A Correlation of the Lowest Hückel Molecular Orbital Transition Energies with the L_b Band Frequencies of Thiapyrylium Ions[1]

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The long-wavelength electronic absorption frequencies of thiapyrylium ion (1) and 11 di-, tri-, and tetra-nuclear benzologs have been correlated with transition energies calculated by Hückel molecular orbital theory. Systematic variation of the coulomb integral for sulfur and the carbon–sulfur bond integral yielded an optimum correlation with the parameters $h_S = 0.9$ and $k_{CS} = 0.6$. The final regression line, $\bar{\nu} = 26.053\Delta m - 0.677$ kcm^{-1} (correlation coefficient, 0.992), passed well within two standard deviations ($S_{\bar{\nu}} = 0.609$ kcm^{-1}) of the origin, thereby conforming unexpectedly to simple theory. Syntheses of several new polynuclear thiapyrylium salts, including 2- and 3-thiaphenanthrenium (6 and 7), 7-thiabenz[a]anthracenium (10), 12-thiabenz[a]anthracenium (11) perchlorates, and 5-thianaphthacenium (12) 2,4,6-trinitrobenzenesulfonate, are described.

Quantitative correlations of electronic spectral band frequencies with transition energies calculated from Hückel molecular orbital (HMO) theory have recently been reported for pyridine and related azines,[2] for a number of substituted pyrylium salts,[3] and for an assortment of heterocyclic sulfur compounds of contemporary interest.[4] Among this last group, salts of the thiapyrylium ion (1) and its benzologs appeared to us particularly suitable for a systematic spectral evaluation of the coulomb and resonance integrals appropriate for thionium sulfur, and we report here a correlation based on such a study of the 12 cations illustrated in formulas 1 to 12 (Chart I).

9-thiaphenanthrenium (9)[8] ions were known. Subsequently, the 1- and 4-thiaphenanthrenium (5 and 8) perchlorates were also disclosed,[9] but the reported yields (8 and 0.3%, respectively) were unattractive, and we therefore present here new preparations of these two salts, along with syntheses of 2- and 3-thiaphenanthrenium (6 and 7), 7-thiabenz[a]anthracenium (10), and 12-thiabenz[a]anthracenium (11) perchlorates, as well as 5-thianaphthacenium (12) 2,4,6-trinitrobenzenesulfonate.

Syntheses of the isomeric thiaphenanthrenium salts all followed the pattern illustrated by the following explicit example (Chart II). S-(1-Naphthylmethyl)-

CHART I
STRUCTURES OF THE THIAPYRYLIUM COMPOUNDS STUDIED[a]
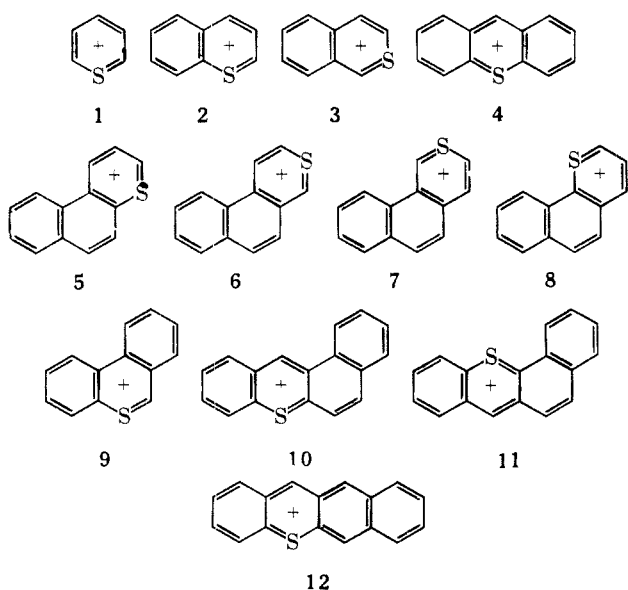
[a] All salts were perchlorates except that of 12 which was the 2,4,6-trinitrobenzenesulfonate.

CHART II
SYNTHESES OF THIAPHENANTHRENIUM PERCHLORATES

When this work was initiated only the perchlorate salts of thiapyrylium (1),[5] 1-thianaphthalenium (2),[6] 2-thianaphthalenium (3),[6] thioxanthylium (4),[7] and

thioglycollic acid (13)[10] was cyclized with phosphorus pentoxide in benzene solution to give a 16% yield of benz[h]isothiochroman-1-one (14),[11] which on reduction with lithium aluminum hydride yielded (92%) the corresponding carbinol (15). On treatment with trityl perchlorate[12] in acetic acid–nitromethane solution, the carbinol underwent both dehydration and hydride abstraction to give a 54% yield of 3-thiaphenanthrenium (7) perchlorate. Analogous procedures

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

(2) R. Zahradník and J. Koutecký, *Advan. Heterocyclic Chem.*, **5**, 79 (1965).

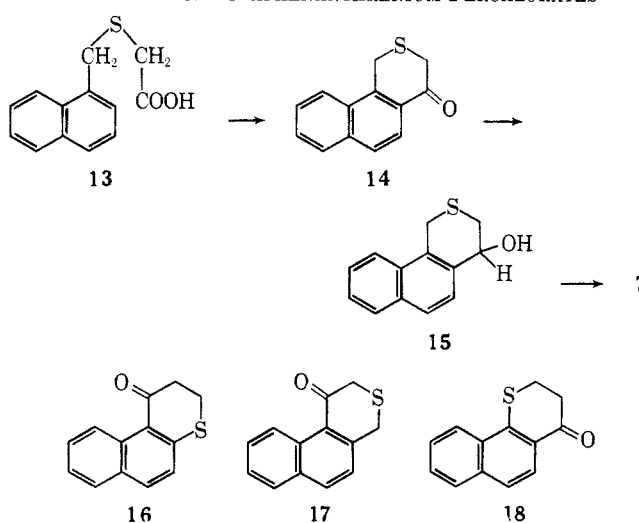(3) G. V. Boyd and N. Singer, *Tetrahedron*, **21**, 1263 (1965).

