wise. The mixture was stirred under nitrogen to 25° for 20 hr. A yellowish solution was obtained, which on cooling to 0° afforded a colorless precipitate. Ether was added to complete the precipitation. The finely divided, colorless needles (1.71 g, 74%) were filtered, washed well with ether, and dried over phosphorus pentoxide (0.03 mm). Recrystallization from chloroform–ether gave the analytical sample: mp 174–175° (resolidification occurred at 185° followed by mp >300°); uv max (H_2O) 218, 254, and 277 mμ (shoulder) at pH 6; nmr (DMSO-d_6) δ 1.93 (s, 3, $C_{(6)}$-acetyl), 2.18 (s, 3), 2.23 (s, 3, $N_{(2)}$- and $N_{(7)}$-acetyls), 7.23 (m, 8, N-phenyl), and 7.55 (m, 8, N protons).

Anal. Calcd for $C_{17}H_{17}N_5O_6$: C, 52.71; H, 4.43; N, 18.08. Found: C, 53.06; H, 4.70; N, 18.55.

When the above reaction was conducted at −15° for 5 hr and followed by the addition of ether to the mixture, 1.14 g of a slightly yellowish solid was collected, mp >300°. This product was not identified, but its nmr spectrum indicated that it was a product of diacetylation of **4**.

Registry No.—**2** (R = Me, R′ = Et), 21823-24-5; **4** (R = H), 21823-25-6; **4** (R = Me), 21823-26-7; **4** (R = Et), 21823-79-0; **4** (R = Bu), 21823-80-3; **4** (R = Ph), 21823-81-4; **4** (R = D-ribosyl), 21823-82-5; **7** (R = H), 21823-83-6; **7** (R = Me), 21823-84-7; **7** (R = Et), 21823-85-8; **7** (R = Bu), 21823-86-9; **7** (R = Ph), 21850-65-7; **8**, 21823-87-0; **9**, 21823-88-1; **10**, 21823-89-2; diethyl N′-methylureidomalonate, 21823-90-5; diethyl N′-ethylureidomalonate, 21823-91-6; diethyl N′-butylureidomalonate, 21823-92-7; diethyl N′-2,3,5-tri-O-benzoyl-β-D-ribofuranosylureidomalonate, 21823-93-8.

Dithia Aromatic Systems. I. The Isomeric Thianaphthenothiapyrylium Perchlorates[1]

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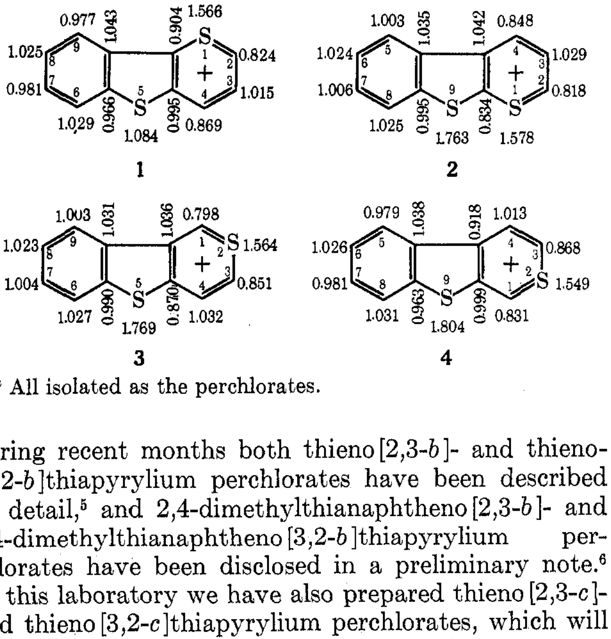
Syntheses of thianaphtheno[3,2-*b*]-, -[2,3-*b*]-, -[3,2-*c*]-, and -[2,3-*c*]thiapyrylium perchlorates (**1–4**, respectively), the prototypes of a class of 14-π-electron dithia aromatic systems, are described. These stable salts exhibit nmr spectra in which protons α and γ to the thionium center of the thiapyrylium rings experience the usually strong deshielding (δ 10.57–9.00 ppm) typical of positions of markedly low electron density. Hückel molecular orbital calculations, based on the assumption that both the thiapyrylium sulfur and the thiophenelike sulfur can be represented by the same set of parameters (h_S = 0.9 and k_{CS} = 0.6), yield predicted first electronic transition frequencies significantly at variance with the observed spectral frequencies.

In a recent article[3] we reported an excellent correlation of the longest wavelength electronic absorption frequencies ($\bar{\nu}$) of thiapyrylium ion and 11 of its polynuclear benzologs with the first transition energies (Δm) calculated by Hückel molecular orbital (HMO) theory. These calculations were based on a simple p-orbital model in which the coulomb integral for sulfur and the carbon–sulfur bond integral were expressed as $\alpha_S = \alpha + h_S\beta$ and $\beta_{CS} = k_{CS}\beta$, respectively.[4] Systematic variation of the parameters yielded an optimum set, h_S = 0.9 and k_{CS} = 0.6, which maximized the correlation coefficient to 0.992 and gave a corresponding regression line, $\bar{\nu} = 26.053\ \Delta m - 0.677$ (kcm^{-1}), having a standard deviation of 0.609 kcm^{-1}. Since such an empirically optimized set of parameters, as well as the spectral correlation, should have broader validity, we sought to extend their use to encompass new classes of dithia heterocycles in which each sulfur is essentially σ-bivalent and formally contributes two electrons to a potentially aromatic π system. The isomeric thienothiapyrylium cations and their various benzo derivatives (*e.g.*, **1–4**), which fulfill the foregoing structural requirements, were selected for initial attention, and we report here the syntheses of several perchlorate salts representative of this novel group, along with some properties appropriate for possible correlations with HMO indices (Chart I).

Chart I

Structures and Electron Densities of the Thianaphthenothiapyrylium Cations[a]



1 2

3 4

[a] All isolated as the perchlorates.

When this work was begun, no examples of the desired thienothiapyrylium salts were known; however, during recent months both thieno[2,3-*b*]- and thieno[3,2-*b*]thiapyrylium perchlorates have been described in detail,[5] and 2,4-dimethylthianaphtheno[2,3-*b*]- and 2,4-dimethylthianaphtheno[3,2-*b*]thiapyrylium perchlorates have been disclosed in a preliminary note.[6] In this laboratory we have also prepared thieno[2,3-*c*]- and thieno[3,2-*c*]thiapyrylium perchlorates, which will be described in a separate communication.[7]

Synthetic sequences leading to the parent thianaphthenothiapyrylium perchlorates having [3,2-*b*], [2,3-*b*], [3,2-*c*], and [2,3-*c*] modes of ring fusion (**1–4**, respectively) are illustrated in Schemes I–IV. In

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[1] Based on the Ph.D. dissertation of C. R. Hamel, Lehigh University, 1969. Supported in part by National Science Foundation Grant GP-8597.

