INTERDIPOLE DISTANCES IN HYDROGEN BONDED COMPLEXES IN SOLUTION

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Abstract—Preliminary dipole moment work is reported which shows promise of estimating the interdipole distance between certain hydrogen bonded species in solution. The dipole moments of $CHX_s(X = Cl, I \text{ and } NO_s)$ have been determined in the solvents, cyclohexane and *p*-xylene and bromoform in cyclohexane.

INTRODUCTION

SEVERAL dipole studies have been made of the hydrogen bond employing phenols, alcohols and amines. Examples of the different types of results obtained in a strong and a weak hydrogen bonding solvent are given in Table 1.

Compounds	$\mu_{\rm D}$	$\mu_{\rm B}$	$\mu_{\rm D} - \mu_{\rm B}$
Anisole1	1.36	1.33	0.03
Phenol ¹	1.86	1.56	0.30
p-Nitrophenol ¹	5.43	5.05	0.38
Isobutanol	1·83ª	1.81*	0.02
Methylsalicylate ¹	2.57	2.53	0.04
Aniline ⁴	1.77	1.53	0.24
4-Nitro-1-naphthylamine ⁵	7.04	6.40	0.64
6-Nitro-2-naphthylamine ⁶	7.13	6.04	1.09
3-Nitro-1-naphthylamine	5.47	5.14	0.33
n-Butylamine ⁶	1.32	1.31	0.01
t-Butylamine ⁶	1.32	1.32	0.00

Table 1. Dipole moments in benzene (μ_B) and dioxan (μ_D) in debye units

The important features which emerge from Table 1 are:

- (i) For compounds which are strongly intramolecularly hydrogen bonded, such as methyl salicylate, there is negligible change in moment between benzene capable of only weak hydrogen bonding—and the strong hydrogen bonding solvent dioxan.¹
- ¹ J. H. Richards and S. Walker, Trans. Faraday Soc. 57, 399 (1961).
- ^a C. P. Smyth and W. S. Walls, J. Amer. Chem. Soc. 53, 2115 (1931).
- ³ P. C. Mahanti, J. Indian Chem. Soc. 6, 743 (1929).
- ⁴ J. W. Smith, *Electric Dipole Moments* Butterworths (1955).
- ⁵ J. H. Richards and S. Walker, Tetrahedron 20, 841 (1964).
- * A. V. Few and J. W. Smith, J. Chem. Soc. 2663 (1949).

(ii) Both phenols and aromatic amines have considerably higher moments in dioxan than in benzene. The $\mu_D - \mu_B$ values are particularly high when the molecule has appreciable resonance contributions from quinonoid forms as with 4-nitro-1- and 6-nitro-2-naphthylamines.⁵ This is to be contrasted with the behaviour of isobutanol, n-butylamine and tertiary butylamine⁶ in which no significant alteration in moment takes place between the two solvents.

From (ii) it would appear that when intermolecular hydrogen bonding takes place an appreciable redistribution of charge occurs only when the $-NH_2$ is directly attached to a conjugated system. Insufficient work has been carried out on the alcohols to draw the same conclusion. However, for the non-conjugated amines $\mu_D - \mu_B \sim 0$. A detailed study of the steric and mesomeric factors influencing the $\mu_D - \mu_B$ value of aromatic amines has been made by Smith and co-workers.⁷⁻¹⁰ Ibbitson *et al.*¹¹ have made similar studies in phenolic systems. In general, the high values of $\mu_D - \mu_B$ are closely related with the mesomeric effect in the phenols and aromatic amines.

On the whole, aromatic amines exhibit the highest charge redistribution with a strong hydrogen bonding solvent such as dioxan. When, however, aniline is measured in cyclohexane and benzene the moments are 1.49D and 1.51D respectively, and the difference is extremely small. Thus, even with an aromatic amine any hydrogen bonding to the π -electrons leads to almost negligible change in moment. The same conclusion may be deduced for alcohols and aliphatic amines from the following data.

