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Dipole Moment and Structure of 1,2-Dinitroethane

by

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Continuing our work on the structure of nitroparaffins [1] we examined the dipole moment of 1,2-dinitroethane in the hope that the results might throw some light on the problem of rotation around the C—C bond in this compound. It was expected that there might be a restricted rotation around this bond, by the analogy with the known example of 1,2-dichloroethane, which in the liquid state exists mainly in *trans* and to *lesser* extent in *gauche* form, and when solid — in *trans* form [2]—[5].

Preliminary geometrical analysis of the *cis* form of 1,2-dinitroethane based on he known bond lengths C—C = 1.54 Å, C—N=1.5 Å, and angles (C—C—N angle = 109°28′) shows that the distance between the nitrogen atoms is *c.* 2.5 Å, whereas the sum of the van der Waals radii around the nitrogen atoms (R_N = 1.58 Å) is *c.* 3.16 Å, i.e. there is an overlapping of these radii around each of the nitrogen atoms by *c.* 0.33 Å.

A similar analysis for 1,2-dichloroethane (C—Cl = 1.76 Å, C—C—Cl angle = 109°28′) shows that the distance between the chlorine atoms is *c.* 2.12 Å, and the sum of van der Waals radii around chlorine atoms (R_{Cl} = 1.8 Å) is *c.* 3.6 Å. The overlapping around each of the chloride atoms is therefore *c.* 0.74 Å.

Thus, it could be expected that a restricted rotation is more probable in 1,2-dinitroethane than in 1,2-dichloroethane.

To approach this problem the dipole moment of 1,2-dinitroethane was measured. The data obtained were compared with those calculated for various possible rotation isomers of the compound. For comparison the same calculation was done for 1,2-dichloroethane.

Experimental

1,2-Dinitroethane (m.p. 38.5—39.5°) was prepared by a conventional method [6] and purified by repeated crystallization from alcohol.

The dipole moment of 1,2-dinitroethane was measured in benzene solution at 20°C by the heterodyne-beat method on a DMI instrument (Wissenschaftliche Technische Werkstätte, Weilheim).

The results of measurement at different concentrations I—V are collected in the Table. The average result of five measurements gave the value of $\mu = 4.4 \pm 0.1$ *D*.

TABLE

	M_1	M_2	ω_2	$\varepsilon_{1,2}$	$\varepsilon_{1,2}-\varepsilon_1$	$n_{1,2}$	$(n^2_{1,2}-n^2_1)$
Benzene	—	—	—	2.2835 (ε_1)	—	1.50034 (n_1)	—
I	34.1010	0.1947	$5.68\cdot10^{-3}$	2.3923	$10.88\cdot10^{-2}$	1.50014	$0.74\cdot10^{-3}$
II	32.3473	0.2610	$8.00\cdot10^{-3}$	2.4273	$14.38\cdot10^{-2}$	1.50004	$1.01\cdot10^{-3}$
III	33.1020	0.4119	$12.23\cdot10^{-3}$	2.5111	$22.76\cdot10^{-2}$	1.49984	$1.62\cdot10^{-3}$
IV	38.1295	0.5158	$13.35\cdot10^{-3}$	2.5213	$23.78\cdot10^{-2}$	1.49969	$1.69\cdot10^{-3}$
V	34.2485	0.7460	$21.32\cdot10^{-3}$	2.6756	$39.21\cdot10^{-2}$	1.49947	$2.74\cdot10^{-3}$

$a_u = -0.129$, $a_\varepsilon = 18.23$, $\mu = 4.4 \pm 0.1$ *D*.

Discussion

The dipole moment of both 1,2-dinitroethane and 1,2-dichloroethane was calculated for various values of the angle θ defining the rotation of C—N (of the CH_2—NO_2 group) and C—Cl (of the CH_2Cl_2 group), respectively, around the C—C axis (Fig. 1), where *X* denotes NO_2 or Cl.

