

QUANTITATIVE STUDIES OF HYDROGEN BONDING  
IN ORTHO-SUBSTITUTED PHENOLS USING  
PROTON MAGNETIC RESONANCE

by

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Chemistry

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## A B S T R A C T

The chemical shift of protons in intramolecular hydrogen bonds has been measured in 41 ortho substituted phenol type compounds. The change in chemical shift " $\Delta\sigma_{OH}$ " on formation of these hydrogen bonds is taken as the difference between the infinite dilution chemical shift of the parent phenol compound in  $CCl_4$  solution and the chemical shift measured for the proton in the intramolecular hydrogen bond. This change in chemical shift is correlated with the corresponding frequency shift " $\Delta\nu_{OH}$ " in the -OH stretching region of the infra-red spectrum.

The dilution chemical shift for the -OH proton in the o-halophenols has been investigated over a concentration range 1 - 5 mole % in  $CS_2$  and a temperature region -53 to 107°C. Using the infinite dilution shift values, the equilibrium constants of the cis-trans conversion were obtained. Values for  $\delta_{CIS}$ , the chemical shift of the completely hydrogen bonded form;  $\delta_{TRANS}$ , the chemical shift of the unbonded form, and  $\Delta H$ , the enthalpy of formation of the hydrogen bond, were also calculated. From these results a value for  $\Delta H$ , the enthalpy of formation for the dimer was calculated, assuming that the major dimer species in solution was formed from the combination of a cis and trans bonded form.

Temperature studies of the change in chemical shift of the -OH proton for 2,4,6-trihalosubstituted phenols is also reported. The temperature range in this case was 0°C to 111°C.

ABSTRACT APPROVED . . . . .

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## CHAPTER I

## INTRODUCTION.

## 1) General Considerations

The study and interpretation of factors which account for the formation of a hydrogen bond has been of considerable interest to chemists for some years. Many experimental techniques, including dielectric constant measurements, vapour pressure studies and spectroscopic methods, particularly in the infrared region, have been adopted for the study of such bonding (1) (2) (3). Since 1953, the use of nuclear magnetic resonance spectroscopy as a means of studying the hydrogen bond has indicated that this relatively new method will equal, if not surpass, other means for obtaining information (4). The recently published work of Pimentel and McClellan (3) is particularly useful, since a general survey of all pertinent literature on hydrogen bonding to 1956, as well as some to 1959, is included as an appendix.

Pimentel and McClellan define a hydrogen bond in the following manner:

"A hydrogen bond exists between a functional group -X-H and an atom or group of atoms Y in the same or different molecule when

- (a) there is evidence of bond formation (association or chelation)
- (b) there is evidence that this new bond linking

-X-H and Y specifically involves the hydrogen already bonded to X." \*

Using this definition, one must distinguish between the two types of hydrogen bonding likely to occur; the intermolecular, where the functional groups -X-H and Y are in different molecules, and the intramolecular, where both -X-H and Y are in the same molecule, with the distance between them favourable to the formation of a bond.

In 1953 Arnold and Packard (5) (6) discovered that the chemical shift of the -OH proton signal of ethyl alcohol was both concentration and temperature dependent. Upon dilution in non-polar solvents or upon an increase in temperature the signal was observed to shift to higher field. No similar shift was observed for the methyl or methylene protons.

The lifetime of the hydrogen bond is very short and the high field shift on dissociation of these bonds is a time average of the various environments in the solution (7) (8). The average shielding parameter thus increases as hydrogen bonds are broken in the system, with consequent resonance at higher field for the proton involved. Further studies on ethanol (9), various phenols (10), and acetic acid (11) seem to confirm this interpretation.

Pople and Marshall (12), in an attempt to explain

\*S.C.Pimentel and A.L.McLellan, The Hydrogen Bond, W.H. Freeman & Co., San Francisco (1960), p.6

the low field shift of a proton on formation of a hydrogen bond, considered the contribution to the chemical shift of a hydrogen atom by an electric field  $E$ . The result obtained

$$\delta = - \frac{881}{216} \frac{a^3 E^2}{m c^2} \quad (1)$$

where  $\delta$  = the chemical shift

$m$  = mass of the proton

$c$  = velocity of light

$a$  = the Bohr radius

gives a shift of 4 p.p.m. for an electric field of 0.14 atomic units, which is the field that would arise from a single electron at a distance of 1.4 Å.

Pople, Schneider and Bernstein (13) also calculated the contribution to the chemical shift produced by the magnetic field induced by the Y atom on bonding, but obtained a result which predicted a shift opposite to that observed. Another term giving a similar result would be the amount of covalent character of the bond  $X \cdots H - Y$ , but this would be difficult to evaluate quantitatively. Pople (12) concluded that electrostatic effects were of considerable importance, since observed chemical shifts are always to lower field when a hydrogen bond is known to be formed.

The major purpose of this work was to evaluate the chemical shift of the -OH group (at low concentrations, to reduce intermolecular effects) for compounds known to

contain an intramolecular hydrogen bond. The change in chemical shift  $\Delta\sigma_{\text{OH}}$  from the infinite dilution chemical shift of the parent compound was then correlated with the change in frequency  $\Delta\nu_{\text{OH}}$  of the -OH stretching frequency in the infrared region. For some weakly bonded species, a study of the chemical shift as a function of temperature and concentration allowed the calculation of a heat of formation  $\Delta H$  for the hydrogen bond.

An ortho substituent on a phenol or naphthol is favourably situated for the formation of an intramolecular bond with the -OH group of the compound. The study was confined to compounds of this type.

(ii) Infrared and Dipole Moment Studies of Intramolecular Hydrogen Bonds in Phenols.

Evans (14) has reported an estimated barrier to rotation for the -OH group in phenol of 3.7 kcal./mole. Upon placing a substituent capable of hydrogen bond formation in the ortho position the two sites would no longer be equivalent and the relative population of the unbonded to the bonded form (trans/cis) would depend on the strength of the hydrogen bond formed, neglecting intermolecular effects. In the -OH stretching region two bands are observed due to the trans and cis forms. If intensity measurements are used, an estimate of the equilibrium constant may be made.

One of the first such studies was made by Wulf and Liddel in 1935 (15) (16). Using dilute solutions of o-chlorophenol in carbon tetrachloride they observed two bands ( $7050\text{ cm}^{-1}$  and  $6910\text{ cm}^{-1}$ ) in the infrared which were attributed by Pauling (17) to the frequency for a free -OH (trans) and a bonded -OH (cis). Several other workers studied similar compounds, but most of the work prior to 1953 was discounted by Rossmly, Lüttke and Mecke (18), who made new measurements on carefully purified o-chloro, o-bromo and o-iodophenol and stated that all earlier quantitative measurements were in error due to the fact that no special care had been taken by earlier workers to remove the phenol which was invariably present. Their

values for the trans/cis ratio (25° C) in o-chloro, o-bromo and o-iodophenol in carbon tetrachloride solution were 1/44, 1/37, and 1/12 respectively. Calculated values of  $\Delta H$  were 1.4 kcal/mole for o-iodophenol and 2.1 kcal/mole for o-bromophenol. It was stated that the value for o-chlorophenol would be higher.

Probably the most reliable, and the most complete, infrared data on the -OH stretching region of o-substituted phenols is that obtained by Baker and co-workers (19-22). For the o-halophenols, after purification by several passes through a gas chromatograph, Baker obtained accurate -OH stretching frequencies and from the band intensities calculated trans/cis ratios of 1/56, 1/38 and 1/13.5 for o-chloro, o-bromo and o-iodophenol respectively at 25° C. Subsequently, he investigated the change in frequency ( $\Delta \nu_{OH}$ ) relative to phenol for a series of o-substituted phenols and concluded that  $\Delta \nu_{OH}$  is roughly a measure of the strength of the hydrogen bond formed. He further studied 2,4,6-trihalosubstituted phenols where two bands are observed if the halogens at the 2,6 positions are different. Jones and Watkinson (23), in their studies of o-halophenols, obtained results markedly different from Baker's.

Richards and Walker (24-27) have investigated a series of similar ortho-substituted compounds in various solvents and, where possible, have attempted to correlate

their dipole moment measurements with the infrared data of Baker. They have measured the trans/cis ratios for the o-halophenols (26) in carbon tetrachloride, cyclohexane, benzene and dioxan. The order in cyclohexane and carbon tetrachloride was found to be  $I > F > Br$  and  $Cl$ ; in benzene  $I > Br > Cl$  and  $F$ ; and in dioxan  $I > Br > Cl > F$ . A previous dipole moment study in carbon tetrachloride by Angilotti and Curran (28) gave the order  $F > Cl > Br$  for the three o-halophenols studied.



## CHAPTER II. EXPERIMENTAL PROCEDURE.

## 1) Preparation of Samples.

Commercially available compounds (i.e. Eastman Kodak or Aldrich Chemicals) known to contain an intramolecular hydrogen bond of the type  $\text{-OH--Y}$  were purified by fractional distillation or recrystallization from suitable solvents such as cyclohexane, chloroform, ether, alcohol or acetone. The synthesized 2,4,6-trihalo-substituted phenols were purified by recrystallization from n-heptane or pentane. For the temperature studies, o-chloro, o-bromo and o-fluorophenol were purified by two passes through a Beckman Megachrom gas chromatograph.

Reagent grade carbon tetrachloride and carbon disulphide which had been dried over phosphorus pentoxide and distilled were used as solvents in the preparation of samples. In each case approximately one mole % of internal standard (cyclohexane or tetramethyl silane) was added to the freshly distilled solvent, which was stored in glass ether bottles.

All solutions were made up by weight using a standard Mettler analytical balance and the mole fraction of phenol calculated. In most cases solutions of approximately 5 ml. volume were made up and a portion of the solution transferred to 5 mm. pyrex tubes which had been dried and stored in a dessicator over phosphorus

pentoxide. The tube was transferred to a vacuum system, the solution was frozen in liquid nitrogen, and the tube sealed after air over the sample had been pumped off.

