The Electric Dipole Moments of Some Hydrogen-bonded Complexes.

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Measurements have been made of the changes of electric dipole moment ($\Delta\mu$) which occur when trimethylamine forms complexes with weakly acidic substances in *cyclo*hexane solution. The change is about 1·0 D for the amine with phenol, the positive pole being on the nitrogen atom. This indicates a contribution of not more than 10% from the structure $\mathrm{O^{-}\ H{-}N^{+}}\!\leqslant$, which is roughly what might be expected from the electronegativities of the atoms, and which confirms that the hydrogen-bond proper is largely ionic. For *p*-cresol the change is less (0·9 D), while for *p*-chlorophenol it is greater (1·26 D); so these moment changes, the $-\Delta H$ values (preceding paper), and the acid dissociation constants in water all increase together, and presumably are due to increase of the O–H bond moment in this order.

In general there is fairly good proportionality between $(\Delta\mu)^2$ and K, the association constant for the complex; this confirms the observation previously reported that the association constant is greater for β-naphthol than for α-naphthol although the acid dissociation constant in water is smaller.

In the preceding paper, approximate values were reported for the association constants, K, for complex formation in *cyclo*hexane solution between trimethylamine and various substances containing a more or less acidic hydrogen atom. In this paper, these are combined with electric polarisation values to give the dipole moments of the complexes. The significance of the values so obtained is considered.

EXPERIMENTAL

Method of expressing and of using the Polarisation Results.—Suppose the initial solution contains a moles of trimethylamine, b of the " acidic " substance, and s of *cyclo*hexane. If, after reaction has taken place, x moles of the 1 : 1 complex are formed, the total number of moles in solution is s of *cyclo*hexane, $a - x$ of trimethylamine, $b - x$ of acidic component, and x of complex, *i.e.*, a total of $a + b + s - x$.

From these, the respective molar fractions of each substance may be obtained. If we assume that molar fractions can be taken as the active masses of each reactant, which is not exactly true but is sufficiently so for our purposes (see preceding paper), the mass action equilibrium constant K is given by

$$K = \frac{x}{(a - x)(b - x)} \times (a + b + s - x)$$

By arranging this as a quadratic equation in x, and, bearing in mind the uncertainties in the K values as obtained in the previous paper, we may assume, K being of the order 75 to 2000 when so expressed, that $K + 1 \approx K$, whence

$$x = [K(a + b) + s - \{[K(a + b) + s]^2 - 4Kab\}^{\frac{1}{2}}]/2K$$

Using the values of x so derived, we may obtain the weight fractions of each molecular species present at equilibrium. Let these be denoted by w_1, w_2, w_3, and w_4 for *cyclo*hexane, trimethylamine, acidic component, and complex, respectively. We may write the total specific polarisation ${}_Tp$ (that is, the sum of the distortion and the orientation polarisations) for the solution as

$${}_Tp = (\varepsilon - 1)v/(\varepsilon + 2) = w_1\,{}_Tp_1 + w_2\,{}_Tp_2 + w_3\,{}_Tp_3 + w_4\,{}_Tp_4$$

where ε is the observed dielectric constant for the solution and v the specific volume. ${}_Tp_1$, etc., represent the total specific polarisations for each component. ${}_Tp_1$ is obtained, as $v_1(\varepsilon_1 - 1)/(\varepsilon_1 + 2)$, by direct observations on the solvent. ${}_Tp_2$ is taken to be 0·5994 c.c. from work by Le Fèvre (*Trans. Faraday Soc.*, 1947, **43**, 374). ${}_Tp_3$ can be obtained from the literature, but for phenol and for triphenylmethanol it has been redetermined. Hence, ${}_Tp_4$ can be calculated and thence the total *molar* polarisation ${}_TP_4 = (M_2 + M_3)\,{}_Tp_4$, where M_2 is the molecular weight of species whose weight fraction is w_2, etc. The molar electron polarisation of the complex may be taken as the sum of those for its constituents, *i.e.*, ${}_EP_4 = {}_EP_2 + {}_EP_3$ which are available in the literature. Thus, the molar orientation polarisation, ${}_OP_4$, for the complex is obtained as ${}_TP_4 - {}_EP_4$, and so the moment of the complex as $\mu = 0{\cdot}2212({}_OP_4)^{\frac{1}{2}}$.

