

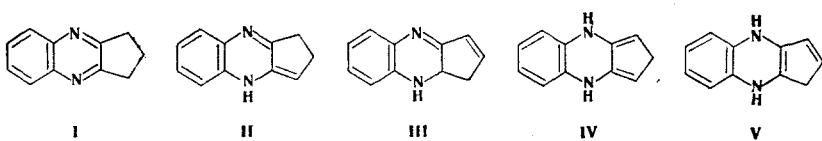
DIHYDRO-1,2,3-TRICARBALKOXYCYCLOPENTA[b]QUINOXALINES

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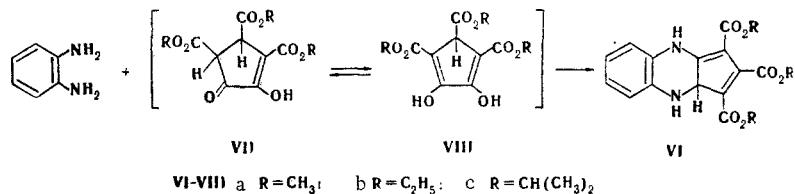
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4,9-Dihydro-3aH-1,2,3-tricarbalkoxycyclopenta[b]quinoxalines, the structure of which was established on the basis of the absorption, fluorescence, PMR, and IR spectra, were synthesized by condensation of o-phenylenediamine with tricarbalkoxycyclopentane-1,2-diones.

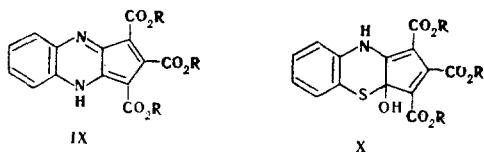
Of the six possible tautomeric forms (I-VI) of dihydrocyclopentaquinoxalines, the I structure, as in the case of cyclopentaquinoxalines [1, 2], is assumed for them, whereas structure II is assumed for their N-alkyl derivatives [4].



We have found that the condensation of o-phenylenediamine with tricarbalkoxycyclopentane-1,2-diones [5], which exist in the form of a tautomeric mixture of keto-enol VII and dienol VIII in solution,* gives 4,9-dihydro-3aH-1,2,3-tricarbalkoxycyclopenta[b]quinoxalines (VI):



Compound VIb is oxidized to cyclopentaquinoxaline IX, which has the same PMR, IR, and electronic spectra as the compound described in [6], when oxygen is bubbled through a solution of it in CCl_4 and the solution is irradiated with a quartz lamp. Dihydrocyclopentaquinoxalines VI are weaker acids (pK_a 10.3 ± 0.15 in 80% aqueous CH_3OH at $25^\circ C$) than IX (pK_a 5.65).



The absorption in the IR spectrum at 3400 cm^{-1} (Table 1) indicates the presence of NH groups in VI. The PMR spectra of these compounds contain singlets of the protons of two NH groups at 8.7 ppm and

* This follows from the data from the PMR spectra (in $CHCl_3$): the ring protons of keto-enol VIIc give a doublet of doublets at δ 3.40 and 4.08 ppm, whereas the ring proton of dienol VIIIc gives a singlet at 4.18 ppm.

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TABLE 1. 4,9-Dihydro-3aH-1,2,3-tricarbalkoxyxycyclopenta[b]-quinoxalines

Com- pound	mp, °C	Empirical formula	Found, %			Calc., %			ν_{NH}^* , cm ⁻¹	Yield, %
			C	H	N	C	H	N		
VI a	212 (dec.)	C ₁₇ H ₁₆ N ₂ O ₆	59.0	4.6	8.2	59.3	4.7	8.1	3400	53
VI b	171—173 (dec.)	C ₂₀ H ₂₂ N ₂ O ₆	61.9	5.7	7.3	62.2	5.7	7.3	3370	97
VI c	138—139	C ₂₃ H ₂₈ N ₂ O ₆	64.6	6.6	6.5	64.5	6.6	6.5	3370	92

* In KBr pellets (3380 cm⁻¹ for VIb in CCl₄).

