QUANTUM-CHEMICAL INVESTIGATION OF SOME OLIGOMERIC HETEROAROMATIC COMPOUNDS

V.* OXAZOLES

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The characteristics of the electronic structures of a number of model aromatic oxazoles realized in aromatic polyoxazoles were obtained within the framework of the Pariser–Parr–Pople method. The UV spectra of most of them were interpreted. The stereoisomerism of dibenzoxazoles is examined.

Continuing our research on the establishment of a correlation between the strength characteristics of bonds (during the degradation of the compounds) and the characteristics of the electronic structures of a number of molecules of heat-resistant polymers [1, 2], we have investigated model aromatic oxazoles and some fragments realized in aromatic polyoxazoles [3]. The characteristics of the electronic structures were obtained within the framework of the Pariser–Parr–Pople method; the details of the calculation and the parameters used were reported in [2]. Thus we calculated oxazole (I), its 2-phenyl and 2,5-diphenyl derivatives [(II) and (III), respectively], benzoxazole (IV), 2-phenylbenzoxazole (V), dibenz[b,e]oxazole (VI), 2,5-diphenyldibenz[b,e]oxazole (VII), a dimer of an aromatic oxazole based on dihydroxydiaminobenzene (VIII), 5,5'-bis(2,2'-diphenylbenzoxazole) (IX), and some models containing differently connected benzoxazole rings (X-XII). The indicated compounds are presented in Figs. 1 and 2.

The calculated rings were assumed to be regular polyhedra with bond lengths of 1.38 Å in the case of oxazole and condensed rings and 1.40 Å in the case of terminal aromatic rings. The C–C bond lengths between the rings were 1.50 Å.

In addition to the usual quantum-chemical characteristics, we calculated the total (E_{tot}), π-bond ($E_{\pi b}$), and resonance (E_{VR}) energies, the resonance energy per π electron (E_{VR}/n), the energy of interaction of the heterorings with one another (E_{int}/m), and the energies of the upper occupied (ε_{uo}) and lower vacant (ε_{lv}) molecular orbitals for the investigated heterocycles. The indicated values are presented in Table 1. Table 1 also includes information on the position of the maxima of the long-wave absorption bands.

Molecular Diagrams. The molecular diagrams of the ground states of the investigated compounds are presented in Figs. 1 and 2. Analysis of the electronic distribution in oxazole I indicates great nonuniformity of the distribution of the π electrons ($\mu_{\pi}^{calc} \approx 3.0$ D) caused by the presence in the ring of heteroatoms of different nature. Moreover, one of the carbon atoms (C_2) is the electrophilic center of the molecule, while two of the others (C_4 and C_5) are nucleophilic centers. The bonds between the carbons and the heteroatoms have the lowest order. It is precisely at these bonds that one should primarily expect disintegration of the heteroring via a homolytic mechanism, and we will therefore subsequently define them as "weak bonds."

Comparison of the molecular diagrams of I and imidazole [1] shows that the oxygen atom in the oxazole ring is a weaker electron donor than the NH group of imidazole. In addition, we direct attention to the facts, first, that the C_4–N bond in I has a lower order, while the C_2–N bond has a higher order than in imidazole, i.e., the "weak" C–N bond is more resistant to homolytic disintegration in the imidazole ring than in the oxazole ring; second, that oxazole already has a dipositive $\overset{+}{C}-\overset{+}{O}$ bond at which its hydrolytic splitting most likely occurs.

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*See [1] for communication IV.

