NEW π-ELECTRON ANALOGS OF AZULENE

II.* 1,2,3-TRICARBALKOXYCYCLOPENTA[b]-1,4-BENZOTHIAZINES

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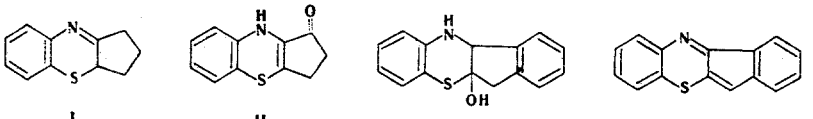
Condensation of o-aminothiophenol with 2-hydroxy-3,4,5-tricarbalkoxycyclopentadienones gave 3a, 9-dihydro-3a-hydroxy-1,2,3-tricarbalkoxycyclopenta[b]-1,4-benzothiazines, which undergo dehydration to give 1,2,3-tricarbalkoxycyclopenta[b]-1,4-benzothiazines. The latter were characterized as π-electron analogs of azulene on the basis of their electronic and PMR spectra and quantum-chemical calculations.

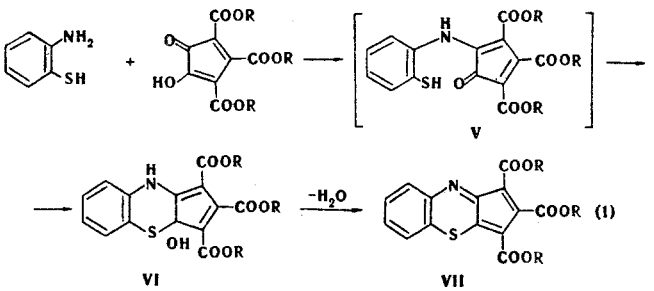
Cyclopentabenzothiazines (I-III) obtained by condensation of o-aminothiophenol with 2-chlorocyclopentanone [1], 3-chlorocyclopentane-1,2-dione [2], and indane-1,2-dione [3] are colorless compounds.



I II III IV

When III is heated above its melting point, water is split out to give deeply colored IV (λ_{max} 519 nm), which, like cyclopentathiopyrans [3, 4], is a π-electron analog of dibenzoazulene.

We have found that the condensation of o-aminothiophenol with 2-hydroxy-3,4,5-tricarbalkoxycyclopentadienones [5] proceeds in accordance with scheme (1):



V VI VII

VI, VII a R=CH_3; b R=C_2H_5; c R=$CH(CH_3)_2$

When the reaction is carried out in methanol, VI† are isolated, whereas VII are isolated when the reaction is carried out in pyridine; VII are new π-electron analogs of azulene (Table 1).

*See [7] for communication I.

†Structure V was assigned to VI in a preliminary communication [6].

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TABLE 1. 3a, 9-Dihydro-3a-hydroxycyclopenta[b]-1,4-benzothiazines (VI) and 1, 2,3-Tricarbalkoxycyclopenta[b]-1,4-benzothiazines (VII)

Compound	mp, °C (dec.)	Empirical formula	Found, %				Calc., %				ν_{NH}*, cm^{-1}	ν_{ON}*, cm^{-1}	Yield, %
			C	H	N	S	C	H	N	S			
VIa	159	$C_{17}H_{15}NO_7S$	54,1	4,0	3,7	8,5	54,0	4,0	3,7	8,8	3310	3520	77
VIb	141—142	$C_{20}H_{21}NO_7S$	57,3	5,1	3,3	7,6	57,3	5,1	3,4	7,9	3315	3520	50
VIc	140—141	$C_{23}H_{27}NO_7S$	59,9	5,9	3,0	7,0	59,8	5,9	3,3	7,1	3305	3510	54
VIIa	187	$C_{17}H_{13}NO_6S$	56,8	3,7	3,9	8,9	56,9	3,7	4,0	8,9	—	—	37
VIIb	125—126	$C_{20}H_{19}NO_6S$	59,8	4,8	3,5	8,0	60,2	4,9	3,6	7,8	—	—	40
VIIc	162—163	$C_{23}H_{25}NO_6S$	62,3	5,7	3,2	7,2	62,0	5,8	2,9	7,4	—	—	34

*In CCl_4; the absorption is at 3300-3400 cm^{-1} in the case of KBr pellets.

† Molecular weight (determined cryoscopically in benzene): Found 437; calculated 443.

