EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing voltage of 50 eV and an inlet temperature 15-20°C lower than the melting point of the sample. The elementary compositions of the fragment ions in the mass spectra of II-V were determined with a JMS-01-SG-2 high-resolution spectrometer (Jeol).

The synthesis of the compounds was published in [5].

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TAUTOMERISM, ELECTRONIC STRUCTURES, AND ELECTRONIC SPECTRA OF INDOLO[2,3-b]QUINOXALINE AND ITS DERIVATIVES

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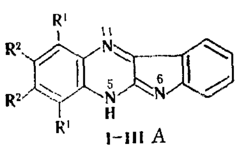
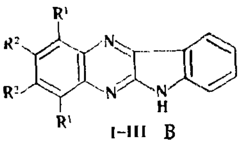
541.62:543.422.6

The tautomerism, electronic spectra, and electronic structures of the ground and excited states of indolo[2,3-b]quinoxaline and its 2,3- and 1,4-dibutoxy derivatives were investigated by the Pariser—Parr—Pople (PPP) method. It is shown that these compounds exist primarily in the 6H form; the long-wave $S_{\pi\pi^*}$ transition is due to transfer of π charge from the indole fragment to the quinoxaline fragment, and in the first excited state many of the bonds in the quinoxaline fragment are loosened significantly. The effect of butoxy substituents on the first $S_{\pi\pi^*}$ transition of indolo[2,3-b]quinoxaline was analyzed by means of perturbation theory within the framework of the Hückel MO method.

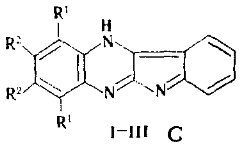
Continuing the synthesis and study of indolo[2,3-b]quinoxaline derivatives [1,2] we have studied the electronic structures of some indolo[2,3-b]quinoxalines that theoretically may exist in three tautomeric forms A, B, and C:



I-III A



I-III B



I-III C

I $R^1=R^2=H$; II $R^1=H$, $R^2=n\text{-}C_4H_9O$; III $R^1=n\text{-}C_4H_9O$, $R^2=H$

We have previously shown on the basis of a comparative investigation of the electronic spectra of I-III and their methyl analogs that in neutral solutions they exist primarily in

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Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1259-1263, September, 1982. Original article submitted May 27, 1981.

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TABLE 1. ΔH and E_{π} Values of the Tautomeric Forms of Indolo[2,3-b]quinoxalines (I-III) Calculated by the MO PPP Method

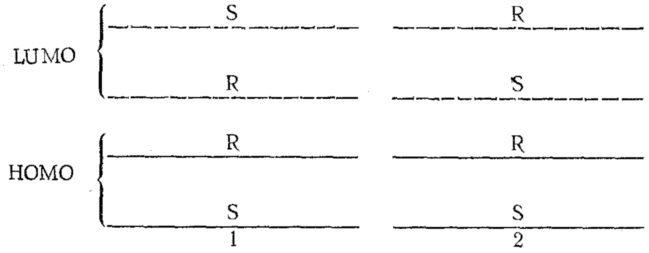
Energies, eV	Compound								
	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
ΔH	−136,75	−137,23	−136,20	−147,34	−147,87	−146,95	−147,38	−147,91	−146,98
E_{π}	−246,20	−246,67	−245,57	−326,82	−327,37	−326,35	−326,84	−327,39	−326,38

the B form [2, 3]. In the present research we studied the electronic structures and electronic spectra of the A-C forms of I-III by the quantum-chemical method of molecular orbitals within the Pariser—Parr—Pople (PPP) approximation.

To evaluate the stabilities of the tautomeric forms of the π-conjugated systems of I-III we used the heats of atomization (ΔH) and the overall π energies of the systems (E_{π}), which generally give more reliable results [4] than the delocalization energies. It is apparent from Table 1 that the B forms are the most stable forms. The C forms have the maximum ΔH and E_{π} values. Consequently, they are the least energetically favorable forms. It is possible that it is precisely for this reason that the formation of 11H-indole[2,3-b]quinoxaline derivatives has not been experimentally observed [5].

