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QUANTUM-CHEMICAL STUDY OF THE ELECTRONIC STRUCTURES AND SPECTRAL PROPERTIES OF OXAZOLE ANALOGS OF 1,4-DISTYRYLBENZENE AND THE ISOMERIC DISTYRYLNAPHTHALENES

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The electronic structures and spectral properties of a number of oxazole analogs of 1,4-distyrylbenzene and the isomeric 2,6-, 1,5-, and 2,7-distyrylnaphthalenes were studied within the framework of the Pariser–Parr–Pople method. The long-wave band of the electronic spectra of these compounds is formed by the $S_0 \rightarrow S_1$ lower electron transition, which has general molecular character and is accompanied by intramolecular charge transfer. Intense electron transitions from fluorescent level S_1 to higher electron-excitation levels are absent over the range of the absorption and fluorescence bands.

In our preceding communication [1] we described the synthesis and spectral-luminescence properties of azole analogs of 1,4-distyrylbenzene and the isomeric distyrylnaphthalenes. The synthesized compounds have intense fluorescence, and some of them are efficient converters of laser radiation. For a more profound study of the observed fluorescence and generation properties one must ascertain the nature of the electron-excitation states and the electron transitions in these compounds. The literature does not contain information regarding a theoretical study of the electronic spectra of such systems, and the available data are restricted to a few diaryl-, styryl-, and stilbenyl-substituted oxazoles [2, 3].

The aim of the present research was to make a quantum-chemical study of the electron structures and electronic absorption spectra of oxazole analogs of 1,4-distyrylbenzene and

TABLE 1. Effect of the Conformation on the Wavelength (λ) and Oscillator Force (f) of the $S_0 \rightarrow S_1$ Transition in the I Molecule

Conformation	λ, nm	f
syn-cis	360,8	2,33
syn-trans	360,1	2,46
anti-cis	360,7	2,34
anti-trans	359,9	2,53

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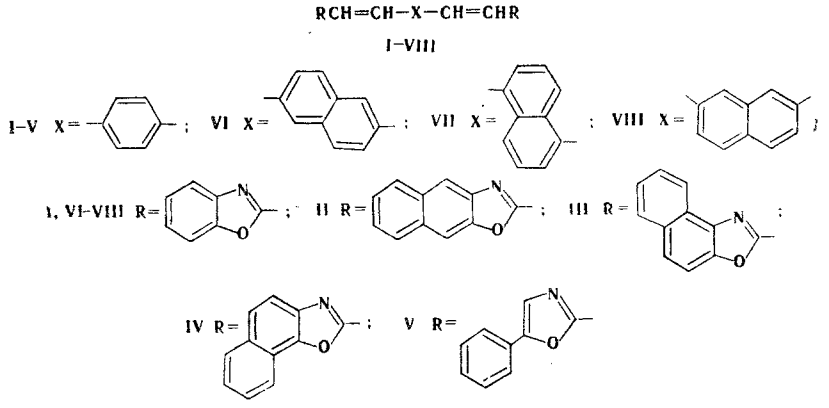
distyrylnaphthalenes within the framework of the Pariser–Parr–Pople method [4, 5] and, above all, to ascertain the nature of the long-wave absorption band, the parameters of which should be taken into account in the study of the fluorescence and generation properties of organic luminophores [6].

Of the series of compounds described in [1] we selected 1,4-bis[β-(2-benzoxazolyl)-vinyl]- (I), 1,4-bis[β-(naphth[2,3-d]oxazol-2-yl)vinyl]- (II), 1,4-bis[β-(naphth[1,2-d]-oxazol-2-yl)vinyl]- (III), 1,4-bis[β-(naphth[2,1-d]oxazol-2-yl)vinyl]- (IV), and 1,4-bis[β-(5-phenyloxazol-2-yl)vinyl]benzene (V) and 2,6- (VI), 1,5- (VII), and 2,7-bis[β-(2-benzoxazolyl)vinyl]naphthalene (VIII) for the theoretical study. Compounds I-V have different terminal fragments R, while I and VI-VIII differ with respect to central fragment X:



