

QUANTUM-CHEMICAL INVESTIGATION OF SOME OLIGOMERIC HETEROAROMATIC COMPOUNDS

IV.* IMIDAZOLES

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Those structures of aromatic imidazoles that can be realized in polybenzimidazoles were investigated within the framework of the computational scheme of the Pariser-Parr-Pople method. The features of the electronic structures of the investigated molecules were exposed. A judgment is expressed relative to the strength characteristics of the bonds in the imidazole rings during thermal or thermal oxidative destruction of aromatic polybenzimidazoles. The stereoisomerism of dibenzimidazoles was examined. The UV absorption spectra of the investigated compounds were interpreted.

The present communication contains information on the results of calculations, within the framework of the Pariser-Parr-Pople method, of molecules containing imidazole rings. In this case, we were first of all interested in structures that may be realized in the construction of polybenzimidazole macromolecules [2]. Imidazole (I), 2-phenylimidazole (II), benzimidazole (III), 2-phenylbenzimidazole (IV), structures of condensed imidazole and benzimidazole rings (V-VIII), and models containing differently linked benzimidazole rings (IX-XI) (Figs. 1 and 2) were investigated. Some of the indicated compounds have already been the subject of quantum-chemical investigation (for example, see [3-5]).

*See [1] for communication III.

TABLE 1. Energy and Spectra Characteristics of Imidazoles

Comp.	E_{tot} , eV	$E_{\pi b}$, eV	E_{VR} , eV	E_{VR}/n , eV	E_{int}/m , eV	$-\epsilon_{\text{UO}}$, eV	$-\epsilon_{\text{LV}}$, eV	$\Sigma\delta$	calc. nm	sym. type	λ_{max} exptl. nm*	literature
I	92,803	9,243	4,367	0,7278	—	9,780	0,139	—	201	—	207	13
II	170,404	19,884	8,384	0,6987	0,583	9,257	1,582	—	267	—	271	13
III	143,069	14,869	6,672	0,6672	—	9,386	1,387	0,431	247	—	245	15
IV	219,499	24,339	10,358	0,6474	0,532	9,167	2,055	0,422	284	—	302	16
											300	2
V	208,967	19,527	9,613	0,6866	—	8,647	1,704	0,418	306†	B_2	295	2
Vi	209,009	19,569	9,655	0,6896	—	8,631	1,743	0,425	293	A_1	—	—
VI	360,824	37,464	16,702	0,6424	0,510	8,547	2,269	0,408	318	B_u	—	—
VII	646,222	66,462	30,362	0,6600	0,508	8,546	2,566	0,406	323	B_2	339	2
VIII	439,529	49,209	21,247	0,6640	0,532	8,780	2,015	0,420	293	B_2	—	—
IX	286,670	30,270	13,876	0,6938	0,532	8,835	1,508	0,430	276	B_2	—	—
IXi	286,675	30,275	13,881	0,6941	0,537	8,837	1,547	0,430	276	B_u	—	—
X	286,675	30,275	13,881	0,6941	0,537	8,799	1,825	0,428	291	B_2	293	2
Xi	286,691	30,291	13,897	0,6949	0,553	8,775	1,816	0,432	289	B_u	—	—
XI	286,688	30,288	13,894	0,6947	0,550	8,806	1,670	0,432	284	—	—	—
XIi	286,674	30,274	13,880	0,6940	0,536	8,796	1,682	0,431	282	—	—	—

* The λ_{max} values, which were taken from [2], were obtained for solutions in H_2SO_4 , while those taken from [13, 15, 16] were obtained for solutions in normal hydrocarbons.

† The calculated oscillator strength was less than 0.08.

