312. *A Comparison of the Dipole Moments of the Isomeric Benzaldoximes and Furfuraldoximes.*

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The dipole moments of monomeric oximes may be calculated from measurements on dilute solutions. Acetoxime, the benzaldoximes, and the furfuraldoximes are taken as examples. Results are compatible with present-day views of the structural relationships of these isomers. Some qualitative high-frequency conductivity comparisons in water are also recorded which parallel known behaviour in liquid sulphur dioxide. Data for benzaldehyde, *o*-nitrobenzaldehyde, and furfuraldehyde are also included.

Hassel and Naeshagen (*Z. physikal. Chem.*, 1924, *B*, **4**, 217) attempted measurements of the dipole moment of benzaldoxime in benzene solution, but refrained from evaluating their results because of the known association of the solute in this solvent (Beckmann, *Ber.*, 1888, **21**, 767). Later, Sutton and Taylor (*J.*, 1931, 2190; 1933, 63), when selecting compounds with which to provide a physical demonstration of the absolute configuration of isomeric oximes, chose to work with the related *N*-ethers, whose unpolymerised condition was definitely established.

However, an inspection of Beckmann's data indicates that, within the concentration ranges usual for dipole-moment determinations, several oximes are monomeric or nearly so; hence, an approach similar to that made with the sulphonamides or the fatty acids (Le Fèvre and Vine, *J.*, 1938, 1790, 1795) should easily reveal the polarity of the single molecules.

Appropriate measurements have therefore been made with the substances named in the title, together with acetoxime, in benzene or chloroform (see Experimental). Evidence of dissociation with increasing dilution is seen by a non-rectilinearity of either dielectric constant or density with composition. When the formulæ $\varepsilon_{12} = \varepsilon_2(1 + \alpha w_1)$ and $d_{12} = d_2(1 + \beta w_1)$ are used (see *J.*, 1937, 1805, for explanation), $\alpha\varepsilon_2$ and βd_2 are not constant but smoothly related to w_1, so that values of α and β for $w_1 = 0$ are available by extrapolation, and from them the moments of the monomeric oximes, *viz.* (in D.) :

	M. p.	In C_6H_6.	In $CHCl_3$.
α-Benzaldoxime	35°	1·2	0·7
β- ,,	128	$1{\cdot}5_5$	$1{\cdot}2_5$
α-Furfuraldoxime	75	1·2	$0{\cdot}8_2$
β- ,,	92	1·9	—
Acetoxime	61	0·9	—

Vectorial analysis is made difficult by possible intramolecular rotation of the angular polar hydroxyl and/or furyl groups. The cases will be discussed separately. To remove ambiguity, we use the prefix *cis*- or *trans*- with respect to the aldoximino- H and HO groups.

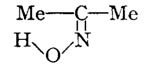
Benzaldoximes.—Maximum and minimum resultant moments will occur when the O–H bond lies in the plane containing the C=N and N–O components. They have been calculated from the following link moments and bond angles : H–C, 0·4; N–O, 0·3; C=N, 2·0; H–O, 1·6; Ph–C–H, 110°; C=N–O, 121°; N–O–H, 105°. The last two are, respectively, the N=N–Ph angle in *trans*-azobenzene (Robertson and Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398) and the H–O–H angle in water (Darling and Dennison, *Physical Rev.*, 1940, **57**, 128). The N–O link moment has been deduced from Sutton and Taylor's second paper (see above). The phenyl nucleus is assumed to have a regular hexagonal form. Accordingly, we estimate that the *trans*-oxime may have μ = 3·6—1·4 D., and its *cis*-counterpart μ = 3·7—1·0 D.

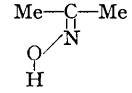
The moments as measured are seen to be of the order of the respective minima. The implication is therefore that the hydroxyl group is not freely rotating. In one configuration, at least, this may be ascribed to steric hindrance, in both perhaps to the mutual potential energy–azimuthal angle relation between the two larger moments, *viz.*, $\mu_{C=N}$ and μ_{HO}.

