

## Dipole Moments of H-Bonded Complexes

*Pierre L. Huyskens*

*University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium*

and

*Georges G. Siegel*

*University of Puerto Rico, 00708 Mayagüez, Puerto Rico*

This paper deals with the information which can be obtained from dielectric measurements about the structure of H-bonded complexes in the liquid phase.

In the first part the basic equations used in the determination of the dipole moments in the liquid phase are discussed. For pure polar liquid Onsager's equations lead to values of the moments which may differ from those of the gas phase. According to Kirkwood these deviations are due to preferential orientation effects between the molecules. In pure liquids these deviations are only very important in the case of the formation of H-bonds.

The interpretation of experimental dipole data for self associated compounds such as alcohols, carboxylic acids, amides, amines, anilines and pyridines is presented.

A method used for the experimental determination of dipole moments for one-one hydrogen bonded complexes is discussed.  $\mu_{ab}$  depends not only on the moments of the separate partners  $\mu_a$  and  $\mu_b$  but also on the angles  $\vartheta_a$  and  $\vartheta_b$  which these moments form with the direction of the hydrogen bond. Furthermore,  $\mu_{ab}$

also depends on the dipole increment,  $\Delta\mu$ , originated by the displacements of electrons and nuclei brought about by the formation of the bond.

$\Delta\mu$  in turn, will depend on the  $\Delta pK_a$ , the difference between the  $pK_a$  of the conjugated acid of the proton acceptor and that of the acid. Sigmoidal curves are obtained which can be interpreted as resulting from a tautomerism between »normal« and »proton transfer« hydrogen bonds.

The dependence of  $\Delta\mu$  on the enthalpy of bond formation,  $-\Delta H_b$ , also gives a sigmoidal curve which is approximately the same for all H-bonds of a given kind (O—H...O, O—H...N etc.) in a given solvent.

This dependence can be used for the calculation of  $\Delta\mu$ . Using this value with the experimental moments  $\mu_{ab}$ ,  $\mu_a$  and  $\mu_b$  it is then possible to deduce angular parameters for a given H-bonded complex. A few examples are discussed.

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## INTRODUCTION

Theoretical and experimental work on hydrogen bonding has been performed since 1920, when Latimer, and Rodebush<sup>1</sup> introduced this concept in chemistry. However, the event which has had perhaps the greatest catalytic effect on research in this field has been the Symposium held at Ljubljana in 1957 and organized by Professor D. Hadži<sup>2</sup>.

In this Conference not only the universal character of H-bonding in chemistry and in biology was underlined, but many scientists specialized in a large variety of disciplines such as crystallography, spectroscopy, thermodynamics, theoretical methods and others got for the first time the opportunity to compare their results in this field.

Among these methods dielectric measurements can be used especially for the study of H-bonds in the liquid state, and a contribution was already presented at the Ljubljana Conference by L. Sobczyk, who carried out pioneering work in this field and who published a few years ago a review on this question<sup>3</sup>.

In this paper we deal with the information which can be obtained from static dielectric measurements about H-bonds in the liquid state.

Although dipole measurements alone can provide already valuable information, the most interesting information is obtained when the dipolar data are combined with those of other methods such as spectroscopy, calorimetry, determination of distribution coefficients etc.

Hydrogen bonds formed between molecules of the same kind lead to self-association of the substance. Such bonds can be studied in the pure compounds and in their solutions in a more or less inert solvent. The enthalpy change of formation ( $-\Delta H_b$ ) of such self-association bonds rarely surpasses 25 kJ mol<sup>-1</sup>.

A much larger variety of bond-energies is encountered in H-bonds between molecules of different kinds where  $-\Delta H_b$  can reach 100 kJ mol<sup>-1</sup> and even higher values.

As a matter of fact the information obtained from dipole methods is always based on the comparison of the dipole moments of the H-bonded entities with those of the separate molecules.

In the first part of this paper we will then briefly discuss the basic equations which are used in the determination of these dipole moments.

## DETERMINATION OF DIPOLE MOMENTS OF H-BONDED COMPLEXES

In the liquid phase the permanent dipole moments  $\mu_i$  are computed from the dielectric constant  $\epsilon$  of the liquid or solution. All the computation methods are based on the relation between the polarization  $P$ , the total moment in the direction of the field  $E$  per unit volume and the magnitude of this field:

$$P \equiv \frac{\sum n_i N_A \langle m_{iz} \rangle}{V} = \frac{(\epsilon - 1)}{4\pi} E \quad (1)$$

In this equation the  $n_i$ 's are the numbers of moles of the various entities present in the volume  $V$  and  $N_A$  is Avogadro's number.

$\langle m_{iz} \rangle$  is the mean value of the moment of the entity in the direction of the field.

When the entity exhibits a permanent dipole moment  $\mu_i$ , a part of  $\langle m_{iz} \rangle$  is due to the *orientation* of the moments by the field and the other part is due to the *distorsion*. Onsager<sup>4</sup> introduced the concept of »internal refractive index  $\nu$ « the square of which corresponds to the dielectric constant which would be observed if the orientation were annihilated, the distorsion remaining unperturbed. It is difficult to find experiments where these two conditions are fulfilled and, generally, the internal refractive index  $\nu$  is estimated from  $\nu_D$ , the index for the sodium D line, using an expression of the type

$$\frac{\nu^2 - 1}{\nu^2 + 2} = \xi \frac{\nu_D^2 - 1}{\nu_D^2 + 2} \quad (2)$$

where  $\xi$  varies from 1.00 to 1.20.

All the theories which tend to establish a relation between  $\langle m_{iz} \rangle$  and  $\mu_i$  replace the latter, which in fact corresponds to a real charge distribution of electrons and nuclei in space, by a model, namely a point dipole in a cavity.

The oldest theory is that of Debye<sup>5</sup>. For a pure liquid the molecules of which exhibit the moment  $\mu_B$  this theory leads to the equation:

$$\mu_B^2 = \left( \frac{9kT \times 10^{39}}{4\pi N_A} \right) \frac{(\epsilon' - \nu'^2) \times 3}{(\epsilon' + 2)(\nu'^2 + 2)} \cdot \frac{1}{F'_B} \quad (3)$$

where  $F'_B$  is the formal concentration of the pure substance in mol dm<sup>-3</sup>.  $\mu_B$  is given in debye when  $k$  is taken in erg K<sup>-1</sup>.

Debye's equation is certainly not correct because it neglects the fact that the reaction field originated by the dipole cannot influence its orientation. The better treatment by Onsager<sup>4</sup> leads to the equation

$$\mu_B^2 = \left( \frac{9kT \times 10^{39}}{4\pi N_A} \right) \frac{(\epsilon' - \nu'^2)(2\epsilon' + \nu'^2)}{\epsilon'(\nu'^2 + 2)^2} \cdot \frac{1}{F'_B} \quad (4)$$

This equation presupposes that in the absence of an external field the neighbouring dipoles do not exhibit preferential orientations with respect to a given one.

