^{13}C Nuclear Magnetic Resonance Spectra of Organic Sulfur Compounds: Cyclic Sulfides, Sulfoxides, Sulfones, and Thiones

M. S. CHAUHAN AND I. W. J. STILL

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1

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^{13}C Chemical shift data have been obtained for more than 50 thiochromanone and related sulfoxide and sulfone derivatives. The assignments of the various resonances in the most important of these have been made using the limited data already available and also by comparison with certain model compounds, such as thioanisole, diphenyl sulfide, and the corresponding sulfoxides and sulfones.

Within each of these three series and in a fourth which comprises derivatives of thiochromone, including three α,β-unsaturated thiones, we have examined the effects on ^{13}C chemical shift of substitution at various positions in the thiochromanone skeleton. Among the substituents examined in this context are methyl, phenyl, methoxyl, bromine, and carbomethoxyl. Attempts to compare the ^{13}C chemical shifts for the thiochromanone series with those in a few oxygen containing analogs and in a small number of structurally similar analogs are also discussed.

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On a déterminé les déplacements chimiques du ^{13}C de plus de 50 thiochromanones ainsi que des sulfoxydes et sulfones correspondantes. On a attribué les positions principales de résonance en faisant appel aux quelques données disponibles et aussi par comparaison avec divers composés modèles comme le thioanisole et le sulfure de diphényle ainsi que les sulfoxydes et les sulfones correspondantes.

Dans chacune de ces trois séries et dans une quatrième comprenant des dérivés de la thiochromone incluant trois thiones α,β non-saturées, on a examiné les effets, sur le déplacement chimique du ^{13}C, de substitutions à diverses positions sur le noyau thiochromanone. Dans ce contexte, on a examiné l'influence des substituants méthyle, phényle, méthoxyle, bromure et carbométhoxyle. On discute des essais que nous avons faits afin de comparer les déplacements chimiques du ^{13}C dans la série de la thiochromanone avec ceux de quelques analogues contenant de l'oxygène et d'un petit nombre d'analogues de structures similaires.

[Traduit par le journal]

Our recent application of ^{13}C n.m.r. chemical shifts to the elucidation of the structure of an unusual rearrangement product from the base-catalyzed methylation of 3-methylthiochroman-4-one (1) demonstrated to us the scarcity of ^{13}C n.m.r. data for even the most common types of sulfur-containing functionality. By way of an example, one (3) of several excellent introductory texts on ^{13}C n.m.r. to appear recently (2–4) contains 500 spectra but reports data for only one sulfone, one thione, and not one sulfoxide. The availability in our laboratory of a considerable number of sulfides, sulfoxides, and sulfones which had been synthesized as part of a continuing investigation of the photochemical behavior of such compounds (5–7) prompted us to undertake an extensive compilation of ^{13}C n.m.r. data for these compounds, and a few related thiones, under identical experimental conditions, the results of which we now wish to discuss.

Experimental

The i.r. spectra were recorded as neat films or Nujol mulls on a Perkin-Elmer 337 grating spectrophotometer and the u.v. spectra on a Unicam SP8000 instrument. ^1H Nuclear magnetic resonance spectra were recorded on Varian T-60 or HA-100 spectrometers with tetramethylsilane (TMS) as internal reference. Mass spectra were recorded on a Bell and Howell 21-490 spectrometer and accurate mass measurements on the A.E.I. MS-902 machine. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Box 25, Herlev, Denmark or by A. B. Gygli, 329 St. George St., Toronto. All melting and boiling points are uncorrected. Satisfactory spectral and analytical data were obtained for all new compounds.