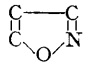
As to the former cause, the annexed figures *a*, *b*, *c*, and *d* correspond to the extreme structures. They show the sections which the constituent atoms would make in the plane of the paper during " free rotation." Being drawn from the data of Pauling and Huggins (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293), they can be regarded as minimum estimates. Superimposed on one version of the *trans*-form is the dotted outline of the " Wirkungs-radien " of the atoms immediately concerned (Stuart, *Z. physikal. Chem.*, 1935, *B*, **27**, 353). A measure of interference with the " free rotation " of the hydroxyl group can therefore be predicted for this isomeride. As a result, its hydrogen atom is likely to inhabit regions more remote from the phenyl. In addition to this cause, however, it is possible that the O–H disposition is strongly affected in all oximes by dipolar repulsions. For a rough approximation we have considered only $\mu_{C=N}$ and μ_{HO}. Using the various dimensions given above in conjunction with enlarged drawings of the two limiting hydroxyl positions in the C=N–OH unit, and making appropriate substitutions in the equation for the potential energy due to the mutual arrangement of two dipoles [*i.e.*, $U = (\cos\chi - 3\cos\alpha_1\cos\alpha_2)\mu_1\mu_2/r^3$; cf. Jeans, " Electricity and Magnetism," Cambridge University Press, 1920, 354], the energy difference calculable is $0{\cdot}36 \times 10^{-12}$ c.g.s unit (*i.e.*, *ca.* 8*kT* at ordinary temperatures) in favour of hydroxyl dispositions such as in *b* and *d*. We therefore suggest that configuration allotment should be made on the basis of the estimated least values, *i.e.*, that in the oximes, m. p. 35° and 128°, the H and HO groups are *cis*- and *trans*-, respectively.

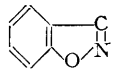
Furfuraldoximes.—*A priori* calculation of resultants requires the resolution of one fixed vector with two others, each rotating around its own axes. A general solution for this type of problem appears to be cumbersome; that of Fuchs (*Z. physikal. Chem.*, 1931, *B*, **14**, 339) is a special case. We have therefore again had recourse to scale drawings ; taking μ = 0·7 D. (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230) symmetrically through the oxygen atom as the appropriate vector for the furan nucleus (regarded as a regular pentagon), and other values as above, maxima and minima are calculable as 3·7 and 0·3 D. for the *cis*- and 3·4 and 1·3 for the *trans*-furfuraldoxime, respectively. By parallel arguments to those used above, the observed moments should follow the minima expected, *i.e.*, the oxime, m. p. 75°, is the *cis*-compound, and that of m. p. 92° the *trans*-.

Acetoxime.—Comparison of the moment found (*ca.* 1 D.) with those expected on the basis of the values used above again suggests that the configuration conforms much more to (II) than to (I).

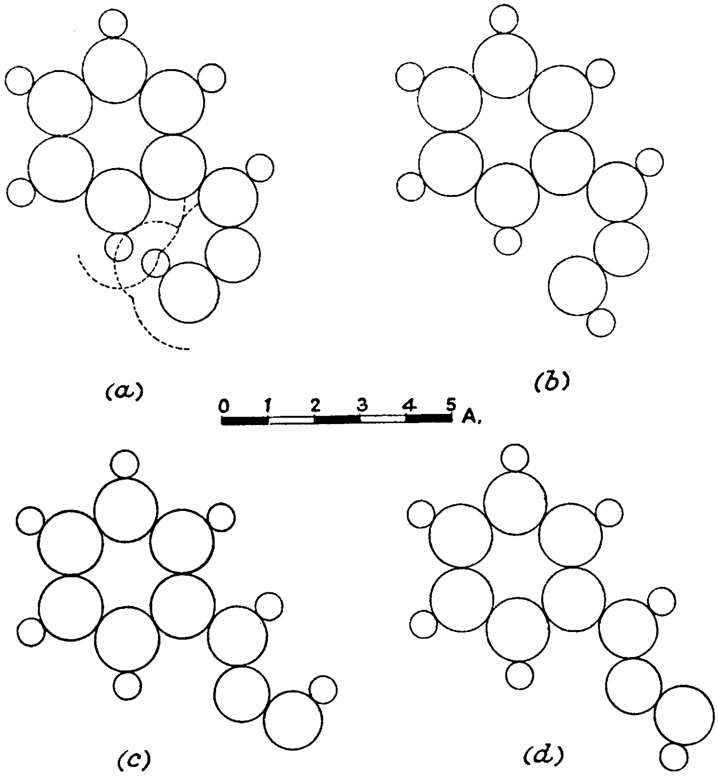

(I; μ = 3·0 D.)


