

The electronic configurations and dipole moments of the ground and excited states of perimidine, imidazole, and benzimidazole were calculated by means of the self-consistent-field molecular orbital (SCF MO) method using the Pariser-Parr-Pople (PPP) approximation. The reactivity of perimidine is discussed. The results of the calculations by the PPP method are compared with earlier calculations based on the simple MO method. An interpretation of the electronic spectrum of perimidine is given.

In [1,2] we studied several peculiarities of the structures and properties of perimidine (I) and some of its derivatives. The data on the reactivities, dipole moments, and absorption spectra of I were interpreted by means of the simple MO method [1]. In this communication we present the results of calculations carried out with the more rigorous SCF MO PPP approximation [3]. The results are compared with the data for analogs of I, viz., imidazole (II) and benzimidazole (III) which, like I, have an  $\text{NH}-\text{CH}=\text{N}$  amino grouping which, however, is included in a five-membered ring rather than in a six-membered ring.

**Dipole Moments.** The  $\pi$ -electron configurations of I-III in the ground state, the  $\pi$  components of the dipole moments, and the total moments are presented in molecular diagrams Ia-IIIa. The experimental values of the dipole moments ( $\mu_{\text{exp}}$ )\* are also presented for comparison. The  $\sigma$  components of the dipole moments were calculated as the hybridization moments of the  $\text{sp}^2$  pair of nitrogen [4].

It can be seen that the deviation between the experimental and theoretical results is 0.2-0.5 D, while the moments calculated by means of the simple MO method exceed the experimental values of the dipole moments of perimidines by 2-3 D [1]. Despite the satisfactory agreement between the calculated moment and the experimental value, it still remains unclear why both the simple MO theory and the PPP method predict higher moments for perimidines than for azoles (II and III), while the reverse order in the moments is observed experimentally. To explain this effect we must have a calculation that allows for polarization of the  $\sigma$  framework of the molecule (the method in [7], for example). The calculated dipole moments of the excited states of perimidine ( $\mu_e$ ) are given in Table 1.

**Reactivities.** The conclusions regarding the reactivity of perimidine which follow from the results of calculations via the PPP method (molecular diagram Ia) are in agreement with those previously drawn on the basis of Hückel calculations [1]. Electrophilic substitution in I should proceed at the 4-, 9-, 6-, and 7-positions, and the 4- and 9-positions, which are adjacent to the heteroatoms, are particularly reactive. The carbon atom in the amidine grouping of heterocycles I-III has a high positive charge, the magnitude of which increases in the order  $q_{\text{II}} < q_{\text{III}} < q_{\text{I}}$ . The simple MO theory predicts the same order [1]. Since N-methylimidazole is not aminated by sodium amide, while N-methylbenzimidazole does undergo this nucleophilic substitution, we pointed out in [1] that amination of N-methylperimidine should proceed with great ease. In fact, the introduction of an amino group into the heterocyclic ring of perimidine was recently accomplished in [8].

\*The  $\mu$  values for the N-methyl derivatives of I-III are presented in view of the strong association of I-III in solutions [1-5] and the associated inaccuracy in the determination of the orientation polarization by extrapolation to infinite dilution.

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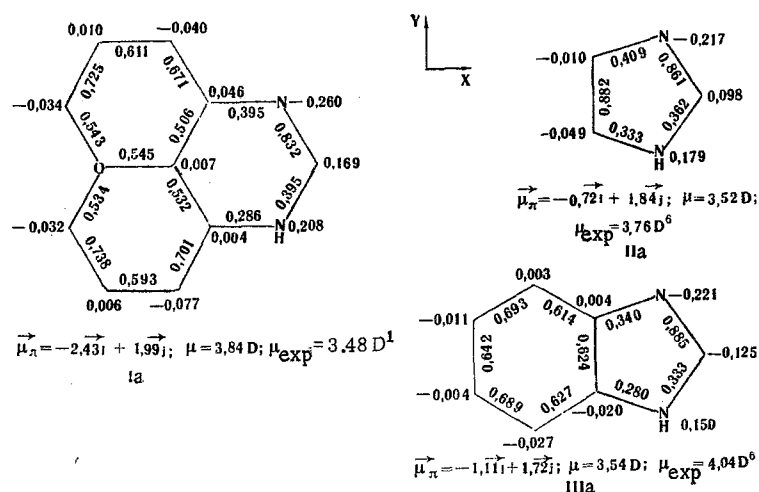


Fig. 1

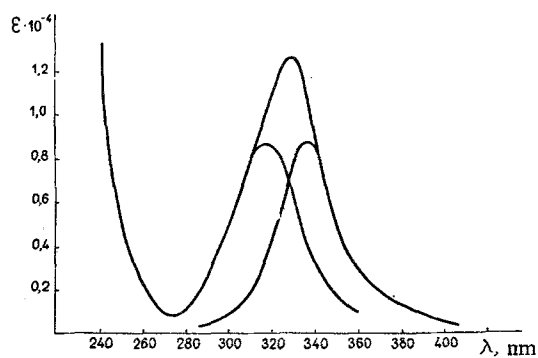


Fig. 2. Electronic absorption spectrum of perimidine (in ethanol).

