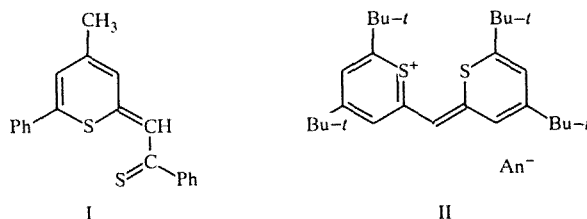


α -THIENYL-SUBSTITUTED THIOPYRILIUM SALTS

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The perchlorates of 2,6-di(2-thienyl)-4-methylpyrilium and -thiopyrilium, and the isomeric 2,4-di(2-thienyl)-6-methyl derivatives, as well as the perchlorates of 2,4-di(2-thienyl)pyrilium with tri- and tetramethyl groups in the 5,6 position have been synthesized. Their UV and PMR spectra have been studied. Based on data on Oberhauser's nuclear effect it was concluded that the sulfur atoms of 2(6)-thienyl substituents and the O(S) atoms of heteroaromatic cations are present in the cis position.

It is known that compounds, in which sulfur atoms are separated by a trimethine chain, such as 2-(thiobenzoylmethylene)-2H-pyran I [1] and thiopyrilo-2-monomethinecyanine II, possess a Z,Z-configuration, established in the latter instance for the crystalline state of the substance [2], as well as for its solutions [3]. On the other hand, in systems in which the sulfur atoms are separated only by two carbon atoms, the conformation can change depending on the conditions. Thus, it has been shown that in the solid state of the substance the poly- α -thienyl molecules exist in the everywhere planar trans-form [4-6]. In solution 2,2-dithienyl can exist mostly as the S-cis-conformer [7] or as a mixture of conformers [8] in which the planes of the thiophene radicals are rotated at an angle to each other.



In the present study a series of α -thienyl-substituted thiopyrilium salts was obtained and their three-dimensional structure in solution investigated. The reaction of 2-acetylthiophene with acetaldehyde gave the 1,5-diethienyl-substituted diketone III, which by the reaction with acetyl perchlorate was converted to the 2,6-diethienyl-substituted pyrilium salt IV. The thioanalog V

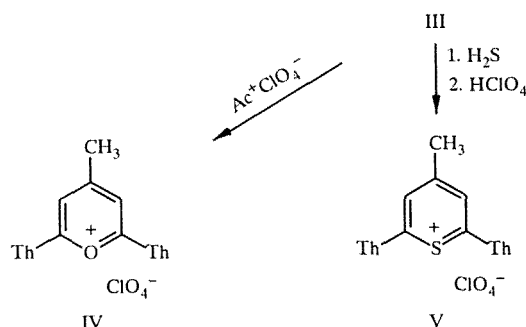
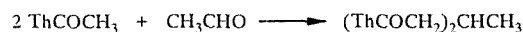
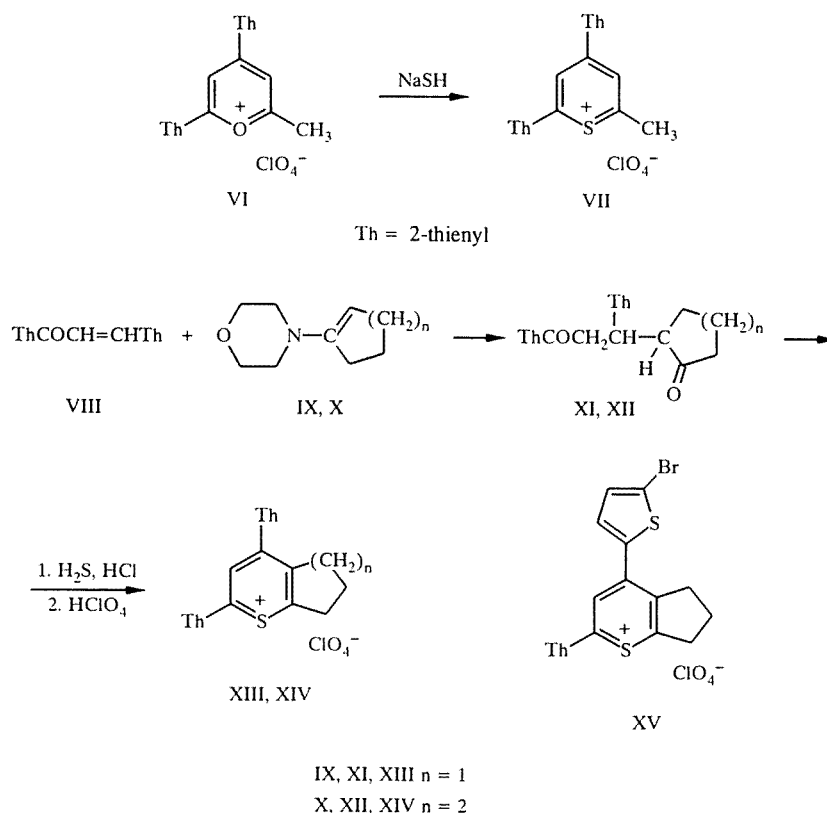


TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp*, °C	Yield, %
III	C ₁₄ H ₁₄ O ₂ S ₂	68...70	65
IV	C ₁₄ H ₁₁ ClO ₅ S ₂	247...248	72
V	C ₁₄ H ₁₁ ClO ₄ S ₃	245...247	14
VII	C ₁₄ H ₁₁ ClO ₄ S ₃	246...247	54
XIII	C ₁₆ H ₁₃ ClO ₄ S ₃	217...218	33
XIV	C ₁₇ H ₁₅ ClO ₄ S ₃	194...195	16
XV	C ₁₆ H ₁₂ BrClO ₄ S ₃	> 300	7

*Compound III crystallizes from ethanol; IV from a mixture of acetonitrile—acetic acid (1:10); V from acetonitrile; VII is reprecipitated from acetonitrile with ether; XIII-XV crystallizes from glacial acetic acid.

was synthesized by treating the diketone III with a mixture of hydrogen sulfide and hydrogen chloride; boron trifluoride etherate can be used instead of the latter. The 2,4-di(2-thienyl)-6-methylthiopyrilium perchlorate VII was obtained by the reaction of sodium hydrosulfide with the corresponding pyrilium salt VI [9]. We have also synthesized the perchlorates of 2,4-di(2-thienyl)-5,6-trimethylenethiopyrilium XIII and 2,4-di(2-thienyl)-5,6,7,8-tetrahydrobenzo-1-thiopyrilium XIV. For this purpose the 1,3-di(2-thienyl)-2-propen-1-one VIII was treated with the enamines of cyclopentenone or cyclohexenone IX, X respectively; the diketones XI, XII, created hereby, formed rings by the action of hydrogen sulfide and hydrogen chloride. The 4-(5-bromothieryl-2)-substituted analog XV was synthesized in the same way as the salt XIII.



Data derived from the electron absorption spectra of the synthesized salts IV-VII, XIII-XV and of their phenyl-substituted analogs IVa-VIIa, XIIIa, XIVa are presented in Table 2. The replacement of the phenyl radicals by the stronger electron donors α -thienyls causes in all instances a bathochromic shift of the long-wave absorption bands. The spectra of the 2,6-dithienyl-substituted pyrilium and thiopyrilium salts IV and V contain, like their phenyl-substituted analogs, one long-wave

TABLE 2. Electron Absorption Spectra of Thienyl-Substituted Pyriliium and Thiopyriliium Salts IV-VII, XIII-XV and of Their Phenyl-Substituted Analogs IVa-VIIa, XIIIa, XIVa in Methylene Chloride

Com- pound	λ_{\max} , nm ($\epsilon \cdot 10^{-4}$)	Com- pound	λ_{\max} , nm ($\epsilon \cdot 10^{-4}$)
IV	304(1,78), 330s(1,33), 470(2,66)	IVa	241(1,28), 281(1,54), 402(2,29)
V	280(2,62), 340(0,62), 492(2,65)	Va	267(2,89), 326(0,39), 405(2,06)
VI	279(1,07), 334s(0,67), 378(2,05), 443(4,40)	VIa	260(1,05), 355(1,62), 384(1,64)
VII	260(0,74), 305(1,14), 415(2,34), 458(2,64)	VIIa	253(1,04), 278s(0,81), 372(2,61)
XIII	265(1,72), 280(1,85), 420(3,12), 452(2,52)	XIIIa	251(1,57), 272s(1,20), 374(2,27)
XIV	270(1,02), 302(1,07), 420(2,08), 455(2,27)	XIVa	256(1,63), 279s(0,86), 378(1,89)
XV	307(1,34), 434(3,35), 464(3,22)		