The moments obtained for each of three or four separate solutions are averaged. The errors quoted are obtained by considering the scatter of these values, on the assumption that the K value is definitive, and therefore they reflect only the uncertainties of the polarisation measurements.

As already mentioned, the electric dipole moments of phenol and of triphenylmethanol were also measured to check existing data. The dielectric constants, ε, specific volumes, v, and the differences of the refractive indices from that of the pure solvent, Δn, were measured for a series of benzene solutions containing various weight fractions, w, of the solute; and they were used for calculating the moments in the usual way (see Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417). The molar electron polarisations were also calculated, as ${}_EP = 10^{-5}M(29{,}312\beta + 57{,}145\gamma + 33{,}566)$, β and γ being the gradients of the v–w, and the n–w plots, respectively.

Apparatus and Techniques.—The dielectric constants were measured by means of the apparatus and technique described by Hill and Sutton (*J.*, 1953, 1482). Specific volumes were measured by means of a Sprengel–Ostwald type pyknometer. Refractive index differences were measured on a Pulfrich refractometer.

Solutions were made up as follows. The solid solute was weighed into a conical flask having a well-fitting ground-glass stopper. The *cyclo*hexane was added to this and the flask re-weighed. When solution was complete, about 2 ml. of a 5% solution of trimethylamine in *cyclo*hexane were added, and the flask again weighed. The mixture was transferred to the dielectric cell by replacing the stopper by a cork bearing an inverted U-tube and a short capillary connected to the dry air supply. The concentration of trimethylamine was back-titrated acidimetrically in a weighed amount of solution taken from the dielectric cell immediately after measurement.

Purification of Materials.—*cyclo*Hexane was purified as described in the preceding paper save that the passage through activated charcoal was omitted, and instead it was subjected to two successive fractional freezing processes in which the residual one-sixth was rejected each time.

Benzene (" AnalaR ") was purified by triple fractional freezing.

Both *cyclo*hexane and benzene were dried (P_2O_5), and were then distilled from fresh pentoxide in a stream of dry air.

p-*Fluorophenol.* A specimen supplied by Imperial Chemical Industries Limited was distilled in an all-glass apparatus, the fraction of b. p. 184·5—186° being collected. This was crystallised and was stored in a desiccator (P_2O_5) until required [m. p. 48·3° (cf. 48·2°, Swartz, *J. Chim. phys.*, 1919, **17**, 26)].

Other materials were purified as described in the preceding paper. The results are shown in Tables 1 and 2.

TABLE 1. *Electric dipole moments of individual compounds in benzene.*

Phenol

w	ε	v	Δn
0·002483	2·27733	1·14438	0·000209
0·004138	2·28315	1·14388	0·000223
0·006288	2·28912	1·14340	0·000327
0·007794	2·29344	1·14305	0·000404
0·008535	2·29494	1·14292	0·000494
0·010432	2·30046	1·14246	0·000523
0·014840	2·31449	1·14132	0·000784

Whence, $\varepsilon = 2{\cdot}2710 + 2{\cdot}84\,w$; $v = 1{\cdot}14485 - 0{\cdot}228\,w$; $n = 0{\cdot}000018 + 0{\cdot}0483\,w$
$_0P = 48{\cdot}09$ c.c.; $_EP = 27{\cdot}90$ c.c.; $\mu = 1{\cdot}53(4)$ D.

Triphenylmethanol

w	ε	v	Δn
0·002602	2·2763	1·14411	0·000135
0·004111	2·2785	1·14383	0·000412
0·006121	2·2809	1·14317	0·000602
0·001737	2·2755	—	0·000105

Whence, $\varepsilon = 2{\cdot}2732 + 1{\cdot}240\,w$; $v = 1{\cdot}14493 - 0{\cdot}286\,w$; $n = 0{\cdot}000118 + 0{\cdot}1176\,w$
$_0P = 43{\cdot}93$ c.c.; $_EP = 83{\cdot}05$ c.c.; $\mu = 1{\cdot}46(6)$ D.

