QUANTUM-CHEMICAL INVESTIGATION OF SOME OLIGOMERIC HETEROAROMATIC COMPOUNDS

II.* 1,3,4-OXADIAZOLES

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The electronic structures of a number of oligomeric 1,3,4-oxadiazoles and their phenyl derivatives were calculated by the Pariser–Parr–Pople method. The energy characteristics and molecular diagrams for the ground and excited states are discussed. It is shown that the effectiveness of conjugation between the rings in polyoxadiazole is close to that in polyphenylene.

Continuing our investigation of the effect of the electronic structure of macromolecules on their strength characteristics in destruction processes [1], in the present communication we examine polyoxadiazoles – one of the promising classes of heat-resisting compounds.

The literature contains individual quantum-chemical calculations of 1,3,4-oxadiazoles and some of their phenyl derivatives by the Hückel method [3-6]. In the present communication we present the results of calculations by the Pariser–Parr–Pople (PPP) method of the ground and excited states of a number of oxadiazoles with different chain lengths and addition isomerism. The methodical details of the calculation and the parameters used were reported in [1]. The geometrical characteristics of the oxadiazole ring were borrowed from [7]. It was assumed that all of the compounds are coplanar, that the benzene rings in them are regular hexagons with bond lengths of 1.40 Å, and that the bonds between the benzene and oxadiazole rings are directed along the bisectors of the corresponding external angles and are 1.50 Å long.

Molecular Diagrams

The molecular diagrams of the examined compounds are presented in Fig. 1 (the numbering of the compounds will subsequently be used in conformity with this figure). The π components of the dipole moments ($\vec{\mu}_\pi$) and other calculated values are presented in Table 1.

It is seen from the molecular diagrams that there is a rather strong interaction between the atoms within the oxadiazole ring, which leads to considerable polarization of the electron cloud.

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*See [1] for communication I.

TABLE 1. Energy Characteristics of 1,3,4-Oxadiazoles

Comp.	μ_π (D)	$\varepsilon_{v.o.}$, eV	$\varepsilon_{l.v.}$, eV	E_{tot}, eV	$E_{\pi b}$, eV	E_{int}, eV	ε_{int}, eV
I	3,88	−10,677	−0,410	−104,182	9,352	—	—
II	3,75	−9,768	−1,717	−181,770	19,980	0,570	0,570
III	3,58	−9,382	−1,971	−259,363	30,613	1,144	0,572
IV	6,80	−9,219	−2,365	−441,702	51,162	2,284	0,571
V	9,38	−9,177	−2,526	−624,040	71,710	3,422	0,570
VI	11,08	−9,169	−2,615	−806,375	92,255	4,557	0,570
VII	4,86	−9,408	−2,181	−441,680	51,140	2,262	0,561

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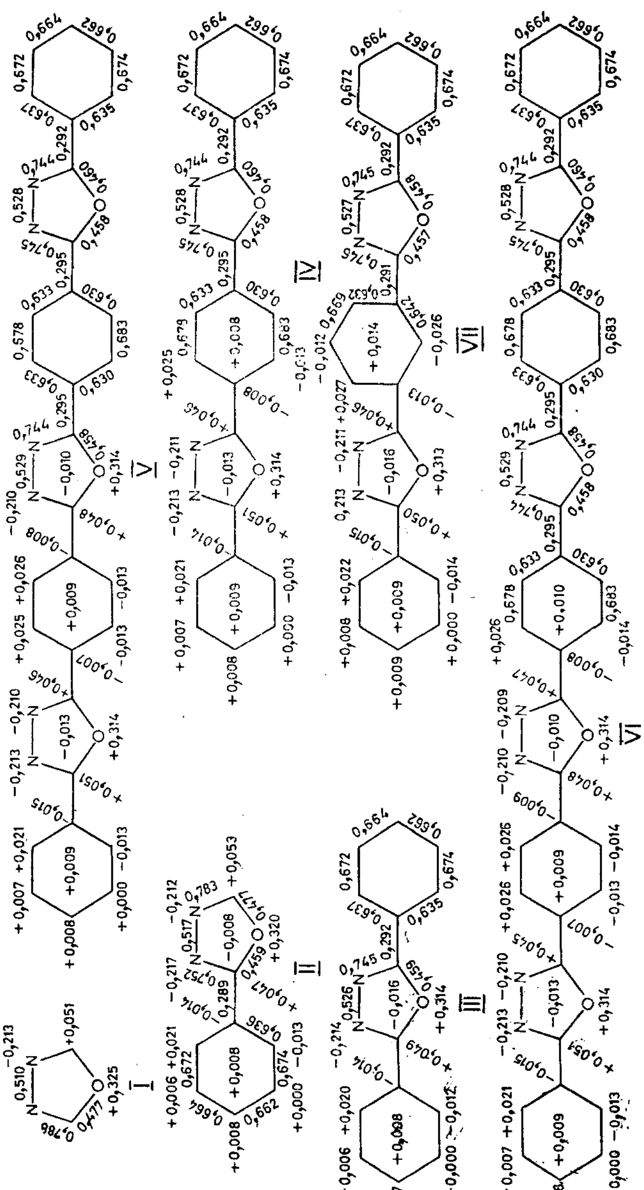

Fig. 1. Molecular diagrams of aromatic 1,3,4-oxadiazoles in the ground state.