The ^{13}C n.m.r. spectra were obtained in 12–15% $CDCl_3$ solution for natural abundance compounds on a Varian Associates XL-100-15 instrument at 25.16 MHz, with approximately 5% TMS added as internal reference. The deuterium of the solvent was used as lock and primary reference and the chemical shifts were obtained from listings supplied by the 16K-620i computer, with an accuracy of ±0.1 p.p.m. Normal operating conditions included an acquisition time of 0.9 s/transient with a delay of 0.3 s and a routine spectral width of 6000 Hz, at an r.f. pulse width of 35 μs and a probe temperature of

32 ± 3 °C. Off-resonance proton decoupled spectra were obtained for all compounds. Of the model compounds for which data are recorded in Table 1, the diphenyl sulfide, sulfoxide, and sulfone were used as commercially supplied. Thiobenzophenone was prepared from benzophenone by refluxing with P_2S_5 in toluene.

Thiochroman-4-one (now commercially available) and its 5-, 6-, 7-, and 8-methyl analogs, as well as the 6-methoxy derivative were all prepared by the base-catalyzed reaction of the appropriate benzenethiol with β-propiolactone, followed by ring closure of the resulting acid with concentrated sulfuric acid (5). The preparation of the 2- and 3-methyl and the 2- and 3-methoxycarbonyl analogs of **1**, and of isothiochromanone **4** also followed our previously outlined procedures (5). The preparation of 3-bromothiochroman-4-one (8), thiochroman-3-one (9), and 2-phenylthiochroman-4-one (10) closely followed the literature methods, although a modified procedure for 6-methyl-2-phenylthiochroman-4-one is described below. 3,3-Dimethylthiochroman-4-one was prepared by methylation of **1** with sodium hydride – methyl iodide, and similar methylation of isothiochroman-4-one and of 2,2-dimethylthiochroman-4-one produced 3,3-dimethylisothiochromanone and 2,2,3,3-tetramethylthiochroman-4-one respectively.

2,2-Dimethylthiochroman-4-one

A mixture of thiophenol (30 g), β,β-dimethylacrylic acid (20 g) and hydrobromic acid in acetic acid (30%, 100 ml) was heated under reflux for 12 h after which it was diluted with water and extracted with ether. The ether extract was washed, dried, and evaporated. The oil obtained was distilled under reduced pressure. Distillate collected up to 120 °C (2 Torr) was discarded. This was found to be a mixture of thiophenol and some products arising from reactions of the unsaturated acid. The temperature was maintained at 120 °C until no more distillate collected. The residue in the flask was cooled, extracted with ether and the ether solution was then extracted four times with saturated sodium bicarbonate solution. The bicarbonate extracts were combined, acidified with concentrated hydrochloric acid, and the precipitated acid was extracted with ether, washed, and dried. The product (17.6 g, 42%) obtained on evaporation of the solvent was recrystallized from petroleum ether, m.p. 60–61 °C. Infrared 3300–2500, 1705 cm^{-1}; n.m.r. δ 1.4 (s, 6H), 2.55 (s, 2H), 7.15–7.65 (m, 5H), 12.9 (s, 1H) p.p.m. This acid, 3-methyl-3-phenylthiobutanoic acid, was cyclized to 2,2-dimethylthiochroman-4-one by the following procedure.

The acid (15.5 g) was dissolved in dry benzene (60 ml). A paste of phosphorus pentoxide (25 g) and Hyflo Super Cel (15 g) was prepared with dry benzene (80 ml) and the paste was added in small amounts to the solution of the acid with stirring. The mixture was then heated under reflux at 100 °C for 5 h, stirring all the time. The solution was filtered and the residue was extracted with boiling benzene three times. The benzene solutions were combined, washed with water, sodium hydroxide solution, and again water, dried and evaporated. The oil so obtained crystallized (8.0 g, 56%) and was recrystallized from petroleum ether, m.p. 44–45 °C Infrared, 1680, 1590, and 1315 cm^{-1}; n.m.r. δ 1.45 (s, 6H), 2.85 (s, 2H), 7.25 (m, 3H), 8.15 (br d, 1H) p.p.m.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.73; H, 6.29; S, 16.64. Found: C, 68.49; H, 6.29; S, 16.65.

