Electric Dipole Moments and Molecular Conformations of Acetophenone Oximes and Benzaldoximes

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The electric dipole moments of 30 oximes have been measured in benzene or 1,4-dioxan solution at 25·0 °C and the results interpreted in terms of molecular conformations. The hydroxyimino-group has either conformation (I) or (I′) in every molecule studied.

ANALYSIS of the electric dipole moment of a molecule provides one method for obtaining information about the conformation in solution. Results are available for acetophenone oximes and for benzaldoximes but it seems desirable to extend these to a wider range of compounds including some with substituents in the phenyl ring.

EXPERIMENTAL

The electric dipole moments were determined as described previously.[1] The total polarisation (P_T), molar refractivity (R_D), and dipole moments (μ) are recorded in Table 1 where the other parameters are the limiting slopes of the electric permittivities (α), specific volumes (β), and refractive indices squared (γ) against weight fraction of the solute. The measurements were made in benzene solution except for five compounds whose solubility in benzene was too low for the results to be reliable and 1,4-dioxan was employed instead.

Preparation and Purification of Compounds.—The purification of the solvents has been described.[2] Each oxime was prepared by a standard method [3] and recrystallised from one or two solvents to a constant m.p. which was in agreement with literature values; *syn*-benzaldoxime was purified by fractionation, b.p. 92·5 °C at 1·4 mmHg. The final purification of each compound was performed immediately before its solutions were made and their electric permittivities measured.

DISCUSSION

In order to analyse electric dipole moments in terms of the structure and conformations of molecules a knowledge of relevant angles and bond or group moments is required. The latter are frequently available [4] but those for the C=N and N–O bond moments in solution are not easily obtained and their literature values [5] are not particularly reliable. In oximes the situation is complicated by an interaction between these two bond moments; conjugation between the three atoms results in some delocalisation of lone pair electrons on the oxygen atom into the C=N bond. The results for the parent and *para*-substituted compounds studied are best satisfied by taking the C=N bond moment as 1·80 D and that of the N–O bond in conjunction with it as —0·20 D, relative to a zero value for the C–H bond. The group moment from the phenyl ring to the C(=N) bond has been taken as 0·50 D and the other values from a compilation of electric bond and group moments.[4]

The bond angles employed in these calculations are the *X*-ray values reported for *syn*- and *anti*-*p*-chlorobenzaldoximes: [6] *syn* $\mathrm{Ph{-}\hat{C}{=}N}$ 123°, $\mathrm{C{=}\hat{N}{-}O}$ 112°; *anti* $\mathrm{Ph{-}\hat{C}{=}N}$ 130°, $\mathrm{C{=}\hat{N}{-}O}$ 118° (the N–O bond is 19° out of the molecular plane).

The parent molecules have low dielectric relaxation times measured [7] at 9·82 GHz in benzene solution at 25·0 °C; acetophenone oxime, 5·4 ps; *syn*-benzaldoxime, 9·0 ps; *anti*-benzaldoxime, 6·2 ps. These results indicate that relaxation occurs not only by rotational diffusion but also by an internal mechanism such as the libration or rotation of the hydroxy or phenyl group. Further, over an 80° temperature range down to —40 °C, the ^{1}H n.m.r. spectra of *anti*-benzaldoxime and of its *p*-chloro-derivative indicated that there was no distinction between the two *ortho*-protons thus implying rotation about the Ph–C bond. In acetophenone oxime conformation (I) (Figure) is sterically more likely than (II) and might be stabilised by a favourable interaction between the oxygen atom and a methyl hydrogen atom; this could also be one reason why the *anti*-isomers of acetophenone oxime have not been isolated. The situation in *syn*-benzaldoximes is similar except that the possible stabilising effect in conformation (I) would not be present. Conformation (II′) for the *anti*-isomers is sterically impossible; even in (I′) an interaction between the oxygen atom and phenyl hydrogen atom forces the former 19° out of the molecular plane in the crystalline phase.

Table 2 lists the dipole moments computed for the various molecular conformations. For each series it is evident that the molecules exist primarily, if not entirely, in conformations (I) or (I′).

Acetophenone and Related Oximes.—The replacement of the phenyl ring by a saturated hydrocarbon or by a hydrogen atom (acetoxime) gives a marginal increase in the experimental dipole moment but with the two naphthyl compounds the values would seem to be influenced slightly by altered mesomeric moments. A

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[1] C. W. N. Cumper, A. A. Foxton, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 1964, 430.