(4) R. Zahradník, *Advan. Heterocyclic Chem.*, **5**, 42 (1965).

(5) A. Lüttringhaus and N. Engelhard, *Angew. Chem.*, **73**, 218 (1961).

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

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

(8) A. Lüttringhaus and A. Kolb, *Z. Naturforsch.*, **16b**, 762 (1961).

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

(10) W. Gündel, German Patent 814, 596 (Sept 24, 1951); *Chem. Abstr.*, **47**, 1741 (1953).

(11) The enumeration adapted in the fused system corresponds to that of the analogous benzenoid hydrocarbon, in this case, phenanthrene.

(12) K. A. Hoffman and H. Kirmreuther, *Ber.*, **42**, 4856 (1909).

starting from the known benzo[f]thiochroman-4-one (16),[13] benz[f]isothiochroman-4-one (17),[14] and benzo-[h]thiochroman-1-one (18)[13] led to the isomeric 1-, 2-, and 4-thiaphenanthrenium (5, 6, and 8, respectively) perchlorates.

Preparations of the tetranuclear thiapyrylium salts are shown in Chart III. Reduction of benzo[b]thio-

CHART III

SYNTHESES OF TETRANUCLEAR THIAPYRYLIUM SALTS
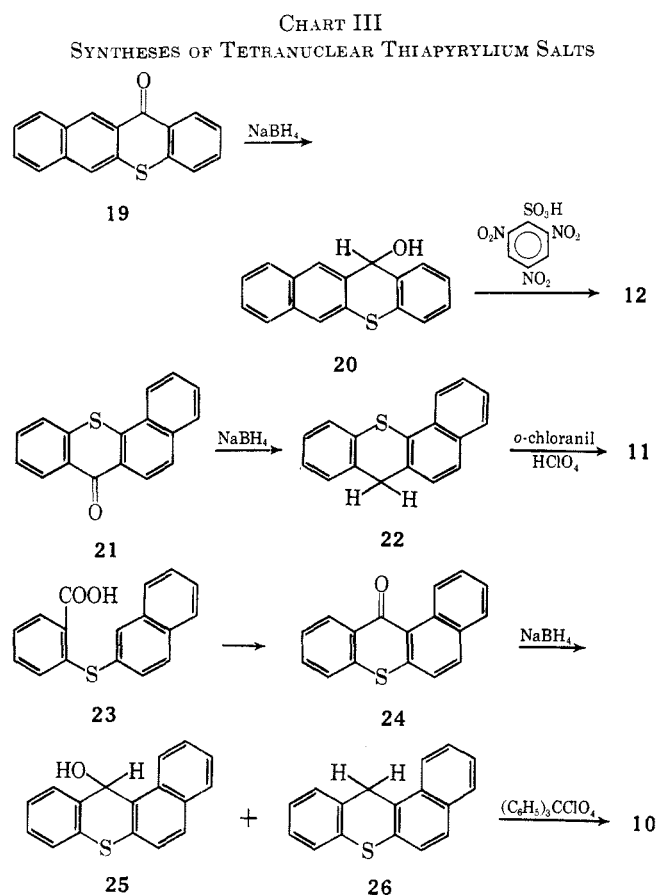
xanthen-12-one (19)[15] with excess sodium borohydride in refluxing 95% ethanol also gave a clean reduction to the colorless alcohol (20) in 79% yield   Reaction of this alcohol with perchloric acid immediately gave a dark blue precipitate (presumably 12 perchlorate) which was extremely sensitive to atmospheric moisture and rapidly turned green, then yellow, on exposure to air.   However, treatment of the alcohol 20 with 2,4,6-trinitrobenzenesulfonic acid dihydrate[16] in acetic acid containing acetic anhydride yielded dark blue crystals of 5-thianaphthacenium (12) 2,4,6-trinitrobenzenesulfonate in excellent yield.   This salt was stable to atmospheric moisture, and, although it was discolored rapidly by the 1% perchloric acid in acetonitrile normally used to obtain the electronic spectra, it could be recrystallized conveniently from acetic acid–acetic anhydride solution, and was sufficiently stable in acetic acid to determine its ultraviolet–visible spectrum.

Attempted reduction of benzo[c]thioxanthen-7-one (21)[15,17] with sodium borohydride in methanol or with

1 equiv of lithium aluminum hydride in ether gave only unreacted ketone. Reduction of 21 with excess sodium borohydride in refluxing isopropyl alcohol for 2 days gave a mixture (infrared, $\tilde{\nu}_{OH}$ 3350 cm^{-1} and no carbonyl absorption) of the corresponding alcohol and benzo[c]thioxanthene (22).[18] Column chromatography of a sample of the mixture on silica gel gave 27% of 22 (mp 86–87.5°) and 72% of the starting ketone (21) apparently resulting from facile oxidation or disproportionation of the alcohol on the column. Finally, reduction of the ketone 21 by excess sodium borohydride in refluxing pyridine gave only benzo[c]thioxanthene (22) in 34% yield. Treatment of 22 with o-chloranil and perchloric acid[19] then yielded 12-thiabenz[a]anthracenium (11) perchlorate as dark red crystals.

Ring closure of 2-(2-naphthylthio)benzoic acid (23),[20] via the acid chloride with stannic chloride, afforded benzo[a]thioxanthen-12-one (24) in high yield. This ketone also yielded mixtures of the corresponding carbinol (25) and benzo[a]thioxanthene (26) on reduction with sodium borohydride in either methanol or pyridine. No conditions were found for formation of either discrete compound, nor could the two products be effectively separated. However, treatment of the mixture (25 and 26) with trityl perchlorate yielded a dark red salt having spectral properties, as well as acceptable elemental analysis, corresponding to 7-thiabenz[a]anthracenium (10) perchlorate.