6-Methyl-2-phenylthiochroman-4-one

A mixture of *p*-thiocresol (30 g), methyl cinnamate (33 g), absolute ethanol (100 ml), and piperidine (4.0 g) was heated under reflux at 100 °C for 72 h. The unreacted thiocresol was removed from the mixture by steam distillation. Hydrochloric acid (6 *N*) (350 ml) and acetone (20 ml) were then added and the mixture was heated under reflux for 12 h; on cooling, crystals of the acid, 3-[*p*-methylphenylthio]hydrocinnamic acid, were formed. The product was filtered off and purified by dissolving it in saturated sodium bicarbonate solution and reprecipitating with concentrated hydrochloric acid. Recrystallization from petroleum ether – benzene gave the pure product (28 g, 52%), m.p. 106–107 °C, lit. (8) m.p. 106 °C.

The acid (13 g) was mixed with phosphorus oxychloride (60 g) and heated on a steam bath for 25 min after which the mixture was cooled and then poured over ice. Extraction with ether gave an impure product (8 g, 66%) which was recrystallized from ethanol, m.p. 95–96 °C, lit. (8) m.p. 96 °C. Infrared 1670, 1600, 1465, 1400, 1300, 1280 cm^{-1}; n.m.r. δ 2.30 (s, 3H), 3.2 (m, 2H), 4.65 (m, 1H) 7.15–7.45 (m, 7H), 8.0 (m, 1H) p.p.m.

2,3-Dimethylthiochroman-4-one

A mixture of tiglic acid (2-methyl-*cis*-2-butenoic acid) (15.0 g), thiophenol (12.0 g), and piperidine (6 drops) was heated at 170–180 °C for 12 h and then distilled under vacuum to remove unreacted thiophenol and tiglic acid. The fraction collected at b.p. 170–172 °C/0.5 Torr was the required acid (23.0 g, 85%). Infrared 3600–2500, 1700 cm^{-1}; n.m.r. δ 1.17–1.40 (m, 6H), 2.62 (m, 1H), 3.51 (m, 1H), 7.10–7.57 (m, 5H), 11.65 (br s, 1H) p.p.m.

The thioacid (5.0 g) and concentrated sulfuric acid (40 g) were kept at room temperature for 4 h. The viscous reddish brown mixture was poured over ice and the solution extracted with ether. The combined ether extracts were dried ($MgSO_4$) and then evaporated. The residue was chromatographed on silica, elution with benzene affording 2,3-dimethylthiochromanone (3.0 g, 64%). Infrared 1670 cm^{-1}; n.m.r. δ 1.14–1.47 (m, 6H), 2.33–3.74 (m, 2H), 6.84–7.42 (m, 3H), 7.99 (br d, 1H) p.p.m.

1-Thiaindan-3-one (6)

This was prepared essentially by the route described in the literature (11, 12) via cyclization of the acid chloride of *S*-phenylthioglycolic acid (prepared from thiophenol and bromoacetic acid in alkali) using aluminum chloride as the catalyst. Yields of the acid chloride (attempted with various chlorinating agents) and of the final product were invariably poor. The product was recrystallized from *n*-hexane – petroleum ether as a pink solid, m.p. 67–69 °C (lit. (13) m.p. 71 °C), which rapidly turned purple if allowed to stand at room temperature. Infrared 1665 cm^{-1}; n.m.r. δ 3.7 (s, 2H), 6.95–7.55 (m, 3H), 7.6–7.85 (m, 1H) p.p.m.

The preparations of thiochromone **7***a* and of 4*H*-thiochromene-4-thione **9** described below illustrate the general methods also used to prepare the 2- and 3-methyl and the 2,3-dimethyl analogs of **7***a*, and the other thiones listed in Table 3, respectively.