Smyth and Dornte reported a value of 2·11 (*J. Amer. Chem. Soc.*, 1931, **53**, 546); recalculation from their observations gives 1·64 D.

TABLE 2. *Electric dipole moments of complexes.*

s	a	b	ε	v	x	$_TP_4$
		Phenol–trimethylamine complex				
0·44677	0·001606	0·002278	2·0479	1·2836	0·001098	260·3
0·46904	0·003662	0·004328	2·0851	1·2826	0·002577	262·1
0·48080	0·001797	0·002010	2·0449	1·2840	0·001088	267·6
*cyclo*Hexane		—	2·0139	1·2849	—	—

$K = 800 \pm 200$; $_Tp_3 = 0{\cdot}8081$ c.c.; $_EP_3 = 27{\cdot}90$ c.c.
Hence, average $_TP_4 = 263{\cdot}3$ c.c.; $\mu = 3{\cdot}24 \pm 0{\cdot}03$ D.

s	a	b	ε	v	x	$_TP_4$
		p-*Cresol–trimethylamine complex*				
0·474971	0·001661	0·002108	2·0146	1·2837	0·000977	244·6
0·472827	0·001725	0·003303	2·0556	1·2827	0·001247	270·0
0·521781	0·002222	0·003711	2·0578	1·2826	0·001578	259·3
*cyclo*Hexane		—	2·0141	1·2848	—	—
0·450732	0·001778	0·002275	2·0472	1·2835	0·001089	256·4
0·442700	0·001596	0·001383	2·0347	1·2842	0·000742	234·7
0·482380	0·001477	0·002080	2·0399	1·2838	0·000884	250·7
*cyclo*Hexane		—	2·0141	1·2849	—	—

$K = 600 \pm 200$; $_Tp_3 = 0{\cdot}7571$;* $_EP_3 = 31{\cdot}3$ c.c.*
Hence, average $_TP_4 = 252{\cdot}6$ c.c.; $\mu = 3{\cdot}13 \pm 0{\cdot}06$ D.

s	a	b	ε	v	x	$_TP_4$
		o-*Cresol–trimethylamine complex*				
0·479932	0·001832	0·001234	2·0323	1·2848	0·000737	240·2
0·445901	0·001609	0·001444	2·0352	1·2843	0·000787	237·8
0·496711	0·001816	0·001992	2·0388	1·2839	0·001018	237·1
*cyclo*Hexane		—	2·0142	1·2850	—	—

$K = 650 \pm 100$; $_Tp_3 = 0{\cdot}6652$ c.c.;* $_EP_3 = 31{\cdot}3$ c.c.*
Hence, average $_TP_4 = 238{\cdot}4$ c.c.; $\mu = 3{\cdot}02 \pm 0{\cdot}02$ D.

s	a	b	ε	v	x	$_TP_4$
		α-*Naphthol–trimethylamine complex*				
0·469264	0·001107	0·000242	2·0201	1·2921	0·000162	261·4
0·470012	0·001216	0·000408	2·0230	1·2920	0·000272	264·6
0·489603	0·001154	0·000352	2·0222	1·2921	0·000231	275·9
*cyclo*Hexane		—	2·0149	1·2922	—	—

$K = 1000 \pm 200$; $_Tp_3 = 0{\cdot}5935$ c.c.;† $_EP_3 = 45{\cdot}5$ c.c.†
Hence, average $_TP_4 = 267{\cdot}3$ c.c.; $\mu = 3{\cdot}14 \pm 0{\cdot}05$ D.