Electronic Spectra and HMO Calculations.—Ultraviolet–visible spectra were measured for the perchlorate salts of 2, 4, 5, 6, 7, 8, 10, and 11 in acetonitrile containing 1% by volume of 70% perchloric acid. Since the absorption maxima of 2,[6] 5,[9] and 8[9] did not differ significantly from values obtained in acetic acid solution, spectral data in acetic acid for 1,[5] 3,[6] and 9[8] from the literature were directly included in this study. The spectrum of the blue 2,4,6-trinitrobenzenesulfonate of 12 was also measured in acetic acid for reasons already cited.

These polynuclear thiapyrylium compounds all exhibit electronic spectra (cf. the Experimental Section for specific data) which are similar to, but red shifted from, those of the corresponding polynuclear hydrocarbons,[21] suggesting that the first absorption bands of the thiapyrylium compounds should be designated ^1L_b in Platt notation.[21] With the exception of 1 and 4, both of which have C$_{2v}$ symmetry, all of the thiapyrylium ions studied belong to the C$_s$ point group in which all transitions ($^1A' \rightarrow {}^1A'^*$) are symmetry allowed in the molecular plane. The first $\pi \rightarrow \pi^*$ transition of the parent thiapyrylium ion (1) is $^1A_1 \rightarrow {}^1B_2^*$ and is also formally allowed in the molecular plane and perpendicular to the twofold rotation axis. Similarly, from the HMO calculations, the first $\pi \rightarrow \pi^*$ transition of thioxanthylium ion (4) proves to be $^1A_1 \rightarrow {}^1A_1^*$,

(13) F. Krollpfeiffer and H. Schultze, Ber., 56, 1819 (1923).

(14) P. Cagniant, G. Jecko, and D. Cagniant, Bull. Soc. Chim. France, 2217 (1964).

(15) R. Martin, N. Defay, F. Geerts-Evrard, P. Given, J. R. Jones, and R. W. Wedel, Tetrahedron, 21, 1833 (1965).

(16) D. J. Pettitt and G. K. Helmkamp, J. Org. Chem., 29, 2702 (1964).

(17) E. G. Davis and S. Smiles, J. Chem. Soc., 97, 1290 (1910).

(18) M. Kamel and H. Shoeb [Tetrahedron, 20, 483 (1964)] have similarly reported that dibenzo[a,h]- and dibenzo[b,h]xanthone also give mixtures of carbinol and methylene derivatives on hydride reduction, but yield exclusively the carbinols with sodium amalgam.

(19) Cf. A. Lüttringhaus, N. Engelhard, and A. Kolb, Ann., 654, 189 (1962), and D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, Tetrahedron Letters, No. 15, 530 (1961), for other hydride abstractions with these reagents.

(20) J. Goldberg, Ber., 37, 4527 (1904).

(21) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 13.
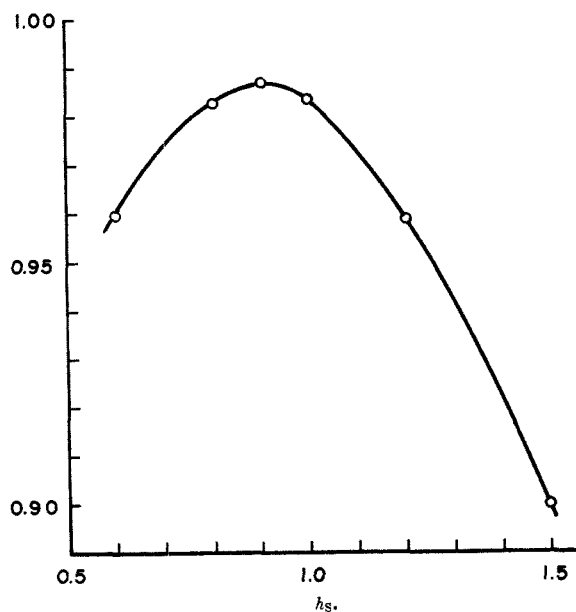
Figure 1.—Variation of the least-squares correlation coefficient (r) with the coulomb parameter (h_S) for k_{CS} = 0.6.
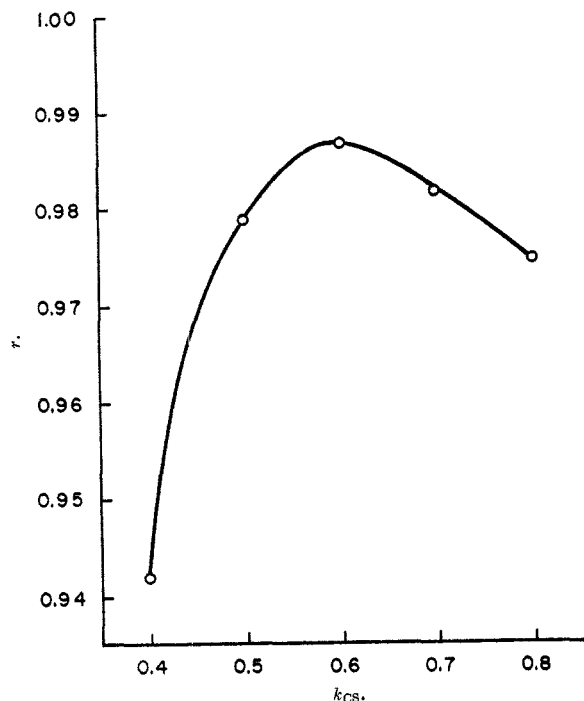

Figure 2.—Variation of the least-squares correlation coefficient (r) with the bond-integral parameter (k_{CS}) for h_S = 0.9.

which is also allowed parallel to the twofold axis. As a consequence of the low symmetry the L_b bands are all quite strong, and, except for **12**, exhibit log ϵ values from about 3 to 4.