Thiochromone (7a) (14)

The crude red triphenylmethyl perchlorate (prepared just before use by dissolving triphenylmethanol (13.0 g) in 60% perchloric acid (50 ml), warming briefly, cooling, and filtering) was added to thiochroman-4-one (6.0 g) in

TABLE 1. Carbon-13 chemical shifts[a] and aromatic shielding parameters[b] of model compounds

Compound[c]	C-1	C-2, 6(*o*)	C-3, 5(*m*)	C-4(*p*)
Thioanisole (3)	138.6[d]	126.6	128.7	124.9
(—S—)	(+10.0)	(−2.0)	(+0.1)	(−3.7)
Diphenyl sulfide	135.8	131.0	129.1	127.0
(—S—)	(+7.2)	(+2.4)	(+0.5)	(−1.6)
Methyl phenyl sulfoxide	145.9[e]	123.4	129.7	130.8
(—SO—)	(+17.3)	(−5.2)	(+0.6)	(+2.2)
Diphenyl sulfoxide	145.7	124.7	129.2	131.0
(—SO—)	(+17.1)	(−3.9)	(+0.6)	(+2.4)
Methyl phenyl sulfone	140.6[f]	127.1	129.3	133.6
($—SO_2—$)	(+12.0)	(−1.5)	(+0.7)	(+5.0)
Diphenyl sulfone	141.6	127.6	129.3	133.2
($—SO_2—$)	(+13.0)	(−1.0)	(+0.7)	(+4.6)
Thiobenzophenone	147.2	129.5	127.9	131.9
(—CS—)	(+18.6)	(+0.9)	(−0.7)	(+3.3)

[a]In p.p.m. downfield from TMS. [b]In p.p.m. from benzene (128.6). Positive value indicates a downfield shift, relative to TMS. [c]In $CDCl_3$ solution. [d]Methyl, 15.6q. [e]Methyl, 43.7q. [f]Methyl, 44.2q.

glacial acetic acid (60 ml). After addition of acetic anhydride (9 ml) an exothermic reaction occurred and the mixture was then boiled for 10 min before cooling in ice and filtering off the yellow 4-hydroxy-1-thiobenzo[*b*]pyrylium perchlorate. This salt, after being washed with anhydrous ether, was stirred briefly with saturated sodium bicarbonate solution and the liberated thiochromone filtered off in almost quantitative yield. Recrystallization from petroleum ether – benzene (4:1) gave white prisms, m.p. 78–80 °C, lit. (8) m.p. 78 °C. Infrared 1635, 1590 cm^{-1}; u.v. $\lambda_{max}^{CH_3OH}$ 248 (ε, 11 100), 256sh (ε, 10 900), 280 (ε, 4300), 333 (ε, 9500) nm; n.m.r. δ 6.9 (d, J = 10 Hz, 1H), 7.8 (d, J = 10 Hz, 1H) 7.5–7.6 (m, 3H), 8.4–8.6 (m, 1H) p.p.m.

4H-Thiochromene-4-thione (9)

Thiochromone (3.24 g) was refluxed in dry benzene for 4 h with phosphorus pentasulfide (4.45 g). The red solution was cooled, filtered, and the solvent evaporated. The crude residue was extracted with boiling petroleum ether (60–80 °C). Filtration of the hot solution and concentration gave red crystals of the thione (2.89 g, 81%), m.p. 90–91 °C, lit. (15) m.p. 91 °C. Infrared 1150 cm^{-1} (C=S); u.v. $\lambda_{max}^{CH_3OH}$ 236 (ε, 16 000), 289 (ε, 6450), 405 (ε, 15 400) nm; n.m.r. δ 7.3 (d, J = 9 Hz, 1H), 8.1 (d, J = 9 Hz, 1H), 7.5–7.7 (m, 3H), 8.9–9.1 (m, 1H) p.p.m.

Using the general procedure illustrated below for the case of 3-methylthiochroman-4-one we have experienced no difficulty in converting the thiochromanones into the corresponding sulfoxides in yields (isolated) ranging from 43–90% with virtually no contamination by the corresponding sulfones. Similarly, the general procedure previously described (5) converted the sulfides into the corresponding sulfones in isolated yields of 42–91%.