[2] National Science Foundation Trainee, 1967–1969.

[3] T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 444 (1967).

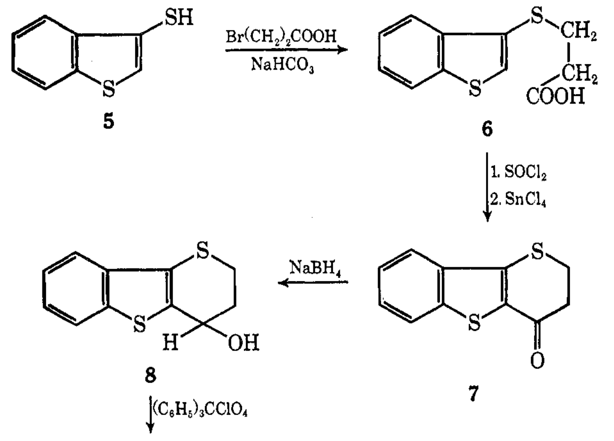
[4] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 5.

[5] I. Degani, R. Fochi, and G. Spunta, *Ann. Chim.* (Rome), **58**, 263 (1968).

[6] J. Fabian and H. Hartmann, *Tetrahedron Lett.*, 239 (1969).

[7] T. E. Young and C. R. Hamel, *J. Org. Chem.*, **35**, 821 (1970).

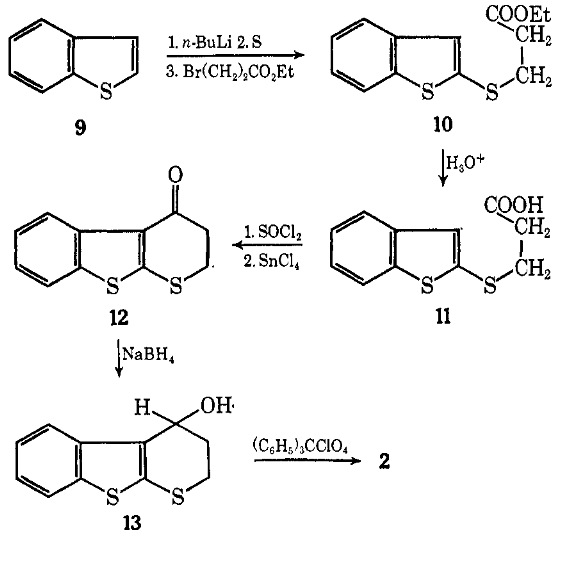
SCHEME I



the first sequence (Scheme I), 3-mercaptothianaphthene (**5**)[8] reacted with 3-bromopropionic acid in absolute ethanol in the presence of sodium bicarbonate to yield 72% of S-(3-thianaphthenyl)-3-mercaptopropionic acid (**6**). This acid was converted by thionyl chloride into the acid chloride, which was then cyclized *in situ* by the action of stannic chloride to give 3,4-dihydro-2H-thianaphtheno[3,2-*b*]thiapyran-4-one (**7**) in 97% overall yield. Reduction of the ketone **7** with sodium borohydride in refluxing isopropyl alcohol afforded essentially quantitative conversion into the carbinol **8**, which underwent dehydration and hydride abstraction with trityl perchlorate in acetic acid–nitromethane solution to give green-yellow crystals of thianaphtheno[3,2-*b*]thiapyrylium perchlorate (**1**) in 88% yield.

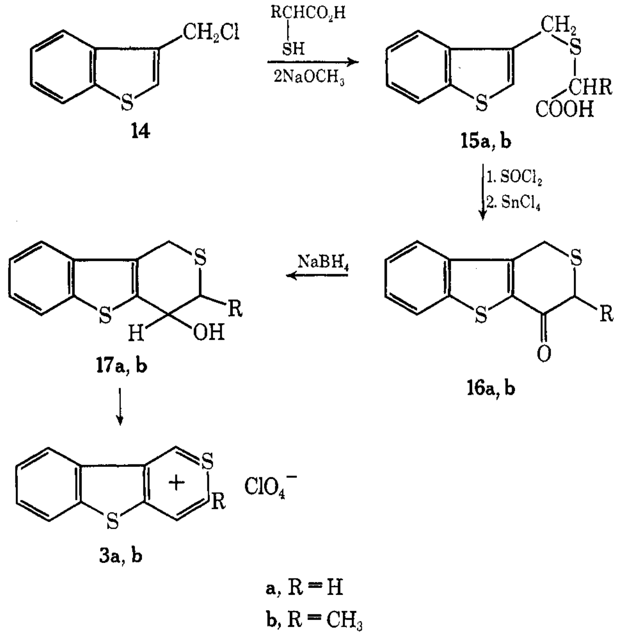
Preparation of thianaphtheno[2,3-*b*]thiapyrylium perchlorate (**2**) followed a similar pattern (Scheme II), except that the lithium salt of 2-mercaptothianaphthene, generated by reaction of 2-thianaphthenyllithium[9] with sulfur,[10] was directly alkylated *in situ* with ethyl 3-bromopropionate to give ethyl S-(2-thianaphthenyl)-3-mercaptopropionate (**10**). Acidic hydrolysis of this ester to the acid **11** was rather poor (25% yield), but alkaline hydrolysis gave none of the desired product. The subsequent steps (**11** → **12** → **13** → **2**) are self-explanatory and afforded the green thiapyrylium salt (**2**) in an overall yield (**11** → **2**) of 56%.

SCHEME II



Thianaphtheno[3,2-*c*]thiapyrylium perchlorate (**3a**) and its 3-methyl derivative (**3b**) (required to clarify a proton assignment in the nmr spectra) were both obtained by initial reaction of 3-chloromethylthianaphthene (**14**)[11] with the appropriate mercapto acid (mercaptoacetic and 2-mercaptopropionic acids, respectively) and 2 equiv of sodium methoxide in dry glyme, as shown in Scheme III. The resulting carboxylic acids (**15a**, **b**) weret hen cyclized anda romatized as before. It should be noted that the carbinol **17b** bearing a 3-methyl group was isolated and used as a mixture of *cis* and *trans* isomers, as shown by a broad melting range, 120–132°, and two clearly separated methyl absorptions centered at δ 1.32 and 1.48 ppm in the nmr spectrum.