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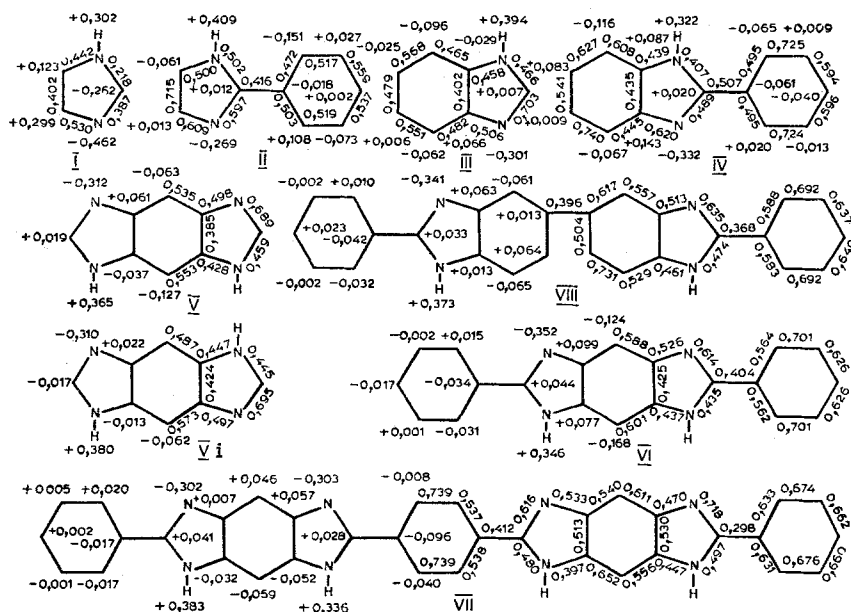


Fig. 1. Molecular diagrams of aromatic imidazoles in the ground state.

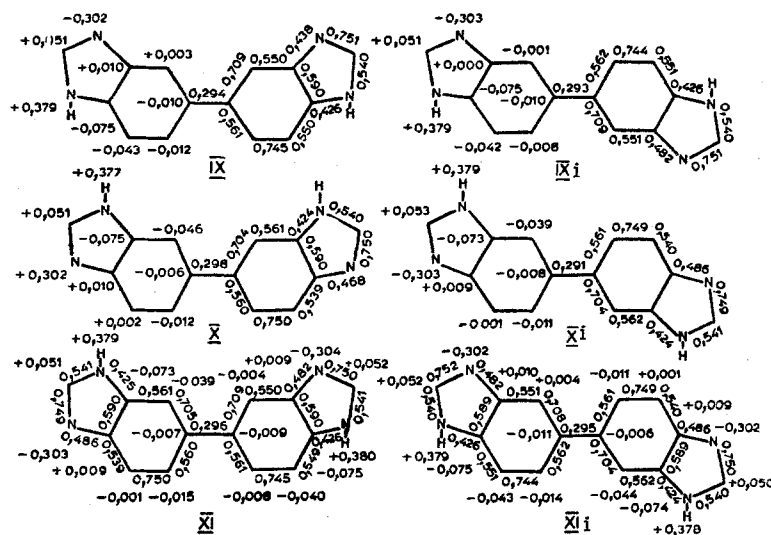


Fig. 2. Molecular diagrams of stereoisomeric dibenzimidazoles in the ground state.

The details of the calculation and the parameters used were reported in [6]. All of the calculated rings were assumed to be regular polyhedra with bond lengths of 1.38 Å in the case of imidazole and condensed rings and 1.40 Å for terminal aromatic rings. The C-C bond lengths between the rings were assumed to be 1.50 Å. The following energy characteristics (Table 1) were calculated for the investigated heterocycles: total (E_{tot}), π -bond ($E_{\pi b}$), and resonance (E_{VR}) energies, resonance energy per π electron (E_{VR}/n), energy of interaction of the heterorings with one another (E_{int}/m) [7], and energies of the upper occupied (ϵ_{UO}) and lower vacant (ϵ_{LV}) MO. In addition, the magnitudes of dipositive character of bond a of the imidazole rings ($\Sigma \delta^+$) and the positions of the maxima of the long-wave absorption bands (λ_{max}) are indicated in Table 1.