band each, while the spectra of the 2,4-dithienyl-substituted pyriliium salt VI, isomeric to IV, and of its phenyl-substituted analog contain two bands. This difference is explained by the fact that the intensity of the second long-wave transition in the discussed symmetrically substituted compounds is so low that it is not detected or that it appears as a shoulder on the curve in the region 300-350 nm. In distinction from the absorption spectra of 2,4-dithienyl- and 2,4-diphenyl-substituted thiopyriliium salts, the spectra of the salts VII, XII, XIV and VIIa, XIIIa, XIVa differ from each other. While the spectra of the first three compounds contain two long-wave bands each, the spectra of the latter compounds contain one band only (Fig. 1). An analysis of the data in Table 2 shows that the transition from the pyriliium salt VI to the thiopyriliium salt VII is accompanied by a shift of both bands to the long-wave region and by a shortening of the distance between the first and the second maxima ($\lambda_1 - \lambda_2$ for VI is equal to 65 nm, for VII 43 nm). A comparison of the corresponding pair of the 2,4-diphenyl-substituted compounds VIa and VIIa shows that this difference is even smaller in the pyriliium salt VIa ($\lambda_1 - \lambda_2 = 29$ nm); the single long-wave band of the thiopyriliium salt VIIa is not shifted to the long-wave region, but to the short-wave region of the spectrum, in comparison with the long-wave band of compound VIa by 12 nm. This indicates that in the salt VIIa, as evidently also in XIIIa and XIVa, the energies of the first and second transition are so close that the corresponding absorption bands combine into one band. An analogous combination of two bands into one has been observed also in the spectra of pyriliium salts, for instance, when the phenyl group in position 4 in the 2,4,6-triphenyl-substituted pyriliium cation is replaced by the α -furyl substituent [10].

The PMR spectra of compounds IV and V contain four multiplet groups. The analysis of the integral intensities of the signals in these spectra, as well as the use of COSY binuclear spectroscopy and the calculation of the theoretical spectra, determined this spin system as $A_2B_2C_2D_2X_3$. Based on these data the proton signals were assigned for compounds IV and V (Table 3). The signals for the other compounds were assigned, based on the comparison of the spectra of all compounds investigated; in some instances the data were also confirmed experimentally by double homonuclear resonance. In particular, when irradiating a solution of the thiopyriliium XIII cation with a signal at 7.41 ppm, which we assigned to the 4-H proton of the 2- α -thienyl substituent, we observed a degeneration of 3-H and 5-H multiplets near 8.00 ppm into singlets. Based on the characteristics of the PMR spectra of the compounds studied, let us point out that the signals of the 3-H and 5-H protons of α -thienyl substituents, present in positions 2 as well as 4 of the heterocyclic salts, differ relatively little from each other and are located at 0.6-0.8 ppm in the weaker field, as compared to the signals of the 4-H protons of the same substituents. This indicates a strong conjugation of the latter with the heteroaromatic cations. Owing to the same electron-donor effect of the thienyl substituents, the protons of the methyl groups in the discussed cations are located by 0.4 ppm in the stronger field than in their phenyl-substituted analogs [11].

For compounds IV, V, VII, and XIII the preferable conformation of the thienyl substituents was established by means of Oberhauser's nuclear effect. Thus, when saturating the 3(5)-H protons of the pyriliium IV and thiopyriliium V cations, a positive response is observed on the band of the 3-H protons of the 2(6)- α -thienyl substituents, whereby the intensity of the signals increases by 9 and 3%, respectively. In the thiopyriliium VII and XIII cations saturation of the 3-H protons leads to an increase in the intensity of the signals of the 3-H protons of both thienyl substituents. For a substituent in position 2 of the

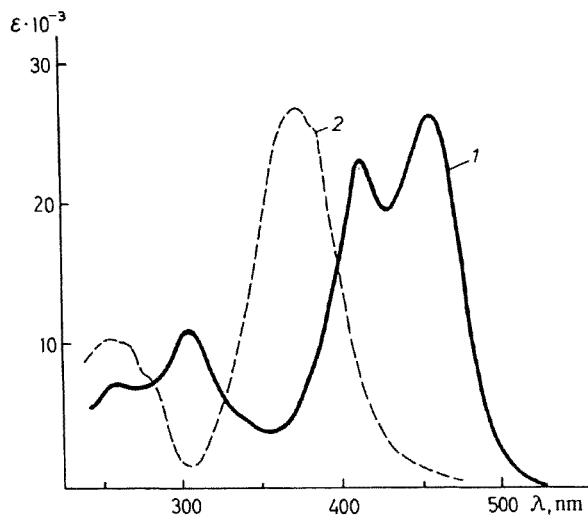


Fig. 1. Electron absorption spectra of 1) 2,4-di(2-thienyl)-6-methylthiopyrilium salt (VII) and 2) 2,4-diphenyl-6-methylthiopyrilium salt (VIIa) in methylene chloride.