In the case of pure non-polar liquids the difference  $\epsilon' - \nu'^2$  vanishes and  $\mu_B^2$  is zero. However when, as said before,  $\nu_D^2$  is used instead of the internal index  $\nu$ , an error is made which leads to the calculation of an »apparent« value of  $\mu_B^2$  for the nonpolar substance. Examples are given in Table I.

TABLE I

Apparent Values of  $\mu_B^2$  of Non-polar Substances Resulting from the Use of  $\nu_D$  Instead of  $\nu$  in Onsager's Equation ( $T = 298.16$  K)

Substance	$F'_B$ /mol dm <sup>-3</sup>	$\epsilon'$	$\nu_D^2$	$\xi$	»apparent« $\mu_B^2/D^2$
Cyclohexane	9.217	2.015	2.030	0.989	-0.015
Hexane	7.623	1.882	1.886	0.997	-0.006
Benzene	11.191	2.274	2.247	1.015	+0.019
Tetrachloromethane	10.311	2.228	2.126	1.064	+0.084
1,4-Dioxane	11.672	2.209	2.018	1.134	+0.144
1,4-Dichlorobenzene	8.444	2.460	2.330	1.066	+0.119

The apparent values can be positive or negative. They are larger when the non-polar character of the molecules is only due to a compensation between group dipoles of opposite direction. In such case the error may, at least partially, originate from a residual dipole moment in some of the molecules in the liquid.

When equation (4) is used for polar substances (taking  $\nu_D^*$  for  $\nu^*$ ) differences appear between the dipole moment determined in the liquid phase and the dipole moment  $\mu_1$  of the isolated molecule (obtained mostly from measurements in the gas phase). Examples are given in Table II.

TABLE II

Squares of the Dipole Moments of Pure Liquids Computed by Means of Onsager's Equation ( $T = 298.16$  K)

Substance	$F_B$ mol dm <sup>-3</sup>	$\epsilon$	$\nu_D^2$	Onsager $\mu^2/D^2$	isolated $\mu_1^2/D^2$	$g$
Class A						
Diethylether	9.582	4.235	1.825	2.04	1.64	1.25
Chlorobenzene	9.775	5.621	2.329	2.13	2.56	0.83
Acetone	13.533	20.70	1.842	9.67	8.58	1.13
Nitroethane	13.918	28.63	1.932	12.53	10.43	1.20
Nitrobenzene	9.729	34.82	2.415	17.31	15.13	1.14
Acetonitrile	19.045	36.00	1.803	12.39	15.29	0.81
Class B						
Methanol	24.577	32.63	1.762	8.94	2.89	3.09
Ethanol	17.047	24.30	1.848	9.06	2.89	3.13
Water	55.500	78.54	1.777	9.61	3.42	2.81
Acetamide	19.523	105.40	2.094	31.14	13.84	2.25
N-methyl- propionamide	10.91	163.10	2.04	89.04	12.74	6.99
Acetic acid	17.385	6.18	1.877	1.85	2.89	0.64
Propanoic acid	13.334	3.32	1.919	0.86	1.89	0.30

The difference between the  $\mu_{\text{Onsager}}^*$  values and that of the isolated molecule was ascribed by Kirkwood<sup>6</sup> to the fact that preferential orientations exist between neighbouring dipoles. According to Kirkwood:

$$\frac{\mu_{\text{Onsager}}^2}{\mu_1^2} = g = 1 + \langle \sum_{j \neq i} \cos \vartheta_{ij} \rangle \quad (5)$$

wherein  $\vartheta_{ij}$  is the angle between a given dipole  $i$  and its  $j$ th neighbour, the sum being taken over all neighbours. When no preferential orientations occur  $\langle \sum_{i \neq j} \cos \vartheta_{ij} \rangle$  equals zero and  $g$  equals one.

The substances considered in Table II can be classified in two categories: those for which the  $g$  values deviate only moderately from one ( $0.80 < g < 1.25$ ) and those which deviate strongly from one, indicating strong preferential orientations.



It now seems that all substances appearing in class B are those having molecules which bear both proton donor and proton acceptor sites and which can thus self associate through the formation of H-bonds.

Preferential orientations in pure liquids thus originate mainly from the formation of H-bonded associates.

From this point of view, *the associated liquid is not formed by one kind of molecules with a given dipole moment  $\mu_B$  but by a collection of »i-mers« each characterized by a dipole moment  $\mu_i$  and a concentration  $C_i$ .*

$$F_B' = \sum i C_i \quad (6)$$

If we disregard the effects on the correlation parameter which are not due to H-bond formation (according to Table II, pure dipole-dipole interactions do not trigger deviations of  $g$  from unity of more than 0.25) we can write

$$g \mu_1^2 F_B' = \sum \mu_i^2 C_i \quad (7)$$

This leads to

$$g = \frac{\sum (\mu_i^2/i) i C_i}{\sum i C_i} = \frac{\langle \mu_i^2/i \rangle}{\mu_1^2} \quad (8)$$

Thus the correlation parameter  $g$  of the pure substance differs from one if the mean contribution  $\langle \mu_i^2/i \rangle$  per molecule in the square of the dipole moments of the various entities differs from  $\mu_1^2$ .

This procedure (which ascribes all the orientation effects to the formation of H-bonds) can also be extended to solutions of one or several substances in a non-polar solvent.

In the case where all the entities exhibit the same internal refractive index  $\nu$ , the Onsager treatment leads to the equation

$$\sum \mu_i^2 C_i = \left( \frac{9kT \times 10^{39}}{4\pi N_A} \right) \frac{(\varepsilon - \nu^2)(2\varepsilon + \nu^2)}{\varepsilon(\nu^2 + 2)^2} \quad (9)$$

where  $\varepsilon$  is the dielectric constant of the solution.

If we replace in this expression the internal index by the experimental value  $\nu_D$ , the refractive index of the solution for the D line of sodium, this constitutes an approximation. We can correct part of this approximation for the solvent molecules considering the following quantity which can be completely calculated from experimental data:

$$D \equiv \left( \frac{9kT \times 10^{39}}{4\pi N_A} \right) \left\{ \frac{(\varepsilon - \nu_D^2)(2\varepsilon + \nu_D^2)}{\varepsilon(\nu_D^2 + 2)^2} - \frac{F_S}{F_S'} \frac{(\varepsilon_s - \nu_{Ds}^2)(2\varepsilon + \nu_{Ds}^2)}{\varepsilon_s(\nu_{Ds}^2 + 2)^2} \right\} \quad (10)$$

$F_S$  is the actual concentration of the solvent in the solution,  $F_S'$  its concentration in mol dm<sup>-3</sup> in the pure state and the subscript s for the other symbols refers to the pure solvent.

Thus, if the internal refractive index of all the dissolved substances can be put equal to the experimental value  $\nu_D$  of the solution, one can write

where the sum is extended to all dissolved species at the exclusion of solvent molecules.

