IR-SPECTRA AND DIPOLE MOMENTS OF HYDROGEN-BONDED COMPLEXES. PART II. POLARITY OF DIPHENYLAMINE AND 2.4.6-TRIMETHYLPHENOL ADDUCTS

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Dipole moments of hydrogen-bonded adducts of diphenylamine and 2.4.6-trimethyl-phenol as well as of the proton donor and acceptor components, were determined in CCl_4, at 25°C. The calculated polarities of hydrogen bonds are approximately constant in series of complexes of one donor with acceptors of varying basicity. The results, together with IR data obtained in a previous paper, lead to the conclusion, that electrostatic inductive forces are dominant in weak hydrogen-bonded systems.

The effect of an increase of the dielectric polarization in hydrogen-bonded systems was known for some time. Much work has been done in the study of the "dioxane effect": the dipole moments of amines [1–4], phenols [5–6] and alcohols [7] are higher in dioxane than in inert solvents, such as cyclohexane, heptane *etc.* The $\overrightarrow{\Delta \mu}$ (polarity of hydrogen bonding, *i. e.* excess dipole moment along the AH-bond axis due to H-bond formation) value, calculated on the base of these results is usually about 0.3–0.6 D. No relation between $\overrightarrow{\Delta \mu}$ and acidity or dipole moment of the donor could be established from these data. Ibbitson *et al.* [5–6] reported, that $\overrightarrow{\Delta \mu}$ increases with the acidity of the phenol derivative, but some of their results are too high, because the intramolecular interaction dipole moments in free molecules of phenols were not taken into account.

The effect of dipole moment enhancement occurs not only in dioxane. Malarski and Sobczyk [8] proved, that for haloforms, phenylacetylene, diphenylamine, triphenylcarbinol even in such a weak proton acceptor as benzene, an increase of the dipole moment is observed. Detailed investigations, involving different donors and acceptors, were performed by Lumbroso *et al.* [9–11]. Interesting results for HF, HCl, HBr, HJ in different solvents were obtained by Weith *et al.* [12]; the dependence of $\overrightarrow{\Delta \mu}$ on the acidity of the donor used is evident in these case.

The investigations of binar systems (donor-solvent), mentioned above, are performed basing on the assumption that the proton donor is completely bound to the molecules of the

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solvent. The validity of this assumption is supported by IR-data. The number of non-polar solvent with more pronounced basic properties is, however, limited. On the other hand, the correct interpretation of experimental data obtained in polar solvents is difficult on account of the choice of the local field model. Thus, the investigation of three-component systems (inert solvent–donor–acceptor) seems to be more promising.

An important question in the discussion of H-bond polarity is the problem of the life times of hydrogen-bonded adducts. If the life time is considerably greater than the dielectric relaxation time, the whole complex orientates in the electric field; but if both these quantities are of the same order, the interpretation of results of dielectric measurements may not be clear. Little attention has been paid to this problem hitherto. For complexes with weak or moderately strong H-bond usually values of 10^{-9}–10^{-6}s have been found [13–16]. They are at least one order greater than the relaxation time of molecules in such solvents as C_6H_6 and CCl_4, hence reliable results should be expected.

The determination of the molar polarization of the hydrogen-bonded complex in a three--component system requires the knowledge of its formation constant. A simultaneous esti-mation of both these quantities by the method of Cleverdon, Collins and Smith [17] is possible, but the necessity of an independent determination of the formation constant is emphasized by many authors. Data on dipole moments of about 20 complexes with weak hydrogen bonding, involving such donors as water, alcohols, phenol, pyrrole, and acceptors: pyridine, triethylamine, dioxane, tetrahydrofurane, acetone in different solvents were pub-lished [9–11, 17–21]. $\overrightarrow{\Delta\mu}$ changes irregularly and does not exceed 0.7 D; often it is even negative. It is difficult to discuss these results, obtained in different conditions, e. g. in different solvents, what is reflected dramatically in the stability constant [22] and may also affect other physical properties of the complexes, especially the dipole moments. The need of more systematic and accurate investigations seems to be evident. More systematic data are available for systems with stronger hydrogen-bonds, especially for complexes of phenols with amines [23–25] and carboxylic acids with amines; [26–28] although in the latter case the discrepancies between the results obtained by various workers are considerable. In the mentioned systems a distinct correlation between $\Delta\mu$ and the acidity of the proton donor is observed, probably due to proton transfer, e. g. in a series of complexes of phenols with triethylamine, investigated by Ratajczak and Sobczyk [24b]. Data for complexes of carbo-xylic acids with oxygen bases are also available [29].

