

# IR-SPECTRA AND DIPOLE MOMENTS OF HYDROGEN-BONDED COMPLEXES. PART I. INTEGRATED INTENSITIES OF THE STRETCHING VIBRATION BAND OF THE PROTON DONOR GROUP

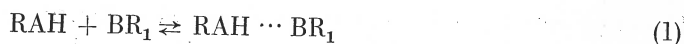
BY J. P. HAWRANEK, AND L. SOB CZYK

Laboratory of Physical Chemistry, Institute of Chemistry, University of Wrocław\*

(Received October 8, 1970)

Stability constants for hydrogen-bonded complexes of diphenylamine and 2,4,6-trimethylphenol with various bases, mainly pyridine-derivatives, were determined, in  $\text{CCl}_4$ , at  $25^\circ\text{C}$ . The spectral shift, half-width and integrated intensity of the stretching vibration band of the proton donor group in these complexes were also measured. Some correlations between spectral data, predicted by H-bond theories, are verified.

The formation of the hydrogen bond



leads to a variation in the charge distribution, mainly in the AH-group of the proton-donor RAH and in the lone electron pair of the atom B of the proton-acceptor  $\text{BR}_1$ . A measure of this effect is the polarity of H-bond,  $\overline{\Delta\mu}$ , *i.e.* the difference between the dipole moment vectors of the resulting adduct and the sum of dipole moments of the components

$$\overline{\Delta\mu} = \vec{\mu}_{\text{AD}} - \vec{\mu}_{\text{A}} - \vec{\mu}_{\text{D}} \quad (2)$$

where  $\vec{\mu}_{\text{D}}$ ,  $\vec{\mu}_{\text{A}}$  and  $\vec{\mu}_{\text{AD}}$  are the dipole moments of the proton-donor (D), proton-acceptor (A) and adduct (AD), respectively.

The polarity of the hydrogen bond reflects the change in the static dipole moment due to the bond formation. From the measurements of the IR-intensity of various modes of vibrations, mainly of the stretching vibration of the proton-donor group AH, and its change caused by H-bond formation, some important informations on the dynamics of hydrogen bonding may be derived. Thus, from the well-known formula for the fundamental stretching vibration in the harmonic oscillator approximation it follows

$$\left( \frac{\partial \mu_{\text{AH}}}{\partial r_{\text{AH}}} \right)_{r_0} = \pm \sqrt{\frac{3c^2 10^3 m_r}{\pi N}} B \quad (3)$$

where  $r_0$  is the equilibrium distance,  $m_r$  — the reduced mass of the AH-oscillator,  $N$  — Avogadro's number.

\* Address: Zakład Chemii Fizycznej Instytutu Chemii, Uniwersytet Wrocławski, Wrocław, F. Joliot-Curie 14, Poland.

gadro's number,  $c$  — the velocity of light;  $B$  is the integrated intensity of the fundamental stretching vibration:

$$B = \frac{1}{C \cdot l} \int_{-\infty}^{\infty} A(\nu) d\nu \quad (4)$$

where  $A(\nu)$  is the shape function of the absorption band ( $A(\nu) = \ln \left( \frac{I_0}{I} \right)_\nu$ ),  $\nu$  — the wave-number [ $\text{cm}^{-1}$ ],  $C$  — concentration [moles/l],  $l$  — the path length [cm].

Both quantities:  $\Delta\vec{\mu}$  and  $B$  play an important role in understanding the nature of the hydrogen bond, and further experimental data are needed. Earlier investigations of the IR intensity in hydrogen-bonded systems were discussed by Pimentel and McClellan [1]. In the majority of cases two-component systems were studied, *i.e.* proton-donors in solvents of different activity. In such measurements a part of the observed intensity enhancement is caused by the macroscopic solvent-effect, which may be considerable in some cases.

In the measurements of IR-intensities of hydrogen bonded complexes in ternary systems (*i.e.* in an inert solvent) the solvent effect remains approximately constant in the whole series of complexes, however the determination of equilibrium constants of complexation is required. Becker [2] investigated some complexes of methanol, ethanol and tert.-butanol with various proton-acceptors (in  $\text{CCl}_4$ ). Thompson *et al.* [3] studied complexes of phenol and 2,6-di-tert-butylphenol with organic cyanides (in tetrachloroethylene). Yoshida and Osawa [4] investigated complexes of phenol with aliphatic and aromatic  $\pi$ -bases (in  $\text{CCl}_4$ ). A number of data for *t*-butylalcohol, pyrrole, phenol,  $\alpha$ -naphthol, trifluoroacetic acid and hydrogen chloride complexes have been collected by Szczepaniak and Tramer [5], and for phenol and amine complexes by Yogansen *et al.* [6, 7]. Recently Chayredtinova *et al.* [8] published data on a series of complexes formed by alcohols of different acidity with  $\text{CH}_3\text{CN}$ . Perkampus *et al.* [9] have examined adducts of methanol and ethanol with a series of 15 pyridine derivatives. The importance of systematic investigations seems to be evident in the light of these works.

