STRUCTURE AND PROPERTIES OF PERIMIDINE AND ITS DERIVATIVES

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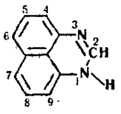
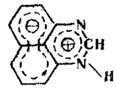
The electronic absorption spectra, luminescence spectra, and vibrational spectra of perimidine and its derivatives have been studied. On the basis of the dipole moments and vibrational spectra, the conformations of 2-(o-hydroxyphenyl)perimidine and 2-(o-hydroxyphenyl)perimidine and 2-(o-methoxyphenyl)perimidine, which are stabilized by intramolecular hydrogen bonds, have been established. The electronic configurations of the perimidines in the ground and first excited states have been calculated by Hückel's MO method. The results have been compared with data on the reactivity and electronic absorption spectra of the perimidines.

Perimidine (I), a heterocyclic isoelectronic analog of pleiadylene and the naphthazoles, was synthesized by Sachs as long ago as 1909. In later papers [2–7] a number of modifications of the initial method have been proposed and some reactions of the perimidines have been studied with a bias in the direction of the synthesis of dyes. At the same time, with the exception of fragmentary information in the IR [8] and UV [6] spectra, the problem of the structure of the perimidines has not been previously considered. In the present work we undertook a study of the dipole moments, electronic and vibrational spectra, and luminescence spectra of perimidine and some of its 2-derivatives and compared the results with those of a calculation by Hückel's MO method (HMO).



I



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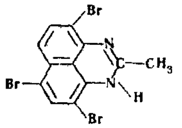
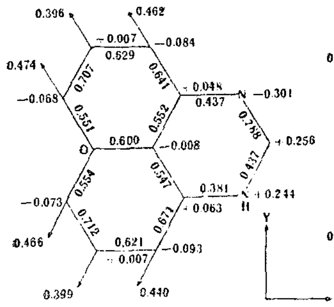


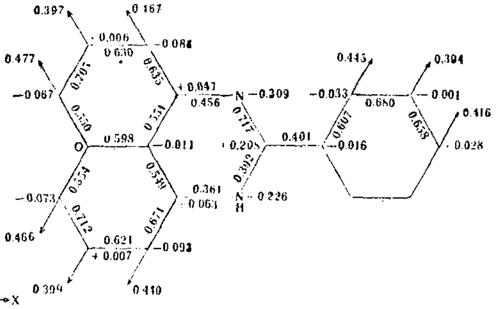
III

The complete π-electron system of perimidine consists of 14 π-electrons and satisfies the basic requirements of aromaticity: in the closed electron cloud the delocalization energy $DE = E^{\pi} - 2\alpha_{N_1} - 5E_{C=C}^{\pi} - E_{C=N}^{\pi} = 4.497\beta^0$, which corresponds to $0.32\beta^0$ per electron. However, the six-membered heterocycle that perimidine contains includes seven electrons and, consequently, must have a tendency to expel the superfluous electron into the naphthalene system that is peri-condensed with it (contribution of structure II),



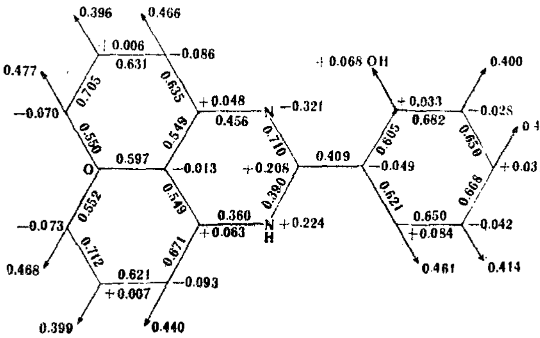
IV. $DE = 4.497\beta^0$

$\vec{\mu}_\pi = -4.52\vec{i} + 3.10\vec{j}$; $\mu = 5.22$ D



V. $DE = 6.920\beta^0$

$\vec{\mu}_\pi = -5.71\vec{i} + 2.93\vec{j}$; $\mu = 6.84$ D



VI. $DE = 7.133\beta^0$

$\vec{\mu}_\pi = -5.57\vec{i} + 2.56\vec{j}$; $\mu = 6.45$ D which has an analogy with the well-known examples of azulene, sesquifulvalene, etc. The results of a calculation of the π-electronic configuration of perimidine by the HMO method (molecular diagram IV) will illustrate this position although, as usual, they overestimate the separation of charges.