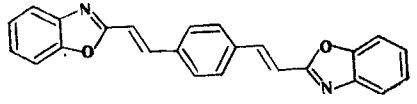
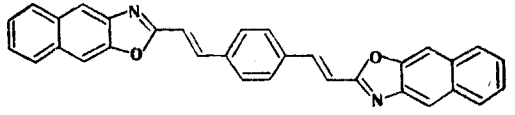
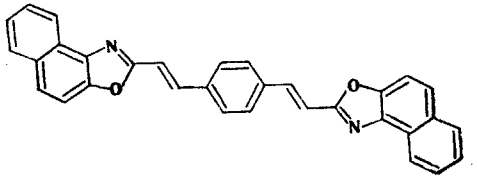
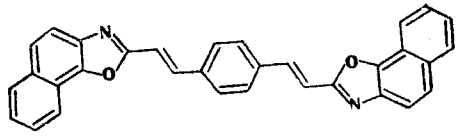
The quantum-chemical calculations for the I-VIII molecules were made within the Pariser–Parr–Pople π-electron approximation [4,5], which is widely used for the theoretical of study of heteroaromatic molecules. The standard values of the semiempirical parameters, viz., the ionization potentials of the valence states and the coulombic integrals, for the C, N, and O atoms were used [7]. The resonance integrals were varied during the iteration procedure and were calculated from the bond orders with the aid of the linear Nishimoto–Forster expression [8]. The two-center integrals of electronic repulsion were calculated from the Mataga–Nishimoto formula [9, 10]. The bond lengths were made self-consistent with respect to the bond orders during the calculation [11]. The excited states and the corresponding electron transitions were calculated within the approximation of configuration interaction with allowance for 25 singly excited configurations.

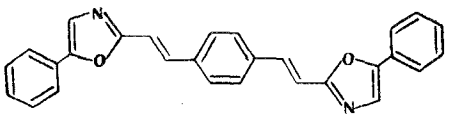
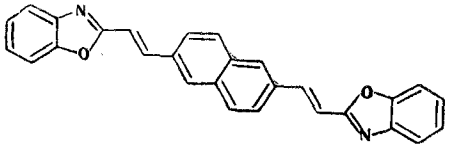
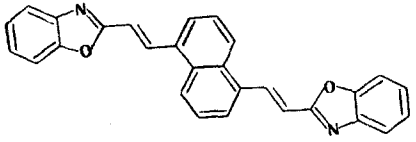
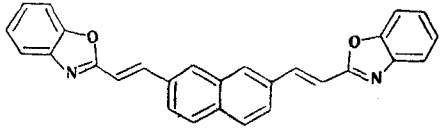
The existence of various conformations that differ with respect to the spatial orientation of the ethylene bonds (S-cis and S-trans) and the oxazole rings (S-syn and S-anti) is possible for the molecules under consideration. The results of the calculation, which are presented in Table 1 for various conformations of the I molecule, show that the wavelengths (λ) and oscillator forces (f) of the electron transitions depend slightly on the choice of conformation. The calculations for the remaining molecules were therefore made only for one conformation, viz., the syn-cis conformation in the case of VIII and the anti-trans conformation in the remaining cases (Table 2). On the basis of the IR spectra and the PMR spectrum we demonstrated [1] that the molecules of these compounds have a trans configuration relative to the C=C bonds.

A comparison of the calculated wavelengths and the oscillator forces of the electron transitions with the experimental electronic absorption spectra of I-VIII (Table 2) shows that only one intense $S_0 \rightarrow S_1$ transition (f = 2.2-2.9) is found in the region of the long-wave band. The oscillator force of the adjacent transitions that fall into the region of this band is equal or close to zero. The next intense transition — $S_0 \rightarrow S_3$ in the II molecule, $S_0 \rightarrow S_4$ in the III and V-VIII molecules, and $S_0 \rightarrow S_5$ in the IV molecule — is shifted 65-140 nm to the shortwave side and falls in the region of the second spectral band. The long-wave absorption band in all cases is consequently formed by one electron transition, viz., $S_0 \rightarrow S_1$. In the case of I, III-VI, and VIII this band has a vibrational structure that is displayed even more distinctly in the fluorescence spectra, which are mirror-symmetrical with respect to the long-wave band.

The calculation showed that the $S_0 \rightarrow S_1$ transition is polarized in all cases along the long axis of the molecule and is accompanied by intramolecular π-charge transfer (Δq), the magnitude of which ranges from 0.10 to 0.25 e (Table 2). An analysis of the distribution

TABLE 2. Electronic Absorption Spectra of I-VIII and Results of a Quantum-Chemical Calculation of the Electron Transitions in Their Molecules*