Two tubes of each solution were made.

For the work on correlation of chemical shift with infrared stretching frequency, carbon tetrachloride was used as solvent, but since its melting point is too high for low temperature work ( $-23^{\circ}\text{C}$ ), carbon disulphide was used for the subsequent temperature studies (m.p.  $-108^{\circ}\text{C}$ ). Benzene, acetone, chloroform, or similar solvents are unsuitable for this type of study, since hydrogen bonding with solvent molecules would occur.

ii) Synthesis of 2,4,6 trisubstituted halophenols.

(a) 2-Fluoro-4,6-diiodophenol and 2-Chloro-4,6-diiodophenol

The procedure followed was essentially that outlined by Baker (21). Eight grams of potassium hydroxide and 0.10 mole of the 6-halophenol were dissolved in 150 ml. of water. In a second beaker, 54 gm. of pulverized iodine were dissolved in a cold solution of 26 gm. of potassium hydroxide in 400 ml. of water and immediately added to the phenol solution. Cold, 25% sulphuric acid was added dropwise until a pH of 7. was reached. The excess of iodine was removed by the addition of solid sodium thiosulphate. The oil which formed solidified on cooling in ice and was recrystallized twice from n-heptane.

melting pt.(obs.) reported (21)  
(corr.)

2-fluoro-4,6-diiodophenol	56-56.5° C	56-57° C
2-chloro-4,6-diiodophenol	93-95° C	96° C

(b) 2-Fluoro-4,6-dibromophenol and 2-Chloro-4,6-dibromophenol

Prepared by the method of Raiford and Le Rosen(29). Twenty ml. of glacial acetic acid and 0.10 mole of the ortho halophenol were cooled in ice and 12 ml. of bromine were slowly added. The solution was left

for one hour and was then poured into ice water. A 20% solution of sodium bisulphite was added to remove excess bromine. The crude product was dissolved in a 5% solution of sodium hydroxide, decolorized with charcoal, and filtered. The resulting solution was acidified with dilute sulphuric acid to precipitate the product, which was recrystallized twice from n-heptane.

	m.p. (obs.) (corr.)	m.p.(reported)
2-Fluoro-4,6-dibromophenol	33-34.5°C	34-35°C
2-Chloro-4,6-dibromophenol	70-71°C	-

## iii) Measurement of Chemical Shifts.

A standard Varian 40 Mc/sec V4300 High Resolution Spectrometer was used for all measurements, except where noted. In order to achieve the base line stability required for measurements at concentrations of one mole %, a twelve volt battery was placed in parallel with the filament supply to the V-4310 Varian RF unit. Chemical shifts were measured using the side band technique, and side band frequencies were measured simultaneously by adopting the circuit recommended by Varian NMR Instrument Owner Bulletin, February 1, 1960, which allowed the Hewlett Packard model 522B Electronic Frequency Counter to continuously monitor the side bands applied. A Hewlett Packard 200 CD Oscillator was used to supply side bands. The variable temperature apparatus was that described by Reid and Connor (30).

For the work on correlation of chemical shifts with -OH stretching frequency, the measurements were made by superimposing a sideband for the internal cyclohexane standard upon the phenol -OH band using a Dumont type 304 AR Oscilloscope. Two measurements on each of the two samples were considered sufficient. The estimated accuracy is  $\pm 1.5$  cycles/sec, or 0.04 p.p.m. Since chemical shifts were required to  $\pm 0.1$  cycles/sec for the temperature studies, another technique was adopted. The phenol -OH band

was recorded on chart paper with side bands before and after it, using a Speedomax model H recorder (see figure 1). The side band was switched off and changed while sweeping through the -OH band. The distance between side bands was from 10-12 cycles/sec and sweep rates were such that the length on the chart paper was approximately 1 cm./cycle. Five to eight measurements were taken for each sample at all temperatures. The internal standard for the o-halophenols was cyclohexane, while for the 2,4,6 trisubstituted halophenols tetramethyl silane was used and the values reduced to that for cyclohexane. As measured in this laboratory, the cyclohexane signal is 57.6 cycles/sec (40 Mc/sec RF) or 1.44 p.p.m. to low field from tetramethyl silane. The average standard deviation for o-chloro and o-bromophenol measurements was  $\pm 0.1$  cycles/sec.; for o-fluorophenol  $\pm 0.2$  cycles/sec. and for the trisubstituted phenols  $\pm 0.5$  cycles/sec.

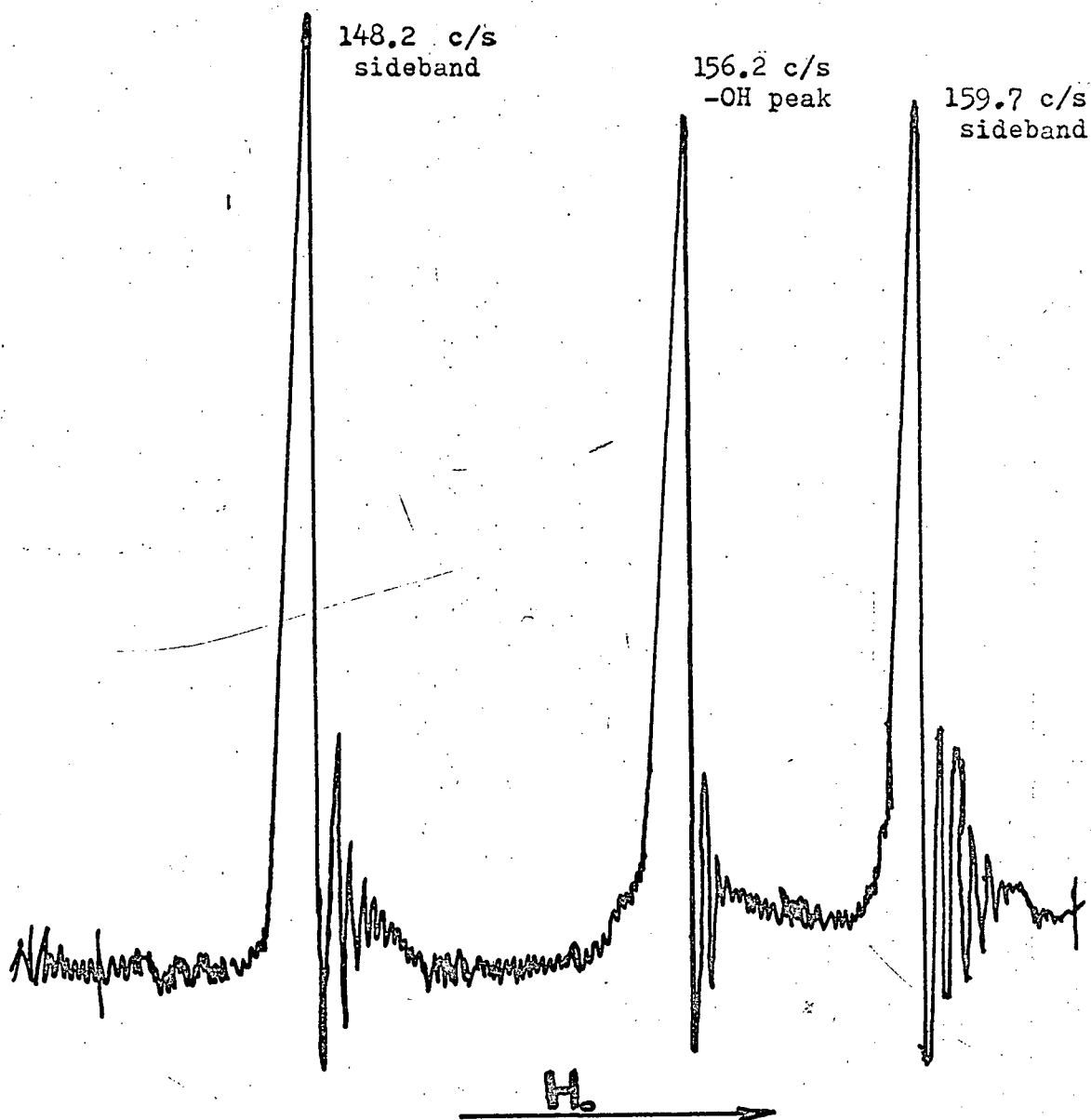


Figure 1. Representative pmr spectrum of o-halophenols showing sidebands applied before and after the phenol -OH resonance peak. The sample in this case was o-chlorophenol (2 mole%) at 27 °C. The sweep rate was .86 cm./cycle.

i) Correlation of Chemical Shift with infrared stretching frequency.

The values for the chemical shift at infinite dilution and the -OH stretching frequency for the parent compounds phenol, 1-naphthol and 2-naphthol are given in Table 1 below:

TABLE 1

Compound (referred to infinite dilution in $\text{CCl}_4$ )	(1)	(2)	(3)
	$(\sigma_{\text{C}_6\text{H}_5} - \sigma_{\text{OH}})$ (Observed) p.p.m.	$(\sigma_{\text{C}_6\text{H}_5} - \sigma_{\text{OH}})$ (Corrected) p.p.m.	$\nu_{\text{OH}}$ cm <sup>-1</sup>
phenol	3.12	2.80	3604
1-naphthol	3.78	2.86	3594
2-naphthol	3.49	2.66	3601

Column 1 gives the observed infinite dilution shift of the compound, while column 2 gives the chemical shift corrected for ring current using the model of Pople (31). The circulating  $\pi$  electrons of the benzene ring lead to an additional magnetic field at the protons near the ring which reinforces the main field  $H_0$ , leading to resonance at lower values of  $H_0$  than would normally be the case. This leads to an approximate correction for the chemical shift, given by:



$$\Delta\sigma = - \frac{e^2 a^2}{2mc^2 R}$$

where:  $e$  = charges on the electron

$m$  = mass of an electron

$a$  = radius of the benzene ring (1.4 Å)

$c$  = velocity of light

$R$  = distance from the proton under consideration to the centre of the ring

$\Delta\sigma$  = the change in chemical shift due to the influence of the  $\pi$  electrons.

