QUANTUM-CHEMICAL INVESTIGATION OF SOME OLIGOMERIC HETEROAROMATIC COMPOUNDS

I. INDIGO AND ITS OLIGOMERS

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Indigo and its dimer, trimer, dehydro, and leuco forms were investigated within the framework of the Pariser–Parr–Pople method. The electronic structures of the compounds in the ground and excited states and the effect of chain lengthening are discussed, and the UV absorption spectra are interpreted. Several characteristics of the chromaticity of the investigated compounds as representatives of vat dyes are examined. The estimated (from calculations) energetic favorability of the indigoid, dehydro, and leuco forms of indigo is used in discussing the observed and experimental ease of redox transformations of indigo.

In connection with our investigation of the thermal decomposition and photodestruction characteristics of representatives of classes of polymers in order to establish a correlation between the indicated characteristics and the electronic structures of macromolecules [1], we have performed quantum-chemical calculations of a number of aromatic heterocyclic compounds with chain, cyclic chain, and ladder structures within the framework of a single computational scheme and system of orbital parameters. The literature contains papers dealing with quantum-chemical calculations of individual representatives of monomeric heteroaromatic compounds (for example, see [2, 3]), but these studies are difficult to compare, since the calculations in them were made with different schemes (must often by the Hückel MO method) with different systems of parameters. As for polymeric heteroaromatic compounds, the data accumulated up to now are mainly the result of an experimental investigation of the most diverse of their characteristics [4, 5]. Indirect information regarding the electronic structures is used in explaining the observed effects in terms of the characteristics of the electronic structures of the investigated molecules, since the results of quantum-chemical investigations of the indicated polymers are usually lacking. The present series of communications contains information regarding the electronic structures of several oligomeric heteroaromatic compounds, which, as will be shown below, are identical to the structures in the polymers.

The calculations were carried out by the self-consistent-field molecular-orbital method [Pariser–Parr–Pople method (PPP)] by means of the program described by one of us, which was specially modified [6] by the inclusion of operators that realize the so-called "variable β" method [7] and also calculate such values as the total π-electron energies (E_π) of the molecules (which take the repulsion of the framework nuclei into account), the π-bond energies ($E_{\pi b}$), and the vertical resonance energies (E_{VR}). These values were calculated within the PPP method from the formulas in [8]. The system of atomic parameters in [7] was used, and the γ_{pq} integrals were calculated from the Mataga–Nishimoto formula [9]. The characteristics of the excited states were obtained using the multiconfiguration approximation. In particular,

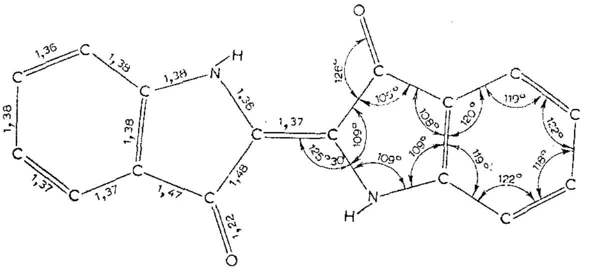

Fig. 1. Geometrical characteristics of the monomer link in indigo and its oligomers.

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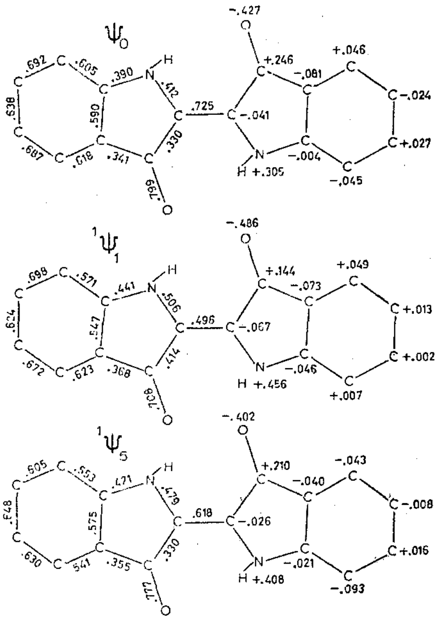

Fig. 2. Molecular diagrams of indigo in the ground (Ψ_0) and some singlet excited ($^1\Psi_a$) states.

the elements of the density matrices for the molecules in the excited states were calculated from the formula

$$P_{pq}{}^{a} = P_{pq}{}^{\mathrm{gr}} + \sum_{i\to k} \sum_{j\to l} A_{a,i\to k} A_{a,j\to l} [\delta_{ij} C_{pk} C_{ql} - \delta_{kl} C_{pi} C_{qj}],$$

where $P_{pq}{}^{\mathrm{gr}}$ are the corresponding values for the ground state, $A_{a,i\to j}$ are the coefficients of expansion of the wave function of the excited state with respect to the determinant functions of the states obtained by a single-stage excitation of an electron from an occupied (in the ground state) MO (ψ_i) to a vacant MO (ψ_j), C_{pi} are the coefficients of expansion of the MO with respect to AO, and δ_{ij} is the Kronecker symbol. The interaction of nine singly excited configurations was taken into account in the calculations of all of the compounds.