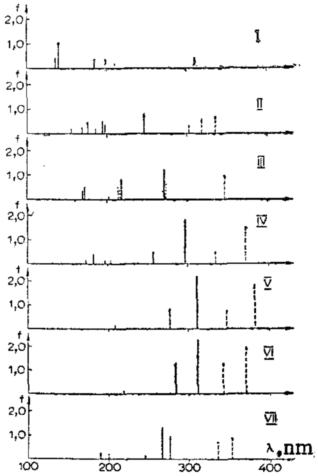

Fig. 2. Calculated electronic spectra of aromatic 1,3,4-oxadiazoles for transitions to singlet (——) and triplet (- - -) excited states (the transitions with $f >$ 0,1 are indicated).

The addition of a phenyl group to the oxadiazole ring in the 2 position leads to a small shift in the electron density away from the phenyl group to the heteroring.

When phenyl groups are simultaneously introduced into the 2 and 5 positions, the charge distribution is obtained as a result of the superimposition of the effects of each phenyl group separately – the charges on the atoms of the $C=N$ bonds become close in magnitude to those in I, but the order of these bonds decreases appreciably. The charges on the carbon atoms of the benzene rings have almost the same values as in II.

The transition from III to IV is accompanied by a change in the charges only on the carbon atoms of the phenyl group that connects the 2-phenyl-1,3,4-oxadiazole fragments. The molecular diagrams of the fragments themselves remain practically unchanged in the process. The magnitude of the charge that develops on any carbon atom of the phenyl bridge group is close to the sum of the charges that develop on this atom from interaction with each of the fragments separately. The same effects that are observed on passing from the monomer to the dimer are observed as the length of the molecular chain is increased further, i.e., on passing to the trimers and tetramers (V and VI, respectively).

A comparison of the molecular diagrams of the m- (VII) and p- (IV) substituted dimers demonstrates that competitive acceptance of the electrons of the phenylene bridge group from the 2-phenyl-1,3,4-oxadiazole fragments is absent in VII.

In comparing the molecular diagrams of I-III that we obtained within the framework of the PPP method with those previously obtained by the Hückel method, it may be noted that the electron density distributions obtained when the Orgel parameters [4] are used in the Hückel MO method prove to be closest to our values. However, the addition of a benzene ring to the oxadiazole ring leads to somewhat different qualitative results in [4].

The energy characteristics of I-VII are presented in Table 1.

The effectiveness of the interaction among all of the rings in the molecule can be estimated by means of the so-called total interaction energies (E_{int}), which are determined as the differences between the π-

TABLE 2. Comparison of the Calculated and Experimental Characteristics of the $\Psi_0 \rightarrow {}^1\Psi_1$ Electron Transitions in Oxadiazoles

Compound	Calculated*		Experimental†		
	$E_{0\rightarrow 1}$, nm	$f_{0\rightarrow 1}$	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	literature
I	185	0,300	—	—	—
II	264	0,011		—	
	246	0,791	248^{e}		8
III	271	1,163	282^{cy}	2,6	9,11
IV	298	1,755	315^{ch}	4,8	11
			318^{cy}	—	9
V	310	2,155	—	—	—
VI	311	2,297	327^{d}	—	8
VII	276	0,932	285^{d}	—	9

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*The terms of the excited states have B_2 (C_{2v} group) symmetry.

†Solvents: e is ethanol, cy is cyclohexane, ch is chloroform, and d is dimethylformamide.