These corrections were also made for the compounds containing intramolecular hydrogen bonds. The experimentally observed values, along with corrected values for  $\sigma$  are given in Table 2. Column 3 gives the value of  $\Delta\sigma_{on}$  (corrected) from the parent compound while column 4 gives the change in frequency  $\Delta\nu_{on}$  ( $\text{cm}^{-1}$ ). A graph of  $\Delta\nu_{on}$  against  $\Delta\sigma_{on}$  is given in figure 2, the numbers on the graph referring to the compounds in Table 2 (32). Infrared data were obtained on a Perkin Elmer model 21 Double Beam infrared spectrometer using 3mm. or 1mm. sodium chloride cells. All measurements were checked, where possible, with those of Baker (20) (21). With the exception of  $\Delta\nu_{on}$  for o-nitrophenol, where Baker's value of  $346 \text{ cm}^{-1}$  disagrees with our value of  $364 \text{ cm}^{-1}$ , there was good agreement. The 2,4,6 trihalo substituted phenols, where the 2,6 positions contain different halogens, are not included in figure 2, since two bands are observed in the infrared, corresponding

to the two different bonds formed. As stated previously, the magnetic resonance signal observed is an average of these two forms (8).

TABLE 2.

Compound	$(\sigma - \sigma_{OH})$ p.p.m.	$(\sigma - \sigma_{OH})$ corrected p.p.m.	$\Delta\sigma_{OH}$ corrected p.p.m.	$\Delta\nu_{OH}$ cm <sup>-1</sup>
1. Salicylaldehyde	-9.51	-8.83	6.71	471
2. 5-Nitrosalicylaldehyde	-10.05	-9.37	7.25	500
3. 5-Bromosalicylaldehyde	-9.38	-8.70	6.58	454
4. o-Nitrophenol	-9.14	-8.46	6.34	*346, 364
5. 2,4 Dinitrophenol	-9.64	-8.96	6.84	388
6. Methyl Salicylate	-9.12	-8.44	6.32	395
7. o-Bromo Benzoic Acid	-11.25	-10.70	8.58	570, 96
8. o-Chlorophenol	-3.97	-3.27	1.17	61
9. 2,4 Dichlorophenol	-3.99	-3.31	1.19	63
10. 2,4,6 Trichlorophenol	-4.20	-3.52	1.40	75
11. o-Bromophenol	-3.95	-3.27	1.15	92
12. 2,4-Dibromophenol	-3.98	-3.30	1.18	83
13. o-Iodophenol	-3.68	-3.00	0.98	105
14. o-Methoxyphenol	-3.98	-3.30	1.18	60
15. 2,6 Dimethoxyphenol	-3.82	-3.14	1.02	56
16. o-Allylphenol	-3.87	-3.19	1.07	63
17. o-Cresol	-3.12	-2.44	0.32	-8

\* cf. ref. 20.

TABLE 2 (cont'd)

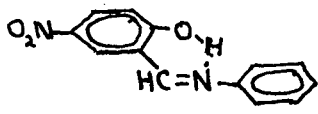
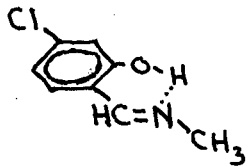
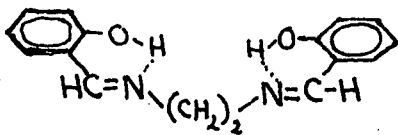
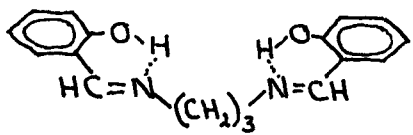
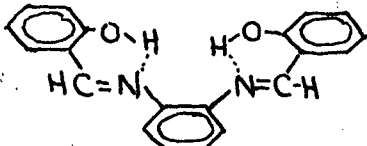
Compound	$(\sigma - \sigma_{\text{OH}})$ p.p.m.	$(\sigma - \sigma_{\text{OH}})$ corrected p.p.m.	$\Delta\sigma_{\text{OH}}$ corrected p.p.m.	$\Delta\nu_{\text{OH}}$ cm <sup>-1</sup>
18. 	-12.49	-11.54	9.42	(Overlaps -C-H stretch 3000cm <sup>-1</sup> )
19. 	-11.27	-10.59	8.47	
20. 	-11.13	-10.45	8.33	544
21. 	-11.36	-10.68	8.56	532
22. 	-11.03	-10.08	7.96	531

TABLE 2 (cont'd)

Compound	( $\sigma - \sigma_{OH}$ ) p.p.m.	( $\sigma - \sigma_{OH}$ ) corrected p.p.m.	$\Delta\sigma_{OH}$ corrected p.p.m.	$\Delta\nu_{OH}$ cm <sup>-1</sup>
23. 1-Nitro-2-naphthol	-10.53	-9.70	7.04	538
24. 2,4 Dinitro-1-naphthol	-11.20	-10.28	7.42	543
25. 2,5 Dichlorophenol	-4.02	-3.34	+ 1.22	65
26. o-Fluorophenol	-3.62	-2.94	0.82	18
27. o-Phenylphenol	-3.67	-2.99	0.87	45
28. 4-Chloro-2-nitrophenol	-9.06	-8.38	6.26	354
29. 2-Bromo-4-phenylphenol	-3.93	-3.25	1.13	75
30. 1-Bromo-2-naphthol	-4.45	-3.62	1.79	82
31. 2,4-Dibromo-1-naphthol	-4.40	-3.48	1.54	89
32 <sup>a</sup> o-(Methylthio)phenol	-4.67	-3.99	1.87	194
33 <sup>a</sup> 2 Methyl-6(Methylthio) phenol	-5.20	-4.52	2.40	208
34 <sup>a</sup> o-(isopropylthio)phenol	-5.18	-4.50	2.30	205
35. 2,3,4,6-Tetrachlorophenol	-4.43	-3.75	1.63	80
36. 2-Chloro-4,6-dibromophenol	-4.27	-3.59	1.47	-
37. 2-Chloro-4,6-diiodophenol	-4.32	-3.64	1.52	-
38. 2,4,dichloro-6-iodophenol	-4.28	-3.60	1.48	-
39. 2-Fluoro-4,6-dibromo- phenol	-3.85	-3.17	1.05	-
40. 2-Fluoro-4,6-diiodophenol	-4.06	-3.38	1.26	-
41. 2,4 dibromo-6-iodophenol	-4.27	-3.59	1.47	-

(a) I wish to express my thanks to Dr. A.W. Baker for supplying these compounds.

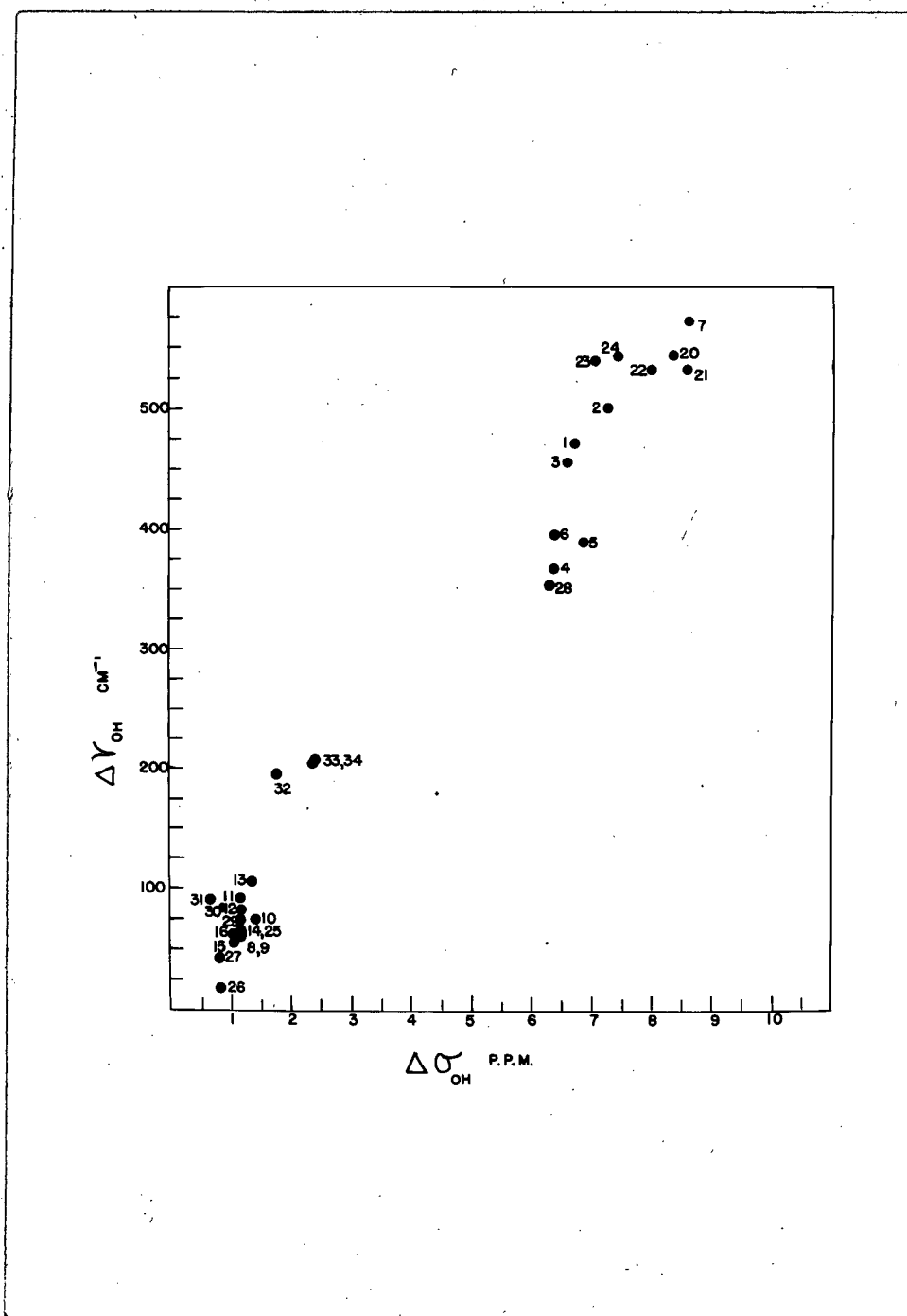


Figure 2. Plot of  $\Delta\sigma_{OH}$  vs  $\Delta\nu_{OH}$  for the compounds given in Table 2. Numbered points refer to compounds as listed.