It follows from an analysis of the energies of the σ and π bonds of tautomeric forms A-C of I-III that the energy of the π bonds is responsible for the highest stability of the B form. In fact, the σ-bond energies for all of the forms (for example, those of I) remain virtually unchanged (IA = −71.29, IB = −71.29, and IC = −71.37 eV), whereas the π-bond energies undergo significant changes (IA = −25.76, IB = −26.33, and IC = −25.13 eV). Let us note that the ΔH and E_{π} energies (Table 1) and the π-bond energies increase ∿1 eV on passing from the most stable B form to the least stable C form of I-III.

If one regards the indole[2,3-b]quinoxaline molecule as a combination of two fragments, viz., indole and quinoxaline, a problem arises as to how the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) of both fragments are oriented relative to one another with respect to their energies in the energy spectrum of the indolo[2,3-b]quinoxaline molecule. It is natural that as a result of interaction, they will be perturbed [6, 7]. Two variants of the mutual orientation of the perturbed HOMO and LUMO of the R and S fragments in the spectrum of the energies of compound RS, which can be represented schematically as shown below, are possible:



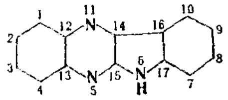
The first variant demonstrates the bathochromic effect of one fragment (S) on the maximum of the long-wave absorption band (LAB) of the other (R) [7]. The second variant is an example of the development of a new absorption maximum in the long-wave region that is associated with a π-electron transition from the perturbed HOMO of one fragment to the perturbed LUMO of the other fragment, i.e., with intramolecular transfer of π charge from one fragment to the other [7].

From considerations associated with the principles of the interaction of the HOMO and the LUMO of the fragments in the formation of a complex molecule [6, 7], we deduced conditions superimposed on the energies of the as yet nonperturbed HOMO and LUMO of starting fragments R and S from which a new RS compound will be composed for the realization of the two cases cited above [(1)-(2)]:

TABLE 2. Energies of the HOMO and LUMO (eV) Calculated by the MO PPP Method

MO	Compound										
	indole	quinoxaline	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
LVMO	−1,128	−2,622	−3,178	−2,746	−3,625	−2,763	−2,229	−3,119	−2,848	−2,238	−3,301
HOMO	−9,081	−9,722	−8,765	−9,079	−8,447	−8,046	−8,118	−7,997	−7,993	−7,541	−7,859

TABLE 3. π-Electron Charges (Q_r) and Bond Orders (p_{rs}) in the Ground and First Excited States of 6H-Indolo[2,3-b]quinoxaline:



Atom No., r	Q_r^0	Q_r^1	r—s bond	p_{rs}^0	p_{rs}^1	Atom No., r	Q_r^0	Q_r^1	r—s bond	p_{rs}^0	p_{rs}^1
1	0,005	−0,051	1—2	0,779	0,697	11	−0,194	−0,352	7—17	0,594	0,577
2	−0,002	0,050	1—12	0,495	0,542	12	0,054	0,141	8—9	0,623	0,617
3	0,008	−0,016	2—3	0,539	0,521	13	0,074	0,104	9—10	0,706	0,659
4	−0,007	−0,037	3—4	0,777	0,723	14	0,062	0,050	10—16	0,598	0,585
5	−0,258	−0,337	4—13	0,499	0,505	15	0,068	0,077	11—14	0,686	0,577
6	0,301	0,434	5—13	0,564	0,553	16	−0,058	−0,079	11—12	0,569	0,512
7	−0,043	0,036	5—15	0,656	0,535	17	−0,023	−0,074	12—13	0,530	0,438
8	0,011	−0,020	6—15	0,443	0,526				14—15	0,474	0,448
9	−0,019	0,013	6—17	0,385	0,400				14—16	0,373	0,419
10	0,022	0,062	7—8	0,706	0,667				16—17	0,600	0,544

$$E^{S}_{\mathrm{HOMO}} < E^{R}_{\mathrm{HOMO}}\,;\; E^{S}_{\mathrm{LUMO}} > E^{R}_{\mathrm{LUMO}} \qquad (1)$$

$$E^{S}_{\mathrm{HOMO}} < E^{R}_{\mathrm{HOMO}}\,;\; E^{S}_{\mathrm{LUMO}} < E^{R}_{\mathrm{LUMO}} \qquad (2)$$

A comparison of the experimental and calculated characteristics of the electronic absorption spectra of I-III (Fig. 1) and an analysis of the coefficients of the configuration interaction matrices provide evidence that 80-90% of the long-wave absorption bands (LAB) is due to the HOMO → LUMO $S_{\pi\pi}{}^{*}$ electron transition, 80-90% of the second absorption maximum at 350-370 nm is due to an $S_{\pi\pi}{}^{*}$ transition from the next occupied MO to the LUMO, while the remaining absorption bands are the superimposition of several mixed electron transitions of the $S_{\pi\pi}{}^{*}$ type.