Molecular Diagrams

The diagrams of the distribution of the π electrons for all of the investigated molecules are presented in Figs. 1 and 2. The imidazole ring itself (I) is characterized by an uneven distribution of the π -electron density ($\mu_{\text{calc}} \approx 3.5$ D). A significant fraction of the unshared pair of electrons of the pyrrole nitrogen, namely, about 0.4e, migrates to the remaining atoms of the ring, so that they all have excess

electron density. The most nucleophilic of the ring carbon atoms turns out to be $C_{(5)}$. The data on the distribution of charges in the imidazole ring are in good agreement with the known high polarity of imidazole ($\mu \approx 3.8\text{--}4.0$ D [8]) and its reactivity (electrophilic substitution in the neutral form of the molecule occurs at the 5, 4, and – to a somewhat lesser extent – 2 positions [9]). Of the bonds between the carbon and nitrogen atoms in the heteroring, the $N_{(1)}\text{--}C_{(5)}$ (bond e in the imidazole ring) has the lowest order and it can therefore be considered to be the least resistant to homolytic disintegration. The molecular diagram of I obtained in the present study seems preferable to the one presented in [5] if only because the $C_{(2)}$ atom in [5] turns out to be the center of attack by a nucleophilic agent, while it is known [10] that imidazole is incapable, for example, of undergoing amination at this carbon atom.

Judging from the molecular diagrams, the phenyl group in the 2 position of imidazole (see II) leads to a certain increase in the aromaticity of the heteroring. This is particularly manifested in the tendency for equalization of the bond orders. Despite the general electron-acceptor character of the benzene ring with respect to the imidazole ring, the order of bond e increases somewhat.

The principal effect of annelation of imidazole and benzene rings (III) from the point of view of the electron distribution in the imidazole ring should be considered to be the appearance of a dipositive $\begin{smallmatrix} + & + \\ C & -N \end{smallmatrix}$ bond (bond a of the imidazole ring); according to the existing concepts [11], this should lead to the possibility of hydrolytic disintegration of the heteroring at this bond. A measure of the dipositive character of this bond is the magnitude of the overall effective positive charge on the atoms that make up this bond ($\Sigma\delta^+$). In benzimidazole (III), the electron density is shifted to a considerable degree from the imidazole ring to the benzene ring. Moreover, the order of bond e is reduced considerably.

The dipositive character of bond a in 2-phenylbenzimidazole (IV) is reduced as compared with benzimidazole, but bond e in this case has somewhat increased order.

The formation of benzodiimidazole structure (V) is characterized by an appreciable change in the distribution of the electron density. Moreover, the dipositive character of bond a is somewhat reduced, and the decrease in the order of bond e is extremely noticeable. A comparison of the molecular diagrams of V and dibenzimidazoles on the basis of diaminobenzidine (IX) shows an increase in the latter of the orders of bond e and the $\Sigma\delta^+$ values. Similar effects are observed when VI is compared with VIII. We also note that the carbon-carbon bond between the benzimidazole rings in VIII has only a somewhat larger order than the corresponding bonds between the heterorings and the terminal phenyl groups.

A comparison of the molecular diagrams of VI and VII confirms the judgment we expressed in previous communications regarding the invariable character of the distribution of charges when the chain of the macromolecule is lengthened (also see [12]).

Thus an analysis of the molecular diagrams obtained makes it possible to conclude: 1) the weakest bond in the imidazole rings of polybenzimidazoles for homolytic disintegration is bond e, while the most electrophilic bond is bond a. This means that the disintegration of the imidazole ring of polybenzimidazole should occur primarily due to homolytic disintegration of the $N_{(1)}\text{--}C_{(5)}$ bonds and hydrolysis (or other type of nucleophilic cleavage) of the $N_{(1)}\text{--}C_{(3)}$ bonds; 2) a phenyl group in the 2 position in all structures leads to a certain strengthening of weak bonds, i.e., to an increase in the homolytic stability of the imidazole rings; the heterolytic stability is also increased in this case; 3) the electron density on the nitrogen atoms in the heterorings changes only slightly when a phenyl group is introduced into the 2 position, while annelation with a ring of aromatic character leads to a sharp decrease in the effective positive charge on NH and an increase in the electron density on the pyridine nitrogen atom; 4) the simultaneous presence of acid and basic properties in the imidazole rings should promote association of the polybenzimidazole macromolecules through the formation of strong hydrogen bonds; 5) the imidazole rings in polybenzimidazoles based on diaminobenzidine should be more resistant to homolytic reactions and less resistant to hydrolysis than in the case of analogs based on tetraminobenzene.

