

DONOR-ACCEPTOR PROPERTIES  
OF  
PHOSPHORUS-SULPHUR COMPOUNDS

by

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## ABSTRACT

The cage molecule  $P_4S_3$  has been examined by a variety of spectroscopic and chemical methods in order to determine some information about its stability, its distribution of electronic density, and also about its donor-acceptor properties.  $P_4S_3$  has been shown to be a poor  $\sigma$ -donor as indicated by its lack of reactivity toward either  $BCl_3$  or  $BF_3$ , its failure to be protonated by  $HBF_4$ , and its failure to be quaternized by either  $MeSO_3F$  or  $Et_3OBF_4$ . It does however show evidence of acceptor properties by its reaction with certain thiophiles. Numerous attempts were made to prepare transition metal complexes of  $P_4S_3$ . The formation of complexes is most favoured with the later and heavier transition metals in low oxidation states. In these complexes, optimum donor-acceptor interaction is expected and results reveal that  $P_4S_3$  is a good  $\pi$ -acceptor.

The infrared and Raman spectra of  $P_4S_3$  were obtained and complete vibrational assignments have been made. The spectra are in substantial agreement with recently published information but there is some difference in interpretation.

Tetraphosphorus trisulphide diiodide,  $\alpha$ - $P_4S_3I_2$ , has been shown to behave chemically as little more than a molecular association of  $P_4S_3$  and  $I_2$ . Attempts to prepare the cation

$P_4S_3^{2+}$  were unsuccessful and experiments designed to replace iodide by other groups such as -CN, -SCN and -OEt invariably resulted in loss of molecular iodine and regeneration of  $P_4S_3$ .

Continuing experimental difficulties with  $P_4S_3$  and its complexes brought about a change in the direction of this research. Instead, various cyclic organophosphorus-sulphur compounds were examined chemically and spectroscopically, a major portion of the work involving the interrelationship between the compounds  $Ph_4P_4S$ ,  $Ph_3P_3S_3$  and  $Ph_2P_2S_4$ . At the time that this work was begun, the structures of  $Ph_4P_4S$  and  $Ph_3P_3S_3$  were uncertain and the establishment of these structures was naturally essential for an understanding of their chemistry. The crystal structure of  $Ph_4P_4S$  has been determined, and the molecule, contrary to literature reports, consists of a non-planar five-membered  $P_4S$  ring. The structure of  $Ph_3P_3S_3$  has been elucidated by interpretation of the phosphorus and fluorine n.m.r. spectra of its para-fluorophenyl analogue.  $Ph_3P_3S_3$  consists of an unsymmetrical five-membered  $P_3S_2$  ring, again contrary to literature reports, the remaining sulphur atom being bonded exocyclically to one of the phosphorus atoms.

The meta- and para-fluorophenyl analogues of the compounds  $Ph_4P_4S$ ,  $Ph_3P_3S_3$  and  $Ph_2P_2S_4$ , and also those of



(PhP)<sub>n</sub> and (PhPI)<sub>2</sub>, have been prepared; using the methods of Taft et al, inductive and resonance parameters have been calculated from the <sup>19</sup>F n.m.r. shifts. Acceptor properties (both  $\sigma$ - and  $\pi$ -) are greatest in those compounds richest in sulphur and Ph<sub>2</sub>P<sub>2</sub>S<sub>4</sub>, in particular, exhibits very large inductive and conjugative withdrawal.

The infrared and Raman spectra of the phenyl and p-fluorophenyl derivatives have been obtained and a number of vibrational assignments have been made. The mass spectra of the phenyl and p-fluorophenyl derivatives have been obtained, and considerable rearrangement of molecular fragments is a common feature.

TABLE OF CONTENTS

|  | PAGE |
|--|------|
| ABSTRACT   | i    |
| TABLE OF CONTENTS                                      | iv   |
| LIST OF TABLES   | vi   |
| LIST OF FIGURES  | viii |
| ACKNOWLEDGEMENTS                                       | ix   |
| INTRODUCTION   | 1    |
| PART 1: TETRAPHOSPHORUS TRISULPHIDE                    |      |
| I. EXPERIMENTAL  |      |
| A. INTRODUCTION  | 10   |
| B. EXPERIMENTAL DETAIL                                 | 20   |
| C. INFRARED AND RAMAN SPECTRA                          | 54   |
| II. DISCUSSION   | 61   |
| PART 2: ORGANOPHOSPHORUS-SULPHUR COMPOUNDS             |      |
| I. EXPERIMENTAL  |      |
| A. INTRODUCTION  | 81   |
| B. EXPERIMENTAL DETAIL                                 | 87   |
| II. RESULTS AND DISCUSSION                             | 111  |
| THE DIIODODIPHENYL DIPHOSPHINES<br>( $R_2P_2I_2$ )     | 123  |
| THE FOUR-MEMBERED RING SYSTEM<br>( $R_2P_2S_4$ )       | 135  |
| THE CYCLOTETRAPHOSPHINE MONOSULPHIDES<br>( $R_4P_4S$ ) | 146  |
| THE CYCLOTRIPOSPHINE TRISULPHIDES<br>( $R_3P_3S_3$ )   | 153  |

TABLE OF CONTENTS(cont.)

|   | PAGE |
|---|------|
| THE FLUOROPHENYL CYCLOPOLYPHOSPHINES<br>$(\text{FC}_6\text{H}_4\text{P})_n$ | 163  |
| ELECTRONIC INTERACTIONS OF THE<br>FLUOROPHENYL DERIVATIVES                  | 165  |
| SUMMARY   | 180  |
| REFERENCES  | 183  |

LIST OF TABLES

| TABLE | TITLE   | PAGE |
|-------|---|------|
| I     | Vibrational spectra of $P_4S_3$   | 57   |
| II    | Shielding parameters and Taft inductive and resonance parameters of compounds prepared in this work | 113  |
| III   | Mass spectra of $Ph_2P_2I_2$ and $(p-FC_6H_4PI)_2$  | 124  |
| IV    | Characteristic infrared frequencies of phenyl and fluorophenyl groups                               | 116  |
| V     | Low frequency infrared and Raman absorption of compounds $R_2P_2I_2$                                | 127  |
| VI    | Raman spectral results for $PhPH_2$ , $PhPCl_2$ , $m-FC_6H_4PH_2$ and $(m-FC_6H_4PI)_2$ in solution | 120  |
| VII   | Mass spectra of $Me_2P_2S_4$ , $Ph_2P_2S_4$ and $(p-FC_6H_4PS_2)_2$                                 | 136  |
| VIII  | Solid state Raman spectra of compounds $R_2P_2S_4$  | 138  |
| IX    | Solid state infrared spectra of compounds $R_2P_2S_4$   | 140  |
| X     | Molecular structure of $Ph_4P_4S$   | 148  |
| XI    | Mass spectral results for $Ph_4P_4S$ and $(p-FC_6H_4P)_4S$  | 150  |

LIST OF TABLES(cont.)

| TABLE | TITLE   | PAGE |
|-------|---|------|
| XII   | Vibrational spectra of $\text{Ph}_4\text{P}_4\text{S}$<br>and $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$       | 152  |
| XIII  | Mass spectral results for $\text{Ph}_3\text{P}_3\text{S}_3$<br>and $(\text{p-FC}_6\text{H}_4\text{PS})_3$         | 155  |
| XIV   | Vibrational spectra of $\text{Ph}_3\text{P}_3\text{S}_3$ and<br>its fluorophenyl analogues                        | 160  |
| XV    | Mass spectra of compounds $(\text{p-FC}_6\text{H}_4\text{P})_n$   | 164  |
| XVI   | Shielding parameters and Taft inductive<br>and resonance parameters of compounds<br>referred to in the discussion | 166  |
| XVII  | Effect of fluorine in the <u>para</u> -<br>position on various infrared<br>stretching frequencies                 | 171  |

LIST OF FIGURES

| FIGURE | TITLE   | PAGE |
|--------|---|------|
| 1      | E.s.r. electrolysis cell                                    | 29   |
| 2      | Orientation of p-orbitals as<br>used in the calculation     | 71   |
| 3      | Energy levels of $P_4S_3$ as derived<br>by HMO calculations | 72   |
| 4      | Reactions of organophosphorus<br>sulphur ring compounds     | 112  |
| 5      | Vibrations of a monosubstituted<br>phenyl group             | 115  |
| 6      | Molecular structure of $Ph_4P_4S$                           | 146  |
| 7      | Arrangement of phenyl groups<br>in $Ph_4P_4S$               | 147  |
| 8      | $^{19}F$ n.m.r. spectrum of<br>$(p-FC_6H_4PS)_3$            | 157  |
| 9      | $^{31}P$ n.m.r. spectrum of<br>$(p-FC_6H_4PS)_3$            | 158  |

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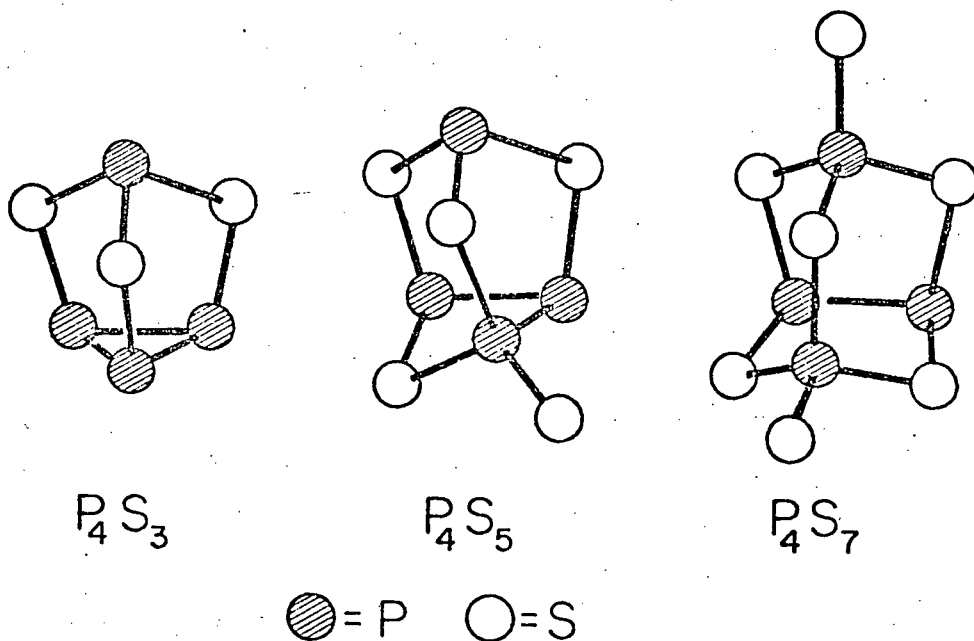
## INTRODUCTION

The reaction between the elements phosphorus and sulphur was first noted by Margraff<sup>1</sup> in 1740. In the following one hundred and fifty years, chemical individuality was claimed for more than a dozen phosphorus-sulphur compositions ranging from  $P_4S$  to  $P_2S_{12}$ . Many of these so-called compounds were prepared simply by varying the P/S ratio so that undoubtedly there were mixtures of phosphorus sulphides present. It was not until the beginning of the twentieth century that the careful work of Alfred Stock and his co-workers<sup>2-4</sup> resulted in the knowledge that only three compounds, tetraphosphorus trisulphide ( $P_4S_3$ ), tetraphosphorus heptasulphide ( $P_4S_7$ ) and tetraphosphorus decasulphide ( $P_4S_{10}$ ) could be made by the thermal reaction of phosphorus with sulphur. Since that time, the existence of several other phosphorus sulphides of lower thermal stability has been recognized. Tetraphosphorus pentasulphide ( $P_4S_5$ ) cannot be made by direct union of the elements, and is best prepared photochemically<sup>21</sup> by exposing a carbon disulphide solution of stoichiometric quantities of  $P_4S_3$  and sulphur, plus a trace of iodine, to diffuse daylight for several days. Recently, tetraphosphorus nonasulphide ( $P_4S_9$ ) has been prepared<sup>5</sup> by the hydrolysis of thiophosphoryl chloride in sealed tubes. In addition, a brief communication<sup>6</sup> has claimed the existence of  $P_4S_2$ , formed from the reaction of  $P_4S_3$  with white phosphorus; however, in view of the



past history of errors in P-S chemistry, it would be prudent to consider the existence of  $P_4S_2$  as uncertain. A phosphorus sulphide of non-stoichiometric composition was noted by Rodley and Wilkins<sup>7</sup> in their work on phosphorus-sulphur compositions in the range  $P_4S_5$  to  $P_4S_{6.9}$ . A particular phase observed by these workers, of approximate composition  $P_4S_{6.5}$ , was later shown by X-ray diffraction<sup>8</sup> to possess the same basic structure as  $P_4S_7$ , except that some terminal sulphur atoms were missing. It does not seem unlikely considering these results, that additional phosphorus sulphides will be prepared in the future.

The crystal structures of  $P_4S_3$ <sup>33</sup>,  $P_4S_7$ <sup>10</sup>,  $P_4S_9$ <sup>11</sup> and  $P_4S_{10}$ <sup>12</sup> have been reported and the molecular structures of  $P_4S_3$ ,  $P_4S_5$  and  $P_4S_7$  are reproduced below. The molecular structure of  $P_4S_{10}$ , like that of  $P_4O_{10}$ , possesses tetrahedral symmetry, each phosphorus atom being

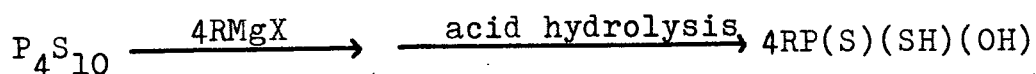


pentavalent and tetracoordinate; the structure of  $P_4S_9$  is similar to that of  $P_4S_{10}$  with the exception that a terminal sulphur atom is missing. The structures of the phosphorus sulphides are quite distinctive in that they are based on the cage-like tetrahedral structure of  $P_4$ , and like  $P_4$  itself, contain many small rings and bond angles. Indeed, the structure of  $P_4S_3$  as illustrated above was considered<sup>22</sup> unlikely as recently as 1949 on the basis that it did not possess the least strained structure that could be devised from four phosphorus atoms and three sulphur atoms. The completely unsymmetrical structure of  $P_4S_5$  is surely the most unusual of all the phosphorus sulphide structures in that it contains a four-membered ring, two five-membered rings and a six-membered ring. Even in  $P_4S_7$ , not all the P-P bonds have been broken by bridging sulphur atoms, and the solitary P-P bond in  $P_4S_7$  is considerably longer ( $2.35\text{\AA}$ ) than a normal P-P bond length ( $2.22\text{\AA}$ ); in addition, there are eight different types of bond angle in  $P_4S_7$ . Although the structures of the more common phosphorus sulphides have been known for some time now, the chemistry of this family has remained comparatively undeveloped. It would not be an understatement to say that, despite their unusual structures, little research has been carried out with the phosphorus sulphides and not much is understood about their bonding and reactivity.

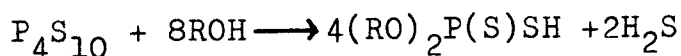
The phosphorus sulphides have been used extensively for industrial purposes for quite some time, and although the commercial importance of these compounds should not be underestimated, their industrial uses have not contributed much to an understanding of their structures or reactions. Thus,  $P_4S_3$  has long been used in the manufacture of ordinary "strike-anywhere" matches in which it replaced the more dangerous white phosphorus that was formerly used. There exists a large number of patents in the literature relating to the use of phosphorus sulphides in the preparation of lubricant oil additives and flotation reagents. Halogenated paraffins and phosphorus sulphides, in the presence of a Friedel-Crafts catalyst at elevated temperatures, give P- and S- containing organic compounds which are useful as oil addition agents because they possess anti-oxidant properties and inhibit corrosion<sup>13</sup>. Useful lubricating oil additives are also obtained from the reaction of  $P_4S_3$  with organic compounds such as esters, alcohols and olefinic hydrocarbons<sup>14</sup>; it has also been shown<sup>15</sup> that the number and severity of surface ignitions in internal combustion engines is reduced by the addition of small quantities of phosphorus-sulphur compounds to automotive gasolines. Phosphorus sulphides have also been used extensively in the manufacture of insecticides. Compounds referred to<sup>16</sup> as tridialkyl phospho thiophosphates are produced by heating together  $P_4S_{10}$  and alkyl phosphates; compounds of

this type with lower alkyl groups such as methyl and ethyl have a quick insecticidal action, but the higher alkyl derivatives retain their toxicity longer and are more resistant to hydrolysis. Concentrations as low as 1:2,000 parts of water are effective against roaches, aphids, spiders and flies. The possibility of using  $P_4S_3$  as a coolant for nuclear reactors has been investigated<sup>17</sup>. Studies were made to determine the corrosion and heat transfer characteristics of  $P_4S_3$  at 1200°F and thereby determine the feasibility of extracting energy from a nuclear reactor using a boiling  $P_4S_3$  cycle. Results showed that  $P_4S_3$  was better suited as a coolant than was molten sulphur, which proved to be more corrosive and less efficient as a coolant.

Some of the better characterized reactions of the phosphorus sulphides have been reviewed previously<sup>18,22</sup>. The majority of the reactions involve nucleophilic attack and destruction of the cage structures; thus,  $P_4S_3$ ,  $P_4S_7$  and  $P_4S_{10}$  have been found to react with Grignard reagents<sup>24</sup>.



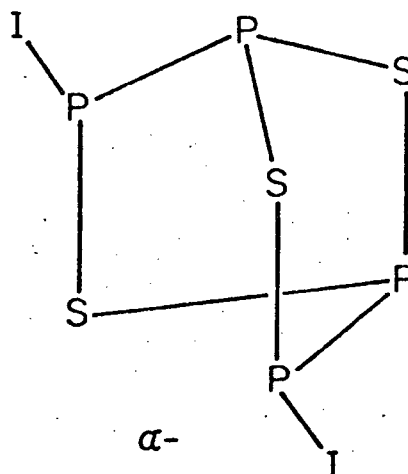
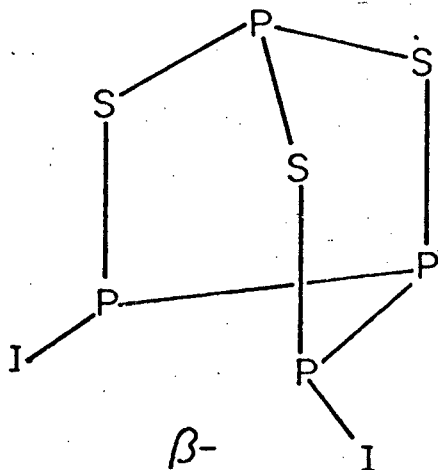
Compounds with X-H bonds (X=O,S,N) react with  $P_4S_{10}$  by elimination of  $H_2S$ . Alcohols and phenols give predominantly secondary dithiophosphates<sup>19,20,39</sup>.



$P_4S_{10}$  is used extensively in organic chemistry for con-

verting C=O, COOH and P=O into their corresponding sulphur analogues. Alcohols also react with  $P_4S_5$  and  $P_4S_7$  to give products<sup>40</sup> of composition  $(RO)_2PSH$ ,  $(RO)_2P(S)SH$  and  $(RO)_2P(S)SR$ . The phosphorus sulphides react with amines<sup>41,42</sup> and also with liquid ammonia,<sup>25,43,45</sup> the usual result being a cleavage of the P-S-P bridges. The phosphorus sulphides range in hydrolytic stability from  $P_4S_3$ , which reacts only slowly with cold dilute HCl or  $H_2SO_4$ , to  $P_4S_7$  which is hydrolyzed by atmospheric moisture. The sequence of hydrolytic stability appears<sup>21</sup> to be  $P_4S_3 > P_4S_{10} > P_4S_7$ . All the phosphorus sulphides are hydrolyzed by aqueous alkalis to give products which include hydrogen, hydrogen sulphide, phosphine, hypophosphorous acid, phosphorous acid and phosphoric acid<sup>21</sup>.

The reaction of  $P_4S_3$  with iodine is quite complex. With an excess of iodine,  $P_4S_3$  is oxidized<sup>21</sup> to  $P_4S_7$ . Under milder conditions, stoichiometric amounts of iodine and  $P_4S_3$  can react to produce  $\alpha$ - or  $\beta$ - $P_4S_3I_2$ . The  $\alpha$ -isomer<sup>31</sup> is the more stable of these two forms; indeed,

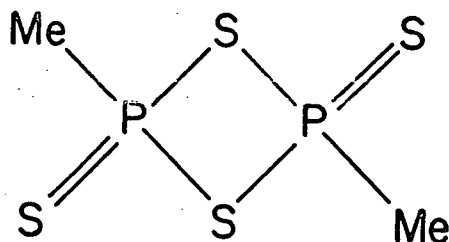


the existence of  $\beta\text{-P}_4\text{S}_3\text{I}_2$  has only recently been established<sup>32</sup>.  $\beta\text{-P}_4\text{S}_3\text{I}_2$  can be converted to  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  by inversion of an S-P-I group, the transformation readily occurring when  $\beta\text{-P}_4\text{S}_3\text{I}_2$  is melted. These reactions constitute an excellent example of the general mobility of bonding in the phosphorus sulphides.

At the time that this work was undertaken, only one report had appeared in the literature regarding complex formation with the phosphorus sulphides. Nixon *et al.*<sup>29</sup> have prepared the complexes  $\text{cis-(P}_4\text{S}_3)_2\text{M(CO)}_4$  [M=Cr, Mo, W],  $\text{cis-(P}_4\text{S}_3)_3\text{M(CO)}_3$  [M=Cr, Mo] and  $\text{Ni(P}_4\text{S}_3)_4$  and have shown that  $\text{P}_4\text{S}_3$  coordinates through its unique apical phosphorus. In the intervening years, only a few additional papers have appeared and these will be referred to later in this thesis.

One of the major aims of this work has been to investigate the donor-acceptor properties of phosphorus-sulphur compounds in the hopes of obtaining more knowledge of the factors important in their bonding. The lowest sulphide,  $\text{P}_4\text{S}_3$  was examined extensively in this regard because it is the most stable and most tractable of these cage molecules. However, continuing experimental difficulties forced a change in the direction of this research, and instead of pursuing work with the cage phosphorus sulphides, various cyclic organophosphorus-sulphur

compounds were examined instead. Chief amongst these were the compounds  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$ , all of which can be prepared by the reaction of phenylphosphine with sulphur. At the time that this work was undertaken, the structures of the first two had not been conclusively established and it was, of course, necessary to establish these structures beyond any doubt. On the other hand, the structure of the third compound has been shown to consist of a four-membered planar  $\text{P}_2\text{S}_2$  ring, with each phosphorus atom being pentavalent and tetracoordinate. For example, the structure<sup>121</sup> of  $\text{Me}_2\text{P}_2\text{S}_4$  is shown below.



The reactions of compounds of this type have been examined in detail<sup>46</sup> and ring cleavage is the usual result.

Bond mobility is a common feature of the cage phosphorus sulphides and so experiments were undertaken to determine whether the ring analogues are capable of similar behaviour. Whereas some insight into the electronic interactions in  $\text{P}_4\text{S}_3$  has been gleaned by an examination of its basic general chemistry, donor-acceptor

interactions within the phosphorus-sulphur ring compounds have been assessed by interpretation of their m- and p-fluorophenyl derivatives. Finally, evidence is presented to show similarities between the cage phosphorus sulphides and the P-S ring compounds.

In the following chapters, experiments undertaken with  $P_4S_3$  will be described, and then a discussion of their results will be presented; the second half of this thesis will deal analogously with the P-S ring systems.



PART 1: TETRAPHOSPHORUS TRISULPHIDE

I - EXPERIMENTAL

A. INTRODUCTION

Much of the reported work on tetraphosphorus trisulphide ( $P_4S_3$ ) has involved reactions in which the cage structure of  $P_4S_3$  has been destroyed. Typical reactions of this type include acid<sup>21</sup> and basic hydrolysis<sup>21,22,23</sup>, as well as reactions with Grignard reagents<sup>24</sup> and with amines<sup>25</sup>. The curious structures of the phosphorus sulphides are perhaps their most interesting feature however and this work was mostly concerned in pursuing reactions in which the cage of  $P_4S_3$  remained intact. Consequently, if it became apparent during the work-up of a reaction that decomposition of the cage had occurred, then the reaction mixture was discarded after minimal attempts to identify the decomposition products.

The first sequence of experiments presented was designed to test the basicity of  $P_4S_3$ . A freshly-prepared saturated solution of  $BF_3$  in  $H_2O$  was added to  $P_4S_3$ ; no visible reaction or dissolution of  $P_4S_3$  occurred over a number of days. The stronger but similarly non-oxidizing acid  $HF$  was also tested with  $P_4S_3$ ; again no visible dissolution or reaction occurred, even over a number of days. With 100% sulphuric acid, no immediate reaction

occurred, but over a period of a week the yellow crystals of  $P_4S_3$  slowly disappeared and simultaneously there appeared a small amount of whitish crystalline material which was identified as elemental sulphur. The addition of  $P_4S_3$  to oleum (20%  $SO_3$  in  $H_2SO_4$ ) resulted in an immediate vigorous reaction. The pungent smell of  $SO_2$  was detected and the solution of oleum turned a variety of colours and then remained blue, indicating the probable presence of  $S_8^{2+}$ . It is evident that  $P_4S_3$  is readily oxidized by  $SO_3$ . When fluorosulphuric acid was distilled onto  $P_4S_3$ , a vigorous reaction set in following a brief induction period; elemental sulphur was again isolated from the reaction mixture. It is apparent then that  $P_4S_3$  is at most very weakly basic; it is not protonated by strong non-oxidizing acids and is decomposed by oxidizing acids.

To test further the possible donor properties of  $P_4S_3$ , the molecule was treated with  $BF_3$  and then with  $BCl_3$ . In each case, there was no reaction. Many trivalent phosphorus compounds can be quaternized with relative ease but attempts to quaternize  $P_4S_3$  yielded results similar to those obtained from the protonation experiments. The very strong methylating agent methyl fluorosulphate,  $MeSO_3F$ , slowly reacted with  $P_4S_3$  but analytical and spectroscopic data of the product revealed that decomposition had occurred. Triethyloxonium tetrafluoroborate and  $P_4S_3$  produce no reaction when heated under reflux in methylene chloride.

The lack of reaction with these strong alkylating agents is further evidence of the weak donor properties of  $P_4S_3$ .

The following sequence of reactions was designed to test the stability of the cage of  $P_4S_3$  toward a variety of oxidants. In particular it was of interest to see if a radical cation of  $P_4S_3$  could be produced. If a radical could be formed, then electron spin resonance measurements would be expected to yield useful information regarding the possible mobility of an unpaired electron. The hexachloroantimonate ion,  $SbCl_6^-$ , has been shown to be a one-electron oxidant with respect to aromatic amines, ferrocene and iodide ion<sup>26</sup>. However, triphenylmethyl hexachloroantimonate and  $P_4S_3$ , heated under reflux in  $CH_2Cl_2$ , failed to react. Antimony pentachloride itself has become a useful reagent for the generation of cation radicals from polynuclear aromatic molecules<sup>27,28</sup>. Treatment of  $P_4S_3$  with  $SbCl_5$  either as a neat liquid or in solution, results in decomposition of the cage. The reaction products are elemental sulphur and what appears to be  $PCl_4^+ SbCl_6^-$ . In view of this result, it is not surprising that antimony pentafluoride is found to react violently with  $P_4S_3$ . Sulphur cations and  $Sb_2S_3$  are apparently formed as part of the decomposition products. The reaction of  $P_4S_3$  with  $AsF_5$  proceeded along similar lines. When  $AsF_5$  was condensed onto  $P_4S_3$ , fuming and frothing occurred and the

variety of colour changes observed are attributed to formation of sulphur cations. When the unreacted  $\text{AsF}_5$  was removed from the reaction flask, it was found that the weight of the product was less than the original weight of  $\text{P}_4\text{S}_3$  indicating that volatile products had been formed.  $\text{P}_4\text{S}_3$  reacts vigorously with liquid dinitrogen tetroxide at room temperature and elemental sulphur can be isolated. Dimethylsulphoxide, a very weak oxidizing agent, will also destroy  $\text{P}_4\text{S}_3$  and again the formation of sulphur is observed.

The stability of  $\text{P}_4\text{S}_3$  toward reduction was examined polarographically.  $\text{P}_4\text{S}_3$  was found to undergo irreversible reduction at a very low potential; the reduced species did not exhibit any electron spin resonance spectrum.

In general the preceding reactions show that the cage of  $\text{P}_4\text{S}_3$  is rather fragile and incapable of withstanding even moderate stress. In further experiments designed to test the strength of the P-S framework,  $\text{P}_4\text{S}_3$  was subjected to treatment with thiophiles of varying strength. Sulphite ion is incapable of removing sulphur from  $\text{P}_4\text{S}_3$  under the conditions used; cyanide ion will react to a limited degree to form  $\text{SCN}^-$  under similar conditions. Triphenylphosphine in boiling  $\text{CS}_2$  or benzene does not react with  $\text{P}_4\text{S}_3$ ; in boiling toluene there is a slight reaction, and in boiling xylene a significant reaction, with formation of

triphenylphosphine sulphide and an insoluble scarlet material. Analytical data show that this material is of variable composition but consists predominantly of phosphorus. If  $\text{Ph}_3\text{P}$  and  $\text{P}_4\text{S}_3$  are melted together in a sealed tube, the reaction takes place quite rapidly.

It might be expected, given the apparently weak donor properties of  $\text{P}_4\text{S}_3$ , that stable transition metal complexes would be obtained only with difficulty. Such was the case for the particular metals of the first and second transition series that were tested initially. Thus bis(acetylacetonato)oxovanadium (IV), which is known to form complexes with  $\text{Ph}_3\text{PO}$  and pyridine, does not combine with  $\text{P}_4\text{S}_3$  in refluxing benzene. The reaction of bis(triphenylphosphine)nickel dicarbonyl with  $\text{P}_4\text{S}_3$  led to a variety of products, amongst them a black, apparently polymeric<sup>29</sup> material and triphenylphosphine sulphide. The formation of triphenylphosphine sulphide indicates that  $\text{P}_4\text{S}_3$  has decomposed and so the reaction was not pursued. Antimony trichloride did not react with  $\text{P}_4\text{S}_3$  when heated under reflux in  $\text{CS}_2$ . When fused together with  $\text{P}_4\text{S}_3$ , there was limited decomposition and a small amount of  $\text{Sb}_2\text{S}_3$  was isolated. The reactions of  $\text{P}_4\text{S}_3$  with low valent metals in the second and third transition series were somewhat more successful but in general the products proved exceedingly difficult to characterize; in all but one case the products proved to be completely insoluble in all solvents tested. This lack

of solubility severely hampered efforts to purify and characterize the complexes and was a major reason for discontinuing work on  $P_4S_3$  in favour of the more tractable organophosphorus sulphur compounds. Thus, although palladous chloride failed to react with  $P_4S_3$  either in solution or when fused together, bis(benzonitrile) palladium dichloride and  $P_4S_3$  reacted immediately to form a dark brown precipitate. An infrared spectrum of the solid showed no absorption due to  $C\equiv N$  stretching, indicating that both benzonitrile groups had been displaced. The product was insoluble in all solvents tested. Similarly, bis(benzonitrile)platinum dichloride and  $P_4S_3$  react to produce an orange solid which is insoluble in all common solvents. Vaska's compound<sup>30</sup>, trans-chlorocarbonylbis(triphenylphosphine)iridium (I) reacts with  $P_4S_3$  to yield the green complex  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$ . Efforts to replace both  $Ph_3P$  molecules were unsuccessful and again only  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$  was obtained. It is somewhat surprising that this complex too is completely insoluble. In an attempt to prepare a soluble derivative of this product,  $BCl_3$  was bubbled through a suspension of  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$  in benzene. The colour of the mixture slowly changed from green to orange, presumably as a result of formation of a species such as  $[IrCl(H)(CO)(Ph_3P)(P_4S_3)]^+ [BCl_4]^-$ . It was found however that vacuum-drying of the orange solid was sufficient to

cause it to revert to the original green complex. Apparently the orange complex is in equilibrium with free  $\text{BCl}_3$

$$\left[\text{IrCl}(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)\right]^+ \left[\text{BCl}_4^-\right] \rightleftharpoons$$

$\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3) + \text{BCl}_3$  and so removal of  $\text{BCl}_3$  by pumping causes complete reversion to the initial complex. An infrared spectrum proved that the green material isolated was identical to the starting material. It was felt that the instability of the tetrachloroborate salt might be due in part to the disparate sizes of anion and cation. Consequently experiments with larger anions were undertaken. However sodium tetraphenylborate failed to react with  $\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$  in boiling tetrahydrofuran; similarly the chloride acceptors  $\text{CoCl}_2$  and  $\text{SnCl}_2$  failed to react. Although  $\text{SbCl}_5$  is a powerful chloride acceptor, it has also been shown to attack  $\text{P}_4\text{S}_3$  and so this reaction was not attempted.  $\text{P}_4\text{S}_3$  will also combine with  $\text{RhCl}(\text{Ph}_3\text{P})_3$ ,  $\text{RhBr}(\text{Ph}_3\text{P})_3$  and  $\text{Pt}(\text{Ph}_3\text{P})_4$  but again only intractable powders are obtained. Extensive analytical data for the  $\text{RhCl}(\text{Ph}_3\text{P})_3 - \text{P}_4\text{S}_3$  complex give somewhat curious results, and in general these three complexes remain rather ill-defined.

The reaction of  $\text{P}_4\text{S}_3$  with cis-( $\text{PBu}_3$ ) $_2\text{PtCl}_2$  is very interesting. When heated under reflux in benzene, the reactants produce a soluble brown complex which can be precipitated by addition of alcohol or light petroleum ether.

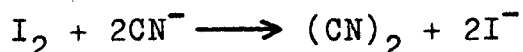
Infrared and Raman spectra indicate the presence of coordinated  $P_4S_3$ , but more significantly, they reveal the lack of Pt - Cl stretching. This is confirmed by analytical data showing that only residual chloride is present. The carbon and hydrogen analyses are in agreement with the formulation  $Pt(PBu_3)(P_4S_3)_2$ , a complex of platinum (0). Presumably the displaced tributylphosphine functions as a reducing agent and is itself oxidized to  $PBu_3Cl_2$ . Unfortunately the complex could not be crystallized and purification was hampered by the fact that the complex is strongly adsorbed by such usual column material as florisil and silica gel.

Despite the difficulties experienced with these Group VIII metal complexes the mere fact that complexation has occurred is encouraging; furthermore useful information has been derived from the  $C\equiv O$  stretch of  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$  and also from the Raman spectrum of  $Pt(PBu_3)(P_4S_3)_2$ . These experiments were amongst the last attempted with  $P_4S_3$  and as stated previously, the lack of tractability of these, the only really promising complexes, resulted in discontinuation of work with  $P_4S_3$  in favour of organophosphorus sulphur compounds.

$P_4S_3$  has been shown to react with iodine to produce two different isomers<sup>31,32</sup> of  $P_4S_3I_2$ . The more stable isomer, denoted  $\alpha$ - $P_4S_3I_2$  was treated with silver hexa-



fluoroantimonate. An immediate precipitation of AgI was observed but from its weight it was determined that additional byproducts were also present. An orange water-insoluble powder believed to be  $\text{Sb}_2\text{S}_3$  was also isolated, indicating that decomposition had occurred.  $\alpha\text{-P}_4\text{S}_3\text{I}_2$ , when mixed with sodium tetraphenylborate in benzene, gives a wine-red solution. However,  $\text{NaBPh}_4$  was recovered unchanged.  $\text{P}_4\text{S}_3$  was also recovered and therefore the wine-red colour is attributed to formation of molecular iodine. With potassium thiocyanate,  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  again reverts to  $\text{P}_4\text{S}_3$  and molecular iodine. Potassium cyanide and  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  react to yield a similar wine-red solution. The colour slowly faded to a pale yellow and removal of solvent gave two products,  $\text{P}_4\text{S}_3$  and KI. The potassium iodide is formed as liberated molecular iodine oxidizes cyanide ion,



This reaction accounts for the observed colour change and for the subsequent formation of KI. Under the action of  $\text{SbCl}_5$ ,  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  again decomposes to form  $\text{P}_4\text{S}_3$  and  $\text{I}_2$ ; in this case the liberated  $\text{P}_4\text{S}_3$  is then decomposed by  $\text{SbCl}_5$ . Treatment of  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  with mercury resulted in a heavy precipitation of HgS. Complex formation with

$\alpha\text{-P}_4\text{S}_3\text{I}_2$  was equally unsuccessful. With  $\text{Mo}(\text{CO})_6$ , in solution, decomposition occurred with the formation of a black powder thought to be either molybdenum iodide or sulphide. When  $\text{Mo}(\text{CO})_6$  and  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  were melted together

obvious decomposition occurred as iodine sublimed out of the mixture. With  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , an orange intractable compound was obtained but triphenylphosphine sulphide was also isolated indicating that at least partial decomposition of  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  had occurred.

Polarographic reduction of  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  was unsuccessful as the molecule again decomposed into  $\text{P}_4\text{S}_3$  and  $\text{I}_2$ , apparently under the influence of the electrolyte, tetra-n-butylammonium iodide. The solution turned bright orange indicating formation of the triiodide ion and the polarographic wave observed at  $-0.95$  v. was identical to that previously obtained for  $\text{P}_4\text{S}_3$ .

## B. EXPERIMENTAL DETAIL

### $\text{BF}_3 \cdot \text{H}_2\text{O}$ with $\text{P}_4\text{S}_3$ :

$\text{BF}_3 \cdot \text{H}_2\text{O}$  was freshly-prepared by bubbling  $\text{BF}_3$  through distilled water for about one and one half hours. The viscous yellowish liquid was added to  $\text{P}_4\text{S}_3$  but no reaction or dissolution of  $\text{P}_4\text{S}_3$  was observed, even upon heating the solution.

### $\text{HBF}_4$ solution with $\text{P}_4\text{S}_3$ :

$\text{BF}_3$  was bubbled vigorously through a 49% HF aqueous solution for about one hour. The resulting clear fuming solution was added to  $\text{P}_4\text{S}_3$  in a polyethylene container. Again no visible dissolution or reaction occurred even after a number of days.

### 100% $\text{H}_2\text{SO}_4$ with $\text{P}_4\text{S}_3$ :

A small volume of 100%  $\text{H}_2\text{SO}_4$  was added to a small amount of  $\text{P}_4\text{S}_3$  in a dry box. No immediate reaction or dissolution was observed. Over a period of a week it was observed that the yellow  $\text{P}_4\text{S}_3$  was slowly disappearing accompanied by the simultaneous formation of small whitish crystals. These crystals were collected on sintered glass, washed with acetone and dried with nitrogen; a melting point of  $119^\circ\text{C}$  indicated that the product was elemental sulphur.

Oleum with  $P_4S_3$ :

The addition of  $P_4S_3$  to cold oleum results in a vigorous but not violent reaction. Sulphur dioxide is apparently liberated (detected by smell) and a blue solution eventually forms. This blue colour is attributed to the formation of  $S_8^{2+}$ .

$HSO_3F$  with  $P_4S_3$ :

Doubly distilled fluorosulphuric acid was added to  $P_4S_3$  in a dry atmosphere. There was an immediate effervescence and very shortly thereafter yellow crystals began appearing. These crystals were collected on sintered glass, washed and dried. A melting point of  $119^\circ C$  indicated the formation of elemental sulphur.

$BF_3$  with  $P_4S_3$ :

(i) in solution:  $BF_3$  was bubbled through a solution of  $P_4S_3$  in dry chloroform for approximately one hour. Apart from some initial cloudiness believed to be caused by formation of a small amount of  $BF_3 \cdot H_2O$  there was no obvious reaction. Removal of chloroform gave only unreacted  $P_4S_3$ , m.p.  $171-2^\circ C$ .

(ii) neat:  $BF_3$  was condensed onto  $P_4S_3$  in a vacuum line until the yellow crystals were completely covered by liquid. No reaction was observed and the mixture was allowed to warm to room temperature. At this temperature, all the  $BF_3$  was gaseous. The two compounds were left in

contact together at room temperature overnight but no reaction had occurred by the following morning.

(iii) in an autoclave: A small amount of  $P_4S_3$  was placed in an autoclave. The air was removed from the autoclave and  $BF_3$  was condensed onto the  $P_4S_3$ . The autoclave was sealed and then heated with an infrared lamp for 20 hours. At that time, the gases were removed from the autoclave; an infrared spectrum of the solid remaining was identical to that of pure  $P_4S_3$  indicating that no reaction had occurred.