TABLE 2. (*Continued.*)

s	*a*	*b*	ε	*v*	*x*	${}_TP_4$
		β-Naphthol–trimethylamine complex				
0·477239	0·000890	0·000402	2·0221	1·2919	0·000291	364·4
0·490948	0·001029	0·000438	2·0231	1·2917	0·000328	371·6
*cyclo*Hexane		—	2·0150	1·2922	—	—
0·467755	0·001033	0·000448	2·0254	1·2919	0·000310	348·1
*cyclo*Hexane		—	2·0150	1·2922	—	—

$K = 2100 \pm 400$; ${}_Tp_3 = 0·6568$ c.c.;† ${}_EP_3 = 45·5$ .c.c.†
Hence, average ${}_TP_4 = 361·4$ c.c.; $\mu = 3·80 \pm 0·08$ D.

s	*a*	*b*	ε	*v*	*x*	${}_TP_4$
		p-*Chlorophenol–trimethylamine complex*				
0·470831	0·003213	0·003720	2·1334	1·2897	0·002391	436·44
0·472245	0·003213	0·003577	2·1296	1·2904	0·002533	417·53
0·437883	0·003372	0·003949	2·1660	1·2892	0·003359	413·1
*cyclo*Hexane		—	2·0170	1·2950	—	—

$K = 1700 \pm 300$; ${}_Tp_3 = 1·0859$ c.c.;* ${}_EP_3 = 31·6$ c.c.*
Hence, average ${}_TP_4 = 422·3$ c.c.; $\mu = 4·30 \pm 0·08$ D.

s	*a*	*b*	ε	*v*	*x*	${}_TP_4$
		p-*Fluorophenol–trimethylamine complex*				
0·448273	0·001753	0·000941	2·0445	1·2844	0·000746	369·7
0·454988	0·001154	0·000801	2·0380	1·2844	0·000554	381·4
0·463336	0·001541	0·000838	2·0397	1·2843	0·000643	365·1
*cyclo*Hexane		—	2·0142	1·2851	—	—

K (assumed) $= 1700$; ${}_Tp_3 = 1·0695$ c.c.;‡ ${}_EP_3 = 38·6$ c.c.‡
Hence, average ${}_TP_4 = 372·1$ c.c.; $\mu = 3·93 \pm 0·04$ D.

s	*a*	*b*	ε	*v*	*x*	${}_TP_4$
		Indole–trimethylamine complex				
0·470194	0·002428	0·002549	2·0469	1·2828	0·0006263	214·1
0·487530	0·001996	0·003123	2·0532	1·2823	0·0006084	261·7
0·470423	0·001751	0·004416	2·0665	1·2807	0·0007029	218·1
*cyclo*Hexane		—	2·0140	1·2848	—	—
0·464169	0·001681	0·002370	2·0455	1·2832	0·0004391	263·3
*cyclo*Hexane		—	2·0142	1·2851	—	—

$K = 85$; ${}_Tp_3 = 1·0452$ c.c.;§ ${}_EP_3 = 36·5$ c.c.§
Hence, average ${}_TP_4 = 239·3$ c.c.; $\mu = 2·99 \pm 0·18$ D.

s	*a*	*b*	ε	*v*	*x*	${}_TP_4$
		Triphenylmethanol–trimethylamine complex				
0·504443	0·000783	0·000389	2·0185	1·2913	0·0000535	161·1
0·497091	0·001051	0·000494	2·0197	1·2911	0·0000868	162·6
0·474395	0·001029	0·000581	2·0204	1·2908	0·0001027	151·8
*cyclo*Hexane		—	2·0149	1·2921	—	—

$K = 110 \pm 20$; ${}_Tp_3 = 0·4878$ c.c.; ${}_EP_3 = 83·05$.
Hence, average ${}_TP_4 = 158·5$ c.c.; $\mu = 1·65 \pm 0·06$ D.

* Donle and Gehrckens, *Z. phys. Chem.*, 1932, *B*, **18**, 316.
† Higashi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1933, **12**, 780.
‡ Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.
§ Cowley and Partington, *J.*, 1936, 47.

DISCUSSION

The results obtained, together with other relevant matter, are shown in Table 3. From the gross moment of the complex, the moments of trimethylamine and of the acidic component, and from a knowledge of the directions of these moments relative to their

TABLE 3.

