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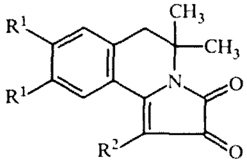
# ELECTRONIC SPECTRA OF PYRROLO[2,1-*a*]ISOQUINOLINES AND PYRROLO[1,2-f]PHENANTHRIDINES

**A. G. Mikhailovskii and V. S. Shklyaev**

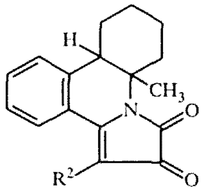
*The electronic absorption spectra of dioxo-compounds of the pyrrolo[2,1-a]isoquinoline and pyrrolo[1,2-f]phenanthridine series and products of their condensation with o-phenylenediamine were studied. The influence of substituents was demonstrated; halochromic phenomena in sulfuric acid medium were described; the fluorescence spectra are discussed.*

Dioxo-compounds of the pyrrolo[2,1-*a*]isoquinoline and pyrrolo[2,1-f]phenanthridine series are of interest for the chemistry of alkaloids and their synthetic analogs [1-8]. The studies cited are devoted to the reactivity of these compounds. At the same time, one vital property of the substances synthesized — their bright color, due to the peculiarities of the electronic structure — was not noted in the publications mentioned. The aim of this work was to investigate the electronic spectra of these compounds and to establish the relationship of structure to the spectral properties.

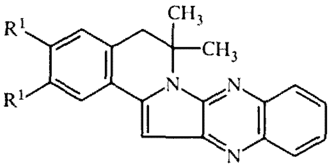
Substances I—IV, produced in [8], were selected as an example, since this series provides a rather broad variety of substituents (Table 1). Substances I and II are colored various shades of bright red. Quinoxalines III and IV, representing products of the condensation of compounds I and II with o-phenylenediamine, are lemon yellow. When their solutions are irradiated with a laser beam, fluorescence can be observed visually.



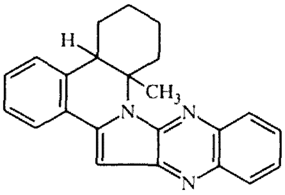
I a-h



IIa,b



IIIa, b



IV

The UV absorption spectra of I-IV were observed in methanol (see Table 1), beginning with the wavelength 200 nm. All the substances contain aromatic fragments, which is clearly manifested in the spectra. Thus, all the compounds are characterized by the presence of the $\beta$-band of a $\pi \rightarrow \pi^*$ transition [9—11] in the region of 200-234 nm, $\log \varepsilon = 3.55\text{-}4.62$. An aromatic p-band (245-294 nm, $\log \varepsilon = 3.60\text{-}4.62$) is another common feature. In the spectra of all the compounds a K-band of the total $\pi$—$\pi$ conjugation of the molecule [12] is observed in the region of 315-413 nm, $\log \varepsilon = 3.89\text{-}4.47$. At the same time, the spectra of the quinoxalines III and IV differ substantially from the spectra of the dioxopyrrolines I and II. The spectra of the quinoxalines have more intense absorption in the aromatic region; moreover, the K-band of the spectra of the bases III and IV (374-413 nm) experiences a bathochromic shift in comparison with compounds I and II (3.15-3.75 nm).

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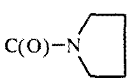
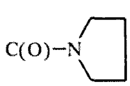
Institute of Technical Chemistry, Urals Branch of the Russian Academy of Sciences, Perm' 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 650-653, May, 1995. Original article submitted March 14, 1995.