Numerous empirical linear correlation have been found:  $2b$  (the half-width of the absorption band) and  $\Delta B$  (the intensity increment) *vs.*  $\Delta\nu$  [1-3, 9] (the spectral shift of the stretching band, accompanying H-bond formation);  $2b$  and  $B$  *vs.*  $\frac{\Delta\nu}{\nu_0}$  [8] and several linear relations between thermodynamic and spectral data. A new type of correlation between H-bond energy and intensity of the stretching vibration band has been proposed by Yogansen [6, 7].

Special attention should be paid to the work by Chaykin and Tchulanovsky [10] who determined the intensities of the fundamental and first overtone of the NH stretching vibration of diethylamine and diphenylamine and for HCl, in various solvents. From these data the dipole moment function,  $\mu(r)$ , for the free and bound AH oscillator can be constructed and hence the polarity of hydrogen bond can be deduced.

The aim of this and subsequent papers in this series is to collect more systematic data on polar properties of weak hydrogen bonds, in order to obtain information on the nature

of bonding forces, mainly to establish the role of the electrostatic inductive and CT effects in these bonds.

The purpose of this work was the determination of the formation constants for diphenylamine and 2,4,6-trimethylphenol (mesitol) complexes with a number of proton acceptors in  $\text{CCl}_4$  and the estimation of integrated intensities and other IR-spectral data for the NH and OH stretching vibration bands in H-bonded complexes.

### Experimental

Resolution of overlapping bands. The absorption band of the stretching vibration of the N—H group of diphenylamine in complexes overlaps the band corresponding to the free molecule (Fig. 1). The calculation of the equilibrium constants as well as of absolute intensities requires the resolution of the composite envelope.

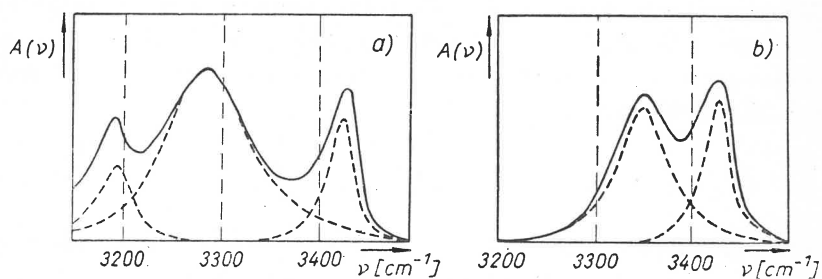


Fig. 1. The NH-stretching vibration band of diphenylamine in the presence of: a) pyridine, b) dioxane, in  $\text{CCl}_4$  solution

For the description of an individual absorption band the Cauchy-Gauss product function [11] was used

$$A(\nu) = a_1(1 + a_2^2(\nu - a_3)^2)^{-1} * \exp(-a_4^2(\nu - a_3)^2) \quad (5)$$

where  $A(\nu) = \log_{10} \left( \frac{I_0}{I} \right)_\nu$  is the shape function,  $a_1$  represents the peak height,  $a_3$  — the

frequency at the center of the band,  $a_2$  and  $a_4$  are the shape parameters. If  $\frac{a_2}{a_2 + a_4} = 0$ ,

Eq. (1) reduces to a Gauss function, if it equals 1, the equation corresponds to a Cauchy (Lorentz) curve. Starting from approximate input values, the parameters for each band were found by means of iteration procedures based on Levenberg's and Meiron's [11, 12] methods.

The iteration steps are given by the equations:

$$\vec{a}^{(m+1)} = \vec{a}^{(m)} - (\mathbf{B}^{(m)} + d\mathbf{C}^{(m)})^{-1} \vec{G}^{(m)} \quad (6a)$$

$$\vec{a}^{(m+1)} = \vec{a}^{(m)} - (\mathbf{B}^{(m)} + d\mathbf{E})^{-1} \vec{G}^{(m)} \quad (6b)$$

where  $\vec{a}$  is the column vector of the determined parameters. The matrix  $\mathbf{B}$  and the vector  $\vec{G}$  are defined as

$$\mathbf{B} = \mathbf{J}^T \mathbf{P} \mathbf{J}, \quad \vec{G} = \mathbf{J}^T \mathbf{P} \vec{r}$$

$C$  is a matrix obtained from  $B$  by omitting all the off-diagonal elements, and  $E$  is a unity matrix.  $P$  is a diagonal matrix of weight factors,  $P_i$ . The matrix  $J$  is defined as

$$J = \{J_{ij}\} \quad J_{ij} = \frac{\partial r_i}{\partial a_j} \quad \begin{array}{l} i = 1, 2 \dots M \\ j = 1, 2 \dots N \\ i \geq j \end{array}$$

$M$  denotes the number of experimental points;  $v_i$ ,  $A_i$ ;  $N$  is the number of parameters ( $N = 4L$ , where  $L$  denotes the number of absorption bands). The vector  $\vec{r}$  has the components:

$$r_i = A_{i_{\text{exp}}} - A_{i_{\text{calc}}}$$

$d$  denotes the damping factor, chosen on each iteration step to minimize the quantity  $\sum_{i=1}^M P_i r_i^2$ .