TABLE 2. PMR Spectra of VI-VIII

Compound	Solvent	Group	Chemical shift, δ, ppm	No. of protons and multiplicity *
VIa	$CHCl_3$	CH_3	3,78	3 s
			3,84	3 s
			3,96	3 s
		OH	3,50	s
		NH	10,01	s
VIb	$CHCl_3$	CH_3	1,25	3 t
			1,28	3 t
			1,37	3 t
		CH_2	4,25	2 q
			4,30	2 q
			4,40	2 q
		OH	3,52	s
		NH	10,00	s
VIc	$CHCl_3$	CH_3	1,23	6 d
			1,28	6 d
			1,39	6 d
		CH	5,25	3 m
		OH	3,64	1 s
		NH	10,03	s
VIIb	$CHCl_3$	CH_3	1,37	6 t
			1,40	3 t
		CH_2	4,50	4 q
			4,61	2 q
VIIb	Pyridine	CH_3	1,29	3 t
			1,32	3 t
			1,45	3 t
		CH_2	4,35	2 q
			4,46	2 q
			4,67	2 q
VIIIb	CF_3CO_2H	CH_3	0,98	3 t
			1,08	6 t
		CH_2	4,07	2 q
			4,10	4 q
VIIa	Pyridine	CH_3	3,88	3 s
			3,94	3 s
			4,15	3 s
VIIIa	CF_3CO_2H	CH_3	3,60	3 s
			3,64	3 s
			3,72	3 s

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

Bands at 3300 and 3500 cm^{-1}, which are characteristic for intramolecular NH and OH hydrogen bonds (Table 1) appear in the IR spectra of CCl_4 solutions of VI; the absorption at 2500 cm^{-1} that is characteristic for the SH group is absent. The PMR spectra of these compounds contain signals at 3.5 and 10 ppm, which we assigned to the protons of OH and NH groups, respectively (Table 2). The assignment of the protons of the NH group was made on the basis of the fact that its signal in the spectrum of tricarbalkoxy-4H-cyclopentaquinoxalines [7] is found at 12 ppm, as compared with 11 ppm in the spectrum of α-formylpyrrole [8]. Absorption in the indicated regions is not observed in the PMR and IR spectra of VII.

Compounds VIa-c, which are stable in the crystalline state and in inert aprotic solvents, undergo dehydration to give VII when they are heated in carboxylic acids, pyridine, or acetic anhydride. Rapid

TABLE 3. Electronic Spectra of VI-VIII, X, and XI

Compound	λ_{max}, nm	lg ε	Medium
VIa	427, 300, 228	4,00; 4,39; 4,41	C_2H_5OH
VIb	420, 302, 225	3,97; 4,41; 4,41	C_2H_5OH
VIc	425, 300, 228	3,99; 4,38; 4,37	C_2H_5OH
VIIa	556, 392*, 376, 289, 231*	3,48; 4,09; 4,12; 4,64; 4,25	C_2H_5OH
VIIb	558, 392*, 376, 290, 232*	3,49; 4,10; 4,14; 4,65; 4,24	C_2H_5OH
VIIc	556, 392*, 376, 290, 231*	3,48; 4,11; 4,16; 4,66; 4,30	C_2H_5OH
VIIIa	720, 440, 301*, 294	3,14; 4,33; 4,62; 4,69	VIIa in 70% H_2SO_4
VIIIb	720, 439, 300*, 294	3,16; 4,32; 4,66; 4,73	VIIb in 70% H_2SO_4
VIIIc	720, 444, 300*, 293	3,16; 4,35; 4,62; 4,70	VIIc in 70% H_2SO_4
VIIIa	720, 439, 302*, 294	3,13; 4,29; 4,63; 4,67	VIa in 70% H_2SO_4
Xa	457, 330, 268	3,91; 4,26; 4,29	VIIa + EtONa in EtOH
XIa	392, 298, 219†	3,95; 4,40	VIIa + NaOH in 25% EtOH
XIa	395, 300, 220†	3,96; 4,41	VIa + NaOH in 25% EtOH
XIa	396, 300, 223†	3,89; 4,45	VIa + EtONa in EtOH

*Shoulder.

†The determination of the intensity is difficult because of the absorption of the solvent.

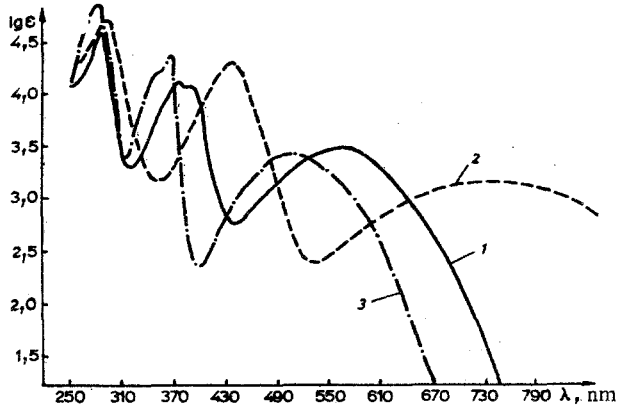
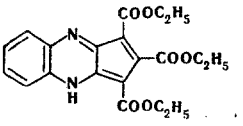


Fig. 1. Electronic spectra of VIIb (1), VIIIb (2), and 1,2,3-tricarbethoxy-4H-cyclopenta[b]quinoxaline (IX) (3).

hydration occurs even at room temperature when they are dissolved in 70% H_2SO_4 to give cation VIII [scheme (2)]. A comparison of the electronic spectra of solutions of VIIa and VIa in 70% H_2SO_4 (the absorption in both cases pertains to VIIIa) shows that this reaction proceeds quantitatively (Table 3).

