

ELECTRONIC SPECTRA OF 5,6-POLYMETHYLENETHIAPYRYLIUM SALTS AND CERTAIN OXYGEN ANALOGS

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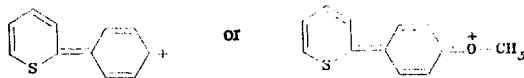
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Electronic absorption and emission spectra of substituted 5,6-tri- and 5,6-tetramethylenethiapyrylium salts are examined to determine the influence of the degree and character of substitution of the heterocycle, the size of the condensed alicycle, the nature of the heteroatom and the counterion, and the polarity of the solvent.

5,6-Tri- and 5,6-tetramethylenethiapyrylium salts, obtained by reaction of 1-aryl- and 1,3-diaryl-3-(2-oxocycloalkyl)-1-propanones with hydrogen sulfide and acids [1-4], are used as intermediates in the synthesis of condensed thiopyrans [1, 5] and thiapyrylocyanines [6-8], and they are also used as fluorescent materials [9], as photosensitizers [10-12], and in lasers [13-15]. Therefore, there is an urgent need for studies of the electronic absorption and emission spectra of thiapyrylium salts and their oxygen analogs (Table 1).

In Table 2 we present the spectra data for the 5,6-polymethylenethiapyrylium perchlorates I-XIV. The degree and character of substitution in the heterocycle have the greatest influence on the energy of the first transition, which is responsible for the long-wave absorption band. The substantial bathochromic shift and the increase in intensity of this band upon introduction of substituents participating in conjugation with the heterocycle are indications of π electron excitation (it is assumed that only one electron changes in state). Judging from the high intensity, the other absorption bands of compounds I-XIV (Table 2) are also due to $\pi \rightarrow \pi^*$ transitions. In the electronic spectra of all thiapyrylium and pyrylium salts thus far studied, no transitions with the participation of the unshared pair of electrons of the heteroatom have been manifested. Quantum-chemical calculations have shown that the stationary state of these electrons in pyrylium and thiapyrylium salts is characterized by a lower energy than, for example, in pyridine [16, 17]. Therefore, the energy of $n \rightarrow \pi^*$ transitions in the present case is so great that the corresponding absorption bands do not fall into the near-UV region.

It was noted previously that low-frequency electronic excitation of substituted thiapyrylium and pyrylium salts having phenyl or heteroatomic substituents is accompanied by substantial transfer of electron density to the heterocycle [17-19]. Intramolecular charge transfer (ICT) upon excitation can be interpreted as an increase in the contribution to the resonance made by valence schemes of the type

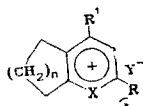


In order to estimate the degree of localization of the positive charge on the carbon or oxygen atoms in the electronically excited state of the thiapyrylium cation, we investigated the influence of solvent polarity on the position of the ICT absorption band. Increases in the solvating power of the solvent lead to a hypsochromic shift of the long-wave absorption band in these systems (Table 1).

The greatest hypsochromic shift is observed for thiapyrylium salts containing one methoxyl substituent (Table 1). This indicates that the dipole moment of the methoxyphenyl derivatives of the compounds is changed to the greatest degree as a result of electronic excitation; however, the shift $\Delta\lambda$ is no greater than 15 nm. Obviously, the energy of reorganization of the

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TABLE 1. Position of Long-Wave Absorption Band of 2-R-4-R¹-5,6-Polymethylenethiapyrylium Salts and Corresponding Pirylium Salts