## ii) Temperature Studies of o-Halophenols.

The results of the chemical shift measurements (relative to cyclohexane) at various temperatures are given in tables 3 to 6, along with the values of  $\delta_{M\infty}$ , the extrapolated infinite dilution shift. The graphical results for obtaining  $\delta_{M\infty}$  are given in figure 3 for o-chlorophenol, figure 4 for o-bromophenol, and figure 5 for o-iodophenol and o-fluorophenol. Figure 6 shows a plot of  $\delta_{M\infty}$  against temperature for o-bromophenol, which was used to obtain a trial value for  $\delta_{c_{15}}$ , the chemical shift of the phenol -O-H when completely hydrogen bonded. Similar plots were made for o-chloro and o-iodophenol (see discussion). The solid points on the graph for o-fluorophenol (fig. 5) represent data obtained by L. W. Reeves at 60 Mc/s during a visit to the National Research Council in the summer of 1961. The measurements were reduced to 40 Mc/s for inclusion in the same figure.

Table 3.

Values of chemical shift  $\delta_m$  in cycles/sec from cyclohexane obtained at various concentrations and temperatures for o-chlorophenol, along with the extrapolated values for  $\delta_{m\infty}$  obtained from Figure 3.

	C O N C E N T R A T I O N ( M O L E % )					
TEMPERATURE	0	1.22	2.02	3.18	4.03	4.99
107°C	151.2	151.5	152.3	152.6	153.1	153.4
82°C	152.6	153.2	153.5	154.0	154.6	155.3
68°C	153.3	-	154.7	155.5	155.9	-
27°C	156.1	158.6	159.6	160.0	161.1	162.3
-1°C	157.4	159.7	161.5	163.5	165.5	166.9
-53°C	159.2	-	176.6	185.9	-	196.9



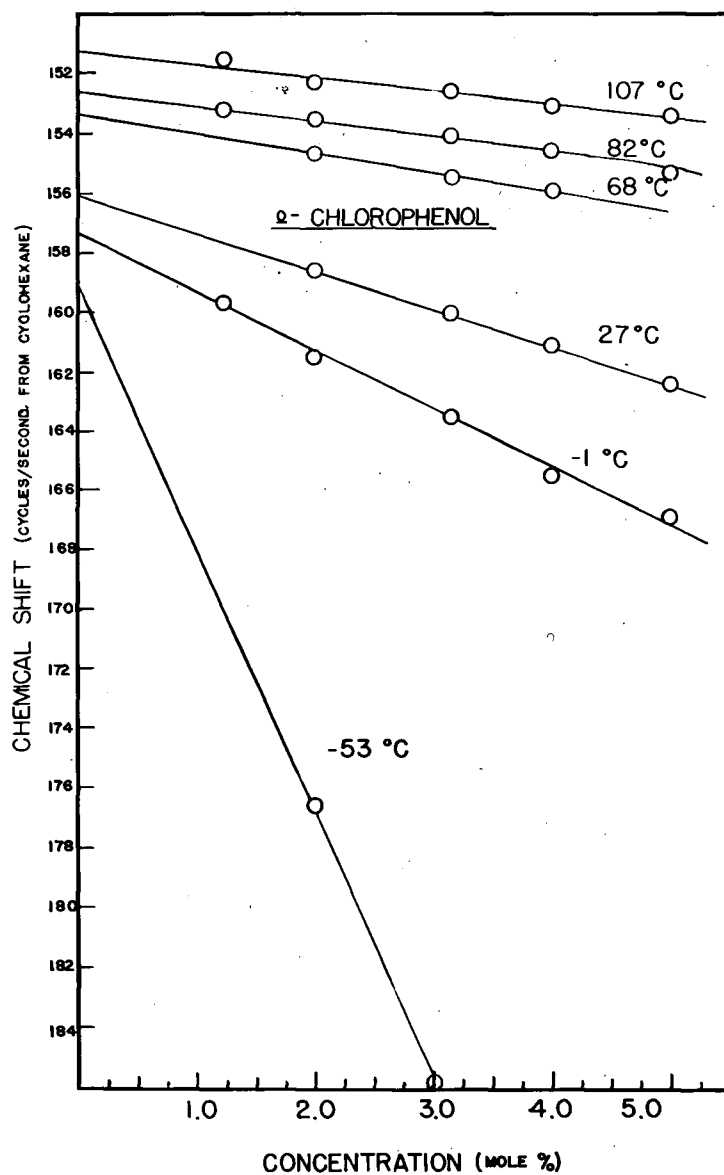


Figure 3. Dilution chemical shifts at six temperatures for the -O-H proton in o-chlorophenol at 1-5 mole % of the phenol in carbon disulphide. The numbers refer to cyclohexane as an internal standard.

Table 4.

Values of chemical shift  $\delta_m$  in cycles/sec from cyclohexane obtained at various concentrations and temperatures for o-bromophenol, along with the extrapolated values for  $\delta_{m\infty}$  obtained from Figure 4.

TEMPERATURE	C O N C E N T R A T I O N ( M O L E % )					
	0	1.16	2.02	3.13	3.74	4.61
107°C	150.4	-	151.5	-	152.0	152.8
82°C	-	152.4	153.1	153.3	154.1	154.3
68°C	152.7	153.2	153.7	154.0	154.7	155.3
27°C	154.5	155.5	156.2	157.2	157.9	159.0
-1°C	155.4	156.8	158.1	159.4	160.7	161.9
-18°C	156.0	157.8	159.0	161.6	-	164.1
-53°C	156.6	162.5	167.9	173.0	177.4	183.5

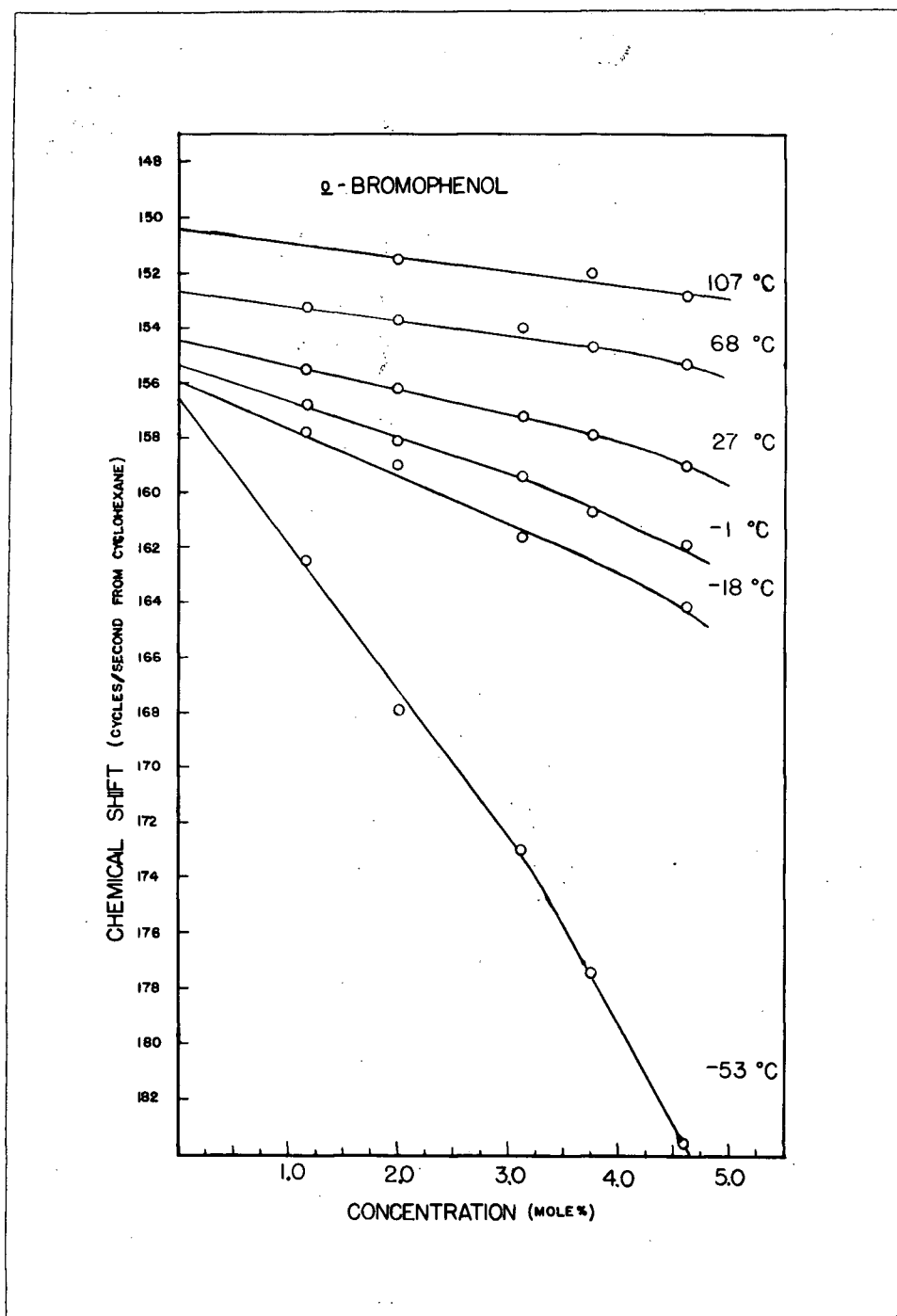


Figure 4. Dilution chemical shifts at six temperatures for the -O-H proton in o-bromophenol.