HMO calculations for cations **1–12** were carried out in the usual way[22] using a simplified model[23] in which the coulomb integral for sulfur and the carbon–sulfur

(22) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(23) The unlabeled α is the usual coulomb integral for carbon and β is the corresponding carbon–carbon bond resonance integral. R. Gerdil and E. A. C. Lucken [*J. Am. Chem. Soc.*, **87**, 213 (1965)] have recently shown that the Longuet-Higgins d-orbital model predicts a completely incorrect odd-electron distribution in dibenzothiophene radical anion and have further criticized this model on theoretical grounds. We have therefore chosen the simple p-orbital model for the present work.

bond integral were expressed as $\alpha_S = \alpha + h_S\beta$ and $\beta_{CS} = k_{CS}\beta$, respectively,[23] and in which no auxiliary inductive parameter for carbon adjacent to sulfur was employed. As a starting point we used the parameters h_S = 1.0 and k_{CS} = 0.6, which correspond to Zahradnik's model B2,[24] then repeated the calculations for five additional values (0.6, 0.8, 0.9, 1.2, and 1.5) of h_S. Computations were performed on the full secular determinants using a G.E. 225 computer and a standard-matrix diagonalization program.

For each set of parameters, the observed wavenumbers ($\bar{\nu}$, kcm^{-1}) of the longest wavelength electronic absorption bands of ions **1–10** were correlated with the calculated transition energies expressed as Δm (the change in coefficient of β between the lowest unoccupied and the highest occupied molecular orbitals)[25] by means of a least-squares fit to the linear equation ($\bar{\nu} = a\Delta m + b$) of slope (a) and intercept (b). For a fixed value of k_{CS} = 0.6, a plot of the correlation coefficient (r) vs. the coulomb parameter (h_S) showed a distinct maximum in the region h_S = 0.9 (Figure 1). The coulomb parameter (h_S = 0.9) was then held constant; the computations were repeated for additional values (0.4, 0.5, 0.7, and 0.8) of k_{CS}. A plot of the correlation coefficient (r) vs. k_{CS} exhibited a maximum at k_{CS} = 0.6 (Figure 2); hence the parameters h_S = 0.9 and k_{CS} = 0.6 constitute a self-consistent optimum set for this correlation and yielded a regression line ($\bar{\nu} = 26.226\cdot\Delta m - 0.880$ kcm^{-1}) characterized by a high correlation coefficient (r = 0.987) and low standard deviation of the residuals ($S_{\bar{\nu}}$ = 0.638 kcm^{-1}). The various regression line constants and corresponding data for Figures 1 and 2 are summarized in Table I.

TABLE I

REGRESSION LINES ($\bar{\nu} = a\Delta m + b$) FOR VARIOUS SETS OF PARAMETERS h_S AND k_{CS}

| h_S | k_{CS} | Regression line constants | | Correlation coefficient, | Std dev, |
		a	b	r	$S_{\bar{\nu}}$ (kcm^{-1})
0.6	0.6	21.470	3.603	0.960	1.103
0.8	0.6	24.558	0.651	0.983	0.720
0.9	0.6	26.226	−0.880	0.987	0.638
1.0	0.6	27.436	−1.920	0.984	0.690
1.2	0.6	28.302	−2.385	0.959	1.111
1.5	0.6	27.589	−1.220	0.900	1.710
0.9	0.4	31.169	−2.375	0.942	1.314
0.9	0.5	29.229	−2.200	0.979	0.807
0.9	0.7	23.296	0.675	0.982	0.736
0.9	0.8	20.852	2.072	0.975	0.873

Salts of ions **11** and **12**, which were successfully synthesized only after most of the above calculations had been completed, exhibited long-wavelength absorption bands, the frequencies of which fell within one standard deviation of the optimum regression line for compounds **1–10**, thus lending further support to the correlation, as well as corroborating the structural assignments of compounds **11** and **12**.

All twelve compounds (**1–12**) were then included in the computation of a final regression line ($\bar{\nu} = 26.053\cdot\Delta m - 0.677$ kcm^{-1}) based on the data summarized in Table II and illustrated in Figure 3. The high cor-

(24) R. Zahradnik, *Advan. Heterocyclic Chem.*, **5**, 10 (1965).

(25) The HMO energy levels are usually expressed as $E_j = \alpha + m_j\beta$. Zahradnik[24] uses the notation $E(N \rightarrow V_1)$ in place of Δm. See ref 3 for a concise summary of pertinent notation and theory.

relation coefficient (r = 0.992) and low standard deviation of the residuals ($S_{\bar{\nu}}$ = 0.609 kcm^{-1}) for this line support the assignment of these long-wavelength bands as the first $\pi \rightarrow \pi^*$ transitions.

TABLE II

LONGEST WAVELENGTH ELECTRONIC ABSORPTION BANDS OF THIAPYRYLIUM COMPOUNDS AND HMO TRANSITION ENERGIES (Δm) BASED ON OPTIMUM PARAMETERS (h_S = 0.9 AND k_{CS} = 0.6)

Compd	λ_{max}, mμ^a	$\bar{\nu}$, kcm^{-1}	Δm, β
1	284	35.2	1.3692
2	384	26.0	1.0269
3	385	26.0	0.9827
4	510	19.6	0.7945
5	432	23.2	0.9283
6	425	23.5	0.9368
7	411	24.4	0.9825
8	430^b	23.3	0.9127
9	424	23.6	0.9773
10	454	22.0	0.8354
11	508^b	19.7	0.7604
12	692^b	14.5	0.5909

^{a} All spectra were measured in acetonitrile containing 1% of 70% perchloric acid except 1,^{5} 3,^{3} 9,^{8} and 12 (this work) which were measured in acetic acid solution. ^{b} Shoulder.