I–XIX X=S; XX–XXV X=O; I–IX, XV–XVIII, XX–XXIII n=2; X–XIV, XIX, XXIV, XXV n=1

Compound	Y	R	R ¹	λ _{max} , nm		Δλ, nm
				CH ₂ Cl ₂	CH ₃ CN	
I	CF ₃ COO	H	H	307†	—	—
II	ClO ₄	C ₆ H ₅	H	382	372	10
III	ClO ₄	C ₆ H ₅	CH ₃	368	361	7
IV	ClO ₄	C ₆ H ₅	C ₆ H ₅	368	368	0
V	ClO ₄	C ₆ H ₅	C ₆ H ₄ OCH ₃ -4	420	420	0
VI	ClO ₄	C ₆ H ₅	C ₆ H ₃ (OCH ₃) ₂ -3,4	425	—	—
VII	ClO ₄	C ₆ H ₄ OCH ₃ -4	H	440	425	15
VIII	ClO ₄	C ₆ H ₄ OCH ₃ -4	C ₆ H ₅	442	429	13
IX	ClO ₄	C ₆ H ₄ OCH ₃ -4	C ₆ H ₄ OCH ₃ -4	432	426	6
X	ClO ₄	C ₆ H ₅	H	381	372	9
XI	ClO ₄	C ₆ H ₅	CH ₃	379	—	—
XII	ClO ₄	C ₆ H ₅	C ₆ H ₅	367	359	8
XIII	ClO ₄	C ₆ H ₄ OCH ₃ -4	H	442	427	15
XIV	ClO ₄	C ₆ H ₄ OCH ₃ -4	C ₆ H ₅	440	432	8
XV	FeCl ₄	C ₆ H ₅	H	375	367	8
XVI	FeCl ₄	C ₆ H ₅	C ₆ H ₅	372	366	6
XVII	BF ₄	C ₆ H ₅	C ₆ H ₅	370	366	4
XVIII	Br	C ₆ H ₅	C ₆ H ₄ OCH ₃ -4	435	421	14
XIX	I	C ₆ H ₅	H	379	374	5
XX	ClO ₄	C ₆ H ₅	H	376	362	14
XXI	ClO ₄	C ₆ H ₅	C ₆ H ₅	370	365	5
XXII	ClO ₄	C ₆ H ₅	C ₆ H ₄ OCH ₃ -4	420	—	—
XXIII	ClO ₄	C ₆ H ₅	C ₆ H ₃ (OCH ₃) ₂ -3,4	435	—	—
XXIV	ClO ₄	C ₆ H ₅	H	374	366	8
XXV	ClO ₄	C ₆ H ₅	C ₆ H ₅	375	368	7

†In CF₃COOH solution.

solvent is small in all cases, and the charge transfer in the process of the electronic transition cannot be significant. This statement is supported by the fact that the energy of the first transition of the thiapyrylium salts is very little dependent on the structure of the anion,[†] the value of λ_{max} remains almost unchanged in the series of compounds II–XV–XIX and IV–XVI–XVII in both of the solvents that were used (Table 1). Thus, we should consider that the first electronic transition is a π → π* transition with very little redistribution of electron density. The shift of electron density from the substituents to the heterocycle is not large enough that we can speak of ICT.

A phenyl substituent in position 2 gives a very marked shift in the long-wave absorption band of the thiapyrylium heterocycle toward longer wavelengths, which can be explained by the extension of the conjugation chain. According to our approximate estimate (the anions are different in compounds I and II), the bathochromic shift is 75 nm (Table 1). At the same time, the introduction of an additional phenyl group at position 4 gives a small hypsochromic effect, as we can see by comparing the values of λ_{max} for the compounds II and IV, X and XI, XIII and XIV, and XV and XVI. An analogous picture is observed in the electronic spectra of monocyclic thiapyrylium perchlorates. The values of λ_{max} for the long-wave absorption band of thiapyrylium, 2,6-diphenylthiapyrylium, and 2,4,6-triphenylthiapyrylium are 285, 419, and 415 nm [20]. In contrast to the phenyl groups in position 2, each of which apparently produces a bathochromic shift on the order of 70 nm, the introduction of a phenyl group into position 4 gives a slight shift of this band toward the short-wave region. A breakdown of additivity in the influence of phenyl substituents is also observed in the pyrylium salts: The long-wave absorption bands for the perchlorates of pyrylium, 2,6-diphenylpyrylium, and 2,4,6-triphenylpyrylium are found in the respective regions 270, 416, and 419 nm [20].