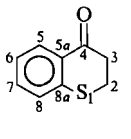
3-Methylthiochroman-4-one 1-oxide

A solution of 3-methylthiochroman-4-one (9.0 g) in acetic acid (35 ml) was cooled in an ice bath and 30% hydrogen peroxide (6.4 g) was added slowly with stirring. The mixture was allowed to remain for 12 to 16 h at 25 °C before dilution with water and extraction with ether to remove unreacted sulfide. Extraction with methylene chloride, followed by washing ($NaHCO_3$, water) and drying gave the sulfoxide (6.0 g, 66%). Final purification was achieved by chromatography on silica (eluting with 30% acetone – methylene chloride) and recrystallization from *n*-hexane–benzene, m.p. 116–117 °C. Infrared 1689, 1031 cm^{-1}.

Anal. Calcd. for $C_{10}H_{10}O_2S$: C, 61.86; H, 5.15; S, 16.49. Found: C, 61.64; H, 5.17; S, 16.62.

Results and Discussion

Carbon-13 chemical shift data for a series of cyclic keto-sulfides derived mainly from thiochroman-4-one (**1**) and including also the isomeric isothiochromanone (**4**) and thiochroman-3-one (**5**), as well as 1-thiaindan-3-one (**6**) and the oxime derived from **1**, are collected in Table 2. A number of other oximes were also available but their insolubility in $CDCl_3$ rendered them unsuitable for the present study. The simple oxygen analogs of **1** and of thioflavanone (**3***a*) (chromanone (**2**) and flavanone (**3***b*)) are also included to provide some comparisons between S- and O-series of compounds.



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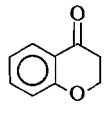

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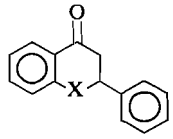
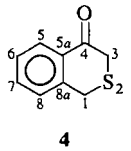


3*a* X = S
3*b* X = O



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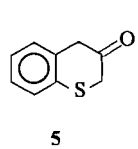

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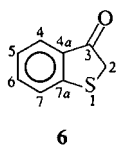
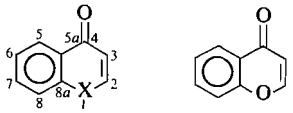


6

The assignments of the six aromatic chemical shifts in thiochroman-4-one were made using the

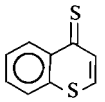
aromatic shielding parameters of the $COCH_3$ group (2) and by subtracting from the various chemical shifts of thioanisole (3) (Table 1) the chemical shift of benzene, which was 128.6 p.p.m. under the present conditions. This rather simplifying assumption gave remarkably good agreement between theory and prediction for the four unsubstituted carbons, C-5 to C-8, none of the deviations exceeding 1.0 p.p.m. Not unexpectedly, as other authors have noted (16), the agreement between prediction and observation for C-5*a* and C-8*a* was much poorer, the deviations being 4.8 and 3.4 p.p.m., respectively. The relative lack of data for the shielding parameters of sulfur-containing substituents as compared to the carbonyl substituent and the presence of the second (heterocyclic) ring may account for this result. Results from the 6-methyl and 6-methoxy analogs, however, reveal *para*-substituent effects of −3.3 and −8.7 p.p.m. respectively and give excellent corroboration of the correctness of the C-5*a* and C-8*a* assignments in **1**. A similar procedure was carried out for chromanone using the well documented aromatic shift parameters for $COCH_3$ and OCH_3 (2) groups. The maximum deviation observed was 3.6 p.p.m. (for C-8), while the agreement for the ring fusion carbons C-5*a* and C-8*a* was very good in this case, neither of the deviations exceeding 2.0 p.p.m. The assignment of the resonance at 26.2 to C-2 and that at 39.5 p.p.m. to C-3 in thiochromanone was obvious from an examination of the chemical shifts in tetrahydrothiophene, cyclopentanone and cyclopentane, as well as being in accord with the substituent effects produced in the C-2 and C-3 methylated analogs.

