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INFLUENCE OF THE ELECTRIC PERMITTIVITY OF THE MEDIUM ON THE POLARITY OF HYDROGEN BONDING IN COMPLEXES OF PHENOLS AND TRIETHYLAMINE

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Assuming a double minimum model *i. e.* tautomeric equilibrium of two forms $A\text{–H}...B \rightleftharpoons A^{-}...\text{H}-B^{+}$ of the hydrogen bridge differing in energy by ΔU, theoretical dependences of ΔU and the mean dipole moment μ on the electric permittivity of the medium are proposed using Onsanger's theory, and checked by measuring μ for 8 complexes of phenol derivatives (with pK_a varying from 10.8 to 3.4) and triethylamine in 3 solvents: cyclohexane ($\varepsilon = 2.0$), toluene ($\varepsilon = 2.4$), and trichloroethlaene ($\varepsilon = 3.5$). The dipole moment μ_k of the complexes was found to depend strongly on of the solvent. The curve ΔU *vs* ε agrees well with the theory and leads to $\mu_2 = 11.4$ D for the form of bridge with shifted proton in excellent agreement with the directly measured value.

Also, the theoretical shape of μ *vs* $\Delta U(\varepsilon)/RT$ agrees well with the present experimental results throughout a wide range of $\Delta U/RT$-values appearing to prove the existence of such tautomeric equilibria in hydrogen bonds.

1. *Introduction*

The properties of hydrogen bonded systems are primarily defined by the state of the bonded proton. In determining this state, one considers essentially two possibilities: proton localization $A-\text{H}...B$ or $A^{-}...\text{H}-B^{+}$, and proton delocalization $A...\text{H}...B$. In the first case, one assumes tautomeric equilibrium:

$$A-\text{H}...B \rightleftharpoons A^{-}...\text{H}-B^{+}, \tag{1.1}$$

with a potential energy curve of the proton presenting two minima, one for either state. Figs 1a, b, c show the shapes of the proton's potential energy curves postulated for such cases.

In the case of delocalization of the proton, the energy curve has a single minimum (Fig. 1d).

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A number of facts suggest that, except for some few particular cases, the proton does not occupy a position symmetrical with respect to the atoms A and B. This has been confirmed by various electron and neutron diffraction studies as well as by NMR, and so it appears that proton delocalization is not the typical kind of hydrogen bond.

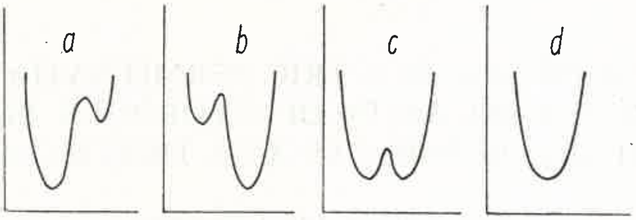

Fig. 1. The various types of potential energy curves of the hydrogen bonded proton

A tautomeric equilibrium (1.1) brought about by a potential energy with two minima has obviously to be dynamical and hence related with a kinetics of the proton along the $A...B$ bond.

Many proofs exist that the proton can change its position in the bridge [1–10], although the nature of its motion is still controversial.

One of the strongest arguments in favour of tautomeric equilibrium with proton shift (1.1) resides in the *UV* spectra of complexes of phenols (particularly *p*-nitrophenol) [2, 11] and organic bases (chiefly triethylamine) revealing a band (at about 400 nm), characteristic of the phenolate anion, and of an intensity depending on such factors as the polarity of the solvent, or temperature.

Bell and Barrow [12] draw the same conclusion from the IR spectra of complexes of deuterated phenols and bases. Barrow [13] made assessments of the contribution of structures with shifted proton for systems of pyridine and carboxylic acids.

Dielectric saturation studies by Małecki have shown that, in hydrogen bonded systems, nonlinearity of the medium is especially large. The unusually large negative values of correlation factors for dielectric saturation $R^{(s)}$, which in not highly concentrated solutions of alcohols in neutral solvents are of the order of -100, mean that the observed effect not only is of opposite sign to that which would result from the orientation of the molecule in the electric field but that moreover its absolute value is 100 — fold larger than that to be expected from the dipole moment of the alcohol molecule. In order to explain such very large negative values of $R^{(s)}$, one has to assume the existence of two energy states of the complex differing slightly in energy but very strongly differing as to their dipole moments. On the assumption that the two energy states of the hydrogen bridge correspond to states described by a tautomeric equilibrium of the type (1.1), Piekara [14] and Małecki [15, 16] explained the experimental effect of dielectric saturation and evaluated the dipole moment of the complex with shifted proton. For *n*-hexanol dimers, this moment amounted to about 13 D.

Also, the results of Ratajczak and Sobczyk [17–19] on hydrogen bond polarity are in agreement with the theoretical calculations once one assumes the presence of the tautomeric equilibrium (1.1).

The shape of the potential energy curve and the kinetics of the proton in the hydrogen bridge are subjects of the utmost interest to numerous research workers, and play a central role *int. al.* in the theory of a class of ferroelectrics, as well as in molecular biology. Löwdin [20], using the concept of proton tunnelling in the bridge, proposed a theory of spontaneous point mutations in DNA. Proton photo-transfer is probably of vast importance in biological processes, especially with regard to the arising of point mutations [21].

2. Polarity of the hydrogen bond

The application of dielectric methods to the study of systems with hydrogen bonds appears highly suitable, since the assumptions required for the interpretation of these results are in many cases less arbitrary than when using other methods.

Calculations and a correct interpretation of the experimental results become feasible once the stoichiometry and geometry of the complexes are known. In general, the true composition of hydrogen bonded associated solutions is not known and, as yet, there is no method of solving this problem univocally.