$BCl_3$  with  $P_4S_3$ :

(i) neat (at  $0^\circ C$ ): A sample of  $P_4S_3$  was placed in a pear flask and attached to a vacuum line. Sufficient  $BCl_3$  to cover all the  $P_4S_3$  was condensed in the flask. The flask was warmed to  $0^\circ C$  but there was no evidence of reaction.

(ii) neat (in an autoclave): Approximately 4-5 mls. of  $BCl_3$  were condensed into an evacuated autoclave containing a small amount of  $P_4S_3$ . The autoclave was then heated overnight with an infrared lamp. Gaseous products were removed from the autoclave leaving behind unreacted  $P_4S_3$ , m.p.  $171-2^\circ C$ .

$P_4S_3$  with  $MeSO_3F$ :

A small amount of  $P_4S_3$  was treated with an excess of  $MeSO_3F$  and the mixture was heated under reflux with

stirring in a nitrogen atmosphere. For the first two hours no visible reaction occurred; then  $P_4S_3$  was observed to very slowly disappear accompanied by simultaneous formation of a whitish product. After an additional two hours, more of the white product had formed but not all the  $P_4S_3$  had reacted. It was found however that continued refluxing at this stage brought about rapid formation of a dark brown solution and so the reaction was stopped. Excess  $MeSO_3F$  was removed on the vacuum line and the remaining product was washed with  $CS_2$  to remove any unreacted  $P_4S_3$ . The whitish material was found to be insoluble in non-polar organic solvents but was soluble in dimethylsulphoxide, acetonitrile and dimethylformamide although recovery from these latter three solvents was extremely difficult. However the product was successfully crystallized from hot water to yield well-formed crystals, m.p.  $> 270^\circ C$ .

Found: C 16.33% H 4.34%

$CH_3P_4S_3^+SO_3F^-$  requires C 3.59% H 0.90%

Obviously this product is not what was hoped for. A  $^{19}F$  n.m.r. spectrum showed a singlet at + 130 p.p.m. (ext.  $CFCl_3$ ) indicating the presence of ionic fluoride. The fluorosulphate anion has a  $^{19}F$  chemical shift of -39.2 p.p.m. with respect to  $CFCl_3$ . The  $^1H$  n.m.r. spectrum showed a singlet at 7.067. The methyl group must be attached to sulphur therefore, as a doublet would be expected if it were attached to phosphorus.

It is quite apparent that total decomposition has occurred and consequently this reaction was discarded.

$P_4S_3$  with Triethyloxonium tetrafluoroborate:

Triethyloxonium tetrafluoroborate is extremely hygroscopic and was weighed and transferred in a dry box.  $Et_3O^+BF_4^-$  (0.4018 gms, 2.12 mmoles) and  $P_4S_3$  (0.4655 gms, 2.12 mmoles) were combined in dry methylene chloride and heated under reflux in a nitrogen atmosphere. Upon distilling off the solvent,  $P_4S_3$  was recovered unreacted and identified by its melting point,  $171-2^\circ C$ .

$P_4S_3$  with Triphenylmethyl hexachloroantimonate:

20.0 mls. of a solution of  $Ph_3C^+SbCl_6^-$  (0.0299 M in  $CH_2Cl_2$ ) were added to  $P_4S_3$  (0.1318 gms, 0.597 mmoles) in  $CH_2Cl_2$  under a blanket of dry nitrogen. No reaction was apparent and so the solution was heated under reflux for 2 hours in a nitrogen atmosphere. The solution was concentrated and then cooled in ice to yield  $P_4S_3$ , identified by its melting point,  $173^\circ C$ , sharp.

$P_4S_3$  with  $SbCl_5$ :

In the absence of solvent,  $P_4S_3$  and  $SbCl_5$  react together extremely exothermically. If  $SbCl_5$  is added to a mixture of  $P_4S_3$  in dry chloroform, then the  $P_4S_3$  reacts rapidly and white crystals are formed. These crystals

were collected on sintered glass in a glove bag filled with nitrogen, washed with a little dry chloroform and vacuum-dried. Analytical results showed that the crystals contained no sulphur; obviously complete decomposition had occurred. The crystals are extremely hygroscopic in air and are capable of oxidizing iodide to iodine, indicating the presence of  $\text{Sb}^{\text{V}}$ . It is therefore likely that these crystals are  $\text{PCl}_4^+\text{SbCl}_6^-$ .

$\text{P}_4\text{S}_3$  with  $\text{SbF}_5$ :

- (i) neat: After a brief induction period, solid  $\text{P}_4\text{S}_3$  reacted violently with liquid  $\text{SbF}_5$ . Products included brown fumes and brown powder flecked with dark blue colours.
- (ii) in liquid  $\text{SO}_2$ : Approximately 2 mls. of  $\text{SbF}_5$  were added to about 30 mls. of liquid sulphur dioxide and then solid  $\text{P}_4\text{S}_3$  was added in portions under nitrogen. The solution turned brown immediately. The sulphur dioxide was allowed to evaporate overnight. The only solid product observed was a mass of yellow-orange material which did not melt below  $250^\circ\text{C}$ , and turned black at  $230^\circ\text{C}$ . The two crystal modifications of  $\text{Sb}_2\text{S}_3$  are orange and black; in addition this orange material dissolved in hot, concentrated hydrochloric acid. A portion of this solution was diluted with water and a piece of zinc was added. An immediate black coating formed on the zinc indicating the presence of antimony ions. The phosphorus



is presumably lost as volatile phosphorus-fluorine compounds such as  $\text{PF}_3$ ,  $\text{PF}_5$  and  $\text{S}=\text{PF}_3$ .

$\text{P}_4\text{S}_3$  with  $\text{AsF}_5$ :

A sample of  $\text{P}_4\text{S}_3$  (0.1407 gms, 0.64 mmoles) was placed in a round-bottom flask; the flask was evacuated and gaseous  $\text{AsF}_5$  was introduced to the system. Immediately brownish fumes evolved.  $\text{AsF}_5$  was condensed onto the  $\text{P}_4\text{S}_3$  by cooling the flask to  $-196^\circ\text{C}$ . When the flask was warmed and the  $\text{AsF}_5$  melted, there was much frothing and a bluish solution formed.  $\text{AsF}_5$  was condensed onto  $\text{P}_4\text{S}_3$  several times to ensure complete reaction. Finally the flask was evacuated overnight. The weight of material remaining was 0.1173 gms. indicating that at least partial decomposition into volatile products had occurred. As a result the reaction was not investigated further.

$\text{P}_4\text{S}_3$  with  $\text{N}_2\text{O}_4$ :

Liquid dinitrogen tetroxide was poured into a beaker and a small amount of  $\text{P}_4\text{S}_3$  was added. There was an immediate exothermic reaction and elemental sulphur was the only solid material isolated. Any phosphorus oxides formed are undoubtedly converted to acids very quickly.

$\text{P}_4\text{S}_3$  with dimethylsulphoxide:

$\text{P}_4\text{S}_3$  is slightly soluble in dimethylsulphoxide at

room temperature but gives no evidence of reaction. Upon warming the mixture to 60-70°C a reaction is initiated which proceeds very vigorously and rapidly. The reaction is accompanied by popping noises and the evolution of a gas which was most likely dimethylsulphide as evidenced by its foul smell. As the  $P_4S_3$  reacted, a yellow oil formed; when the solution was concentrated after the reaction had finished, the oil crystallized. The melting point of the product (118-119°C, sharp), its poor infrared absorption and finally its mass spectrum (peaks observed only at multiples of 32) establish beyond doubt that another novel route to the synthesis of elemental sulphur had been found.

#### POLAROGRAPHY

For experiments involving the polarographic reduction of  $P_4S_3$ , it was important to exclude both water and oxygen. The solvents used, benzene and acetonitrile, were dried overnight with  $CaH_2$  and then distilled under nitrogen. A 1:1 benzene-acetonitrile mixture was found to be ideal as it allowed dissolution of enough  $P_4S_3$  and of enough tetra-n-butylammonium iodide, the supporting electrolyte, to obtain good polarograms. The solutions used were 0.002 M with respect to  $P_4S_3$  and 0.1 M with respect to tetra-n-butylammonium iodide. Solutions were prepared in a nitrogen atmosphere and, to remove the last traces of oxygen, were vigorously flushed with high purity nitrogen for at least fifteen minutes

prior to use. It was particularly important to remove oxygen because its second reduction wave occurring at  $E_{\frac{1}{2}} = -0.78\text{v}$  was very close to the wave found for  $\text{P}_4\text{S}_3$ .

All polarograms were run on a Sargent Polarograph, Model XXI. The electrodes used were a dropping mercury electrode and a standard calomel electrode. The solvent mixture used was found to be stable in the region 0 to  $-2.5\text{v}$ . At more negative reduction potentials, acetonitrile is reduced. The supporting electrolyte, tetra-n-butylammonium iodide is stable in the region  $-0.5$  to  $-3.0\text{v}$ . Polarograms could therefore only be recorded in the region  $-0.5$  to  $-2.5$  volts, but as preliminary tests showed that there were no waves in the region  $-1.5$  to  $-2.5\text{v}$ ., subsequent polarograms were generally run only in the range  $-0.5$  to  $-1.5\text{v}$ .  $\text{P}_4\text{S}_3$  has a reproducible half-wave potential of  $-0.95\text{v}$ .; no visible colour change occurred during this reduction. The reduction is apparently irreversible as Nernst plots from several different polarograms gave values of  $n$ , the number of electrons transferred in the reduction process, ranging from 0.5 to 0.7. The cause of the irreversibility is unknown; however cage fracture or reaction with mercury are two possibilities.

#### E.S.R. ATTEMPTS:

To test the possibility of radical anion formation

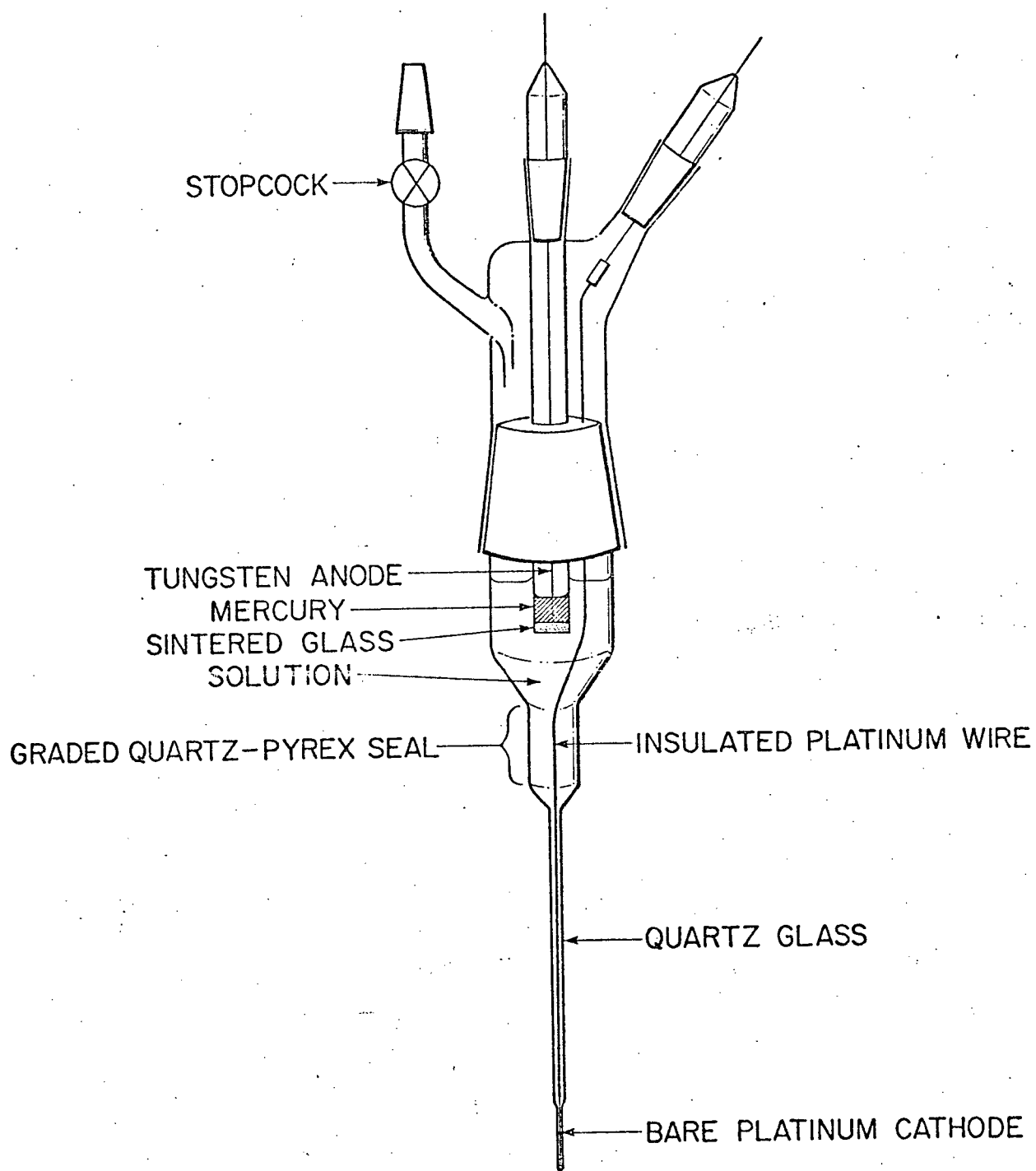


FIG. 1: E.s.r. electrolysis cell

during the reduction of  $P_4S_3$ , a controlled electrolysis was carried out using the apparatus illustrated in Fig.1. This apparatus is designed to fit into a Varian E3 electron spin resonance (e.s.r.) spectrometer so that the generation of a radical can immediately be detected. Sufficient solution is introduced to the cell so that the tungsten anode is immersed. The platinum wire cathode is insulated except at the very tip so that reduction is concentrated in a very small volume. The system was successfully tested by electrolytic generation of the nitrobenzene radical anion. The complete 54-line spectrum of this species was observed.

To test the formation of a radical anion of  $P_4S_3$ , solutions of dry 1:1 benzene-acetonitrile were prepared; these were 0.001 M with respect to  $P_4S_3$  and 0.2 M with respect to tetra-n-butylammonium iodide. Once placed in the electrolysis cell, the solutions were degassed by vacuum so far as was possible. A potential of -1.2 v. was applied to the cell, sufficient to ensure that a reasonable amount of the reduced species would be present, but no e.s.r. spectrum could be obtained. Variation of the applied potential was equally unsuccessful in obtaining a spectrum.

#### ULTRAVIOLET SPECTRUM

Ultraviolet spectra were recorded using a Perkin Elmer Coleman 124 Double Beam Spectrophotometer.

Two solutions were prepared for determination of the molecular extinction coefficients. The first was a  $3.49 \times 10^{-3} \text{ M}$  solution of  $\text{P}_4\text{S}_3$  in Spectrograde chloroform; the second was a  $3.50 \times 10^{-5} \text{ M}$  solution of  $\text{P}_4\text{S}_3$  in 95% ethanol. The UV spectrum of  $\text{P}_4\text{S}_3$  exhibits two peaks in the region 380-200 nm., one at 343 nm. ( $\epsilon=217$ ) and another at 206 nm. ( $\epsilon=1.38 \times 10^4$ ). A concentrated solution of  $\text{P}_4\text{S}_3$  in carbon disulphide did not give any absorption in the region 800-350 nm.

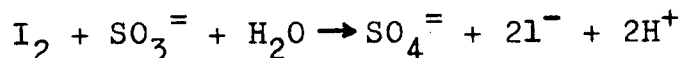
$\text{P}_4\text{S}_3$  with thiophiles:

with  $\text{Na}_2\text{SO}_3$

A solution of  $\text{P}_4\text{S}_3$  (0.6323 gms, 2.87 mmoles) in  $\text{CS}_2$  was stirred vigorously overnight with an aqueous solution containing sodium sulphite (0.6509 gms, 5.17 mmoles). The aqueous layer was separated, and the  $\text{CS}_2$  layer and the reaction vessel were washed with several portions of distilled water. The washings were combined with the bulk of the aqueous layer and this solution was placed in a 100 ml. volumetric flask and diluted to the mark. 25 ml. aliquots were withdrawn, a few mls. of freshly-prepared starch indicator were added and the solution was titrated with 0.0531 M iodine solution. (The standard iodine solution was prepared by adding an accurately weighed portion of  $\text{KIO}_3$  to a solution of KI in dilute sulphuric acid.) The titre of iodine required to neutralize an aliquot was exactly that required assuming that only sulphite ion, and not thiosulphate,

was present.

The reaction of sulphite with iodine is:



whilst that of thiosulphate with iodine is:



Thus formation of any thiosulphate should reduce the volume of standard iodine solution required for neutralization. But as stated previously, the volume of iodine required for neutralization indicates that no significant amounts of thiosulphate had formed.

#### with KCN

A solution of  $\text{P}_4\text{S}_3$  (0.9981 gms, 4.54 mmoles) was stirred vigorously overnight with an aqueous solution of KCN (0.8834 gms, 13.6 mmoles.) The aqueous layer was separated from the  $\text{CS}_2$  layer in a separatory funnel. The  $\text{CS}_2$  layer was washed with water several times and the combined aqueous portions were poured into a volumetric flask and diluted to the mark. To test for the presence of thiocyanate, three aliquots were withdrawn and each treated with 0.5 mls  $\text{Br}_2$  and 1 ml concentrated  $\text{HNO}_3$ . Oxidation apparently proceeded smoothly and the solutions were concentrated to 20 mls. Concentrated HCl was added to destroy the nitrate ions and when no more  $\text{NO}_2$  was evolved, the solutions were neutralized with concentrated NaOH and then slightly acidified with HCl to prevent co-precipitation of phosphates. The solutions

were then diluted to 100 mls. heated to boiling and a hot dilute  $\text{BaCl}_2$  solution was added dropwise until no further precipitation occurred. The precipitated  $\text{BaSO}_4$  was collected on sintered glass, washed with water and acetone and dried at  $100^\circ\text{C}$ . The average weight of  $\text{BaSO}_4$  was  $0.048 \pm 0.003$  gms. This corresponds to removal of  $7.5 \pm 0.4\%$  of the total sulphur atoms available from  $\text{P}_4\text{S}_3$ .

with  $\text{PPh}_3$ :

(i) A mixture of  $\text{P}_4\text{S}_3$  (0.4034 gms, 1.83 mmoles) and  $\text{Ph}_3\text{P}$  (0.4888 gms, 1.83 mmoles) was melted together in a sealed tube at  $100^\circ\text{C}$ . After one hour at this temperature the mixture had turned red-orange. The reaction was left overnight and then the mixture was cooled and the tube broken under nitrogen. This mixture can be spontaneously inflammable so an inert atmosphere was essential. The red material was ground to a fine powder and then extracted with  $\text{CS}_2$ . The  $\text{CS}_2$  solution was put down a column of 80-200 mesh alumina and approximately twenty fractions were collected. A small portion of impure  $\text{P}_4\text{S}_3$  was isolated (m.p.  $164-168^\circ\text{C}$ , lit.  $172-3^\circ\text{C}$ ) but by far the major amount of material melted at  $159-161^\circ\text{C}$ . This material was recrystallized from ethanol to yield needle-like crystals.

Found:      C 73.13%      H 5.33%

$\text{Ph}_3\text{P}=\text{S}$  requires      C 73.45%      H 5.14%

No unreacted  $\text{Ph}_3\text{P}$  was isolated so that it appears the reacting ratio of  $\text{Ph}_3\text{P}$  is considerably more than 1:1.



(ii) In order to obtain a somewhat more pure sample of the red byproduct, the reaction of  $\text{Ph}_3\text{P}$  with  $\text{P}_4\text{S}_3$  was tested in solution. Assuming that this material is polymeric, the use of solvent might help prevent impurities from being trapped in its network.  $\text{Ph}_3\text{P}$  and  $\text{P}_4\text{S}_3$  do not react in boiling  $\text{CS}_2$  or in boiling benzene. In boiling toluene, there is very little reaction as evidenced by formation of the red byproduct. In boiling xylene the reaction is somewhat faster and a very fine red precipitate was obtained. All these reactions were carried out under nitrogen. This red material was then extracted with  $\text{CS}_2$  and then dried in vacuo with heating. Carbon and hydrogen analyses gave values of 1.71%C and 0.51%H. A phosphorus analysis gave a value of 77.21%P. The remainder is presumably sulphur. A mass spectrum of this product showed the base peak to be  $m/e$  124 ( $\text{P}_4^+$ ) but significant peaks were also seen for  $\text{P}_4\text{S}_3$ ,  $\text{PPh}_3$  and  $\text{S=PPh}_3$ .

$\text{P}_4\text{S}_3$  with  $\text{VO}(\text{acac})_2$ :

A mixture of  $\text{P}_4\text{S}_3$  (0.1291 gms, 0.587 mmoles) and bis(acetylacetonato)oxovanadium IV (0.1560 gms, 0.587 mmoles) was heated together in refluxing benzene in a nitrogen atmosphere. After five hours the solution was cooled and poured into pet ether (30-60°). An infrared spectrum of the precipitated blue material was identical to that of pure  $\text{VO}(\text{acac})_2$ . No reaction occurred.

$(\text{NbCl}_5)_2$  with  $\text{P}_4\text{S}_3$ :

Niobium pentachloride dimer (0.6269 gms., 2.35 mmoles) and  $\text{P}_4\text{S}_3$  (0.5165 gms., 2.35 mmoles) were mixed together in benzene in a nitrogen atmosphere. The mixture was heated under reflux overnight, allowed to cool and then transferred to a glove bag. The apparent product, a light brown powder, was collected on sintered glass and then vacuum-dried. The infrared spectrum of this brownish material was essentially the same as that of  $(\text{NbCl}_5)_2$  with the exception of a few minor peaks which were attributed to impurities. Concentration of the red filtrate resulted in precipitation of  $\text{P}_4\text{S}_3$ , identified by its melting point,  $172-3^\circ\text{C}$ .

P<sub>4</sub>S<sub>3</sub> with (PPh<sub>3</sub>)<sub>2</sub>Ni(CO)<sub>2</sub>:

A mixture of P<sub>4</sub>S<sub>3</sub> (0.1207 gms, 0.549 mmoles) and (PPh<sub>3</sub>)<sub>2</sub>Ni(CO)<sub>2</sub> (0.3533 gms, 0.549 mmoles) was heated under reflux in benzene in a nitrogen atmosphere. Almost immediately a black precipitate appeared. The reaction was left overnight and then the solution was filtered. An infrared spectrum of the black material showed only broad weak absorption and no bands that could be assigned to either CO or Ph<sub>3</sub>P. Nixon et al.<sup>29</sup> apparently isolated similar material during the course of their work on Ni(P<sub>4</sub>S<sub>3</sub>)<sub>4</sub>. The brownish filtrate from this reaction was passed through an alumina column. The only compound isolated had a broad melting range. This material was dissolved in carbon tetrachloride and filtered through activated charcoal. White crystals were obtained and an infrared spectrum of these crystals was indistinguishable from that of triphenylphosphine sulphide. As obvious decomposition had occurred, this reaction was not pursued.

P<sub>4</sub>S<sub>3</sub> with SbCl<sub>3</sub>:

(i) A mixture of P<sub>4</sub>S<sub>3</sub> (1.8470 gms, 8.40 mmoles) and SbCl<sub>3</sub> (3.7614 gms, 16.5 mmoles) was heated under reflux in carbon disulphide in a nitrogen atmosphere. After sixty hours there had been no visible reaction.

(ii) A mixture of P<sub>4</sub>S<sub>3</sub> (1.0529 gms, 4.79 mmoles) and SbCl<sub>3</sub> (2.1500 gms, 9.47 mmoles) was fused in vacuo at

110°C. A reddish precipitate appeared in the yellowish liquid. Fusion was continued for about sixty hours. Unreacted  $P_4S_3$  (m.p. 172-4°C) was recovered from the fused mass by washing with  $CHCl_3$ . The fused mass was ground to a fine state and then washed with several portions of  $CS_2$ , in which both starting materials are very soluble. An orange precipitate remained whose infrared spectrum showed only broad weak bands. The orange material did not melt below 270°C but turned black at 90-100°C. It was undoubtedly  $Sb_2S_3$  as the two crystal modifications of  $Sb_2S_3$  are orange and black.

P<sub>4</sub>S<sub>3</sub> with PdCl<sub>2</sub>:

P<sub>4</sub>S<sub>3</sub> (0.2412 gms., 1.1 mmoles) and a suspension of PdCl<sub>2</sub> (0.1914 gms., 1.1 mmoles) in a small volume of 1:1 chloroform-acetone were heated together under nitrogen for thirty-six hours. As no visible reaction had occurred, the solvent mixture was removed by distillation and the reactants fused together in vacuo at 180°C. No visible reaction occurred over a period of 3 hours after which time most of the P<sub>4</sub>S<sub>3</sub> had sublimed out.

P<sub>4</sub>S<sub>3</sub> with (PhCN)<sub>2</sub>PdCl<sub>2</sub>:

Solid P<sub>4</sub>S<sub>3</sub> (0.1492 gms., 0.678 mmoles) was added to a red solution of bis(benzonitrile)palladous chloride (0.1123 gms., 0.339 mmoles) in benzene at room temperature. The solution rapidly turned dark brown and a precipitate of the same colour quickly appeared. The precipitate was collected on sintered glass and washed with several portions of benzene; it was insoluble in all solvents tested and had a broad melting range, with decomposition occurring, of 225-240°C. An infrared spectrum of the product was of very poor quality, but indicated that the benzonitrile groups had been displaced as no C≡N stretching was visible. Broad absorptions were seen centred at 525 cm<sup>-1</sup>, 470 cm<sup>-1</sup> and 390-440 cm<sup>-1</sup>. The latter two peaks are in the general region that uncomplexed P<sub>4</sub>S<sub>3</sub> exhibits absorption. There was no obvious band that could be assigned to palladium-

chlorine stretching even though  $(\text{PhCN})_2\text{PdCl}_2$  has moderate absorption at  $366\text{ cm}^{-1}$  which has been assigned as  $\nu(\text{Pd-Cl})$ . A mass spectrum of the product was of equally poor quality, apparently due to the lack of volatility of the complex. Because of the intractability of this complex, its platinum analogue was prepared instead.

$\text{P}_4\text{S}_3$  with  $(\text{PhCN})_2\text{PtCl}_2$ :

$\text{P}_4\text{S}_3$  (0.1349 gms., 0.613 mmoles) was added to a benzene solution of  $(\text{PhCN})_2\text{PtCl}_2$  (0.1659 gms., 0.307 mmoles). After one hour of heating under reflux in a nitrogen atmosphere a dark red-brown powder had precipitated. The powder was collected on sintered glass, washed several times with benzene and air-dried. A melting point determination was attempted but no change in colour or state was observed up to  $250^\circ\text{C}$ . The infrared spectrum of the product was very similar to that obtained for the analogous palladium complex. Broad absorptions were seen centred at  $520\text{ cm}^{-1}$ ,  $470\text{ cm}^{-1}$  and  $440\text{-}390\text{ cm}^{-1}$ .

No band was seen that could be assigned as Pt-Cl stretching even though  $(\text{PhCN})_2\text{PtCl}_2$  has medium absorption attributable to  $\nu(\text{Pt-Cl})$  at  $340\text{ cm}^{-1}$ . This product too was insoluble in all solvents tested; it was therefore not investigated further.

trans-IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub> with P<sub>4</sub>S<sub>3</sub>: (1:1 mole basis)

P<sub>4</sub>S<sub>3</sub> (0.1087 gms., 0.492 mmoles) and trans-IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub> (0.3835 gms., 0.492 mmoles) were mixed together in about 20 mls. of dry benzene in a nitrogen atmosphere. The solution was heated under reflux for one hour to yield a mass of very small green crystals. The crystals were collected on sintered glass, washed with benzene and dried in vacuo overnight. The product was insoluble in tetrahydrofuran, chloroform, water, acetone, methanol, acetonitrile, benzene, carbon disulphide, xylene and was decomposed by triglyme and sulfolane. The material was extracted for two days with chloroform in a nitrogen atmosphere. Analytical data revealed that nitrogen was present in the sample, presumably due to displacement of carbon monoxide by molecular nitrogen. All further manipulations of this complex were therefore carried out in a helium atmosphere. A fresh sample was extracted with chloroform for two days but none of the complex dissolved. A few soluble impurities were removed and a reasonable analysis was obtained.

Found: C 30.44% H 2.10% P 19.92% S 12.25%  
Cl 8.19% m.p. > 270°C

IrCl<sub>2</sub>(H)(CO)(Ph<sub>3</sub>P)(P<sub>4</sub>S<sub>3</sub>) requires: C 29.45% H 2.07%  
P 20.02% S 12.40% Cl 9.17%

The isolation of the expected product, IrCl(CO)(Ph<sub>3</sub>P)(P<sub>4</sub>S<sub>3</sub>), as its hydrochloride in an 80% yield is somewhat surprising in view of the fact that a maximum

of 50% would be expected had all the chloride originated from  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ .

The infrared spectrum of  $\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$  exhibits  $\text{C}\equiv\text{O}$  stretching at  $2045\text{ cm}^{-1}$ , characteristic phenyl absorption at  $745\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$  as well as numerous bands in the  $400\text{--}550\text{ cm}^{-1}$  region. Attempts to obtain a Raman spectrum were unsuccessful.

$\text{trans-IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  with  $\text{P}_4\text{S}_3$ : (1:2 mole basis)

$\text{P}_4\text{S}_3$  (0.1746 gms., 0.794 mmoles) and  $\text{trans-IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (0.3094 gms., 0.397 mmoles) were dissolved in benzene and heated under reflux for twenty-four hours in a helium atmosphere. The insoluble olive green product was washed with chloroform and carbon disulphide to yield light green material whose infrared spectrum was identical to that of the previously characterized  $\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$ .

$\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$  with  $\text{BCl}_3$ :

$\text{IrCl}_2(\text{H})(\text{CO})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$  (denoted Ir-1) (0.0983 gms., 0.120 mmoles) was suspended in dry benzene that had been denitrogenated by bubbling a stream of helium through the solution. As boron trichloride was bubbled through the suspension, a colour change from green to orange occurred within twenty minutes.  $\text{BCl}_3$  was bubbled through the suspension for an additional hour but no further colour change was observed. Excess  $\text{BCl}_3$  was removed by flushing



the solution with helium. The solid product was collected on sintered glass in a glove bag filled with nitrogen. As the product was dried in vacuo, it slowly changed colour from orange to green. An infrared spectrum confirmed that the green material was Ir-1.

Ir-1 with NaBPh<sub>4</sub>:

A mixture of Ir-1 (0.0896 gms., 0.11 mmoles) and NaBPh<sub>4</sub> (0.0419 gms., 0.11 mmoles) in tetrahydrofuran was shaken for two days. No visible reaction occurred. The mixture was then heated under reflux for two days. The supernatant liquid was filtered off and tested with AgNO<sub>3</sub>. No precipitate formed, indicating the absence of Cl<sup>-</sup> in solution.

Ir-1 with CoCl<sub>2</sub>:

Ir-1 (0.2264 gms., 0.277 mmoles) and CoCl<sub>2</sub> (0.0202 gms., 0.138 mmoles) were heated under reflux overnight in dry methanol in a helium atmosphere. Ir-1 was filtered off washed with acetone and air-dried; it was identified by its infrared spectrum. The filtrate was purple indicating that CoCl<sub>2</sub> was in solution.

Ir-1 with SnCl<sub>2</sub>:

Ir-1 (0.2010 gms., 0.246 mmoles) and SnCl<sub>2</sub>.2H<sub>2</sub>O (0.0523 gms., 0.246 mmoles) were heated under reflux in methanol overnight and in a helium atmosphere. The

mixture was then filtered to remove the green material; it was washed with water and methanol to remove stannous chloride. An infrared spectrum of the green material showed that it was Ir-1.

RhCl(Ph<sub>3</sub>P)<sub>3</sub> with P<sub>4</sub>S<sub>3</sub>:

A mixture of RhCl(Ph<sub>3</sub>P)<sub>3</sub> (0.7138 gms., 0.785 mmoles) and P<sub>4</sub>S<sub>3</sub> (0.1726 gms., 0.785 mmoles) was heated under reflux in benzene in a nitrogen atmosphere. Almost immediately a dark brown precipitate occurred. After several hours, the reaction mixture was cooled and the product was collected on sintered glass in a nitrogen atmosphere.

It was dried in vacuo at 70°C for several hours. The complex did not melt below 250°C nor was it soluble in a wide range of common solvents. The analytical data are as follows: C 26.70% H 2.59% Cl 4.5% P 20.71% S 14.11%. If it is assumed that the remaining weight is due solely to rhodium, then the percentage of Rh in the complex is 31.4%. The analytical data correspond not at all well to any expected composition. The empirical formula which provides the closest fit is Rh<sub>2</sub>(Cl)(Ph<sub>3</sub>P)(P<sub>4</sub>S<sub>3</sub>) for which the following composition is expected: C 29.85%, H 2.07%, Cl 4.9%, P 19.28%, S 13.27%, Rh 28.47%.

The infrared spectrum of this brown product exhibits characteristic phenyl absorption at 740(s), 720(m), 690(s), 517(s) and 505(sh)  $\text{cm}^{-1}$ . There is also broad unresolved absorption of medium intensity between 450 and 420  $\text{cm}^{-1}$ . There is no evidence of Rh-Cl stretching but this vibration is quite weak at 296  $\text{cm}^{-1}$  in  $\text{RhCl}(\text{Ph}_3\text{P})_3$ . Because of the very dark colour of the complex, its Raman spectrum was very weak but distinct bands were seen at 369  $\text{cm}^{-1}$ , 420  $\text{cm}^{-1}$ , and 1003  $\text{cm}^{-1}$ . The 1003  $\text{cm}^{-1}$  band is a phenyl ring vibration. Because of the usual difficulties involved in work with these intractable complexes, no further work was done on this compound.

$\text{RhBr}(\text{Ph}_3\text{P})_3$  with  $\text{P}_4\text{S}_3$ :

A mixture of  $\text{RhBr}(\text{Ph}_3\text{P})_3$  (1.1635 gms., 1.22 mmoles) and  $\text{P}_4\text{S}_3$  (0.2679 gms., 1.22 mmoles) were heated under reflux in benzene in a nitrogen atmosphere. Almost immediately a dark brown precipitate formed. The product was collected on sintered glass and washed with numerous aliquots of  $\text{CS}_2$  in which both starting materials are very soluble. The compound was found to smell of  $\text{H}_2\text{S}$  upon prolonged exposure to the atmosphere. It was therefore stored in a nitrogen atmosphere but quick manipulations were performed in the air. The complex was completely insoluble in all solvents tested and did not melt up to 275°C. It was dried in vacuo at 70°C to remove solvent and the following analytical data were obtained:

C 27.62% H 2.25% Br 10.55%. Assuming that this complex is similar to the analogous chloro- complex, for which more complete analytical data are available, then the empirical formula  $\text{Rh}_2(\text{Br})(\text{Ph}_3\text{P})(\text{P}_4\text{S}_3)$  would require the following proportions: C 28.13% H 1.95% Br 10.42%. An infrared spectrum is very similar to that of the chloro- analogue. Absorption is seen at 740(s), 720(m), 688(s), 517(s) and 492(m)  $\text{cm}^{-1}$ . In addition there is broad unresolved absorption of medium intensity between 420-450  $\text{cm}^{-1}$ . Because of the dark brown colour of this complex, a Raman spectrum was of limited success. Only two relatively broad bands centred at 366 and 420  $\text{cm}^{-1}$  were seen; the normally intense phenyl ring vibration at 1000  $\text{cm}^{-1}$  could not be seen.

$\text{Pt}(\text{Ph}_3\text{P})_4$  with  $\text{P}_4\text{S}_3$ :

A mixture of  $\text{P}_4\text{S}_3$  (0.1662 gms., 0.0755 mmoles) and  $\text{Pt}(\text{Ph}_3\text{P})_4$  (0.9453 gms., 0.0755 mmoles) was heated under reflux overnight in benzene in a nitrogen atmosphere. A pale brown precipitate was filtered off, washed with chloroform and dried in vacuo at 80°C for thirty minutes. This material did not melt up to 255°C nor was it soluble in any of a wide range of solvents. Carbon and hydrogen analyses are as follows: C 28.47% H 2.2%. If one assumes that platinum remains tetracoordinate, then for species  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{P}_4\text{S}_3)_2$  and  $(\text{Ph}_3\text{P})\text{Pt}(\text{P}_4\text{S}_3)_3$ , the carbon

and hydrogen analyses should be C 37.27%, H 2.59% and C 19.34%, H 1.34% respectively. The possibility of a tricoordinate platinum complex cannot be excluded. The complex  $(\text{Ph}_3\text{P})\text{Pt}(\text{P}_4\text{S}_3)_2$  would be expected to have carbon and hydrogen analyses of 24.08% and 1.67% respectively. It is apparent that none of these formulations is correct for the experimental analytical data. When  $\text{Pt}(\text{Ph}_3\text{P})_4$  was reacted under similar conditions with an excess of  $\text{P}_4\text{S}_3$  (1:5 mole ratio), an intractable brown complex of composition 21.47%C and 2.46%H was isolated. The infrared spectra of the two complexes were identical and absorption bands were seen at 744(m), 724(m), 690(s), 524(s), 509(m), 494(sh) and 450-420 (broad)  $\text{cm}^{-1}$ . A Raman spectrum of the first complex was of poor quality but the following peaks were seen: 1030(m), 1002(s), 620(w), 414(w, broad) and 365(w, broad)  $\text{cm}^{-1}$ .

$\text{cis-Pt}(\text{PBu}_3)_2\text{Cl}_2$  with  $\text{P}_4\text{S}_3$ :

$\text{cis-Pt}(\text{PBu}_3)_2\text{Cl}_2$  was prepared according to literature methods<sup>32a</sup>. In a typical reaction,  $\text{cis-Pt}(\text{PBu}_3)_2\text{Cl}_2$  (1.0355 gms., 1.57 mmoles) and  $\text{P}_4\text{S}_3$  (0.3456 gms., 1.57 mmoles) were heated under reflux in benzene in a nitrogen atmosphere. The colour of the solution slowly changes from a pale yellow to a clear red-brown solution. The solvent was then removed under reduced pressure to yield a brown oil; precipitation was effected by addition of very cold ( $-10^\circ\text{C}$ ) ethanol. The resulting pale brown

powder was washed with pet ether or acetone and dried in vacuo. Upon prolonged exposure to air, the complex was observed to smell of  $H_2S$ ; it was therefore stored in vacuo but in general further manipulations were carried out in the air. Attempts to crystallize the product by slow evaporation of the following solvents were unsuccessful: benzene, chloroform/petroleum ether, chloroform/acetone, chloroform/ethanol, carbon disulphide/petroleum ether. The complex is very soluble in chloroform and carbon disulphide, somewhat less soluble in benzene and insoluble in alcohols or petroleum ether. It does not melt up to  $275^{\circ}C$ . Analytical results are as follows: C 17.14% H 3.00% Cl 1.85%  $Pt(PBu_3)(P_4S_3)_2$  requires C 17.20% H 3.22% Cl 0. Attempts to rid this complex of its residual chloride have been hindered by the fact that it is strongly adsorbed by such common column materials as florisil and silica gel. The complex could not be freed from florisil even in boiling chloroform. Experiments are continuing in an attempt to purify this interesting complex. The following spectral data have been obtained:

(i) n.m.r. Attempts to obtain a  $^{31}P$  n.m.r. spectrum were unsuccessful. A  $^1H$  n.m.r. spectrum exhibits methyl resonances centred at  $1.0\delta$  and methylene resonances centred at  $1.6\delta$ . The relative intensities are 1:2 as expected. The proton chemical shifts are identical to those seen in

cis-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. A proton spectrum scanned to 437 did not reveal any resonance that might be attributed to a platinum hydride complex.

(ii) infrared: A nujol mull of Pt(PBu<sub>3</sub>)(P<sub>4</sub>S<sub>3</sub>)<sub>2</sub> showed only weak to medium absorption. Bands associated with P<sub>4</sub>S<sub>3</sub> were seen at 480(w), 438(m), 422(m), and 395(sh) cm<sup>-1</sup>. On the same Perkin-Elmer 457 grating spectrophotometer, the corresponding bands of uncomplexed P<sub>4</sub>S<sub>3</sub> are seen at 478(m), 434(s), 419(s) and 395(sh) cm<sup>-1</sup>. No Pt-Cl stretching was seen; this vibration is very easily seen in both cis- and trans-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.