The 2-methyl, 3-methyl, 2,2-dimethyl, and 3,3-dimethyl analogs of **1** were also examined in the analogous sulfoxide (Table 5) and sulfone (Table 6) series and the substituent effects have been compared in Table 7 for all three series. Generally speaking, methyl substitution at C-2 produces a more pronounced downfield shift at that carbon than does methyl substitution at C-3, α to the carbonyl group. Roberts and Weigert (17) observed this effect in simple methylcyclohexanones. As Table 7 reveals, however, there are a number of curious variations in the methyl substituent effect pattern and the likelihood that the heterocyclic ring may exist in both the half-chair and the sofa conformations, as well as the widely different electronic effects of S, SO, and SO_2 and the existence of diastereomeric sulfoxides (in some cases) make rationalization difficult. As expected, substitution of methyl (or phenyl) groups on C-2 or C-3 has in general no significant influence on the chemical shifts of C-5*a*, C-8*a* or the carbonyl carbon (C-4). The one exception to this is in the downfield shift of the carbonyl carbon in the 3-methyl compound (+2.4 p.p.m.) and in the 3,3-dimethyl compound (+4.5 p.p.m.). The shift of the carbonyl carbon on going from cyclohexanone to 2-methylcyclohexanone is +1.5 p.p.m. Significant shifts in the position of the carbonyl carbon were noted in thiochroman-3-one (**5**), where the downfield shift is attributable to the loss of conjugation with the aromatic ring, and in 1-thiaindan-3-one (**6**), where the downfield shift is due to the five-membered ring. In thiochroman-4-one oxime the C-2 and C-3 signals had almost identical chemical shifts and the C-4 carbon appeared in the normal range for oximes (2) at 153.6 p.p.m.



7*a* X = S
7*b* X = SO_2

8



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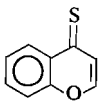


10

The 10 compounds appearing in Table 3 under the generic heading 'thiochromones' strictly include only four members of that class of compound. However, the three thiones **9**, **10**, and the 2-phenyl analog of **10**, the thiochromone sulfone (**7***b*), and the oxygen analogs chromone (**8**) and flavone all possess as a common structural feature a double bond between C-2 and C-3 and furthermore all contain an α,β-unsaturated ketone (or thione) moiety in a six-membered ring, with an electron-withdrawing group (O, S, SO_2) attached to the β-carbon, and we have thus felt justified in treating them for the present purpose as a related group of compounds. Finding suitable model compounds is more difficult for this series, but at least for the ketone members of the series we have utilized the well-documented effects of α- and β-methyl substitution in 2-cyclohexen-1-one (2) and the generally much lower field position observed for the β-carbon in assigning the C-2 and C-3 resonances. In assigning the aromatic carbon reson-

TABLE 2. Carbon-13 chemical shifts[a] of cyclic sulfides (thiochromanones)

