The Diamagnetic Susceptibilities of Some Oximes and Oxime Ethers.

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The diamagnetic susceptibilities of six oximes of various structural types and four oxime ethers have been measured by the Gouy method. The values obtained are in poor agreement with those calculated by Pascal's method, nor can they be satisfactorily interpreted on the basis of the recent " Modified Bond Additivity System " (French and Harrison, *J.*, 1955, 1990). It is suggested that the origin of the divergences lies in interactions between groups attached to the C:N bond, an effect analogous to that postulated by Lacher, Pollock, Johnson, and Park (*J. Amer. Chem. Soc.*, 1951, **73**, 2838) in methyl-substituted ethylenes. Other factors which may influence the susceptibilities of oximes and oxime ethers are briefly discussed.

DIAMAGNETIC susceptibilities of many compounds containing only carbon, hydrogen, and oxygen have recently been investigated, but since the early work of Pascal (*e.g.*, *Bull. Soc. chim. France*, 1911, **9**, 336) little attention has been paid to simple compounds containing also nitrogen.

In building up his system of additive and constitutive constants, Pascal found more difficulty with compounds containing nitrogen than with those formed from carbon, hydrogen, and oxygen only, especially with compounds with functional groups containing both oxygen and nitrogen, such as oximes and oxime ethers. In Pascal's method of calculation, correction terms for tertiary and quaternary carbon atoms near functional groups containing oxygen are included, and in order to apply these terms to compounds containing nitrogen and oxygen Pascal assumed that a system such as >C:N·O· could be treated as equivalent to >C:CMe·O, the same correction terms being applicable in each case. This rather extraordinary procedure was supported in the case of oximes by measurements on four compounds only, two of which had by no means simple structures; Pacault (*Rev. sci.*, 1948, **86**, 38), reviewing Pascal's method, adopted this procedure without comment or modification.

It seemed of interest to measure the susceptibilities of some simple oximes and oxime ethers in order to test the validity of Pascal's method of calculation in such compounds. Oxime ethers were included because, although tautomerism in simple oximes is now regarded as highly improbable, it cannot be ruled out (cf. Dunitz and Robertson, *Ann. Reports*, 1952, **49**, 378). Susceptibilities of the parent carbonyl compounds were also measured, in order to evaluate the susceptibility increment for the transition >C:O → >C:N·OH.

EXPERIMENTAL

Materials.—Benzene (B.D.H. extra pure for molecular-weight determinations) was shaken three times with concentrated sulphuric acid, washed with distilled water, and dried ($CaCl_2$) for 3 days. It was then fractionally frozen three times (the last third to freeze being rejected each time), dried (P_2O_5), and carefully fractionated at 1 atm., all but the middle third of the distillate being rejected, through a column packed with Fenske helices (efficiency approximately 15 theoretical plates), which was also used for the fractionation of the ketones and oximes.

Acetone (" AnalaR ") was refluxed with alkaline potassium permanganate for 6 hr., filtered, dried (K_2CO_3) for 1 week, and then twice fractionated, with rejection of all but the middle third in each case. Ethyl methyl ketone, diethyl ketone, and *n*-hexyl methyl ketone were dried (K_2CO_3) and purified by repeated fractionation. *n*-Hexyl methyl ketone was fractionated under reduced pressure, since there were signs of decomposition at atmospheric pressure. As a check, small amounts of these ketones were also purified *via* the semicarbazone (Cowan, Jeffery, and Vogel, *J.*, 1940, 171).

Acetophenone was dried for 3 days ($CaCl_2$) and then purified by fractional freezing, as described by Morgan and Lammert (*J. Amer. Chem. Soc.*, 1924, **46**, 881), followed by fractional

distillation (15 mm.). *iso*Butyraldehyde was dried (Na_2SO_4) and repeatedly fractionated at atmospheric pressure. It was found essential to use the aldehyde immediately after purification, because of the great difficulty in preventing oxidation. *cyclo*Hexanone, after preliminary fractionation at atmospheric pressure, was purified *via* the bisulphite compound (Vogel, " A Text-book of Practical Organic Chemistry," Longmans, London, 1948, p. 340) and finally fractionated (20 mm.).

