Nuclear Magnetic Resonance Spectra of Some Polynuclear Thiapyrylium Cations[1]

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Analysis of the nmr spectra of 11 polynuclear thiapyrylium perchlorates (**1**–**11**) in deuteriotrifluoroacetic acid shows that the most strongly deshielded protons (δ 10.69–9.42) are associated with the positions of lowest electron density (q_r = 0.722–0.869) α and γ to the thionium center of the thiapyrylium rings. Protons β to the sulfur, unless additionally deshielded by angular benzo rings, yield resonance bands on the low-field edge of the normal aromatic region. Despite their strong deshielding (δ_2 10.50 and δ_4 9.70), the 2 and 4 protons of 1-thianaphthalenium ion undergo no apparent deuterium exchange in CF$_3$COOD–D$_2$O at room temperature. 2-Thia- and 3-thiaphenanthrenium perchlorates (**6** and **7**, respectively), each of which possesses two different hydrogens α to the sulfur atom, exhibit pronounced α,α′ coupling ($J_{\alpha,\alpha'}$ = 3.0–3.4 cps) suggesting significant through conjugation *via* the thionium sulfur. Syntheses of 2- and 4-methyl-1-thianaphthalenium (**2** and **3**) and of 6,7,8,9-tetrahydrobenzo[*g*]-1-thianaphthalenium (**4**) perchlorates, required as model compounds for spectral assignments, are also described.

As part of an earlier investigation of indolothiapyrylium compounds we reported[2] that the nmr spectrum of 1-thianaphthalenium perchlorate (**1**)[3] in dimethyl-d_6 sulfoxide exhibited an unusually low-field absorption (δ 12.12)[4] tentatively associated with the structure CH=S$^+$, in which the large downfield shift from the normal aromatic region was attributed to the high electronegativity of the adjacent thionium center. This strongly deshielded proton showed an anomalous lack of splitting, and indeed nmr studies with additional analogs of **1** in dimethyl-d_6 sulfoxide revealed further irregularities suggesting possible reaction of the solvent with these cations. Subsequent investigation showed that the use of deuteriotrifluoroacetic acid as solvent leads to well-defined and interpretable nmr spectra of members of this series, and we therefore wish to report more definitive studies of **1**, of its three alkylated derivatives (**2**, **3**, and **4**), and of the series of polynuclear benzologs (**5**–**11**) (Chart I), which clearly reflect the low electron densities characteristic of the thiapyrylium ring.

The electron densities (q_r) summarized in Chart I were obtained in the usual way from HMO calculations based on a set of sulfur coulomb and carbon–sulfur bond integral parameters (h_S = 0.9 and k_{CS} = 0.6, respectively) which gave an optimum correlation of the lowest HMO transition energies with the L$_b$ band frequencies of 12 thiapyrylium cations, as described in more detail in another article.[5] No special calculations were performed for ions **2**–**4** since another arbitrary parameter would have been required and since the alkyl substituents were expected to introduce only a small perturbation of the parent system (**1**).

The perchlorate salts of 1-thianaphthalenium (**1**),[3] 1-, 2-, 3-, and 4-thiaphenanthrenium (**5**, **6**, **7**, and **8**, respectively),[5,6] thioxanthylium (**9**),[7] 7-thiabenz[*a*]anthracenium (**10**),[5] and 12-thiabenz[*a*]anthracenium (**11**)[5] ions were prepared as previously described, while the perchlorates of **2**, **3**, and **4** were synthesized as illustrated in Scheme I.

2-Methylthiochroman-4-one (**12**)[8] on reduction with lithium aluminum hydride gave an excellent yield of the corresponding carbinol (**13**), which readily underwent dehydration and hydride abstraction with dicyanodichloroquinone and perchloric acid to form 2-methyl-1-thianaphthalenium perchlorate (**2**) in 31% yield. The known 4-methylthiochroman-4-ol (**14**)[9] reacted similarly with *o*-chloranil and perchloric acid to give a 78% yield of 4-methyl-1-thianaphthalenium perchlorate (**3**). As discussed below, the nmr spectra of both **2** and **3** were consistent with the assigned structures. Their ultraviolet–visible spectra in the range 220–420 mμ were also very similar to that of the green-yellow parent compound (**1**) thus corroborating their electronic structures (*cf.* the Experimental Section for pertinent data). However, both **2** and **3** were a deep blue color and exhibited additional, unexpected, visible maxima at 616 mμ, not shown by the parent compound. 6,7,8,9-Tetrahydrobenzo[*g*]thiochroman-4-one (**15**)[10,11] was also reduced with lithium aluminum hydride to the corresponding carbinol (**16**), which reacted directly with trityl perchlorate in acetic acid–nitromethane solution to give 6,7,8,9-tetrahydrobenzo[*g*]-1-thianaphthalenium perchlorate (**4**) as green-yellow crystals. The ultraviolet–visible spectrum of **4** was again very similar to, but slightly red shifted from, that of the parent compound (**1**), and no new maxima appeared in this case.

