A STUDY OF NITROGEN-CONTAINING BISHETEROCYCLIC SYSTEMS

III. Dipole Moments and Structure of N-(Benzimidazol-2-yl)azoles[*]

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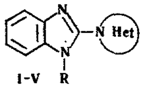
On the basis of determinations of dipole moments and quantum-mechanical calculations for a series of N-(benzimidazol-2-yl)azoles, it has been concluded that they have a nonplanar structure. The calculation of the total π-electronic charges on the individual fragments of the molecules studied has shown that the benzimidazol-2-yl radical possesses electron-accepting properties with respect to a N-heteryl residue.

It has been shown previously [1] that considerable induction and mesomeric interaction exists between the heterocyclic nuclei in the molecules of I-V.



I-V

I-IV $R = CH_3$; V $R = H$

Het = I imidazolyl;
II benzimidazolyl;
III pyrazolyl;
IV, V indazolyl;

The present communication is devoted to a determination of the conjugation effect in I-V and the elucidation of the probable spatial structure of the compounds studied. To solve these questions we have measured the dipole moments and carried out quantum mechanical calculations of the molecules by the LCAO MO method[†]

RESULTS

Compounds I-V were synthesized and purified by methods described previously [1]. The dipole moments were determined in absolute dioxane at 25 ± 0.1°C on a IDM-2 instrument [5].

The calculations by Hückel's MO method were performed on an M-20 electronic computer using the program given by Ostroumov [6].

The calculated values of the π-electronic charges and of the bond orders for compounds I-IV on the assumption that they have a planar structure, and also the various angles of rotation φ relative to the C−N bond between the heterocyclic moieties for II and III are given in Figs. 1 and 2. In the calculations of the nonplanar conformation, the resonance integral of the C−N bond between the rings was taken as $0.8\beta \cos \varphi^2$. The delocalization energies ΔE_π were calculated as the difference between the total π-electronic energy of the bisheterocycle (E_π) and the total π-electronic energies of its individual moieties [4].

On the basis of the calculation of the π-electronic charges and of the geometry of the molecules the π-electronic moments for various angles of rotation φ were calculated. In order to simplify the calculations, the pyrazole and imidazole rings were considered as true pentagons and the lengths of all the bonds were taken as equal to the length of the aromatic C−C bond. The calculation of the σ-component of the dipole moment was carried out by a vectorial scheme on the basis of generally-accepted values of the σ-moments of the bonds [7]. The values of the dipole moments calculated theoretically and found by experiment are given in the table.

DISCUSSION

Starting from the fact that in the bisheterocyclic systems studied a considerable steric interaction between the N-methyl group of the benzimidazole moieties and the hydrogen atoms of the N-heteryl residues is possible, a nonplanar

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[*] For part II, see [1].

[†] The calculations were carried out with the values of the parameters recommended by Streitwieser [2], which ensure good agreement of the experimental and calculated values of the dipole moments [3, 4].

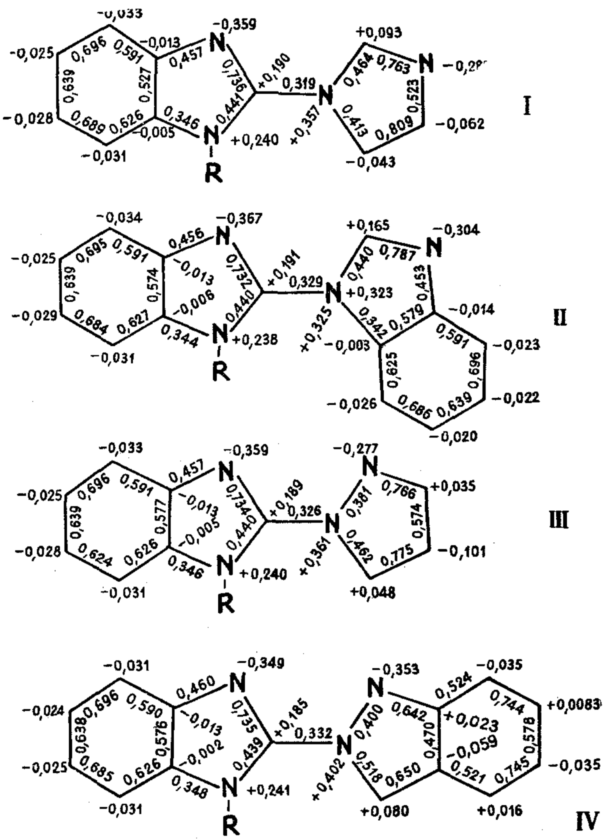


Fig. 1. π-Electronic charges and bond orders of the molecules of I-IV (cis-, form, $\varphi = 0°$).