	μ_{hexane}	$\mu_{\rm oyclohexane}$	$\mu_{\mathbf{B}}$
2-Propanol	1.6412		1.6418
t-Butanol	1.5612		1.5612
1-Pentanol	1.6718		1.6713
n-Butylamine	1.3314	1.3214	1.3215

It seemed that if there was no redistribution of charge due to hydrogen bonding of the alcohols and aliphatic amines with benzene and for aniline in benzene, then it would also be the case for the C—H in haloforms and trinitromethane in benzene since C—H of chloroform forms very weak hydrogen bonds.¹⁶ If then the increase in moment of the CHX₃ solute between the weakly hydrogen bonding solvent and cyclohexane could be attributed to an inductive effect (i.e. if the contributions from the charge transfer valence bond structures¹⁷ of the hydrogen bond were negligible), it would seem feasible to estimate the distance between the polarizing CHX₃ dipole and the π -electrons of the solvent. *p*-Xylene was chosen in preference to benzene

- ⁷ A. V. Few and J. W. Smith, J. Chem. Soc. 753 (1949).
- ⁹ J. W. Smith, J. Chem. Soc. 2532 (1950).
- * J. W. Smith, J. Chem. Soc. 109 (1953).
- ¹⁰ J. W. Smith and S. M. Walshaw, J. Chem. Soc. 3217 (1957).
- ¹¹ E. V. Goode and D. A. Ibbitson, J. Chem. Soc. 4265 (1960).
- ¹² C. Hennings, Z. Physik. Chem. B28, 267 (1935).
- 13 K. Higashi, Bull. Inst. Phys. Chem. Res., Tokyo, 11, 729 (1932).
- ¹⁴ E. G. Cowley, Nature, Lond. 168, 705 (1951).
- ¹⁸ B. C. Curran and G. K. Estok, J. Amer. Chem. Soc. 72, 4575 (1950).
- ¹⁶ G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* p. 197. W. H. Freeman and Co., San Francisco and London (1960).
- ¹⁷ C. A. Coulson, Research 149 (1957).

since it was considered that the steric effect of the methyls might tend to stabilize the position of a hydrogen bonded complex. In addition, the choice of $CHX_3(X = Cl, I, NO_2)$ was favoured by its being a symmetric-top molecule which, when hydrogen bonded, had its dipole perpendicular to the ring. Furthermore, since the moments of chloroform and iodoform differed so much from that of nitroform, this provided a means of indicating whether the change in moment between *p*-xylene and cyclohexane could be attributed to an inductive mechanism.

Dipole moments and results

For each system a range of 5–9 solutions was prepared up to a weight fraction of solute (w_2) of mainly 0.02, and the following precautions were taken:

(a) Chloroform and bromoform. About 30 ml solvent were weighed in a stoppered flask, an appropriate volume of liquid solute dispensed from an "Agla" micrometer syringe, and the flask reweighed.

(b) *Iodoform*. The dried crystals were weighed into the empty flask before the solvent was added, and the solutions kept in the dark until used.

(c) Nitroform. To exclude contact with atmospheric moisture the cold, dry crystals were added directly to the weighed amount of solvent, and the flask was reweighed.

To minimize change in composition, particularly in the iodoform solutions, the Guggenheim procedure¹⁸ was adopted, as this facilitated more rapid working. In addition, each solution was measured immediately after preparation. However, in order to check the validity of this method for these solutes and solvents, two systems were examined by the more traditional procedure employing the following equations:

$$\epsilon_{12} = \epsilon_1 + \alpha w_2, \quad v_{12} = v_1 + \beta w_2 \quad \text{and} \quad n_{12}^2 = n_1^2 + \nu w_2$$

where ϵ = dielectric constant, v = specific volume, n = refractive index and w = weight fraction. Subscript 1 is employed for the solvent, 2 for the solute and 12 for the solution.