The most highly complicated situation arises in the case of associates of molecules having bi-functional groups *i. e.* ones containing donor as well as acceptor atoms (OH, NH, *etc.*), as here different associates (monomers, dimers, trimers, *etc.*) can occur simultaneously, in open and cyclic form. Such is the situation with solutions of alcohols, phenols, as well as primary and secondary amines in neutral solvents. Data relating to the stoichiometry, formation constants and dipole moments of associates can be calculated by methods proposed by Małecki resorting to results of dielectric polarization and dielectric saturation measurements [22–24].

The situation becomes increasingly intricate if the solvent is an active one, since the associates enter into complexes with the solvent molecules. An interesting method of analyzing the composition of such complexes from dielectric data is due to Huyskens *et al.* [25].

In a good approximation, the composition can be determined for a certain class of ternary solutions containing molecules of an acid, a base and a neutral solvent. Among others, dielectric titration measurements by Ratajczak [26] showed that, in the case of bases of the type of ternary and pyridine amines at appropriately low concentrations of the acid (as long as association is weak) and at appropriately high excess of the base, complexes of 1:1 composition are given rise to. This, obviously, holds for sufficiently strong acids, when the equilibrium constants of complex formation are sufficiently large, and thus concerns *e. g.* systems involving a phenol, triethylamine, and a neutral solvent, when all the molecules of the acid can be assumed to have entered complexes with those of the base. Unless this is so, the determination of the dielectric polarization of the complex requires the equilibrium constant of formation of the latter to be known.

In the case of the above-mentioned complexes of phenols and triethylamine (or pyridine), the geometry of the complex can be determined in a satisfactory approximation. In bondings of this type, the atoms A and B are situated on the axis of the lone electron pair of nitrogen; consequently, in interpreting the experimental results, one can resort to a rather simple model of the complex based on directional additivity of dipole moment vector components.

Once the composition of the solution is known, dielectric polarization results can serve for the calculation of the dipole moment $\vec{\mu}_k$ of the complex. If, moreover, the geometry of the latter is known, its dipole moment resulting from vector addition of the dipole moments of the acid ($\vec{\mu}_a$) and base ($\vec{\mu}_b$) can be calculated.

Now, it turns out that, for hydrogen bonded complexes, the experimentally determined dipole moment ($\vec{\mu}_k$) is larger than the one calculated from the geometry. The difference:

$$\Delta\vec{\mu} = \vec{\mu}_k - (\vec{\mu}_a + \vec{\mu}_b) \tag{2.1}$$

is referred to as the polarity of the hydrogen bond.

The quantity $\Delta\vec{\mu}$ is due to changes in the charge distribution in the complex R_1AH...

...BR_2 as compared with the charge distributions of the isolated molecules. Such changes occur in the entire system, but are strongest in the fragment $A-$H...B directly engaged in the bond. Although the literature provides very little data concerning the changes in charge distribution in the rest of the complex, it seems a good assumption that they are negligible in a first approximation.

Since, on the above assumption, $\Delta\vec{\mu}$ represents the changes occuring in the system $A-$H...B, in the case of linear hydrogen bonds $\Delta\vec{\mu}$ is the increase in dipole moment along the bond $A-$H...B, often referred to simply as the dipole moment of the hydrogen bond.

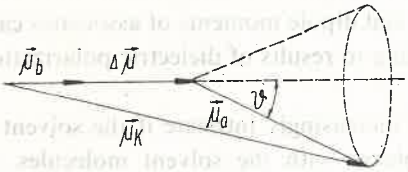

Fig. 2. Geometrical interpretation of the quantity $\Delta\vec{\mu}$

Fig. 2 gives a geometrical interpretation of $\Delta\vec{\mu}$ for the case of a phenol + triethylamine type complex of composition 1:1.

As yet, the literature dealing with the hydrogen bond contains no papers on the theoretical prediction of the value of $\Delta\vec{\mu}$. The methods of quantum mechanics, which permit the evaluation of this quantity, are applicable only if the wave function of the hydrogen bonded complexes is known exactly. The problem, however, still awaits its solution.

The experimental papers lay stress on the essential importance of the inductional effect, electron delocalization and proton transfer with regard to the dipole moment of hydrogen bonds.

The contribution of the effects of induction and delocalization to the polarity of the hydrogen bond, as evaluated *int. al.* by Sobczyk and Syrkin [27], Ratajczak [28], Kollmann and Allen [29] and Hoyland and Kier [30], is of the order of 0.5 D. It is generally thought that these effects are decisive for the polarity of weak hydrogen bonds, and that these values of $\Delta\mu$ represent the lower limit of polarity.

For complexes of strongly acid and basic molecules, one obtains rather large values of $\Delta\mu$ (of the order of 10 D), a fact most authors explain by invoking the existence of a polar form of the bond: $A^{-}...\mathrm{H}-B^{+}$.

Sutton *et al.* [31] measured the dipole moment of phenoltriethylamine complexes and found that the calculated $\Delta\mu$ values increased with growing acidity of the phenol. Huyskens *et al.* [25] also found a dependence of $\Delta\mu$ on pK_a in their measurements of the dipole moment of complexes of phenols and triethylamine. These results point to a growing part of the ionic form in the equilibrium (1.1) with increasingly strong acidic properties (decreasing pK_a) of the proton donor.

Huyskens and Zeegers-Huyskens [32] established theoretically the following relation between the equilibrium constant K_{PT} of the proton transfer process and the ionisation constants of the acid (K_a) and base (K_b):

$$\log K_{PT} = -pK_a - pK_b + 14 + \Delta, \tag{2.2}$$

where Δ depends on the nature of the solvent and type of the complex, but generally remains constant within a family of similar complexes.

The earliest investigation of $\Delta\mu$ *vs* pK_a is due to Ratajczak and Sobczyk [17–19], who obtained a well-defined correlation between the two quantities for complexes of phenols with triethylamine and pyridine. Fig. 3 shows their results [17].