When differences exist between  $\nu_i$  and  $\nu_D$  of the solution the equation varies for the different treatments. Onsager's theory leads to:

$$D = \sum \mu_i^2 \left( \frac{\nu_i^2 + 2}{\nu_D^2 + 2} \right)^2 \left( \frac{2\varepsilon + \nu_D^2}{2\varepsilon + \nu_i^2} \right) C_i \quad (12)$$

while from the theory of Fröhlich<sup>7</sup> one derives

$$D = \sum \mu_i^2 \left( \frac{\nu_i^2 + 2}{\nu_D^2 + 2} \right)^2 C_i \quad (13)$$

In equations (12) and (13) the  $\nu_i$ 's are not known but can be approximated by the  $\nu_{Di}$ 's.

Thus, when  $\nu_i$  differs from  $\nu_D$ , different values of the dipole moments will be calculated from the experimental quantity  $D$  according to which of the three equations is used.

Furthermore the three equations suppose the molecules to be spherical. Böttcher<sup>8</sup> and others extended the treatment to ellipsoidal molecules which leads to more sophisticated expressions. Anyway a major problem still remains in the fact that the dipole moments of the entities are not point dipoles. However when dealing with H-bond studies, one is generally interested not in the correct absolute value of the dipole moment of an H-bonded entity but rather in the values compared to those of the non bonded entities, that is in relative values.

For this comparison equation (11) is sufficiently accurate. Of course, when solvent effects are studied, equations (12) and (13) are more appropriate.

In studying H-bond formation by a substance B dissolved at a concentration  $F_B$  in a non-polar solvent it is interesting to consider the following experimental function:

$$\Omega_B = \frac{D}{F_B} \quad (14)$$

#### DIPOLE MOMENTS OF H-BONDED ASSOCIATES

If the substance B exhibits self-association, equation (11) leads to

$$\Omega_B = \frac{\sum \mu_i^2 C_i}{F_B} = \langle \mu_i^2 / i \rangle \quad (15)$$

Now, in a *non-cyclic* aggregate, the angle between the dipoles of two consecutive H-bonded molecules is usually smaller than  $90^\circ$ . Under these circumstances:

$$\mu_i^2 / i > \mu_1^2 \quad (\text{for non-cyclic aggregates}) \quad (16)$$

On the contrary, in *cyclic* aggregates

$$\mu_i^2 / i < \mu_1^2 \quad (17)$$

Thus, the function  $\Omega_B$  will be larger than  $\mu_1^2$  when non-cyclic polymolecules predominate whereas this function is smaller than  $\mu_1^2$  when the majority of molecules are involved in cyclic aggregates.

### 1. Alcohols

$\Omega_B$  varies with  $F_B$  qualitatively in the same way for all the alcohols (see Figure 1). The curves pass through a minimum and then approach, in principle, a limiting value of approximately  $3\mu_1^2$ . However, for tertiary alcohols, even at the highest concentration (this is in the pure state) the curve is still far below the limiting value. The position of the minimum depends on the nature of the alcohol and on the temperature. This behaviour was first observed by Mecke<sup>9</sup> and after him by numerous other workers<sup>10-16</sup> (The existence of the minimum was already recognized as early as 1929 by Smith and Stoops<sup>17</sup>).

It shows that aggregates with a not too large number of molecules tend to cyclize whereas this tendency is negligible for higher aggregates. However from the curves of Figure 1 alone it is not possible to determine for which values of  $i$ , the number of molecules in the aggregate, the tendency to cyclize predominates.

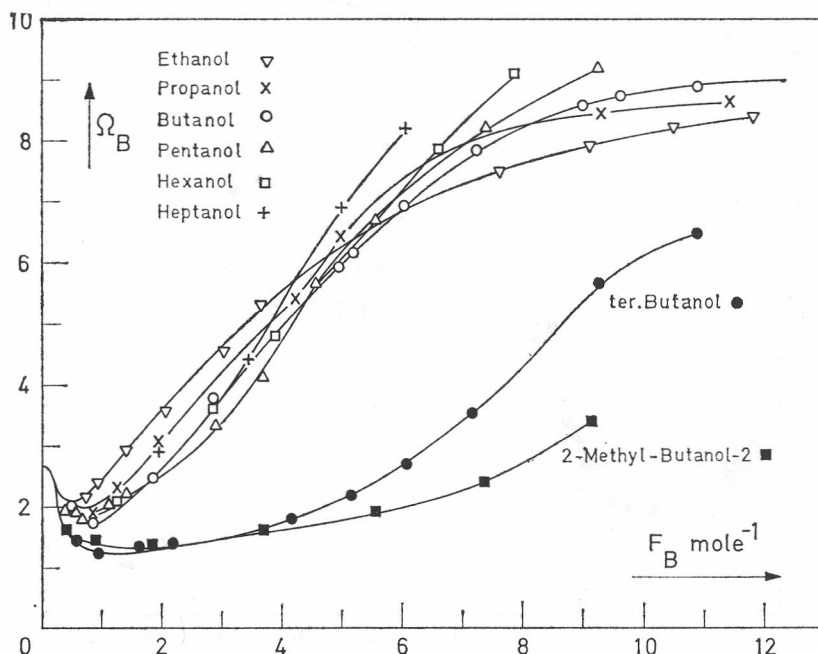


Figure 1. Experimental values of the quantity  $\Omega_B/D^2$  as a function of the formal concentration  $F_B/\text{mol dm}^{-3}$  of alcohols in cyclohexane at 298.16 K.<sup>18</sup>

The comparison of dipole moments with data obtained by other methods can provide valuable information about the characteristics of self association bonds.

From the distribution coefficient of an associated substance between an inert solvent and water, one can obtain the mean degree of association  $\langle i \rangle$ , defined as

$$\langle i \rangle \equiv \frac{\sum i^2 C_i}{F_B} \quad (18)$$

and also the mean number of molecules per entity  $\langle n \rangle$ , defined as

$$\langle n \rangle \equiv \frac{F_B}{\sum C_i} \quad (19)$$

These values were determined for alcohols in cyclohexane solution. When the dipole function  $\Omega_B$  is plotted against  $\langle i \rangle$  or  $\langle n \rangle$  (Figure 2 and 3) one observes that, for all the alcohols, the minimum occurs at the same value of  $\langle i \rangle$  (between 4 and 5) and of  $\langle n \rangle$  (between 3 and 4). From these results one can thus conclude that the tendency for cyclization is maximum for trimers and tetramers<sup>18</sup>. When  $\langle n \rangle$  equals 2, the values of  $\Omega_B$  calculated from the data of Ibbitson and Moore<sup>19</sup> and of Jadzyn and Malecki<sup>14</sup> are higher, indicating that dimers possess less tendency to cyclize.