The oximes were prepared from the carbonyl compounds and hydroxylamine hydrochloride by standard methods. The solid oximes (*i.e.*, of acetone, *cyclo*hexanone, and acetophenone) were purified by repeated recrystallisation from " AnalaR " light petroleum (b. p. 60—80°), and the liquids by fractional distillation under reduced pressure.

Acetoxime *O*-methyl ether was prepared by Ponzio and Charrier's method (*Gazzetta*, 1907, **37**, 506). The best yields were obtained by cooling the mixture in ice and separating the product from the aqueous residue as soon as possible after reaction had ceased.

Acetophenone oxime *O*-methyl ether was obtained by a modification of Dunstan and Goulding's method (*J.*, 1901, **79**, 628). Dry acetophenone oxime (40 g.) was dissolved in a solution of sodium (7 g.) in dry ethanol (150 ml.). Methyl iodide (43 g.) was added in small portions and the mixture refluxed gently for 5 hr. Most of the ethanol was distilled off, and the residue poured into cold water. Ether was added, the ethereal layer was separated and dried ($CaSO_4$), and the ether removed. The residue was distilled at 12 mm. The middle fraction (b. p. 91—92°) was acetophenone oxime *O*-methyl ether (19·6 g.) (Found: C, 72·7; H, 7·4; N, 9·2. Calc. for $C_9H_{11}ON$: C, 72·5; H, 7·4; N, 9·4%). The product was redistilled twice before use.

*cyclo*Hexanone oxime *O*-methyl ether was prepared by Hudlicky and Hockr's method (*Coll. Czech. Chem. Comm.*, 1949, **14**, 561). Although acetoxime *O*-benzyl ether was prepared by Janny (*Ber.*, 1883, **16**, 174) it does not appear to have been previously obtained *pure*. Sodium (6·3 g.) was dissolved in absolute ethanol (150 ml.), and to the solution were added in turn dry acetoxime (20 g.) and redistilled benzyl chloride (31 ml.). The mixture was gently refluxed for 2 hr. When cool, it was poured into ice-cold water (250 ml.), and the oil extracted with ether (2 × 100 ml.). The extract was washed with small portions of water and dried ($CaSO_4$), and the ether was distilled off. The residue was fractionally distilled (1·5 mm.), the acetoxime *O*-benzyl ether being obtained as a fraction, b. p. 65—66° (20 g.) (Found: C, 73·5; H, 8·1; N, 8·7. Calc. for $C_{10}H_{13}ON$: C, 73·6; H, 8·0; N, 8·6).

The identity of the oxime ethers was confirmed by hydrolysis with 20% hydrochloric acid, and isolation of the corresponding substituted hydroxylamine hydrochloride and ketone. The boiling (or melting) points, densities, and refractive indices of all the compounds studied are recorded in Table 1.

TABLE 1.

		RR'CO			RR'C:NOH		
R	R'	B. p./mm.	n_D^{20}	d_4^{20}	B. p./mm.	n_D^{20}	d_4^{20}
Me	Me	56·0°/755	1·3591	0·7903	(m. p. 59—60°)	—	1·05
Et	Me	79·4—79·6/760	1·3785	0·8054	71·5—72/26	1·4427	0·9238
Et	Et	101·5—102/763	1·3925	0·8143	75—75·5/15	1·4463	0·9139
n-Hexyl	Me	75·5/24	1·4156	0·8185	121—122/20	1·4515	0·8852
Ph	Me	87—88/15	1·5341	1·0279	(m. p. 59—60)	—	1·17
Pr^i	H	64/760	1·3733	0·7931	51/15	1·4301	0·8949
RR' =	$<[CH_2]_5$	51—52/20	1·4501	0·9478	(m. p. 87—88)	—	1·01
		RR'C:N·OMe			RR'C:N·O·CH_2Ph		
Me	Me	72·5—73/763	1·3997	0·8331	65—66/1·5	1·5137	0·9852
Ph	Me	58—59/15	1·4656	0·9472	—	—	—

Physical Measurements.—Magnetic susceptibilities were measured by the Gouy method. The magnet was a copy of that described by Bates and Lloyd Evans (*Proc. Phys. Soc.*, 1933, **45**, 425), with a pole gap of 17 mm. and exciting current of 12·5 A producing a field of 12,750 gauss at the centre of the pole gap. It was calibrated with pure benzene ($\chi = -0{\cdot}702 \times 10^{-6}$ e.m.u. g.$^{-1}$). With solids, great care was taken to ensure uniformity of packing, and the formula given by French and Harrison (*J.*, 1953, 2538) was used. The standard deviation of the χ value was calculated in each case, although it is not certain that application of such statistical methods to susceptibility measurements (in which errors are often of a

systematic nature) is justified. The standard deviations were roughly $0{\cdot}001 \times 10^{-6}$ for liquids and $0{\cdot}004 \times 10^{-6}$ for solids.