Table 5.

Values of chemical shift  $\delta_m$  in cycles/sec from cyclohexane at various concentrations and temperatures for o-iodophenol, along with the extrapolated values for  $\delta_{m\infty}$  obtained from Figure 5.

TEMPERATURE	C O N C E N T R A T I O N ( M O L E % )					
	0	1.37	2.11	3.00	4.21	4.78
107°C	141.5	142.2	-	142.6	143.5	143.6
82°C	142.8	143.4	143.6	143.9	144.5	145.0
68°C	-	-	-	144.8	145.7	146.6
27°C	145.8	147.0	147.6	148.2	149.9	150.7
-1°C	146.5	148.4	149.8	151.2	153.2	154.7
-22°C	-	152.4	152.8	154.6	160.0	161.6
-53°C	-	157.8	164.9	168.6	179.5	182.7

Table 6.

Values of chemical shift  $\delta_m$  in cycles/sec from cyclohexane obtained at various concentrations and temperatures for o-fluorophenol.

	C O N C E N T R A T I O N ( M O L E % )				
TEMPERATURE	0.966	1.91	2.85	3.62	5.35
50°C	-	136.4	140.1	143.1	149.0
<sup>a</sup> 27°C	138.5	144.6	149.5	152.6	160.9
23°C	-	144.7	150.7	153.7	162.1
-1°C	-	156.8	166.1	171.7	182.6
-18°C	-	165.1	178.3	183.2	186.9

<sup>a</sup> Data obtained by L.W. Reeves at 60 Mc/sec while at the National Research Council, Ottawa, in August 1961. Values are reduced to those for 40 Mc/sec for comparison.

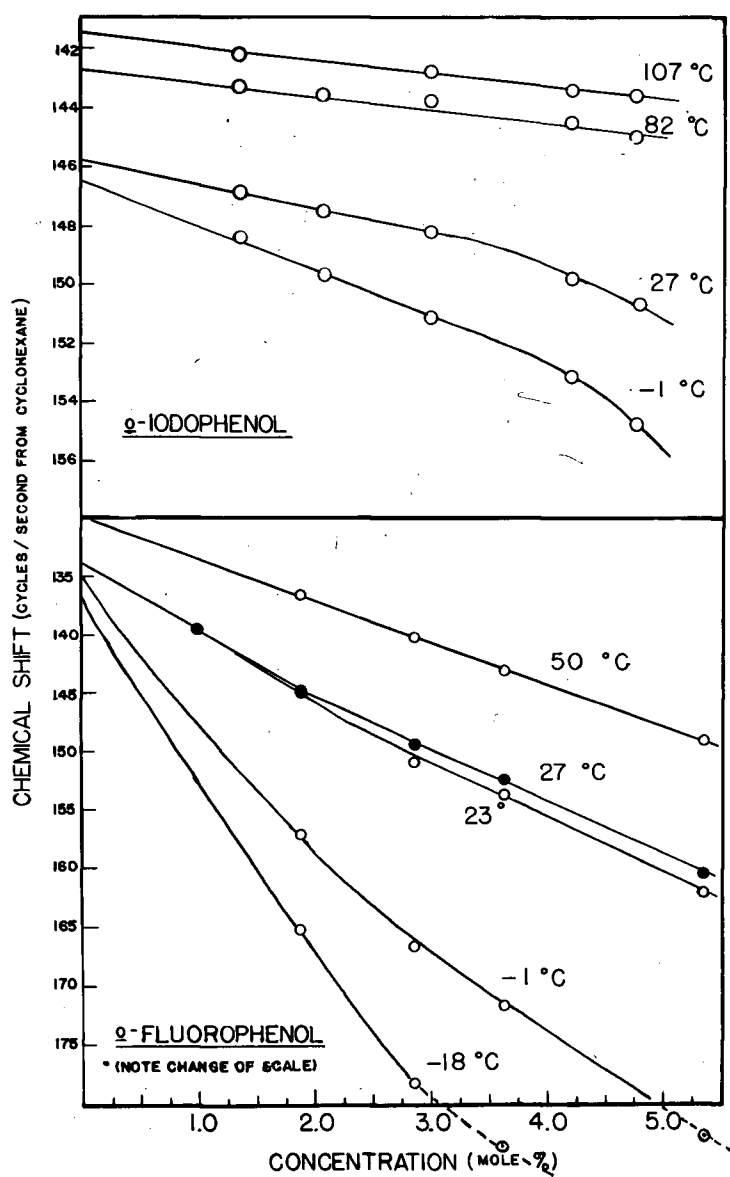


Figure 5. Dilution chemical shifts for the -O-H proton in o-iodo and o-fluorophenol.

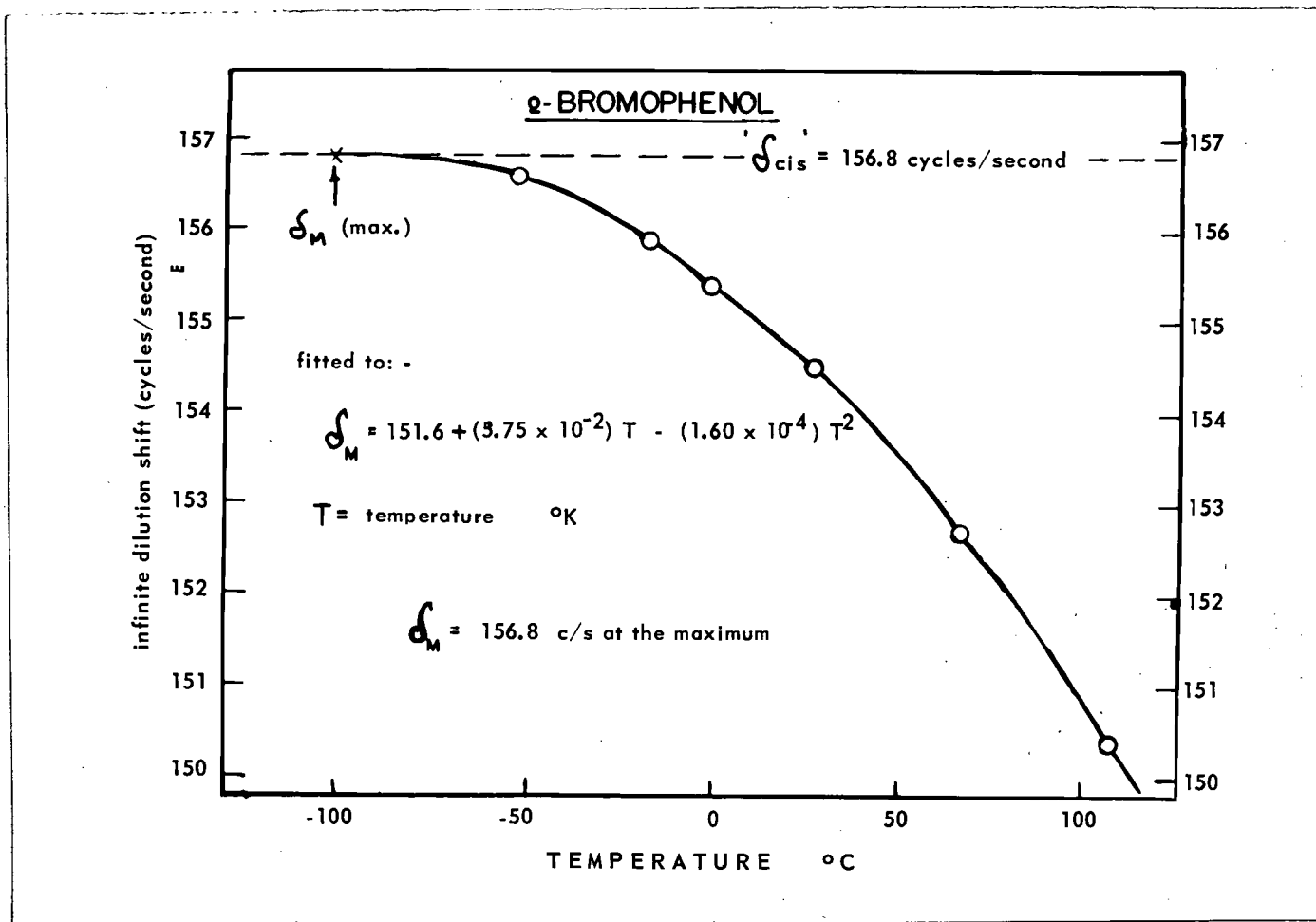


Figure 6. The values of  $\delta_{M\infty}$  obtained from Figure 4 plotted against temperature.

iii) Temperature Studies of 2,4,6-Trisubstituted Phenols.

