HETEROCYCLIC NITRO COMPOUNDS

IX.* DIPOLE MOMENTS OF 3(5)-NITRO-1,2,4-TRIAZOLES

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The dipole moments of some 3(5)-nitro-1,2,4-triazoles in dioxane were measured. Hydrogen is attached to the N_1 heteroatom in nitrogen-unsubstituted 3-nitrotriazoles. The dipole moments of the triazoles in chloroform are lower than in dioxane.

The dipole moments of 1,2,4-triazole and its derivatives were investigated in [2, 3].

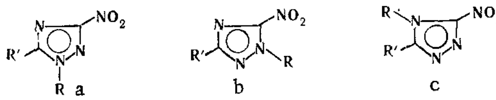
In the course of a study of nitro derivatives of 1,2,4-triazole we decided to measure the dipole moments of some 3(5)-nitro-1,2,4-triazoles in order to establish the position of the proton in heteronitrogen-unsubstituted nitro compounds and to clarify some problems ofthe interaction of nitrotriazole molecules with solvents.

The objects of the investigation were 3-nitro-1,2,4-triazole (I), 3-nitro-5-methyl-1,2,4-triazole (II), 1-methyl-3-nitro-1,2,4-triazole (IIIa), 1-methyl-5-nitro-1,2,4-triazole (IIIb), 4-methyl-3-nitro-1,2,4-triazole (IIIc), 1-methyl-3,5-dinitro-1,2,4-triazole (IV), and 1-methyl-3-nitro-5-chloro-1,2,4-triazole (V).

The dipole moments of dioxane solutions were measured. The experimentally found dipole moments of the investigated compounds were compared with the vectorially calculated values.

In the vector calculation of the dipole moments we used the method of calculation [3] from the magnitude and direction of the dipole moment of unsubstituted 1,2,4-triazole and the moment of the N-methyl group in the triazole. The moments of the nitro group, the C-methyl group, and chlorine were assumed to be the same as in [3]. It was also assumed that the direction of the vector of the dipole moment of the substituent coincided with the direction of the ring–substituent bond.

Tautomeric forms (a, b, and c) are possible as a function of the position of the hydrogen in the nitrogen-unsubstituted triazole derivatives. However, these compounds are known in one form.



I R = R′ = H; II R = H, R′ = CH_3; IIIa-c R = CH_3, R′ = H

To establish the location of hydrogen in I and II, we measured their dipole moments and compared them with the vectorially calculated values for tautomers a, b, and c (Table 1).

The experimentally determined dipole moments of nitrotriazoles I and II are closest to the calculated moments for structures a, which makes it possible to assign the structure of 1-H derivatives (Ia and IIa) to I and II. This assumption is also confirmed by the dipole moments of the corresponding N-methylnitrotriazoles (IIIa-c), which are close to the calculated moments of tautomeric forms Ia-c.

The satisfactory agreement between the experimental dipole moments of N-methyl-substituted nitrotriazoles and the values calculated on the basis of unsubstituted nitrotriazole attests to the absence of an

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* See [1] for communication VIII.

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TABLE 1. Comparison of the Experimental and Calculated Dipole Moments of Nitrotriazoles

Compound	Tautomeric form	Dipole moment	
		found	calculated
I	a	6,74	7,02
	b		3,52
	c		5,61
II	a	7,19	7,28
	b		3,57
	c		5,93
III	a	6,78	6,95*
	b	3,30	3,67
	c	5,96	5,80
IV	a	4,96	5,10*
V	a	6,05	5,98*

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* The experimental value of the dipole moment of I was used in the vector calculation of the moments of these compounds.

TABLE 2. Determination of the Dipole Moments of Nitrotriazoles

Compound	Solvent	α	β	$P_O = P_{tot} - (P_E + P_A)$	$P_E + P_A = P_D$	μ, D
I	Dioxane	50,40	−0,4877	951,88	21,90	6,74
II	Dioxane	51,98	−0,2593	1108,50	26,01	7,19
IIIa	Dioxane	45,15	−0,2511	966,70	28,02	6,78
	Chloroform	80,43	−0,1571	536,20	28,02	4,98
IIIb	Dioxane	11,10	−0,5016	248,64	28,36	3,30
	Chloroform	19,91	−0,1082	153,02	28,36	2,47
IIIc	Dioxane	35,20	−0,3115	754,60	28,40	5,96
	Chloroform	50,72	−0,1127	318,30	28,40	3,76
IV	Dioxane	17,97	−0,4031	534,25	32,28	4,96
	Chloroform	27,76	−0,1122	266,55	32,28	3,32
V	Dioxane	28,13	−0,3124	780,20	31,87	6,05
	Chloroform	52,00	−0,06907	428,10	31,87	4,40

appreciable "dioxane effect." Otherwise, the calculated dipole moments of IIIa, IV, and V would be considerably higher.

