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Abstract

Full Text

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DIPOLE MOMENTS OF SOME NITRONES

We have measured the dipole moments of seven nitrones listed in Table 1. The measurements were carried out in dilute benzene solutions at 25° by the heterodyne method, and the results were calculated according to Hedestrand. Table 1 gives, in sequence: the name of the compound, structural formula, melting point, range of concentrations studied, total polarizations extrapolated to infinite dilution, electronic polarizations (for compound I determined experimentally, and for the others calculated from bond refractions), then orientation polarizations and dipole moments in debyes.

Compounds I, II, and V were described previously ([1-3]). Compound IV was synthesized for the first time*. I, II, IV, and V were obtained in 70–80% yield by boiling N-phenyl- or N-benzylhydroxylamine with an equimolar amount of the corresponding aldehyde in benzene (2 hours with a water separator). Compounds VI and VII were synthesized by the action of $Pb(OCOCH_3)_4$ on I and II, respectively ([4]). Substance III was obtained by the method described earlier ([5]).

In the polarity of the compounds measured, the determining factor is the presence of the N-oxide group. In the case of the simplest aliphatic N-oxide $(CH_3)_3N \rightarrow O$, the dipole moment in benzene is 5.02 D ([6]).

In the method of consideration from the standpoint of valence schemes, the N-oxide group is constructed from positively charged nitrogen in sp^3 hybridization and oxygen in the form of a negative ion,

$$\backslash \overset{+}{\mathrm{N}} - \mathrm{O}^{-} \\ /$$

If one takes into account that the N—O distance is 1.35 Å, then the product of the electric charge by this distance would lead to a moment of ~ 6.5 D.

From the moment of $N(CH_3)_3$, equal to ~ 0.62, and assuming that this moment vector is retained in the molecule, the moment of $(CH_3)_3N \rightarrow O$ would be ~ 5.9 D. It must be borne in mind, however, that oxygen has no vacant orbitals and that the displacement of the electron cloud of the electron of the unshared pair of nitrogen is incomplete. This decreases the effective charges on nitrogen and oxygen. Data are available on the dipole moment of pyridine N-oxide. It is 4.24 D ([6]). The reason for the lowering of the moment is apparently the circumstance that the carbons of the ring can, to some extent, compete with oxygen for possession of the electron. We note that the electron affinity of oxygen is 35 kcal, and that of carbon is 25 kcal; therefore some additional electron density falls on the α- and γ-atoms of the ring, which may be represented by three valence schemes of type A:

$$O=\overset{+}{N}(\ \text{benzene ring}\ )^{-} \qquad \text{(A)}$$

It is possible that, to some extent, the positive charge of nitrogen is dispersed over the α- and γ-carbons in the ring in accordance with scheme B:

$$\overline{O}=N(\ \text{benzene ring}\ )^{+} \qquad \text{(B)}$$

* Found, %: N 11, 11. $C_{16}H_{17}N_2O$. Calculated, %: N 11.02

Table 1

Compound No.	Name	Formula	m.p., °C	f_2	P_{total}	P_{el}	P_{or}	$\mu \cdot 10^{18}$
I	C,N-diphenylnitrone	$C_6H_5-CH=N^+(O^-)-C_6H_5$	112 (from alcohol)	0.00492	310.3	63.7	246.6	3.37
II	C-phenyl-N-benzylnitrone	$C_6H_5-CH=N^+(O^-)-CH_2-C_6H_5$	82 (from ether)	0.00351	320.3	68.4	251.9	3.47
III	C,C-diphenyl-N-benzylnitrone	$(C_6H_5)_2C=N^+(O^-)-CH_2-C_6H_5$	120 (from benzene–hexane)	0.00187	334.0	92.7	241.3	3.40
IV	C-(*n*-dimethylaminophenyl)-N-benzylnitrone	$(CH_3)_2N-C_6H_4-CH=N^+(O^-)-CH_2-C_6H_5$	122 (from benzene)	0.00190	299.2	299.2	0.5	3.79

Compound No.	Name	Formula	m.p., °C	f_2	P_{total}	P_{el}	P_{or}	$\mu \cdot 10^{18}$
V	C-(*m*-nitrophenyl)-N-benzylnitrone	$m-NO_2-C_6H_4-CH=N^+(O^-)-CH_2-C_6H_5$	148 (from benzene)	0.00092	531.6	76.2	455.4	4.67
VI	C-acetoxy-C,N-diphenylnitrone	$C_6H_5-C(OCOCH_3)=N^+(O^-)-C_6H_5$	157 (from petroleum ether)	0.00097	410.1	74.8	325.3	3.95
VII	C-phenyl-N-(α,α-diacetoxybenzyl)nitrone	$C_6H_5-CH=N^+(O^-)-C(OCOCH_3)_2-C_6H_5$	102 (from ether)	0.00428	506.1	93.1	413.0	4.44

But such a charge distribution, if it is at all possible, is represented by a structure of small weight, since in this case the unshared pair of nitrogen electrons is not used.

According to scheme A the molecular moment is lowered as a result of the appearance of a moment in the opposite direction; according to scheme B the moment increases. In this connection it is interesting to note that in pyridine N-oxide the γ-position is the most reactive toward both electrophilic and nucleophilic reagents, for example toward nitration (the reagent is the nitronium ion $\overset{+}{N}O_2$) and toward methoxylation (the reagent is $\overline{OCH_3}$). This is presumably connected with the structure of the active complex in the reaction. The approach of a negatively charged group favors charge distribution according to scheme B, whereas the approach of positive charges increases the weight of the state according to scheme A. The decrease of the moment in the case of possible conjugation with the aromatic ring can apparently be explained by an increase in electron density in the ortho- and para-positions. In compound I the decrease of the moment is probably connected with an increase in the weight of the structure:

$$Ph-\overset{+}{N}(=O)-C(H)=\text{(cyclohexadienyl ring with negative charges)}$$

Conjugation of this type in compound I is naturally represented to a greater extent than in pyridine N-oxide. The same applies to compound II, the moment of which differs little from that of compound I. Correspondingly, the moment of

$$C_6H_5-CH=N-CH_3$$

has a close value, equal to 3.55 D ([7]). In the presence of two phenyl groups at an angle of 120° (compound III), the resultant moment of these two groups is directed toward the N-oxide group at the same angle of 120°, and therefore the moment changes little.

In compound IV the group $(CH_3)_2N-$ increases the electron density in the ortho- and para-positions of the ring. This should increase the moment if the group $(CH_3)_2N-C_6H_4-$ forms an angle of 180° with the N-oxide group (trans form).

In the case of compound V a configuration is possible in which the nitro group (in the meta-position) forms an angle of 60° with the N-oxide group. If such a configuration is realized, then the molecular moment should increase.

Compounds VI and VII contain too many vectors of individual moments, so that an unambiguous interpretation of the results obtained in these cases does not appear possible.

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CITED LITERATURE

1. E. Bestann, *Ann.*, **367**, 273 (1909).
2. L. W. Jones, M. C. Sneed, *J. Am. Chem. Soc.*, **39**, 677 (1917).
3. H. Goldschmidt, *Ber.*, **23**, 2174 (1890).
4. M. M. Shemyakin, V. I. Maimind et al., *Izv. AN SSSR, ser. khim.*, 1964 (in press).
5. A. C. Cope, A. C. Haven, *J. Am. Chem. Soc.*, **72**, 4896 (1950).
6. E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).
7. R. Huisgen, *Angew. Chem.*, **75**, 626 (1963).

Note: Figure translations are in progress. See original paper for figures.