Studies of Hydrogen Bonding. Part XXXIV. Dipole Moments of Carbonyl Compounds and of their Hydrogen-Bonded Complexes with Phenol

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The dipole moments of fourteen carbonyl compounds and of their hydrogen-bonded complexes with phenol have been determined in carbon tetrachloride at 20 °C.

In general there is no smooth correlation between the dipole moments and the ability of the carbonyl compounds to associate with phenol. The influence of substituents on the $C=O$ bond moment and on the molecular dipole moment is discussed.

The vectorially calculated dipole moments of the various hydrogen-bonded complexes are smaller than the corresponding dipole moments obtained experimentally. The vectorial difference between experimental and vectorially calculated dipole moment, $\Delta\mu$, was found to be greatest for carbonyl compounds containing the $N-C_6H_4-C=O$, $C_6H_5-C=O$ and $N-C=O$ groups.

In a previous publication[1] the dipole moments of several phosphoryl compounds and of their hydrogen-bonded complexes with phenol were determined. The dipole moments were related to the ability of the phosphoryl compounds to associate with phenol and to the hydrogen bond strength. A similar study using carbonyl compounds was then of interest.

Experimental

Materials. Phenol and carbon tetrachloride were purified as described elsewhere.[1] The carbonyl compounds, not commercially available, were prepared by literature methods.[2] The compounds were purified by redistillation or recrystallization immediately before use. The purity was checked by GLC and mass spectroscopy.

Experimental dipole moments. The dipole moment measurements were carried out in carbon tetrachloride at $20 \pm 0.05\,°C$. The instruments and methods of evaluation of the dipole moments were the same as reported in detail elsewhere.[3–5] The concentration range of phenol was 0.01–0.05 M and of the carbonyl compounds 0.03–0.15 M. The K_{ass} values from Ref. 2 were used to evaluate the experimental dipole moments of the hydrogen-bonded complexes. The concentration of proton acceptor was kept 3–5 times greater than the concentration of the proton donor to minimize the formation of complexes

other than the 1:1 hydrogen-bonded complex.[6] The experimental polarization data α, β, γ, P_∞, R_D and the corresponding dipole moments of the carbonyl compounds, μ_A^{exp}, and of the hydrogen-bonded complexes, μ_{DA}^{exp}, are tabulated in Tables 1 and 2. The μ_A^{exp} and μ_{DA}^{exp} values are 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}. As seen from Table 1 and Fig. 1, the dipole moments, μ_A^{exp}, of the various carbonyl compounds do not, in general, give a smooth correlation with the carbonyl stretching frequency, v_{CO}, or with the phenol O–H stretching frequency shift, Δv_{OH}, accompanying the complexation of the carbonyl compounds with phenol (Δv_{OH} = stretching frequency of free phenol O–H minus the frequency of hydrogen-bonded O–H). The plot μ_A^{exp} vs. Δv_{OH} is virtually a scatter diagram, but we have drawn, as shown in Fig. 1, the best straight line through eight (**1, 9, 10, 5, 11, 12, 13** and **7**) of fifteen data points. The correlation is given by eqn. (1).

$$\mu_A^{exp} = 4.60 \times 10^{-3}\Delta v_{OH} + 2.49$$
$$n = 8 \qquad r = 0.97 \tag{1}$$

We believe that the deviating behaviour of the symmetrical carbonyl compounds **3, 15, 4** and **14** from this line has to do with the fact that we are dealing with symmetrical and unsymmetrical molecules. The four sym-

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* For Part XXXIII see Ref. 1.

Table 1. Experimental dipole moments, μ_A^{exp}, the corresponding total polarization, P_∞, molar refraction, R_D, the parameters α, β, γ and IR data of various carbonyl compounds at 20°C. Solvent: carbon tetrachloride.