Compound	Structure	Absorption in n-octane, λ_{max}, nm	Wavelengths (nm) and oscillator forces of the electron transitions	Charge transfer for $S_0 \rightarrow S_1$ (e)	Probability of localization of the $S_0 \rightarrow S_2$ on the L_{fr} fragments
I		394 sh, 374, 358 sh 238	$S_0 \rightarrow S_1$ 360 (2,53) $S_0 \rightarrow S_2$ 294 (0,0) $S_0 \rightarrow S_3$ 265 (0,0) $S_0 \rightarrow S_4$ 261 (0,25)	0,164 O: 0,014 N: 0,001 C=C: 0,046	X 0,30 C=C 0,36 R 0,34
II		380 240	$S_0 \rightarrow S_1$ 371 (2,88) $S_0 \rightarrow S_2$ 328 (0,0) $S_0 \rightarrow S_3$ 315 (0,59) $S_0 \rightarrow S_4$ 299 (0,0)	0,205 O: 0,013 N: −0,011 C=C: 0,056	X 0,25 C=C 0,32 R 0,43
III		428 sh, 404, 386 sh 308 250	$S_0 \rightarrow S_1$ 373 (2,70) $S_0 \rightarrow S_2$ 316 (0,0) $S_0 \rightarrow S_3$ 270 (0,0) $S_0 \rightarrow S_4$ 268 (0,20)	0,250 O: 0,017 N: 0,004 C=C: 0,068	X 0,25 C=C 0,32 R 0,43
IV		416 sh, 394, 376 sh 272 258	$S_0 \rightarrow S_1$ 366 (2,44) $S_0 \rightarrow S_2$ 308 (0,0) $S_0 \rightarrow S_3$ 288 (0,01) $S_0 \rightarrow S_4$ 282 (0,0) $S_0 \rightarrow S_5$ 263 (0,50)	0,202 O: 0,014 N: 0,010 C=C: 0,060	X 0,27 C=C 0,34 R 0,39

V		408 sh, 390, 375 sh 272 238	$S_0 \rightarrow S_1$ 376 (2,33) $S_0 \rightarrow S_2$ 314 (0,0) $S_0 \rightarrow S_3$ 268 (0,0) $S_0 \rightarrow S_4$ 260 (0,79)	O: N: C=C:	0,236 0,022 0,0 0,058	X 0,26 C=C 0,32 R 0,42
VI		396 sh, 376 288 sh, 280 250	$S_0 \rightarrow S_1$ 357,5 (2,18) $S_0 \rightarrow S_2$ 302 (0,0) $S_0 \rightarrow S_3$ 295 (0,06) $S_0 \rightarrow S_4$ 272 (1,40)	O: N: C=C:	0,176 0,012 0,003 0,064	X 0,42 C=C 0,29 R 0,29
VII		360 282 248	$S_0 \rightarrow S_1$ 379 (2,26) $S_0 \rightarrow S_2$ 317 (0,0) $S_0 \rightarrow S_3$ 289 (0,0) $S_0 \rightarrow S_4$ 270 (0,49)	O: N: C=C:	0,104 0,010 0,0 0,034	X 0,49 C=C 0,26 R 0,25
VIII		358 sh, 343, 330 sh 278 272 250	$S_0 \rightarrow S_1$ 336 (2,8) $S_0 \rightarrow S_2$ 312 (0,08) $S_0 \rightarrow S_3$ 304 (0,09) $S_0 \rightarrow S_4$ 280 (0,73)	O: N: C=C:	0,216 0,015 0,004 0,061	X 0,36 C=C 0,29 R 0,35

*The absorption spectra were recorded with a Hitachi-356 spectrophotometer. The quantitative spectra could not be obtained because of the low solubilities of I-VIII in n-octane.

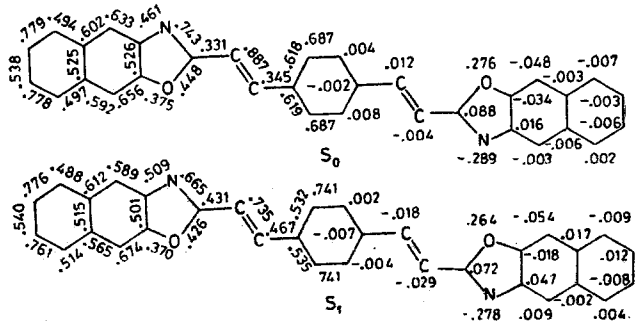


Fig. 1. Electronic structure of the II molecule in the ground S_0 and excited S_1 states.

