DIPOLE MOMENT OF THE INTRAMOLECULAR HYDROGEN BOND. 2-NITROPHENOL AND ITS DERIVATIVES

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Dipole moments of substituted 2-nitrophenols *VIa*—*VIf* and substituted 2-nitroanisoles *VIIa* to *VIIf* were measured in benzene and dioxan solutions. Infrared spectroscopy confirmed that nitrophenols *VI* exist in either solvent and at different concentrations as non-associated molecules with an intramolecular hydrogen bond. Therefore, the difference between the experimental dipole moment and that calculated from group moments can be attributed to charge redistribution raised by the hydrogen bond. Only a minute part of it may be due to electron transfer through the ring (conjugation of the functional groups) as follows particularly from the comparison with nitroanisoles *VII*. Nevertheless, the charge transfer, expressed as the vector μ_H, amounts only 1·7 . . 10^{-30} Cm (at an angle of 138° to the H—O bond), *i.e.* several times less than observed previously in compounds with more powerful hydrogen acceptors. CNDO/2 and MNDO calculations agree fairly with the gross dipole moments of the compounds investigated but are unable to predict μ_H, not even as far as its direction is concerned.

The effect of an intramolecular hydrogen bond on the dipole moment of the molecule was investigated by us in preceding papers of this series[1-4] as well as by other authors[5-9]. The result may be represented as vector difference (μ_H) between the experimental dipole moment (μ_{exp}) and its anticipated value for a molecule in the actual conformation but without the hydrogen bond (μ_{calc}):

$$\mu_H = \mu_{exp} - \mu_{calc} . \tag{1}$$

The latter value is evidently hypothetical in character. In our previous work[1-4] it was calculated from standard bond moments[10] or from group contributions, alternatively quantum chemical calculations can be used[9]. We have investigated in particular three model systems $(I-III)$ in which the substituents on the aromatic ring served only to determine the direction of the experimental dipole moment. The following results were obtained[1,2,4]: *a)* The contribution of the intramolecular hydrogen bond is well outside the possible error. *b)* Its absolute value is rather different in the three compounds, increasing from 4·5 to 8·3. (All dipole moment values in this paper are given in the units 10^{-30} C m.) *c)* The direction of the vector is rather similar

in all the compounds (approximately $-150°$ with respect to the H—O bond), but it is unexpected in terms of common theories of the hydrogen bond[11].
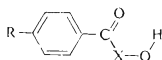

I; $X = CH_2$
II; $X = NH$
III; $X = O$

Further possible model systems[5,6,8,12] $IV - VI$ were considered[1] to be less suitable since the hydrogen acceptor and hydrogen donor are conjugated through the benzene nucleus, and formation of the hydrogen bond is accompanied by redistribution of the electron density in the aromatic ring. It follows that the conjugation might affect the dipole moment value even if it were no hydrogen bond, and the small values of μ_H obtained[5,8] may result from compensation of several factors. In the case of 2-nitrophenol (VIa) an attempt was made[8] to bisect the formal value of μ_H into the contribution of the hydrogen bond itself and that of the conjugation of the hydroxyl with the nitro group. However, this proceeding is open to criticism since it is based on minimal number of derivatives of which 2,6-dinitrophenol is evidently in a non-planar conformation and hence possesses an anomalous dipole moment (see Discussion). In an alternative approach[9] use was made only of quantum chemical calculations, and the calculated dipole moment of 2-nitrophenol was compared with the sum calculated for the two functional groups; the resulting difference vector should include the effects of hydrogen bond as well as of conjugation. Its direction was, however, opposite to that found on the experimental basis[5,8].