Refractive indices for the sodium-D line were measured at 20·0° ± 0·05° with a Bellingham and Stanley critical-angle refractometer. Densities of liquids were measured, at 20·0° ± 0·02°, in a 5 c.c. density bottle with tightly-fitting cap. Densities of powdered solids were measured in the same density bottle, with either conductivity water or light petroleum (b. p. 60—80°) as filling liquid.

In Table 2 the experimentally determined values of the specific susceptibility (χ) and the molar susceptibility (χ_m) are recorded. For some ketones agreement with other recently recorded values is less good than expected. We believe this to be due partly to the difficulty of purifying these compounds. For this reason, the methods of purification and physical constants of the materials used have been given in full. We advise that this practice should be generally adopted, so that at least some discrepancies in recorded susceptibility values could be explained.

TABLE 2.

Compound	$-10^6\chi$	$-10^6\chi_m$	Other recorded values
Acetone	$0{\cdot}581_4$	$33{\cdot}7_8$	24 values—see ref. 1
Ethyl methyl ketone	$0{\cdot}632_2$	$45{\cdot}5_8$	45·60 [2]; 47·74 [3]; 46·97 [4]; 45·86 [5]; 45·60 [1]
Diethyl ketone	$0{\cdot}675_1$	$58{\cdot}1_4$	58·31 [5]; 57·32 [1]
n-Hexyl methyl ketone	$0{\cdot}713_1$	$91{\cdot}4_2$	91·6 [6]; 93·31 [2]; 92·07 [1]
Acetophenone	$0{\cdot}603_5$	$72{\cdot}5_0$	72·38 [2]; 72·95 [7]; 72·2 [8]; 72·05 [9]
*iso*Butyraldehyde	$0{\cdot}655_9$	$47{\cdot}2_9$	46·2 [6]; 45·6 [10]; 47·45 [3]; 46·38 [1]
*cyclo*Hexanone	$0{\cdot}632_3$	$62{\cdot}0_4$	63·46 [11]; 61·98 [12]
Acetoxime	$0{\cdot}607_6$	$44{\cdot}4_2$	—
Ethyl methyl ketoxime	$0{\cdot}658_0$	$57{\cdot}3_2$	—
Diethyl ketoxime	$0{\cdot}675_4$	$68{\cdot}3_1$	—
n-Hexyl methyl ketoxime	$0{\cdot}716_2$	$102{\cdot}5_8$	102·43 [13]
Acetophenone oxime	$0{\cdot}592_0$	$79{\cdot}9_0$	—
*iso*Butyraldoxime	$0{\cdot}644_3$	$56{\cdot}1_3$	55·87 [13]
*cyclo*Hexanone oxime	$0{\cdot}632_1$	$71{\cdot}5_4$	—
Acetoxime *O*-methyl ether	$0{\cdot}629_8$	$54{\cdot}8_7$	—
Acetophenone oxime *O*-methyl ether	$0{\cdot}618_8$	$92{\cdot}3_1$	—
*cyclo*Hexanone oxime *O*-methyl ether	$0{\cdot}652_3$	$82{\cdot}9_6$	—
Acetoxime *O*-benzyl ether	$0{\cdot}642_7$	$104{\cdot}8_9$	—

Refs. :—[1] Angus, Llewelyn, and Stott, *Trans. Faraday Soc.*, 1955, **51**, 241. [2] Pascal, *Bull. Soc. chim. France*, 1911, **9**, 177. [3] Bhatnagar and Dhawan, *Phil. Mag.*, 1928, **5**, 536. [4] Cabrera and Madinaveitia, *Anales Fis. Quim.*, 1932, **30**, 528. [5] Seguin, *Compt. rend.*, 1947, **224**, 928. [6] Henrichsen, *Ann. Phys.*, 1888, **34**, 180. [7] Angus, *Bull. Soc. chim. France*, 1949, **16***D*, 483. [8] Cherrier, *Compt. rend.*, 1948, **226**, 1016. [9] Angus and Llewelyn, *Trans. Faraday Soc.*, 1955, **51**, 245. [10] Pascal, *Compt. rend.*, 1909, **149**, 343. [11] Pascal, *Bull. soc. chim. France*, 1911, **9**, 809. [12] Farquharson and Sastri, *Trans. Faraday Soc.*, 1937, **33**, 1474. [13] Pascal, *Bull. Soc. chim. France*, 1911, **9**, 336.