In the present communciation, we present the results of the calculation of indigo and its dimer, trimer, dehydro, and leuco forms. The geometric characteristics of the monomer link of indigo were taken from [10] and are presented in Fig. 1; it was assumed that they do not change as the molecular chain grows. Since no accurate data are available regarding the bond lengths and valence angles for the leuco and dehydro forms, the lengths of all of the bonds in the rings were assumed to be 1.38 Å, while the C = C bonds (in indigo), the C – C bonds (in the leuco and dehydro forms), and the C =O and C–OH bonds were assumed to be 1.37, 1.52, 1.22, and 1.40 Å, respectively. The rings were assumed to be regular polygons.

Molecular Diagrams

It follows from the molecular diagrams (Figs. 2-4) of indigo in the monomeric, dimeric, and trimeric forms in the ground state (Ψ_0) and some singlet excited states ($^1\Psi_a$) that the carbon – carbon bond between the condensed systems in indigo has a high multiplicity (0.725) and is formed by atoms with surplus π-electron density (0.041 e). The charges on the carbon atoms alternate in the condensed system of rings.

Lengthening the molecular chain, i.e., successive transition to diindigo and triindigo, leaves the π-electron charges and the bond orders in the structural elements of the monomeric link practically unchanged, and this makes it possible to assume that they remain the same in polymers.

A comparison of the electron distribution in the ground and first excited states of indigo demonstrates that the long-wave excitation is accompanied by an increase in the multiplicity of the bonds in the heterocycles, while the order of the C = C bond decreases by a factor of about two. This sort of considerable reduction in the order of the C = C bond in the excited state explains the ease of trans – cis isomerization of indigo under the influence of light.*

The largest fraction of the charge of the migrating (during excitation) unshared pairs of electrons of the N atoms is transferred to the exocyclic C atoms, during which a certain loosening of the C =O bonds is observed. Excitation to the $^1\Psi_5$ state is accompanied chiefly by charge redistribution within the condensed rings. It follows from the molecular diagrams calculated for the triplet excited states that they are similar with respect to the character of electron distribution to the corresponding singlet states.

The molecular diagrams of 5,5'-diphenylindigo (the monomeric link of the polyindigo reported in [11]), dehydroindigo, and leuco indigo are presented in Fig. 5. It is easy to see that the charge distributions in the indigoid fragment of 5,5'-diphenylindigo and of indigo itself are practically identical. A characteristic peculiarity of the electron distribution in dehydroindigo and leuco indigo is its high degree of nonuniformity in the heterocycles, which leads to the fact that all of the C atoms in the 4-7 and 4'-7' positions in the condensed benzene rings in dehydroindigo have a deficit of π electrons, while all the corresponding C atoms in leuco indigo have a surplus of π electrons. One's attention is also drawn to the fact that the carbon–

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*Professor V. I. Minkin pointed out to us this aspect of the use of the results obtained.

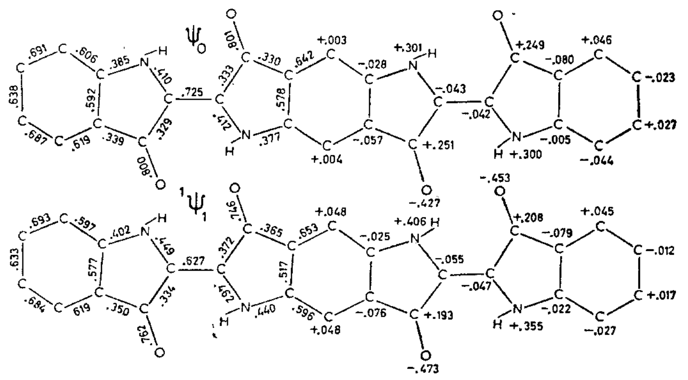

Fig. 3. Molecular diagrams of diindigo in the ground (Ψ_0) and in the first excited (${}^1\Psi_1$) states.

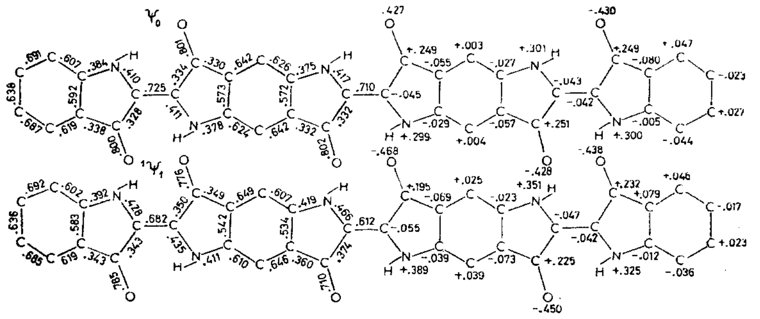

Fig. 4. Molecular diagrams of triindigo in the ground (Ψ_0) and first excited (${}^1\Psi_1$) states.

