UDC 541.67 + 547.77

ELECTRON DENSITY DISTRIBUTION IN HETEROCYCLIC SYSTEMS WITH TWO VICINAL NITROGEN ATOMS. III*. DIPOLE MOMENTS OF SOME ALKYL, ARYL, AND NITRO PYRAZOLE DERIVATIVES

S. A. Giller, I. B. Mazheika, I. I. Grandberg

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 107-111, 1965

Dipole moments of 13 alkyl and aryl derivatives of pyrazole are determined. It is found that fundamentally it is the pyrazole ring that determines the values of these dipole moments. The phenyl group behaves as a weak electron donor with respect to the pyrazole ring. It is shown that under the action of powerful electron-accepting substituents, such as the nitro group, the electron cloud of the pyrazole ring is polarized toward the electron acceptor.

The preceding paper [1] gives the results of measuring the dipole moment of pyrazole (I). From the valence state of the nitrogen atoms in the molecule of I and X-ray measurements of its geometry [2] a vector calculation was made of the angle between the total dipole moment vector and the N — H bond (118° 15').

The present paper gives the dipole moments of a series of pyrazole derivatives and determines the interaction of substituents and pyrazole ring.

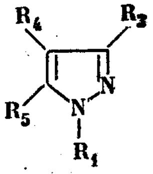
To determine the polarities of substituents in various positions in the pyrazole ring, vector calculations were made of their dipole moments from the dipole moments of pyrazole and the corresponding derivatives, using the above-mentioned direction for the total vector of the dipole moment of I and average values for the valence angles in this molecule, taken from [2]: $\sphericalangle 1 = 110^\circ$; $\sphericalangle 2 = 105{,}4^\circ$; $\sphericalangle 3 = 113{,}2^\circ$; $\sphericalangle 4 = 104^\circ$; $\sphericalangle 5 = 108{,}6^\circ$.

I

The dipole moments of alkyl and aryl pyrazoles show that, as with imidazole derivatives [3], the value of the dipole moment is mainly determined by the moment of the pyrazole ring itself.

TABLE 1

Dipole moments of pyrazole derivatives



Compound	R_1	R_3	R_4	R_5	μ, D
I	H	H	H	H	2.06
II	C_6H_5	H	H	H	2.00
III	CH_3	H	H	H	2.28
IV	H	C_6H_5(H)	H	H(C_6H_5)	2.26
V	CH_3	C_6H_5	H	H	2.30
VI	CH_3	H	H	C_6H_5	2.45
VII	H	C_6H_5	H	C_6H_5	2.30
VIII	H	CH_3	H	CH_3	2.31
IX	C_6H_5	C_6H_5	H	C_6H_5	2.47
X	C_6H_5	CH_3	H	C_6H_5	2.48
XI	p-$NO_2 \cdot C_6H_4$	H	H	H	4.40
XII	H	CH_3(Cl)	NO_2	Cl(CH_3)	5.92
XIII	p-$NO_2 \cdot C_6H_4$	CH_3	NO_2	Cl	2.97

Within the limits of experimental error, substitution of a phenyl group in position 1 does not alter the dipole moment for 1-phenylpyrazole (II) as compared with I, although the basicity of II is appreciably less than that of I [4].

---

*For Part II see [1].

TABLE 2

Data for determination of dipole moments of pyrazole derivatives

Compound	f, mole fraction	ε	d	P_{total}, cm³	MR, cm³	P_O, cm³	μ, D
II	0.000000	2.2740	0.8735	127.17	44.12	83.05	2.00
	0.001063	2.2807	0.8743				
	0.001692	2.2849	0.8749				
	0.005603	2.3057	0.8757				
	0.008048	2.3202	0.8760				
III	0.001844	2.2875	—	131.58	23.44	108.14	2.28
	0.002128	2.2895	0.8736				
	0.003506	2.2999	0.8737				
	0.003728	2.3009	0.8738				
	0.004733	2.3082	0.8740				
IV	0.001858	2.2864		151.47	44.86	106.61	2.26
	0.002893	2.2911	0.8746				
	0.003881	2.2968	0.8751				
	0.004945	2.2999	0.8755				
V	0.001260	2.2838	0.8740	158.15	47.94	110.21	2.30
	0.002348	2.2927	0.8743				
	0.003011	2.2968	0.8746				
VI	0.001255	2.2849	0.8740	172.64	47.94	124.70	2.45
	0.002492	2.2963	0.8744				
	0.004005	2.3082	0.8744				
VII	0.000902	2.2797	0.8743	176.57	66.82	109.75	2.30
	0.000997	2.2833	0.8741				
	0.001269	2.2844	0.8746				
	0.001555	2.2870	0.8746				
VIII	0.002758	2.2903	0.8739	139.54	28.10	111.44	2.31
	0.003423	2.2913	0.8738				
	0.004989	2.2966	0.8743				
	0.006702	2.3015	0.8744				
IX	0.001860	2.2922	0.8748	218.18	90.93	127.25	2.47
	0.002168	2.2942	0.8751				
	0.002444	2.2962	0.8759				
X	0.000709	2.2802		195.13	67.60	127.53	2.48
	0.001326	2.2864	0.8742				
	0.002429	2.2961	0.8743				
	0.002873	2.2997	0.8752				
XI	0.000514	2.2884	—	451.45	48.40	403.05	4.40
	0.000690	2.2926	—				
	0.000792	2.3003	0.8740				
	0.000899	2.2993	0.8743				
	0.004159	2.3880	0.8766				
XII	0.000738	2.3107	0.8744	762.81	34.11	728.70	5.92
	0.000993	2.3215	0.8747				
	0.001141	2.3291	0.8748				
	0.001159	2.3246					
XIII	0.001737	2.2900	0.8736	155.51	32.83	122.68	2.43
	0.002452	2.2936	0.8742				
	0.003298	2.2967	0.8750				
	0.004816	2.3127	0.8776				