Compound[b]	C-2	C-3	C-4 (C=O)	C-5a	C-8a	C-5, 6, 7, 8
Thiochroman-4-one, **1**	26.6t	39.5t	193.8s	130.9s	142.1s	124.9d (C-6); 127.5d (C-8); 129.1d (C-5); 133.1d (C-7)
Chromanone, **2**	66.9t	37.7t	191.4s	121.4s	161.8s	117.8d (C-8); 121.2d (C-6); 127.0d (C-5); 135.8d (C-7)
2-Methyl-**1**[c]	36.2d	47.6t	193.9s	130.2s	141.6s	124.6d (C-6); 127.3d (C-8); 128.8d (C-5); 133.1d (C-7)
2,2-Dimethyl-**1**[d]	44.5s	53.8t	194.5s	129.7s	141.2s	124.6d (C-6); 127.5d (C-8); 128.6d (C-5); 133.5d (C-7)
3-Methyl-**1**[e]	33.0t	42.1d	196.2s	130.4s	141.8s	124.7d (C-6); 127.2d (C-8); 129.4d (C-5); 133.3d (C-7)
3,3-Dimethyl-**1**[f]	39.1t	40.9s	198.3s	129.5s	141.4s	124.8d (C-6); 127.1d (C-8); 130.0d (C-5); 132.7d (C-7)
2,3-Dimethyl-**1**[g] (cis- + trans-)	40.6, 41.7 d	46.9, 48.7 d	196.3, 196.7 s	129.7, 129.9 s	140.4, 140.8 s	124.6d (C-6); 127.0, 127.3d (C-8); 129.0, 129.3d (C-5); 133.0d (C-7)
6-Methyl-**1**[h]	26.7t	39.8t	194.3s	130.8s	138.8s	127.5d (C-8); 129.3d (C-5); 134.4d (C-7); 134.9s (C-6)
8-Methyl-**1**[i]	26.0t	39.1t	194.3s	131.1s	141.7s	124.1d (C-6); 126.9d (C-5); 134.3d (C-7); 135.4s (C-8)
6-Methoxy-**1**[j]	26.8t	39.6t	193.6s	131.5s	133.4s	111.3d (C-5); 121.9d (C-7); 128.7d (C-8); 157.3s (C-6)
2-Phenyl-**1** (thioflavanone, **3***a*)	45.4d	46.6t	194.0s	130.4s	142.0s	125.1–133.5d[k]; 138.4s (C-1′)
Flavanone, **3***b*	79.5d	44.6t	191.6s	120.9s	161.5s	118.0d (C-8); 121.5d (C-6); 126.1–128.7d[l]; 136.0d (C-7); 138.8s (C-1′)
1, oxime	26.3t[r]	26.0t[r]	153.6[m]	129.5s	136.3s	125.6–129.3d[r]
Isothiochromanone, **4**	30.5t[n]	37.0t	190.8s	131.8s	141.8s	127.7–128.9d[r]; 132.9d (C-7)
Thiochroman-3-one, **5**	46.5t	204.7s[o]	37.3t	132.8s	134.0s	127.0–129.0d[r]
1-Thiaindan-3-one, **6**	39.1t	199.8s[o]	—	130.9s[p]	155.2s[q]	124.6–126.5d[r]; 135.5s (C-6)

[a]In p.p.m. downfield from TMS; numbering of carbons as in **1**. [b]In $CDCl_3$ solution. [c]Methyl, 20.3q. [d]Methyls, 28.5q. [e]Methyl, 14.9q. [f]Methyls, 23.5q. [g]Methyls, 15.9, 19.9q(C-2); 11.1, 13.4q(C-3) [h]Methyl, 20.8q. [i]Methyl, 20.0q. [j]Methoxyl, 55.4q. [k]C-5, C-6, C-7, C-8, C-2′, C-3′, C-4′. [l]C-5, C-2′, C-3′, C-4′. [m]C=NOH. [n]C-1. [o]C=O. [p]C-4*a*. [q]C-7*a*.
[r]Individual assignments uncertain.

TABLE 3. Carbon-13 chemical shifts[a] of unsaturated cyclic sulfides (thiochromones)

Compound[b]	C-2	C-3	C-4 (C=O)	C-5*a*	C-8*a*	C-5, 6, 7, 8
Thiochromone, **7***a*	137.9d	126.6d	179.4s	132.2s	137.5s	125.7d (C-6); 127.7d (C-8); 128.5d (C-5); 131.4d (C-7)
Chromone, **8**	145.5d	113.0d	177.6s	125.0s	156.6s	118.3d (C-8); 125.3, 125.8d (C-5, C-6)[j]; 133.8d (C-7)
2-Methyl-**7***a*[c]	151.0s	124.6d	179.9s	130.5s	137.4s	125.9d (C-6); 127.3d (C-8); 128.2d (C-5); 131.2d (C-7)
3-Methyl-**7***a*[d]	132.7d	133.0s	179.3s	130.6s	137.4s	126.3d (C-6); 127.0d (C-8); 128.5d (C-5); 131.0d (C-7)
2,3-Dimethyl-**7***a*[e]	144.3s	129.8s	179.3s	130.7s	136.8s	125.3d (C-6); 126.9d (C-8); 128.9d (C-5); 130.5d (C-7)
2-Phenyl-**8** (flavone)	163.3s	107.6d	178.3s	124.0s	156.3s	118.1d (C-8); 125.2–131.6[f]d; 131.8s (C-1′); 133.7d (C-7)
Thiochromone1,1-dioxide, **7***b*	140.6d	132.2d	177.8s	128.2s	141.1s	123.1d (C-8); 128.5d (C-5); 133.0d (C-7); 135.0d (C-6).
4*H*-Thiochromene-4-thione, **9**	137.6d	131.4d	204.4s[g]	132.5s	138.4s	127.3–129.0[h]d; 132.0d (C-7)
4*H*-Chromene-4-thione, **10**	146.0d	126.2d	202.8s[g]	130.9s	151.4s	118.6d (C-8); 124.8d (C-6); 128.6d (C-5); 134.2d (C-7)
2-Phenyl-**10**	153.8s	120.1d	201.4s[g]	130.8s	151.3s	118.3d (C-8); 125.9-131.7[i]d; 129.7s (C-1′); 133.9d (C-7)

