CALCULATION OF THE ELECTRONIC STRUCTURES OF BENZIMIDAZOLE, PERIMIDINE, AND 5H-DIBENZO[d,f]-1,3-DIAZEPINE WITH THE INCLUSION OF ALL OF THE VALENCE ELECTRONS

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The distributions of the σ and π charges in benzimidazole,perimidine, and 5H-dibenzo[d,f]-1,3-diazepine molecules, as well as several other characteristics of these compounds, were calculated by the SCF LCAO MO method with the inclusion of all of the valence electrons using the approximation of complete neglect of differential overlap (CNDO). In accordance with the calculations carried out using the π-electron approximation, this method predicts increased basicity and nucleophilicity in this series of compounds. It was demonstrated that the mechanism for the development of a positive charge on the meso carbon atom is substantially different for these compounds.

The amidine grouping in benzimidazole (I), perimidine (II), and 5H-dibenzo[d,f]-1,3-diazepine (III) is structurally included in the composition of the five-, six-, and seven-membered rings, respectively, and this leads to substantial differences in the electron distributions and properties of the compounds. We have previously studied [1-3] the electronic structures of these heterocycles by means of the Pariser–Parr–Pople (PPP) and Hückel methods using the π-electron approximation. The present communication contains the results of calculations of the electronic structures of I-III that were performed by the SCF LCAO MO method with the inclusion of all of the valence electrons using the CNDO (complete neglect of differential overlap) approximation [4].

The calculations were performed with a BÉSM-6 computer from a somewhat modified original program [5] using the parameters of Pople and Segal [4]. The molecular geometries of benzimidazole and perimidine were assumed to be the same as in previous calculations [3]. The calculation for dibenzodiazepine III was carried out for the most stable nonplanar conformation, in which, according to our calculations [2], the angle between the planes of the benzene ring is 40°. Several principal results of the calculations that make it possible to compare the properties of I-III are presented in Tables 1 and 2.

The most important features of the chemical behavior of I-III are associated with reactions that involve the amidine fragment of their molecules. The charge separation (Δq) in this heterocyclic grouping increases appreciably from I to III, although the overall charge does not vary significantly. The increase in the electron density on the $N_{(2)}$ atom, which is the center of protonation of the molecules in acidic media, leads to an observable increase in the basicity that is especially significant on passing from perimidines to dibenzodiazepines [6, 7].

The noted polarization of the amidine group is also manifested in an increase in the positive charge on the meso carbon atom in the order I-III; this atom ($C_{(3)}$) acts as the nucleophilic center. The calculations, which take into account the contributions of all of the valence electrons, confirm the conclusion previously drawn within the framework of the π-electron approximation that the nucleophilic properties are intensified in the series under study [1-3]. However, the data obtained make it possible to elucidate the mechanism of

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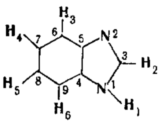
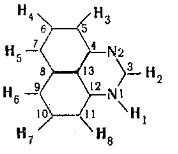
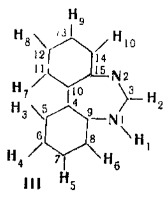
TABLE 1. Distribution of the σ, π, and Total Charges on the Atoms in Molecules of I-III



I



II



III

Atom	Compound						
	I			II			III
	Δq^{σ}	Δq^{π}	Δq	Δq^{σ}	Δq^{π}	Δq	Δq*
$N_{(1)}$	−0,4577	0,3343	−0,1234	−0,4437	0,2909	−0,1528	−0,1915
$N_{(2)}$	−0,0126	−0,2038	−0,2164	0,0057	−0,2382	−0,2325	−0,2791
$C_{(3)}$	0,1313	0,0364	0,1677	0,0596	0,1380	0,1976	0,2559
$C_{(4)}$	0,1056	−0,0310	0,0746	0,0662	0,0777	0,1439	0,0011
$C_{(5)}$	0,0940	−0,0166	0,0774	0,0347	−0,1077	−0,0730	0,0050
$C_{(6)}$	0,0064	−0,0228	−0,0164	−0,0150	0,0524	0,0374	−0,0092
$C_{(7)}$	0,0171	−0,0263	−0,0092	0,0357	−0,0964	−0,0607	0,0132
$C_{(8)}$	0,0171	−0,0171	0,0000	0,0125	0,0583	0,0708	−0,0403
$C_{(9)}$	0,0183	−0,0531	−0,0348	0,0232	−0,0919	−0,0587	0,1210
$C_{(10)}$	—	—	—	−0,0706	0,0473	0,0397	−0,0239
$C_{(11)}$	—	—	—	0,0468	−0,1372	−0,0904	0,0072
$C_{(12)}$	—	—	—	0,0954	0,0517	0,1471	−0,0203
$C_{(13)}$	—	—	—	0,0071	−0,0449	−0,0378	0,0151
$C_{(14)}$	—	—	—	—	—	—	−0,0416
$C_{(15)}$	—	—	—	—	—	—	0,1432
$H_{(1)}$			0,1096			0,1186	0,1199
$H_{(2)}$			0,0009			0,0061	−0,0338
$H_{(3)}$			−0,0048			−0,0040	−0,0021
$H_{(4)}$			−0,0079			−0,0141	−0,0055
$H_{(5)}$			−0,0074			−0,0098	−0,0050
$H_{(6)}$			−0,0101			−0,0081	−0,0017
$H_{(7)}$			—			−0,0118	−0,0100
$H_{(8)}$			—			−0,0074	−0,0088
$H_{(9)}$			—			—	−0,0090
$H_{(10)}$			—			—	0,0001