TABLE 1. UV Spectra of Compounds I-IV in Methanol

| Compound | $R^1$ | $R^2$ | Absorption bands, $\lambda_{max}$, nm (log $\varepsilon$) | | |
|---|---|---|---|---|---|
| | | | $\beta$ | $p$ | $K$ |
| Ia | H | H | 200 sh. (4,02), 212 sh. (4,00) | 276 (3,97), 303 sh. (3,72) | 372 (4,25), 383 sh. (4,08) |
| Ib | $OCH_3$ | H | 203 (4,20) | 246 (4,12), 292 (3,60) | 375 (4,45), 388 sh. (4,40) |
| Ic | H | $CO_2C_2H_5$ | 212 (3,55) | 255 (3,91), 276 sh. (3,70) | 308 sh. (3,83), 352 (4,09) |
| Id | $OCH_3$ | $CO_2C_2H_5$ | 210 (3,88) | 246 (4,25) | 309 sh. (3,70), 354 (4,19), 443 sh. (3,39) |
| Ie | H |  | 204 (4,58) | 260 (3,96), 300 (3,78) | 364 (4,10) |
| If | $OCH_3$ |  | 203 sh. (4,20) | 248 (4,28), 288 sh. (3,92) | 362 (4,32), 370 sh. (4,08) |
| Ig | H | $C(O)C_6H_5$ | 204 (4,62), 229 sh. (4,12) | 254 (4,18), 291 (4,02) | 356 (4,00) |
| Ih | H | $C(O)CCl_3$ | 200 (4,14), 218 sh. (4,01) | 294 (3,85) | 315 (3,89) |
| IIa | — | H | 200 sh. (4,13), 209 sh. (4,11), 225 sh. (3,90) | 280 (3,85), 299 sh. (3,78) | 374 (4,21), 388 sh. (4,20) |
| IIb | — | $CO_2C_2H_5$ | 200 sh. (4,13), 209 sh. (4,20), 226 sh. (4,01) | 256 (4,01), 278 (3,90), 313 sh. (3,90) | 351 (4,08) |
| IIIa | H | — | 207 sh. (4,34), 210 sh. (4,37), 222 (4,46), 232 (4,45) | 267 sh. (4,51), 274 (4,60) | 362 sh. (4,41), 374 (4,44), 408 (4,11), 427 sh. (3,94) |
| IIId | $OCH_3$ | — | 206 sh. (4,26), 220 sh. (4,44), 230 (4,49) | 245 (4,50), 274 sh. (4,35), 283 (4,38) | 385 (4,47), 413 (4,39) |
| IV | — | — | 207 sh. (4,34), 210 sh. (4,38), 224 (4,46), 234 (4,47) | 268 sh. (4,53), 274 (4,62) | 362 sh. (4,39), 376 (4,43), 408 (4,11), 427 sh. (3,94) |

In the series of dioxopyrrolines I and II, a number of spectral patterns are noteworthy. Just as should have been expected, the appearance of a hydrocarbon superstructure $(CH_2)_4$ (compounds IIa,b) virtually does not change the picture of the spectrum in comparison with the corresponding structures Ia,c. The effect of the auxochromic group $OCH_3$ appears rather clearly. Thus, in all three cases (pairs of substances Ia,b, esters Ic,d, and amides Ie,f) the hyperchromic effect of this group is present: The value of log $\varepsilon$ for the K-band increases by 0.20, 0.10, and 0.22, respectively. The position of the K-band is directly dependent on the acceptor properties of the substituent $R^2$: As the latter increase, this band is hypsochromically shifted from 375 nm, log $\varepsilon$ = 4.45 (substance Ib, $R^2$ = H), reaching a minimum in the case of the most electronegative substituent $C(O)CCl_3$ in compound Ih ($\lambda_{max}$ = 315 nm, log $\varepsilon$ = 3.89), which is accompanied by a hypochromic effect.

Analogously to the patterns mentioned, in the spectra of the quinoxalines III and IV the tetramethylene superstructure (compound IV) virtually does not change the spectrum in comparison with the corresponding isoquinoline IIIa. The $OCH_3$ group induces an 11 nm bathochromic shift of the K-band.

Halochromic phenomena were detected for compounds IIIa,b and IV. Thus, for example, when substance IIIb is dissolved in 95% $H_2SO_4$ or 70% $HClO_4$ the solution acquires a dark blue color. The color of a halochromic solution of this compound depends on the dilution: 1:1 dilution (by volume) changes the color to light green, and 1:3 (three parts water) gives an orange color. Other concentrated acids (nitric, phosphoric, hydrochloric, trifluoroacetic, and acetic) gave no changes of this kind. Solutions of substance IIIb in them have the same crimson color, similar to the color of a solution of compounds IIIa and IV. The latter are crimson colored in all the acids mentioned, including 95% $H_2SO_4$ and 70% $HClO_4$.

