ORGANIC METALS: STUDIES RELATED TO THE
SYNTHESIS OF ACCEPTORS DERIVED FROM TCNQ

by

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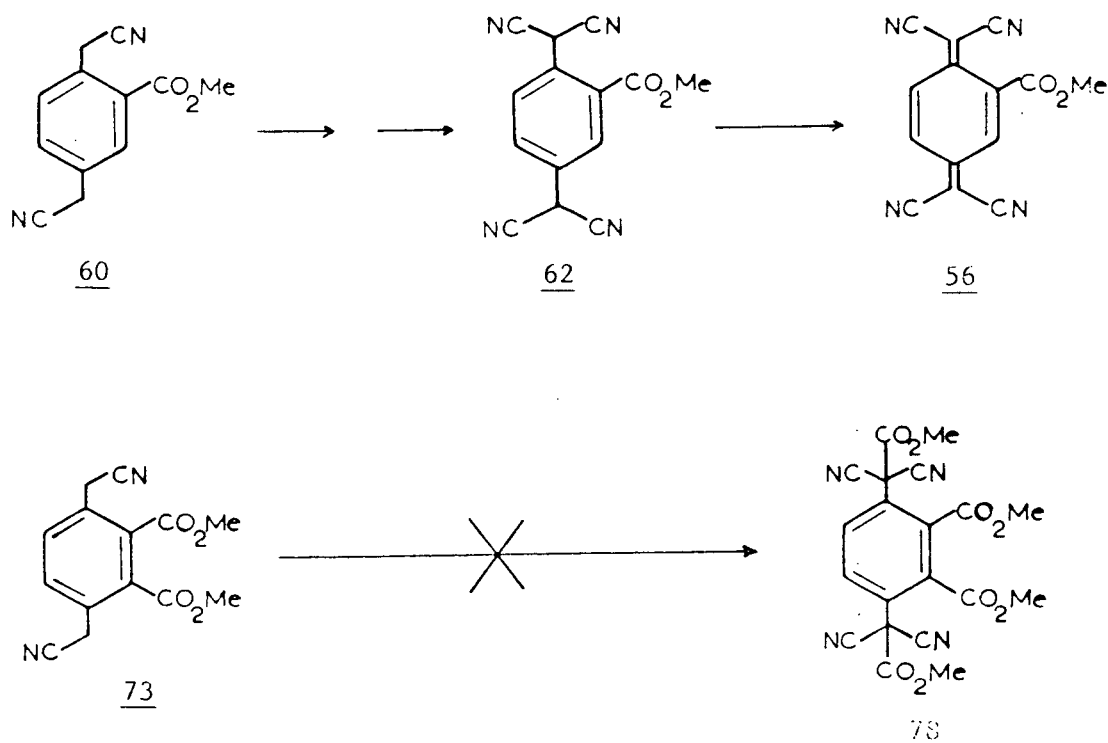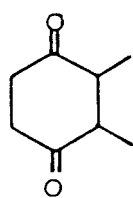Vancouver, Canada
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ABSTRACT

Since a report that the complex of TTF.TCNQ showed novel solid
state properties including high room temperature conductivity, there
has been considerable interest in the study of these so called "organic
metals." This thesis describes the synthesis of new acceptors derived
from TCNQ. First the synthesis of 2-methoxycarbonyl-7,7,8,8-tetracyanoquino-
dimethane (56) is presented. Bromination of methyl 2,5-dimethylbenzoate
followed by treatment with sodium cyanide yielded the dicyano compound
60 which was converted to the dihydro-TCNQ 62 via the corresponding
phenylenetetracyanodiacetate intermediate. Oxidation of 62 afforded 2-
methoxycarbonyl-7,7,8,8-tetracyanoquinodimethane (56), which was found
to be unstable. The synthesis of 2,3-dimethoxycarbonyl-7,7,8,8-tetra-
cyanoquinodimethane was attempted in the following manner: the Diels-
Alder cyclization of trans,trans-2,4-hexadiene and dimethyl acetylenedi-
carboxylate followed by dehydrogenation of the adduct gave dimethyl 3,6-
dimethylphthalate. Benzylic bromination of this material followed by
displacement of the bromines by cyanide yielded the dicyano compound
73. However, several attempts to convert 73 to the corresponding tetraester
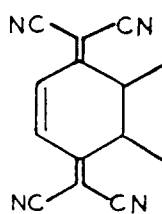78 were unsuccessful.

The synthesis of 2,3-dimethyl-7,7,8,8-tetracyanoquinodimethane is
presented. The intermediate 2,3-dimethylcyclohexane-1,4-dione (87) was
prepared from 2,3-dimethylphenol by standard means. It was then condensed
with malononitrile, and the product was treated with bromine/pyridine to
give the dihydro-DMTCNQ 89. When this compound was treated with a mixture
of palladium and sulfur at 180°C the desired 2,3-dimethyl-TCNQ 83 was
obtained in low yield.

The second part of this thesis describes the preparation of 11,11,
12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (TCNTP)
from mesitylene. This compound was bisbrominated to give 3,5-bis-
(bromomethyl)toluene, which was then coupled with 3,5-bis(mercaptomethyl)-
toluene to produce the dithia[3.3]metacyclophane 98. This was converted
to the dimethyl[2.2]metacyclophane 96 via Wittig rearrangement followed
by reduction with lithium in liquid ammonia. This cyclophane was then
brominated and the resulting dibromo compound was converted to the
corresponding dicyano-94. The latter compound was treated with bromine
in the presence of iron powder to produce 2,7-bis(cyanomethyl)-4,5,9,10-
tetrahydropyrene. Introduction of the remaining two nitrile groups was
accomplished via use of the tetracyanodiacetate intermediate 92. Hydrolysis
and decarboxylation of 92 followed by oxidation with NBS/triethylamine
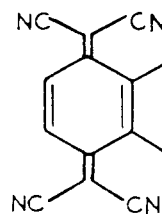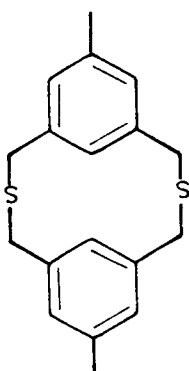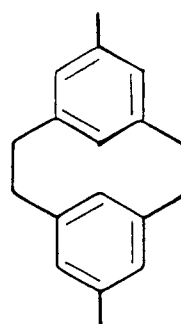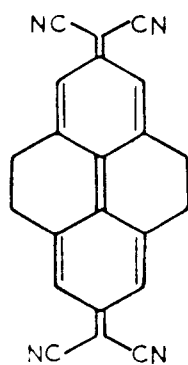at -78°C furnished the desired TCNTP (90).

87

89

83

98

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90

92

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Acknowledgements

I am very grateful to Dr. Larry Weiler for his guidance, kind encouragement and understanding throughout my period of research.

I also wish to express my gratitude to all the members of the Organic Metals group, past and present, for their many helpful discussions. Special thanks are due to Drs. Y. Hoyano and M. R. Bryce, and Ms. J. Lee. I also thank Anna Wong for typing the manuscript.

....If a man does not keep
   pace with his companions, perhaps
   it is because he hears a different drummer.
   Let him step to the music which he
   hears, however measured or far away...

                     H. D. Thoreau

                              A mis padres, con todo el amor
                              que solo ellos son capaces de
                              inspirar

1. INTRODUCTION

In 1973 researchers at Johns Hopkins University[1] detected signs of very high conductivity (around 1500 ohms^{-1}cm^{-1} at room temperature) from a 1:1 organic complex of 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) (1), and tetrathiafulvalene (TTF)(2). There quickly followed an exciting and controversial report from a group at U. of Pennsylvania[2] who claimed that some crystals of TTF.TCNQ showed "superconducting fluctuations," with increases in conductivity at 58°K of several hundred times the room temperature value. Research in the field of organic conductors has been very active ever since.

$\underline{1}$ $\underline{2}$
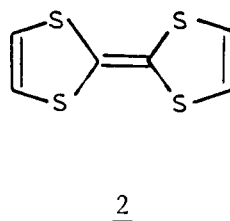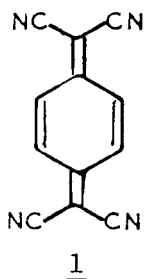
This new class of organic solids, typified by TTF.TCNQ, displays unexpected "metallic like" behavior over a wide temperature range. The materials are composed solely of non-metallic atoms, such as carbon, nitrogen, sulphur and oxygen; hence, the term "organic metal" has been used to describe these solids. These organic metals are part of a larger class of compounds known as charge-transfer salts; they are formed when an electron is transferred from an organic donor to an acceptor molecule.

The interest in the novel transport properties of these organic metals can be fully appreciated by comparing the conductivities of most

organic compounds: typical values are 10^{-11} to 10^{-7} ohm^{-1}cm^{-1} (insulators) and 10^{-5} to 10^{-3} ohm^{-1}cm^{-1} (semiconductors). However, the complex of hexamethylene-tetraselenafulvalene (HMTSF) and TCNQ has a room temperature conductivity of 2×10^{3} ohm^{-1}cm^{-1} - the highest of any known organic substance.[3]

log σ

	+ 6	Metals
Organic Metals	+ 4	
	+ 2	
	0	Molten salts
Nichrome	-2	
Silicon	-4	Alkali TCNQ salts
	-6	
	-8	
	-10	Carbazole-iodine complex
Most molecular crystals	-12	
		Ferrocene
	-14	
	-16	Anthracene
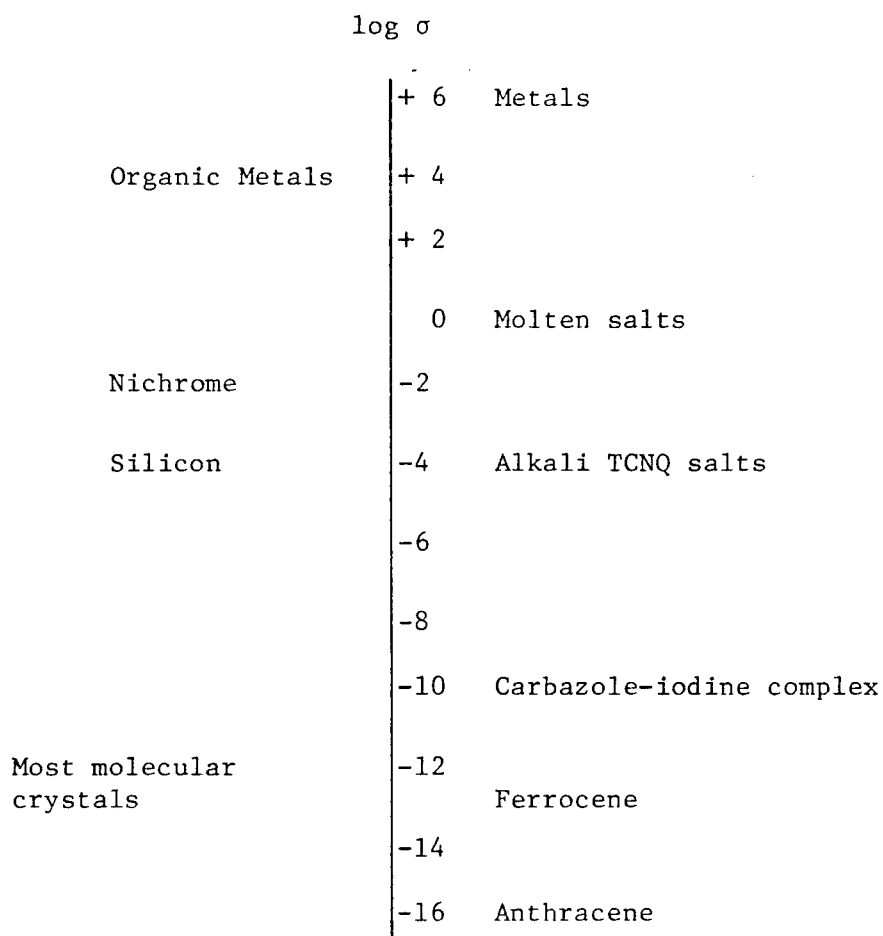
Figure 1. Scale of approximate conductivities

The organic molecules which form these complexes are relatively large and planar. They form stacks in the solid state with their π-molecular orbitals interacting strongly along the stacks, and only weakly

between them, which gives them a quasi-one dimensional nature that is reflected in their physical and electronic properties. TTF.TCNQ was identified as the first organic metal and has become the prototype organic conductor. The crystals are highly anisotropic, and diverse studies of their electronic and physical properties are all consistent with a metallic nature at room temperature.

The driving force behind the considerable amount of research done on one-dimensional metals has been the search for high temperature superconductivity. The quest for a totally organic superconductor remains a major but unsuccessful goal. Nevertheless, a by-product of this ambition has been the wealth of exciting physics and chemistry which came as a result of these endeavors, and that is finding practical applications in an ever growing number of areas, such as electrolytic capacitors, solid state batteries and printing systems.

2. GENERAL BACKGROUND

2.1 TCNQ Complexes and Salts

Research in organic conductors has been progressing for some time and the published data have centered around charge-transfer complexes, free radicals and free radical salts, long chain compounds and polymers.[4] Charge transfer complexes have been studied extensively although in many cases their structures were not well characterized. It was found that a surprising minority of these complexes had conductivities above 10^{-3} $ohm^{-1}cm^{-1}$. These types of complexes containing iodine and aromatic hydrocarbons or aromatic amines provided the first examples of moderately high electrical conductivity in organic materials (graphitized complexes are not included).

It was found that tetracyanoethylene (TCNE)(3) could polymerize with some metal chelates[4,5] forming charge transfer complexes that had relatively low resistivities (around 0.04 ohm cm). These results increased the exploration of the chemistry of other unsaturated systems containing the highly electronegative nitrile group, particularly, structures in which the double bond of TCNE is replaced by a conjugated system. On the other hand, quinones are known to be good electron acceptors, also forming stable complexes with some electron donors.[6]

$$NC \diagdown \quad \diagup CN$$
$$C = C$$
$$NC \diagup \quad \diagdown CN$$

3
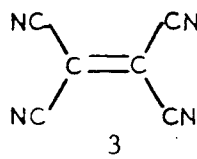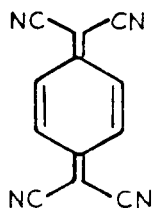
TCNQ (1)

In 1962, D. S. Acker and W. R. Hertler[7] synthesized a substituted quinodimethane, namely 7,7,8,8-tetracyanoquinodimethane (1), a compound with several exceptional properties; among them the formation of stable anion radical derivatives which have unusually low electrical resistivities in the solid state. The synthesis of TCNQ is illustrated in Scheme I. It involves the Knoevenagel condensation of 1,4-cyclohexanedione (4) with malononitrile in the presence of the Prout catalyst, β-alanine, to give the tetrahydro intermediate 5, in 94% yield; this compound is then dehydrogenated either with bromine/pyridine at 0°C in acetonitrile, or with manganese dioxide by brief refluxing in toluene.[8]

4   5

$$\underline{5} \xrightarrow{\quad Br_2/Pyridine \quad} TCNQ \ (\underline{1})$$
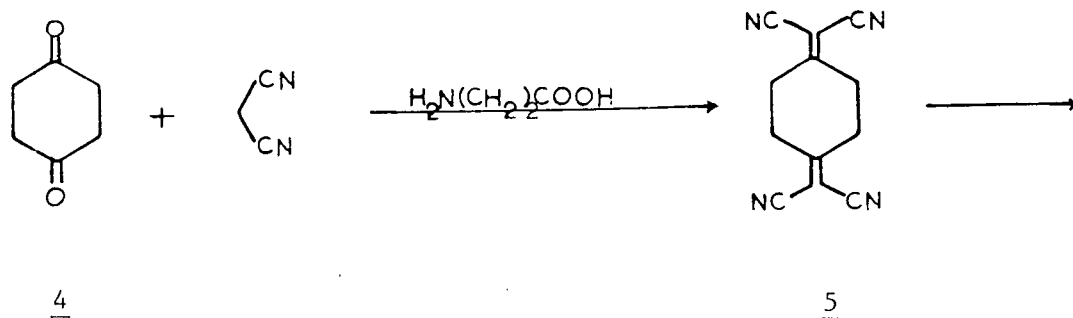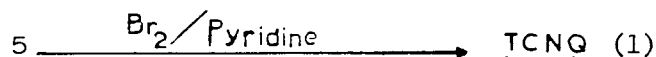
Scheme I. Synthesis of TCNQ $(\underline{1})$[7]

The unique characteristics of this molecule, namely, its high electron affinity, its planar structure and high symmetry, allowed the formation of electrically conducting donor-acceptor complexes, with TCNQ as the acceptor. According to Melby et al.[9] these complexes could be subdivided into three groups characterized by their composition and conduction behavior:
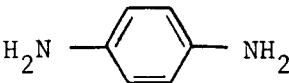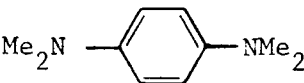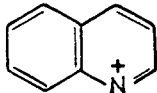
i) TCNQ π Complexes. These are crystalline complexes formed with aromatic hydrocarbons, amines, chelates, and other neutral compounds, usually in a ratio of 1:1. They have conductivities ranging from 10^{-3} to 10^{-12} $ohm^{-1}cm^{-1}$. From these early studies it was clear that there was no correlation between the basicity of the donor and the electrical conductivity of the complex. Steric factors and crystal packing seemed to play an important role.

ii) TCNQ salts of the composition $M^{+n}(TCNQ^-)_n$. The conductivity of salts of this group (M^{+n} stands for a metal ion or an organic cation) is usually in the range of 10^{-4} to 10^{-12} $ohm^{-1}cm^{-1}$. The esr absorption is very weak. Usually the conductivity in these simple salts is isotropic.

iii) TCNQ Salt Complexes of the composition $M^{+n}(TCNQ^-)_n$ $TCNQ°$. These complex TCNQ salts which, beside the $TCNQ^-$ radical anion, contain a neutral TCNQ molecule, display high conductivities ranging from 10^{-3} to 10^{+2} $ohm^{-1}cm^{-1}$. They show variable esr absorption. Furthermore, the

conductivity of single crystals displays strong anisotropy. Table I shows

some examples of the different molecular complexes of TCNQ.

Table I. Conductivities of some TCNQ Complexes and Salts.

Type	Donor	Conductivity $(ohm^{-1}cm^{-1})$
π-complex	H_2N—⟨benzene⟩—NH_2	3×10^{-4}
"	Me_2N—⟨benzene⟩—NMe_2	10^{-6}
Simple salts	Cs^+	3×10^{-5}
"	Cu^+	5×10^{-3}
Complex salts	⟨quinolinium N^+⟩	100
"	$(C_2H_5)_3N^+$	1.5×10^{-1}

During the mid 1960's the search for new and better organic semi-

conductors failed to yield a true organic metal. Some of the different

theories of organic conductivity in organic solids that emerged were

controversial and lacked experimental support. However, some facts

received attention. It was realized that if a low resistivity 1:1 complex

is to be formed, there should be considerable, but not complete, charge

transfer. Acker and Blomstron[10] found that a condition for high conductivity

is that the cation be a planar, aromatic, heterocyclic molecule. Further-
more, Le Blanc[11] suggested the importance of having a polarizable cation.

In 1965, Melby[12] made a complex between N-methylphenazinium (NMP)(6)
and TCNQ. Its single crystal conductivity reached 380 ohm^{-1}cm^{-1} at room
temperature. This remained the most conductive organic solid until 1973,
when Perlstein, Cowan et al.[1] mixed TCNQ and TTF to produce a new compound
with exciting and novel solid state properties, including a room tem-
perature conductivity ranging from 600 to 1800 ohm^{-1}cm^{-1} (variable from
sample to sample). The conductivity of this 1:1 complex increases with
decreasing temperature down to 60°K (metallic region) where there is a
transition to an insulating state (T<60°K). The peak conductivity at
T=59°K is comparable to the conductivity found in some metals such as
lead and tin (around 10^4 ohm^{-1}cm^{-1}).

The organic donor, TTF, is a planar molecule with an extensive π
electron system; it is highly symmetric and very similar in size to TCNQ.
This molecule is also highly polarizable because of the presence of four
sulfur atoms, and it can be readily oxidized to a radical ion, thereby
forming conducting cation radical salts with some halides.[13] A number
of synthetic pathways to TTF and its derivatives are available.[14,15,16]
One route to TTF developed by Melby et al.[16] (Scheme II) involves depro-
tonation of a 1,3-dithiolium ion, synthesized from the commercially
available dimethyl acetylenedicarboxylate (7) and ethylene trithio-
carbonate (8).

6

Scheme II. Synthesis of TTF ($\underline{2}$)[16]
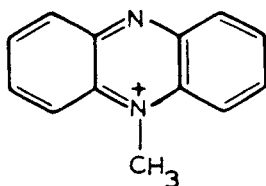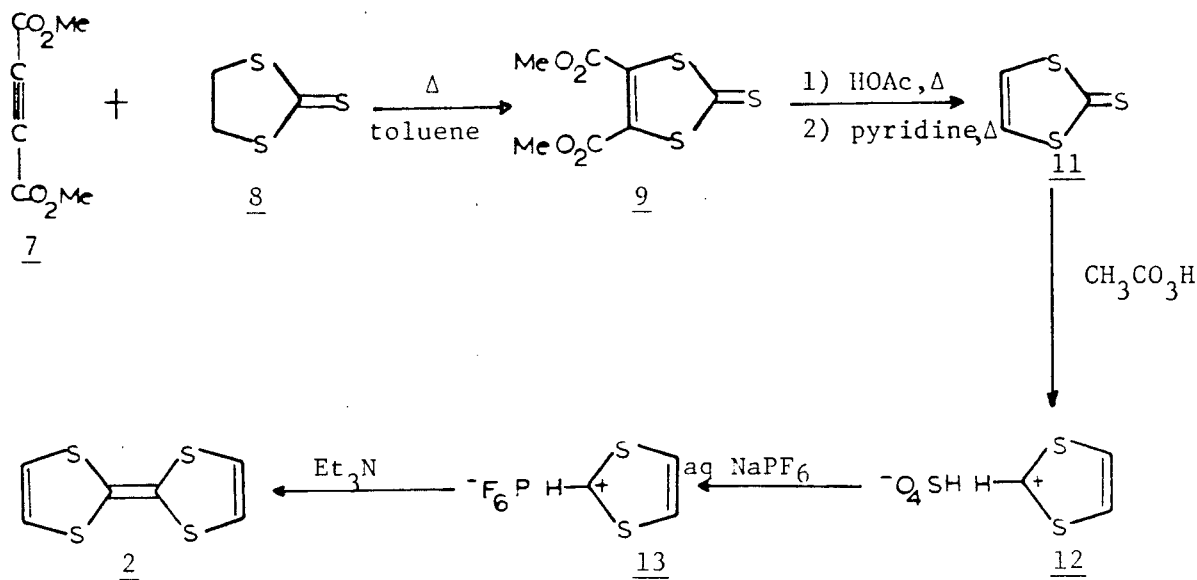
The 1:1 complex of TCNQ and TTF produces lustrous black plates when recrystallized from acetonitrile. Figure 2 shows a diagramatic representation of a single crystal, including approximate dimensions, along with the corresponding room temperature conductivities.[17] This material exhibits a highly anisotropic conductivity which reaches a

$$\sigma_b \approx 600\text{-}1800 \text{ ohm}^{-1}\text{cm}^{-1}$$

$$\frac{\sigma_b}{\sigma_a} \approx 10^3$$

$$\frac{\sigma_b}{\sigma_c*} \approx 150$$
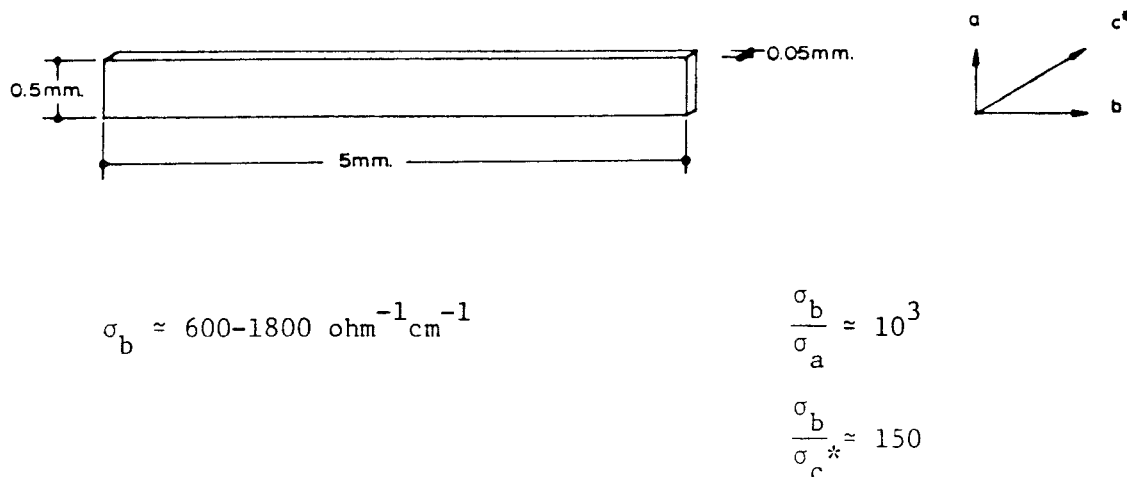
Figure 2. Dimensions and relative conductivities of a TTF·TCNQ crystal.

maximum along the crystallographic b axis. The temperature dependence

of the dc conductivity along the b axis is shown in Figure 3.[15] The

conductivity peaks at 59-60°K and begins to fall at lower temperatures, going

through two transitions at 53°K and 38°K. The magnitude of $\sigma T_{max}/\sigma 300°K$

is still a subject of controversy: it is found to be around 20 in most

cases, although a case was reported[2] in which the values for certain

crystals reached as high as 150.
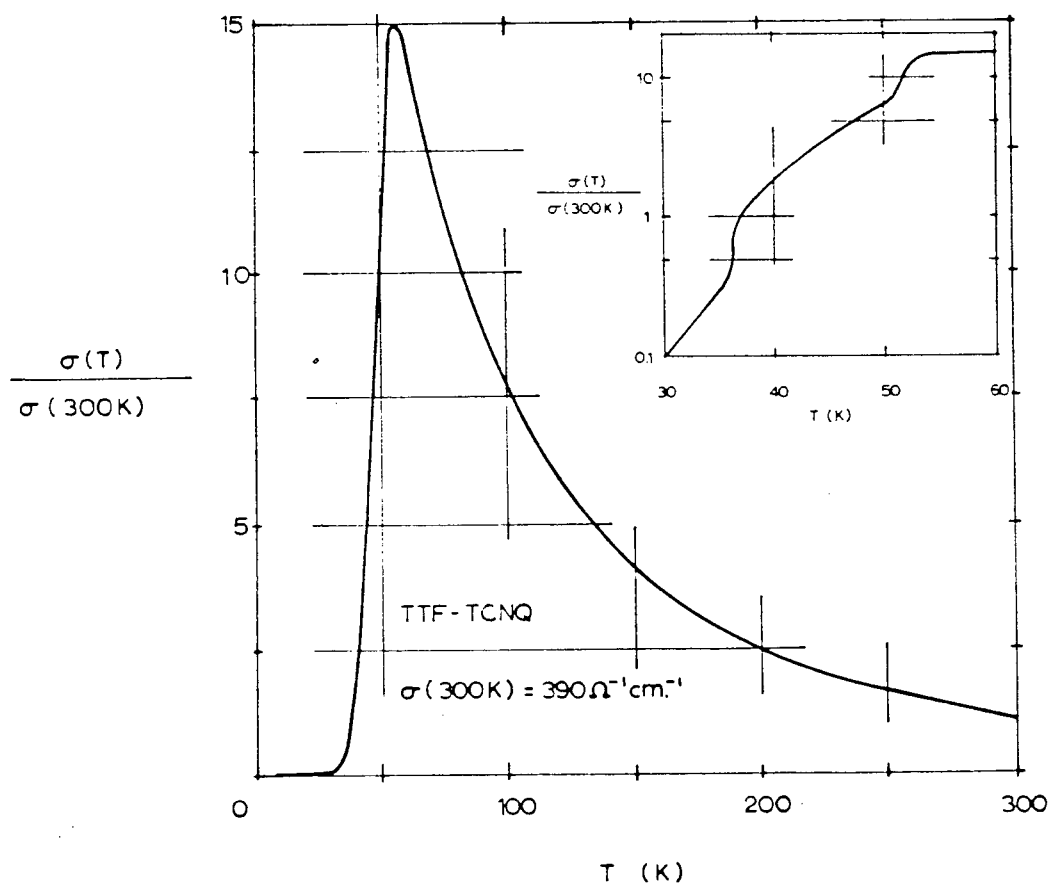
Figure 3.   Temperature dependence of d.c. conductivity (σ)
            of TTF.TCNQ[15] Insert shows the transitions at 53°K
            and 38°K.