The aim of this work is to determine the $\overrightarrow{\Delta\mu}$-values of weak hydrogen-bonded com-plexes formed by one donor with a series of proton-acceptors of varying basicity (complexes of diphenylamine and mesitol [30]), and to correlate these data with IR-features of the com-plexes, obtained previously [30].

Experimental

The electric permittivity of solution (CCl_4 was used as solvent throughout this work) was measured by the heterodyne beat method using the substitution technique, at a fre-quency 400 kHz. A liquid cell with three coaxial cylindrical platinum electrodes, of a capa-city of *ca* 50 pF, was used. The dipolmeter was equipped with a high precision Sullivan and

Griffiths condenser. The capacity could be measured with an error, $\dfrac{\Delta C}{C}$, less than $1 \cdot 10^{-4}$.

The density was measured by means of a 10 ml picnometer, provided with a calibrated capillary tube, with an error less than $1 \cdot 10^{-4}$ g/cm³ (the repeatability was $\pm 2 \cdot 10^{-5}$ g/cm³). All measurements were carried out at 25.0°C. The purification of the compounds used in this work was described earlier [30].

The dipole moments of the investigated compounds were calculated by Hedestrand's method [31]. The molar polarization, extrapolated to infinite dilution, is given by

$$P_{2\infty} = \frac{3\varepsilon_1 M_1}{(\varepsilon_1+2)^2 d_1}\alpha + \frac{\varepsilon_1-1}{(\varepsilon_1+2)d_1}(M_2 - \beta M_1) \tag{1}$$

where

$$\alpha = \frac{1}{\varepsilon_1}\left(\frac{\partial \varepsilon}{\partial x_2}\right) \cong \frac{\Delta\varepsilon}{\varepsilon_1 x_2}; \quad \beta = \frac{1}{d_1}\left(\frac{\partial d}{\partial x_2}\right) \cong \frac{\Delta d}{d_1 x_2} \tag{2}$$

ε — electric permittivity, d — density, M — molecular weight, and x — mole fraction; the index "1" denotes the solvent, "2" — the solute. The sum of atomic and electronic polarizations was replaced by refraction for the sodium D-line; the molar refractions of the compounds were calculated using exlusively the values given by Smith [31].

The dipole moments of the $1:1$ complexes were determined by measuring the electric permittivity and density of systems containing known initial concentrations of the donor (D) and acceptor (A) in CCl_4. The knowledge of stability constants estimated previously [30], permitted to calculate the equilibrium concentrations of A, D and AD (complex) and the molar polarization of the complex, P_{AD}. The polarization was calculated in three different ways.

Method 1. Firstly the dependence of the molar polarization of the donor (P_D) and acceptor (P_A) on the concentration was described by means of a quadratic curve:

$$P_2 = a_0 + a_1 x_2 + a_2 x_2^2 \tag{3}$$

where x_2 is the mole fraction of the solute and a_0, a_1, a_2 are constants, found by the least squares method. Thus, the effective polarization of A and D at equilibrium concentration in the three-component systems could be evaluated, and then from the additivity scheme

$$P = \sum_i P_i x_i = P_s x_s + P_A x_A + P_D x_D + P_{AD} x_{AD} \tag{4}$$

where s denotes the solvent, the molar polarization of the complex, P_{AD}, could be calculated, and hence its dipole moment. The total polarization, P, was calculated in the usual way

$$P = \frac{\varepsilon-1}{\varepsilon+2}\frac{\overline{M}}{d} \tag{5}$$

where $\overline{M}$ denotes the mean molecular weight of the mixture.

