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Studies of Hydrogen Bonding. Part XXXVI.* Dipole Moments of Pyridines, Quinolines and Acridine, and of their Hydrogen-Bonded Complexes with Phenol

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The dipole moments of eight pyridines, three quinolines and acridine, and of their hydrogen-bonded complexes with phenol have been determined in carbon tetrachloride solution at 20°C. The data points for the correlation of the dipole moments with the ability of the proton acceptors to associate with phenol and with their basicity, are separated into two groups. In one group the compounds possess a resultant of the group moments that reinforces, whereas in the other group the resultant opposes the molecular dipole moment.

The vectorially calculated dipole moments of the hydrogen-bonded complexes were found to be smaller than the corresponding dipole moments obtained experimentally.

We have previously determined the dipole moments of several phosphoryl[2] and carbonyl[3] compounds, and of their hydrogen-bonded complexes with phenol. The dipole moments were related to hydrogen-bond strength and to the ability of the proton acceptors to associate with phenol. A similar study by using pyridines, quinolines and acridine was then of interest.

Experimental

The purification of the chemicals and the method of evaluation of the dipole moment were the same as reported in detail elsewhere.[4,5] The concentration range of phenol was 0.01–0.05 M and of the proton acceptors 0.03–0.15 M. The concentration of the acceptor was kept

Table 1. Experimental dipole moments, μ_A^{exp}, the corresponding total polarization, P_∞, molar refraction, R_D, the parameters α, β, γ and the basicity, pK_a, of the proton acceptors.[a] Solvent: carbon tetrachloride; $T = 20°C$.

Proton acceptor	pK_a	α	β	γ	P_∞	R_D	μ_A^{exp}/D
1 Quinoline	4.90	8.2758	0.2857	0.7857	147.152	43.643	2.23
2 Pyridine	5.27	13.3333	0.3684	0.4090	133.628	12.340	2.41
3 Isoquinoline	5.40	11.0256	0.2045	0.9500	181.521	43.126	2.58
4 Acridine	5.58	6.1224	0.3594	1.3983	166.969	76.164	2.09
5 3-Methylpyridine	5.75	13.7931	0.5000	0.4138	165.695	33.043	2.52
6 2-Methylpyridine	6.05	9.6552	0.5000	0.4167	125.167	33.079	2.10
7 4-Benzylpyridine	5.59	8.4444	0.2800	0.5057	195.682	51.886	2.63
8 2-Methylquinoline	5.83	6.2857	0.3182	0.8536	134.460	50.728	2.01
9 4-Methylpyridine	6.10	15.9091	0.6111	0.3928	189.389	38.668	2.72
10 2,6-Dimethylpyridine	6.64	8.8461	0.5854	0.2262	137.666	38.327	1.89
11 2,4-Dimethylpyridine	6.85	10.3226	0.5263	0.2143	152.464	36.452	2.36
12 2,4,6-Trimethylpyridine	7.25	8.0000	0.6087	0.2241	145.731	43.731	2.22

[a] **13** 3,5-Dimethylpyridine ($pK_a = 6.19$, $\mu_A^{exp} = 2.66$ D, $K_{ass} = 80.9$ M^{-1}); **14** 4-ethylpyridine (6.03, 2.78, 87.1); **15** 4-methoxypyridine (6.58, 3.07, 107.6); **16** 4-aminopyridine (9.12, 4.10, 261.9); **17** 4-dimethylaminopyridine (9.61, 4.44, 347.4); **18** 3-ethylpyridine (5.70, 2.56, 72.4); **19** 2,3-dimethylpyridine (6.70, 2.33, 90.2); **20** 2,5-dimethylpyridine (6.55, 2.28, 86.4); **21** 2-ethylpyridine (5.99, 2.06, 78.3); **22** 2-aminopyridine (6.86, 2.19, 95.6). The pK_a values are from Ref. 16, the K_{ass} values at 20°C from this work and the μ_A^{exp} values for compounds **13–22** from Ref. 7. The literature values of μ_A^{exp} measured in benzene are, following Sharpe and Walker,[9] corrected for carbon tetrachloride as the solvent by adding 0.13 D.