The crystal structure[18] of this material is shown in Figure 4.

TTF.TCNQ consists of segregated, uniform columns of TTF and TCNQ molecules

stacked face-to-face along the highly conducting b axis. The molecular

planes are tilted with respect to the b stacking axis, and TTF and

TCNQ have opposite tilts relative to each other. The intrastack

distances are shorter than the van der Waals radii of TTF or TCNQ,

and permit a strong overlap of π-molecular orbitals along the stacks.

a)

b)
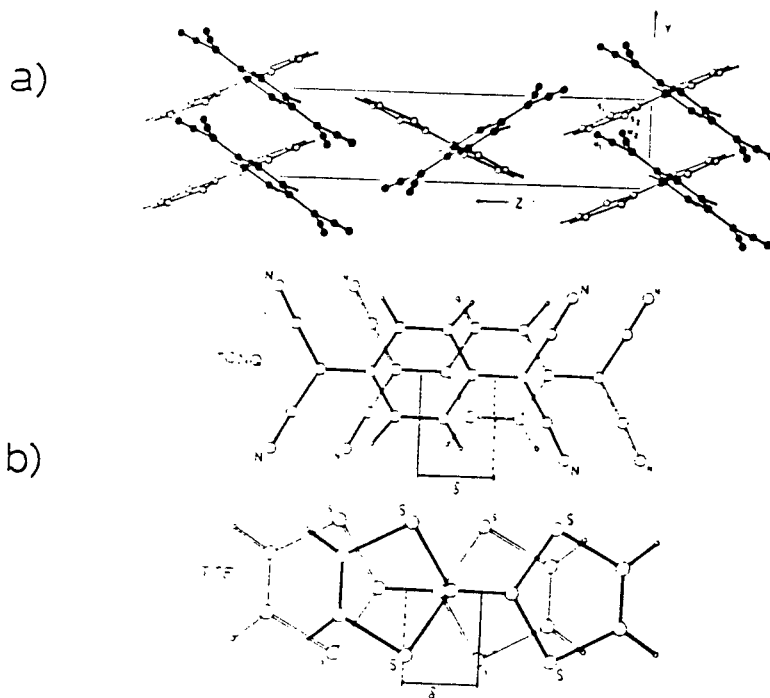
Figure 4. a) Crystal structure of TTF.TCNQ. b) molecular overlap
in the columnar stacks of TTF and TCNQ, showing the
lateral displacements of their molecular centres (δ).

Above the transition temperature the TTF and TCNQ molecules are uniformly

spaced within the stack.

As mentioned earlier, TTF is a good electron donor, and TCNQ is a

good electron acceptor. According to several recent investigations[18],

the charge transfer in the solid state in TTF.TCNQ amounts to 0.6±0.01

of one electron.

In TCNQ radical anion the HOMO is a π-MO. The interaction of these

MO's on two adjacent TCNQ⁻ within the same stack is bonding, when each

molecule is displaced laterally with respect to the molecule below. This gives rise to the "ring-double bond" overlap shown in Figure 4. In addition, calculations of the energy surface for the dimer $(TCNQ)_2^-$ show a well defined minimum when δ, distance between the molecular centres (Figure 4), is $2.2\overset{\circ}{A}$[19] (observed value: $2.14\overset{\circ}{A}$). Similar calculations on TTF^+ ions show a strong interaction of the HOMO's, but the energy surface calculations for TTF dimer show a minimum only for the case of two TTF's stacked directly over each other. The fact that this type of TTF packing has been observed in the highly conducting mixed valence halides such as $TTF.I_{0.71}$[13c], indicates that the interaction of HOMO's on the TCNQ stack and crystal forces are responsible for the packing of the solid in TTF.TCNQ. The picture for TTF.TCNQ that emerges at this point is one of segregated stacks containing planar, partially charged molecules arranged so as to allow relatively strong π-orbital overlap within the stack; thus parallel conducting linear chains are formed which are only weakly coupled.

There is still controversy over which description best explains the conductivity in these compounds. A useful model that describes the room temperature conductivity of TTF.TCNQ can be obtained by extending the MO approach of an individual $TCNQ^-$ and TTF^+ to an infinite array of linear chains. Thus the corresponding HOMO's of the radical ions generate a conduction band consisting of MO's delocalized along the stack. Calculations[20] using the extended Huckel Method of Hoffmann, showed that the largest overlap occurs along the highly conducting b axis, and that the TCNQ band is wider than the TTF band. There can be metallic type conductivity in the TCNQ or TTF band as long as it is partially filled, as in normal metals. These 1-D organic solids, however, are subject to lattice distortions (Peierls instability)[21] that can create an energy gap in the

electronic band. In the case of a half-filled band this will cause the molecules within a stack to dimerize. This will lead to a semiconducting behavior. It has been proposed[22] that such a distortion may be suppressing the metallic conductivity at 59°K in TTF.TCNQ.

The partial, as opposed to full, charge transfer in TTF.TCNQ has two important consequences: it provides crystal stabilization by minimizing intrastack repulsive interactions, and it lowers on site electron-electron repulsive interactions in both the donor and acceptor stacks. This effect is important if we are to consider another approach to the conductivity in these systems: that is, a hopping model, in which charge migrates along the donor and acceptor stacks, with some donors bearing two positive charges and some acceptors bearing two negative charges. This is illustrated in Figure 5. An additional requirement then, would be that these molecules

$$D^+D^+D^+....D^+D^+$$
$$A^-A^-A^-....A^-A^-$$

(a)

$$^+\left| \begin{array}{c} D\ D^+D^+....D^+D^{\pm} \\ A^=A^-A^-....A^-A \end{array} \right|^-$$

(b)

$$2D^+ \rightleftharpoons D + D^{++}$$
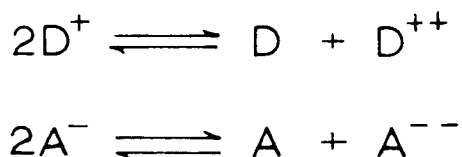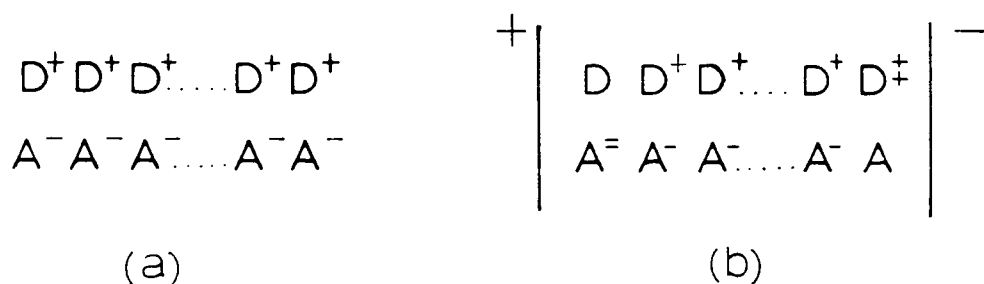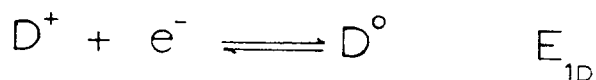
$$2A^- \rightleftharpoons A + A^{--}$$

Figure 5. Charge migration using a hopping model; (a) stacked charge transfer salt; (b) the same salt under the effect of an electric field.

should be able to localize two charges. A measurement of the redox

potentials of the different species in solution could be useful in

providing some information and suggestions for the design of new organic

metals. The redox potentials would provide a measure of the electron

accepting or donating ability of the components in the charge transfer salt.

$$D^+ + e^- \rightleftharpoons D^\circ \qquad E_{1D}$$

$$A^\circ + e^- \rightleftharpoons A^- \qquad E_{1A}$$

$$D^\circ + A^\circ \rightleftharpoons D^+ + A^- \qquad E_{1A} - E_{1D} = \Delta E$$

Finally, an approach that regards the organic metals as resulting

from the intermolecular migration of aromaticity was first proposed by

Perlstein.[23] Under this concept, the most efficient conductors should

contain molecules (a) whose radical ions form a new aromatic sextet upon

one-electron oxidation or reduction, and (b) whose aromaticity can

migrate by mixed valence interaction.

Since the initial report on TTF.TCNQ, an ever-growing number of new

compounds have been added to this class of metallic-like organic solids.

Much of this effort has focused on preparing derivatives of TTF, either

through replacement of the ring heteroatoms, or by addition of substituents.

Table II contains the electrical conductivity data of TCNQ salts of TTF

and some of its derivatives. From this Table it is apparent that sub-

stitution on the basic skeleton of TTF may produce solids that have similar

conductivities to TTF.TCNQ. Indeed, the substitution of selenium for sulfur in TTF seems to improve the room temperature conductivity. This may result from the greater orbital extent of selenium, which could lead to stronger overlap along the donor stack and, hence, to an increased band width. Nevertheless, the maximum conductivity for these new salts is similar to that of TTF.TCNQ, although the metallic state has been stabilized to higher temperatures.

Table II. Electrical conductivity data on the TCNQ salts of TTF and derivatives

$$\begin{array}{c} R_1 \\ R_2 \end{array}\!\!>\!\!\begin{array}{c} X_1 \\ X_2 \end{array}\!\!>\!\!=\!\!<\!\!\begin{array}{c} X_3 \\ X_4 \end{array}\!\!<\!\!\begin{array}{c} R_3 \\ R_4 \end{array}$$

Name		Conductivity data for TCNQ salt		
		σ_{RT} [b] ohm^{-1}cm^{-1} [a]	σ_{max} [c] ohm^{-1}cm^{-1} [a]	T_p [d] (°K)
Tetrathiafulvalene (TTF)	X_{1-4}=S, R_{1-4}=H	400–500	$>10^4$	58
Diselenadithia-fulvalene (DSDTF)	$X_{1,3}$=S, $X_{2,4}$=Se, R_{1-4}=H	500	3×10^3	64
Tetraselena-fulvalene (TSF)	X_{1-4}=Se, R_{1-4}=H	800	$>10^4$	40
Hexamethylene-tetrathiafulvalene (HMTTF)	X_{1-4}=S, $R_{1,2}$=$R_{3,4}$ =$(CH_2)_3$	500	2×10^3	80
Benzo-tetrathia-fulvalene	X_{1-4}=S, $R_{1,2}$= $R_{3,4}$=(C_4H_4)	10^{-4}	–	–
Tetramethyl – TSF	X_{1-4}=Se, R_{1-4}= CH_3	10^3	6×10^3	71
Hexamethylene – TSF	X_{1-4}=Se, $R_{1,2}$= $R_{3,4}$=$(CH_2)_3$	2×10^3	7×10^3	45–75[e]

[a] single-crystal measurement. [b] σ_{RT} = room temperature conductivity.
[c] σ_{max} = maximum conductivity at T_p. [d] Temperature of maximum conductivity.
[e] Still highly conducting below T_p.

Some of the chemical and structural features that may be required

for metallic behavior are summarized below:[2,15,24]

   - the existence of unpaired electrons within molecular units.

   - a uniform crystal structure consisting of parallel and

segregated stacked columns of planar molecules with delocalized π-

molecular orbitals. These π-orbitals must have significant intermolecular

overlap.

   - large π-systems in which the open shell cation and anion are of

similar size.

   - a polarizable cation

   - a certain amount of disorder (including doping) in the one-

dimensional system may prevent a uniform periodic distortion of the

lattice, and thus may stabilize the metallic state.

   A different approach to the design of organic metals has been

given by Torrance.[25] According to him, the most important properties

to consider are stacking, degree of charge transfer, and stoichiometry.

Although most of the characteristic features of these organic metals are

widely accepted, the relative importance of each of these parameters is

still a matter of discussion.

2.2   Extended TCNQ's

   The unpaired electron in the anion radical salts of TCNQ is largely

localized on the terminal dicyano methylene groups. It is the ability of

TCNQ to accommodate two electrons at opposite ends of the molecule which

distinguishes it from most other acceptors. Another potential quino-

dimethane acceptor would be 11, 12, 11', 12' - tetracyanonaphtho-2,6-

quinodimethane (TNAP)(14), an extended, conjugated analog of TCNQ. The

preparation of TNAP, first described by Hertler et al.[26], is shown in

Scheme III. The synthesis started with 2,6-dimethylnaphthalene (15)

which was brominated with NBS (N-bromosuccinimide) to yield the dibromide

16. Displacement of bromide with cyanide gave 17 in poor yield. This

was then treated with diethyl carbonate and base to give diethyl 2,6-

naphthalenedicyanoacetate (18). Treatment of the cyano ester 18 with

aqueous ammonia gave the corresponding amide 19 as a mixture of diastereo-

mers. After purification, 19 was dehydrated with $POCl_3$ to give 2,6-

naphthalenedimalononitrile (20). Finally, oxidation of the dimalononitrile

(20) with N-iodosuccinimide gave TNAP in 40% yield.
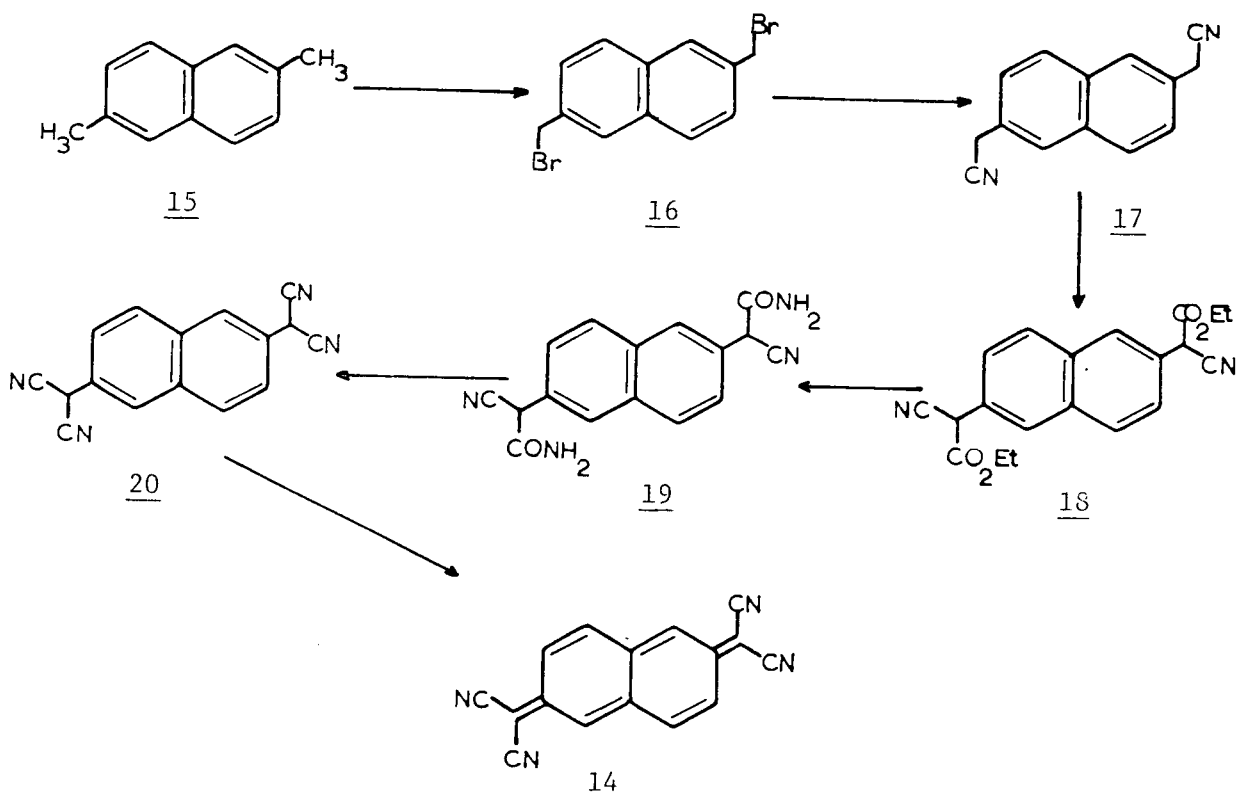

Scheme III. Synthesis of TNAP (14).[26]

This synthetic route was later improved by Sandman and Garito[27] with
a procedure that both avoided the stereochemical problem of the earlier
synthesis, and improved the overall yield. The reaction of 17 with
sodium ethoxide and diethyl carbonate in toluene, followed by reaction
of the resultant dianion with cyanogen chloride, led to a 60% yield of
diethyl 2,6-naphthalene α,α,α´,α´-tetracyanodiacetate (21). Hydrolysis
and decarboxylation of 21 gave 20 which was oxidized in situ with aqueous
bromine to afford TNAP in essentially quantitative yield (Scheme IV).
The anion radical salts of TNAP have compaction resistivities similar
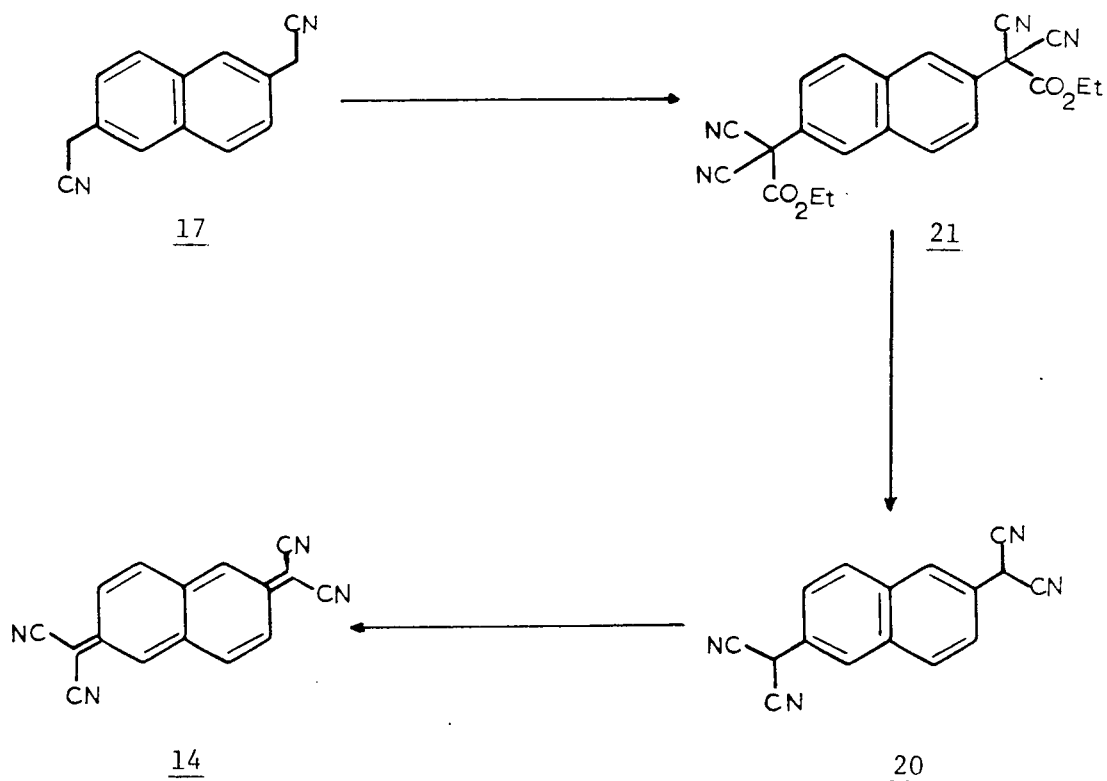
Scheme IV. Improved synthesis of TNAP (14).[27]

to those reported for salts of TCNQ.[26] Single crystals of TTF.TNAP. obtained via a slow diffusion process[28], show uniform, segregated stacks of cation and anion radicals. However, the room temperature conductivity is only 40 ohm^{-1}cm^{-1} and exhibits little temperature dependence; a sharp "metal-insulator" transition occurs at 185°K.

Next in the series is 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ)(22), which has not been isolated as a neutral species. Attempts to prepare it have led only to formation of polymeric material.[27,29a,b] However, a number of salts of the anions of TCNDQ have been prepared, and their physical properties studied.[29a] The preparation of the dihydro-TCNDQ 27[29a], the immediate precursor of TCNDQ, was accomplished using biphenyl (23) as the starting material. Bisbromomethylation followed by displacement of the bromide with sodium cyanide afforded the dicyano-25 which was converted to the dihydro – TCNDQ 27 following the procedure of Sandman and Garito[27] (Scheme V). Garito and Heeger[24a] suggested that a strong π-conjugation between the distant withdrawing groups is required to maintain the molecular stability. If the conjugation is weakened,

22
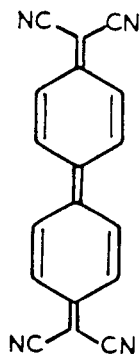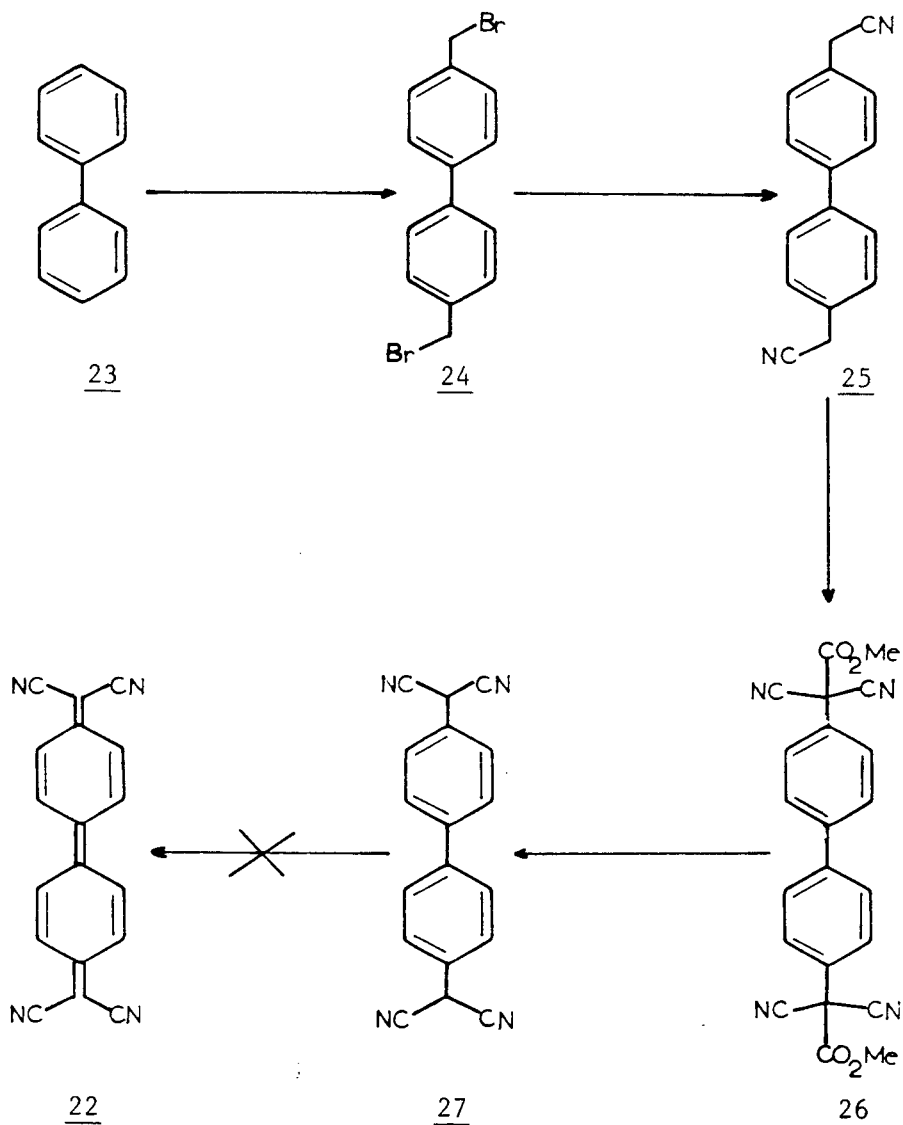
Scheme V. Synthesis of the dihydro - TCNDQ 27.[27,29a,b]

unwanted polymerization occurs. This could explain the difficulty in obtaining a neutral TCNDQ; the inter-ring hydrogen repulsions could account for the weakening of the π-conjugation.[30]

As stated previously, an analysis of the redox potentials of the donors and acceptors in solution could serve as an experimental approximation in the evaluation of the Coulombic repulsion energies[24a], and

therefore, it could be a practical guide in the search for new donors and acceptors. Table III lists the redox properties of some of these acceptors.

Table III. Redox Potential of Acceptors[a] [29a,31b,c]

Acceptor	E_1	E_2	ΔE
TCNE	0.15	-0.57	0.72
TCNQ	0.13	-0.29	0.42
F_4-TCNQ	0.52	0.03	0.49
TNAP	0.21	-0.17	0.38
TCNDQ	0.08	-.08	0.16

a) reduction potentials, in volts, vs SCE in CH_3CN reference electrode

The experimental conductivities of the charge transfer salts obtained from some of these acceptors are in agreement with the observed trends in ΔE (difference between the first two polarographic reduction potentials). All complexes of TCNE are insulators, whereas complexes of TCNQ and TNAP are metallic. A few complexes of F_4-TCNQ are semi-conductors. In the case of TCNDQ, the proximity of the two reduction potentials would indicate a clear reduction of the Coulombic repulsions in the dianion.