SCHEME III



a, R = H
b, R = CH_3

Synthesis of the interestingly bronze-colored salt, thianaphtheno[2,3-*c*]thiapyrylium perchlorate (**4**), proceeded analogously starting from 2-bromomethylthianaphthene (**18**)[12] as shown in Scheme IV and requires no additional comment.

All of the intermediate thianaphthene derivatives in these reaction sequences were well-defined compounds whose structures were corroborated particularly well by their nmr spectra as detailed in the Experimental Section, and virtually all of them deteriorated badly on prolonged storage. In contrast, the final thianaphthenothiapyrylium salts (**1**–**4**) were quite stable and showed no significant changes after being kept for many months. These salts all exhibited nmr spectra (in deuteriotrifluoroacetic acid) in which pro-

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[8] D. E. Boswell, J. A. Brennan, P. S. Landis, and P. G. Rodewald, *J. Heterocycl. Chem.*, **5**, 69 (1968).

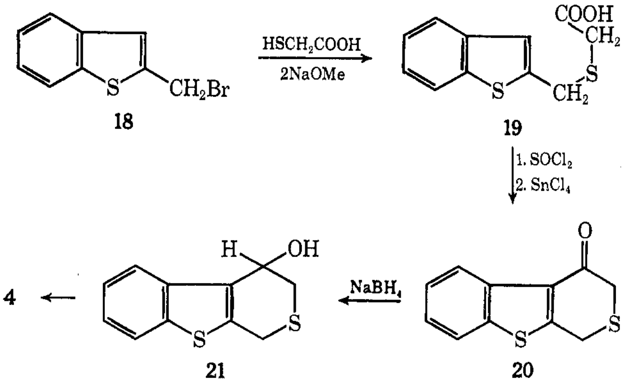
[9] D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, **74**, 664 (1952).

[10] R. B. Mitra, L. J. Pandya, and B. D. Tilak, *J. Sci. Ind. Res.*, **16B**, 345 (1957); *cf. Chem. Abstr.*, **52**, 5371*h* (1958).

[11] F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, **70**, 3768 (1948).

[12] Y. Matsuki and B. C. Li, *Nippon Kagaku Zasshi*, **87**, 186 (1966); *cf. Chem. Abstr.*, **65**, 1530*l* (1966).

SCHEME IV



tons α and γ to the thiapyrylium sulfur were strongly deshielded, appearing in the range δ 10.57–9.00 ppm, as previously observed in benzenoid thiapyrylium derivatives[13] and qualitatively expected on the basis of the low electron densities (summarized in Chart I) associated with these positions.

HMO calculations for cations **1**–**4** as well as the four isomeric thienothiapyrylium ions,[5,7] were carried out in the usual way[4,13] using the same parameters ($h_S = 0.9$ and $k_{CS} = 0.6$) previously defined by our thiapyrylium spectral correlation (*cf.* the introductory paragraph). Since the sulfur atoms in the thiophene ring and the thiapyrylium ring both formally contribute a dipositive, bicovalent sulfur core ($-\overset{2+}{\underset{\cdot\cdot}{S}}-$) to the σ framework, the same set of parameters was used for each type of sulfur atom, a practice commonly used in other HMO treatments of sulfur heterocycles.[14] The calculated transition energies, expressed as Δm (the change in coefficient of β between the lowest unoccupied and the highest occupied molecular orbital),[4,13] were then converted into transition frequencies, using the equation given in the first paragraph as derived from the earlier thiapyrylium correlation.[3] Comparison of the calculated results with the experimentally observed transition frequencies for the longest wavelength electronic absorption band (summarized in Table I) reveals a gross disagreement, with deviations averaging (2.1 kcm^{-1}) nearly three and one-half times the standard deviation for the earlier correlation.

These results are clearly unsatisfactory and suggest that, aside from the inherent deficiencies of HMO theory, the assumption of a single set of parameters to represent the two heteroelements, despite their diverse environments in these molecules, is particularly unwarranted.[15] While in principle it should be possible to determine experimentally a second set of parameters appropriate for the thiophenelike sulfur in these molecules, the total range of absorption frequencies observed for the dithia compounds presently available did not provide sufficient scope for confident correlation; hence this further extrapolation of simple HMO theory was considered to lack immediate justification and was deferred pending further experimental investigation of other dithia aromatic molecules.

TABLE I

COMPARISON OF THE OBSERVED AND CALCULATED FREQUENCIES OF THE LOWEST ENERGY ELECTRONIC TRANSITIONS OF THIANAPHTHENO- AND THIENOTHIAPYRYLIUM CATIONS

Cation	λ_{max}, mμ[a]	$\tilde{\nu}_{obsd}$, kcm^{-1}	Δm[b]	$\tilde{\nu}$,[b] kcm^{-1}
1	379	26.4	0.949	24.1
2	417	24.0	1.065	27.1
3	384	26.0	0.945	23.9
4	433	23.1	1.105	28.1
Thieno[3,2-*b*]-thiapyrylium	396[c]	25.3	1.025	26.0
Thieno[2,3-*b*]-thiapyrylium	361[d,e]	27.7	1.011	25.0
Thieno[3,2-*c*]-thiapyrylium	357[e]	28.0	1.020	25.9
Thieno[2,3-*c*]-thiapyrylium	381[e]	26.2	1.033	26.2

[a] Spectra were determined on the perchlorates in acetonitrile containing 1% of 85% perchloric acid, except as noted. [b] Calculated from the equation $\tilde{\nu} = 26.053\,\Delta m - 0.677$ (kcm^{-1}).[3] [c] In sulfuric acid solvent, as reported.[5] [d] The same maximum was observed in sulfuric acid[5] and in acetonitrile containing perchloric acid.[7] [e] Reference 7.

Experimental Section[16]

S-(3-Thianaphthenyl)-3-mercaptopropionic Acid (6).—To 9.00 g (0.054 mol) of 3-mercaptothianaphthene[8] in 250 ml of absolute ethanol was added 13.6 g (0.162 mol) of sodium bicarbonate and 8.30 g (0.054 mol) of 3-bromopropionic acid. The reaction mixture was refluxed for 6 hr, cooled, and evaporated to near dryness on a rotary evaporator. Water was added and the resulting emulsion was acidified (foaming) to litmus with concentrated hydrochloric acid. The resulting oil was extracted into benzene, which was dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Dilution with petroleum ether and scratching produced solids, which were collected on a filter and air dried to yield 9.20 g (72%) of S-(3-thianaphthenyl)-3-mercaptopropionic acid (**6**), mp 61–65°. Sublimation at 90° (0.12 mm) gave an analytical sample: mp 70–72°; ir (KBr) 3300–2300 (bonded OH), 1695 (acid C=O), and strong bands at 1438, 1420, 1400, 1335, 1256, 1198, 938, 838, 752, and 731 cm^{-1}; nmr ($CDCl_3$) δ 11.55 (s, 1, CO_2H), 8.08–7.70 (m, 2, ArH), 7.58–7.18 (m, 3, ArH), 3.22–2.92 (m, 2, SCH_2), and 2.72–2.42 ppm (m, 2, CH_2CO_2H).