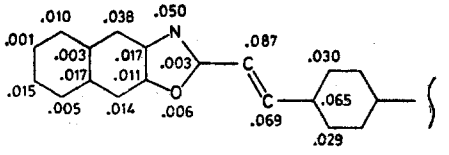


Fig. 2. Distribution of the probabilities of the localization of the $S_0 \rightarrow S_1$ transition on the atoms in the II molecule.

of the π-electron density in the ground and excited states shows that transfer of the electron density in the I-V molecules in the case of the $S_0 \rightarrow S_1$ transition is realized from the peripheral carbocyclic fragments (the benzene or naphthalene fragment in I-IV, the benzene ring together with the carbon atoms of the oxazole ring that are closest to it in V) to the central part of the molecule (X, the C=C bonds, and part of the oxazole ring, including the heteroatoms). On passing to the VI-VIII molecules the character of charge transfer changes: the central naphthalene fragment now displays electron-donor properties when it is excited, and transfer of the electron density is realized from this fragment and the peripheral parts of the molecule to the C=C bonds and the —N=C—O— fragment of the oxazole ring.

The greatest degree of transfer of the π-electron density in the case of the $S_0 \rightarrow S_1$ transition occurs in the C=C bond and is 50-70% of the total value of the intramolecular charge transfer. The degree of transfer of the π-electron density to the heteroatoms is relatively low: the positive charge on the O atom decreases 0.01-0.02 during excitation, whereas the negative charge on the N atom in III, IV, VI, and VIII increases 0.003-0.01; it remains unchanged in the remaining cases, except for II, in which the nitrogen atom behaves like an electron donor. The changes in the π charges on the nitrogen and oxygen atoms and on the C=C bond are presented in Table 2.

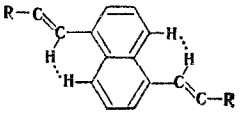
The electronic structure (π charges on the atoms and π bond orders) of the II molecule in the ground S_0 and excited S_1 states is depicted in Fig. 1 as an example.

In order to ascertain the contributions of the various fragments of the molecule to the development of the $S_0 \rightarrow S_1$ transition we made a thorough analysis of the character of the localization of this transition on the atoms. The probability of localization of the electron transition on the μ atom is determined by the diagonal element of the square of the density matrix of the transition ($D^2_{\mu\mu}$) [12]. It is apparent that the sum of $D^2_{\mu\mu}$ with respect to the atoms of the fragment of the molecule gives the probability of localization of the electron transition in this fragment: $L_{fr} = \Sigma D^2_{\mu\mu}$ (if the summation is performed over all of the atoms of the molecule, $\Sigma D^2_{\mu\mu} = 1$). The calculated probabilities (L_{fr}) of localization of the $S_0 \rightarrow S_1$ transition on the central fragment X, the C=C bonds, and the terminal fragments R are presented in Table 2. The L_{fr} values for these fragments are comparable with respect to their bond orders and show that all of these fragments participate in the production of the $S_0 \rightarrow S_1$ transition. The atoms of the ethylene fragments make the greatest contributions to the development of the $S_0 \rightarrow S_1$ transition (Fig. 2): this transition is 32-36% localized on the C=C bonds in the case of I-V, as compared with 26-29%

in the case of VI-VIII (for comparison let us point out that the number of atoms of the two C=C fragments is 11-14% of the total number of atoms of the π-electron system). The distribution of the probabilities of localization of the $S_0 \rightarrow S_1$ transition on the atoms in the II molecule is shown in Fig. 2 as an example.

The results of the calculation of the wavelengths of the $S_0 \rightarrow S_1$ transition (λ_{th}) in the I-V molecules reproduce the experimental λ_{max} values for the principal maximum of the long-wave band with the accuracy that is usually observed for the computational method employed. The λ_{th} values are shifted 14-28 nm to the shortwave region as compared with the corresponding λ_{max} values. According to the results of measurements with solutions in a nonpolar solvent (n-octane), λ_{max} (in nanometers) increases in the order I (374) < II (380) < V (390) < IV (394) < III (404). It is apparent that the difference in the λ_{max} values for the adjacent members of the series is 4-10 nm. The accuracy of the calculation is not accurate enough for reproduction of such small shifts in the absorption spectra, and the calculation actually predicts a different sequence for the wavelengths of the $S_0 \rightarrow S_1$ transition: I (360) < IV (366) < II (371) < III (373) < V (376).