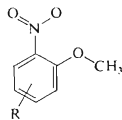

IV; $X = H$
V; $X = CH_3$

VI
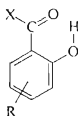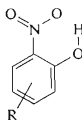
VII

a; $R = H$
b; $R = 4\text{-}CH_3$
c; $R = 5\text{-}CH_3$
d; $R = 4\text{-}NO_2$

e; $R = 5\text{-}NO_2$
f; $R = 6\text{-}NO_2$
g; $R = 4\text{-}Cl$
h; $R = 3\text{-}NO_2$

For these reasons we decided to investigate substituted 2-nitrophenols *VI* once more. By systematic comparison within this series we intended to eliminate the anomalous behaviour of some members (conjugation in 2,4-dinitrophenol, possible non-planarity of 2,6-dinitrophenol), by referring to the methyl ethers *VII* the effect of conjugation should be estimated separately. Although the dipole moments of some of the compounds had been already reported several times[5,8,12-14], we repeated most of the measurements in two solvents, benzene and dioxan, in order to have strictly comparable results. We also extended early IR studies[12,15], searching for possible associates and/or non-bonded forms at various concentrations. Finally, we attempted to support the experimental results by quantum chemical calculations using the CNDO/2 method (with experimental geometry) and MNDO method (with optimized geometry).

EXPERIMENTAL

Materials

All the compounds investigated are known. Substituted nitrophenols *VI* were commercial products (EGA), their methyl ethers *VII* were prepared by methylation with dimethyl sulphate. All samples were recrystallised at least twice from aqueous ethanol and dried several days on phosphorus pentoxide. The m.p. is agreed with literature data.

Physical Measurements

The electric dipole moments were determined at 25°C in benzene or dioxan solution using the method of Guggenheim–Smith[16]. Solutions were prepared at five concentrations within the range $3 \cdot 10^{-3} - 3 \cdot 10^{-2}$ mol l^{-1}. Their relative permittivities (ε_{12}) were measured on a heterodyne apparatus at the frequency of 1·2 MHz, the refractive indices (n_{12}) on an immersion refractometer Carl Zeiss, Jena. The plots of ε_{12} and n_{12}^2 against the weight fraction w_2 were linear within the whole concentration range (slopes α and γ, respectively). The dipole moment was calculated according to the equation:

$$\mu^2 = \frac{27kT\varepsilon_0 M_2}{N_A d_1} \left[\frac{\alpha}{(\varepsilon_1 + 2)^2} - \frac{\gamma}{(n_1^2 + 2)^2} \right]. \tag{2}$$

The physical constants of the solvents were: $d_1^{-1} = 1 \cdot 1448_0$, $\varepsilon_1 = 2 \cdot 2763$, $n_1 = 1 \cdot 49792$ for benzene, and $d_1^{-1} = 0 \cdot 9732_0$, $\varepsilon_1 = 2 \cdot 2090$, $n_1 = 1 \cdot 41929$ for dioxan. The results are listed in Table I. We included also measurements from the literature[5], concerning the compounds *VIg* and *VIIg*, since the remaining values given in the same paper agree reasonably with ours (compounds *VIa*, *VIb*, and *VIIa*). In the case of compound *VIh* the agreement with the literature[13] was less satisfactory but this compound is not important for further conclusions.

In previous papers[1-4] the dipole moments were measured by the method of Halverstadt–Kumler[17] instead of Guggenheim–Smith[16]. According to a recent statistical analysis[18] the two methods yield equal results except for some strongly coloured compounds. Therefore, we carried out a comparative measurement on *VId*, the most deeply coloured compound of our series. The agreement was very good (Table I). A further test was obtained by recalculating the dipole mo-

ments of *VIa*, *VId*, and *VIf*, measured by Richards and Walker[12] according to the Guggenheim–Smith formula[16]; the difference between both methods was always less than 0·1.

The infrared absorption spectra were scanned on a Perkin–Elmer model 580 spectrometer, calibration with NH_3 and H_2O vapour, cell thickness 0·01 cm (CCl_4 and $CHCl_3$ solutions at a concentration of 0·2 mol l^{-1}, or dioxan solutions) or 2 cm (CCl_4 solution at a concentration of 0·006 mol l^{-1}).