(II; μ = 0·7 D.)


(III; μ = 2·8 D.)


(IV; μ = 3·0 D.)

General support for our discussion is also seen in the moments reported for *iso*oxazole (III) and indoxazen (IV) by Jensen and Friediger (*Kgl. Danske Videnskab. Selskab.*, 1943, **20**, No. 20), since it is reasonable (μ_{C-O} being less than μ_{H-O}) that the polarity of (III) (2·8) should approach but fall slightly short of that of (I) (3·0, estimated), and similarly (IV) (3·0) that of Fig. *a* (3·6, estimated). Hassel and Naeshagen (*loc. cit.*) found the moment of the *O*-methyl ether of α-benzaldoxime to be *ca.* 0·9 D., a fact which likewise falls into line with our present conclusions.



(*a*) (*b*) (*c*) (*d*)

Further, it is helpful to note that the infra-red spectrum of acetoxime in carbon tetrachloride (Buswell, Rodebush, and Roy, *J. Amer. Chem. Soc.*, 1938, **60**, 2239, 2444, 2528) displays no indication of the N–H frequency (as would be the case if an appreciable quantity of nitrone form were present), but instead gives clear signs of normal hydroxyl absorption at 2·76 μ together with " associated " hydroxyl absorption at *ca.* 3 μ. As the concentration increases, the latter peak becomes relatively more pronounced (as with alcohols; Buswell, Deitz, and Rodebush, *J. Chem. Physics*, 1937, **5**, 501; Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419). The 3 μ band is still slightly visible in 0·001M-solutions. The Raman spectrum of acetoxime shows the characteristic hydroxyl displacement (Bernstein and Martin, *Trans. Roy. Soc. Canada*, 1937, **31**, III, 95, 105).

Evidence from Other Sources.—The conclusions regarding the benzaldoximes and furfuraldoximes are in agreement with those reached *via* chemical considerations by Brady, Meisenheimer, Beckmann, and others (see *Ann. Reports*, 1925, **22**, 105 for summary and references).

Physical evidence has not been entirely unequivocal. Brady and Goldstein (*J.*, 1926, 1918) commented that the dissociation constants (deduced indirectly through the sodium salts) of the two benzaldoximes would be in discordance with Ostwald's experience with olefinic acids (*Z. physikal. Chem.*, 1892, **9**, 553) *if*, in the form m. p. 35°, the phenyl and the hydroxyl were not vicinal. The difficulty has since been cleared by conductivity observations directly on the two oximes themselves in liquid sulphur dioxide by Patwardhan and Deshapande (*J. Indian Chem. Soc.*, 1947, **21**, 135) who, however, examined only one furfuraldoxime (that of m. p. 92°).

We have made several comparisons of the benz- and furfur-aldoximes in aqueous solutions of high dilution using the high-frequency conductivity apparatus described by Blake (*Chem. and Ind.*, 1946, 28; *J. Sci. Instr.*, 1945, **22**, 174; 1947, **24**, 77, 101). The most conductive was the furfuraldoxime, m. p. 92°, followed in turn, by its isomer of m. p. 75°, then by the benzaldoxime of m. p. 128°, and lastly by that of m. p. 35°. We infer, therefore, that the oximes of m. p. 92° and 128° have the *trans*-hydrogen–hydroxyl arrangement.

Finally, we note that the refractometric data, due to Auwers and Ottens (*Ber.*, 1924, **57**, 446), for certain aldoximes and their *O*-ethers, also support configurations which are the inversion of those originally written by Hantzsch (*Ber.*, 1891, **24**, 13). It follows from Silberstein's treatment (*Phil. Mag.*, 1917, **33**, 92, 521) that of two isomers that which is more elongated will have the greater molecular refraction. Thus the forms of $R\cdot CH\colon N\cdot OH$ in which the H and OH are *cis* (*i.e.*, R and HO, *trans*-) should be distinguishable by larger values of $[R_L]$. The following examples are from Auwers and Ottens's paper (*loc. cit.*) and refer to determinations in quinoline :

	M. p.	$[R_L]_D$.		M. p.	$[R_L]_D$.
Benzaldoximes	35°	$36\cdot8_2$	Furfuraldoximes	73—74°	29·85
	128	36·5—36·6		89	29·4

In each case therefore the lower-melting form appears to contain a *cis*-disposition of H and OH. A similar conclusion, but based upon ultra-violet absorption spectra, has recently been reached by Raffauf (*J. Amer. Chem. Soc.*, 1946, **68**, 1765) for the furfuraldoximes.