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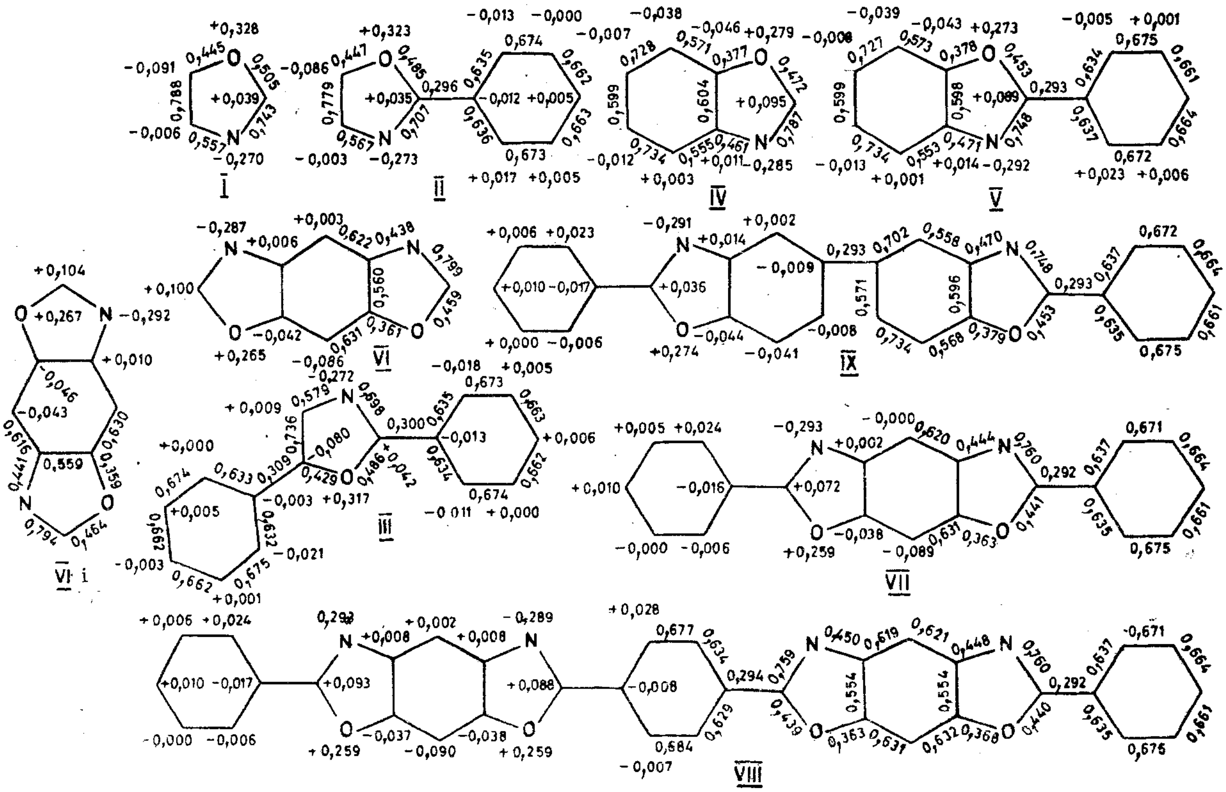

Fig. 1. Molecular diagrams of aromatic oxazoles in the ground state.

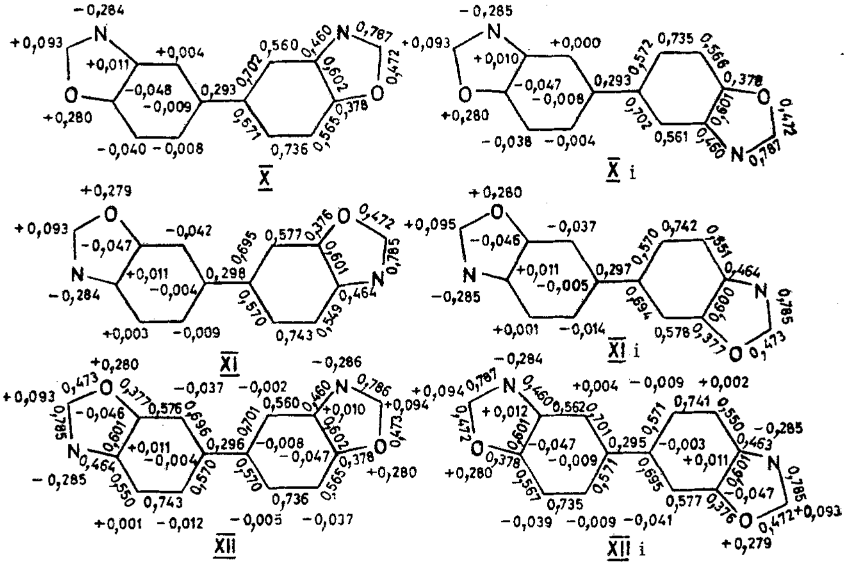

Fig. 2. Molecular diagrams of stereoisomeric dibenzoxazoles in the ground state (X 5,5'-cis, Xi 5,5'-trans, XI 6,6'-cis, XIi 6,6'-trans, XII 5,6'-cis, and XIIi 5,6-trans.

The oxazole and benzene rings in 2-phenyloxazole have identical electronegativities, of course, with a certain tendency for electron-donor character of the benzene ring with respect to the oxazole ring. A more detailed examination of the distribution of charges in II attests to a certain redistribution of the π-electron cloud of the heterocycle in the direction of equalization of the charges on the atoms and of the bond orders. Moreover, the orders of the "weak" bonds remain practically unchanged, while the bonds of that carbon atom to which the phenyl group is attached are most significantly weakened. The electrophilicity of the C_2 atom in II is somewhat depressed.

