ELECTRON DENSITY DISTRIBUTION IN HETEROCYCLIC SYSTEMS WITH TWO ADJACENT NITROGEN ATOMS

VI. Dipole Moments of Some Bispyrazole Systems and Multicondensed Systems Containing the Pyrazole Ring*

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Dipole moments found are compared with those calculated vectorially. Bis(3,5-dimethylpyrazol-4-yl) has a constant dipole moment, which indicates inequality of nitrogen atoms in the pyrazole ring. Dipole moments of condensed pyrazolopyridines can be found by adding vectorially the dipole moments of pyridine and pyrazole. Involvement of a nitrogen atom and formation of two aromatic rings does not significantly alter the dipole moment of pyrazolo[2,3-a]pyridine as compared with pyrazole.

The present work is devoted to elucidating the configurations of molecules of some bicyclic systems containing the pyrazole ring. In addition, the distribution of charges in condensed pyrazolepyridines is considered.

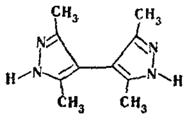
We previously studied the dipole moment of pyrazole and its derivatives [1–3]. The method used to determine the dipole moments is given in [4]. All measurements were made at 25°.

Table 1 gives the results of measuring the dipole moments of compounds I–IX.

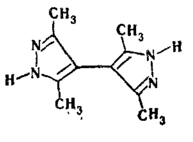
The values of the dipole moment found by experiment were compared with those calculated vectorially. In the calculations the dipole moment of pyrazole was taken as 2.06 D, and the angle relative to the N—H bond as 118°15' [2]. The dipole moment of the pyridine ring is 2.20 D [5], of the furan ring 0.71 D [5], in both cases the moment being directed from the heteroatom towards the center of the ring. The sulfur valence angle is taken as 105°, and the C_{ar}—S bond has dipole moment 1.2 D [6].

Some problems relating to the structures of compounds I–IX can be settled by comparing experimental and vectorially calculated dipole moments.

The molecule is bis(3,5-dimethylpyrazol-4-yl) (I) can exist as the cis and trans configurations (Ia and b).



Ia



Ib

The experimental dipole moment of I is 3.54 D, while vector addition gives a value of 4.10 D for Ia, and 0 for Ib. This obviously shows that coplanarity of the two rings is destroyed because of the large volumes of the spatially close methyl groups.

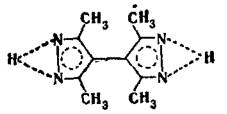
Table 1
Dipole Moments of Pyrazole Derivatives

Compound	Compound	μ, D
I	Bis(3,5-dimethylpyrazol-4-yl)	3.54
II	3(5)-Phenyl-5(3)furyl-2-pyrazole	2.60
III	Bis(1-phenylpyrazol-4-yl)sulfide	3.15
IV	Bis(1,3,5-trimethylpyrazol-4-yl)sulfide	3.52
V	Bis(1-phenylpyrazol-4-yl)-sulfone	5.23
VI	1-Phenylpyrazolo[3,4-b]pyridine	4.29
VII	1-Phenylpyrazolo[4,5-b]pyridine	2.03
VIII	Pyrazolo[2,3-a]pyridine	2.15
IX	4-Bromopyrazolo[2,3-a]pyridine	2.44

For the cis configuration Ia the angle θ through which the two rings are turned relative to one another, as calculated from the formula $\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta$, is 58° 40'.

According to [7, 8], the hydrogen atom in pyrazole is not fixed to one nitrogen atom, but linked with both.

We pointed out in [1] that the dipole moments of symmetrically substituted pyrazole indicate that the hydrogen atom in these compounds is fixed to one nitrogen atom. The dipole moment of bis(3,5-dimethylpyrazol-4-yl) is 3.54 D, and also indicates the location of the hydrogen atom on one nitrogen atom. If the hydrogen atom is considered to be linked to both nitrogen atoms in the ring, the molecule of bis(3,5-dimethylpyrazole-4-yl) has a center of symmetry (Ic), when its dipole moment must be zero, which does not correspond to the experimentally found value.