	Proton acceptor	v_{CO}/cm^{-1}	α	β	γ	P_∞	R_D	μ_A^{exp}/D
1	2-Naphthaldehyde	1709	14.5161	0.2308	1.1636	278.003	56.946	3.26
2	Ethyl acetate	1746	7.2000	0.3519	−0.1795	91.897	21.918	1.83
3	Benzophenone	1670	10.2040	0.3000	0.7500	244.890	61.495	2.97
4	Cyclohexanone	1723	18.6404	0.4167	0.3125	222.728	31.532	3.03
5	Cinnemaldehyde	1693	21.1538	0.2857	0.9565	329.829	47.138	3.69
6	p-(Dimethylamino)benzaldehyde	1696	39.1670	0.2890	0.8570	625.855	51.515	5.38
7	Ethoxycarbonylmethylenetriphenyl-phosphorane[a,b]	1610	12.9032	—	0.4668	—	—	4.29
8	N,N-Diphenyl-4-nitrobenzamide	1673	13.8889	0.1034	0.8947	532.629	95.276	4.59
9	N,N-Diphenylbenzamide	1674	9.6552	0.1628	0.5833	341.155	76.999	3.56
10	N,N-Diphenylpropionamide	1685	10.9091	0.1875	0.4286	330.808	64.731	3.58
11	N,N-Dimethylformamide	1692	41.5380	0.3570	−0.8750	339.449	12.655	3.96
12	N-Propionylpiperidine	1651	19.4737	0.3889	0.3077	363.189	48.466	3.89
13	N,N-Dimethylacetamide[b]	1657	35.7143	—	−0.0741	—	—	3.97
14	Tetramethylurea[b]	1638	21.4286	—	−0.0638	—	—	3.54

[a] Solvent: carbon disulfide. [b] The Hedestrand method was used, Ref. 14.

Table 2. Experimental dipole moments, μ_{DA}^{exp}, the corresponding total polarization, P_∞, molar refraction, R_D, the parameters α, β, γ and IR data of hydrogen-bonded complexes between phenol and various carbonyl compounds at 20°C. Solvent: carbon tetrachloride.

Proton acceptor	$\Delta v_{OH}/cm^{-1}$	K_{ass}/M^{-1}	α	β	γ	P_∞	R_D	μ_{DA}^{exp}/D
1	178	4.9	17.7778	0.1925	0.6895	514.617	61.223	4.67
2	182	9.8	11.1111	0.8700	0.1632	251.031	30.502	3.26
3	186	7.8	15.0000	0.1829	0.7273	501.272	83.669	4.48
4	245	16.8	17.5000	0.3704	0.2456	410.319	58.386	4.11
5	255	12.6	18.1818	0.6905	0.5926	487.296	65.661	4.50
6	265	20.9	40.0000	0.0714	0.1578	1070.569	50.801	7.00
7[a,b]	400	462.3	16.8421	—	1.6000	—	—	6.58
8	202	15.3	16.4444	0.1618	0.5238	809.433	114.372	5.78
9	240	34.8	12.6829	0.1026	1.1228	569.327	119.384	4.65
10	250	45.5	16.8428	0.5000	0.5384	629.094	122.795	5.26
11	283	78.6	30.0000	0.4250	0.2500	577.411	52.766	5.05
12	310	129.1	22.7273	0.3261	0.3200	664.168	73.937	5.33
13[b]	336	152.1	31.5789	—	0.3750	—	—	5.34
14[b]	340	164.0	25.4902	—	0.4545	—	—	5.15

[a] Solvent: carbon disulfide. [b] The method of Hedestrand was used, Ref. 14.

metrical compounds have two identical groups attached to the carbonyl carbon atom. This implies that the resultant of all bond moments in the molecule is directed along the $C=O$ axis, i.e., the molecular dipole moment, μ_A^{exp}, coincides with the $C=O$ bond moment direction. In unsymmetrical carbonyl compounds this is not the case. We feel therefore that there exists for symmetrical compounds a general linear correlation between the molecular dipole moment and the hydrogen bond strength (Δv_{OH}). This linear correlation has been demonstrated, albeit with measurement of only a few symmetrical carbonyl compounds, in Fig. 1 by drawing the regression line through the data points of diphenyl ketone (3), acetone (15),[7,8]

cyclohexanone (4) and tetramethylurea (14). The correlation is given by eqn. (2).