[2] C. W. N. Cumper and A. Singleton, *J. Chem. Soc.* (*B*), 1967, 1096.

[3] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, Green, London, 1956, 3rd edn.; O. L. Brady, A. N. Cosson, and A. J. Roper, *J. Chem. Soc.*, 1925, **127**, 2427; C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, 1955, **20**, 1491.

[4] C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

[5] C. P. Smyth, *J. Amer. Chem. Soc.*, 1938, **60**, 183.

[6] B. Jerslev, *Nature*, 1957, **180**, 1410.

[7] G. A. Balogun and C. W. N. Cumper, unpublished results.

TABLE 1

Polarisation data and dipole moments (μ) of oximes in benzene or 1,4-dioxan solution at 25·0 °C

Compound	α	β	γ	P_T/cm³	R_D/cm³	μ/D	Lit. μ/D	
Acetoxime	$0{\cdot}71_5$	−0·060	−0·245	33·59	19·81	0·82	0·88 [a]	1·06 [b]
Cyclohexanone oxime	$0{\cdot}75_6$	−0·177	0·044	42·02	28·37	0·82	0·83 [b]	
Cyclohexyl methyl ketoxime	$0{\cdot}41_6$	−0·133	−0·042	53·69	40·68	0·80		
Methyl α-naphthyl ketoxime	$0{\cdot}75_6$	−0·322	0·312	71·75	59·65	0·77		
Methyl β-naphthyl ketoxime	$0{\cdot}64_3$	−0·310	0·401	68·44	59·46	0·66		
Acetophenone oxime	$0{\cdot}67_5$	−0·254	0·296	53·26	42·87	0·71		
p-Methyl-	$0{\cdot}71_2$	−0·170	0·256	62·37	49·88	0·81		
p-Chloro-	$1{\cdot}21_2$	−0·369	0·225	74·65	43·94	1·22		
p-Bromo-	$1{\cdot}02_1$	−0·472	0·282	84·03	53·70	1·22		
p-Nitro-	$8{\cdot}80_0$	−0·353		535·8	(49·2)	4·87		
p-Hydroxy-	$3{\cdot}80_5$	−0·161	0·543	139·8	45·75	2·15 *		
p-Methoxy-	$1{\cdot}75_8$	−0·338	0·248	94·30	46·86	1·52		
syn-Benzaldoxime	$0{\cdot}95_5$	−0·251	0·300	53·99	38·63	0·87	0·87 [c]	0·99 [b]
p-Methyl-	$1{\cdot}10_9$	−0·227	0·227	65·13	42·19	1·06		
p-Isopropyl-	$1{\cdot}04_0$	−0·171	0·167	79·70	51·74	1·17		
p-Chloro-	$1{\cdot}13_2$	−0·357	0·556	69·92	52·39	0·92		
p-Nitro-	$9{\cdot}49_5$	−0·409	0·343	476·5	44·73	4·60		
p-Methoxy-	$2{\cdot}38_6$	−0·297	0·303	106·1	46·30	1·71		
o-Chloro-	$2{\cdot}06_0$	−0·301	0·214	99·39	44·83	1·63		
o-Nitro-	$10{\cdot}0_5$	−0·405	0·139	320·7	36·50	3·73		
o-Hydroxy-	$1{\cdot}48_6$	−0·349	0·266	70·31	38·64	1·25		
m-Nitro-	$9{\cdot}47_1$	−0·413	0·270	303·9	39·90	3·60		
anti-Benzaldoxime	$0{\cdot}94_5$	−0·241	0·203	54·43	36·75	0·91	0·71 [b]	
p-Methyl-	$1{\cdot}20_2$	−0·229	0·277	67·85	43·39	1·09		
p-Isopropyl	$1{\cdot}00_4$	0·201	0·183	96·88	50·00	1·52		
p-Chloro-	$2{\cdot}50_0$	−0·211	0·504	92·04	44·02	1·53 *		
p-Nitro-	$12{\cdot}4_8$	−0·245	0·468	386·4	44·81	4·09 *		
p-Methoxy-	$2{\cdot}93_4$	−0·220	0·504	113·3	42·46	1·86 *		
o-Chloro-	$2{\cdot}13_8$	−0·368	0·245	99·43	42·69	1·67		
m-Nitro-	$12{\cdot}1_9$	−0·242	0·475	364·2	44·54	3·95 *		

* Measured in 1,4-dioxan solution.

