DIPOLE MOMENTS OF NITRO DERIVATIVES OF INDAZOLE

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The dipole moments of indazole and a number of its nitro derivatives in dioxane solution were measured. The directions of the vectors of the dipole moments of indazole in the tautomeric 1-H and 2-H forms were determined to solve the problems associated with the tautomerism and the position of the substituents in the molecules. The experimental values of the dipole moments of the investigated compounds were compared with the values calculated via a vector additive scheme. As a result it was shown that the mononitro and dinitro derivatives of indazole exist primarily in the 1-H tautomeric form, whereas the trinitro and tetranitroindazoles exist in the 2-H tautomeric form. The ratios of the isomers were calculated for compounds that have dipole moments intermediate between the 1-H and 2-H forms. A deviation between the experimental and calculated dipole moments of compounds containing two nitro groups in the ortho position was established; this may be explained by disruption of the coplanarity of the molecules or by deviation from additivity because of the introduction of strong electron-acceptor substituents.

Although the chemistry of indazole has been developed quite extensively [1, 2], not enough study has been devoted to the physicochemical properties of indazole derivatives. The literature does not contain data on the dipole moments of indazoles, except for indazole itself [3, 4] and 1- and 2-methylindazoles [4], whereas a study of the dipole moments may give valuable information regarding the structures of indazoles, the electron-density distributions in the molecules, and the effect of substituents on the ratios of the tautomers. To clear up these problems we measured the dipole moments of indazole (I) and a number of its nitro derivatives — 5-nitroindazole (II), 6-nitroindazole (III), 5,6-dinitroindazole (IV), 5,7-dinitroindazole (V), 1-methyl-5,6-dinitroindazole (VI), 2-methyl-5,6-dinitroindazole (VII), 3,5,7-trinitroindazole (VIII), 3,4,6-trinitroindazole (IX), 3,5,6-trinitroindazole (X), 2,3,5,6-tetranitroindazole (XI), and 1-(2,4-dinitrophenyl)-4,6-dinitroindazole (XII). The measurements were made in dioxane solutions at 25°C (Table 1). The experimental values of the dipole moment of indazole I in dioxane (1.75 D) and in benzene (1.85 D) are in satisfactory agreement with the values presented in the literature [3, 4].

The experimentally determined dipole moments of II-XII (Table 1) were compared with the dipole moments calculated via the vector additive scheme for the tautomeric 1-H and 2-H forms.

In contrast to imidazole derivatives [5], annelation of the benzene ring with the pyrazole ring has a substantial effect on the magnitude and direction of the dipole moment; this is apparent from a comparison of the experimental dipole moments of pyrazole and indazole (2.32 and 1.83 D, respectively [3, 4]). However, the computational schemes [6, 7] do not make it possible to detect these differences; when they are used, the calculated dipole moments of pyrazole and indazole turn out to be identical (about 2.3 D). In addition, the difference between the 1-H and 2-H tautomeric forms of indazole is disregarded, although the difference between the dipole moments of 1-methyl- and 2-methylindazoles is significant (1.5 D and 3.4 D, respectively) according to the experimental data [4]. In this connection, the experimental values of the dipole moments of 1- and 2-methylindazoles in conjunction with the group moments of the substituents introduced into the molecule were used for the calculations.

A comparison of the calculated dipole moments of compounds with "ideal" geometry (valence angles of 120° in the benzene fragment and 108° in the pyrazole fragment) with the

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TABLE 1. Dipole Moments of Nitroindazoles

Compound	Name	α	ν	MR, cm^3	P_{or}, cm^3	μ_{exp}, D	μ_{calc}, D	
							1-H	2-H
I	Indazole	5,33	0,67	36,1	62,99	1,75[a]	2,30[b]	3.26[c]
II	5-Nitroindazole	30,91	1,46	41,2	420,98	4,51	4,59	4,65
III	6-Nitroindazole	13,44	1,29	41,2	172,25	2,88	2,78	6,79
IV	5,6-Dinitroindazole	55,33	1,13	46,2	779,93	6,14	6,50	8,55
V	5,7-Dinitroindazole	16,57	1,33	46,2	214,50	3,22	2,87	6,79
VI	1-Methyl-5,6-dinitroindazole	60,34	1,00	50,2	854,20	6,43	6,70	—
VII	2-Methyl-5,6-dinitroindazole	116,25	1,37	50,2	1659,39	8,96	—	8,22
VIII	3,5,7-Trinitroindazole	18,53	1,66	51,2	237,17	3,39	3,69	3,53
IX	3,4,6-Trinitroindazole	67,70	1,31	51,2	955,89	6,80	7,50	4,26
X	3,5,6-Trinitroindazole	62,88	0,99	57,2	891,26	6,57	7,31	6,76
XI	2,3,5,6-Tetranitroindazole	9,28	1,87	56,3	99,09	2,19	—	2,22[d]
XII	1-(2,4-Dinitrophenyl)-4,6-dinitroindazole	21,62	2,11	79,9	271,78	3,62	5,45(a) 2,96(b)	—

