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COMPARATIVE CHARACTERISTICS OF THE ELECTRONIC STRUCTURES OF PERIMIDINE AND NAPHTHIMIDAZOLES WITHIN THE FRAMEWORK OF THE CNDO-2 (COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP) METHOD

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UDC 547.856.7'785.5:541.67

The 1H-naphth[1,2-d]imidazole, 3H-naphth[1,2-d]imidazole, and 1H-naphth[2,3-d]-imidazole molecules were calculated by the CNDO-2 method. The dipole moments of N-methyl derivatives of perimidine and linear naphthimidazole were measured. The π-donor character of N-methyl derivatives of perimidine and naphthimidazoles with respect to 1,3,5-trinitrobenzene was also measured. The study showed that the CNDO-2 method, except for individual details associated with the distribution of the σ electrons, leads to the same conclusions relative to the overall pattern of the effective charges on the atoms in the perimidine and naphthimidazole molecules as the π-approximation methods.

It has been previously shown that the perimidine molecule (I) has an extremely peculiar set of physicochemical properties, the principal feature of which is the simultaneous manifestation of clearly expressed π-surplus character and π-deficient character [1]. Since perimidine is formally peri-naphthimidazole, it also seems of interest to compare it with other naphthimidazoles. The goal of the present research was to compare the electronic characteristics of perimidine and both angular (II and III) and linear (IV) naphthimidazoles within the framework of the CNDO-2 (complete neglect of differential overlap) method, i.e., with the inclusion of all of the valence electrons.

The I molecule was calculated by the CNDO-2 method in [2]. We calculated the naphthimidazole molecules from a similar program with a BÉSM-6 computer with the use of the parameters in [3]. In view of the lack of experimental data on the geometry of the II-IV molecules, the benzene and imidazole rings in them were considered to be regular hexagons and pentagons with internal angles of 120 and 108°, respectively. The C—C and C—N bond lengths were assumed to be 1.39 Å, and the C—H bond length was assumed to be 1.07 Å. The numbering of the atoms and the selection of the system of coordinates are indicated in the formulas.

The Δq^{σ} and Δq^{π} values and the total charges on the atoms of the I-IV molecules presented in Table 1 make it possible to draw the following conclusions.

1. In all four compounds there is a shift of the π-electron density from the heteroring to the naphthalene system. The overall π charges on the nonbridged C atoms of the naphthalene ring in I-IV are, respectively, − 0.3335, − 0.0848, − 0.0879, and − 0.1654. Thus the intensity of the shift of the π-electron cloud is maximal in perimidine and minimal in the isomers of angular naphthimidazole. The linear naphthimidazole molecule occupies an intermediate position. A similar regularity was observed in calculations of the I-IV molecules within the framework of the Hückel MO method [4]. It should be noted that one can arrive at the same conclusions by analyzing the total charges on the atoms of the I-IV mole-

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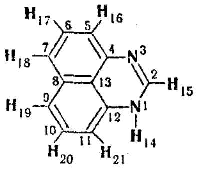
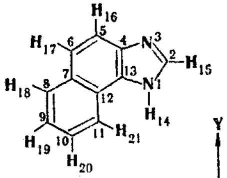
0009-3122/79/1505-0564$07.50

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



I



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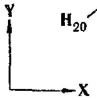
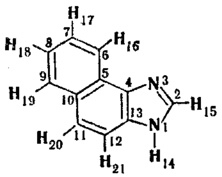
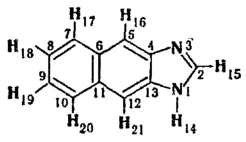