TABLE 2. Electronic Spectra of Dihydrocyclopentaquinoxalines VI, Anion XIb, and Cation XIIb

Com- pound	λ_{max} , nm	1g ε		Medium
		λ ₁	λ ₂	
VIa	414, 390, 367, 350, 313*, 261	4.06, 4.23, 4.23, 4.19, 3.85, 4.12		C ₂ H ₅ OH
VIb	412, 388, 366, 349, 313*, 261	4.11, 4.28, 4.29, 4.25, 3.88, 4.67		C ₂ H ₅ OH
VIc	412, 389, 366, 349, 313*, 262	4.07, 4.25, 4.26, 4.21, 3.83, 4.60		C ₂ H ₅ OH
XIb	495, 298, 218	4.13, 4.19, 4.15		0.01 mole/liter KOH in C ₂ H ₅ OH
XIIb	444, 413, 388, 364, 356, 345*, 333*, 313*, 261	4.11, 4.14, 4.22, 4.27, 4.27, 4.24 4.16, 3.99, 4.61		70% H ₂ SO ₄

* Shoulder.

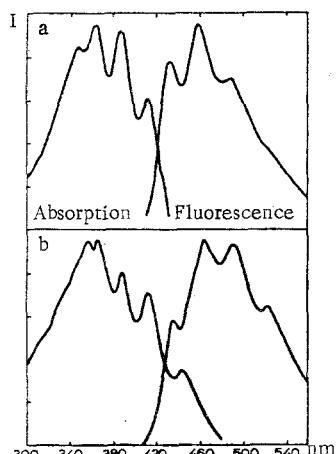


Fig. 1. Absorption and fluorescence spectra of VIb (a) and its anion XIb (b) in alcohol (I is the relative intensity of the absorption and fluorescence).

investigated compounds are close to the electronic spectra of 4,9-dihydro-3a-hydroxy-1,2,3-tricarbalkoxyxycyclopenta[b]-1,4-benzothiazines (X) [7] in which there is no doubt about the structure of the chromophore [for X in C₂H₅OH λ_{max} (log ε): 427 (4.0), 300 (4.4), and 228 (4.4)], both with respect to the position of the maxima and their intensities. The small bathochromic shift observed on passing from VI to X is evidently due to the fact that sulfur is a stronger auxochrome than the NH group. The absence of a vibrational structure in the spectrum of X may be due to the effect of the OH group. As in the case of X [7], the formation of anion XI from VI leads to a bathochromic shift (Table 2), which is explained by reinforcement of the auxochromic properties of the nitrogen atom in the 9 position. (See scheme on following page.)

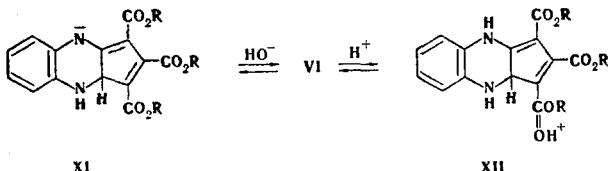
A bathochromic shift is also observed when VI is treated with acid (Table 2), and this is apparently associated with protonation of the carbonyl group (formation of XII); protonation of any of the NH groups should lead to a hypsochromic shift.

a 3aH signal (4.5 ppm). The NH signal in the PMR spectrum of IX is found at 12 ppm, as compared with 10 ppm for X [7]. The fact that the protons of both groups give one narrow signal indicates rapid intramolecular exchange of hydrogen between the nitrogen atoms. All of these data constitute evidence that tautomers I-III are formed in appreciable amounts in our case. Tautomer IV can be excluded on the basis of the fact that the protons of the carbalkoxy groups are not equivalent (CHCl₃).

The electronic spectra of the compounds and their ions (XIb and XIIb) are presented in Table 2. It is surprising that VI and anion XIb display spectra with a well-resolved vibrational structure at 350–450 nm (see Fig. 1), which is the mirror image of their fluorescence spectra at 430–530 nm (λ_{ex} 366 nm). The equivalence of the fluorescence spectra of VIb and anion XIb indicates that the NH bond undergoes dissociation in the excited state of VI to give anion XI.

The existence of fluorescence in the case of the dihydrocyclopentaquinoxalines indicates that they have structure VI rather than structure V, inasmuch as in the latter case the central ring containing eight π electrons would not be coplanar [8]. Structure VI is also confirmed by the fact that the electronic spectra of the

investigated compounds are close to the electronic spectra of 4,9-dihydro-3a-hydroxy-1,2,3-tricarbalkoxyxycyclopenta[b]-1,4-benzothiazines (X) [7] in which there is no doubt about the structure of the chromophore [for X in C₂H₅OH λ_{max} (log ε): 427 (4.0), 300 (4.4), and 228 (4.4)], both with respect to the position of the maxima and their intensities. The small bathochromic shift observed on passing from VI to X is evidently due to the fact that sulfur is a stronger auxochrome than the NH group. The absence of a vibrational structure in the spectrum of X may be due to the effect of the OH group. As in the case of X [7], the formation of anion XI from VI leads to a bathochromic shift (Table 2), which is explained by reinforcement of the auxochromic properties of the nitrogen atom in the 9 position. (See scheme on following page.)