The results are in agreement with the data of an investigation of the acid-base properties of nitrotriazoles [4] and with the Charton assumption [5] that in aromatic nitrogen heterocycles with several nitrogen heteroatoms (which are capable of tautomeric transformations) the predominating tautomer is that which contains a proton on the heteroatom which is furthest removed from the electron-accepting substituent.

Substitution in the 5-position of the triazole ring has an appreciable effect on the dipole moment. As would be expected, the introduction into this position of an electron-donating substituent (methyl group) increases the dipole moment (compare I and II); electron-accepting substituents in the same position decrease the dipole moment (compare IIIa, IV, and V). A similar phenomenon was noted in [3].

As a consequence of the low solubility of the compounds in nonpolar solvents, the dipole moments of IIIa-c, IV, and V could also be determined in chloroform ($\varepsilon_{25} = 4.795$) in addition to dioxane. The dipole moments in chloroform were considerably lower than in dioxane (Table 2).

The decrease in the dipole moment of V in chloroform–dioxane mixtures with increasing chloroform content was linear, which indicates the absence of molecular compounds of V and the solvent.

A comparison of the IR spectra of chloroform solutions in carbon tetrachloride before and after the introduction of V did not indicate an appreciable shift in the band of the valence vibrations of the C−H bond of chloroform (3034 cm^{-1}) or a change in its intensity. No substantial changes in the absorption maxima and extinction coefficients were indicated in the UV spectra of solutions of V in dioxane and chloroform.

Thus, no indications of the presence of a direct interaction of the triazole ring with the hydrogen of the chloroform molecule could be obtained from the spectral data.

The decrease in the dipole moment for substituted nitrotriazoles in chloroform is apparently associated with the mutual orientation of the dipoles of the dissolved substance and solvent, which leads to partial compensation of the charges and, as a consequence, to a decrease in the polarization. Since we observed the same decrease for benzotriazole (the dipole moment in dioxane was 4.21 D compared with 3.33 D in chloroform) but did not observe a decrease, for example, in the case of acetophenone (the dipole moment in dioxane was 3.03 D compared with 2.96 D in chloroform), it is possible that this sort of interaction is specific for nitrogen heterocycles.

EXPERIMENTAL

The dipole moments of the nitro-1,2,4-triazoles were determined in dioxane and chloroform solution. The solvents were purified by the methods recommended in [6]. The synthesis of the compounds is described in [7-9].

The dielectric permeability (ε) of the solutions was determined by the beat method at 1 MHz with an accuracy of 0.1% with an IDM-2 meter (designed by the Kazan Aviation Institute).

The density of the solutions was determined in a 10-ml pycnometer with an accuracy of 0.0001 g/cm^3. The dipole moments were calculated via the method in [10] with the modification in [11].

The experimentally found R_D value for the appropriate crystalline nitro derivative of 1,2,4-triazole was taken for the values of the electronic and atomic polarizations ($P_E + P_A$). The latter was calculated from the refraction of a solution of the compound in dioxane according to the additivity rule from the expression

$$r_2 = \frac{r - r_1}{g_2} + r_1; \quad R_2 = M_2 \cdot r_2,$$

where r and r_1 are the specific refractions of the solution and solvent, respectively, g_2 is the weight fraction of dissolved substance, and M_2 is the molecular weight of the compound.

Special investigations, which we carried out for various crystalline aliphatic and heterocyclic nitro compounds, indicated that the accuracy of the determination of the molecular refraction for crystalline substances is not inferior to the accuracy of the determination for liquids when the methods in [12, 13] and improvements in the IRF-23 refractometer [14] are used.

The experimental data for the calculation of the dipole moments of the investigated compounds are presented in Table 2.

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