TABLE 3. Parameters of the PMR Spectra of the Pyrilium and Thiopyrilium Salts

Compound	Chemical shifts, δ , ppm								
	2(6)-thienyl			4-thienyl			3-H (s)	5-H (s)	CH ₃ (s)
	3'-H (m*)	4'-H (m*)	5'-H (m*)	3'-H (m*)	4'-H (m*)	5'-H (m*)			
IV	8,17	7,44	8,24	—	—	—	8,04	8,04	2,72
V	8,10	7,42	8,11	—	—	—	8,38	8,38	2,81
VII	8,29	7,39	8,12	8,02	7,34	8,00	8,54 (br.)	8,37 (br.)	2,89
XIII*	8,19	7,41	8,14	7,95	7,31	7,93	8,61	—	—
XIV**	7,72	7,14	7,71	7,68	7,11	7,56	8,35	—	—

*Center of multiplet.

**In the PMR spectra of compounds XIII and XIV the signals of the methylene groups adjacent to the heterocycle have chemical shifts of 3.44 and 3.48 ppm (XIII), and 3.02 and 3.14 ppm (XIV); for the intermediate methylene groups the chemical shift is equal to 2.34 and 1.84 ppm, respectively.

thiopyrilium ring the intensity of these signals increases by 11 and 9%, for a substituent in position 4 by 9 and 5%, respectively. These data indicate that the sulfur atoms of the α -thienyl substituents in position 2(6) and the oxygen (sulfur) atoms of the heteroaromatic cations are present in the discussed compounds with symmetrical as well as asymmetrical structures in Z-conformation and the sulfur atoms of α -thienyl substituents in positions 2 and 4 in E,E,E,E-conformation with respect to each other (Fig. 2a, b). The relatively small values of the nuclear effect indicate that a certain torsion angle exists between the thienyl substituents and the heteroaromatic cations. The somewhat lower response intensity for the thiopyrilium V cation (3%) in comparison with the pyrilium IV cation (9%) can be related to a larger angle in the latter instance. This probably also explains the drop in the response intensity of the 3-H proton of the 4- α -thienyl substituent in the cation XIII (5%) in comparison with VII (9%), due to additional sterical hindrances, caused by annelated carbon ring.

In distinction from the compounds, containing the conjugated fragment $S \equiv C \equiv C \equiv S$, where the interaction of the uncombined sulfur atoms stabilizes the Z-conformer (compounds I, II), in the 2-thienyl-substituted thiopyrilium salts as in other

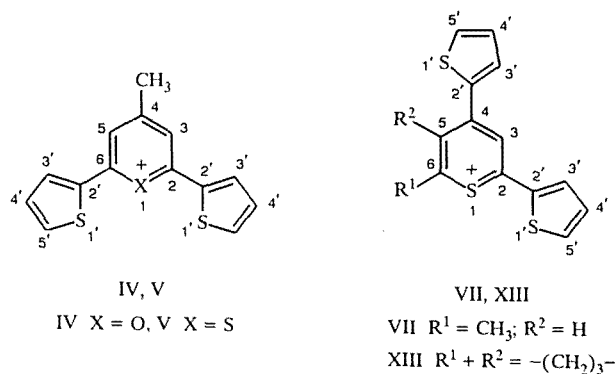


Fig. 2. Three-dimensional structure of the thienyl-substituted pyrylium and thiopyrylium cations (IV, V, VII, and XIII).

compounds containing the fragment $\text{S}=\text{C}=\text{C}=\text{S}$, this interaction must not necessarily lead to stabilization. In fact, calculation in the PPP approximation shows that, taking into account the interaction of the sulfur atoms through space, leads in the first instance to a decrease in the total π -energy of the system ($\delta E^\pi = 0.07 \text{ eV}$, at $\beta_{\text{SS}} = -0.3 \text{ eV}$), and on the other hand in the second instance to its increase ($\delta E^\pi = -0.042 \text{ eV}$). The geometry of all discussed compounds can also not be attributed to single steric causes. Thus, while the geometry of the cation XIII, calculated with account of the bond lengths and valence angles, shows that the 4-thienyl substituent in the established conformation suffers less from steric disturbances (the angle φ between the planes of the thiophene and thiopyrylium fragments is equal to 54.12°) than in the alternative conformation (angle $\varphi = 65.14^\circ$), the torsion angle between the thiopyrylium cycle and the 2-thienyl substituent for Z- and E-conformers is small and virtually the same (3.46 and 2.77°). Evidently, other factors, caused by solvation, have a determining effect on the three-dimensional structure of the discussed thienyl-substituted heterocyclic cations in solutions.