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*Division into σ and π orbitals is complicated because of the noncoplanarity of compound III.

development of positive charge on the meso carbon atom in a novel way. The positive charge on the $C_{(3)}$ atom in the benzimidazole molecule is achieved almost exclusively through polarization of the σ framework, while a shift of the π-electron density from the p_z atomic orbital of the meso carbon atom plays the major role in the perimidine molecule. In the case of imidazole IV, calculations using the CNDO approximation [8] indicate that the total charge on the meso carbon atom is +0.031 and is made up of a positive σ charge (+0.145) and a negative π charge (−0.114). It is hence clear why, in contrast to the N-methyl derivatives of benzimidazole and perimidine, N-methylimidazole does not undergo amination by sodium amide [9, 10]. A similar division of the overall charge on the $C_{(3)}$ atom of dibenzodiazepine III is complicated because of the merging of the σ and π orbitals as a consequence of the nonplanar structure of the molecule. However, the maximum positive charge on the meso carbon atom in the I-III series is reached in this compound.

Thus the relative success of the π-electron calculations in predicting an increase in the nucleophilic reactivity in the order IV, I-III is explained by the fact that these calculations correctly describe the tendency for a decrease in the π-electron density on the meso carbon atom in these compounds. However, when the σ, π interactions are disregarded, they are not capable of predicting the role of polarization of the σ framework, which leads, in particular, to a negative π charge on the meso carbon atom of imidazole.

The significant increase in the overall electron density on the $N_{(1)}$ atom induces a decrease in the acidity of the NH group in the order I-III, which is manifested in increased difficulty in carrying out exchange reactions at this group in perimidines [11] and (from our observations) in dibenzodiazepines.

In general outline, the distribution of the total charges in the arene portion of I-III is in agreement with a purely π-electron distribution and leads to the same predictions regarding the occurrence of electrophilic substitution reactions that were previously made in [1-3]. A substantially different characteristic of perimidine is the distinct alternation of charges ($\sigma + \pi$ and π) on the carbon atoms of the naphthalene system, which is associated with the alternant nature of this heterocycle.

TABLE 2. Some Calculated and Experimental Characteristics of I-III

Property	Computational method	Compound		
		I	II	III
Ionization potential, eV	CNDO	11,26	8,79	10,09
	PPP	9,64	8,26	9,35
Electron affinity, eV	CNDO	−3,28	−2,35	−2,93
	PPP	1,33	1,97	2,24
μ_π, D	CNDO	3,36	4,21	—
	PPP	2,05[3]	3,14[3]	2,17
μ_σ, D	CNDO	1,56	2,30	—
μ_{sp}, D	CNDO	2,37	2,08	1,47
μ, D	CNDO	4,03	3,77	3,01
$\mu_{\text{exp.}}$, D	—	4,04[14]	3,18[1]	2,67*

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* The dipole moment for meso-phenyldibenzodiazepine [2] is presented, since the dipole moment of unsubstituted III was not determined. The latter should range from 2.9 to 3.1 D, since the introduction of a phenyl substituent into the meso position of benzimidazole and perimidine lowers their dipole moments by 0.41 and 0.15 D, respectively [2, 15].

Perimidine also has the lowest ionization potential (Table 2), which, as demonstrated by the calculations, corresponds to detachment of an electron from the π-molecular orbital. This is evidence that perimidine is the strongest π donor and the most inclined to undergo oxidation of all of the compounds examined here. In parametrization [4], the CNDO approximation usually leads to somewhat elevated ionization potentials [12], but the same order of magnitudes of the ionization potentials is also retained in calculations by the PPP method (with the coulombic integrals calculated by Mataga and Nishimoto [13]). The most substantial difference in the results of the calculations by the PPP and SCF LCAO MO methods with allowance for all of the valence electrons using the CNDO approximation consists in the prediction of the different signs of the electron affinities. The absence of experimental data hinders an analysis of this result, but preference should apparently be given to the results obtained by the PPP method.

The dipole moments calculated using the CNDO approximation (Table 2) are in rather good agreement with the experimental values, correctly reflecting the decrease in the moments in the order I-III. This effect could not be reproduced in calculations by the PPP method [3]; this is associated with the fact that the method for estimating the σ and hybridization components of the total dipole moment in the π-electron calculations is too inaccurate. In the CNDO approximation, these components are calculated in the explicit form

$$\vec{\mu} = \vec{\mu}_\pi + \vec{\mu}_\sigma + \vec{\mu}_{sp}$$

$$\mu_{sp}(x) = -14{,}674 \sum_a z_A^{-1} P(2s_A, 2p_{x,A}),$$

where μ_π, μ_σ, and μ_{sp} are the π, σ, and hybridization dipoles, respectively; z is the Slater exponent; and P is the order of the bond between the corresponding orbitals. The data in Table 2 demonstrate that the contributions of μ_σ (and particularly μ_{sp}) may be extremely great and, what is of paramount importance, different for different compounds. It is impossible to take these differences into account in the π-electron approximation.

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