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.61; H, 4.45; S, 26.99.

3,4-Dihydro-2H-thianaphtheno[3,2-*b*]thiapyran-4-one (7).—A stirred solution of 5.00 g (0.021 mol) of **6**, 1.5 ml (0.021 mol) of thionyl chloride, and 0.2 ml of pyridine in 50 ml of dry ether was refluxed for 15 min. Another 1.5 ml of thionyl chloride was added and reflux was continued for 15 min. The solvent was removed by distillation at atmospheric pressure and replaced by an equal volume of dry benzene. The solution was cooled to 5° and 12.3 ml (0.105 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 23° and the red slurry was then stirred for 3 hr. The slurry was poured onto 100 ml of concentrated hydrochloric acid and 100 g of ice and the flask was rinsed with benzene and concentrated hydrochloric acid. The water–benzene mixture was stirred for 1 hr and the layers were separated. The aqueous layer was extracted with three 100-ml portions of benzene and the benzene extracts were combined,

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(13) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 1558 (1967).

(14) R. Zharadnik and J. Koutecky, *Advan. Heterocycl. Chem.*, **5**, 1 (1965).

(15) *Cf.* M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, p 245.

(16) Melting points were determined in capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Box 68, Cambridge, Mass.) precalibrated with standards having known corrected melting points. The microanalyses were performed by the late Dr. V. B. Fish of Lehigh University and by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 257 instrument. Solid samples were run, at a concentration of *ca.* 1% by weight, in potassium bromide disks. Liquid samples were run neat between sodium chloride plates. Ultraviolet spectra were recorded on a Beckman Model DK-2A spectrophotometer in the solvents specified with the recorded spectra. The nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer in deuteriotrifluoroacetic acid for the salts and other specified solvents using tetramethylsilane (δ 0) as an internal standard and are presented in the order δ (multiplicity, number of protons, assignment). The petroleum ether used was the fraction boiling at 60–70° unless otherwise noted.

washed with 100 ml of 10% sodium carbonate, dried (MgSO$_4$), and evaporated on a rotary evaporator. The residual solids were slurried with petroleum ether, collected on a filter, and air dried to yield 4.25 g (97%) of 3,4-dihydro-2H-thianaphtheno[3,2-*b*]thiapyran-4-one (**7**), mp 121–124° with prior shrinking. Recrystallization from methanol–water (Norit) gave pure **7**: mp 123.5–125.0°; ir (KBr) 1630 (C=O), and strong bands at 1480, 1290, 1275, 1188, 931, 754, and 724 cm^{-1}; nmr (CDCl$_3$) δ 7.90–7.20 (m, 4, ArH), 3.38–3.27 (m, 2, SCH$_2$), and 3.08–2.80 ppm (m, 2, CH$_2$CO).

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.06; H, 3.87; S, 28.99.

3,4-Dihydro-2H-thianaphtheno[3,2-*b*]thiapyran-4-ol (8).—To a solution of 2.0 g (0.009 mol) of **7** dissolved in 500 ml of warm isopropyl alcohol was added 0.342 g (0.009 mol) of sodium borohydride. The reaction mixture was stirred magnetically at reflux overnight and then cooled, and the solvent was evaporated to near dryness on a rotary evaporator. After dilution with water, the mixture was extracted with three 100-ml portions of benzene. The combined benzene layers were washed with 50 ml of water, dried (MgSO$_4$), filtered, and evaporated to an oil on a rotary evaporator. On dilution with petroleum ether, the oil became a solid which was collected on a filter and air dried to yield 2.00 g (100%) of 3,4-dihydro-2H-thianaphtheno[3,2-*b*]thiapyran-4-ol (**8**), mp 104–105°. Sublimation at 92° (0.07 mm) gave an analytical sample: mp 104–105°; ir (KBr) 3440–3060 (bonded OH), 3050 (aromatic H), 2910 (methylene), and strong bands at 1430, 1257, 1155, 1050, 1020, 758, and 730 cm^{-1}; nmr (CDCl$_3$) δ 7.87–7.08 (m, 4, ArH), 4.87 (t, 1, J = 4.5 Hz, HOCH), 3.45–2.83 (m, 2, CH$_2$S), 2.68 (s, 1, CHOH, disappeared on exchange with D$_2$O), and 2.50–1.83 ppm (m, 2, CH$_2$CHOH).

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.69; H, 4.57; S, 28.85.

Thianaphtheno[3,2-*b*]thiapyrylium Perchlorate (1).—To 1.00 g (0.0045 mol) of **8** in 20 ml of refluxing glacial acetic acid was added 1.54 g (0.0045 mol) of trityl perchlorate[17] in 20 ml of nitromethane. Reflux was continued for 15 min and the reaction mixture was allowed to cool to room temperature. Evaporation on a rotary evaporator produced an oil, which solidified on dilution with ether. After 3 hr of refrigeration, the solid was collected on a filter and air dried to yield 1.20 g (88%) of thianaphtheno[3,2-*b*]thiapyrylium perchlorate (**1**). Four recrystallizations from glacial acetic acid, the first with Norit, gave the analytical sample: mp 199.0–200.5°; visible and uv max (1% perchloric acid in acetonitrile) 233 mμ (log ϵ 4.47), 270 (3.95), 297 (4.05), and 379 (4.12); nmr (CF$_3$CO$_2$D) δ 9.92 (d, 1, J = 8 Hz, H-2), 9.52 (d, 1, J = 8 Hz, H-4), 8.75 (t, 1, J = 8 Hz, H-3), and 8.75–8.60 (m, 1) and 8.40–7.70 ppm (m, 3, H-6–9) ppm.

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.89; H, 2.52; S, 20.95.