Acid	μ_{acid}	$\mu_{complex}$	$\Delta\bar{\mu}$	$\Delta\mu$	K	$10^{10}k$
β-Naphthol	1·53	3·80 ± 0·08	—	1·41	2100 ± 400	1·17
p-Chlorophenol	2·22	4·30 ± 0·08	1·26	1·22	1700 ± 300	1·32 *
α-Naphthol	1·41	3·41 ± 0·05	—	0·87	1000 ± 200	1·40
Phenol	1·53	3·24 ± 0·03	1·00	0·84	800 ± 200	1·10
o-Cresol	1·41	$3·02_5$ ± 0·02	—	0·75	650 ± 100	0·63
p-Cresol	1·57	3·13 ± 0·06	0·91	0·70	600 ± 100	0·67
Triphenylmethanol	1·46	1·65 ± 0·06	—	–0·67	110 ± 20	—
Indole	2·05	2·99 ± 0·18	—	(0·08)	85 ± 15	—

* In aqueous ethanol (30% ethanol by volume), Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.
Electric dipole moment values are from Wesson, " Tables of Electric Dipole Moments," Massachusetts Institute of Technology Press, 1948.

respective atomic frameworks, it should be possible to calculate the vector changes of dipole moment which occur when the complex is formed. This is, in fact, practicable if the direction of the moment of the acidic component can be taken as fixed relative to the –X–H bond. Otherwise, the problem is not rigorously soluble with the information that we can hope to have available. This condition is satisfied by *p*-substituted phenols, but not by *o*- or *m*-substituted ones, the naphthols, or indole. Accordingly, this calculation has been done for the complexes formed with phenol, *p*-cresol, and *p*-chlorophenol; the results are given in the Table under $\Delta\bar{\mu}$. A less clearly significant measure of the interaction, but one which is easy to calculate, is the scalar difference of moment between that of the complex and the sum of those for the amine and for the acidic component : these values are given under $\Delta\mu$. In addition, the association constant, *K*, and the acidic dissociation constants in water, *k*, are included (cf. Table 3 of preceding paper).

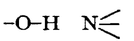
For the calculation of $\Delta\bar{\mu}$ the direction of the resultant moment of the *p*-substituted phenol, relative to the 1 : 4-axis therein, was obtained by vectorial combination of the moments of this substance, of phenol itself, and of the corresponding substituted benzene (*e.g.*, *p*-cresol, phenol, and toluene); and the following values were found :

Phenol, 91°; *p*-cresol, 101°, *p*-chlorophenol, 44° (the values of 101° and 44° mean that the resultant vector is respectively obtuse and acute relative to the O–C bond). The C–O–H angle was assumed to be 120°, the O–H · · · N bond was assumed to be linear, and the moment of trimethylamine was taken to be 0·86 D (Le Fèvre, *Trans. Faraday Soc.*, 1947, **43**, 374).

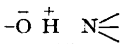
The errors quoted for μ_{complex} reflect only the uncertainties of the polarisation measurements (see p. 3902). The effect of uncertainty in *K* has, however, been considered. A 20% error in *K* produces the following errors in μ_{complex} : for β-naphthol 0·6%, for α-naphthol 2·5%, for phenol 3%, for *p*-cresol 2·5%; while a 12% error in *K* for indole gives a 6% error in the moment. The error from this cause in the moments of the more stable complexes is therefore relatively small.

It is immediately apparent from the $\Delta\bar{\mu}$ values that (*a*) there is an appreciable increase of moment when the complex is formed, *i.e.*, the positive pole of the moment thus generated is towards the amine nitrogen atom, (*b*) the increase with *p*-cresol is less than that with phenol, while that with *p*-chlorophenol is greater. Some of this change is probably due to the induction of moments by trimethylamine in the phenol and *vice versa*. Now, such induction as arises in those parts of the molecules outside the O–H bond of the phenol and the N atom of the amine may be considered as extraneous to that which is proper to the formation of the hydrogen bond; but induction within this bond and in this atom is a classical, electrostatic interpretation of the perturbation arising therefrom. Interest is focused especially on the changes which occur between the hydrogen atom and the nitrogen atom, but the change in the O–H bond is coupled with this, so it is to be regarded as part of the whole change due to hydrogen-bond formation. Accordingly, it is necessary only to estimate the extraneous induced moments : this can be done, *e.g.*, by Hampson and Weissberger's method (*J.*, 1936, 393) which gives a value of the order of 0·2 D.