[†]The structure of the anion in this case should have the same influence on the energy of an ICT electronic transition as does the solvent.

TABLE 2. Position and Intensity of Bands in Electronic Absorption Spectra of Perchlorates I-XIV in Methylene Chloride

Compound	λ_{\max} , nm (and $\epsilon_{\max} \cdot 10^3$ liters/mole \cdot cm)
I [†]	244 (-), 307 (-)
II	251 (12,3), 276 (5,8) Sh., 382 (13,7)
III	256 (20,0), 278 (8,7) Sh., 368 (17,0)
IV	248 (18,6), 269 (14,3), 368 (27,5)
V	258 (34,0), 374 (29,5), 420 (24,0)
VI	254 (30,0), 372 (28,5), 425 (19,8)
VII	264 (12,7), 300 (12,0), 440 (23,0)
VIII	262 (13,0), 300 (14,7), 353 (11,2), 442 (26,3)
IX	268 (31,6), 298 (24,0), 432 (47,5)
X	247 (12,6), 274 (6,3) Sh., 381 (12,6)
XI	248 (13,5), 274 (7,6) Sh., 379 (12,9)
XII	248 (19,1), 275 (13,2) Sh., 367 (26,2)
XIII	258 (10,0), 300 (10,2), 442 (18,6)
XIV	254 (11,5), 304 (16,9), 355 (19,4), 440 (26,9)

[†]Trifluoroacetate in CF₃COOH solution.

CNDO/S calculations of substituted pyrylium cations can provide an explanation of the specific effect of the phenyl group in position 4, the two highest occupied MOs of which do not interact with the filled π MOs of the heterocycle and, having a high energy, in the absence of phenyl groups in position 2, participate directly in low-frequency $\pi \rightarrow \pi^*$ transitions [17]. Since the energy of the lowest unoccupied MO is not changed by the introduction of phenyl substituents at any position in the heterocycle, the 4-phenyl group by itself gives a bathochromic effect on the long-wave absorption band, this effect being on the same order as that of the 2-phenyl substituent [17]. However, in the presence of the 2-phenyl substituent, the energy of the HOMO of the heterocycle is increased so much that the π MOs of the 4-phenyl group are positioned lower on the energy scale and do not participate in the low-frequency transition.

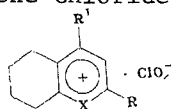
A methoxyphenyl substituent in position 2 gives a bathochromic shift of the maximum of the first absorption band for compound I amounting to 130 nm, almost twice that for a phenyl group (Table 1). The additional shift can be explained qualitatively in terms of a lengthening of the conjugation chain at the expense of the unshared electron pair of the oxygen atom of the methoxyl group. At the same time, the introduction of a methoxyl substituent at position 4 when such is present in position 2 (compounds VII and VIII[†]) gives a hypsochromic shift. In this case, obviously, the 4-methoxyphenyl substituent does not participate in forming the frontier MOs of the thiapyrylium salts. At the same time, compounds V, XVIII, and XXII absorb in a longer-wave region than the corresponding salts II, XV, and XX. In these phenyl-substituted compounds, apparently, the HOMO is localized on the 4-methoxyphenyl substituent, similar to the situation in 2,4-dimethyl-6-phenylpyrylium, where the highest occupied MO is the π MO of the 4-phenyl group [17].

The size of the alicycle has practically no influence on the energy of any of the $\pi \rightarrow \pi^*$ transitions, including the low-frequency transition (Table 2). The alicycle itself produces a bathochromic shift of the long-wave absorption band of the unsubstituted thiapyrylium cation amounting to approximately 20 nm: In the series of compounds thiapyrylium, 5,6-tetramethylene-thiapyrylium, and sym-octahydrothioxanthylum, λ_{\max} increases in the series 285, 307, and 327 nm [20, 21]. The influence of the condensed alicycle is the same as the overall bathochromic effect of α - and β -methyl substituents (13 and 9 nm, respectively [22, 23]).