Ethyl S-(2-Thianaphthenyl)-3-mercaptopropionate (10).—To 3.47 g (0.50 g-atom) of lithium metal stirred under a helium atmosphere in 250 ml of dry ether (distilled from lithium aluminum hydride) was added, at −10 to 0°, 27.4 g (0.20 mol) of *n*-butyl bromide over a 1-hr period. After the mixture was stirred at 0° for 1 hr, the remaining lithium wire was removed with tweezers and 40.26 g (0.30 mol) of thianaphthene (**9**) in 50 ml of dry ether was added at 0° over a 1-hr period. The reaction mixture was stirred at 0° for 1 hr and 6.4 g (0.20 g-atom) of sulfur was added. The temperature rose to 26°. The mixture was refluxed for 3 hr, and then 36.2 g (0.20 mol) of ethyl 3-bromopropionate was added and refluxing was continued overnight. The suspension was cooled and 100 ml of water was added dropwise during a 1-hr period, so that the vigorous reaction was kept under control. The layers were separated and the aqueous layers were extracted with two more 100-ml portions of ether. The combined ether extracts were dried (MgSO$_4$), filtered, and evaporated to leave an oil, which was distilled to give 30.8 g (58%) of ethyl S-(2-thianaphthenyl)-3-mercaptopropionate (**10**), bp 148–154° (0.12 mm). Redistillation gave an analytical sample: ir (neat) 3050 (weak, aromatic H), 2950 and 2920 (strong) and 2865 (medium) (methyl and methylene), 1730 (ester C=O), and other strong bands at 1452, 1420, 1370, 1345, 1278, 1242, 1178, 747, and 725 cm^{-1}; nmr (C$_6$D$_6$) δ 7.70–7.05 (m, 5, ArH), 4.00 (q, 2, J = 7.5 Hz, OCH$_2$CH$_3$), 3.05 (t, 2, J = 7 Hz, SCH$_2$), 2.53 (t, 2, J = 7 Hz, SCH$_2$CH$_2$), and 1.02 ppm (t, 3, J = 7.5 Hz, CH$_2$CH$_3$).

Anal. Calcd for $C_{13}H_{14}O_2S_2$: C, 58.61; H, 5.30; S, 24.08. Found: C, 58.71; H, 5.21; S, 24.20.

S-(2-Thianaphthenyl)-3-mercaptopropionic Acid (11).—A mixture of 12.0 g (0.045 mol) of **10** and 1.0 l. of 50% hydrochloric acid was stirred at reflux overnight. Upon cooling, the oil solidified and was collected by filtration. The gummy solid was taken up in 400 ml of benzene, which was washed with three 75-ml portions of water, dried (MgSO$_4$), filtered, treated with Norite, filtered, and the benzene removed on a rotary evaporator. Dilution of the residual oil with petroleum ether produced a solid which was collected on a filter and dried to give 6.0 g, mp 60–90°. Recrystallization from cyclohexane gave 2.7 g (25%) of S-(2-thianaphthenyl)-3-mercaptopropionic acid (**11**), mp 109–114°. Sublimation at 166° (0.05 mm) gave an analytical sample: mp 115.5–118.0°; ir (KBr) 3300–2500 (bonded OH), 1684 (acid C=O), and strong peaks at 1418, 1392, 1233, 923, 918, 813, 749, 740, and 722 cm^{-1}; nmr (CDCl$_3$) δ 11.37 (s, 1, CO$_2$H), 7.78 (m, 2, ArH), 7.50–7.25 (m, 3, ArH), 3.30–3.03 (m, 2, SCH$_2$CH$_2$), and 2.90–2.55 ppm (m, 2, SCH$_2$CH$_2$).

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.53; H, 4.31; S, 26.68.

3,4-Dihydro-2H-thianaphtheno[2,3-*b*]thiapyran-4-one (12).—Reaction of 3.00 g (0.012 mol) of **11** with 1.8 ml (0.025 mol) of thionyl chloride and 0.5 ml of pyridine in 30 ml of ether afforded the acid chloride, which was cyclized by 7.0 ml (0.06 mol) of stannic chloride in 30 ml of benzene following the general procedure for the preparation of **7**. Recrystallization of the product from benzene–petroleum ether (Norit) gave 2.2 g (79%) of 3,4-dihydro-2H-thianaphtheno[2,3-*b*]thiapyran-4-one (**12**), mp 122–125°. Sublimation at 120° (0.15 mm) followed by two recrystallizations from ethanol–water (the last with Norit treatment) gave an analytical sample: mp 123.5–125.0°; ir (KBr) 1640 (C=O) and strong bands at 1445, 1402, 1358, 1162, 740, and 736 cm^{-1}; nmr (CCl$_4$) δ 8.67–8.47 (m, 1, ArH), 7.75–7.20 (m, 3, ArH), 3.58–3.27 (m, 2, SCH$_2$), and 3.03–2.72 ppm (m, 2, SCH$_2$CH$_2$).

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.16; H, 3.69; S, 29.05.

3,4-Dihydro-2H-thianaphtheno[2,3-*b*]thiapyran-4-ol (13).—This compound was obtained by reduction of 1.90 g (0.0086 mol) of **12** with 0.325 g (0.0086 mol) of sodium borohydride in 150 ml of isopropyl alcohol (*cf.* details for the preparation of **8**) to give 1.7 g (83%) of 3,4-dihydro-2H-thianaphtheno[2,3-*b*]thiapyran-4-ol (**13**), mp 115.0–116.5°. Sublimation at 103° (0.12 mm) gave an analytical sample: mp 115.0–118.0°; ir (KBr) 3400–3000 (bonded OH), 2880 (weak, methylene), and strong bands at 1400, 1260, 1240, 1018, 905, and 728 cm^{-1}; nmr (CDCl$_3$) δ 7.82–7.55 (m, 2, ArH), 7.48–7.08 (m, 2, ArH), 5.05 (m, 1, HOCH), and 3.75–1.72 ppm (m, 5, HOCHCH$_2$CH$_2$).

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.62; H, 4.61; S, 28.97.

Thianaphtheno[2,3-*b*]thiapyrylium Perchlorate (2).—To a magnetically stirred, refluxing solution of 0.60 g (0.0027 mol) of **13** in 16 ml of glacial acetic acid was added 0.93 g (0.0027 mol) of trityl perchlorate in 16 ml of nitromethane. Reflux was continued for 15 min and the reaction mixture was allowed to cool ambiently for 4 hr with stirring. The solvent was removed on a rotary evaporator and the resulting oil solidified on dilution to 400 ml with ether. After overnight refrigeration, the golden yellow product was collected on a filter and air dried to give 0.70 g (86%), mp 214–216° dec. Recrystallization from boiling glacial acetic acid gave an analytical sample: mp 215–218° dec; visible and uv max (1% perchloric acid in acetonitrile) 243 mμ (log ϵ 4.49), 268 (4.38), 302 (4.18), 361 (3.64), and 423 (3.74); nmr (CF$_3$CO$_2$D) δ 9.93–9.60 (m, 2, H-2 and H-4) and 9.13–7.75 ppm (m, 5, H-2, H-5–8).