The search for larger acceptors led Wudl et al.[30] to attempt the synthesis of 2,7-bisdicyanoquinomethano-2,7,H,H-quinazolino[6,5,4-def]-quinazoline (TCQQ)(28). This is a pyrene analog of TCNDQ in which four carbon atoms have been replaced by nitrogen. This substitution was expected to both enhance the electron affinity of the acceptor,and to increase the number of available oxidation states (Scheme VI). The attempted preparation of TCQQ is outlined in Scheme VII. The tetrahydro intermediate 35 could not be purified and was treated directly with base in acetonitrile
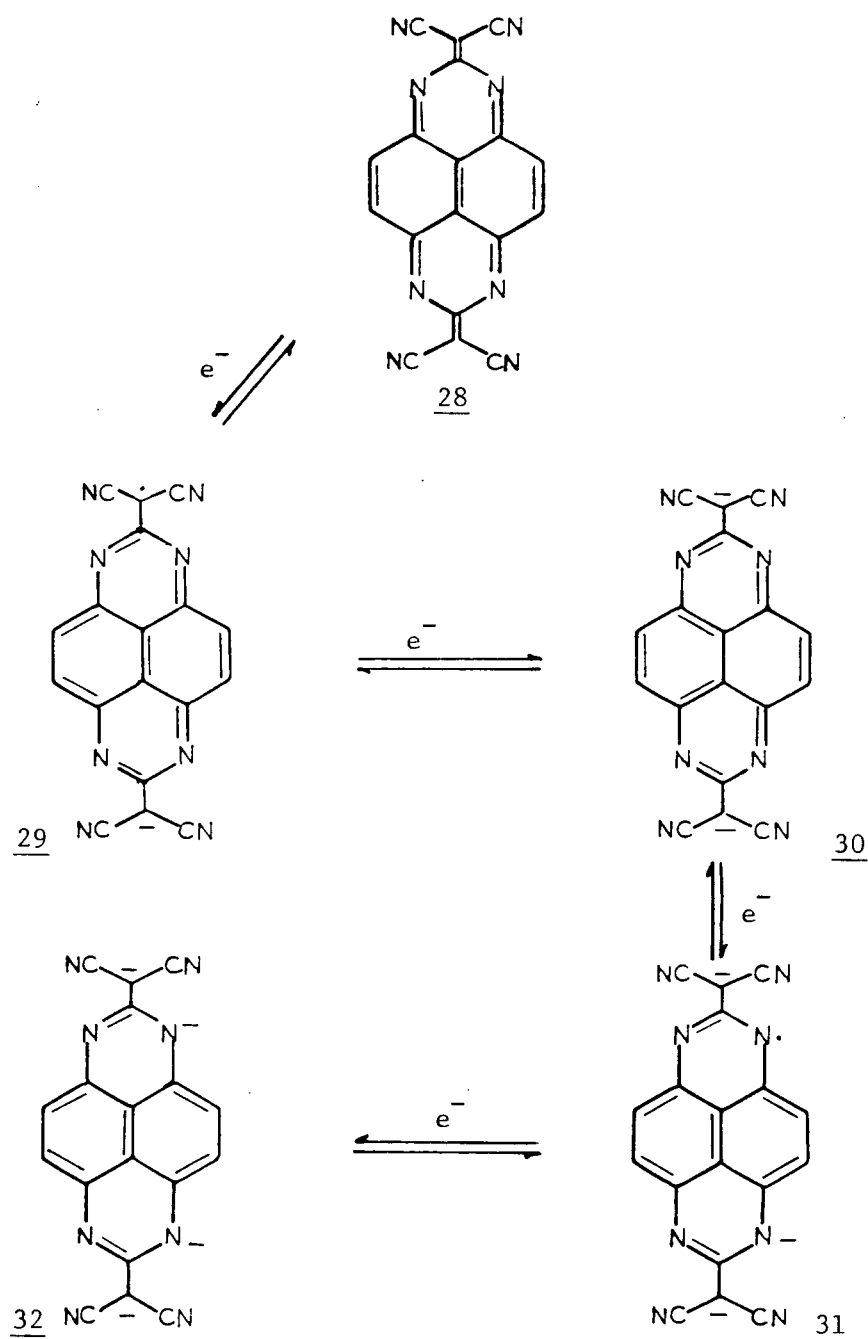
Scheme VI. Oxidation states of TCQQ (28)

in the presence of either tetrabutylammonium or tetraphenylarsonium chloride to give the dianion 30 as the only characterizable product. Unfortunately, attempted oxidations of 30 to 29 or 28 were not successful.
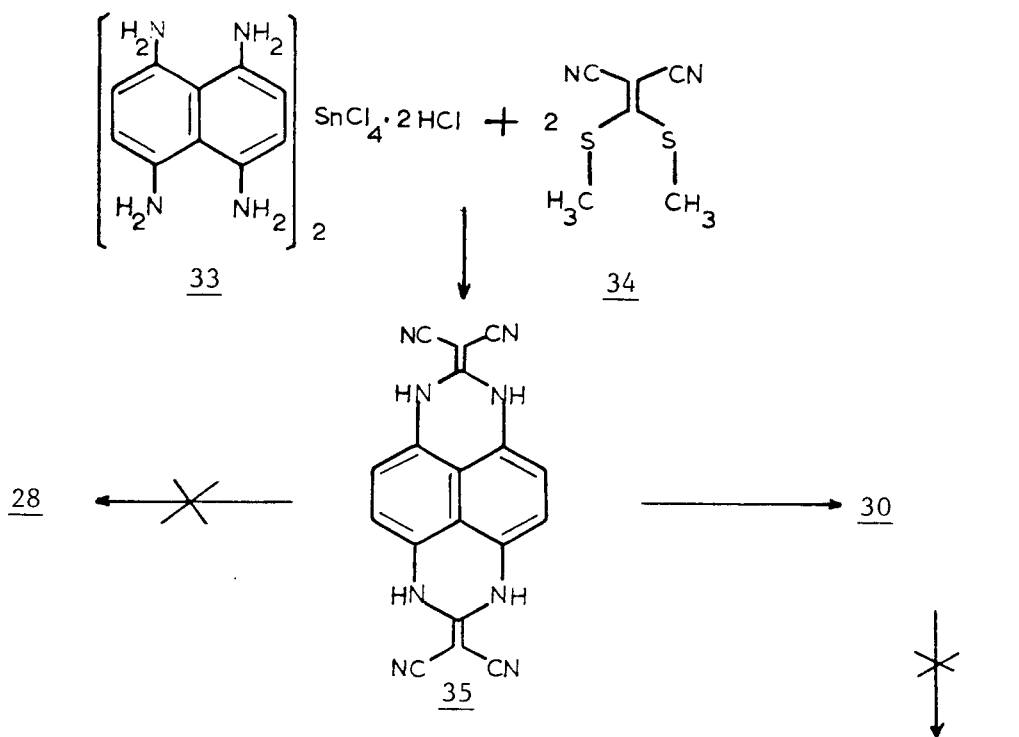
Scheme VII. Attempted synthesis of TCQQ (28)[30]

2.3 Substituted TCNQ's

A systematic study of the synthesis of substituted TCNQ's, together with the observed conducting properties of their charge transfer complexes with a series of donors, has been performed by Wheland.[31] The reported TCNQ derivatives have substituents in the ring; these include alkyl groups (e.g. Me, Et, i-Pr), halogens (F, Cℓ, Br, I), ethers and thio-ethers (e.g. OMe, O-i-Pr, O-i-Bu, SMe), and nitriles.

These syntheses most frequently started with the corresponding p-xylylene dihalide which in most cases could be prepared by direct bis-chloromethylation of an appropriately substituted benzene 36 as shown in Scheme VIII. For some dihalides and haloethers derivatives, the p-xylylene dihalide was prepared according to Scheme IX, starting with an

R_2=H
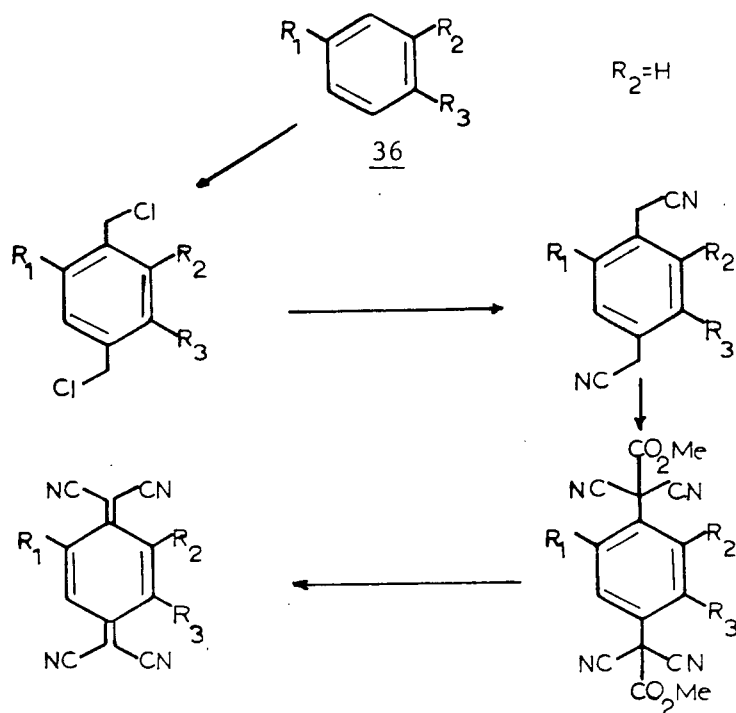
Scheme VIII. General method for the preparation of
substituted TCNQ's.[31a]

appropriately substituted p-xylene $\underline{37}$. The corresponding terephthalic

acid $\underline{38}$ was converted to the acid chloride $\underline{39}$ which was reduced to the

glycol $\underline{40}$. This was then treated with hydrogen halide to give the p-

xylylene dihalide $\underline{41}$. Once the p-xylylene dihalides had been obtained,
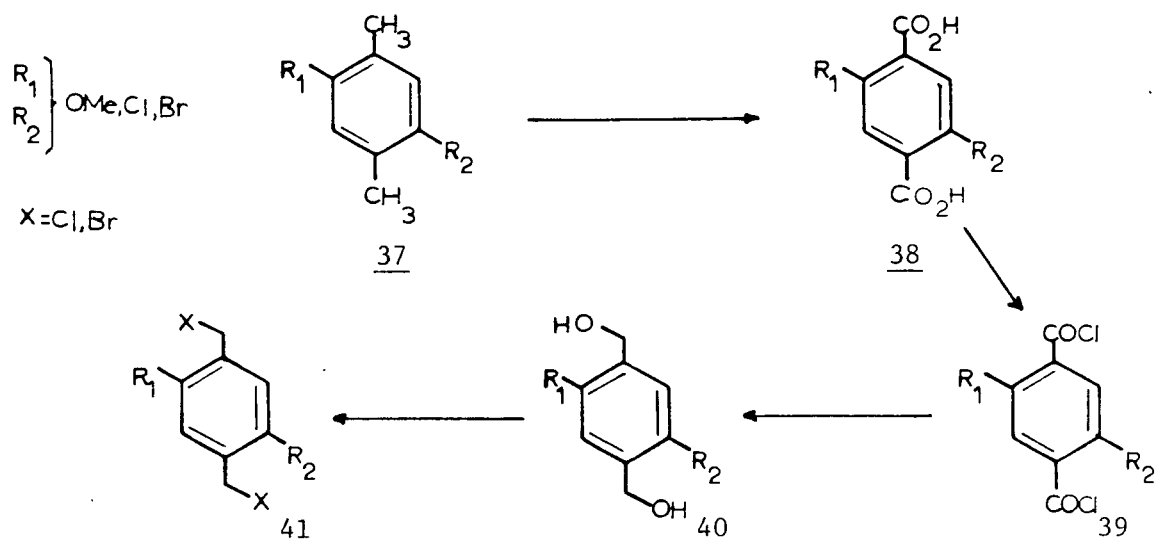
Scheme IX. Synthesis of some p-xylylene dihalides.[31a]

the syntheses of all the substituted TCNQ's were similar, as summarized

in Scheme VIII. For the tetrafluoro derivative 42 and the dicyano-TCNQ

43, the first step involved initial nucleophilic displacement of aromatic

halogen by the anion of tert-butylmalononitrile (44). Thermolysis of the

resulting product with the loss of isobutylene, followed by oxidation

with aqueous bromine, gave the TCNQ's 42 and 43 (Scheme X).

42 R₁=R₂=R₃=F

43 R₁=Cl
   R₂=CN
   R₃=H
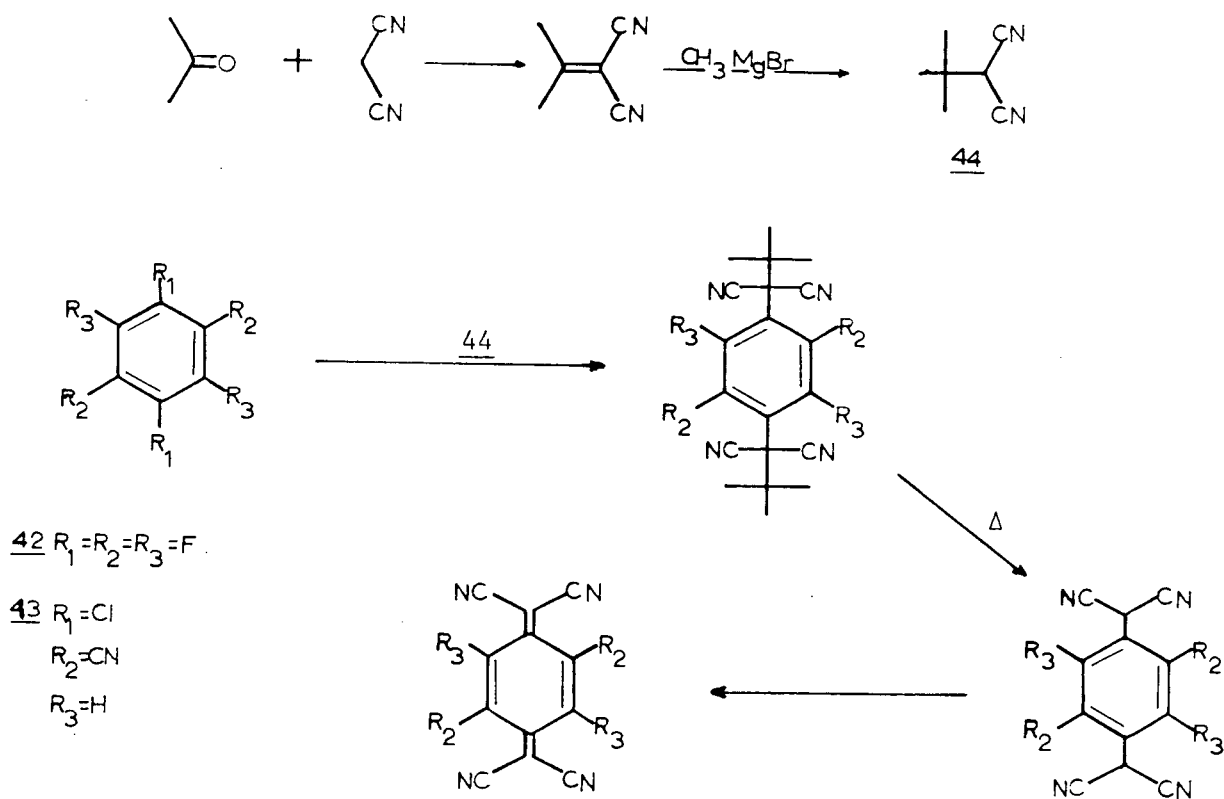
Scheme X. Synthesis of tetrafluoro-TCNQ (42) and 2,5-
   dicyano-TCNQ (43).[31a]

A correlation of the electrical conductivity of different charge transfer complexes, with the redox potentials[31c] of each of the components, shows that strong acceptors, for which complete electron transfer is most likely, give poorly conductive complexes; whereas weaker electron acceptors give highly conductive complexes. On the other hand, lowering donor strength to the point where significant electron transfer is unlikely, uniformly gives poorly conductive complexes. Therefore, it can be speculated that the conductivity will increase with increasing amounts of charge transfer up to a maximum occurring at less than full electron transfer; and then conductivity will decrease as one electron transfer is approached. For optimum charge transfer, the redox potentials of both donor and acceptor should be closely matched ($|E_A - E_D| < 0.25$ V). However, regardless of how favourable these factors are, conductivity will be poor if the requirements of crystal structure are not met. In the characteristic segregated stacked structure of TTF.TCNQ, the spacing of the molecules in their stacks is closer than their van der Waals radii. The consequences of this close encounter have been described in previous sections. Steric factors may play a major role in the crystal packing. The effect of substitution[31c] on the TCNQ ring with increasingly larger groups appears to have minor effects until five or six side chain carbons or oxygens have been added. Beyond this point there is a sudden decrease in conductivity of the complex, and in some cases the complex does not form at all. Furthermore, the lowest resistivities are found when the acceptor length/donor length ratio is approximately equal to 1, suggesting that mismatching of donor and acceptor sizes upsets the crystal structure.

The need for highly polarizable substituents close to the conductive stack has been suggested in several recent theories.[1,2,24a] In accord with

this, the complex of TCNQ with tetraselenafulvalene (in which the sulfur of TTF has been replaced by heavier selenium) shows a higher conductivity at room temperature than does TTF·TCNQ. The conductivity of the complexes of substituted TCNQ's increases when a chlorine substituent is replaced by the heavier and more polarizable bromine or iodine atom. This effect is cumulative in that two bromines or iodines are more effective than one. However, there is only a slight increase in conductivity in going from bromine to iodine, suggesting that the larger size of the iodine might be altering other variables.

Some alkyl derivatives of TCNQ have been used to form charge transfer salts with derivatives of TTF and TSF. Results from these studies show that when small amounts of methyl-TCNQ 49 are added as a dopant to TSF.TCNQ, the characteristic sharp phase transition is broadened, and the conductivity at low temperatures is 10^4 times greater than for the corresponding undoped system.[32]

Interest in synthesizing on organic polymer having metallic conductivity led to the preparation of a polymer containing covalently bound TCNQ's. Hertler[33] synthesized 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane (45) starting from 1,4-bis(2-acetoxyethoxy) benzene (46). A charge transfer polymer was prepared by reaction of 45 with 1,1-diisocyanatoferrocene (47) to give a black polyurethane 48, which contained electron acceptor TCNQ units alternating with electron donating ferrocene units (Scheme XI). However, the conductivity of the compacted powder was only 3×10^{-3} ohm^{-1} cm^{-1}.
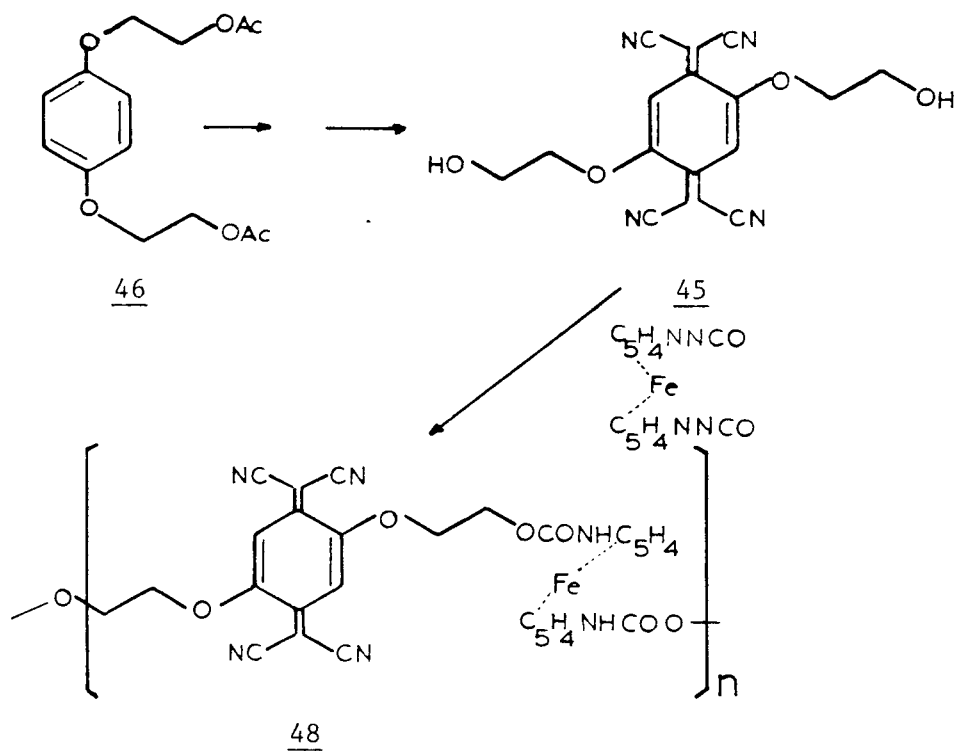
Scheme XI. Synthesis of the polyurethane 48.[33]

3. RESULTS AND DISCUSSION

3.1 Studies related to the synthesis of substituted TCNQ's

In view of the interesting properties observed in TCNQ and its
derivatives, it was decided to initiate a synthetic program leading to
various analogs of this molecule. It seemed particularly attractive to
investigate the possible formation of derivatives having C-substituents
with oxidation levels different from that of saturated hydrocarbons.
Furthermore, the construction of symmetrical or unsymmetrical dimers
containing the TCNQ moiety could be facilitated by the use of functionalized
substituents serving as synthetic handles to achieve dimerization. In the
past, work done in this area[31a] included the preparation of ethers, thio-
ethers, halides, nitriles and alkyl groups as substituents on the TCNQ ring.

Our initial study involved the functionalization of an alkyl
derivative of TCNQ, in particular, 2-methyl-7,7,8,8-tetracyanoquinodi-
methane (MTCNQ) (49). The synthesis of 49 is outlined in Scheme XII. The
preparation of the intermediate 2-methyl-1,4-cyclohexanedione (52) was
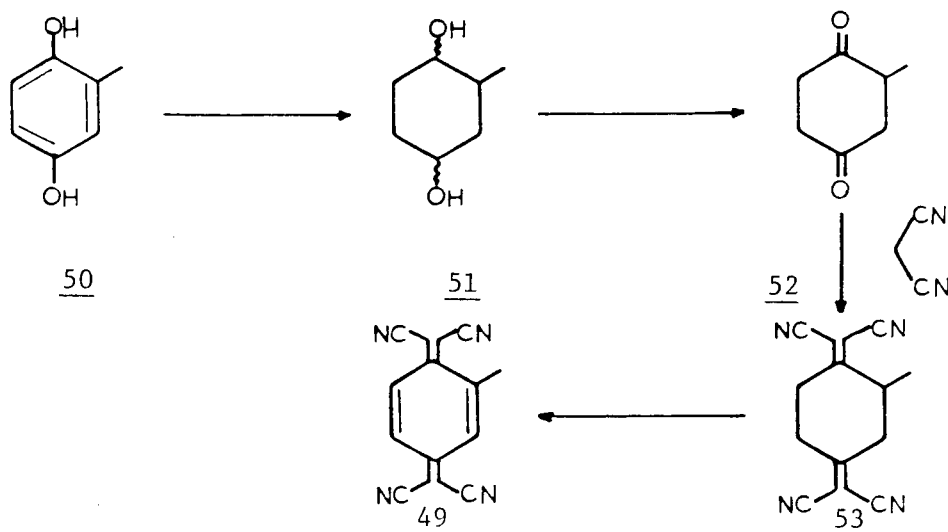

Scheme XII. Synthesis of MTCNQ (49).

accomplished by a modification of the procedure reported by Hertler et al.[26]

shown below. The starting material in both cases was the readily available
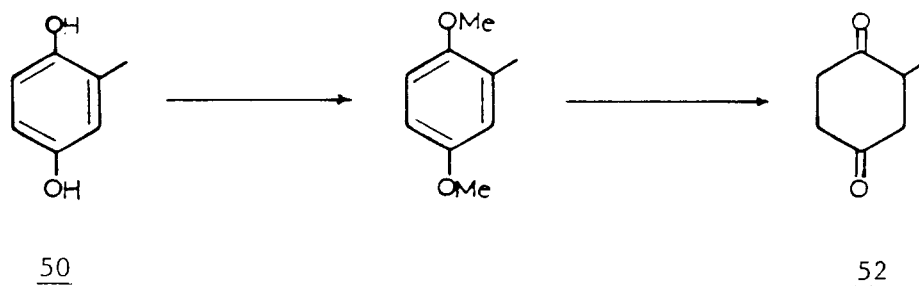
methyl-p-hydroquinone (50). In our case it was hydrogenated to the

corresponding diol–51 with rhodium on powdered charcoal as a catalyst,

in 90% yield. The crude mixture of stereoisomers was oxidized with a

modification of Jones reagent[34] to produce the dione–52 in 54% yield.2-

Methylcyclohexane-1,4-dione (52) was condensed with malononitrile in

the presence of β-alanine to give 2-methyl-1,4-bis(dicyanomethylene)-

cyclohexane (53)(85% yield). This could be used without further puri-

fication in a reaction with bromine and pyridine to produce 49 in 54%

yield after purification by sublimation. The low yield in this reaction

is attributed[26] to the simultaneous formation of a dimer of 49. The

physical and spectroscopic data of 49 were similar with those reported.[26]

Its ^{1}H nmr spectrum showed two singlets, at δ2.70 (3H,-CH$_3$) and δ7.15 (1H,

-C=CH), and   two doublets at δ7.43 (2H,J=4Hz, vinyl).
 |
 CH$_3$

Initial attempts to functionalize the methyl group of 49 with NBS

in carbon tetrachloride were unsuccessful. A change of solvent or initiator

had no positive effect, and in all cases starting material was recovered

-31-

unchanged. It was hoped that the vinyl methyl group of 49 could undergo

an allylic oxidation on treatment with selenium dioxide. However, when

SeO_2 was added to a solution of MTCNQ in refluxing ethanol, starting

material was still present after 24 hours (by tlc analysis). The

resistance of 49 to oxidation might be due to its high oxidation potential,[26]

this would make the olefinic bond less accessible for electrophilic attack

to form the intermediate allylic selenite ester[35] 54.

54
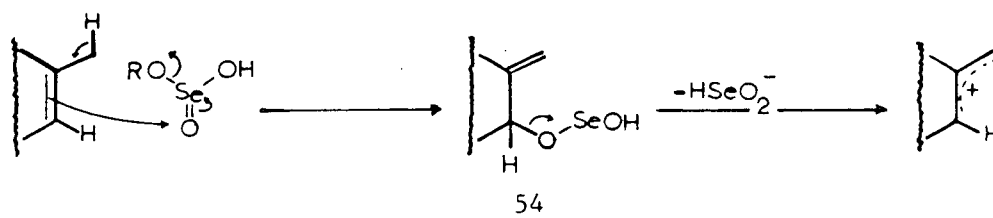
Treatment of MTCNQ with sodium hydride in THF (tetrahydrofuran)

at room temperature, followed by addition of phenyl selenium chloride

at -78°C, yielded only starting material. Similar results were obtained

when potassium hydride in DME (1,2-dimethoxyethane) was used, followed by

addition of bromine. Warming the reaction mixture to room temperature led,

in both cases, to complex mixtures of compounds (at least four by tlc),

including starting material. In light of the difficulty encountered

with the above experiments, a different approach to substituted TCNQ's

was taken. It involved introduction of an alkyl halide group onto the

ring of a dihydro derivative of TCNQ, namely p-phenylenedimalononitrile

(55). This compound was prepared by reduction of TCNQ with thioglycolic

acid in glacial acetic acid[7] (85% yield). Haloalkylation was attempted

with paraformaldehyde and hydrogen bromide following the procedure

developed by Reynolds and Durham.[36]   Hydrogen bromide was bubbled through

a refluxing suspension of the dihydro-TCNQ 55 and paraformaldehyde in
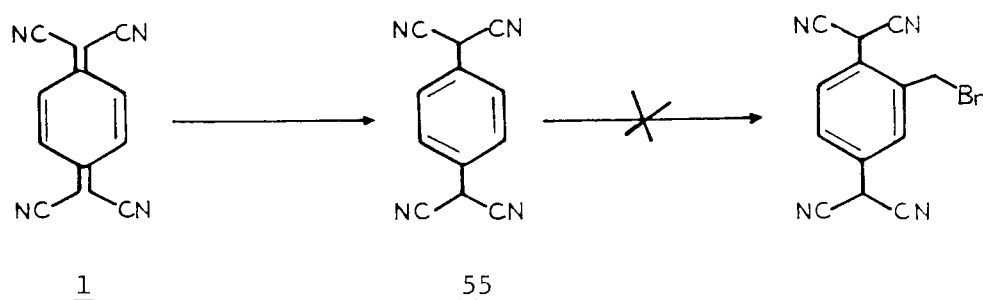
acetic acid.   Analysis of the resulting gummy solid showed disappearance

of the nitrile band in the ir spectrum.   In addition, strong bands at

3600-3200 cm^{-1} and 1710 cm^{-1} indicated that hydrolysis of the nitriles

had taken place.

It was decided at this point to introduce the functionalized carbon

substituent at the beginning of the synthesis, prior to the construction

of the TCNQ frame.   An ester functionality seemed an appropriate choice,

and the synthesis of 2-methoxycarbonyl-7,7,8,8-tetracyanoquinodimethane

(56) was designed in the manner illustrated in Scheme XIII.

56
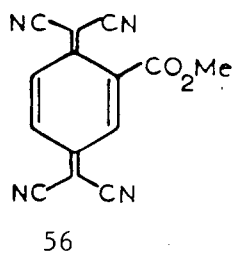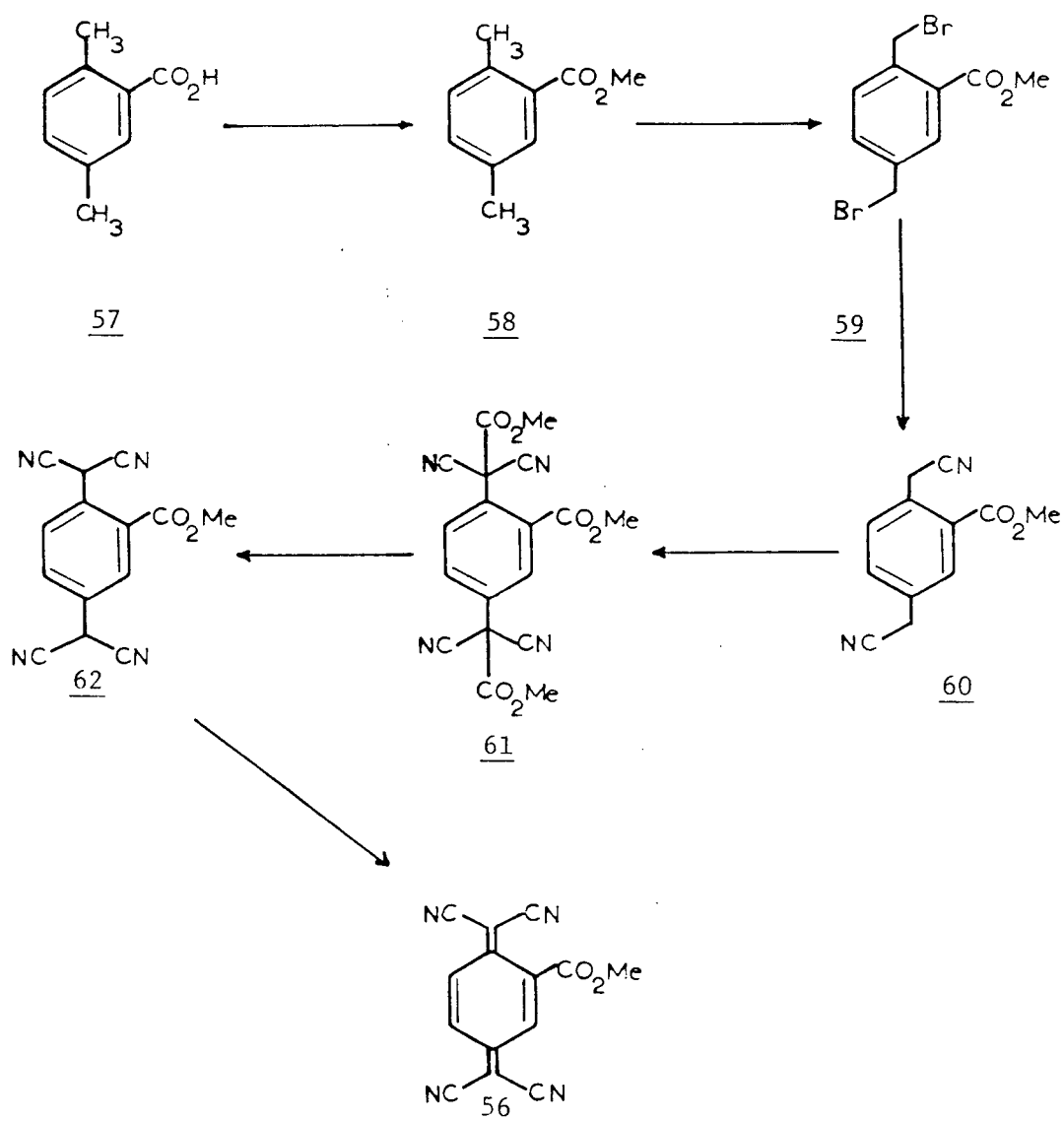
Scheme XIII. Synthesis of 2-methoxycarbonyl-7,7,8,8-tetracyano-quinodimethane (56).