$$\mu_A^{exp} = 4.26 \times 10^{-3}\Delta v_{OH} + 2.05$$

$$n = 4 \qquad r = 0.95 \qquad (2)$$

Eqn. (1) exhibits a better correlation coefficient than eqn. (2): the slope is comparable, but the intercept differs. The difference in the intercept value of 0.44 D may be ascribed to the asymmetry of the molecules. Since we were unable to find a reasonable explanation for the deviating behaviour of the symmetrical compounds from the regression line correlating the unsymmetrical carbonyl com-
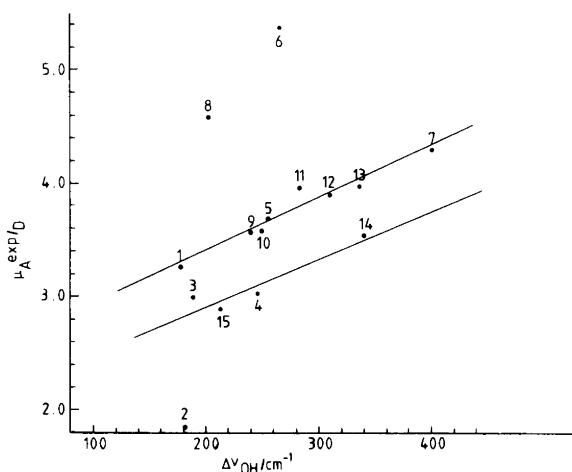
Fig. 1. Correlation between the dipole moments, μ_A^{exp}, of various carbonyl compounds and the stretching frequency shift, Δv_{OH}, of the phenol O–H bond upon complexation with carbonyl compounds [for numbering see Table 1, data for acetone (15) are from Refs. 7 and 10].

Table 3. The vector, $^*\mu_{CO}$, along the C=O axis calculated by using eqn. (1), the group moment, μ_s, and the angle, α, between μ_A^{exp} and $^*\mu_{CO}$.

Proton acceptor	$^*\mu_{CO}/D$	μ_s/D	$\alpha/°$
1	2.81	0.96	10.6
3	2.86	—	0
4	3.09	—	0
5	3.14	0.90	12.1
6	3.18	3.01	29.0
7	3.75	—	—
8	2.91	—	—
9	3.07	—	—
10	3.12	0.60	6.8
11	3.28	1.12	14.2
12	3.37	0.87	11.2
13	3.48	0.74	8.7
14	3.50	—	0

pounds, we have, as discussed later, related the unsymmetrical to the symmetrical compounds. Hence we can, by using eqn. (2), calculate the vector, $^*\mu_{CO}$, directed along the C=O axis [$\mu_A^{exp} = {}^*\mu_{CO}$ in eqn. (2)] for various carbonyl compounds with two different substituents. The results are tabulated in Table 3. Furthermore, by assuming the C–H and C–alkyl bond moments to be comparatively small and hence negligible, we were able, by means of the calculated $^*\mu_{CO}$ values, to determine the group moment, μ_s, and the angle, α, between μ_A^{exp} and $^*\mu_{CO}$. The calculations are shown for N,N-dimethylformamide in Fig. 2. The results are listed in Table 1.

As can be seen from Fig. 1, p-dimethylaminobenzaldehyde (6) is farthest away from the straight line. The large deviation is caused by the large group moment of the $(CH_3)_2NC_6H_4$ group ($\mu_s = 3.01$ D). This implies a

large angle between μ_A^{exp} and $^*\mu_{CO}$ ($\alpha = 29°$) which explain the observed deviation. Ethyl acetate (2) is the only compound that is situated below the straight line, i.e., the μ_A^{exp} value (1.83 D) is small in comparison with its proton accepting ability ($\Delta v_{OH} = 182$ cm^{-1}). The low μ_A^{exp} value may be explained by the fact that the group moment of the C_2H_5O group opposes the C=O bond moment direction, i.e., that the inductive withdrawing effect of an ethoxide group dominates over its resonance effect. Furthermore, it should be emphasized that there is no simple correlation between μ_A^{exp} and the carbonyl stretching frequency, v_{CO}.

μ_{DA}^{exp}, μ_{DA}^{calc} and $\Delta\mu$. As shown above there is a fairly good linear correlation between μ_A^{exp} and Δv_{OH} for carbonyl compounds with two identical groups attached to the carbonyl carbon atom. Similar linearity does not exist between the dipole moments, μ_{DA}^{exp}, of the hydrogen-bonded complexes of the corresponding carbonyl com-
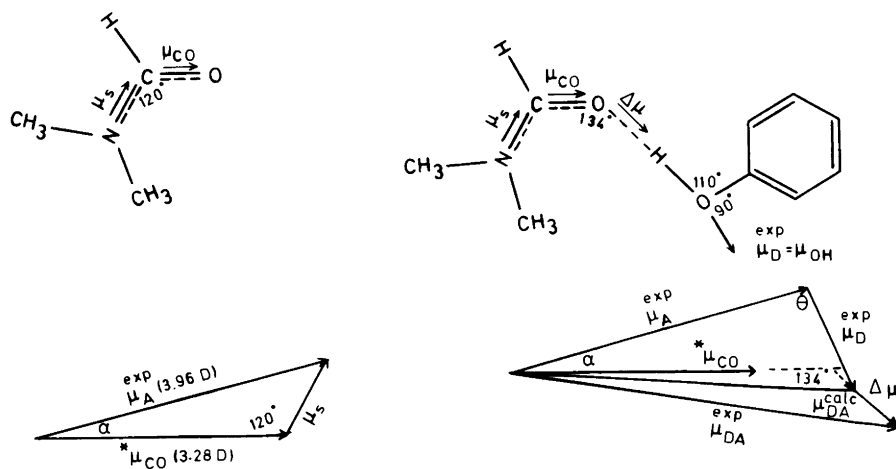

Fig. 2. The hydrogen-bonded complex between phenol and N,N-dimethylformamide showing the various angles used to calculate the group moment, μ_s, the dipole moment of the complex, μ_{DA}^{calc}, and the dipole increment, $\Delta\mu$.