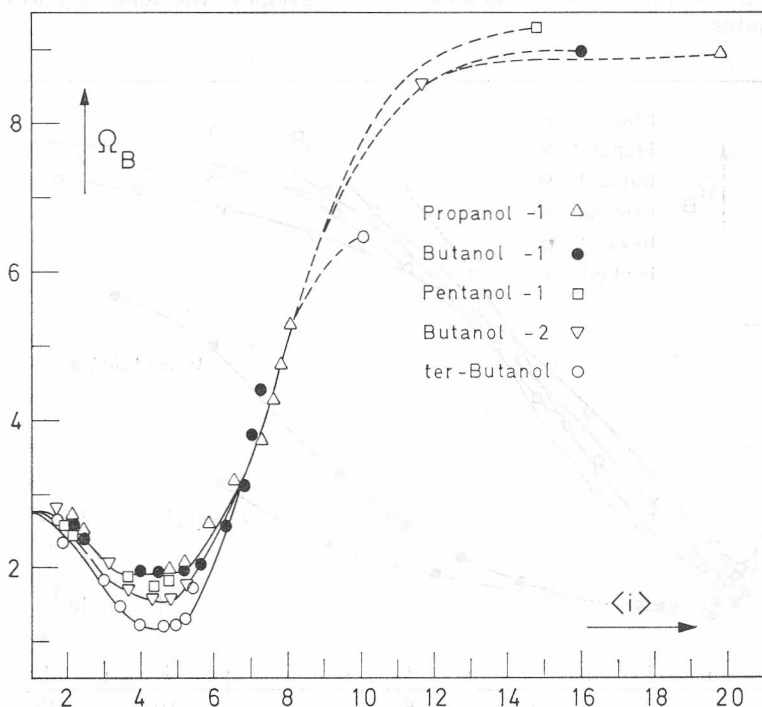


Figure 2. Experimental quantity  $\Omega_B/D^2$  as a function of the mean degree of association  $\langle i \rangle$  for several alcohols in cyclohexane at 298.16 K.<sup>18</sup>

## 2. Carboxylic Acids

In principle the evolution of  $\Omega_B$  with  $F_B$  is here qualitatively the same as for the alcohols<sup>20</sup> but the stability of the cyclic dimers is so large that in the

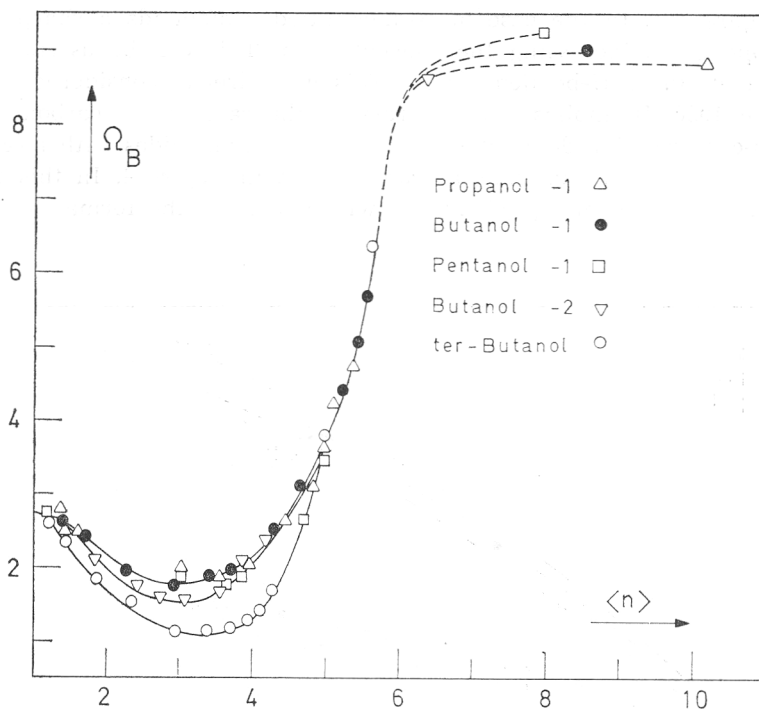
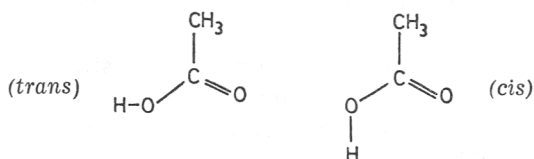


Figure 3. Experimental quantity  $\Omega_B/D^2$  as a function of the mean number of molecules per entity  $\langle n \rangle$ , for several alcohols in cyclohexane at 298.16 K.<sup>18</sup>

higher unsubstituted acids at room temperature  $\Omega_B$  is still very near to its minimum value. The stability of the cyclic dimers is related to the fact that, in the free molecule, where on account of the hindrance of rotation around the C—O bond one must consider a *trans*-isomer and a *cis*-isomer:



the *cis*-isomer predominates. Only this *cis*-isomer can form cyclic dimers.

In the case of formic acid, the situation is reversed.

As a consequence  $\Omega_B$  increases as the concentration increases and the dielectric constant of pure formic acid is fairly large (57.5 at 298.16 K).

### 3. Amides

In most cases the values of  $\Omega_B$  cannot be determined for the whole range of concentration because of the lack of solubility in non-polar solvents. For the N,N disubstituted amides which cannot form H-bonds,  $\Omega_B$  remains con-

stant (Figure 4)<sup>21</sup>. In the case of *N*-substituted compounds a sharp increase of  $\Omega_B$  appears on increasing the concentration. This can be ascribed to the formation of linear H-bonded chains. This was already considered by Mirushima<sup>22</sup> in 1950. It implies that contrary to the case of the carboxylic acids the *trans*-conformation dominates. *N*-substituted formamides with large substituents do not follow this rule, as can be seen in Figure 4. In this case the *cis*-conformation becomes predominant which leads to the formation of cyclic dimers.

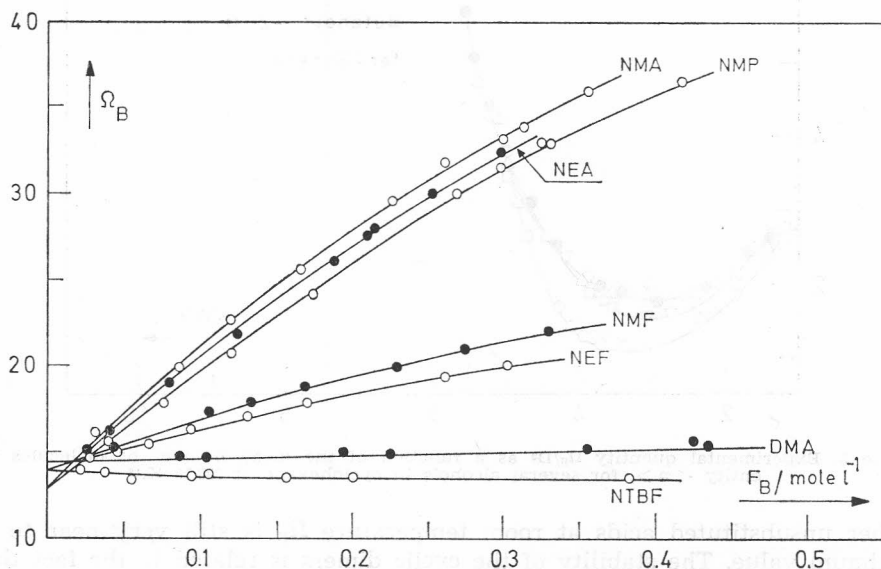


Figure 4. Dipolar quantity  $\Omega_B/D^2$  as a function of the formal concentration  $F_B/\text{mol dm}^{-3}$  of amides in benzene at 298.16 K. NMA : *N*-methylacetamide; NEA : *N*-ethylacetamide; NMP : *N*-methylpropionamide; NMF : *N*-methylformamide; NEF : *N*-ethylformamide; DMA : dimethyl acetamide; NTBF : *N*-tributylformamide.<sup>21</sup>

It is worthwhile to note that for the pure *N*-substituted amides, as shown by Bass et al.<sup>23</sup>,  $\Omega_B$  can reach exceptionally high values which increase when the temperature is lowered. This explains the very high values of the dielectric constant for these liquids.