A large excess of trityl perchlorate also converted **16** to **4** with no evidence for dehydrogenation of the tetrahydro ring to give **19**. However, the ketone (**15**) was easily dehydrogenated by dicyanodichloroquinone to benzo[*g*]thiochroman-4-one (**17**), which, as expected, afforded the corresponding carbinol (**18**) with lithium aluminum hydride. Various attempts to convert **18** to 1-thiaanthracenium perchlorate (**19**) yielded only a violet tar which could not be readily purified.

Discussion of Nmr Spectra.—The nmr spectrum of 1-thianaphthalenium perchlorate (**1**, Figure 1 and Table I) in deuteriotrifluoroacetic acid showed two strongly deshielded doublets at δ 10.50 (J = 9.0 cps)

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(1) Based on part I of the Ph.D. dissertation of C. J. Ohnmacht, Lehigh University, 1966.

(2) T. E. Young and P. H. Scott, *J. Org. Chem.*, **30**, 3613 (1965).

(3) A. Lüttringhaus and N. Engelhard, *Chem. Ber.*, **93**, 1525 (1960).

(4) All values of δ (parts per million) are positive downfield from tetramethylsilane as internal standard.

(5) T. E. Young and C. J. Ohmacht, *J. Org. Chem.*, **32**, 444 (1967). Electron densities based on a different set of parameters have previously been reported for compounds **1** and **9** by R. Zahradník and J. Koutecký, *Collection Czech. Chem. Commun.*, **28**, 1117 (1963).

(6) N. Engelhard and A. Kolb, *Ann.*, **673**, 136 (1964).

(7) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963).

(8) J. Petropoulos, M. McCall, and D. Tarbell, *ibid.*, **75**, 1130 (1953).

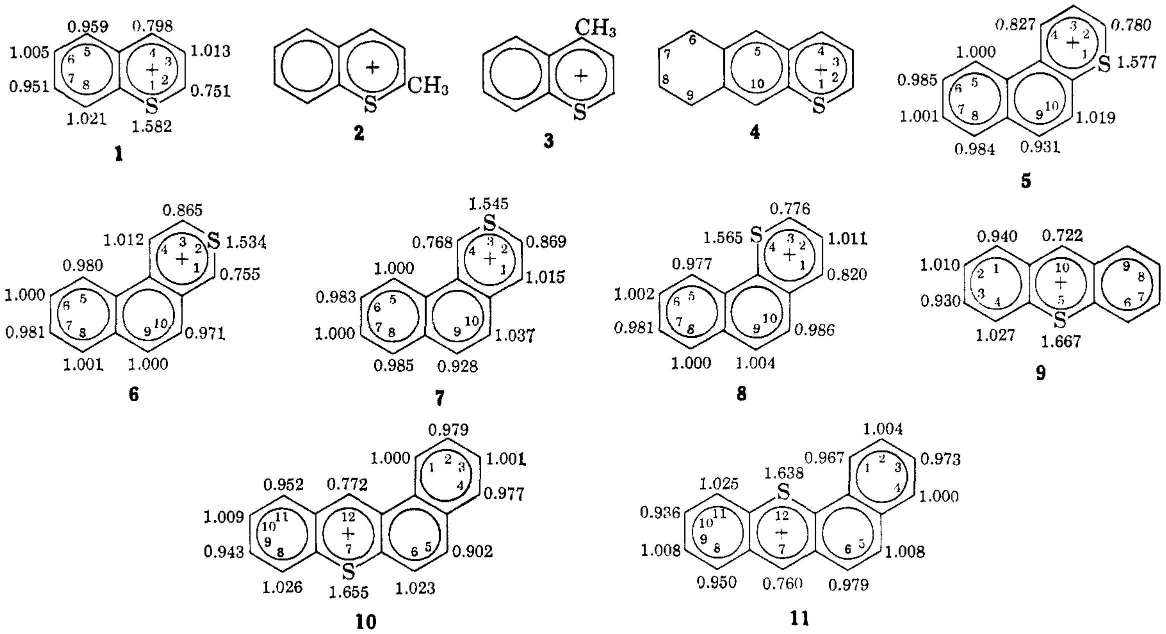
(9) F. Krollpfeiffer, H. Schultze, E. Schumbohm, and E. Sommermeyer, *Ber.*, **58**, 1654 (1925).

(10) F. Krollpfeiffer and H. Schultz, *ibid.*, **56**, 1819 (1923).

(11) T. E. Young and P. H. Scott, *J. Org. Chem.*, **31**, 343 (1966).