The commercially available 2,5-dimethyl benzoic acid (57) was esterified under Fischer conditions[37] to produce the corresponding methyl ester 58 in 85% yield. The next step involved bromination on the two methyl groups. When NBS in carbon tetrachloride was used with benzoyl peroxide (radical initiator), the desired dibromo compound 59 was obtained in 38% yield. By-products included both monobromo isomers and the tribromo

derivative. The amount of side products obtained, together with the low

yield of 59 prompted the search for better reaction conditions. Vögtle

et al.[38] reported that the use of methylene chloride as solvent in the

benzylic bromination of 1,8-di-p-tolylnaphthalene (63) afforded the

dibromo product 64 in 80% yield; in carbon tetrachloride the yield was

around 50%. In our case best results were obtained when a slight excess

63   64
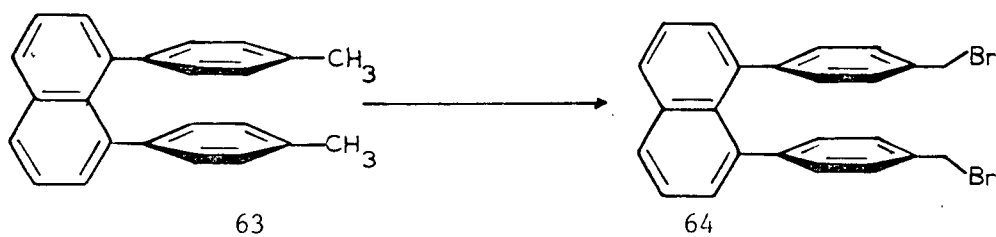
of NBS (2.2 equivalents) was added to a mixture of 58 and AIBN (azobis-

isobutyronitrile) in methylene chloride, followed by refluxing for 2.5

hours. The resulting dibromo ester 59 was isolated from the reaction

mixture by fractional crystallization in methanol. The yield was 70%

after recrystallization. The ^{1}H nmr spectrum of this compound showed

absorptions at $\delta 3.93$ (s,3H,-OCH$_3$), $\delta 4.43$(s,2H,-CH$_2$Br), $\delta 4.90$(s,2H,-CH$_2$Br),

$\delta 7.40$(s,2H,aryl) and $\delta 7.93$(s,1H,aryl), which were consistent with

structure 59.

Reeves et al.[39] have reported the facile conversion of primary alkyl

bromides into alkyl cyanides under phase transfer conditions employing

primary, secondary or tertiary amines as catalysts. They noted that

several requisites are apparent for efficient catalysis: in particular,

the use of long chain aliphatic amines, with a chain length of at least

six carbons. In addition, cyanide displacements are known[40] to occur more

rapidly when acetonitrile is used as solvent. Displacement of the bromines

in 59 by cyanide took place when a solution of the dibromo ester in

acetonitrile was stirred at room temperature for ten hours with an excess

of aqueous sodium cyanide. Tri-n-octylamine was used as catalyst; the

yield in this reaction was 70%. The absorption at 2290 cm^{-1} in the ir

spectrum of 60 showed the presence of the nitrile group, and the aryl ester

carbonyl has an absorption at 1720 cm^{-1}. The ^{1}H nmr spectrum of the dicyano

product showed an upfield shift for the methylene protons.

Introduction of the remaining two nitrile groups was accomplished

via the phenylenetetracyanodiacetate intermediate 61, according to the

procedure of Wheland and Martin.[29a] Toluene instead of benzene was used

as solvent for the reaction. Treatment of 60 with sodium methoxide in

toluene-dimethyl carbonate establishes an equilibrium with dianion 65

which may be driven to completion by distilling off a toluene-methanol

azeotrope. Addition of cyanogen chloride to the reaction mixture at 0°C,

is followed by gradual warming of the mixture up to 80°C. The tetracyano-

diacetate 61, is obtained in relatively good yield (59%). The ir spectrum

60

61   65
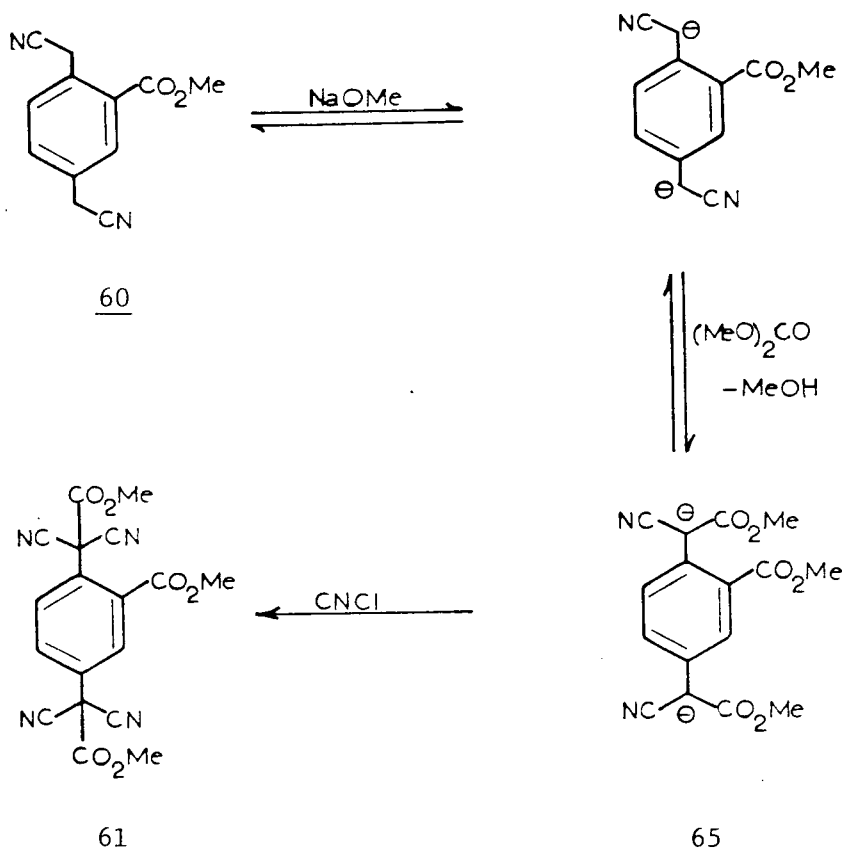
of the crude product showed a new absorption band at 1770 cm^{-1} indicating

the presence of a saturated ester. Its ^{1}H nmr spectrum had a new singlet

at δ4.00 corresponding to the new methoxycarbonyl groups at C-7 and C-8,

and lacked the two singlets at δ3.77 and 4.12 attributed to the cyano-

methylene groups. The mass spectrum of the compound showed the expected

parent peak at m/e 380. Attempted purification of the crude oil by

chromatography on silica gel, resulted in partial hydrolysis of the

triester. The crude product could be used without further purification

in the next reaction; this involved hydrolysis and decarboxylation of the

ester groups to produce the dihydro-TCNQ 62. Wheland[31a] had used aqueous

potassium hydroxide or sodium hydroxide, either hot (70°C) or at room

temperature, to effect hydrolysis and decarboxylation of a number of TCNQ

derivatives. In our case, milder conditions were desired in order to avoid
total or partial hydrolysis of the aryl ester group. Sodium carbonate,
being a weaker base, served our purposes. Indeed, when a solution of the
triester 61 in THF was stirred at room temperature with an excess of aqueous
sodium carbonate, in the presence of small amounts of sodium borohydride,
the dianion 66 was formed. Neutralization with hydrochloric acid gave
the dihydro compound 62. Its ir spectrum lacked the absorption band at
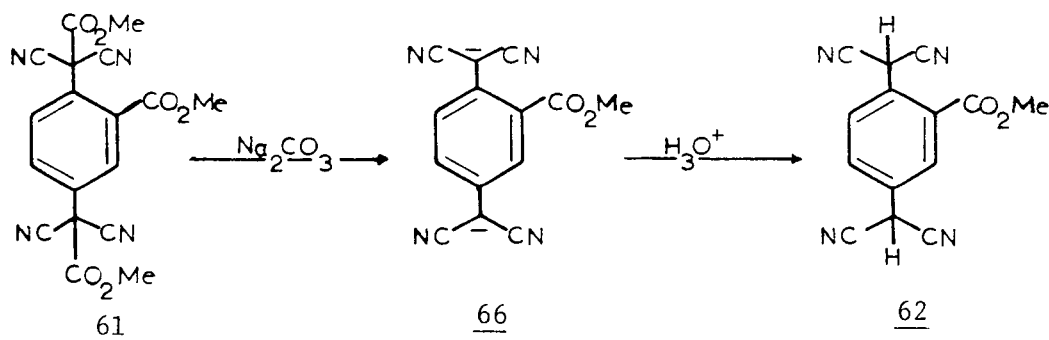
$1770 \ cm^{-1}$ but retained the aryl ester band. Purification of this compound
presented great difficulties. The crude material streaked on tlc; attempted
recrystallization proved unsuccessful; and sublimation in vacuum only de-
composed the product. However, the acidity of the methine protons in 62
permitted purification via acid-base extraction. After work-up the resulting
greenish oil partially crystallized on standing. Gradual darkening of the
solid occurred on standing at room temperature after several days. The
overall yield after purification was 32% (from the dicyano-60).

Oxidation to the desired ester-TCNQ 56 was carried out with aqueous bromine[31a] at room temperature. Attempted purification of the resulting light green solid proved difficult. Sublimation at 190°C/0.01 mm Hg yielded a green-yellow solid (3%), m.p. 220°-224° (decomp.), which darkened gradually on standing. The ^{1}H nmr spectrum of this material was of poor quality and was unreliable; this was due to low solubility, and to the presence of radical anions formed by reaction with solvent impurities. Its ir spectrum showed a weak absorption band at 2220 cm^{-1} (conjugated C≡N) and a strong band at 1725 cm^{-1} (unsaturated ester C=O). Its mass spectrum further substantiated the proposed structure by having 262 (100) as the molecular ion peak. The product could not be purified for elemental analysis. However, high resolution mass spectrometry established the molecular formula of the product to be $C_{14}H_6N_4O_2$, as required by structure 56. Its electronic spectrum showed an absorption band at 396 nm (36,800) with a shoulder at 375 nm. If this solution is left standing, its color darkens and the UV spectrum shows a shift to 409 nm. Attempts to form a charge transfer complex with TTF in acetonitrile failed.

A large planar molecule containing two identical acceptor sites at both ends could be of interest in the study of new acceptors. If one of the acceptor sites was a TCNQ molecule, the resulting system could have a structure such as:
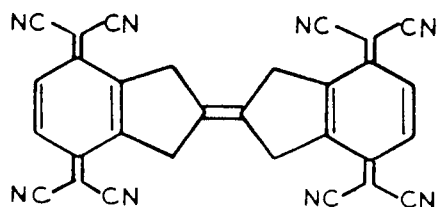
In order to build this symmetrical carbon skeleton, a vicinal disubstituted

TCNQ was needed. Initially, it was hoped that the use of a Diels-Alder

reaction between TCNQ and an appropriate diene would serve our purposes.

However, it has been reported[7] that this reaction has not given any

characterizable adducts when various dienes were used, and in some cases

TCNQ was recovered unchanged. It was decided that the use of a disubstituted

TCNQ with appropriate functional groups would be more convenient. Accordingly,

the synthesis of 3,6-bis(cyanomethyl)phthalic anhydride (67) was planned

as follows (Scheme XIV). It was hoped that this compound could be converted

to the corresponding TCNQ derivative.
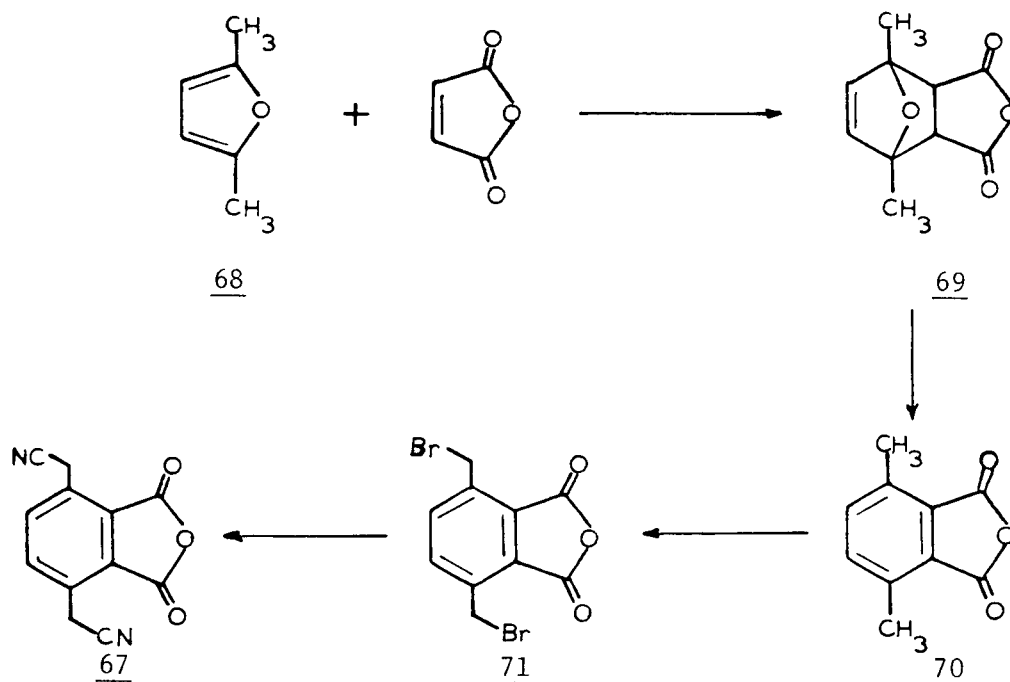
Scheme XIV. Synthesis of 3,6-bis(cyanomethyl)phthalic anhydride (67).

3,6-Dimethylphthalic anhydride (70) was prepared by a Diels-Alder

reaction of 2,5-dimethylfuran (68) and maleic anhydride. The corresponding

adduct was dehydrated directly by treatment with concentrated sulfuric acid[41] at -10°C to give 70 in 24% overall yield. The low yield obtained might be partially explained by the occurrence of an acid catalyzed reversal[42] of the Diels-Alder reaction, which competes with the acid-catalyzed dehydration to 70. When the phthalic anhydride was bisbrominated under Wohl-Ziegler conditions[43], a mixture of mono and dibromo derivatives was obtained. The dibromo-71 precipitated out from the mixture and was purified by recrystallization (26% yield). Its ^{1}H nmr spectrum showed resonances at δ4.86 (s,4H,-CH_2Br) and δ7.82 (s,2H,aryl). Its ir spectrum retained the three absorption bands at 1856, 1777 and 1260 cm^{-1} corresponding to the acid anhydride.

Displacement of bromide by cyanide in the presence of sodium iodide under anhydrous conditions[44] led to a mixture of compounds. Based on the ^{1}H nmr spectrum of the crude mixture, the formation of a five-membered ring lactone was suspected. In addition, signals at δ4.72 and δ4.96 were indicative of cyanomethylene and bromomethylene groups, respectively. The formation of a lactone was explained in terms of an intramolecular displacement of bromide by a carboxylate from the anhydride. It was hoped that substitution of the anhydride by an ester group would permit a cleaner substitution of bromine by nitrile. However, an attempt to convert the anhydride 71 into the diester 76, using methanol and p-toluenesulfonic acid[45], produced only the bromolactone ester 72 in 51% yield. The ^{1}H nmr spectrum of 72 contained a three proton singlet at δ4.01 attributed

71   72
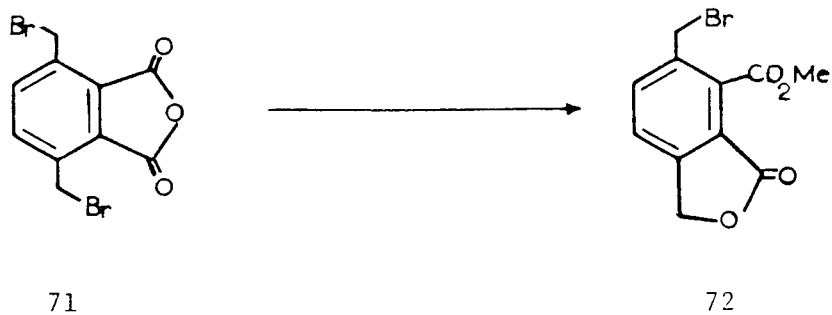
to the methoxy group, while at $\delta 4.55$ occurred a two proton singlet

which was assigned to the methylene protons of the bromomethyl group.

The singlet at $\delta 5.24$ corresponded to the two protons of the γ lactone

ring, while the aromatic protons gave rise to an AB-pattern (J=8Hz)

centered at $\delta 7.55$. Its ir spectrum showed sharp, strong absorptions

at 1775 cm^{-1} (lactone C=O) and 1735 cm^{-1} (aryl ester C=O).

It was decided at this point to try to synthesize the corresponding

diester 73 as outlined in Scheme XV. The preparation of dimethyl 3,6-

dimethylphthalate (75) via a Diels-Alder reaction of trans,trans-2,4-

hexadiene and dimethyl acetylenedicarboxylate has been reported.[46] The

Diels-Alder cyclization took place in refluxing benzene to give the

adduct 74 in essentially quantitative yield. Dehydrogenation with DDQ

(5,6-dichloro-2,3-dicyano-p-benzoquinone) in benzene overnight, led to

the desired dimethylphthalate 75 in 80% overall yield. Its physical and

spectral data were in agreement with those reported in the literature.[46]
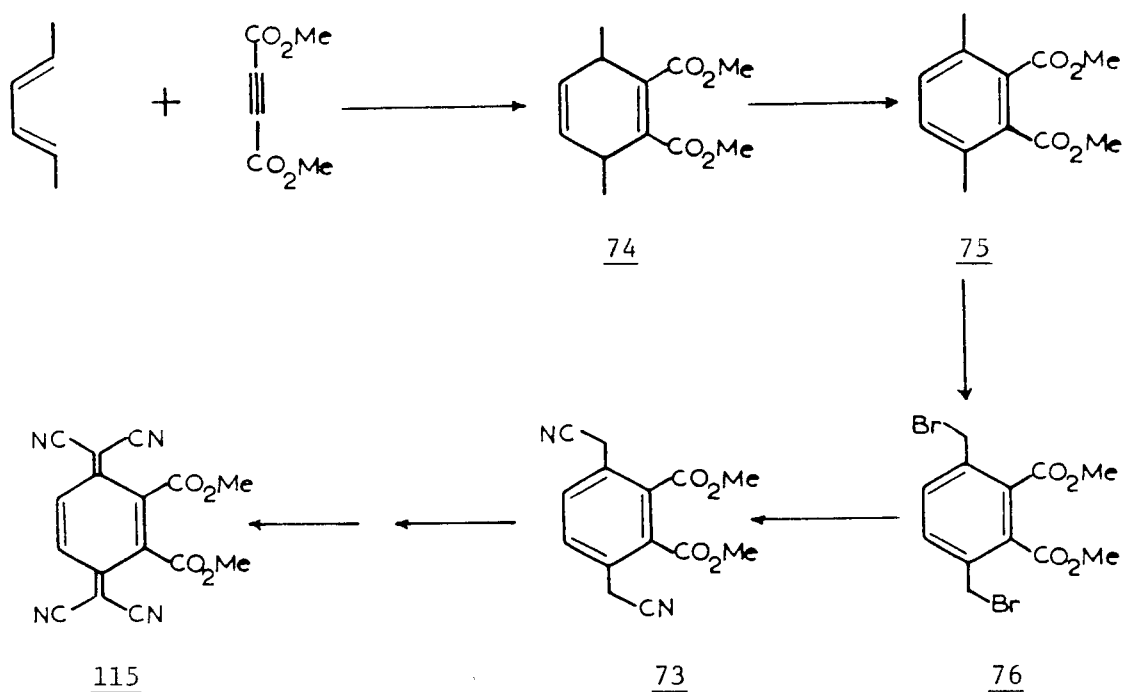
Scheme XV. Proposed synthesis of 2,3-dimethoxycarbonyl-7,7,8,8-tetracyanoquinodimethane (115)

Gundermann et al.[46] have bisbrominated 75 under Wohl-Ziegler conditions[43], in 37% yield, by using 1.7 equivalents of NBS. When a stoichiometric amount of NBS was used, the tribromoderivative 77 was obtained. In our hands, the bromination of 75 was effected using the


77
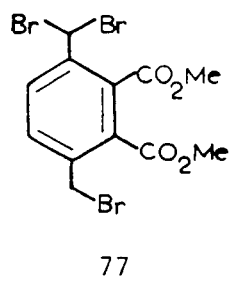
conditions developed for the monoester 58. In this case, a mixture of di- and tribromo compounds 76 and 77 was produced. The tribromo derivative could be separated from the crude product by dissolving the solid mixture

in minimum amounts of boiling ethanol followed by overnight cooling and

selective crystallization by addition of methanol. The crude dibromo-

76 (64% yield) was treated directly with sodium cyanide, in a manner

similar to that described for the monoester 59. The yield of the desired

dimethyl 3,6-bis(cyanomethyl)phthalate (73) was 44% after purification

by preparative column chromatography. Analytical and spectroscopic data

are consistent with structure 73. Notably, the ir spectrum shows a weak

band at 2290 cm^{-1} corresponding to nitrile absorption, and again shows a

sharp, strong band at 1730 cm^{-1} (aryl ester C=O).

Attempts to introduce the remaining two nitrile groups via use of

a phenylenetetracyanodiacetate intermediate failed to give the desired

tetraester 78. An unidentified mixture was obtained and no further charac-

73   78
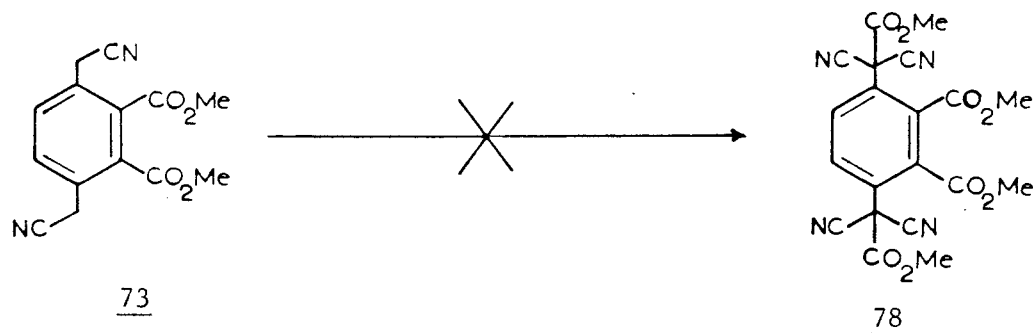
terizations were made. Use of potassium hydride and methyl chloroformate

in DME led to similar results. Treatment of 73 with base followed by

direct alkylation with cyanogen chloride proved unsuccessful. In both

cases complex mixtures of compounds were obtained. It has been reported[48]

that intramolecular electrophilic cyclization of the acid chloride 79

leads to the isoquinolone derivative 80. In light of this fact, it is

79 → 80
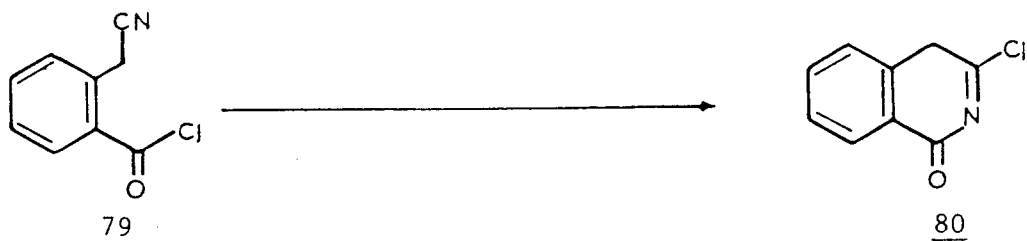
possible that a similar rearrangement occurs in 73, to produce an

intermediate such as 81 a,b,c.

81a

81b

81c
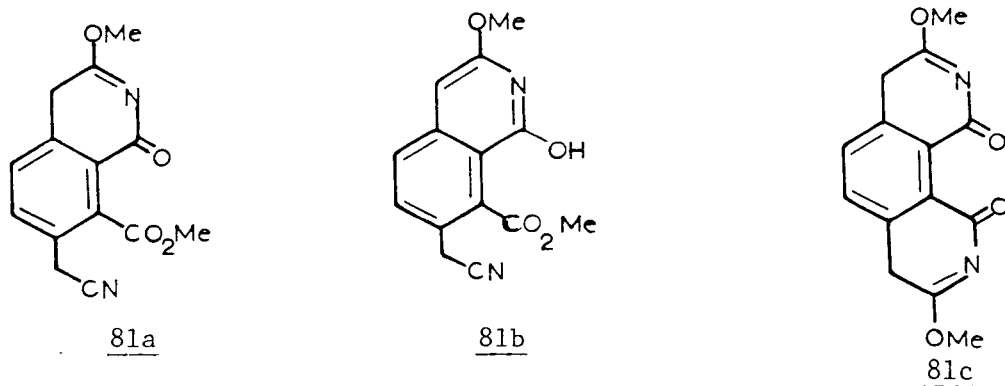
To our knowledge, the synthesis of a vicinal dialkyl derivative of

TCNQ has not been reported in the literature. Studies[49] of the tetrathia-

and tetraselenafulvalene salts of 2,5-dimethyl-7,7,8,8-tetracyanoquinodi-

methane (82) have shown that the conductivities of these salts are comparable

82

83

to that of other TCNQ analogs. However the metal-insulator transition

temperature is lower in the case of the dialkyl derivative 82. This

could arise from disorder effects in the solid, or these results might

indicate that solid state properties are mainly dominated by the actual

crystal structure rather than by electronic properties of donors and

acceptors. 2,3-Dimethyl-7,7,8,8-tetracyanoquinodimethane (2,3-DMTCNQ)

(83) is larger than TCNQ and has a different molecular symmetry than TCNQ.