EXPERIMENTAL.

Materials.—The benzaldoximes were prepared by Beckmann's method (*Ber.*, 1890, **23**, 1684), followed by three recrystallisations, effected by raising benzene solutions of the α-oxime or ether solutions of the β-oxime to saturation point at room temperature by adding light petroleum, and cooling. The directions of Brady and Goldstein (*J.*, 1927, 1960) were used for the furfuraldoximes. The α-form was thrice recrystallised from light petroleum–benzene, and the β-form similarly from 10% ethyl alcohol, m. p.s being then 75—76° and 92—93°, respectively. The aldehydes were distilled, immediately before use, in an atmosphere of nitrogen. The *o*-nitrobenzaldehyde used (from *o*-nitrotoluene, see *Org. Synth.*, **24**, 95) had m. p. 87—88°, and the acetoxime, m. p. 60—61°.

Observations.—The apparatus, technique, and symbols used have been explained previously (Le Fèvre and Calderbank, *J.*, 1948, 1949; Le Fèvre and Northcott, *J.*, 1948, 333). In Table I, the total polarisations of the solutes are evaluated for each concentration by Sugden's mixture rule (*Trans. Faraday Soc.*, 1934, **30**, 720) to display the manner of their dependence upon w_1.

Results.—In Table II we show *inter alia* the values of $\alpha\varepsilon_2$ and β at infinite dilution, extrapolated from the preceding data; the calculations otherwise follow our normal routine (see *J.*, 1937, 1805; or " Dipole Moments," Methuen, 2nd edn., 1948, 41).

Previous or Related Measurements.—Coomber and Partington (*J.*, 1938, 1444), in recording the moment of benzaldehyde as 2·96 D., commented upon the disagreement between their value and those of Williams (2·75; *J. Amer. Chem. Soc.*, 1928, **50**, 2350) and Goebel and Wenzke (2·77; *ibid.*, 1937, **59**, 2301). Our redetermination ($2\cdot9_8$) thus supports the work of the first-named authors. For furfuraldehyde, Hassel and Naeshagen (*Z. physikal. Chem.*, 1930, *B*, **6**, 441) reported 3·57 D. (against $3\cdot6_3$ D. now found by us) at an unstated temperature; however, their orientation polarisation (270·7 c.c.) is not greatly less than ours (272·4 c.c.) and is shown as P_{A+O}. The differences in final μ may therefore come from the ways in which allowances have been made for P_A.

Dobroserdow (see " Tables annuelles," 1913, **2**, 350; Russian original not available) in **1911** measured the dielectric constants (at λ = 60 cm.) of the four pure oximes listed in the following table, and Walden later (*Z. physikal. Chem.*, 1910, **70**, 580) repeated the first at $\lambda = \infty$. Combination of their figures with the densities and refractive indices given by Trapesonzjanz (*Ber.*, 1893, **26**, 1433) and Brühl (*Z. physikal. Chem.*, 1895, **16**, 216) enables the respective orientation polarisations to be calculated by Onsager's formula ${}_{O}P = M(\varepsilon - n^2)(2\varepsilon + n^2)/\varepsilon d(n^2 + 2)^2$ (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) :

	t.	$\varepsilon_{t°}$.	$d_{4°}^{t°}$.	n_D^2.	$({}_{O}P)_{t°}$.	μ_{Onsager}.
Acetaldoxime (Dobr.)	20·5°	3·52	0·9656	2·03	14·5	$0\cdot8_3$
,, (Walden)...............	22·6	2·98	0·9590	2·02	9·8	$0\cdot6_9$
Benzaldoxime	20·1	3·55 *	1·1111	2·50	15·3	$0\cdot8_5$
Methyl ethyl ketoxime	19·8	3·4	0·9232	2·08	19·5	$0\cdot9_6$
Methyl propyl ketoxime	19·8	3·27	0·9095	2·09	20·7	$0\cdot9_9$

* Dobroserdow's value coincides with the mean of earlier determinations by Löwe and Drude, listed in Landolt–Börnstein's " Tabellen," 1912 edn., p. 1219.