The UV spectra of quinoxalines IIIa,b and IV, taken in 95% $H_2SO_4$ solutions and more dilute solutions, are presented in Table 2. A comparison of the spectra in methanol (see Table 1) with the spectra in 95% $H_2SO_4$ shows a sharp bathochromic shift of the K-band under the action of the acid, and most important — a direct influence of the $OCH_3$ group. The bathochromic

TABLE 2. UV Spectra of Compounds IIIa,b and IV in Sulfuric Acid

| Compound | Solvent | Absorption band, $\lambda_{max}$, nm (log $\varepsilon$) | | |
|---|---|---|---|---|
| | | $\beta$ | *p* | $\kappa$ |
| IIIa | $H_2SO_4$ | 220 (4,46) | 265 sh. (3,60), 269 (4,23), 287 (4,15), 298 (4,15), 298 (4,15) | 323 (3,56), 455 (4,30), 461 (4,43), 515 (4,22), 547 (4,26), 588 (4,03) |
| III b | $H_2SO_4$ | 214 (4,38) | 245 (4,42), 270 (4,04) | 319 (4,00), 391 sh. (3,87), 4,31 (4,02), 468 (4,55), 617 (4,57) |
| | $H_2SO_4 : H_2O$, 1 : 1 | 225 (4,47) | 250 (4,24), 261 sh. (4,16) | 319 (4,05), 357 sh. (4,18), 472 (4,36), 588 (3,88) |
| | $H_2SO_4 : H_2O$, 1 : 3 | 220 sh. (4,31) | 248 (3,89), 256 sh. (4,11), 292 sh. (3,91), 3,09 (3,99) | 357 (3,88), 472 (3,85) |
| IV | $H_2SO_4$ | 220 (4,38) | 260 sh. (4,12), 269 (4,17), 287 (4,03), 299 (3,98) | 327 (3,38), 435 (4,18), 465 (4,29), 515 sh. (4,15), 547 (4,20), 588 sh. (4,00) |

shift for compound IIIb in comparison with substances IIIa and IV is 156 and 151 nm, respectively, which is accompanied by the corresponding hyperchromic effect.

The observed halochromy is probably associated with the possibility of formation of a stable pyrrolo[2,3-b]quinoxalinium cation, in which the positive charge is stabilized on account of delocalization over the three rings of the total aromatic system. If we assume that the $OCH_3$ group is completely protonated in 95% $H_2SO_4$ [13, 14], then the possibility of its direct polar conjugation with the heteroaromatic cation is ruled out; the molecule should contain only positive charges. A complex cation, solvated by $H_2SO_4$, is formed and gives a blue color. When it is diluted with water, the degree of protonation of the $OCH_3$ group decreases, which is accompanied by a change in the degree of solvation and, correspondingly, in the absorption. In this case the band at 617 nm, corresponding to the blue color, disappears.

The fluorescence spectra of the quinoxalines III and IV consist of broad structureless bands (half-width 70-80 nm, lying in the visible region of the spectrum). The fluorescence maxima ($\lambda_{max}$) and quantum yields ($\gamma$) relative to rhodamine 6Zh are 484 nm (85%), 490 nm (90%), and 482 nm (80%) for IIIa, b, and IV, respectively.

The presence of fluorescent properties in compounds IIIa,b and IV confirms the coplanarity of the heteroaromatic fragment in their molecule. The comparatively large value of the Stokes shift (more than 100 nm) shows that when the molecule is excited it undergoes structural changes [15]. The $OCH_3$ group induces a small bathofloric shift and increases the value of $\gamma$. Just as we should have expected, the spectra of compounds IIIa and IV are virtually identical, since the tetramethylene chain does not participate in the general aromatic $\pi$-conjugation.

As can be seen from the data presented, the quantum yields of the compounds studied are rather large. We should consider that up to this time no luminophores were known among condensed isoquinolines and phenanthridines. This makes further searches for luminophores in the series of heterocyclic systems mentioned of interest.

## EXPERIMENTAL

The electronic absorption spectra were taken on a Specord M-40 instrument; in all solvents $c = 5 \cdot 10^{-5}$ M. The fluorescence spectra were recorded for the same methanol solutions as the absorption spectra, but with fivefold dilutions of the solution, i.e., in a concentration of $10^{-5}$ M.

To obtain the fluorescence spectra we used a DFS-24 spectrometer-monochromator with DVK-3 recording unit. Fluorescence was excited with an LGI-21 nitrogen laser with excitation wavelength 337 nm. The quantum yields were calculated by a relative method according to a standard — rhodamine 6Zh, the absolute quantum yield of which is equal to 95%. The relative error in the measurement of $\gamma$ is 5-7%.

The purity of the substances [8] was monitored by thin-layer chromatography on Silufol UV-254 plates in an acetone—chloroform (1:9) system with development in UV light.

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