Chart I

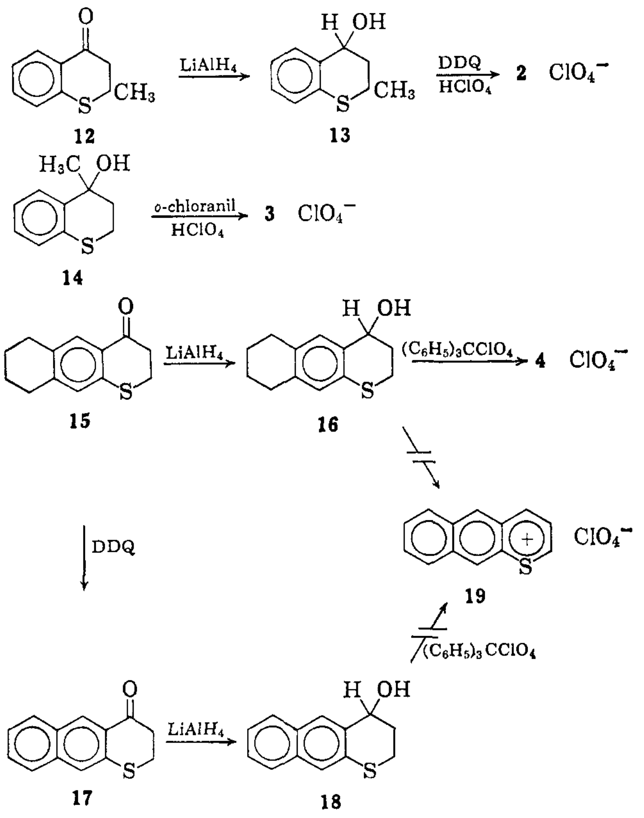
Structures and Electron Densities (q_r) of the Thiapyrylium Cations Studied[a]



[a] The position enumeration shown within each ring is based on the systematic IUPAC 1957 rules [*J. Am. Chem. Soc.*, **82**, 5545 (1960)] except for the thiaphenanthrenes (**5**–**8**) for which the common phenanthrene numbering has been retained.

Scheme I

Syntheses of Substituted Thianaphthalenium Perchlorates[a]



[a] DDQ is dicyanodichloroquinone.

and δ 9.70 (J = 9.0 cps), integrating for one proton each, as well as a complex multiplet in the range δ 9.07–8.35, representing the remaining five protons. The most deshielded doublet (δ 10.50) was assigned to H-2 because of its absence from the spectrum of the 2-methyl derivative (**2**), while the doublet at δ 9.70 was assigned to H-4 since introduction of a 4-methyl substituent in **3** deleted this band. The spectrum of the 2-methyl compound (**2**) retained the characteristic low-field doublet assignable to H-4 at δ 9.43, and the spectrum of 4-methylthianaphthalenium ion (**3**) exhibited the H-2 doublet at δ 10.23. In all three cases (**1**, **2**, and **3**) the 2- and 4-position protons showed splitting by H-3 consistent with the coupling constants $J_{23} = J_{34}$ = 9.0 cps. Therefore the protons at positions 2, 3, and 4 of the parent compound (**1**) comprise a degenerate AMX spin system[12] in which H-3 should appear as a 1:2:1 triplet because of the equivalence of J_{23} and J_{34} while J_{24} = 0 cps.

Table I

Nmr Chemical Shifts of 1-Thianaphthalenium Perchlorate (1) and Its Alkylated Derivatives (2, 3, and 4)[a]

Compd 1	Compd 2	Compd 3	Compd 4	Assignments
10.50 (1) d[b]	...	10.23 (1) d[b]	10.12 (1) d[b]	H-2
9.70 (1) d[b]	9.43 (1) d[b]	...	9.42 (1) d[b]	H-4
...	...	...	8.67 (1) t[b]	H-3
9.07–8.35 (5) m	8.78–8.23 (5) m	9.10–8.32 (5) m	...	H-3, 5, 6, 7, 8
...	...	...	8.45 (2) s	H-5, 10
...	...	...	3.30 (4) s[c]	CH_2-6, 9
...	...	...	2.08 (4) s[c]	CH_2-7, 8
...	3.44 (3) s	3.41 (3) s	...	CH_3

[a] Spectra were determined on a Varian A-60 spectrometer in deuteriotrifluoroacetic acid with tetramethylsilane as internal standard. Data are presented in the order δ (number of protons) and multiplicity as s, d, t, q, and m for singlet, doublet, triplet, quartet, and multiplet, respectively. [b] Coupling constants were 9.0 cps. [c] Broad envelope.

Although the complex multiplet regions of compounds **1**, **2**, and **3** did not permit unambiguous discernment of the expected H-3 triplet, the spectrum

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[12] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, p 63.