A characteristic of the conducting solids formed by TCNQ is the occurrence

of separate stacks of acceptors and donors. The dimethyl-TCNQ 83 carries

the possibility of different stacking patterns. Stacks of 83 might be

formed in an alternating arrangement to facilitate minimum steric repulsion

of methyl groups of adjacent molecules. Alternatively, the methyl groups

can be randomized causing disorder in the lattice. This latter possibility

could cause a broadened phase transition and greater conductivities at

low temperatures, as is the case when small amounts of methyl-TCNQ 49 are

added as a dopant to TSF-TCNQ.[32] In view of these interesting features

offered by 2,3-DMTCNQ (83), a synthesis of this molecule was attempted,

as depicted in Scheme XVI. Synthesis of the dione-87 was accomplished
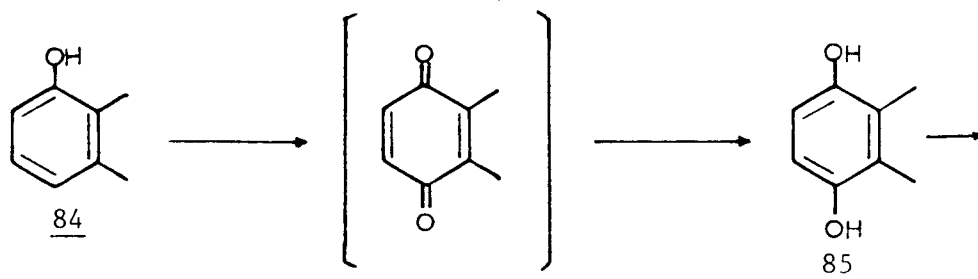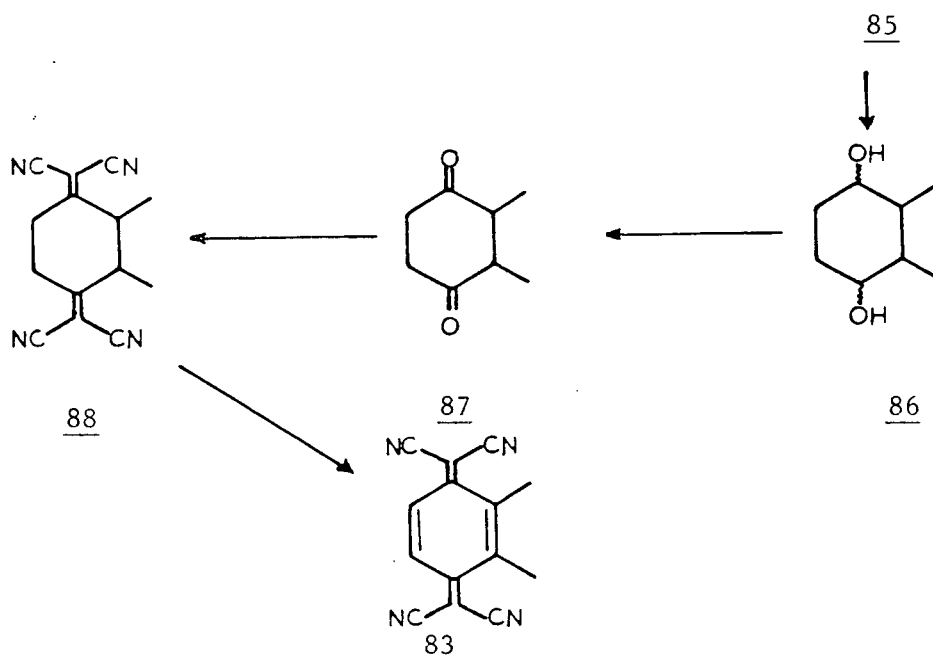
Scheme XVI. Proposed route for the synthesis of 2,3-DMTCNQ (83).

following Yamakawa's route.[50] Oxidation of 2,3-dimethyl phenol (84) was

readily achieved via the Teuber reaction[51], with two equivalents of

potassium nitrosodisulfonate (Fremy's salt) to produce an intermediate p-

benzoquinone. This quinone is reduced in situ during the work-up with

aqueous sodium thiosulphate, giving the hydroquinone 85 in 75% yield;

its m.p. was 167-170°C (lit.[48] m.p. 163-164°C). The hydrogenation step

that follows was carried out using the same procedure as for the hydro-

quinone 50. The crude oil containing a mixture of isomers was isolated

in 95% yield. Oxidation of the diol-86, in the manner described for 51,

gave 2,3-dimethylcyclohexane-1,4-dione (87) in 75% yield. Its ir and

^{1}H nmr spectra were identical to those supplied by Yamakawa.[48]

The dione-87 was condensed[7] with malononitrile to produce the

expected tetracyano-88 in 67% yield. The white solid thus obtained

lacked a carbonyl absorption in its ir spectrum, but contained a new

absorption band at 2250 cm^{-1} (conjugated C≡N). Treatment of 88 with

bromine/pyridine[7] failed to give the desired dimethyl-TCNQ 83. Instead,

the partially oxidized dihydro derivative 89 was obtained in 86% yield.

Its ^{1}H nmr spectrum showed a singlet at δ7.06 corresponding to the two
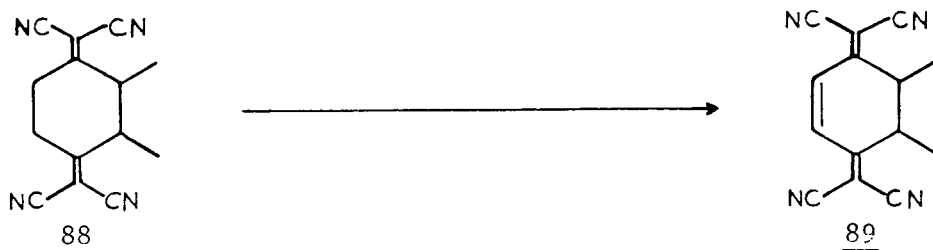
vinyl protons, and it included signals at δ1.16 (d,J=7Hz,6H,CH$_3$-CH) and

δ3.17 (m,2H,-CH-CH$_3$). Further evidence for structure 89 came from its ir

and mass spectra and microanalysis. Efforts to oxidize the allylic

position in 89 with either NBS or NCS (N-chlorosuccinimide) were un-

successful. In both cases starting material was recovered. The

following conditions led to a similar result: manganese dioxide in

refluxing toluene, or DDQ in refluxing dioxane. The search for stronger

dehydrogenation conditions prompted the use of a mixture of sulfur and

palladium as dehydrogenating agents.[52] Small amounts of this mixture

were finely ground with 89 and the resulting powder was heated to 180°C

for 3 hours. Analysis of the extract (by tlc) showed several colored

spots including starting material. The band at R$_f$ 0.5 (eluent methylene

chloride) was collected and found to be the desired product 83. Its

[1]H nmr spectrum showed two singlets at δ2.35 (6H,-CH$_3$) and δ7.43 (2H,

vinyl). Its mass spectrum further substantiated this assignment by

having 232 as the highest molecular ion recorded. Unfortunately, when
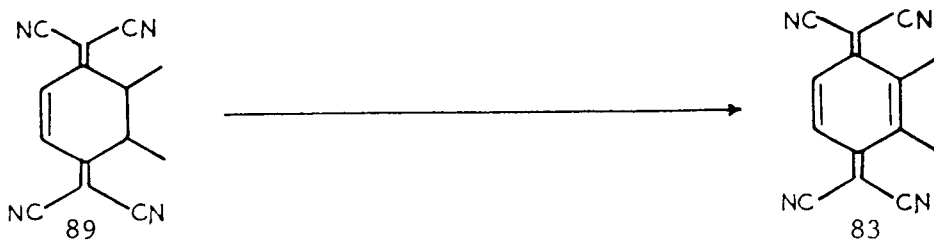
this reaction was scaled up the results were different and 83 could not

be obtained. No further investigations were made.

3.2 Synthesis of 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-

quinodimethane (TCNTP) (90).

Among the extended conjugated analogs of TCNQ studied to date, TCNDQ

(22) suggested some interesting possibilities for further studies. Un-

fortunately, the neutral species has not been isolated.[27,29] It was hoped

that the TCNDQ analog 90, with its pyrene skeleton, would be more stable

because biphenyl inter-ring hydrogen repulsions are eliminated.[30] The
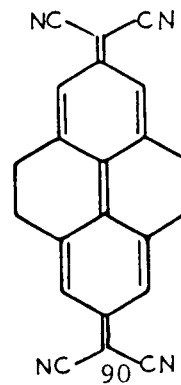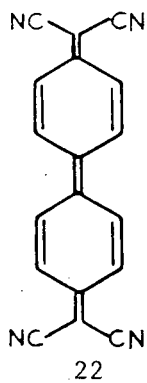
proposed synthesis of TCNTP (90) is outlined in Scheme XVII. This scheme

shows how a figurative dissection to simpler systems could help in the

search for an appropriate starting material. TCNTP could be obtained

from the dihydro precursor 91 using mild oxidation conditions. In turn

91 could be prepared from the dicyano-93 via hydrolysis and decarboxylation

of the phenylenetetracyanodiacetate intermediate 92. Moving backwards in

stepwise fashion, obtention of 93 requires a transannular reaction of the

dicyano[2.2]metacyclophane 94. This compound can be formed from 95 by

displacement of bromide with cyanide. The dibromo metacyclophane 95 is

available from the corresponding dimethyl compound 96 by treatment with

NBS.[53]

90   91   92
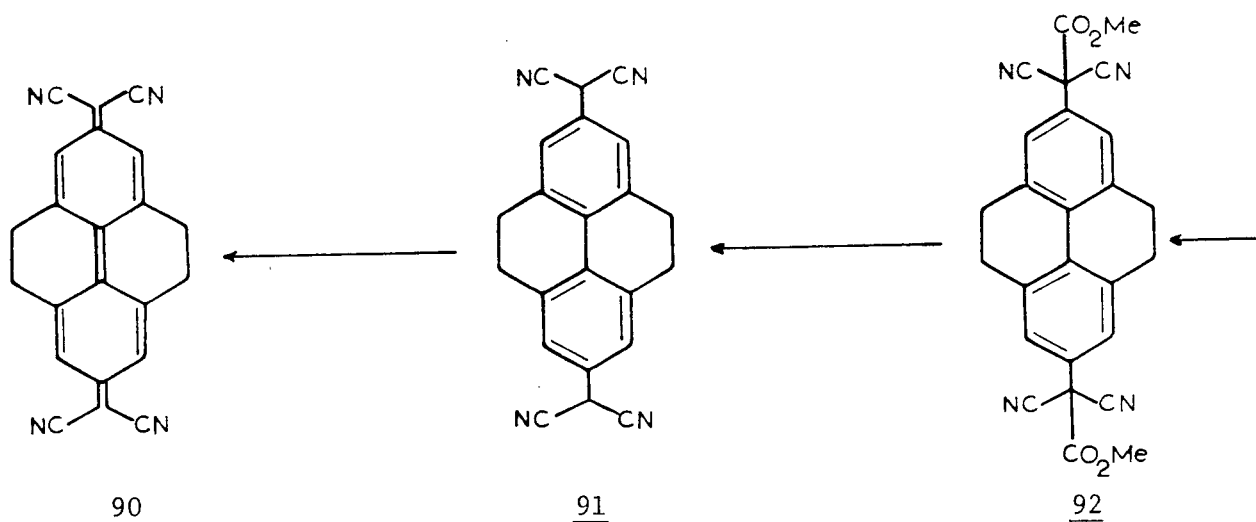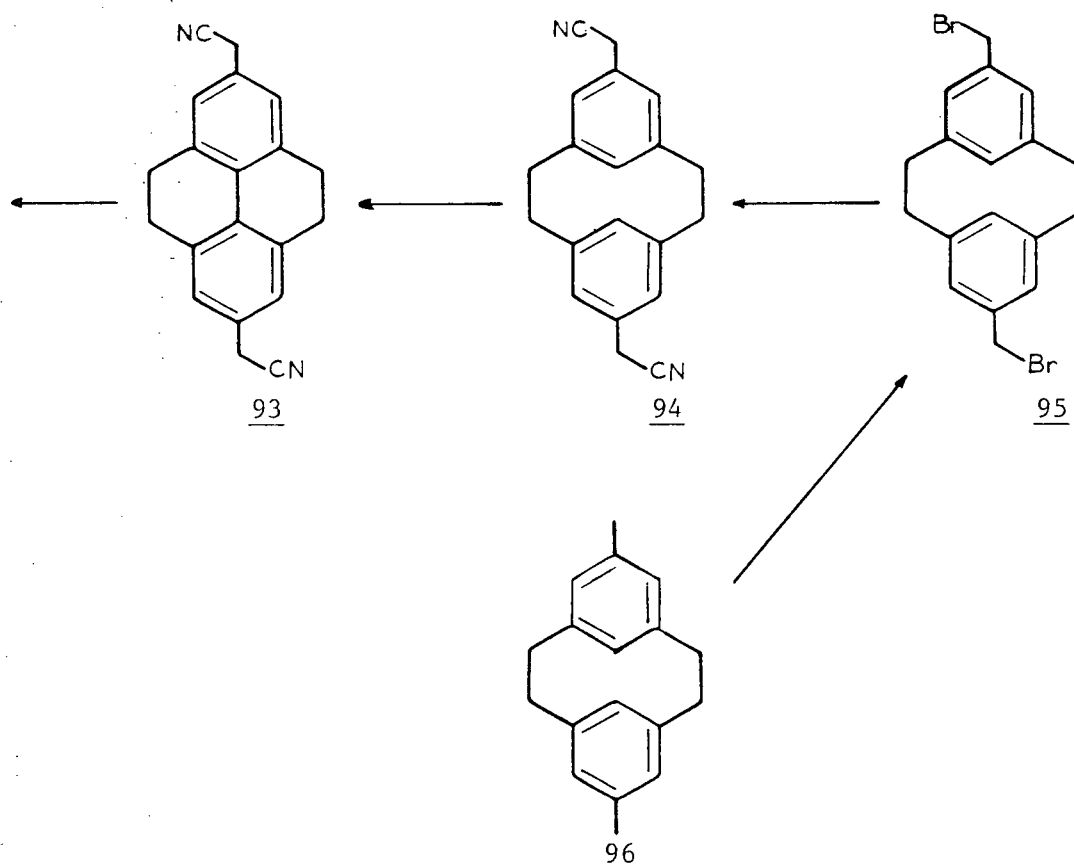
Scheme XVII. Proposed synthesis of TCNTP (90) from 5,13-dimethyl-
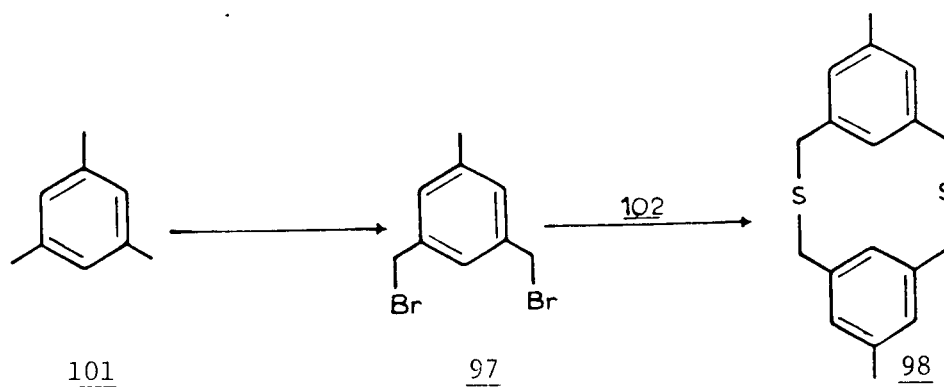   [2.2]metacyclophane   (96).

The metacyclophane 96 contained all the necessary elements for the

synthesis of 90; and it has been prepared in the past by intermolecular

coupling of 3,5-bis(bromomethyl)toluene   (97), via use of the Wurtz

reaction, in the presence of sodium[54] (12% yield), or phenyllithium[55]

(no yield reported). The yields in this type of reaction are usually low

and the amounts of by-products large.[56] On the other hand, the formation

of the corresponding dithiacyclophane 98 generally occurs in high yield,

and so it has been used as precursor for the synthesis of 96 in three

ways: (i) the extrusion of sulphur has been accomplished by conversion

into the corresponding bis-sulphone 99, followed by elimination of

sulphur dioxide on pyrolysis[53] at 800°C (76%)(Scheme XVIII a); (ii)

the extrusion of sulphur has been achieved in one step by irradiation

of small amounts of 98 in the presence of trimethyl phosphite;[57] (iii)

recently, Mitchell et al.[58] found that the Wittig rearrangement of 98,

with n-butyllithium, followed by alkylation with methyl iodide, gave

100 as a mixture of isomers in excellent yield. This mixture was

converted cleanly to anti-5,13-dimethyl[2.2]metacyclophane (96) by

reduction with lithium in liquid ammonia (Scheme XVIII b).

It was decided to use Mitchell's route[58] to 96 in view of the fact

that both steps could be carried out on a large scale and in good yields.

The synthesis of 6,15-dimethyl-2,11-dithio[3.3]metacyclophane (98) is

depicted in Scheme XIX. Bromination[59] of mesitylene (101) with NBS

afforded 3,5-bis(bromomethyl)toluene (97) in 50% yield after recrystalli-

zation. Conversion of the dibromo-97 to the dithiol-102 was achieved in

95% yield using the thiourea method.[59,60] This method involves the

formation of the diisothiouronium bromide 103, via nucleophilic attack

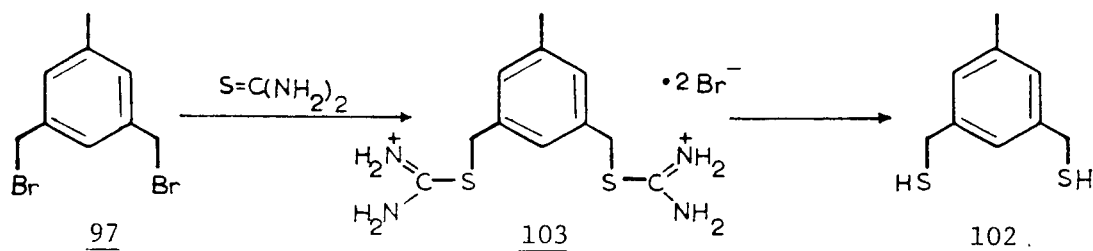on the halide by the sulfur. Hydrolysis of this salt in refluxing potassium
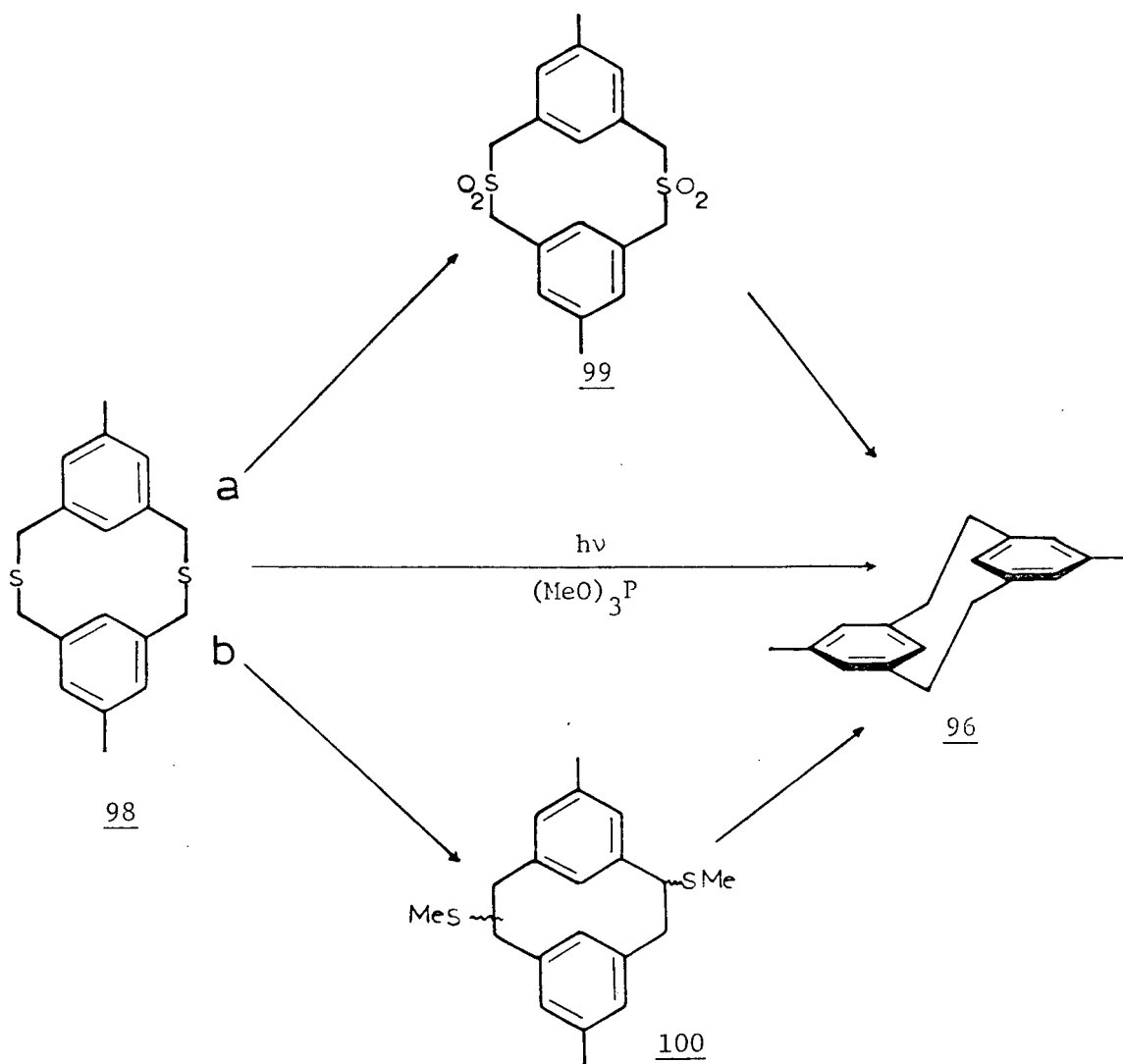
Scheme XVIII. Alternate pathways to anti-5,13-dimethyl[2.2]metacyclo-
phane(96).

Scheme XIX. Synthesis of 6,15-dimethyl-2,11-dithia[3.3]-
metacyclophane (98).

hydroxide gave 102. Its ^{1}H nmr spectrum showed signals at δ1.72 (t,J=8Hz,

2H,-SH), δ2.31 (s,3H,-CH$_3$), δ3.64 (d,J=8Hz,4H,-CH$_2$-) and δ6.97 (s,3H,aryl).

Coupling of 97 and 102 occurred in an ethanolic solution of potassium

hydroxide under high dilution conditions[61] and over a period of 7 days.

The crude product was purified by filtration through silica gel. Thus,

the dithiacyclophane 98 was obtained in 85% yield. A recrystallized

sample had a melting point 101.5-103.5°C (lit.[53] mp 102-102.5°C).

Spectral data were in agreement with those reported previously[59].

Treatment of 98 with n-butyllithium in THF at -20°C, followed by

methylation of the resulting thiolate afforded the mixture of isomers

100. The crude mixture was not purified but was used directly in the

reduction step that follows. Cleavage of the carbon-sulfur bond was

achieved by reduction of 100 with lithium in liquid ammonia. The crude

reaction product was purified by preparative column chromatography;

subsequent recrystallization from ethanol furnished 96 in 30% overall

yield, mp 145-146°C (lit.[53] mp 145-146°C).

It was found that NBS bromination of 96 displayed a remarkable

solvent dependence: in methylene chloride a transannular reaction occurred

with the consequent formation of the tetrahydropyrene 104; while in

carbon tetrachloride, the bisbromide 95 was formed exclusively, in 70%

yield. The ^{1}H nmr spectrum of 95 showed the characteristic pattern of

104

96

95
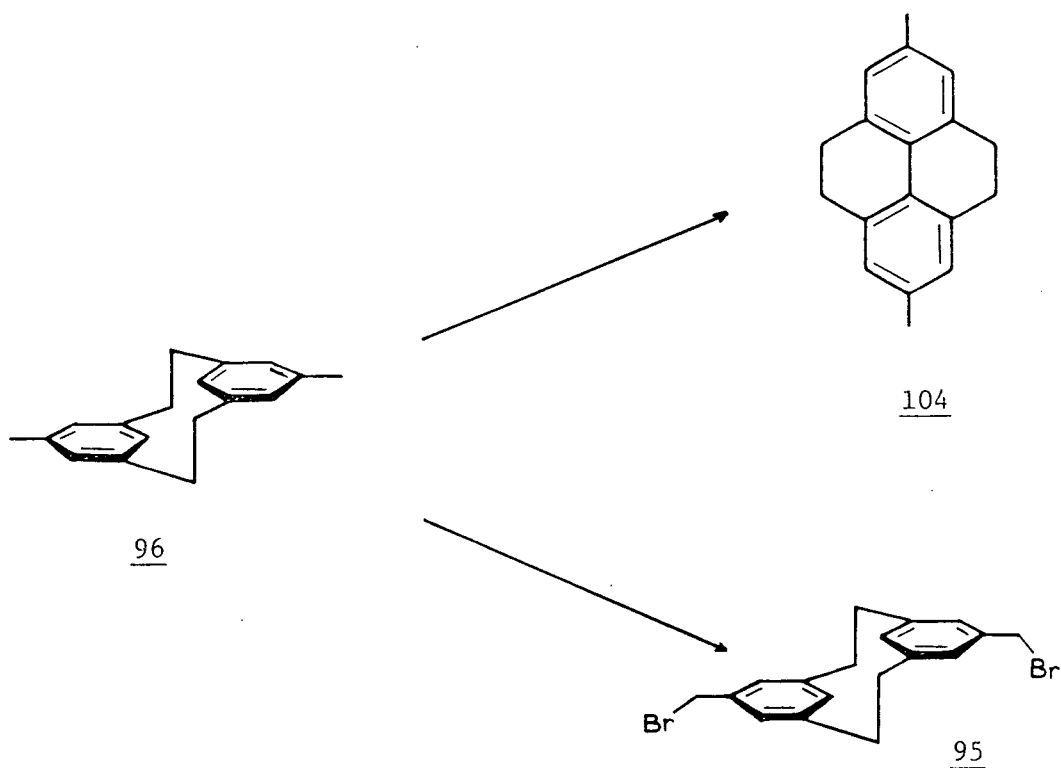
[2.2]metacyclophanes.[62]   In particular, the intraannular protons

exhibited an unusual high field shift at δ4.25 (s) due to the ring

current effect of the other benzene ring. Since the ten-membered ring

system of 95 exists in a rigid chair conformation, the bridging ethylene

signal appears as an A_2B_2-pattern arising from axial and equatorial

protons: δaxial=2.14, δ equatorial=3.13. Furthermore, the benzylic

methylene groups bearing bromine appear as a singlet at $\delta 4.56$. In the case of 104, its ^{1}H nmr spectrum consists of three singlets at $\delta 2.36$ (methyl), $\delta 2.87$ (methylene) and $\delta 6.96$ (aryl) in a ratio of 3:4:2 respectively.

It has been reported that in the NBS bromination of naphthaleno-paracyclophane[38] 105, when methylene chloride was used as solvent, bromination occurred exclusively in the aromatic ring to form the cyclophane 106 while if carbon tetrachloride was used, the mono bromo-107 was formed alongside the gem-dibromo-108.