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.76; H, 2.59; S, 21.08.

S-(3-Thianaphthenylmethyl)mercaptoacetic Acid (15a).—To 14.1 g (0.153 mol) of mercaptoacetic acid dissolved in 100 ml of dry glyme (distilled from lithium aluminum hydride) was added, with stirring and ice-bath cooling, 16.5 g (0.306 mol) of sodium methoxide. The resulting thick white precipitate was broken up and 28.0 g (0.153 mol) of 3-chloromethylthianaphthene (**14**)[11] was rinsed into the flask with 100 ml of dry glyme. The mixture was stirred at reflux overnight and then cooled. The thick white precipitate was dissolved by 100 ml of water, and 50 ml of concentrated hydrochloric acid was added. The two-phase system was evaporated to an oily solid on a rotary evaporator. The

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[17] K. A. Hoffman and M. Kirmreuther, *Ber.*, **42**, 4856 (1909).

residue was extracted into 500 ml of benzene, which was washed with two 100-ml portions of water, dried ($MgSO_4$), filtered, and evaporated to leave an oil which, after dilution with petroleum ether, scratching, and overnight refrigeration, gave 19.6 g of a gummy semisolid. Recrystallization from cyclohexane gave 11.5 g (31.6%) of crude **15a**, mp 91–103°. Sublimation at 100° (0.10 mm) gave an analytical sample: mp 103–105.5°; ir (KBr) 3630–2500 (bonded OH), 1690 (acid C=O), and strong bands at 1420, 1290, 1128, 930, 760, and 730 cm^{-1}; nmr ($CDCl_3$) δ 11.80 (s, 1, CO_2H), 8.00–7.67 (m, 2, ArH), 7.53–7.20 (m, 3, ArH), 4.10 (s, 2, CH_2S), and 3.07 ppm (s, 2, SCH_2) ppm.

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.32; H, 4.47; S, 27.01.

S-(3-Thianaphthenylmethyl)thiolactic Acid (15b).—In a similar manner 16.25 g (0.153 mol) of thiolactic acid and 28.0 g (0.153 mol) of 3-chloromethylthianaphthene afforded 33.8 g of crude product, mp 75–90°. Recrystallization from cyclohexane (Norit) gave 19.8 g (51%) of **15b**, mp 93.5–96.0°. Sublimation at 90° (0.05 mm) gave an analytical sample: mp 94.0–97.0°; ir (KBr) 3300–2500 (bonded OH), 1680 (acid C=O), and strong bands at 1445, 1420, 1281, 1231, 1059, 925, 758, and 730 cm^{-1}; nmr ($CDCl_3$) δ 12.15 (s, 1, CO_2H), 8.13–7.70 (m, 2, ArH), 7.50–7.18 (m, 2, ArH), 4.33 (d, 1, J = 14 Hz, CH_2S), 4.05 (d, 1, J = 14 Hz, CH_2S), 3.40 (q, 1, J = 7 Hz, $SCHCH_3$), and 1.43 ppm (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{12}H_{12}O_2S_2$: C, 57.11; H, 4.79; S, 25.41. Found: C, 57.33; H, 4.78; S, 25.40.

3,4-Dihydro-1H-thianaphtheno[3,2-*c*]thiapyran-4-one (16a).—This compound was prepared by cyclization of 10.5 g (0.044 mol) of **15a** *via* the acid chloride following the procedure described for **7**. The crude product weighed 6.9 g (71% yield), mp 153–155°. Recrystallization from carbon tetrachloride–benzene (Norit) gave 4.2 g (43%) of ketone, mp 158–161°. Sublimation at 132° (0.18 mm) and further recrystallization from methanol–water gave pure **16a**: mp 159–160°; ir (KBr) 1640 (C=O) and strong bands at 1355, 1280, 1255, 989, and 760 cm^{-1}; nmr ($CDCl_3$ and CCl_4) δ 8.00–7.25 (m, 4, ArH), 4.02 (s, 2, CH_2S), and 3.60 ppm (s, 2, SCH_2CO).

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.25; H, 3.49; S, 28.93.

3-Methyl-3,4-dihydro-1H-thianaphtheno[3,2-*c*]thiapyran-4-one (16b).—This compound was similarly obtained from 10.09 g (0.04 mol) of **15b**, yield [7.4 g (79%), mp 97–103°]. Successive recrystallization from carbon tetrachloride (Norit), sublimation at 105° (0.10 mm), and final recrystallization from methanol gave pure **16b**: mp 105.0–106.5°; ir (KBr) 2990, 2920, 2880 (weak) (methyl and methylene), 1650 (strong, C=O), and strong bands at 1525, 1425, 1360, 1300, 1242, 912, 882, 753, and 725 cm^{-1}; nmr ($CDCl_3$) δ 7.98–7.28 (m, 4, ArH), 4.37–3.60 (m, 3, CH_2-SCH), and 1.57 ppm (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.50; H, 4.30; S, 27.37. Found: C, 61.30; H, 4.27; S, 27.09.

3,4-Dihydro-1H-thianaphtheno[3,2-*c*]thiapyran-4-ol (17a).—Reduction of 2.20 g (0.01 mol) of **16a** with 0.38 g (0.01 mol) of sodium borohydride in 200 ml of isopropyl alcohol (as detailed for reduction of **7** to **8**) gave 1.90 g (86%) of **17a**, mp 128–132°. Sublimation at 110° (0.20 mm) followed by recrystallization from methanol–water (Norit) gave an analytical sample: mp 139.0–140.5°; ir (KBr) 3500–3140 (bonded OH), 3040 (weak, aromatic H), 2880 (medium, methylene), and strong bands at 1430, 1408, 1378, 1260, 1188, 1150, 1060, 1040, 755, and 728 cm^{-1}; nmr ($CDCl_3$) δ 7.95–7.27 (m, 4, ArH), 5.00 (m, 1, HOCH), 3.80 (s, 2, CH_2S), 3.12 (m, 2, SCH_2CHOH), and 2.75 ppm (m, 1, OH, exchanges with D_2O).

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.62; H, 4.57; S, 28.83.