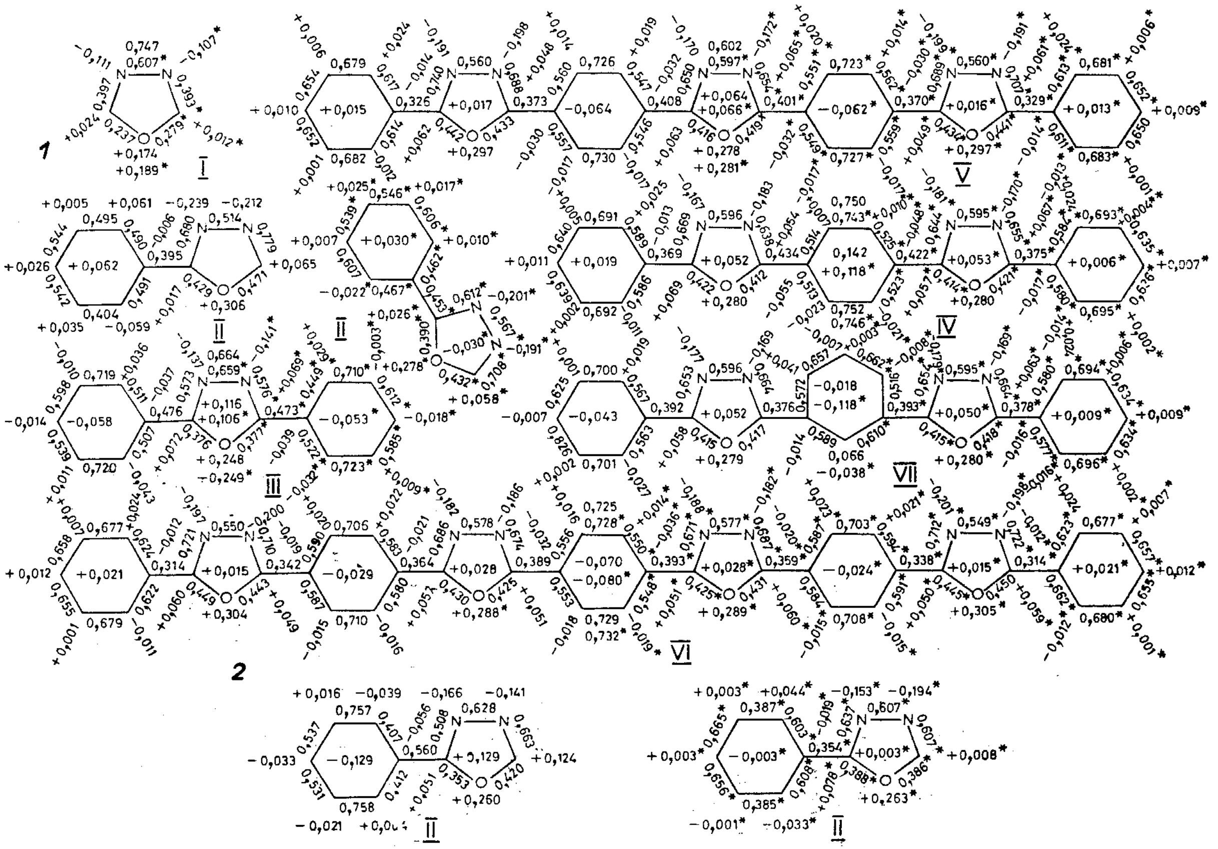

Fig. 3. Molecular diagrams of aromatic 1,3,4-oxadiazoles in the first (1) and second (2) singlet and triplet (*) excited states.

bond energies for the entire molecule ($E_{\pi b}$) and the isolated rings.† The E_{int} value, which is related to the number of bonds between the rings, was assumed to be equal to the energy of interaction (ε_{int}) between the oxadiazole and benzene rings.

The E_{int} value increases on phenylation of the oxadiazole rings and on further lengthening the chain of the molecule, since the number of interacting groups increases. Moreover, the energies of the upper occupied MO ($\varepsilon_{u.o.}$) increase, and the energies of the lower vacant MO ($\varepsilon_{l.v.}$) decrease. However, ε_{int} remains unchanged regardless of whether the interacting rings are terminal or bridge.

A different result is obtained on passing from III to VII: the energy of interaction of the oxadiazole and m-substituted benzene rings proved to be less than ε_{int} in the individual molecules (see Table 1).

It should be noted that ε_{int} for II-VII proved to be close to the energy of interaction of the benzene rings in diphenyl, which we also calculated and found to be 0.588 eV.

Characteristics of the Excited States

The calculated electronic absorption spectra for all of the investigated compounds are presented schematically in Fig. 2. The calculated energies of the $\pi \rightarrow \pi^*$ transitions ($E_{0\rightarrow 1}$) to the first singlet states ($^1\Psi_1$), the oscillator forces ($f_{0\rightarrow 1}$), and the corresponding experimental values are presented in Table 2. The molecular diagrams of I-VII in several excited states are presented in Fig. 3. By comparing the experimental and calculated spectral characteristics, one is easily convinced that they are in good agreement.‡

We will next consider the redistribution of electron density that occurs in the molecules when they are excited. Since it turned out that excitation to singlet and the corresponding triplet states is accompanied by qualitatively similar effects, the reasoning will be equally valid for the two types of excitations.

