

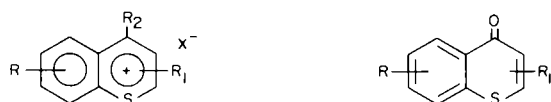
NMR Spectral Evidence for the 4-Hydroxy-1-benzothiopyrylium Ion (Ia)

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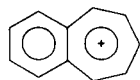
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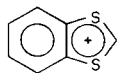
In connection with related research from our laboratory (2) this note presents several significant observations regarding nmr spectral data for a variety of substituted 4-hydroxy-1-benzothiopyrylium trifluoroacetates (I) as a probe into the question (3) of pseudo-heteroaromaticity



I: $R_2 = \text{OH}$, $X = \text{CF}_3\text{COO}^-$
 II: $R_2 = \text{H}$, $X = \text{ClO}_4^-$



IV



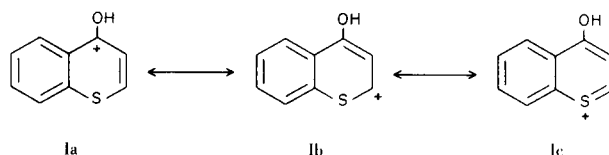
V

for the 10 π -electron benzothiopyrylium salts (e.g., II), which are part of a series of isoelectronic non-benzenoid aromatic systems including IV (4) and V (5). The compounds of interest (I) did not require isolation and could be observed directly in trifluoroacetic acid (TFA) as a consequence of the recognized (6) facility with which the readily available (7) precursor thiochromones (III) undergo carbonyl protonation forming species of type I.

Upon examination of Table I several trends, in addition to the *peri*-effect (8) of the 5-hydrogen, become apparent. In all cases, when the spectra in TFA are compared to those in deuteriochloroform, the protons and methyl groups on the thiopyrone ring are shifted downfield to a greater extent than those of the benzene ring (*cf.*, VII) and in those compounds which possess a 3-hydrogen (VI, VII, VIII) this resonance becomes indistinguishable from the remaining benzene aromatic protons including the 2-phenyl of VIII. Additionally, and of considerable significance, is the fact that the 3-methyl and 6-methyl of X become equivalent in TFA while the 2-methyl is deshielded to a greater degree than the 3-methyl indicating a greater localization of the positive charge on the 2-

carbon and/or sulfur consistent with related observations of Young and Ohnmacht (9). It is also interesting that in TFA the 2-methyl of VII becomes a singlet and is no longer conjugated with the 3-hydrogen (10).

From these observations the data seems best accommodated by suggesting that compounds of type III in TFA can satisfactorily be represented by a series of resonance structures (Ia, Ib and Ic; R groups and counterion trifluoroacetate omitted for simplicity) in which a greater



proportion of the positive charge is localized within the sulfur containing ring and, even more explicitly, to a greater extent on the 2-carbon and/or sulfur atom (Ib and Ic). However, the existence of definite deshielding, relative to the deuteriochloroform spectra, within the benzene portion of the molecule as well as a merging of the 3-hydrogen with the benzene protons stipulates that a 10 π -electron heteroaromatic system of the type I should not and cannot be wholly ruled out in favor of Ia, Ib or Ic or any of their hybrids.

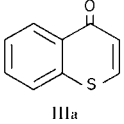
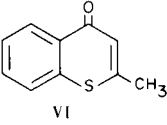
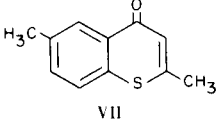
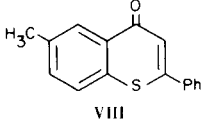
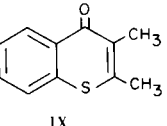
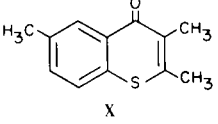
For reference purposes Table II contains nmr data for a variety of related thiochromanones which also exhibit some interesting properties, the interpretation of which must await additional study.

EXPERIMENTAL (13)

4-Thiochromones.