To avoid giving undue weight to the results in the most dilute solutions α , β and ν are calculated from the following quotients:

$$\frac{\Sigma(\epsilon_{12} - \epsilon_1)}{\Sigma w_2} = \alpha, \qquad \frac{\Sigma(v_{12} - v_1)}{\Sigma w_2} = \beta \quad \text{and} \quad \frac{\Sigma(n_{12}^2 - n_1^2)}{\Sigma w_2} = \nu$$

For the two solutions the molar polarization at infinite dilution $P_{2\infty}$ was obtained from the equation:

$$P_{2\infty} = M_2 \{ 3\alpha v_1 / (\epsilon_1 + 2)^2 + (\epsilon_1 - 1) (v_1 + \beta) / (\epsilon_1 + 2) \}$$

and the dipole moment μ'' from the relationship:

$$\mu'' = 0.01281(P_0'T)^{1/2}D$$

where P_0' is the orientation polarization which is derived from the expression $P_0' = P_{2\infty} - R_D$; R_D , the molar refraction of solute for the sodium D line, is given by:

$$R_{\rm D} = M_2 \{ 3vv_1/(n_1^2 + 2)^2 + (n_1^2 - 1)(v_1 + \beta)/(n_1^2 + 2) \}$$

¹⁸ E. H. Guggenheim, Trans. Faraday Soc. 45, 714 (1949).

Seven dipole moments were evaluated by the Guggenheim method employing:

(i)
$$(\mu')^2 = \frac{10^{36}}{N} \cdot \frac{9kT}{4\pi} \cdot \frac{3}{(\epsilon_1 + 2)^2} \cdot \frac{M_2}{d_1} (\alpha - \nu)$$

and also:

(ii)
$$P_0 = \frac{M_2}{d_1} \left[\frac{3\alpha}{(\epsilon_1 + 2)^2} - \frac{3\nu}{(n_1^2 + 2)^2} \right] + C$$

and Smith¹⁹ showed C to be:

$$C = \frac{M_2}{d_2} \left[\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right]$$

then:

 $\mu = 0.01281\sqrt{P_0T}$

Table 2 gives weight fractions, dielectric constants, specific volumes and the squares of the refractive indices. The polarization data $(\mu, \mu' \text{ and } \mu'')$ are in Table 3. On comparison of the μ , μ' and μ'' values it is apparent that the Smith correction factor is negligible for these systems and that all three values correspond within experimental error.

The literature values of the dipole moments of the CHX_3 solutes in a variety of solvents are given in Table 4. Unfortunately, in most cases, the variation in values by different workers made it necessary to re-measure the quoted ones since the dipole moment differences in the two solvents were anticipated to be small.

TABLE 2. DIELECTRIC CONSTANTS, SPECIFIC VOLUMES AND REFRACTIVE						
indices squared data for CHX_s (X = Cl, Br, I, NO _s)						
Solutes in cyclohexane and <i>p</i> -xylene						

		2			
Solute	Solvent	10 ⁵ w ₂	€18	v12	n ² ₁₂
Chloroform	Cyclohexane	0	2 ·0199		2.02647
	,	527	2.0252		2.02650
		750	2.0272		2.02641
		994	2.0302	_	2.02647
		1250	2.0322		2.02632
		1540	2.0359		2.02630
		1859	2.0395	<i>—</i>	2.02647
		2103	2.0424		_
		3693	2.0563	—	—
Chloroform	p-Xylene	0	2.2711	_	2.23000
		538	2.2775	_	2.22.308
		645	2.2789	_	2.22902
		1018	2.2831		2.22887
		1238	2·2863		2·22851
		1556	2.2915	_	2.22851
		1836	2.2.345		2.22815
		2074	2.2985		2.22800
		3803	2-3205	_	2.22627

¹⁹ J. W. Smith, Trans. Faraday Soc. 46, 394 (1950).