* For part XXXV see Ref. 1.

Table 2. Experimental dipole moments, μ_{DA}^{exp}, the corresponding total polarization, P_∞, molar refraction, R_D, and the parameters α, β and γ of the hydrogen-bonded complex between phenol and the proton acceptors. Solvent: carbon tetrachloride; $T = 20°C$.

Proton acceptor	K_{ass}/M^{-1} [a]	α	β	γ	P_∞	R_D	μ_{DA}^{exp}/D
1	57.4	15.9895	0.1143	0.8125	419.971	66.619	4.13
2	59.8	20.5000	0.1250	0.5000	410.369	45.242	4.18
3	61.4	18.9814	0.1487	0.9944	497.312	72.228	4.52
4	67.2	13.5000	0.2500	0.9756	457.838	95.252	4.17
5	73.1	20.3704	0.2500	0.6000	448.833	57.483	4.34
6	74.7	16.8750	0.3696	0.5000	386.576	61.527	3.95
7	78.3	15.4412	0.1818	0.6739	490.892	78.238	4.45
8	79.8	13.7931	0.2037	0.7463	402.325	73.726	3.97
9	80.0	22.2973	0.2917	0.5200	489.015	57.951	4.55
10	95.2	16.3043	0.4808	0.4444	410.308	71.065	3.75
11	103.9	18.0000	0.4255	0.4524	442.973	68.207	4.24
12	137.1	16.3461	0.4166	0.4091	435.833	71.412	4.19

[a] The K_{ass} data at 20°C are from Ref. 5.

3–5 times greater than the concentration of the donor to minimize the formation of complexes other than the 1 : 1 hydrogen-bonded complex.[1,6] The experimental polarization data α′, β, γ, P_∞, R_D and the corresponding dipole moments of the proton acceptors, μ_A^{exp}, and of the hydrogen-bonded complexes, μ_{DA}^{exp}, are tabulated in the Tables 1 and 2. The μ_A^{esp} and μ_{DA}^{exp} values were estimated to be accurate to within ±0.05 and ±0.10 D, respectively. Our data are, when a comparison is possible, in good agreement with literature values.[7]

Results and discussion

μ_A^{exp} and μ_s. As seen from Fig. 1, the data points for the correlation between the dipole moments, μ_A^{exp}, and the basicity, pK_a, of the proton acceptors are separated into two groups. We have drawn the best straight line through the data points for both groups. Those clustered around the regression line I in Fig. 1 are mono- and di-substituted pyridines with one electron-releasing group in the 2-position (**6**, **11**, **19**, **20**, **22**) and 2-methylquinoline (**8**). The correlation is given by eqn. (1). Compounds with two electron-releasing substituents one of which is in the 2-position (**10**, **12**) and acridine (**4**) are situated away from this line. The compounds clustered around the regression line II are compounds with no substituent in the 2-position. They are pyridine (**2**), monosubstituted pyridines with an electron-releasing group in the 3- or 4-position (**5**, **7**, **9**, **14**, **15**, **16**, **17**, **18**), 3,5-dimethylpyridine (**13**), quinoline (**1**) and isoquinoline (**3**). The correlation is given by eqn. (2).

$$pK_a = 2.802\mu_A^{exp} + 0.268 \qquad (1)$$
$$n = 7 \qquad r = 0.885$$

$$pK_a = 2.163\mu_A^{exp} + 0.098 \qquad (2)$$
$$n = 12 \qquad r = 0.993$$

In this connection it should be emphasized that pyridines with electron-withdrawing substituents and amines, e.g., 4-cyanopyridine ($pK_a = 1.90$, $\mu_A^{exp} = 1.65$ D), 4-chloropyridine (3.84, 0.84) and trimethylamine (9.8, 0.79) are situated far away from the regression lines I and II.