Ic

Unlike I, the molecule of 3(5)-phenyl-5(3)-furyl-2'-pyrazole (II) does not exhibit steric hindrance, destroying the uniplanarity of the molecule. This compound can have 4 configurations, due to the exchange of the hydrogen between N-1 and N-2, and on account of rotation of the furan ring around the C-5—C-2 bond.

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*For Part V see [1].

Table 2
Experimental Dipole Moment Data

Compound	Solvent*	*f*, mole fraction	ε	*d*	P_{total}, cm³	*MR*, cm³	$P_{or.}$, cm³	μ, *D*
I	d	0.001741	2.2484	1.0306	314.43	54.14	260.28	3.54
		0.001030	2.3641	1.0304				
		0.000831	2.2312	1.0302				
		0.000820	2.2311	1.0301				
II	d	0.001551	2.2415	1.0306	201.66	61.30	140.36	2.60
		0.001046	2.2376	1.0303				
		0.000913	2.2368	1.0300				
		0.000862	2.2363	1.0299				
		0.000469	2.2337	1.0299				
III	d	0.000764	2.2275	1.0305	301.26	94.11	207.15	3.15
		0.000502	2,2255	1.0303				
		0.000498	2.2197	1.0302				
		0.000366	2.2171	—				
IV	d	0.001614	2.2349	1.0312	329.21	71.62	257.59	3.52
		0.001437	2.2345	1.0314				
		0.001030	2.2317	1.0311				
		0.000939	2.2281	1.0310				
V	d	0.000579	2.2375	1.0314	665.22	96.39	568.83	5.23
		0.000315	2.2260	1.0309				
		0.000288	2.2241	1.0308				
VI	b	0.001329	2.3136	0.8749	444.86	56.59	386.27	4.29
		0.000949	2.3005	0.8744				
		0.000781	2.2959	0.8747				
		0.000564	2.2886	0.8746				
VII	b	0.002973	2.2918	0.8752	143.95	57.89	86.06	2.03
		0.002560	2.2909	0.8749				
		0.002492	2.2886	0.8747				
VIII	b	0.002940	2.2958	0.8744	131.00	34.68	96.32	2.15
		0.002205	2.2875	0.8743				
		0.001433	2,2839	—				
IX	b	0.002427	2.3012	0.8762	166.74	42.39	124.35	2.44
		0.001883	2.2907	0.8755				
		0.001632	2.2883	—				
		0.000000	2.2740	0.8734				

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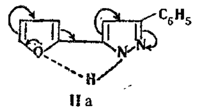
*d = dioxane, b = benzene

The calculated dipole moments are:

cis-3-phenyl-5-furylpyrazole	(IIa)	2.25 D
trans-3-phenyl-5-furylpyrazole	(IIb)	2.48 D
cis-3-furyl-5-phenylpyrazole	(IIc)	2.06 D
trans-3-furyl-5-phenylpyrazole	(IId)	1.50 D

The experimental dipole moment of the II molecule is 2.60 D, somewhat greater than any of the calculated values, but closest to that found for structures **IIb** and **IIa.** So structure IIa is most probable, since it can be stabilized by formation of an intermolecular hydrogen bond between the oxygen of the furan ring and the hydrogen of the NH group of the pyrazole ring.

The observed difference of 0.35 D between the found and calculated dipole moments of structure IIa is probably due to shift of electrons from the furan ring towards the pyrazole one. This is confirmed by the experimental dipole moments being higher than the calculated ones for pyrazole derivatives with +C substitutents at position 3 or 4 [1].

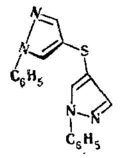


IIa

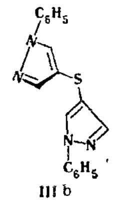
Planar structures are impossible for bis (1-phenylpyrazol-4-yl) sulfide (III), since according to [5] the valence angle in aromatic sulfides is only 105°, and must be about the same in compounds III and IV. In III the separation of the pyrazole rings is too small to give a planar molecule.