Characteristics of the Excited States

The calculated electronic absorption spectra of the investigated compounds are represented schematically in Figs. 4 and 5. The molecular diagrams of the states corresponding to the long-wave electronic excitation are presented in Fig. 3.

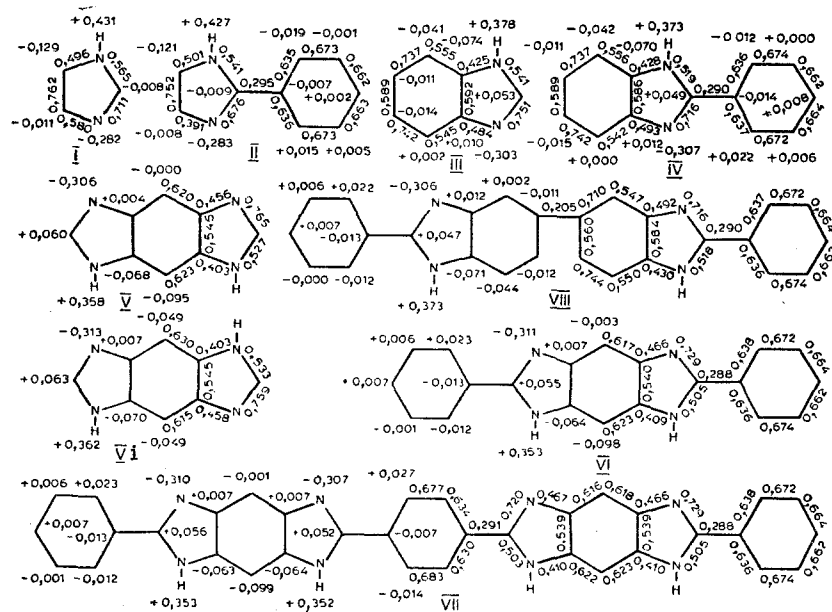


Fig. 3. Molecular diagrams of aromatic imidazoles in the long-wave excited state.

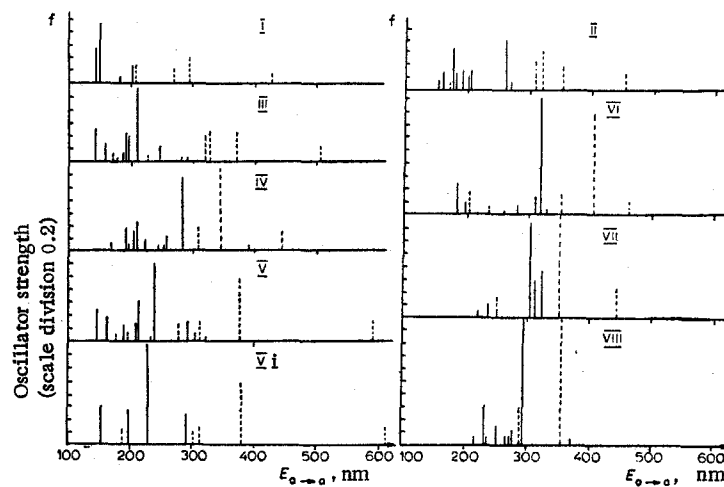


Fig. 4. Calculated singlet-singlet (—) and singlet-triplet (---) transitions in aromatic imidazoles (I-VIII).

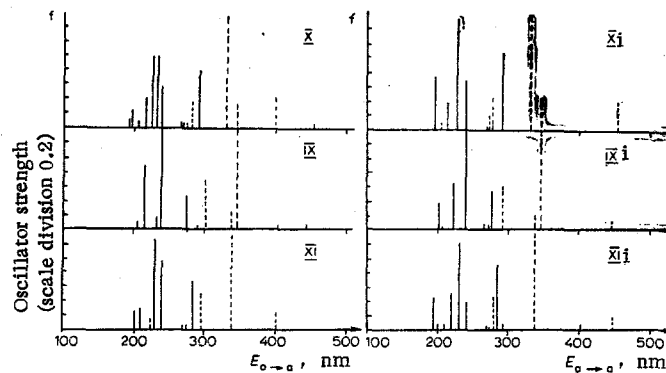


Fig. 5. Calculated singlet-singlet (—) and singlet-triplet (---) transitions in stereoisomeric dibenzimidazoles (IX-XI).