Method 2. The values of $P_{A\infty}$ And $P_{D\infty}$, obtained by Eq. (1), were used and P_{AD} calculated from Eq. (4).

Method 3. It can be shown, that the sum of the molar polarizations at infinite dilution is given by:

$$P_{A\infty} + P_{D\infty} + P_{AD\infty} = \frac{3\varepsilon_1 M_1}{(\varepsilon_1+2)^2 d_1}\,\alpha_t + \frac{\varepsilon_1-1}{(\varepsilon_1+2)d_1}\,(M_A+M_D+M_{AD}-\beta_t M_s) \qquad (6)$$

where

$$\alpha_t = \lim_{x_A,\,x_D,\,x_{AD}\to 0} \frac{1}{\varepsilon_1}\left[\left(\frac{\partial\varepsilon}{\partial x_A}\right)_{x_A,\,x_{AD}} + \left(\frac{\partial\varepsilon}{\partial x_D}\right)_{x_A,\,x_{AD}} + \left(\frac{\partial\varepsilon}{\partial x_{AD}}\right)_{x_A,\,x_D}\right] = \alpha_A + \alpha_D + \alpha_{AD}$$

$$\beta_t = \lim_{x_A,\,x_D,\,x_{AD}\to 0} \frac{1}{d_1}\left[\left(\frac{\partial d}{\partial x_A}\right)_{x_D,\,x_{AD}} + \left(\frac{\partial d}{\partial x_D}\right)_{x_A,\,x_{AD}} + \left(\frac{\partial d}{\partial x_{AD}}\right)_{x_A,\,x_D}\right] = \beta_A + \beta_D + \beta_{AD}.$$

Hence, from Eq. (6) it can be derived, that

$$P_{AD\infty} = \frac{3\varepsilon_1 M_1}{(\varepsilon_1+2)^2 d_1}\,\alpha_{AD} + \frac{\varepsilon_1-1}{(\varepsilon_1+2)d_1}\,(M_{AD}-\beta_{AD} M_S) \qquad (7)$$

in analogy with Hedestrand's equation (1). The results obtained in this way have the meaning of values which would be obtained dissolving the pure complex in an inert solvent, with extrapolation to infinite dilution; such an experiment cannot be performed, of course. α_{AD} and β_{AD}, used in Eq. (7), were calculated from ε and d-measurements of ternary solutions, assuming the validity of the relations:

$$\varepsilon = \varepsilon_1(1+\alpha_A x_A + \alpha_D x_D + \alpha_{AD} x_{AD}) \qquad (8a)$$

$$d = d_1(1+\beta_A x_A + \beta_D x_D + \beta_{AD} x_{AD}) \qquad (8b)$$

$\alpha_A, \alpha_D, \beta_A, \beta_D$ were known from independent measurements (Eq. (2)). It should be mentioned that in a rigorous treatment all these quantities should be taken at infinite dilution.

TABLE I

The dipole moment (in [D]) of 2.4.6-trimethylphenol-4-picoline complex, calculated by different methods (in CCl_4, 25°C; $x_D = 0.002$–0.005; $x_{AD} = 0.004$–0.007)

x_A	Method 1	Method 2	Method 3
0.015	4.49	4.02	4.32
0.025	4.16	3.80	4.31
0.035	3.91	3.58	4.34
0.043	3.72	3.40	4.33
0.055	3.37	3.03	4.35

In Table I the comparison of results obtained by the three discussed methods is presented for 2.4.6-trimethylphenol-4-picoline complex in CCl_4 (the equilibrium concentrations are given). The best coincidence for different concentrations is obtained by Method 3; these values seem to be the most reliable ones. It has been tested, that for strong complexes (e. g. 2.6-dichloro-4-nitrophenol with pyridine bases), when the measurements could be performed at very low concentrations, all three methods give approximately the same results.