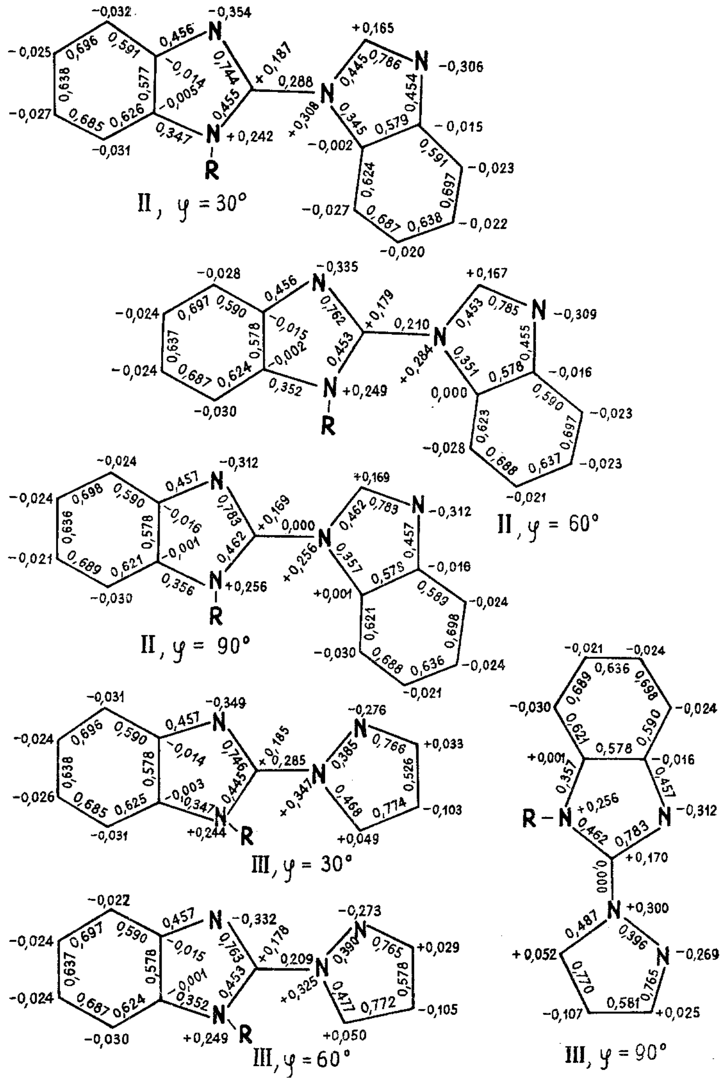
structure of I-IV seemed more likely. In actual fact, bipyridyls [8], bipyrazolyls [9], and other bicyclic systems [5, 10] of analogous structure have nonplanar forms in solution. A confirmation of the noncoplanar structure of the compounds I-IV studied is the considerable decrease in the experimental value of the dipole moment of N-(benzimidazol-2-yl)indazole (V) as compared with the moment of its N-methyl derivative IV (1.41 and 2.77 D). This is due to the flattening of the molecule of V either as the result of a decrease in steric interaction or through the formation of an intramolecular hydrogen bond of the type $\mathrm{N{-}H \cdots N}\!<$ stabilizing the planar trans form ($\varphi = 180°$).

The temperature dependence of the dipole moment of IV in the range from 20 to 70°C (20°—2.71 D; 25°—2.77 D; 35°—2.89 D; 50°—3.08 D; 70°—3.15 D) reflects a decrease in the mean value of the angle φ and does not correspond to a shift in the equilibrium between the planar cis and trans isomers.