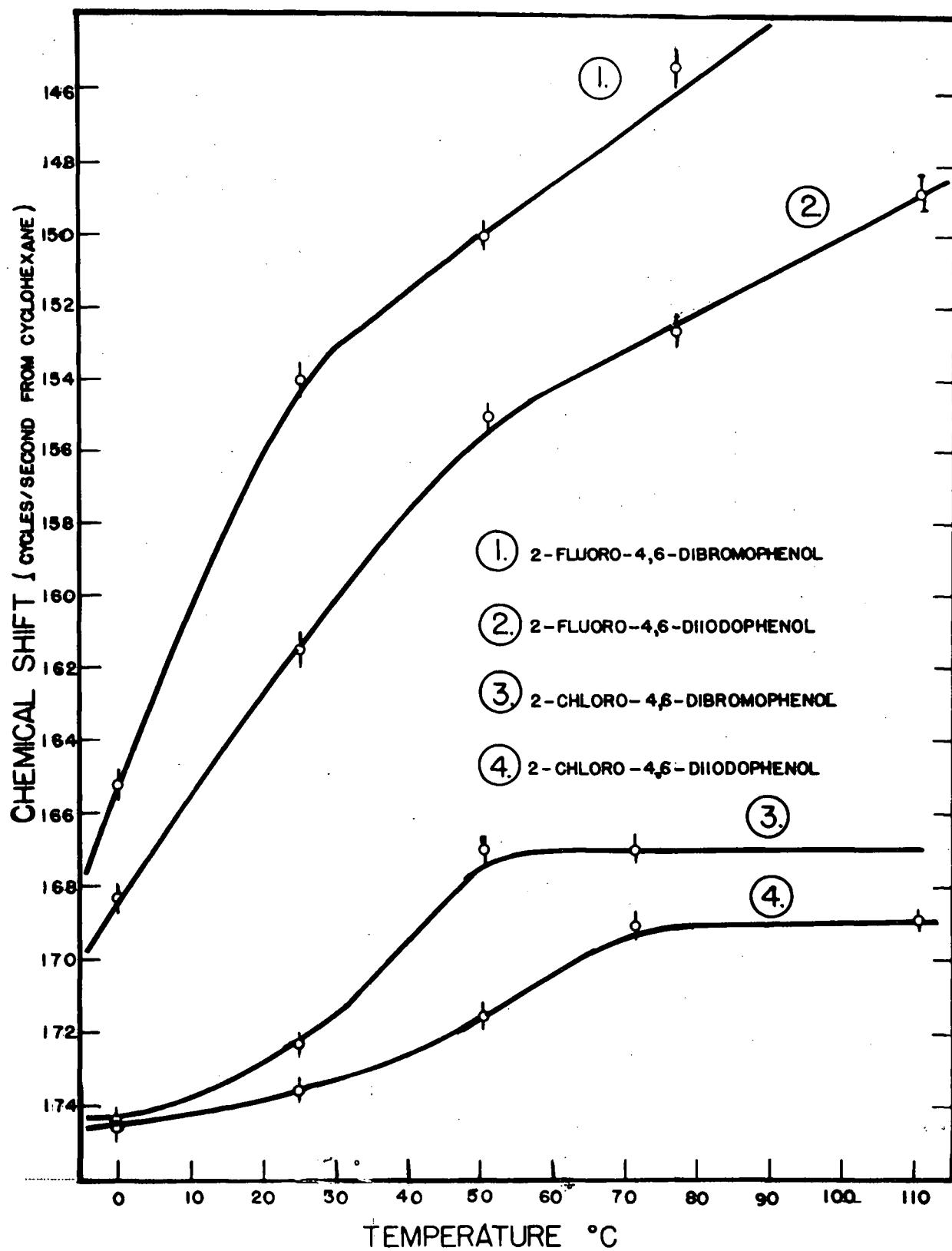
Chemical shift measurements over the temperature range 0 to 110° C for 2-fluoro-4,6-dibromophenol, 2-fluoro-4,6-diiodophenol, 2-chloro-4,6-dibromophenol, and 2-chloro-4,6-diiodophenol are given in table 7. In these cases the chemical shifts were independent of concentration in the range studied (to 4 mole %). Figure 7 is a graph of these results plotted against temperature.



TABLE 7

Values of chemical shift  $\delta_m$  in cycles/sec from cyclohexane for some 2,4,6-trisubstituted phenols at various temperatures. The chemical shift was independent of concentration in the range studied.

COMPOUND	TEMPERATURE				
	0°C	25°C	51°C	73°C	111°C
2-Chloro-4,6-diiodophenol	174.6	173.6	171.6	169.1	168.9
2-Chloro-4,6-dibromophenol	174.3	172.3	167.0	167.0	-
2-Fluoro-4,6-diiodophenol	168.3	161.5	155.0	152.6	149.9
2-Fluoro-4,6-dibromophenol	165.2	154.0	150.0	145.7	147.6

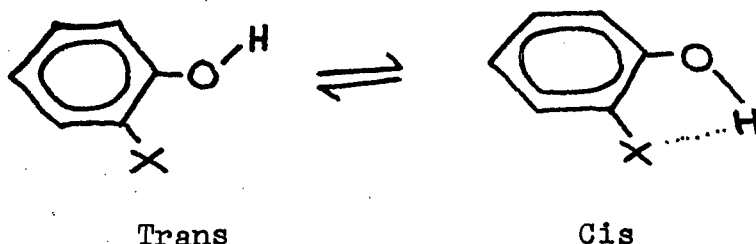


## CHAPTER IV.

## DISCUSSION.

## 1) Correlation of Chemical Shifts with Infrared Stretching Frequency.

An ortho-substituted phenol or naphthol is favourably situated for the formation of an intramolecular hydrogen bond with the -OH group of the phenol. If the possibility of a strong hydrogen bond exists, the measured chemical shift will be that of the hydrogen bonded species (33) (34), but for the weakly bonded compounds, an equilibrium of the type

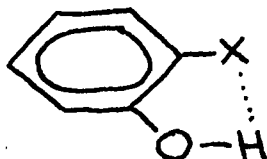


will exist, and the chemical shift will be a weighted average of the two forms (8). If the chemical shift is measured in a non polar solvent at low concentrations ( $\sim 1$  mole %) the value obtained will be very nearly that of the completely hydrogen bonded form.

Plotting the values obtained for  $\Delta\sigma_{\text{OH}}$ , the change in chemical shift, against  $\Delta\nu_{\text{OH}}$ , the change in infrared stretching frequency, shows that there is a degree of correlation (figure 2), in spite of scatter. One may say that the greater the change in chemical shift, the greater the change in stretching frequency,

and the stronger the bond formed.

Upon examination of figure 2, one can see that the compounds measured fall into three main classes. The first class consists primarily of five membered hydrogen bonded rings of the type:



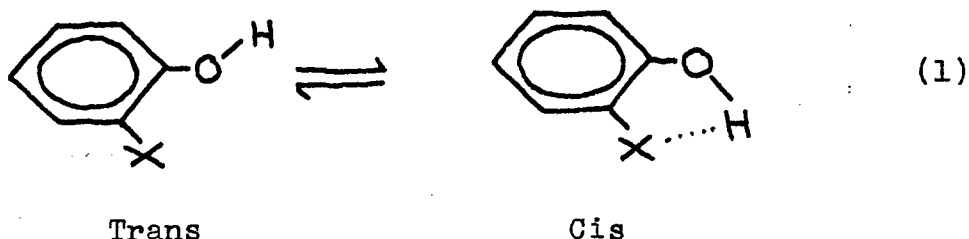
where X can be O, Cl, Br, I or F. The second group consists of five membered rings containing an -O-H...S bond, which appears to be stronger than the previous series. It is possible that the larger sulphur atom makes the distances for bonding more favourable. The third class consists of six membered rings with the hydrogen bonded to an oxygen or nitrogen atom, e.g. o-nitrophenol. The larger size of the ring and the directional nature of the donor orbitals favours a stronger hydrogen bond providing one assumes that the predominant term is electrostatic (35) (36).

J. R. Merrill (38) has recently published a correlation of  $\Delta\sigma_{OH}$  with  $\Delta\nu_{OH}$  for several substituted o-hydroxybenzophenones, and Gutowsky (39) has established a similar correlation of  $\Delta\sigma_{OH}$  with  $\Delta\nu_{C=O}$ , the change in carbonyl stretching frequency, for a series of compounds, with results similar to those in figure 2.

Two exceptions to the classes given above must be noted. o-Allylphenol has a  $6\frac{1}{2}$  membered ring with the hydrogen bond formed with the  $\pi$  electrons of the allyl group and is found in the weakly bonded first class. The large chemical shift obtained for o-bromobenzoic acid is believed to be due to the formation of a hydrogen bonded dimer rather than an intramolecular bond with the bromine. The chemical shift is approximately that which would be expected for a dimer (37) (11) and the infrared spectrum shows frequency shifts of 96 and 570  $\text{cm}^{-1}$  respectively. The first, a very weak bond, is that which would be expected for an -O-H...Br bond (21) (table 2), while the second is that expected for a dimer (11). One may conclude that even at concentrations of one mole % there is little formation of an intramolecular bond.

ii) Calculation of Enthalpies of Formation for the Intramolecular Hydrogen Bond in o-Halophenols.

The observable chemical shift for a compound containing a strong intramolecular hydrogen bond is that of the hydrogen bonded species (33) (34) (38), and the chemical shift is independent of concentration as long as there are no intermolecular contributions. However, for a weakly bonded species (the first class discussed in the previous section) at any concentration there will exist an equilibrium



which will contribute to an average chemical shift.

A further contribution will be obtained from any intermolecular bonding. By measuring the chemical shift ( $\delta_M$ ) over a range of concentrations one is able to obtain an extrapolated infinite dilution shift ( $\delta_{M\infty}$ ) which may be attributed to the equilibrium as in (1), since the extrapolation will eliminate intermolecular effects. Using the analysis of Gutowsky and Saika (8), one may express the infinite dilution shift  $\delta_{M\infty}$  as:

$$\delta_{M\infty} = \chi_T \delta_T + \chi_C \delta_C \quad (2)$$

where  $\chi_T$  = mole fraction of the phenol in the trans form.

$\chi_c$  = mole fraction of the phenol in the cis form.

$\delta_T$  = chemical shift of the trans form.

$\delta_c$  = chemical shift of the cis form.

$\delta_c$  and  $\delta_T$  are assumed to be invariant.