Results and discussion

The dipole moments of the majority of compounds used in this work were known previously [32]; however, to fix the systematic error (stemming from the solvent, temperature, refraction data, calculational procedure *etc.*), all the values were reestimated. The results are given in Table II; arithmetic means (from 6–10 measurements) and mean deviations are quoted.

TABLE II

Dipole moments (in CCl_4, 25°C)

Compound	conc. range (x_2)	$\overline{\alpha\varepsilon_1}$	$\overline{\beta}$	R_D [cm³]	$\overline{P}_{2\infty}$[cm³]	$\overline{\mu}$ [D]
Diphenylamine	0.001—0.01	2.218	−0.5002	54.45	81.21	1.14±0.02
2.4.6-Trimethylphenol	0.003—0.015	2.267	−0.5347	41.92	77.11	1.30±0.01
2.4.6-Collidine	0.003—0.03	6.538	−0.5758	38.59	144.2	2.26±0.02
4-Picoline	0.004—0.009	9.569	−0.3894	29.29	183.9	2.73±0.01
Pyridine	0.003—0.011	6.857	−0.3043	24.64	134.8	2.31±0.02
3-Chloropyridine	0.01 —0.035	5.654	−0.2248	29.48	119.0	2.08±0.01
3.5-Dichloropyridine	0.01 —0.045	1.418	−0.1300	34.31	53.98	0.98±0.01
Piperidine	0.01 —0.05	2.215	−0.4478	26.84	64.31	1.35±0.01
Acetone	0.009—0.06	10.19	−0.3798	16.14	186.9	2.87±0.02
Dioxane	0.01 —0.08	0.0752	−0.3028	22.16	25.79	0.42±0.01

The dipole moments for diphenylamine complexes together with mean square errors, equilibrium concentrations and other data, are collected in Table III; using the dipole moments of the complex, donor and acceptor, it was possible to calculate the polarity of hydrogen bonding in these complexes. The direction of the dipole moment vectors in the molecules of donor and acceptor and the configuration of the complexes must be known exactly to perform such calculations. After that, in a detailed discussion, a possibility of the existence of a distribution of configurations with bent hydrogen bonding should be

TABLE III

Diphenylamine complexes: dipole moments and polarities of hydrogen bonding

Proton acceptor	Concentration range (%)			$\overline{\alpha}_{AD}$	$\overline{\beta}_{AD}$	$P_{AD\infty}$ [cm³]	$\overline{\mu}_{AD}$ [D]	$\overrightarrow{\Delta\mu}$ [D]
	x_A	x_D	x_{AD}					
Piperidine	1—4	0.5—0.7	0.09—0.2	3.261	−0.721	185	2.24±0.01	0—0.16
4-Picoline	0.4—1.5	0.3—0.5	0.03—0.08	8.754	−0.738	386	3.82±0.01	0.08
Pyridine	0.5—3	0.3—0 5	0 03—0.15	7.186	−0.746	327	3.48±0.02	0.15
3.5-Dichloropyridine	1—4	0.6—0.9	0.03—0.07	2.24	−0.405	148	1.68±0.18	—
Dioxane	0.9—9	0.3—0.4	0.03—0.2	1.395	−0.634	114	1.34±0.04	0—0.24
Acetone	0.7—4.5	0.3—0.6	0.1 —0.3	6.066	−0.775	284	3.20±0.06	0—0.20

taken into account. The angle between the dipole moment of the diphenylamine molecule and the NH-bond was taken as equal to 149° [33] (Fig. 1). An angle of 36° between the lone electron pair axis and the dipole moment vector in piperidine was assumed (Fig. 2), similarly to that in dimethylamine [34]. Assuming a rigid complex of a configuration with a minimum resultant dipole moment, $\overrightarrow{\Delta\mu} = 0.16$ D for the adduct with piperidine is obtained, whereas, from
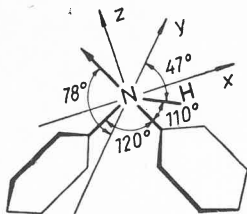
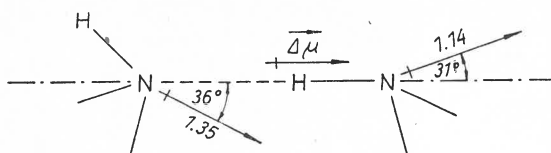Fig. 1. Vector scheme of the diphenylamine molecule