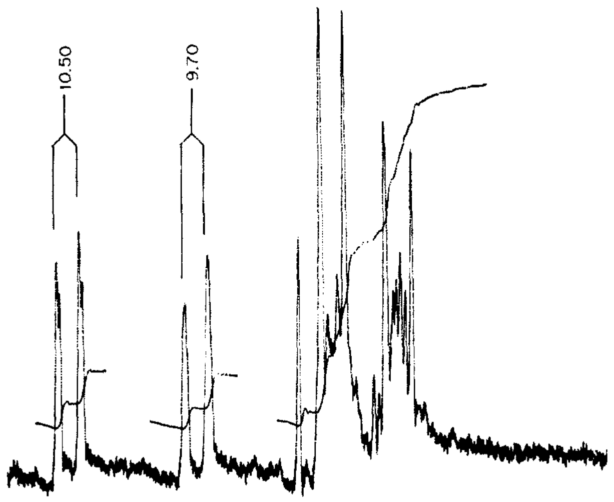

Figure 1.—Nmr spectrum of 1-thianaphthalenium perchlorate (**1**).

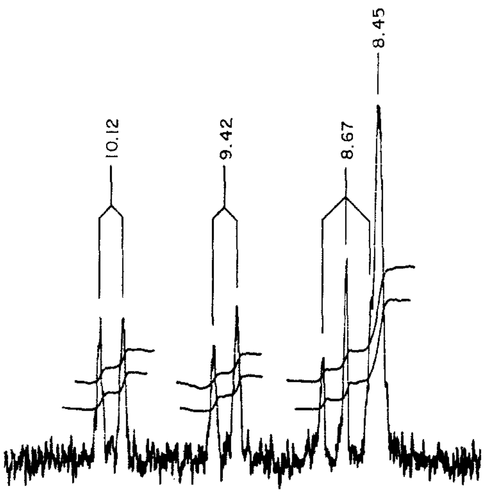

Figure 2.—Nmr spectrum of 6,7,8,9-tetrahydrobenzo[*g*]-1-thianaphthalenium perchlorate (**4**); aromatic protons only.

of 6,7,8,9-tetrahydrobenzo[*g*]-1-thianaphthalenium perchlorate (**4**, *cf.* Figure 2 and Table I) clearly revealed H-3 as a triplet (J = 9.0 cps) centered at δ 8.67 with the high-field band appearing as a sharp shoulder on a more intense singlet at δ 8.45 (integration for 2.28 protons) assignable to the remaining two aromatic protons at C-5 and C-10. The methylene groups of compound **4** appeared in two separate broad bands (integration for four protons each), of which the lower field envelope was assigned to the C-6 and C-9 methylene protons deshielded by the aromatic ring.[13]

Comparison of the chemical shifts of the 2- and 4-position protons of 1-thianaphthalenium ion (**1**) with the calculated electron densities (*cf.* Chart I) shows clearly that both the strong deshielding and the relative order ($\delta_2 > \delta_4$) of the absorption bands are in accord with the unusually low electron densities at these positions (q_2 = 0.751 and q_4 = 0.798). Since comparably deshielded 2-position protons of both 4-methylthiazolium[14] (δ 9.83 in CF_3COOH) and 4-methyl-1,3-dithiolium[15] (δ 11.12 in CF_3COOD-D_2O) ions show pronounced acidity and undergo rapid deuterium exchange in CF_3COOD-D_2O solution,[14,15] we expected 1-thianaphthalenium ion to behave similarly. However, the nmr spectrum of **1** in 50:50 CF_3COOD-D_2O solution showed no decrease in the relative integrated areas of the deshielded protons even after the solution had stood at room temperature for 1 month; hence, high deshielding is not necessarily equivalent to high C-H acidity in the thiapyrylium systems under consideration.

In the spectrum of thioxanthylium perchlorate (**9**) only the C-10 proton, which appeared as an isolated singlet at δ 10.25, could be assigned with certainty. Similarly the *meso* proton at C-12 of 7-thiabenz[*a*]anthracenium (**10**) and at C-7 of 12-thiabenz[*a*]anthracenium (**11**) ions appeared as the expected singlets at δ 10.62 and 9.87, respectively. In each of these three cases the remaining aromatic protons were observed as very complex multiplets at higher fields extending from δ 9.2 through the normal aromatic region to *ca.* 7.5. The large δ values of the *meso* protons of **9**, **10**, and **11** again corroborate the unusually low electron densities (0.722, 0.772, and 0.760, respectively) calculated for these positions. It should be noted, however, that the reasonance peak of H-12 in compound **10** is qualitatively out of sequence on the basis of electron densities alone, and lies at lower field, probably owing to the proximity of, and additional deshielding by, the angular benzo[*a*] ring.