DISCUSSION

Susceptibility values calculated by Pascal's method, using Pacault's revised constants (*loc. cit.*), often differ considerably from our experimental values, even for ketones. A few of the more serious divergences are given in Table 3.

TABLE 3.

Compound	χ_m (exp.)	χ_m (calc.) Pascal	Compound	χ_m (exp.)	χ_m (calc.) Pascal
n-Hexyl methyl ketone	91·4	93·2	Acetoxime	44·4	42·3
*cyclo*Hexanone	62·0	60·6	Acetophenone oxime	79·9	81·4

For the oximes, agreement is poor in all but two cases. It is concluded that Pascal's method of calculation is not in general reliable for this class of compound. The more recent set of constants given by Pascal, Pacault, and Hoarau (*Compt. rend.*, 1952, **233**, 1078) is unlikely to give better agreement, particularly since it has a CH_2 increment of only 11·4, in spite of the fact that all recent experimental work, in various homologous series, indicates a value near to 11·7.

French and Harrison (*J.*, 1955, 1990) have shown that the observed susceptibilities of some simple organic compounds for which the Pascal system is unsatisfactory can

be better reproduced by a "Modified Bond Additivity System." In this, the molar susceptibility is expressed as the sum of terms characteristic of each bond in the molecule, together with a small number of bond-interaction terms. It was hoped that this system would serve as a better basis for the discussion of the present results. Unfortunately, it is not possible to determine independently all the bond or interaction terms required for the calculation of the susceptibilities of oximes and oxime ethers, owing to the scarcity of measurements on other organic compounds containing nitrogen. This difficulty can be overcome, for the present purpose, by treating the sum of a number of bond and interaction terms as a single term β. Then, by using the notation and numerical values of the previous paper (*J.*, 1955, 1990) the susceptibility of acetoxime can be written as:

$$\begin{aligned}\chi_m &= 6\chi_{C-H} + 2\chi_{C-C} + \chi_{O-H} + \chi_{C=N} + \chi_{N-O} + 2\lambda_{C-C=N} + \lambda_{O-N=C} - \lambda_{C-C-C} \\ &= 6\chi_{C-H} + 2\chi_{C-C} + \chi_{O-H} - \lambda_{C-C-C} + \beta \\ &= 35{\cdot}85 + \beta\end{aligned}$$

Similar calculations can be carried out for the other oximes and oxime ethers, provided the assumption is made that the interaction terms depend principally on the multiplicity and steric relationship of the bonds concerned, and only to a negligible extent on the particular atoms. This was shown to be reasonable in the previous work on compounds containing only carbon, hydrogen, and oxygen, and its use here enables relationships such as $\lambda_{N-O-C} = \lambda_{C-C-C}$ to be used.

It was found that when a "theoretical" susceptibility value had been calculated in this way for each compound studied, the value of β required to produce agreement with the experimental value varied considerably from compound to compound. The values suggested earlier for the bond terms such as χ_{C-C}, although indicating the general principles of the method, may, as observed previously, require modification in the light of subsequent experimental work. In the more complex structures inaccuracies in assessing the contributions to the susceptibility from parts of the molecule other than the oxime group may be partly responsible for the observed variation in β. This possibility can be avoided by comparing, instead of the actual susceptibility values, the differences: χ_m(oxime or oxime ether) $-\chi_m$(carbonyl compound), which should be practically independent of errors in the fundamental constants. In Table 4 are given D, the experimental value of this difference, and the value of β required to produce agreement between experimental and calculated values of D. (*Note.* Throughout this section, all susceptibility values are recorded in 10^{-6} c.g.s. units and the negative signs are omitted.)

TABLE 4.