An examination of the energies of the HOMO and LUMO of indole, quinoxaline, and indolo-[2,3-b]quinoxaline (Table 2) with allowance for the conditions proposed above [(1) and (2)] makes it possible to conclude that the maximum of the long-wave absorption band of the B form of I is due to transfer of a π electron from the perturbed HOMO of indole to the perturbed LUMO of quinoxaline (i.e., case 2 is realized; see the scheme presented above). Thus the first $S_{\pi\pi}{}^{*}$ transition in I is virtually transfer of the π charge from the indole fragment to the quinoxaline fragment.

This is also confirmed by calculations of the distribution of the π-electron charges in the ground ($Q_r{}^0$) and first excited ($Q_r{}^1$) states of the B form of I (Table 3). In fact, it is apparent from a comparison of the $Q_r{}^0$ and $Q_r{}^1$ states that in the first excited state of IB the π-electron charge on the atoms of the quinoxaline fragment increases significantly.

An analysis of the bond orders in the ground and first excited states of IB reveals that the C=N and C=C bonds (11—14 and 5—15, 1—2 and 12—13) in the quinoxaline fragment are loosened considerably upon excitation, while the C=C bonds in the indole fragment are loosened slightly, whereas the C—N and C—C (14—16) bonds in this fragment become considerably stronger (Table 3).

The introduction of C_4H_9O substituents in the 2,3 and 1,4 positions leads to bathochromic shifts (17 and 31 nm, respectively) of the maximum of the long-wave absorption band of IB (Fig. 1). It seems of interest to ascertain how the energies of the HOMO and LUMO of IB change in this case, i.e., what their contributions to the observed bathochromic shift are.

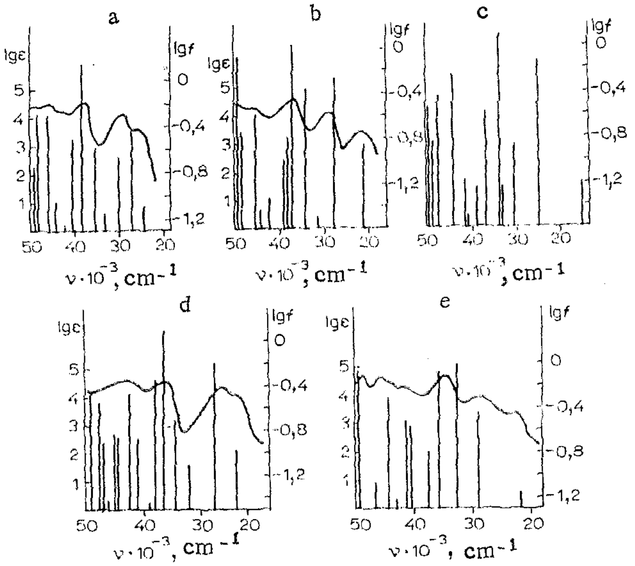


Fig. 1. Calculated (vertical lines) and experimental electronic absorption spectra of indolo[2,3-b]quinoxalines in ethanol: a) IB; b) IA (spectrum of the 5-octadecyl analog); c) IC; d) IIB; e) IIIB.