Table 1

π-Electronic Charges q_2 and Anionic Localization Energies in the 2 Positions of Imidazoles and Perimidine

Compound	q_2	α_2^- ($\beta°$)	Capacity for undergoing amination [12]
Imidazole	+0.094	3.290	—
4,5-Diphenylimidazole	+0.107	2.182	—
Phenanthrimidazole	+0.137	1.976	—
3H-Naphtho[1,2]imidazole	+0.151	1.964	+
1H-Naphtho[1,2]imidazole	+0.152	1.940	+
Benzimidazole	+0.170	1.931	+
Perimidine	+0.256	1.701	?

Reactivity. A consideration of the molecular diagram IV–VI shows that the 4.9 and the 6.7 positions should be most active in electrophilic substitution reactions. The 6.7-positions are characterized by the highest free valence indices and, consequently [9], the lowest energies of cationic localization; these positions are also distinguished by the highest electron densities in the limiting orbital. The 4.9 positions correspond to the highest effective negative charges. What has been said permits the expectation that in various electrophilic substitution reactions, depending on the particular features of their mechanism [10], the attacking reagent will be directed either to the 4.9-positions (if the limiting stage of the reaction is the formation of an intermediate σ-complex) or into the 6.7-positions (if the limiting stage is the decomposition of the σ-complex).

There is very limited information in the literature [11] on the reactivity of the perimidines. The structure of a 4(9)- or 6(7)-derivative has been suggested for the monobromo derivative arising by the bromination of 2-methylperimidine. When the amount of bromine is increased, products can be obtained with the structure of 4.6-, 7.9-, 4.7-, 6.7-, 6.9- or 4.9-dibromo-2-methylperimidine. Structure III has been established fairly reliably for the tribromo derivative. As may be expected on the basis of the molecular diagram V, the nitration of 2-phenylperimidine does not affect the 2-phenyl nucleus and takes place in a similar manner to bromination.

Table 2

Molecular Polarizations, Refractions, and Dipole Moments of the Perimidines. Dioxane, 30° C

No.	Compound	P_∞, cm^3	R_D, cm^3	μ, D
1	Perimidine	254.2	50.2	3.18
2	N-Methylperimidine	300.8	56.4	3.48
3	2-Methylperimidine	269.3	56.3	3.25
4	2-Phenylperimidine	259.1	74.1	3.03
5	2-(p-Nitrophenyl)perimidine	343.8	79.8	3.62
6	2-(o-Hydroxyphenyl)perimidine	370.4	77.4	3.82
7	2-(o-Methoxyphenyl)perimidine	395.2	84.1	3.94