Evidently the decrease in basicity is due to lengthening of the conjugated chain with consequent delocalization of the unshared electron pair of the nitrogen atom 2 at both rings. Here is possible that there is a definite shift of electron density toward the phenyl ring, which should to some extent cause a decrease in the dipole moment of II as compared with that of I. However, such a decrease in dipole moment is not confirmed experimentally (because of some association of molecules of I it may remain unchanged).

Substitution of a methyl group in position 1 leads to the dipole moment of compound III being somewhat greater than that of I. This increase can be explained by the electron-donor action of a methyl group and partial fission of hydrogen bonds existing between molecules of I. Vector calculation of the moment of the methyl group in compound III gives a value 0.41 D, close to that for the methyl group in toluene, 0.37 D.

A phenyl group in position 3 (5) has a more noticeable effect on the dipole moment than one in position 1. As is known, because of the rapid proton exchange between the two nitrogen atoms, it is impossible to differentiate between 3- and 5-substituted pyrazoles unsubstituted at a nitrogen atom. If the nitrogen atom at position 1 carries a substituent, such exchange is impossible, and the 1, 3- and 1, 5-disubstituted pyrazoles can be separated. It follows from the dipole moments of 1-methyl-3-phenylpyrazole (V) and 1-methyl-5-phenylpyrazole (VI) that a phenyl group at position 5 affects the dipole moment, but not one at position 3 (dipole moments of V and III are practically equal). The value of the dipole moment of the phenyl group in VI, as calculated vectorially, is 0.18 D, with the moment from the phenyl group to the pyrazole ring. Evidently an adjacent (vicinal), positively charged nitrogen atom at position 1 to some extent draws off the mobile π-electron cloud of the phenyl ring, although usually the phenyl group acts as a weak electron acceptor.

Substitution of a second phenyl group at position 3 in the molecule of IV does not alter the dipole moment (cf. compound VII).

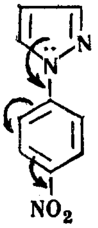
Phenyl and methyl groups at positions 3 and 5 have a similar effect on the dipole moment of the pyrazole ring (cf. compounds VII and VIII), although according to published results [4, 5] the phenyl groups in VII behave as electron acceptors, and the methyl groups in VIII as electron donors.

Introduction of a third phenyl group at position 1 leads to some rise in the dipole moment of 1, 3, 5-triphenylpyrazole (IX) as compared with 3, 5-diphenylpyrazole. When a Stewart-Brigleb model is made of molecule IX it is evident that, due to their large volumes, the coplanarity of the phenyl rings in positions 1 and 5 is disturbed.

The same departure from coplanarity is observed with 1, 5-diphenyl-3-methylpyrazole (X), and here replacement of a group at position 3 by a methyl group does not change the dipole moment of X from that of 1, 3, 5-triphenylpyrazole.

Taking the dipole moment of the p-nitrophenyl substituent in 1-p-nitrophenylpyrazole (XI) as 3.95 D, the dipole moment of the latter as calculated vectorially is 2.36 D. The experimental value is 4.40 D.

The much greater difference between the calculated and the observed dipole moment is attributable to the very high polarizability of the pyrazole ring under the action of a powerful electron acceptor. This powerful polarizability is also observed with the imidazole ring under the action of the p-nitrophenyl substituent [6]. In molecule XI the polarization of the pyrazole ring is so great that the center of negative charge travels towards the nitrophenyl substituent, and the dipole moment of the pyrazole ring changes direction toward the nitro group.



XI

A large dipole moment is also observed with 3(5)-chloro-4-nitro-5(3)-methylpyrazole (XII). Obviously, with this compound too, there is strong polarization with a shift of electron density toward the nitro group, i.e., on moving from XI to XII the direction of the pyrazole ring dipole moment changes.

In the molecule of 1-p-nitrophenyl-3-methyl-4-nitro-5-chloropyrazole (XIII), with two nitro groups opposite one another, such polarization is diminished, and so the dipole moment of XIII is considerably less.

All measurements were made in benzene solutions at 25°. The experimental method and purification of the benzene were previously described in [7].

REFERENCES

1. S. A. Giller, I. B. Mazheika, and I. I. Grandberg, KhGS, no. 1, 103, 1965.

2. W. W. Ehrlich, Acta Cryst., 13, 946, 1960.
3. V. I. Minkin, O. A. Osipov, A. D. Garnovskii, and A. M. Simonov, ZhFKh, 36, 470, 1962.
4. I. I. Grandberg, A. N. Kost, ZhOKh, 32, 1556, 1962.
5. I. I. Grandberg, ZhOKh, 33, 504, 1963.
6. O. A. Osipov, A. M. Simonov, V. I. Minkin, and A. D. Garnovskii, ZhFKh, 36, 1466, 1962.
7. I. Mazheika, L. Avota, G. Sokolov, and S. Giller, ZhOKh, 34, 3380, 1964.

15 October 1964

Institute of Organic Synthesis AS Latvian SSR, Riga
Lomonosov Moscow State University