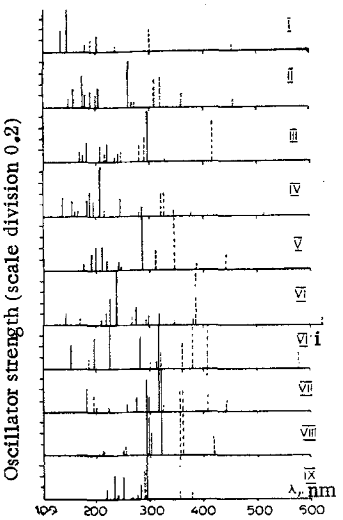

Fig. 3. Calculated singlet–singlet (—) and singlet–triplet (---) transitions in aromatic oxazoles.

2,5-Diphenyl-substitution of oxazole (III) is accompanied by a further decrease in the order of the carbon–carbon multiple bond of the heterocycle, the charge density from which migrates to the adjacent benzene ring. We note a difference in the electronic effects of benzene rings attached to the 2 and 5 positions. The first acts as an electron donor with respect to the oxazole ring (empirical charge Q is +0.005), while the second displays an electron-acceptor effect (Q = −0.027). As compared with I and II, the "weak" C−O bond in III is somewhat weakened, while the "weak" C−N bond is strengthened. The electrophilicity of the $\overset{+}{C}-\overset{+}{C}$ bond in III remains the same as in II.

Annelation of the oxazole and aromatic rings (IV) considerably decreases the orders of the "weak" bonds. The electrophilicity of the C−O bond in this case increases and is the greatest of all of the investigated oxazoles. Of the investigated heterocycles, IV should apparently undergo nucleophilic attack most readily.

The effect of 2-phenyl-substitution of benzoxazole (V) is similar to the effect of substitution of the oxazole ring.

The formation of dibenz[b,e]oxazole structure VI is accompanied by a still greater decrease in the orders of the "weak" bonds and, generally, the bonds between the carbon atoms of the benzene ring and the hetero-atoms of the ring. With respect to the electrophilicity of the $\overset{+}{C}-\overset{+}{O}$ bond, IV occupies a middle position among all of the investigated compounds.

Isomeric dibenz[b,e]oxazole VIi has almost the same characteristics of charge distribution as VI. A comparison of their energy characteristics (Table 1) indicates the advantageousness of the "transoid" configuration.

2,2'-Diphenyl-substitution in VI (see VII) leads to the same shift in electron density as in III and V. Further lengthening of the molecular chain (see VIII) has practically no effect on the characteristics of the charge distribution in the heterocycle.

It is interesting to compare the characteristics of the electronic structure of VII with those of IX, since the first compound is a model of a polybenzoxazole based on dihydroxydiaminobenzene, while the second is a model of a polybenzoxazole based on dihydroxybenzidine. It was found that the bonds in the heterocycles in IX have higher orders; however, the electrophilicity of the C_2 atom is somewhat lower. This means that, according to the results of the quantum-chemical calculations, the polybenzoxazole based on di-

TABLE 1. Energy and Spectral Characteristics of Oxazoles

Compound	$-E_{tot}$, eV	$E_{\pi b}$, eV	E_{VR}, eV	$E_{VR/n}$, eV	$E_{int/m}$, eV	$-\varepsilon_{UO}$, eV	$-\varepsilon_{LV}$, eV	$\Sigma\delta^+$	λ_{max}, nm calc.	symmetry type	exptl.
I	100,703	8,833	3,957	0,6595	—	9,913	0,317	0,367	201	—	
II	178,305	19,475	79,75	0,6646	0,584	9,356	1,701	0,358	267	—	
									260	—	
III	255,933	30,143	12,019	0,6677	0,597	8,941	1,983	0,359	296	—	303[4]
IV	151,007	14,497	6,300	0,6300	—	9,528	1,484	0,374	281	—	276[5]
									243	—	231[5]
V	227,441	23,971	9,990	0,6244	0,536	9,227	2,147	0,362	286	—	299[4]
VI	224,915	18,855	8,941	0,6386	—	8,962	1,798	0,365	298	B_2	—
VIi	224,945	18,885	8,971	0,6408	—	8,909	1,863	0,371	301	B_u	—
VII	376,782	36,802	16,040	0,6169	0,515	8,795	2,339	0,351	317	B_2	—
VIII	678,141	65,141	29,041	0,6313	0,514	8,772	2,668	0,347	321	B_2	—
IX	455,415	48,475	20,513	0,6410	0,536	8,928	2,101	0,360	294	B_2	—
					0,533						
X	302,547	29,527	13,133	0,6567	0,533	9,013	1,576	0,373	273	B_2	—
Xi	302,551	29,531	13,137	0,6569	0,537	9,015	1,613	0,373	274	B_u	—
XI	302,555	29,535	13,141	0,6571	0,541	8,899	1,941	0,372	292	B_2	—
XIi	302,566	29,546	13,152	0,6576	0,552	8,882	1,934	0,375	290	B_u	—
XII	302,562	29,542	13,148	0,6574	0,548	8,938	1,766	0,373	282	—	—
XIIi	302,552	29,532	13,138	0,6569	0,538	8,932	1,777	0,374	281	—	—