The equilibrium expression for (1) at any temperature may be written

$$K_{1(T)} = \frac{[\text{TRANS}]}{[\text{CIS}]} = \frac{[\chi_T]}{[\chi_c]} = \frac{[1 - \chi_c]}{[\chi_c]} \quad (3)$$

since  $\chi_T + \chi_c = 1$ . From (2), one obtains

$$\chi_c = \left\{ \frac{\delta_{\text{moo}} - \delta_T}{\delta_T + \delta_c} \right\} \quad (4)$$

Substituting for  $\chi_c$  in (3), an expression for the equilibrium constant  $K_{1(T)}$  at any temperature (T) is obtained in terms of  $\delta_T$ ,  $\delta_c$  and  $\delta_{\text{moo}}$ :

$$K_{1(T)} = \left\{ \frac{\delta_{\text{moo}} - \delta_c}{\delta_T - \delta_{\text{moo}}} \right\} \quad (5)$$

$\delta_{\text{moo}}$  is known from the extrapolations of figures 3, 4 and 5 for the compounds o-chloro, o-bromo and o-iodophenol. If one observes the slopes of the lines for o-fluorophenol

(figure 5), it is evident that they differ from those of the previous three compounds and in fact resemble the curve one obtains for phenol (33), where there is no possibility of an intramolecular hydrogen bond being formed. This was taken as evidence that the intramolecular bond formed, if any, is so weak that the previous analysis would not apply, since intermolecular effects are still considerable at 1 mole %, which is the limit of sensitivity for the spectrometer used.

For the other three phenols, lower temperatures will shift the equilibrium so that the concentration of the cis form is increased. At sufficiently low temperatures the phenol will be almost 100% cis form, which will give a value for  $\delta_c$ . In order to obtain a value for  $\delta_c$ ,  $\delta_{mo}$  for each phenol was plotted against temperature as in figure 6, and an extrapolation to the maximum value made. The results were also fitted to an equation of the type

$$\delta_{mo} = A + BT + CT^2 \quad (6)$$

where  $T$  = temperature  $^{\circ}\text{K}$

$A, B, C$  are constants to be determined.

It was possible to fit experimental values of  $\delta_{mo}$  to equation 6 within  $\pm .1$  cycles/sec for o-bromo and o-chlorophenol and to within  $\pm .2$  cycles/sec for o-iodophenol. The equations obtained were:



for o-bromophenol,

$$\delta_{m\infty} = 151.6 + (5.75 \times 10^{-2})T - (1.60 \times 10^{-4})T^2$$

for o-chlorophenol,

$$\delta_{m\infty} = 153.6 + (6.83 \times 10^{-2})T - (2.00 \times 10^{-4})T^2$$

and for o-iodophenol,

$$\delta_{m\infty} = 147.4 + (2.41 \times 10^{-2})T - (9.86 \times 10^{-5})T^2.$$

Using these equations, one may obtain an estimated value for  $\delta_c$ , since it is possible to determine the value for which the equation is a maximum; that is, when

$$\frac{d(\delta_{m\infty})}{d(T)} = 0$$

Having found the temperature at which  $\delta_{m\infty}$  is a maximum, one can substitute back into the equation to obtain  $\delta_{m\infty}(\text{max.})$ , which is approximately equal to  $\delta_c$ .

The results of this method are given below:

o-bromophenol:  $\delta_{m\infty}(\text{max.}) \approx \delta_c = 156.8$  cycles/sec at  $172^\circ\text{K}$

o-chlorophenol:  $\delta_{m\infty}(\text{max.}) \approx \delta_c = 159.5$  cycles/sec at  $171^\circ\text{K}$

o-iodophenol:  $\delta_{m\infty}(\text{max.}) \approx \delta_c = 148.9$  cycles/sec at  $121^\circ\text{K}$

Thus, in order to determine values for the equilibrium constant  $K_{1(T)}$ , it remains to evaluate  $\delta_T$ , the chemical shift of the trans form. In order to do this, one may make use of the following relationship:

$$\Delta F = \Delta H - T\Delta S = -RT \ln K_{1(T)} \quad (7)$$

According to Jaffe (38), entropy terms for these systems are very close to zero, so one may write

$$\Delta H \approx \Delta F = -RT \ln K_{1(\tau)} \quad (8)$$

A reasonable value for  $\delta_\tau$  will be that which makes (8) approximately constant for all measured temperatures. In addition, one then obtains a value for  $\Delta H$ , the enthalpy of formation of the hydrogen bond, which should be reasonably good. The results of this analysis for the three o-halophenols studied are given in Table 8. Values of  $K_{1(\tau)}$  at 25°C agree reasonably well with those of Baker (21), and also with those of Rossmly, Lüttke and Mecke, but not with those of Jones and Watkinson (23). However, n.m.r. data do not support Baker's contention that the -O-H...F bond is stronger than the -O-H...I bond in these phenols.

TABLE 8.

Values of  $K_{1(\tau)}$  and  $\Delta H$  for o-chloro, o-bromo and o-iodophenol.

## o-Chlorophenol

Temp., °K	$K_{1(\tau)}$	$\Delta H$ (cal mole <sup>-1</sup> )
380	1/23	2334
355	1/27	2320
341	1/30	2308
300	1/56	2392
272	1/91	2432

mean value  $\Delta H = 2356$  cal mole<sup>-1</sup>

$\delta_c = -159.5$  cycles/sec from cyclohexane

$\delta_T = +34$  cycles/sec from cyclohexane

## o-Bromophenol

Temp., °K	$K_{1(\tau)}$	$\Delta H$ (cal mole <sup>-1</sup> )
380	1/14	2011
341	1/22	2095
300	1/38	2161
272	1/58	2182
253	1/87	2254

mean value  $\Delta H = 2141$  cal mole<sup>-1</sup>

\*  $\delta_c = -157.2$  cycles/sec from cyclohexane

$\delta_T = -51.9$  cycles/sec from cyclohexane

TABLE 8 (cont'd)

## o-Iodophenol

Temp., °K	$K_{1(\tau)}$	$\Delta H$ (cal mole <sup>-1</sup> )
380	1/7.6	1529
355	1/9.5	1581
300	1/19	1748
272	1/26	1746

mean value  $\Delta H = 1650$  cal mole<sup>-1</sup>

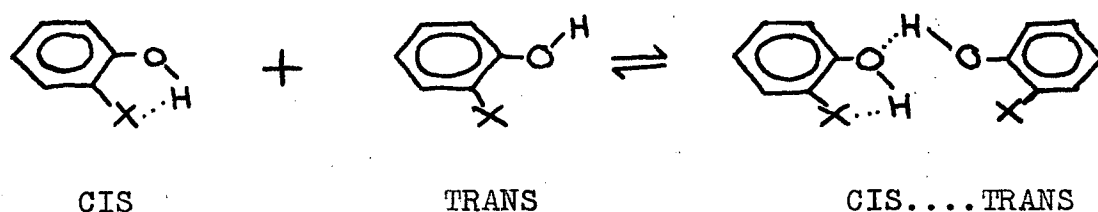
$\delta_c = -148.9$  cycles/sec from cyclohexane

$\delta_\tau = -84.9$  cycles/sec from cyclohexane

\* In order to obtain more reasonable values for o-bromophenol, it was found necessary to change the value of  $\delta_c$  by 0.4 cycles/sec to -157.2 cycles/sec. This is within the error in extrapolation. The value in  $\delta_\tau$  is extremely sensitive to small changes in  $\delta_c$ , since  $K_{1(\tau)}$  is so small. However,  $\Delta H$  is not appreciably altered by this, and therefore the values for  $\Delta H$  are more reliable than those for  $\delta_\tau$ .

iii) Calculation of Enthalpies of Formation of the Cis-trans Dimer for o-Halophenols.

If one assumes that the change in chemical shift from the extrapolated infinite dilution shift  $\delta_{m_{\infty}}$  at low concentrations is due principally to the formation of dimers of the type



a further analysis may be made to obtain enthalpies of formation for these dimers. It is considered that the concentration of the trans-trans dimer is always very much less than that of the cis-trans dimer, since the concentration of the trans form is low, as shown by the values for  $K_{\tau}$  in table 8. One further assumes that this value of  $K_{\tau}$  is applicable at concentrations of one mole %.

If there are initially 'a' moles of phenol and 'm<sub>s</sub>' moles of CS<sub>2</sub>, and one lets 'm<sub>c</sub>' = number of moles of cis form and 'm<sub>d</sub>' = number of moles of dimer, one may write as the number of moles present at equilibrium for each form:

	Moles	Mole Fraction	
Trans	$(a - m_c - m_d)$	$\frac{(a - m_c - m_d)}{(a - m_d) + m_s}$	
Cis	$(m_c - m_d)$	$\frac{(m_c - m_d)}{(a - m_d) + m_s}$	(1)
Cis...trans dimer	$m_d$	$\frac{m_d}{(a - m_d) + m_s}$	

One can then define an equilibrium constant  $K_{2(\tau)}$  in mole fraction units:

$$K_{2(\tau)} = \frac{[\text{cis...trans}]}{[\text{cis}][\text{trans}]} = \frac{m_d (a - m_d + m_c)}{[a - m_c - m_d][m_c - m_d]} \quad (2)$$

The following chemical shifts are needed:

$\delta_{m_c}$  = measured chemical shift at finite concentration 'c'

$\delta_T, \delta_c$  = chemical shifts of the trans and cis forms, respectively, as determined in section (ii)

$\delta_{Td}, \delta_{cd}$  = chemical shifts of the trans and cis forms in the dimer.