Fig. 2. Mutual orientation of components in the diphenylamine-piperidine complex

the free rotation model, a value of — 0.06 D results. The first possibility is, without doubt, more probable. The exact calculation of $\overrightarrow{\Delta\mu}$ for the adduct with dioxane is not possible. The dipole moment of dioxane (0.42 D) results from the presence of molecules in the boat conformation, besides the non-polar chair form. $\overrightarrow{\Delta\mu} = 0.24$ D is obtained assuming that all molecules are chair-conformers; hence, the real value is lower than 0.24 D. In the case
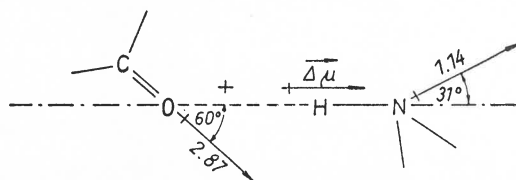
Fig. 3. Configuration of the diphenylamine-acetone complex

of the acetone complex it was assumed that the hydrogen bonding forms an angle of 60° with the axis of the carbonyl group (Fig. 3); for a rigid complex $\overrightarrow{\Delta\mu} = 0.20$ D is obtained, for free rotation model —0.48 D. Thus the structure of the complex is probably nearly rigid, and $\overrightarrow{\Delta\mu}$ is 0–0.2 D. Besides these difficulties, the $\overrightarrow{\Delta\mu}$ values are burdened with a considerable experimental error (~ 0.05 D). It is evident, however, that they are small and that no correlation between $\overrightarrow{\Delta\mu}$ and donor-acceptor properties of interacting molecules exists. The observed polarities are probably caused by the electrostatic inductive effect; in fact, using the relation

$$\mu_{\mathrm{ind(AH)}} = \mu\alpha_{\parallel\,(\mathrm{AH})}\,\frac{\varepsilon_a+2}{3\varepsilon_b r^3}\,(3\cos^2\Theta-1) \qquad (9)$$

where μ is the inductive moment, $\alpha_{||}(AH)$ — the longitudinal polarizability of the AH-bond, ε_a, ε_b — electric permittivity of the environment and the polarized center, respectively, r — the distance between the centre of the dipole and the polarized centre, θ — angle between $\vec{\mu}$ and $\vec{r}$, $\overrightarrow{\Delta\mu}$-values of 0.1–0.2 D for the considered systems can be expected.

TABLE IV

Dipole moments and polarities of hydrogen bonding in 2.4.6-trimethylphenol complexes

Proton acceptor	Concentration range (%)			$\bar{\alpha}_{AD}$	$\bar{\beta}_{AD}$	$\bar{P}_{AD\infty}$ [cm³]	$\bar{\mu}_{AD}$[D]	$\overline{\Delta\mu}$ [D]	
	x_A	x_D	x_{AD}					a	b
Piperidine	1—6	0.1—0.5	0.5—0.7	5.449	−0.931	265	3.08±0.01	0.71* 0.51**	0.70* 0.50**
2.4.6-Collidine	1—4	0.3—0.7	0.4—0.8	8.984	−1.024	403	3.95±0.02	0.43	0.42
4-Picoline	1—5	0.2—0.4	0.4—0.7	10.800	−0.880	459	4.33±0.01	0.36	0.35
Pyridine	2—6	0.2—0.4	0.4—0.7	9.289	−0.800	400	4.01±0.03	0.44	0.42
3-Chloropyridine	2—7	0.3—0.6	0.3—0.5	6.509	−0.639	300	3.33±0.02	0.25*	0.24*
3.5-Dichloropyridine	2—5	0.8—1	0.2—0.3	3.898	−0.690	213	2.58±0.02	0.44*** 0.35	0.43*** 0.33

a, b — see the text,

* free rotation (around the H-bond),   ** rigid structure with minimum steric hindrances,   *** rigid structure with minimum resultant dipole moment of the complex.