Of the thiaphenanthrenium perchlorates (**5**, **6**, **7**, and **8**) the nmr spectrum of the 2-thia isomer (**6**, Figure 3) was most definitive. On the basis of the preceding unambiguous assignments, the three lowest field protons of **6**, integrating for one proton each, were again assigned to the thiapyrylium ring. The spin-spin splitting pattern of H-1, 3, and 4 was consistent with the assignments given in Table II. While the sequence $\delta_1 > \delta_3$ conforms to the electron density pattern, the intermediate δ_4 value must again be attributed to additional ring-current deshielding by the angular

TABLE II

NMR CHEMICAL SHIFTS OF THE ISOMERIC THIAPHENANTHRENIUM PERCHLORATES (**5**, **6**, **7**, AND **8**)[a]

Compd				
5	**6**	**7**	**8**	Assignments
...	10.68 (1) d[b]	9.25 (1) d[c]	9.58 (1) d[c]	H-1
10.24 (1) d[d]	...	9.55 (1) q[e]	8.95 (2) t[f]	H-2
9.02 (2) t[f]	9.64 (1) q[g]	...	10.28 (1) d	H-3
10.39 (1) d[h]	10.09 (1) d[i]	11.41 (...) d[j]	...	H-4
...[k]	9.02 (1) m	9.08 (1) m	...[k]	H-5
8.69 8.49 } (2) q[l]	8.30 (1.6)[m]	{ 8.81 (1) d[n] 8.38 (0.8) s	8.45 (1.8)[m]	H-9, 10
8.17 (3) m	8.16 (3.5) m	8.22 (3.2) m	8.16 (3.2) m	H-6, 7, 8

[a] *Cf.* footnote *a*, Table I. [b] J_{13} = 3.4 cps. [c] J_{12} = 9.0 cps. [d] J_{23} = 9.0 cps. [e] J_{12} = 9.0 cps, J_{24} = 3.0 cps. [f] These triplets (J = 9.0 cps) stand out clearly above a lower lying multiplet which probably also contains H-5. [g] J_{13} = 3.4 cps, J_{34} = 9.6 cps. [h] J_{34} = 9.0 cps. [i] J_{34} = 9.6 cps. [j] This band was nearly merged with that of the trifluoroacetic acid impurity in the solvent. Since paucity of this particular compound required determination in dilute solution, a solvent correction could not be easily applied to the integration. [k] See H-2 assignments and footnote *f*. [l] δ values of the two doublets of a nearly symmetrical AB quartet ($J_{9,10}$ = 9.0 cps). [m] Center of an AB quartet ($J_{9,10}$ = 9.0 cps) similar to that in compound **5** but with the low-intensity upfield branch immersed in the δ 8.16 singlet. [n] J = 9.0 cps.

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(13) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp 57-59.

(14) P. Haake and W. B. Miller, *J. Am. Chem. Soc.*, **85**, 4044 (1963).

(15) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem. Intern. Ed. Engl.*, **4**, 435 (1965).

benzo ring. Martin and co-workers[16] have similarly reported that the 4 and 5 protons (designated as H-α3 protons in their notation) of substituted phenanthrenes are the most deshielded. For analogous reasons, in our present compound, the broad asymmetric multiplet at δ 9.02 was assigned to H-5. The remaining assignments for **6** and analogous assignments for the other thiaphenanthrenium perchlorates (**5**, **7**, and **8**) are summarized in Table II.

Probably the most interesting feature to emerge from the spectra of the thiaphenanthrenium series is the coupling which occurs across the thionium sulfur. The coupling constants [J_{13} = 3.4 cps for 2-thiaphenanthrenium ion (**6**) and J_{24} = 3.0 cps for the 3-thia isomer (**7**)] are slightly larger than the range of J_{25} values (2.7–3.2 cps) observed for 3-substituted thiophenes[17] or of 4-methylthiazolium[14] ion (J_{25} = 2.39 cps), and are distinctly greater than J_{26} = 0.4 observed for pyridines,[17] suggesting significant through conjugation possibly *via* the *d* orbitals of the thionium sulfur.

Although empirical linear correlations of π-electron densities with proton chemical shifts of mononuclear nitrogen heterocycles have been reported,[18] and reliable methods for prediction of ring-current effects in polynuclear aromatic hydrocarbons have also recently appeared,[19] additional contributions to resonance shifts owing to anisotropic effects of heteroatoms in polycondensed systems[20] are not easily evaluated. We have, therefore, been unable to find any quantitative correlation of nmr shifts with electron densities in this series. It is nevertheless apparent that judicious use of HMO electron densities, in conjunction with other relevant data, serves well as a qualitative guide in the assignment of proton chemical shifts in these polynuclear thiapyrylium systems.