The calculations were performed on the Elliott 803 computer in the Wrocław University Computing Centre, following original programs written in Mark III.

Determination of equilibrium constants. The formation constant of the complexation (Eq. (1)) is given by:

$$K = \frac{C_D^0 - C_D}{C_D(C_A^0 - C_D + C_D)} \quad (8)$$

where  $C_D$  is the equilibrium concentration of the proton-donor (D);  $C_A^0$  and  $C_D^0$  are the initial concentrations.  $C_D$  was determined by measuring the peak height or the band intensity of the "free" AH-group absorption, obtained from the resolved envelope of the complex absorption. It has been tested during our calculations, that only with the product function (5) a good description of single absorption bands and a reliable resolution of composite envelopes can be achieved. The use of "pure" Cauchy or Gauss curves is not justified and produces errors in band intensities and equilibrium constants. Both procedures, based on the peak height or band intensity give approximately the same results. It has been proved that in all cases simple complexes of 1:1 stoichiometry are formed, at least in the concentration range considered in this work.

Calculations of integrated intensities. As the result of the numerical resolution procedures performed in this work, all the absorption bands were described by means of the symmetric product function (5). This enabled the numerical integration of the bands. The following integration methods were used.

1. Method of direct integration. It may be shown that the integral of the product function (5) can be expressed by

$$\int_{-\infty}^{\infty} A(v) dv = \pi \frac{a_1}{a_2} \left[ 1 - \frac{2a_4}{\sqrt{\pi}} \int_0^{\frac{1}{a_2}} \exp(-a_4^2 t^2) dt \right] \exp\left(\frac{a_4^2}{a_2^2}\right) \quad (9)$$

This method provides very satisfactory results in cases when  $0.5 < \frac{a_2}{a_2 + a_4} \leq 1$ . The integral of the function  $\exp(-a_4^2 t^2)$  was calculated by means of the trapezium formula.

2. Gauss-Laguerre-method. In cases of high Gauss-percentage of the curve described by Eq. (5), the numerical error of integration based on Eq. (9) becomes considerable. More suitable for the range  $0 \leq \frac{a_2}{a_2+a_4} \leq 0.5$  is the Gauss-Laguerre method:

$$\int_{-\infty}^{\infty} A(v)dv = 2 \int_0^{\infty} e^{-x}f(x)dx \quad (10)$$

where

$$\int_0^{\infty} e^{-x}f(x)dx = \sum_{k=1}^n c_k f(x_k)$$

$$f(x) = a_1(1+a_2^2x^2)^{-1} * \exp(x(1-a_4^2x))$$

$$x = v - v_0 = v - a_3.$$

$c_k$  and  $x_k$  are the coefficients and nodes of the correspondent Laguerre polynomial. Also the simple trapezium formula gives satisfactory results, however the problem of integration limits arises. The calculations were performed following Elliott-Algol procedures.

Experimental details. The spectra were recorded on a Unicam SP-700 Spectrophotometer at constant temp.  $25 \pm 0.2^\circ\text{C}$ . The density of the solutions was always measured also at  $25 \pm 0.05^\circ\text{C}$  with a precision of  $\pm 1 \cdot 10^{-4} \text{ g/cm}^3$ . "Infrasil" absorption cells with teflon stopcocks were used. As a reference the solution of the proton-acceptor (A) at the same concentration as in the sample studied was applied. In the region  $4300\text{--}2800 \text{ cm}^{-1}$  the instrument works with a diffraction grating monochromator; the spectral slit width was exactly known ( $2\text{--}3 \text{ cm}^{-1}$ ). The peak height was corrected for the slit distortion by means of Ramsay's [13] tables. The correction factors were usually  $\sim 1.01\text{--}1.02$ . For the peak height and area for the very broad absorption bands, typical for the stretching vibration bands of the hydrogen-bonded A-H-group, the corrections were negligible.

The solvents used in this work were purified by using standard methods [14]. Piperidine and liquid pyridine bases (*puriss.*) were dried and fractionally distilled. Molecular sieves were used as a desiccant. 3,5-dichloropyridine and diphenylamine were purified by repeated crystallization from ethanol and dried in a vacuum desiccator over KOH and  $\text{K}_2\text{CO}_3$ . 2,4,6-trimethylphenol was twice crystallized from benzene and dried in vacuum desiccator over  $\text{MgSO}_4$ . The physical constants such as b. p., f. p., density and electric permittivity were consistent with literature data.