[a] R. Raman and S. Soundararajan, *Proc. Indian Acad. Sci. A*, 1958, **47**, 357. [b] R. J. W. Le Fèvre, R. K. Perrins, and K. D. Steel, *Austral. J. Chem.*, 1966, **19**, 1769. [c] J. Brassin and H. Lumbroso, *Bull. Soc. chim. France*, 1961, 492.

TABLE 2

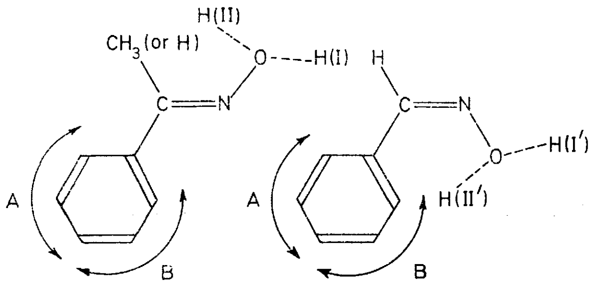
Calculated dipole moments of oximes corresponding to the conformations in the Figure

	Dipole moment (μ/D)				Experimental value
	(IA)	(IB)	(IIA)	(IIB)	
Acetoxime	0·80		3·11		0·82
Cyclohexanone oxime					0·82
Cyclohexyl methyl ketoxime	0·80		3·11		0·80
Methyl α-naphthyl ketoxime	0·71		2·94		0·77
Methyl β-naphthyl ketoxime	0·71		2·94		0·66
Acetophenone oxime	0·71		2·94		0·71
p-Methyl-	1·02		3·06		0·81
p-Chloro-	1·17		2·94		1·22
p-Bromo-	1·14		2·93		1·22
p-Nitro-	3·51		4·28		4·87
p-Hydroxy-	1·95	1·05	4·25	1·49	2·15 *
p-Methoxy-	1·90	1·00	4·20	1·56	1·52
syn-Benzaldoxime	0·70		2·72		0·87
p-Methyl-	1·06		2·85		1·06
p-Isopropyl-	1·12		2·89		1·17
p-Chloro-	0·95		2·65		0·92
p-Nitro-	3·35		4·00		4·60
p-Methoxy-	1·61	1·17	3·39	1·51	1·71
o-Chloro-	1·76	2·15	2·02	4·30	1·63
o-Nitro-	4·09	4·55	2·96	6·73	3·73
o-Hydroxy-	2·16 [a]	2·05	3·57	3·57	1·25
	1·10 [b]	1·60	1·28	3·94	
m-Nitro-	3·49	4·01	1·44	6·19	3·60
anti-Benzaldoxime	0·86		3·48		0·91
p-Methyl-	1·16		3·72		1·09
p-Isopropyl-	1·21		3·78		1·52
p-Chloro-	1·15		2·40		1·53
p-Nitro-	3·44		1·52		4·09 *
p-Methoxy-	1·92	1·12	3·55	2·40	1·86 *
o-Chloro-	1·89	2·29	3·97	4·78	1·67
m-Nitro-	3·45	4·02	2·50	4·91	3·95 *

* Measured in 1,4-dioxan solution.

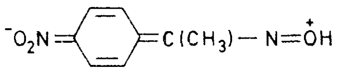
[a] With the O–H group directed away from the C=N bond. [b] With the O–H group directed towards the C=N bond.

small interaction moment in *p*-chloro- and bromoacetophenone oximes would explain[8] why their predicted values are slightly low. The *p*-hydroxy- and -methoxy-groups can undoubtedly rotate about the Ph–O bond and results for these oximes are consistent with them spending roughly equal times in the two stable planar conformations (IA) and (IB) with the O–H or O–CH_3 on either side of the phenyl ring. (The experimental result for *p*-hydroxyacetophenone oxime would be expected to be *ca.* 0·3—0·4 D high[2,9] since the measurements were made in 1,4-dioxan solution.)



The *syn*-conformations of acetophenone oximes and the *syn*- and *anti*- conformations of benzaldoximes. The letters A and B differentiate the two sides of the phenyl ring in substituted compounds

One apparently inconsistent result is that for *p*-nitroacetophenone oxime; if it also exists in conformation (I) the predicted dipole moment is 1·36 D less than the experimental value. Nitro-compounds frequently possess considerable interaction moments and a substantial increment might be expected in this case from the canonical form (Z) which would increase the dipole moment calculated for conformation (I) but would have a smaller resultant effect on (II). That some electronic effect is present in this molecule is confirmed by the ^1H n.m.r. resonance of the methyl group being shifted by 0·07 p.p.m. upfield compared with the other acetophenone oximes studied.