3-Methyl-3,4-dihydro-1H-thianaphtheno[3,2-*c*]thiapyran-4-ol (17b).—In a similar manner 2.00 g (0.0086 mol) of **16b** was reduced with an equimolar amount of sodium borohydride in 250 ml of isopropyl alcohol to yield 1.90 g of crude **17b**. Recrystallization from methanol–petroleum ether gave an analytical sample, mp 120–132°, which appeared to be a mixture of *cis* and *trans* isomers: ir (KBr) 3500–3100 (bonded OH), 3040 (weak, aromatic H), 2850 (weak, methyl and methylene), and strong bands at 1430, 1370, 1015, 750, and 728 cm^{-1}; nmr (C_6D_6 and $CDCl_3$) δ 7.98–7.15 (m, 4, ArH), 4.67 (d, 1, J = 2 Hz, HCOH), 4.42–2.90 (m, 3, CH_2SCHCH_3), 2.77 (s, 1, OH), exchanges with D_2O), and 1.48 and 1.32 ppm (both m, 3, CH_3).

Anal. Calcd for $C_{12}H_{12}OS_2$: C, 60.98; H, 5.12; S, 27.13. Found: C, 61.09; H, 5.08; S, 26.96.

Thianaphtheno[3,2-*c*]thiapyrylium Perchlorate (3a).—A refluxing solution of 1.00 g (0.0045 mol) of **17a** in 16 ml of acetic acid was allowed to react with a solution of 1.54 g (0.0045 mol) of trityl perchlorate in 16 ml of nitromethane, and then treated as in the preparation of **2**. The crude yellow solids (1.45 g) were recrystallized from glacial acetic acid (Norite) to give 0.87 g (95%) of pure **3a** as yellow needles: mp 178–180°; visible and uv max (1% perchloric acid in acetonitrile) 233 mμ (sh, log ϵ 4.13), 237 (sh, 4.18), 254 (4.56), 265 (4.32), 283 (4.25), 314 (3.81), and 384 (3.80); nmr (CF_3CO_2D) δ 10.57 (m, 1, H-1), 9.60–9.15 (m, 2, H-3 and H-4), 8.73–8.47 (m, 1, ArH), and 8.27–7.67 ppm (m, 3, ArH).

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.78; H, 2.63; S, 21.28.

3-Methylthianaphtheno[3,2-*c*]thiapyrylium Perchlorate (3b).—This compound was similarly prepared from 1.00 g (0.0042 mol) of **17b**. The crude product, yield 1.20 g (90%), mp 204–206°, was recrystallized from glacial acetic acid to give pure material: mp 211–212° dec; visible and uv max (1% perchloric acid in acetonitrile) 240.5 mμ (log ϵ 4.28), 258 (4.40), 265 (sh, 4.39), 283 (4.28), 312 (3.91), and 385 (3.81); nmr (CF_3CO_2D) δ 10.33 (s, 1, H-1), 9.00 (s, 1, H-4), 8.50 (m, 1, Ar-H), 8.20–7.70 (m, 3, Ar-H), and 3.17 (s, 3, CH_3) ppm.

Anal. Calcd for $C_{12}H_9ClO_4S_2$: C, 45.50; H, 2.86; S, 20.24. Found: C, 45.68; H, 3.09; S, 20.26.

S-(2-Thianaphthenylmethyl)mercaptoacetic Acid (19).—This compound was obtained from 4.80 g (0.052 mol) of mercaptoacetic acid, 5.62 g (0.104 mol) of sodium methoxide, and 11.8 g (0.052 mol) of 2-bromomethylthianaphthene[12] in 300 ml of dry glyme in the manner described for the preparation of **15a**. The yield was 6.00 g (48%) of crude product, mp 60–70°. Recrystallization from benzene–cyclohexane followed by sublimation at 110° (0.07 mm) afforded pure **19**: mp 95–96.5° (with prior softening); ir (neat) 3400–2500 (bonded OH), 1705 (acid C=O), and strong bands at 1432, 1295, 748, 728, and 679 cm^{-1}; nmr ($CDCl_3$) δ 11.35 (s, 1, CO_2H), 7.87–7.50 (m, 2, ArH), 7.47–7.12 (m, 3, ArH), 4.12 (s, 2, CH_2S), and 3.17 ppm (s, 2, SCH_2).

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.66; H, 3.98; S, 26.67.

3,4-Dihydro-1H-thianaphtheno[2,3-*c*]thiapyran-4-one (20).—A solution of 2.00 g (0.0084 mol) of **19**, 0.6 ml (0.0084 mol) of thionyl chloride, and 0.2 ml of pyridine in 150 ml of dry ether was stirred at reflux for 15 min; another 0.6 ml of thionyl chloride was added and reflux was continued for 15 min. The ether was removed by distillation and replaced with 150 ml of benzene. The mixture was cooled to 6° and 4.9 ml (0.042 mol) of anhydrous stannic chloride was added in one portion. The resulting slurry was stirred at 25° for 3 hr and then poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid, and the flask was rinsed with concentrated hydrochloric acid and benzene. The water–benzene mixture was stirred for 1 hr and a black tar was removed by filtration. The layers were separated and the aqueous layer was extracted with two 100-ml portions of benzene. The combined benzene layers were washed with 100 ml of water and 100 ml of 10% sodium carbonate solution with a filtration before each separation. The benzene solution was dried ($MgSO_4$), filtered, and evaporated on a rotary evaporator to a maroon solid, which was slurried with petroleum ether. The solids were collected on a filter, washed with petroleum ether, and air dried to give 0.75 g (41%) of **20**, mp 110–120°. Recrystallization from carbon tetrachloride–methanol, sublimation at 110° (0.18 mm), and two recrystallizations from methanol–water, the second with a Norit treatment, gave an analytical sample: mp 120.0–121.5°; ir (KBr) 3060 (weak, aromatic H), 2970 and 2890 (weak, methylene), 1650 (C=O), and strong bands at 1455, 1428, 1365, 1200, 760, and 724 cm^{-1}; nmr ($CDCl_3$) δ 8.60 (m, 1, ArH), 7.70 (m, 1, ArH), 7.47–7.18 (m, 2, ArH), 3.92 (d, 2, J = 1.5 Hz, CH_2S), and 3.44 ppm (d, 2, J = 1.5 Hz, SCH_2CO).

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.15; H, 3.70; S, 29.17.

3,4-Dihydro-1H-thianaphtheno[2,3-*c*]thiapyran-4-ol (21).—A 1.75-g (0.008 mol) sample of **20** was reduced with 0.30 g (0.008 mol) of sodium borohydride in 250 ml of isopropyl alcohol and the product was isolated as described for the preparation of **8**. The crude carbinol, yield 1.30 g (74%), was recrystallized from methanol–water (Norit) and then sublimed at 95° (0.10 mm) to give pure **21**: mp 89–91°; ir (KBr) 3500–3100 (bonded OH), 2875 (medium, methylene), and strong bands at 1435, 1411, 1190, 1045, 1018, 740, and 720 cm^{-1}; nmr ($CDCl_3$) δ 8.00–7.55 (m, 2, ArH), 7.48–7.22 (m, 2, ArH), 5.00 (m, 1, HOC**H**), 4.00 (d, 2, J = 17 Hz, CH_2S), 3.50 (d, 2, J = 17 Hz, CH_2S), 3.03 (m, 2, $SC\mathbf{H}_2CHOH$), and 2.77 ppm (m, 1, CHO**H**, disappeared on exchange with D_2O).