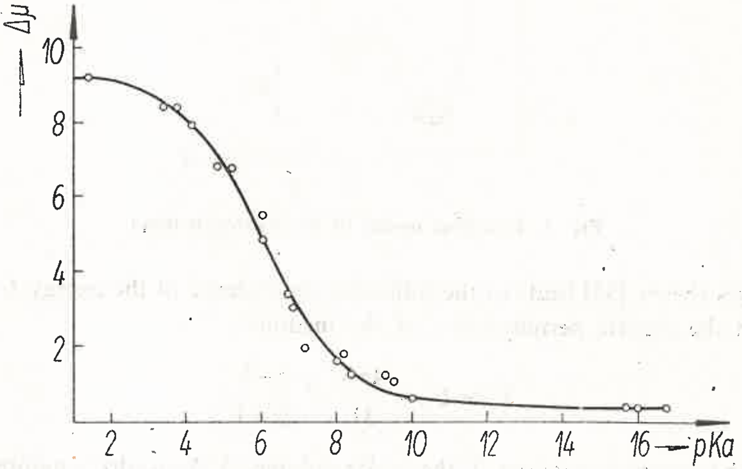

Fig. 3. Experimental dependence of $\Delta\mu$ on pK_a for complexes of phenols and triethylamine (after [17])

These results enabled the authors to check experimentally the theoretical formula of Huyskens (2.2). It was found that in order to adjust the theoretical curve to the experimental one, Huyskens' formula has to be modified as follows:

$$\log K_{PT} = \xi[-pK_a - pK_b + 14 + \Delta]. \tag{2.3}$$

On assuming $\xi = 0.4$ and calculating Δ on the assumption of $K_{PT} = 1$ for $pK_a = 6$, they succeeded in obtaining a good agreement of the theoretical and experimental results.

3. *On the possibility of a modification of the equilibrium constant K_{PT} of the proton transfer process by changes in the electric permittivity of the medium*

The interpretation of the experimental facts relative to hydrogen bonding based on the double-minimum model of the bond *i. e.* on the existence of tautomeric equilibrium between its two forms:

$$\underset{(1)}{A{-}\mathrm{H}\ldots B} \rightleftharpoons \underset{(2)}{A^{-}\ldots\mathrm{H}{-}B^{+}}$$

the "usual" form (1) and the "polar" form (2), leads to vastly important consequences.

Denoting the energy difference between these two states of the bond by ΔU (Fig. 4), the equilibrium constant of the process of proton transfer K_{PT} can be written as:

$$K_{PT} = \exp\left[-\Delta U/RT\right] = \omega_2/\omega_1, \tag{3.1}$$

where ω_1 and ω_2 are the relative investments of the two states, obviously with $\omega_1+\omega_2 = 1$. Assuming furthermore for the bond $A{-}\mathrm{H}\ldots B$ a dipole moment μ_1 and for $A^{-}\ldots\mathrm{H}\ldots B^{+}$ a moment μ_2, one can express the experimentally determined mean dipole moment as:

$$\mu^2 = \omega_1\mu_1^2+\omega_2\mu_2^2. \tag{3.2}$$

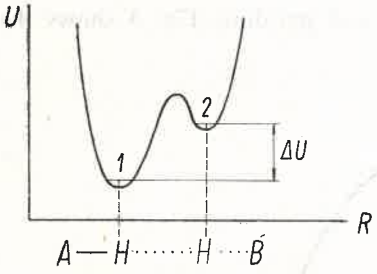

Fig. 4. Two-level model of the hydrogen bond

Onsager's theory [33] leads to the following dependence of the energy U of a dipolar molecule on the electric permittivity ε of the medium

$$U = U_0-\frac{4\pi N}{3V}\mu^2\frac{\varepsilon-1}{2\varepsilon+1}, \tag{3.3}$$

with U_0 — the energy in vacuum, V the molar volume, N Avogadro's number, and μ the dipole moment of the molecule under consideration.

On resorting to a relation of the above form for either state of the bond, one obtains a dependence of ΔU on ε in the form:

$$\frac{\Delta U}{RT} = \frac{\Delta U_0}{RT}-A\frac{\varepsilon-1}{2\varepsilon+1}, \tag{3.4}$$

where

$$A = \frac{4\pi N}{3RTV}(\mu_2^2-\mu_1^2). \tag{3.5}$$

Assessment of A leads to a value of about 30 on the assumption that $\mu_2 = 12$ D. This is to say that the dependence of $\Delta U/RT$ on ε is very steep.

Figs 5a, b show schematically, from Eq. (3.3), the variation of ΔU in function of the parameter $(\varepsilon-1)/(2\varepsilon+1)$ describing the medium in which the complex is immersed. The

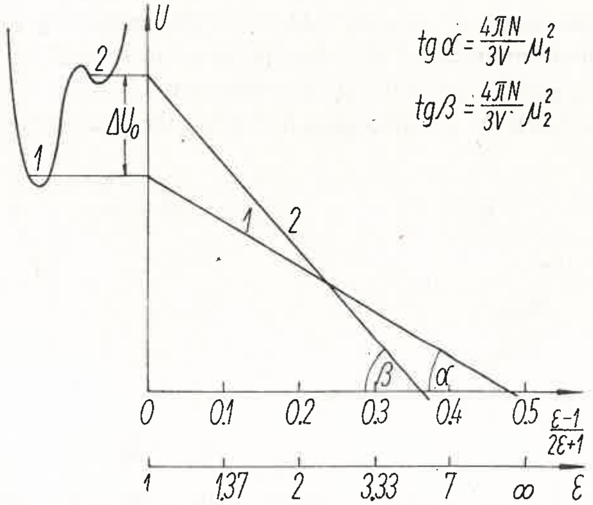

Fig. 5a. Graph of the energies of the two states of the hydrogen bond *versus* the parameter $(\varepsilon-1)/(2\varepsilon+1)$