107 X=H, Y=Br
108 X=Y=Br
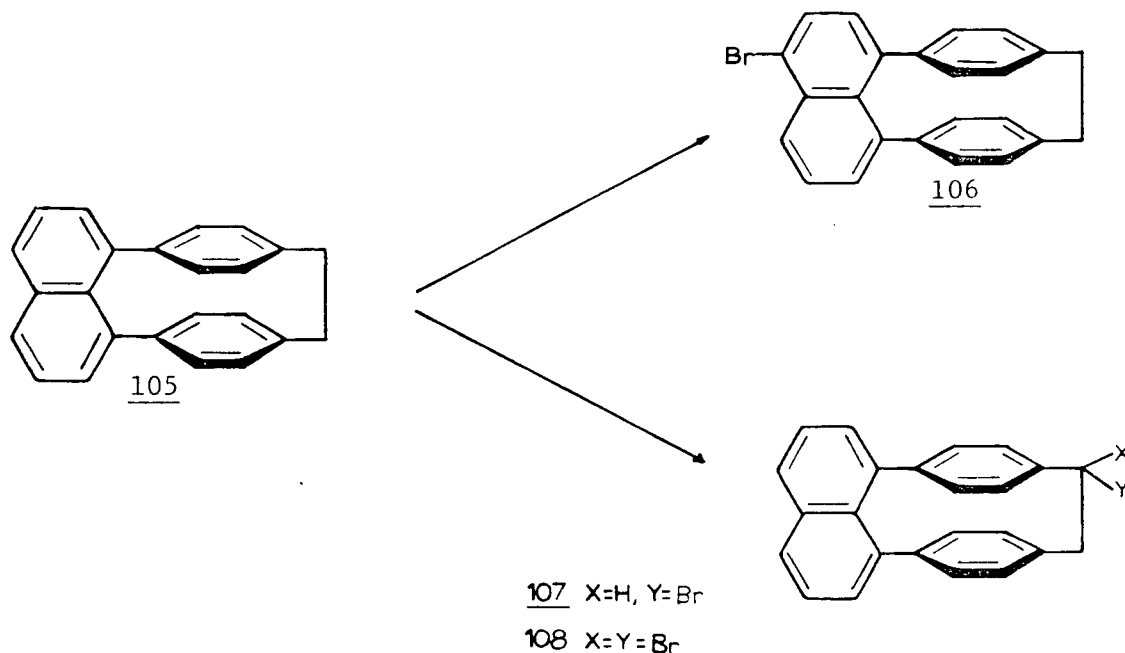
A similar solvent effect may be operating in the NBS bromination of 96. The tetrahydropyrene 104 now has six benzylic positions, and NBS bromination on this molecule would be expected to yield a mixture of

compounds. When 104 is treated with NBS in carbon tetrachloride, one

of the major products of the mixture is 2,7-dimethylpyrene (109). Its

^{1}H nmr spectrum showed two singlets at δ2.80 (6H,-CH$_3$) and δ7.98 (8H,aryl)

which are consistent with the literature values.[61]

Displacement of bromine in dibromo-95 by cyanide was achieved in a

manner similar to that described for the mono- and diester 59 and 76

respectively. Due to solubility problems, the reaction was carried out

in refluxing THF. The resulting dicyano compound 94 was obtained in

70% yield. It exhibited an absorption band in the ir, at 2300 cm^{-1}

(C≡N), and its ^{1}H nmr spectrum showed an expected upfield shift for the

cyanomethyl groups to δ3.80 (s,4H). Compound 94 could now be converted

into the desired pyrene framework by transannular reaction between the

two rings. It has been reported[64] that treatment of 110 with bromine

in the presence of catalytic amounts of iron powder, leads to the

formation of 111. More recently, Misumi et al.[53] have used these

109   104
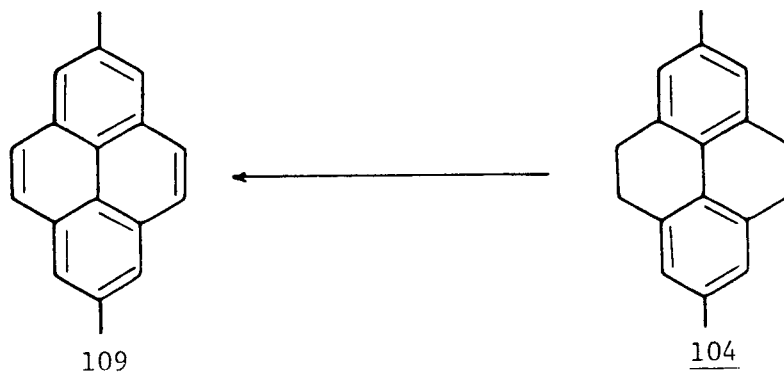
conditions to achieve a transannular oxidation of 95. The cyclophane 94

110   111

95   113
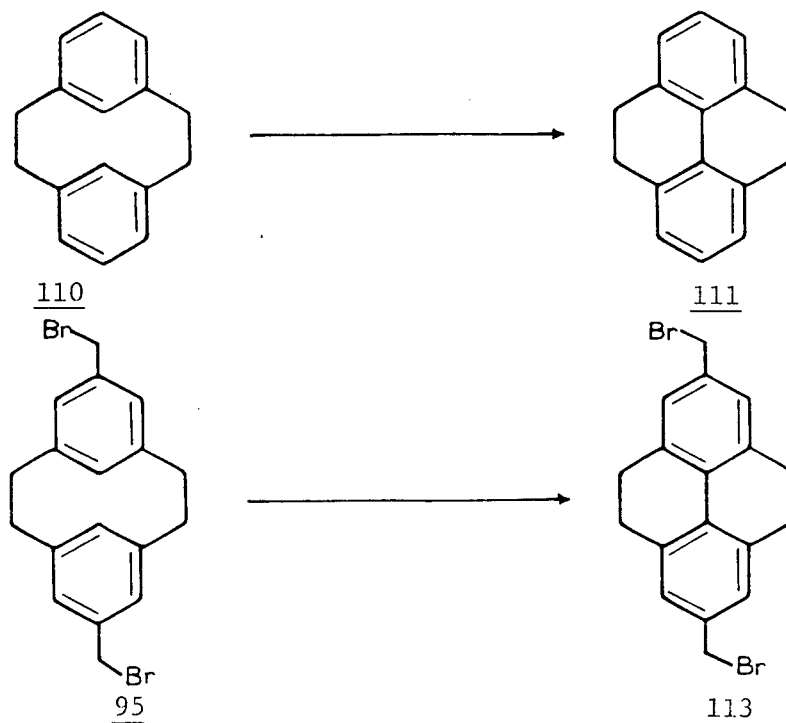
was converted into the dicyanopyrene 93 by stirring the mixture of 94,

bromine in chloroform, and iron powder at 0°C for 1.5 hours. After

work-up the crude reaction mixture is chromatographed, and the dicyano-

pyrene is obtained in 70% yield. Evidence for structure 93 was supplied

by its ^{1}H nmr spectrum which showed the disappearance of the signal at

δ4.24 (intraannular aromatic protons). In addition, since structure 93

is planar, the bridging ethylene protons are all equivalent, and the

A_2B_2-pattern collapsed to a singlet at δ2.83 (8H). Based on the

mechanistic studies[64] on the transformation of 110 into 111, the

following mechanism was suggested for the transannular reaction of 94.

Intermediate 112 is formed by the electrophilic attack of the bromonium

ion on one ring, accompanied by a simultaneous transannular attack of

the generated phenonium ion on the second ring. Regeneration of the

aromatic character by loss of a proton followed by elimination of the

elements of hydrogen bromide gave rise to the observed product.

112
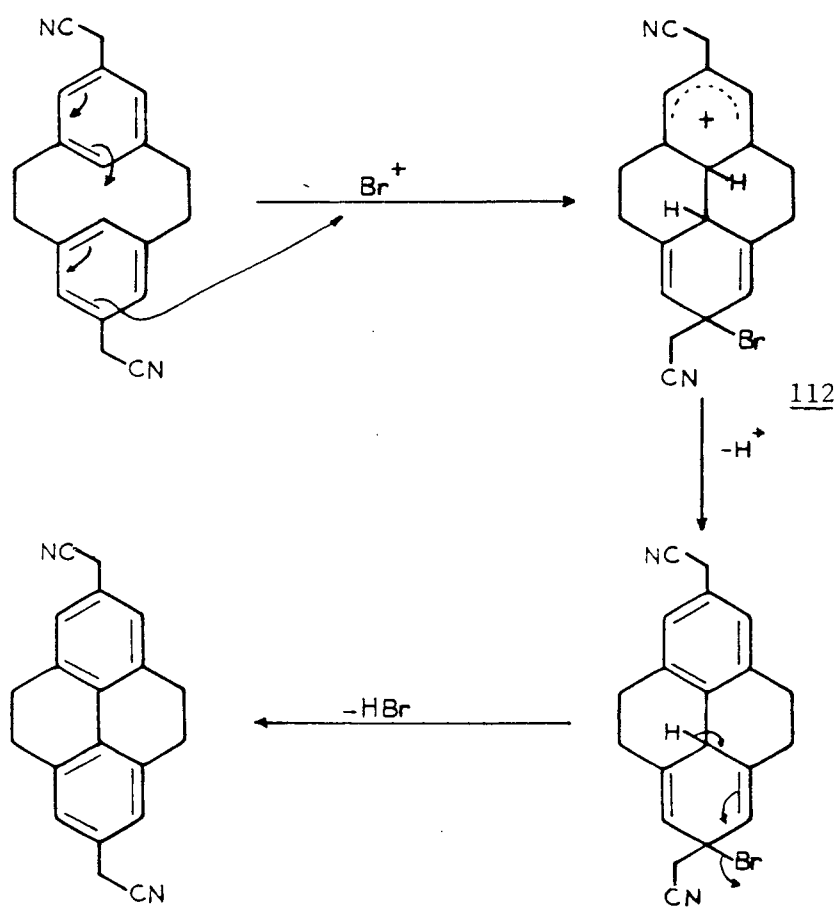
Introduction of the remaining two cyano groups was achieved via formation of the diester 92, in a manner similar to that described previously for the synthesis of the triester 61. The ir spectrum of 92 showed a strong absorption at 1745 cm^{-1} (saturated ester C=O). Its ^{1}H nmr spectrum exhibited a new signal at δ3.91 (s,6H,-OCH$_3$), and its mass spectrum showed the expected M$^+$ at 450. The crude product was not purified any further but was used directly in the hydrolysis step that follows.

Hydrolysis and decarboxylation of 92 afforded the dihydro-TCNTP 91. This reaction was carried out using the same procedure as for the triester 61. Disappearance of the signal corresponding to the methoxy carbonyl group in the ^{1}H nmr spectrum of 91 is accompanied by the appearance of a new singlet at δ5.00 (2H,(CN)$_2$CH-). Purification methods such as chromatography, recrystallization and sublimation failed to give any positive results, and, as yet, this compound has not been obtained in the pure state. It was decided, however, to attempt the synthesis of TCNTP (90) using crude compound 91 in view of the fact that, from our past experience, TCNQ derivatives have been more easily purified than the corresponding dihydro compounds.

Oxidation of 91 to the desired TCNTP proved more difficult than anticipated. The use of manganese dioxide in refluxing toluene[8] led only to unidentified products; treatment with aqueous bromine at room temperature produced a highly insoluble green-brown solid, mp 206-210°C (decomp.). Its ir spectrum showed a band at 2220 cm^{-1} indicative of a conjugated nitrile, (TCNQ shows a band at 2220 cm^{-1})[7]. Furthermore its mass spectrum showed two peaks at 334 and 332 in a 2:1 ratio, together with small peaks at 412 and 414 (1:1 ratio). The latter peaks were believed

to be due to the presence of some bromine containing impurities and will

be discussed later. It was felt that the M^+ + 2 peak observed at 334 ori-

ginated from compound 91, formed by aromatization of TCNTP in the probe

(T=270°C). A small sample (5 mg) was recrystallized from acetonitrile

(ca. 400 ml), mp 210-212°C (decomp). This compound gave an intense

purple color in solution. Elemental analysis, however, did not correspond

with the desired values. Its UV-Vis spectrum is shown in Figure 6. When

this compound was treated with thioglycolic acid in acetic acid under the
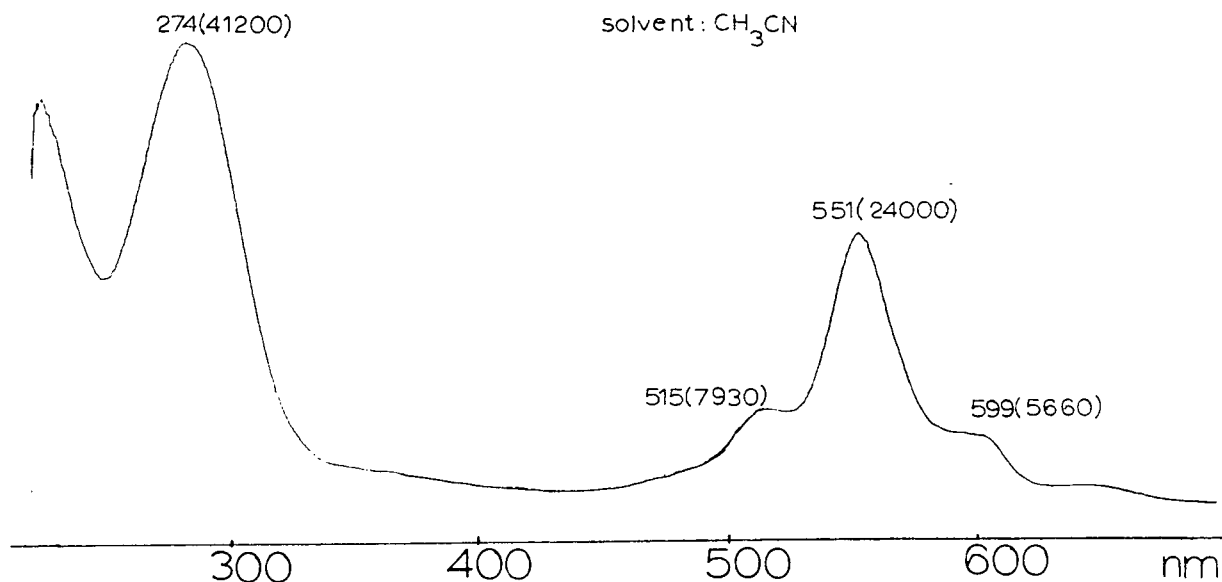
Figure 6. UV-Vis spectrum of 2,7-bis(dicyanomethyl)-4,5,9,10-tetrahydropyrene (91) after treatment with aqueous bromine.

same conditions used for the reduction of TCNQ to the dihydro-TCNQ 55,

the corresponding dihydropyrene 91 was the only material isolated from

the reaction mixture.

Other oxidation conditions were tried, among them, the use of NCS

and triethylamine in methylene chloride, at -20°C; in this reaction a

drastic color change took place when triethylamine was added, and the

color of the reaction mixture turned intense purple. A tlc examination

of the product mixture revealed the presence of two main products; analysis

of the less polar band isolated by preparative tlc (eluent chloroform)

yielded a blue solid, mp 227-230°C, readily soluble in most organic

solvents. The presence of two chlorine atoms in the molecule was evident

by the characteristic isotopic distribution exhibited by the molecular

ions at 402, 404, 406 (9:6:1) in its mass spectrum. In addition, its ^{1}H nmr

spectrum showed two singlets at δ3.50 and δ7.56 in a 4:1 ratio, perhaps

suggesting chlorine substitution on the benzene rings. Treatment of 91

with NBS in methylene chloride at -78°C followed by addition of triethylamine

yielded a yellow-brown solid. Tlc analysis showed one spot, Rf∿0.5 (eluent

chloroform); the solution ir spectrum of the crude reaction product showed

a weak absorption at 2228 cm^{-1} (conjugated C≡N). Purification of the crude

product was attempted by filtration through silica-gel followed by recry-

stallization from benzene; the green microcrystals so obtained melted at

206-208°C (decomposition). Its ir spectrum (KBr pellet) showed two weak

absorptions at 2225 and 2265 cm^{-1}; the ^{1}H nmr spectrum showed signals at

δ2.94 and δ7.20, assigned to the methylene and vinyl protons of 90

respectively. However, due to the presence of unidentified products an

accurate percentage yield of 90 could not be calculated. The mass spectrum

of 90 contained peaks at 332 and 334 corresponding to TCNTP (90) and dihydro-

TCNTP 91 respectively, together with two lower intensity peaks at 412 and

414 indicating the presence of some bromine containing impurities, as

observed previously. The mass spectrum was then recorded at different

temperatures ranging from 280°C to 450°C. In this interval, the ratio

of the peaks at 334 and 332 decreased gradually with increasing

temperature, from a value of 3.1 at 280°C to a value of 1.8 at 450°C.

At the same time the peaks at 412 and 414 disappeared gradually. These

results seem to indicate: (a) the peaks at 412 and 414 are derived from

a compound other than 90; (b) the dihydro compound (m/e=334) is probably

formed from TCNTP (m/e=332) in the mass spectrometer. The UV-Vis spectrum

of 90 is shown below.
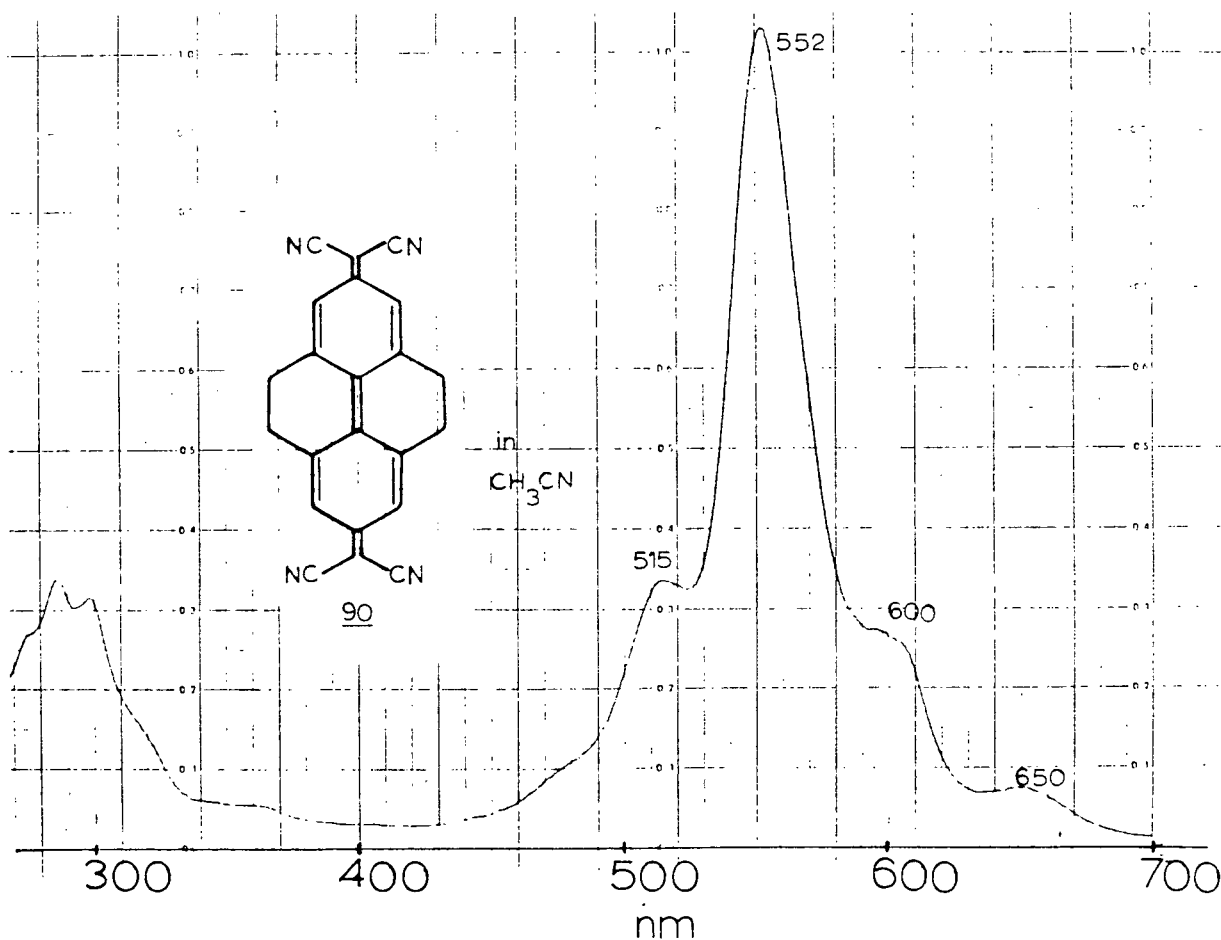
On treatment of <u>90</u> with excess tetrabutylammonium iodide in benzene at room temperature, the color of the solution went from purple to light red. After evaporation of the solvent, a mixture of $TCNTP^-$ TBA^+ (<u>114</u>) (TBA^+:tetrabutylammonium cation) and unreacted tetrabutylammonium iodide was obtained. Its ir spectrum showed a strong sharp nitrile absorption at 2180 cm^{-1} and a smaller absorption at 2145 cm^{-1}. Such a low absorption frequency for the nitriles is consistent with the value of 2200-2175 cm^{-1} observed for the tetraethylammonium salt of $TCNQ^{[9]}$. Furthermore the UV-Vis spectrum of <u>114</u> in benzene is similar to that observed for the radical anion of TCNDQ (<u>22</u>), as would be expected for the formation of $TCNTP^-$. Both spectra are shown in Figure 7.

$$I^- + TCNTP \rightarrow \tfrac{1}{2}I_2 + TCNTP^-$$
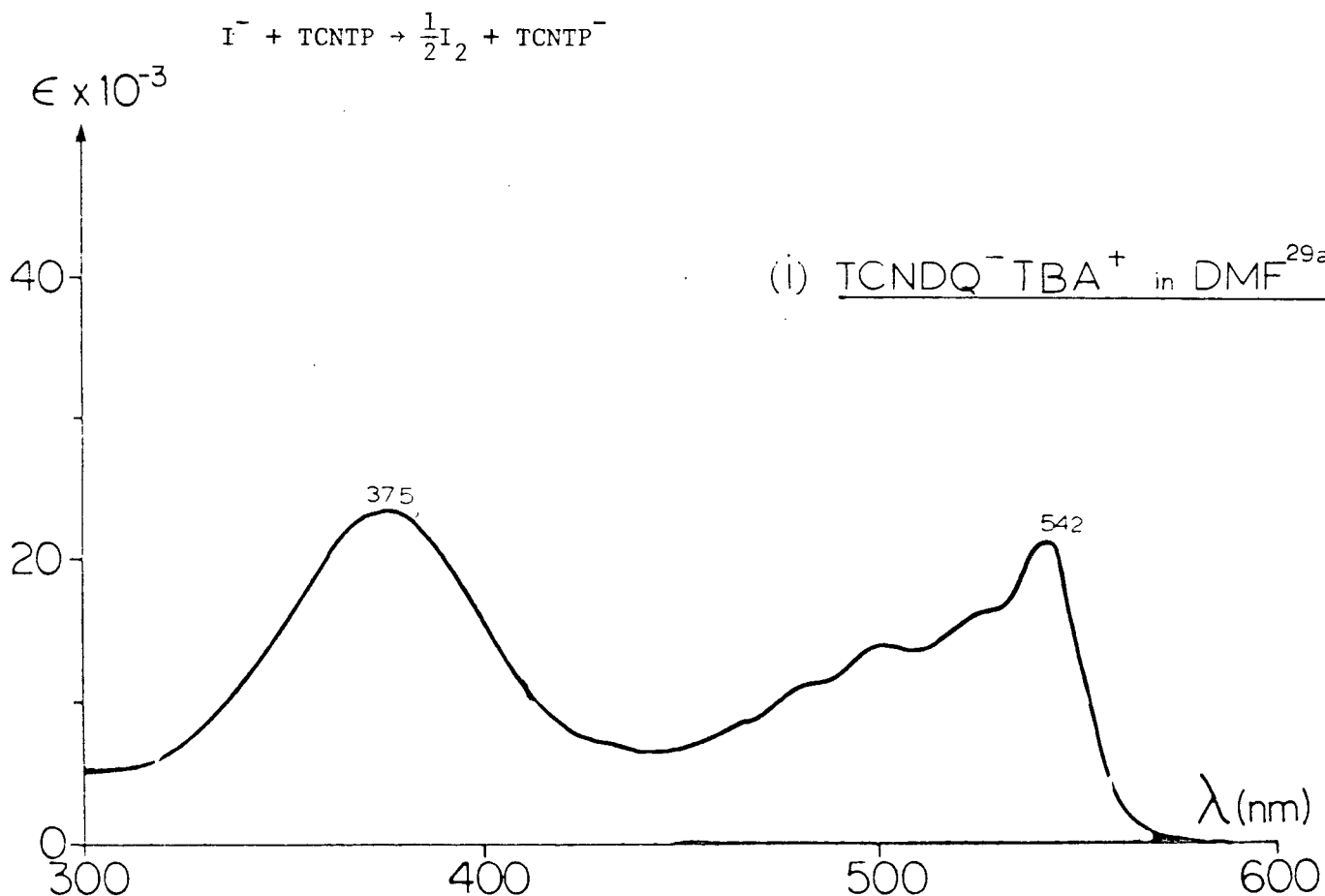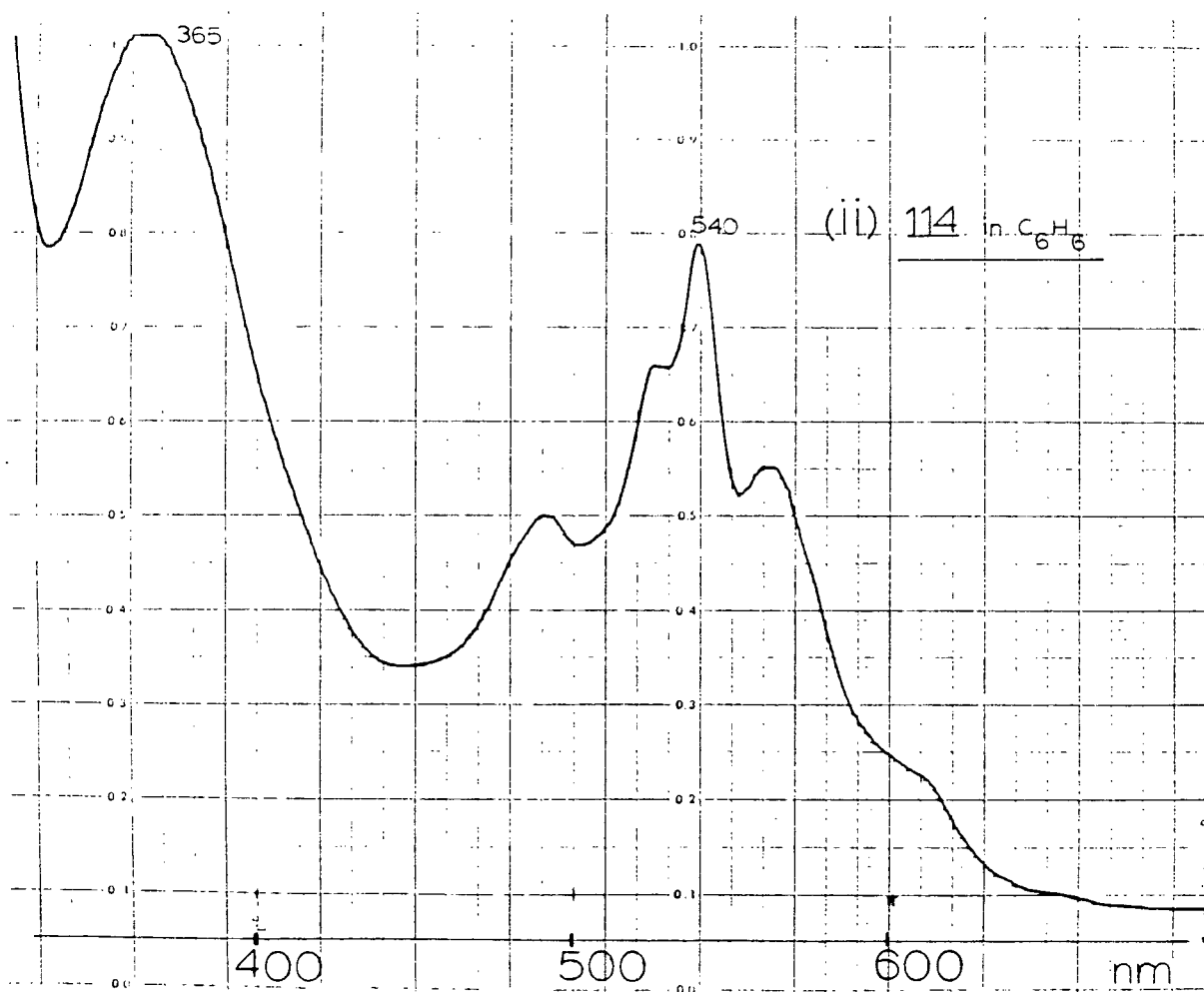
Figure 7. UV-Vis spectrum of (i) TBA$^+$TCNDQ$^-$ and (ii) TBA$^+$TCNTP$^-$ (114).

3.3 Overall Results

In summary, the work done towards the synthesis of a pyrene analog

of TCNDQ (22) has resulted in the preparation of 11,11,12,12-tetracyano-

4,5,9,10-tetrahydropyreno-2,7-quinodimethane (TCNTP)(90). Preliminary

results obtained from some exploratory experiments show that this molecule

could be potentially useful in the study of new donors derived from
extended TCNQ analogs. From the work described in the first section of
this chapter it can be concluded that the synthesis of new TCNQ deri-
vatives containing functionalized carbon substituents should start with
appropriately substituted benzene or cyclohexane derivatives as opposed
to the rather unreactive alkyl substituted TCNQ's. This viewpoint
resulted in the synthesis of 2-methoxycarbonyl-7,7,8,8-tetracyano-
quinodimethane (<u>56</u>). Finally, the synthesis of 2,3-dimethyl-7,7,8,8-
tetracyanoquinodimethane (<u>83</u>) has proved surprisingly difficult because
of the stability of compound <u>89</u> to oxidation. A new route should be
devised, in view of interesting structural features in <u>83</u>.

EXPERIMENTAL

GENERAL

Spectral Data

All infrared (IR) spectra were taken in chloroform solution, unless otherwise stated. They were recorded on a Perkin-Elmer model 700 spectrophotometer and were calibrated with the 1601 cm^{-1} band of poly-styrene. The assignment of each band is noted in parentheses after it.

^{1}H NMR spectra were recorded on a Varian model T-60 or model XL-100 spectrometer. The solvent used is reported in parentheses at the beginning of each spectrum. Chemical shifts (δ) are quoted in p.p.m. downfield from tetramethylsilane, used as an internal standard. The multiplicity, coupling constants (quoted in Hz), integrated peak areas and proton assignments are indicated in parentheses after each signal.

Ultraviolet-visible (UV-Vis) spectra were recorded on a Cary 17D spectrometer. The molar extinction coefficients of the main bands are listed in parentheses after the absorptions and are expressed in cm^{2} mole^{-1}.

Mass spectra were obtained using an Atlas CH-4B mass spectrometer, and high resolution determinations were obtained using an AEI MS-902 or MS-50 mass spectrometer. Both instruments were operated at an ionising potential of 70 eV. The value in parentheses after each mass is its relative intensity.

Physical Data.

Melting points (mp) were determined on a Kofler hot stage microscope and are uncorrected. Elemental microanalyses were performed by Mr. Peter

Borda, University of British Columbia.

