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STUDY OF THE STRUCTURE OF UNSATURATED NITRO COMPOUNDS BY THE METHOD OF DIPOLE MOMENTS

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Study of the structure of unsaturated nitro compounds by the method of dipole moments made it possible for the first time to establish their configuration and considerably broadened ideas about the distribution of electron densities in them.*

The substances studied (I–XI, see Table 1) could equally well have been assigned a planar (cis- or trans- with respect to the C=C bond) or a nonplanar configuration. Withdrawal of the nitro group from the plane of the benzene ring is energetically unfavorable because of the loss of π-conjugation in β-nitrostyrenes; moreover, violation of coplanarity should bring their moments closer to the moments of aliphatic nitro compounds, which is not the case. Consequently, the assumption of a nonplanar structure for the substances studied is ruled out.

In planar configurations the cis structure was excluded because the measured moments (μ) did not coincide with the vector sums of the moments of the individual bonds calculated for the cis forms ($\mu\Sigma_1$ cis), and because of the considerable steric hindrance arising from overlap of the hydrogen atoms of the benzene ring and the oxygen of the nitro group (the distance between the centers of these atoms in β-nitrostyrenes is ~ 0.3 Å, Fig. 1; in furyl-nitroethylene, ~ 0.5 Å).

The closeness of the values of the experimental moments and those calculated for the trans configuration ($\mu\Sigma_1$ trans), and the absence of steric hindrance, make it possible to assign a trans structure to the β-nitrostyrenes; thus, for example, for substance V, $\mu = 7.68$, $\mu\Sigma_1$ trans $= 6.120$, $\mu\Sigma_1$ cis $= 3.84$; for substance VI, $\mu = 1.00$, $\mu\Sigma_1$ trans $= 0.50$, $\mu\Sigma_1$ cis $= 7.38$.

Conjugation of the nitro group with the double bond and the benzene ring causes the appearance of an additional conjugation moment, which should increase with an increase in the number of conjugated π bonds and in the distance between δ^- and δ^+; vectorially adding with the moment of the NO_2 group itself ($\mu C_2H_5NO_2 = 3.2$ D), it should lead to an increase in the total moment in the series

Structural formulas labeled (I), (XII), and (II), illustrating charge distribution and dipole direction.

Figure 1: Structural formulas labeled (I), (XII), and (II), illustrating charge distribution and dipole direction.

$$\mu C_2H_5NO_2(3.2\text{ D}) < \mu_I(3.41\text{ D}) < \mu_{XII}(4.01\text{ D}) < \mu_{II}(4.51\text{ D}),$$

which is in fact observed.

For the same reason, and also because owing to the stronger electron deficiency at the α-carbon atom the polarity of the C_α—H bond is greater than that of C_β—H, the moment vector of the β-nitrovinyl group should deviate–

* The dipole moments of unsaturated nitro compounds had not been determined systematically.

removed from the direction of the phenyl-C_α bond, i.e., this group must be "irregular."

A good verification of this conclusion is provided by the moments of substances X and XI. In 1,4-bis-(β-nitrovinyl)benzene (X) the two nitrovinyl groups may be arranged with respect to the benzene ring in the trans- or in the cis-

Table 1

Experimental values of dipole moments (in debyes)

Compound	No. of compound, $R = H$	M.p., °C, $R = H$	μ, $R = H$	No. of compound, $R = CH_3$	M.p., °C, $R = CH_3$	μ_1, $R = CH_3$	$\mu - \mu_1$, $R = CH_3$
$CH_2 = CHNO_2$	I	b.p. ([1]) 36°/100 mm	3.41	–	–	–	–
$C_6H_5-CH = C(NO_2)R$	II	57-59 ([2])	4.51	II[a] ([3])	65-66	4.14	−0.37
p-$CH_3-C_6H_4-CH = C(NO_2)R$	III	101 ([3])	5.00	III[a] ([3])	52-53	4.55	−0.45
p-$CH_3O-C_6H_4-CH = C(NO_2)R$	IV	87 ([4])	5.43	IV[a] ([3])	43-44	5.09	−0.34
p-$(CH_3)_2N-C_6H_4-CH = C(NO_2)R$	V	184 ([3])	7.61	V[a] ([3])	123.5-124	7.18	−0.43