### Results and discussion

The spectral characteristics and the formation constants of the diphenylamine complexes are given in Table I. Concentrations of  $0.001\text{--}0.07$  moles/l of diphenylamine were used; in this range the selfassociation of this donor is negligible. Diphenylamine is a weak acid ( $pK_a \sim 23$ ), therefore in all cases the absorption band of the stretching vibration of the "bonded" NH-group overlaps considerably the correspondent band of the "free" group. In stronger complexes and additional band at  $3190 \text{ cm}^{-1}$  appears (Fig. 1). The participation

of this band in the total intensity of the composite envelope of the "bonded" absorption (column 9, Table I) increases with the spectral shift of the complex band to lower frequencies, whereas its position remains unchanged. This seems to support the conclusion, that this absorption may be explained as the Fermi resonance between the overtone of the NH-bending vibration and the fundamental stretching vibration of the bonded NH-group.

TABLE I  
Stability constants and spectral characteristics of diphenylamine complexes (25°C, CCl<sub>4</sub>)

Proton-acceptor	$pK_a(B)$	$K[1 \text{ mol}^{-1}]$	$\nu_s(\text{NH})$ [cm <sup>-1</sup> ]	$\Delta\nu$ [cm <sup>-1</sup> ]	$2b$ [cm <sup>-1</sup> ]	$10^{-3}B$ [1 mol <sup>-1</sup> cm <sup>-2</sup> ]	$\frac{B}{B_0}$	$\frac{B'}{B} 100$
Piperidine	11.22	0.85±0.05	3258	176	127	36.0±0.6	9.3	—
3,5-Lutidine	6.09	2.06±0.02	3274	160	83	27.7±0.9	7.1	9
4-Picoline	6.00	1.76±0.02	3279	155	85	30.0±0.5	7.8	8
Pyridine	5.19	1.35±0.02	3285	149	85	29.3±0.7	7.6	7
3,5-Dichloropyridine	0.49	0.31±0.04	3321	113	70	25.3±0.5	6.5	3
Dioxane	-2.92	0.76±0.04	3357	77	47	18.2±0.3	4.7	0
Acetone	-7.2	2.27±0.20	3378	56	64	11.7±0.1	3.0	0
Diphenylamine	—	—	3433.5	—	25	3.87±0.05	1	0

In Table I the arithmetic means (from 5-7 estimations) with mean square errors are given; the errors of  $\nu$ ,  $\Delta\nu$ - and  $2b$ - values are ±1 cm<sup>-1</sup>.

In Table II the spectral characteristics of diphenylamine dissolved directly in some acceptors are given; additional spectral shift towards lower frequencies (15-20 cm<sup>-1</sup>) and broadening (5-10<sup>-1</sup> cm) of the band is observed, compared with the values obtained in an

TABLE II  
Spectral data of some diphenylamine complexes in binary and ternary systems (25°C)

Acceptor	Binary system			Ternary system (in CCl <sub>4</sub> )		
	$\Delta\nu$	$2b$	$10^{-3} \cdot B$	$\Delta\nu$	$2b$	$10^{-3} \cdot B$
4-Picoline	169	93	31.3	155	85	30.0
Pyridine	164	93	32.9	149	85	29.3
Dioxane	90	52	18.9	77	47	18.2
Acetone	77	76	21.7	56	64	11.7

inert solvent. The variation of the integrated intensity is surprisingly small, except for the complex with acetone. The above comparison supports once more the conclusion that the spectral shift of the stretching vibration band, the band broadening and intensity enhancement are caused mainly by hydrogen-bond formation and not by the environment effect.

The equilibrium constants for some diphenylamine-complexes were known previously; for the adduct with pyridine a value of 1.5 moles l<sup>-1</sup> [15] with dioxane 0.88 [15] and 0.58

[16] (from UV-data), with acetone 2.2 [15] and 2.25 [17] were obtained, in good agreement with our results, although the above values were estimated in non-thermostated conditions.

It can be seen in Table I that the  $\Delta\nu$ -,  $2b$ - and  $B$ -values increase with increasing basic properties of the proton-acceptor (higher  $pK_a$ ), whereas the formation constant changes regularly only in complexes with a series of bases of the same type. The small formation

TABLE III

Formation constants and spectral characteristics of 2,4,6-trimethylphenol complexes

