A STUDY OF NITROGEN-CONTAINING BISHETEROCYCLIC SYSTEMS

V*. DIPOLE MOMENTS AND THE CONFORMATION OF ARYLIMIDAZOLES

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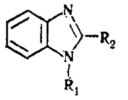
The dipole moments of N- and C-aryl and N- and C-furyl derivatives of imidazole and benzimidazole have been determined. A comparison of the dipole moments of the aryl derivatives found experimentally and calculated vectorially has shown they have a nonplanar structure. Conversely, derivatives of 2-(α-furyl)-4,5-diphenylimidazole contain a planar bicyclic fragment. The hypothesis is put forward that the conformation of the bicyclic compounds studied is determined by a combination of steric and electronic factors.

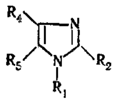
It has been shown [2, 3] that in solution conjugated bicyclic systems have a nonplanar configuration due to the rotation of the nuclei around the single C–C or C–N bonds, which possess a certain degree of double-bond character. It appeared of interest to study the conformation of 1- and 2-aryl and 1- and 2-furyl derivatives of imidazole and benzimidazole in solution in connection with their electronic structure and steric factors.

To solve the problem posed, the dipole moments of compounds I-XVIII were determined experimentally (μ_{exp}) and were calculated (μ_{calc}) by the vectorial scheme.



I-III, XV, XVI

I $R_1 = H$, $R_2 = m\text{-}C_6H_4NO_2$;
II $R_1 = C_2H_5$, $R_2 = m\text{-}C_6H_4NO_2$;
III $R_1 = H$, $R_2 = o\text{-}C_6H_4NO_2$;
XV $R_1 = m\text{-}C_6H_4NO_2$, $R_2 = H$;
XVI $R_1 = o\text{-}C_6H_4NO_2$, $R_2 = H$



IV-XIV, XVII, XVIII

IV-XIV $R_1 = H$;
IV-XII $R_4 = R_5 = C_6H_5$;

IV $R_2 = m\text{-}C_6H_4NO_2$; V $R_2 = H$;
VI $R_2 = C_6H_5$; VII $R_2 = p\text{-}C_6H_4CH_3$;
VIII $R_2 = p\text{-}C_6H_4NO_2$; IX $R_2 = p\text{-}C_6H_4N(CH_3)_2$;
X $R_2 = p\text{-}C_6H_4Br$; XI $R_2 = p\text{-}C_6H_4OCH_3$;
XII $R_2 = \alpha\text{-}C_4H_3O$;
XIII $R_2 = \alpha\text{-}C_4H_3O$, $R_4 = C_6H_5$, $R_5 = p\text{-}C_6H_4CH_3$;
XIV $R_2 = \alpha\text{-}C_4H_3O$, $R_4 = C_6H_5$, $R_5 = p\text{-}C_6H_4OC_2H_5$;
XVII $R_1 = m\text{-}C_6H_4NO_2$, $R_2 = R_4 = R_5 = H$;
XVIII $R_1 = o\text{-}C_6H_4NO_2$, $R_2 = R_4 = R_5 = H$

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*For Communication IV, see [1].

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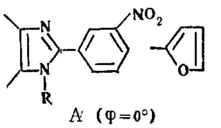
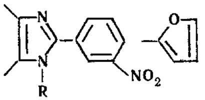
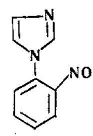
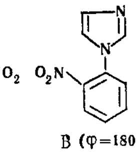
The calculation of the dipole moments of compounds I-XIV was performed as described previously [2] using the value of μ_{exp} of compound VI and its methyl derivative VII. The dipole moments of compounds XV-XVIII were calculated on the basis of MO data taking into account the π-moment of the interaction (μ_c^π) of the imidazole and N-phenyl nuclei (0.68 D) [4]. The calculation of the dipole moments of compounds I-IV, XII, XIII, and XV-XVIII was carried out for two possible planar conformations A (φ = 0°) and B (φ = 180°).

The following values of the group and bond moments were taken: $C_{ar}-CH_3$ 0.4 D; moment of the furan ring 0.71 D [5]; $C_{ar}-OCH_3$ 1.28 D (θ = 72°); $C_{ar}-Br$ 1.54 D [6]; and $C_{ar}-N(CH_3)_2$ 1.61 D (θ = 29.5°) [7].


A (φ=0°)


B (φ=180°)


A (φ=0°)


B (φ=180°)

The experimental values of the dipole moments and the results of the calculation are given in Table 1.