The dipole moments of 2.4.6-trimethylphenol complexes are collected in Table IV (the denotations are the same as in Table III). The μ-values were obtained using Method 3 and stability constants, determined previously [30]. The dipole moment of 2.4.6-trimethylphenol, 1.30 D, indicates that the values: $\mu_{OH} = 1.58$ D and $\sphericalangle COH = 115°$, accepted for phenol, are not the same in this case; therefore the calculations of $\overrightarrow{\Delta\mu}$ were performed for two sets of these quantities: a) $\mu_{OH} = 1.58$ D, $\sphericalangle COH = 131°$ (deformation caused by steric hindrances), and b) $\mu_{OH} = 1.42$ D, $\sphericalangle COH = 115°$. Both these sets reproduce the resultant dipole moment of the 2.4.6-trimethylphenol molecules, 1.30 D. Fortunately enough, the choice of μ_{OH} and $\sphericalangle COH$ has a negligible influence on the obtained results, as can be seen from $\overrightarrow{\Delta\mu}$-values, given in Table IV.

Two effects should be taken into account, considering the polarity of weak hydrogen-bonds: the electrostatic inductive effect, resulting in the $\overset{(-)\,(+)}{A-H...B}$ structure, and the CT effect, given schematically as $\overset{(-)\quad(+)}{A-H...B}$. The role of these effects is controversial; while some workers ignore the inductive forces (Refs [6, 7], Part I), others emphasize their importance in CT- and hydrogen bonded complexes [36–38]. The proton-transfer effect, probably responsible for the polarity of strong hydrogen bonds [24], may be neglected in this case. Let us assume that in the considered series of mesitol complexes $\overrightarrow{\Delta\mu} = \mu_{ind}$ (AH), i. e. the dipole moment enhancement is caused entirely by the inductive effect. Assuming

further, that ε_a, ε_b and r in Eq. (9) are constant in the series, it should be expected that:

$$\overrightarrow{\Delta\mu}_1 : \overrightarrow{\mu\Delta}_2 : \ldots : \overrightarrow{\Delta\mu}_n = \mu_{||1} : \mu_{||2} : \mu_{||n} \tag{10}$$

where $\mu_{||i}$ denotes the component of the inductive moment, parallel to AH-bond; the results are given in Table V. The observed discrepancies between the $\dfrac{\mu_{||i}}{\mu_{||6}}$ and $\dfrac{\overrightarrow{\Delta\mu}_i}{\overrightarrow{\Delta\mu}_6}$ ratios are probably not an argument against the inductive effect, because without doubt more important than the dipole moment of the whole acceptor molecule is the moment of the free electron pair, which should be approximately constant in the series of pyridine derivatives. This could be a possible explanation of the observed constancy of the $\overrightarrow{\Delta\mu}$ values. The free electron pair moment is for aliphatic amines greater than that for aromatic amines, hence the elevated value for piperidine could be explained.

TABLE V

Verification of Eq. (10)

i	Proton acceptor	μ_i [D]	$\mu_{||i}$[D]	$\dfrac{\mu_{||i}}{\mu_{||6}}$	$\dfrac{\overrightarrow{\Delta\mu}_i}{\overrightarrow{\Delta\mu}_6}$
1	Piperidine	1.35	1.09	1.11	1.7
2	2.4.6-Collidine	2.26	2.26	2.31	1.2
3	4-Picoline	2.73	2.73	2.79	1.0
4	Pyridine	2.31	2.31	2.36	1.3
5	3-Chloropyridine	2.08	1.71	1.74	1.0
6	3.5-Dichloropyridine	0.98	0.98	1	1