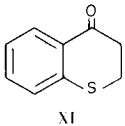
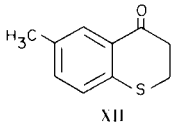
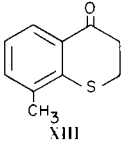
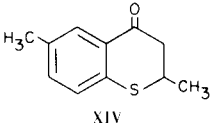
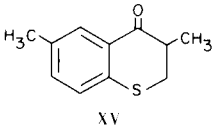
The procedure utilized was adapted from Bossert (7) by warming a polyphosphoric acid (600 g.) solution of equimolar amounts of benzenethiol or *p*-toluenethiol and the desired substituted ethyl acetoacetate on a steam bath for 45 minutes. The brown solution was poured into 1 l. of water at room temperature and allowed to stand overnight. The product was filtered and recrystallized from benzene, benzene-petroleum ether or ethanol as white plates. Compounds V, VI, VII, VIII and IX were

TABLE I
NMR Data for Thiochromones (11)

Compound	Chemical Shift, δ in ppm (12)		Assignment
	CDCl ₃	TFA	
 IIIa	7.00 (d) (a) 6.83 (d) (a) 6.55 (m) 8.54 (m)		2-H 3-H 6-H, 7-H, 8-H 5-H
 VI		3.04 (s) 7.91-8.13 (m) 8.58-8.74 (m)	2-CH ₃ 3-H, 6-H, 7-H, 8-H 5-H
 VII	2.31 (d) (b) 2.38 (s) 6.71 (q) (b) 7.26 (b,d) (c) 8.21 (b) (c)	3.09 (s) 2.70 (s) 7.93-8.18 (m) 8.60-8.65 (b,s) (c)	2-CH ₃ 6-CH ₃ 3-H 7-H, 8-H 3-H, 7-H, 8-H 5-H
 VIII	2.43 (s) 7.18 (s) 7.34-7.70 (m) 8.30 (b) (c)	2.70 (s) 7.59-8.29 (m) 8.64-8.68 (b,s) (c)	6-CH ₃ 3-H 7-H, 8-H, 2-Ph 3-H, 7-H, 8-H, 2-Ph 5-H
 IX	2.16 (s) 2.30 (s) 7.31-7.52 (m) 8.28-8.50 (m)	2.71 (s) 3.07 (s) 7.95-8.28 (m) 8.75-8.92 (b,s) (c)	3-CH ₃ 2-CH ₃ 6-H, 7-H, 8-H 5-H
 X	2.17 (s) 2.30 (s) 2.40 (s) 7.29 (b,s) (c) 8.23 (b,s) (c)	3.07 (s) 2.68 (s) 7.96-8.08 (m) 8.58-8.70 (m)	3-CH ₃ 2-CH ₃ 6-CH ₃ 3-CH ₃ , 6-CH ₃ 7-H, 8-H 5-H

(a) $J = 8$ Hz. (b) $J = 1$ Hz. (c) b = broad.

TABLE II
NMR Data for Thiochromanones (11)

Compound	Chemical Shift, δ in ppm (12)		Assignment
	CDCl ₃	TFA	
 XI	2.80-3.35 (m) 6.98-7.40 (m) 7.92-8.11 (m)		2-H, 3-H 6-H, 7-H, 8-H 5-H
 XII	2.30 (s) 2.75-3.32 (m) 7.25 (d) (a) 7.89 (b,s) (e)	2.32 (s) 3.04-3.12 (b,t) (e) 6.97-7.32 (m) 7.82 (b,s)	6-CH ₃ 2-H, 3-H 7-H, 8-H 5-H
 XIII	2.30 (s) 2.76-3.30 (m) 7.00-7.21 (m) 7.89-8.03 (m)		6-CH ₃ 2-H, 3-H 6-H, 7-H 5-H
 XIV	1.37 (d) (b) 2.31 (s) 2.67-2.90 (d) (c) 3.17-3.83 (m) 7.11 (d) (d) 7.88 (b,s) (e)	1.41 (d) (b) 2.32 (s) 2.79-3.78 (m) 7.01-7.40 (m) 7.88 (b,s) (e)	2-CH ₃ 6-CH ₃ 3-H 2-H 2-H, 3-H 7-H, 8-H 5-H
 XV	1.28 (m) 2.23 (s) 2.62-3.22 (m) 7.00 (d) (d) 7.72 (d) (d)		3-CH ₃ 6-CH ₃ 2-H, 3-H 7-H, 8-H 5-H

(a) $J = 2$ Hz. (b) $J = 7$ Hz. (c) $J = 4$ Hz. (d) $J = 1$ Hz. (e) $b = \text{broad}$.

prepared by this route and found to possess m.p. data identical to those reported (7).