Substance	D	β	Substance	D	β
Acetoxime	10·6	8·65	*cyclo*Hexanone oxime	9·5	7·55
Ethyl methyl ketoxime	11·7	9·75	Acetoxime *O*-methyl ether	21·1	8·45
Diethyl ketoxime	10·2	8·25	Acetophenone oxime *O*-methyl ether	19·8	7·15
n-Hexyl methyl ketoxime	11·2	9·25	*cyclo*Hexanone oxime *O*-methyl ether	21·0	8·35
Acetophenone oxime	7·4	5·45	Acetoxime *O*-benzyl ether	71·1	7·61
*iso*Butyraldoxime	8·8	7·85			

There are two important facts which can be deduced from this Table. First, the value of the molar susceptibility increment associated with the transition

$$>C{=}O \longrightarrow >C{=}N{\cdot}OH \text{ (or } >C{=}O \longrightarrow >C{=}N{\cdot}O{\cdot}CH_3)$$

is not independent of the nature of the rest of the molecule. Secondly, in spite of the elimination of possible errors in contributions assigned to other parts of the molecule, a constant value of β is not obtained. Hence it appears that the simple modified scheme will not satisfactorily account for the susceptibilities of oximes and oxime ethers. If the very low value for acetophenone oxime (this compound is very difficult to purify adequately or to pack uniformly into a susceptibility tube) is neglected the values of β lie between 7·15 and 9·75. Whilst this variation is not large, it is greater than normally observed by the use of this system.

In order to explain the breakdown of the modified scheme in this case, a search was

made for previously recorded examples of a similar type. A case of considerable interest is the system of methyl-substituted ethylenes (Lacher, Pollock, Johnson, and Park, *J. Amer. Chem. Soc.*, 1951, **73**, 2838). These authors were only able to interpret the observed susceptibilities by the inclusion of interaction terms between *groups* both parallel and perpendicular to the double bond. We have verified that in this case also our scheme will not satisfactorily account for the experimental values, divergences being similar to those obtained with the oximes. It has already been shown that the system is satisfactory for certain compounds containing double bonds, *e.g.*, carbonyl compounds. Oximes and substituted ethylenes differ from carbonyl compounds in that substituent groups are attached to the atoms at both ends of the double bond.

The modified system implicitly includes interactions between groups attached to the same atom (in the form of bond interactions) but ignores interactions between groups attached to different ends of a double bond. Further, the interactions between *gem.*-dialkyl groups, as calculated by the system in its present form, would be independent of the particular alkyl groups concerned. The bond angles in acetoxime (Bierlin and Lingafelter, *Acta Cryst.*, 1951, **4**, 450) seem to indicate that the methyl and hydroxyl groups are sufficiently close for some kind of interaction to occur. It is suggested that neglect of the parallel type of interactions, and oversimplified treatment of the perpendicular type, are at least partly responsible for the breakdown of the system in this case. Any system of calculation satisfactory for unsaturated compounds must allow for these interactions, but the best method cannot be decided upon until more experimental values for simple unsaturated compounds become available.

With regard to the actual values of β given in Table 4, it may be significant that the symmetrical ketoximes ($R_2C{:}N{\cdot}OH$) give values of β very roughly 1 unit less than the corresponding unsymmetrical compounds ($RR'C{:}N{\cdot}OH$). A similar alternation effect is evident in the susceptibilities of the ketones themselves.

Finally, other factors bearing on the observed susceptibilities may be :

Tautomerism.—The lack of constancy of β values for the oxime ethers, in which tautomerism is impossible, prevents any definite conclusions being drawn about the influence of tautomerism in the oximes on the variation in β in the latter.

Geometrical Isomerism.—The variations in β values cannot be explained completely by varying amounts of *cis*- and *trans*-forms since the symmetrical oximes, which are incapable of geometrical isomerism, fail to yield a constant value of β. If *cis*- and *trans*-forms do have different susceptibilities, this may be due to the operation of the parallel type of interaction term previously discussed.

Difference in Susceptibility between Liquid and Solid States.—In spite of many investigations, it is still not completely certain how large a change in susceptibility (if any) accompanies the change of state from liquid to solid. There is no evidence of a systematic difference between the values of β found for solids and liquids in the present work, high and low values being found in both states.

Whilst not affecting the value of the method for systems of the type discussed in our previous paper, the present work does indicate that the modified bond-additivity system will not deal satisfactorily with all types of unsaturated compounds, unless further interaction terms are included, the investigation of which is proceeding.

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