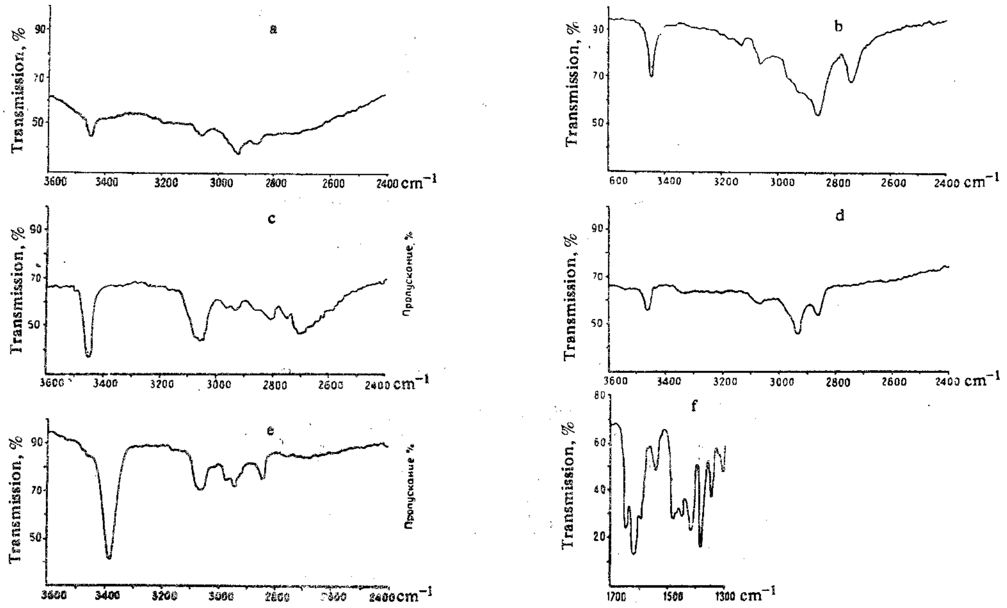


Fig. 1. IR spectra of perimidines: a) perimidine (CCl_4); b) 2-methylperimidine (CCl_4); c) 2-phenylperimidine (CCl_4); d) 2-(o-hydroxyphenyl)perimidine (CCl_4); e) 2-(o-methoxyphenyl)perimidine (CCl_4); f) 2-methylperimidine (paraffin oil).

If the naphthalene system of perimidine is the object of electrophilic attack, its hetero ring must be inclined to nucleophilic substitution reactions in position 2. It is known [12] that N-alkylbenzimidazoles and napthimidazoles undergo amination smoothly with sodium amide. This is explained by the high effective positive charges in the 2 positions of the imidazole ring and the low anionic localization energies. A comparison of these magnitudes with the corresponding figures for perimidine calculated with identical parameters for the hetero atoms (Table 1) permits the assumption that in the perimidine series the amination reaction must be capable of taking place even more readily.

A comparison of thermolecular diagrams IV–VI clearly shows the characteristic feature of the perimidines. In contrast to the 2-substituted benzimidazoles [13], the introduction of a substituent into position 2 has no effect whatever on the electron distribution in the hydrocarbon fragment attached to the heterocyclic ring. Thus, the six-membered heterocyclic ring of perimidine in the ground electronic state is a poor conductor of electronic influences.

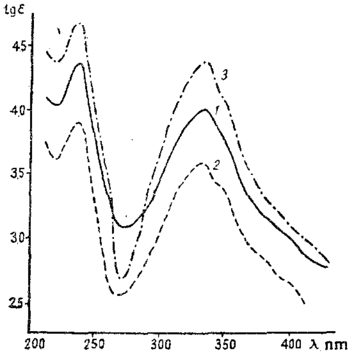
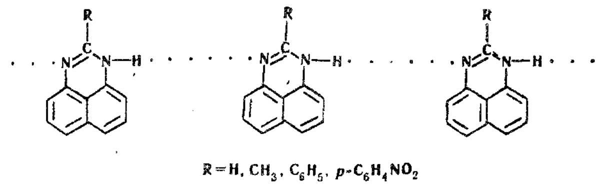


Fig. 2. UV spectra of perimidines (dioxane): 1) N-methylperimidine; 2) perimidine; 3) 2-methylperimidine.

The dipole moments (DM) of perimidine and and its derivatives are characterized by fairly high figures (Table 2) and agree with ideas on the considerable polarity of their molecules. As in the case of imidazole derivatives [14], the dependence of the dielectric permeability of dioxane solutions of perimidine and of 2-methyl-, 2-phenyl-, and 2-(p-nitrophenyl)perimidines on the concentration is not linear, and the molecular polarization P_∞ decreases with dilution.

This type of relationship $P_\infty = f(C)$ and $\varepsilon = f(C)$ shows the association of the molecules of perimidine in solutions, as is the case for the imidazoles [12].



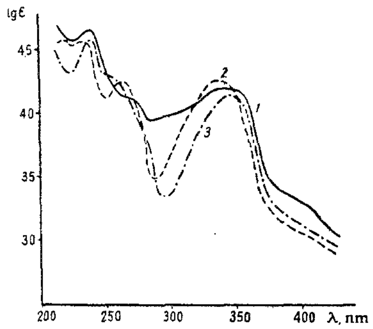


Fig. 3. UV spectra of perimidines (dioxane): 1) 2-(o-methoxyphenyl)perimidine; 2) 2-(o-hydroxyphenyl)perimidine; 3) 2-phenylperimidine.