The dipole moments of the proton acceptors have also been correlated with their ability (log K_{ass}) to associate with phenol as shown in Fig. 1. Again the data points are separated in the same way into two groups, i.e., we have found the same trend for the relationship log K_{ass} vs. μ_A^{exp}

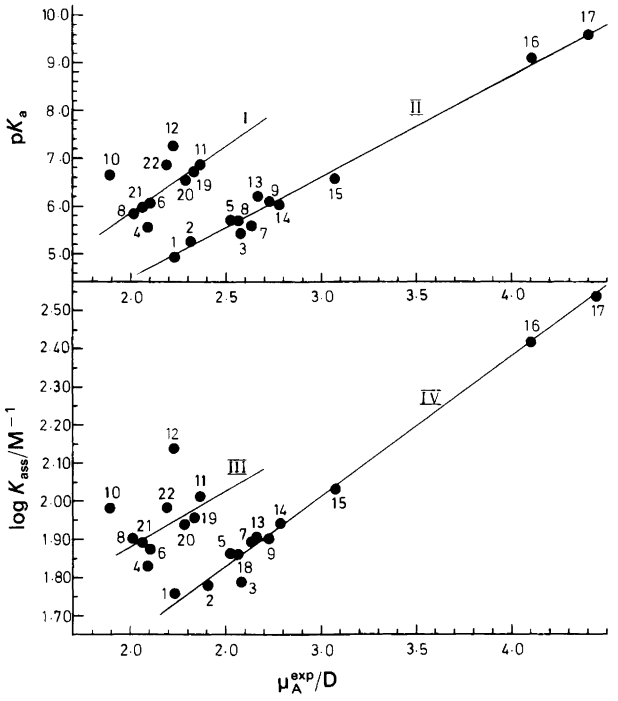

Fig. 1. The correlation between the dipole moments, μ_A^{exp}, and the pK_a values of various proton acceptors, and the tendency, log K_{ass}, of the acceptors to associate with phenol.

as for pK_a vs. μ_A^{exp}. The correlations for the regression lines III and IV are given by eqns. (3) and (4).

$$\log K_{ass} = 0.296\mu_A^{exp} + 1.288 \qquad (3)$$
$$n = 7 \qquad r = 0.795$$

$$\log K_{ass} = 0.365\mu_A^{exp} + 0.918 \qquad (4)$$
$$n = 12 \qquad r = 0.994$$

The obvious reason for the separation of the data points into two groups is that in one group (the compounds situated on the regression lines II and IV) the resultant of the group moments reinforces the dipole moment of the pyridine ring, whereas in the other group the resultant opposes the μ_{Py} direction. The main reason for the poor linear correlation of the data points in the latter group of compounds is the deviating behaviour of the 2-aminopyridine (**22**). The compounds with substituents in 2- and 6-position (**10**, **12**) are too basic in comparison with their dipole moments to fall onto the regression lines, i.e., the molecular dipole moment does not increase to the same extent as the basicity on increasing the number of substituents. The basicity is dependent mainly on the number of substituents, whereas the dipole moment, in addition, is strongly dependent on the location of the substituents in the pyridine ring. We believe that the linear correlation of the data points for the compounds situated on the regression lines II and IV is due to the fact that, in these compounds, all the individual group moments reinforce the molecular dipole moment. Quinoline (**1**) is in fact the only compound situated on the regression lines II and IV that is less basic than and possesses a smaller dipole moment than pyridine, i.e., the condensed benzene ring acts as an electron-withdrawing group. In contrast, the condensed benzene ring in isoquinoline (**3**) and the two benzene rings in acridine (**4**) act as electron-releasing groups (see pK_a values in Table 1). The resultant of the group moments in isoquinoline reinforces the molecular dipole moment, whereas in acridine the resultant opposes the μ_{Py} direction. The methyl group and the condensed benzene ring in 2-methylquinoline (**8**) have a combined effect that acts as an electron-releasing group, however, the resultant opposes the μ_{Py} direction (see pK_a and μ_A^{exp} values in Table 1).