(iii) A Raman spectrum of Pt(PBu<sub>3</sub>)(P<sub>4</sub>S<sub>3</sub>)<sub>2</sub> was obtained. The following bands were observed in the region 500-160 cm<sup>-1</sup>: 488(w), 446(s), 345(m) and 290(m) cm<sup>-1</sup>. These correspond to Raman bands at 488, 443, 342, and 288 cm<sup>-1</sup> in uncomplexed P<sub>4</sub>S<sub>3</sub>. An additional band at 420 cm<sup>-1</sup> is seen in Pt(PBu<sub>3</sub>)(P<sub>4</sub>S<sub>3</sub>)<sub>2</sub> but it is not sufficiently sharp to permit an exact evaluation. No bands that could be assigned as Pt-P stretching were observed.

P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> with AgSbF<sub>6</sub>:

Cl-P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> was prepared as described in the literature. A dry benzene solution of P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> (0.5647 gms., 1.20 mmoles) was prepared and solid AgSbF<sub>6</sub> (0.8192 gms., 2.40 mmoles)

was added to the solution under a nitrogen atmosphere. An immediate precipitation occurred but the weight of the precipitate (0.8146 gms.) was significantly more than could correspond solely to formation of AgI (0.5596 gms. maximum). An undetermined amount of sharp-smelling gas was also released in this reaction; in addition, an insoluble orange product was isolated. It gave a positive test for antimony after treatment with HCl and was therefore assumed to be  $\text{Sb}_2\text{S}_3$ . The liberated gas was likely  $\text{PF}_3$  and to some degree HF.

$\text{P}_4\text{S}_3\text{I}_2$  with  $\text{NaBPh}_4$ :

$\alpha\text{-P}_4\text{S}_3\text{I}_2$  (0.2280 gms., 0.481 mmoles) and  $\text{NaBPh}_4$  (0.1639 gms., 0.96 mmoles) were stirred together in a 1:1 dry solvent mixture of benzene and acetonitrile under nitrogen. Immediately a wine-red solution resulted. The mixture was heated under reflux overnight and then the solvent was removed under reduced pressure to yield a yellow-orange product. The product was extracted with  $\text{CS}_2$  to yield pale yellow crystals whose melting point ( $171\text{-}2^\circ\text{C}$ ) confirmed that they were  $\text{P}_4\text{S}_3$ . The material which was not extracted by  $\text{CS}_2$  was found to dissolve completely in acetonitrile; removal of acetonitrile gave a pale yellow compound whose infrared spectrum was identical to that of  $\text{NaBPh}_4$  except for a few weak peaks. The initial formation of a red solution is attributed to loss of molecular iodine from  $\text{P}_4\text{S}_3\text{I}_2$ .



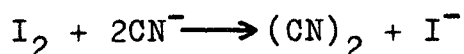
P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> with NaSCN:

Sodium thiocyanate was dried in vacuo with heating prior to use. P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> (0.4750 gms., 1.0 mmoles) and dry NaSCN (0.1815 gms., 2.0 mmoles) were stirred together in dry 1:1 benzene acetonitrile in a nitrogen atmosphere. An immediate red solution formed. The presence of free I<sub>2</sub> was confirmed using KI-starch paper.

The solvent mixture was removed under reduced pressure and extraction of the remaining solids with CS<sub>2</sub> yielding P<sub>4</sub>S<sub>3</sub>, identified by its melting point 171-2°C.

P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> with KCN:

A mixture of P<sub>4</sub>S<sub>3</sub>I<sub>2</sub> (0.3368 gms., 0.71 mmoles) and KCN (0.0190 gms., 1.42 mmoles) were heated under reflux in dry 1:1 benzene-acetonitrile in a nitrogen atmosphere. Initially the solution turned deep red but after having been left overnight, the solution was a pale yellow colour. Removal of solvent gave solid material from which P<sub>4</sub>S<sub>3</sub> (m.p. 172°C, sharp) was extracted with CS<sub>2</sub>. The remaining white product gave no infrared spectrum indicating that it was not KCN. It was however water soluble and was oxidized by an acidic iodate solution to yield a straw-brown colour. The white product is therefore assumed to be KI, formed by oxidation of cyanide ion by molecular iodine:



$P_4S_3I_2$  with  $Mo(CO)_6$ :

- (i) in solution:  $P_4S_3I_2$  (0.1656 gms., 0.35 mmoles) and  $Mo(CO)_6$  (0.0901 gms., 0.35 mmoles) were mixed in degassed benzene and refluxed under nitrogen overnight. A heavy black precipitate had formed. No other solids could be isolated from the reaction mixture. The likelihood of decomposition was so great that the reaction was not pursued.
- (ii) molten:  $P_4S_3I_2$  (0.2387 gms., 0.50 mmoles) and  $Mo(CO)_6$  (0.1317 gms., 0.50 mmoles) were melted together under a slight pressure of nitrogen. After two hours only a small volume of CO had been released and a small amount of solid iodine had sublimed out of the reaction. It would appear therefore that dissociation of  $P_4S_3I_2$  is occurring followed by slow displacement of CO with  $P_4S_3$ .

$P_4S_3I_2$  with  $SbCl_5$ :

A small portion of  $P_4S_3I_2$  was added to an excess of  $SbCl_5$  in dry  $CH_2Cl_2$ . An exothermic reaction was observed and the solution turned dark orange. Continued addition of  $P_4S_3I_2$  gave a dark red solution and formation of white crystals. The solution was tested with KI-starch paper and gave a strong positive test for molecular iodine. The white crystals were not investigated but are undoubtedly the same as those obtained from the decomposition of  $P_4S_3$  with  $SbCl_5$  (assumed to be  $PCl_4^+SbCl_6^-$ ).

$P_4S_3I_2$  with Hg:

A solution of  $P_4S_3I_2$  in  $CS_2$  was added to a small amount of stirred mercury. The reaction was continued overnight in a nitrogen atmosphere at room temperature. A heavy black precipitate had formed; it was insoluble in water, but was soluble in concentrated alkali and in aqua regia. The material is undoubtedly HgS. The reaction solution was concentrated by removal of solvent to yield a foul-smelling yellow oil.

$P_4S_3I_2$  with  $IrCl(CO)(Ph_3P)_2$ :

$P_4S_3I_2$  (0.1843 gms., 0.389 mmoles) and  $IrCl(CO)(Ph_3P)_2$  (0.3028 gms., 0.389 mmoles) were mixed together in benzene and allowed to reflux overnight under helium. Almost immediately an orange precipitate formed; a work-up of the mother liquors revealed that triphenylphosphine sulphide had formed; it was identified by comparison of its infrared spectrum with that of an authentic sample. The orange precipitate was therefore not examined as it was obvious that  $P_4S_3I_2$  had decomposed.

Attempted Polarography of  $P_4S_3I_2$ :

A 0.001 M solution of  $P_4S_3I_2$  in dry 1:1 benzene-acetonitrile was prepared. When sufficient tetra-n-butylammonium iodide to form 0.1 M solution was added, the mixture turned a bright orange. Nonetheless the solution was vigorously deoxygenated and a polarogram of

the solution showed only one wave at -0.95 v. identical to that previously obtained for  $P_4S_3$ . It is apparent therefore that  $P_4S_3I_2$ , under the influence of iodide ion, has dissociated to form  $P_4S_3$  and  $I_2$ . The liberated iodine complexes with free iodide ion to form the  $I_3^-$  ion accounting for the initial colour change.

C. INFRARED & RAMAN SPECTRA OF  $P_4S_3$

Structural mobility is a characteristic of many of the compounds whose chemistry is described in this thesis. The structure of  $P_4S_3$  in the solid state is known<sup>33</sup>, but its cage structure is changed under very mild conditions by reaction with elemental sulphur to give  $P_4S_5$ , and it seemed possible that the structure of  $P_4S_3$  itself might not be the same in solution as in the crystal. A study of its vibrational spectra in the liquid and solid phases was therefore undertaken. Previous work<sup>34</sup> (Gerding, Maarsen, Nobel) had indeed shown some differences between the spectra in the solid and in  $CS_2$  solution, and their work did not entirely agree with the later infrared results of Steger and Blechschmidt<sup>35</sup>. While the present work was being carried out, a more detailed paper<sup>36</sup> appeared, which showed that for the phosphorus sulphides  $P_4S_5$ ,  $P_4S_7$  and  $P_4S_{10}$ , structural changes do indeed take place in solution, probably through migration of sulphur atoms in P=S bonds. In agreement with the present work, no such migrations were detected in  $P_4S_3$ , but there are some differences between the two sets of results, which are reported in detail below.

EXPERIMENTAL:

Commercial  $P_4S_3$  was recrystallized twice from toluene

under nitrogen to yield pale yellow crystals, m.p. 171-172°C (lit.<sup>37</sup> 172-173°C). This was the material used for routine spectra. The spectra obtained with this sample were entirely consistent with those obtained from a highly purified sample. To test the hypothesis that certain bands were due to impurities, a highly purified sample of  $P_4S_3$  was prepared.  $P_4S_3$  was twice recrystallized from toluene under nitrogen; these crystals were ground to a fine powder and treated with boiling distilled water for one hour to remove higher sulphides. This procedure was also carried out under nitrogen to avoid any possible oxidation.  $P_4S_3$  was then collected on sintered glass and washed with ethanol and ether. It was subsequently recrystallized from benzene under nitrogen, powdered and sublimed in vacuo at 130°C. The crystals were collected in a nitrogen atmosphere, powdered and placed in a Raman tube fitted with a B 10 joint.

All Raman spectra were recorded with a Cary 81 spectrometer using 6328A<sup>0</sup> excitation from a Spectra Physics Model 125 He-Ne continuous gas laser. To obtain accurate depolarization ratios, the instrument was calibrated using depolarization ratios previously reported<sup>38</sup> for various bands of  $CS_2$ ,  $CH_2Cl_2$  and  $CCl_4$ . Freshly prepared saturated solutions of  $P_4S_3$  in  $CS_2$  were filtered prior to use in the depolarization measurements.

The infrared spectrum of  $P_4S_3$  was recorded between 625 and  $160\text{ cm}^{-1}$  using a Perkin Elmer Model 310 infrared spectrophotometer. The spectrum was obtained in the solid state as a nujol mull between polythene plates.

#### RESULTS:

The results obtained are given in Table I. The infrared spectrum is weak and does not extend above  $488\text{ cm}^{-1}$ . The measured spectrum agrees with that of Steger and Blechschmidt as far as their frequency range extends, and with that of Gardner with the exception of a possible i.r. band at  $185\text{ cm}^{-1}$ , which Gardner reports as strong in a KBr disc. There are several differences between the present Raman results and those in the literature.

- 1) The weak band reported by Gerding et al. at  $109\text{ cm}^{-1}$  was not observed, possibly because it was obscured by Rayleigh scattering.
- 2) The band at  $146\text{ cm}^{-1}$  in the solid is affected by Rayleigh scattering, but appears to be of moderate intensity, not weak as reported by Gardner.
- 3) Gardner suggests that the bands at  $371\text{ cm}^{-1}$  in the Raman and  $390\text{ cm}^{-1}$  in the infrared are due to impurities. However, these lines appear clearly in the spectra of both normally and highly purified samples, at the same intensities, though purification sharpens the bands. Gardner was able to determine that the band at  $187\text{ cm}^{-1}$

TABLE I (in  $\text{cm}^{-1}$ )

| Symmetry<br>Species | Infrared<br>Spectrum | Melt | Raman                                |                      | Assignment                        |
|---------------------|----------------------|------|--------------------------------------|----------------------|-----------------------------------|
|                     |                      |      | $\text{CS}_2$<br>solution ( $\rho$ ) | Solid<br>(intensity) |                                   |
| E                   |                      |      |                                      | 146 (1.6)            | $\nu_{10}$                        |
| $A_1$               | 185(vw)?             |      |                                      | 184 (0.2)            | $\nu_4$                           |
| E                   | 221(s)               | 224  | 224 (0.72)                           | 219 (1.0)<br>225     | $\nu_9$                           |
| E                   | 287(mw)              | 288  | 288 (0.73)                           | 288 (2.4)            | $\nu_8$                           |
| E                   | 341(mw)              | 341  | 342 (0.68)                           | 342 (4.5)<br>346     | $\nu_7$                           |
| E                   | 390(sh)?             |      |                                      | 371 (0.045)<br>390   | $\nu_6$                           |
| $A_1$               | 419(s)               |      | 424 (0.25)                           | 421 (2.3)            | $\nu_3$                           |
| $A_1$               | 435(s)               | 445  | 445 (0.18)                           | 443 (10)             | $\nu_2$                           |
| $A_1$               | 478(m)               | 486  | 488 (0.33)                           | 488 (2.1)            | $\nu_1$                           |
|                     |                      |      |                                      | 627                  | $\nu_7 + \nu_4$                   |
|                     |                      |      |                                      | 681                  | $2\nu_7$                          |
|                     |                      |      |                                      | 730                  | $\nu_2 + \nu_8$                   |
|                     |                      |      |                                      | 765                  | $\nu_3 + \nu_7$                   |
|                     |                      |      |                                      | 781                  | $\nu_2 + \nu_7$                   |
|                     |                      |      |                                      | 812                  | $\nu_2 + 371$ or<br>$\nu_3 + 391$ |
|                     |                      |      |                                      | 825                  | $\nu_1 + \nu_7$                   |
|                     |                      |      |                                      | 845                  | $2\nu_3$                          |
|                     |                      |      |                                      | 865                  | $\nu_2 + \nu_3$                   |
|                     |                      |      |                                      | 968                  | $2\nu_1$                          |

w - weak  
 m - medium  
 s - strong  
 sh - shoulder  
 $\rho$  - depolarization ratio



is polarized. Polarization measurements are otherwise in agreement.

For the symmetry group  $C_{3v}$ , the fundamental vibrations of  $P_4S_3$  are expected to be of species  $4A_1 + A_2 + 5E$ . The  $A_2$  vibration (antisymmetric torsion) is inactive in both infrared and Raman. The others are all active, the  $A_1$  vibrations being polarized. There is no doubt that the three bands of highest frequency are polarized, and are three of the  $A_1$  bands. The fourth (by Gardner's results) is at  $184\text{ cm}^{-1}$ . The assignment of the bands at 224, 288 and  $342\text{ cm}^{-1}$  ( $CS_2$  solution) is equally certain, not only because of their polarizations, but also because the first and third are split in the solid ( $219/225$  and  $342/346\text{ cm}^{-1}$ ) probably as a result of the low site symmetry ( $C_s$ ). The assignment of the band of lowest frequency is less certain. Since its intensity is "moderate" it is unlikely to be the  $A_2$  vibration made active by local interactions, and such a vibration is unlikely to occur at higher frequencies. The observed band is therefore likely to be of species E. The assignment of the two lines at  $371/390\text{ cm}^{-1}$  as fundamentals is confirmed by the appearance of a weak combination-band at  $812\text{ cm}^{-1}$ , which can only be described in terms of one of these weak bands. It is perhaps significant that Gerding reported weak Raman absorption at  $384\text{ cm}^{-1}$ , intermediate between 371 and  $390\text{ cm}^{-1}$ , and these two bands are here assigned to the fifth E mode, resolved in the solid into  $A'$  and  $A''$ .

components. This explanation obviates the need to assume accidental overlap of A and E modes in the  $488\text{ cm}^{-1}$  band as Gardner does; no splitting could be detected in this band even under the highest resolution ( $0.5\text{ cm}^{-1}$ ). The symmetry species seem therefore to be satisfactorily assigned, and the structure of the  $\text{P}_4\text{S}_3$  cage is therefore unchanged when it is melted or dissolved.

Allocation of the frequencies to particular atomic motions is difficult, because the angular internal coordinates have no clear meaning in a small cage molecule. However some qualitative conclusions seem possible. The band at  $488\text{ cm}^{-1}$  is considered to be polarized and is assigned as symmetric P-P stretching. It is logical that this vibration should occur at the highest frequency; moreover, it gives a value in good agreement with P-P stretching frequencies derived for other compounds which form part of this thesis. These include a value of  $504\text{ cm}^{-1}$  in  $\text{Ph}_2\text{P}_2\text{I}_2$ ,  $478\text{ cm}^{-1}$  in  $(\text{p-FC}_6\text{H}_4\text{PI})_2$ ,  $489\text{ cm}^{-1}$  in  $(\text{m-FC}_6\text{H}_4\text{PI})_2$ ,  $476\text{ cm}^{-1}$  in  $(\text{p-FC}_6\text{H}_4\text{P})_n$ . White phosphorus exhibits infrared absorption at  $465\text{ cm}^{-1}$ . The totally symmetric vibrations at  $443$  and  $421\text{ cm}^{-1}$  are assigned as symmetric P-S stretching. The remaining totally symmetric vibration, assigned by Gardner to the weak  $184\text{ cm}^{-1}$  band, can be considered as a symmetrical deformation of the apical phosphorus. The three E vibrations involving P-P and P-S stretching are con-

sidered to be those at  $390/371\text{ cm}^{-1}$ ,  $346/342\text{ cm}^{-1}$  and  $288\text{ cm}^{-1}$ . The very strong degenerate vibration at  $342\text{ cm}^{-1}$  is most likely due to asymmetric P-S stretching. The lower frequency vibrations at  $225/219\text{ cm}^{-1}$  and  $142\text{ cm}^{-1}$  represent asymmetric deformations.

## II. DISCUSSION

Tetraphosphorus trisulphide has been subjected to a wide variety of chemical and spectroscopic tests.  $P_4S_3$  has been shown to be at most very weakly basic; it cannot be protonated by strong non-oxidizing acids and is decomposed by strong oxidizing acids.  $P_4S_3$  cannot be quaternized with strong alkylating agents and does not complex with such powerful  $\sigma$ -acceptors as  $BF_3$  and  $BCl_3$ . These experiments illustrate forcefully that  $P_4S_3$  is a poor  $\sigma$ -donor with respect to species that can act only as  $\sigma$ -acceptors. The very weak basicity of  $P_4S_3$  is illustrated strikingly in the attempt to perform a polarographic reduction of  $Cl-P_4S_3I_2$ . The fact that  $Cl-P_4S_3I_2$  is decomposed to  $P_4S_3$  and  $I_3^-$  by iodide ion indicates that  $I^-$  is a stronger base towards iodine than is  $P_4S_3$ . Considering that the heat of formation of  $I_3^-$ , as determined<sup>47</sup> by partition experiments with water and carbon tetrachloride, is only -4.34 Kcal/mole, then it is apparent that  $P_4S_3$  is a very weak base indeed.

Although  $P_4S_3$  is thermally stable at  $190^\circ C$ , it is nonetheless very sensitive to both oxidative and reductive stress. While it is perhaps not surprising that  $P_4S_3$  is decomposed by such strong oxidants as  $SO_3$ ,  $SbF_5$ ,  $SbCl_5$ ,  $AsF_5$  and  $N_2O_4$ , it is remarkable that such a weak oxidant as dimethylsulphoxide can exert a similar effect. It is characteristic of elemental sulphur that despite its

profusion of formally unshared electrons, the  $S_8$  ring is mainly susceptible to nucleophilic attack. The fact that aqueous cyanide and triphenylphosphine can slowly attack  $P_4S_3$  indicates similar properties in the cage. The polarographic experiments have been interpreted to give an indication of the stability of the  $P_4S_3$  cage toward reduction. The polarographic wave at  $E_2 = -0.95v.$  is considered to involve a two-electron reduction of  $P_4S_3$  resulting in cleavage of a P-P bond. Other workers<sup>48</sup> have examined a variety of compounds containing P-P bonds, including cyclopolyphosphines, diphosphines, diphosphine mono-sulphides and diphosphine disulphides. In all cases a two-electron irreversible reduction occurs and a P-P bond is cleaved. All compounds examined were observed to exhibit waves in the region -1.5 to -2.5 volts, for example,  $Ph_5P_5$  -1.725v.,  $Ph_4P_2$  -2.050v.,  $Ph_4P_2S_2$  -1.795v.,  $Me_4P_2S_2$  -2.480v. As  $P_4S_3$  exhibits only one wave in the region -0.5 to -2.5 v., this wave is considered to be due to P-P cleavage. The very low value of -0.95v. illustrates the ease with which the  $P_3$  ring can be broken. Although it cannot be said with complete certainty from the simple experiments performed that reduction of  $P_4S_3$  involves cleavage of the  $P_3$  ring, the weight of evidence favours this explanation; the failure to observe an e.s.r. spectrum is also in agreement with such a two-electron reduction. In general therefore,  $P_4S_3$  is stable within fairly narrow limits as defined by oxidation and reduction.

In view of results that  $P_4S_3$  has been shown to be a poor  $\sigma$ -donor, it is not surprising that  $P_4S_3$  does not complex with metals of rather high effective nuclear charge such as  $VO(acac)_2$  and  $SbCl_3$ . In these types of metal complexes, the possibility of synergistic effects is greatly reduced. The importance of such effects is illustrated by the fact that  $P_4S_3$  is found to react with every Group VIII metal complex tested. In these complexes, the metal is in a low- or zero-valent oxidation state and so there is ample opportunity for  $\pi$ -back-donation from filled metal d-orbitals to unfilled  $\pi$ -orbitals in  $P_4S_3$ . The iridium complex isolated,  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$ , exhibits a  $C\equiv O$  stretch at  $2045\text{ cm}^{-1}$  whereas that of the analogous complex  $IrCl_2(H)(CO)(Ph_3P)_2$ <sup>49</sup> is found at  $2024\text{ cm}^{-1}$ . The shift of the  $C\equiv O$  stretching vibration to a higher frequency implies that  $P_4S_3$  is a stronger  $\pi$ -acceptor than is  $Ph_3P$ . The importance of donor-acceptor interactions is supported by the earlier work of Nixon and colleagues<sup>29</sup>:  $P_4S_3$  was found to form metal carbonyl complexes of the type  $\text{cis}-(P_4S_3)_2Mo(CO)_4$  [ $M=Cr, Mo, W$ ] and  $\text{cis}-(P_4S_3)_3M'(CO)_3$  [ $M'=Cr, Mo$ ]. The  $C\equiv O$  stretching frequencies of these complexes lie between those quoted for the related  $P(OMe)_3$  and  $PCl_3$  compounds<sup>50</sup>, substantiating the argument that  $P_4S_3$  is a strong  $\pi$ -acceptor. The formation and stability of  $Pt(PBu_3)(P_4S_3)_2$  is also a good indication of the acceptor properties of  $P_4S_3$ . The well-known<sup>51</sup> strong  $\pi$ -acceptor properties of  $PF_3$  apparently

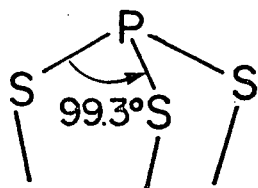
stabilize Pt(0) to the extent that treatment of  $\text{PtCl}_2$  with high pressures of  $\text{PF}_3$  results in reduction of Pt(II) and formation<sup>52</sup> of  $\text{Pt}(\text{PF}_3)_4$  and  $\text{Cl}_2\text{PF}_3$ . Similarly the acceptor properties of  $\text{P}_4\text{S}_3$  are found to stabilize Pt(0) to the extent that cis- $\text{Pt}(\text{PBu}_3)_2\text{Cl}_2$  is reduced to  $\text{Pt}(\text{PBu}_3)(\text{P}_4\text{S}_3)_2$ , presumably with simultaneous formation of  $\text{Cl}_2\text{PBu}_3$  although no attempts were made to isolate this byproduct. Several tricoordinate complexes of platinum (0) are known including  $\text{Pt}(\text{Ph}_3\text{P})_3$ ,  $\text{Pt}(\text{MePPh}_2)_3$ <sup>54</sup> and  $\text{Pt}(\text{PEt}_3)_3$ <sup>59</sup>. The complexes containing triarylphosphines are significantly more stable than the complex of triethylphosphine.

Tris(triethylphosphine)platinum(0) is an extraordinarily strong nucleophile and is known to undergo addition reactions with  $\text{PhCN}$  and  $\text{PhCl}$ , in contrast to  $\text{Pt}(\text{PPh}_3)_3$ .

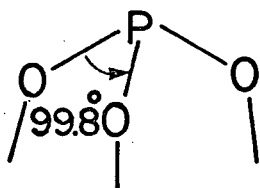
$\text{Pt}(\text{PEt}_3)_3$  will also extract protons from water or ethanol to form the cationic species  $[\text{H Pt}(\text{PEt}_3)_3]^+$ . No rigorous experiments have been performed with  $\text{Pt}(\text{PBu}_3)(\text{P}_4\text{S}_3)_2$ , but it is known that this complex is stable to ethanol and that it is very slow to decompose in moist air; moreover, the smell of  $\text{H}_2\text{S}$  detected indicates that the cause of decomposition may well be hydrolysis of  $\text{P}_4\text{S}_3$ . It is apparent therefore that  $\text{Pt}(\text{PBu}_3)(\text{P}_4\text{S}_3)_2$  more closely resembles the  $\text{Pt}(\text{PPh}_3)_3$  complex, in which increased  $\pi$ -back-donation from platinum to phosphorus decreases chemical reactivity at the metal site. The crystal structure<sup>56</sup> of  $\text{Pt}(\text{PPh}_3)_3$  confirms that  $\pi$ -bonding occurs between platinum and phosphorus; the reported Pt-P bond length of  $2.26\text{\AA}$ <sup>0</sup> is  $0.16\text{\AA}$ <sup>0</sup>.

shorter than the sum of the covalent radii of platinum and phosphorus. A very recent crystal structure<sup>57</sup> of the complex  $P_4S_3Mo(CO)_5$  indicates that metal-phosphorus  $\pi$ -bonding is important in this complex also. The Mo-P bond length of  $2.477(6) \text{ \AA}$  is shorter than the majority of molybdenum-phosphorus bond distances which have been reported<sup>57</sup>, and  $0.23 \text{ \AA}$  shorter than the sum of the covalent radii of Mo and P<sup>58</sup>. As might be expected, the effect of Mo-P  $\pi$ -bonding is seen also in the Mo-C bond lengths, which at  $2.06(2) \text{ \AA}$  are longer than the distances usually found in substituted carbonyls, but are equal to the average values found in  $Mo(CO)_6$ <sup>59</sup> and in  $Mo(CO)_5PF_3$ <sup>60</sup>.

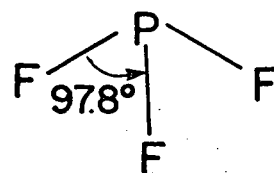
To place  $P_4S_3$  within a wider chemical perspective, it is useful to compare and contrast  $P_4S_3$  with molecules which it appears to resemble either structurally or chemically. Other workers<sup>29,57</sup> have shown that, in the complexes examined to date,  $P_4S_3$  prefers to bond through the apical phosphorus atom. The stereochemistry at this apical phosphorus is illustrated below, along with similar data for  $P_4O_6$  and  $PF_3$ .



Ref. 33



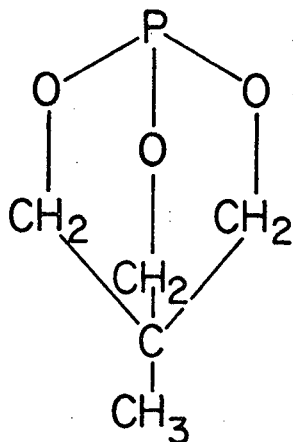
Ref. 61



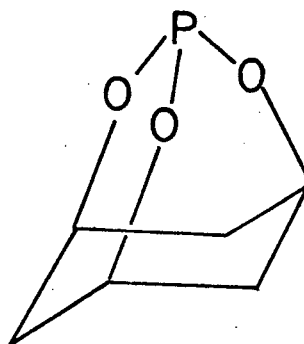
Ref. 62



The configuration at the coordinating phosphorus atoms are very similar and neither  $P_4S_3$  nor  $P_4O_6$  has any substituents so that steric effects should be minimized. A comparison of the donor and acceptor properties of these three compounds should prove useful in attempting to decide what factors are important in the bonding of  $P_4S_3$ . The chemistry of the cage molecule  $P_4O_6$  has not been studied to a great degree, but it has been shown to possess quite strong donor properties. For example, the reaction of  $P_4O_6$  with diborane in solution<sup>63</sup> results in formation of crystalline complexes  $P_4O_6 \cdot 2BH_3$  and  $P_4O_6 \cdot 3BH_3$ . In addition there is evidence presented for the existence of  $P_4O_6 \cdot 4BH_3$  in solution.  $P_4O_6$  will react with an excess of  $Ni(CO)_4$  to produce  $P_4O_6 \cdot 4Ni(CO)_3$  within ten minutes<sup>64</sup>; in this complex all four phosphorus atoms are coordinated to  $Ni(CO)_3$  moieties. The reaction of  $P_4O_6$  with  $BF_3 \cdot Et_2O$  results in decomposition and such products as  $PF_3$ ,  $PF_2OPF_2$  and  $PF_2OEt$  can be isolated<sup>65</sup>. Although information is limited with respect to coordination of  $P_4O_6$ , many papers have been published about the chemistry of the cage bicyclopophosphites, 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane<sup>66</sup> (L) and 2,8,9-trioxa-1-phosphaadamantane<sup>67</sup> (L'). Although the crystal structures of these molecules have not been determined, it is unlikely that the configuration at phosphorus is vastly different from that found in  $P_4O_6$ .



L



L'

Compounds L and L' exhibit very striking donor properties. L will form complexes<sup>68</sup> with  $\text{BH}_3$ ,  $\text{B}_3\text{H}_7$ ,  $\text{BMe}_3$  and  $\text{BF}_3$ ; in addition, it tends to bring out the maximum coordination number in metals. Various examples include  $\text{L}_4\text{CuClO}_4$ <sup>69</sup>,  $\text{L}_4\text{AgClO}_4$ <sup>69</sup>,  $\text{CoL}_6(\text{ClO}_4)_3$ <sup>70</sup> and  $\text{CoL}_5\text{ClO}_4$ <sup>70</sup>. Although L is not sufficiently basic to displace trimethylamine from its borane adduct, L' has been shown<sup>67</sup> to be capable of doing so. The high reactivity of these bicyclopophosphites has been attributed<sup>66</sup> to their minimal steric hindrance, their high symmetry and the increased availability of the phosphorus lone pair electrons. Even though there appears to be no reason, on geometrical considerations, why these factors should be substantially changed in  $\text{P}_4\text{S}_3$ , the diversity of this work has illustrated that donor properties of  $\text{P}_4\text{S}_3$  are strikingly different from those of the bicyclopophosphites L and L'.

On the basis of electronegativities, the phosphorus atoms in  $P_4S_3$  are expected to be much more basic than the phosphorus atoms in  $P_4O_6$  or in the constrained bicyclop-phosphites. The reduced polarity of the P-S bond with respect to P-O bonds is illustrated, for example, by the generally weak infrared absorption of  $P_4S_3$ ; at the same time, the increased polarizability results in extremely strong Raman absorption. Further proof of reduced polarity can be furnished by comparison of the reactions of  $P_4O_6$  and  $P_4S_3$  with water;  $P_4O_6$  is instantly decomposed by cold water with quantitative production of  $H_3PO_3$ ; on the other hand,  $P_4S_3$  is only very slowly decomposed by boiling water. Despite the fact that sulphur is much less electronegative than oxygen, there is no evidence of increased basicity at phosphorus. In fact quite the reverse is observed:  $P_4S_3$  has considerably poorer donor properties than, for example, the constrained bicyclop-phosphites. The most reasonable explanation of the properties of the  $P_4S_3$  cage would appear to involve postulation of significant  $\pi$ -bonding between phosphorus and sulphur, resulting in partial deactivation of the phosphorus lone pairs normally used for  $\sigma$ -donation.

Trivalent phosphorus has been shown in this work (vide infra) and in previous work<sup>71</sup> to be capable of  $\pi$ -donation to its substituents in compounds where (i) substituent atoms or groups are capable of  $\pi$ -acceptance,

and where (ii) substituent atoms or groups capable of  $\pi$ -acceptance are not outweighed by the effects of other more electronegative groups. For example, work with the m- and p-fluorophenyl derivatives<sup>71</sup> of  $\text{PhPMe}_2$  and  $\text{PhPPh}_2$  show that the  $-\text{PMe}_2$  and  $-\text{PPh}_2$  groups are weak but net  $\pi$ -donors to the fluorophenyl groups. However, from similar data obtained with  $\text{PhPF}_2$ , it is apparent that the accumulation of positive charge on phosphorus, resulting from  $\sigma$ -electron withdrawal by fluorine, will increase  $\text{Ph} \rightarrow \text{P}$  and  $\text{F} \rightarrow \text{P}$   $p\pi$ - $d\pi$  acceptor action and generally tend to decrease  $\text{P} \rightarrow \text{Ph}$   $p\pi$ - $p\pi$  donor action<sup>71</sup>. Considering that the electronegativities of carbon and sulphur, based on the Allred-Rochow formula, are 2.50 and 2.44 respectively, it is not unreasonable to suppose, on the basis of inductive effects alone, that the accumulation of positive charge at phosphorus in  $\text{P}_4\text{S}_3$  is not greatly different from that in  $\text{PhPPh}_2$  or  $\text{PhPMe}_2$ . Since it has been shown that the  $-\text{PPh}_2$  and  $-\text{PMe}_2$  moieties are weak  $\pi$ -donors to the attached fluorophenyl rings, it seems reasonable to suppose that the phosphorus atoms in  $\text{P}_4\text{S}_3$  are capable of similar action with respect to sulphur. At the same time, the acceptor properties of sulphur are well-known<sup>72-74</sup>; indeed the second part of this thesis will reveal the important acceptor properties of sulphur in cyclic phosphorus-sulphur systems.

In further attempts to obtain some indication of the factors important in the bonding of this compound, simple Hückel molecular orbital (HMO) calculations have been carried out on  $P_4S_3$  with the following assumptions. The molecular geometry was considered to be that of the determined crystal structure<sup>33</sup>. Interactions were included between 3p-orbitals only, overlap being neglected except for the purpose of estimating resonance integrals. The coulomb integral of phosphorus was taken as 0, and that of sulphur as -0.4eV. Resonance integrals were estimated by multiplying the numerical overlap by -2.0eV., the overlaps for the two standard orientations ( $\sigma$ - and  $\pi$ -) being taken from the tables of Mulliken<sup>75</sup> for the appropriate internuclear distances, the bond asymmetry parameter  $t$  being taken as 0. The orientation of the p-orbitals is shown in Fig. 2. Because 3p $\sigma$ -3p $\sigma$  overlap is still substantial at large internuclear distances, calculations were carried out for (i) interactions between directly bonded atoms and (ii) interactions between all atoms, so including P-P interactions across a sulphur atom, S-S interactions and remote S-P interactions. Typical energy diagrams are shown in Fig. 3. The following general results were obtained:

A. Total binding energies (eV.)

|   |       |
|---|-------|
| Directly bonded atoms only, $\sigma$ -interactions only:      | -17.3 |
| Directly bonded atoms only, $\sigma$ - + $\pi$ -interactions: | -18.4 |
| All bonds, $\sigma$ -interactions only:                       | -17.6 |
| All bonds, $\sigma$ - + $\pi$ -interactions:                  | -18.9 |

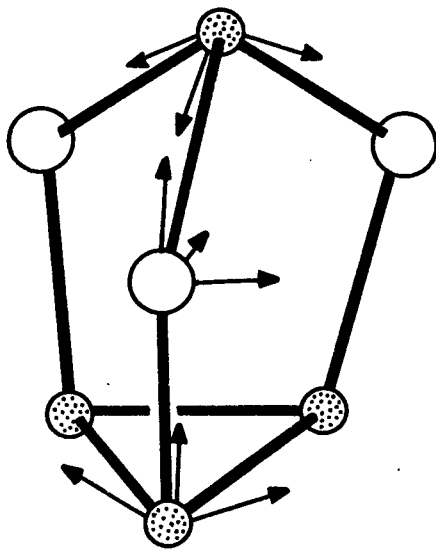


FIG. 2: Orientation of p-orbitals as used in the calculation

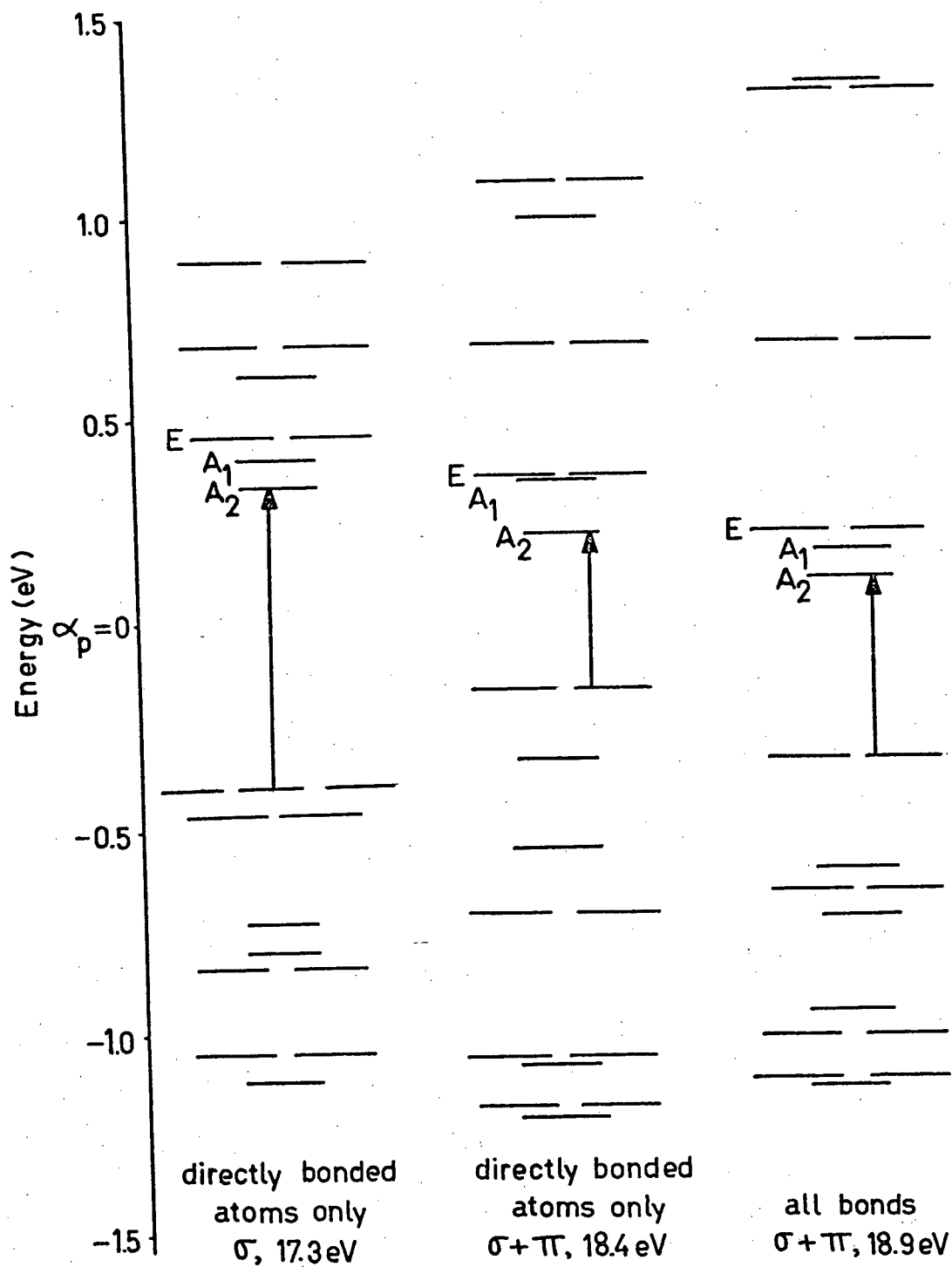


FIG. 3: Energy levels of  $P_4S_3$  as derived by HMO calculations

Inclusion of the more remote bonds has a significant stabilizing effect on the molecule, but the inclusion or exclusion of  $\pi$ -interactions is more important.

B. The total charge density at individual atoms decreases in the order  $S > P_{\text{base}} > P_{\text{apex}}$ . For two cases, the values are as follows

|  | $P_{\text{apex}}$ | S    | $P_{\text{base}}$ |
|--|-------------------|------|-------------------|
| $\sigma$ -interactions of direct bonds:      | 2.15              | 4.54 | 2.75              |
| All bonds, $\sigma$ - + $\pi$ -interactions: | 2.11              | 4.55 | 2.75              |

C. For all the cases considered, the energetically lowest acceptor orbitals are of species  $A_2$ ,  $A_1$ , and E, usually increasing in that order. The energy gap between the highest occupied (always species E) and lowest unoccupied orbitals is dependent mainly on the extent of the  $\pi$ -bonding; the energy gap is (eV.)

|  |       |
|--|-------|
| directly bonded atoms, $\sigma$ -interactions only:      | 0.73  |
| directly bonded atoms, $\sigma$ - + $\pi$ -interactions: | 0.28  |
| All bonds, $\sigma$ -interactions only:                  | 0.51* |
| All bonds, $\sigma$ - + $\pi$ -interactions:             | 0.39  |

\*first acceptor level E;  $A_1$ ,  $A_2$  0.02, 0.03 eV higher

D. All three levels are close enough to the occupied levels to accept electrons significantly, but they do so differently.