No attempt was made to choose a coulomb parameter for sulfur which would yield a regression line slope comparable with that for benzenoid hydrocarbons, an arbitrary device recently reported for similar correlations of pyrylium salt spectra;^{3} hence the slope of the present regression line yields a value of β (−74.5 kcal/mole) considerably higher than those observed for benzenoid molecules.^{22,26} For comparison, Table III summarizes the regression line constants for this correlation along with those of other correlations in which certain spectral band frequencies show linear dependence on Δm. The purely empirical treatment of parameters used here has revealed the additional point of interest that *the optimum regression line passes well within two standard deviations of the origin* as required by simple theory,^{3} and indeed is closest to the origin when the optimum parameters are used [*cf.* the frequency intercepts (*b*) in Table I]. It would therefore be of further interest to determine whether the large intercepts observed on the frequency axis in previous correlations (*cf.* Table III), and rationalized in terms of singlet–triplet splitting,^{27} could more generally be accommodated in the simple theory by a more appropriate selection of empirical parameters.

TABLE III

COMPARISON OF REGRESSION LINES FOR CORRELATION OF SPECTRAL BANDS DEPENDENT ON Δm FOR VARIOUS SERIES OF COMPOUNDS

Series	Constants in $\bar{\nu}$ = $a\Delta m$ + b		Ref
	a	b	
Pyridine and its benzologs	24.031	5.584	2
Benzenoid hydrocarbons	19.207	10.234	22
Pyrylium salts	14.700	10.500	3
Benzothiophenes	19.865	7.478	4
Thiapyrylium salts	26.053	−0.677	This work

(26) R. Zahradník and J. Koutecký, *Collection Czech. Chem. Commun.*, **28**, 904 (1963).
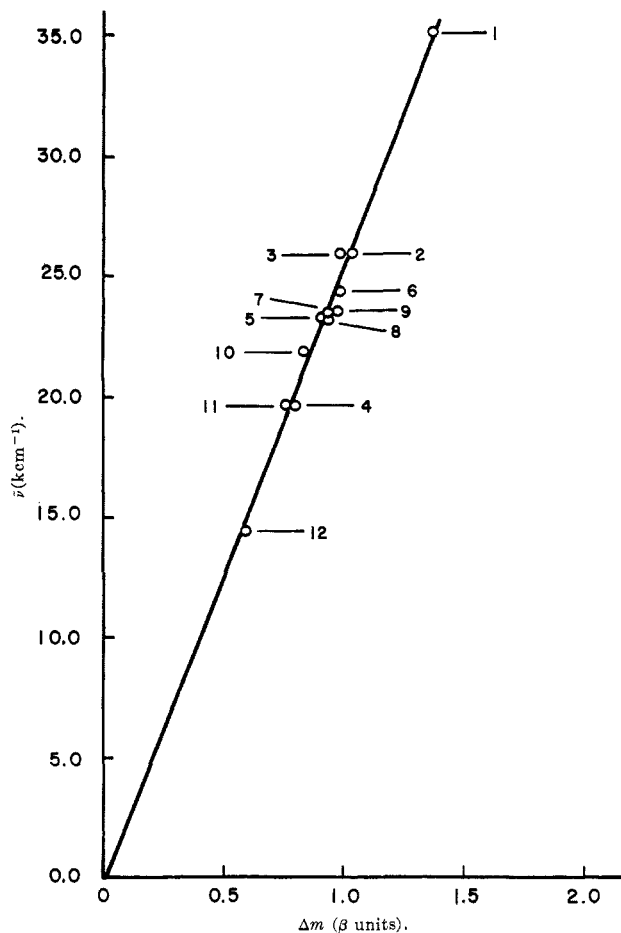(27) Reference 22, p 213.

Figure 3.—Final regression line ($\bar{\nu}$ = 26.053Δm − 0.677) for correlation of the L$_b$ bands of thiapyrylium ions 1–12 with the HMO transition energies (Δm) based on the parameters h_S = 0.9 and k_{CS} = 0.6. Correlation coefficient: r = 0.992; standard deviation of residuals: $S_{\bar{\nu}}$ = 0.609 kcm^{-1}.

Experimental Section[28]

1-Thianaphthalenium (2) Perchlorate.—This compound, prepared as already described:^{6} had mp 221–223° dec; ultraviolet-visible spectrum $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 258 mμ (log ϵ 4.53), 335 (3.70), 384 (3.50); lit.^{6} mp 219–220° dec.

Thioxanthylium (4) Perchlorate.—This salt was prepared as previously described^7 and had mp 224–225° dec; ultraviolet-visible spectrum $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 243 mμ (log ϵ 3.98), 278 (4.97), 380 (4.36), 485 (3.50), 510 (3.42); lit.^{7} mp 229° dec.

Anal. Calcd for C$_{13}$H$_9$ClO$_4$S: C, 52.62; H, 3.06; S, 10.81. Found: C, 52.56; H, 3.08; S, 10.96.

Benzo[*f*]thiochroman-4-ol.—To a stirred solution of 12.2 g (0.0568 mole) of benzo[*f*]thiochroman-4-one (16)^{13} in 200 ml of boiling methanol was added dropwise during 20 min a solution of 4.0 g (0.105 mole) of sodium borohydride, 5 ml of 2 N sodium hydroxide and 20 ml of water. The mixture was then poured into 500 ml of ice water, and the resulting pale yellow crystals were collected and air dried to yield 11.9 g (97%) of product, mp 100–112°. Two recrystallizations from petroleum ether (bp 60–70°) gave 5.3 g (43% yield) of pure product, mp 128–130°.

Anal. Calcd for C$_{13}$H$_{12}$OS: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.09; H, 5.81; S, 14.62.

1-Thiaphenanthrenium (5) Perchlorate.—A solution of 7.30 g (0.0212 mole) of trityl perchlorate^{12} in 60 ml of nitromethane was added in 5 min to a stirred refluxing solution of 4.60 g (0.0212 mole) of benzo[*f*]thiochroman-4-ol in 150 ml of acetic acid. The mixture was then refluxed for 15 min during which the solution turned dark brown. The reaction mixture was cooled and

the resulting green-yellow crystals were collected. Concentration of the liquors to one-third volume afforded a second crop, bringing the total yield to 5.95 g (79%), mp 217–220° dec. One recrystallization from acetic acid gave bright green crystals (5.80 g), mp 218–220° dec, lit.[9] mp 208–210°.