The introduction into position 2 of a voluminous aryl substituent apparently creates some steric hindrance to the association which is particularly large in the case of 2-(o-R-aryl) substituents. Thus, compounds Nos. 6 and 7, and also No. 2 [here and below the compounds are denoted by the numbers shown in Table 2] are not associated in solutions: the magnitudes of P_∞ are constant and do not depend on the concentrations. However, there is another reason for the absence of the association of compounds Nos. 6 and 7. Compound No. 7 is a structural analog of salicylidene-α-naphthylamine, in which the naphthalene ring is kept in the plane of the molecule by the cyclic NH group. According to this, one may assume that in Compound No. 6, as in the salicylidenearylamines [15–17] and 2-(o-hydroxyaryl)benzazoles [18] there is an intramolecular hydrogen bond (IHB) of the type O—H. . . N.

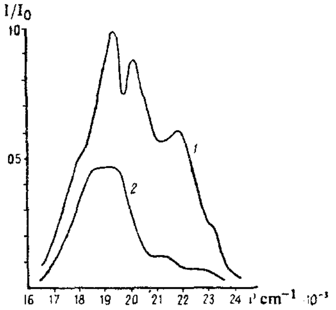


Fig. 4. Luminescence spectra of: 1) 2-methylperimidine; 2) 2-phenylperimidine.

By making use of the method of calculating DM for various conformations based on the vectorial combination of the DM's of phenol, anisole, and 2-phenylperimidine* and described in detail previously [18–20],

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*The vector DM of 2-phenylperimidine was determined on the basis of the magnitude of the DM of compounds nos. 4 and 5. At the given position of the axis of coordinates, it is equal to $-1.51\vec{i} + 2.63\vec{j}$ (D).

it is possible to determine which conformation is preferable for compounds 6 and 7.

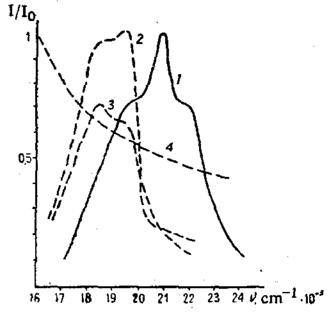
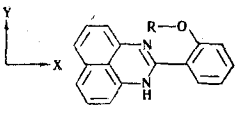


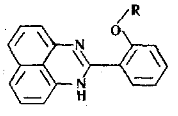
Fig. 5. Luminescence spectra of 2-(o-hydroxyphenyl)perimidine: 1) in ethanol (T = 90° K); 2) in hexane (T = 77° K) before irradiation; 3) in hexane (T = = 77° K) after irradiation for 3 min; 4) kinetic quenching for $\lambda_{max} = 19 \cdot 10^3$ cm^{-1}.

The DMs calculated for the various conformations VII-IX of compounds Nos. 6 and 7 (μ_{calc}) are given below.



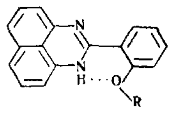
μ_{calc} = 3.42 *D*
2.89 *D*

VII R=H
R=CH_3



VIII R=H
R=CH_3

μ_{calc} = 2.62 *D*
2.83 *D*



IX R=H
R=CH_3

μ_{calc} = 4.44 *D*
4.27 *D*

A comparison of the experimental values of the DMs (Table 2) with μ_{calc} shows that compound No. 6 exists mainly in conformation VII with a six-membered quasiaromatic ring chelated by a IHB, while for compound VII the most probable configuration is IX, which is also stabilized by a IHB. In both cases, therefore, the possibilities of the association of the molecules of the compounds are greatly reduced. The greater deviations of μ_{calc} from the experimental values of the DMs than for the compounds studied previously—hydroxyanils and benzazoles [18, 20]—are due both to the greater approximation of the present calculation and to the possible existence of an equilibrium between the conformations VII ⇄ IX for compound No. 6 and IX ⇄ VIII for compound No. 7 and also to an equilibrium with the associates.