EXPERIMENTAL

The absorption spectra of compounds IV-VII, XIII-XV, and their phenyl-substituted analogs IVa-VIIa, XIIIa-XIVa were taken on a Specord M-40 spectrophotometer in methylene chloride, stabilized with 1% absolute ethanol. The experimental PMR data were obtained on a VARIAN VXR-300 spectrometer in D_3 acetonitrile at 25°C , compound XIV was measured on a Bruker WP-200 spectrometer in $\text{CF}_3\text{CO}_2\text{D}$ (with TMS as the internal standard). The purity of the preparations was checked by TLC on Silufol UV-254 sheets with acetonitrile as the eluent. The elemental analysis data for C, H, Cl, and S agreed with the calculated values.

1,5-Di(2-thienyl)-3-methylpentanedione-1,5 (III). A mixture of 37.8 g (0.3 mole) 2-acetylthiophene and 0.4 g (0.01 mole) sodium hydroxide, dissolved in 35 ml ethanol, heated to 70°C , is slowly treated dropwise with 4.4 g (0.1 mole) acetaldehyde. When the addition is completed, the mixture is stirred for 30 min, cooled, and treated with 0.1 N sulfuric acid to a weakly acidic reaction. The oily phase is separated, ethanol is stripped in vacuum from the aqueous ethanolic layer, and the residue extracted with ether ($3 \times 120 \text{ ml}$). The extracts and the oil are combined, washed with water to a neutral reaction, and dried with anhydrous magnesium sulfate. The ether is removed and the residue distilled in vacuum: bp $185\text{--}190^\circ\text{C}$ at 0.45 mm Hg .

2,6-Di(2-thienyl)-4-methylpyrylium Perchlorate (IV). A solution of 2.8 g (0.01 mole) of the diketone III in 25 ml acetic anhydride is treated with cooling to $0 \pm 5^\circ\text{C}$ dropwise with stirring in 5 min with a mixture of 5 ml acetic anhydride and 1.5 ml 70% perchloric acid, prepared at the same temperature. The reaction mixture is then diluted with ether and the precipitated salt filtered off (see Table 1).

2,6-Di(2-thienyl)-4-methylthiopyrylium Perchlorate (V). A stream of dry hydrogen sulfide is bubbled for 1 h through a solution of 7.5 g (27 moles) diketone III in 45 ml glacial acetic acid at $17\text{--}18^\circ\text{C}$ and then simultaneously a stream of hydrogen sulfide and hydrogen chloride for 3 h at $35\text{--}40^\circ\text{C}$. The reaction mixture is cooled to 15°C , treated with 40 ml 42% perchloric acid and allowed to stand overnight at 5°C . The salt is filtered off and washed consecutively with acetic acid, water, and ether.

2,4-Di(2-thienyl)-6-methylthiopyrilium Perchlorate (VII). A suspension of 0.25 g (0.7 mole) of salt VI in 8 ml acetonitrile is treated with 2 ml of a saturated solution of anhydrous sodium hydrosulfide in absolute ethanol; the mixture is stirred for 15 min. The suspension is filtered and 1 ml 70% perchloric acid added to the filtrate. The salt is precipitated with ether, filtered off, and washed with ether.

2,4-Di(2-thienyl)cyclopenta[1,2:b]thiopyrilium Perchlorate (XIII). Hydrogen sulfide is bubbled for 1 h through a solution of 2.7 g (8.9 moles) of the diketone XI, prepared in the same way as the 1,3-diphenyl-substituted analog, in 20 ml glacial acetic acid at 20°C, and then a mixture of hydrogen sulfide and hydrogen chloride for 1.5 h at 30-35°C. The reaction mixture is cooled to 15°C and the salt precipitated with 42% perchloric acid. The precipitate is filtered off and washed with water and ether.

2,4-Di(2-thienyl)-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (XIV) is prepared in the same way as compound XIII, starting from the diketone XII.

2-(2-Thienyl)-4-(2-bromothieryl-5)cyclopenta[1,2:b]thiopyrilium perchlorate (XV) is synthesized in the same way as compound XIII, by using 1-(2-thienyl)-3-(2-bromothieryl-5)-3-(2-oxocyclopentanyl)-propan-1-one, obtained in the same way as XI.

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