TABLE I.

$10^6 w_1$.	$\varepsilon^{25°}$.	$\alpha\varepsilon_2$.	$d_{4°}^{25°}$.	βd_2.	${}_{T}P_1$.
(a) *Solvent :* Benzene.					
(i) *Benzaldehyde.*					
0	2·2725	—	0·87378	—	—
5,057	2·3194	9·27	0·87456	0·154	212·6
10,166	2,3696	9·55	0·87537	0·156	215·7
14,883	2·4121	9·38	0·87597	0·147	210·9
20,985	2·4681	9·32	0·87686	0·147	207·4
24,932	2·4977	9·03	0·87736	0·144	200·8
(ii) o-*Nitrobenzaldehyde.*					
3,217	2·3160	13·5	0·87480	0·317	412·7
17,513	2·5132	13·7	0·87906	0·301	401·4
(iii) *Benzaldoxime,* m. p. 35°.					
0	2·2725	—	0·87165	—	—
1,891	2·2755	1·59	0·87210	0·238	58·7
4,047	2·2774	1·21	0·87255	0·222	58·4
5,738	2,2794	1·20	0·87279	0·199	62·0
7,191	2·2810	1·18	0·87303	0·192	61·2
(iv) *Benzaldoxime,* m. p. 128°.					
1,555	2·2754	1·87	0·87189	0·154	76·4
1,989	2·2761	1·81	0·87192	0·136	76·0
3,724	2·2777	1·40	0·87227	0·166	65·4
(v) *Furfuraldehyde.*					
0	2·2725	—	0·87145	—	—
3,128	2·3225	16·0	0·87258	0·361	304·1
5,359	2·3542	15·3	0·87306	0·282	291·4
8,157	2·3960	15·2	0·87370	0·276	288·0
9,824	2·4177	14·8	0·87402	0·262	280·9
11,733	2·4485	15·0	0·87456	0·265	282·7
(vi) *Furfuraldoxime,* m. p. 75—76°.					
1,812	2·2749	1·32	0·87180	0·193	56·3
2,413	2·2754	1·20	0·87182	0·153	55·9
4,160	2·2777	1·25	0·87224	0·190	55·6
6,152	2·2800	1·22	0·87280	0·219	53·8
8,978	2·2832	1·19	0·87346	0·222	53·0

$10^6 w_1$.	$\varepsilon^{25°}$.	$\alpha\varepsilon_2$.	$d_{4°}^{25}$.	βd_2.	${}_{T}P_1$.
(vii) *Furfuraldoxime,* m. p. 92—93°.					
17,70	2·2800	4·24	0·87214	0·390	120·0
3,295	2·2859	4·07	0·87279	0·407	140·6
4,011	—	—	0·87308	0·406	—
5,288	2,2883	2·99	0·87333	0·356	83·3
7,895	2·2928	2·57	0·87400	0·323	77·2
11,408	2·2968	2·13	0·87485	0·298	69·2
16,939	2·3041	1·87	0·87590	0·263	65·1
(viii) *Acetoxime.*					
0	2·2725	—	0·87378	—	—
2,154	2·2753	1·30	0·87385	0·033	41·8
3,469	2·2767	1·21	0·87385	0·020	40·8
5,221	2·2786	1·17	0·87399	0·040	39·7
8,985	2,2810	0·95	0·87417	0·043	36·6
17,026	2·2862	0·81	0·87454	0·045	34·6
(b) *Solvent :* Chloroform.					
0	4·7240	—	1·4678	—	—
(i) *Benzaldoxime,* m. p. 35°.					
1,442	4·7216	−1·66	1·4674	−0·277	44·7
2,392	4·7182	−2·42	1·4668	−0·418	45·1
4,024	4,7133	−2·66	1·4661	−0·422	44·5
6,359	4·7029	−3·32	1·4646	−0·500	41·9
(ii) *Benzaldoxime, m. p.* 128°.					
1,910	4·7195	−2·36	1·4664	−0·733	55·8
2,470	4·7166	−3·00	1·4660	−0·729	47·7
3,606	4·7113	−3·52	1·4655	−0·638	46·3
4,923	4·7000	−4·88	1·4635	−0·873	46·1
(iii) *Furfuraldoxime,* m. p. 75—76°.					
2,114	4·7191	−2·32	1·4672	−0·284	37·7
3,776	4·7156	−1·99	1·4665	−0·344	41·6
6,861	4·7108	−1·92	1·4660	−0·262	39·9

TABLE II.

