ABSORPTION AND LUMINESCENCE SPECTRA OF INDOLO[2,3-b]QUINOXALINE

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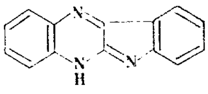
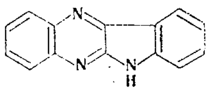
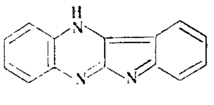
The spectral-luminescence properties of indolo[2,3-b]quinoxaline, which at 77°K has fluorescence and phosphorescence of the $\pi\pi^*$ type, were investigated. Retarded fluorescence and nonexponential quenching of the phosphorescence were observed; this is explained by photochemical processes with subsequent recombination luminescence.

Previously, on the basis of a study of the electronic absorption spectra [1-3] and the electronic structure [3] of indolo[2,3-b]quinoxaline (I) and some of its derivatives it was shown that I in neutral solutions exists primarily in the most stable of the three theoretically possible tautomeric forms, viz., in the 6H form:


5H-I


6H-I


11H-I

In the present paper we report the peculiarities of the electronic absorption spectra and luminescence properties of the 6H form of I.

The luminescence properties of indole [4, 5] and quinoxaline [6, 7] have been studied quite adequately. Indole has fluorescence and phosphorescence, whereas quinoxaline has only phosphorescence.

This is explained by the corresponding orientations of the energy levels of the lowest singlet (S) and triplet (T) $\pi\pi^*$ and $n\pi^*$ states [6-8] for quinoxaline (Fig. 1), which is classified as a type III molecule [8]. In the case of this mutual orientation of the energy levels in the molecule fluorescence is suppressed by intercombination conversion of the $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ type, the probability of which is high [6-8]. It seems of interest to examine how the peculiarities of the spectral properties of indole and quinoxaline show up in the spectrum of I, which is a combination of the indicated compounds, as well as the relative orientation of the lowest S and T energy levels of the $\pi\pi^*$ and $n\pi^*$ type in I.

In contrast to quinoxaline, solutions of I at 77°K have both fluorescence and phosphorescence (Fig. 2 and Table 1). Retarded fluorescence, which is adjacent to the phosphorescence spectrum on the short-wave side, is observed in heptane solution (Fig. 2, spectrum 4).

The fluorescence band is partially overlapped with the long-wave absorption band (LWAB) and is mirror-symmetrical to it (Fig. 2). The LWAB and fluorescence maxima are shifted by a value corresponding to the band half width relative to the 0–0 transition. The energy of the fluorescent state $[E(S_1)]$ of I corresponds to the frequency of the point of intersection of the absorption and fluorescence spectra.

On passing from a solution in heptane to a solution in a more polar (ethanol) solvent the fluorescence and phosphorescence spectra of I experience a bathochromic shift (Table 1); this is characteristic for $\pi\pi^*$ bands.

The magnitude of the singlet–triplet interval of I (Fig. 1) also confirms the assignment of the fluorescence and phosphorescence to the $\pi\pi^*$ type.

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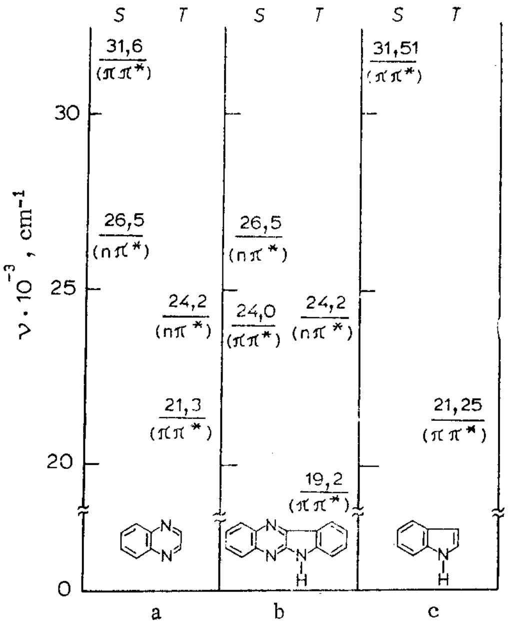