(i) The  $A_2$  level is composed of 'tangential' p-orbitals at sulphur, and pairs in the base plane antisymmetric to the symmetry planes of  $C_{3v}$ . The atomic orbitals have



only a  $\pi$ -interaction, and no s, p or d orbital of an apically-attached atom has the right symmetry to interact with it. It is essentially a non-bonding combination which can accept electrons, but can hardly be considered a 'lone-pair'.

(ii) The  $A_1$  combination contains contribution from all three atoms. Energies and charge densities are as follows:

|  | $P_a$ | S    | $P_b$ |
|--|-------|------|-------|
| $\sigma$ -interactions of directly bonded atoms (0.38 eV.)           | 1.06  | 0.22 | 0.09  |
| $\sigma$ - + $\pi$ -interactions of directly bonded atoms (0.34 eV.) | 1.06  | 0.13 | 0.19  |
| All bonds, $\sigma$ - + $\pi$ -interactions (0.16 eV.)               | 0.87  | 0.21 | 0.17  |

Increasing the number of interactions lowers the energy, but the density remains strongly localized on  $P_a$ . This combination is therefore a strong  $\sigma$ -acceptor orbital, of the same symmetry as a  $d_{z^2}$  orbital of an apically attached metal atom.

(iii) The E combination again contains contributions for all atoms, energies and charge densities being given below.

|  | $P_a$ | S    | $P_b$ |
|--|-------|------|-------|
| $\sigma$ -interactions of directly bonded atoms (0.45 eV.)           | 0.50  | 0.42 | 0.38  |
| $\sigma$ - + $\pi$ -interactions of directly bonded atoms (0.35 eV.) | 0.13  | 0.54 | 0.75  |
| All bonds, $\sigma$ - + $\pi$ -interactions (0.19 eV.)               | 0.24  | 0.46 | 0.79  |

Again, inclusion of more interactions lowers the orbital

energy, but has a much bigger effect on the electron distribution of the E orbital than it has on the  $A_1$  orbital; electron density is distributed from  $P_a$  onto S and  $P_b$ . This orbital should be able to accept charge effectively from both the  $d_{xy}$ ,  $d_{x^2-y^2}$  and the  $d_{xz}$ ,  $d_{yz}$  degenerate pairs.

E. Finally it should be emphasized that these are model calculations only, designed to find out the likely most important factors involved in bonding and donor-acceptor interactions. Apart from some obvious limitations arising from the use of the Hückel model and the omission of s-orbitals, there is another inherent in these calculations, in that  $\pi$ -interactions are overestimated for two reasons. (i) The overlap calculations use nodeless 3p-orbitals; omission of the spherical node gives too high a  $\pi$ -overlap. (ii) The  $\pi$ -overlap takes place in a weaker nuclear field than the  $\sigma$ -overlap, so a smaller, but unknown, proportionality constant than -2.0 eV. should be used. It seems unlikely that use of a better value would invalidate the above qualitative conclusions.

This model calculation has revealed the importance of additional through-cage  $\sigma$ - and  $\pi$ -interactions and the observed chemistry of  $P_4S_3$  is consistent with this idea. Treatment of  $P_4S_3$  with a wide variety of oxidants invariably leads to cage breakdown, implying that even

though  $\pi$ -bonding is formally of secondary importance, any removal of electrons from  $P_4S_3$  is sufficient to induce cage fracture. Similarly, experiments with  $\alpha-P_4S_3I_2$  have shown that formation of the cation  $P_4S_3^{2+}$  is not favoured.

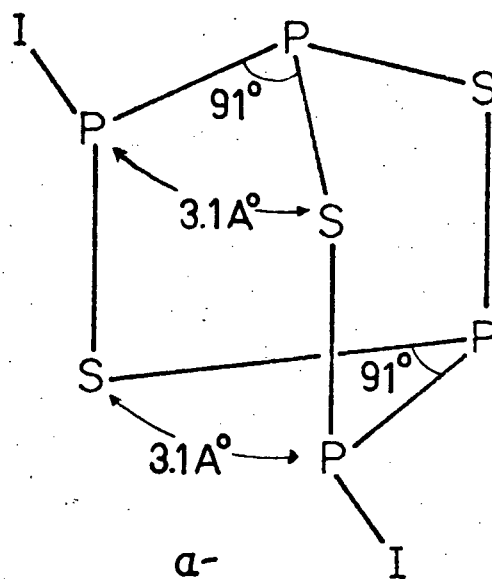
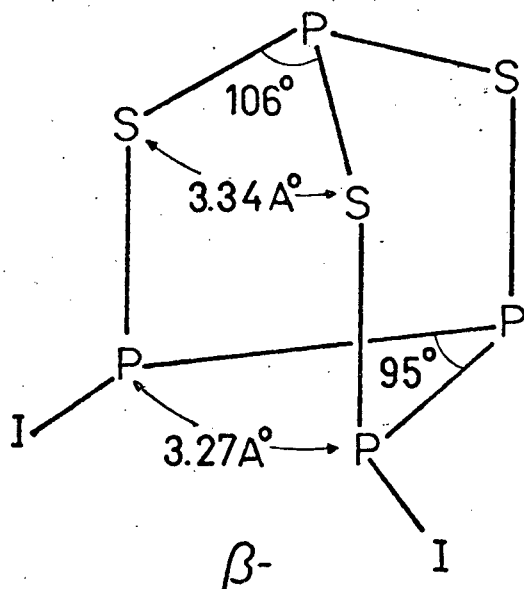
The values of charge density at the apical and basal phosphorus atoms have confirmed that the apical phosphorus atom ( $P_a$ ) is expected to be less basic than the basal phosphorus atoms. Despite the lower charge density at  $P_a$ ,  $P_4S_3$  is known to coordinate through this phosphorus atom. The most likely explanation for this behaviour is that, since it has been established that  $P_4S_3$  will only complex with those metals capable of synergistic interactions,  $\pi$ -density received by  $P_a$  can, in part, be shared equally by the three sulphur atoms to which it is directly bonded. As yet no complexes have been isolated in which it is known that  $P_4S_3$  coordinates through a basal phosphorus atom (or to the entire  $P_3$  ring), but such coordination is entirely possible, particularly in view of the fact that  $P_4$  is known<sup>76</sup> to form coordination complexes.

Since the lowest unoccupied molecular orbitals of  $P_4S_3$  are non-bonding in the case of the  $A_2$  level, or anti-bonding in the case of the  $A_1$  and E levels, acceptor action by  $P_4S_3$  is not expected to strengthen the cage structure. The recently published crystal structure of  $P_4S_3Mo(CO)_5$

is the only transition metal complex of  $P_4S_3$  examined in this way to date. Although the authors<sup>57</sup> argue that all the P-S bond lengths have increased and are therefore weakened with respect to uncomplexed  $P_4S_3$ , the structure determination is unfortunately not sufficiently accurate to claim that significant changes have occurred. Moreover the reported infrared bands belonging to  $P_4S_3$  in this complex (475, 435 and 415  $cm^{-1}$ ) differ very slightly from those of uncomplexed  $P_4S_3$  (478, 434 and 419  $cm^{-1}$  respectively). Such minor changes seem inconsistent with significant bond weakening; also, it has been established that the infrared bands at 434 and 419  $cm^{-1}$  are due to P-S stretching so that these two bands would be expected to change the most if the strength of the P-S bond is altered. The infrared and Raman spectra of  $Pt(PBu_3)(P_4S_3)_2$  confirm that the vibrational frequencies of  $P_4S_3$  change little upon complex formation, in that the largest shift of frequency is only 4  $cm^{-1}$ . The fact that the vibrational frequencies of  $P_4S_3$  change so little upon coordination suggests that the non-bonding  $A_2$  level may be the primary recipient of  $\pi$ -charge from the metal.

The chemistry of  $\alpha-P_4S_3I_2$  is intriguing, and as pointed out earlier, is useful in giving an idea of the base strength of  $P_4S_3$ . The failure to replace iodine by other substituents defies a ready explanation. It has been shown that the  $\pi$ -system in  $P_4S_3$  is of small but crucial

proportions. Iodine has an electronegativity intermediate between those of phosphorus and sulphur and is also capable of participation in  $\pi$ -bonding. It is possible therefore that iodine may be ideally suited to the bonding scheme in  $P_4S_3$  whereas the relatively 'harder' groups such as  $-CN$  and  $-SCN$  are not. The importance of indirect bonding interactions in the  $P_4S_3I_2$  system may well account for the greater stability of  $\alpha$ - $P_4S_3I_2$ . The 'angles of fold' in  $\alpha$ - $P_4S_3I_2$  (shown below<sup>149</sup>) are  $91^\circ$  and the closest intramolecular P-S distances are  $3.1\text{\AA}$ ,  $0.6\text{\AA}$  less than the sum of the van der Waals radii. By contrast the angles of fold in  $\beta$ - $P_4S_3I_2$  are  $95^\circ$  and  $106^\circ$



and the intramolecular P-P and S-S distances are increased to  $3.27$  and  $3.34\text{\AA}$  respectively<sup>32</sup>.

The problem of intractability should be mentioned as other workers<sup>29,77,78</sup> have experienced similar difficulties. The possibility of multiple coordination sites on  $P_4S_3$  could lead to formation of polymeric complexes by way of bridging ligands. The fact that  $P_4$  has been found<sup>76</sup> to form coordination complexes reinforces the idea that the apical phosphorus in  $P_4S_3$  may not be the only site capable of coordination. It is not yet known how  $P_4$  coordinates but Ginsberg and Lindsell<sup>76</sup> favour coordination through the centre of a  $P_3$  ring in view of the bonding scheme that has been proposed<sup>79,101</sup> for  $P_4$ . A similar type of bond through the  $P_3$  ring in  $P_4S_3$  is therefore not unreasonable. There is little chance of polymerization in  $IrCl_2(H)(CO)(Ph_3P)(P_4S_3)$ , but it is worth noting that the analogous triphenylphosphine complex<sup>49</sup>,  $IrCl_2(H)(CO)(Ph_3P)_2$ , is reportedly too insoluble to allow either molecular weight or n.m.r. measurements. Thus, even though complexes may be monomeric, they may also be inherently insoluble.

In conclusion, the belief that sulphur atoms in  $P_4S_3$  act as acceptors leads one to speculate that donor properties will decrease in the higher phosphorus sulphides. On this basis, it is not surprising that the attempts of Nixon *et al.*<sup>29</sup> to prepare a complex of  $P_4S_7$  by heating  $cis-(P_4S_3)_2Mo(CO)_4$  with sulphur were unsuccessful and led only to isolation of free  $P_4S_7$ . Acceptor properties of the higher sulphides would be expected to be greater than

those of  $P_4S_3$  and it has been found<sup>21</sup>, for example, that the higher sulphides are much less stable toward hydrolysis than is  $P_4S_3$ . A recent publication<sup>102</sup> of the reactions of  $P_4S_{10}$  with nucleophiles such as  $N_3^-$  and  $CN^-$  confirms that  $P_4S_{10}$  has strong  $\pi$ -acceptor properties. In addition, these workers were able to prepare the anion  $P_4S_9N^-$  in which a bridging sulphur is replaced by nitrogen. This anion was isolated as its tetra-n-propylammonium salt and could not be methylated with dimethylsulphate, implying that there is considerable electronic delocalization. The failure of  $P_4S_3$  to be quaternized by  $MeSO_3F$  or  $Et_3OBF_4$  is more interesting in light of these experiments.

## PART 2 ORGANOPHOSPHORUS-SULPHUR COMPOUNDS

### I EXPERIMENTAL

#### A. INTRODUCTION:

The problem of intractability which characterized so much of the work involving  $P_4S_3$  led to experiments with cyclic organophosphorus-sulphur compounds instead. The presence of organic groups on phosphorus would be expected to make these compounds more soluble and thus simplify purification and characterization; the presence of such groups eliminates, of course, the possibility of cage formation.

A characteristic feature of the chemistry of the cage phosphorus sulphides is their considerable bond mobility, quite drastic changes in structure occurring under very mild reaction conditions. One of the aims of this work has been to investigate the possibility of similar properties in cyclic organophosphorus-sulphur compounds. A second important aim has been to examine the electronic interactions within these compounds by preparing their meta- and para- fluorophenyl derivatives. An analysis of the  $^{19}F$  n.m.r. chemical shifts according to the methods of Taft et al<sup>80</sup> would be expected to be quite informative. In order to properly interpret these n.m.r. data, and indeed the rest of this work, it is important to know the structures of the compounds



being examined. Although many of the compounds prepared in this section are not new, the structures of several were uncertain or disputed at the time this work was undertaken. These structures have therefore been elucidated using crystallographic and spectroscopic methods. In addition, the spectroscopic properties of those compounds of known structure were examined in greater detail than has been reported previously.

The reaction of phenyldichlorophosphine with hydrogen sulphide was reported by Michaelis<sup>81</sup> to give  $\text{Ph}_2\text{P}_2\text{S}_2$ . No further reports have been made regarding a compound of this composition and since the proposed structure,  $\text{Ph}_2\text{P}(\text{S})-\text{P}=\text{S}$ , did not seem very likely in view of present knowledge, this reaction was reinvestigated. Phenyldichlorophosphine and hydrogen sulphide were heated together in an autoclave at  $95^\circ\text{C}$ ; the solid material isolated from the oily reaction mixture was shown to be cyclotriphenyltriphosphine trisulphide,  $\text{Ph}_3\text{P}_3\text{S}_3$ , by analytical results and by comparison with the minimal data reported in the literature<sup>82-84</sup>. Since the structure of this compound was by no means certain,<sup>82-85</sup>  $\text{Ph}_3\text{P}_3\text{S}_3$  was investigated more fully. The yields of  $\text{Ph}_3\text{P}_3\text{S}_3$  from the Michaelis method were low and large amounts of oily products were formed; therefore, new synthetic routes to  $\text{Ph}_3\text{P}_3\text{S}_3$  were examined. Zinc sulphide and phenyldichlorophosphine did not react; however,

anhydrous sodium sulphide and phenyldichlorophosphine were found to produce  $\text{Ph}_3\text{P}_3\text{S}_3$  in generally better yields than the Michaelis method. As the yields were not consistently high, the method of Maier<sup>82</sup> was used for routine preparation of  $\text{Ph}_3\text{P}_3\text{S}_3$ .

Several attempts were made to prepare alkyl-substituted analogues of  $\text{Ph}_3\text{P}_3\text{S}_3$ , but none were successful. Thus, although ethyldichlorophosphine appeared to react with both  $\text{K}_2\text{S}$  and  $\text{Na}_2\text{S}$ , no product would be isolated from the reaction mixture. Methylphosphine was found to react with sulphur to give methylthionophosphine sulphide dimer,  $\text{Me}_2\text{P}_2\text{S}_4$ ; <sup>86, 87</sup> surprisingly, the same product was isolated when methylphosphine was treated with an equimolar amount of sulphur dichloride.

In an attempt to prepare  $\text{Ph}_3\text{P}_3\text{S}_3$ , anhydrous potassium sulphide was fused with phenyldichlorophosphine. Extraction of the fused mass yielded a small amount of yellow crystals which were identified as tetraphenylcyclo-tetraphosphine monosulphide,  $\text{Ph}_4\text{P}_4\text{S}$ , from analytical data and from a literature report;<sup>82</sup> the reaction of phenylphosphonothioic dichloride,  $\text{PhP(S)Cl}_2$ , with phenylphosphine was also found to produce  $\text{Ph}_4\text{P}_4\text{S}$ . The structure of  $\text{Ph}_4\text{P}_4\text{S}$  proved to be rather difficult to elucidate as the vibrational spectra were inconclusive and a <sup>31</sup>P n.m.r. spectrum was of poor quality. This compound was

therefore structurally characterized by a single crystal X-ray study.

The original work of Maier<sup>82</sup> has shown that it is possible to prepare the higher sulphur-containing cyclic compounds  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$  by reaction of  $\text{Ph}_4\text{P}_4\text{S}$  with the proper stoichiometric amounts of sulphur. To elaborate this work, and to determine the possible reversibility of sulphur addition, the following set of experiments was undertaken. It is known<sup>21</sup> that an excess of iodine is capable of oxidizing  $\text{P}_4\text{S}_3$  to  $\text{P}_4\text{S}_7$ ; similarly, when  $\text{Ph}_3\text{P}_3\text{S}_3$  is treated with an equimolar amount of iodine at room temperature, it is immediately oxidized to phenylthionophosphine sulphide dimer,  $\text{Ph}_2\text{P}_2\text{S}_4$ . On the other hand, the reaction of  $\text{Ph}_4\text{P}_4\text{S}$  with iodine at room temperature results in ring cleavage and the production of 1,2-diphenyl- 1,2-di-iododiphosphine,<sup>88</sup>  $\text{Ph}_2\text{P}_2\text{I}_2$ . Triphenylphosphine has been shown to be capable of removing sulphur from  $\text{P}_4\text{S}_3$ ; similarly, the strong thiophile, tributylphosphine, is capable of removing sulphur from  $\text{Ph}_3\text{P}_3\text{S}_3$  to give  $\text{Ph}_4\text{P}_4\text{S}$ . The remaining sulphur is firmly held however, and can not be removed by tributylphosphine in boiling xylene. The reaction of tributylphosphine,  $\text{Bu}_3\text{P}$ , with  $\text{Ph}_2\text{P}_2\text{S}_4$  has been examined previously,<sup>89</sup> and  $\text{Bu}_3\text{P}$  has been found to cleave the dimer and subsequently add to the monomer giving the species  $\text{Ph}-\overset{\text{S}}{\underset{\text{S}^-}{\text{P}}}^+\text{PBu}_3$ . The desulphurization of

$\text{Ph}_2\text{P}_2\text{S}_4$  was therefore attempted using elemental mercury. At room temperature  $\text{Ph}_2\text{P}_2\text{S}_4$  and mercury slowly react to produce a white, mercury-containing compound; the reaction of  $\text{Ph}_3\text{P}_3\text{S}_3$  with mercury under similar conditions produces the same compound. However, if the reaction is allowed to proceed for a longer period of time, the amount of mercury-containing intermediate decreases and  $\text{Ph}_4\text{P}_4\text{S}$  can be isolated. These experiments, together with those in the literature,<sup>82</sup> illustrate that it is indeed possible, by addition or removal of sulphur, to interconvert between  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$  with remarkable ease.

Several diverse experiments were attempted with the compounds whose chemistry is outlined in this introduction. For example, both  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_4\text{P}_4\text{S}$  were treated with tungsten hexacarbonyl in boiling tetrahydrofuran but neither was found to react. Fusion of  $\text{Ph}_3\text{P}_3\text{S}_3$  with molybdenum hexacarbonyl resulted in decomposition and apparent formation of  $\text{MoS}_2$ . Chlorotris-(triphenylphosphine)rhodium (I) was found to react quickly with  $\text{Ph}_3\text{P}_3\text{S}_3$  but triphenylphosphine sulphide was isolated as a byproduct indicating that ligand rearrangement or decomposition had occurred and therefore the reaction mixture was discarded. In an attempt to prepare a novel type of phosphorus-sulphur compound,

$\text{Ph}_2\text{P}_2\text{I}_2$  was treated with ethanethiol but no reaction was observed. Surprisingly, an attempt to prepare 1,2-diphenyl- 1,2-diiododiphosphine disulphide by the reaction of  $\text{Ph}_2\text{P}_2\text{I}_2$  with elemental sulphur was unsuccessful and both starting materials were recovered unreacted.

To assess electronic interaction within the phosphorus-sulphur rings, and to take advantage of the fact that the phenyl group is apparently a favoured substituent, the  $^{19}\text{F}$  chemical shifts of the meta- and para-fluorophenyl derivatives of  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$  were obtained and analyzed using the established methods of Taft et al.<sup>80</sup> For comparison purposes, the  $^{19}\text{F}$  chemical shifts of the related compounds  $(\text{FC}_6\text{H}_4\text{P})_n$  and  $(\text{FC}_6\text{H}_4\text{PI})_2$  were also obtained.

Finally, the mass spectra of many of these compounds have been obtained; they exhibit numerous molecular fragments which have undergone considerable rearrangement, indicating once again the considerable bond mobility of these compounds. The infrared and Raman spectra of many of these compounds have been recorded; numerous band assignments were possible because of the close similarities of the compounds.

## B. EXPERIMENTAL DETAIL

The organophosphorus-sulphur compounds examined were found to be quite as tractable as was hoped. In general, these compounds are crystalline and are readily soluble in common solvents; they are, however, sensitive to both oxidation and hydrolysis and so virtually all the experiments reported here were carried out in an inert atmosphere. In many cases, satisfactory microanalyses could be obtained only when the analyses were performed in an inert atmosphere, as significant decomposition was found to occur in the brief time required to handle the samples in the atmosphere.

PhPCl<sub>2</sub> with H<sub>2</sub>S: (All manipulations and reactions were performed in vacuo or in a nitrogen atmosphere.)

- (i) PhPCl<sub>2</sub> (15.62 gms., 0.087 moles) was placed in an autoclave in a nitrogen atmosphere; the nitrogen was removed on a vacuum line and approximately 0.087 moles of H<sub>2</sub>S (27 cms. pressure in a 5.65 l. gas bulb) were condensed into the autoclave. The reaction mixture was heated to 95°C overnight and then cooled. The autoclave was opened and a clear pale yellow liquid was removed. A qualitative test for chloride revealed that large amounts of unreacted phenyldichlorophosphine remained. An

excess of  $\text{H}_2\text{S}$  was condensed onto the oil at  $-80^\circ\text{C}$  and allowed to remain there for ten hours. Large rosettes of white crystals slowly appeared at the  $\text{H}_2\text{S}$  - oil interface. The hydrogen sulphide was then pumped off and the crystalline product was collected on sintered glass and washed with cyclohexane. A sample was purified by sublimation in vacuo at  $185^\circ\text{C}$ .

Found: C 51.36% H 3.56% m.p.  $148^\circ\text{C}$  (lit.<sup>82</sup>  $148^\circ\text{C}$ )

$\text{Ph}_3\text{P}_3\text{S}_3$  requires C 51.42% H 3.59%

$^1\text{H}$  n.m.r.: complex multiplet centred at 2.37  
(int. TMS) in  $\text{CS}_2$ .

- (ii)  $\text{PhPCl}_2$  and  $\text{H}_2\text{S}$  were allowed to react together in a carbon tetrachloride solution in the presence of triethylamine. It was hoped that the triethylamine would assist the reaction by removal of the liberated  $\text{HCl}$ . Great difficulty was experienced in removing the last traces of  $\text{Et}_3\text{NH}^+\text{Cl}^-$  from  $\text{Ph}_3\text{P}_3\text{S}_3$  however and this method was discarded.

#### ZnS with $\text{PhPCl}_2$ :

$\text{PhPCl}_2$  (7.6831 gms., 0.0429 moles) and ZnS (4.1790 gms., 0.0429 moles) were mixed together under nitrogen and then heated under reflux at the boiling point of  $\text{PhPCl}_2$ ,  $222^\circ\text{C}$ , for 15 hours. No visible reaction occurred. The mixture was then cooled and diluted with dry  $\text{CCl}_4$ . Unreacted ZnS was removed by filtration and removal of

$\text{CCl}_4$  in vacuo left an oily liquid whose infrared spectrum was identical to that of  $\text{PhPCl}_2$ , proving that no reaction had occurred.

$\text{Na}_2\text{S}$  with  $\text{PhPCl}_2$ :

Anhydrous  $\text{Na}_2\text{S}$  was prepared from the elements in liquid ammonia according to literature methods<sup>90</sup>.  $\text{PhPCl}_2$  (7.43 gms., 0.0415 moles) and  $\text{Na}_2\text{S}$  (3.23 gms., 0.0415 moles) were mixed together in 150 mls. of dry ( $\text{LiAlH}_4$ ) benzene in a nitrogen atmosphere. The mixture was heated to reflux for 24 hours; at that time, a solution spectrum of the reaction mixture showed no reaction. The benzene was removed by distillation and the reactants were fused together at  $222^\circ\text{C}$  for two days. Extraction of this fused mass with benzene resulted in clear solutions from which  $\text{Ph}_3\text{P}_3\text{S}_3$  could be isolated by removal of the solvent.  $\text{Ph}_3\text{P}_3\text{S}_3$  was identified by its infrared spectrum; it was not always formed in good yields, however and the preparation of  $\text{Na}_2\text{S}$  was cumbersome. Consequently the method of Maier<sup>82</sup>, involving the reaction of  $\text{PhPH}_2$  with sulphur, was used for routine preparation of  $\text{Ph}_3\text{P}_3\text{S}_3$ .

$\text{PhPH}_2$  with sulphur:

$\text{PhPH}_2$  was prepared by reduction of  $\text{PhP(S)Cl}_2$  with  $\text{LiAlH}_4$ . Reported literature methods<sup>91</sup> for the preparation of  $\text{PhPH}_2$  usually involve reduction of  $\text{PhPCl}_2$ . However



$\text{PhP(S)Cl}_2$  is much cheaper and very much less obnoxious to handle than is  $\text{PhPCl}_2$ . In a typical reaction,  $\text{LiAlH}_4$  (16.5 gms., 0.44 moles) was added to 150 mls. of dry ( $\text{LiAlH}_4$ ) ether in a nitrogen atmosphere. The slurry was cooled, with stirring, to  $0^\circ\text{C}$  in an ice bath. A solution of  $\text{PhP(S)Cl}_2$  (71 gms., 0.34 moles) in 50 mls. of dry ether was added dropwise to the slurry at such a rate that the temperature of the solution did not exceed  $5^\circ\text{C}$ . When the addition was completed, the reaction mixture was allowed to warm to room temperature and was stirred overnight. Then 200 mls. of 1:1  $\text{HCl}$  were added to the cooled mixture to destroy excess  $\text{LiAlH}_4$ . Stirring was continued until no more gas evolution was observed. The ether layer was separated and dried with anhydrous  $\text{Na}_2\text{SO}_4$  and then distilled to give 25.3 gms. of  $\text{PhPH}_2$  (b.p.  $158-161^\circ\text{C}$ ). Yield: 68.3%

Phenylphosphine and sulphur were reacted together according to the method of Maier<sup>82</sup>. The stoichiometry of the reactants is important as either  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$  or  $\text{Ph}_2\text{P}_2\text{S}_4$  can be obtained depending on the amount of sulphur present.

$\text{EtPCl}_2$  and  $\text{K}_2\text{S}$ :

$\text{EtPCl}_2$  (4.07 gms., 31.1 mmoles) and anhydrous  $\text{K}_2\text{S}$  (3.42 gms., 31.1 mmoles) were mixed together in dry benzene in a nitrogen atmosphere. The reaction mixture was heated under reflux overnight with stirring. Benzene

was then distilled off and the reactants were fused for two days. Extraction of the fused mass with dry benzene yielded only a very small amount of yellow oil which was insufficient for characterization.

EtPCl<sub>2</sub> and Na<sub>2</sub>S:

EtPCl<sub>2</sub> (5.82 gms., 44.4 mmoles) and anhydrous Na<sub>2</sub>S (3.46 gms., 44.4 mmoles) were mixed together in high boiling (60°-120°) dry petroleum ether in a nitrogen atmosphere. The reaction mixture became very hot immediately. The mixture was heated under reflux overnight and then the solution was decanted from the solid residues. Removal of solvent from the filtrate left behind only a trace of oily material whose infrared spectrum showed the presence of EtPCl<sub>2</sub>. On the assumption that the reaction was incomplete, an excess of aluminum chloride (13 gms.) was added to the solid residue followed by a small volume of dry petroleum ether. This mixture was heated under reflux overnight to yield a clear solution and a gum. The solution was decanted and was found to consist entirely of solvent. Because of the possibility that AlCl<sub>3</sub> had complexed EtPCl<sub>2</sub>, instead of removing a chloride ion, the gum was fused at 150°C in vacuo overnight to yield a red-brown mixture. Extraction of this mixture with CH<sub>2</sub>Cl<sub>2</sub> yielded a red-brown oil whose infrared spectrum did not correspond to any likely compound. This reaction was therefore not pursued.

MePH<sub>2</sub> and S<sub>8</sub>:

MePH<sub>2</sub> was prepared by the reduction of MeP(O)(OMe)<sub>2</sub> with LiAlH<sub>4</sub> according to the method of Sheldrick<sup>92</sup> and was purified by trap-to-trap distillation until the vapour pressure (73 mm. at -63°C) was in agreement with literature data<sup>93</sup>. A mixture of benzene (5 mls.) and sulphur (7.33 gms., 28.6 mmoles) was placed in an autoclave and the benzene was degassed by several freeze-thaw cycles. (The amount of sulphur used corresponds to a 1:2 P:S ratio based on the expected yield of MePH<sub>2</sub>.) Methylphosphine was condensed into the autoclave which was then sealed and placed in an oven at 65°C for 12 hours. The autoclave was then cooled to -196°C and opened to the vacuum line; non-condensable gases were removed and then the autoclave was allowed to warm to room temperature. Condensable gases were collected at -196°C; the pressure of these gases at -63°C was almost one atmosphere indicating that the gas mixture was predominantly H<sub>2</sub>S. An infrared spectrum of this gas mixture did reveal bands characteristic<sup>94</sup> of MePH<sub>2</sub> indicating that the reaction had not gone to completion. The autoclave was resealed and then opened in a nitrogen atmosphere. The presence of unreacted sulphur confirmed that the reaction had not gone to completion. The benzene solution was decanted from the unreacted sulphur and the solvent was removed on the vacuum line to give an additional small amount of

sulphur and an oil. The addition of a small volume of  $\text{CS}_2$  caused precipitation of a white powder while at the same time dissolving the residual sulphur. The white powder was filtered off and washed with  $\text{CS}_2$ . It was observed to be extremely hygroscopic and was therefore recrystallized twice from benzene under nitrogen.

Found: C 11.10% H 2.73% m.p. 208-212°C

$\text{Me}_2\text{P}_2\text{S}_4$  requires C 10.91% H 2.82% m.p. 210-212°C (ref.<sup>86</sup>)

$^1\text{H}$  n.m.r.: one doublet at 7.50  $\tau$ ,  $J_{\text{PH}} = 14\text{Hz}$

#### $\text{MePH}_2$ and $\text{SCl}_2$ :

$\text{MePH}_2$  was prepared as described above. Sulphur dichloride,  $\text{SCl}_2$ , was freshly distilled from  $\text{PCl}_3$  to remove the possible impurities of sulphur and chlorine. The weight of  $\text{MePH}_2$  was determined to be 2.16 gms. (46.0 mmoles) on the basis of its pressure (13.7 cms.) in a 5.61 l. gas storage bulb. Therefore the correct stoichiometric amount of  $\text{SCl}_2$  (4.65 gms., 46.0 mmoles) was placed in an autoclave in a small volume of benzene and the solution was degassed by several freeze-thaw cycles. The methylphosphine was then condensed into the autoclave which was sealed and placed in an oven at 85°C for 15 hours. The autoclave was then connected to a vacuum line and cooled to -196°C. Non-condensable gases were pumped off, and condensable gases were transferred to a storage bulb. The autoclave was resealed and then opened in a nitrogen atmosphere; the contents of the autoclave were

washed out with benzene and placed in a flask. The solvent was removed on the vacuum line to give a small amount of white powder which was collected under nitrogen, washed with anhydrous ether and then vacuum-dried. An infrared spectrum of this material was identical to that of the previously identified  $\text{Me}_2\text{P}_2\text{S}_4$ .

$\text{PhPCl}_2$  and  $\text{K}_2\text{S}$ :

Anhydrous  $\text{K}_2\text{S}$  was prepared in the same way as has been described for  $\text{Na}_2\text{S}$ .  $\text{K}_2\text{S}$  (6.74 gms., 61.2 mmoles) and  $\text{PhPCl}_2$  (10.95 gms., 61.2 mmoles) were mixed together in a small volume of benzene in a nitrogen atmosphere. The solvent was then removed by distillation and the reactants fused at  $222^\circ\text{C}$  for 48 hours. The reaction mixture was then extracted with dry benzene overnight. Removal of benzene on the vacuum line yielded a small amount of pale yellow crystals. Large needle-like crystals were obtained by passing nitrogen slowly over a saturated solution of this material in 1:1 chloroform-acetone.

Found: C 62.04% H 4.32% m.p.  $154-6^\circ\text{C}$

$\text{Ph}_4\text{P}_4\text{S}$  requires C 62.07% H 4.31% m.p.  $154-6^\circ\text{C}$  (ref.<sup>82</sup>)

$^1\text{H}$  n.m.r.: two multiplets of equal area centred at 2.55 $\tau$  and 2.83 $\tau$  (in  $\text{CS}_2$ , with TMS as an internal standard.)

$\text{PhPH}_2$  with  $\text{PhP(S)Cl}_2$ :

$\text{PhP(S)Cl}_2$  (3.84 gms., 18.2 mmoles) was added to

$\text{PhPH}_2$  (2.0 gms., 18.2 mmoles) in 5 mls. of dry benzene. The reactants were heated under reflux overnight and then the solvent was removed by distillation. The reactants were heated together for an additional 24 hours to yield a deep yellow solution. Upon cooling, virtually the entire mixture solidified to a mass of pale yellow crystals. The crystals were collected in a nitrogen atmosphere and were identified as  $\text{Ph}_4\text{P}_4\text{S}$  by their melting point and by their infrared spectrum.

$\text{Ph}_3\text{P}_3\text{S}_3$  with  $\text{I}_2$ : (All manipulations performed in a nitrogen atmosphere.)

Iodine (0.287 gms., 1.13 mmoles) was added in one portion to a slurry of  $\text{Ph}_3\text{P}_3\text{S}_3$  (0.4297 gms., 1.13 mmoles) in 15 mls. of benzene. The purple colour of iodine immediately disappeared and a bright yellow solution resulted. The reaction mixture was stirred overnight at room temperature. Removal of benzene on a vacuum line afforded tiny yellow crystals. This product was recrystallized from benzene to give block-shaped crystals.

Found: C 41.96% H 2.91% m.p.  $242^\circ\text{C}$  (sharp)

$\text{Ph}_2\text{P}_2\text{S}_4$  requires C 41.86% H 2.93% m.p.  $233-243^\circ\text{C}$  (ref.<sup>86</sup>)

$\text{Ph}_4\text{P}_4\text{S}$  with  $\text{I}_2$ : (All manipulations performed in a nitrogen atmosphere.)

Iodine (0.4893 gms., 1.93 mmoles) was added in one portion to a slurry of  $\text{Ph}_4\text{P}_4\text{S}$  (0.9136 gms., 1.93 mmoles) in 15 mls. of benzene. The purple colour of iodine

immediately disappeared and a bright yellow-orange solution resulted. The reaction mixture was stirred at room temperature until all the solid iodine had disappeared. Benzene was then removed on a vacuum line to yield a mass of orange material. This material was crystallized from benzene-chloroform (10:1) to yield brilliant orange needles.

Found: C 30.53% H 2.00% m.p. 183-185°C

$\text{Ph}_2\text{P}_2\text{I}_2$  requires C 30.65% H 2.13% m.p. 178-180°C (ref.<sup>95</sup>)

A better yield of  $\text{Ph}_2\text{P}_2\text{I}_2$  was obtained when  $\text{Ph}_4\text{P}_4\text{S}$  and iodine were allowed to react in a 1:2 molar proportion.

$\text{Ph}_3\text{P}_3\text{S}_3$  with  $\text{PBu}_3$ : (All manipulations performed in a nitrogen atmosphere.)

A mixture of  $\text{Ph}_3\text{P}_3\text{S}_3$  (0.3804 gms., 0.904 mmoles) and  $\text{Bu}_3\text{P}$  (0.1826 gms., 0.904 mmoles) was heated under reflux in xylene overnight. The solvent was removed on a vacuum line to yield pale yellow crystals whose infrared spectrum was identical with that of an authentic sample of  $\text{Ph}_4\text{P}_4\text{S}$ .

$\text{Ph}_4\text{P}_4\text{S}$  with  $\text{PBu}_3$ : (All manipulations performed in a nitrogen atmosphere.)

- (i) A mixture of  $\text{Ph}_4\text{P}_4\text{S}$  (0.3752 gms., 0.817 mmoles) and  $\text{PBu}_3$  (0.165 gms., 0.817 mmoles) was dissolved in 15 mls. of benzene and heated under reflux overnight. Removal of the solvent on a vacuum line yielded unreacted  $\text{Ph}_4\text{P}_4\text{S}$  which was identified by its infrared spectrum.

- (ii) The experiment was repeated in boiling xylene to encourage reaction.  $\text{Ph}_4\text{P}_4\text{S}$  (0.2890 gms., 0.630 mmoles) and  $\text{PBU}_3$  (0.1272 gms., 0.630 mmoles) were heated under reflux in xylene for 24 hours but again no reaction occurred. Unreacted  $\text{Ph}_4\text{P}_4\text{S}$  was identified by its infrared spectrum.

$\text{Ph}_3\text{P}_3\text{S}_3$  with Hg: (All manipulations performed in a nitrogen atmosphere.)

- (i) A solution of  $\text{Ph}_3\text{P}_3\text{S}_3$  in benzene was stirred with a large excess of mercury for 16 hours - by which time a small amount of white solid had appeared. This white material and the benzene solution were decanted from the mercury, and then the solid material was isolated by filtration. The solid was vacuum-dried and its infrared spectrum was recorded. Benzene was removed from the filtrate on a vacuum line to yield a clear oil. Addition of a small amount of anhydrous ether caused precipitation of an off-white powder whose infrared spectrum was identical to that of the previously isolated solid. It appears therefore that only one product is obtained under these conditions. The two fractions of solid were combined and extracted with  $\text{CS}_2$ . The white powder obtained in this manner was dried in vacuo

Found: C 28.40% H 2.28% m.p. 210-220°C

The empirical formula of  $\text{Ph}_2\text{P}_2\text{S}_3\text{Hg}$  would require C 28.12% and H 1.97%.



The mass spectrum confirms the presence of elemental mercury but no mercury-containing fragments were observed. The base peak of the mass spectrum occurs at  $m/e$  172 and is considered to be  $\text{PhPS}_2^+$ . The infrared spectrum exhibits strong absorption at 1438, 1090, 760, 742, 672, 628, 607, 569, 495 and  $470\text{ cm}^{-1}$ . The band at  $628\text{ cm}^{-1}$  is the strongest and broadest of the low frequency vibrations and is considered to be due to P=S stretching. The Raman spectrum exhibits strong bands at 1001, 503, 336 and  $263\text{ cm}^{-1}$ . This compound remains incompletely characterized.

- (ii) The reaction of  $\text{Ph}_3\text{P}_3\text{S}_3$  with mercury was repeated as before except that vigorous stirring was continued for 22 hours. A fine white precipitate had again formed and its infrared spectrum was identical to that of the compound isolated in part (i). The benzene filtrate was concentrated by removal of benzene on a vacuum line to yield small yellow crystals. An infrared spectrum of these crystals proved that they were  $\text{Ph}_4\text{P}_4\text{S}$ . It appears, therefore, that the mercury-containing compound may be an intermediate between  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_4\text{P}_4\text{S}$ .

$\text{Ph}_2\text{P}_2\text{S}_4$  with Hg: (All manipulations performed in a nitrogen atmosphere)

A slurry of  $\text{Ph}_2\text{P}_2\text{S}_4$  in benzene was stirred vigorously

with about 3 mls. of mercury until all the  $\text{Ph}_2\text{P}_2\text{S}_4$  had disappeared (about 25 hours.) At the end of this period a heavy precipitate of  $\text{HgS}$  had formed. The reaction mixture was filtered and the solids were washed with  $\text{CS}_2$  (3 x 10 mls.) Solvent was removed from the filtrate on the vacuum line to yield a clear oil; the addition of anhydrous ether induced precipitation of a white solid whose infrared spectrum was identical to that of the mercury-containing compound isolated from the reaction of  $\text{Ph}_3\text{P}_3\text{S}_3$  with mercury.