Compounds VIIa-c are dark-violet substances (Table 1) and form green solutions of cations VIII when they are dissolved in CF_3CO_2H or mineral acids.

The similarity between the electronic spectra of VII and the spectra of azulene and, particularly, 1,2,3-tricarbalkoxy-4H-cyclopenta[b]quinoxaline (LX) [7] (Fig. 1) indicates the presence in them of a unified cyclic system of π electrons, i.e., that they are aromatic compounds.



IX

The analogy with azulene shows up distinctly upon comparing cyclopentabenzotriazines (VII) with their cations (VIII) (Table 3 and Fig. 1) – in conformity with the rules of the effect of the electronegativities of the atoms in the 4 and 8 positions of the azulene ring, protonation of VII in the 9 position leads to a strong bathochromic shift of the longwave band. On passing from cyclopentaquinoxalines IX to cyclopentathiazine VII, i.e., on replacing the nitrogen atoms by a sulfur atom, we also observe a bathochromic shift, and this effect is considerably more pronounced in the cations (115 nm) than in the bases (50 nm). When considering bases VII and IX and their cations as pseudoazulenes, one must bear in mind the fact that the NH group in IX or the sulfur atom in VII replaces two CH groups of azulene in the 4 and 5 positions, which have opposite charges and, consequently, opposite substituent effects. Replacement of the nitrogen atom by a sulfur atom may therefore lead both to hypsochromic and bathochromic shifts. In fact, both types of effects have been described for pseudoazulenes [3]. In the case of the cyclopentaquinoxaline cation, in view of the symmetry of the nitrogen atom, the character of the 4 and 8 positions of azulene should predominate, and the bathochromic shift on replacement of one of the nitrogen atoms by a sulfur atom, which gives its electrons to the overall conjugation system less readily, is completely explainable without invoking additional

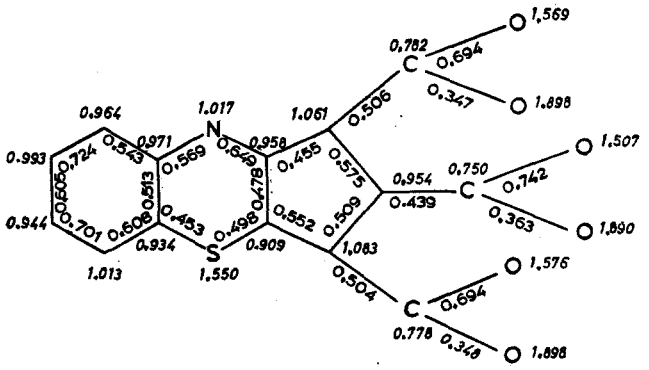
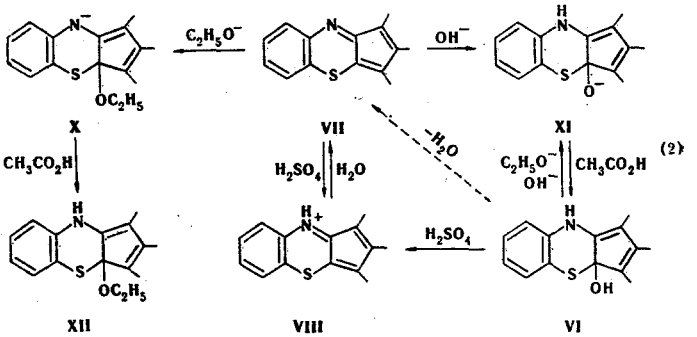


Fig. 2. Molecular diagram of 1,2,3-tricarbalkoxycyclopenta[b]-1,4-benzothiazine (VII).

assumptions, for example, participation of the d orbitals [3].

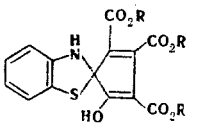
The absorption spectra of hydrated derivatives VI (Table 3) differ considerably from the spectra of the pseudoazulenes. The decrease in the number of bands and the strong hypsochromic shift indicate a substantial change in the π-electron structure. In contrast to cyclopentathiazines I–III, VI are colored, and this may be explained by the presence of a system of conjugation between the carbalkoxy groups and the aniline residue.