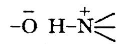
It is, therefore, reasonably certain that the major part (*ca.* 0·8 D) of the change of moment observed is due to bond formation proper. The non-classical significance of this may be shown as follows. If we adopt the simple view that the actual O–H bond may be described as a resonance hybrid of a covalent and of an ionic structure (I and II respectively), we could say that the only way in which the hydrogen atom can form any but a rigid dipole complex with the amine, involving no deformation of the nitrogen atom, would be through the ionic structure (II) which would make possible an " ammonium " structure (III). Structure (III) would involve movement of the unshared pair of electrons on the


$-O{-}H\quad N\leqq$

I)


$-\overset{-}{O}\ \overset{+}{H}\quad N\leqq$

(II)


$-\overset{-}{O}\ H{-}\overset{+}{N}\leqq$

(III)

nitrogen atom towards the proton, and a transfer of a formal positive charge from hydrogen to nitrogen, so its formation would generate a moment of $el_{(\text{H}\ldots\text{N})}$. If $l_{(\text{H}\ldots\text{N})}$ be taken as 1·5 Å, this is 7·2 D; or if 2·0 Å then 9·6 D. The actual change attributed to this cause being only about 0·8 D, we conclude that structure (III) contributes to the extent of not more than 10%. According to Pauling's estimate that the O–H bond (in water) is 39% ionic ("Nature of the Chemical Bond," Cornell Univ. Press, 1940, Chap. 2), the contributions of the three forms, ignoring any perturbation of the O–H bond by the proximity of the amine, would be: (I) 61%, (II) 29%, and (III) 10%. Since structures (II) and (III) would be the only ones, on this point of view, which contribute to any kind of hydrogen bond, we could then say that this bond is about 75% ionic [(II)/(II + III)] and 25% covalent [(III)/(II + III)]. This is equivalent to saying that there is resonance between a "no-bond" state (I) and a polar bond state (II and III). The perturbing effect of the amine will actually increase somewhat the contribution of structure (II), perhaps to 40%, and part of the moment change will be due to this, so that a better assessment of the hydrogen bond character in this instance seems likely to be 80% ionic and 20% covalent, or even 85% ionic and 15% covalent.

It is interesting to compare these conclusions with estimates made by using Pauling's formalism.* According to this, the electronegativity of the nitrogen atom in structure (III) would be increased to about 3·3 by its positive charge. The difference (1·2) between this and hydrogen would give the bond 30% ionic character only. However, the proximity of the $-O^-$ ion will, in effect, decrease the electronegativity of the hydrogen atom and increase that of the nitrogen atom, so that the actual difference of electronegativity may well be about 2·2, which corresponds to 70% ionic character, and even more. This picture is not necessarily to be accepted as correct; but it provides a useful way of presenting and of discussing the results.