#### 4. Amines

Tertiary aliphatic amines are not self associated liquids and hence  $\Omega_B$  is a constant in cyclohexane<sup>24</sup>. In the case of secondary amines  $\text{N}-\text{H} \dots \text{N}$  bonds can be formed which lead to self-association. This self-association was studied by means of several methods by Wolff and his coworkers<sup>25</sup>. According to Clerbaux and Huyskens  $\Omega_B$  increases slightly with concentration in cyclohexane. For primary amines the increase of  $\Omega_B$  with  $F_B$  is still weaker, as shown by Siegel et al.<sup>26</sup>. This behaviour could be explained by the formation of some cyclic aggregates which competes with the formation of open chains.

## 5. Anilines

Anilines with N—H groups are associated through N—H...N hydrogen bonds. According to Gomez<sup>27</sup>  $\Omega_B$  of unsubstituted aniline shows a slight increase when its formal concentration in cyclohexane rises. N—N disubstituted anilines are still self associated as shown by calorimetric measurements<sup>25</sup>, presumably by  $\pi \dots \pi$  interactions.

## 6. Pyridines

In the case of pyridines, the behaviour of  $\Omega_B$  as a function of the concentration is markedly influenced by the position and nature of the substituents. For pyridine itself Smets<sup>28</sup> observed a very slight increase of  $\Omega_B$  when the concentration rises. For 4-CH<sub>3</sub>-pyridine he finds that  $\Omega_B$  decreases while the reverse is true for 2-Cl-pyridine. The results can be interpreted by the competition between several specific bonds:  $\pi \dots \pi$  interactions and C—H...N hydrogen bonds between the  $\alpha$  or  $\gamma$  CH groups and the nitrogen atom of a neighbouring molecule<sup>29</sup>.

### ONE-ONE H-BONDED COMPLEXES BETWEEN MOLECULES OF DIFFERENT KIND

#### A. Experimental Determination of the Dipole Moments of *ab* Complexes

When substances A and B are dissolved in a non-polar solvent at the formal concentrations  $F_A$  and  $F_B$  and if these compounds form only H-bonded complexes of one-one stoichiometry, one can write

$$F_A = C_a + C_{ab} = C_a (1 + KC_b) \quad (20)$$

$$F_B = C_b + C_{ab} = C_b (1 + KC_a) \quad (21)$$

where  $C_a$ ,  $C_b$  and  $C_{ab}$  are the actual concentrations of the entities and  $K$  is the equilibrium constant for complex formation.

The function  $D$  obeys then the relation

$$D = \mu_a^2 C_a + \mu_b^2 C_b + \mu_{ab}^2 C_{ab} \quad (22)$$

Dividing by  $F_B$  and taking the equilibrium constant into account this can be written as:

$$\Omega_B = \mu_b^2 + (\mu_{ab}^2 - \mu_b^2) \left\{ \frac{1}{1 + (KC_b)^{-1}} \right\} \frac{F_A}{F_B} + \mu_a^2 \frac{(KC_b)^{-1}}{1 + (KC_b)^{-1}} \frac{F_A}{F_B} \quad (23)$$

Let us now consider the case where

$$KC_b \gg 1 \quad (24)$$

This is obtained when

$$F_B - F_A \gg K^{-1} \quad (25)$$

Under these circumstances (23) reduces to

$$\Omega_B = \mu_b^2 + (\mu_{ab}^2 - \mu_b^2) \frac{F_A}{F_B} \quad (26)$$

Thus when, in an excess of B sufficient to ensure inequality (25), the experimental value  $\Omega_B$  is plotted against the ratio  $F_A/F_B$ , one obtains a straight line

with intercept  $\mu_b^2$  and slope  $\mu_{ab}^2 - \mu_b^2$ . (When  $K$  is known, the more accurate equation (23) can be used).

The appearance of higher complexes  $a_2b$ ,  $a_3b$ ... generally provokes an upward curvature of the line.

### B. Factors Influencing the Value of $\mu_{ab}$ . Dipole increment

One of the most important characteristics of hydrogen bonds is their directional character. This is the consequence of the fact that their formation requires an adequate overlapping of the orbitals of the electron donor and electron acceptor. If we consider for example an O—H...N bond, it is necessary that the  $n$ -orbital of the nitrogen atom overlaps the antibonding  $\sigma_{OH}^*$  orbital of the O—H group.

A first consequence of this is that the dipole moment  $\vec{\mu}_b$  of the base forms a specific angle  $\theta_b$  (within the margin of the vibrations) with the O—H direction. We will assume further that the last direction is also that of the H-bond (this is generally the case in the liquid state when only one H-bond between a and b has to be considered). The dipole moment  $\vec{\mu}_a$  of the proton donor forms also a definite angle  $\theta_a$  with the O—H (or more generally A—H) direction.

In the liquid phase and in the gas phase however the condition of overlapping of orbitals can be fulfilled for several positions of the other parts of one molecule with respect to the other and one can foresee the existence of several rotamers around the hydrogen bond. Each rotamer is characterized by a given value of the azimuthal angle  $\varphi$  (Figure 5). (This is not the case in crystals where on account of the requirements for lattice formation, generally only one rotamer exists).

A second characteristic of H-bonds is that their formation is accompanied by the displacement of electrons and nuclei (especially the proton which is

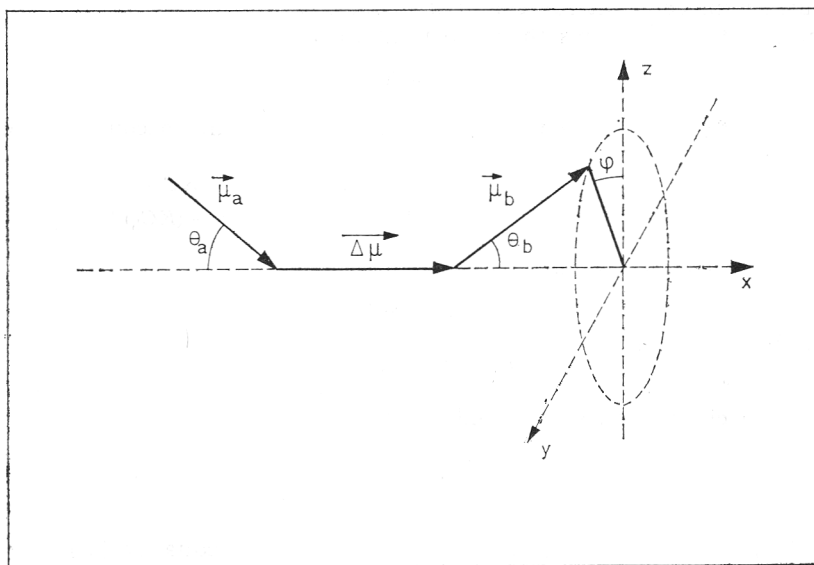


Figure 5. Angular parameters in hydrogen bonds.



directly involved in the H-bond). As a consequence, the dipole moment  $\vec{\mu}_{ab}$  of a hydrogen bonded complex differs from the vector sum of the moments of the components by a vector which we will call the *dipole increment*:

$$\vec{\mu}_{ab} = \vec{\mu}_a + \vec{\mu}_b + \Delta\vec{\mu} \quad (27)$$

The absolute value of the dipole moment  $\mu_{ab}$  of a hydrogen bonded complex will thus not only depend on the absolute value of  $\mu_a$  and  $\mu_b$  but also on the angles  $\theta_a$  and  $\theta_b$  these dipoles form with the direction of the H-bond and on the dipole increment  $\Delta\mu$ .