TABLE I

The results of dipole moment measurement

Compound	Solvent	α^a	γ^a	$\mu\,10^{-30}$ Cm	Literature data
VIa	Bz	8·00	0·070	10·6	10·7[12], 10·6[13,b]
	Diox	8·94	0·408	10·3	10·2[12], 9·8[13,b]
VIb	Bz	8·80	0·086	11·7	11·6[5]
	Diox	9·56	0·380	11·3	—
VIc	Bz	9·90	0·140	12·4	—
	Diox	10·80	0·260	12·0	—
VId	Bz	5·44	0·276	9·8^c	10·1[12], 10·7[13], 9·8[8]
	Diox	8·72	0·420	11·7	11·7[12], 12·0[13]
VIe	Bz	1·22	0·206	4·4	5·1[13], 4·4[8]
	Diox	1·97	0·460	4·9	5·1[13]
VIf	Bz	9·00	0·325	12·8	13·0[12], 12·9[13], 11·5[8]
	Diox	8·80	0·336	11·8	11·6[12], 11·5[13]
VIg	Bz	—	—	7·8^d	
VIh	Bz	—	—	16·9^e	
VIIa	Bz	19·0	0·104	16·6	16·1[5]
	Diox	20·4	0·289	16·6	—
VIIb	Bz	16·6	0·104	16·8	—
	Diox	19·2	0·320	16·8	—
VIIc	Bz	19·2	0·096	18·0	—
VIId	Bz	17·6	0·196	18·8	18·4[14]
	Diox	20·7	0·358	19·0	—
VIIe	Bz	1·08	0·185	4·2	—
	Diox	2·00	0·303	5·5	—
VIIf	Bz	6·67	0·068	11·6	11·7[14]
	Diox	8·00	0·270	11·7	—
VIIg	Bz	—	—	15·3^d	

^{a} Slopes of the plots ε_{12} vs w_2 and n_{12}^2 vs w_2, respectively; ^{b} Numerous further measurements are available[25]; ^{c} measured also by the method of Halverstadt–Kumler in benzene with the results: α 5·4, β −0·516, $\mu(5)$ 9·9, $\mu(15)$ 9·8; ^{d} ref.[5]; ^{e} ref.[13].

Calculations

The calculations within the framework of bond moment scheme were accomplished with the following standard values[10] (10^{-30} C m): $H\!-\!C_{al}$ 1, $H\!-\!C_{ar}$ 0, $C_{ar}\!-\!Cl$ 5·33, $C_{ar}\!-\!NO_2$ 13·33. The OH group moment of 5·15 at an angle of 90° to the O—C bond was taken according to the previous studies[5,8], the OCH_3 group moment 4·17 (74° to the O—C bond) was redetermined by us[4]; both values in essential agreement with a recent estimate[19]. The benzene nucleus was assumed hexagonal.

The CNDO/2 and MNDO calculations were carried out with the standard parametrization[20,21]. In MNDO the geometry of the H-bond was optimized. In CNDO/2 the X-ray geometry of 2-nitrophenol[22] and 2,6-dinitrophenol[23] was used except the length of the O—H bond[24], equal to 100 pm; the same geometry was used for 2-nitroanisole together with the ap conformation on the C—O bond. The calculated dipole moments and energies are given in Table II.

RESULTS AND DISCUSSION

Before discussing the dipole moments of nitrophenols $VIa-VIg$, we can state that these compounds exist in solution solely in the form of non-associated, intramolecularly hydrogen bonded molecules. This opinion was offered already on the basis of IR spectra of 2-nitrophenol[15] and 2,4-dinitrophenol[12], we are now able to confirm it more quantitatively in virtue of the concentration dependence. Within the concentration range 0·006—0·2 mol l^{-1} only one O—H stretching band was observable (for 2-nitrophenol at 3 242 cm^{-1} in tetrachloromethane, at 3 256 cm^{-1} in chloroform), neither intermolecular associates nor non-bonded hydroxyl were detected. Similar observations were made in dioxan at concentrations between 0·1 and 1 mol . l^{-1}, the absorption coefficient was exactly constant ($\bar{\nu}$ for 2-nitrophenol 3 285 cm^{-1}). We can thus confirm the finding[12,15] that the intramolecular hydrogen bond persists even in dioxan; nevertheless, its strength might be somewhat reduced as inferred[15] from the shift of the O—H band. Also the dipole moments in dioxan and benzene differ more than usual, and quite irregularly (Table I, in agreement with ref.[12,13]). A formal explanation assumed an additional moment raised by complex formation with dioxan[12].