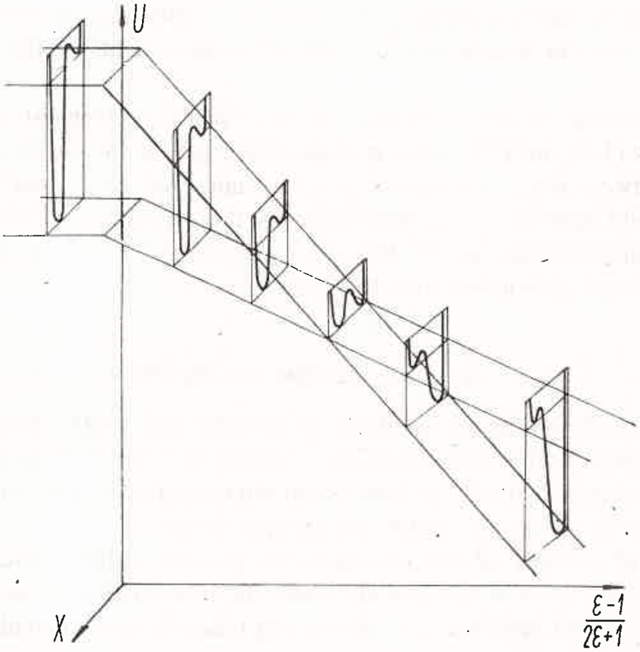

Fig. 5b. The shape of the potential energy curve of the proton in the hydrogen bridge, in function of the parameter $(\varepsilon-1)/(2\varepsilon+1)$. The x-axis is pointed in the direction of the bond, from atom B to atom A

straight lines *1* and *2* in Fig. 5a represent the variations in energy of the complex in state *1* and *2* respectively; their slopes are proportional to the square of the respective dipole moment. Fig. 5a also shows the scale of ε-values corresponding to given values of $(\varepsilon-1)/(2\varepsilon+1)$. Fig. 5b is a counterpart of Fig. 5a in the three-dimensional coordinate system $[u, (\varepsilon-1)/(2\varepsilon+1), x]$, with x pointing along the bond $A-\mathrm{H}...B$, from B to A.

Fig. 6 shows the shape of $\Delta U_0/RT-\Delta U/RT=f(\varepsilon)$ according to Eq. (3.5), on the assumption of a dipole moment of 12D for the bond in state *2*.

The preceding graphs reveal a strong dependence of ΔU on ε. Clearly, the strongest changes in ΔU occur when the complex goes over from the gaseous to the liquid state *i. e.* in the range from $\varepsilon \approx 1$ to $\varepsilon \approx 2$. This seems to account essentially for the lack of agreement between the theoretical predictions based on calculations performed for isolated hydrogen bonds and the experimental results of measurements in the solid and liquid states.

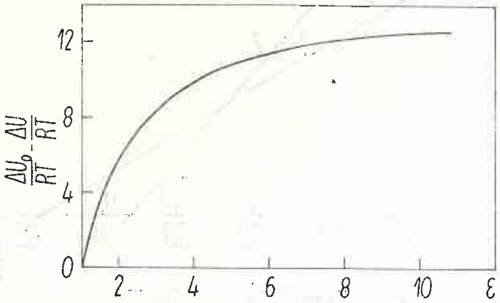

Fig. 6. Graph of the function $\Delta U_0/RT-\Delta U/RT=f(\varepsilon)$, on the assumption of $\mu_2 = 12\,\mathrm{D}$

The graphs moreover lead to predict, in liquid phase, a strongest dependence $\Delta U(\varepsilon)$ and thus, by Eqs (3.1) and (3.2) a strong dependence $\mu(\varepsilon)$ in the range of small ε-values of the solvent, between $\varepsilon \approx 2$ (neutral non-polar solvents) and $\varepsilon \approx 4$ (weakly polar solvents).

It was our aim here to verify experimentally the dependence of the dipole moment of hydrogen bonded systems on the dielectric permittivity ε of the medium by studying complexes of phenol derivatives and triethylamine.

4. Choice of experimental materials

We studied three-component solutions of phenols and triethylamine in 3 solvents: cyclohexane, toluene, and trichloroethylene. Ternary systems present the advantage of allowing, by going over from one solvent to another, to change systematically and previsibly the medium in which the complexes are immersed.

The choice of phenols in our measurements proved highly convenient and useful. They represent a rare class of compounds where the introduction of various substituents yields a series of phenol derivatives of almost continuously varying acidity, preserving at the same time an almost unchanged spatial configuration of the hydrogen bonded complexes. The numerous available papers on phenol complexes with various bases, in particular triethylamine, admit of a rather univocal definition of the complexes with regard to their configuration and stoichiometry.

We resorted to solvents, the permittivity of which lay within the range of the largest predicted effects ($\varepsilon \approx 2 \div 3.5$). These solvents can be regarded as neutral with respect to the systems under investigation, since the competitive interaction of the phenols with the electrons of the toluene ring or the double bond of trichloroethylene is negligible as compared with the interaction between the phenolic OH group and the nitrogen of triethylamine.

5. *Preparation of chemical reagents*

Cyclohexane, Special for Spectroscopy, produced by the Carlo Erba, was preliminarily dried with P_2O_5 and then twice distilled over this oxide; the fraction boiling at 80.5–81.0°C was collected.

Toluene, pure, from Zakłady Koksochemiczne (Coke and Chemical Factories) "Hajduki", Chorzów, was dried and twice distilled over metallic sodium. Boiling temperature was 110–111°C. The purified liquid was stored over sodium.