III



IV

Atom	Compound											
	I			II			III			IV		
	Δq^{σ}	Δq^{π}	Δq	Δq^{σ}	Δq^{π}	Δq	Δq^{σ}	Δq^{π}	Δq	Δq^{σ}	Δq^{π}	Δq
$N_{(1)}$	−0,4437	0,2909	−0,1528	−0,4787	0,3677	−0,1110	−0,4769	0,3639	−0,1130	−0,4593	0,3171	−0,1422
$C_{(2)}$	0,0596	0,1380	0,1976	0,1321	0,0184	0,1505	0,1315	0,0228	0,1542	0,1021	0,0801	0,1822
$N_{(3)}$	0,0057	−0,2382	−0,2325	−0,0036	−0,2224	−0,2261	−0,0008	−0,2239	−0,2246	0,0161	−0,2514	−0,2353
$C_{(4)}$	0,0662	0,0777	0,1439	0,0873	−0,0225	0,0648	0,0820	−0,0268	0,0552	0,0742	0,0088	0,0830
$C_{(5)}$	0,0347	−0,1077	−0,0730	−0,0026	−0,0033	−0,0059	0,0174	−0,0003	0,0171	0,0285	−0,0473	−0,0188
$C_{(6)}$	−0,0150	0,0524	0,0374	0,0125	−0,0420	−0,0295	0,0025	−0,0091	−0,0066	0,0322	0,0083	0,0405
$C_{(7)}$	0,0357	−0,0964	−0,0607	0,0243	0,0055	0,0298	0,0048	−0,0030	0,0018	−0,0063	−0,0077	−0,0140
$C_{(8)}$	0,0125	0,0583	0,0708	−0,0041	−0,0099	−0,0140	0,0059	−0,0042	0,0017	−0,0081	−0,0090	−0,0171
$C_{(9)}$	0,0322	−0,0919	−0,0587	0,0001	−0,0045	−0,0044	0,0037	−0,0120	−0,0083	0,0024	−0,0046	−0,0022
$C_{(10)}$	−0,0076	0,0473	0,0397	0,0078	−0,0064	0,0014	0,0246	0,0049	0,0295	0,0148	−0,0189	−0,0041
$C_{(11)}$	0,0468	−0,1372	−0,0904	0,0132	−0,0187	−0,0055	0,0157	−0,0359	−0,0202	0,0158	0,0089	0,0247
$C_{(12)}$	0,0954	0,0517	0,1471	0,0244	−0,0076	0,0168	0,0054	−0,0237	−0,0183	0,0222	−0,0779	−0,0557
$C_{(13)}$	0,0071	−0,0449	−0,0378	0,1074	−0,0543	0,0531	0,1058	−0,0529	0,0529	0,0779	−0,0058	0,0721
$H_{(14)}$	—	—	0,1186	—	—	0,1197	—	—	0,1186	—	—	0,1208
$H_{(15)}$	—	—	0,0061	—	—	0,0121	—	—	0,0132	—	—	0,0136
$H_{(16)}$	—	—	−0,0040	—	—	−0,0063	—	—	−0,0035	—	—	−0,0117
$H_{(17)}$	—	—	−0,0141	—	—	−0,0068	—	—	−0,0102	—	—	0,0068
$H_{(18)}$	—	—	−0,0098	—	—	−0,0070	—	—	−0,0103	—	—	−0,0052
$H_{(19)}$	—	—	−0,0081	—	—	−0,0088	—	—	−0,0097	—	—	−0,0080
$H_{(20)}$	—	—	−0,0118	—	—	−0,0069	—	—	−0,0063	—	—	−0,0188
$H_{(21)}$	—	—	−0,0074	—	—	−0,0158	—	—	−0,0132	—	—	−0,0105

TABLE 2. Dipole Moments and Ionization Potentials of the Investigated Compounds

Property	*Compound			
	I	II	III	IV
μ_π, D	4,21[2]	3,40	3,68	3,75
μ_σ, D	2,30[2]	3,74	1,52	1,78
μ_{sp}, D	2,08[2]	2,36	2,39	2,48
μ_{calc}, D	3,77[2]	3,93	4,25	3,88
μ_{exp}, D (in dioxane at 30°C)	3,66 †	4,04 ‡	3,86	4,05
Ionization potential, eV, CNDO-2	8,79	10,26	10,02	9,76
From charge-transfer-complex data	6,78	—	7,72	7,44
λ_{max} of the π-complex with trinitrobenzene (in chloroform), nm	550	—	400**	435

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*All of the calculated values are presented for unsubstituted I-IV, while the experimental data are presented for their N-methyl derivatives. †According to the data in [7], 3.48 D. ‡For 1-ethylnaphth[1,2-d]imidazole [8]. **Broad shoulder on the end absorption of the donor.

cules. This is explained by the fact that the σ charges make a relative small contribution to the total charges on the C atoms of the naphthalene rings of I-IV.

