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# CHEMISTRY

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chemical structural formulas labeled (I), (II), and (III)

Figure 1: chemical structural formulas labeled (I), (II), and (III)

## Abstract

## Full Text

*CHEMISTRY*

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# DIPOLE MOMENTS OF IMIDAZOLE AND ITS DERIVATIVES

*(Presented by Academician M. M. Shemyakin, 14 XII 1960)*

The classical structural formula of imidazole (I) does not explain the large values of the dipole moments of its derivatives, which, according to data from a number of authors, vary within the range 3.6–6.2 D. Hückel, Datow, and Zimmerbach (1) determined the dipole moments of imidazole and 4-methylimidazole in nonpolar solvents and assigned to them values of 6.2–4.8 D. The authors came to the conclusion that the structure of imidazole corresponds to the structure of a bipolar ion (II), the positive center of which is concentrated on the immonium nitrogen, while the negative center, as a result of delocalization of charge over the ring, is located at the center of the five-membered cycle. The calculated dipole moment of such a structure is 5.5 D and agrees satisfactorily with the experimental data.

However, the much lower value of the dipole moment of N-methylimidazole (3.6-3.8 D), the data of Jensen and Fridiger (2) on the determination of the dipole moments of imidazole (3.84 D) and benzimidazole (3.98 D), of Syrkin and Shott-L' vova (3) (4.08 D), as well as calculations by the method of molecular orbitals (4), are in poor agreement with the amphionic structure of imidazole.

An original interpretation of the structure of benzimidazole derivatives in solutions was proposed by L. S. Efros and B. A. Porai-Koshits (5), who assumed the possibility of formation of intermolecular ionic compounds (III)

In connection with the foregoing, it seemed of interest to verify the data of various authors (1-3) on dipole moments and to discuss certain questions concerning the fine chemical structure of imidazole and its derivatives.

In our experiments, the dielectric permittivity of dioxane solutions was measured by the resonance method in combination with the substitution method at 25° and with imidazole concentrations from 0.002 to 0.02 mole fraction. The electronic polarization was calculated from the sum of bond refractions; atomic polarization was not taken into account. The detailed measurement procedure has been described previously ($^6$).

Table 1 contains the data obtained on the dipole moments of a series of imidazole derivatives, as well as of N,N′-diphenylformamidine (IV).

The data of Table 1 show that the magnitude of the dipole moment of the imidazole ring determines the values of the moments of its derivatives containing weakly polar substituents. At the same time, the character of the carbocyclic nuclei condensed with imidazole does not exert a substantial influence

the value of the moment, to which, according to our measurements and the data of other authors ($^{2,3}$), a value of approximately 4 D may be assigned. This value characterizes the polarity of the imidazole ring as a whole and is not determined by the moment of the —NH—CH=N—grouping, as is shown by the value 2.20 D obtained by us for the dipole moment of N,N′-diphenylformamidine (IV), in good agreement with that calculated according to the vector-additive scheme.

**Table 1**

| No. | Substance | $P_\infty$, cm$^3$ | $P_{el}$, cm$^3$ | $\mu$, D |
|---|---|---|---|---|
| 1 | Imidazole | 349.0 | 17.95 | 3.99 |
| 2 | 4,5-Diphenylimidazole | 438.9 | 66.20 | 4.34 |
| 3 | N-ethyl-4,5-diphenylimidazole | 427.0 | 75.69 | 4.11 |
| 4 | Benzimidazole | 374.2 | 34.74 | 4.03 |
| 5 | N-methylbenzimidazole | 380.4 | 39.58 | 4.04 |
| 6 | 5, 6, 7, 8-Tetrahydrobenzimidazole | 354.8 | 34.48 | 3.98 |
| 7 | Naphtho-(1,2)-imidazole | 398.4 | 51.53 | 4.12 |
| 8 | 3-Methylnaphtho-(1,2)-imidazole | 360.3 | 56.37 | 3.86 |
| 9 | 1-Ethylnaphtho-(1,2)-imidazole | 394.4 | 61.02 | 4.04 |
| 10 | N-ethylphenanthreno-(9,10)-imidazole | 424.0 | 77.81 | 4.11 |

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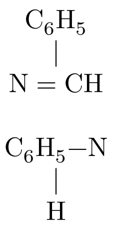
| No. | Substance | $P_\infty$, cm$^3$ | $P_{\text{el}}$, cm$^3$ | $\mu$, D |
|---|---|---|---|---|
| 11 | 5 (6)-Nitrobenzimidazole | 765.1 | 40.43 | 5.95 |
| 12 | N,N′-Diphenylformamidine | 160.3 | 60.93 | 2.20 |

The observed values of the dipole moments of imidazole derivatives do not agree with assumptions of complete ionization of the imidazole ring (II), and also contradict the concept of the existence of acid-base interaction leading to the formation of an intermolecular ionic compound (III).

The dipole moments of compounds of type (III) are quantities on the order of 14–19 D (7). Moreover, with such a structure of imidazole and benzimidazole derivatives, one would have to expect greater differences between the moments of nonalkylated and alkylated compounds, since the latter, lacking a mobile hydrogen, are incapable of such salt formation. The results given in Table 1 show that the dipole moments of alkylated and nonalkylated imidazole derivatives almost coincide.

Thus, neither the classical structural formula of imidazole (I), nor the structure of an internal salt (II) or of an intermolecular ionic compound (III), explains the values of the dipole moments of imidazole derivatives. The anomalously large values of the moments of imidazole and 4-methylimidazole reported by Hückel (1,8) may apparently be attributed to the fact that in the cited works measurements were made on excessively concentrated solutions, as a result of which it was not possible to avoid superposition of the association effect.

The deviation of the experimentally found values of the dipole moments from the additive values is explained by polarization of the imidazole ring in the direction of the C=N bond (V), although the degree of polarization is far from the formation of an ionic structure.



$$\begin{array}{c} C_6H_5 \\ | \\ N = CH \\ \\ C_6H_5{-}N \\ | \\ H \end{array}$$

(IV)

imidazole ring structure
with polarization toward the C=N bond

(V)

The direction of the moment of the imidazole ring can be determined from the values of the dipole moments of 5-(6)-nitrobenzimidazole (5.95 D), imidazol-

of the ring and the nitro group (3.95 D). The angle $\theta$ between the directions of the moments of the nitro group and the imidazole ring is

$$\theta = \mathrm{Arc}\cos\frac{\mu^2 - \mu^2_{\mathrm{NO_2}} - \mu^2_{\mathrm{im}}}{2\mu_{\mathrm{NO_2}}\mu_{\mathrm{im}}} = 9^\circ.$$

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*Note: Figure translations are in progress. See original paper for figures.*

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