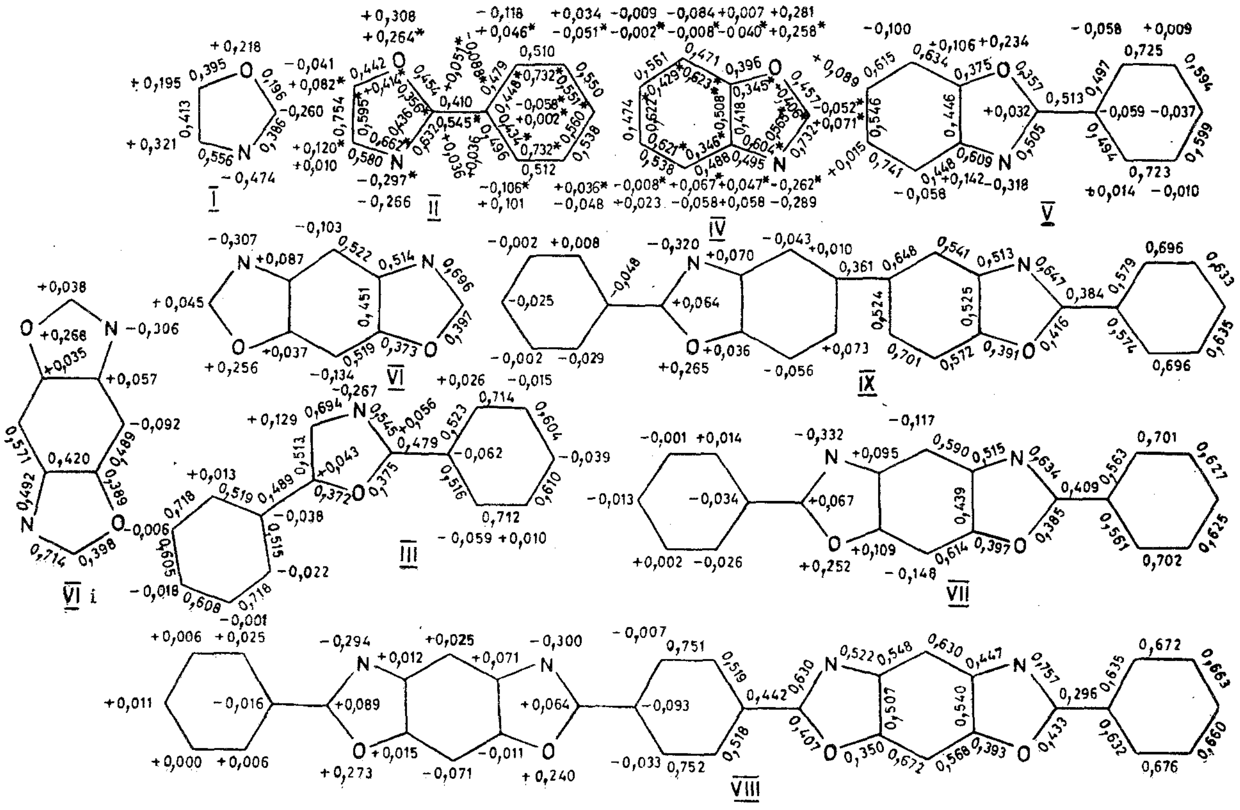

Fig. 4. Molecular diagrams of aromatic oxazoles in the first and second (*) singlet excited states.