The values of the dipole moments of compounds I-IV calculated vectorially for the planar conformations A (φ = 0°) and B (φ = 180°) differ considerably from the experimental values, which is due to their nonplanar structure. The deviation from coplanarity of the structure in the case of the ortho-nitro-substituted III is greater than for the meta derivatives I and IV (I, IV, $\varphi \simeq$ 150°; III, φ = 90°). The latter is completely explained by the steric interaction in III between the ortho substituents relative to the C–C bond between the rings (Fig. 1). A confirmation of this is the increase in the angle φ (II, φ = 119°) with the introduction of a C_2H_5 group into position 1 of benzimidazole, which increases the steric repulsion because of the considerable overlapping of the van der Waals radii of the hydrogen atoms of the ethyl group and the phenyl ring.

In spite of the absence of appreciable steric hindrance to the existence of a planar structure for compounds I and IV, these molecules, even when the dioxane effect is taken into account, do not exist in solution in the form of planar isomers. This is apparently due to the insufficient energy of stabilization of the planar forms as a result of conjugation between the rings through the C_2-C_{Ar} bond. The low degree of conjugation between the rings is evidently due to countereffects arising as a result of the electron-accepting nature of both the benzimidazol-2-yl radical [3, 13] and the nitrophenyl radical. What has been said above is in harmony with the absence of an interaction moment for 2-(p-nitrophenyl)-4,5-diphenylimidazole (VIII, μ_{exp} = 6.10, μ_{calc} = 6.09 D). The electron-accepting nature of the benzimidazol-2-yl radical is confirmed by a consideration of the dipole moments of compounds V-VII and X. In particular, the introduction of an electron-donating bromine atom into the para position of the phenyl ring present in position 2 of the heterocycle leads to a lowering of the experimental dipole moment in comparison with that calculated vectorially (X, μ_{exp} = 4.10; μ_{calc} = 4.46 D). Obviously, in this case the participation of the p-electrons of the bromine in the total conjugation plays a greater role than the inductive capacity of bromine for attracting electrons to itself.

The experimental dipole moments of compounds XII-XIV (taking into account a dioxane effect of 0.15-0.30 D [12]) show the formation in solution of the planar structure A (φ = 0°C). The stabilization of the planar conformation probably takes place because of the existence of an intramolecular hydrogen bond (IHB) of the NH...O type. It is not excluded, either, that structure A is preferable because the dipoles not participating in the π bonding of the hybrid electron pairs of the oxygen and nitrogen have an energetically more favorable arrangement for this conformation than for conformation B. An IR spectroscopic study of compounds VI and XII that we have performed (IKS-14A instrument, LiF prism, hexachlorobutadiene) tends to confirm the second hypothesis: their spectra in the 3600-2500 cm^{-1} region are practically identical, while in VI an IHB is not feasible.

For compound XIV, the dipole moments were calculated for various angles of rotation φ of the phenyl ring with the $p-OC_2H_5$ substituent. The experimental values of the dipole moment (3.94 D) (allowing for the dioxane effect) corresponds to a rotation of the $p-C_2H_5-O$ phenyl ring relative to the C_5-C_{Ar} ring of approximately 90° (μ_{calc} = 3.69 D), which is due to the considerable steric interaction of the 4- and 5-phenyl radicals.

TABLE 1. Dipole Moments of 1- and 2-Aryl-(α-furyl) Derivatives of Imidazole and Benzimidazole in Dioxane

Compound	Name	μ_{exp}, D	μ_{calc} A (φ=0°)	μ_{calc} B (φ=180°)	Angle φ, deg
I	2-(m-Nitrophenyl)benzimidazole	3,24	7,84	2,73	152
II	1-Ethyl-2-(m-nitrophenyl)benzimidazole	4,59	7,84	2,73	119
III	2-(o-Nitrophenyl)benzimidazole	5,32	7,46	1,38	89
IV	2-(m-Nitrophenyl)-4,5-diphenylimidazole	3,48	7,84	2,73	146
V	4,5-Diphenylimidazole	4,40 (4,39)*		(3,81) ‡	
VI	2,4,5-Triphenylimidazole	3,92		(3,81)‡	
VII	2-(p-Tolyl)-4,5-diphenylimidazole	3,87		(3,82)‡	
VIII	2-(p-Nitrophenyl)-4,5-diphenylimidazole	6,10		6,09	
IX	2-(p-Dimethylaminophenyl)-4,5-diphenylimidazole	4,76		(4,59)**	
X	2-(p-Bromophenyl)-4,5-diphenylimidazole	4,10		4,46	
XI	2-(p-Methoxyphenyl)-4,5-diphenylimidazole	4,21		(4,19)**	
XII	2-(α-Furyl)-4,5-diphenylimidazole	3,45	3,22	4,63	0
XIII	2-(α-Furyl)-4-phenyl-5-(p-tolyl)-imidazole	3,76	3,51	4,91	0
XIV	5-(p-Ethoxyphenyl)-2-(α-furyl)-4-phenylimidazole	3,94		(3,74)**	0
XV	1-(m-Nitrophenyl)benzimidazole	3,45	4,50	3,04	122
XVI	1-(o-Nitrophenyl)benzimidazole	5,91	6,92	6,07	
XVII	1-(m-Nitrophenyl)imidazole	(3,63)*	4,50	3,04	108
XVIII	1-(o-Nitrophenyl)imidazole	5,89 (5,90)†	6,92	6,07	

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*Values of μ_{exp} from the literature [5, 14].