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.35; H, 4.71; S, 28.58.

Thianaphtheno[2,3-*c*]thiapyrylium Perchlorate (4).—A refluxing solution of 0.88 g (0.004 mol) of **21** in 15 ml of acetic acid was treated with a solution of 1.37 g (0.004 mol) of trityl perchlorate in 15 ml of nitromethane, and the product was isolated as in the preparation of **1**. The crude product, yield 1.10 g (91%), was recrystallized several times from glacial acetic acid to give the pure thiapyrylium salt (**4**): mp 207.0–208.0°; visible and uv max (1% perchloric acid in acetonitrile) 292 mμ (log ε 4.24), 354 (4.18), and 433 (3.52); nmr (CF_3CO_2D) δ 10.40 (m, 1, J = 2 Hz, H-1), 9.55 (2 s, 2, H-3 and H-4), 8.77 (m, 1), and 8.32–7.68 ppm (m, 3, H-6–9).

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.82; H, 2.37; S, 21.10.

Registry No.—**1,** 22482-76-4; **2,** 22482-77-5; **3a,** 22482-78-6; **3b,** 22482-79-7; **4,** 22482-80-0; **6,** 22316-07-0; **7,** 22314-71-2; **8,** 22294-31-1; **10,** 22482-83-3; **11,** 22482-84-4; **12,** 22482-85-5; **13,** 22482-86-6; **15a,** 22482-87-7; **15b,** 22482-88-8; **16a,** 22482-89-9; **16b,** 22482-90-2; **17a,** 22482-91-3; *cis*-**17b,** 22528-36-5; *trans*-**17b,** 22486-17-5; **19,** 22482-92-4; **20,** 22482-93-5; **21,** 22482-94-6; thieno[3,2-*b*]thiapyrylium perchlorate, 22482-95-7; thieno[2,3-*b*]thiapyrylium perchlorate, 22482-96-8; thieno[3,2-*c*]thiapyrylium perchlorate, 22431-16-9; thieno[2,3-*c*]thiapyrylium perchlorate, 22482-98-0.

Notes

Dithia Aromatic Systems. II. Thieno[3,2-*c*]- and Thieno[2,3-*c*]thiapyrylium Perchlorates[1]

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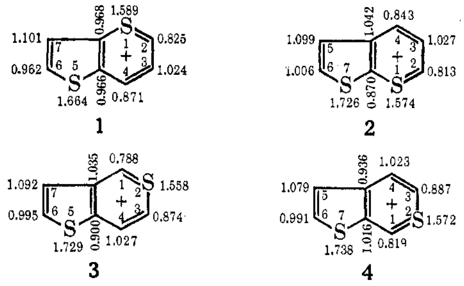
For reasons cited more explicitly in a companion article,[3] we became interested in the isomeric thienothiapyrylium cations (**1**–**4**) as representatives of a new class of dithia aromatic systems having 10 π electrons. While this work was in progress, the first examples of this class of compounds, thieno[3,2-*b*]- and thieno[2,3-*b*]thiapyrylium perchlorates (**1** and **2**, respectively), were reported by Degani and coworkers,[4] who made a quantitative study of the hydrolysis equilibria ($pK_R{}^+$) of these two cations and interpreted their nmr spectra in the light of electron densities calculated from Hückel molecular orbital (HMO) theory. More recently, syntheses of the 2,4-dimethyl derivatives of **1** and **2** have also been revealed in a preliminary communication, along with charge densities and bond orders for all four cations (**1**–**4**) and electronic transition frequencies predicted (for ions **1**–**3**) from semiempirical SCF calculations.[5] We have already presented syntheses of thianaphtheno[3,2-*c*]- and -[2,3-*c*]thiapyrylium perchlorates[3] and now wish to complete this picture with a description of some salts containing the isomeric thieno[*c*]thiapyrylium nuclei (**3** and **4**), which were readily obtained as shown in the accompanying formulas (**5** → **6** → **3** and **7** → **8** → **4**).

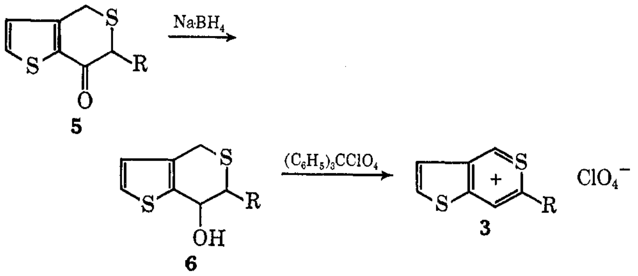
CHART I

STRUCTURES AND ELECTRON DENSITIES OF THE THIENOTHIAPYRYLIUM CATIONS[a]



[a] All isolated as the perchlorates.

Reduction of 3-methyl-3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-one (**5b**)[6] with sodium borohydride in refluxing isopropyl alcohol gave the corresponding carbinol (**6b**) (84%), which had a broad melting range (64–75°) and was clearly a mixture of *cis* and *trans* isomers, as shown by the appearance of the methyl resonance as two well-defined doublets centered at δ 1.23 and 1.12 ppm (J = 8.0 Hz) in the nmr spectrum (in deuteriobenzene). On reaction with trityl perchlorate in refluxing acetic acid–nitromethane solution, this carbinol underwent both dehydration and hydride abstraction to give 3-methylthieno[3,2-*c*]thiapyrylium perchlorate (**3b**), a blue-green salt, in 11% yield.



a, R = H
b, R = Me

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[1] Based on the Ph.D. Dissertation of C. R. Hamel, Lehigh University, 1969. Supported in part by National Science Foundation Grant GP-8597.

[2] National Science Foundation Trainee, 1967–1969.

[3] Part I: T. E. Young and C. R. Hamel, *J. Org. Chem.*, **35**, 816 (1970).

[4] I. Degani, R. Fochi, and G. Spunta, *Ann. Chim.* (Rome), **58**, 263 (1968).

[5] J. Fabian and H. Hartmann, *Tetrahedron Lett.*, 239 (1969).

[6] P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, 2597 (1967).