One may then write (8):

$$\delta_{m_c} = \chi_T \delta_T + \chi_c \delta_c + \chi_d \delta_{Td} + \chi_d \delta_{cd} \quad (3)$$

where  $\chi_T, \chi_c, \chi_d$  are respectively the mole fractions of trans, cis and dimer forms. Substituting, one obtains:

$$\delta_{Mc} = \left( \frac{a - m_c - m_d}{a - m_d} \right) \delta_T + \left( \frac{m_c - m_d}{a - m_d} \right) \delta_c + \left( \frac{m_d}{a - m_d} \right) \delta_{Td} + \left( \frac{m_d}{a - m_d} \right) \delta_{cd} \quad (4)$$

Assuming that the chemical shift of the cis proton in the dimer is approximately equal to that of the free cis proton; that is,  $\delta_{cd} \approx \delta_c$ , it is possible to rewrite (4) as:

$$\delta_{Mc} = \left( \frac{a - m_c - m_d}{a - m_d} \right) \delta_T + \left( \frac{m_c}{a - m_d} \right) \delta_c + \left( \frac{m_d}{a - m_d} \right) \delta_{Td} \quad (5)$$

From the previous section,

$$\delta_{M\infty} = \left( \frac{a - m_c}{a} \right) \delta_T + \left( \frac{m_c}{a} \right) \delta_c \quad (6)$$

Also,  $\delta_{Mc} \longrightarrow \delta_{M\infty}$  as  $m_d \longrightarrow 0$

Since  $m_d$  is small, if one assumes that  $a - m_d \approx a$  equation (5) may be rewritten as:

$$\delta_{Mc} \approx \delta_{M\infty} - \left( \frac{m_d}{a} \right) \delta_T + \left( \frac{m_d}{a} \right) \delta_{Td} \quad (7)$$

Solving for  $m_d$ ,

$$m_d = \left\{ \frac{\delta_{Mc} - \delta_{M\infty}}{(\delta_{Td} - \delta_T) + (\delta_{Mc} - \delta_{M\infty})} \right\} a \quad (8)$$

Let  $A = \left\{ \frac{\delta_{Mc} - \delta_{M\infty}}{(\delta_{Td} - \delta_T) + (\delta_{Mc} - \delta_{M\infty})} \right\}$

Substituting in the expression for  $K_2(\tau)$  (2),

$$K_2(\tau) = \frac{aA (a - aA + m_s)}{(a - m_c - aA) (m_c - aA)} \quad (9)$$

From the previous section (ii),

$$m_c = \frac{a}{1 + K_1(\tau)} \quad (10)$$

Substituting this in ( ), and neglecting terms in  $(K_1(\tau))^2$  and  $(A)^2$ , which are small, the following expression is obtained for  $K_2(\tau)$  :

$$K_2(\tau) = \frac{A (1 + 2K_1(\tau))}{K_1(\tau)} \left[ \frac{a + m_s}{a} \right] \quad (11)$$

With the exception of the chemical shift for  $\delta_{Td}$ , all values are known. From the work done in section (i), a reasonable value for a proton in an -O-H...O- hydrogen bond would be approximately 8 p.p.m. or 320 cycles/sec. Therefore, this value was used in calculating  $K_2(\tau)$ . Values for  $\delta_{Mc}$  were taken from figures, 3, 4 and 5 at one mole %. The analysis will not apply for the higher temperatures (108°C), since the concentration of the trans form is appreciable, which will make the assumptions made in deriving  $K_2(\tau)$  invalid.

By plotting  $\log K_2(\tau)$  against  $1/T$ , one obtains  $\Delta H$  from the slope of the straight line formed.



The graph of these results is given in figure 8. As would be expected,  $\Delta H$  for the dimer is more or less independent of a particular phenol, since the X substituent would play little part in dimer formation. The estimated accuracy is  $\pm .5$  kal mole<sup>-1</sup>. The values of 5.8, 5.6, 5.4 kcal-mole<sup>-1</sup> for the o-bromo, o-chloro, and o-iodophenol dimer are what would be expected for an -O-H...O hydrogen bond.

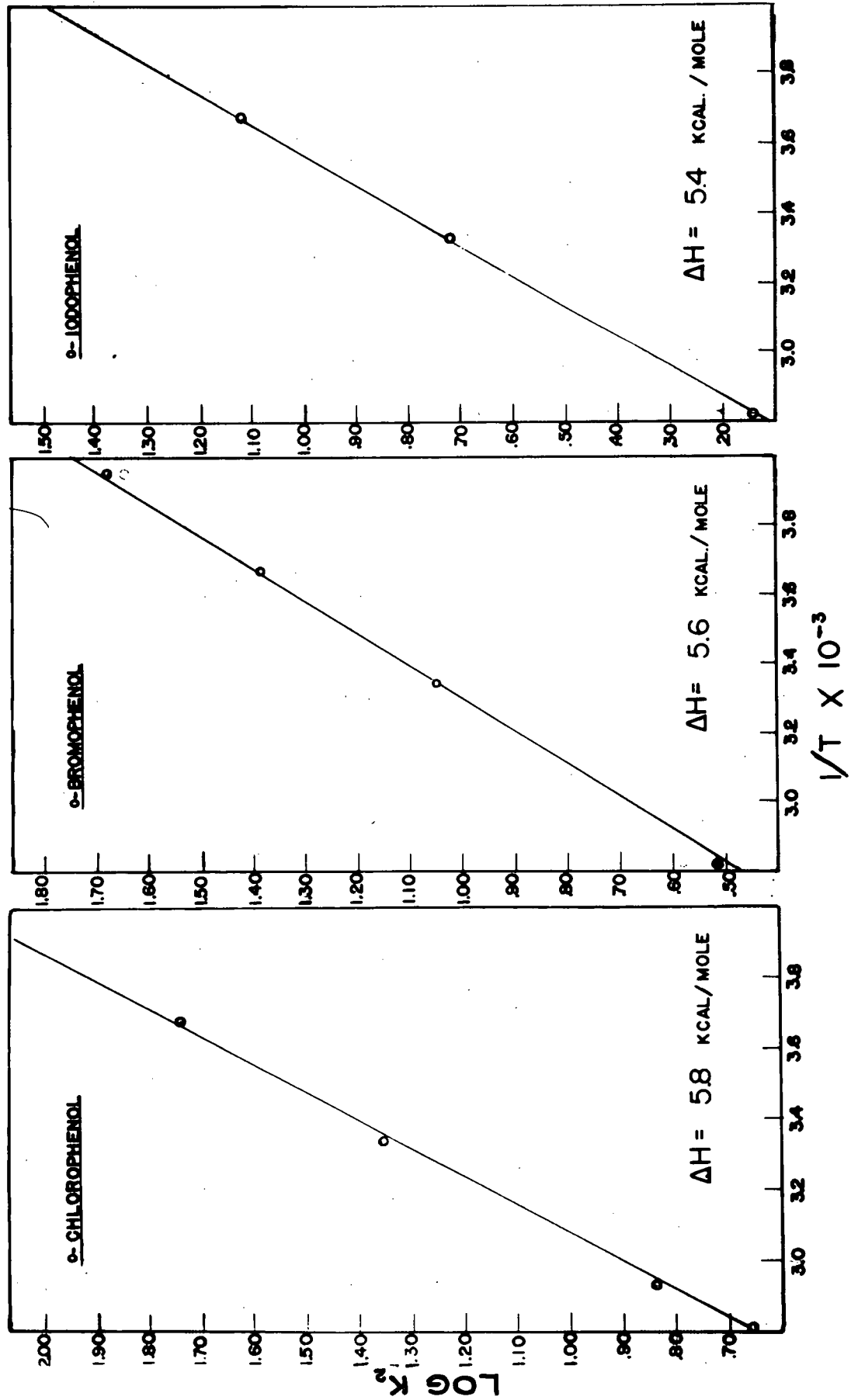


TABLE 9.

Compound	Temperature °K	$K_2(\tau)$
o-bromophenol	380	2.57
"	341	3.78
"	300	11.22
"	272	24.10
"	253	46.89
o-chlorophenol	355	4.54
"	341	7.04
"	300	23.48
"	272	55.08
o-iodophenol	380	1.5
"	355	1.52
"	300	5.24
"	272	12.9

iv) Variable Temperature Studies of 2,4,6-trisubstituted phenols.

As stated previously, the chemical shift of the -OH proton of the 2,4,6-trisubstituted phenols was found to be independent of concentration in the range studied (2-4 mole %). This may be attributed to the fact that the bulky effect of the halogens prevents intermolecular association.

It was thought that such compounds might also have a chemical shift which would be independent of solvent, but a study of 2,4,6-trichlorophenol showed that this was not the case, since a shift was observed. Although the chemical shift of the phenol proton is the same for inert solvents such as CS<sub>2</sub>, CCl<sub>4</sub> and cyclohexane (-4.32 p.p.m.), there is a shift in benzene to -3.83 p.p.m., in chloroform to -4.24 p.p.m., and in acetone, to 8.94 p.p.m., indicating that there is still solvent interaction.

In phenol itself there is a very strong concentration dependence (10) but the infinite dilution shift should be independent of temperature, since there is a symmetrical barrier for the rotation of the hydroxy group about the C-O bond (14). This should also be true for any phenol symmetrically substituted at the 2,6 positions. However, where the substituents at the 2,6 positions are different, and there is a possibility of hydrogen bonding or steric hindrance, the barrier to rotation will be unsymmetrical. This should result in a temperature dependent chemical shift

for the phenol proton, since the populations at each ortho position will vary with temperature. If the difference in energy between the two forms is larger, one should expect a large temperature dependence; while a smaller dependence would be expected if the energy difference is small. At higher temperatures the chemical shift will tend to become temperature independent.

An examination of the results for the four compounds studied (figure 7) will show that this is the result obtained. For 2-chloro-4,6-dibromophenol and 2-chloro-4,6-diiodophenol, where the difference in energy between the two hydrogen bonded forms is small, the chemical shift becomes independent of temperature at about 50° C. for 2-chloro-4,6-dibromophenol and at about 70°C. for the other. Since the energy difference is greater for the chloro-iodo compound, one would expect a constant chemical shift to occur at a higher temperature, as is the case.

For 2-fluoro-4,6-dibromophenol and 2-fluoro-4,6-diiodophenol, where the difference in energy is much greater, there is no indication that the measured chemical shift is tending to a constant value in the range studied. Baker (21) measured infra-red intensities for these compounds at various temperatures and reported similar behaviours.

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