For this, let us use perturbation theory within the framework of the Hückel MO (HMO) method [6,7]. Let us model the p-C_4H_9O substituent by means of the OCH_3 group with coulombic and resonance parameters h_O and k_{CO}. The energies of the HOMO and LUMO of IB (in β units) will then change when substituents are introduced in, for example, the 2 and 3 positions in the following way:

$$E^{IIB}_{HOMO}=E^{IB}_{HOMO}+\frac{a^2_{2,HOMO}+a^2_{3,HOMO}}{E^{IB}_{HOMO}-h_O}\cdot k_{CO}^2 \qquad (3)$$

$$E^{IIB}_{LUMO}=E^{IB}_{LUMO}+\frac{a^2_{2,LUMO}+a^2_{3,LUMO}}{E^{IB}_{LUMO}-h_O}\cdot k_{CO}^2, \qquad (4)$$

where the squares of the coefficients of the atomic orbitals (AO) of the C_2 and C_3 atoms in the wave functions of the HOMO and LUMO of IB are found in the numerators of the fractions.

For compound IB: $E^{IB}_{HOMO} = 0.682$, $E^{IB}_{LUMO} = -0.439$, $h_o = 1.8$, $a^2_{2,HOMO} = 0.064$, $a^2_{3,HOMO} = 0.070$, $a^2_{2,LUMO} = 0.044$, and $a^2_{3,LUMO} = 0.061$. When these values are substituted into Eqs. (3) and (4), we obtain

$$E^{IIB}_{HOMO}=E^{IB}_{HOMO}-0.12k_{CO}^2$$

$$E^{IIB}_{LUMO}=E^{IB}_{LUMO}-0.047k_{CO}^2$$

It is hence apparent that the observed bathochromic shift of the long-wave absorption band is due to the effect of the substituent on the HOMO of IB, which exceeds its effect on the LUMO by a factor of approximately two. Similarly, for IB substituted in the 1 and 4 positions

$$E^{IIIB}_{HOMO}=E^{IB}_{HOMO}-0.338k_{CO}^2$$

$$E^{IIIB}_{LUMO}=E^{IB}_{LUMO}-0.097k_{CO}^2$$

The bathochromic effect of the substituents here is considerably greater, which is in agreement with the experimental data presented above. It is apparent that the difference in the effect of the substituents in the 2,3 and 1,4 positions on the long-wave absorption band of IB is due to the different contributions of the corresponding AO to the HOMO and LUMO.

EXPERIMENTAL

Indolo[2,3-b]quinoxalines I-III and 5-octadecylindolo[2,3-b]quinoxaline were obtained by the methods described in [1,2]. The electronic spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. Quantum-chemical calculations of the ground and excited states of the neutral tautomeric forms of I-III, indole, and quinoxaline were made by the MO LCAO method within the PPP approximation with allowance for the configuration interaction by means of our program, which realizes the Dewar algorithm [4] with optimization of the internuclear distances with respect to the minimum of the atomization energy. In the calculations it was assumed that the molecules are planar, whereas the geometries adopted in [8, 9] were used for the quinoxaline and indole fragments, respectively. Calculations by the Huckel MO method were made by means of the following parameters: $h_{\dot{N}} = 0.4$, $h_{\ddot{N}} = 2.0$, $k_{C-C} = k_{C-N} = 0.7$, and $k_{C=C} = k_{C=N} = 1.0$. 1.0.

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SYNTHESIS AND RING-CHAIN TAUTOMERISM OF SALTS OF ALKYLIDENE(ARYLIDENE) DERIVATIVES OF AMIDRAZONES

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A number of salts of alkylidene(arylidene) derivatives of amidrazones was obtained by the reaction of S-methylthioamidium iodides with hydrazones of monocarbonyl compounds. According to the ^{1}H and ^{13}C NMR data, these compounds in solutions are capable of ring-chain tautomerism of the 1-alkylideneamidrazone—1,2,4-triazoline type. The position of the equilibrium is determined chiefly by steric interactions of the substituents attached to the $C-N_2$ bond.

We have previously found [1] that acetone hydrazone and methylhydrazone react smoothly with S-methylthioamidium iodide to give the corresponding salts of 2-propylidene derivatives of acetamidrazone. In the present paper we report additional results of an investigation of the reaction of hydrazones with thioamidium iodides, which are of interest in connection with the problem of the structures of the final products, which are capable of ring-chain tautomeric transformations of the 1-alkylideneamidrazone—1,2,4-triazoline type [1,2]. The information on the factors that determine the position of the equilibria in systems of this type can be used to ascertain the principles of ring-chain transformations in series of related compounds, viz., thioacylhydrazones [3], semicarbazones [4, 5], and thiosemicarbazones [6].

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