Substance and mol. wt.	Data source.	p_2.	C.	$a\varepsilon_2$.	β.	${}_{\infty}P_1$.	$[R_L]_D$.	μ, D.
Benzaldehyde (106·1)	*a* (i)	0·3409	0·1881	9·31	0·171	215·8	32·0	2·9$_8$
o-Nitrobenzaldehyde (151·1)	*a* (ii)	0·3409	0·1881	13·6	0·354	420·4	37·3	4·3$_0$
Benzaldoxime, m. p. 35° (121·1)	*a* (iii)	0·3417	0·1885	1·65	0·294	68·1	36·8 *	1·2$_3$
	b (i)	0·3773	0·0452	−1·43	−0·183	46·2	36·8 *	0·6$_8$
Ditto, m. p. 128° (121·1)	*a* (iv)	0·3417	0·1885	2·23	0·150	86·1	36·6 *	1·5$_5$
	b (ii)	0·3773	0·0452	−0·879	−0·619	69·2	36·6 *	1·2$_5$
Furfuraldehyde (96·1)	*a* (v)	0·3418	0·1886	15·2	0·332	297·8	25·4	3·6$_3$
Furfuraldoxime, m. p. 75°	*a* (vi)	0·3418	0·1886	1·29	0·184	58·0	29·8$_5$ *	1·1$_7$
(111·0)	*b* (iii)	0·3773	0·0452	−2·40	−0·328	43·6	29·8$_5$ *	0·8$_2$
Ditto, m. p. 92° (111·0)	*a* (vii)	0·3418	0·1886	4·23	0·558	105·3	29·4 *	1·9$_2$
Acetoxime (73·1)	*a* (viii)	0·3409	0·1881	1·33	0·032	40·9	24·0	0·9$_0$

* Data from Auwers and Ottens, *loc. cit.*

The moments so estimated for the two ketoximes are only slightly higher than that now found for acetoxime in dilute benzene solution, and accordingly we infer that for them also type (II) is a preferred configuration. The same is probably true for the one known form of acetaldoxime (Beilstein, "Handbuch," **1**, 608). For benzaldoxime, μ_{Onsager} appears to be definitely less than that determined in benzene. This disparity could be either a dispersion or a solvent effect. We suspect the latter since a somewhat parallel diminution of apparent moment occurs when benzene is replaced by chloroform (compare corresponding *a* and *b* data in Tables I and II). No exact regularity should, however, be expected, since the so-called "solvent effects" in dipole-moment measurements often include contributions which are solute-dependent (cf. Le Fèvre, *op. cit.*, Chap. III). The following data for five assorted solutes illustrate the point:

Solute.	Apparent μ in C_6H_6.	Apparent μ in $CHCl_3$.	Ratio.
C_6H_5Cl *	1·59	1·18	1·35
$C_6H_5NO_2$ *	4·05	3·05	1·33
$CHCl_3$ *	1·22	1·10	1·11
Paraldehyde †	2·03	2·26	0·90
Benzil ‡	3·76	3·21	1·17

* Le Fèvre and Russell, *J.*, 1936, 491.
† Le Fèvre and Russell, *J.*, 1936, 496.
‡ Caldwell and Le Fèvre, *J.*, 1939, 1614.

Our results (Table II) show a similarly inconstant " solvent " influence :

Benzaldoxime, m. p. 35°	1·23	0·68	1·81
,, m. p. 128°	1·55	1·25	1·24
Furfuraldoxime, m. p. 75°	1·17	0·82	1·43

Equilibrium between the Furfuraldoximes.—Patterson, Buchanan, and Summers (*J.*, 1941, 606) noted that, although these oximes are not interconverted at 20° in ethyl tartrate, yet at 70° an equilibrium is eventually produced. Polarimetrically this appeared to contain 45% and 55%, respectively, of the higher- and the lower-melting form.