EXPERIMENTAL

The electronic spectra of the compounds were recorded with a Unicam SP-8000 spectrophotometer. At concentrations of 10^{-4} to 10^{-5} mole/liter, all of the investigated solutions followed the Lambert-Beer law. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-477 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The fluorescence spectra of $1 \cdot 10^{-5}$ mole/liter solutions of the compounds were recorded with an ISP-51 spectrometer with an FEP-1 photoelectric adapter (λ_{ex} 366 nm). The spectral sensitivity of the apparatus was evaluated from the results of measurements of the fluorescence of quinine sulfate [9]. A solution of anion XIB was obtained by dissolving VIb in an alcohol solution of KOH (0.01 mole/liter). The ionization constant of VIIa was determined potentiometrically at 25° with a pH-340 potentiometer.

4,9-Dihydro-3aH-1,2,3-tricarbethoxycyclopenta[b]quinoxaline (VIb). A solution of 0.54 g (5 mmole) of o-phenylenediamine in 10 ml of methanol was added to 1.26 g (3.3 mmole) of tricarbethoxycyclopentane-1,2-dione dissolved (by heating) in ~20 ml of CH₃OH, after which a large amount of the solvent was removed by gentle distillation. The residual solution was cooled, a few milliliters of water were added, and the resulting precipitate was removed by filtration and crystallized from methanol. PMR spectrum (in CHCl₃), δ, ppm: 1.27 (6H, t*), 1.32 (3H, t), 4.22 (2H, q), 4.26 (2H, q), 4.30 (2H, q), 4.65 (1H, s, ring CH), 6.82 (4H, m, aromatic CH), 8.68 (2H, s, NH); (in CF₃CO₂H): 1.00 (9H, t), 3.96 (4H, q), 4.01 (2H, q), 4.30 (1H, s, ring CH), 6.88 (4H, m, aromatic CH). IR spectrum: (KBr): 1595, 1630, 1665, 1730, and 3370 cm⁻¹.

Compounds VIIa, b were similarly obtained and crystallized from methanol.

Compounds VI (Table 1) were obtained as light-yellow crystalline substances (oblong prisms) that were quite soluble in CHCl_3 , CH_3CN , and DMF; VIc was readily soluble in most organic solvents, and VIa, b were soluble in hot alcohols, but only slightly soluble in hexane and ether. The molecular weight of VIb was 379 (determined cryoscopically in $\text{CH}_3\text{CO}_2\text{H}$), as compared with 386.4 calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$.

LITERATURE CITED

1. E. J. Moriconi, R. E. Misner, and T. E. Brady, *J. Org. Chem.*, **34**, 1651 (1969).
2. R. M. Scribner, *J. Org. Chem.*, **30**, 3657 (1965).
3. G. R. Wendt and K. W. Ledig, US Patent No. 3,485,837 (1969); *Chem. Abstr.*, **72**, 55, 504 (1970).
4. G. R. Wendt and K. W. Ledig, US Patent No. 3,376,284 (1968); *Chem. Abstr.*, **69**, 52, 181 (1968).
5. W. Wislicenus and A. Schwanhausser, *Ann.*, **297**, 107 (1897).
6. N. V. Sumlivenko, G. F. Dvorko, and G. G. Dyadyusha, *Khim. Geterotsikl. Soedin.*, 1148 (1973).
7. N. V. Sumlivenko, E. A. Ponomareva, G. G. Dyadyusha, and G. F. Dvorko, *Khim. Geterotsikl. Soedin.*, 699 (1975).
8. V. West (editor), *Applications of Spectroscopy in Chemistry* [Russian translation], Inostr. Lit., Moscow (1959), p. 590.
9. E. Lippert, W. Nagele, I. Seibold-Blankenstein, W. Stiger, and W. Voss, *Z. Anal. Chem.*, **170**, 1 (1959).
10. N. K. Davidenko and A. A. Zholdakov, *Zh. Neorgan. Khim.*, **12**, 1196 (1967).

* Abbreviations: s is singlet, q is quartet, t is triplet, and m is multiplet.