When one compares the calculated absorption spectra of VI-VIII (λ_{th} = 358, 379, and 336 nm, respectively), it is apparent that the calculated spectra of VI and VIII are shifted to the shortwave region relative to the experimental spectra (as in the case of I-V), while a significant long-wave shift of λ_{th} relative to λ_{max} is noted in the case of the VII molecule. For the VII molecule one should take into account the possibility of steric repulsion between the H atom of the ethylene fragment and the peri-H atom of the naphthalene fragment, which is closest to it. It is known that this repulsion arises in hydrocarbons at H...H distances of less than 2 Å [13]. For the planar structure of the VII molecule this distance, which was estimated from the standard bond lengths and bond angles, does not exceed 1.75 Å:



Steric hindrance in the VII molecule will promote twisting about the exocyclic bonds of the naphthalene fragment and the development of a nonplanar structure; this leads to weakening of the conjugation in the molecule and consequently to a shift of the $S_0 \rightarrow S_1$ transition to the shortwave region. The assumption of a nonplanar structure for the VII molecule also explains the absence of a vibrational structure for the long-wave band, characteristic for nonplanar conjugated systems [14]. The distance between the closest H atoms in the VI and VIII molecules is no less than 2.1 Å, and a repulsion effect is therefore not displayed for them.

In conformity with the observed similarity in the absorption and fluorescence spectra for I and VI [1], the calculation indicates the closeness of the energies of the $S_0 \rightarrow S_1$ transitions in these molecules. A calculation of the transitions from fluorescent state S_1 to the high-lying excited S_i states did not reveal any intense $S_1 \rightarrow S_i$ transitions in the region of the absorption and fluorescence spectra of the investigated molecules; this indicates the absence of a secondary singlet-singlet absorption in these molecules and makes it possible to explain their high efficiency as generating compounds [15].

Thus a quantum-chemical study of a number of oxazole analogs of 1,4-distyrylbenzene and the isomeric distyrylnaphthalenes made it possible to ascertain the nature of the long-wave (most intense) band of the electronic absorption spectra of these compounds. The long-wave band is formed by the lower $S_0 \rightarrow S_1$ electron transition with a large oscillator force; the structure of this band observed in individual cases has vibrational character. The wavelength of the $S_0 \rightarrow S_1$ transition is virtually independent of the conformation of the molecule. The $S_0 \rightarrow S_1$ transition is accompanied by intramolecular charge transfer. In compounds with a central benzene fragment X the electron density is transferred from the peripheral carbocyclic parts of the molecule to the central part: X, the C=C bonds, and the —N=C—O— fragments; in compounds with a naphthalene X fragment, the density is transferred from the peripheral parts and the X fragment to the C=C bonds and the —N=C—O— fragment. All of the fragments of the molecule make a contribution to the formation of the $S_0 \rightarrow S_1$ transition, i.e., this transition has whole-molecule character. The calculation indicates the absence in the region of absorption and fluorescence bands of any intense electron transitions from the fluorescent S_1 level to the higher electronically excited levels.

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STEREOSPECIFIC SYNTHESIS OF ALL OF THE POSSIBLE ISOMERS OF 4-UREIDO-3-HYDROXY-2-(5'-ALKOXYCARBONYLBUTYL)THIOPHAN

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and V. M. Berezovskii

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All four possible isomers of 4-ureido-3-hydroxy-2-(5'-alkoxycarbonylbutyl)-thiophan were synthesized by the action of potassium isocyanate on the corresponding hydrochlorides (or hydrobromides) of the stereoisomers of 4-amino-3-hydroxy-2[5'-methoxy(or ethoxy)carbonylbutyl]thiophans, which were obtained by several methods. The configurations of the compounds obtained were proved by PMR spectroscopy.

As a further development of our earlier research [1-3] in the present study we accomplished the stereospecific synthesis of all four isomers of 4-ureido-3-hydroxy-2-substituted thiophans, which are of interest for the synthesis of biologically active compounds.

We synthesized all four isomers (the cis, epi, allo, and epiallo configurations) of 4-ureido-3-hydroxy-2-(5'-alkoxycarbonylbutyl)thiophan (XI-XIV) by the action of potassium isocyanate on the corresponding hydrochlorides (or hydrobromides) of the stereoisomers of 4-amino-3-hydroxy-2-(5'-alkoxycarbonylbutyl)thiophans (VII-X), which were obtained by several methods.

r-4-Benzamido-t-3-hydroxy-c(and t)-2-(5'-methoxycarbonylbutyl)thiophans (III and VI) were converted to r-4-benzamido-c-3-hydroxy-c(and t)-2-(5'-methoxycarbonylbutyl)thiophans (I and IV) by cleavage of the intermediate oxazoline derivatives [2] by heating in an aqueous pyridine medium; these compounds were previously obtained by the method in [1]. r-4-Benzamido-t-3-chloro-c(and t)-2-(5'-methoxycarbonylbutyl)thiophans (II and V) were also obtained from III and VI by the method in [2].

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