Chromatography

Preparative thin layer chromatography (TLC) was carried out using 0.9 mm thickness silica gel (E. Merck, grade PF-254 + 366) on either 20 x 20 cm or 5 x 20 cm glass plates. Small analytical plates were prepared by dipping microscopic slides into a stirred solution of silica gel in chloroform. Column chromatography was done using silica gel of grade finer than 200 mesh.

Solvents

The term "dry" in this thesis refers to solvents dried in the following ways: ethyl ether and tetrahydrofuran (THF) were dried by re-fluxing over lithium aluminium hydride. Toluene and benzene were dried over sodium. Carbon tetrachloride, methylene chloride and acetonitrile were distilled from phosphorous pentoxide. Methanol was dried by refluxing over magnesium methoxide.

Techniques

Anhydrous magnesium sulfate was used to dry organic solutions and was removed by filtration. All stirring, unless otherwise noted, was carried out using teflon-coated magnetic stirring bars.

2-Methyl-1,4-cyclohexanedione (52)*

Methyl-p-hydroquinone (50) (8.8 g, 0.071 mole), rhodium (10%) on powdered charcoal (1.55 g) and a methanol-water mixture (198 ml, 10:1 V/V) were placed in a hydrogenation bottle which was then attached to a Parr-low-pressure apparatus. Air was evacuated and the flask was flushed with hydrogen several times. The reduction was then carried out at room

temperature at an initial hydrogen pressure of 50-60 psi. The reaction was complete when a constant hydrogen pressure was reached (approximately 22 hours). The catalyst was removed by filtration, washed with methanol (50 ml), and dried in vacuo. The catalyst could be used again after it had been reactivated - two days in the oven at 110°C. Solvents from the filtrate were removed under reduced pressure; traces of methanol and water were azeotropically distilled with chloroform (30 ml). The resultant oil (8.3 g, 90%) was shown, by ir and ^{1}H nmr spectra, to be 2-methyl-1,4-cyclohexanediol (51) which was not purified but was used directly in the oxidation step that follows. A solution of chromium trioxide (26.72 g, 9.27 mole), water (77 ml), concentrated sulfuric acid (23 ml), and manganese sulfate (0.2 g) was prepared, and added slowly to a stirred solution of the crude diol-51 (1.52 g, 0.012 mole) in chloroform (50 ml) at 5°C. The addition was stopped after 3 equivalents (13 ml) of chromium trioxide had been introduced (30 minutes). Stirring was continued for 4 hours, and then the chloroform layer was separated. The aqueous layer was extracted with chloroform (3 x 50 ml) and the combined extracts were washed with an aqueous solution of concentrated ammonium hydroxide (1 ml) in saturated sodium chloride (10 ml). After drying, the solvent was removed under reduced pressure to yield 2-methyl-1,4-cyclohexanedione (52) (0.79 g, 54%).

IR ν_{max} 1715 cm^{-1} (C=O).

^{1}H NMR(CDCℓ_3)δ 1.15(d,J=6,3H,-CH$_3$), 2.3-2.95(m,3H,-C$\underline{H}_2$-C$\underline{H}$-) and 2.60 ppm(s,4H,-CH$_2$-).

Mass spectrum m/e 55(54) 56(100), 57(41), 68(58), 69(75), 71(32), 82(16), 83(19), 111(43) and 126(91).

* Experiment first performed by Ms. J. Lee.

2-Methyl-7,7,8,8-tetracyanoquinodimethane (49)

The compound was prepared by the same procedure as that reported by

Hertler et al.[26] The reagents used were: 2-methyl-1,4-cyclohexanedione

(52) (939 mg, 7.45 mmole), malononitrile (993 mg, 15.1 mmole) and a 2%

aqueous solution of β-alanine (1.68 ml), which gave 1.407 g (85%) of 2-

methyl-1,4-bis(dicyanomethylene)cyclohexane (53), identified by its ir

and nmr spectra. Compound 53 (440 mg, 1.98 mmole) was not purified but

was treated with a 10% solution of bromine in acetonitrile (2 ml) and

pyridine (1 ml) to give 460 mg of 2-methyl-7,7,8,8-tetracyanoquino-

dimethane (49). Purification of compound 49 was achieved by sublimation

at 150°C/0.01 mm (250 mg, 54%), mp 198-200°C (lit[26] mp 200-201°C). Its

ir, ^{1}H nmr and mass spectra were in accord with the proposed structure.

Methyl 2,5-dimethylbenzoate (58)

The preparation of methyl 2,5-dimethylbenzoate (58) followed the

method described by Falk and Schlogl.[37] The reagents used were: 2,5-

dimethylbenzoic acid (57) (16.82 g, 0.112 mole), methanol (46 ml) and

concentrated sulfuric acid (5 ml), which gave 15.20 g (82%) of methyl

2,5-dimethylbenzoate (58) after vacuum distillation, bp 70-72°C/0.5 mm

(lit[37] bp 106-107°C/13 mm).

IR ν_{max} 1715 cm^{-1} (aryl ester C=O).

^{1}H NMR (CDCl$_3$) δ2.28 (s,3H,m-CH$_3$), 2.48 (s,3H,o-CH$_3$) 3.77 (s,3H,-OCH$_3$);
6.97 (s,2H,aryl) and 7.55 ppm (s,1H,aryl).

Mass spectrum m/e 77(21), 104(32), 105(58), 132(88), 133(100), 149(17)

and 164(62).

Methyl 2,5-bis(bromomethyl)benzoate (59)

An oven-dried 200-ml flask was equipped with a condenser, magnetic stirrer, and heating mantle. The condenser was stoppered with a septum cap, fitted with nitrogen inlet and outlet syringe needles, and flushed with nitrogen. The reaction vessel was then charged with methyl 2,5-dimethyl benzoate (58) (5.53 g, 0.034 mole), NBS (recrystallized from water, 13.5 g, 0.075 mole), azobisisobutyronitrile (0.3 g) and dry methylene chloride (60 ml). The mixture was stirred and heated to reflux for 2.5 hours, during which time it turned yellow and then orange. The reaction mixture was then cooled and filtered. The filtrate was diluted with 100 ml of methylene chloride and washed successively with saturated aqueous solutions of sodium bisulphate (1 x 25 ml) and sodium bicarbonate (1 x 25 ml) to remove excess bromine and hydrobromic acid. After washing with water (2 x 30 ml), the organic layer was dried and the solvent removed under reduced pressure. The resulting oily solid was covered with methanol and kept at -5°C overnight. The white solid was collected by vacuum filtration and recrystallized from methanol-pentane to yield 7.66 g (70%) of pure compound (59) as white crystals, mp 81.5-82.5°C.

IR ν_{max} 1720 cm^{-1} (aryl ester C=O).

^{1}H-NMR(CDCℓ_3) δ3.93(s,3H,-OCH$_3$), 4.43(s,2H,m-CH$_2$Br), 4.90(s,2H, o-CH$_2$Br), 7.40(s,2H,aryl) and 7.93 ppm(s,1H,aryl).

Mass spectrum m/e 77(26), 119(25), 121(22), 122(17), 147(35), 162(67), 163(48), 209(17), 211(19), 241(100), 243(96), 291(13), 320(10), 321(17), 322(20) and 324(10).

Analysis calculated for C$_{10}$H$_{10}$Br$_2$O$_2$: C 37.30, H 3.13, Br 49.63; found: C 37.25, H 2.98, Br 49.40.

Methyl 2,5-bis(cyanomethyl)benzoate (60)

Sodium cyanide (9.0 g, 0.183 mole) was weighed into a 250-ml

flask and then dissolved in 30 ml of water. A solution of 59 (9.15 g,

0.028 mole) in acetonitrile (73 ml) was added, followed by 0.33 ml of

tri-n-octylamine (3% by weight of 59). The mixture was stirred for 10

hours at room temperature and poured into water (200 ml). The mixture

was extracted with methylene chloride (3 x 100 ml), and the extracts were

washed successively with aqueous sodium bisulphate (50 ml), dilute

hydrochloric acid (50 ml), and saturated sodium chloride solution (50

ml). After drying, the solvents were evaporated under reduced pressure

to give 6.1 g of a buff-colored solid. Purification of 60 was achieved

by careful recrystallization from methanol, followed by chromatography of

the mother liquors using a carbon tetrachloride-ethyl ether mixture

(9:1 V/V). Methyl 2,5-bis(cyanomethyl)benzoate (60) was isolated as a

white microcrystalline powder (4.19 g, 70%), mp 98-100°C.

IR ν_{max} 2290(C≡N) and 1722 cm^{-1} (aryl ester C=O).

^{1}H NMR(CDCl$_3$) δ3.77(s,2H,m-CH$_2$CN), 3.90(s,3H,-OCH$_3$), 4.17(s,2H,

o-CH$_2$CN), 7.50(s,2H,aryl) and 7.95 ppm(s,1H,aryl).

Mass spectrum m/e 83(26), 101(18), 127(19), 128(26), 154(26),

155(33), 177(20), 172(19), 182(100), 183(68) and 214(84).

Analysis calculated for C$_{12}$H$_{10}$N$_2$O$_2$:C 67.28, H 4.71, N 13.08; found

C 67.32, H 4.88, N 12.66.

Dimethyl α,α,α´,α´-tetracyano-2-methoxycarbonyl-1,4-phenylenediacetate (61).

An oven-dried, three-neck, 250-ml round-bottom flask was equipped

with a 2 in magnetic stirring bar, an oil bath and distillation head. The

flask was stoppered with a ground glass bubbler and a septum cap fitted

with a nitrogen inlet needle. The whole system was flamed and allowed
to cool to room temperature under a nitrogen flow. Fresh sodium
methoxide was prepared in situ by addition of sodium metal (0.8 g,
0.034 mole) to dry methanol (10 ml) followed by removal of the excess
alcohol under reduced pressure. The methoxide was suspended in dry
toluene (80 ml) and a solution of methyl 2,5-bis(cyanomethyl)benzoate
(60)(2.632 g, 0.0123 mole) in dry THF-toluene mixture (40 ml, 6:4 V/V)
was syringed into the flask. The reaction mixture was stirred for 15
minutes at room temperature; the mixture turned dark brown. Dimethyl
carbonate (freshly distilled from molecular sieves, 10.3 ml, 0.123 mole)
was syringed in and the reaction mixture was then heated to gentle boiling
and refluxed for 4 hours. Then methanol was distilled off azeotropically
with toluene. Distillation was continued until the temperature of
the vapor reached 110°C (approximately one hour). After cooling the
mixture to 0°C in an ice bath, an additional 95 ml of toluene was added.
Cyanogen chloride (2.7 ml, 0.052 mole) was condensed inside a graduated
cylinder fitted with a septum cap and cooled in an ice bath. Then the
cyanogen chloride was distilled into the reaction flask through a
stainless steel canulae, when the ice bath was removed. The mixture
loosened up and was stirred at 0°C for 1 hour. The flask was then
warmed to room temperature, gradually heated and kept at 80°C for 1
hour. After stirring overnight at room temperature, the reaction mixture
was evaporated to dryness under reduced pressure. The crude solid
mixture of 61 and sodium chloride was stirred with cold water. The
brown cake obtained by filtration was dissolved in methylene chloride,
treated with Norite and magnesium sulfate, and filtered using Celite.

Evaporation of the solvent gave 2.68 g (58.6%) of 61 as a green thick
oil.

IR ν_{max} 2280 (nonconjugated C≡N), 1770 (saturated ester C=O) and
1720 cm^{-1} (aryl ester C=O).

^{1}H NMR(CDCℓ$_3$) δ3.95(s,3H,-OCH$_3$), 4.00(s,6H,-(CN)$_2$C-CO$_2$CH$_3$), 8.02
(s,2H,aryl) and 8.40 ppm(s,1H,aryl).

Mass spectrum: a) high resolution calculated for C$_{18}$H$_{12}$N$_4$O$_6$:380.0757
amu, found 380.0779 m/e;

b) low resolution m/e 59(68),
91(30), 92(21), 139(7), 175(11), 177(13), 193(15), 203(12), 247(14),
262(14), 277(100), 278(21), 303(24), 316(15), 336(25), 349(21) and
380(1).

2-Methoxycarbonyl-1,4-phenylenedimalononitrile (62)

A solution of 61 (450 mg, 1.18 mmole) in THF (20 ml) was added
into a 100-ml flask. The flask was fitted with a magnetic stirring
bar, septum cap and flushed with nitrogen. Sodium borohydride (2 mg)
was added and the mixture was stirred at room temperature while a
5% aqueous solution of sodium carbonate (16 ml, 7.8 mmole) was syringed
in dropwise (8 minutes). After stirring for 1 hour, the dark solution was
acidified with 1.5 N hydrochloric acid, extracted with methylene chloride
(2 x 50 ml), and washed with water (2 x 25 ml). The extracts were dried
and the solvents removed under reduced pressure to yield 268 mg (86%) of
compound 62. The crude product was purified as follows. Crude product
(120 mg) was dissolved in aqueous sodium carbonate (50 ml) and extracted
with ethyl acetate (3 x 30 ml). The aqueous layer was acidified with 6 N
hydrochloric acid and extracted with ethyl acetate (2 x 30 ml). After

drying, the solvent was evaporated under reduced pressure to give 72 mg

of 62 as a light green oil which partially crystallized on standing.

After standing several days the color of this product darkened gradually.

IR ν_{max} 2260 (nonconjugated C≡N) and 1725 cm^{-1} (aryl ester C=O).

^{1}H NMR (acetone-d$_6$) δ3.93(s,3H-OCH$_3$), 6.0(bs,2H,(CN)$_2$CH-); 7.87(s,

2H,aryl) and 8.2(s,1H,aryl).

Mass spectrum m/e 59(28) 87(77) 85(52) 151(26) 152(26) 177(25),

178(37), 207(27), 208(22), 221(26), 222(26), 232(74), 233(100), 238(33),

249(33), 263(28), 264(93) and 265(22).

2-Methoxycarbonyl-7,7,8,8-tetracyanoquinodimethane (56)

Ester 62 (0.38 g) was dissolved in 5% aqueous sodium carbonate (50

ml) and neutralized with 6 N hydrochloric acid. A slight excess of 0.1 M

bromine solution in water was added gradually at room temperature

(positive test with starch-iodine paper). The resulting green solid

was filtered, washed with water (50 ml), and dried in vacuo over phos-

phorous pentoxide to yield 0.38 g. A small scale purification was

achieved by sublimation of 56 (36 mg) at 190°C/0.01 mm overnight; the

resulting green-yellow solid (1 mg, 3%) had a mp 220-224°C (decomposition).

IR(KBr)ν_{max} 2220 (conjugated C≡N) and 1725 (unsaturated ester C=O).

UV-Vis(CH$_3$CN) λ_{max} 396 nm (36,800) and 375 nm (sh).

^{1}H NMR(CDCℓ$_3$) δ 4.4(s,3H,OCH$_3$) and 7.4-8.6 ppm (m,3H,vinyl).

Mass spectrum; high resolution calculated for C$_{14}$H$_6$N$_4$O$_2$: 262.0491 amu

found 262.0495 m/e;

low resolution m/e 55(72), 57(100), 69(64),

71(71), 111(44), 123(33), 125(39), 149(89), 203(37), 204(42), 231(97),

232(58), 262(100) and 263(26).

3,6-Dimethylphthalic anhydride (70)

To a well-stirred suspension of maleic anhydride (24.3 g, 0.247 mole) in dry ethyl ether (40 ml) was added slowly 2,5-dimethylfuran (68) (26.4 ml, 0.247 mole). After stirring at room temperature for 20 hours, during which the maleic anhydride dissolved and crystals of the adduct began to separate, the mixture was cooled in an ice-salt bath for 1 hour. The crystals of adduct 69 (32.8 g, 69%) were collected and dried, mp 57-59°C (lit[41] mp 59-63°C). Compound 69 was dehydrated directly by slow addition into concentrated sulfuric acid (322 ml) at -10°C. The solution was stirred for 1 hour at -10°C before it was allowed to rise to 10°C. After pouring onto 1 kg of crushed ice the light brown precipitate was collected, washed with ice water and air-dried. After successive re-crystallizations from benzene and toluene, the desired 3,6-dimethylphthalic anhydride (70) was obtained in 24% yield (9.96 g), mp 137-138°C (lit[41] mp 142-143°C).

IR ν_{max} 1845 and 1765 cm^{-1} (aryl acid anhydride C=O) and 1260 cm^{-1} (C-O anhydride).

^{1}H NMR(CDCl$_3$) δ2.60 (s,6H,-CH$_3$) and 7.39 ppm (S,2H,aryl).

Mass spectrum m/e 103(30), 104(68), 120(25), 132(55), 148(65) and 176(100).

3,6-Bis(bromomethyl)phthalic anhydride (71)

Recrystallized NBS (37 g, 0.208 mole) was weighed into an oven-dried 2-ℓ flask equipped with a magnetic stirring bar. The flask was fitted with a reflux condenser stoppered with a septum cap, and the whole system was flushed with nitrogen. A solution of 3,6-dimethyl-phthalic anhydride (70) (8.33 g, 0.047 mole) in dry carbon tetrachloride (710 ml) was added through the condenser followed by 0.1 g of benzoyl peroxide, and the mixture was heated at reflux. After 8 hours, heating was stopped and the reaction mixture was allowed to cool to room temperature. Succinimide and unreacted NBS were filtered off and the filtrate was evaporated under reduced pressure. The resulting oil containing a mixture of mono- and dibromo derivatives was left to stand at room temperature. The desired dibromo compound 71 crystallized on standing (4.1 g, 26%) and was further purified by recrystallization from a carbon tetrachloride-hexanes mixture (3:7 V/V). The white crystals obtained had a mp 121-125°C.

IR ν_{max} 1856 and 1777 cm^{-1} (C=O, aryl anhydride) and 1260 cm^{-1} (C-O anhydride).

^{1}H NMR(CDCℓ$_3$) δ4.86(s,4H,-CH$_2$Br) and 7.82 ppm(s,2H,aryl).

Mass Spectrum m/e 63(13), 74(12), 75(15), 76(16), 102(34), 117(13), 129(9), 146(43), 173(24), 174(100), 175(40), 252(75), 253(87), 254(84), 255(87), 332(7), 334(12) and 336(6).

Analysis calculated for C$_{10}$H$_6$Br$_2$O$_3$:C 36.85, H 1.85, Br 49.02; found: C 36.52, H 1.87, Br 49.20.

6-(Bromomethyl)-7-methoxycarbonylphthalide (72)

A 50-ml flask was equipped with a magnetic stirring bar, a heating

mantle, and a reflux condenser protected by a calcium chloride tube.
The reaction vessel was charged with 2,5-bis(bromomethyl)phthalic
anhydride (71) (0.5 g, 1.5 mmole), methanol (25 ml) and p-toluenesulfonic
acid (10 mg). The mixture was refluxed for 2 hours and then cooled to
room temperature. Methanol was evaporated under reduced pressure and
the resulting solid was dissolved in ethyl ether (50 ml). The ethereal
solution was extracted with a saturated solution of sodium bicarbonate
(2 x 20 ml) and washed with saturated sodium chloride solution (25 ml);
after drying, the solvent was removed by evaporation under reduced pressure
to yield 0.216 g (50%) of crude compound 72. A small sample was purified
by preparative tlc (chloroform); the band between R_f 0.6 and 0.8 was
removed and extracted with methylene chloride. After evaporation of the
solvent white crystals of 72 were obtained, mp 125-128°C.

IR ν_{max} 1775 (lactone C=O) and 1735 cm^{-1} (aryl ester C=O).

^{1}H NMR(CDCl$_3$) δ4.01(s,3H,-OCH$_3$), 4.55(s,2H,-CH$_2$Br), 5.24(s,2H,-CH$_2$-
O-CO) and 7.55 ppm (dd,J=8.0,2H,aryl).

Mass spectrum: a) high resolution calculated for C$_{11}$H$_9$BrO$_4$: 283.9684
amu, found 283.9685 m/e;

b) low resolution m/e 89(31), 90(18), 91(9),
117(17), 118(25), 129(12), 145(16), 146(24), 147(14), 149(15), 173(60),
174(75), 175(33), 176(18), 205(100), 206(23), 252(87), 253(28), 254(90),
255(28), 284(11) and 286(11).

Dimethyl 3,6-dimethylphthalate (75)

A 100-ml flask was equipped with a reflux condenser and a calcium
chloride tube, a magnetic stirring bar, and a heating mantle. Dimethyl
acetylenedicarboxylate (12.34 ml, 0.10 mole), trans,trans-2,4-hexadiene

(13.88 ml, 0.12 mole) and dry benzene (25 ml) were added to the flask and the mixture was stirred and refluxed for 24 hours. The light yellow solution was cooled to room temperature and the solvent was removed under reduced pressure. The crude oil obtained was distilled in vacuo to afford the adduct 74; bp 101-103°C (0.4 mm). Its spectroscopic data were in agreement with structure 74. This compound (13.336 g, 0.0595 mole) was treated directly with one equivalent of DDQ (13.97 g, 0.0615 mole) in benzene (100 ml) and the mixture was stirred and refluxed for 20 hours. The reaction mixture was then diluted with two volumes of petroleum ether, bp 30-60°C, and the precipitate of 2,3-dichloro-5,6-dicyano hydroquinone and unchanged DDQ was filtered off. The filtrate was passed through a short (16 cm x 5 cm) alumina column which was washed with additional petroleum ether until no more 75 could be eluted. The eluates were evaporated to give dimethyl 3,6-dimethylphthalate (10.5 g, 80% overall yield), mp 74-77°C (lit.[46] mp 72-75°C). Its ir, ^{1}H nmr and mass spectra were in agreement with those reported.[46]

Dimethyl 3,6-bis(bromomethyl)phthalate (76)

This compound was prepared by a similar procedure as that employed in the preparation of methyl 2,5-bis(bromomethyl)phthalate (59). The only difference was that the refluxing time was 3 hours in the case of 75. The reagents used were: dimethyl 3,6-dimethylphthalate (75) (10.5 g, 0.047 mole) in 130 ml of dry methylene chloride, NBS (19.3 g, 0.108 mole), and AIBN (0.5 g). The crude solid obtained after work-up was dissolved in the minimum amount of boiling ethanol and the solution was left to stand overnight. On addition of methanol white crystals of dimethyl 6-bromo-methyl-3-dibromomethylphthalate (77) precipitated and were collected by

filtration (3.8 g), mp 118-126°C (lit.[47] mp 123°C). Its ir, ^{1}H nmr and mass spectra were consistent with structure 77. The filtrate was evaporated under reduced pressure to give 11.4 g (64%) of crude dimethyl 3,6-bis(bromomethyl)phthalate (76). A small sample (187 mg) was purified by tlc, using chloroform as eluent. The band at R_f 0.6 was removed and eluted with methylene chloride. Evaporation of the solvent gave 115 mg (40%) of compound 76 as a colorless oil.

IR ν_{max} 1730 cm^{-1} (aryl ester C=O)

^{1}H NMR(CDCℓ$_3$) δ3.77(s,6H,-OCH$_3$),4.60(s,4H,-CH$_2$Br) and 7.38 ppm (s,2H,aryl).

Mass spectrum a) high resolution calculated for $C_{12}H_{12}Br_2O_4$: 377.9102 amu, found 377.9095 m/e;

b) low resolution m/e 77(31), 89(27), 90(21), 102(30), 103(26), 118(21), 129(22), 132(19), 145(67), 162(20), 174(19), 189(50), 205(86), 220(22), 267(40), 269(43), 299(64), 301(67), 347(53), 349(100), 350(44), 351(58), 378(5), 380(8) and 382(5).

Dimethyl 3,6-bis(cyanomethyl)phthalate (73)

The procedure used in this reaction was the same to that employed in the preparation of compound 60. The following reagents were used: dimethyl 3,6-bis(bromomethyl)phthalate (76) (7.1 g, 0.0186 mole) in acetonitrile (91 ml), 30% aqueous sodium cyanide (8.8 g, 0.18 mole), and tri-n-octylamine (0.4 ml). After the work-up the crude mixture was purified using a 4 cm x 26 cm column of silica gel eluted with carbon tetrachloride-ethyl ether (95:5 V/V). The band corresponding to a spot at R_f 0.65 on analytical tlc was collected and, after evaporation of the solvents, gave 73 (2.2 g, 44%), mp 66-68°C.

IR ν_{max} 2290 (C≡N) and 1730 cm^{-1} (aryl ester C=O)

^{1}H NMR(CDCl$_3$) δ3.88(s,6H,-OCH$_3$), 3.91(s,4H,-CH$_2$CN) and 7.58 ppm (s,2H,aryl).

Mass Spectrum m/e 127(7), 128(8), 153(7), 154(10), 182(18), 213(4), 214(5), 225(5), 240(100), 241(59) and 272(1.2).

Analysis calculated for C$_{14}$H$_{12}$N$_2$O$_4$:C 61.76, H 4.44, N 10.29; found: C 61.89, H 4.34, N 10.17.

2,3-Dimethyl-1,4-cyclohexanedione (87)

This compound was prepared by a similar procedure to that employed in the preparation of 2-methyl-1,4-cyclohexanedione (52). The following reagents were used: 2,3-dimethylhydroquinone (85) (1.09 g, 0.0079 mole), rhodium catalyst (0.41 g) and methanol-water mixture (22 ml, 10:1 V/V), which gave 7.08 g (95%) of 2,3-dimethyl-1,4-cyclohexanediol (86), identified by its ir and ^{1}H nmr spectra. Compound 86 (0.94 g, 6.5 mmole) was not purified but was oxidized directly with three equivalents of chromium trioxide solution (7.22 ml) in chloroform (25 ml) at 5°C. After the addition of chromium trioxide (10 minutes), the reaction mixture was stirred for 2 hours, and worked up as described previously for 51, to give 0.684 g (75%) of 2,3-dimethyl-1,4-cyclohexanedione (87).

IR ν_{max} 1710 cm^{-1} (C=O).

^{1}H NMR(CDCl$_3$) δ1.08(d,J=7,6H,-CH$_3$), 2.70(s,4H,-CH$_2$-), and 2.2-3.0 ppm (m,2H,-CH-).

Mass spectrum m/e 56(61), 69(21), 73(24), 125(87) and 140(100).

2,3-Dimethyl-1,4-bis(dicyanomethylene)cyclohexane   (88)

To 2,3-dimethyl-1,4-cyclohexanedione (87) (335 mg, 2.39 mmole)

in a 50-ml flask, was added a mixture of malononitrile (347 mg, 5.25

mmole) and a catalytic amount of β-alanine (30 mg) in water (10 ml).

The reaction mixture was heated at reflux for 3.5 hours. The product

was isolated by filtration and was washed with water (40 ml). The

yield of crude 2,3-dimethyl-1,4-bis(dicyanomethylene)cyclohexane (88)

was 379 mg (67%). A small sample, recrystallized from acetonitrile,

melted at 186-189°C.

IR(KBr) ν_{max} 2250 (C≡N)   and 1600 cm^{-1} (C=C).

^{1}H NMR(acetone-d$_6$) δ1.30(d,J=7,6H,-CH$_3$), 3.10(s,4H,-CH$_2$-) and

3.33 ppm(q,2H,-CH-).

Mass spectrum m/e 91(6), 92(6), 118(12), 119(18), 131(16), 145(100),

146(12), 194(18), 207(6), 208(9), 209(6), 219(8), 221(28), 222(5), 234(8),

235(6) and 236(14).

Analysis calculated for C$_{14}$H$_{12}$N$_4$: C 71.17, H 5.12, N 23.71; found:

C 71.27, H 5.16, N 23.96.

5,6-Dimethyl-1,4-bis(dicyanomethylene)-2-cyclohexene (89)

An oven-dried, 50-ml flask containing compound 88 (304 mg, 1.29

mmol), acetonitrile (15 ml) and bromine (0.073 ml, 1.42 mmol) was stoppered

with a septum cap and fitted with a magnetic stirring bar. It was flushed

with nitrogen while cooled to 0-5°C in an ice bath. Pyridine (0.42 ml,

5.16 mmol) was slowly syringed into the reaction flask over a period of

15 minutes. After completion of the addition, the mixture was stirred

at 0°C for 30 minutes and then for two more hours at room temperature. Cold

water was added and the mixture was stirred for about 15 minutes. The resultant solid product was removed by filtration, washed with cold water (50 ml), and dried over phosphorous pentoxide in vacuo (258 mg, 86%). An analytical sample was recrystallized from acetonitrile, mp 203-205°C.

Ir ν_{max} 2260 (C≡N) and 1560 cm^{-1} (conjugated C=C).

^{1}H NMR(CD$_3$CN) δ1.16(d,J=7,6H,-CH$_3$), 3.17(m,2H,-CH-) and 7.06 ppm (s,2H,vinyl).