The scalar difference between the dipole moment of 4-monosubstituted pyridine and pyridine was taken to be equal to the group moment, μ_s, of that particular substituent. In this way the 4-methyl, 4-ethyl, 4-benzyl, 4-methoxy, 4-amino and 4-dimethylamino group moments were calculated to be 0.31, 0.37, 0.22, 0.69, 1.66 and 2.03 D, respectively. It should be noted, however, that the corresponding group moments are substantially different when they are substituted in a benzene ring,[8,9] A large difference in the methyl group moment can also be demonstrated by comparison of 2-methylpyridine with 4-methylpyridine. By using the experimental dipole moments of 2-methylpyridine and pyridine, the 2-methyl group moment, μ_s, was calculated, as shown in Fig. 2(a),

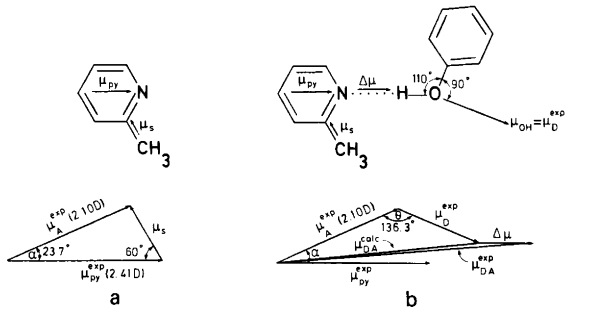

Fig. 2. The hydrogen-bonded complex between phenol and 2-methylpyridine showing the various angles used to calculate the group moment, μ_s, the dipole moment of the complex, μ_{DA}^{calc}, and the dipole increment, $\Delta\mu$.

to be -0.97 D ($-$ means that the group moment opposes the μ_{Py} direction). This value should be compared with the value of 0.31 D found for the 4-methyl group moment in 4-methylpyridine. Similarly, the 3-methyl group moment in 3-methylpyridine was calculated to be 0.21 D. Furthermore, since the dipole moment of 2,4-dimethylpyridine (2.36 D) and pyridine (2.41 D) is comparable, the two methyl group moments must nearly compensate each other. This implies that the 2-methyl group moment is much larger than the 4-methyl group moment and hence strengthens the results reported above. In 2,6-dimethylpyridine the resultant of the two group moments is parallel to and opposes the μ_{Py} direction. The vectorial sum of the two methyl group moments was calculated to be -0.52 D (1.89–2.41 D), i.e., the scalar value of μ_s for a methyl group in the 2- and 6-position is equal to 0.52 D. This value differs very much from the value of 0.97 D found for the 2-methyl group moment in 2-methylpyridine. In 3,5-dimethylpyridine the resultant of the group moments is also parallel to but reinforces the μ_{Py} dipole. The resultant is determined to be 0.25 D (2.66–2.41 D). This means that the group moment is 0.25 D which differs from that found for 2,6-dimethylpyridine. Furthermore, in 2,4,6-trimethylpyridine the resultant (-0.19 D) of the three methyl group moments is parallel to and opposes the μ_{Py} direction. The above observations clearly show that the group moment of a methyl group not only varies from one position to another in monosubstituted methylpyridines, but is also dependent on the number of substituents and on their mutual position in the ring.

μ_{DA}^{exp}, μ_{DA}^{calc} *and* $\Delta\mu$. The experimental dipole moments, μ_{DA}^{exp}, of twelve hydrogen-bonded complexes between phenol and several proton acceptors are listed in Table 2. The dipole moments of the complexes have been correlated (not shown) with the ability of the acceptors to associate with phenol and with their basicity. The data are again separated into two groups of compounds. Those with a resultant of the group moments that reinforces the pyridine ring dipole moment, μ_{Py}, and those with a resultant that opposes the μ_{Py} direction. Within each group of

compounds the data points form more of a scatter diagram than is the case for the corresponding correlation with μ_A^{exp}, i.e., the data points for the correlations μ_{DA}^{exp} vs. $\log K_{ass}$ and μ_{DA}^{exp} vs. pK_a do not form linear correlations. The reason for this might be that the enhancement of the bond moments on complexation with phenol, differs from acceptor to acceptor. For example, owing to the two benzene rings, acridine is much more enhanced than pyridine on complexation with phenol (see Tables 1 and 2).

