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ELECTRON DENSITY DISTRIBUTION IN HETEROCYCLIC SYSTEMS WITH TWO VICINAL NITROGEN ATOMS. II*. PYRAZOLE DIPOLE MOMENTS

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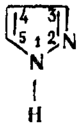
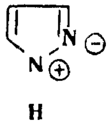
The dipole moment of pyrazole is determined and found to agree well with that calculated vectorially. From vector calculation the angle between the dipole moment and the N—H bond is found to be 118° 15'.

Previous papers [1] have dealt with the dipole moments of pyridazine derivatives. In the present paper these are compared with the data for 5-membered heterocyclic rings also with two vicinal nitrogen atoms, the prototype being pyrazole. The dipole moment of pyrazole was determined by the heterodyne beat method and compared with the values given in the literature. Its direction was also determined.



I

II



III

By analogy with imidazole and its derivatives [2], it is to be expected that the pyrazole ring will exhibit appreciable polarizability and change in the direction of the moment with a polarizing substituent.

For this reason it appeared impossible to calculate the direction of the dipole moment of pyrazole (I) from the experimentally determined moments of pyrazole itself and some derivative, using a known value of the moment of the substituent.

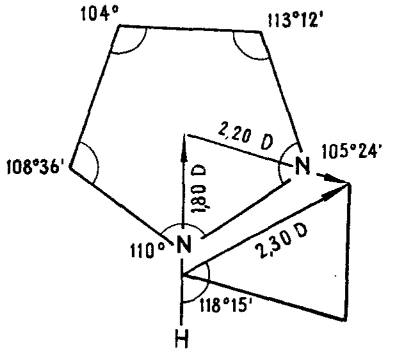
Hence the experimentally determined value of the dipole moment was compared with that calculated vectorially, and from this the direction of the total dipole moment of the molecule was established.

In making the calculation the following assumptions were made:

1. The nitrogen atom in position 1, forming two endocyclic and one exocyclic σ-bonds, like the nitrogen atom in pyrrole, puts its unshared electron pair into the aromatic sextet of the ring and has a fractional positive charge. The dipole moment depending on the presence of a nitrogen atom in position 1 is taken equal to the dipole moment of pyrrole (1.80 D), with direction from the nitrogen atom to the center of the ring.

2. The nitrogen atom in position 2, forming two endocyclic σ bonds, puts its third valence electron into the aromatic sextet of the molecule. The unshared electron pair in the aromatic sextet does not participate. Thus, in I, nitrogen atom 2, like the nitrogens in pyridine and pyridazine, has a fractional negative charge. The dipole moment depending on nitrogen atom 2 is assumed equal to the moment of pyridine (2.20 D), with direction from the center of the ring to the nitrogen atom.

3. In accordance with X-ray investigations, the molecule I is regarded as a planar pentagon with average values for the angles as shown in the figure.



Valence angles and distribution of vector components of the dipole moment of pyrazole

4. By contrast with [3], the N—H bond is assumed coplanar with the ring, since the configuration of the hydrogen atom cannot be determined precisely by X-rays; and electron diffraction data, which are more useful in this connection, indicate coplanarity of ring and N-methyl group in pyrrole and tetrazole derivatives [4, 5].

Calculation of the dipole moment of the pyrazole molecule, carried out in this way, gives a value 2.38 D, and 118° 15' for the angle between the dipole moment and the N—H bond.

According to the literature data the dipole moment of I in benzene at 20° is 1.46 D [6], 1.57 D at 25° [7], while in dioxane it is 2.19 D at 20° [6].

The experimental value of the dipole moment of I now found at 25° in benzene is 2.06 D, and in dioxane 2.33 D. Because the dipole moment is so low, Hückel's hypothesis that I has an ion-dipole structure, (II or III [6, 8]), is

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* For Part I see [1].

excluded. The authors of [7] also express doubt about this. The dipole moment in benzene is somewhat lower than in dioxane, and evidently this is due to some molecular association caused by hydrogen bonding.

The present experimental value of the dipole moment of I in benzene is appreciably greater than that given in the literature [6-8]. This may be due to association of molecules of I through hydrogen bonding, leading to formation of cyclic dimers and trimers. Such association is greatly dependent on concentration, as is shown by IR spectroscopy [9] and cryoscopic molecular weight determinations [6]. In more concentrated solution ($f = 0.044 - 0.66$ [7] or $f = 0.092 - 0.11$ [6]), such association can lower the value of the dipole moment found. The present work was done at concentrations $f = 0.0026 - 0.0057$. Furthermore, one of the measurements was repeated at a concentration close to that stated in [7], and similar results were obtained.