Trichloroethylene, pure, from Zakłady Chemiczne (Chemical Factory) "Oświęcim", was dried and distilled twice over P_2O_5. The boiling temperature was 86.5–87.0°C.

The degree of purity of the solvents was checked by gas chromatography.

Triethylamine, pure, produced by the VEB Laborchemie Apolda, was preliminarily dehydrated by heating with KOH under reflux cooler at 40°C during 10 hrs and then distilled twice. The fraction boiling at 89.0–89.5°C was collected.

Phenols were purified by repeated recrystallization. On purification, the phenols were dried and stored in exsiccators over P_2O_5 or silicagel. Their melting temperatures are given in Table II.

6. *Method of measurement*

The solutions were prepared by weighing. Guided by the dielectric titration results of Ratajczak [26], we introduced triethylamine in (about 20-fold) excess in relation to the phenol concentration. In this way, a three-component solution was obtained consisting of the molecules of the complex (of 1 : 1 composition), unbonded triethylamine, and the solvent.

The concentration range applied was such that, in the presence of excess triethylamine, self-association of phenol molecules could be neglected. The concentration of complexes in the systems investigated did not exceed 1.10^{-3} (in molar fractions).

All the measurements were carried out at 20±0.1°C.

The dielectric permittivity ε was measured with a DMO1 DIPOLMETER, made by WTW. The device operates on the beat principle, at measuring frequency 2 MHz. A liquid measuring condenser of type DFL 2, with an electric capacitance of 7 pF, made by the same firm, was used. The condenser was scaled by means of liquids of well-known ε, namely: hexane ($\varepsilon = 1.8893$), cyclohexane ($\varepsilon = 2.0230$), benzene ($\varepsilon = 2.2825$), and carbon tetrachloride ($\varepsilon = 2.2364$).

The permittivity ε of the solutions was measured with an accuracy of $\pm 5.10^{-4}$.

Density was measured with a picnometer of volume about 17 cm^3, ending in a calibrated capillary of diameter about 2 mm and a length of approximately 25 cm. The picnometer was filled by means of a syringe and appropriately long needle. The volume of the picnometer was calibrated with water thrice—distilled from quartz vessels.

The density was measured to within $\pm 5.10^{-4}$ g/cm^3.

Values of the refractive indices and molar refraction coefficients were taken from the literature.

Dielectric polarization was calculated using Onsager's formula [33].

The calculated maximal error due to experimental error in determining the dipole moment of the complexes was of the order of 0.1 D.

7. Experimental results, and their interpretation

The results of measurements are assembled in Tables I–III. Table I contains data relating to the properties of the initial reagents, namely the solvents and triethylamine; Table II contains those of the phenol derivatives; and Table III gives the results for the dipole moment μ_k of the complexes measured in cyclohexane, toluene and trichloroethylene.

TABLE I

Properties of the liquid reagents (at 20°C)

Substance	ε	d	n	R_D	p^{dip}	μ
Cyclohexane	2.0228	0.7783	1.4262	27.73	0	0
Toluene	2.3916	0.8674	1.4962	31.06	2.63	0.35
Trichloroethylene	3.4605	1.4642	1.4775	46.37	17.26	0.91
Triethylamine	μ was determined in solutions in cyclohexane			33.74	12.48	0.78

In order to calculate the polarity $\Delta\mu$ of the hydrogen bond, one has to know the values of the dipole moment $\vec{\mu}_a$ of the acid and that $\vec{\mu}_b$ of the base as well as their directions in respect to the straight line defined by the system O–H...N.

The direction of the dipole moment $\vec{\mu}_a$ of the phenols was determined from a vector model of the molecule constructed so that, on assuming vectorial additivity of the dipole moments of the bonds, a value of μ_a should result in accordance with the experimental values in Table II. Obviously, such a procedure implies some assumptions, the most important of which concerns the additivity of the bond moments. This seems a good assumption in most cases but, for some molecules, can lead to considerable divergence.

There are numerous reasons why the agreement to within ± 0.1 D between the results of such simple calculations and the experimental data should be considered satisfactory. The divergencies are due, among other factors, to:

a) the arising of additional induced moments by interaction between the dipole and the rest of the molecule or complex;

TABLE II

Properties of the phenol derivatives

Phenol	T_f	pK_a	R_D	P^{dip}	μ	References	
3,4,5-trimethylophenol	70°	10.8	42.17	58.29^a	1.68^a	1.68	[34]
p-cresol	34°	10.26	32.55	47.85^b	1.52^b	1.57 1.53 1.55	[35] [36] [26]
phenol	40.5°	9.95	27.90	46.40^b	1.50^b	1.45 1.47 1.54 1.54	[37] [36] [38] [26]
m-nitrophenol	97°	8.35	35.93	317.8^a	3.92^a	3.91 3.90	[27] [39, 40]
p-nitrophenol	114°	7.15	35.93	530.0^a	5.06^a	5.05 5.02 5.06	[40] [35] [26]
2,4,6-trichlorophenol	67°	6.0	42.54	45.8^a	1.50^a	1.42 1.62	[26] [41]
pentachlorophenol	190°	4.82	86	87.81^b	2.05^b	1.95	[17]
2,6-dibromo- -4-nitrophenol	144°	3.39	85	208.82^a	3.17^a	3.36	[17]

^{a} determined in solutions in toluene, ^{b} determined in solutions in cyclohexane.