Mass Spectrum m/e 138(20), 139(20), 140(20), 142(33), 156(16), 165(26), 169(33), 192(22), 206(22), 207(32), 219(100), 233(33), 234(90) and 235(18).

Analysis calculated for C$_{14}$H$_{10}$N$_4$:C 71.78, H 4.30, N 23.92; found: C 71.96, H 4.40, N 24.02.

2,3-Dimethyl-7,7,8,8-tetracyanoquinodimethane (83)

5,6-Dimethyl-1,4-bis(dicyanomethylene)-2-cyclohexene (89) (64 mg, 0.27 mmole), 10% palladium on powdered charcoal (22 mg) and sulfur (32 mg) were ground in a mortar. The homogeneous mixture was placed inside a small sublimation apparatus and heated to 180°C for 3 hours. Some of the sulfur deposited on the cold finger, and the black residue was extracted with boiling acetonitrile. After filtration, the acetonitrile was evaporated under reduced pressure. Purification was achieved by tlc: 50 mg of the crude material was chromatographed on a 5 cm x 20 cm silica coated plate, using methylene chloride as eluent. The two main components isolated from this chromatography were, in order of elution, starting material and compound 83 (20 mg, 32%). 2,3-Dimethyl-7,7,8,8-tetracyano-quinodimethane (83) was identified by its ^{1}H nmr and mass spectra.

^{1}H NMR(CD$_3$CN) δ2.35(s,6H,-CH$_3$) and 7.43 ppm (s,2H,vinyl).

Mass spectrum m/e 81(100), 100(61), 120(28), 132(43), 170(26), 182(78), 220(14) and 232(16).

3,5-Bis(bromomethyl)toluene (97)

A 2-ℓ three neck flask equipped with two efficient condensers and a strong mechanical stirrer was charged with dry carbon tetrachloride (400 ml), distilled mesitylene (138 ml, 1 mole), NBS (recrystallized from water, 356 g, 2 mole) and benzoyl peroxide (3 g). The mixture was stirred and heated at reflux. After 15-30 minutes of reflux, a vigorous reaction took place and the heating mantle was then replaced by an acetone-dry ice bath. Vigorous reflux continued for about 15 minutes, after which time the reaction was complete. The reaction mixture was then cooled and filtered and the filtrate was evaporated under reduced pressure. The product 96 (128 g, 46%) was obtained by direct recrystallization of the crude reaction mixture from ethanol, mp 45-50°C (lit.[65] mp 60°C). Its spectroscopic data were in agreement with the proposed structure.

3,5-Bis(mercaptomethyl)toluene (102)

In a 250-ml flask fitted with an efficient reflux condenser and a heating mantle, were placed thiourea (10.9 g, 0.143 mole) and 95% ethanol (60 ml). The mixture was brought to the reflux temperature and 3,5-bis(bromomethyl)toluene (97) (19.8 g, 0.071 mole) was added in batches (ca 10 minutes), and the reflux continued for 2 hours. After cooling, the white precipitate was filtered and dried. The crude salt 103 so obtained was mixed with potassium hydroxide (51 g, 0.92 mole) in water (110 ml) and boiled under reflux for 6 hours. The reaction mixture was

then cooled in an ice bath and acidified with 9 M sulfuric acid; it was

extracted with ethyl ether (3 x 100 ml), and washed with water (100 ml).

After drying, the solvent was removed under reduced pressure to give

12.47 g (95%) of 3,5-bis(mercaptomethyl)toluene (102) as a colorless

oil. It was not purified but was used directly in the next reaction.

^{1}H NMR(CDCℓ$_3$) δ1.72(t,J=8,2H,-SH), 2.31(s,3H,-CH$_3$), 3.64(d,J=8,4H,

-CH$_2$-), and 6.97 ppm (s,3H,aryl).

6,15-Dimethyl-2,11-dithia[3.3]metacyclophane (98)*

A 5-1 three neck flask was fitted with nitrogen inlet and outlet

syringe needles, 3 in magnetic stirring bar and a Hershberg dropping

funnel. The reaction vessel was charged with potassium hydroxide (9 g,

0.16 mole) dissolved in ethanol-water (9:1 V/V, 2ℓ) and was stirred under

argon at room temperature. A solution of 3,5-bis(bromomethyl)toluene (97)

(19.02 g, 0.0684 mole) and 3,5-bis(mercaptomethyl)toluene (102)(12.47 g,

0.0677 mole) in benzene (1.6ℓ) was placed in the funnel; it was then

added dropwise over a period of seven days. After the addition was

complete, the reaction mixture was filtered; the filtrate was evaporated

under reduced pressure and the crude product was purified by column

chromatography, using silica-gel (10 cm x 20 cm) and a mixture of benzene

and petroleum ether, bp 30-60°C, (2.5:7.5 V/V) to give compound 98 in

86% yield (17.48 g). An analytical sample, prepared by recrystallization

from cyclohexane, melted at 101.5-103.5°C (lit.[53] mp 102-102.5C).

IR v_{max} 1601 cm^{-1} (C=C aromatic).

^{1}H NMR(CDCℓ$_3$) δ2.13(s,6H,-CH$_3$), 3.62(s,8H, -CH$_2$), 6.58(bs,2H,

internal ArH) and 6.66(bs,4H,ArH).

Mass spectrum m/e 119(68), 120(80), 149(27), 150(42), 151(52) and

300(100).

Analysis calculated for $C_{18}H_{20}S_2$: C 71.95, H 6.71, S 21.34; found: C 72.15, H 6.74, S 21.22.

5,13-Dimethyl[2.2]metacyclophane (96)*

An oven-dried, 1-1 flask in charged with 6,15-dimethyl-2,11-dithia[3.3]metacyclophane (98) (17.48 g, 0.058 mole) dissolved in dry THF (290 ml), equipped with a magnetic stirring bar and stoppered with a septum cap. The flask was then fitted with a nitrogen inlet and outlet needle, flushed with nitrogen and cooled to -20°C (carbon tetrachloride - dry ice). n-Butyllithium, as a 1.55 M solution in hexane, (94 ml, 0.145 mole) was added dropwise to the reaction which was stirred for a further 40 minutes before the addition of methyl iodide (18 ml, 0.29 mole). The mixture turned yellow and a yellow precipitate was formed. The reaction mixture was stirred for an additional 30 minutes at -20°C and then warmed to room temperature. It was quenched with cold water (200 ml), extracted with ethyl ether (2 x 100 ml) and washed with water (100 ml). The aqueous layer was further extracted with methylene chloride (100 ml). The combined organic extracts were washed with saturated sodium chloride solution (100 ml), dried, and the solvents were evaporated under reduced pressure to yield 100 (17.72 g), which was identified by its ir and nmr spectra. Compound 100 was dissolved in dry THF-ether (200 ml, 6:4 V/V) and added to 250 ml of a blue solution of liquid ammonia containing chips of lithium. The reaction vessel was kept at -78°C during the addition, and lithium chips were added whenever the blue color faded. After the addition was over, the reaction mixture was stirred for 1.5 hours before ammonium chloride was added to discharge the blue color. The flask was

then warmed to room temperature and ammonia was allowed to evaporate overnight. Water (100 ml) was added to the resulting mixture which was then acidified with 6 N hydrochloric acid. It was extracted with ethyl ether (2 x 100 ml), washed with water (100 ml), and saturated sodium chloride solution (100 ml). After drying, the solvents were evaporated under reduced pressure. The resultant light yellow solid was purified by filtration through silica gel using petroleum ether, bp 30-60°C, subsequent recrystallization from ethanol afforded 96 (3.8 g, 30%), as white crystals, mp 145-146°C (lit.[53] mp 145-146°C).

IR ν_{max} 1600 cm^{-1} (aromatic C=C).

^{1}H NMR(CDCl$_3$) δ2.02(d,J=8,4H,axial CH$_2$), 2.93(d,J=8,4H,equatorial CH$_2$), 2.23(s,6H,-CH$_3$), 4.03(s,2H,aryl) and 6.67 ppm(s,4H,aryl).

Mass spectrum m/e 118(21), 205(18), 206(28), 208(23), 219(20), 221(88), 222(24), 235(18), 236(100) and 237(26).

Analysis calculated for C$_{10}$H$_{20}$: C 91.47, H 8.53; Found: C 91.30, H 8.52.

* Due to the possible toxicity of an intermediate or unknown by-products, this reaction should be totally carried out in a well vented hood.

5,13-Bis(bromethyl)[2.2]metacyclophane (95)

An oven-dried, 200-ml flask was equipped with a magnetic stirring bar, a reflux condenser fitted with a nitrogen inlet, and a heating mantle. The reaction vessel was charged with 5,13-dimethyl[2.2] metacyclophane (96) (580 mg, 2.46 mmole), NBS (recrystallized from water, 920 mg, 5.16 mmole), dry carbon tetrachloride (83 ml) and benzoyl peroxide (40 mg). The reaction mixture was then stirred and heated at reflux for 1.5 hours under nitrogen. Heating was discontinued and the mixture was stirred at room temperature overnight. It was then filtered and the solvent from the filtrate was removed by evaporation under reduced pressure. The residue was washed with petroleum ether, bp 30-60°C, and dried in vacuo to give 686 mg (70%) of compound 95. A small sample was recrystallized from acetonitrile, mp 209-210°C (lit.[53] mp 205-206°C)

IR ν_{max} 1600 cm^{-1} (C=C aromatic) and 1780, 1755 cm^{-1} (1,3,5 trisubstituted benzene).

^{1}H NMR(CDCl$_3$) 2.14(d,J=8Hz,4H,axial-CH$_2$-), 3.13(d,J=8Hz,4H, equatorial-CH$_2$-), 4.25(s,2H,aromatic), 4.56(s,4H,-CH$_2$Br), 7.10(s,4H,aromatic).

Mass spectrum m/e 101(14), 108(12), 109(11), 115(11), 116(25), 202(15), 203(18), 204(11), 217(11), 219(29), 220(15), 233(42), 234(69), 235(18), 299(11), 301(11), 313(100), 314(26), 315(95), 316(24), 392(24), 394(43) and 396(23).

5,13-Bis(cyanomethyl)[2.2]metacyclophane (94)

A 200-ml flask was equipped with a magnetic stirring bar, a reflux condenser and a heating mantle. The reaction vessel was charged with 5,13-bis(bromomethyl)[2.2]metacyclophane (95)(264 mg, 0.67 mmole), sodium cyanide (197 mg, 4.02 mmole) in water (1 ml), THF (20 ml), and tri-n-octylamine(one drop). The mixture was stirred and heated at reflux

overnight. It was then allowed to cool to room temperature, poured into
cold water (25 ml) and extracted with methylene chloride (3 x 30 ml). The
organic layer was washed with water (30 ml), saturated sodium chloride
(30 ml) and dried. After evaporation of the solvents under reduced pressure
a light yellow solid was obtained, this was then recrystallized from methanol
(with cooling in a carbon tetrachloride-dry ice bath) to give compound 94
(135 mg, 70%). An analytical sample, mp 190-195°C, was prepared by
sublimation at 180°C/0.2 mm.

IR ν_{max} 2300 (C≡N), 1600 (C=C aromatic).

^{1}H NMR(CDCl$_3$) δ2.14(d,J=8,4H,axial-CH$_2$-), 3.13(d,J=8,4H,equatorial-CH$_2$-),
3.80(s,4H,-CH$_2$CN), 4.24(s,2H,aromatic) and 7.06 ppm(s,4H,aromatic).

Mass spectrum m/e 203(12), 205(19), 206(100), 207(23), 245(13),
246(47), 247(11), 254(12), 286(59) and 287(13).

Analysis calculated for C$_{20}$H$_{18}$N$_2$:C 83.88, H 6.34, N 9.78; found:
C 83.49, H 6.30, N 9.62.

2,7-Bis(cyanomethyl)-4,5,9,10-tetrahydropyrene (93)

5,13-Bis(cyanomethyl)[2.2]metacyclophane (94)(0.28 g, 1 mmole) was
dissolved in dry chloroform (passed through alumina, 15 ml) and added to
an oven-dried 50 ml flask. The reaction vessel was then charged with a
catalytic amount of iron powder (350 mesh), equipped with a magnetic
stirring bar and flushed with nitrogen. The mixture was stirred at 0°C
in an ice bath for 5 minutes before a 10% solution of bromine in chloroform
(1.5 ml, 2.9 mmol) was added dropwise with a syringe; then, the reaction
mixture was stirred vigorously for 1.5 hours at 0°C. The reaction was
quenched when saturated solution of sodium thiosulfate (15 ml) was added
followed by stirring at room temperature for 15 minutes. The color of the

solution went from red-orange to light green. The reaction mixture was then extracted with methylene chloride (2 x 25 ml), washed with water (2 x 20 ml) and dried. The solvents were evaporated under reduced pressure to give the crude compound 93, which was purified by column chromatography, using chloroform as eluent, to give 199 mg (70%) of compound 93, mp 230-235°C.

IR ν_{max} 2300(C≡N) and 1620 cm^{-1} (C=C aromatic).

^{1}H NMR(CDCl$_3$): 2.84(s,8H,-CH$_2$-), 3.66(s,4H,-CH$_2$CN) and 6.95 ppm (s,4H,aromatic).

Mass spectrum: a) high resolution calculated for C$_{20}$H$_{16}$N$_2$:284.1313 amu, found 284.1317 m/e;

b) low resolution m/e 206(100), 246(40), 258(28), 284(97) and 285(23).

2,7-Bis(methyl α,α-dicyanoacetate)-4,5,9,10-tetrahydropyrene (92)

This compound was prepared by a similar procedure as that employed in the preparation of dimethyl-α,α,α´,α´-tetracyano-2-methoxycarbonyl-1,4-phenylenediacetate(61). The only difference was that the refluxing time was 1.5 hours in this case as opposed to 4 hours in the case of the monoester 60. The reagents used were: 2,7-bis(cyanomethyl)-4,5,9,10-tetrahydropyrene (93) (519 mg, 1.83 mmole), fresh sodium methoxide (5.13 mmole from 118 mg of sodium) dry toluene (30 ml + 25 ml) dry THF (10 ml), distilled dimethyl carbonate (2 ml, 24 mmol) and cyanogen chloride (0.47 ml, 9.09 mmole). Work-up: solvents and volatile components of the reaction mixture were distilled off under reduced pressure and the resulting light brown solid was stirred with 1.5 N hydrochloric acid (40 ml) and extracted with ethyl acetate (3 x 50 ml). After drying, the solvent was evaporated under reduced pressure to yield compound 92 as a dark brown solid, mp 110-115°C (662 mg).

IR ν_{max} 2265 and 2210 cm^{-1} (C≡N) and 1770 (saturated ester C=O)

^{1}H NMR(CDCl$_3$) δ2.94(s,8H,-CH$_2$-), 3.91(s,6H,-OCH$_3$) and 7.33 ppm (s,4H,aryl).

Mass spectrum: a) high resolution calculated for C$_{26}$H$_{18}$N$_4$O$_4$: 450.1328 amu, found 450.1335 m/e;

b) low resolution m/e 59(100), 69(57), 91(36), 92(29), 202(25), 203(16), 206(20), 217(16), 219(15), 258(46), 282(17), 317(39), 341(31), 355(17), 400(15) and 450(5).

2,7-Bis(dicyanomethyl)-4,5,9,10-tetrahydropyrene (91)

A solution of 92 (250 mg, 0.55 mmole) in THF (13 ml) was added into a 50-ml flask. The flask was fitted with a magnetic stirring bar, septum cap and flushed with nitrogen. Sodium borohydride ($\sim$2 mg) was added and the mixture was stirred at room temperature while a 5% aqueous solution of sodium carbonate (8 ml, 4.0 mmol) was syringed in dropwise (5 minutes). After stirring for 1.5 hours, the dark solution was acidified with 6 N hydrochloric acid, extracted with ethyl acetate (3x50 ml), and washed with water (2x25 ml). The extracts were dried and the solvents removed under reduced pressure to yield 162 mg of 2,7-bis(dicyanomethyl)-4,5,9,10-tetrahydropyrene (91), mp 70-80°C. The crude product was identified by its ir and ^{1}H nmr spectra, and was used directly in the reaction that follows.

IR ν_{max} 2260 and 2215 cm^{-1} (C≡N)

^{1}H NMR (CDCℓ$_3$) δ2.93 (s,8H,-CH$_2$-), 5.00 (s,2H,-CH(CN)$_2$) and 7.14 ppm (s,4H,aryl).

11,11,12,12-Tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (90)

Compound 91 (116 mg, 0.34 mmol) was dissolved in dry methylene chloride (25 ml) and placed in an oven-dried 50-ml flask. The flask was fitted with a magnetic stirring bar, septum cap and flushed with nitrogen. The solution was cooled to -78°C (dry ice-acetone bath) and NBS (26 mg, 0.15 mmole) was added followed by triethylamine (2 drops). The solution turned dark red instantaneously and it was stirred for 5 minutes at -78°C before it was warmed up to 0°C. Hydrochloric acid was then added to acidify the reaction mixture and this was diluted with methylene chloride (25 ml). The mixture was washed with water (1x10 ml) and the solvent was dried and evaporated under reduced pressure to yield a dark brown solid (99 mg).

The crude product was filtered through a short silica gel column

(eluent: methylene chloride); evaporation of the solvent gave 24 mg

of compound 90. This compound was further purified by recrystallization

from benzene to give compound 90 (19 mg) as green microcrystals, mp

206-208°C (decomposition).

IR(KBr) ν_{max} 2265 and 2225 cm^{-1} (C≡N)

^{1}H NMR (CDCℓ$_3$) δ2.94 (s,8H,-CH$_2$-) and 7.20 ppm (bs,4H,vinyl).

Mass spectrum a) high resolution calculated for C$_{22}$H$_{12}$N$_4$:

332.1062 amu, found 332.1071 m/e;

b) low resolution m/e 99(23), 202(33), 203(25), 204(37),

332(35), 334(100) and 335(25).

BIBLIOGRAPHY

1.   J. Ferraris, D. O. Cowan, V. Walatka Jr., J. H. Perlstein,

J. Am. Chem. Soc., 95, 948 (1973).

2.   L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F.

Garito, A. J. Heeger, Solid State Commun., 12, 1125 (1973).

3.   A. N. Bloch, D. O. Cowan, K. Bechgaard, T. O. Poehler, Phys.

Rev. Lett., 34, 741 (1975).

4.   F. Gutmann, L. E. Lyons, "Organic Semiconductors", Wiley, N.Y.,

1967, Chapter 8.

5.   S. D. Levina, Dokl. Akad. Nauk SSSR, 145, 602 (1962).

6.   a) M. E. Peover, J. Chem. Soc., 4540 (1962).

b) M. E. Peover, Nature, 193, 475 (1962).

7.   D. S. Acker, W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).

8.   A. J. Fatiadi, Synthesis, 133 (1976).

9.   L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson,

W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).

10. D. Acker, D. Blomstrom, U.S. Pat. 3,162,641 (1964); Chem.Abst.60, 11918(1964).

11. O. H. Le Blanc Jr., J. Chem. Phys., 37, 916 (1962).

12. L. Melby, Can. J. Chem., 43, 1448 (1965).

13. a) F. Wudl, D. Wubschall, E. J. Hufnagel, J. Am. Chem. Soc., 94,

670 (1972).

b) S. J. la Placa, P. W. R. Coofield, R. Thomas, B. A. Scott,

Solid State Commun., 17, 635 (1975).

c) C. K. Johnson, C. R. Watson Jr., J. Chem. Phys., 64, 2271 (1976).

14. M. Narita, C. U. Pittman, Synthesis, 489 (1976).

15. D. Cowan, P. Shu, C. Hu, W. Krug, T. Carruthers, T. Poehler, A. Bloch in "Chemistry and Physics of One-Dimensional Metals" edited by H. J. Keller, Plenum, N.Y., 1977, p.25.

16. L. R. Melby, H. D. Hartzler, W. A. Sheppard, J. Org. Chem., 39, 2456 (1974).

17. A. J. Heeger, A. F. Garito in "Low-Dimensional Cooperative Phenomena" edited by H. J. Keller, Plenum, N.Y., 1975, p.89.

18. E. M. Engler, Chemtech. 6, 274 (1976) and references cited therein.

19. A.J.Berlinsky, L. Weiler, Solid State Commun., 19, 1165 (1976).

20. A. J. Berlinsky, J. F. Carolan, L. Weiler, Solid State Commun., 15, 795 (1974).

21. R. E. Peierls, "Quantum Theory of Solids", Oxford University Press, London, 1955, p.108.

22. A. F. Garito, A. J. Heeger, Acc. Chem. Res., 7, 232 (1974).

23. J. H. Perlstein, Angew. Chem. Int. Ed. Engl., 16, 519 (1977).

24. a) A. F. Garito, A. J. Heeger, Acc. Chem. Res., 7, 232 (1974).
    b) A. N. Bloch in "Energy and Charge Transfer in Organic Semiconductors" edited by K. Masuda and M. Silver, Plenum Press, N.Y., 1974, p.159.

25. J. B. Torrance, Acc. Chem. Res., 12, 79 (1979).

26. J. Diekmann, W. R. Hertler, R. E. Benson, J. Org. Chem., 28, 2719 (1963).

27. D. J. Sandman, A. F. Garito, J. Org. Chem., 39, 1165 (1974).

28. P. Berger, D. Dahm, G. Johnson, M. Miles, J. Wilson, Phys. Rev. B, 12, 4085 (1975).

29. a) A. W. Addison, N. S. Dalal, Y. Hoyano, S. Huizinga, L. Weiler, Can. J. Chem., 55, 4191 (1977).
    b) W. R. Hertler, U.S. Patent No. 3 153 658 (1964); Chem. Abstr. 62, 4145 (1965).

30. F. Wudl, M. L. Kaplan, B. K. Teo, J. Marshall, J. Org. Chem.,
    42, 1666 (1977).

31. a) R. C. Wheland, E. I. Martin, J. Org. Chem., 40, 3101 (1975).

    b) R. C. Wheland, J. L. Gillson, J. Am. Chem. Soc., 98, 3916 (1976).

    c) R. C. Wheland, J. Am. Chem. Soc., 98, 3926 (1976).

32. E. M. Engler, R. A. Craven, Y. Tomkiewicz, B. A. Scott, K. Bechgaard,
    J. R. Andersen, Chem. Commun., 337 (1976).

33. W. R. Hertler, J. Org. Chem., 41, 1412 (1976).

34. P. Eaton, R. Mueller, G. Carlson, D. Cullison, G. Cooper, T. Chou,
    E. Krebs, J. Am. Chem. Soc., 99, 2751 (1977).

35. a) V. Bhalerao, H. Rapoport, J. Am. Chem. Soc., 93, 4835 (1971).

    b) J. P. Schaefer, B. Horvath, H. P. Klein, J. Org. Chem., 33,
    2647 (1968).

36. D. D. Reynolds, K. R. Durham, US Patent #2789971 (1957); Chem.Abst.51,14814c(195?

37. H. Falk, K. Schlögl, Monatshefte für Chemie, 49, 578 (1968).

38. F. Vögtle, W. Bieber, Angew. Chem. Int. Ed. Engl., 16, 175 (1977).

39. W. P. Reeves, M. R. White, Syn. Commun., 193 (1976).

40. F. L. Cook, C. W. Bowers, C. L. Liotta, J. Org. Chem., 39, 3416 (1974).

41. M. S. Newman, B. T. Lord, J. Am. Chem. Soc., 66, 734 (1944).

42. M. S. Newman, V. Lee, J. Org. Chem., 42, 1478 (1977).

43. a) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and
    Structure." McGraw-Hill, N.Y., 1968, p.535.

    b) K. Ziegler, A. Spath, E. Schaaf, W. Schumann, E. Winkelmann, Annalen,
    551, 80 (1942).

44. K. Rorig, J. D. Johnston, R. W. Hamilton, T. J. Telinski, Org. Syn.,
    Coll. Vol. IV, 576.

45. A. C. Cope, E. C. Herrick, Org. Syn., Coll. Vol. IV, 304.

46. H. J. Kuhn, K. Gollnick, Chem. Ber., 692 (1973).

47. D. Gundermann, D. Röker, J. Liebigs Ann.Chem., 140 (1976).

48. G. Simchen, Angew. Chem. Int. Ed. Engl., 5, 663 (1966).

49. J. R. Andersen, C. S. Jacobsen, G. Rindorf, H. Soling, K. Bechgaard, Chem. Commun., 883 (1975).

50. K. Yamakawa, private communication.

51. H. J. Teuber, Chem. Ber., 86, 1036 (1953).

52. M. Crawford, V. R. Supanekar, J. Chem. Soc., 2380 (1964).

53. T. Umemoto, S. Satani, Y. Sakata, S. Misumi, Tet. Lett., 3159 (1975).

54. T. Sato, S. Akabori, S. Muto, K. Hata, Tet., 24, 5557 (1968).

55. H. Irgantinger, R. G.Kirrstetter, C. Krieger, H. Rodewald, H. A. Staab, Tet. Lett., 1425 (1978).

56. F. Vögtle, P. Newmann, Synthesis, 85 (1973).

57. V. Boekelheide, D. Reingold, M. Tuttle, Chem. Commun., 406 (1973).

58. R. H. Mitchell, R. Carruthers, J. Zwinkels, Tet. Lett., 2585 (1976).

59. R. H. Mitchell, R. Carruthers, Can. J. Chem., 52, 3054 (1974).

60. A. J. Speziale. Org. Synt., Coll. Vol. IV, 401.

61. R. H. Mitchell, T. Otsubo, V. Boekelheide, Tet. Lett., 219 (1975).

62. a) F. Vögtle, P. Neumann, Angew. Chem. Int. Ed. Engl., 11, 73 (1972).

    b) S. Akabori, T. Sato, K. Hata., J. Org. Chem., 33, 3277 (1968).

63. E. Clar, B. A. McAndrew, M. Zander, Tet, 23, 985 (1967).

64. T. Sato, M. Wakabayashi, Y. Okamura, T. Amada, K. Hato, Bull. Chem. Soc. Japan, 40, 2363 (1967).

65. W. Ried, F. J. Konigstein, Chem. Ber., 92, 2532 (1959).

SPECTRAL INDEX

RELATIVE INTENSITY

M/E

58

126

FREQUENCY (CM⁻¹)

TRANSMITTANCE (%)

52

RELATIVE INTENSITY

0.0 25.0 50.0 75.0 100.0

0.0
50.0
100.0
133
150.0
164
200.0
250.0
300.0
350.0
400.0
450.0

M/E

-98-

58

CO$_2$Me

TRANSMITTANCE (%)

0
10
20
30
40
50
60
70
80
90
100

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

FREQUENCY (CM)

8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

RELATIVE INTENSITY

0.0 25.0 50.0 75.0 100.0

TRANSMITTANCE (%)

FREQUENCY (CM⁻¹)

M/E

-99-

241

322

59

Br

Br

CO_2Me

RELATIVE INTENSITY

100.0

75.0

50.0

25.0

0.0

182

214

M/E

0.0   50.0   100.0   150.0   200.0   250.0   300.0   350.0   400.0   450.0

CN

CO$_2$Me

NC

60

FREQUENCY (CM⁻¹)

4000   3600   3200   2800   2400   2000   1800   1600   1400   1200   1000   800   600

TRANSMITTANCE (%)

100
90
80
70
60
50
40
30
20
10

500   400   300   200   100   0 Hz

8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   0

61

RELATIVE INTENSITY

100.0

75.0

50.0

25.0

0.0

0.0   50.0   100.0   150.0   200.0   250.0   300.0   350.0   400.0   450.0

M/E

FREQUENCY (CM⁻¹)

4000   3600   3200   2800   2400   2000   1800   1600   1400   1200   1000   800   600

TRANSMITTANCE (%)

100
90
80
70
60
50
40
30
20

500   400   300   200   100   0 Hz

8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   0

62

PERCENT TRANSMISSION

FREQUENCY (CM)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400

RELATIVE INTENSITY

0.0   25.0   50.0   75.0   100.0

0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0

M/E

-103-

262

56

NC   CN
NC   CN
CO$_2$Me

70

71

106

105

286

72

RELATIVE INTENSITY

M/E

FREQUENCY (CM⁻¹)

TRANSMITTANCE (%)

76

73

87

88

89

83

102

PERCENT TRANSMISSION

FREQUENCY (CM⁻¹)

RELATIVE INTENSITY

M/E

-114-

98

96

RELATIVE INTENSITY

313

34

95

M/E

FREQUENCY (CM⁻¹)

TRANSMITTANCE (%)

94

93

92

91

PERCENT TRANSMISSION

FREQUENCY (CM⁻¹)

RELATIVE INTENSITY

0.0   25.0   50.0   75.0   100.0

M/E

90

NC—C—CN   NC—C—CN