The transition of I to the excited state is accompanied by migration of the electron density from the atoms of the C=N bonds to the oxygen atom. The long-wave excitation in III-VII additionally leads to migration of the charge to the adjacent phenyl groups, with an attendant increase in the orders of the bonds between the rings and a decrease in the order of the C–O bond. The maximum redistribution of charge in long molecules is observed in the center of the molecule (Fig. 3). The amount of charge that migrates from the heterorings also decreases as the chain length of the molecule increases.

The character of the low-intensity long-wave transition in II is different. In this compound, the electron density is transferred from the benzene ring to the oxadiazole ring during excitation. The molecular diagram of II for the second excited state, the transition to which is more probable, is therefore also presented in Fig. 3. An analysis of the molecular orbitals and molecular diagrams demonstrated that the second electron transition in II is of precisely the same nature as the long-wave electron transitions in the remaining compounds.

Having ascertained that the long-wave transitions in I and III-VII and the second transition in II are of the same nature, it can be asserted that a bathochromic shift of the long-wave absorption band and an increase in its intensity occur on phenylation of the 1,3,4-oxadiazole ring and on further lengthening of the molecules of aromatic oxadiazoles. The same result is also obtained in an analysis of the experimental data (see Table 2). A bathochromic shift is noted during excitation to the triplet states only on passing from the monomer to the dimer (from III to IV); the position of the long-wave absorption band remains practically unchanged as the chain length is increased further.

There are several qualitative differences in the shifts of the electron density in IV and VII during excitation to the singlet states. Thus, while the electron density in p-substituted IV is shifted from the oxadiazole rings and the terminal phenyl groups to the central benzene ring, the electron density in m-substituted compound VII is shifted from the oxadiazole rings principally to the terminal phenyl groups. These differences are not detected during excitation to the triplet states.

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† The value that we calculated for $E_{\pi b}$ of benzene is 10.058 eV.

‡ The small systematic deviations of the calculated $E_{0\rightarrow 1}$ values from the experimental λ_{max} values could have been excluded by correction of the parameters. However, it is not compulsory to do this for a comparative study of one class of compounds.

The λ_{max} value is greater in p-substituted IV on passing to both the singlet and triplet excited states. This is also experimentally observed. This relationship is apparently also retained in polymers.

It is known [9] that oxadiazole rings are unstable to heat, radiation, and chemical action, and that their stability increases considerably when benzene rings are added. This is evidence for, first, the large role of conjugation in these systems and, second, the participatory character of π-electron interactions in similar sorts of characteristics of the macromolecules. The conjugation between the oxadiazole and benzene rings in polyoxadiazoles can be judged from the ε_{int} values and from the observed shift of the long-wave absorption bands. It turns out that if ε_{int} is used, the effectiveness of conjugation between the rings in polyoxadiazole is close to that in diphenyl. The following experimental fact also attests to this: replacement of the benzene ring in polyphenylene by the 1,3,4-oxadiazole ring alters the position of the long-wave absorption band of the polymer in the UV spectrum only very slightly [8, 11, 13].

As the conjugation chain length increases, the effect of the electronic shifts during excitation is extended to the entire molecule, decreasing from its center to its ends. The magnitudes themselves of the shifts of the electron density on the atoms of the fragments in the central portion of the molecule also decrease simultaneously. The high photostability and radiation stability of polymers with a system of conjugated bonds and, in general, of compounds with extended conjugation chains is apparently associated with this.

Since it turned out that the electronic structure in the ground state remains practically unchanged as the chain length of the molecule increases, it is easy to predict the electronic structure of the polymer molecule from the data for the monomer or dimer link. Because of the constancy of the ε_{int} value, the energy of the polymer molecule is determined from the formula

$$E_{\pi b} = n \cdot E_{\pi b}^{\mathrm{ox}} + (n+1) E_{\pi b}^{\mathrm{benz}} + 2n\varepsilon_{\mathrm{int}},$$

where n is the number of oxadiazole groups.

Additional stabilization of the bonds between the oxadiazole and phenyl rings in the polymer, as compared with the monomer, due to conjugation, as proposed in [5], is not detected from either the magnitudes of the corresponding bonds or from the ε_{int} values. This also holds for other bonds in the polymer.

It was experimentally established in [14, 15] that cleavage of the C−O and N=N bonds is most probable in polyoxadiazoles during thermal destruction. The results of the calculations, from which the high degree of double bond character of the C=N bonds follows, and the absence of uniformity of the bond orders in the oxadiazole rings do not contradict this fact.

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