Proton-acceptor	$pK_a(B)$	$K$ [l mol <sup>-1</sup> ]	$\nu_s(\text{OH})$ [cm <sup>-1</sup> ]	$\Delta\nu$ [cm <sup>-1</sup> ]	$2b$ [cm <sup>-1</sup> ]	$B \cdot 10^{-4}$ [l mol <sup>-1</sup> cm <sup>-2</sup> ]	$B/B^0$	$2b/2b^0$
Piperidine	11.22	9.27±0.23	2900*	721*				
2,4,6-Collidine	7.52	6.03±0.04	3140	481	391	16.27±0.46	24.61	24.44
4-Picoline	6.00	6.44±0.13	3202	419	348	15.42±0.17	23.32	21.75
Pyridine	5.19	4.61±0.12	3226	395	334	14.46±0.28	21.87	20.88
3-Chloropyridine	2.84	2.01±0.10	3291	330	261	11.25±0.20	17.01	16.31
3,5-Dichloropyridine	0.49	0.74±0.04	3350	271	253	12.56±0.45	19.00	15.81
2,4,6-Trimethylphenol	—	—	3621.4	—	16.0	0.6610±0.0079	1	1

\* ±50 cm<sup>-1</sup>

constants of the piperidine-complex results probably from steric hindrances whereas the relatively high values for dioxane and acetone are difficult to explain. It is worth mentioning that no complexation of diphenylamine with triphenylamine, tri-*n*-butylamine, tribenzylamine, tripropylamine, trisopropylamine and triallylamine was detected, even using a large excess of the acceptor concentration. This reflects the special role of steric effects during the complexation, *i. e.* the considerable contribution of the entropy change to the thermodynamic potential change of the process.

TABLE IV

Dipole moment derivatives of the NH-group in diphenylamine complexes

Proton-acceptor	$\left(\frac{\partial \mu_{\text{NH}}}{\partial r_{\text{NH}}}\right)_{r_0} \left[\frac{\text{D}}{\text{\AA}}\right]$	$\left(\frac{\partial \mu_t}{\partial r_{\text{NH}}}\right)_{r_0} \left[\frac{\text{D}}{\text{\AA}}\right]$
Piperidine	2.83	1.90
3,5-Lutidine	2.48	1.55
4-Picoline	2.59	1.66
Pyridine	2.55	1.62
3,5-Dichloropyridine	2.37	1.44
Dioxane	2.01	1.08
Acetone	1.62	0.69
Diphenylamine	0.928	—

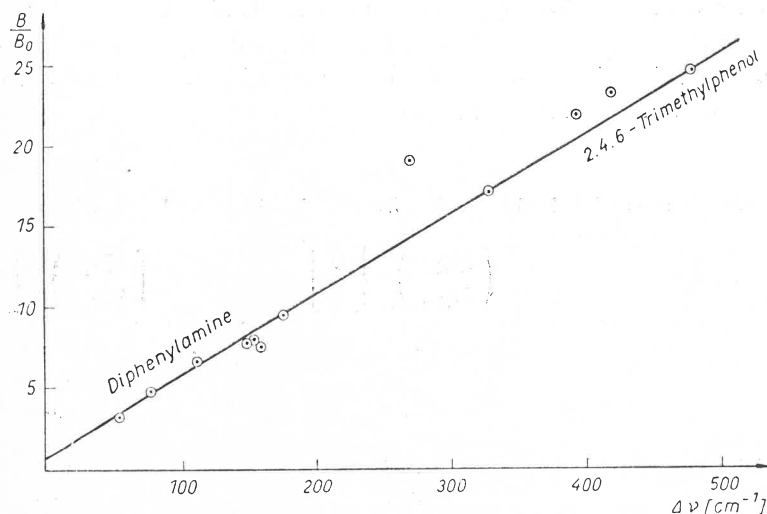
Similar results were obtained for a series of 2,4,6-trimethylphenol complexes, which have not been hitherto investigated. The absorption band of the stretching vibration of the free OH group fulfils the Lambert-Beer's law; the measurements were carried out in the concentration range  $9 \cdot 10^{-4}$ — $5 \cdot 10^{-3}$  moles  $l^{-1}$  (for the donor); the bases were used in 5- to

TABLE V

Dipole moment derivatives of the OH-group in 2,4,6-trimethylphenol complexes

Proton-acceptor	$\left( \frac{\partial \mu_{OH}}{\partial r_{OH}} \right)_{r_0} \left[ \frac{D}{\text{\AA}} \right]$	$\left( \frac{\partial \mu_t}{\partial r_{OH}} \right)_{r_0} \left[ \frac{D}{\text{\AA}} \right]$
2,4,6-Collidine	6.04	4.82
4-Picoline	5.88	4.66
Pyridine	5.70	4.48
3-Chloropyridine	5.03	3.81
3,5-Dichloropyridine	5.31	4.09
2,4,6-Trimethylphenol	1.218	—

20-fold excess. There is practically no overlap between the absorption bands of the bonded and free OH-group, as the complexes are stronger than in the case of diphenylamine. For the intensity measurements of the absorption band of the bonded OH-group only the short-wavelength side with the maximum of this band was accessible due to the interfering CH stretching vibration band. Symmetry of this band was assumed during the calculation of integrated intensity. The spectral data of the complexes and their formation constants are