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pounds and Δv_{OH}. The reason for this behaviour is that the enhancement of bond moments, on complexation with phenol, is much greater in tetramethylurea and diphenyl ketone than in cyclohexanone owing to the presence of N–C=O and C_6H_5–C=O groups.

To calculate the vectorial dipole moment, μ_{DA}^{calc}, of a hydrogen-bonded complex we need to know the direction of μ_D^{exp} and μ_A^{exp} in, respectively, the proton donor and acceptor molecule. The direction of μ_D^{exp} in phenol has previously[9] been estimated to be 90° in relation to the C_6H_5–O axis. The direction of μ_A^{exp} in the various carbonyl compounds, i.e., the angle between μ_A^{exp} and *μ_{CO} has been determined as outlined above (see Fig. 2). To find the direction in which μ_A^{exp} and μ_D^{exp} are acting in the complex we must know the geometrical structure of the various hydrogen-bonded complexes. As a model for such complexes, we have used the crystal structure of the stable hydrogen-bonded complex between pentafluorophenol and 4,4'-bis(dimethylamino)benzophenone.[10] The C=O $\cdots$ H angle was found to be 134° and the angle θ between μ_A^{exp} and μ_D^{exp} was then calculated by using the phenol/N,N-dimethylformamide complex (see Fig. 2, right). We assumed that the dimethylamino group is coplanar and *trans* to the phenol ring. The coplanarity is in agreement with what was found for the pentafluorophenol/4,4-bis(dimethylamino)benzophenone complex[10] and with CNDO/2 calculations on the phenol/acetonitrile complex.[4] The *trans* position was preferred because in this position the calculated dipole moment is less than that found experimentally and hence in accordance with the results found for the complexes phenol/tetramethylurea, phenol/diphenyl ketone and phenol/cyclohexanone in this work and also with previously reported results.[3–5] The μ_{DA}^{calc} and θ values for the various complexes are presented in Table 4.

If the formation of a hydrogen bond does not bring about displacement of electrons, the experimental dipole moments and the vectorial sum of the components should

be the same. In most cases,[3–5, 11–13] however, the experimental values exceed the vectorial sum. The difference can be expressed in terms of a dipole increment, $\Delta\mu$, defined by the vector equation

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

The calculation of $\Delta\mu$ for the system phenol/N,N-dimethylformamide is shown in Fig. 2. It has been assumed that the additional dipole moment, $\Delta\mu$, is directed along the hydrogen bond, from the proton acceptor towards proton donor,[1, 12, 13] i.e., we do not take into account the electronic redistribution in other parts of the hydrogen-bonded complex. The $\Delta\mu$ values are listed in Table 4. As can be seen the $\Delta\mu$ vary from 0.26 D for the system phenol/cyclohexanone to 2.43 D for phenol/ p-dimethylaminobenzaldehyde. We believe that the additional dipole moment in the cyclohexanone complex is mainly due to polarization along the hydrogen bond, whereas in the p-dimethylaminobenzaldehyde complex the polarization of the $(CH_3)_2NC_6H_4$ group is the main contributor to the $\Delta\mu$ value. The contribution from the phenol molecule is negligibly small,[1, 13] of the order of 0.1 D.

Table 4. Vectorial calculated dipole moments, μ_{DA}^{calc}, the additional dipole moments, $\Delta\mu$, and the angle, θ, between the direction in which μ_A^{exp} and μ_D^{exp} are acting in the hydrogen-bonded complex.

Proton acceptor	μ_{DA}^{calc}/D	$\Delta\mu/D$	$\theta/°$
1	3.87	0.94	103.37
3	3.81	0.73	114.00
4	3.87	0.26	114.00
5	4.25	0.31	101.88
6	5.45	2.43	85.02
10	4.50	0.82	107.16
11	4.45	0.76	99.83
12	4.45	1.07	102.81
13	4.58	0.96	105.28
14	4.35	0.89	114.00

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