$\text{Ph}_3\text{P}_3\text{S}_3$  with  $\text{W}(\text{CO})_6$ :

$\text{Ph}_3\text{P}_3\text{S}_3$  (0.0770 gms., 0.183 mmoles) and  $\text{W}(\text{CO})_6$  (0.1303 gms., 0.183 mmoles) were mixed together in tetrahydrofuran and heated under reflux in a nitrogen atmosphere for 36 hours. No visible reaction occurred and an infrared spectrum of the solution showed only one peak at  $1970\text{ cm}^{-1}$ , characteristic of  $\text{W}(\text{CO})_6$ . Therefore no reaction occurred.

$\text{Ph}_4\text{P}_4\text{S}$  with  $\text{W}(\text{CO})_6$ :

$\text{Ph}_4\text{P}_4\text{S}$  (0.0079 gms., 0.017 mmoles) and  $\text{W}(\text{CO})_6$  (0.0059 gms., 0.017 mmoles) were heated under reflux in tetrahydrofuran for 36 hours in a nitrogen atmosphere. At the end of this period, only one strong peak was observed in the  $\text{C}\equiv\text{O}$  stretching region and it was characteristic of  $\text{W}(\text{CO})_6$  implying that no reaction had occurred.

Ph<sub>3</sub>P<sub>3</sub>S<sub>3</sub> with Mo(CO)<sub>6</sub>:

A mixture of Ph<sub>3</sub>P<sub>3</sub>S<sub>3</sub> and Mo(CO)<sub>6</sub> were fused together under nitrogen to give a brownish-black mass. Extraction of this mass with chloroform yielded a solution whose infrared spectrum showed only one C≡O stretch, that characteristic of Mo(CO)<sub>6</sub>, proving that no coordination complex had been formed. The black material observed is undoubtedly MoS<sub>2</sub>.

Ph<sub>3</sub>P<sub>3</sub>S<sub>3</sub> with RhCl(Ph<sub>3</sub>P)<sub>3</sub>: (All manipulations were performed in a nitrogen atmosphere.)

Ph<sub>3</sub>P<sub>3</sub>S<sub>3</sub> (0.1322 gms., 0.315 mmoles) and RhCl(Ph<sub>3</sub>P)<sub>3</sub> (0.2854 gms., 0.315 mmoles) were mixed together in 15 mls. of dry benzene and heated under reflux for 24 hours in a nitrogen atmosphere. At the end of this period, the solution was concentrated in vacuo and an excess of light petroleum ether was added to precipitate a pale brown powder whose infrared spectrum was strongly similar to that of the starting material RhCl(Ph<sub>3</sub>P)<sub>3</sub>. The mother liquors of this mixture were evaporated to dryness to yield crystals whose infrared spectrum was identical to that of an authentic sample of triphenylphosphine sulphide. The formation of Ph<sub>3</sub>P=S implies that Ph<sub>3</sub>P<sub>3</sub>S<sub>3</sub> has either decomposed or rearranged and this reaction was not pursued.

Ph<sub>2</sub>P<sub>2</sub>I<sub>2</sub> with EtSH:

A slurry of Ph<sub>2</sub>P<sub>2</sub>I<sub>2</sub> (0.3016 gms., 0.642 mmoles) in

20 mls. of benzene was stirred under nitrogen at room temperature in a flask fitted with a septum cap. EtSH (95 microlitres, 1.284 mmoles) was added dropwise via syringe through the septum. The mixture was stirred for 1 hour at room temperature and then heated under reflux for ten minutes. Removal of solvent on a vacuum line resulted in precipitation of a yellow solid which was identified as  $\text{Ph}_2\text{P}_2\text{I}_2$  by its melting point and by its Raman spectrum. Therefore no reaction occurred.

$\text{Ph}_2\text{P}_2\text{I}_2$  with  $\text{S}_8$ : (All manipulations were performed in a nitrogen atmosphere.)

$\text{Ph}_2\text{P}_2\text{I}_2$  (0.5949 gms., 1.27 mmoles) and  $\text{S}_8$  (0.0800 gms., 0.313 mmoles) were mixed together in benzene and heated under reflux for 25 hours. Removal of part of the solvent on the vacuum line caused precipitation of  $\text{Ph}_2\text{P}_2\text{I}_2$  which was identified by its melting point and by its Raman spectrum. Elemental sulphur was recovered by concentration of the mother liquors and was identified by its melting point,  $112^\circ\text{C}$ .

FLUOROPHENYL DERIVATIVES: (All manipulations performed in a nitrogen atmosphere.)

The phosphines  $\text{m-FC}_6\text{H}_4\text{PH}_2$  and  $\text{p-FC}_6\text{H}_4\text{PH}_2$  were used to prepare the fluorophenyl derivatives of  $(\text{PhP})_n$ ,  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$ . The fluorophenyl derivatives of  $\text{Ph}_2\text{P}_2\text{I}_2$  were prepared by the reaction of iodine with the fluorophenyl derivatives of  $\text{Ph}_4\text{P}_4\text{S}$  or

(PhP)<sub>n</sub>. The syntheses of *m*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> and *p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> are outlined below.

*p*-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>:

This was prepared from the reaction of fluorobenzene with phosphorus trichloride in the presence of aluminum trichloride according to the method of Schindlbauer<sup>96</sup>.

*p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub>:

The method employed was essentially that of Schindlbauer<sup>97</sup> except that the addition of *p*-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> to an ethereal suspension of LiAlH<sub>4</sub> was carried out in such a manner that the temperature of the reaction mixture did not exceed 0°C. The yield of *p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> (15.3 gms., 50%) is somewhat improved by this method (lit. <sup>97</sup> 45%.) Significant amounts of (*p*-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> are formed during the reduction of *p*-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>, thus accounting for the rather low yield of *p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub>.

The boiling point of *p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> was observed to be 154-158°C (lit.<sup>97</sup> 154-155°C). A <sup>1</sup>H n.m.r. spectrum of *p*-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> shows a doublet for the phosphine hydrogens centred at 6.85 τ, J<sub>PH</sub> = 202 Hz (lit. <sup>100</sup> 199 Hz.) The phenyl resonance is centred at 3.42 p.p.m. A 56.4 MHz <sup>19</sup>F n.m.r. spectrum indicated that only one type of fluorine was present.

(p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub>:

During the preparation of p-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> a white solid was also formed. The solid was removed by filtration and extracted with benzene to give large well-formed crystals. Analytical results revealed the presence of essentially one mole of benzene per mole of cyclopolyphosphine; therefore, the crystals were powdered and dried in vacuo with heating (100°C) for several hours.

Found: C 56.92% H 3.21% m.p. 225-230°

(p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> requires C 57.15% H 3.20%

The p-fluorophenylcyclopolyphosphine system is apparently as complex as that of phenylcyclopolyphosphine<sup>84</sup>.

Schindlbauer<sup>97</sup> reports the melting point of (p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> as 167-169°C when recrystallized from tetrahydrofuran and water, and as 196-197°C when recrystallized from benzene-ethyl acetate. The different value obtained here indicates that several modifications of (p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> exist.

(p-FC<sub>6</sub>H<sub>4</sub>P)<sub>4</sub>S:

p-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> (4.6389 gms., 36.3 mmoles) and sulphur (1.1546 gms., 4.51 mmoles) were reacted together in accordance with the method published by Maier<sup>82</sup>. Solvent was removed in vacuo to yield pale yellow crystals which were recrystallized twice from benzene, powdered and dried at 85°C for 2 hours in vacuo.

Found: C 53.55% H 3.20% m.p. 194-196°C

(p-FC<sub>6</sub>H<sub>4</sub>P)<sub>4</sub>S requires C 53.73% H 2.99%

(p-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub>:

p-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> (4.06 gms., 31.7 mmoles) and sulphur (2.03 gms., 7.93 mmoles) were reacted together in accordance with the method published by Maier<sup>82</sup>. Solvent was removed in vacuo to yield a white powder which was crystallized twice from benzene, powdered and dried in vacuo at 80°C for 3 hours.

Found: C 45.31% H 2.66% m.p. 115-117°C

(p-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub> requires C 45.57% H 2.53%

(p-FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub>:

(p-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub> (0.7610 gms., 1.61 mmoles) and sulphur (0.1528 gms., 0.597 mmoles) were heated under reflux in toluene for 48 hours. Solvent was removed in vacuo to yield yellow crystals which were recrystallized from benzene, powdered and dried in vacuo at 110°C for 2 hours.

Found: C 37.55% H 2.35% m.p. 203-206°C

(p-FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub> requires C 37.89% H 2.11%

(p-FC<sub>6</sub>H<sub>4</sub>PI)<sub>2</sub>:

(p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> (0.5197 gms.) and iodine (0.5220 gms.) were stirred together in benzene at room temperature. The solution was filtered to remove a small amount of unreacted (p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> and then the solvent was removed in vacuo to yield an orange powder which was crystallized from cyclohexane. The crystals were collected on sintered glass and vacuum-dried.

Found: m.p. 156-159°C (lit.<sup>95</sup> 138-140°C)

<sup>31</sup>P n.m.r.: singlet at +21.8 p.p.m. relative to external P<sub>4</sub>O<sub>6</sub>.

The synthesis of m-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> essentially follows the method published by Schindlbauer and Prikozovich<sup>98</sup>.

(NEt<sub>2</sub>)<sub>2</sub>PCl:

This was prepared by the method published by Chantrell et al<sup>99</sup>.

(NEt<sub>2</sub>)<sub>2</sub>P(m-FC<sub>6</sub>H<sub>4</sub>):

m-FC<sub>6</sub>H<sub>4</sub>Li (0.75 moles) was prepared by addition of 0.75 moles of n-BuLi to 0.75 moles of m-FC<sub>6</sub>H<sub>4</sub>Br in 200 mls. of anhydrous ether at -78°C. (NEt<sub>2</sub>)<sub>2</sub>PCl (0.67 moles) was then added dropwise to the solution of m-FC<sub>6</sub>H<sub>4</sub>Li with stirring. Immediately a fine white precipitate of LiCl was formed. Addition of (NEt<sub>2</sub>)<sub>2</sub>PCl was carried out over a period of several hours and then the mixture was allowed to warm to room temperature. LiCl was removed by filtration in the open and the solvents were removed by distillation to yield a dark brown oil. This oil was vacuum-distilled to yield 73 gms. (40%) of colourless (NEt<sub>2</sub>)<sub>2</sub>P(m-FC<sub>6</sub>H<sub>4</sub>), b.p. 140-147°C, 9.5 mm. (lit.<sup>98</sup> b.p. 147°C, 10 mm.)

m-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>:

This was prepared from (NEt<sub>2</sub>)<sub>2</sub>P(m-FC<sub>6</sub>H<sub>4</sub>) by the action



of HCl in accordance with the method published by Schindlbauer<sup>98</sup>. The boiling point of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> was found to be 97-107°C, 20 mm. (lit.<sup>98</sup> 99-101°C, 20 mm.) A 94.1 MHz fluorine spectrum exhibited only one fluorine multiplet.

$\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub>:

The reduction of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> by LiAlH<sub>4</sub> results in a rather low (38%) yield of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> according to the published method<sup>98</sup>. The cause of such a low yield is undoubtedly cyclopolyphosphine formation and therefore the reduction was carried out with a large excess of LiAlH<sub>4</sub>. In addition, the reaction mixture was kept very cold and addition of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> was carried out very slowly.

LiAlH<sub>4</sub> (9.2 gms., 0.242 moles) was added to 250 mls. of dry ether and cooled to -5°C in an ice-salt bath. A solution of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> (43 gms., 0.218 moles) in 75 mls. of dry ether was added dropwise over a period of 8 hours such that the temperature of the reaction solution did not exceed 0°C. The mixture was allowed to warm to room temperature overnight and then excess LiAlH<sub>4</sub> was destroyed by addition of 1:1 hydrochloric acid. The ether layer was then separated, dried with Na<sub>2</sub>SO<sub>4</sub> and the ether was removed by distillation to yield a pale yellow oily liquid. This liquid was vacuum-distilled to yield 16.4 gms. (61%) of  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub>, b.p. 54-56°C, 21 mm. (lit.<sup>98</sup> 52-53°C, 21 mm.)

A  $^1\text{H}$  n.m.r. spectrum of  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  shows that the phosphine hydrogen resonance occurs as a doublet centred at  $6.17\tau$ ,  $J_{\text{PH}} = 202$  Hz. The phenyl resonance occurs as a multiplet centred at  $3.00\tau$ . A 94.1 MHz fluorine n.m.r. spectrum showed that only one type of fluorine was present.

$(\underline{m}\text{-FC}_6\text{H}_4\text{P})_4\text{S}$ :

$\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  (2.5320 gms., 19.8 mmoles) and sulphur (0.6348 gms., 2.48 mmoles) were reacted together in accordance with the method published by Maier<sup>82</sup>. Solvent was removed in vacuo to yield pale yellow crystals which were recrystallized from benzene, powdered and dried in vacuo at  $110^\circ\text{C}$  for 3 hours.

Found: C 53.37% H 2.98% m.p.  $173\text{--}175^\circ\text{C}$

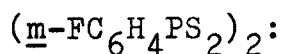
$(\underline{m}\text{-FC}_6\text{H}_4\text{P})_4\text{S}$  requires C 53.73% H 2.99%

$(\underline{m}\text{-FC}_6\text{H}_4\text{PS})_3$ :

$\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  (1.8474 gms., 14.4 mmoles) and sulphur (0.9255 gms., 3.62 mmoles) were reacted together in accordance with the method published by Maier<sup>82</sup>. Solvent was removed in vacuo to yield a white powder which was crystallized from benzene, powdered and dried in vacuo at  $100^\circ$  for 3 hours.

Found: C 45.54% H 2.55% m.p.  $142\text{--}145^\circ\text{C}$

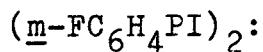
$(\underline{m}\text{-FC}_6\text{H}_4\text{PS})_3$  requires C 45.57% H 2.53%



$\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> (1.8397 gms., 14.4 mmoles) and sulphur (1.38 gms., 5.4 mmoles) were reacted together in accordance with the method published by Maier<sup>82</sup>. Solvent was removed in vacuo to yield yellow crystals which were recrystallized from benzene, powdered and dried in vacuo at 100°C for 3 hours.

Found: C 37.55% H 2.40% m.p. 225-230°C

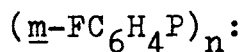
( $\underline{m}$ FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub> requires C 37.89% H 2.11%



( $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>P)<sub>4</sub>S (1.8305 gms., 3.4 mmoles) and iodine (1.7160 gms., 6.8 mmoles) were stirred together in cyclohexane to yield an orange precipitate which was crystallized from cyclohexane and vacuum-dried for 1 hour at room temperature.

Found: C 28.39% H 1.80% m.p. 110-112°C

( $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PI)<sub>2</sub> requires C 28.46% H 1.58%



$\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> (1.22 gms., 8.84 mmoles) and  $\underline{m}$ -FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> (1.74 gms., 8.84 mmoles) were heated under reflux in high boiling (65-110°) petroleum ether to form a white powder. This compound is extremely soluble in all other solvents that have been tested and was therefore difficult to crystallize. A sample of the white powder was dried

in vacuo at 70°C for 7 hours.

Found: C 56.75% H 3.40% m.p. 88-92°C

(m-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> requires C 57.15% H 3.20%

FLUORINE N.M.R. SPECTRA:

The <sup>19</sup>F n.m.r. spectra of these fluorophenyl derivatives were recorded using a Varian XL-100 n.m.r. spectrometer operating at 94.07 MHz. All spectra were recorded using dilute solutions in CDCl<sub>3</sub> with fluorobenzene as an internal standard. Fourier transform techniques were required for the compounds (m-FC<sub>6</sub>H<sub>4</sub>P)<sub>4</sub>S, (m-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub>, (p-FC<sub>6</sub>H<sub>4</sub>P)<sub>4</sub>S, (m-FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub> and (p-FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub>. The <sup>19</sup>F n.m.r. spectrum of (p-FC<sub>6</sub>H<sub>4</sub>P)<sub>n</sub> could not be obtained due to the extreme insolubility of this compound.

Since all the spectra were recorded using solutions in CDCl<sub>3</sub>, the degree of solvent-solute interaction will hopefully be minimized. To obtain some idea of the solvent effect, the fluorine spectra of p-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> and of m-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> were obtained in deuteriochloroform, cyclohexane and benzene. The chemical shifts (relative to internal fluorobenzene) of p-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub> were found to be -7.79 ppm. in CDCl<sub>3</sub>, -7.48 ppm. in C<sub>6</sub>H<sub>12</sub> and -7.52 ppm. in C<sub>6</sub>H<sub>6</sub>.

The fluorine chemical shift of m-FC<sub>6</sub>H<sub>4</sub>PH<sub>2</sub> has been determined<sup>98</sup> to be +0.1 ppm. relative to fluorobenzene. No resolution of these two peaks could be observed in the

three solvents tested. From a comparison of both the half-height widths and the base widths of the resonance observed, the differences in chemical shift between  $m\text{-FC}_6\text{H}_4\text{PH}_2$  and  $\text{FC}_6\text{H}_5$  could not have exceeded 0.2 ppm. in any of the solvents, and was probably less than or equal to 0.1 ppm. The fluorine chemical shifts are tabulated in Table II of the following section.

#### MASS SPECTRA:

All mass spectra were recorded using a Metropolitan Vickers MS 9 mass spectrometer.

#### VIBRATIONAL SPECTRA:

All infrared spectra were recorded in the solid state using a nujol mull. A Perkin-Elmer Model 457 grating infrared spectrophotometer was used for routine spectra (in the  $4000\text{-}250\text{ cm}^{-1}$  region.) The far-infrared spectrum of  $\text{Me}_2\text{P}_2\text{S}_4$  was recorded as a nujol mull using a Perkin-Elmer Model 310 infrared spectrophotometer.

All Raman spectra were recorded with a Cary 81 spectrometer using  $6328\text{\AA}^0$  excitation from a Spectra Physics Model 125 He-Ne continuous gas laser. To obtain accurate depolarization ratios, the instrument was calibrated using depolarization ratios previously reported<sup>38</sup> for various bands of  $\text{CS}_2$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ .

## II. RESULTS AND DISCUSSION

In this section, the systematic chemical relationship between the organic phosphorus-sulphur compounds will be presented and the structures of those compounds which are presently uncertain will be determined. For one of these compounds,  $\text{Ph}_4\text{P}_4\text{S}$ , the structure was determined crystallographically; for other compounds, structures were deduced spectroscopically. Finally, the types of electronic interaction between the basic skeletal structures and their phenyl substituents will be examined by an interpretation of the  $^{19}\text{F}$  n.m.r. results of their *m*- and *p*-fluorophenyl analogues.

As a result of experiments outlined in the previous section, it has been established that organophosphorus-sulphur ring compounds possess the same structural mobility as cage phosphorus-sulphides; the interrelationship between members of the former group is illustrated in Fig. 4, in which starred reactions represent original work. The  $^{19}\text{F}$  n.m.r. chemical shifts of the fluorophenyl derivatives, together with the inductive and resonance parameters deduced from them, are listed in Table II. Spectroscopic data for the compounds  $\text{Ph}_2\text{P}_2\text{I}_2$ ,  $\text{Ph}_3\text{P}_3\text{S}_3$ ,  $\text{Ph}_4\text{P}_4\text{S}$ ,  $\text{Ph}_2\text{P}_2\text{S}_4$  and their fluorophenyl derivatives will now be presented in detail along with similar results for the fluorophenyl derivatives of  $(\text{PhP})_n$ . Much of the

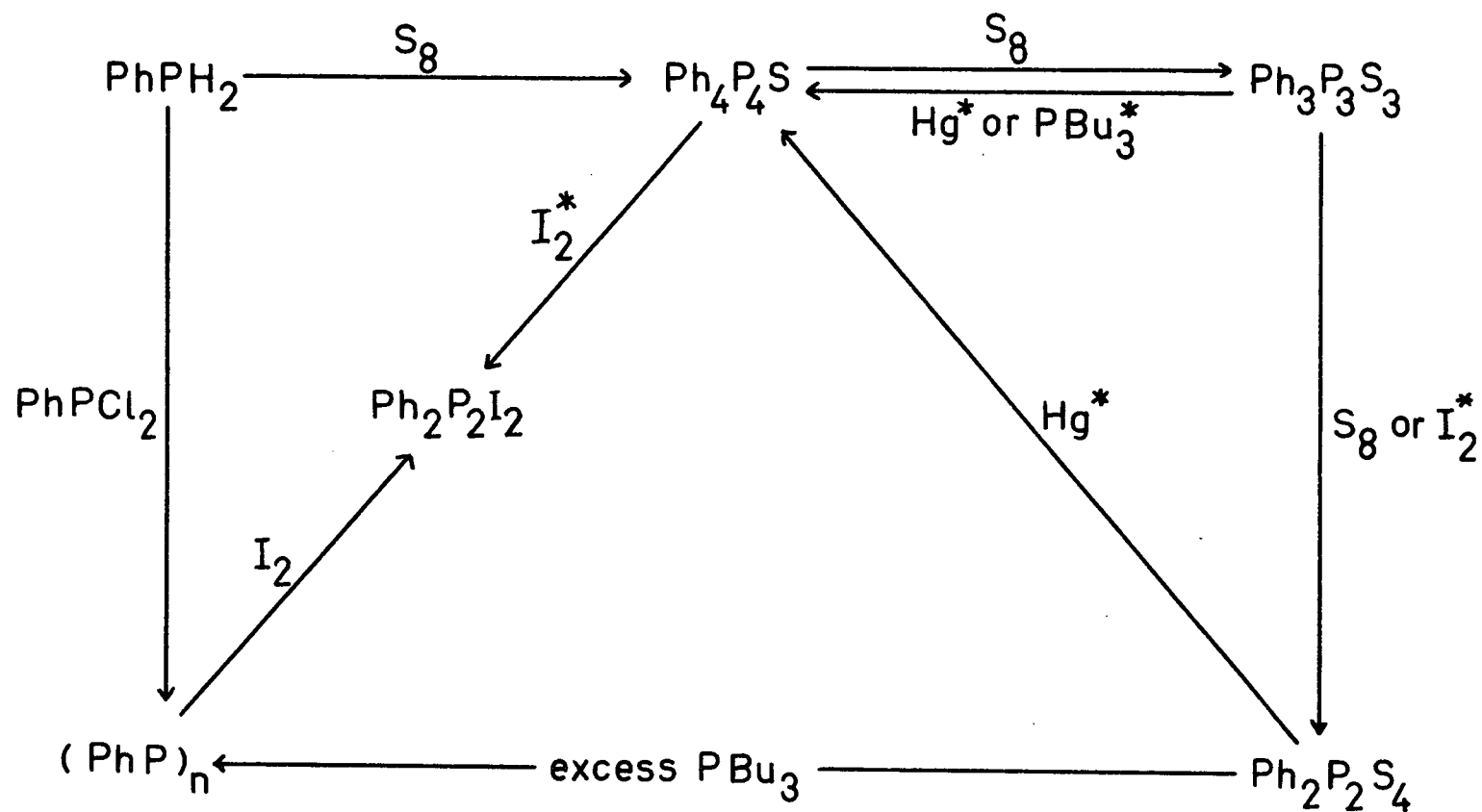


FIG. 4: Reactions of Organophosphorus Sulphur Ring Compounds

TABLE II

SHIELDING PARAMETERS<sup>e</sup> AND TAFT INDUCTIVE AND RESONANCE PARAMETERS

| COMPOUND                                    | $\delta(\underline{m}\text{-F})$ | $\delta(\underline{p}\text{-F})$ | $\sigma_I^a$ | $\sigma_{Ro}^b$ |
|---|----------------------------------|----------------------------------|--------------|-----------------|
| $\text{FC}_6\text{H}_4\text{PH}_2$          | +0.1 <sup>c</sup>                | -0.6 <sup>d</sup>                | +0.07        | +0.02           |
| $\text{FC}_6\text{H}_4\text{PCl}_2$         | -2.8                             | -7.8                             | +0.48        | +0.17           |
| $(\text{FC}_6\text{H}_4\text{P})_4\text{S}$ | -1.14, -1.35                     | -0.60, -0.82                     | +0.25, +0.27 | -0.02           |
| $(\text{FC}_6\text{H}_4\text{PS})_3$        | -2.65(1)                         | -6.9                             | +0.46(1)     | +0.14           |
|   | -2.51(2)                         | -3.7, -3.2                       | +0.44(2)     | +0.04, +0.02    |
| $(\text{FC}_6\text{H}_4\text{PS}_2)_2$      | -3.5                             | -9.4                             | +0.58        | +0.20           |
| $(\text{FC}_6\text{H}_4\text{PI})_2$        | -1.9                             | -6.3                             | +0.35        | +0.15           |
| $(\text{FC}_6\text{H}_4\text{P})_n$         | -1.65, -1.39                     | unobtainable                     | +0.32, +0.26 | ---             |

$$a \quad \sigma_I = 0.1409(0.6 - \int H^{m-x})$$

$$b \quad \sigma_{Ro} = 0.0339(\int H^{m-x} - \int H^{p-x})$$

c from ref. 98, in  $\text{CFCl}_3$

d from ref. 97, in benzene

e p.p.m. relative to internal fluorobenzene, in  $\text{CDCl}_3$



spectroscopic work presented here involves vibrational assignments derived from infrared and Raman spectra. The assignments were made for the simplest molecules first and were then extended to the more complicated molecules. In this way, frequency ranges of various characteristic groupings were obtained and the vibrational spectroscopic work could be used to confirm the structures of various compounds.

Much of the difficulty involved in making vibrational assignments has been to eliminate the internal vibrations of the phenyl groups. There are numerous low-frequency vibrations which are of similar energy to those of, for example, P=S, P-S or P-P bonds. To simplify these assignments, the vibrational spectra of  $\text{PhPH}_2$  and  $\text{PhPCl}_2$  (Table VI) were examined. With the aid of these two compounds, it has been possible to determine many of the lower-frequency phenyl vibrations. Table IV lists the higher-frequency infrared vibrations characteristic of phenyl and fluorophenyl groups. These vibrations were found in virtually all the phenyl and fluorophenyl derivatives of the compounds examined; consequently, this list will not be repeated for each compound discussed.

Whiffen<sup>103</sup> has examined the vibrations of monosubstituted phenyl groups, denoted  $\text{C}_6\text{H}_5\text{X}$ , and has found that

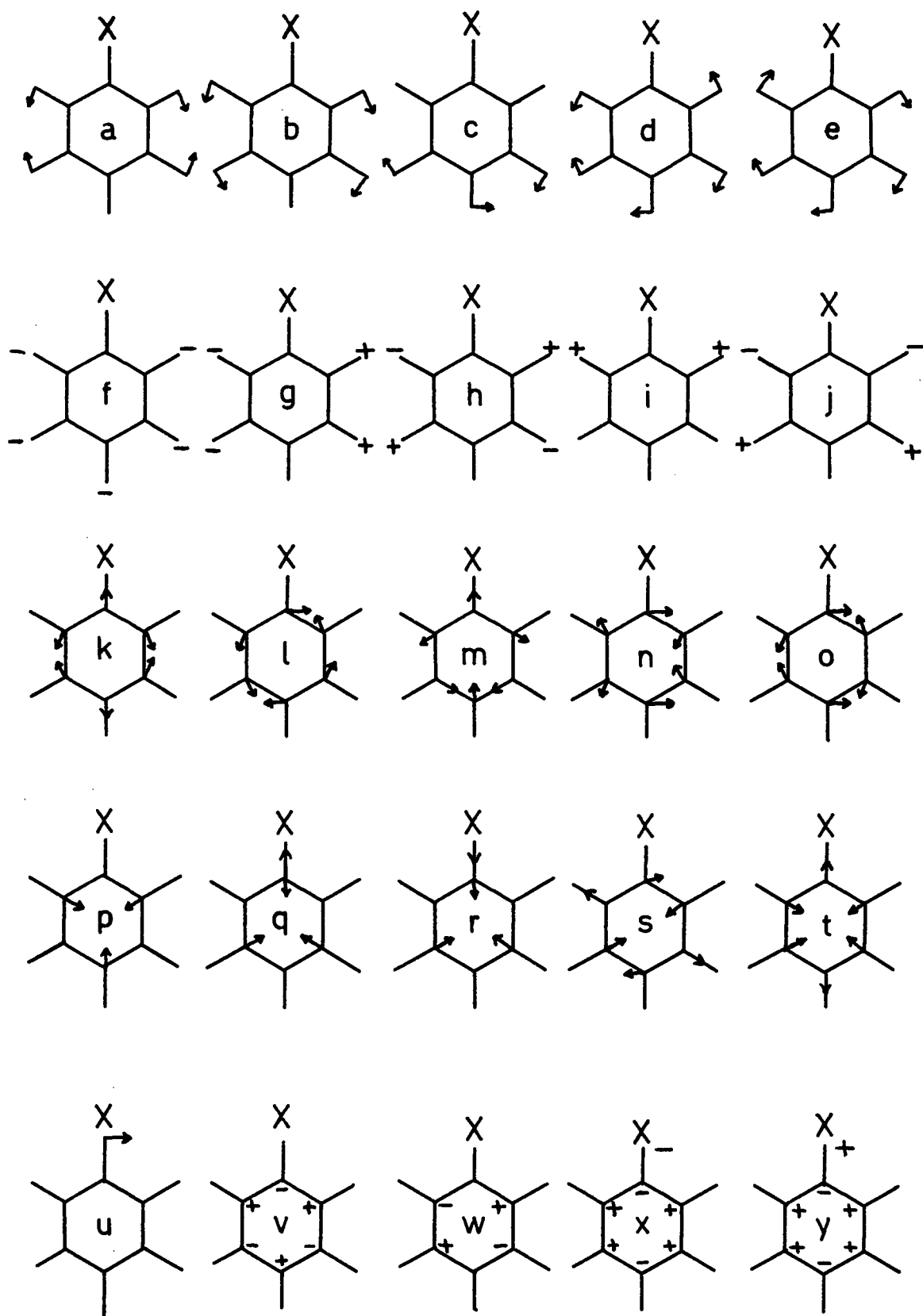


FIG. 5: Vibrations of a monosubstituted phenyl group<sup>103</sup>

TABLE IV

CHARACTERISTIC INFRARED FREQUENCIES OF PHENYL AND FLUOROPHENYL GROUPS

| <u>PHENYL</u>                     |                                 | <u>m-FLUOROPHENYL</u>             |                                 |
|-----------------------------------|---------------------------------|-----------------------------------|---------------------------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ ) | ASSIGNMENT                      | FREQUENCY<br>( $\text{cm}^{-1}$ ) | ASSIGNMENT                      |
| 1570(var.)                        | aromatic C-C stretch            | 1595(var.)                        | aromatic C-C stretch            |
| 1430(sharp)                       | aromatic C-C stretch            | 1575(s)                           | aromatic C-C stretch            |
| 1270(sharp)                       | C-H in-plane bend               | 1470(s)                           | aromatic C-C stretch            |
| 1180(var.)                        | C-H in-plane bend               | 1420(s)                           | aromatic C-C stretch            |
| 996(sharp)                        | ring vibration                  | 1265(sharp)                       | C-H in-plane bend               |
| 800(broad)                        | C-H out-of-plane bend           | 1220(s)                           | C-F stretching                  |
| 740(sharp,s)                      | C-H out-of-plane bend           | 1160(var.)                        | C-H in-plane bend               |
| 680(s)                            | out-of-plane ring deformation   | 1090(var.)                        | C-H in-plane bend               |
| 465(m-s)                          | out-of-plane skeletal vibration | 1000(sharp)                       | ring vibration                  |
|                                   |                                 | 900(sharp)                        |                                 |
|                                   |                                 | 870(vs)                           | C-H out-of-plane bend           |
|                                   |                                 | 780(vs)                           | C-H out-of-plane bend           |
|                                   |                                 | 675(vs)                           | out-of-plane ring deformation   |
|                                   |                                 | 520(ms)                           | out-of-plane skeletal vibration |
|                                   |                                 | 440(ms)                           | out-of-plane skeletal vibration |

var.=variable; v=very; m=medium; s=strong; w=weak

(continued overleaf)

TABLE IV(cont.)

p-FLUOROPHENYL

| FREQUENCY<br>(cm <sup>-1</sup> ) | ASSIGNMENT                      |
|----------------------------------|---------------------------------|
| 1580(s)                          | aromatic C-C stretch            |
| 1490(s)                          | aromatic C-C stretch            |
| 1390(m)                          |                                 |
| 1298(m)                          | C-H in-plane bend               |
| 1240(vs)                         | C-F stretching                  |
| 1165(vs)                         | C-H in-plane bend               |
| 1080,1090(m)                     | C-H in-plane bend               |
| 1020(w)                          | C-H in-plane bend               |
| 820(vs)                          | C-H out-of-plane bend           |
| 510(ms)                          | out-of-plane skeletal vibration |
| 405(w)                           | out-of-plane skeletal vibration |

there are six vibrational modes in which the substituent X moves with appreciable amplitude and consequently, these frequencies are sensitive to the mass of X (See Fig. 5.) Of these six X-sensitive vibrations, three belong to the totally symmetric  $A_1$  class and will give rise to polarized Raman lines; Whiffen denotes these vibrations as X-sens.(q), X-sens.(r) and X-sens.(t). All these modes involve some degree of C-X stretching, and it is therefore not justifiable to consider any of these vibrations as "the" C-X stretching frequency. The fourth substituent-sensitive vibration, X-sens.(u), belongs to the  $B_1$  class and may be called the C-X in-plane deformation mode. The remaining frequencies, denoted X-sens.(x) and X-sens.(y), belong to the  $B_2$  class and may be considered as out-of-plane deformation modes.

Since these X-sensitive vibrations involve considerable motion of the substituent atom, it is reasonable to assume that at least some of these vibrations might be a function not only of X, but also of any additional groups attached to X. To test this hypothesis, the Raman spectra of  $\text{PhPH}_2$  and  $\text{PhPCl}_2$  were analyzed. The vibrational assignments of  $\text{PhPH}_2$ , as reported by Amster and Colthup<sup>104</sup>, are in complete agreement with the work of Whiffen; in fact, the phenyl frequencies are easy to assign as they are very close to those reported for chlorobenzene, no doubt because of the similar masses of the chlorine atom and the  $\text{PH}_2$

group.  $\text{PhPCl}_2$  is inadequately described in the literature with respect to polarization measurements; therefore, these data were obtained and are presented in Table VI. Other workers<sup>105-107</sup> have examined the infrared and Raman spectra of  $\text{PhPCl}_2$  but their assignments have suffered from an absence of polarization data; for example, Goubeau et al.<sup>106</sup> assigned the apparently polarized band at  $455\text{ cm}^{-1}$  as asymmetric  $\text{PCl}_2$  stretching. The strongest peaks in the Raman spectrum of  $\text{PhPCl}_2$  are assigned to various P-Cl modes. The very strong absorption at  $504\text{ cm}^{-1}$  is obviously due to symmetric  $\text{PCl}_2$  stretching. Green and Kynaston<sup>108</sup> assigned the strong depolarized band at  $293\text{ cm}^{-1}$  as  $\text{PCl}_2$  wagging; the same workers considered the depolarized band at  $190\text{ cm}^{-1}$  to be a  $\text{PCl}_2$  scissor vibration. Such a vibration would be expected to give rise to a polarized band, however, and this vibration is therefore more likely to be a  $\text{PCl}_2$  rocking vibration. Frankiss and Miller<sup>109</sup> have examined the vibrational spectra of  $\text{P}_2\text{Cl}_4$  and have assigned a depolarized band at  $189\text{ cm}^{-1}$  as a  $\text{PCl}_2$  rocking vibration. Having corrected and eliminated  $\text{PCl}_2$  vibrational modes, the remaining vibrations can be considered to be due to the phenyl group. By comparison with the spectrum of  $\text{PhPH}_2$ , several obvious assignments can be made. The band at  $619\text{ cm}^{-1}$  in  $\text{PhPCl}_2$ , and that at  $622\text{ cm}^{-1}$  in  $\text{PhPH}_2$ , is obviously Whiffen's vibration(s), a C-C-C in-plane ring deformation (which is not substituent-sensitive.) The polarized band at  $693\text{ cm}^{-1}$  in  $\text{PhPH}_2$  correlates with

TABLE VI

RAMAN SPECTRAL RESULTS

| $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$ in $\text{CS}_2$ |              | neat $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$ |                       |                        |            |
|---|--------------|---|-----------------------|------------------------|------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ )                                   | $\rho$       | FREQUENCY<br>( $\text{cm}^{-1}$ )                     | RELATIVE<br>INTENSITY | $\rho$                 | ASSIGNMENT |
| 675   | not measured | 680   | 10                    | 0.18(p)                | P-sens.(r) |
| 567   | 0.65(dp)     | 539   | 1.2                   | 0.69(dp)               |            |
| 523   | 0.38(p?)     | 523   | 4.3                   | 0.31(p?)               | F-sens.(t) |
| 486   | 0.35(p?)     | 433   | 0.8                   | $\sim 0.3(\text{p??})$ | see text   |
| 431   | 0.35(p?)     | 384   | 10                    | 0.18(p)                | P-sens.(t) |
| 343   | 0.28(p)      | 245   | 4.2                   | 0.75(dp)               | F-sens.(x) |
| 245   | 0.77(dp)     | 217   | 1.2                   | 0.63(dp?)              |            |
| 201   | 0.24(p)      | 179   | 3.2                   | 0.82(dp)               | P-sens.(x) |
| 178   | 0.20(p)      |   |                       |                        |            |

$\rho$  = depolarization ratio; p = polarized; dp = depolarized

(continued overleaf)

TABLE VI (cont.)

RAMAN SPECTRAL RESULTS

| neat $\text{PhPH}_2^a$            |                       |        |            |
|-----------------------------------|-----------------------|--------|------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | $\rho$ | ASSIGNMENT |
| 693                               | 6                     | (p)    | X-sens.(r) |
| 622                               | 4                     | (dp)   | vib.(s)    |
| 438                               | 2                     | (dp)   | X-sens.(y) |
| 394                               | 8                     | (p)    | X-sens.(t) |
| 255                               | 2                     | (dp)   | X-sens.(u) |
| 179                               | 6                     | (dp)   | X-sens.(x) |

| neat $\text{PhPCl}_2$             |                       |              |                             |
|-----------------------------------|-----------------------|--------------|-----------------------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | $\rho$       | ASSIGNMENT <sup>b</sup>     |
| 701                               |                       | not measured | X-sens.(r)                  |
| 619                               |                       | not measured | vib.(s)                     |
| 504                               |                       | 0.18(p)      | sym. $\text{PCl}_2$ stretch |
| 455                               | (4)                   | 0.30(p)      | see text                    |
| 423                               | (1)                   | 0.70(dp)     | see text                    |
| 293                               |                       | 0.78(dp)     | $\text{PCl}_2$ wag          |
| 256                               | weak                  | --           | see text                    |
| 244                               | weak                  | --           | see text                    |
| 190                               |                       | 0.70(dp)     | see text                    |

a. from Amster and Colthup, ref. 104

b. assignment based in part on work of Green and Kynaston, ref. 108



the  $701\text{ cm}^{-1}$  band in  $\text{PhPCl}_2$ ; by comparison with Whiffen's work on monosubstituted halobenzenes, these bands are attributed to the totally symmetric X-sens.(r) vibration. The X-sens.(u) vibration occurs at  $255\text{ cm}^{-1}$  in  $\text{PhPH}_2$ . Two bands occur in this region in the spectrum of  $\text{PhPCl}_2$ , one at  $244\text{ cm}^{-1}$  and one at  $256\text{ cm}^{-1}$ . Green and Kynaston<sup>108</sup> have assigned these bands as the X-sens.(u) vibration and  $\text{PCl}_2$  twisting respectively. Both these vibrations would be expected to give rise to depolarized bands so there is little chance of distinguishing between them. The depolarized band at  $179\text{ cm}^{-1}$  in  $\text{PhPH}_2$  is considered to be the X-sens.(x) vibration. This band could not be located in the Raman spectrum of  $\text{PhPCl}_2$ ; it may possibly be obscured by the strong  $\text{PCl}_2$  rocking vibration at  $190\text{ cm}^{-1}$ . Finally, there remain two bands in each spectrum: in  $\text{PhPH}_2$ , these bands occur at  $394\text{ cm}^{-1}$  (p, intensity 8) and  $438\text{ cm}^{-1}$  (dp, intensity 2) and Amster and Colthup<sup>104</sup> have assigned these bands as the X-sens.(t) and X-sens.(y) vibrations respectively, in agreement with Whiffen<sup>103</sup> who has shown that they are  $A_1$  and  $B_2$  vibrations respectively. In  $\text{PhPCl}_2$ , similar bands are seen at  $423\text{ cm}^{-1}$  ( $\rho = 0.70$ , intensity 1) and  $455\text{ cm}^{-1}$  ( $\rho = 0.30$ , intensity 4) and are considered to be the X-sens.(y) and X-sens.(t) vibrations respectively; Green and Kynaston<sup>108</sup> have incorrectly reversed these two assignments in their work on  $\text{PhPCl}_2$ .