Fig. 2. Plot of  $\frac{B}{B_0}$  vs.  $\Delta \nu$



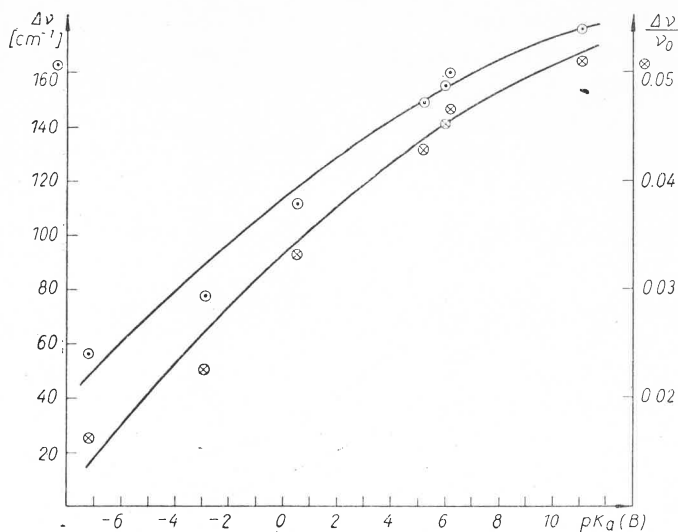


Fig. 3. The dependence of  $\Delta\nu$  and  $\frac{\Delta\nu}{\nu_0}$  on  $pK_a(B)$  for diphenylamine complexes

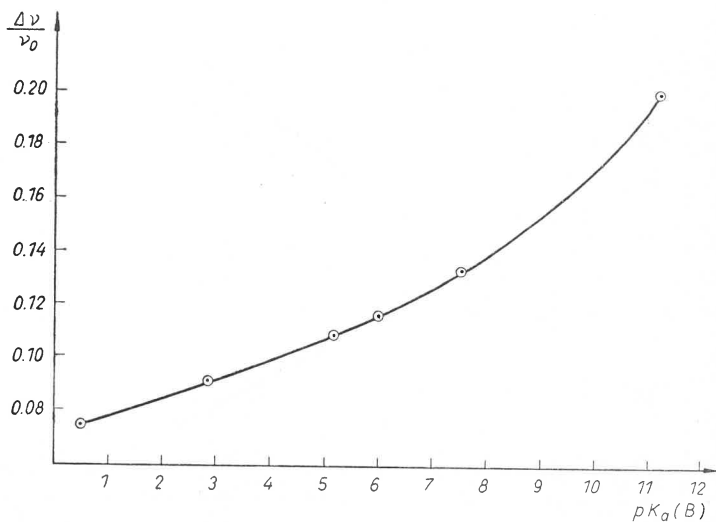


Fig. 4. The dependence of  $\frac{\Delta\nu}{\nu_0}$  on  $pK_a(B)$  for mesitol complexes

collected in Table III; the denotations of Table I are used. The error of the values:  $\nu$ ,  $\Delta\nu$  and  $2b$  is here  $\pm 2\text{cm}^{-1}$ . It is evident from the data in Table III, that the  $K$ -,  $\Delta\nu$ -,  $2b$ - and  $B$ -values fall systematically with decreasing basicity of the acceptor. The variation of these quantities during H-bond formation are larger than in diphenylamine-complexes, according to the more pronounced acidic character of the donor and, respectively, more stable ad-

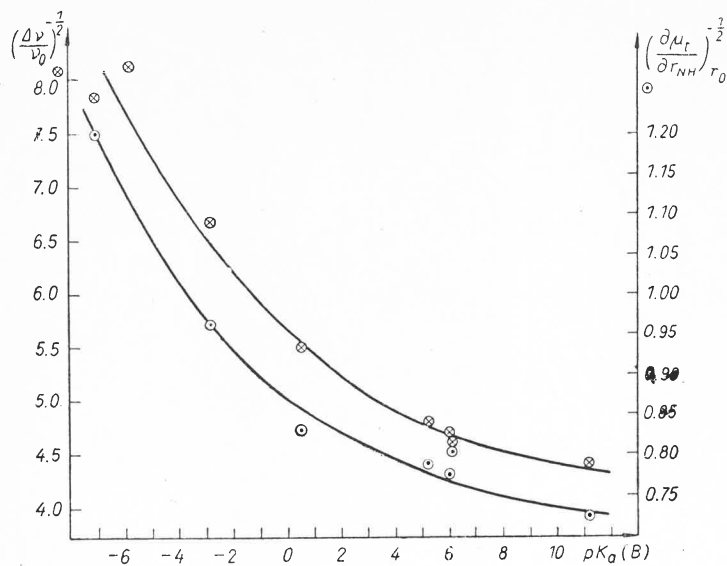


Fig. 5. The relationship between  $\left(\frac{\Delta\nu}{\nu_0}\right)^{-\frac{1}{2}}$  or  $\left(\frac{\partial\mu_t}{\partial r_{NH}}\right)^{-\frac{1}{2}}$  and  $pK_a(B)$  for diphenylamine complexes