TABLE III

Dipole moments of complexes of phenol derivatives and triethylamine in the various solvents

Solvent / Phenol	Cyclohexane			Toluene			Trichloroethylene		
	P	P^{dip}	μ_k	P	P^{dip}	μ_k	P	P^{dip}	μ_k
3,4,5-trimethylophenol	208.8	132.9	2.5	257.0	181.1	2.9	312.7	236.8	3.4
p-cresol	229.1	162.8	2.8	243.3	177.0	2.9	384.8	318.5	3.9
phenol	215.2	153.5	2.7	299.6	238.0	3.3	331.8	270.0	3.6
m-nitrophenol	610.3	540.6	5.1	702.2	632.0	5.6	961.0	891.0	6.6
p-nitrophenol	984.6	914.9	6.7	1263.5	1193.5	7.6	1924.1	1854.4	9.45
2,4,6-trichlorophenol	592.9	504.1	4.9	1166.5	1090.2	7.2	1735.8	1659.5	8.9
pentachlorophenol	1105.7	985.7	6.9	2043	1923	9.6	2410	2290	10.6
2,6-dibromo-4-nitrophenol	too low solubility			3047.8	2916.6	11.8	3459	3340	12.7

b) non-coaxial disposition of the moments of the group with respect to the $X-Y$ bond direction;

c) resonance and delocalizing effects, leading to considerable changes in the effective moments of the groups in the various derivatives.

In calculating $\Delta\vec{\mu}$, the following assumptions were made:

1. the orbital of the nitrogen lone pair *i. e.* the dipole moment $\vec{\mu}_b$ of triethylamine was assumed as directed along the hydrogen bond;
2. the dipole moment of the C–OH group was assumed equal to 1.56 D and the angle between this vector and the direction of the C–O bond to about 90°;
3. the COH angle in the phenols was taken equal to 115°.

TABLE IV

Moments of the bonds, and calculated angle ϑ between the vector $\vec{\mu}_a$ and the direction of the O–H bond

Phenol	Moments of bonds	ϑ
3,4,5-trimethylophenol	0.4 $\overset{\longleftarrow +}{(\mathrm{C-CH_3})}$	49°
p-cresol	0.4 $\overset{\longleftarrow +}{(\mathrm{C-CH_3})}$	34°
phenol		25°
m-nitrophenol	4.1 $\overset{+\longrightarrow}{(\mathrm{C-NO_2})}$	~19°
p-nitrophenol	4.1 $\overset{+\longrightarrow}{(\mathrm{C-NO_2})}$	49°
2,4,6-trichlorophenol	1.55 $\overset{+\longrightarrow}{(3-\mathrm{Cl})}$	25°
pentachlorophenol	1.55 $\overset{+\longrightarrow}{(\mathrm{C-Cl})}$	16°
2,6-dibromo-4-nitrophenol	1.55 $\overset{+\longrightarrow}{(\mathrm{C-Br})}$ 4.1 $\overset{+\longrightarrow}{(\mathrm{C-NO_2})}$	35°

With the above assumptions, it was possible to determine the angle ϑ between the moment $\vec{\mu}_a$ vectors and the O–H bond direction. The results of these calculations as well as the data concerning the values and senses of the dipole moments of the bonds are given in Table IV.

Fig. 7 exemplifies the vector model of the 2,6-dibromo-4-nitrophenol molecule.

When $\vec{\mu}_a$, $\vec{\mu}_b$, ϑ and the dipole moment $\vec{\mu}_k$ of the complex are known, $\Delta\mu$ (Fig. 2) can be calculated from the formula:

$$\Delta\mu = \sqrt{\mu_k^2 - \mu_a^2 \sin^2\vartheta} - \mu_b - \mu_a \cos\vartheta. \tag{7.1}$$

Also, the dipole moment of the hydrogen bridges:

$$\mu = \mu_{\mathrm{OH}} + \Delta\mu + \mu_b \tag{7.2}$$

can be calculated, on the assumption of $\mu_{\mathrm{OH}} = 1.6$ D. The results of these calculations are assembled in Table V.

TABLE V

Polarity $\Delta\mu$ of the hydrogen bond and dipole moment μ of the hydrogen bridge O–H...N in complexes of phenol derivatives and triethylamine in various solvents

Solvent / Phenol	Cyclohexane		Toluene		Trichloroethylene	
	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ
3,4,5-trimethylophenol	0.4	2.8	0.7	3.1	1.2	3.6
p-cresol	0.5	2.9	0.7	3.1	1.6	4.0
phenol	0.4	2.8	0.9	3.3	1.3	3.7
m-nitrophenol	0.6	3.0	1.2	3.6	2.5	4.9
p-nitrophenol	1.4	3.8	2.6	5.0	4.7	7.1
2,4,6-trichlorophenol	2.7	5.1	5.1	7.5	6.8	9.2
pentachlorophenol	4.2	6.6	6.9	9.3	7.9	10.3
2,6-dibromo-4-nitrophenol			8.3	10.7	9.2	11.6

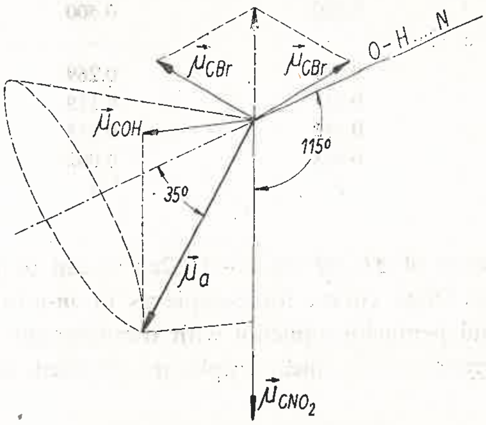

Fig. 7. Vector model of the 2,6-dibromo-4-nitrophenol molecule

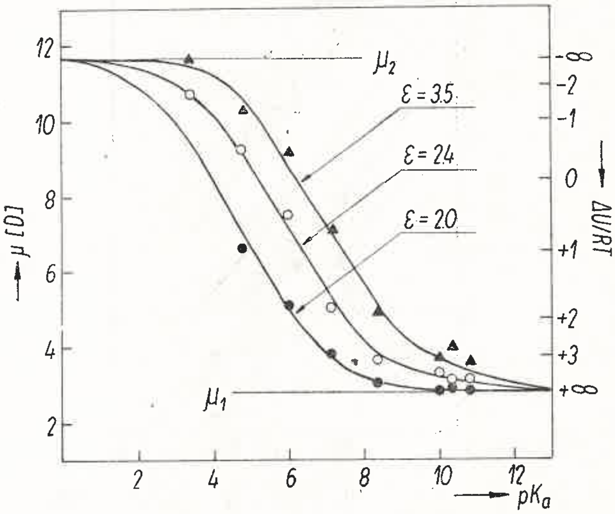

Fig. 8. Mean dipole moment μ of the O–H...N bond *vs* pK_a of the phenol

Fig. 8 shows the mean dipole moment of the O—H...N bond in function of pK_a of the phenols, as well as the $\Delta U/RT$-scale assigned to the U-values, after Eqs (3.1) and (3.2) (Table VI).