No precise conclusions can be drawn as to the origin of the hydrogen-bond energy; but some interesting qualitative ones emerge. Two rigid dipolar systems have a negative energy of approach; but, *ex definitio*, there could be no dipole moment change, $\Delta\bar{\mu}$, of the complex relative to the correct vector sum of the moments of the two components, so $\Delta\mu$, the scalar difference, could only be zero or negative. This energy may be calculated (cf. Moelwyn-Hughes, *J.*, 1938, 1243; Davies, *Trans. Faraday Soc.*, 1940, **36**, 341) from the bond moments and the interatomic distances, and this has been done by Dr. A. Gilchrist. The most important assumptions are that the O · · · N distance is 3·0 Å (cf. the N–H · · · O bond length; Pauling, *op. cit.*, p. 334), and the O–H bond length is 1·04 Å (increased from 0·97 Å by the perturbation, cf. Davies, *Ann. Reports*, 1946, **43**, 17), making the N · · · H distance 1·96 Å. The other bond lengths are all taken to have the standard values (see *e.g.*, Pauling, *op. cit.*; Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46). Formal charges can then be calculated for each atom: the O–H moment has been taken as 2·3 D by adding to the conventional value (Pauling, *op. cit.*) the whole of the increase of 0·8 D calculated as the actual $\Delta\mu$, in order to make the calculated approach energy as large as possible, μ(C–O) is taken as 0·8 D, μ(C–N) as 0·31 D, and μ(H–C) as 0·30 D. The dielectric constant (ε) of the medium between the charges is taken to be unity which would be strictly correct if the system were electrically non-polarisable. The energy decrease then calculated is *ca.* 3 kcal./mole. It is very sensitive to the value assumed for l(H · · · N): if this were decreased to 1·5 Å (cf., the O · · · O distance, Pauling, *op. cit.*) the energy would be doubled. On the other hand, the effective value of ε must be somewhat greater than unity: if it were equal to the macroscopic value for hydrocarbons it would be *ca.* 2, and the energy would be halved. The correct value of $-\Delta H$ for rigid dipoles is therefore unlikely to exceed 3 kcal./mole. If, now, the dipolar systems be considered polarisable, this energy is found to be increased, but only by *ca.* 0·1 kcal./mole (ε again assumed to be unity), so classical electrostatic calculations can account for only about a half of the observed 5·8 kcal./mole of approach energy.

The qualitative parallel between the $\Delta\bar{\mu}$ values (0·91, 1·00, and 1·26 D respectively) and the $-\Delta H$ values (3·8, 5·8, 7·0 kcal./mole respectively) of the series *p*-cresol, phenol, and *p*-chlorophenol suggests, despite the foregoing, that the approach energy is largely determined by polarisation processes; the classical treatment of these ceases to be adequate at high field strengths (cf. Coulson, Maccoll, and Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106).

The preceding non-classical interpretation of the $\Delta\bar{\mu}$ value in terms of a resonance

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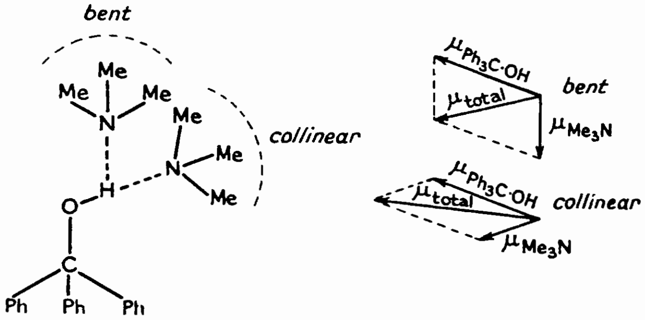
* In discussion in 1948, Professor Pauling made suggestions which the senior author believes to be reproduced in essence here.

between ionic and covalent structures cannot be used at all precisely to obtain a revised estimate of the polarisation energy, but if the primitive assumption be made that the contribution of the 10% of covalent character for the N • • • H bond adds 10% of the covalent N–H bond energy (taken as $\frac{1}{2}[H(\text{N–N}) + H(\text{H–H})]$, this increment is 6·2 kcal./mole, which is more than enough to close the gap between the estimated rigid dipole energy and the observed value. It seems likely, therefore, that a considerable part of the energy of these hydrogen bonds is due to the development of covalency between H and N.

The ΔH value mainly determines ΔF and hence K at 25° (see preceding paper). Moreover, there is a parallel between the K values and the acid dissociation constants in water (k). Therefore, since ΔH must be a function of the polarity * of the phenolic O–H bond, whatever the precise mechanism may be, it follows that K must be mainly so determined, and there is an indication that k must be too. The existence of a connection between k and the polarity of the bond from which the proton is released has long been accepted, but the present demonstration is a relatively direct one. The absence of any relation between K and k for benzenethiol shows, however, that the connection is not general.