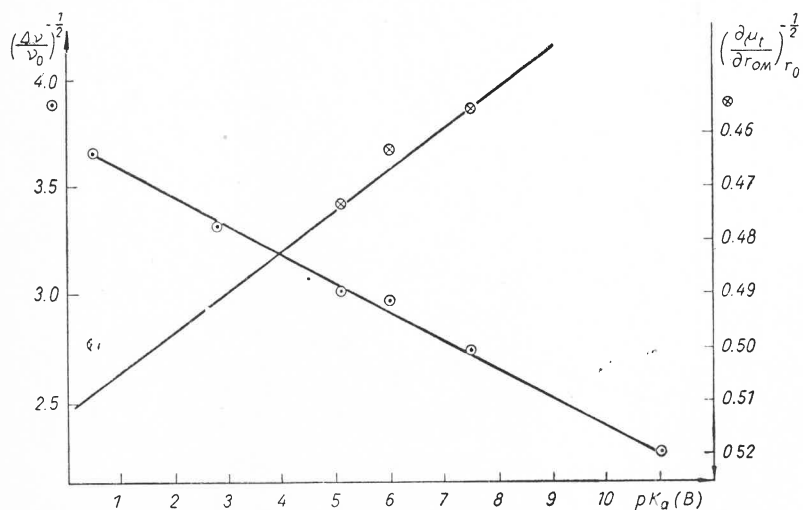


Fig. 6. The relation between  $\left(\frac{\Delta\nu}{\nu_0}\right)^{-\frac{1}{2}}$  or  $\left(\frac{\partial\mu_t}{\partial r_{OH}}\right)^{-\frac{1}{2}}$  and  $pK_a(B)$  for 2,4,6-trimethylphenol complexes

ducts. It is interesting to notice, that the  $\frac{B}{B^0}$  and  $\frac{2b}{2b^0}$  ratios are close; this results from the known fact, that in the hydrogen bonding the intensity enhancement is produced mainly by the broadening of the absorption band, whereas the molar extinction coefficient remains almost unchanged.

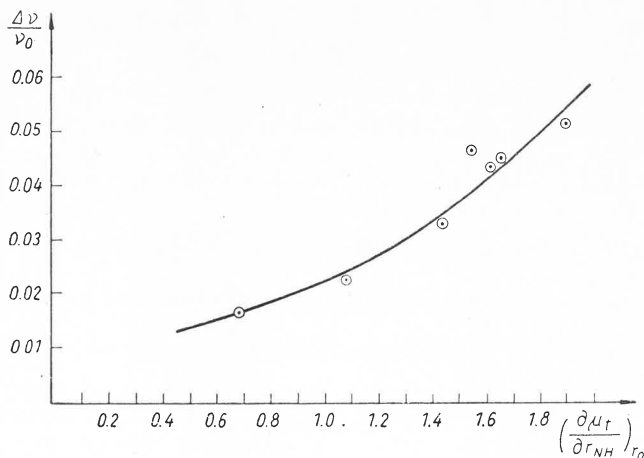


Fig. 7. Plot of  $\frac{\Delta \nu}{\nu_0}$  vs.  $\left(\frac{\partial \mu_t}{\partial r_{NH}}\right)_{r_0}$ : diphenylamine complexes

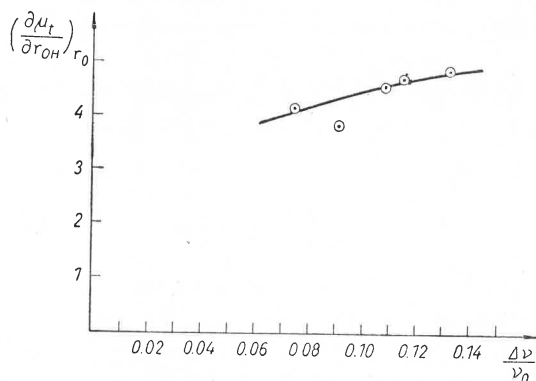


Fig. 8. Plot of  $\left(\frac{\partial \mu_t}{\partial r_{OH}}\right)_{r_0}$  vs.  $\frac{\Delta \nu}{\nu_0}$ : mesitol complexes

In Table IV the values of the dipole moment derivative,  $\left(\frac{\partial \mu}{\partial r}\right)_{r_0}$ , for the NH-group of diphenylamine, are given, calculated following relation (3):

$$\left(\frac{\partial \mu_{NH}}{\partial r_{NH}}\right)_{r_0} = 1.491 \cdot 10^{-2} \sqrt{B} \left[\frac{D}{\text{\AA}}\right]. \quad (11)$$

Similar data for the OH group of mesitol are collected in Table V; in this case the relation (3) reduces to:

$$\left(\frac{\partial \mu_{OH}}{\partial r_{OH}}\right)_{r_0} = 1.498 \cdot 10^{-2} \sqrt{B} \left[\frac{D}{\text{\AA}}\right]. \quad (12)$$

In both Tables also the increments,  $\left(\frac{\partial \mu_t}{\partial r_{AH}}\right)_{r_0}$ , *i. e.* the derivatives of the intermolecular transition moments, are quoted.