Anal. Calcd for $C_{13}H_9ClO_4S$: C, 52.62; H, 3.06; S, 10.81. Found: C, 52.62; H, 3.25; S, 10.85.

Ultraviolet–visible spectrum showed $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 244 mμ (log ϵ 4.60), 290 (4.12), 307 (4.12), 432 (3.91).

Benz[*f*]isothiochroman-4-ol.—A solution of 1.90 g (0.0085 mole) of benz[*f*]isothiochroman-4-one (17)[14] in 170 ml of dry ether was slowly added to a stirred suspension of 1.70 g (0.045 mole) of lithium aluminum hydride in 170 ml of dry ether. The mixture was then stirred for an additional 15 min and a 20-ml portion of ethyl acetate was added cautiously, followed by addition of 10 ml of water. The ether solution was filtered to remove precipitated salts, dried over magnesium sulfate, filtered, and then evaporated to dryness yielding 1.75 g (92%) of off-white solid, mp 109–113°. One recrystallization from petroleum ether (bp 60–70°) followed by two sublimations at 85° (0.05 mm) gave the pure carbinol, mp 111.5–113.5°.

Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 71.92; H, 5.72; S, 14.68.

2-Thiaphenanthrenium (6) Perchlorate.—A solution of 3.35 g (0.0097 mole) of trityl perchlorate in 30 ml of nitromethane was added during 5 min to a stirred refluxing solution of 2.10 g (0.0097 mole) of benzo[*f*]thiochroman-4-ol and 130 ml of acetic acid. After refluxing for 5 min the solution was quickly cooled and filtered to yield 0.4 g of a black solid, mp >300°. The solvent volume was then reduced to one-third of its initial volume and 150 ml of dry ether was added to precipitate 2.20 g (76%) of brown crystals, mp 208–214° dec. Recrystallization three times (twice with charcoal) from acetic acid gave 1.20 g (42%) of greenish yellow crystals, mp 216–218°.

Anal. Calcd for $C_{13}H_9ClO_4S$: C, 52.62; H, 3.06; Cl, 11.94; S, 10.81. Found: C, 52.68; H, 3.24; Cl, 12.05; S, 10.78.

Ultraviolet–visible spectrum showed $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 238 mμ (log ϵ 4.42), 255 (4.04), 298 (4.49), 357 (4.06), 425 (3.40).

Benz[*h*]isothiochroman-1-one (14).—A paste of 30 g of phosphorus pentoxide, 15 g of Celite, and 150 ml of dry toluene was added with rapid stirring to a solution of 27.20 g (0.117 mole) of S-(1-naphthylmethyl)thioglycollic acid (13)[10] in 100 ml of refluxing dry toluene. The slurry was allowed to reflux with vigorous stirring for 15 min then a paste of 30 g of phosphorus pentoxide in 60 ml of dry toluene was added. After refluxing for an additional 15 min another identical paste was added and the mixture then refluxed for an additional 30 min. The toluene slurry was filtered hot and the red, insoluble mass was extracted with two 300-ml portions of boiling benzene. The extracts were combined and washed with two 250-ml portions of 5% sodium bicarbonate followed by 250 ml of water. The solution was dried (MgSO₄) and filtered, and the solvent was removed *in vacuo* to yield a yellow oil which solidified on standing at 5° overnight. The solid was dissolved in 250 ml of boiling 95% ethanol and decanted from a small amount of insoluble red oil. After 1 hr at 5° an orange oil along with some pale yellow solid precipitated. The solution was warmed just enough to put the crystals back into solution and the solution was decanted from the red gum. On cooling overnight the ethanol solution yielded 6.00 g (24%) of pale yellow crystals, mp 115–121°. (Concentration of the liquors yielded an oil.) Sublimation at 110° (0.05 mm) followed by recrystallization from 95% ethanol yielded 3.90 g (16%) of pale yellow plates, mp 126–128°. A resublimed analytical sample also had a melting point of 126–128°.

Anal. Calcd for $C_{13}H_{10}OS$: C, 72.86; H, 4.70; S, 14.96. Found: C, 72.81; H, 4.78; S, 14.80.

Benz[*h*]isothiochroman-1-ol (15).—A solution of 1.30 g (0.00607 mole) of benz[*h*]isothiochroman-1-one (14) in 225 ml of dry ether was slowly added to a stirred suspension of 1.00 g (0.0264 mole) of lithium aluminum hydride in 100 ml of dry ether. The mixture was stirred for 10 min then 20 ml of ethyl acetate was cautiously added followed by 10 ml of water. The lithium salts were filtered off and the ether solution was dried (MgSO₄), filtered, and evaporated *in vacuo*. The white crystalline residue weighed 1.20 g (92%), mp 114–118°. Recrystallization from benzene–petroleum ether (bp 60–70°) followed by sublimation at 105° (0.05 mm) gave pure 15, mp 119–120°.

Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.32; H, 5.74; S, 14.84.

3-Thiaphenanthrenium (7) Perchlorate.—A solution of 1.32 g (0.00385 mole) of trityl perchlorate in 15 ml of nitromethane was added in one portion to a stirred solution of 0.83 g (0.00385 mole) of 15 in 75 ml of refluxing acetic acid. The solution turned greenish brown immediately. As the solution was refluxed for 10 min black crystals formed on the wall of the reaction flask. The mixture was then cooled and the black crystals (0.40 g, mp >250°) were removed by filtration. The nitromethane was removed *in vacuo* and the remaining solution treated with 200 ml of dry ether. The greenish brown crystals which precipitated were collected by filtration and dried *in vacuo* over potassium hydroxide. The yield was 0.55 g (44%), mp 221–225° dec. Repeated recrystallizations from acetic acid gave small yellow needles, mp 231.5–232°.