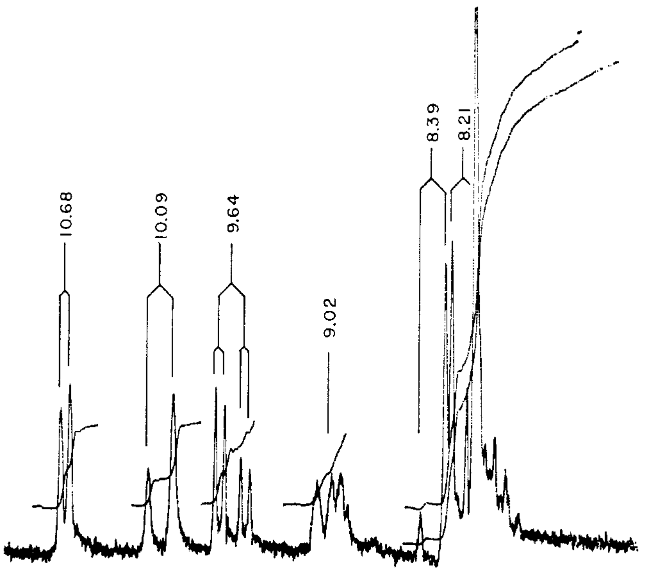

Figure 3.—Nmr spectrum of 2-thiaphenanthrenium perchlorate (**6**).

Experimental Section[21]

2-Methylthiochroman-4-ol (**13**).—To a stirred slurry of 2.12 g (0.056 mole) of lithium aluminum hydride in 250 ml of dry ether was added, over a period of 15 min, 5.00 g (0.028 mole) of 2-methylthiochroman-4-one (**12**).[8] The mixture was stirred for an additional 10 min then cautiously decomposed by the addition of 20 ml of ethyl acetate followed by 15 ml of water. The lithium salts were removed by filtration and the ether solution was evaporated to dryness. The wet crystals were then recrystallized from 175 ml of petroleum ether (bp 60–70°) to yield 4.17 g (83%) of white crystals, mp 73–75°. Recrystallization followed by sublimation at 35° (0.05 mm) gave an analytical sample, mp 74–75.5°.

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.78. Found: C, 66.34; H, 6.56; S, 17.75.

2-Methyl-1-thianaphthalenium Perchlorate (**2**).—A solution of 5.30 g (0.0233 mole) of dicyanodichloroquinone in 15 ml of acetic acid and 10 ml of nitromethane was added at room temperature in one portion to a solution of 4.20 g (0.0233 mole) of 2-methylthiochroman-4-ol (**13**) in 40 ml of acetic acid. The green solution was cooled in an ice bath as 25 g (15 ml) of 70% perchloric acid was added dropwise with stirring. The nitromethane was removed *in vacuo* and the solution was treated with ten times its volume of dry ether. The resulting green crystals, which were contaminated with 2,3-dicyano-5,6-dichlorohydroquinone, were then dissolved in 50 ml of hot acetic acid and cooled, and the insoluble material was collected by filtration and discarded. The liquors were then treated with dry ether to yield 1.92 g (32%) of blue plates, mp 117–121°. Recrystallization several times from acetic acid gave pure material, mp 123–126°.

Anal. Calcd for $C_{10}H_9ClO_4S$: C, 46.07; H, 3.48; S, 12.30. Found: C, 46.20; H, 3.46; S, 12.31.

The ultraviolet-visible spectrum showed $\lambda_{\max}^{1\%\ \mathrm{HClO_4\ in\ CH_3CN}}$ 261 mμ (log ϵ 4.59), 340 (3.94), 370 (3.62) sh, 579 (2.34) sh, 616 (2.72) sh.

4-Methyl-1-thianaphthalenium Perchlorate (**3**).—A solution of 6.83 g (0.0276 mole) of *o*-chloranil in 15 ml of acetic acid was added at room temperature in one portion to a solution of 5.00 g (0.0276 mole) of 4-methylthiochroman-4-ol (**14**)[9] in 40 ml of acetic acid. The blue solution was then cooled in an ice bath as 25 g (15 ml) of 70% perchloric acid was added dropwise with stirring. The color of the solution changed to blue-green and a precipitate formed after about two-thirds of the acid had been added. After addition was complete 400 ml of dry ether was added and the mixture was allowed to stand for 1 hr then filtered to yield 5.62 g (78%) of green crystals, mp 122–128°. Recrystallization several times from acetic acid yielded dark blue crystals of **3**, mp 119–123°.

Anal. Calcd for $C_{10}H_9ClO_4S$: C, 46.07; H, 3.48; S, 12.30. Found: C, 46.21; H, 3.53; S, 12.23.

The ultraviolet-visible spectrum showed $\lambda_{\max}^{1\%\ \mathrm{HClO_4\ in\ CH_3CN}}$ 257 mμ (log ϵ 4.60), 333 (3.71), 380 (3.65), 580 (2.72) sh, 616 (3.09).