Solutes in cyclohexane and p-xylene.							
Solute	Solvent	10 ⁵ w ₂	€12	v_{12}	n12 ²		
Bromoform	Cyclohexane	0	2.0199		2.02655		
		396	2.0217		2.02701		
		576	2.0220		2.02721		
		795	2.0234		2.02729		
		933	2.0240		2.02749		
		1462	2.0266		2.02787		
		1748	2.0277		2.02822		
Iodoform	Cyclohexane	0	2.0199	1.28974	2.02632		
		368	2.0211				
		380	2.0213				
		391		1.28596			
		414	2.0216				
		439	2.0214		2.02698		
		662			2.02792		
		694	2.0225		<u></u>		
		819	-	1.28151			
		882	2.0230				
		943			2.02812		
		1111	2.0243				
		1239			2.02892		
		1243	2.0240				
		1484	2.0252				
		1501	2.0252		2.02940		
		2048	_		2.03074		
Iodoform	p-Xylene	0	2.2708	1.16406	2.23002		
		355			2.23069		
		435		1.16004			
		461	2.2726				
		602			2.23111		
		718			2.23165		
		760	2.2741				
		913		1.15603			
		919			2.23180		
		1148	2.2755				
		1329			2.23278		
		1670			2.23338		
		1810	2.2784		—		
Nitroform	Cyclohexane	0	2.0199		2.02641		
		394	2.0342	-	2.02621		
		763	2.0461		2.02593		
		1175	2.0599	_	2.02573		
		1615	2.0792		2.02547		
Nitroform	<i>p</i> -Xylene	0	2.2700		2.22968		
	-	402	2.2913		2.22902		
		784	2.3112		2.22836		
		1200	2.3313		2.22797		
		1646	2.3526		2.22771		
		2015	2.3718		2.22714		

TABLE 2 (contd.)

Solute	Solvent	α	v	μ' (D)	P ₀ (cm. ³)	C (cm.³)	P + C (cm. ³)	μ (D)	μø
CHCI _s	Cyclohexane	1.024	0.000	1.20	29.32	-0.10	29.22	1.196	
-	p-Xylene	1.274	-0.102	1.24	31.56	0.55	32-11	1·25a	
CHBr _s	Cyclohexane p-Xylene*	0.440	0-098	1.01	20.71	−0 ·11	20.60	1.004	
CHI,	Cyclohexane	0.359	0.207	0.83	13.97	-0.11	13.86	0.82	0.82
-	p-Xylene	0.418	0.202	0.88	15.87	0.65	16.52	0.89,	0.89
CH(NO ₃) ₃	Cyclohexane p-Xylene	3·540 5·129	-0·056 -0·136	2·52 2·72	130·1 152·3	0·11 0·60	130-01 152-9	2·52₂ 2·73₅	

TABLE 3. POLARIZATION DATA AND μ , μ' , and μ'' values

* The moment of bromoform in *p*-xylene was not determined because the difference in moment of chloroform in *p*-xylene and cyclohexane was of the same order as for iodoform, and the moment of bromoform in cyclohexane came in between those of the other two in this solvent.

Solute	Gaseous	Solvent				
	state	n-hexane	benzene	carbon tetrachloride		
Chloroform	1.00-1.07	1.06-1.20	1.11-1.28	1.00-1.21		
Bromoform	1.00		1.00-1.02	1.00		
Iodoform		1.01	0.80-1.16	1.00		
Nitroform			2.63	2.73		

TABLE 4. THE RANGE OF LITERATURE DIPOLE MOMENT VALUES¹⁶ (IN D) OF CHX₃ (X = Cl, Br, I and NO₂) in the gaseous state and in solvents