TABLE VI

Attribution of $\Delta U/RT$-scale to the μ-values

$\Delta U/RT$	ω_1	ω_2	μ
$-\infty$	0	1	11.6
-6	0.002	0.998	11.6
-4	0.018	0.982	11.5
-2	0.119	0.881	10.9
-1	0.268	0.732	10.0
0	0.500	0.500	8.4
$+1$	0.731	0.269	6.5
$+2$	0.881	0.119	4.7
$+4$	0.982	0.018	3.2
$+6$	0.998	0.002	2.9
$+\infty$	1	0	2.8

Hence, the dependence of $\Delta U/RT$ on $(\varepsilon-1)/(2\varepsilon+1)$ can be plotted for the various complexes. Fig. 9 shows these curves for complexes of *m*-nitrophenol, *p*-nitrophenol, 2,4,6-trichlorophenol, and pentachlorophenol with triethylamine.

In a satisfactory approximation, linear graphs are obtained, as predicted by Eq. (3.4).

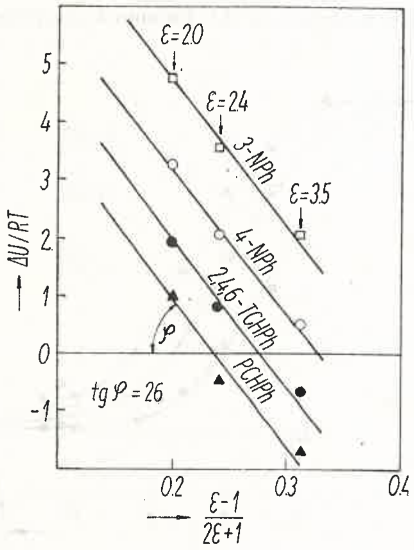

Fig. 9. $\Delta U/RT$ *vs* $(\varepsilon-1)/(2\varepsilon+1)$ for some complexes

The steepness of the straight lines amounts to 26. On insertion of this experimental value into Eq. (3.5), one obtains a value $\mu_2 = 11.4$ D in excellent agreement with the value of 11.6 D resulting by direct measurement.

However, Fig. 9 shows that, with increasing pK_a of the phenol, the divergence from Onsager's formula (3.4) also exhibits a slight increase.

A confrontation of experimental results like that of Fig. 9 and the drawing of conclusions regarding different complexes is meaningful only as long as one compares hydrogen bridges of identical geometry; in the case of linear bonds this condition concerns the $A...B$ distance. In fact, it is well known that this distance decreases (the bond becomes shorter) with growing energies of the hydrogen bond. The distance $A...B$ has a direct bearing on the value of the dipole moment μ_2 — since we have approximately:

$$\mu_2 = e \cdot R_{A...B}. \tag{7.3}$$

This interdependence entails consequences of much importance: indeed, in the case of weak bonding (small μ), μ_2 is large ($R_{A...B}$ is long), whereas in that of strong bonding (large μ), μ_2 is small ($R_{A...B}$ is short); in the case a symmetrical bond A...H...B, one has $\mu_1 = \mu_2 = \mu$.

Such variability of μ_2 can lead to divergences from Onsager's formula as well as from the calculated polarity values of hydrogen bridges.

This, too, is probably the reason for the relatively low polarity of strong hydrogen bonds reported by various authors. Sobczyk and Syrkin [42] determined $\Delta\vec{\mu}$ for complexes of pyridine and acetic, chloroacetic and trichloroacetic acid as amounting respectively to 0.5, 1.05 and 4.31 D in spite of the fact that *e.g.* for the complex with trichloroacetic acid IR spectra suggested the presence of almost 100 per cent of ion pairs [43].

The tendency to form symmetrical hydrogen bonds seems to be exhibited by oxygen bases. Hadži, Ratajczak and Sobczyk [44] obtained for complexes of carboxylic acids and oxygen bases $\Delta\mu$-values ranging from 0.4 to 3.2 D — apparently accessible to an explanation by the preceding considerations.

A decrease in polarity of the hydrogen bridge form with shifted proton on going over to growingly strong bonds results also from the work of Małecki [45, 46] on dielectric saturation in alcohols.

The theoretical assignment of a scale of $\Delta U/RT$-values to those of μ performed on grounds of Eqs (3.1) and (3.2) permits the plotting of $\mu = f(\Delta U/RT)$; into the graph thus obtained, the experimental values of μ from Table III can then be inserted on resorting to the dependence of $\Delta U/RT = f(\varepsilon)$. Fig. 10 shows the theoretical dependence $\mu = f[\Delta U(\varepsilon)/RT]$ together with the experimental dipole moments in the various solvents.

The good agreement between the experimental and theoretically predicted values in the wide interval of $\Delta U/RT$-values appears to be a sound proof that hydrogen bonds present tautomeric equilibrium of the type $A-$H$...B \rightleftharpoons A^-...H-B^+$.