In analogy to CT-complexes [35], let us write the expression for the force constant of the stretching vibration of the hydrogen-bonded AH-group in the form

$$k_c = (a^2 + abS) k_0 + (b^2 + abS) k_1 \tag{11}$$

where k_0 and k_1 denote, respectively, the force constants for the free AH-group, and the (AH)$^-$-group, created by the electron-transfer from the lone pair of the atom B to anti-bonding orbital of the AH-group; a and b are coefficients of the no-bond (AH...B) and dative $(\overset{(-)}{A}-H-\overset{(+)}{B})$ structure in the wave-function describing the complex, S is connected with the overlap integral. From Eq. (11) it results that the weight of the dative structure is given by

$$b^2 + abS = \frac{k_0 - k_c}{k_0 - k_1} = \frac{\nu_0^2 - \nu_c^2}{\nu_0^2 - \nu_1^2} \tag{12}$$

where ν denotes the wavenumber of the correspondent vibration. On the other hand, from the expression for the dipole moment of a CT-complex

$$\mu_c = (a^2 + abS) \mu_0 + (b^2 + abS) \mu_1 \tag{13}$$

where μ_0 and μ_1 are dipole moments of the no-bond and dative structure, respectively, it may be derived, that

$$\overrightarrow{\Delta\mu} = \mu_{ind} + (b^2 + abS)(\mu_1 - \mu_0) \tag{14}$$

or, combining (12) and (14):

$$\overrightarrow{\Delta\mu} = \mu_{ind} + \frac{\nu_0^2 - \nu_c^2}{\nu_0^2 - \nu_1^2} \tag{15}$$

if only inductive- and CT-contributions to the polarity of the hydrogen bonding are taken into account. Thus, the dependence of $\overrightarrow{\Delta\mu}$ vs. $\nu_2^0 - \nu_c^2$ should be linear, with a slope $\frac{\mu_1 - \mu_0}{\nu_0^2 - \nu_1^2}$, intercepting the ordinate axis at μ_{ind}. Within experimental error, $\overrightarrow{\Delta\mu}$ is constant; thus, the amount of the CT structure is small in these weak complexes, and the observed $\overrightarrow{\Delta\mu}$ values seems to be caused mainly by the inductive effect.

TABLE VI

Verification of relation (16) for hydrogen-bonded complexes of mesitol

Proton acceptor	$10^{-6} \cdot (\nu_0^2 - \nu_c^2)$ [cm^{-2}]	$\dfrac{\Delta\nu}{\nu_0}$	$b^2 + abS$	$\overrightarrow{\Delta\mu}_{calc.}$ [D]	$\overrightarrow{\Delta\mu}_{exp}$ [D]
Piperidine	4.705	0.199	0.5312	6.9	0.61
2.4.6-Collidine	3.255	0.133	0.355	4.6	0.43
4-Picoline	2.862	0.116	0.309	4.0	0.36
Pyridine	2.707	0.109	0.291	3.8	0.44
3-Chloropyridine	2.284	0.091	0.243	3.2	0.35
3.5-Dichloropyridine	1.892	0.075	0.200	2.6	0.35

Another attempt to discuss the data on the basis of the CT-theory can be made in the following way. ν_1 cannot be measured directly, but Person [35] reports, that for many CT-complexes $\nu_1 \cong \frac{\nu_0}{2}$; it holds also (at least, formally) for hydrogen-bonded adducts; in many systems with strongest H-bonds the stretching vibration frequency diminishes approximately to one-half. In this case relation (15) reduces to

$$\overrightarrow{\Delta\mu} = \mu_{ind} + \frac{8}{3}\frac{\Delta\nu}{\nu_0}(\mu_1 - \mu_0). \tag{16}$$

In Table VI, $\overrightarrow{\Delta\mu}$-values calculated from this relation, assuming $\mu_1 - \mu_0 = 13$ D (Ref. [5], Part I) and neglecting μ_{ind} are given; considerable disagreement between the calculated and experimental values is observed. This visualizes the difficulties in describing the hydrogen-bonded systems by means of the CT-theory in its simple form.

REFERENCES

[1] V. G. Vassiliev, Y. K. Syrkin, *Zh. Fiz. Khim.*, **14**, 414 (1941).

[2] A. V. Few, J. W. Smith, *J. Chem. Soc.*, 753, 2781 (1949).

