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Abstract

Full Text

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Dipole Moments of Some Halopolynitroalkanes

The dipole moments of aliphatic polynitro compounds containing carbon-halogen bonds are of interest for clarifying the question of how the accumulation of nitro groups affects polarity and how this effect is reflected in chemical properties.

For this purpose we measured the dipole moments of eight compounds at 25° in benzene by the heterodyne method. All compounds were synthesized by us and obtained analytically pure. The electronic polarizations were in some cases taken from experiment, and in others calculated from bond refractions. From experimental data for the refraction of the $C{-}NO_2$ group, a value of 7.65 cm^3 was obtained in those cases where three nitro groups are attached to one carbon atom, and 7.5 cm^3 when one carbon atom is bonded to two nitro groups. The atomic polarization of each nitro group was estimated as 2 cm^3. Hedestrand’ s formulas were used to calculate the dipole moments.

Table 1

Formula	f	P_∞	$P_{el} + P_{at}$	$\mu \cdot 10^{18}$
$CCl(NO_2)_3$	0.003–0.006	133.5	35.7	2.17
$CBr(NO_2)_3$	0.005–0.012	174.1	38.1	2.56
$CJ(NO_2)_3$	0.002–0.004	341	43.5	3.79
$CH_3C(NO_2)_3$	0.002–0.007	243.8	35.3	3.17
$CH_3CH(NO_2)_2$	0.005–0.01	276.8	27	3.47
$CH_3CBr(NO_2)_2$	0.003–0.015	254.6	34.7	3.26
$CH_3CCl(NO_2)_2$	0.004–0.008	226.1	31.85	3.06
$CH_3CHBr(NO_2)$	0.006–0.014	206	26.9	2.94

Table 1 gives, in sequence, the formulas, the range of measured concentrations in mole fractions, the total polarization, the sum of the atomic and electronic polarizations, and the value of the dipole moment in debyes.

Let us compare the dipole moments of the C—Cl, C—Br, and C—J bonds in compounds of the type CH_3Hal and $CHal(NO_2)_3$.

If one conventionally takes for the moment of the C—H bond the value 0.31, as has recently been proposed for the case of sp^3 hybridization (with the positive charge directed toward hydrogen) (^{1}), then from the values of the dipole moments in benzene solutions for CH_3Cl 1.86; CH_3Br 1.82, and CH_3J 1.48 D, we obtain values for the moments of the C—Cl, C—Br, and C—J bonds of 1.55, 1.51, and 1.17 D.

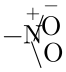
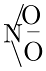
The accumulation of halogen atoms at one carbon atom leads to a decrease in the bond moments. With the same assumption concerning the C—H bond, from experimental data on the moments of $CHCl_3$ 1.2; $CHBr_3$ 1.06, and CHJ_3 0.95 D, we obtain for the C—Cl, C—Br, and C—J bonds, respectively, the values 0.89, 0.75, and 0.64 D.

From the magnitude of the dipole moment of nitromethane in benzene, 3.15, we find for the $C—NO_2$ moment 2.84 D. The moment of nitroform $CH(NO_2)_3$, known from literature data and also from our measurements, is 2.71, which gives 2.4 for the $C—NO_2$ bond. Using this value and the magnitudes found by us for the moments of $CCl(NO_2)_3$ 2.17, $CBr(NO_2)_3$ 2.56, and $CJ(NO_2)_3$ 3.79, we find that in these compounds the moments of the carbon-halogen bonds are: C—Cl 0.23 (with the negative charge directed toward chlorine), C—Br 0.15 (with the positive charge directed toward bromine), and C—J 1.39 D (with the plus at iodine). In comparison with compounds of the type CH_3Hal, the moments are changed for the C—Cl bond by 1.32, C—Br by 1.66, and C—J by 2.56.

Consequently, in halotrinitromethanes chlorine has a small negative charge, bromine a slight positive charge, and iodine already a considerable positive charge. The essential point, of course, is not in the absolute quantitative values, but in the fact that the increase in the dipole moment of the molecule from $CCl(NO_2)_3$ to $CBr(NO_2)_3$ and to $CJ(NO_2)_3$ (whose moment is greater than that of nitroform by 1.08 D) indicates that, in the C—J bond, iodine is the positive end of the dipole. Irrespective of the accuracy of the quantitative comparisons (for the C—H bond, a single value was taken as a conventional quantity for all halogen derivatives of methane), it is obvious that in the series of halotrinitromethanes the electropositivity increases rapidly from chlorine to iodine. This is connected with the fact that, in the presence of three $C—NO_2$ bonds at one carbon atom, the interaction of iodine with carbon is not exhausted by the formation of an ordinary two-electron bond with a partially ionic state

$$\overset{+}{C} - \overset{-}{J}.$$

Apparently, iodine here partly acts as a donor on account of its unshared pair of *p*-electrons, and the displacement of electrons from iodine to carbon causes a further displacement of electrons and a partial conversion of the nitro group

 $-\overset{+}{N}(\overset{-}{O})O$ into the nitrito group  $N(O)\overset{-}{O}$.

The peculiar polarization of the carbon—halogen bond in halotrinitromethanes accounts for the specific chemical properties of these compounds, for example their ability to hydrolyze with formation of hydrohalic acids (2), to oxidize hydrazine (3) or potassium iodide (4), and to be rapidly reduced at a mercury electrode (5). The ease of these reactions increases on going from chlorotrinitromethane to bromo-, and especially to iodotrinitromethane (for example, the hydrolysis constants of the indicated compounds are, respectively, $8 \cdot 10^{-12}$, $3 \cdot 10^{-11}$, and $4 \cdot 10^{-7}$ (2)). In the same sequence the electropositivity of the halogen in halotrinitromethanes increases, as is evident from their dipole moments.

If the dipole moment of the $C(NO_2)_3$ group is taken to be 2.4 D and this value is used for the molecule $CH_3C(NO_2)_3$ (3.17 D), then the moment of CH_3—C is found to be 0.77 D. Consequently, in the neighborhood of three nitro groups the electropositivity of the methyl group is increased and the acidic properties of the hydrogen atoms are intensified, which is in good agreement with the chemical behavior of 1,1,1-trinitroethane, which readily loses the elements of nitrous acid with formation of 1,1-dinitroethylene (6).

Taking the indicated values of the moments C—CH_3, C—H, and C—NO_2, one can calculate the resultant dipole moments of a series of gem-dinitro compounds. Thus, for $CH_3CH(NO_2)_2$ the calculation gives 3.38 D, instead of the experimental value 3.47 D; for $CH_3CCl(NO_2)_2$ the calculated value is 3.15 D, and the experimental value is 3.06 D; for the molecule $CH_3CBr(NO_2)_2$ the calculation gives 3.29 D, in satisfactory agreement with the experimental value 3.26 D. Hence it follows that also in the case of dinitro compounds experiment agrees with the fact of a considerable decrease in the dipole moment of the carbon—halogen bond.

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