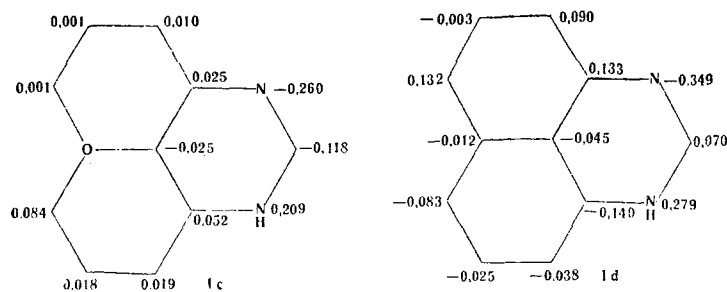


Fig. 3

TABLE 1. Transition Energies and Other Characteristics of the Excited States of Perimidine

Excited state	Transition energy		Oscillator strength		$\mu e, D$
	calc.	exptl.	calc.	exptl.	
$S_1$	3.65	3.69	0.448	0.143	6.34
$S_2$	4.00	3.92	0.210	0.125	1.90

We estimated the basicities of I-III from the equation  $\varepsilon = q_n \sum_{\mu} \frac{q_{\mu}}{r_{\mu n}}$ , where  $\varepsilon$  is the electrostatic energy

of the interaction of the unshared pair of nitrogen, which forms a bond with the proton in the conjugate acid;  $q_n$  is the charge of this pair,  $q_{\mu}$  is the  $\pi$ -electron charge of the  $\mu$ -th atom, and  $r_{\mu n}$  is the distance between the  $\mu$ -th atom and the centroid of the charge of the p pair. According to [12], the centroid of the  $sp^2$  pair of nitrogen is 0.4 Å from the nucleus of nitrogen along the line of the bisector of the valence angle. The results of the calculations give  $\varepsilon_I = 16.4$  eV,  $\varepsilon_{II} = 12.1$  eV, and  $\varepsilon_{III} = 12.4$  eV, values which correctly predict the higher basicity of perimidine as compared with azoles II and III (see [13]), but they do not explain the differences in the basicities of II and III [14]. The  $\sigma$  charges must apparently be taken into account for a more accurate examination.

**Electronic Absorption Spectra.** The electron absorption spectrum of perimidine is shown in Fig. 2. The only observable absorption band is the result of superimposition of the bands of two electron transitions, which were exposed graphically by the method in [9]. The longer-wave band is the band corresponding to charge transfer from the naphthalene fragment of the molecule to the hetero ring. The electronic configuration of the corresponding excited state is presented in molecular diagram Ic (Fig. 3). The nature of the electron transition responsible for the second absorption band can be ascertained from a comparison of the electronic configurations of the ground (Ia) and corresponding excited (Id) states.

The energies of the electron transitions were calculated as

$$\begin{aligned} S_{i \rightarrow k} &= \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik}, \\ T_{i \rightarrow k} &= \varepsilon_k - \varepsilon_i - J_{ik}, \end{aligned}$$

where S and T are symbols for the singlet and triplet transitions,  $\varepsilon$  are the orbital energies, and J and K are the coulombic and exchange integrals for the i and k MO, respectively. The values obtained and some other calculated characteristics of the excited states are presented in Table 1. Allowance for the configurational interactions has virtually no effect on the magnitudes of the transition energies. The following values were obtained for the energies of transitions to the triplet states:  $E_{S_0 \rightarrow T_1} = 2.14$  eV and  $E_{S_0 \rightarrow T_2} = 2.83$  eV.

**Computational Method.** The calculations were carried out with a Razdan computer from a program composed by E. N. Malysheva. The parameters were selected in accordance with the data in [10]. The matrix of the coulombic repulsion integrals was calculated by the Mataga-Nishimoto method [11]. The lengths of all of the bonds were taken as 1.39 Å, the angles in the six-membered rings were assumed to be 120°, while those in the five-membered rings were taken as 108°.

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