Anal. Calcd for $C_{13}H_9ClO_4S$: C, 52.62; H, 3.06; S, 10.81. Found: C, 52.60; H, 2.96; S, 10.56.

Ultraviolet–visible spectrum showed $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 240 mμ (log ϵ 4.40), 252 (4.40), 262 (4.38), 280 (4.33), 312 (3.73), 411 (4.05).

Benzo[*h*]thiochroman-1-ol.—A solution of 0.76 g (0.020 mole) of sodium borohydride and 1 drop of 50% sodium hydroxide in 10 ml of water was added dropwise to a stirred slurry of 4.1 g (0.019 mole) of benzo[*h*]thiochroman-1-one (18)[13] in 75 ml of boiling methanol. After addition was complete (10 min) the solution was poured into 750 ml of ice water and stirred for 1.5 hr to promote crystal growth. The product was collected and air dried to yield 3.35 g (81%) of colorless crystals, mp 87–89°. Two recrystallizations from petroleum ether (bp 60–70°) followed by sublimation [65° (0.1 mm)] gave an analytical sample, mp 94–95.5°.

Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 71.96; H, 5.88; S, 14.65.

4-Thiaphenanthrenium (8) Perchlorate.—A solution of 10.0 g (0.029 mole) of trityl perchlorate in 75 ml of nitromethane was added in about 10 min to a stirred solution of 6.3 g (0.029 mole) of benzo[*h*]thiochroman-1-ol in 150 ml of refluxing acetic acid. After addition was complete the mixture was refluxed for an additional 15 min, the nitromethane was removed *in vacuo*, and the residue was diluted to 200 ml with acetic acid. The dark green crystals (5.05 g, 59% mp 157–160° dec) which separated on cooling were collected by suction filtration and the filtrate was treated with an equal volume of ether, precipitating a second crop of crystals (2.00 g, 23%, mp 154–157° dec). Combination of the crops and recrystallization four times from acetic acid yielded 3.8 g (44%) of green crystals, mp 161–163° dec, lit.[9] mp 152–153° dec.

Anal. Calcd for $C_{13}H_9ClO_4S$: C, 52.62; H, 3.06; S, 10.81. Found: C, 52.82; H, 3.61; S, 10.65.

Ultraviolet–visible spectrum gave $\lambda_{max}^{1\% \ HClO_4 \ in \ MeCN}$ 240 mμ (log ϵ 4.75), 307 (4.27), 385 (3.83), 430 (3.28) sh.

Benzo[*b*]thioxanthen-12-ol (20).—To a stirred slurry of 2.62 g (0.010 mole) of benzo[*b*]thioxanthen-12-one (19)[15] in 125 ml of refluxing 95% ethanol was added, in one portion, a solution of 1.60 g (0.043 mole) of sodium borohydride and 2 drops of 50% sodium hydroxide in 30 ml of water. The mixture was then stirred at reflux until the yellow color disappeared (1 hr). The mixture was filtered and poured into 300 ml of cold water to give, after air drying, 2.63 g of white crystals, mp 150–156°. Recrystallization from benzene–cyclohexane gave 2.10 g (79%) of white crystals, mp 187–190° (sealed tube), the sample turning yellow about 100°. Recrystallization five times from benzene–cyclohexane gave an analytical sample, mp 188–190° (sealed tube).

Anal. Calcd for $C_{17}H_{12}OS$: C, 77.24; H, 4.57; S, 12.13. Found: C, 77.39; H, 4.82; S, 12.07.

5-Thianaphthacenium (12) 2,4,6-Trinitrobenzenesulfonate.—To a stirred solution of 0.87 g (0.0033 mole) of 20 in 30 ml of acetic acid (warmed to dissolve) was added, in one portion, a solution of 1.08 g (0.0033 mole) of 2,4,6-trinitrobenzenesulfonic acid dihydrate,[16] 6 ml of acetic anhydride, and 20 ml of acetic acid. A slightly exothermic reaction occurred as a dark green precipitate formed immediately. The mixture was stirred for an additional 45 min and the precipitate was collected by filtration, washed with dry ether, and dried *in vacuo* over potassium hydroxide. The yield of green solid was 1.61 g (91%), mp 215–218° dec, with shrinking at 210°. A sample recrystallized twice from 1-l. portions of acetic acid, containing a few milliliters of acetic anhydride, gave dark blue, almost black, microneedles, mp 225–227° dec.

Anal. Calcd for $C_{23}H_{13}N_3O_9S_2$: C, 51.21; H, 2.43; S, 11.89. Found: C, 51.05; H, 2.46; S, 11.64.

Ultraviolet–visible spectrum showed λ_{max}^{HOAc} 265 mμ (log ϵ 4.60), 290 (4.08) (sh), 304 (3.98), 321 (3.52) (sh), 424 (3.30), 652 (2.34), 692 (2.32) (sh).

Benzo[c]thioxanthene (22).—A stirred solution of 6.56 g (0.025 mole) of benzo[c]thioxanthen-7-one (21)[15,17] and 3.50 g (0.088 mole) of sodium borohydride in 250 ml of pyridine was refluxed for 20 hr. The reddish brown solution was concentrated to 50 ml then poured into water, cautiously neutralized with 10% sulfuric acid, and then extracted with two 100-ml portions of benzene. The benzene layers were combined, washed successively with 100-ml portions of 10% sulfuric acid, water, and 5% sodium bicarbonate, then dried over magnesium sulfate, filtered, and evaporated to dryness. The residual orange oil was extracted into boiling 95% ethanol until only a red, insoluble material remained; then the extract was filtered (charcoal) and treated hot with water until the solution became cloudy. The pale orange crystals which separated on cooling weighed 2.15 g (34%), mp 80–84°. Sublimation at 80° (0.1 mm) followed by recrystallization from 95% ethanol gave colorless crystals, mp 86–87.5°.