According to the data of [6, 9], one of the phenyl rings of aromatic sulfides is in the plane of the C—S—C bonds, and the other is perpendicular to it. Assuming the disposition of the pyrazole rings to be the same in III, vector calculations were made of the two possible rotational isomers IIIa and IIIb.

The experimentally found dipole moment of III is 3.15 D, an average of the two calculated values (μIIIa = 3.72 D, μIIIb = 2.26 D), and close to the dipole moment of a mixture containing equimolecular concentrations of the two forms IIIa and IIIb



IIIa

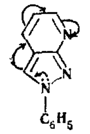


IIIb

The dipole moment of the mixture is calculated from the formula [10] $\mu^2 = c_1\mu_1^2 + c_2\mu_2^2$, where μ_1 and μ_2 are the dipole moments of IIIa and IIIb, c_1 and c_2 are the concentrations of IIIa and IIIb (mole fractions). It is 3.08 D. The results do not, however, make it possible to decide definitely that III is a mixture of **IIIa** and **IIIb**, since the possibility of rotation of the pyrazole rings around the C–S bond, or formation of an additional interaction dipole moment due to the involvement of the free d orbitals of the sulfur atom in conjugation with the pyrazole rings are not excluded.

The dipole moment of bis(1,3,5-trimethylpyrazol-4-yl) sulfide (V) is 3.52 D, and greater by 0.37 D than the dipole moment of III. This can be explained by displacement of electron density from the methyl group to the sulfur atom.

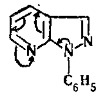
The dipole moment of 4.13 D calculated for the 1-phenylpyrazolo[3,4-b]pyridine (VI) molecule, is 0.16 D less than the experimental value. Obviously, the reason for the increase in the experimental value of the dipole moment of VI compared with the theoretical value is the increase in negative charge on the nitrogen atom of the pyridine ring, due to interaction with the N-1 nitrogen atom via the chain of conjugated bonds.



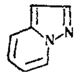
VI

We showed [1] that when a –C substituent was present at position 4, the experimental dipole moment of the molecule is greater than the calculated one. Precisely the same thing is found with 1-phenylpyrazolo[3,4-b]pyridine (VI), where the pyridine ring can be regarded as an electron-accepting substituent.

A similar thing is found with the 1-phenylpyrazolo[4,5-b]pyridine (VIII) molecule. There the experimental dipole moment, 2.03 D, is greater than the calculated one, 1.63 D, by 0.40 D.



VII



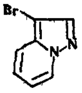
VIII

The dipole moment of pyrazolo[2,3-a]pyridine (VIII), 2.15 D, is close to those for pyrazole 2.06 D [2] and 1-methylpyrazole 2.28 D [3].

Obviously, this is due to the valence state of the nitrogen atoms just as the degree of participation of their unshared electron pairs in the formation of an aromatic system of π electrons is the same in the pyrazole molecule as in the pyrazolo[2,3-a]pyridine (VIII) one.

Ten π electrons are needed to form the aromatic system of the molecule VIII. Each carbon atom and N-2 nitrogen atom supples one π electron, due to its valence electron. The N-1 nitrogen atom contributes two π electrons from its unshared electron pair. Like pyrazole [2], the N-1 nitrogen atom in the VIII molecule has fractional positive charge due to the extension of its unshared electron pair, while the N-2 nitrogen atom, whose unshared electron pair does not participate in conjugation, has a fractional positive charge. The vectorial calculation of the value and direction of the dipole moment of VIII is similar to that for pyrazole [2].

To confirm that the reported agreement between the dipole moments of pyrazole and VIII was not fortuitous, and that there is no substantial change in charge distribution in the molecule on formation of a condensed system with a nitrogen atom common to the two rings, we measured the dipole moment of 4-bromopyrazolo[2,3-a]pyridine (IX).



IX

It was found to be 2.44 D, close to the value 2.28 D [1] found for 1-phenyl-4-bromopyrazole.

Hence the dipole moment of pyrazolo[2,3-a]pyridine differs little, either in value or direction, from that of pyrazole.

Thus from what has been said it can be concluded that vectorial calculation can be used to determine expected dipole moments for the condensed ring systems of pyrazolopyridines, including systems with a nitrogen atom common to both rings.

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