DISCUSSION

It is assumed that the CHX₃ solute molecules exhibit no specific interaction with cyclohexane, and the moment in this solvent has been taken to be that of the non-interacting dipole CHX₃ in solution. This value should then correspond with μ in equation 1. The difference in moment between the solute in *p*-xylene and cyclohexane—termed $\Delta\mu$ —in the absence of any redistribution of charge due to the hydrogen bond itself as a result of charge transfer structures should equal the moment induced (μ_{ind}) by the polarizing CHX₃ dipole in the π -electrons. The CHX₃ dipole has been taken to lie symmetrically along the six-fold axis of symmetry with the hydrogen nearest the ring.[†] The distance along this axis from the centre of the π -electron cloud to the centre of the CHX₃ dipole is the value of r in:

$$\mu_{\rm ind} = \frac{2\mu v(\epsilon + 2)}{3\epsilon r^3} \tag{1}$$

which is the equation employed by Frank²⁰ when $\theta = 0^{\circ}$. ϵ is the dielectric constant (2.27) of *p*-xylene at 25°, and ν was taken to be the polarizability of the π -electron

† NMR measurements on the proton in HCX₃ (X = I, NO₂) confirmed that the proton was hydrogen bonded. This work will be published later in conjunction with Dr. J. Homer. ³⁰ F. C. Frank, *Proc. Roy. Soc.* A152, 171 (1936). cloud perpendicular to the ring and was approximated to the value for benzene (i.e. the b_3 value of 7.33×10^{-24} cc).²¹

(i) The hydrogen-bonded complex between p-xylene and chloroform. The value of μ was taken as 1.20D—the value in cyclohexane and the estimated induced moments for various values of r are given in Table 5.

TABLE	5. Calc chlorof	ORM SYST	NDUCED TEM FOR V r Value	MOMENTS VARIOUS S	FOR THE VALUES C	B <i>p</i> -Xylene)f <i>f</i>
	3	3.5	4 ∙0	4.5	5∙0	5·5Å
μ_{ind}	0.41	0.26	0.17	0.12	0.09	0·07 <i>D</i>

The value of $\Delta\mu$ is 0.06 \pm 0.02D, and if $\Delta\mu$ is taken to be equal to μ_{ind} , then the interdipole distance would be ~ 5.5 Å. However, the $\Delta \mu$ values are based on all the chloroform being complexed which is most improbable. It follows that if the $\Delta \mu$ values were obtained from a three component system with the molecules present at low concentration in an inert solvent such as cyclohexane and the association constant was determined, then the true value of $\Delta \mu$ could be estimated. On equating $\Delta \mu$ and μ_{ind} a lower value of r would result.

(ii) The hydrogen-bonded complex between p-xylene and iodoform. μ was taken to be 0.82D, and the estimated induced moments for various values of r are given in Table 6.

SYSTEM FOR VARIOUS VALUES OF r r Values 5-5Å 3 3.5 4·0 4.5 5.0 0.18 0.12 0.08 0.06 0.05D 0.28 μ_{ind}

TABLE 6. CALCULATED INDUCED MOMENTS FOR THE p-XYLENE-IODOFORM

The value of $\Delta\mu$ is 0.08 \pm 0.02*D*, and hence the interdipole distance is probably less than ~ 5 Å.

(iii) The hydrogen-bonded complex between p-xylene and nitroform. μ was taken 'o be 2.52D, and the estimated induced moments are given in Table 7.

Fable 7. (Calculati Si	ED INDUC YSTEM FOI	ED MOME R VARIOU r Values	NTS FOR S VALUES	тне <i>р</i> -хі оf <i>r</i>	'LENE-NITROI	'ORM
	3	3.5	4,0	4 ·5	5,0	5·5Å	
μ_{ind}	0.86	0.54	0.36	0.25	0.19	0·14D	

The value of $\Delta \mu$ is 0.21D and, therefore, the interdipole distance is probably less than ~ 5 Å.

¹¹ Physical Methods In Organic Chemistry (Edited by A. Weissberger) Vol. 1, Part 3, p. 2493. Interscience, N.Y. (1959).