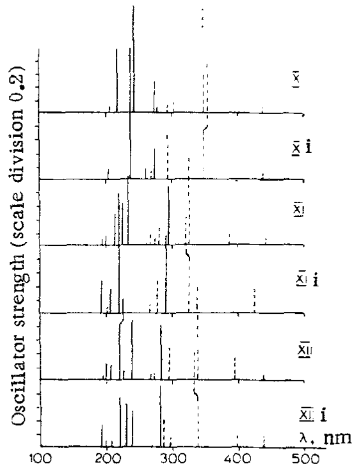

Fig. 5. Calculated singlet–singlet (—) and singlet–triplet (---) transitions in stereoisomeric dibenzoxazoles.

hydroxybenzidine should have higher heat resistance because of the greater homolytic and heterocyclic stability of the oxazole ring. We also note the identical strengths of the C–C bonds between the rings of the diphenyl fragment and between the benzoxazole and benzene ring and a certain tendency for weakening of the terminal C–C bond as the chain of the molecule is lengthened.

Characteristics of the Excited States. The calculated electronic absorption spectra of the investigated compounds are schematically represented in Fig. 3; the λ_{max} values of the long-wave absorption are also presented in Table 1. The molecular diagrams of the compounds in states corresponding to the long-wave excitation are presented in Fig. 4. Comparison of them with the molecular diagrams of the ground state lead to the following results.

Excitation in oxazole is accompanied by a considerable decrease in the orders of all of the bonds except the N–C_4 bond, and especially of the multiple bonds. The electron density was shifted to such an extent from the C=C bonds that the atoms that form it were converted from centers of addition of electrophilic agents to sites of possible attack of nucleophilic agents. Moreover, a large excess of π-electron density is formed on C_2.

The longest-wave excitation in II (ΔE ≃ 267 nm, f ≃ 0.07) is related to the phenyl fragment of the molecule with partial participation of the C=C bond of the oxazole ring. However, the intense transition with ΔE ≃ 260 nm is accompanied by charge transfer (about 0.2 e) from the oxazole ring to the benzene ring with considerable strengthening of the bond between them. In other words, the electron-acceptor properties of the phenyl group are appreciably intensified in the excited state.

The same polarization of the π-electron cloud is also noted for the excited state of III. In this case, the nonequivalence of the benzene ring is retained – the ring in the 2 position has the greater electron-acceptor effect. A more detailed examination of the molecular diagram of III indicates that the orders of all of the bonds of the oxazole ring decrease during excitation, while the orders of the N=C bonds increase. The bonds between the rings are also strengthened.

Two bands of different intensity with λ_{max} 276 and 231 nm [4] are observed in the long-wave region of the UV spectrum of benzoxazole IV. They are satisfactorily reproduced by our calculations (see Table 1). Moreover, it turns out that the low-intensity band corresponds to primary migration of the π-electron density through the benzene ring, while the intense long-wave absorption is accompanied by charge redistribution throughout the entire molecule.

As in all of the 2-phenyl-substituted oxazoles, the excited state of V is characterized by a shift of the π-electron density from the heterorings to the benzene rings. This shift is accompanied by strengthening of the bond between the rings. Moreover, the orders of the "weak" bonds remain practically unchanged, while the electrophilicity of the $\overset{+}{O}-\overset{+}{C}$ bonds turns out to be considerably reduced.

The long-wave excitation of dibenz[b,e]oxazole is of a nature that indicates involvement of the entire molecule. Moreover, the charges on the carbon atoms (the nucleophilicities of C_2 and $C_{2'}$ decrease as the electrophilicities of C_4 and $C_{4'}$ increase) and the orders of all of the bonds except the C–O bond change most significantly.

Substituent effects similar to those described above are observed in the excited states of VII-IX (see their molecular diagrams).

Stereoisomerism of Dibenzoxazoles. The molecular diagrams and calculated electronic absorption spectra of various stereoisomeric dibenzoxazoles are presented in Figs. 2 and 5.

A comparison of the molecular diagrams of the isomers shows insignificant differences in the characteristics of the electron distribution. The examined isomers also differ only insignificantly with respect to energy characteristics (Table 1). However, their comparison makes it possible to note that the cis orientation of the oxazole rings proved to be somewhat more advantageous than the trans configuration only in the case of XII.

The data in Fig. 5 make it possible to expect identical character of the long-wave absorption of dibenzoxazoles with cis or trans orientation of the oxazole rings and a certain difference in their UV spectra in the short-wave region. Stereoisomers with different fusions of the benzoxazole rings (5,5'-, 6,6'-, or 5,6'-) are spectrally different.

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