For the reasons given we processed first the dipole moments values of $VIa-VIg$ in benzene. The direction of the vector can be determined from experimental values for the substituted and unsubstituted compound, and from the known moment[10] of the substituent. In geometrical terms it means to construct a triangle given its three sides; the procedure has to be repeated for each substituent. Fig. 1 reveals a good agreement for compounds VIb, VIc, VIe, and VIg. In the case of 2,4-dinitrophenol (VId) an enhanced moment of the substituent 4-NO_2 has to be applied accounting for its conjugation with the hydroxyl group. According to Fig. 1 a suitable value would be between 13·3 and 15 but the fit is not particularly sensitive to it. In any case the value of 16·1 as derived from 4-nitrophenol[8] would be too high; the conjugation

in 2,4-dinitrophenol is evidently weakened. The example proves that substituents strongly interacting with functional groups are not dependable for the purpose of vector analysis of dipole moments, preferable are those with weaker effects (4-Cl in *VIg*) or without conjugation (5-NO$_2$ in *VIe*). A still more striking example is 2,6-dinitrophenol *VIf*. Its deviation could be attributed to non-planar conformation of the 6-nitro group not engaged in the hydrogen bond, although the molecule is planar in the crystalline phase[23]. The fit is actually improved by introducing a reduced NO$_2$ group moment, *e.g.* 12·3 as in nitromesitylene[26] but a perfect coincidence would require a still lower value, approximately 10. Further corroboration may be seen in the dipole moment of 2,3-dinitrophenol[13] (*VIh*) which would require a similar group moment for 3-NO$_2$. In case of sterically hindered nitroanisoles, the moment of 10·3 was used for a non-coplanar nitro group[14]. Nevertheless, the anomalous behaviour of these compounds could have still other reasons which can be generally denoted as *ortho*-effect. Instead of searching for them, we preferred to disregard
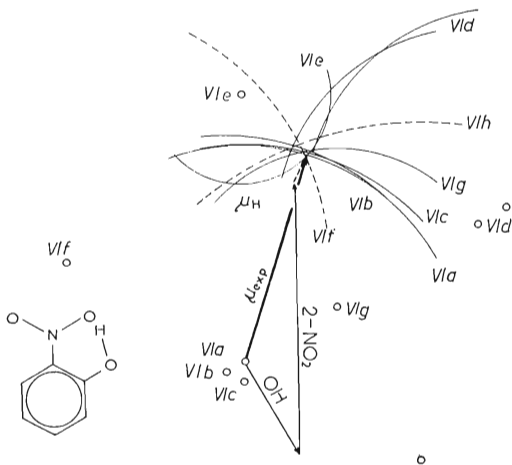

Fig. 1

Direction of the experimental dipole moment of 2-nitrophenol *VIa* (heavy arrow) as determined by comparison with the compounds *VIb*—*VIe* and *VIg*. When the group moments (light arrows) are substracted, the resulting vector (broken arrow) represents the contribution of the hydrogen bond μ_H.

the compounds in further discussion; in Fig. 1 the pertinent circles are traced by dashed lines and have not been accounted for when calculating the group moment. The remaining derivatives determine the dipole moment of 2-nitrophenol to 11·0 at an angle of 43° to the C—O bond.