From Fig. 10, the shapes of μ *vs* $\Delta U/RT$ and μ *vs* pK_a (Fig. 8) are found to be identical. This proves that the pK_a-scale expresses directly the values of $\Delta U/RT$. One should expect a similar dependence of $\Delta U/RT$ on the pK_b-values of the base. However, in the present study, only one base, triethylamine, was applied, with a value of $pK_b = 3.45$.

Consequently, on comparing the curves of Figs 8 and 10, the following empirical relation can be written:

$$\frac{\Delta U}{RT} = pK_a + f(pK_b) + C(\varepsilon), \tag{7.4}$$

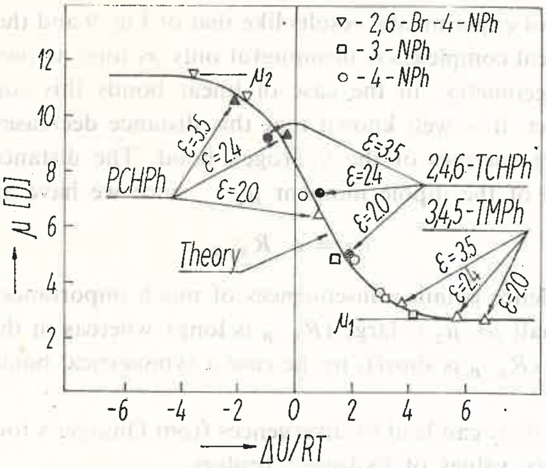

Fig. 10. Theoretical dependence of $\mu = f[\Delta U(\varepsilon)/RT]$, and the experimental results

where the function $f(pK_b)$ is not determined in the present instance for a lack of experimental data, and $C(\varepsilon)$ accounts for the displacement of the centre of coordinates and the dependence on ε.

With Eq. (3.1), the Eq. (7.4) can be rewritten as follows:

$$\log K_{PT} = 0.43\,[-pK_a - f(pK_b) - C(\varepsilon)]. \tag{7.5}$$

The difference between this equation and the one proposed by Huyskens, (2.2), resides essentially in the coefficient at pK_a which, experimentally, amounts to 0.43 whereas the theoretical values is 1. As mentioned in Section 2, this circumstance was noticed by Ratajczak and Sobczyk [17], who introduced an empirical coefficient at pK_a amounting to 0.4 so as to obtain good agreement between the theoretical curve and the results of experiment.

8. *Conclusion*

A reviewal of the available literature data with the aim of reaching a decision as to the state of the proton in the hydrogen bridge *i.e.* of deciding between delocalization and localization of the proton, makes the latter of the two possibilities appear the more probable one. Numerous authors are inclined to think that the assumption of two energy states $A-\mathrm{H}\ldots B \rightleftharpoons A^{-}\ldots\mathrm{H}-B^{+}$, corresponding to a potential energy curve with two minima for the proton, provides an explanation of the essential experimental facts.

This hypothesis served as the starting point of the present dielectric study of hydrogen bonded complexes. The assumption of tautomeric equilibrium between two states of the bond entailed a dependence of the equilibrium constant K_{PT} of the proton transfer process on the electric permittivity ε of the medium in which the hydrogen bonds are immersed. Since this is an equilibrium between two forms differing strongly as to dipole moment ($\mu_1 \approx 3$ D; $\mu_2 \approx 12$ D), one has to expect a dependence of the measured mean dipole moments of the hydrogen bonded complexes on the permittivity ε of the solvent.

With the aim of verifying these considerations, the dipole moments of phenol derivative-triethylamine complexes were measured in the three solvents: cyclohexane ($\varepsilon \approx 2$), toluene ($\varepsilon \approx 2.4$), and trichloroethylene ($\varepsilon \approx 3.5$). In fact, these measurements revealed a strong dependence of μ_k *vs* ε (Table V; Fig. 8). Thus *e.g.* the dipole moment values for pentachlorophenol-triethylamine complex amounted to 6.9, 9.6 and 10.6 D respectively for permittivities of 2.0, 2.4 and 3.5. This is a fact which has to be taken into account when comparing experimental results obtained in various solvents.

Onsager's local field theory permits to derive a relationship between the difference in energy of the two states of the bridge ΔU (and consequently K_{PT}) and the electric permittivity ε of the medium. The equation predicts a linear dependence of $\Delta U/RT$ on the parameter $(\varepsilon-1)/(2\varepsilon+1)$.

This relationship, plotted from the experimental results, is shown in Fig. 9 for several complexes. In a good approximation, the dependence is linear, and the slope yields $\mu_2 = 11.4$ D in excellent agreement with the directly measured value 11.6 D.

Onsager's equation (3.4) moreover permits the theoretical plotting of $\mu = f[\Delta U(\varepsilon)/RT]$ and thus its comparison with the experimental results. Fig. 10 points to very good agreement between theory and experiment.

The fact that the results of the present experiments are in good agreement with the theory throughout a wide range of acidity of the proton donor appears to prove the initial assumptions *i.e.* the existence of tautomeric equilibria of the form (1.1).

It should be stressed that the quantity ΔU defined here is meaningful only in the case of two energy states of the hydrogen bridge. In that of delocalization, *i.e.* when an "averaged" state is attributed to the proton, ΔU is physically meaningless.

The omission of other effects able (beside tautomeric equilibrium) to influence the polarity of the bond is an obvious approximation. Nevertheless, in the present case of phenol derivative — triethylamine complexes, tautomeric equilibrium appears to predominate totally, bearing out this simplification.

The considerations of this paper moreover lead to a strong dependence of the energy of the hydrogen bond on the electric permittivity of the medium at almost constant entropy able to affect the direction of conformational transitions in hydrogen bonded systems, particularly biological ones, where the micro-surroundings of a bond can change their properties from those typical of hydrocarbons (within protein structures) to those characteristic of an aqueous medium.

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