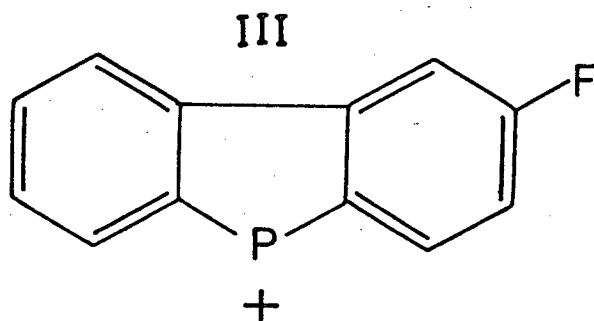
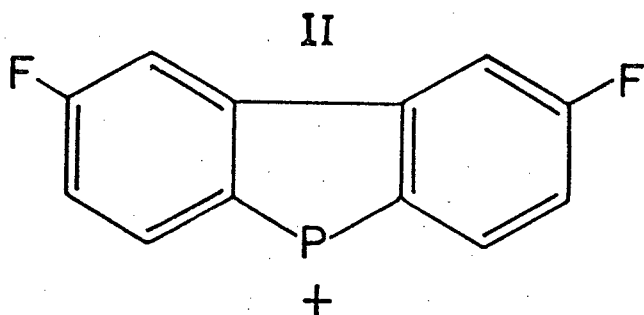
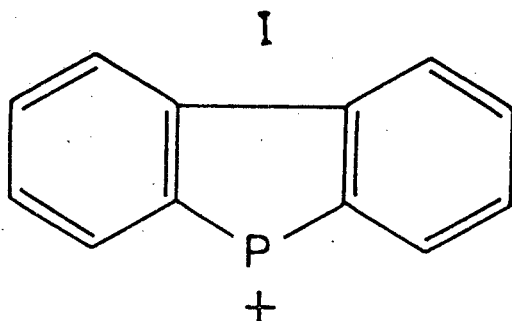
# The Diiododiphenyldiphosphines ( $R_2P_2I_2$ )

For the sake of continuity with respect to discussion of the vibrational work, the structurally simple diiododiphenyldiphosphine,  $Ph_2P_2I_2$ , will be considered first. The dimeric nature of this compound is confirmed by its mass spectrum (Table III), in which a weak parent ion is seen. The major fragment of the spectrum is  $PhPI^+$ , indicating that the P-P bond is cleaved rather easily. Significant rearrangement has obviously occurred in order to yield species such as  $Ph_4P_4^+$ ,  $Ph_3P_3^+$  and  $Ph_3P^+$ . It is apparent that  $Ph_2P_2I_2$  can regenerate the cyclopolyphosphine  $Ph_4P_4$  via elimination of iodine. The same reaction was observed to occur when  $Ph_2P_2I_2$  was left in solution for a long period of time; a  $^{31}P$  n.m.r. spectrum of a partly decomposed sample of  $(\underline{m}\text{-}FC_6H_4PI)_2$  showed the presence of  $(\underline{m}\text{-}FC_6H_4P)_n$ . The most likely explanation for the appearance of the  $Ph_4P_4^+$  peak is that  $Ph_2P_2I_2$  can associate in the vapour phase, as evidence has been presented<sup>110</sup> to show that symmetrical diphosphines can associate in solution. The loss of molecular iodine is reminiscent of the behaviour of  $\alpha\text{-}P_4S_3I_2$  which has been shown to revert to  $P_4S_3$  even under very mild conditions. The peak  $Ph_3P^+$  is no doubt derived from  $Ph_4P_4^+$ ; the reported<sup>111</sup> base peak in the mass spectrum of  $Ph_5P_5$  is  $Ph_3P^+$ . The very intense peak at  $m/e$  183 appears in most of the mass spectra reported here and is assigned structure I.

TABLE III

MASS SPECTRA OF  $\text{Ph}_2\text{P}_2\text{I}_2$  AND  $(\text{p-FC}_6\text{H}_4\text{PI})_2$

| Peak(m/e) | Abundance | Assignment <sup>(+)</sup>          | Peak(m/e) | Abundance | Assignment <sup>(+)</sup>                               |
|-----------|-----------|------------------------------------|-----------|-----------|---|
| 470       | 1.1       | $\text{Ph}_2\text{P}_2\text{I}_2$  | 506       | 37.8      | $(\text{FC}_6\text{H}_4\text{PI})_2$                    |
| 432       | 10.2      | $\text{Ph}_4\text{P}_4$            | 379       | 100       | $(\text{FC}_6\text{H}_4\text{P})_2\text{I}$             |
| 362       | 11.4      | $\text{PhPI}_2$                    | 316       | 54.0      | $(\text{FC}_6\text{H}_4)_3\text{P}$                     |
| 343       | 44.9      | $\text{Ph}_2\text{P}_2\text{I}$    | 284       | 8.9       | $(\text{FC}_6\text{H}_4)_2\text{P}_2\text{I}$           |
| 324       | 6.8       | $\text{Ph}_3\text{P}_3$            | 253       | 81.6      | $\text{FC}_6\text{H}_4\text{PI}$                        |
| 262       | 10.7      | $\text{Ph}_3\text{P}$              | 221       | 53.4      | $(\text{FC}_6\text{H}_4)_2\text{P}$                     |
| 235       | 100       | $\text{PhPI}$                      | 219       | 47.5      | $(\text{FC}_6\text{H}_3)_2\text{P}$                     |
| 216       | 9.8       | $\text{Ph}_2\text{P}_2$            | 201       | 25.8      | $(\text{FC}_6\text{H}_3)\text{P}(\text{C}_6\text{H}_4)$ |
| 185       | 9.7       | $\text{Ph}_2\text{P}$              | 157       | 48.6      | $\text{FC}_6\text{H}_4\text{P}_2$                       |
| 183       | 43.4      | $(\text{C}_6\text{H}_4)_2\text{P}$ |           |           |   |
| 139       | 6.2       | $\text{PhP}_2$                     |           |           |   |
| 138       | 12.1      | $\text{C}_6\text{H}_4\text{P}_2$   |           |           |   |
| 108       | 73.6      | $\text{PhP}$                       |           |           |   |
| 107       | 82.8      | $\text{C}_6\text{H}_4\text{P}$     |           |           |   |
| 77        | 41.2      | $\text{Ph}$                        |           |           |   |



Similarly, the mass spectrum of  $(p\text{-FC}_6\text{H}_4\text{PI})_2$  exhibits peaks at  $m/e$  219 and 201 which are assigned structures II and III respectively. These three ions are most likely stabilized by the aromatic character of the 14-electron system that results if phosphorus donates its remaining lone pair to the  $\pi$ -system. The fact that these molecular ions occur so frequently, and in generally large abundance, confirms that they must possess special stability. Even though there are several fragments of high intensity in which it is apparent that there are two phenyl groups attached to a phosphorus atom, one of these phenyl groups must have migrated from elsewhere during molecular re-

arrangement. The  $^{31}\text{P}$  n.m.r. spectrum of  $(\text{p-FC}_6\text{H}_4\text{PI})_2$  exhibits a single peak at +21.8 p.p.m. (ext.  $\text{P}_4\text{O}_6$ ) confirming that only one type of phosphorus environment is present and that this compound is 1,2-diiodo-1,2-di(p-fluorophenyl)diphosphine.

The low frequency infrared vibrations of  $\text{Ph}_2\text{P}_2\text{I}_2$ ,  $(\text{m-FC}_6\text{H}_4\text{PI})_2$  and  $(\text{p-FC}_6\text{H}_4\text{PI})_2$  are listed in Table V together with the low-frequency Raman-active vibrations. The Raman spectrum of  $(\text{m-FC}_6\text{H}_4\text{PI})_2$  in carbon disulphide, and that of liquid  $\text{m-FC}_6\text{H}_4\text{PH}_2$ , are reported in Table VI, together with the degree of polarization of each vibration.

Consider first the Raman spectrum of  $\text{Ph}_2\text{P}_2\text{I}_2$ . The extremely strong band at  $337\text{ cm}^{-1}$  is due to symmetric stretching of the highly polarizable P-I bond; according to Corbridge<sup>112</sup>, P-I stretching would be expected to be found in this region. The bands at  $457\text{ cm}^{-1}$  and  $426\text{ cm}^{-1}$  in  $\text{Ph}_2\text{P}_2\text{I}_2$  are considered to be the X-sens.(t) and X-sens.(y) vibrations, respectively, by analogy to similar bands at  $455\text{ cm}^{-1}$  and  $423\text{ cm}^{-1}$  in  $\text{PhPCl}_2$ . It may be argued that these vibrations should shift by a larger frequency upon replacement of chlorine by iodine; however, the work of Whiffen has shown that a levelling effect occurs in the X-sensitive vibrations as the mass of X is increased. Furthermore, the primary effect is due to the phosphorus atom and the secondary effect of the phosphorus substi-

TABLE V

LOW FREQUENCY INFRARED AND RAMAN ABSORPTION

| INFRARED ABSORPTION (cm <sup>-1</sup> )            |                        | RAMAN ABSORPTION (cm <sup>-1</sup> ) (Ph <sub>2</sub> P <sub>2</sub> I <sub>2</sub> ) |                       |                       |
|--|------------------------|---|-----------------------|-----------------------|
| Ph <sub>2</sub> P <sub>2</sub> I <sub>2</sub>      | ASSIGNMENT             | FREQUENCY<br>(cm <sup>-1</sup> )  | RELATIVE<br>INTENSITY | ASSIGNMENT            |
| 398,388  | see text               | 618   | 0.07                  | vib.(s)               |
| 341(s)   | ν <sub>as.</sub> (P-I) | 504   | 0.9                   | ν(P-P)                |
| 258(mw)  |                        | 457   | 0.5                   | P-sens.(t)            |
|  |                        | 426   | 0.4                   | P-sens.(y)            |
|  |                        | 404   | 0.04                  | vib.(w)               |
| (p-FC <sub>6</sub> H <sub>4</sub> PI) <sub>2</sub> | ASSIGNMENT             | 337   | 10                    | ν <sub>s.</sub> (P-I) |
|  |                        | 228   | 2.3                   |                       |
| 363(m)   | ν <sub>as.</sub> (P-I) | 202   | 3.4                   |                       |
| 351  |                        | 140   | 0.7                   |                       |
| (m-FC <sub>6</sub> H <sub>4</sub> PI) <sub>2</sub> | ASSIGNMENT             | v=very  |                       |                       |
|  |                        | w=weak  |                       |                       |
| 550(vw)  |                        | m=medium  |                       |                       |
| 388(s)   | see text               | s=strong  |                       |                       |
| 334(s)   | ν <sub>as.</sub> (P-I) | s.=symmetric  |                       |                       |
|  |                        | as.=antisymmetric   |                       |                       |

(continued overleaf)

TABLE V (cont.)

LOW FREQUENCY RAMAN ABSORPTION

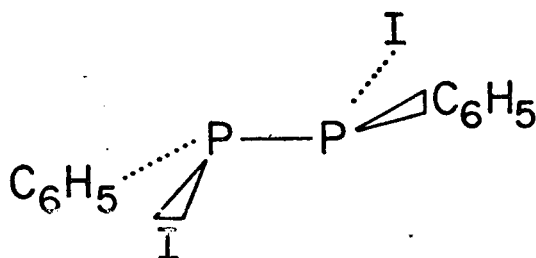
| $(p\text{-FC}_6\text{H}_4\text{PI})_2$ |                       |                               | $(m\text{-FC}_6\text{H}_4\text{PI})_2$ |                       |                               |
|--|-----------------------|-------------------------------|--|-----------------------|-------------------------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ )      | RELATIVE<br>INTENSITY | ASSIGNMENT                    | FREQUENCY<br>( $\text{cm}^{-1}$ )      | RELATIVE<br>INTENSITY | ASSIGNMENT                    |
| 632,622                                | 0.6                   | vib.(s)                       | 675                                    | 0.3                   | P-sens.(r)                    |
| 525                                    | 0.7                   | F-sens.(t)                    | 569                                    | 0.3                   | see text                      |
| 478                                    | 5.4                   | $\nu(\text{P-P})$             | 522                                    | 0.1                   | F-sens.(t)                    |
| 424                                    | 1.0                   | P-sens.(t)                    | 489                                    | 1.0                   | $\nu(\text{P-P})$             |
| 414                                    | 0.1                   | P-sens.(y) or vib.(w)         | 431                                    | 1.3                   | P-sens.(t)                    |
| 387                                    | 2.2                   | see text                      | 410                                    | 0.2                   | P-sens.(y) or vib.(w)         |
| 366                                    | 10                    | $\nu_{\text{s.}}(\text{P-I})$ | 340                                    | 10                    | $\nu_{\text{s.}}(\text{P-I})$ |
| 318                                    | 2.7                   | see text                      | 245                                    | 0.1                   | F-sens.(x)                    |
| 206                                    | 6.9                   |                               | 203                                    | 0.7                   |                               |
| 171                                    | 0.1                   |                               | 178                                    | 4.7                   |                               |
| 157                                    | 0.1                   |                               | 136                                    | 0.7                   |                               |

tuent would be expected to be much less in replacing one chlorine atom by iodine (assuming the other substituent, phosphorus, to have approximately the same mass effect as the chlorine which it replaces) than it was in replacing two hydrogen atoms by two chlorine atoms. In any case, the only other vibration of moderate intensity in this region occurs at  $504\text{ cm}^{-1}$  and it does not seem plausible that such a further large frequency shift could occur for either the X-sens.(t) or the X-sens.(y) vibration. By process of elimination, this band at  $504\text{ cm}^{-1}$  is considered to be due to P-P stretching; Corbridge<sup>112</sup> suggests that the typical range of P-P stretching frequencies extends from 390 to  $510\text{ cm}^{-1}$ . Reported P-P stretching frequencies include  $437\text{ cm}^{-1}$  for  $\text{P}_2\text{H}_4$ <sup>113</sup>,  $445\text{ cm}^{-1}$  in  $\text{Me}_4\text{P}_2\text{S}_2$ <sup>114</sup>,  $510\text{ cm}^{-1}$  in  $(\text{n-C}_4\text{H}_9)_4\text{P}_2\text{S}_2$ <sup>114</sup>, and 606 and  $465\text{ cm}^{-1}$  in  $\text{P}_4$ <sup>115</sup>. The very weak absorption at  $404\text{ cm}^{-1}$  may be due to Whiffen's vibration (w), an out-of-plane  $\text{A}_2$  ring deformation; the weak absorption at  $618\text{ cm}^{-1}$  is certainly Whiffen's vibration(s), a C-C-C in-plane ring deformation. The remaining low-frequency Raman vibrations at 228, 202 and  $140\text{ cm}^{-1}$  are viewed as deformation modes and have not been assigned definitive motions.

Three low-frequency infrared bands (Table V) remain to be assigned. The split band at 398,  $388\text{ cm}^{-1}$  apparently also occurs<sup>116</sup> in the infrared spectrum of  $\text{Ph}_2\text{P}_2\text{Br}_2$ , indicating that it is not halogen-dependent; however, the



vibration that causes this absorption has not been deduced and neither has that which causes weak absorption at  $258\text{ cm}^{-1}$ . The strong band at  $341\text{ cm}^{-1}$  is considered to be due to P-I stretching. If this vibration is considered to be an antisymmetric P-I stretch, then the only infrared and Raman coincident band (to  $250\text{ cm}^{-1}$ ) is the X-sens.(t) phenyl vibration, implying that  $\text{Ph}_2\text{P}_2\text{I}_2$  has a centre of symmetry. The structure of  $\text{Ph}_2\text{P}_2\text{I}_2$  in the solid state is therefore believed to be as illustrated below.



Any other conformation of  $\text{Ph}_2\text{P}_2\text{I}_2$ , or a change in configuration at phosphorus, would result in species whose molecular symmetry would permit complete coincidence of infrared and Raman fundamentals.

The Raman spectra of  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  and of  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  in solution are reported in Table VI. In meta-disubstituted benzenes, the local symmetry of the ring is lowered to  $\text{C}_s$ ; consequently, all in-plane deformations will be totally symmetric and will give rise to polarized Raman lines. Conversely, all out-of-plane deformations will be asym-

metric and will give rise to depolarized Raman lines. The effect of various substitution patterns on the vibrations of a benzene ring is a complex problem and has been the subject of an exhaustive book<sup>117</sup>. The vibrational assignments of  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  and of  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  are therefore less complete than those of their phenyl analogues. Since there are now two types of X-substituents, the fluorine-sensitive vibrations will be denoted F-sens. and the phosphorus-sensitive vibrations will be denoted P-sens. The strong polarized band at  $680\text{ cm}^{-1}$  is assigned to the totally symmetric P-sens.(r) vibration seen at  $693\text{ cm}^{-1}$  in  $\text{PhPH}_2$ . The  $680\text{ cm}^{-1}$  band cannot correlate with the strong infrared band seen at  $675\text{ cm}^{-1}$  in  $\underline{m}$ -fluorophenyl derivatives (Table IV), as this vibration is an out-of-plane ring deformation and could not give rise to a polarized Raman line. The  $680\text{ cm}^{-1}$  band in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  is considered to correlate with the  $675\text{ cm}^{-1}$  band of  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$ , although by an oversight the state of polarization of the latter vibration was not measured. The depolarized band at  $539\text{ cm}^{-1}$  in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  appears to correlate with the depolarized band at  $567\text{ cm}^{-1}$  in  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$ . Both compounds have apparently polarized bands at  $523\text{ cm}^{-1}$  which are assigned as the symmetric F-sens.(t) vibration; this vibration occurs at  $519\text{ cm}^{-1}$  in fluorobenzene<sup>103</sup>. The extremely strong polarized band at  $343\text{ cm}^{-1}$  is undoubtedly the symmetric P-I stretch. The strong polarized band at  $384\text{ cm}^{-1}$  in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  is con-

sidered to be the P-sens.(t) vibration seen at  $394\text{ cm}^{-1}$  in  $\text{PhPH}_2$ . This vibration was observed to increase to  $455\text{ cm}^{-1}$  in  $\text{PhPCl}_2$ ; therefore, the strong polarized band at  $431\text{ cm}^{-1}$  in  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  is considered to be the P-sens.(t) vibration. It is felt that this band cannot correlate with the very weak  $433\text{ cm}^{-1}$  band in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  because the relative intensities are very different; although Table VI lists this  $433\text{ cm}^{-1}$  band as being perhaps polarized, the vibration is so weak that the state of polarization must be considered to be uncertain. In fact, this vibration may be the P-sens.(y) vibration seen at  $438\text{ cm}^{-1}$  in  $\text{PhPH}_2$ . Since the frequency of this vibration did not change much in passing from  $\text{PhPH}_2$  to  $\text{Ph}_2\text{P}_2\text{I}_2$ , then it is likely that this band is either not seen in  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  or is obscured by the P-sens.(t) vibration. By process of elimination, the symmetric P-P stretch is assigned to the  $486\text{ cm}^{-1}$  absorption, in good agreement with the P-P stretching frequency found in  $\text{Ph}_2\text{P}_2\text{I}_2$ . The depolarized band at  $245\text{ cm}^{-1}$  in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  cannot correlate with the P-sens.(u) vibration seen at  $255\text{ cm}^{-1}$  in  $\text{PhPH}_2$ , as the latter vibration involves an in-plane deformation which would give rise to a polarized vibration under the  $C_s$  symmetry of a meta-disubstituted benzene ring. The bands at  $245\text{ cm}^{-1}$  in both  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  and  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  are therefore attributed to the F-sens.(x) vibration, an out-of-plane C-F deformation; the F-sens.(x) vibration of fluorobenzene occurs at  $242\text{ cm}^{-1}$  according to Whiffen<sup>103</sup>.

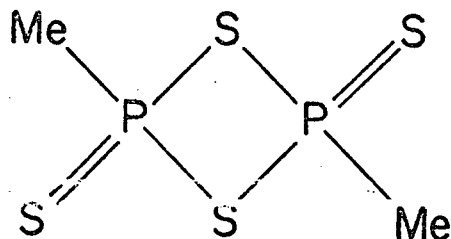
The depolarized band at  $179\text{ cm}^{-1}$  in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  is most likely due to the P-sens.(x) vibration seen at  $179\text{ cm}^{-1}$  in  $\text{PhPH}_2$ . In contrast, the absorption at  $178\text{ cm}^{-1}$  in  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  is due to a strongly polarized vibration which is very much greater in intensity than the  $179\text{ cm}^{-1}$  band in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$ . (Compare, for example, the relative intensities of these bands with respect to the F-sens.(x) vibrations at  $245\text{ cm}^{-1}$  in each of these compounds.) The depolarized vibration at  $217\text{ cm}^{-1}$  in  $\underline{m}\text{-FC}_6\text{H}_4\text{PH}_2$  and the polarized band at  $201\text{ cm}^{-1}$  in  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  have not been assigned definitive motions. Finally, the infrared-active vibration observed at  $388\text{ cm}^{-1}$  (Table V) is believed to be the same vibration observed at  $388, 398\text{ cm}^{-1}$  in  $\text{Ph}_2\text{P}_2\text{I}_2$ ; no such band is observed in the infrared spectrum of  $(\underline{p}\text{-FC}_6\text{H}_4\text{PI})_2$ , suggesting that the vibration is dependent upon the substitution pattern of the benzene ring. The strong band at  $334\text{ cm}^{-1}$  is considered to be due to asymmetric P-I stretching. Again the lack of coincident infrared and Raman frequencies suggests that  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  has molecular symmetry  $C_1$ . A comparison of the Raman spectra of  $(\underline{m}\text{-FC}_6\text{H}_4\text{PI})_2$  in solid state and in solution illustrates that no gross structural changes have occurred upon dissolution and that the conformation of the molecule is essentially the same in solution as in the crystal. The bulky iodine and phenyl substituents no doubt hinder rotation about the P-P bond.

The vibrational spectra of  $(p\text{-FC}_6\text{H}_4\text{PI})_2$  are more difficult to interpret since no  $p\text{-FC}_6\text{H}_4\text{PH}_2$  was available for comparison purposes. However, several assignments have been made by comparison with  $\text{Ph}_2\text{P}_2\text{I}_2$  and  $(m\text{-FC}_6\text{H}_4\text{PI})_2$ . The split Raman band at 622, 632  $\text{cm}^{-1}$  is considered to be Whiffen's vibration(s); the same vibration occurs at 618  $\text{cm}^{-1}$  in  $\text{Ph}_2\text{P}_2\text{I}_2$ . The band at 525  $\text{cm}^{-1}$  is believed to be the F-sens.(t) vibration that occurs at 522  $\text{cm}^{-1}$  in  $(m\text{-FC}_6\text{H}_4\text{PI})_2$ . The strong absorption at 478  $\text{cm}^{-1}$  is assigned as P-P stretching by comparison with both  $\text{Ph}_2\text{P}_2\text{I}_2$  and  $(m\text{-FC}_6\text{H}_4\text{PI})_2$ . The relatively strong band at 424  $\text{cm}^{-1}$  is likely the P-sens.(t) vibration; such an assignment is supported by the fact that  $p\text{-FC}_6\text{H}_4\text{PCl}_2$  has a polarized band at 424  $\text{cm}^{-1}$ . The weak vibration at 414  $\text{cm}^{-1}$  may be Whiffen's vibration(w), an out-of-plane ring deformation; the weak bands at 404  $\text{cm}^{-1}$  in  $\text{Ph}_2\text{P}_2\text{I}_2$  and 410  $\text{cm}^{-1}$  in  $(m\text{-FC}_6\text{H}_4\text{PI})_2$  are most likely due to the same vibration. By virtue of its great strength, the band at 366  $\text{cm}^{-1}$  is assigned as P-I stretching. This shift to higher frequency with respect to  $\text{Ph}_2\text{P}_2\text{I}_2$  and  $(m\text{-FC}_6\text{H}_4\text{PI})_2$  indicates that the P-I bond has been significantly strengthened in  $(p\text{-FC}_6\text{H}_4\text{PI})_2$ . The effect of para-fluorophenyl groups on certain vibrational frequencies will be considered later in the discussion.  $p\text{-FC}_6\text{H}_4\text{PCl}_2$  has a weak band at 385  $\text{cm}^{-1}$  while  $(p\text{-FC}_6\text{H}_4\text{PI})_2$  has a moderately strong band at 387  $\text{cm}^{-1}$  but whether or not the same vibration is responsible is uncertain. The band at 318  $\text{cm}^{-1}$  is found to occur in the

spectra of other para-fluorophenyl compounds and may be due to a fluorine-sensitive vibration of the phenyl ring.

#### The Four-Membered Ring System ( $R_2P_2S_4$ )

A wide variety of compounds of general formula  $R_2P_2S_4$  has been synthesized<sup>118-120</sup>. The crystal structure of  $Me_2P_2S_4$  has been solved<sup>87</sup> and the molecule has been found to possess a planar four-membered  $P_2S_2$  ring as shown below.



Space group data<sup>19</sup> for  $Ph_2P_2S_4$  show that this molecule also has a centre of symmetry. Despite the diversity of compounds of this type that have been made, very few spectroscopic data have been reported. Thus, Maier<sup>82</sup> reports the infrared spectrum of  $Ph_2P_2S_4$  in the region  $800-640\text{ cm}^{-1}$  and assigns the strong absorption at  $655\text{ cm}^{-1}$  as  $\nu(P=S)$ ; Fluck and Binder<sup>122</sup> report the  $^{31}P$  n.m.r. of  $Ph_2P_2S_4$  as consisting of a singlet at  $-15.4$  p.p.m. relative to  $P_4O_6$ . As a result, the compounds  $Me_2P_2S_4$ ,  $Ph_2P_2S_4$  and its fluorophenyl analogues have been examined spectroscopically in very much greater detail than has been

TABLE VII

MASS SPECTRA OF  $\text{Me}_2\text{P}_2\text{S}_4$ ,  $\text{Ph}_2\text{P}_2\text{S}_4$  and  $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$

| $\text{Me}_2\text{P}_2\text{S}_4$ |           |                                   |
|-----------------------------------|-----------|-----------------------------------|
| Peak(m/e)                         | Abundance | Assignment(+)                     |
| 220                               | 49.1      | $\text{Me}_2\text{P}_2\text{S}_4$ |
| 110                               | 100       | $\text{MePS}_2$                   |
| 95                                | 20.7      | $\text{PS}_2$                     |
| 78                                | 19.2      | $\text{MePS}$                     |
| 63                                | 73.1      | $\text{PS}$                       |
| 47                                | 19.2      | $\text{SMe/MePH}$                 |
| 45                                | 12.9      | $\text{CH}_2\text{P}$             |

| $\text{Ph}_2\text{P}_2\text{S}_4$ |           |                                   |
|-----------------------------------|-----------|-----------------------------------|
| Peak(m/e)                         | Abundance | Assignment(+)                     |
| 344                               | 2.8       | $\text{Ph}_2\text{P}_2\text{S}_4$ |
| 249                               | 2.2       | $\text{Ph}_2\text{PS}_2$          |
| 172                               | 100       | $\text{PhPS}_2$                   |
| 109                               |           | $\text{PhPH}$                     |
| 108                               | 9.9       | $\text{PhP}$                      |
| 107                               |           | $\text{C}_6\text{H}_4\text{P}$    |
| 77                                | 11.8      | $\text{C}_6\text{H}_5$            |
| 63                                | 53.8      | $\text{PS}$                       |

| $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$ |           |   |
|--|-----------|---|
| Peak(m/e)                                | Abundance | Assignment(+)                               |
| 380                                      | 6.1       | $(\text{FC}_6\text{H}_4\text{PS}_2)_2$      |
| 285                                      | 3.8       | $\text{FC}_6\text{H}_4\text{P}_2\text{S}_4$ |
| 253                                      | 1.7       | $\text{FC}_6\text{H}_4\text{P}_2\text{S}_3$ |
| 190                                      | 100       | $\text{FC}_6\text{H}_4\text{PS}_2$          |
| 158                                      | 7.1       | $\text{FC}_6\text{H}_4\text{PS}$            |
| 126                                      | 13.4      | $\text{FC}_6\text{H}_4\text{P}$             |
| 95                                       | 4.6       | $\text{FC}_6\text{H}_4$                     |
| 63                                       | 70.4      | $\text{PS}$                                 |

reported previously.

The mass spectra of  $\text{Me}_2\text{P}_2\text{S}_4$ ,  $\text{Ph}_2\text{P}_2\text{S}_4$  and  $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$  are reported in Table VII. In each case, the fragmentation pattern is similar, the base peak being the monomeric species  $\text{RPS}_2^+$  and a strong peak occurring for the  $\text{PS}^+$  ion. In contrast to other mass spectra reported in this section, the spectra of these three compounds do not exhibit molecular ions which have undergone considerable rearrangement.

As reported in the experimental section, the proton n.m.r. of  $\text{Me}_2\text{P}_2\text{S}_4$  consists of a doublet centred at the very low chemical shift value of 7.50  $\tau$ ,  $J_{\text{PH}} = 14$  Hz. This result will be considered later in the discussion together with the  $^{19}\text{F}$  n.m.r. data of the fluorophenyl derivatives.

The infrared and Raman spectra of  $\text{Me}_2\text{P}_2\text{S}_4$ ,  $\text{Ph}_2\text{P}_2\text{S}_4$  and  $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$  are reported in Tables VIII and IX. Complete vibrational assignments are impossible as none of these compounds are sufficiently soluble to allow a determination of the degree of polarization of the various vibrations. The assignment of vibrations is aided by the fact that  $\text{Me}_2\text{P}_2\text{S}_4$  and  $\text{Ph}_2\text{P}_2\text{S}_4$  are known to possess a centre of symmetry and consequently the mutual exclusion principle must prevail. The vibrational spectra of  $\text{Me}_2\text{P}_2\text{S}_4$  are



TABLE VIII

SOLID STATE RAMAN SPECTRA OF COMPOUNDS  $R_2P_2S_4$ 

| R=Me | FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | ASSIGNMENT                  |
|------|-----------------------------------|-----------------------|-----------------------------|
|      | 2993                              | neg.                  | $\nu_{\text{as.}}$ (C-H)    |
|      | 2905                              | 0.2                   | $\nu_{\text{s.}}$ (C-H)     |
|      | 1407,1402                         | neg.                  | $\delta_{\text{as.}}$ (C-H) |
|      | 1276,1274                         | neg.                  | $\delta_{\text{s.}}$ (C-H)  |
|      | 905                               | 0.3                   | $\rho$ (C-H)                |
|      | 752                               | 0.3                   | $\nu_{\text{s.}}$ (P-C)     |
|      | 658                               | 0.7                   | $\nu_{\text{s.}}$ (P=S)     |
|      | 447                               | 10                    | $\nu$ (P-S)                 |
|      | 421                               | 4.2                   | $\nu$ (P-S)                 |
|      | 318                               | 0.5                   |                             |
|      | 269                               | 0.9                   |                             |
|      | 228                               | 0.3                   |                             |
|      | 179                               | 4.5                   |                             |
|      | 103                               | 0.4                   |                             |

| R=Ph | FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | ASSIGNMENT |
|------|-----------------------------------|-----------------------|------------|
|------|-----------------------------------|-----------------------|------------|

higher frequencies not recorded

|     |     |             |
|-----|-----|-------------|
| 726 | 1.2 | see text    |
| 686 | 1.9 | P-sens.(r)  |
| 616 | 0.6 | vib.(s)     |
| 502 | 10  | $\nu$ (P-S) |
| 470 | 2.1 | P-sens.(t)  |
| 410 | 4.9 | see text    |
| 396 | 6.1 | see text    |
| 328 | 1.0 |             |
| 270 | 2.0 |             |
| 210 | 2.1 |             |
| 191 | 3.4 |             |
| 174 | 3.1 |             |
| 143 | 1.8 |             |

(continued overleaf)

neg.= negligible

TABLE VIII (cont.)

| R=p-FC <sub>6</sub> H <sub>4</sub> | FREQUENCY<br>(cm <sup>-1</sup> ) | RELATIVE<br>INTENSITY | ASSIGNMENT |
|------------------------------------|----------------------------------|-----------------------|------------|
|                                    | higher frequencies not recorded  |                       |            |
|                                    | 698                              | 2.5                   |            |
|                                    | 645                              | 0.2                   |            |
|                                    | 626                              | 0.3                   |            |
|                                    | 481                              | 10                    |            |
|                                    | 419                              | 8.3                   |            |
|                                    | 404                              | 2.0                   |            |
|                                    | 387                              | 5.3                   |            |
|                                    | 353                              | 1.8                   |            |
|                                    | 310                              | 0.5                   |            |
|                                    | 225                              | 1.2                   |            |
|                                    | 196                              | 0.7                   |            |
|                                    | 173                              | 3.1                   |            |
|                                    | 91                               | 2.5                   |            |

TABLE IX

SOLID STATE INFRARED SPECTRA OF COMPOUNDS  $R_2P_2S_4$

| R=Me                         |                       |                   | R=Ph <sup>a</sup>            |                       |             | R=p-FC <sub>6</sub> H <sub>4</sub> <sup>b</sup> |                       |             |
|------------------------------|-----------------------|-------------------|------------------------------|-----------------------|-------------|---|-----------------------|-------------|
| FREQ.<br>(cm <sup>-1</sup> ) | RELATIVE<br>INTENSITY | ASSIGNMENT        | FREQ.<br>(cm <sup>-1</sup> ) | RELATIVE<br>INTENSITY | ASSIGNMENT  | FREQ.<br>(cm <sup>-1</sup> )                    | RELATIVE<br>INTENSITY | ASSIGNMENT  |
| 1276                         | m                     | $\nu_{s.}$ (C-H)  | 719                          | s                     | see text    | 758   | w                     |             |
| 900,892                      | s                     | $\rho$ (C-H)      | 655                          | vs                    | $\nu$ (P=S) | 685   | vs                    | $\nu$ (P=S) |
| 756                          | s                     | $\nu_{as.}$ (P-C) | 610                          | m, sharp              | vib.(s)     | 625   | s                     |             |
| 617                          | vs                    | $\nu_{as.}$ (P=S) | 563                          | s                     | $\nu$ (P-S) | 602   | s                     |             |
| 531                          | s                     | $\nu$ (P-S)       | 473                          | s                     | P-sens.(t)  | 555   | s                     |             |
| 422                          | s                     | $\nu$ (P-S)       | 448                          | s                     | $\nu$ (P-S) | 450   | s                     |             |
| 263                          | mw                    |                   | 346                          | w                     |             | 415   | sh                    |             |
| 239                          | m                     |                   | 292                          | w                     |             | 331   | m                     |             |
| 150                          | m                     |                   |                              |                       |             |   |                       |             |

v=very; w=weak; m=medium; s=strong; sh=shoulder

a. spectrum includes those peaks listed in Table IV, column I (exc. 465 cm<sup>-1</sup>)

b. spectrum includes those peaks listed in Table IV, column III(exc.510 and 405 cm<sup>-1</sup>)

easiest to interpret. Antisymmetric C-H stretching is seen at  $2993\text{ cm}^{-1}$ , and symmetric C-H stretching, at  $2905\text{ cm}^{-1}$ . Symmetric C-H bending is seen at  $1274$  and  $1276\text{ cm}^{-1}$ ; antisymmetric C-H bending is seen at  $1407$  and  $1402\text{ cm}^{-1}$ . The C-H rocking vibration is seen at  $905\text{ cm}^{-1}$  (Raman) and at  $892, 900\text{ cm}^{-1}$  (infrared). Absorptions at  $752\text{ cm}^{-1}$  (Raman) and  $756\text{ cm}^{-1}$  (infrared) are assigned to the symmetric and antisymmetric P-C stretch respectively. These values are typical of pentavalent phosphorus-carbon stretching frequencies<sup>112</sup>. The strong band at  $617\text{ cm}^{-1}$  in the infrared spectrum is the only band which falls in the normal region for  $\nu(\text{P}=\text{S})$  and it is therefore assigned as the antisymmetric P=S stretch. The only band in this region in the Raman spectrum ( $658\text{ cm}^{-1}$ ) is considered to be the symmetric P=S stretch. Cowley and White<sup>114</sup> also found the symmetric P=S stretch to occur at higher frequencies than the antisymmetric P=S stretch in the diphosphine disulphides  $\text{Me}_4\text{P}_2\text{S}_2$ ,  $\text{Et}_4\text{P}_2\text{S}_2$  and  $\text{Bu}_4\text{P}_2\text{S}_2$ . In addition, the antisymmetric stretch is listed as being a very strong absorption while the Raman-active symmetric stretch is listed as being of only medium intensity. These observations are consistent with what has been obtained for  $\text{Me}_2\text{P}_2\text{S}_4$ . Corbridge<sup>112</sup> considers the normal P-S stretching frequency range to lie between  $400$  and  $550\text{ cm}^{-1}$ . Such a frequency range is much more reasonable than the region  $550\text{--}600\text{ cm}^{-1}$  which has been suggested by some workers<sup>85</sup>. Neither  $\text{Me}_2\text{P}_2\text{S}_4$  nor  $\text{P}_4\text{S}_3$  has any

absorption in the region  $550\text{--}600\text{ cm}^{-1}$ ; in fact, the highest absorption in  $\text{P}_4\text{S}_3$  occurs at  $489\text{ cm}^{-1}$ . Four absorption bands are seen in the region  $400\text{--}550\text{ cm}^{-1}$ , two in the infrared spectrum ( $531, 422\text{ cm}^{-1}$ ) and two in the Raman spectrum ( $447, 421\text{ cm}^{-1}$ ) as would be expected. By virtue of its great intensity, the strongest Raman band ( $447\text{ cm}^{-1}$ ) is most likely the totally symmetric P-S stretch. The infrared-active band at  $422\text{ cm}^{-1}$  and the Raman-active band at  $421\text{ cm}^{-1}$  are considered to belong to different symmetry species as both are very strong peaks. As mentioned previously,  $\text{Me}_2\text{P}_2\text{S}_4$ , having a centre of symmetry, is not expected to have any infrared and Raman coincidences; if such coincidences do occur, it is unlikely that the vibration would be very strong in both the infrared and Raman spectra. In any case, an accidental coincidence is not unreasonable since the various P-S stretching vibrations are closely related and would be expected to require similar energies. The remaining vibrations are too difficult to assign without polarization data; nine Raman-active fundamentals are expected however, (treating the methyl groups as point masses) and nine are observed. Seven of the nine infrared-active fundamentals are seen, if the infrared-Raman coincidences of  $422\text{--}421\text{ cm}^{-1}$  and  $263\text{--}269\text{ cm}^{-1}$  are treated as being accidental.