CONCLUSIONS

The difference in moment of the CHX₃ solute in an interacting solvent (*p*-xylene) and the non-interacting cyclohexane may be accounted for by the inductive effect of the C—X dipoles on the solvent. It would seem unlikely that there is any appreciable redistribution of charge as a direct result of hydrogen bond formation. This is strongly supported by the approximate proportionality between the inducing dipole and that of the difference in moment when measured in the hydrogen bonding solvent and cyclohexane. Although the interdipole distances would not be expected to be identical for the CHCl₃, CHI₃ and CH(NO₂)₃ hydrogen bonded to the π -electrons of *p*-xylene, the fact that they come out of the same order gives support to the procedure. However, the interdipole distance evaluated should be regarded as greater than that existing in the complex, since in *p*-xylene not all the HCX₃ molecules would be complexed. On the whole, this would diminish the inductive contribution and hence increase the estimated value of the interdipole distance.

The results indicate a certain potential for this approach with regard to an estimation of the distance between the hydrogen bonding species. Such values, of course, are interdipole distances, but for suitably chosen systems ought to yield some appreciation of the distances apart of the complexed species. Initially, at least, the hydrogen group should not be conjugated with the remainder of the molecule. Ideally, three component systems ought to be employed with the interacting molecules present at low concentration in an inert solvent such as cyclohexane. In addition, the association constant ought to be evaluated and the appropriate inductive contribution to the resulting dipole moment of the complex estimated. From Table 7 it follows that if the inducing dipole is of a similar magnitude to that of nitroform, then the ensuing values of r could be significant to about ± 0.1 Å.

It is now intended to follow up this work by examining mixtures of nitroform, *p*-xylene and cyclohexane and then to extend the procedure to other systems.

EXPERIMENTAL

Materials

(1) Chloroform. Commercial grade CHCl_s was purified by the method of Smyth and Rogers;²² i.e. washing with conc H_2SO_4 was followed by water, alkali and further water washings. After standing over anhydrous CaCl₂, it was refluxed over and finally distilled from P_2O_5 . This was stable for many weeks in a dark, ground-stoppered bottle.

(2) *Iodoform*. Commercial grade iodoform was recrystallized once from absolute alcohol, filtered and briefly washed with ice-cold acetone and dried in the dark at 56° under partial vacuum for about 1 hr.

(3) Bromoform was treated in the same manner as $CHCl_3$, and this left more than 1% of unidentifiable impurities. These were considerably diminished—as estimated by gas chromatographic analysis—by two elutions through an alumina column.

(4) Nitroform. The preparation was based on the method of Chattaway and Harrison.³³ Tetranitromethane (5 g) were shaken for 1 hr with a solution of 25 g K₄Fe(CN)₆ in 75 ml distilled water. The yellow precipitate of the potassium salt of nitroform was filtered, briefly washed with alcohol and dried for 30 min under partial vacuum. The dry salt was suspended in 10–15 ml light petroleum (60–80°) and gently shaken during the slow addition of 10 ml conc H₂SO₄ from a burette. The free nitroform released was extracted in the solvent, and after separation from the acid layer was crystallized from light petroleum at -50° in an acetone-solid CO₂ freezing mixture.³⁴ After 2 further

22 C. P. Smyth and H. E. Rogers, J. Amer. Chem. Soc. 52, 1824-30 (1930).

²³ F. P. Chattaway and F. M. Harrison, J. Chem. Soc. 171 (1916).

²⁴ H. Shechter and H. L. Cates, J. Org. Chem. 26, 51 (1961).

recrystallizations the residual light petroleum was removed in a vacuum desiccator. The white crystalline nitroform (m.p. 27°) was stored in a stoppered bottle in a small vacuum desiccator at 0° and used the following day.

The cyclohexane (spectrosol) and p-xylene (analaR) were purified by refluxing over sodium and distilled from a 20-plate column.

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