schematic configurations a, b, c

Figure 2: schematic configurations a, b, c

Compound	No. of compound, $R = H$	M.p., °C, $R = H$	μ, $R = H$	No. of compound, $R = CH_3$	M.p., °C, $R = CH_3$	μ_1, $R = CH_3$	$\mu - \mu_1$, $R = CH_3$
p-$O_2N-C_6H_4-CH=C(NO_2)R$	VI	206-207 (5)	1.00	VI[a] (10)	114-115	0.41	−0.59
$C_6H_5-CH=C(NO_2)Br$	VII	75 (6)	–	VII[a] (11)	67-68	4.05	–
furyl$-CH=C(NO_2)R$	VIII	147-148 (7)	5.00	VIII[a] (12)	74-75	4.59	−0.41
$O_2NCH=CH-CH=CHNO_2$	IX	230-232 (8)	0.71	–	–	–	–
$O_2N-C(R)=CH-C_6H_4-CH=C(NO_2)R$	X	202-203 (9)	1.05	X[a] (8)	122-123	1.65	$\pm$0.60
$O_2N-C(R)=CH-C_6H_4-CH=C(NO_2)R$	XI	203 (9)	3.65	XI[a] (10)	108-109	4.20	$\pm$0.55

positions*. The dipole moment of the trans form should be equal to zero owing to complete compensation of the moment vectors of the NO_2 groups. The cis configuration should give a small moment as a consequence of the irregularity of the β-nitrovinyl groups, which is what is observed.

$$O_2N-CH=CH-C_6H_4-CH=CH-NO_2$$

(X)

* With respect to the bond of the $C = C$ group and of the phenyl–there can be only two trans positions, for the reasons set forth above.

The structure of the nitrovinyl group makes it possible to predict for (XI) the possibility of three configurations:

a b c

Fig. 1

Figure 3: Fig. 1

Fig. 2

Figure 4: Fig. 2

Because of the irregularity of the β-nitrovinyl group, the angle between the moments of the nitrovinyl groups will be, in configuration a), smaller; in b), larger; and in c), equal to 120°, while the resultant moment will accordingly be greater than, less than, and equal to 4.3 D. The experimentally found moment, 3.65 D, argues in favor of structure b) for 1,3-bis-(β-nitrovinyl)benzene.

Fig. 1

If regularity of the nitrovinyl group in 1,3-bis-(β-nitrovinyl)benzene (XII) is assumed, its moment would be equal to 4.3 D, i.e., to the moment of nitrostyrene (4.51 D) decreased by 0.2 D (analogously to the case of *m*-dinitrobenzene (3.8 D) and nitrobenzene (4.01 D)). Replacement by a methyl group of the hydrogen atom at the β-carbon of β-nitrostyrenes leads to a decrease in the dipole moments by 0.4 D (II –IX , Table 1).

In β-methyl-β-nitrostyrenes, owing to the superposition of the atomic volumes of the methyl group (its van der Waals radius is ~2 Å), the *o*-hydrogen of the benzene ring, and the oxygen of the nitro group, the coplanarity of the molecules is disturbed (Fig. 2).

Fig. 2

The result of the disturbance of coplanarity is a weakening of π-conjugation in β-methyl-β-nitrostyrenes involving the benzene ring, vinyl, and nitro groups; however, less effective π,σ-conjugation of the C–H bonds of the methyl group and the double bonds of the vinyl residue will be preserved. Since the magnitudes of the dipole moments are the result of vector addition of the moments of the individual polar bonds and groups and of the dipole moment of conjugation, the weakening of conjugation naturally leads to a decrease in the dipole moments found.

In 1,4- and 1,3-bis-(β-nitro-β-methylvinyl)benzenes (Xa and XIa), the role of the moment due to π,σ-conjugation of the methyl group and the ethylenic residue becomes decisive; it is directed along the C_β—CH_3 bond, with the positive end on the methyl group. The geometry of Xa and XIa is similar to the geometry of 1,4- and 1,3-bis-(β-nitrovinyl)benzenes (X and XI), which have a cis configuration with respect to the benzene ring. Therefore, the addition of the transverse components of the moments of the nitrovinyl groups gives an observed moment, naturally, larger than in X and XI. These data are in agreement with the results of a study of the combination-scattering spectra of arylnitroalkenes ([13]).

The dipole moments (μ) in debyes were measured in benzene at 25° by the beat method and were calculated from the formula:

$$\mu = 0.0127\sqrt{(P_\infty - P_E - P_A)T},$$

or, at T 298° K,

$$\mu = 0.220\sqrt{P_\infty - P_E - P_A},$$

where P_∞ is the molar polarization of the substance at infinite dilution, P_E is the electronic polarization, and P_A is the atomic polarization. The electronic polarization (P_E) was taken equal to the molar refraction MR_D and was calculated additively, as the sum of the refractions of atoms and bonds for the sodium D-line; the atomic polarization was estimated by an additive rule derived by one of us ([14]), with the following group increments for P_A: O_2N 3.9 cm^3, $-CH=CHNO_2$ 7.9 cm^3, CH_3 0.9 cm^3.

In two cases (substances IV, V, XIV, and XV), when it was not possible to estimate the value of P_A by this method, P_A was taken to be approximately equal to $0.15MR_D$, which is fully justified for large dipole moments.

The compounds investigated were synthesized according to published procedures and were carefully purified to constant melting or boiling points.

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