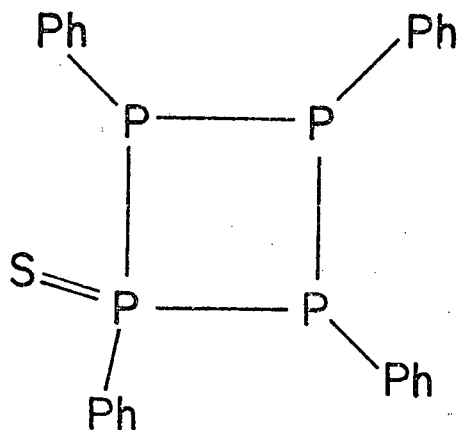
The vibrational spectra of  $\text{Ph}_2\text{P}_2\text{S}_4$  are somewhat more complicated; the very strong broad infrared-active band

at  $655\text{ cm}^{-1}$  is assigned as antisymmetric P=S stretching, not only because of its strength but also because of the similarity of the band shape to that observed for the antisymmetric P=S stretch in  $\text{Me}_2\text{P}_2\text{S}_4$ . The only other band in this region which might qualify as the antisymmetric P=S stretch is the strong sharp infrared-active band at  $719\text{ cm}^{-1}$ . No assignment has been made for this band even though it appears repeatedly in compounds containing  $\text{Ph-P(S)}\text{<}$  linkages; for example, a comparison of the infrared spectra of  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{P=S}$  reveals that strong absorptions appear at  $712\text{ cm}^{-1}$  and  $632\text{ cm}^{-1}$  in the spectrum of  $\text{Ph}_3\text{P=S}$ . The band at  $632\text{ cm}^{-1}$  has been assigned<sup>124</sup> as P=S stretching but no mention was made of the  $712\text{ cm}^{-1}$  band even though it is slightly more intense than the  $632\text{ cm}^{-1}$  band. Chittenden and Thomas<sup>125</sup> have suggested that the P=S bond is characterized by two infrared absorptions; however, according to other workers<sup>126</sup> the association of two absorptions with P=S stretching seems to be incorrect. The sharp bands at  $610\text{ cm}^{-1}$  in the infrared spectrum, and  $616\text{ cm}^{-1}$  in the Raman spectrum, are assigned as the C-C-C in-plane ring deformation, vibration(s) in Whiffen's notation. The Raman-active band at  $686\text{ cm}^{-1}$  is considered to be the P-sens.(r) vibration of the phenyl ring; this vibration was observed to be relatively unaffected in passing from  $\text{PhPH}_2$  ( $693\text{ cm}^{-1}$ ) to  $\text{PhPCl}_2$  ( $701\text{ cm}^{-1}$ ). The Raman-active band at  $726\text{ cm}^{-1}$  may be the symmetric P=S stretch but the possibility that it is due to

the same vibration as is observed at  $719\text{ cm}^{-1}$  in the infrared spectrum cannot be excluded. The infrared active band at  $473\text{ cm}^{-1}$ , and the Raman-active band at  $470\text{ cm}^{-1}$ , are assigned as the P-sens.(t) vibration that was observed at  $465\text{ cm}^{-1}$  for  $\text{Ph}_2\text{P}_2\text{I}_2$ . The strong infrared-active absorptions at  $563$  and  $448\text{ cm}^{-1}$  are considered to be the two expected infrared-active P-S stretches; the strongest Raman band,  $502\text{ cm}^{-1}$ , is assigned as the totally symmetric P-S stretch by analogy to  $\text{Me}_2\text{P}_2\text{S}_4$ . The other Raman-active P-S stretch occurs at either  $410$  or  $396\text{ cm}^{-1}$ . No further assignments have been attempted for  $\text{Ph}_2\text{P}_2\text{S}_4$ . The P=S stretching frequencies have been identified as occurring at  $652\text{ cm}^{-1}$  in  $(\text{m-FC}_6\text{H}_4\text{PS}_2)_2$  and at  $687\text{ cm}^{-1}$  in  $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$ . The higher frequency observed in  $(\text{p-FC}_6\text{H}_4\text{PS}_2)_2$  indicates that the P=S bond has been strengthened by conjugative interaction with the p-fluorophenyl group.

#### The Cyclotetraphosphine Monosulphides ( $\text{R}_4\text{P}_4\text{S}$ )

Tetraphenylcyclotetraphosphine monosulphide ( $\text{Ph}_4\text{P}_4\text{S}$ ) has been prepared by Maier<sup>82</sup> who reported its infrared spectrum in the region  $800\text{-}600\text{ cm}^{-1}$  and a molecular weight determination. On the basis of this rather scant information, Maier postulated that  $\text{Ph}_4\text{P}_4\text{S}$  consists of a four-membered phosphorus ring as shown.



A close inspection of the vibrational spectroscopic data (Table XII) reveals that there is no band which can be readily assigned as a P=S stretching frequency. There remains, however, the possibility of accidental overlap with the strong infrared-active phenyl vibrations at 680 and 740  $\text{cm}^{-1}$ . Such a coincidence apparently occurs in the infrared spectrum of  $\text{PhP(S)Cl}_2$ , in which only these two strong phenyl vibrations are seen<sup>127</sup> in the region 600-800  $\text{cm}^{-1}$ . Because of this possibility, and also because of the failure to obtain an adequate  $^{31}\text{P}$  n.m.r. spectrum, the structure of  $\text{Ph}_4\text{P}_4\text{S}$  was determined by a single crystal X-ray diffraction study<sup>128</sup>, and was found to consist of a five-membered  $\text{P}_4\text{S}$  ring, and not a four-membered phosphorus ring as Maier<sup>82</sup> had postulated. The  $\text{P}_4\text{S}$  ring is non-planar, as shown in Figures 6 and 7, deviations from the mean plane being: P(1), 0.19; P(2), -0.24; P(3), 0.24; P(4), -0.15; S, -0.02  $\text{\AA}$ . The mean bond lengths are: P-P, 2.190(5)  $\text{\AA}$ ;



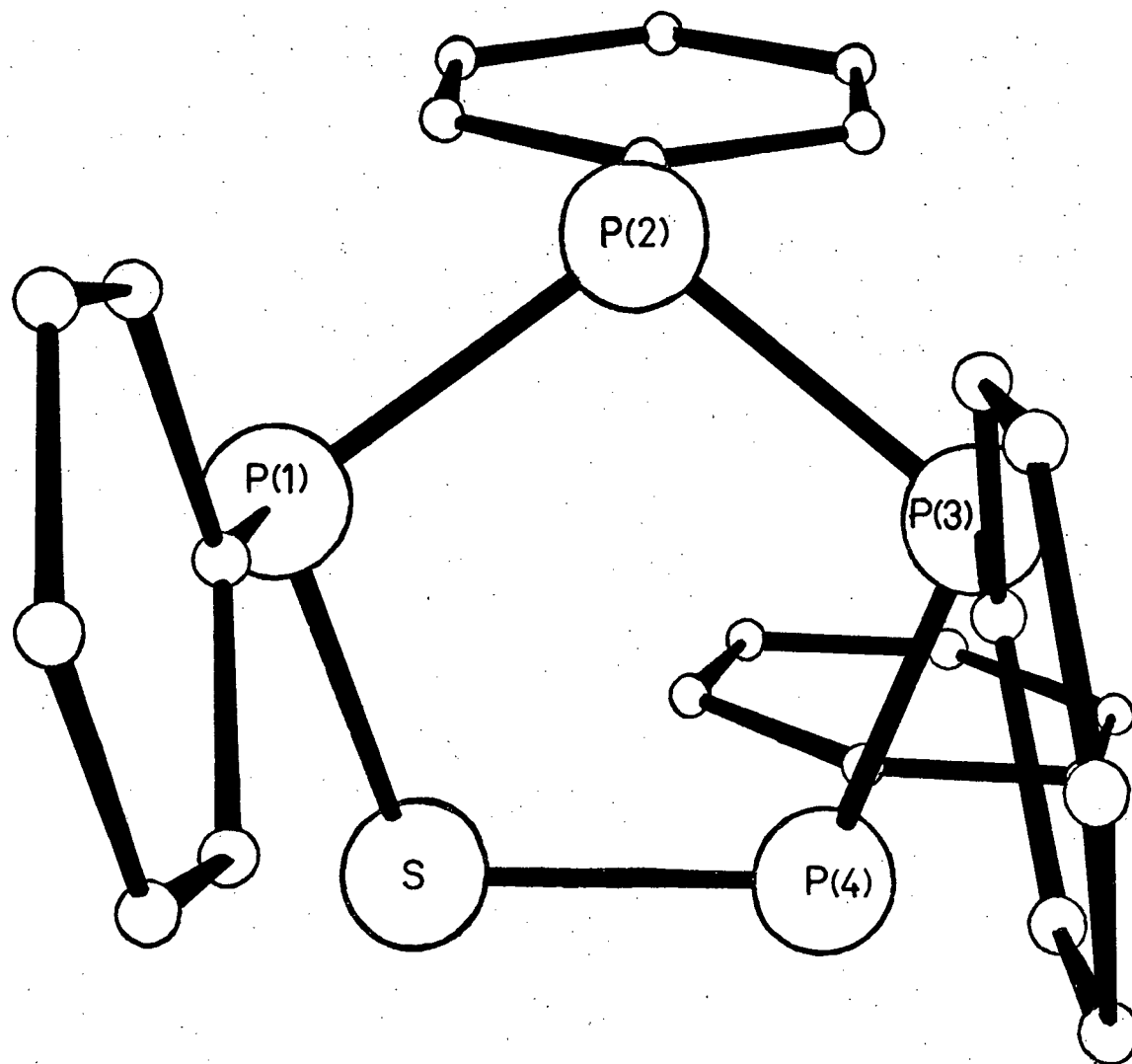


FIG.6: Molecular structure of  $\text{Ph}_4\text{P}_4\text{S}$

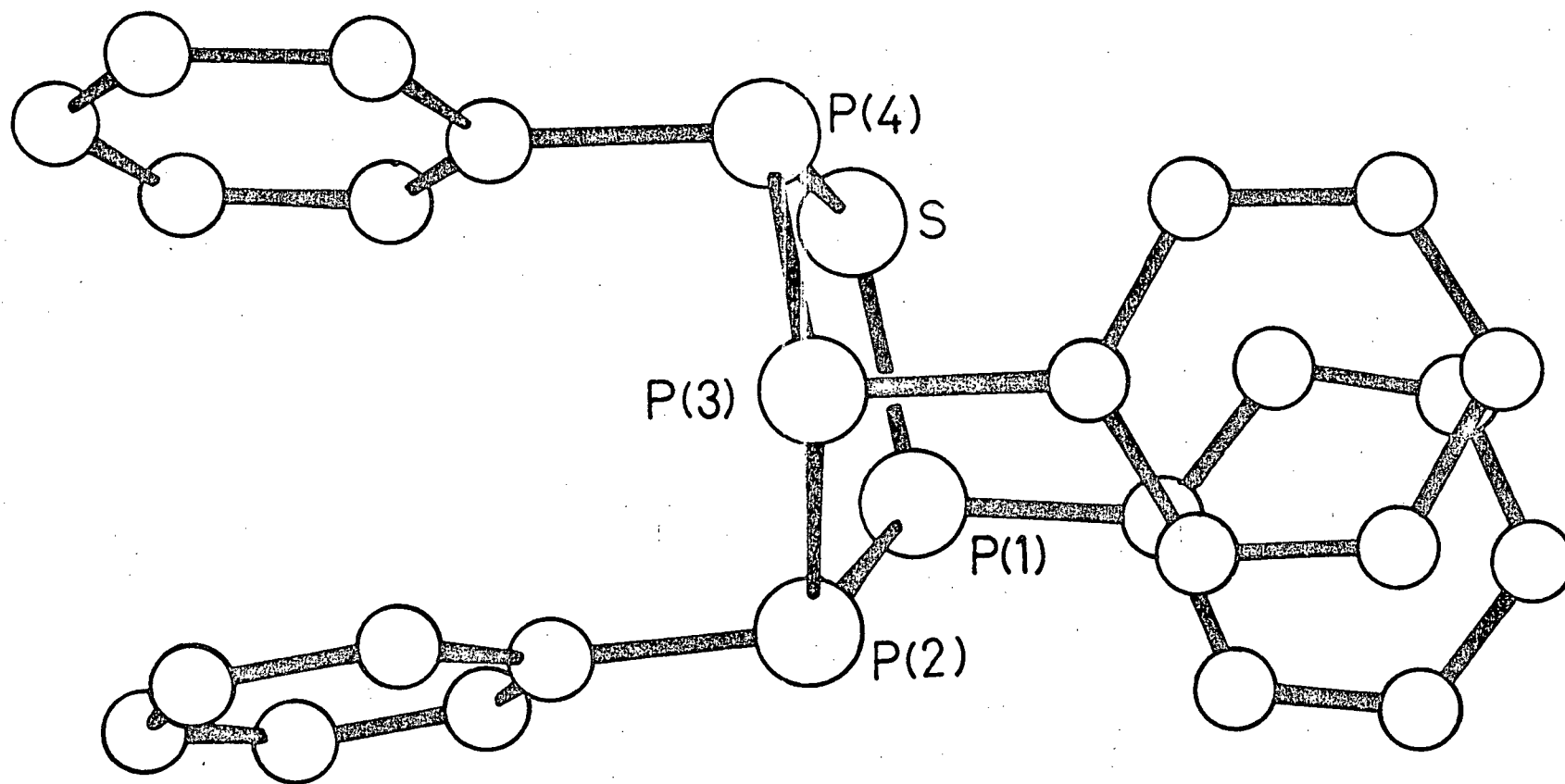


FIG. 7: Arrangement of phenyl groups in  $\text{Ph}_4\text{P}_4\text{S}$

TABLE X

MOLECULAR STRUCTURE OF  $\text{Ph}_4\text{P}_4\text{S}$

a. Mean bond lengths ( $\text{\AA}$ )

|     |           |
|-----|-----------|
| P-S | 2.116(5)  |
| P-P | 2.190(5)  |
| P-C | 1.831(22) |
| C-C | 1.382(16) |

b. Endocyclic bond angles (deg.)

|                        |          |
|------------------------|----------|
| $\angle \text{P}_1$    | 105.9(2) |
| $\angle \text{P}_2$    | 104.2(2) |
| $\angle \text{P}_3$    | 105.1(2) |
| $\angle \text{P}_4$    | 105.6(2) |
| mean $\angle \text{P}$ | 105.2    |
| $\angle \text{S}$      | 110.4(2) |

c. Dihedral angles (deg.) in the  $\text{P}_4\text{S}$  ring

| <u>Atoms</u>        | <u>Angle</u> |
|---------------------|--------------|
| P(1)-P(2)-P(3)-P(4) | -29.9        |
| P(2)-P(3)-P(4)-S    | +23.0        |
| P(3)-P(4)-S-P(1)    | -7.1         |
| P(4)-S-P(1)-P(2)    | -11.7        |
| S-P(1)-P(2)-P(3)    | +25.6        |

P-S,  $2.116(5)\text{\AA}$ ; P-C,  $1.831(22)\text{\AA}$ ; C-C,  $1.382(16)\text{\AA}$ . Other useful data are presented in Table X. The phenyl groups are nearly perpendicular to the mean plane of the  $\text{P}_4\text{S}$  ring, the pairs on the same side of the ring being roughly parallel to each other, but perpendicular to the other pair. The near equality of the angles at phosphorus (Table X) is to be contrasted with the variability of those in  $\text{Ph}_5\text{P}_5^{129}$ , in which the angles range from  $94.1^\circ$  to  $107.2^\circ$ , mean  $100^\circ$ . The stability of the monosulphide, indicated by the variety of synthetic methods and the difficulty of removing the remaining sulphur with tributylphosphine, may be due in part to the larger and more regular angles at phosphorus, themselves a result of reduced steric repulsions of the phenyl groups.

The mass spectra of  $\text{Ph}_4\text{P}_4\text{S}$  and  $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$  are presented in Table XI. Surprisingly, the strongest peaks are those in which either one or two phenyl groups have migrated to the same phosphorus atom; hence, the strongest peaks in the mass spectrum of  $\text{Ph}_4\text{P}_4\text{S}$  are due to the ions  $\text{Ph}_3\text{P}^+$ ,  $\text{Ph}_2\text{P}^+$  and  $(\text{C}_6\text{H}_4)_2\text{P}^+$ ; the latter fragment is believed to be the molecular ion of 9-phosphafluorene that is also prominent in the mass spectrum of  $\text{Ph}_2\text{P}_2\text{I}_2$ . The *p*-fluorophenyl analogues of these three ions are the most intense peaks in the mass spectrum of  $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$ . Several other fragments are seen in the mass spectrum of  $\text{Ph}_4\text{P}_4\text{S}$  which indicate that significant rearrangement has occurred,

TABLE XI

MASS SPECTRAL RESULTS FOR  $\text{Ph}_4\text{P}_4\text{S}$  and  $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$

| $\text{Ph}_4\text{P}_4\text{S}$ |           |  | $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$ |           |   |
|---------------------------------|-----------|--|---|-----------|---|
| PEAK<br>(m/e)                   | ABUNDANCE | ASSIGNMENT <sup>(+)</sup>              | PEAK<br>(m/e)                                 | ABUNDANCE | ASSIGNMENT <sup>(+)</sup>                               |
| 540                             | 0.8       | $\text{Ph}_5\text{P}_5$                | 536   | 47        | $(\text{FC}_6\text{H}_4\text{P})_4\text{S}$             |
| 496                             | 0.3       | $\text{Ph}_4\text{P}_4\text{S}_2$      | 378   | 32        | $(\text{FC}_6\text{H}_4\text{P})_3$                     |
| 464                             | 57        | $\text{Ph}_4\text{P}_4\text{S}$        | 347   | 13        | $(\text{FC}_6\text{H}_4)_3\text{P}_2$                   |
| 432                             | 2.3       | $\text{Ph}_4\text{P}_4$                | 316   | 70        | $(\text{FC}_6\text{H}_4)_3\text{P}$                     |
| 401                             | 2.7       | $\text{Ph}_4\text{P}_3$                | 284   | 26        | $(\text{FC}_6\text{H}_4\text{P})_2\text{S}$             |
| 388                             | 2.4       | $\text{Ph}_3\text{P}_3\text{S}_2$      | 252   | 10        | $(\text{FC}_6\text{H}_4\text{P})_2$                     |
| 370                             | 1.5       | $\text{Ph}_4\text{P}_2$                | 221   | 100       | $(\text{FC}_6\text{H}_4)_2\text{P}$                     |
| 356                             | 1.7       | $\text{Ph}_3\text{P}_3\text{S}$        | 219   | 62        | $(\text{FC}_6\text{H}_3)_2\text{P}$                     |
| 324                             | 18        | $\text{Ph}_3\text{P}_3$                | 201   | 27        | $(\text{FC}_6\text{H}_3)\text{P}(\text{C}_6\text{H}_4)$ |
| 293                             | 35        | $\text{Ph}_3\text{P}_2$                | 157   | 32        | $\text{FC}_6\text{H}_4\text{P}_2$                       |
| 279                             | 2.4       | $\text{Ph}_2\text{P}_3\text{S}$        | 126   | 28        | $\text{FC}_6\text{H}_4\text{P}$                         |
| 262                             | 100       | $\text{Ph}_3\text{P}$                  | 125   | 39        | $\text{FC}_6\text{H}_3\text{P}$                         |
| 248                             | 16        | $\text{Ph}_2\text{P}_2\text{S}$        | 107   | 25        | $\text{C}_6\text{H}_4\text{P}$                          |
| 232                             | neg.      | $(\text{Ph}_4\text{P}_4\text{S})^{2+}$ | 95  | 17        | $\text{FC}_6\text{H}_4$                                 |
| 217                             | 8         | $\text{Ph}_2\text{PS}$                 | 63  | 12        | PS  |
| 185                             | 80        | $\text{Ph}_2\text{P}$                  |   |           |   |
| 183                             | 95        | $(\text{C}_6\text{H}_4)_2\text{P}$     |   |           |   |
| 170                             | 8         | $\text{PhP}_3$                         |   |           |   |
| 139                             | 25        | $\text{PhP}_2$                         |   |           |   |
| 108                             | 43        | $\text{PhP}$                           |   |           |   |
| 107                             | 19        | $\text{C}_6\text{H}_4\text{P}$         |   |           |   |
| 77                              | 34        | Ph                                     |   |           |   |
| 63                              | 7         | PS                                     |   |           |   |
| 52                              | 10        | $\text{C}_4\text{H}_4$                 |   |           |   |

specifically the ions  $\text{Ph}_5\text{P}_5^+$ ,  $\text{Ph}_4\text{P}_4\text{S}_2^+$ ,  $\text{Ph}_3\text{P}_3\text{S}_2^+$  and  $\text{Ph}_4\text{P}_2^+$ . The compound  $(\text{CF}_3\text{P})_4\text{S}$  is believed <sup>130</sup> to possess a five-membered  $\text{P}_4\text{S}$  ring on the basis of hydrolysis experiments; its mass spectrum has been reported <sup>131</sup> and shows significant differences from that of  $\text{Ph}_4\text{P}_4\text{S}$ . The spectra are mainly different because of the greatly differing ability of the phosphorus substituents to stabilize the molecular fragment; thus, in the mass spectrum of  $(\text{CF}_3\text{P})_4\text{S}$ , the major ions are of low molecular weight and the parent ion is  $\text{PS}^+$ . Larger fragments are much more stable in the mass spectrum of  $\text{Ph}_4\text{P}_4\text{S}$ ; for example, the abundance of  $\text{PS}^+$  is only 7% of the base peak,  $\text{Ph}_3\text{P}^+$ . The ion  $(\text{CF}_3)_3\text{P}^+$  does not appear in the mass spectrum of  $(\text{CF}_3\text{P})_4\text{S}$  even though its phenyl analogue is the base peak in that of  $\text{Ph}_4\text{P}_4\text{S}$ .

The fluorine chemical shifts of m- and (p- $\text{FC}_6\text{H}_4\text{P}$ )<sub>4</sub>S, together with the calculated inductive and resonance parameters, are reported in Table II. As might be expected, two fluorine resonances of equal area are seen in each spectrum; one resonance is attributed to the fluorophenyl groups attached to the two phosphorus atoms adjacent to sulphur, and the second resonance is attributed to the fluorophenyl groups attached to the remaining two phosphorus atoms. These results indicate that the structure of  $\text{Ph}_4\text{P}_4\text{S}$  is unaltered upon dissolution.

TABLE XII

VIBRATIONAL SPECTRA OF  $\text{Ph}_4\text{P}_4\text{S}$  AND  $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$

INFRARED SPECTRAL RESULTS \*

| <u><math>\text{Ph}_4\text{P}_4\text{S}</math></u> |           | <u><math>(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}</math></u> |           |
|---|-----------|---|-----------|
| FREQUENCY( $\text{cm}^{-1}$ )                     | INTENSITY | FREQUENCY( $\text{cm}^{-1}$ )                                   | INTENSITY |
| 505   | w         | 615   | w         |
| 483   | w         | 490   | sharp     |
| 464   | m         | 455   | w         |
| 454   | ms        | 435   | w         |
| 429   | w         | 400   | w         |
| 398   | m         | 350   | w         |
| 306   | w         | 328   | w         |

\*includes pertinent vibrations listed in Table II  
w=weak; m=medium; s=strong

RAMAN SPECTRAL RESULTS

| FREQUENCY( $\text{cm}^{-1}$ ) | INTENSITY | FREQUENCY( $\text{cm}^{-1}$ ) | INTENSITY |
|-------------------------------|-----------|-------------------------------|-----------|
| 1029                          | 2.3       | 828                           | 1.2       |
| 1001                          | 5.1       | 634                           | 0.8       |
| 690                           | 0.4       | 618                           | 1.7       |
| 620                           | 0.2       | 460                           | 1.1       |
| 513                           | 0.4       | 446                           | 1.0       |
| 492                           | 0.1       | 422                           | 3.0       |
| 450                           | 1.3       | 406                           | 10        |
| 437                           | 6.4       | 374                           | 0.2       |
| 406                           | 0.2       | 359                           | 0.7       |
| 371                           | 10        | 341                           | 1.6       |
| 315                           | 1.6       | 313                           | 2.5       |
| 300                           | 2.9       | 301                           | 2.8       |
| 284                           | 0.8       | 276                           | 0.8       |
| 264                           | 0.4       | 258                           | 0.4       |
| 252                           | 0.7       | 225                           | 0.1       |
| 218                           | 2.3       | 199                           | 2.0       |
| 184                           | 2.5       | 188                           | 1.4       |

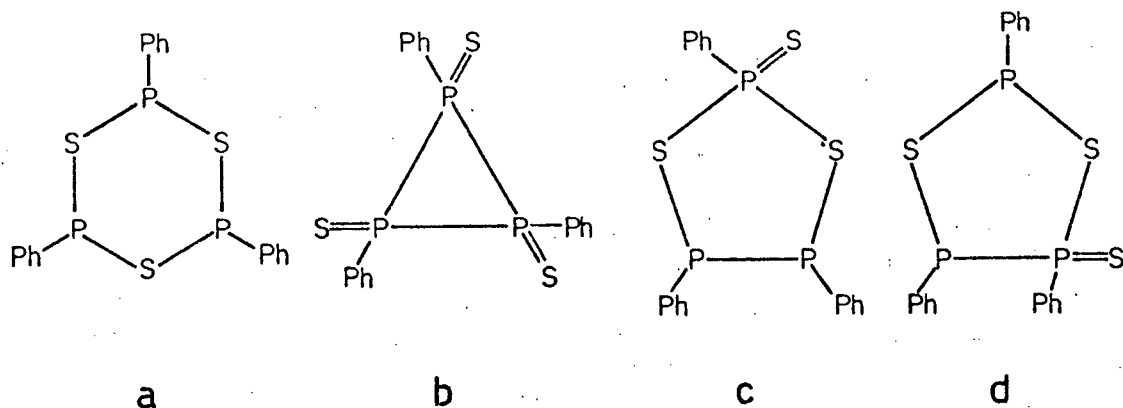
The infrared and Raman spectra of  $\text{Ph}_4\text{P}_4\text{S}$  and  $(\text{p-FC}_6\text{H}_4\text{P})_4\text{S}$  are reported in Table XII. Both compounds are characterized by weak to medium infrared absorption in the region reported in this Table; by contrast, the Raman absorption is quite strong. The strongest bands in the Raman spectrum of  $\text{Ph}_4\text{P}_4\text{S}$  appear at 437 and 371  $\text{cm}^{-1}$ , and can be considered as either P-P or P-S stretching. Amster and Colthup<sup>104</sup> have assigned bands in the region of 488-417  $\text{cm}^{-1}$  and 409-391  $\text{cm}^{-1}$  as asymmetric and symmetric ring stretching modes respectively in alkyl cyclopolyphosphines. The Raman band at 450  $\text{cm}^{-1}$ , and the infrared band at 454  $\text{cm}^{-1}$ , are most likely due to the P-sens(t) vibration. In general, assignments are very difficult because of the great number of vibrations that arise from the low symmetry of these two molecules.

#### The Cyclotriphosphine Trisulphides ( $\text{R}_3\text{P}_3\text{S}_3$ )

The reaction of sulphur with  $\text{Ph}_4\text{P}_4\text{S}$  results in formation of triphenylcyclotriphosphine trisulphide,  $\text{Ph}_3\text{P}_3\text{S}_3$ . As mentioned in the introduction, there has been disagreement and uncertainty about the structure of this compound. An erroneous molecule weight determination<sup>132</sup>, suggesting that this compound was a tetramer, was not detected by Maier<sup>82</sup> and apparently escaped unnoticed until Abel et al.<sup>133</sup> reported a molecular weight determination in agreement with a trimeric structure. Maier and Daly<sup>84</sup> then reported



space group data confirming the trimeric nature of  $\text{Ph}_3\text{P}_3\text{S}_3$ . Six possible structures of  $\text{Ph}_3\text{P}_3\text{S}_3$  have been illustrated in a later article by Maier<sup>135</sup>; four of these structures are illustrated below.



Structure (a) was suggested by Abel *et al.*<sup>133</sup> and was apparently favoured by Maier<sup>136</sup>. Baudler *et al.*<sup>85</sup> favoured structure (b) on the basis of infrared and mass spectral results. The mass spectra of  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $(p\text{-FC}_6\text{H}_4\text{PS})_3$  are reported in Table XIII. In each case, the high reactivity of these compounds results in peaks which can be explained only in terms of oxidation or hydrolysis products of the starting materials; thus, the parent ion (P) of  $\text{Ph}_3\text{P}_3\text{S}_3$  is observed at  $m/e$  420 and peaks present at  $m/e$   $P+16$ ,  $P+32$  and  $P+48$  are most likely due to oxidation although the peak at  $m/e$   $P+32$  may well correspond in part to  $\text{Ph}_3\text{P}_3\text{S}_4^+$ . The molecular ion at  $m/e$  464 has been previously assigned<sup>85</sup> as  $\text{Ph}_3\text{P}_3\text{S}_4\text{CH}_2^+$ . The high reactivity of  $(p\text{-FC}_6\text{H}_4\text{PS})_3$  is illustrated by strong peaks at  $m/e$  128

TABLE XIII

MASS SPECTRAL RESULTS FOR  $\text{Ph}_3\text{P}_3\text{S}_3$  AND  $(\text{p-FC}_6\text{H}_4\text{PS})_3$

| <u><math>\text{Ph}_3\text{P}_3\text{S}_3</math></u> |           |   | <u><math>(\text{p-FC}_6\text{H}_4\text{PS})_3</math></u> |           |   |
|---|-----------|---|--|-----------|---|
| PEAK<br>(m/e)                                       | ABUNDANCE | ASSIGNMENT(+)   | PEAK<br>(m/e)  | ABUNDANCE | ASSIGNMENT(+)                                 |
| 468   | 7.1       | $\text{Ph}_3\text{P}_3\text{S}_3\text{O}_3$                                 | 474  | 2.8       | $(\text{FC}_6\text{H}_4\text{PS})_3$          |
| 464   | 0.8       | $\text{Ph}_3\text{P}_3\text{S}_4\text{CH}_2$                                | 442  | 15.1      | $(\text{FC}_6\text{H}_4\text{P})_3\text{S}_2$ |
| 452   | 3.2       | $\text{Ph}_3\text{P}_3\text{S}_3\text{O}_2/\text{Ph}_3\text{P}_3\text{S}_4$ | 284  | 23.2      | $(\text{FC}_6\text{H}_4\text{P})_2\text{S}$   |
| 436   | 0.9       | $\text{Ph}_3\text{P}_3\text{S}_3\text{O}$                                   | 253  | 6.5       | $(\text{FC}_6\text{H}_4)_2\text{PS}$          |
| 420   | 10.4      | $\text{Ph}_3\text{P}_3\text{S}_3$   | 221  | 37.4      | $(\text{FC}_6\text{H}_4)_2\text{P}$           |
| 388   | 21.3      | $\text{Ph}_3\text{P}_3\text{S}_2$   | 219  | 12.5      | $(\text{FC}_6\text{H}_3)_2\text{P}$           |
| 356   | 9.1       | $\text{Ph}_3\text{P}_3\text{S}$   | 190  | 10.0      | $\text{FC}_6\text{H}_4\text{PS}_2$            |
| 324   | 7.1       | $\text{Ph}_3\text{P}_3$   | 160  | 45.0      | $\text{FC}_6\text{H}_4\text{P}(\text{OH})_2$  |
| 262   | 4.9       | $\text{Ph}_3\text{P}$   | 128  | 76.1      | $\text{FC}_6\text{H}_4\text{PH}_2$            |
| 248   | 100       | $\text{Ph}_2\text{P}_2\text{S}$   | 126  | 100       | $\text{FC}_6\text{H}_4\text{P}$               |
| 217   | 33        | $\text{Ph}_2\text{PS}$  | 63   | 78.3      | PS  |
| 185   | 100       | $\text{Ph}_2\text{P}$   |  |           |   |
| 183   | 85.0      | $(\text{C}_6\text{H}_4)_2\text{P}$  |  |           |   |
| 172   | 21.7      | $\text{PhPS}_2$   |  |           |   |
| 140   | 20.0      | $\text{PhPS}$   |  |           |   |
| 108   | 19.3      | $\text{PhP}$  |  |           |   |
| 107   | 52.1      | $\text{C}_6\text{H}_4\text{P}$  |  |           |   |
| 63  | 45.2      | PS  |  |           |   |

and  $m/e$  160,  $\text{FC}_6\text{H}_4\text{PH}_2^+$  and  $\text{FC}_6\text{H}_4\text{P}(\text{OH})_2^+$  respectively. No molecular ions larger than the parent ion were seen in the mass spectrum of  $(p\text{-FC}_6\text{H}_4\text{PS})_3$ . Baudler *et al.*<sup>85</sup> argued that the presence of peaks  $\text{Ph}_3\text{P}_3\text{S}_2^+$ ,  $\text{Ph}_3\text{P}_3\text{S}^+$  and  $\text{Ph}_3\text{P}_3^+$  in the mass spectrum of  $\text{Ph}_3\text{P}_3\text{S}_3$  was indicative of a stepwise loss of exocyclic sulphur atoms from a  $\text{P}_3$  ring; however, it has been demonstrated that significant rearrangements are a common feature of these compounds and, in particular, it is worth noting that the abundance of  $\text{Ph}_3\text{P}_3^+$  (7.1%) is similar to that of  $\text{Ph}_3\text{P}^+$  (4.9%), and that that of  $\text{Ph}_3\text{P}_3\text{S}_2^+$  (21.3%) is similar to that of  $\text{PhPS}_2^+$  (21.7%). Thus it does not seem justified to propose that  $\text{Ph}_3\text{P}_3\text{S}_3$  is based on a three-membered phosphorus ring; in fact, the  $^{19}\text{F}$  n.m.r. spectrum of  $(p\text{-FC}_6\text{H}_4\text{PS})_3$  (Fig.8) shows three distinct peaks of relative area 1:1:1, indicating the presence of three different phosphorus environments and suggesting that  $\text{Ph}_3\text{P}_3\text{S}_3$  possesses structure (d). The  $^{31}\text{P}$  n.m.r. spectrum (Fig.9) of  $(p\text{-FC}_6\text{H}_4\text{PS})_3$  is of the ABX type,  $\delta_A = -36.8$ ,  $\delta_B = -24.2$ ,  $\delta_X = +45.7$  p.p.m. (ext.  $\text{P}_4\text{O}_6$ ) with  $J_{AB} = 245$  Hz. and  $\sum AB:X = 2:1$ , confirming that  $\text{Ph}_3\text{P}_3\text{S}_3$  consists of an unsymmetrical five-membered ring; furthermore, the very large AB coupling constant is indicative of a direct P-P bond. This unexpected structure is identical to that of one of the rings of  $\text{P}_4\text{S}_5$  and the basic  $(\text{P}_2)(\text{SPS})$  ring is also found in  $\text{P}_4\text{S}_3$  and both forms of  $\text{P}_4\text{S}_3\text{I}_2$ .

FIG. 8:  $^{19}\text{F}$  n.m.r. spectrum of (*p*- $\text{FC}_6\text{H}_4\text{PS}$ )<sub>3</sub>

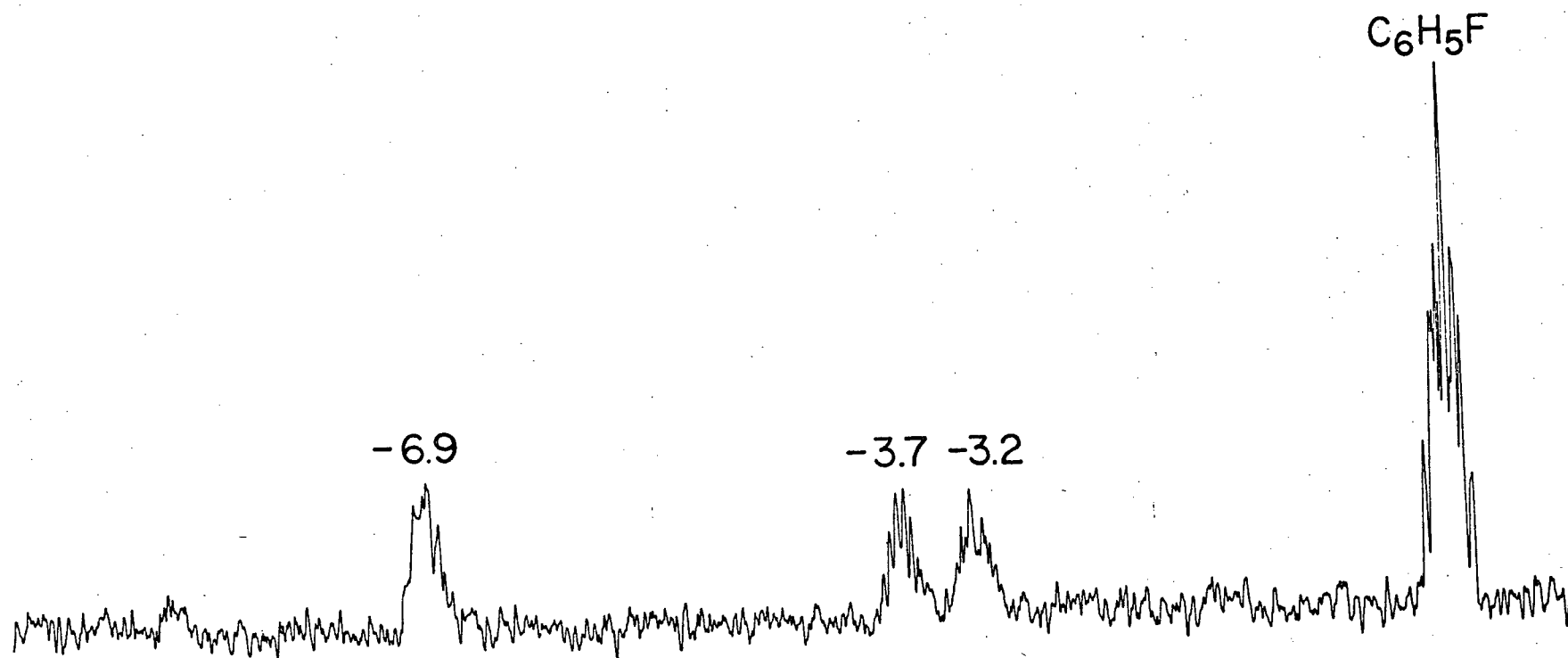


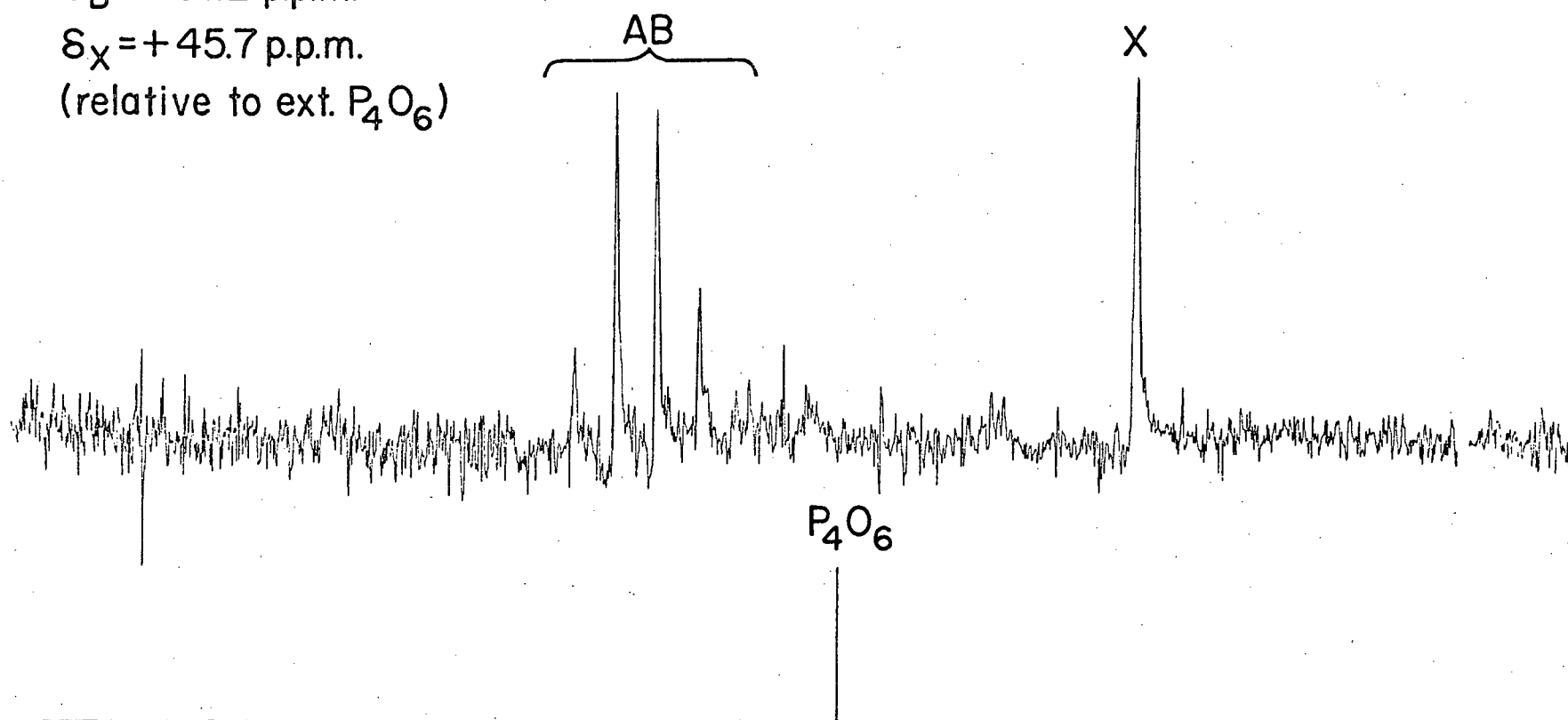
FIG. 9:  $^{31}\text{P}$  n.m.r. spectrum of  $(\text{p-FC}_6\text{H}_4\text{PS})_3$

$\delta_A = -36.8$  p.p.m.

$\delta_B = -24.2$  p.p.m.

$\delta_X = +45.7$  p.p.m.