†In benzene.

‡Values of μ_{calc} from the literature [8].

**Calculated with the assumption of free rotation of the para substituent.

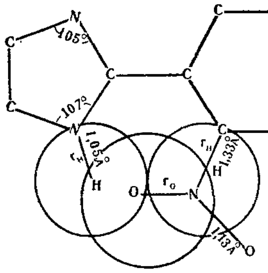

Fig. 1. Geometrical model of 2-aryl-substituted imidazoles (the bond lengths and van der Waals radii from[9-12] are used).

As in the case of the 2-aryl derivatives I-IV, a comparison of the experimental and vectorially calculated moments of 1-(m-nitrophenyl)-benzimidazole (XV) shows that its structure is nonplanar (φ = 122°), because of the steric interaction of the ortho hydrogen atom of the 1-phenyl ring and the hydrogen atom in position 7 of the benzimidazole [12]. However, in spite of the smaller steric hindrance in the case of the imidazole derivative XVII, this is characterized by a greater deviation from a coplanar structure (φ = 108°). This may be due to the increase in the size of the chain of conjugation for compound XV, which promotes the stabilization of a planar structure (see [3]). Still greater π-electronic interaction is apparently found in the o-nitrophenyl derivatives of imidazole and benzimidazole (XVI and XVIII). As is well known [4], the interaction moment (μ_c^π) arising under these conditions decreases the experimental value of the dipole moment. Consequently, μ_{exp} for XVI and XVIII proved to be smaller than the vectorially calculated values of μ even for the planar conformation B. The latter can be explained by the maximum approach of the structure of the molecules mentioned to the planar model B (φ = 180°) in spite of pronounced steric hindrance [12]. However, an accurate determination of the value of the angle φ from the experimental values of the dipole moments of XVI and XVIII using a vectorial scheme does not appear possible. Thus, it may be assumed that the spatial structure of the compounds studied is determined not only by steric factors but also by the degree of conjugation via the bond between the rings.

EXPERIMENTAL

The 2-nitrophenylbenzimidazoles were obtained from o-phenylenediamine (I, III) or its N-ethyl derivative (II) and the corresponding nitrobenzaldehyde in ethanol in the presence of nitrobenzene [14].

2-(m-Nitrophenyl)benzimidazole (I). Dark yellow plates with mp 189°C (from benzene). Yield 60%. Found, %: N 17.41. $C_{13}H_9N_3O_2$. Calculated, %: N 17.57.

1-Ethyl-2-(m-nitrophenyl)benzimidazole (II). Yellow plates with mp 114°C (from aqueous ethanol). Yield 50%. Found, %: N 15.36. $C_{15}H_{13}N_3O_2$. Calculated, %: N 15.72.

2-(o-Nitrophenyl)benzimidazole (III) was characterized with mp 271°C, corresponding to the figure given in the literature [15].

The 1-nitrophenyl derivatives of imidazole and benzimidazole were synthesized by boiling (30 h) mixtures of the corresponding bromonitrobenzenes, azoles, cuprous bromide, and potassium carbonate in bromonitrobenzenes [16, 17].

1-(m-Nitrophenyl)benzimidazole (XV). Pale yellow needles, mp 146°C (from aqueous ethanol); bp 212°C (10 mm). Yield 35%. Found, %: N 17.91. $C_{13}H_9N_3O_2$. Calculated, %: N 17.57.

1-(o-Nitrophenyl)imidazole (XVIII). Pale yellow plates after vacuum distillation at 180°C (13 mm); mp 97°C. Yield 30%. Found, %: N 22.00. $C_9H_7N_3O_2$. Calculated, %: N 22.21.

Compounds XVI and XVII have been described previously [18]. The syntheses of the 2-aryl- and 2-furyl-4,5-diphenylimidazoles IV-XIV were made from benzine and the corresponding aldehydes in acetic acid [19]. The physicochemical characteristics of IV-XIV are given in [20].

The dipole moments of compounds I-XVIII were determined in dioxane and that of XVIII also in benzene, at 25 ± 0.1°C, in the range of molar fractions of $1 \cdot 10^{-3}$-$6 \cdot 10^{-3}$ by a published method [2].

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