When only one bond is formed one can assume to a good approximation that  $\Delta\vec{\mu}$  has the direction of the hydrogen bond.

Under these circumstances the vector equation (27) above can be replaced by the following one:

$$\begin{aligned} \mu_{ab}^2 = \mu_a^2 + \mu_b^2 + (\Delta\mu)^2 + 2\mu_a\mu_b \cos\theta_a \cos\theta_b + 2\mu_a\mu_b \sin\theta_a \sin\theta_b \cos\varphi + \\ + 2\mu_a \cos\theta_a \Delta\mu + 2\mu_b \cos\theta_b \Delta\mu \end{aligned} \quad (28)$$

In this expression  $\varphi$  is the azimuthal angle related to the direction of  $\vec{\mu}_b$  with respect to the plane defined by  $\vec{\mu}_a$  and the direction of the H-bond (Figure 5).

We will take  $\cos\varphi = 0$  by convention when  $\vec{\mu}_b$  lies in the last mentioned plane, the steric group of each partner lying in *cis*-position against each other.

In the liquid phase  $\cos\varphi$  can exhibit several values and the *experimental value*  $\mu_{ab}^2$  obtained by the methods described above corresponds to the mean value of  $\cos\varphi$ ,  $\langle\cos\varphi\rangle$ , in the preceding equation.

The dipole increment  $\Delta\mu$  can be calculated from the experimental values of  $\mu_{ab}$ ,  $\mu_a$  and  $\mu_b$ , by means of equation (28) provided  $\theta_a$ ,  $\theta_b$  and  $\langle\cos\varphi\rangle$  are known.

The value of  $\theta_a$  can be estimated from the contributions of the group moments. In many cases (as for instance for symmetric *N*-bases)  $\theta_b$  is zero for symmetry reasons. In the other cases acceptable approximations for  $\theta_b$  and  $\langle\cos\varphi\rangle$  can be used in the calculation.

The experimental values of  $\Delta\mu$  range from 0 to 12 debye and even more.

### C. Factors Influencing the Dipole Increment in One-One H-bonded Complexes

#### 1. $\Delta pK_a$ of the partners in water

In 1969 Ratajczak and Sobczyk<sup>30</sup> determined  $\Delta\mu$  for complexes between triethylamine and a large variety of phenols differing in their  $pK_a$  values in water. When  $\Delta\mu$  is plotted against  $pK_a$ , the difference between the  $pK_a$  of the conjugated acid of the base and the  $pK_a$  of the acid in water, a sigmoidal curve is obtained.

Such behaviour is quite general and was observed for O—H...N bonds by Debecker and Huyskens<sup>31</sup>, Jadzyn and Malecki<sup>32</sup>, Nouwen and Huyskens<sup>33</sup>, Huyskens et al<sup>34</sup>, Grech et al.<sup>35</sup>, for O—H...O bonds by Pauwels and Huy-

skens<sup>36</sup> and Huyskens et al.<sup>37</sup> and for Cl—H...O bonds by Rospenk et al.<sup>38</sup>. An example is given in Figure 6.

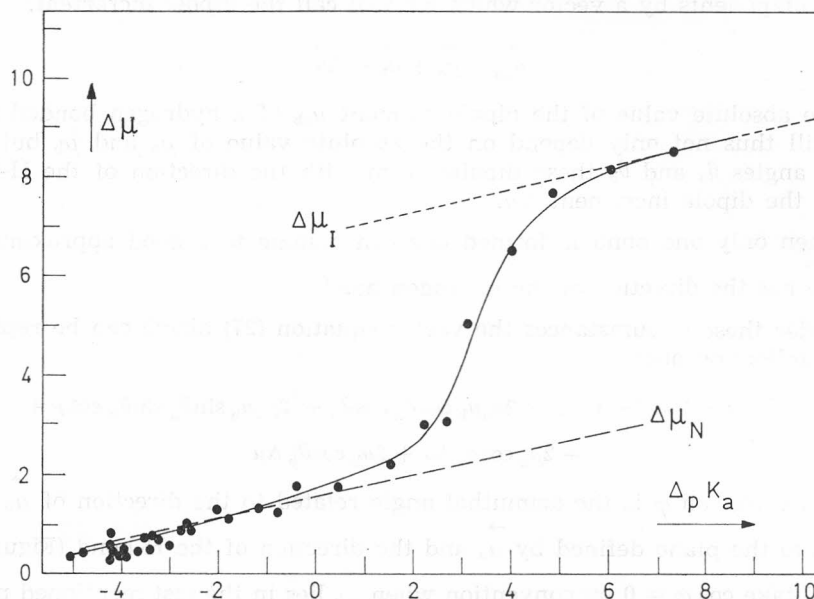
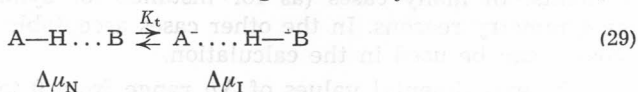


Figure 6. Dipole increment  $\Delta\mu$ /debye against  $\Delta pK_a$  for H-bonded complexes between pyridines and phenols in benzene at 298.16 K.<sup>23</sup>

This behaviour can be interpreted as resulting from a tautomerism between two forms of H-bonding, namely a first one in which the proton is located in the vicinity of the A nucleus and characterized by a low dipole increment  $\Delta\mu_N$  and a second one the »proton transfer« or »ion-pair« form where the proton has jumped to a position near the B nucleus. The last form exhibits a strong dipole increment  $\Delta\mu_I$  due to the considerable charge displacement.

The equilibrium between the two forms is governed by the constant  $K_t$ .



The possibility of simultaneous appearance of the two types of bonds was already considered in 1939 by Elliott and Fuoss<sup>39</sup>.

When  $K_t$  is not too far removed from one the two forms can be detected by their spectral characteristics as was shown first by Bell and Barrow<sup>40</sup> and later by many other authors as Baba et al.<sup>41</sup>, Zeegers-Huyskens<sup>42</sup>, Romanowski and Sobczyk<sup>43</sup>, Gusakova et al.<sup>44</sup>, Zundel and his coworkers<sup>45</sup>, Denisov et al.<sup>46</sup>.

Numerical values of  $K_t$  are tabulated in a recent review on this question by Zeegers-Huyskens and Huyskens<sup>47</sup>.