2,3,6-Trimethyl-4-thiochromone (X).

Prepared by the scheme outlined above using ethyl α -methylacetoacetate led to the isolation of white plates, m.p. 95-97°, recrystallizable from benzene in 59% yield.

Anal. Calcd. for C₁₂H₁₂SO: C, 70.58; H, 5.92; O, 7.84. Found: C, 70.83; H, 5.92; O, 8.04.

4-Thiochromanones.

4-Thiochromanone (XI) (14), 6-methyl-4-thiochromanone (XII) (14,15), 8-methyl-4-thiochromanone (XIII) (16) and 2,6-dimethyl-4-thiochromanone (XIV) (17) were prepared by cyclizing the appropriate 3-arylpropionic acid (2) with sulfuric acid.

3,6-Dimethyl-4-thiochromanone (XV).

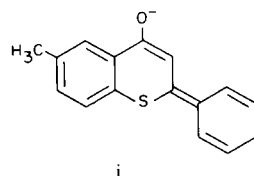
An equimolar amount of XII and sodium hydride were mixed in 75 ml. of cold, anhydrous benzene. The solution was kept

cold and stirred for 1 hour following the mixing after which time an equimolar amount of methyl iodide was added and the stirring continued for 1 hour at room temperature and then refluxed for 5 hours. After allowing the solution to cool, it was washed with dilute sulfuric acid, dilute sodium bicarbonate, and finally, water resulting in a yellow benzene solution. Following drying over anhydrous sodium sulfate, evaporation of the benzene yielded an oil which distilled as a colorless liquid (40%), b.p. 115/0.12 mm.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.74; H, 6.25; O, 8.33. Found: C, 68.60; H, 6.40; O, 8.40.

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- (1a) Contribution No. 1999 from the Chemical Laboratories of Indiana University. We gratefully acknowledge support of this investigation by a research grant (GM-31959) to S. W. S. and by a grant (GM-10366) to Indiana University from the National Institutes of Health. (b) Taken in part from a thesis submitted in partial fulfillment of the requirements for the Ph. D. degree by S. W. S., Indiana University, June, 1968. (c) Address correspondence to this author: Department of Chemistry, University of South Florida, Tampa, Florida 33620.
- (2) E. Campaigne, H. R. Burton, C. D. Blanton, Jr., and S. W. Schneller, *J. Heterocyclic Chem.*, **8**, 65 (1971).
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- (5) E. Campaigne and R. D. Hamilton, *Quart. Rep. Sulfur Chem.*, **5**, 275 (1970).
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- (10) Another noteworthy observation but not directly related to the above discussion is the presence of a deshielding effect exerted by the 2-phenyl of VIII upon the 3-hydrogen in deuteriochloroform indicating that the 2-phenyl must possess some coplanarity with the entire ring system (e.g., i).



- (11) Spectra were determined on a Varian A-60 Spectrometer in deuteriochloroform and trifluoroacetic acid with tetramethylsilane as an internal standard at ambient probe temperatures.
- (12) Multiplicity designated as s, d, t, q and m represents singlet, doublet, triplet, quartet and multiplet, respectively.
- (13) Melting points were taken on a Mel-Temp capillary melting point apparatus and were corrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana.
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- (16) C. D. Hurd and S. Hayao, *J. Am. Chem. Soc.*, **76**, 5065 (1954).
- (17) French Patent 1,365,504, July 3, 1964 to J. R. Boissier and C. Malen; *Chem. Abstr.*, **61**, 14642d (1964).