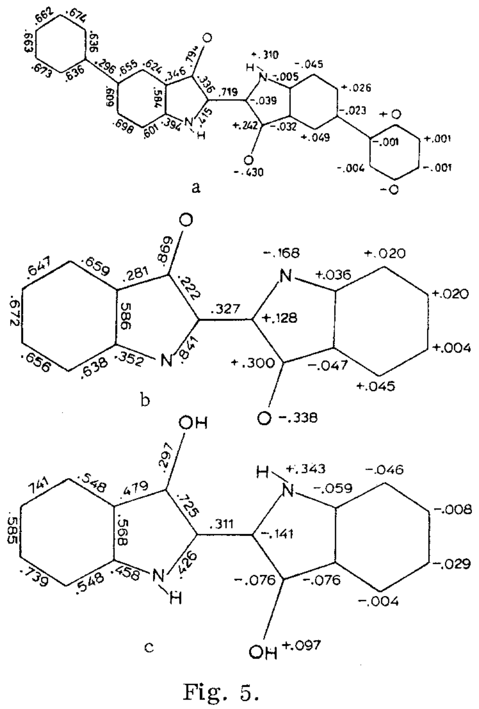

Fig. 5.

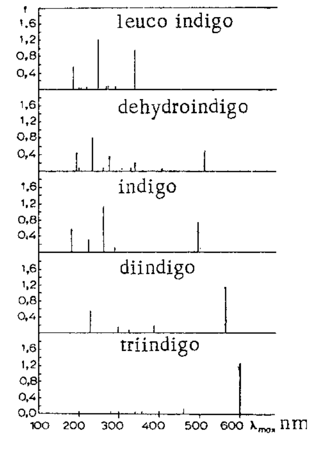

Fig. 6.

Fig. 5. Molecular diagrams of 5,5'-diphenylindigo (a), dehydroindigo (b), and leuco indigo (c) in the ground state.

Fig. 6. Calculated λ_{max} and oscillator forces (f) of the electronic transitions to singlet excited states.

TABLE 1. Energy and Spectral Characteristics of Indigo and Its Dehydro and Leuco Forms

Compound	E, eV	E_{π}, eV	$E_{\pi b}$, eV	E_{VR}, eV	$\frac{E_{VR}}{n}$, eV	ε_{LV}, eV	ε_{UO}, eV	E_{0-1}		f_{0-1}
								eV	Å	
Indigo	−318,120	−1029,713	32,240	12,784	0,5811	−3,457	−8,590	2,504	4951	0,709
5,5'-Diphenylindigo	−471,120	−1806,381	51,320	20,176	0,5934	−3,489	−8,475	2,419	5125	0,869
Dehydroindigo	−274,431	−840,284	32,231	10,027	0,5014	−4,150	−9,435	2,418	5126	0,498
Leuco indigo	−369,321	−1209,528	30,301	14,717	0,6132	−1,634	−7,917	3,659	3388	1,011

carbon bond between the rings in dehydroindigo and leuco indigo has approximately the same multiplicity, but in the first case it is "dipositive," while in the second case there is excess charge (0.141 e) on both C atoms.

Electronic Absorption Spectra

The calculated wavelengths and oscillator strengths of the electronic transitions of all of the investigated compounds are presented graphically in Fig. 6. For indigo itself, they are in satisfactory agreement with the experimental data for indigo blue in the vapor state ($\lambda_{max}=546$ nm, $f=1.0$ [12, 13]). According to the calculated data, a considerable deepening of the color on passing to polyindigoid dyes is predicted – the value that we estimated by extrapolating λ_{max} of the long-wave singlet electron transition should be ~650 nm.

A distinctive peculiarity of the calculated spectra is their gradual simplification on passing from the monomer to the oligomers. During this transition, the number of short-wave absorption bands decreases.

It is known [12] that polymeric indigo has semiconductor properties and paramagnetism. These properties may be associated with the nearness of the triplet level (the $\Psi_0 \rightarrow {}^3\Psi_1$ transition energy in triindigo is 0.992 eV) and the rather high probability of transition to it ($f=0.819$).

An examination of the spectral characteristics of the indigoid, leuco, and dehydro forms of indigo (Fig. 6) confirms the slight deepening of the color of the dehydro form and the considerable increase in the color of the leuco form.

Redox Transitions

The rather facile redox transitions of indigo to the dehydro and leuco forms are well-known [14]. It follows from the energy characteristics presented in Table 1 that the indigoid and dehydro forms of indigo have identical π-bond energies, and these energies are ~2 eV higher than the corresponding energy of leuco indigo. From the magnitude of its resonance energy and its fraction per π electron (E_{VR}/n), the leuco form proved to be the most stable form.

Using the energies of the upper occupied and lower vacant orbitals (ε_{UO} and ε_{LV}) to estimate the tendency of the forms of indigo to undergo photooxidation and photoreduction, it is not difficult to convince oneself that, of the three examined forms of indigo, the indigoid form is the most inclined to undergo reduction, while the leuco form is the most inclined to undergo oxidation.

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