The shape of the curves  $\Delta\mu$  versus  $\Delta pK_a$  can be explained in the following way: At low values of  $\Delta pK_a$  the transfer constant  $K_t$  is much smaller than one, the normal form predominates and  $\Delta\mu$  equals  $\Delta\mu_N$ . At high values of  $\Delta pK_a$  the opposite happens:  $K_t$  is much larger than one, the ionic form predominates and  $\Delta\mu$  is practically equal to  $\Delta\mu_I$ .

In the intermediate region of  $\Delta pK_a$  both forms are present in non negligible proportion and  $\Delta\mu$  is intermediate between  $\Delta\mu_N$  and  $\Delta\mu_I$ .

Starting from equation (28) Nouwen and Huyskens<sup>33</sup> obtained the following relation between  $\Delta\mu$ ,  $K_t$ ,  $\Delta\mu_N$  and  $\Delta\mu_I$ :

$$K_t = \frac{\Delta\mu - \Delta\mu_N}{\Delta\mu_I - \Delta\mu} \left\{ \frac{\Delta\mu + \Delta\mu_N + 2(\mu_a \cos\theta_a + \mu_b \cos\theta_b)}{\Delta\mu + \Delta\mu_I + 2(\mu_a \cos\theta_a + \mu_b \cos\theta_b)} \right\} \quad (30)$$

The values of  $\Delta\mu_N$  and  $\Delta\mu_I$  can be found by extrapolation of the lower and the upper part of the sigmoide respectively (Figure 6) and it is possible to calculate  $K_t$  in the transient region from the experimental value of  $\Delta\mu$ . When the factor within brackets equals unity, equation (30) reduces to that used by Sobczyk and Pawelka<sup>48</sup>.

The inflexion point of the curve of  $\Delta\mu$  against  $\Delta pK_a$  corresponds to a complex for which  $K_t$  is very nearly one.

For a given family of complexes in a given solvent,  $\log K_t$  is to a good approximation linearly related to  $\Delta pK_a$ :

$$\log K_t = \xi \Delta pK_a - \delta \quad (31)$$

This equation was used by Ratajczak and Sobczyk<sup>30</sup> to improve on an equation proposed in 1964 by Huyskens and Zeegers-Huyskens<sup>49</sup>. The values of  $\xi$  and  $\delta$ , as already mentioned, depend on the family of complexes and on the particular solvent used. For instance, for the system phenols triethylamine  $\delta$  is 6.5 in cyclohexane<sup>32</sup>, 5.2 in toluene<sup>32</sup> and in benzene<sup>30</sup> and 4.1 in trichloroethylene<sup>32</sup>. The experimental values of  $\xi$  lie between 0.2 and 1.0 and seem to be lower for the O—H...O than for the O—H...N bonds.

## 2. Enthalpy of H-bond formation

When, in a given solvent, different families of complexes are considered (for instance phenols-pyridine and phenols-triethylamine) the sigmoids describing  $\Delta\mu$  against  $\Delta pK_a$  are displaced with respect to each other (this means that in equation (31)  $\delta$  is different).

When now, instead of  $\Delta pK_a$  one takes  $-\Delta H_b$ , the enthalpy change for bond formation, as the independent variable, all the points relative to the complexes of the same type of bond (O—H...N, O—H...O etc.) in the same solvent lie approximately on the same curve. This was shown by Huyskens et al.<sup>37</sup> and an example involving approximately one hundred complexes with O—H...O bonds in cyclohexane is given in Figure 7.

The curve is also sigmoidal and passes through the origin.

It can be represented by the following general equation<sup>37</sup>:

$$\Delta\mu = \frac{A(-\Delta H_b) + [B + C(-\Delta H_b)] e^{[A_1 + B_1(-\Delta H_b)]}}{1 + e^{[A_1 + B_1(-\Delta H_b)]}} \quad (32)$$

For O—H...O bonds in cyclohexane the coefficients of this equation take the following numerical values,  $\Delta\mu$  being expressed in debye and  $\Delta H_b$  in kJ mol<sup>-1</sup>,  $A = 0.028$ ,  $B = 3.20$ ,  $C = 0.075$ ,  $A_1 = -6.5$ ,  $B_1 = 0.085$ .

For O—H...N bonds in benzene the coefficients become<sup>34</sup>:  $A = 0.0074$ ,  $B = 4.41$ ,  $C = 0.045$ ,  $A_1 = -7.7$ ,  $B_1 = 0.172$ .

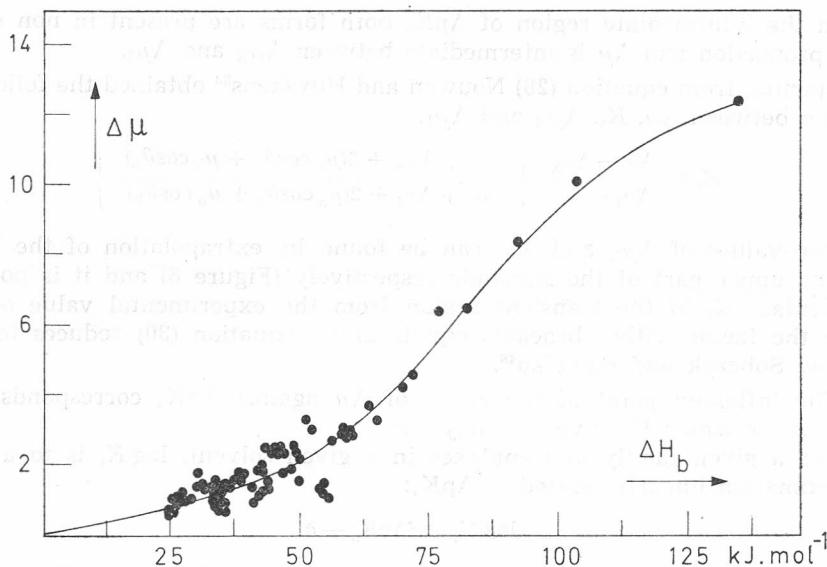


Figure 7. Dipole increment  $\Delta\mu$ /debye as a function of the enthalpy of the hydrogen bond  $-\Delta H_b$ /kJ mol $^{-1}$  for O—H...O complexes in cyclohexane at 298.16 K (data from ref. 37).

For the O—H...O bonds in cyclohexane the inflexion point lies in the vicinity of  $-\Delta H_b = 80$  kJ mol $^{-1}$ , whereas for the O—H...N bonds in benzene it appears at  $-\Delta H_b \approx 50$  kJ mol $^{-1}$ . Of course, as benzene is a more active solvent than cyclohexane, the values of  $-\Delta H_b$  are systematically lower because the specific bonds of the donor and the acceptor with benzene have to be broken before the two partners can form an H-bond. Anyway the solvent effect cannot account for such a large difference in  $-\Delta H_b$  at the inflexion point. One can thus conclude that the proton transfer is favoured in O—H...N bonds when compared to the transfer in O—H...O bonds of the same energy. In our opinion, this is related to the fact that proton transfer produces less changes in the hybridization of the orbitals for the nitrogen atom than for the oxygen atom.