The value found for the dipole moment of I in dioxane agrees, within the limits of experimental error, with that calculated vectorially. Possibly the close agreement is to a certain extent fortuitous, since the following simplifications are made:

1) The moment due to nitrogen atom 2 is assumed equal to the moment of pyridine, although in a 6-membered ring there must be a different distribution of charges on the carbon and nitrogen atoms determining the value of the dipole moment. Furthermore, in the pyridine molecule the valence angle at the nitrogen atom is equal to 117° [10], but the corresponding angle at nitrogen atom 2 in the molecule of I is 105.4° [3]. This should not greatly affect the value of the dipole moment, since basically a change of valence angle somewhat alters the σ moment, which, according to M.O. calculations [11], is the smaller part of the total moment.

2) The mutual interaction of the two nitrogen atoms is not evaluated.

3) The unequal distribution of electron density at the carbon atoms is not taken into account, since the fractional positive charge at carbon atom 4 is less than at the other two carbon atoms. This is indicated by the relative reactivity of that carbon atom in electrophilic attack [12-14].

Dipole moment determination data for pyrazole at 25°

Solvent	f, mole fractions	ε	d	P_{total} cm^3	MR, cm^3	P_O, cm^3	μ, D
Dioxane	0.005599	2.2762	1.0245	132.83	18.98	113.85	2.33
	0.005525	2.2715	1.0244				
	0.003719	2.2617	—				
	0.002787	2.2580	1.0247				
	0	2.2352	1.0243				
Benzene.	0.005651	2.3037	0.8746	107.09	18.98	88.11	2.06
	0.004496	2.2964	0.8740				
	0.003142	2.2912	0.8739				
	0.002664	2.2876	—				
	0	2.2740	0.8735				
	0.051571	2.4223	0.8803	60.73			
	0.05400	2.4456	0.8816	63.42			

Despite these simplifications, the calculated value of the dipole moment for pyrazole agrees well with that found experimentally. It is important to note that the angle of the dipole moment relative to the N—H bond, as found by calculation, is in good agreement with the value 116° 30' found for this angle by the method of M.O.s [15].

Thus, using the method given here, it is possible to calculate with sufficient accuracy, to a first approximation, the value and direction of the dipole moment of pyrazole.

EXPERIMENTAL

The method of measurement and purification of the benzene is similar to that described elsewhere [1].

The acetal impurity in dioxane was removed by refluxing for 7 hr with 1 N hydrochloric acid, while air was bubbled through the liquid. Peroxides were then removed by shaking with stannous chloride. Next, the dioxane was treated with KOH, and the water layer separated. After drying over potassium hydroxide, the dioxane was distilled, twice partly frozen, and dried and twice distilled over sodium. The purified dioxane was stored over sodium in the dark.

Pyrazole was synthesized by Jones's method [16], and purified by two vacuum distillations (m.p. 70°).

Total polarization was calculated by Hedestrand's method. The sum of the electronic and atomic polarizations was assumed equal to MR_D.

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REFERENCES

1. I. Mazheika, L. Avota, G. Sokolov, and S. Giller, ZhOKh, 34, 3380, 1964.
2. O. A. Osipov, A. M. Simonov, V. I. Minkin, and A. D. Garnovskii, ZhFKh, 36, 1466, 1962.
3. H. W. W. Ehrlich, Acta. Cryst., 13, 946, 1960.
4. L. V. Vilkov, P. A. Akishin, and V. M. Presnyakova, ZhSKh, 3, 5, 1962.
5. J. H. Bryden, Acta. Cryst., 9, 874, 1956.
6. W. Hückel, J. Datow, and E. Simmersbach, Z. phys. Chem., 186A, 129, 1940.
7. K. A. Jensen, A. Friediger, Kgl. Danske Videnskab. Selskab. Math.-fys. Medd., no. 20, 20, 1943.
8. W. Hückel, W. Jahnentz, Ber., 74, 652, 1941.
9. D. M. W. Anderson, J. L. Duncan, and F. J. C. Rosotti, J. Chem. Soc., 140, 1961.
10. J. R. de la Vega, H. F. Hameka, J. Am. Chem. Soc., 85, 3504, 1963.
11. A. J. Owen, Tetrahedron, 14, 237, 1961.
12. Heterocyclic Compounds [Russian translation], vol. 5, IL, Moscow 1961.
13. I. I. Grandberg, L. I. Gorbacheva, and A. N. Kost, ZhOKh, 33, 511, 1963.
14. I. I. Grandberg, L. I. Gorbacheva, A. N. Kost, and D. V. Sibiryakova-Fedotova, ZhOKh, 33, 515, 1963.
15. R. D. Brown, M. L. Heffernan, Austr. J. Chem., 13, 49, 1960.
16. R. Jones, J. Am. Chem. Soc., 71, 3997, 1949.

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