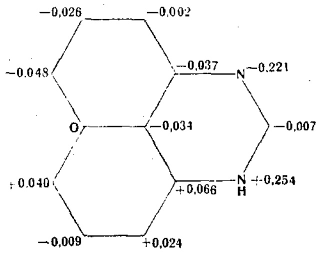
The IR spectra of the perimidines are a further confirmation of the conclusions drawn on the basis of the DM data. The spectra of perimidine and its derivatives in the solid state lack the band of the stretching vibrations of a free NH group, in place of which there is a diffuse band at 2500–3200 cm^{-1} characteristic for the vibrations of associated N—H...N groupings in the imidazoles [8, 12]. However, in solutions, in addition to this band, there is a band of ν_{NH} at 3450 cm^{-1} (Fig. 1a). Other typical examples of spectra are shown in Fig. 1b and c.

The spectrum of compound No. 6 (Fig. 1d) does not show the bands of the stretching vibrations of a free OH group but does show the band of the stretching vibrations of a nonassociated NH group and the diffuse band at 2500–3300 cm^{-1} which is characteristic for the vibrations of O—H...N in a six-membered ring of a IHB [15–17]. All these observations agree with conformation VII for compound No. 6 which was established on the basis of the DM data.

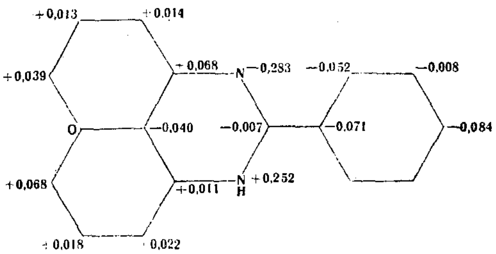
The band of the O—H...N vibrations has a well-defined structure at 2860, 2940, and 3065 cm^{-1}; analogous bands at the same frequencies are present in the spectrum of perimidine (Fig. 1a), which gives grounds for assigning these bands to the ν_{CH} vibrations that are characteristic for the perimidine skeleton.

The spectrum of compound No. 7 (Fig. 1e) shows, in addition to the bands of the stretching vibrations of C—H groups, a strong band at 3385 cm^{-1} (in the crystalline state, tablets with KBr, at 3348 cm^{-1}) which corresponds to the vibration of a N—H group particularly in a IHB of the type N—H ... O<, conformation IX. The form of the spectrum does not exclude the simultaneous presence of associates N—H...N. It is interesting that dilution does not affect the ratio of the intensities of the bands at 3385 cm^{-1} and 2500–3100 cm^{-1}.

In the region of the stretching vibrations of the skeletal bonds of perimidine three bands can be seen at 1598, 1620, and 1646 cm^{-1}. The spectra of all the 2-substituted perimidines also show the band at 1550 cm^{-1} characteristic for 2-substitution. A typical spectrum is shown in Fig. 1f.



X



XI

Table 3

Data on the Synthesis and Constants of the Perimidines

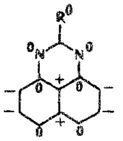
Compound No.*	Mp, °C (solvent for crystallization)	Empirical formula	Found, %		Calculated, %		Mp according to the literature, °C
			C	H	C	H	
1	222 (ethanol)	—	—	—	—	—	222[1]
2	81-82 (methanol)	$C_{12}H_{10}N_2$	78.80	5.35	79.08	5.54	—
3	210-213 (ethanol)	—	—	—	—	—	212[6]
4	178-180 (benzene-petroleum ether)	—	—	—	—	—	182[23]
5	190-192 (50% ethanol)	$C_{17}H_{11}N_3O_2$	70.29	4.01	70.57	3.84	180[23]
6	243-244 (50% dioxane)	$C_{17}H_{12}N_2O$	78.39	4.84	78.43	4.66	—
7	124-126 (benzene-petroleum ether)	$C_{18}H_{14}N_2O$	78.83	5.34	78.80	5.15	—

*For names, see Table 2.

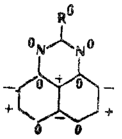
The UV spectra of perimidine and its derivatives are shown in Figs. 2 and 3. The spectrum of perimidine and its N-methyl derivative are characterized by two broad absorption bands with maxima at 235 and 335 nm. They are evidently both the results of the superposition of the bands of several electronic transitions. The greatest contribution to the long-wave band is made by the transition $\pi_1 \to \pi^*_1$, which is connected with the transfer of charge from the naphthalene part of the molecule into the heterocyclic ring with a considerable increase in the electron density on the second carbon atom. This interpretation follows from a comparison of the distribution of the charges in the ground state IV and the first excited state X of perimidine.