In Fig. 2 the plot of the empirical correlation:  $\frac{B}{B^0} = f(\Delta\nu)$  is shown. The data fulfil also the linear correlation:  $\Delta B = f(\Delta\nu)$ ; both (equivalent) relations seem to be well-established features of H-bonded systems [18]. Sokolov [19] on the base of the VB theory of the hydrogen-bonding, predicts a linear relationship between  $\Delta\nu$  (or  $\frac{\Delta\nu}{\nu_0}$ ) and  $I_B^v$  (ionization potential of the base BR<sub>1</sub>); consequently, such a relation between  $\Delta\nu$  (or  $\frac{\Delta\nu}{\nu_0}$ ) and  $pK_a(B)$  should exist. On the other hand, from the CT theory of the hydrogen bonding [5] a linear relation between  $\left(\frac{\partial\mu_r}{\partial r}\right)_{r_0}^{-\frac{1}{2}}$  and  $pK_a(B)$ , and  $\left(\frac{\Delta\nu}{\nu_0}\right)^{-\frac{1}{2}}$  and  $pK_a(B)$ , is expected; the plot of  $\left(\frac{\partial\mu_r}{\partial r}\right)_{r_0}$  vs  $\frac{\Delta\nu}{\nu_0}$  should also be linear and intercept the origin. It can be seen from Figs 3, 5 and 7 that the relations are not fulfilled in the case of diphenylamine. This may be caused by the fact that, as it will be shown later, in this complexes the electrostatic inductive forces are dominant. In the case of 2,4,6-trimethylphenol complexes the  $pK_a$ -range of the bases seems to be too limited to make any conclusions, although the disagreement with the mentioned theories is also evident from Figs. 4 and 8.

The authors are greatly indebted to dr A. Sucharda-Sobczyk for the participation in spectroscopic investigations which were performed in the Central Laboratory of the Chemical Faculty of the Wrocław Technical University.

#### REFERENCES

- [1] G. C. Pimentel, A. L. Mc Clellan, *The Hydrogen Bond*, Freeman, San Francisco 1960.
- [2] E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).
- [3] M. C. S. Lopes, H. W. Thompson, *Spectrochim. Acta*, **24A**, 1367 (1968).
- [4] Zen-ichi Yoshida, Eiji Osawa, *J. Amer. Chem. Soc.*, **87**, 1467 (1965); **88**, 4019 (1966).
- [5] K. Szczepaniak, A. Tramer, *J. Phys. Chem.*, **71**, 3035 (1967).
- [6] B. W. Rassadin, A. W. Yogansen, *Zh. Priklad. Spektrosk.*, **6**, 492, 801 (1967); **10**, 290 (1969); **11**, 828 (1969).
- [7] A. W. Yogansen, C. A. Kurkcz, B. W. Rassadin, *ibid.* **11**, 1054 (1969).
- [8] A. K. Chayredtinova, I. S. Perelygin, *Optika i Spektrosk.*, **26**, 62 (1969).
- [9] H. H. Perkampus, P. M. A. Kerim, *Spectrochim. Acta*, **24A**, 2071 (1968).
- [10] C. J. Chaykin, W. M. Chulanovsky, *Optika i Spektrosk.*, **20**, 234 (1966); **23**, 709 (1967).
- [11] J. Pitha, R. N. Jones, *Canad. J. Chem.*, **44**, 3031 (1966).
- [12] J. I. Hawranek, *Wiad. Chem.*, **24**, 225 (1970) in Polish.
- [13] D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).
- [14] *Technique of Organic Chemistry*, Vol. VII, Organic Solvents, Interscience Publ., London 1955.
- [15] J. Lauransan, P. Pineau, *J. Chim. Phys.*, **65**, 1937 (1968).
- [16] A. B. Sannigrahi, A. K. Chandra, *J. Phys. Chem.*, **67**, 1106 (1963).
- [17] A. E. Lutski, E. I. Goncharova, *Zh. Fiz. Khim.*, **40**, 2735 (1966); **41**, 538 (1967).
- [18] S. Detoni, D. Hadži, R. Smerkolj, J. Hawranek, L. Sobczyk, *J. Chem. Soc.*, **A**, 2851 (1970).
- [19] N. D. Sokolov, *Vodorodnaya Svyaz'*, Nauka, Moskva 1964, p. 7, in Russian.