To obtain a preliminary indication of the rôle of the solvent in such a process, we kept pure specimens of the two isomers at 100° for 14 hours and then made routine polarisation measurements in benzene :

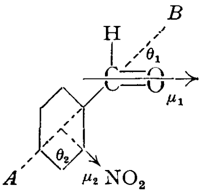
$10^6 w_1$.	$\varepsilon^{25°}$.	$\alpha\varepsilon_2$.	$d_{4°}^{25°}$.	βd_2.	P_1.
0	2·2725	—	0·87145	—	—
Preparation from form, m. p. 92—93°.					
2361	2·2763	1·61	0·87196	0·216	61·4
Preparation from form, m. p. 75—76°.					
3445	2·2780	1·60	0·87236	0·264	59·4

From our previous data (Tables I and II) the total polarisations of the pure oximes at these concentrations are seen to be 105 and 56 c.c. Application of the simple mixture formula to the corresponding orientation polarisations, therefore, shows contents of the higher- and the lower-melting oximes in the ratios *ca.* 7 : 93 and 11 : 89 in the two cases. The inference is, therefore, that the equilibration has a marked solvent dependence.

o-*Nitrobenzaldehyde.*—The moment now recorded for this substance completes the extant data for the three nitrobenzaldehydes :

o-, μ = 4·30 D. (present work).
m-, $3{\cdot}2_8$ D. (Hassel and Naeshagen, *Chem. Zentr.*, 1930, 1956).
p-, 2·4 D. (Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2350).
2·41 D. (Coomber and Partington, *loc. cit.*).

At the outset we expected a higher polarity for the *o*-compound since $\mu_{C_6H_5 \cdot NO_2}$ exceeds that of $\mu_{C_6H_5 \cdot CHO}$, and $\mu_{o\text{-phthalaldehyde}}$ is known to be 4·5 D. (Hassel and Naeshagen, *loc. cit.*). Coomber and Partington (*loc. cit.*) had concluded that, because of induced and mesomeric moments in the aromatic ring, the resultant moment, μ_1, of the benzaldehyde molecule is oriented effectively at $143\tfrac{1}{2}°$ to the 1 : 4-axis, *AB*. In the annexed diagram we put $\mu_1 = 2{\cdot}9_8$, $\mu_2 = 4{\cdot}03$, $\theta_1 = 36\tfrac{1}{2}°$, and θ_2 = 120°, 60°, and 0°, respectively, for the *o*-, *m*-, and *p*-structures, and consider collinear and normal components to *AB* during rotation around *AB* of the planes containing the aldehydo- and the nitrophenyl radicals. Taking χ as the azimuthal angle thus involved, and noting that at all values of χ the components normal to *AB* must produce a resultant which is also normal, we have for the square of the molecular resultant of a given configuration :



$$R^2 = (\mu_1 \cos\theta_1 - \mu_2 \cos\theta_2)^2 + \mu_1^2 \sin^2\theta_1 + \mu_2^2 \sin^2\theta_2 + 2^2\mu_1\mu_2 \sin\theta_1 \sin\theta_2 \cos\chi.$$

" Free rotation " or χ = 90° both require a solution in which the last term is zero. Our calculations may be summarised :

	χ = 0°.	χ = 180°.	" Free rotn."	Obs.
o-$NO_2 \cdot C_6H_4 \cdot CHO$	6·9	4·7	5·9	4·3
m- ,,	5·3	1·8	3·9	3·3
p- ,,	2·4	2·4	2·4	2·4

Although we admit that assumptions which are satisfactory for *m*- or *p*-disubstituted benzenes are uncertain when applied to *o*-isomers (cf., *e.g.*, Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919), we submit that the low moment of *o*-nitrobenzaldehyde now found indicates that its molecule exists extensively as configurations in which χ is *ca.* 180°. As such, the aldehydic hydrogen is correctly disposed for the easy photochemical substitution by oxygen (Zimmer, *Z. physikal. Chem.*, 1933, *B*, **23**, 239; Leighton and Lucy, *J. Chem. Physics*, 1934, **2**, 756) and eventual formation of *o*-nitrosobenzoic acid.

The possibility of following the last change, under controlled conditions of illumination and temperature, *via* dielectric-constant readings, has also been explored, but unsuccessfully owing to the extremely low solubility of the nitroso-acid in all non-conducting solvents tried.

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