In fact, the action of an alkoxide on VIIa gives anion Xa with the charge on the nitrogen atom, and solution of Xa absorb at longer wavelengths than a solution of VIa (Table 3); the deepening of the color is due to the fact that the anilide anion residue is a stronger auxochrome.

Another anion (XI) in which the charge is concentrated on the oxygen atom is formed by the action of aqueous alcoholic alkali on VII. The fact that a solution with precisely the same spectral characteristics (Table 3) is formed by the action of aqueous alcoholic alkali or alkoxide on VI constitutes proof for this. The UV spectra of solutions containing this anion are very similar to the spectrum of VI and differ from it only with respect to the small hypsochromic shift of the longwave band. (Table 3). Solutions of XII formed from anion X after acidification have similar spectra.

The combination of these transformations is incompatible with the alternative structure (XIII) of the hydrated derivatives.



XIII

Spirobenzothiazolines of the XIII type are usually formed in the condensation of cyclenones with o-aminothiophenol [9], although they have not been detected in the condensation with indane-1,2-dione [3]. The color of spirobenzothiazoline XIII should deepen on ionization of the hydroxyl group and should undergo little change on ionization of the NH group. In fact, we observe the opposite effects, which are in good agreement with structure VI. A direct proof that our hydrated compounds have structure VI rather than structure XIII is provided by the fact that their PMR spectra do not contain signals at 1-1.5 ppm (Table 2) a region that is characteristic for the NH group of spirobenzothiazolines [10]. The proton of the NH group in VI gives a signal at 10 ppm, which is natural for a NH group conjugated with strong electron acceptors [7, 8].

In conformity with structure VI, the protons of the carbalkoxy groups in the 1, 2, and 3 positions are nonequivalent, and the signals of the protons of the carbalkoxy groups in conjugation with the NH group (in the 1 and 3 positions) are close to one another and appear at stronger field than the signals of the protons of the carbalkoxy group in the 2 position (Table 2). The protons of the carbalkoxy groups of VII give, as a rule, closely situated nonequivalent signals. This is in agreement with our quantum-mechanical calculations of the electron density distribution in VII (Fig. 2). According to these calculations, the shift

of the signals of the protons of the ester groups to low field should occur in the order 1-3-2, and the difference between the 1 and 3 positions should be slight. This is what we observe experimentally. A similar pattern is also noted for cations VIII (Table 2). In the case of VIIIb it is seen that the signals of the protons of the ester groups in the 1 and 3 positions of the cation are shifted to lower field as compared with the protons of the carbalkoxy group in the 2 -positions. It is also seen from Fig. 2 that the carbon atom in the 3a position stands out appreciably with respect to the magnitude of the positive charge from the other carbon atoms of the heteroxyclic system. This explains the direction of nucleophilic attack during the action of bases on VII (formation of X and XI).

EXPERIMENTAL METHOD

The electronic spectra of the compounds were recorded with a Unicam-SP-8000 spectrograph. All of the investigated solutions followed the Lambert–Beer law at concentrations from 10^{-4} to 10^{-5} mole/liter. 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 molecular diagram of VII was calculated by the MO LCAO method within the Hückel approximation with the Streitwieser parameters [11] and a Minsk-22 computer.

3a, 9-Dihydro-3a-hydroxy-1,2,3-tricarbethoxycyclopenta[b]-1,4-benzothiazine (VIb). A 6.5-mmole sample of o-aminothiophenol was added to a heated mixture of 3.2 mmole of 2-hydroxy-3,4,5-tricarbethoxycyclopentadienone and 15 ml of CH_3OH, after which the mixture was heated for 10 min on a water bath. It was then cooled, and the precipitated yellow crystals were removed by filtration. The product was crystallized from benzene–hexane (1 : 1). Compounds VIa, c were similarly obtained; VIa was crystallized from CH_3OH, and VIc was crystallized from hexane.

1,2,3-Tricarbomethoxycyclopenta[b]-1,4-benzothazine (VIIa). A A solution of 3.8 mmole of o-aminothiophenol in 5 ml of pyridine was added to a heated (100°) solution of 3.8 mmole of 2-hydroxy-3,4-5-tricarbomethoxycyclopentadienone in 15 ml of pyridine, after which the mixture was heated on a water bath for 10 min. The bulk of the solvent was removed by distillation, the concentrated solution was cooled, and the precipitated dark-violet crystals were removed by filtration. The product was crystallized from methanol (acetone).

Compounds VIIb, c were similarly obtained and crystallized from hexane.

B) A solution of $4.95 \cdot 10^{-5}$ mole of VIa in 15 ml of $(CH_3CO)_2O$ was heated on a water bath for 1 h, after which the bulk of the solvent was removed by distillation, the concentrated solution was cooled, and the resulting precipitate was removed by filtration to give $2.76 \cdot 10^{-5}$ mole (56%) of VIIa. The product was crystallized from acetone.

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