2. The most electron-deficient center in I-IV is the μ-carbon atom of the imidazole ring. The total charge and the π charge on it change in conformity with the intensity of the shift of the π electrons to the naphthalene ring: I > IV > II, III. However, this does not mean that the contribution of the σ electrons here is small in all cases. On the contrary, as in the case of the benzimidazole molecule [2], the most important difference between II and III relative to perimidine is the fact that the total charge on the C_2 atom in them is determined mainly by the polarization of the σ electrons of the C=N bond, whereas in the I molecule the dominant factor is π polarization. In this respect, naphth[2,3-d]imidazole occupies an intermediate position: The contribution of σ and π polarization to the induction of a positive charge on the C_2 atom in it are approximately identical.

3. The reduced value of the positive charge on the pyrrole N atom of I and IV constitutes evidence that the shift of the π-electron density from the C_2 atom in them takes place not only in a direction toward the C=N bond but also in a direction toward the pyrrole nitrogen atom. The overall charge on the pyrrole N atom of the I-IV molecules due to the σ-inductive effect has a negative sign, and the $-\Delta q$ values for I and IV are greater than for II and III. This makes it possible to predict that the N—H bonds in perimidine and naphth[2,3-d]imidazole will differ with respect to lower acidities. Unfortunately, there are no quantitative data available with respect to this problem.

4. The total charges on the pyridine N atom are not in complete harmony with the relative basicities of I-IV. Thus, whereas they correctly predict the increased basicities of I and IV as compared with II and III, the observed high basicity of I as compared with IV [5] is not explained by the results of calculations by the CNDO-2 method.

5. The positive charge (Δq) on the μ-hydrogen atom in the I molecule is considerably lower than in the II-IV molecules. This is somewhat surprising if one takes into account the fact that the H atom in perimidine is bonded to a more electron-deficient center than in II-IV. Upon the whole, there is no correlation whatsoever between the magnitude of the charge on the μ-carbon atom and the kinetic C—H acidities of I-IV, as well as their capacity for metallation (N-alkyl derivatives I and IV add organometallic reagents to the C=N bond, while II and III are metallated by them) [6].

Since the CNDO-2 method is parametrized for the calculation of dipole moments, it seemed of interest to compare the dipole moments calculated by means of it with the experimental values. With this end in mind, we measured the previously unknown dipole moment of 1-methylnaphth[2,3-d]imidazole and also made a repeat measurement of the dipole moment of 1-methylperimidine (the dipole moment of a sample that has a substantially reduced melting point was previously measured [7]). The dipole moments of the N-alkyl-substituted derivatives of both angular naphthimidazoles were borrowed from the literature [8].

The data in Table 2 show that the agreement between the calculated and experimental values for I, II, and IV is good and that the deviation does not exceed 3-4% but is somewhat greater (10%) for III.

The calculations further show that the magnitudes of the first ionization potentials of I-IV are determined by detachment of an electron from the upper occupied π orbital and vary in the order (Table 2) II > III > IV > I, i.e., perimidine should have the maximum π-donor character.

This sequence is in good agreement with our measured π-donor character of N-methyl derivatives I, III, and IV with respect to 1,3,5-trinitrobenzene (TNB). All of these substances form crystalline 1:1 molecular complexes with TNB. The I·TNB complex is violet [9], while the complexes of III and IV are orange. The λ_{max} values presented in Table 2 for the charge-transfer bands (CTB) of these complexes made it possible to calculate the first ionization potentials of the donors from the Foster formula [10]. Although the latter differ considerably in absolute value from the potentials calculated by the CNDO-2 method, the trends in their changes for the investigated compounds are identical. Thus the π-donor character of the I-IV molecules is in agreement with the relative π-surplus character of their naphthalene rings. This constitutes evidence that in the case of the formation of π complexes with perimidine and naphthimidazoles the π acceptor is situated above the plane of the naphthalene ring [9].

The research showed that the CNDO-2 method, except for individual details, leads to the same conclusions relative to the overall pattern of the effective charges of the atoms in the perimidine and naphthimidazole molecules as π-approximation methods.

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