6,7,8,9-Tetrahydrobenzo[*g*]thiochroman-4-ol (**16**).—A suspension of 3.0 g (0.014 mole) of 6,7,8,9-tetrahydrobenzo[*g*]thiochroman-4-one (**15**)[10,11] in 300 ml of dry ether was slowly added to a slurry of 1.0 g (0.026 mole) of lithium aluminum hydride in 100 ml of dry ether. The mixture was stirred for 0.5 hr (a green solution resulting), and then 20 ml of ethyl acetate was cautiously added followed by 10 ml of water. The lithium salts were removed by filtration and the filtrate was dried ($MgSO_4$), filtered, and evaporated to dryness. The yield of pale yellow solid was 2.75 g (92%), mp 116–118°. Recrystallization from benzene–petroleum ether (bp 60–70°) followed by sublimation twice at 110° (0.1 mm) gave a colorless analytical sample, mp 117–118°.

Anal. Calcd for $C_{13}H_{16}OS$: C, 70.88; H, 7.32; S, 14.55. Found: C, 71.06; H, 7.04; S, 14.55.

6,7,8,9-Tetrahydrobenzo[*g*]-1-thianaphthalenium Perchlorate (**4**).—A solution of 12.35 g (0.036 mole) of trityl perchlorate[22] in

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[16] R. H. Martin, N. Defay, F. Geerts-Evrard, and H. Figeys, *Bull. Soc. Chim. Belges*, **73**, 199 (1964).

[17] R. F. M. White in, "Physical Methods in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press, Inc., New York, N. Y., 1963, pp 117, 142.

[18] B. M. Lynch and H. J. M. Dou, *Tetrahedron Letters*, 2627 (1966).

[19] H. P. Figeys, *ibid.*, 4625 (1966).

[20] *Cf.* T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963), for a detailed discussion of contributing factors.

[21] Melting points were determined in capillary tubes using a Mel-Temp apparatus and are corrected. Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer. Nmr spectra of the thiapyrylium perchlorates (**1–11**) were determined in nearly saturated solutions (ranging from 10 to 20% by weight) in deuteriotrifluoroacetic acid of 99+% isotopic purity. All nmr spectra were recorded on a Varian A-60 spectrometer at ambient probe temperature (*ca.* 37°).

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

80 ml of nitromethane was added, in 10 min, to a stirred refluxing slurry of 2.30 g (0.012 mole) of tetrahydrobenzo[*g*]thiochroman-4-ol (**16**) in 100 ml of acetic acid. After refluxing for an additional 15 min the nitromethane was removed *in vacuo* and the resulting reddish brown precipitate (4.1 g, mp 140–148°) was collected by filtration. The liquors were then concentrated to *ca.* 20 ml and treated with 100 ml of dry ether to give a second crop of 2.0 g, mp 135–140°. Recrystallization of the first crop from acetic acid revealed it to be trityl perchlorate, mp 141–150° dec (lit.[22] mp 143–144°), while recrystallization of the second crop yielded 1.2 g (33%) of greenish brown crystals, mp 190–195° dec. Recrystallization of the second crop repeatedly from acetic acid gave an analytical sample of bright gold-green crystals of **4**, mp 204–206° dec.

Anal. Calcd for $C_{13}H_{13}ClO_4S$: C, 51.91; H, 4.36; S, 10.66. Found: C, 51.70; H, 4.33; S, 10.62.

The ultraviolet–visible spectrum showed $\lambda_{max}^{1\%\ HClO_4\ in\ CH_3CN}$ 269 mμ (log ε 4.58), 358 (3.96), 405 (3.63).

Benzo[*g*]thiochroman-4-one (**17**).—A solution of 6.81 g (0.030 mole) of dicyanodichloroquinone in 75 ml of warm benzene was added slowly to a refluxing, stirred, solution of 2.18 g (0.010 mole) of 6,7,8,9-tetrahydrobenzo[*g*]thiochroman-4-one (**15**)[10,11] in 25 ml of benzene. The initial green solution gave way to a brown precipitate on refluxing for 1 hr. The resulting mixture was cooled, the precipitate was filtered off, and the benzene solution was evaporated to *ca.* 10 ml, and then treated with petroleum ether (bp 30–40°). The resulting brown precipitate was treated with 10% aqueous base to give yellow solid which was collected and air dried to yield 0.77 g (36%) of product, mp 111–118°. The benzene–petroleum ether liquors were evaporated to dryness and treated with 10% aqueous base to yield a second crop of 0.50 g (23%), mp 88–106°. Recrystallization of this crop from petroleum ether (bp 60–70°) gave 0.45 g of yellow product, mp 115–119°. A sample of the first crop, recrystallized from petroleum ether (bp 60–70°), sublimed at 100° (0.05 mm), recrystallized, and then resublimed, had a melting point of 121–123°.

Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.71; S, 14.97. Found: C, 72.96; H, 4.80; S, 15.03.

An nmr spectrum of **17** in $CDCl_3$ exhibited an A_2X_2 multiplet of ten peaks (4 H of H-2 and H-3) centered at δ 3.15, aromatic singlets at 8.62 (H-5), and 7.65 (H-10) as well as normal aromatic peaks (4 H) in the region 7.27–7.90.

Benzo[*g*]thiochroman-4-ol (**18**).—A solution of 1.95 g (0.0091 mole) of benzo[*g*]thiochroman-4-one (**17**) in 150 ml of warm, dry ether was added dropwise to a stirred slurry of 1.50 g (0.040 mole) of lithium aluminum hydride in 125 ml of ether during 0.5 hr. After being stirred for 1 hr the solution was cautiously hydrolyzed by the addition of 10 ml of ethyl acetate followed by 10 ml of water. The lithium salts were removed by filtration and the filtrate was dried ($MgSO_4$) and evaporated to dryness. The resulting white solid was recrystallized from 500 ml of petroleum ether (bp 60–70°) to yield 1.72 g (87%) of yellow product, mp 118–121°. Sublimation at 100° (0.1 mm) gave an analytical sample as white needles, mp 120–122°.

Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.35; H, 5.66; S, 14.84.

Registry No.—**1**, 3220-72-2; **2**, 10147-15-6; **3**, 10181-99-4; **4**, 10137-42-5; **5**, 7432-90-8; **6**, 7432-91-9; **7**, 7432-92-0; **8**, 7432-93-1; **9**, 2567-20-6; **10**, 7432-95-3; **11**, 7432-96-4; **13**, 6157-10-4; **16**, 10137-50-5; **17**, 10137-51-6; **18**, 10137-52-7.

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Chemistry of Dimethylketene Dimer. VII. Dimers of Dimethylthioketene[1]

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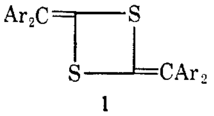
The reaction of tetramethyl-1,3-cyclobutanedione with phosphorus pentasulfide gives tetramethyl-1,3-cyclobutanedithione (**3**) and tetramethyl-3-thio-1,3-cyclobutanedione (**4**). These may be converted into the corresponding unsaturated β-(thio lactones), 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-(thio lactone) (**6**) and 3-mercapto-2,2,4-trimethyl-3-pentenoic acid β-(thio lactone) (**7**). Pyrolysis of **3** gives a third dimer of dimethylthioketene, which is evidently 2,4-diisopropylidene-1,3-dithietane (**10**).

Although the chemistry of ketene and its homologs has been studied intensively for many years, the literature contains only a few references to attempts to prepare monomeric thioketene or its alkyl derivatives. In most cases these attempts were unsuccessful.[2] Recently, however, a process for preparing monomeric thioketene and methylthioketene was patented,[3] and the synthesis and several reactions of hexafluorodimethylthioketene were reported.[4] Earlier, Schönberg, *et al.*,[5-7] had described the preparation of compounds of structure **1** which are dimers of diarylthioketenes.



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We prepared a dimer of dimethylthioketene, tetramethyl-1,3-cyclobutanedithione (**3**),[7a] by refluxing tetramethyl-1,3-cyclobutanedione (**2**) with excess phosphorus pentasulfide in pyridine solution. When **3** is prepared in this way, it is accompanied by a small amount of tetramethyl-3-thio-1,3-cyclobutanedione (**4**, which may be regarded as a mixed dimer of dimethylketene and dimethylthioketene), a minor amount of 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undecane-8-thione (**5**), and several unidentified compounds (see Scheme I). By using

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(1) Paper VI in this series: J. C. Martin, R. D. Burpitt, and H. U. Hostetter, *J. Org. Chem.*, **32**, 210 (1967).

(2) H. Staudinger, G. Rathsam, and F. Kjelsberg, *Helv. Chim. Acta*, **3**, 853 (1920).

(3) E. G. Howard, Jr. (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,035,030 (1962).

(4) M. S. Raasch, *Chem. Commun.*, 577 (1966).

(5) A. Schönberg, L. V. Vargha, and H. Kaltschmidt, *Ber.*, **64**, 2582 (1931).

(6) A. Schönberg, A. Stephenson, H. Kaltschmidt, E. Petersen, and H. Schulten, *ibid.*, **66**, 237 (1933).

(7) A. Schönberg, E. Feese, and K.-H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

(7a) NOTE ADDED IN PROOF.—The preparation of **3** from tetramethyl-1,3-cyclobutanedione and hydrogen sulfide in the presence of hydrogen chloride and zinc chloride was reported after the work in this article had been completed [R. D. Lipscomb (to E. I. du Pont de Nemours and Co., Inc.), U. S. Patent 3,297,765 (Jan 10, 1967)].