When the dipole moments of *VI* in dioxan were treated in the same manner as above, the worst fit was again obtained for compounds *VId* and *VIf*. These compounds also exhibit the largest (and opposite) differences between the two solvent. If the reason is complex formation with dioxan[12], its effect is clearly not constant and manifests itself particularly with polynitro derivatives. When the mentioned compounds were omitted, the result was approximately the same as in benzene.
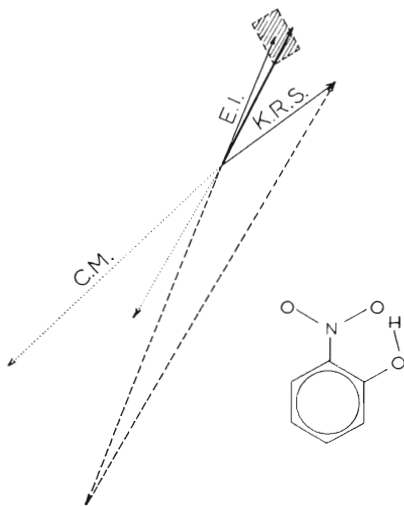

Fig. 2

Direction and value of the moment μ_H due to the hydrogen bond in 2-nitrophenol (*VIa*) according to various determinations: full arrows — experimental values (this paper; Eda and Ito[5] — the uncertainty represented by the hatched area; Koll, Ratajczak and Sobczyk[8]), dotted arrows — quantum chemical calculations (this paper; Catalán and Macias[9]), broken arrows — supposititious bisection[8] into contributions of conjugation and of the hydrogen bond itself.

In the next step of the analysis the gross dipole moment was resolved into components. Comparison with the vector sum of group moment as they are given in Experimental confirms firstly the finding[5,12,13] that the conformation on the C—O bond is *ap*; in fact this follows already from the existence of an intramolecular hydrogen bond. The same comparison also reveals — even in the *ap* conformation — a difference, which can be identified with the contribution of the hydrogen bond. The direction and absolute value of this residual fall within the range given in the pioneer work of Eda and Ito[5] whose result is only of lower accuracy and lower statistical weight, see Fig. 2 for comparison. There is, however, some disagreement with the subsequent result of Koll, Ratajczak and Sobczyk[8], based only on compounds *VIa* and *VId* with reference to 4-nitrophenol; the reason may be the unequal mesomeric interaction in these molecules as mentioned above. In addition, the interpretation of the latter authors[8] differs from ours when they try to bisect the gross effect into two further components: one expressing the conjugation of the *ortho*-standing nitro group with the hydroxyl group, the other representing the pure contribution of the hydrogen bond. This bisection refers to 2,6-dinitrophenol (*VIf*) and 2,4,6-trinitrophenol in order to derive the contribution of the 6-nitro group, and assumes further that the contribution of the 2-nitro group is equal. Just the last assumption is not correct in our opinion, and is the cause of the inacceptable result for the effect of conjugation: firstly its direction is unexpected, secondly and more important the absolute value of 4·9 is too large. We already suggested a possible explanation that the 6-nitro group is not coplanar with the benzene ring. In this case its conjugation effect is not transferable to the 2-nitro group. We conclude that the bisection[8] into the effect of conjugation and of the hydrogen bond is not realistic; according to the following results on 2-nitroanisoles the former is quite small if different from zero. Some misprints in the paper quoted[8] (2, 4, 6-trinitrophenol in Table V) are not relevant in the whole context.

Substituted anisoles were already used by Eda and Ito[5] as reference compounds on which the method of vector addition of bond moment was tested. The presumption was that the mesomeric interaction in anisole is similar as in phenol. In this paper we utilized substituted 2-nitroanisoles *VII* in an attempt to estimate the effect of conjugation between the nitro and hydroxyl groups (the mesomeric moment), assuming that this conjugation is nearly equal in 2-nitrophenol and 2-nitroanisole. The experimental dipole moments of compounds *VII* in benzene and in dioxan are virtually equal except for *VIIe*. Fig. 3 was constructed from the data in benzene, the procedure was the same as in Fig. 1. Again an enhanced group moment has to be applied for the nitro group in 2,4-dinitroanisole *VIId* and a reduced one in 2,6-dinitroanisole *VIIf*, for the latter compound a conformation with one coplanar and one perpendicular nitro group was already inferred[14]. The fit for the remaining compounds is reasonable. A comparison with the vector sum of group moments reveals unambiguously the *ap* conformation on the C—O bond $\left(CH_3 \text{ remote from } NO_2 \right)$ in agreement with the