(Z)

Benzaldoximes.—The *syn*-isomers are structurally very similar to the acetophenone oximes but in the *anti*-isomer conformation (II′) is sterically impossible and even in (I′) the molecules cannot be planar.[6]

The calculated and experimental dipole moments (Table 2) for the benzaldoximes and their derivatives with substituents in the *para*-position are in reasonable agreement bearing in mind that in four cases the experimental results are 0·3—0·5 D high because measurements had to be made in 1,4-dioxan solution. The low solubility of some of the *anti*-benzaldoximes in benzene solution is presumably due to their tending to polymerise; the *anti*-isomer of *p*-chlorobenzaldoximes is polymeric in the solid state whereas the *syn*-form is dimeric.[6]

It would seem that a *p*-methoxy-substituent in the *anti*-isomer has no great preference for either of the two conformations (IA or B) in which it is coplanar with the phenyl ring but in the *syn*-isomer there appears to be a preference for (IA). The experimental result for the *anti*-isomer of *p*-isopropylbenzaldoxime exceeds the calculated value, as was also the case for the corresponding acetophenone oxime.

The *para*-nitro-derivative of *syn*-benzaldoxime is similar to the corresponding acetophenone oxime but the interaction moment in the *anti*-isomer would appear to be small; this could be associated with the non-planarity of the molecule and is supported by a 4 nm reduction in the wavelength maximum of its P absorption band. When the nitro-group is in the *meta*-position there should not be a significant interaction moment and the dipole moment is consistent with it being on either side A or side B (Figure), of the phenyl ring. There is n.m.r. evidence that conformation (IB) predominates. The ^1H chemical shifts, measured relative to tetramethylsilane in $(CD_3)_2SO$ solution, of the aromatic protons are shown in Table 3. Comparing the two benzaldoximes the chemical shifts of 5-H are nearly the same whereas those for 4-, 6-, and 2-H differ progressively in this order, that for 2-H being particularly great. With the (IA) conformation the greatest difference would be expected for 6-H, since this atom would be affected by its proximity to the oxygen atom in the *anti*-isomer and to the lone-pair electrons of the nitrogen atom in the *syn*-isomer. With (IB), however, 2-H should display the greatest difference which is in agreement with the experimental results.

TABLE 3

^1H Chemical shifts [δ (p.p.m.)] in *m*-nitrobenzaldoximes

	Benzaldoxime		
Proton	*syn*	*anti*	Difference
2-H	8·40	8·89	−0·49
4-H	8·21	8·29	−0·08
5-H	7·70	7·72	−0·02
6-H	8·05	8·21	−0·16

When a chlorine atom or a nitro-group is substituted in the *ortho*-position of the phenyl ring then conformation A would be stabilised by favourable Cl · · · H or NO_2 · · · H interactions, whereas B would be destabilised by the interactions of these substituents with the hydroxyimino nitrogen atom. This is supported by the dipole moment results. The *H*–C=N proton resonance in the n.m.r. spectra of the four *ortho*-substituted benzaldoximes was at a lower frequency than in the other benzaldoximes which is also consistent with (IA) being the predominant conformation.

The *ortho*-hydroxy-substituent in *syn*-benzaldoxime may have many conformations and it is difficult to deduce from dipole moment evidence alone which predominates. Conformation (IB) with the hydroxy

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[8] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955, p. 209.

[9] C. W. N. Cumper and J. W. M. Wood, *J. Chem. Soc.* (*B*), **1971**, 1811; C. W. N. Cumper and A. Singleton, *ibid.*, **1967**, 1100; **1968**, 645.

hydrogen atom directed towards the nitrogen atom ($\mu_{calc.}$ 1·60 D) would be stabilised by an O–H · · · N interaction, which in turn would modify its dipole moment, and conformation (IA) in which this hydrogen atom is directed away from the C=N bond ($\mu_{calc.}$ 2·16 D) might be stabilised by a weak H–O · · · H–C=N interaction. On the other hand, the remaining two conformations with the oxime in structure (I) would be destabilised by unfavourable interactions.

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