Fig. 1

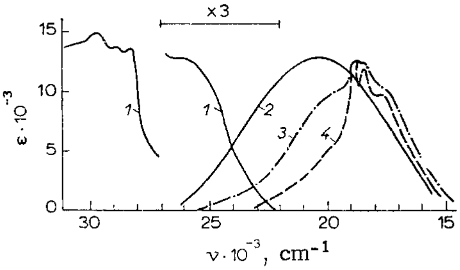


Fig. 2

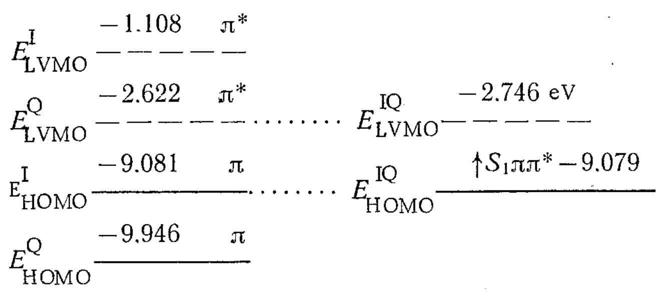
Fig. 1. Energy levels of quinoxaline (a) [6], indoloquinoxaline (b), and indole (c) [4].

Fig. 2. Absorption (1) and fluorescence (2) spectra at 300°K and luminescence spectrum at 77°K (3) and prolonged luminescence at 77°K (4) of indoloquinoxaline in heptane.

Retarded fluorescence with an initial quenching time of ∿0.05 sec and an initial lag time of up to ∿1 sec is observed. The quenching of the phosphorescence is also nonexponential: a log of up to ∿1.6 sec occurs.

The manifestation of retarded fluorescence is associated with photochemical processes that take place with I, which leads to the development of recombination luminescence. The phosphorescence lag can also evidently be explained by recombination luminescence.

In our preceding paper [3] I was regarded as being a combination of two fragments, viz., indole (I) and quinoxaline (Q) fragments. The relative orientations of the calculated energy levels of the highest occupied molecular orbital (E_{HOMO}) and the lowest vacant molecular orbital (E_{LVMO}) of the fragments and the I molecule (or IQ) appear schematically in the following way:



It has been shown [3] that the energies of the HOMO and LVMO of I are the perturbed HOMO and LVMO of indole and quinoxaline, respectively.

The first $S_{\pi\pi^*}$ transition in I is due to intramolecular transfer of π charge from the indole fragment to the quinoxaline fragment [3]. The second $S_{\pi\pi^*}$ transition is primarily a transition from the second occupied MO of I to its LVMO due to the quinoxaline fragment ($E^{IQ}_{VLMO} \approx E^{Q}_{LVMO}$) [3].

In this case one should expect that characteristic vibrational frequencies of the quinoxaline fragment should appear in the vibrational structure of these two $S_{\pi\pi^*}$ absorption

TABLE 1. Spectral-Luminescence Characteristics of the 6H Form of Indolo[2,3-b]quinoxaline

Solvent	λ_{abs} max, nm	λ_{fl}, max, nm		λ_{phos} max, nm	τ_{phos}, sec
		300°K	77°K		
Ethanol	407 354 269 221	520	505	541 556 585	0,7
Heptane	400 354 266 223	500	500	529 544 570	0,6

bands, whereas the characteristic vibrational frequencies of the luminescence spectrum of the indole fragment will appear in the luminescence spectrum of I.

In fact, it is customary to assume that the long-wave absorption band (LWAB) is due to transition of the π electron from the zero vibrational sublevel of the ground electronic state of the molecule (S_0) to various vibrational sublevels of the S_1 state, whereas the luminescence spectrum is determined by transition of the π electron from the zero vibrational sublevel of the first excited singlet (S_1) and triplet (T_1) electronic states to the vibrational levels of the ground state of the molecule (S_0) [8].

It is apparent from the experimental data (Fig. 2 and Table 1) that the long-wave absorption band in the spectrum of I in heptane does not have a pronounced vibrational structure but that the next absorption band displays a satisfactory vibrational structure with vibrational frequencies of 640 and 1000 cm^{-1}, which are close to the most intense vibrational frequencies of 600 and 1021 cm^{-1} in the absorption spectrum of quinoxaline [7]. However, vibrational frequencies at 500 and 1370 cm^{-1}, which are characteristic for the vibrational structure of the fluorescence spectrum of indole [4], are present in the phosphorence spectra of ethanol and heptane solutions of I.

It follows from the information set forth above that our theoretical assumption regarding the long-wave absorption band of I, as well as the assumption regarding the band involving charge transfer from the indole fragment to the quinoxaline fragment, is in good agreement with the experimental data.