Anal. Calcd for C$_{17}$H$_{12}$S: 82.22; H, 4.87; S, 12.91. Found: C, 82.01; H, 4.90; S, 12.87.

12-Thiabenz[a]anthracenium (11) Perchlorate.—A solution of 2.35 g (0.0095 mole) of o-chloranil in 10 ml of acetic acid was added, at room temperature, to a solution of 2.35 g (0.0095 mole) of 22 in 50 ml of acetic acid. After standing for 10 min the dark brownish red solution was cooled and 8 ml of 70% perchloric acid was added dropwise with stirring. After being stirred for an additional 0.5 hr the resulting red precipitate was collected by filtration and dried to yield 1.26 g (37%) of product, mp 208–213° dec. A second crop of red crystals (0.80 g, 24%, mp 190–201° dec) was obtained on treatment of the liquors with dry ether. Repeated recrystallization of a sample from acetic acid gave an analytical sample as dark red microcrystals, mp 220–222° dec.

Anal. Calcd for C$_{17}$H$_{11}$ClO$_4$S: 58.88; H, 3.20; S, 9.25. Found: C, 58.75; H, 3.41; S, 9.21.

Ultraviolet–visible spectrum showed $\lambda_{max}^{1\%\ HClO_4\ in\ MeCN}$ 239 mμ (log ϵ 4.58), 265 (4.32), 289 (4.23) (sh), 302 (4.50), 314 (4.76), 381 (4.02), 428 (4.03), 482 (3.58) (sh), 508 (3.53) (sh).

Benzo[a]thioxanthen-12-one (24).—This method was adapted from procedures described by Campaigne and Heaton.[29]

A mixture of 21.0 g (0.075 mole) of 2-(2-naphthylthio)benzoic acid (23),[20] 0.5 ml of dry pyridine, 40 ml of dry ether, and 19.0 g (11.6 ml, 0.160 mole) of thionyl chloride, added in that order, was refluxed on a water bath for 45 min. After the ether was removed at atmospheric pressure, 40 ml of dry benzene was added and distilled off, followed by another 30-ml portion of benzene to make certain of removal of the excess thionyl chloride. The residual oil was then dissolved in 60 ml of dry benzene and the solution was cooled to 2°. The first of two precooled (2°) solutions of 10 ml of stannic chloride in 10 ml of benzene was then added in one portion, the temperature rising to 45°. When the mixture had cooled to 20° the remaining stannic chloride solution was added, no temperature rise being noted. After 20 min at room temperature the reddish yellow mixture was poured into a

stirred mixture of 350 g of ice and 200 ml of concentrated hydrochloric acid. After the benzene had melted, the organic layer was separated, the water layer was extracted twice with 100-ml portions of benzene, and the organic layers were combined. The benzene solution was washed with 100 ml of 5% sodium bicarbonate solution followed by 100 ml of water and dried over magnesium sulfate and the benzene was then removed *in vacuo.* The resulting yellow solid was recrystallized from 1 l. of 95% ethanol to yield 17.5 g (89%) of yellow plates, mp 128–130°. An analytical sample recrystallized twice from ethanol and sublimed twice at 110° (0.1 mm) had a melting point of 131–133°.

Anal. Calcd for C$_{17}$H$_{10}$OS: C, 77.84; H, 3.84; S, 12.22. Found: C, 77.57; H, 3.85; S, 12.03.

Reduction of Benzo[a]thioxanthen-12-one (24) with Sodium Borohydride in Methanol Solution.—A solution of 2.50 g (0.066 mole) of sodium borohydride and 1 drop of 50% sodium hydroxide solution in 20 ml of water was added, over a period of 30 min, to a stirred slurry of 4.00 g (0.0153 mole) of 24 in 200 ml of refluxing methanol. The solution was refluxed for an additional 10 min, concentrated to approximately 60 ml and then diluted to 200 ml with water. The gummy yellow crystals were collected and air dried to yield 2.4 g of product, which sintered *ca.* 90°, but melted mainly at 215–225° to a red liquid. Repeated recrystallization from acetone gave material which melted at *ca.* 230°. A constant melting point, however, could not be obtained. The fact that the product contained benzo[a]thioxanthen-12-ol was shown by formation of a red solid when the product was treated with mineral acids. Analysis, however, indicated a mixture of alcohol 25 and benzo[a]thioxanthene (26).

Anal. Calcd for C$_{17}$H$_{12}$OS: C, 77.24; H, 4.58; S, 12.13. Calcd for C$_{17}$H$_{12}$S: C, 82.22; H, 4.87; S, 12.91. Found: C, 79.34; H, 4.70; S, 12.33.

7-Thiabenz[a]anthracenium (10) Perchlorate.—One and one-tenth grams of the mixture of benzo[a]thioxanthene (26) and benzo[a]thioxanthen-12-ol (25), obtained by hydride reduction of 24, and 1.52 g of trityl perchlorate in 15 ml of nitromethane was refluxed for 15 min. The solution was cooled and the dark red crystals (mp 280–285° dec) were collected and dried *in vacuo.* A second crop obtained by treatment of the liquors with ether melted at 276–279° dec. The total crude yield was 1.40 g. Recrystallization twice from 4:1 acetic acid–nitromethane gave 0.70 g of dark red needles, mp 287–289° dec.

Anal. Calcd for C$_{17}$H$_{11}$ClO$_4$S: C, 58.88; H, 3.20; S, 9.25. Found: C, 58.69; H, 3.29; S, 9.14.

Ultraviolet–visible spectrum gave $\lambda_{max}^{1\%\ HClO_4\ in\ MeCN}$ 246 mμ (log ϵ 4.44), 272 (4.39), 300 (4.49), 311 (4.67), 454 (4.15).

(29) E. Campaigne and B. G. Heaton, *J. Org. Chem.*, **29**, 2372 (1964).