results with 2,4-dinitroanisole[14], or 2-chloroanisole[19,27] and 2,4-dichloroanisole[19]. On the other hand, the effect of conjugation is rather small, just approaching the limit of accuracy of the whole procedure. If the charge separation were similar as in 4-nitrophenol, the mesometric moment would be approximately one half in virtue of the shorter distance between the functional groups in the *ortho* position. The value found is still one half of this and in addition its direction is almost opposite. Hence we do not hold this minute value to be warranted, and prefer leaving our value of μ_H uncorrected. If the correction were applied, μ_H would be somewhat reduced. Anyhow this correction would be by one order less than recommended by Koll, Ratajczak and Sobczyk[8], in addition to its opposite direction (Fig. 2).

We thus believe that the contribution of the hydrogen bond to the dipole moment of 2-nitrophenol is real, although the value found is less than for any other class of compounds with an O—H⋯O bond[1,2,4−6]. In 2-methyl-2-nitropropanol an intra-molecular hydrogen bond was established[28] but the uncertain orientation of the dipole moment did not allow to evaluate μ_H. In 2-nitro-1-naphthol the effect was stated only qualitatively[29] for the same reason. In the following we have attempted to obtain some estimate of μ_H by quantum chemical calculations.
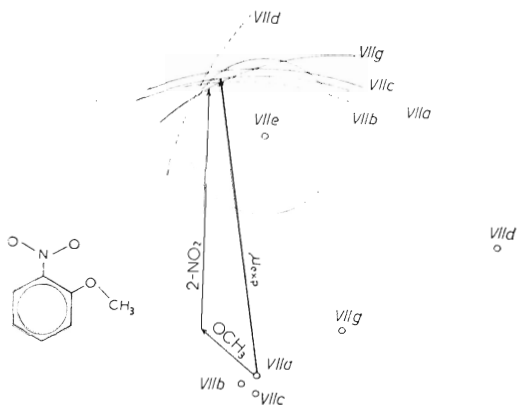

Fig. 3

Analysis of the experimental dipole moment of 2-nitroanisole in the same way as in Fig. 1.

The results with the CNDO/2 method and with experimental geometry were inasmuch satisfying that they unambiguously preferred the hydrogen bonded conformation (difference approximately 40 kJ mol^{-1}, see Table II). However, the calculated dipole moments were all somewhat high even when their direction was reasonably predicted. In Table II these results are compared to those calculated from bond moments with the correction term μ_H, in this comparison the latter figures represent nothing more than smoothed out experimental values. The hydrogen bond itself is not responsible for the discrepancy since the results with 2-nitroanisoles *VII* were essentially the same. Even the method applied is not critical. Our calculation with MNDO and with optimized geometry showed that this method is not superior in this case. While the hydrogen bond was evidenced from the optimized H···O distance (216 pm), the pertinent bond order was only 0·05 and the calculated dipole moments were still higher than from CNDO/2. Previous results on 2-nitrophenol with INDO or PPP methods were also similar in character[9,30]. Our ultimate goal was to calculate μ_H. Within the framework of semiempirical methods we have not seen any possibility how to obtain the dipole moment of a hypothetical form without the hydrogen bond but in the conformation of the real, hydrogen bonded molecule. Hence we adopted a combined empirical procedure: the dipole moment of the *ap* conformation (H remote

TABLE II

The values of calculated dipole moments

Compound	Bond moment, scheme[a]		CNDO/2		
	$\mu\ 10^{-30}$ Cm	θ^b	$\mu\ 10^{-30}$ Cm	θ^b	E^c kJ . mol^{-1}
VIa	11·0	43°	12·5^d	36°^{a}	—
VIb	11·7	39′	13·2	32°	−41·73
VIc	11·9	45°	13·9	39°	−42·57
VId	10·1	143°	11·0	122°	−41·71
VIe	4·3	270°	6·6	332°	−40·29
VIf	13·0	354°	17·1	321°	—
VIIa	16·5	71°	21·6	65°	—
VIIb	17·2	67°	22·1	62°	—
VIIc	17·6	70	23·2	64°	—
VIId	18·4	121°	20·9	112°	—
VIIe	4·2	111°	5·9	70°	—