Let us now examine how the orientations of the lowest $S_{n\pi^*}$ and $T_{n\pi^*}$ states change on passing from quinoxaline to indolo[2,3-b]quinoxaline. Since we classified the fluorescence and phosphorescence of I to the $\pi\pi^*$ type, the precise experimental determination of the energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ states is not possible. However, the energy of the lowest $T_{n\pi^*}$ state can be estimated from the dependence of the fluorescence quantum yield of I on the temperature. The fluorescence quantum yields of I at room temperature are $3 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ in alcohol and heptane, respectively. When the temperature of the solutions is lowered to 77°K, the fluorescence of I increases to $(6.3 \pm 1.3) \cdot 10^{-2}$. It is apparent that this pronounced decrease in the fluorescence quantum yield when the temperature of the solutions is lowered is associated with the fact that intercombination conversion $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ through the $T_{n\pi^*}$ state, which is oriented somewhat higher than the $S_{\pi\pi^*}$ state, occurs in the case of population of the higher vibrational states of the $S_{\pi\pi^*}$ level, which are frozen out at 77°K. This fact makes it possible to estimate the value of the energy of the $T_{n\pi^*}$ state, which does not show up directly in the absorption and luminescence spectra.

The fluorescence quantum yield (Φ_{fl}) is

$$\Phi_{fl} = \frac{K_{fl}}{K_{fl} + K_{st} + K_{bk} + K_e}, \qquad (1)$$

where K_{fl}, K_{st}, and K_{bk} are the fluorescence, intercombination conversion, and internal conversion constants, respectively, and K_e is the constant of thermal activation to the highest vibrational level of the $S_{\pi\pi^*}$ state, from which intercombination conversion to the $T_{n\pi^*}$ state takes place.

The K_e value can be represented in the form

TABLE 2. Dependence of the Energy of Activation on Variations in the $(K_{st} + K_{bk})/K_{fl}$ Values

Energy of activation, cm^{-1}	$(K_{st}+K_{bk})/K_{fl}$					
	0	2	4	6	8	10
ΔE_1	169	176	184	194	205	219
ΔE_2	200	212	227	246	273	316

$$K_e = A\cdot\exp(-\Delta E/RT), \tag{2}$$

where A is the frequency factor, and ΔE is the energy of activation. Substituting (2) into (1) we obtain the expression

$$\frac{1}{\Phi_{fl}} - 1 - \frac{K_{st}+K_{bk}}{K_{fl}} = A/K_{fl}\cdot\exp(-\Delta E/RT), \tag{3}$$

which is similar to expression (89) in [9].

Writing expression (3) for temperatures of 300 and 77°K and dividing them term-by-term by one another we can find the energy of activation

$$\Delta E = \frac{RT_1T_2}{T_1-T_2}\ln\frac{1/\Phi_{fl}{}^1 - 1 - (K_{st}+K_{bk})/K_{fl}}{1/\Phi_{fl}{}^2 - 1 - (K_{st}+K_{bk})/K_{fl}}, \tag{4}$$

where the subscripts 1 and 2 pertain to temperatures of 300 and 77°K, respectively.

Since the fluorescence quantum yield at 77°K is ~0.1, $(K_{st} + K_{bk})K_{fl} \leqslant 10$. By varying the latter value from 0 to 10 with allowance for the error in the measurement of the fluorescence quantum yield we obtain $\Delta E = (240 \pm 70)\ cm^{-1}$ (Table 2). The ΔE_1 and ΔE_2 values in Table 2 pertain to fluorescence quantum yields of $5\cdot 10^{-2}$ and $7.5\cdot 10^{-2}$, respectively, in heptane at 77°K.

Thus it follows from the data obtained that the energy of the $T_{n\pi^*}$ state is $(24{,}240 \pm 70)\ cm^{-1}$.

It has been shown [3] that on passing from quinoxaline to I the energy of its LVMO is determined by the quinoxaline fragment. As a consequence of this, it might be expected that the energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ states of indoloquinoxaline will be the same as in the case of quinoxaline (Fig. 1). The energy of the $T_{n\pi^*}$ state of I that we obtained is in good agreement with the energy of the $T_{n\pi^*}$ state of quinoxaline [6].

From the orientation of the electronic states of I (Fig. 1) it is apparent that it should have luminescence of the $\pi\pi^*$ type, which confirms our assignment of this luminescence.

EXPERIMENTAL

The absorption spectra were recorded with a Specord UV-vis spectrophotometer, while the luminescence spectra were recorded with an apparatus assembled on the basis of an MDR-1 monochromator. The luminescence spectra presented were corrected for the spectral sensitivity of the apparatus. The phosphorescence lifetimes were measured from its quenching by means of an SI-18 oscillograph.

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