The $\Delta\mu$ values have the same sequence as the $\Delta\bar{\mu}$ values. Furthermore, for the complexes generally, the $\Delta\mu$ and the K values are monotonically related (see below). In the less stable complex formed with indole there is very little moment change at all, which indicates " rigid dipole " association and hence a low polarity for the N–H bond.

FIG. 1. *The extreme configurations for the triphenylmethanol-trimethylamine complex, and their total electric dipole moments.*



The negative change found for the triphenylmethanol complex requires comment. Although the concentration of the complex, x, is small in the solutions examined, because the solubility of the carbinol in *cyclo*hexane is low and because K is small, the consistency of the calculated total polarisations is about average. Also, although error in K affects $\Delta\mu$, the error to account for a change in μ of 0·7 D would be impossibly large. It would therefore appear that the effect is real. The most probable explanation is that, as may be seen from a model, the repulsion between the methyl groups of the amine and the phenyl groups of the carbinol causes the axis of the amine to incline towards that of the triphenylmethyl group, and so to bend the O–H • • • N system which otherwise would be linear. This would cause the angle between the phenolic moment and the amine moment to increase, and possibly even to become obtuse (see Fig. 1 wherein the extremes are shown) and so would reduce the moment of the complex to less than the scalar sum of these two.

It is surprising to find that $(\Delta\mu)^2$ is a fairly linear function of K (Fig. 2). On a very simple polarisation treatment of hydrogen-bond formation, as being due to the approach energy between a permanent point dipole and a point of polarisability α, it follows that $E = -(\Delta\bar{\mu})^2/2\alpha$, but the observed relation does not follow rigorously from this result. Nevertheless, it appears sufficiently established to be used as follows. In the preceding paper the association constant K for the β-naphthol complex was anomalously large as judged by the value of k for this acid. From Table 3 it is clear that this is due to the bond's being stronger

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* The term " polarity" in this context may include not only the permanent moment of the bond but the axial polarisability.

than for the α-naphthol, because Δμ is 1·41 D for the β- and 0·87 D for the α-complex. That the value of the former is the higher cannot be attributed to an error in K for the β-complex relative to that for the α-complex, because if it were in fact the same as the latter, *i.e.*, 1000 instead of the 2100 reported, Δμ would be still higher for the β-complex, *viz.*, 1·9 D; the point would not then fall on the curve in Fig. 2.

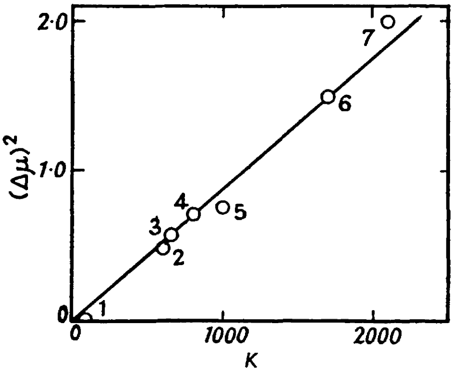

FIG. 2. *The relation between* $(\Delta\mu)^2$ *and* K.
1, Indole; 2, *p*-cresol; 3, *o*-cresol; 4, phenol; 5, α-naphthol; 6, *p*-chlorophenol; 7, β-naphthol.

The monotonic relation between $(\Delta\mu)^2$ and K therefore confirms that the β-complex is anomalous in the sense given; this implies that the greater polarity of the O–H bond in β-naphthol than in α-naphthol does not determine the relative ease of dissociation in water for that particular pair of compounds. Some further indication that the O–H moment is greater in the former substance is that its total electric dipole moment is the greater (Table 3) although this fact by itself is not conclusive. It may also be mentioned that the evidence is against the difference between the naphthols being the result of the greater screening of the hydroxyl group, by the *peri*-hydrogen atom, in the α-compound: were this the reason, there should be evidence of screening in *o*-cresol compared with *p*-cresol, yet in fact the values of K, Δμ, and of k are hardly distinguishable. The discussion of possible reasons for this anomaly is beyond the scope of the present paper.

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