[3] J. W. Smith, *ibid.*, 3532 (1950); 109 (1953).

[4] J. W. Smith, S. M. Walshaw, *ibid.*, 3217 (1957).

[5] B. Erič, E. V. Goode, D. A. Ibbitson, *ibid.*, **55**, 4265 (1960).

[6] D. A. Ibbitson, J. P. B. Sandall, *ibid.*, 4547 (1964).

[7] D. A. Ibbitson, L. F. Moore, *ibid.*, **B**, **76**, 80 (1967).

[8] Z. Malarski, L. Sobczyk, *CR Acad. Sci.* (France), **269**, 874 (1969).

[9] H. Lumbroso, D. M. Bertin, *Bull. Soc. Chim. France*, 532 (1966).

[10] C. Pigenet, H. Lumbroso, *CR Acad. Sci.* (France), **262**, 1221 (1966).

[11] D. M. Bertin, H. Lumbroso, *ibid.*, **263**, 181 (1966).

[12] A. J. Weith, M. E. Hobbs, P. M. Gross, *J. Amer. Chem. Soc.*, **70**, 805 (1948).

[13] M. Magat, in *Hydrogen Bonding*, ed. D. Hadži and H. W. Thompson, Pergamon Press, London 1959, p. 309.

[14] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

[15] T. Yasunaga, N. Tatsumoto, H. Inoue, M. Miura, *J. Phys. Chem.*, **73**, 477 (1969).

[16] G. Hammes, C. A. Park, *J. Amer. Chem. Soc.*, **90**, 4150 (1968); **91**, 956 (1969).

[17] D. Cleverdon, G. B. Collins, J. W. Smith, *J. Chem. Soc.*, 4499 (1956).

[18] K. Kimura, R. Fujishiro, *Bull. Chem. Soc. Japan*, **32**, 433 (1959).

[19] H. Lumbroso, *J. Chim. Phys.*, **61**, 132 (1964).

[20] V. M. Kazakova, L. S. Feldstein, *Zh. Fiz. Khim.*, **35**, 488 (1961).

[21] A. H. Boud, J. W. Smith, *J. Chem. Soc.*, 4507 (1956).

[22] J. C Lasseques, P. V. Huong, *Rev. GAMS*, **5**, 69 (1969).

[23] J. R. Hulett, J. A. Pegg, L. E. Sutton, *J. Chem. Soc.*, 3901 (1955).

[24] a) H. Ratajczak, L. Sobczyk, *Zh. Strukt. Khim.*, **6**, 262 (1965);
b) *J. Chem. Phys.*, **50**, 556 (1969); *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **18**, 93 (1970).

[25] T. Clerbaux, P. Duterme, T. Zeeghers-Huyskens, P. Huyskens, *J. Chim. Phys.*, **64**, 1326 (1967); **65**, 1266 (1968).

[26] L. Sobczyk, J. Syrkin, *Roczniki Chem.*, **30**, 881, 883 (1956), in Polish.

[27] L. Sobczyk, in *Hydrogen Bonding*, ed. D. Hadži and H. W. Thompson, Pergamon Press, London 1959, p. 323.

[28] H. Tsubomura, *Bull. Chem. Soc. Japan*, **31**, 435 (1958).

[29] D. Hadži, H. Ratajczak, L. Sobczyk, *J. Chem. Soc.*, **A**, 48 (1967).

[30] J. Hawranek, L. Sobczyk, *Acta Phys. Polon.*, in press.

[31] J. W. Smith, *Electric Dipole Moments*, London, Butterworths, 1955.

[32] A. L. Mc Clellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco 1963.

[33] A. Koll, *Thesis*, Wrocław 1968.

[34] C. P. Smyth, *Dielectric Behavior and Structure*, Mc Graw-Hill, London 1955, p. 311.

[35] H. B. Friedrich, W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

[36] M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

[37] M. W. Hanna, D. E. Williams, *ibid.*, **90**, 5358 (1968).

[38] J. L. Lippert, M. W. Hanna, P. J. Trotter, *ibid.*, **91**, 4035 (1969).