### 3. Dielectric constant of the medium

The increase of the polarity, described by the dipole increment, will be favoured by an increase of the dielectric constant of the medium. Thus one expects that in a more polar medium the dipole increment of both the normal form  $\Delta\mu_N$  and the proton transfer form  $\Delta\mu_I$  will increase.

However no quantitative information about this effect seems to be available. The effect is presumably weak and is overshadowed by others such as the specific effects of the solvent on  $\mu_a$  or  $\mu_b$  or both.

Another quantity which is perhaps influenced to a larger extent by the dielectric constant is the transfer constant  $K_t$ . Several equations have been proposed<sup>32,41</sup> but again, as pointed out by Sobczyk et al.<sup>3</sup>, the effect may be overshadowed by other effects, such as the formation of specific bonds between the complex and the solvent.

### D. Determination of the Structure of Some H-Bonded Complexes in Solution From Dipole Measurements

Below or beyond the transient region in the  $\Delta\mu/\Delta H_b$  curve,  $\Delta\mu$  can be computed within a few tenths of debye from  $\Delta H_b$ , using equation (32) (this calculation is less accurate in the transient region). Occasionally, when  $\Delta H_b$  is not available, it can be estimated from the displacement  $\Delta\nu_{OH}$ , using a Badger-Bauer relation<sup>50</sup>.

Knowing  $\Delta\mu$  it is then possible to compute  $\langle \cos \varphi \rangle$ , if  $\theta_b$  and  $\theta_a$  are known, from the experimental moments  $\mu_{ab}$ ,  $\mu_a$  and  $\mu_b$  using equation (28). For O—H...O complexes this value is of the order of  $-0.5$  and this can be explained by steric hindrances in the cis conformation<sup>37</sup>. For O—H...N complexes  $\langle \cos \varphi \rangle$  is of the order of zero<sup>34</sup>.

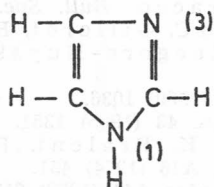
With these values of  $\langle \cos \varphi \rangle$  one can calculate  $\theta_b$  for the bases for which this angle is unknown. This calculation can be performed for a whole series of complexes of the same base, which will give an idea of the accuracy of the method. Of course this accuracy will depend on that of  $\Delta\mu$  and the other variables.

A more sophisticated mathematical treatment can even be developed using multiple regression analysis for all the unknown angles<sup>37</sup>.

Even when  $\theta_b$  is known from this method only within a margin of  $10^\circ$  or  $20^\circ$ , this can provide a clue in cases where there exists some doubt about several possible structures of several H-bonded complexes in the liquid phase.

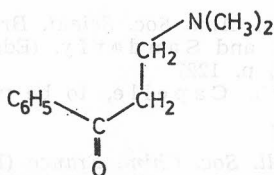
We will give here a few examples.

In imidazoles, for instance, two different base sites exist: the amino nitrogen (1) and the imino nitrogen (3) atom:

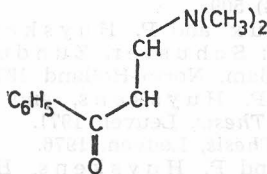


If hydrogen bond formation occurs on the amino nitrogen a value of  $\theta_b$  of the order of  $90^\circ$  can be expected. If the hydrogen bond is formed on the imino nitrogen  $\theta_b$  will be much smaller. The experimental value obtained from the dipole data for 1-methyl and 1,2-dimethylimidazole is  $38^\circ \pm 10^\circ$  indicating that the second hypothesis is correct<sup>34</sup>.

Other examples are the two following compounds



$\beta$ -dimethylamino-1-phenyl-2-propene-1-one



$\beta$ -dimethylaminopropiophenone

Here also several basic sites have to be considered: 1) on the C=O group and 2) on the N atom. The moments for both bases have approximately the C=O direction. If complexation occurs on the C=O group then  $\theta_b$  is expected to be of the order of  $60^\circ$  (which is the angle between the C=O direction and the lone pairs of electrons), while if complexation occurs on the N atom then  $\theta_b$  is expected to be of the order of  $90^\circ$ .

Some nine complexes of  $\beta$ -dimethylaminopropiophenone with various phenols were studied following the method described above. One finds for  $\theta_b$  a value of  $101 \pm 8^\circ$ . The complexation occurs here clearly on the nitrogen atom.

On the contrary, the complexes of the same phenols with the enamino ketone exhibits a value of  $\theta_b = 62 \pm 10^\circ$ . Here, the complexation takes place on the carbonyl group.

These few examples illustrate the variety of problems in H-bonding research for which dipole measurements constitute an adequate tool.

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## IZVLEČEK

### Dipolni momenti vodikovo vezanih kompleksov

*Pierre L. Huyskens in Georges G. Siegel*

Članek obravnava podatke o strukturi vodikovo vezanih kompleksov v tekoči fazi, dobljenimi z dielektričnimi merjenji. V prvem delu razpravlja o osnovnih enačbah za določanje dipolnih momentov v tekočinah. Za čisto polarne tekočine Onsagerjeve enačbe pripeljejo do vrednosti, ki se lahko razlikujejo od tistih za plinsko fazo. Kirkwood je razložil, da te razlike nastanejo zaradi medmolekulskih orientacijskih pojavov. V čistih tekočinah so te razlike zelo pomembne, če gre za vodikove vezi.

V drugem delu je razlaga eksperimentalnih podatkov o dipolnih momentih auto-asociiranih spojin: alkoholov, karbonskih kislin, amidov, aminov, anilinov in piridinov.

V tretjem delu je podana metoda, ki jo uporabljamo za določanje dipolnih momentov  $\mu_{AB}$  vodikovo vezanih kompleksov (1:1).  $\mu_{AB}$  ne zavisi samo od momentov ločenih partnerjev, ampak tudi od kotov  $\vartheta_A$  i  $\vartheta_B$ , ki jih tvorijo ti momenti s smerjo vodikove vezi. Še več  $\mu_{AB}$  je odvisen tudi od dipolnega prirastka  $\Delta\mu$ , ki nastane ob premiku elektronov in jeder, zaradi vodikove vezi.  $\Delta\mu$  bo tako odvisen od  $\Delta pK_A$ , razlike med  $pK_A$  konjugirane kisline protonskega akceptorja in kisline same. Dobljene sigmoidne krivulje si lahko razlagamo s tautomerijo med »normalno« vodikovo vezjo in tisto »s prenosom protona«.

Odvisnost  $\Delta\mu$  od entalpije vodikove vezi,  $-\Delta H_B$  se tudi pokaže v obliki sigmoidne krivulje, ki je približno enaka za vse vodikove vezi iste vrste (OH...O, OH...N, itd.) v danem topilu. Ta odvisnost se lahko uporabi za računanje  $\Delta\mu$ . S tako dobljeno vrednostjo in z merjenimi momenti  $\mu_{AB}$ ,  $\mu_A$  in  $\mu_B$  lahko določamo kote  $\vartheta_A$  in  $\vartheta_B$  za proučevani kompleks. Podani so nekateri primeri.