The long-wave band in the spectrum of 2-phenylperimidine is similar in nature. However, in this case the transfer of charge from the naphthalene nucleus extends both to the heterocyclic ring and to the phenyl ring conjugated with it. The electronic configuration of the first excited state of 2-phenylperimidine is described by structure XI.

The greatest contribution to the absorption band of perimidine with λ_{max} 235 nm is apparently made by the transition $\pi_2 \to \pi^*_3$, due to local excitation and not accompanied by charge transfer. The nature of this transition can be understood from a consideration of the symmetry properties of the corresponding bonding π_2 and antibonding π^*_3 orbitals.



π^*_2-orbital



π^*_3-orbital

Orbitals with such symmetry are characteristic for all 2-substituted perimidines. A band with λ_{max} close to 235 nm corresponding to this is observed in the spectra of various 2-substituted perimidines (Figs. 2 and 3).

The luminescence of perimidine and some of its derivatives at room temperature has been studied by Japanese authors [21], who noted that the total luminescence of the perimidines is less strong than that of the naphthimidazoles. We have studied the luminescence properties of some perimidines in frozen ethanol and hexane solutions at temperatures of 77-90° K (Figs. 4 and 5).

It is interesting that the introduction of a 2-aryl radical leads to a structureless spectrum; in the case of compounds Nos. 1, 3, 5, and 7, irradiation in UV light leads to phosphorescence with an afterglow time of about 1-7 sec; in the case of compound No. 6, on irradiation a considerable (particularly in hexane) quenching of the luminescence is observed (Fig. 5) with a redistribution of the relative intensities in the long-wave luminescence maxima. Analogous effects have been reported in a series of salicylidenearylamines and are connected [22] with the photochemical reaction of proton transfer. By analogy, the proton phototransfer reaction in compound No. 6 can be described by the following equation:

EXPERIMENTAL

The synthesis of perimidine was carried out by Sachs' method [1]. To obtain the 2-substituted perimidines a procedure was used [6] according to which equimolar amounts of 1, 8-naphthalenediamine and the chloride of the appropriate acid in benzene were kept at the boil for 1.5-2 hr (we found that it was preferable to use the higher-boiling mesitylene as solvent). The perimidine hydrochlorides formed were decomposed with ammonia and the perimidines were recrystallized from a suitable solvent. N-Methylperimidine was obtained by the methylation of perimidine with methyl iodide in an alcoholic solution of KOH.

Other data on the perimidines are given in Table 3.

Spectra. The UV absorption spectra were taken on a SF-4 spectrophotometer in dioxane solutions at concentrations of 10^{-3}-10^{-5} M. The IR spectra were obtained on a UR-10 spectrometer in CCl_4 solutions in cells 20 mm long, in the form of mulls with paraffin oil, and in tablets of KBr. The luminescence spectra were measured on a ISP-51 spectrograph with a FEP-1 attachment in a cell formed by an optical Dewar vessel. Thermostatting at low temperatures was effected by means of liquid nitrogen. Details of the procedure have been given previously [24].

Dipole moments were determined as described by Minkin et al. [14] in dioxane at 30° C. The dielectric permeability of dioxane at this temperature, determined with respect to benzene, is 2.025. The values of P_∞ were determined by graphical extrapolation to zero concentration. The molecular refractions were calculated as the sum of the refractions of the bonds for the sodium D line. The atomic polarization was not taken into account.

The calculations by the HMO method were carried out on the M-20 computer using the program compiled by Ostroumov [25]. The following parameters of the heteroatoms were used [56]: $\alpha_{-N=} = \alpha^\circ + 0.5\beta^\circ$, $\alpha_{NH} = \alpha^\circ + 1.5\beta^\circ$, $B_{C-N} = 0.8\beta^\circ$ $\beta_{C=N} = \beta^\circ$. The magnitudes of $\overrightarrow{\mu_\pi}$ were obtained on the basis of a geometry of perimidine molecules in which all the bond lengths were taken as equal to the length of the aromatic C–C bond and all the angles equal to 120°. The values of μ_σ were calculated from the moments of the σ-bonds given by Orgel [27].

The authors express their thanks to M. I. Knyazhanskii for taking the luminescence spectra.

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