The vectorially calculated dipole moments, μ_{DA}^{calc}, of the various hydrogen-bonded complexes were obtained by using the experimental dipole moments of the donor, μ_D^{exp}, and the acceptors, μ_A^{exp}. The dipole moment of phenol has been measured[2] in carbon tetrachloride to be 1.47 D at 20°C and the C–O–H angle was taken[10] to be 110°. The direction of μ_A^{exp} within the various acceptors was determined as shown in Fig. 2(a). To find the angle, θ, between the direction in which μ_A^{exp} and μ_D^{exp} act in the complex, we assumed that the lone electron pair on the nitrogen atom is directed along the hydrogen bond, as shown in Fig. 2(b). Furthermore, CNDO/2 calculations have shown[11] that the phenol ring is *trans* to the methyl group and coplanar with the pyridine ring. The angle, θ, and the dipole moment, μ_{DA}^{calc}, were calculated for the various hydrogen-bonded complexes as shown for the phenol/2-methylpyridine complex in Fig. 2(b). The θ and μ_{DA}^{calc} values are listed in Table 3. The vectorially calculated dipole moments were always found to be smaller than those obtained experimentally. The vectorial difference can be expressed in terms of a dipole increment, Δμ, defined by the vector equation (5)

$$\Delta\mu = \mu_{DA}^{exp} - \mu_{DA}^{calc} = \mu_{DA}^{exp} - (\mu_D^{exp} + \mu_A^{exp}) \quad (5)$$

The stumbling block in these calculations is, however, that we do not know the dipole moments of the donor and acceptor molecules as they occur in the complex. We have therefore assumed that the additional dipole moment, Δμ, is caused only by electronic displacement along the H-bond, i.e., we have not taken into account possible electronic redistribution in other parts of the hydrogen-bonded complex. The direction of Δμ has been shown by CNDO/2 calculation[12] to be from the proton acceptor towards proton donor. The Δμ values are tabulated in Table 3. As can be seen the Δμ values vary from 0.35 D for the system phenol–pyridine to 0.67 D for phenol–acridine. We believe that the additional dipole moment in the pyridine complex is due to polarization in the pyridine ring and along the hydrogen bond, whereas in the acridine complex the polarization of the two benzene rings is an important additional contributor to the Δμ value. The Δμ value of the acridine complex is also larger than of the 2,4,6-trimethylpyridine complex in spite of the fact that the trimethylpyridine is a much stronger proton acceptor than acridine, i.e., our data show no obvious correlation between hydrogen bond strength and the additional dipole moment. Ratajczak and Orville-Thomas have shown,[13,14] however, by using an extension of Mulliken's charge-transfer theory, that there exists for structurally similar hydrogen-bonded complexes, a linear correlation between the square root of the additional dipole moment, $\Delta\mu^{1/2}$, and the enthalpy of formation, ΔH. A linear correlation has also been reported[4] between $\Delta\mu^{1/2}$ and the phenol O–H stretching frequency shift, $\Delta\nu_{OH}$, accompanying the association of phenol with phosphorinanes and diethyl phosphonates. A similar linear correlation between $\Delta\mu^{1/2}$ and pK_a (or $\log K_{ass}$) has not been observed in this work. The reason for this might be, as discussed above, that the contribution to Δμ on complexation with phenol comes not only from the change in the charge distribution along the hydrogen bond, but also from other parts of the complex, especially from the proton-acceptor part. The contribution to Δμ from the polarization of the π-electrons in the phenol molecule has been shown by quantum-mechanics calculations[15] to be small, of the order of 0.1 D, and has hence been neglected in our discussion.

Table 3. Vectorial calculated dipole moments, μ_{DA}^{calc}, group moments, μ_s, additional dipole moments, Δμ, and the angle, θ, between the direction in which μ_D^{exp} and μ_A^{exp} are acting in the hydrogen-bonded complex.

Proton acceptor	μ_{DA}^{calc}/D	μ_s/D	Δμ/D	θ/°
2	3.83	—	0.35	160.0
4	3.51	0.32	0.67	160.0
5	3.91	0.21	0.43	155.8
6	3.32	0.97	0.63	136.3
7	4.04	0.22	0.41	160.0
9	4.13	0.31	0.42	160.0
10	3.31	0.52	0.48	160.0
12	3.64	0.19[a]	0.56	160.0

[a]The vectorial sum of the three methyl-group moments in 2,4,6-trimethylpyridine.

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