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a) In benzene, 1.85 D. b) Calculation via the vector additive scheme [7]. c) Calculation with the experimental values of 2-methylindazole and VII. d) The N—NO_2 group moment is 4.2 D [10].

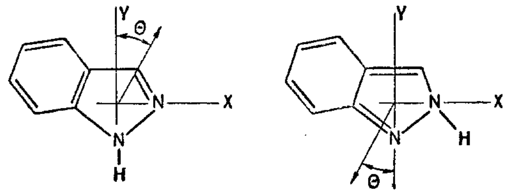


Fig. 1. Direction of the vectors of the dipole moments of the 1-H and 2-H tautomers of indazole.

moments calculated from the real structure of unsubstituted indazole [8] showed that these values differ only slightly (by no more than 0.2 D). The "ideal" structures were therefore subsequently used in the calculations.

The direction of the vector of the dipole moment (angle Θ, see Fig. 1) in the 1-H tautomeric forms was found from the experimental values of the dipole moments of indazole I and 5-nitroindazole II and the group moment of the nitro group (4.01 D) [9] from the vector addition formula. It was found that $\Theta = 38°27'$ for the 1-H tautomer of indazole. A similar calculation with the aid of the experimental value of the dipole moment of 6-nitroindazole III gave a close result ($\Delta\Theta = 1.5°$). The dipole moment of 2-methylindazole [4] (3.4 D) and the experimental value of the moment of 2-methyl-5,6-dinitroindazole VII ($\Theta = 37°15'$) were used for the tautomeric 2-H form in the calculation (Fig. 1).

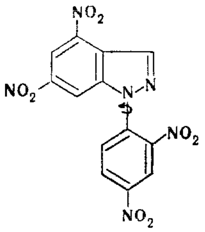
A comparison of the experimental dipole moments of indazole I and 1-methylindazole [4] shows that I exists in the tautomeric 1-H form in dioxane and benzene solutions.

It follows from the data presented in Table 1 that III and IV have 1-H tautomeric structures. The difference between the calculated dipole moments of the 1-H and 2-H forms is only slight for 5-nitroindazole II, and this does not enable one to draw a definite conclusion regarding its structure.

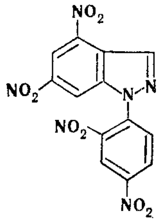
Compounds VIII and X have experimental dipole moments that are close to those calculated for the 2-H forms. This constitutes evidence in favor of their 2-H tautomeric structures.

The experimental dipole moments of V and IX are intermediate between the moments of the 1-H and 2-H forms. A 1-H to 2-H tautomer ratio of 17:1 was calculated for V, and a ratio of 2.8:1 was calculated for IX.

Appreciable deviations between the experimental and calculated dipolar moments are observed for IV, VI, and VII, which contain two nitro groups in the ortho position. From all



XII a



XII b

appearances, this is associated with disruption of the coplanarity of the molecules, but one also cannot exclude the possibility of deviations from additivity because of the introduction of strong electron-acceptor groups.

The dipole moment of 1-(2,4-dinitrophenyl) derivative XII is intermediate between the moments of the two conformers (a and b); this can be explained by rotation of the 2,4-dinitrophenyl fragment about the N^1—C bond at a certain angle, the value of which is about 60° relative to the plane of the indazole ring.

EXPERIMENTAL

The investigated compounds were synthesized by the methods in [11-18] and were recrystallized.

The dielectric permeabilities of the solutions were determined at 25 ± 0.01°C with a Tangens-M apparatus by the heterodyne method with an accuracy of 0.0001 at 1 MHz. The orientation polarization was calculated from the Hedestrand equation in the modification presented in [19, 20]. The molecular refractions were calculated from the group and bond refractions [21], and the atomic polarization was assumed to be 10% of the molecular refraction.

The dioxane was purified by known methods [22].

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