The usual explanation for the reduction of the $\pi \rightarrow \pi^*$ transition energy by alkyl substituents is hyperconjugation, but this explanation meets with objections that are well justified [24]. This is all the more true since a methyl radical in position 4 does not produce a bathochromic, but rather a hypsochromic shift of the long-wave absorption band, amounting to 14 nm, both in our compounds and in monocyclic thiapyrylium cations [22, 23]. The influence of alkyl substituents on the energy of the first transition in thiapyrylium compounds and in their oxygen analogs is apparently governed by the type of frontier π MOs and by the relative contribution to these orbitals from the 2p_z orbitals of the heterocycle carbon atoms.

No definite trend can be observed in the shift of the long-wave absorption band of the thiapyrylium salts when the sulfur atom is replaced by oxygen. Whereas compounds XX and XXIV [†]As in Russian original; appears that it should be compounds VIII and IX — Translator.

TABLE 3. Wavelength (λ_0) of Purely Electronic Transition, and Position (λ_{fl}) and Relative Intensity (Q) of Fluorescence Band, in Methylene Chloride



Compound	λ_{fl} , nm	Q	λ_0 , nm
II	472	50	427
III	457	28	412
IV	468	18	418
V	562	4	491
VI	506	1	466
VII	540	200	490
VIII	537	120	490
IX	530	70	481
XX	419	190	398
XXI	420	166	395
XXII	535	16	478
XXIII	480	4	458

absorb in a shorter-wave region than their sulfur analogs, compounds XXI, XXIII, and XXV show the opposite trend, and the salts XXII and V have the same value of λ_{max} (Table 1).

Investigation of the emission spectra of a number of fluorescing thiapyrylium and pyrylium perchlorates has shown that the wavelength λ_0 of the purely electronic transition[†] is greater for the thiapyrylium perchlorates in all cases (Table 3). This means that the energy of the first purely electronic transition in thiapyrylium salts is smaller than in the corresponding oxygen compounds. The difference in the minimum excitation energy of the S and O analogs decreases with increasing length of the conjugation chain.

The thiapyrylium salts fluoresce at longer wavelengths than the pyrylium salts, but with a lower intensity; this cannot be explained on the sole basis of the difference between the two groups of compounds in absorbance. Apparently, the fluorescence quenching process is more efficient in the thiapyrylium salts.

The influence of substituents at position 4 on the location of the fluorescence band is qualitatively the same as the influence on the location of the long-wave absorption band. The intensity of fluorescence of the substituent decreases in the series $\text{CH}_3 > \text{C}_6\text{H}_5 > n\text{-C}_6\text{H}_4(\text{OCH}_3)$, both in the thiapyrylium salts and in the pyrylium salts. However, in position 2, a methoxyphenyl substituent, on the contrary, substantially increases the fluorescence of the thiapyrylium salts (Table 3).

EXPERIMENTAL

The UV spectra of the salts I-XXV were obtained in an SF-4A spectrophotometer in methylene chloride or acetonitrile solution, with a layer thickness $2.2 \cdot 10^{-5}$ cm and a concentration of 10^{-2} M. The fluorescence spectra were taken in a JY-3 spectrometer. The spectral slit width was 10 nm, scanning rate 1 nm/sec, thickness of layer 1 cm. The solution concentration was $2 \cdot 10^{-5}$ M, and the optical density of the sample in the region of the absorption band was ≈ 0.01 . The accuracy in determining the fluorescence wavelength was ± 2 nm. The relative intensity of fluorescence Q was rated in units of area under the emission curve for compound VI. The accuracy of measurement of the fluorescence band area was approximately 20%.

The salts II-XXV were prepared in accordance with [1-4]. The bromides, fluorides, tetrafluoroborates, and trifluoroacetates were converted to perchlorates by an exchange reaction with 70% HClO_4 . The 5,6-tetramethylenethiapyrylium trifluoroacetate (I) was not isolated. The solution of the trifluoroacetate I in CF_3COOH was prepared by the procedure of [4] from 3-(2-oxocyclohexyl)-1-propanal.

[†]Defined as the half-sum of λ_{max} for the bands of absorption and fluorescence.

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