[a] The contribution μ_H of the hydrogen bond is included; [b] angle between the C—O bond and the dipole moment; [c] energy difference between the *sp* and *ap* conformations on the O—H bond; [d] MNDO method gave μ 14·1 and θ 60°.

from NO_2) was calculated first and the rotation around the C—O bond was formally carried out by adding vectorially two H—O bond moments in proper directions. The result is visualized in Fig. 2 which reveals that the vector obtained is almost opposite to that experimentally found. Remarkably enough, our calculated μ_H agrees qualitatively with that derived from the work of Catalán and Macías[9] and based on a different procedure: from the calculated dipole moment of 2-nitrophenol (INDO method) those of phenol and nitrobenzene were vectorially substracted. The principal disagreement with experiment may be due to combined inaccuracy of the semiempirical quantum methods on the one hand and of the bond moment scheme on the other, the experimental error itself being immaterial. Nevertheless, we have already pointed out that the values of μ_H found for compounds *I* and *II* are at variance with the current theories[11,31] of the hydrogen bond; these values are much higher and more reliable than in the case of our compounds *VI*.

We conclude that the charge transfer connected with the hydrogen bond cannot yet be interpreted theoretically in simple terms. On the other hand we are able to review the results obtained and seek for possible regularities. Let us restrict to hydro-
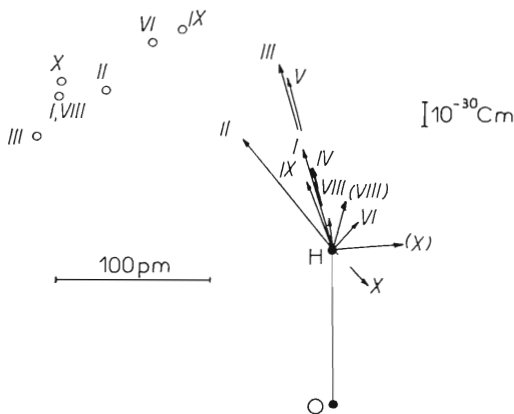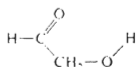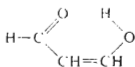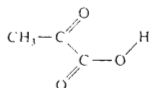

FIG. 4

Dipole moments μ_H raised by the intramolecular hydrogen bond O—H···O in compounds *I—VI*, *VIII—X* and their position with respect to the H—O bond. The circles denote supposed position of the acceptor oxygen atom.

VIII   IX   X

gen bonds of the O—H···O type. In addition to previous findings of Eda and and Ito[5,6] and ours[1,2,4] which all were obtained essentially in the same way as in the present paper, we can derive some further values from gas phase measurements[32-34] (compounds $VIII - X$). The latter results might be somewhat less dependable although the experimental dipole moments in the gas phase are precise. The reason is that the bond moments in use[10] have been derived from solution measurements and may involve some solvent effects. All the results available are summarized in Fig. 4. Before drawing some conclusions, we must take into account that a kind of systematic error is not completely excluded, *e.g.* in a bond moment value. Nevertheless, some regularities emerge. The hydrogen bonds with a carbonyl oxygen as acceptor give rise to rather large dipoles, the direction of the vector being almost uniform. One can assume that the charge separation depends on the strength of the hydrogen bond and hence on the distance from hydrogen to the acceptor atom. These distances are shown in Fig. 4 and give some support for the hypothesis. On the other hand the size of the chelate ring seems to be less relevant: in five- and six-membered rings the dipoles μ_H are of comparable magnitude. Compared to the carbonyl group the nitro group seems to be a less efficient acceptor; the extra dipole moment produced is rather near to the possible error limit. This finding contrasts with the strength of the hydrogen bond assumed according to quantum chemical calculations and to the O—H frequency shift.

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