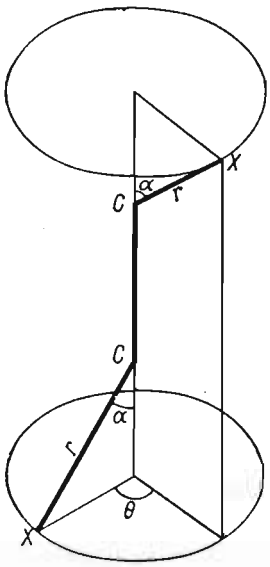

Fig. 1

The values used for calculation were: dipole moments of the groups: NO_2, C—Cl and C—H — 3.5 *D*, 1.8 *D* and 0.4, respectively. The angles α_N and α_{Cl} between the C—C axis and the vectors $r_N = CH_2\text{-}NO_2$ and $r_{Cl} = CH_2\text{-}Cl$ were calculated to be 63°53′ and 56°43′, respectively.

The dipole moments (μ) as a function of θ were calculated from the formula

(1) $$\mu = r \sin \alpha \sqrt{2-2\cos\theta}$$

Figs. 2 and 3 show the change of μ against θ.

As possible forms: *cis*, *trans*, *gauche* and "*perpendicular*" should be considered.

The calculated values may lead to different conclusions as regards the structure of 1,2-dinitroethane in solution:

(i) the substance may exist as a mixture of *gauche* and *cis* forms,

(ii) the substance may exist in a predominant "*perpendicular*" form, where $\theta = 90°$.

(iii) there may be free rotation of the nitro groups around the C—C axis. In this case $\cos \theta = 0$ and Eq. (1) would take the form:

$$\mu = r \sin \alpha \sqrt{2}. \tag{2}$$

This would give $\mu = 4.13$ *D*, a figure very near to the experimental value.

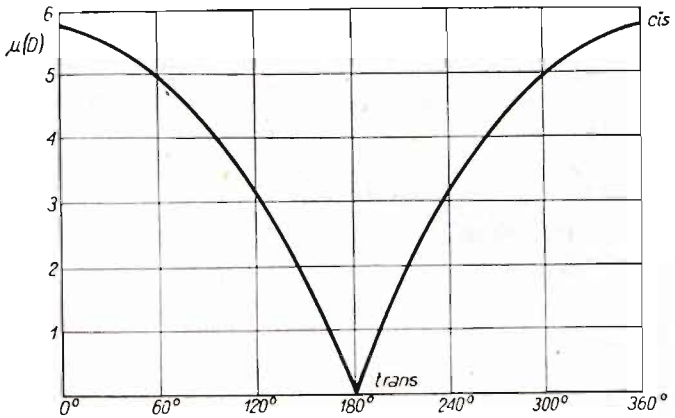

Fig. 2. Dipole moment of 1,2-dinitroethane as a function of θ

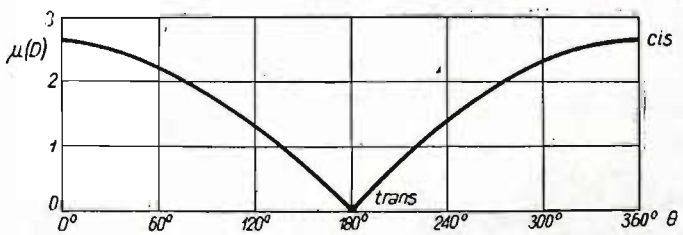

Fig. 3. Dipole moment of 1,2-dichloroethane as a function of θ

As regards (i) and (ii) the suggestion [7] should be borne in mind, that liquid ethylenediamine exists in *cis* form. This was based on examination of infrared spectra.

At present it is difficult to decide which of the three possible explanations is correct. However, it seems that the method of dipole moment calculation as reported in this paper may sometimes be a reliable tool for getting an insight into the rotational isomerism, as seen on the example of the values calculated for 1,2-dichloroethane (Fig. 3).

The known experimental value of the dipole moment of this compound ($\mu = 1.12$ D at 32°C [2]) corresponds to a high proportion (*c.* 70%) of the *trans* form and is in agreement with the existing views.

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