(relative to ext.  $\text{P}_4\text{O}_6$ )



The infrared and Raman spectra of  $\text{Ph}_3\text{P}_3\text{S}_3$  and its fluorophenyl derivatives are reported in Table XIV. The lack of symmetry of these compounds again results in a tremendous number of infrared and Raman vibrations; consequently, few assignments have been made. The P=S stretching frequency is readily seen in each of the infrared spectra, however; the spectrum of  $(\text{p-FC}_6\text{H}_4\text{PS})_3$  is particularly useful in this regard as the strong C-H out-of-plane bending vibration is shifted to much higher frequencies and the region of  $600\text{--}700\text{ cm}^{-1}$  is greatly simplified. The very strong broad band at  $673\text{ cm}^{-1}$  is therefore confidently assigned as P=S stretching; bands of similar shape and intensity occur at  $648\text{ cm}^{-1}$  in  $\text{Ph}_3\text{P}_3\text{S}_3$  and at  $646\text{ cm}^{-1}$  in  $(\text{m-FC}_6\text{H}_4\text{PS})_3$ . Again, the strong unexplained band at  $710\text{ cm}^{-1}$  which appears to be characteristic of  $\text{PhP(S)}\diagdown$  linkages is present in the infrared spectrum of  $\text{Ph}_3\text{P}_3\text{S}_3$ ; the strong sharp band at  $687\text{ cm}^{-1}$  in  $(\text{m-FC}_6\text{H}_4\text{PS})_3$  is believed to be due to the same vibration.

Raman bands at  $467$ ,  $440$  and  $354\text{ cm}^{-1}$  in  $\text{Ph}_3\text{P}_3\text{S}_3$  appear to correlate with bands at  $452$ ,  $433$  and  $340\text{ cm}^{-1}$  in  $(\text{p-FC}_6\text{H}_4\text{PS})_3$ . The vibration appearing at  $467\text{ cm}^{-1}$  in  $\text{Ph}_3\text{P}_3\text{S}_3$  may be the P-sens.(t) vibration but it appears to be rather too strong by comparison with other spectra; either this band, or that at  $511\text{ cm}^{-1}$ , is likely to be due to the P-P stretching vibration. The strong vibrations at  $440$  and  $354\text{ cm}^{-1}$  in the Raman spectrum of  $\text{Ph}_3\text{P}_3\text{S}_3$ , and

TABLE XIV

VIBRATIONAL SPECTRA OF  $\text{Ph}_3\text{P}_3\text{S}_3$  AND ITS FLUOROPHENYL ANALOGUES

| $\text{Ph}_3\text{P}_3\text{S}_3$ |                       |  | I. RAMAN SPECTRA                  |                       |                          | $(\text{p-FC}_6\text{H}_4\text{PS})_3$ |                       |            |
|-----------------------------------|-----------------------|--|-----------------------------------|-----------------------|--------------------------|--|-----------------------|------------|
| FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | ASSIGNMENT                             | FREQUENCY<br>( $\text{cm}^{-1}$ ) | RELATIVE<br>INTENSITY | ASSIGNMENT               | FREQUENCY<br>( $\text{cm}^{-1}$ )      | RELATIVE<br>INTENSITY | ASSIGNMENT |
| 714                               | 1.1                   |  | 682                               | 8.0                   | P-sens.(r)               |  |                       |            |
| 655                               | 3.4                   | $\nu(\text{P}=\text{S})$               | 675                               | 8.0                   | $\nu(\text{P}=\text{S})$ |  |                       |            |
| 619                               | 1.5                   |  | 619                               | 4.1                   |                          |  |                       |            |
| 511                               | 3.7                   | see text                               | 499                               | 1.8                   |                          |  |                       |            |
| 467                               | 5.5                   | P-sens.(t) or $\nu(\text{P}-\text{P})$ | 452p                              | 8.0                   |                          |  |                       |            |
| 440                               | 4.9                   | see text                               | 433p                              | 10                    | see text                 |  |                       |            |
| 405                               | 1.1                   |  | 413p                              | 4.6                   |                          |  |                       |            |
| 378                               | 1.9                   |  | 401                               | 1.7                   |                          |  |                       |            |
| 354                               | 10                    | see text                               | 340p                              | 9.8                   | see text                 |  |                       |            |
| 317                               | 4.3                   |  | 315                               | 2.8                   |                          |  |                       |            |
| 289                               | 3.1                   |  | 304                               | 4.3                   |                          |  |                       |            |
| 270                               | 1.9                   |  | 294                               | 1.9                   |                          |  |                       |            |
| 242                               | 2.0                   |  | 257                               | 2.9                   |                          |  |                       |            |
| 218                               | 2.2                   |  | 242                               | 2.3                   |                          |  |                       |            |

p=polarized

(continued overleaf)

TABLE XIV(cont.)

II. INFRARED SPECTRA\*

| (p-FC <sub>6</sub> H <sub>4</sub> PS) <sub>3</sub> |                       |            | (m-FC <sub>6</sub> H <sub>4</sub> PS) <sub>3</sub> |                       |            |
|--|-----------------------|------------|--|-----------------------|------------|
| FREQUENCY<br>(cm <sup>-1</sup> )                   | RELATIVE<br>INTENSITY | ASSIGNMENT | FREQUENCY<br>(cm <sup>-1</sup> )                   | RELATIVE<br>INTENSITY | ASSIGNMENT |
| 702  | w                     |            | 687  | s                     | see text   |
| 673  | vs                    | ν(P=S)     | 646  | s                     | ν(P=S)     |
| 615,611  | m                     |            | 555  | m                     |            |
| 522  | ms                    |            | 517  | m                     |            |
| 504  | ms                    |            | 507  | m                     |            |
| 492  | ms                    |            | 488  | s                     |            |
| 444  | ms                    |            | 466  | s                     |            |
| 422  | mw                    |            | 438,432  | m                     |            |
| 405  | w                     |            | 371  | m                     |            |
| 365  | w                     |            | 311  | w                     |            |
| 338  | w                     |            | 256  | w                     |            |
| 325  | w                     |            |  |                       |            |

| Ph <sub>3</sub> P <sub>3</sub> S <sub>3</sub> |                       |            |
|---|-----------------------|------------|
| FREQUENCY<br>(cm <sup>-1</sup> )              | RELATIVE<br>INTENSITY | ASSIGNMENT |
| 710   | s                     | see text   |
| 648   | vs                    | ν(P=S)     |
| 610   | w                     |            |
| 504   | m                     |            |
| 478   | m                     |            |
| 468,462                                       | ms                    |            |
| 430   | w                     |            |
| 395   | w                     |            |

v=very; w=weak; m=medium; s=strong

\* includes absorptions listed in Table IV



those at 433 and 340  $\text{cm}^{-1}$  in the Raman spectrum of  $(\text{p-FC}_6\text{H}_4\text{PS})_3$  are believed to be due to stretching vibrations of the  $\text{P}_3\text{S}_2$  ring. The intensity of these absorptions essentially eliminates the possibility that they may be due to vibrations within the phenyl rings. To substantiate the argument that these vibrations are due to the  $\text{P}_3\text{S}_2$  ring, it is worth noting the following points:

- (i)  $\text{P}_4\text{S}_3$ , containing three fused  $\text{P}_3\text{S}_2$  rings, has Raman absorption at 443 and 342  $\text{cm}^{-1}$ ; these two bands are the strongest observed for  $\text{P}_4\text{S}_3$  and are thought to be symmetric and antisymmetric P-S stretching respectively.
- (ii)  $\text{P}_4\text{S}_7$ , containing two fused  $\text{P}_3\text{S}_2$  rings, has very strong Raman absorption<sup>36</sup> at 346  $\text{cm}^{-1}$  and strong absorption at 444  $\text{cm}^{-1}$ .
- (iii)  $\text{P}_4\text{S}_5$ , containing two fused  $\text{P}_3\text{S}_2$  rings, has strong absorption<sup>36</sup> at 388  $\text{cm}^{-1}$  and strong bands at both 434 and 452  $\text{cm}^{-1}$ .

The suggestion by Baudler et al.<sup>85</sup> that the region 550-600  $\text{cm}^{-1}$  is typical of P-S stretching is not justified and the lack of absorption by  $\text{Ph}_3\text{P}_3\text{S}_3$  in this region cannot be considered as evidence that  $\text{Ph}_3\text{P}_3\text{S}_3$  consists of a three-membered phosphorus ring.

The Fluorophenyl Cyclopolyphosphines  $(\text{FC}_6\text{H}_4\text{P})_n$

The mass spectra of the fluorophenyl cyclopolyphosphines are presented in Table XV. These results indicate that  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  most likely has a pentameric structure, whereas  $(\underline{p}\text{-FC}_6\text{H}_4\text{P})_n$  probably has a hexameric structure. Peaks are seen at all values of  $n = 1-5$  for  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  and there appears to be no reason why the  $n = 6$  species should not also appear if it were the parent ion. On the other hand, the abundance of the  $(\text{FC}_6\text{H}_4\text{P})_6^+$  ion is greater than that of the  $(\text{FC}_6\text{H}_4\text{P})_5^+$  ion in the mass spectrum of  $(\underline{p}\text{-FC}_6\text{H}_4\text{P})_n$ , suggesting that the former peak is the parent ion. The mass spectrum of  $(\underline{p}\text{-FC}_6\text{H}_4\text{P})_n$  is much more complex than that of  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  and several high molecular weight fragments can only be explained if it is assumed that a phenyl group has broken up. The infrared and Raman spectra of  $(\underline{p}\text{-FC}_6\text{H}_4\text{P})_n$  have been obtained; in the infrared spectrum, the strongest bands are due to the fluorophenyl groups, whilst in the Raman spectrum, a very strong band at  $476\text{ cm}^{-1}$  is the only intense band in that region and is therefore confidently assigned as P-P stretching.

TABLE XV

MASS SPECTRA OF COMPOUNDS  $(\text{FC}_6\text{H}_4\text{P})_n$

| <u><math>(\text{p-FC}_6\text{H}_4\text{P})_n</math></u> |           |   | <u><math>(\text{m-FC}_6\text{H}_4\text{P})_n</math></u> |           |   |
|---|-----------|---|---|-----------|---|
| PEAK<br>(m/e)   | ABUNDANCE | ASSIGNMENT <sup>(+)</sup>                                   | PEAK<br>(m/e)   | ABUNDANCE | ASSIGNMENT <sup>(+)</sup>                               |
| 756   | 17        | $(\text{FC}_6\text{H}_4\text{P})_6$                         |   |           |   |
| 630   | 14        | $(\text{FC}_6\text{H}_4\text{P})_5$                         | 630   | 4         | $(\text{FC}_6\text{H}_4\text{P})_5$                     |
| 535   | 24        | $(\text{FC}_6\text{H}_4)_4\text{P}_5$                       |   |           |   |
| 504   | 42        | $(\text{FC}_6\text{H}_4\text{P})_4$                         | 504   | 2         | $(\text{FC}_6\text{H}_4\text{P})_4$                     |
| 485   | 16        | $(\text{FC}_6\text{H}_4)_3\text{P}_4(\text{C}_6\text{H}_4)$ |   |           |   |
| 471   | 19        | $\text{FC}_6\text{H}_3\text{P}_6?$                          |   |           |   |
| 456   | 21        | ?   |   |           |   |
| 442   | 31        | $(\text{FC}_6\text{H}_4)_4\text{P}_2$                       |   |           |   |
| 414   | 20        | ?   |   |           |   |
| 409   | 18        | $(\text{FC}_6\text{H}_4)_3\text{P}_4$                       |   |           |   |
| 378   | 26        | $(\text{FC}_6\text{H}_4\text{P})_3$                         | 378   | 77        | $(\text{FC}_6\text{H}_4\text{P})_3$                     |
| 327   | 25        | ?   |   |           |   |
| 316   | 100       | $(\text{FC}_6\text{H}_4)_3\text{P}$                         | 316   | 100       | $(\text{FC}_6\text{H}_4)_3\text{P}$                     |
| 252   | 22        | $(\text{FC}_6\text{H}_4\text{P})_2$                         | 252   | 30        | $(\text{FC}_6\text{H}_4\text{P})_2$                     |
| 221   | 97        | $(\text{FC}_6\text{H}_4)_2\text{P}$                         | 221   | 69        | $(\text{FC}_6\text{H}_4)_2\text{P}$                     |
| 219   | 62        | $(\text{FC}_6\text{H}_3)_2\text{P}$                         | 219   | 51        | $(\text{FC}_6\text{H}_3)_2\text{P}$                     |
| 201   | 35        | $(\text{FC}_6\text{H}_3)\text{P}(\text{C}_6\text{H}_4)$     | 201   | 25        | $(\text{FC}_6\text{H}_3)\text{P}(\text{C}_6\text{H}_4)$ |
| 187   | 41        | $\text{FC}_6\text{H}_3\text{P}_3?$                          |   |           |   |
| 157   | 33        | $\text{FC}_6\text{H}_4\text{P}_2$                           | 157   | 32        | $\text{FC}_6\text{H}_4\text{P}_2$                       |
| 135   | 31        | ?   |   |           |   |
|   |           |   | 126   | 92        | $\text{FC}_6\text{H}_4\text{P}$                         |

# ELECTRONIC INTERACTIONS OF THE FLUOROPHENYL DERIVATIVES

The sensitivity of the shielding of fluorine to small changes in molecular environment is well-known, and for many groups the interpretation of the fluorine chemical shifts of m-fluorophenyl and p-fluorophenyl derivatives in terms of  $\pi$ -electron densities has been justified theoretically<sup>137-139</sup> and the shielding parameters correlated<sup>80</sup> with the Taft reactivity parameters  $\sigma_I$  and  $\sigma_{R^0}$ . More recently<sup>123</sup>, it has been found that there is a good correlation between  $\sigma_{R^0}$  and  $\sum \Delta q(\pi)$ , as obtained from CNDO/2 calculations, so verifying that  $\sigma_{R^0}$  is a measure of  $\pi$ -charge transfer and hence of conjugative interactions. The parameters have also been shown to be applicable to substitution at a phosphorus centre<sup>71</sup>.

The  $^{19}\text{F}$  chemical shifts of the fluorophenyl derivatives prepared in this work, and the calculated inductive and resonance parameters, have been presented in Table II. Related data for previously reported compounds are listed in Table XVI and will be used for comparison purposes. The results for the fluorophenyl cyclopolyphosphines are of great interest because several variables, such as the oxidation state of phosphorus and the presence of sulphur, are eliminated. Unfortunately, the para-fluorophenyl cyclopolyphosphine was too insoluble to obtain a fluorine n.m.r. spectrum; however, the pentafluorophenyl cyclopoly-

TABLE XVI

SHIELDING PARAMETERS<sup>a</sup> AND TAFT INDUCTIVE AND RESONANCE PARAMETERS

| COMPOUND  | $\delta(\underline{m}\text{-F})$ | $\delta(\underline{p}\text{-F})$ | $\sigma_{\text{I}}$ | $\sigma_{\text{R}}^{\circ}$ | REFERENCE |
|---|----------------------------------|----------------------------------|---------------------|-----------------------------|-----------|
| $\text{FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$           | -0.9                             | -0.7                             | +0.21               | -0.01                       | 97,98     |
| $(\text{FC}_6\text{H}_4)_3\text{P}$                               | -1.3                             | -1.2                             | +0.27               | $\sim 0$                    | 97,98     |
| $\text{FC}_6\text{H}_4\text{P}(\text{S})(\text{C}_6\text{H}_5)_2$ | -2.2                             | -5.5                             | +0.39               | +0.16                       | 97,98     |
| $(\text{FC}_6\text{H}_4)_3\text{P}=\text{S}$                      | --                               | -4.8                             | --                  | --                          | 97        |
| $\text{FC}_6\text{H}_4\text{PF}_4$                                | -2.6                             | -12.1                            | +0.45               | +0.32                       | 71        |
| $\text{FC}_6\text{H}_4\text{PF}_2$                                | -2.1                             | -8.3                             | +0.38               | +0.21                       | 71        |
| $\text{FC}_6\text{H}_4\text{N}_n\text{P}_n\text{F}_{2n-1}$        | -3.3                             | -10.2                            | +0.56               | +0.20                       | 146       |
| $\text{FC}_6\text{H}_4\text{Br}$                                  | -2.55                            | +2.55                            | +0.44               | -0.16                       | 80        |
| $\text{FC}_6\text{H}_4\text{F}$                                   | -3.10                            | +6.40                            | +0.52               | -0.32                       | 80        |

a. using dilute solutions with  $\text{C}_6\text{H}_5\text{F}$  as internal standard

phosphine,  $(C_6F_5P)_5$ , has been examined by Cowley and Pinnell<sup>140</sup> who report that "the  $\pi$ -bonding situation in  $(C_6F_5P)_5$  would appear to be about the same as in  $C_6F_5P(C_6H_5)_2$  in terms of the published relationships<sup>141, 142</sup> between the chemical shift of the para  $^{19}F$  resonance and  $\pi$ -bonding in pentafluorophenylphosphine derivatives."

It might be expected, therefore, that the inductive and conjugative effects in the monofluorophenyl cyclopolyphosphines will resemble those in the monofluorophenyl-diphenylphosphines; in fact, the  $\sigma_I$  value of  $\underline{m}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  is +0.21 whereas the average  $\sigma_I$  value of  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  is +0.29. Much of this difference can be attributed to the presence of more than one fluorophenyl group; the effect of additional fluorophenyl groups can be seen by comparing the  $\sigma_I$  values of  $\underline{m}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  and  $(\underline{m}\text{-FC}_6\text{H}_4)_3\text{P}$ , +0.21 and +0.27 respectively (Table XVI). The observed difference of +0.06 is likely greater than the difference that would be expected for  $\underline{m}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_{n-1}$  with respect to  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$ , since the latter compound has only one fluorophenyl group per phosphorus atom. Nonetheless, it is apparent that inductive effects in  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  and  $\underline{m}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  are indeed similar. There are several possible explanations for the appearance of two fluorine resonances in the n.m.r. spectrum of  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$ : perhaps the most likely is that two different

ring sizes are present in solution; the existence of several ring sizes has been noted for the phenyl cyclo-polyphosphine<sup>134</sup>, pentafluorophenyl cyclopolyphosphine<sup>140</sup> and trifluoromethyl cyclopolyphosphine<sup>143</sup> systems.

On the other hand, the mass spectrum of  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  suggests that this compound consists of a five-membered ring in the solid state; the analogous compound  $(\text{PCF}_3)_5$  exhibits two  $\text{CF}_3$  multiplets in its  $^{19}\text{F}$  n.m.r. spectrum and this has been attributed<sup>143</sup> to pseudo-rotation, a cyclic interchange of the role of the P atoms, and hence of the  $\text{CF}_3$  groups, around the ring through a torsional vibration. Pseudo-rotation might well occur in  $(\underline{m}\text{-FC}_6\text{H}_4\text{P})_n$  if this compound does contain a  $\text{P}_5$  ring in solution. Since no  $^{19}\text{F}$  n.m.r. spectrum could be obtained for  $(\underline{p}\text{-FC}_6\text{H}_4\text{P})_n$ , the conjugative interactions within the cyclopolyphosphine ring have been inferred by using Cowley's statement<sup>140</sup> that  $\pi$ -bonding is similar to that observed in  $\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_5)_2$ . The Taft resonance parameter,  $\sigma_{\text{R}0}$ , for the analogous para-fluorophenyl derivative,  $\underline{p}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$ , is -0.01, indicating that the  $\text{P}(\text{C}_6\text{H}_5)_2$  moiety is a weak, but net  $\pi$ -donor to its attached fluorophenyl group. Therefore, the phosphorus ring in phenyl cyclopolyphosphines is apparently a weak  $\pi$ -donor to its attached phenyl rings. The magnitude of  $\sigma_{\text{R}0}$  is so small in  $\underline{p}\text{-FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  that it is entirely possible that the cyclopolyphosphine ring may be a weak  $\pi$ -acceptor; however, there will obviously not be a great transfer of  $\pi$ -density between the phenyl

rings and the skeletal phosphorus ring.

In  $\text{Ph}_4\text{P}_4\text{S}$ , a five-membered ring is again present except that one PhP grouping has been replaced by sulphur. Not surprisingly, the substitution of one sulphur within the ring does not produce drastic changes. The inductive and resonance parameters of the  $\text{P}_4\text{S}$  skeleton are +0.26 (avg.) and -0.02, respectively, very close to those of  $\text{FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  (+0.21 and -0.01 respectively), bearing in mind the likely effects of the presence of additional fluorophenyl groups. The  $\text{P}_4\text{S}$  ring is thus a weak  $\pi$ -donor to its attached fluorophenyl groups; in fact, it must be considered to be a stronger  $\pi$ -donor than these results indicate because of the presence of four fluorophenyl groups. Fluorine itself is known to be a reasonable  $\pi$ -donor<sup>80</sup>, so that the  $\pi$ -donor capacity of the  $\text{P}_4\text{S}$  ring is sufficient to outweigh the combined effects of the four fluorine atoms. The movement of electronic density within the  $\text{P}_4\text{S}$  ring is therefore very similar to that inferred for the cyclopolyphosphine system.

The addition of sulphur to  $\text{Ph}_4\text{P}_4\text{S}$  results in formation of  $\text{Ph}_3\text{P}_3\text{S}_3$  and the  $\text{P}_3\text{S}_2$  ring found in this compound is a characteristic feature of many other phosphorus-sulphur compounds. It is apparent from the results listed in Table II that this addition of sulphur results in significant changes in both the inductive and resonance



parameters.

The most deshielded fluorine atom in both the meta- and para- derivatives is considered to be in the fluorophenyl group attached to the pentavalent phosphorus atom. The remaining two fluorine atoms cannot be distinguished in the spectrum of (m-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub> but are clearly non-equivalent in the spectrum of (p-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub>. Table II illustrates that inductive withdrawal from the fluorophenyl groups is relatively insensitive to the oxidation state of phosphorus, even though conjugative withdrawal is obviously very sensitive to this parameter. The constancy of  $\sigma_I$  suggests that, either there exists very efficient inductive transmission throughout the ring, or that the presence of sulphur plays the major role in causing inductive withdrawal. The magnitude of this withdrawal is surprisingly large, approximating that of a bromine substituent<sup>80</sup>; in fact the  $\sigma_I$  values of the fluorophenyl groups attached to the trivalent phosphorus atoms almost rival the  $\sigma_I$  value found for m-FC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>. The  $\sigma_{R0}$  parameters reveal that  $\pi$ -electron density is withdrawn from all the fluorophenyl groups, but to a varying degree. As stated previously, the largest withdrawal is considered to be from the fluorophenyl group attached to the pentavalent phosphorus; the value of  $\sigma_{R0}$  of +0.14 is very similar to that obtained for m- and p-FC<sub>6</sub>H<sub>4</sub>P(S)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (Table XVI). Further, the difference in  $\sigma_{R0}$  between the

TABLE XVII

EFFECT OF FLUORINE IN THE *para*- POSITION  
ON VARIOUS INFRARED STRETCHING FREQUENCIES

| COMPOUND  | $\nu(\text{P-I})(\text{cm}^{-1})$ |
|---|-----------------------------------|
| $\text{Ph}_2\text{P}_2\text{I}_2$                         | 337                               |
| $(\underline{\text{m}}\text{-FC}_6\text{H}_4\text{PI})_2$ | 340                               |
| $(\underline{\text{p}}\text{-FC}_6\text{H}_4\text{PI})_2$ | 366                               |

| COMPOUND  | $\nu(\text{P=S})(\text{cm}^{-1})$ |
|---|-----------------------------------|
| $\text{Ph}_3\text{P}_3\text{S}_3$                         | 648                               |
| $(\underline{\text{m}}\text{-FC}_6\text{H}_4\text{PS})_3$ | 646                               |
| $(\underline{\text{p}}\text{-FC}_6\text{H}_4\text{PS})_3$ | 673                               |

| COMPOUND  | $\nu(\text{P=S})(\text{cm}^{-1})$ |
|---|-----------------------------------|
| $\text{Ph}_2\text{P}_2\text{S}_4$                           | 655                               |
| $(\underline{\text{m}}\text{-FC}_6\text{H}_4\text{PS}_2)_2$ | 652                               |
| $(\underline{\text{p}}\text{-FC}_6\text{H}_4\text{PS}_2)_2$ | 687                               |

$\text{FC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$  and  $\text{FC}_6\text{H}_4\text{P}(\text{S})(\text{C}_6\text{H}_5)_2$  systems is very close to the difference in  $\sigma_{\text{R}}$  observed between the pentavalent phosphorus atom in the  $(\text{FC}_6\text{H}_4\text{PS})_3$  system and the trivalent phosphorus atoms in the  $(\text{FC}_6\text{H}_4\text{P})_4\text{S}$  system. An examination of the P=S infrared stretching frequencies (Table XVII) reveals that the P=S bond is strengthened significantly in  $(\text{p-FC}_6\text{H}_4\text{PS})_3$ , suggesting that at least part of the  $\pi$ -electron density withdrawn from the fluorophenyl group (attached to the pentavalent phosphorus) is transferred to the P=S bond via  $\pi$ -donor action from fluorine itself, and not just from the benzene  $\pi$ -system. Note that the P=S stretching frequency of  $(\text{m-FC}_6\text{H}_4\text{PS})_3$ , in which conjugative interaction with fluorine is not possible, is essentially unchanged from that of  $\text{Ph}_3\text{P}_3\text{S}_3$ .

Knox et al.<sup>144</sup> studied the meta- and para-substituted derivatives of  $\text{XC}_6\text{H}_4\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$  (X=MeO, Me, F, Cl,  $\text{CO}_2\text{Me}$ , CN) and found a linear correlation between the Hammett  $\sigma$ -constants and the symmetric and antisymmetric infrared stretching frequencies of the CO groups. However, the changes in these frequencies were small,  $\Delta\nu_{\text{asym.}} = 15 \text{ cm}^{-1}$  and  $\Delta\nu_{\text{sym.}} = 12 \text{ cm}^{-1}$ . Stewart and Treichel<sup>145</sup>, on the other hand, prepared the series meta- and para- $\text{XC}_6\text{H}_4\text{Mn}(\text{CO})_5$  (X=H, F, Cl, Br, CN,  $\text{CF}_3$ ) and found that the CO vibrations were practically invariant to both the nature of the substituent X and to its position on the ring; these authors suggest that the larger effects observed by

Knox et al.<sup>144</sup> probably result from the presence of only two CO groups (vs. five in the manganese compounds) in that these two carbonyls would be forced to respond to a greater extent and appear more sensitive to the net electron density change. By contrast, the difference in the P=S stretching frequencies of m- and (p-FC<sub>6</sub>H<sub>4</sub>PS)<sub>3</sub> is 27 cm<sup>-1</sup>, much larger than the frequency change for the CO vibrations. It appears that other workers have not noticed the effect of  $\pi$ -donation from fluorine as distinct from donation from the benzene  $\pi$ -system, perhaps because the effects are usually small; with such highly polarizable bonds as P=S and P-I, the effects are more readily seen. The main conclusion that should be made from these observations is that conjugative interactions with a p-fluorophenyl group reflect the combined effects of the donor-acceptor properties of the benzene  $\pi$ -system and the  $\pi$ -donor properties of fluorine, an extension and modification of the original concepts<sup>80</sup>. Substituents X (in p-FC<sub>6</sub>H<sub>4</sub>X compounds) which exhibit  $\pi$ -donor properties with respect to the fluorophenyl group are thus stronger donors than otherwise appears in that their  $\pi$ -donor capabilities must initially counteract the  $\pi$ -donor action of fluorine. Similarly, a substituent X (in C<sub>6</sub>H<sub>5</sub>X compounds) may actually be a weak  $\pi$ -donor but appear from n.m.r. chemical shifts (in FC<sub>6</sub>H<sub>4</sub>X compounds) to act as a weak  $\pi$ -acceptor if its  $\pi$ -donor capabilities are less than those of fluorine. It is important to keep these effects

in mind when interpreting the conjugative interactions of fluorophenyl derivatives, since it is virtually impossible to distinguish between donor activity from the benzene  $\pi$ -system and from fluorine  $\pi$ -orbitals.

A comparison of the results obtained with monofluorophenyl systems<sup>80</sup> to those obtained with pentafluorophenyl systems<sup>142</sup> reinforces the ideas presented above. According to Taft et al.<sup>80</sup>, the halogens are essentially weak  $\pi$ -donors with  $\sigma_R$  values becoming more negative in the series  $H < I < CH_3 < Br < Cl < F$ . However, according to Graham et al.<sup>142</sup> who used pentafluorophenyl derivatives, the order of  $\pi$ -donor strength is  $I < H < Br < Cl < CH_3 < F$

so that with the exception of fluorine, they might be considered as  $\pi$ -acceptors. A logical explanation of this difference is that in the pentafluorophenyl systems,  $C_6F_5X$ , there are three fluorine atoms capable of donating  $\pi$ -electron density in a conjugative manner to the substituent X. Here, then, is an illustration of the point that was made above: the combined action of  $\pi$ -donation from three fluorine atoms changes the substituent X from being a weak  $\pi$ -donor to being a weak  $\pi$ -acceptor. Of course, the effect of inductive withdrawal by the  $C_6F_5$  group would enable substituent X to successfully compete for  $\pi$ -electron density and cannot be overlooked. In all fairness though, it can be stated that the magnitude of donor-acceptor interactions will be exaggerated if one

uses pentafluorophenyl derivatives instead of monofluorophenyl derivatives.

The fluorine chemical shift of para-fluorophenyl species,  $p\text{-FC}_6\text{H}_4\text{X}$ , will therefore depend not only on the ability of substituent X to receive or donate  $\pi$ -charge, but will also depend, to a certain degree, on the inherent  $\pi$ -donor ability of fluorine. This  $\pi$ -donor ability of fluorine would be expected to remain fairly constant as long as the para- substituent X is capable of  $\pi$ -interactions (excluding  $\text{X}=\text{H}$ , for example) so that the comparisons that have been made, and will be made, remain valid. Even though the magnitude of the  $\sigma_{\text{R}^0}$  values may not be completely accurate in that they should probably be made somewhat more negative, the trends observed within a series will not be affected.

Let us consider once again the  $\pi$ -interactions within the  $(\text{FC}_6\text{H}_4\text{PS})_3$  system. As pointed out by Taft et al.<sup>71</sup>,  $p\pi$ -acceptor interaction by phosphorus is greatly diminished when the phosphorus is tetracoordinate, because  $p$ -orbitals are largely involved in  $\sigma$ -bond formation; consequently, the predominant acceptor interaction will involve use of  $d$  orbitals on phosphorus. It is apparent, therefore, that the  $\text{P}=\text{S}$  bond in  $(p\text{-FC}_6\text{H}_4\text{PS})_3$  is strengthened by enhanced  $d\pi - p\pi$  bonding between P and S, or possibly by  $d\pi - d\pi$  bonding. Conjugative withdrawal

from the fluorophenyl groups attached to the trivalent phosphorus atoms is slight, but distinctly different from the effects observed in the  $P_4S$  ring. It is difficult to determine whether this  $\pi$ -electron density is transferred to sulphur, or whether it remains with phosphorus to compensate for the accumulation of positive charge resulting from inductive withdrawal by sulphur. In all probability, the true bonding picture lies somewhere between these extremes.

Addition of sulphur to  $Ph_3P_3S_3$  results in a structural change to  $Ph_2P_2S_4$ , a four-membered  $P_2S_2$  ring. The fluorophenyl derivatives of this compound are exceptional in that they exhibit both strong inductive and conjugative withdrawal. The presence of only two fluorophenyl groups in this molecule ensures that the effects of one on the other will be lowered and that the results obtained reflect accurately the various interactions within the  $P_2S_4$  framework. Inductive withdrawal from the fluorophenyl groups is extremely large and the value of  $\sigma_I$  (+0.58) is of the same order of magnitude as those found for such strong  $\sigma$ -acceptors as F (+0.52) and  $NO_2$  (+0.56). Conjugative withdrawal is also strong and the magnitude of  $\sigma_{Ro}$  (+0.20) is similar to the values found for such strong  $\pi$ -acceptors as CN and  $NO_2$ , +0.21 and +0.20 respectively. From Table XVI, it is apparent that the value of  $\sigma_{Ro}$  in the  $(FC_6H_4PS_2)_2$  system is not greatly different from the  $\sigma_{Ro}$

values of other compounds in which phosphorus is pentavalent and tetracoordinate. Again, the P=S bond is observed to be strengthened (Table XVII) in the *p*-fluorophenyl derivative; the *m*-fluorophenyl derivative exhibits a P=S stretching frequency at essentially the same frequency as its phenyl analogue, confirming that the P=S bond in (*p*-FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub> is strengthened (with respect to Ph<sub>2</sub>P<sub>2</sub>S<sub>4</sub>) by way of conjugative interaction with fluorine. At the same time, it is important to note that the P=S stretching frequency in Ph<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (655 cm<sup>-1</sup>) occurs at a much higher frequency than in Me<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (617 cm<sup>-1</sup>), illustrating the importance of donation from the benzene π-system. Since both phosphorus atoms in Ph<sub>2</sub>P<sub>2</sub>S<sub>4</sub> are equivalent and are tetracoordinate, π-acceptor activity at phosphorus must involve population of d orbitals for the reasons outlined previously. The ability of pentavalent phosphorus to act as a π-acceptor has been noted by several workers<sup>71,97,98,146</sup> and the value of σ<sub>R</sub>o obtained for the (FC<sub>6</sub>H<sub>4</sub>PS<sub>2</sub>)<sub>2</sub> system appears to be a typical value. As might be expected, larger values of σ<sub>R</sub>o have been obtained (Table XVI) for the FC<sub>6</sub>H<sub>4</sub>PF<sub>4</sub> system and also for the monofluorophenyl phosphonitric fluoride (FC<sub>6</sub>H<sub>4</sub>P<sub>n</sub>N<sub>n</sub>F<sub>n-1</sub>) system. The very large acceptor properties of the P<sub>2</sub>S<sub>4</sub> framework is confirmed by the proton chemical shift of Me<sub>2</sub>P<sub>2</sub>S<sub>4</sub>, which is centred at the low value of 7.50 τ. By comparison, the proton chemical shift<sup>147</sup> of methyl heptafluorocyclotetraphosphonitrile, N<sub>4</sub>P<sub>4</sub>F<sub>7</sub>Me, is



centred at 8.30  $\tau$ . In addition, the following proton chemical shifts have been reported by Nixon and Schmutzler<sup>148</sup>:  $\text{MePF}_4$ , 8.12  $\tau$ ;  $\text{MeP(O)Cl}_2$ , 7.72  $\tau$ ;  $\text{MeP(S)Cl}_2$ , 7.12  $\tau$ . It is thus readily apparent that the proton chemical shift of  $\text{Me}_2\text{P}_2\text{S}_4$  is rather low.

The inductive and resonance parameters obtained for the  $(\text{FC}_6\text{H}_4\text{PI})_2$  system are +0.35 and +0.15 respectively. Inductive withdrawal is intermediate between that observed for  $(\text{m-FC}_6\text{H}_4\text{P})_4\text{S}$  and  $(\text{m-FC}_6\text{H}_4\text{PS})_3$ ; conjugative withdrawal is also of moderate intensity and the effect of the *p*-fluorophenyl group serves to strengthen the P-I bond considerably (Table XVII), again showing that a bond order is raised via conjugative interaction with fluorine. The P-I stretching frequency of  $(\text{m-FC}_6\text{H}_4\text{PI})_2$  is essentially unchanged from the value obtained for  $\text{Ph}_2\text{P}_2\text{I}_2$ .

The effects of the substitution of sulphur into phosphorus ring systems are readily apparent from the n.m.r. results that have been presented in this section. It has been inferred that the phosphorus ring in phenyl cyclopolyphosphine is a weak  $\pi$ -donor to its attached phenyl rings. Replacement of one PhP group with sulphur does not produce a great change and the  $\text{P}_4\text{S}$  ring is also a weak  $\pi$ -donor to its attached phenyl groups. The presence of additional sulphur, as in  $\text{Ph}_3\text{P}_3\text{S}_3$ , results in moderate, but disproportionately large, inductive withdrawal and weak to moderate conjugative withdrawal from

the phenyl rings. Finally, in  $\text{Ph}_2\text{P}_2\text{S}_4$ , the compound with the highest S/P ratio, the acceptor properties of the  $\text{P}_2\text{S}_4$  framework are very large. It is thus readily apparent that the presence of sulphur and pentavalent phosphorus must necessarily play crucial roles in the explanation of these observations. The trend that acceptor properties of P-S compounds increase with increasing sulphur content was also noted for the cage phosphorus sulphides. The  $\sigma_{\text{R}^0}$  values of the organophosphorus sulphur rings cannot be considered exceptional; on the other hand the  $\sigma_{\text{I}}$  values of the  $(\text{FC}_6\text{H}_4\text{PS})_3$  and  $(\text{FC}_6\text{H}_4\text{PS}_2)_2$  systems are larger than would be otherwise expected, and an adequate explanation of these features must await further experimentation.

SUMMARY:

It is worthwhile, by way of summary, to note some of the similarities and differences in the reactions and properties of the ring and cage phosphorus sulphides. Consider first the various ways of preparing these types of compounds; for example, both types can be prepared by the reactions of phosphines with sulphur. Phosphine itself will react<sup>121</sup> with sulphur to produce a mixture of phosphorus sulphides, the major components depending on the stoichiometry of the reactants. The results presented in this thesis, together with the earlier work of Maier, have shown that monosubstituted phosphines are capable of similar reactions to yield ring P-S compounds; again, the end products depend upon the stoichiometry of the reactants.

Another obvious similarity between the ring and cage P-S compounds is that the higher sulphides can be prepared by the reaction of a lower sulphide with sulphur. It has been mentioned previously that  $P_4S_5$  is best prepared<sup>21</sup> by the reaction of  $P_4S_3$  with elemental sulphur; in addition, Mai<sup>134</sup> has shown that  $P_4S_7$  and  $P_4S_{10}$  can be conveniently prepared from  $P_4S_3$  and sulphur. Similarly, Maier<sup>82</sup> has shown that both  $Ph_3P_3S_3$  and  $Ph_2P_2S_4$  can be prepared by the reaction of  $Ph_4P_4S$  with sulphur. The mobility of bonding in P-S compounds has been illustrated several times in this thesis. A typical example of this

mobility is that, for the ring compounds, the last-mentioned reactions are reversible; that is,  $\text{Ph}_4\text{P}_4\text{S}$  can be prepared from both  $\text{Ph}_3\text{P}_3\text{S}_3$  and  $\text{Ph}_2\text{P}_2\text{S}_4$  by the removal of sulphur with mercury, the reactions involving considerable rearrangement of skeletal structures. Limited work of this type has been performed with the cage phosphorus sulphides; in fact, it would appear that the only reaction examined is that of  $\text{P}_4\text{S}_3$  with triphenylphosphine, reported in this thesis. Part of the sulphur was successfully removed and it would be expected that removal of sulphur, particularly the exocyclic sulphur atoms, from the higher sulphides such as  $\text{P}_4\text{S}_5$ ,  $\text{P}_4\text{S}_7$  and  $\text{P}_4\text{S}_{10}$  would be much easier. An investigation of these reactions would be of interest, not only with a view to expanding our knowledge of the chemistry of the phosphorus sulphides, but also because careful removal of sulphur from the higher sulphides might result in formation of new cage compounds.

Treadwell and Beeli<sup>21</sup> have observed that, with an excess of iodine,  $\text{P}_4\text{S}_3$  is oxidized to  $\text{P}_4\text{S}_7$ . The oxidation of a lower sulphide to a higher sulphide by iodine has also been observed with the P-S ring compounds, namely the oxidation of  $\text{Ph}_3\text{P}_3\text{S}_3$  to  $\text{Ph}_2\text{P}_2\text{S}_4$ . By contrast, the lowest ring sulphide,  $\text{Ph}_4\text{P}_4\text{S}$ , again behaves more like a cyclopolyphosphine and undergoes ring cleavage when it reacts with iodine.

Finally, the use of fluorophenyl groups to assess electronic interactions within the P-S ring compounds has illustrated that acceptor properties are greatest in those compounds richest in sulphur and pentavalent phosphorus; in particular, the acceptor properties of the  $P_2S_4$  framework in  $Ph_2P_2S_4$  are unexpectedly large. Although the acceptor properties of the cage phosphorus sulphides have not been examined extensively, it has been noted previously that  $P_4S_3$  will form complexes with certain metal carbonyls, but  $P_4S_7$  apparently will not<sup>29</sup>, implying that the donor properties of  $P_4S_7$  are less than those of  $P_4S_3$ . Finally, the failure of the  $P_4S_9N^-$  anion to react with powerful methylating agents<sup>102</sup> is strong evidence for powerful acceptor properties in this ion. It is undoubtedly significant that in both classes of compounds, acceptor properties are greatest in those compounds richest in sulphur and pentavalent phosphorus; an explanation of these features in electronic terms remains to be developed.

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