In the opinion of Leandri and co-workers [13], the absorption of imidazole at 207-208 nm is due to conversion of the symmetrical and structurally covalent compound to the asymmetrical and polar $\text{NH}=\text{CH}-\text{N}^--\text{CH}=\text{CH}$. However, from our data it turns out that in the presence of long-wave excitation there is considerable impoverishment in π electrons of all the ring carbon atoms, such that the carbon atoms in the 4 and 5 positions are converted from nucleophilic centers of the molecule to electrophilic centers. The orders of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds are reduced in this case (by a factor of approximately two). If one judges from the change in the charge on the nitrogen atoms, the acidity of the NH groups decreases during excitation, while the basicity of the pyridine nitrogen atom increases.

The long-wave absorption bands of II are associated with charge migration toward the aromatic ring. In this case the multiplicity of the bond between the rings increases by a factor of 1.5. If one follows the position of the bands of this nature in the investigated 2-phenyl-substituted imidazoles, their bathochromic shift, which can be interpreted as an increase in the effectiveness of conjugation in the corresponding macromolecules, is apparent. A bathochromic shift of the long-wave absorption of 50-100 nm on passing from the spectrum of the model to that of the polymer was experimentally noted in [2].

From the diagrams of the distribution of electron density in the excited states of the molecules it is seen that the weakest bond in the excited states is bond e, i.e., homolytic cleavage of the imidazole rings in the excited states also should occur primarily at these bonds.

Stereoisomerism of Dibenzimidazoles

In polybenzimidazoles based on diaminobenzidine one can imagine structures in which the imidazole rings are in the cis and trans positions relative to the bond that links the rings. In addition, cis or trans positions of the NH groups are possible for one or another position of the imidazole rings. In other words, six stereoisomers can exist in dibenzimidazoles. All of the indicated stereoisomers were calculated, and the results are presented in Table 1 and in Figs. 2 and 5.

A comparison of the molecular diagrams of all of the possible isomers shows very insignificant changes in the characteristics of the electron distribution. Moreover, since the energies of interaction of the benzimidazole rings (E_{int}) proved to be about 0.5 eV/link, it is difficult to conceive of the possibility of stereoisomerization at room temperature. It is possible only in the presence of these or other energy effects. The energy characteristics of the isomers under consideration (Table 1) also differ only slightly. However, a comparison of them makes it possible to note that trans orientation of both the rings themselves and the NH groups is somewhat more favorable from an energy point of view in all cases.

Thus real polybenzimidazoles based on diaminobenzidine may, with equal probability, contain all of the six stereoisomers. The predominance of one or another isomer should be determined by, for example, the requirements of dense packing of the macromolecules rather than by the energies of the π electrons.

An attempt might have been made to solve the problem of the concentration predominance of one or another stereoisomer by means of UV spectroscopy. The results of a theoretical examination (Table 1 and Fig. 5) have shown that stereoisomers with different types of fusion of the benzimidazole rings (5,5'-, 6,6'-, or 5,6'-) are spectrally different; however, one should not expect differences in the UV spectra of dibenzimidazoles with a cis or trans orientation of the imidazole rings. We also note that the experimental long-wave absorption (λ_{max}) for poly-2,2'-tetramethylene-6,6'-dibenzimidazole (293 nm) [2] is in good agreement with the results obtained by calculation (291 nm). This may serve as a confirmation of the correctness of the structure proposed in [2] for this polymer. The UV absorption on the short-wave wing of the long-wave band should increase in the case of the possible existence of products of prototropic transformation, for example, 5-5' isomers.

In conclusion, we report one of the interesting properties of polybenzimidazole films, namely, the deepening of their color on heating and disappearance of color when the film is removed from the heat source. This thermochromism of polybenzimidazole films was previously described in [14] but has not yet been given a satisfactory theoretical interpretation. Unfortunately, the data on the electronic structure of the macromolecule of aromatic benzimidazole that were obtained in the present study are insufficient for the exposition of the true reasons for the presence of thermochromism in polybenzimidazoles.

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