A comparison of the experimental and the theoretically-calculated values of the dipole moments (μ) for II and III enables the angle φ between the planes of the heterocycles to be evaluated. Attention is attracted by the fact that in II the experimental values of μ correspond to a considerable rotation ($\sim 70°$) of the N-heterocycle from the plane of the cis form. Conversely, III is characterized by a structure of the molecule closer to the coplanar form. The angle φ in this case is $\sim 150°$, which corresponds to a rotation of 30° from the plane of the trans form. The same situation must probably be expected in the case of the benzimidazol-2-yl derivatives of imidazole I and of indazole IV.

In an evaluation of the structures of I-IV, it must be borne in mind that their dipole moments were determined in dioxane. Since for compounds of this type the magnitude of the dioxane effect is 0.15-0.20 D [11], the values of the angles given above must be regarded as 10-15° too high.

Thus, it may be assumed that the higher degree of conjugation in III and IV as compared with I and II that has been established previously is connected with the above-mentioned differences in the three-dimensional structures of these molecules.


II, φ = 30°

II, φ = 60°

II, φ = 90°

III, φ = 30°

III, φ = 60°

III, φ = 90°

Fig. 2. π-Electronic charges and bond order of the molecules of II and III with angles of rotation φ = 30, 60, and 90°.

The results obtained permit a hypothesis to be put forward on the considerable influence of the electronic structure of the hetero moieties on the spatial configuration of the compounds studied. In actual fact, while the smaller order of the C−N bond between the heterocycles in II as compared with III at angles of φ close to the actual values (60 and 30°) is due to the smaller degree of overlapping of the π-electronic orbitals in III, the retention of the same situation for I and II and for III and IV when the hypothetical planar molecules are considered (Fig. 1) definitely shows the greater possibility of π-interaction in the heterocycles III and IV. The latter should lead to a greater stabilization of the planar structures under otherwise similar (steric conditions). The lower degree of conjugation in I and II is obviously due to the greater aromaticity of the imidazoyl and benzimidazolyl radicals as compared with the pyrazolyl and indazolyl radicals. In view of this, the reason for the practical coincidence of ΔE_π in I-III for the planar models of the molecules remains obscure. According to Streitwieser's book [2] the energy of interaction in II and III at angles of, respectively, 60 and 30° can be evaluated as 2.1 and 4 kcal/mole.

A consideration of the molecular diagrams of compounds I-IV (Figs. 1 and 2) enables the question of the direction of the mesomeric interaction in these compounds to be answered. A calculation of the total π-electronic charge on each hetero residue shows that the benzimidazol-2-yl radical exhibits electron-accepting properties in compounds I-V.

Table 1. Dipole Moments of the N-(Benzimidazol-2-yl)azoles

Compound	Name	∠φ, °	μ_{theor}, D	μ^{25}_{exp}, D	E_{π}, β	ΔE_{π}, β
I	N-(1-Methylbenzimidazol—2-yl)imidazole	0	4,76	4,45	23,7964	0,2600
		180	3,70			
II	N-(1-Methylbenzimidazol-2-yl)benzimidazole	0	3,79		29,6378	0,2682
		30	3,95			
		60	4,21	4,38	29,4760	0,1064
		90	4,65			
		120	4,66			
		150	4,78			
		180	4,70			
III	N-(1-Methylbenzimidazol-2-yl)pyrazole	0	6,47		23,7804	0,2660
		30	6,18			
		60	5,49			
		90	4,51			
		120	3,59			
		150	2,79	2,86	23,7130	0,1986
		180	2,51			
IV*	N-(1-Methylbenzimidazol-2-yl)indazole	0	7,21	2,77	29,3752	—
		180	0,86			
V	N-(Benzimidazol-2-yl)indazole	0	7,21			
		180	0,86	1,41		

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*In addition to the quinoid structure shown in Fig. 1, compound IV may be ascribed the structure of a 1-(benzimidazol-2'-yl)-substituted indazole (benzenoid structure). However, calculations of the dipole moments for the benzenoid trans and cis forms (3.69 D and 6.10 D, respectively) lead to the conclusion that IV has a planar structure, which contradicts the results of UV spectroscopy [1] and the decrease in μ on passing to V.

It is interesting to note the existence of a considerable positive charge in position 2 of compounds I and II. In agreement with well-known facts [12], it is to be expected that these positions will be subjected to nucleophilic attack first, for example in amination reactions. The high negative charges on the nitrogen atoms of the "pyridine type" in compounds I-IV makes the use of these compounds as bidentate ligands in complex-forming reactions promising.

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