[a]In p.p.m. downfield from TMS; numbering of carbons as in **7***a*. [b]In $CDCl_3$ solution. [c]Methyl, 23.0q. [d]Methyl, 18.9q. [e]Methyls, 21.6q (C-2), 13.0q (C-3). [f]C-5, C-6, C-2′, C-3′, C-4′. [g]C=S. [h]C-5 C-6, C-8. [i]C-5, C-6, C-2′, C-3′, C-4′.
[j]Individual assignments uncertain.

TABLE 4. Shielding parameters[a] in α,β-unsaturated cyclic ketones

Substituent	Effect on β-carbon[b]	Effect on α-carbon[b]
β-Methyl(2-methyl-7*a*)	+13.1 (+11.5)	−2.0 (−2.8)
α-Methyl(3-methyl-7*a*)	−5.2 (−5.2)	+6.4 (+6.5)
α,β-Dimethyl(2,3-dimethyl-7*a*)	+6.4 (+3.9)	+3.2 (+1.6)

[a]In $CDCl_3$ solution. [b]In p.p.m. from corresponding values in thiochromone (7*a*) and cyclohexenone (in parentheses), respectively. Positive value indicates a downfield shift, relative to TMS.

ances, for example in the parent thiochromone and chromone systems, (7*a* and **8**), we have adopted the guideline that those carbon atoms whose resonances are significantly shifted (upfield or downfield) from the 128.6 p.p.m. value for benzene in $CDCl_3$ will experience much the same electronic effects as those in the saturated analogs, **1** and **2**, and have assigned them accordingly. The carbonyl carbon atoms (C-4) in the first seven members of the series all appear within the narrow range 177.6–179.9 p.p.m., thus indicating that not only methyl substitution (α- or β-), but also β-phenyl substitution or even the replacement of the cyclic β-sulfur substituent with oxygen or sulfone groups, produces little effect at C-4. The same situation occurs for the thiones **9**, **10**, and 2-phenyl-**10**, where the carbon of the C=S group appears within the range 201.4–204.4 p.p.m. Comparison of the chemical shifts in chromone and thiochromone with those in the corresponding thiones, **10** and **9** respectively, reveals a general similarity in the α,β-unsaturated ketone and thione systems. Indeed, in the thiochromone ketone and thione pair the only significant change is a downfield shift of +4.8 p.p.m. in the C-3 resonance on going from the ketone to the thione. A similar downfield shift was observed for C-3 of the alicyclic thione, thiocamphor, compared to C-3 in camphor itself, in an earlier study by Demarco *et al.* (18). In the ketone and thione of the chromone series, where the electronic influence of the ring oxygen is much greater, the corresponding downfield shift of the C-3 signal is +13.2 p.p.m. in going from C=O to C=S. Attempts to prepare thiones corresponding to the thiochromanone series of compounds in Table 2 unfortunately met with no success.

Some justification for comparing the thiochromone ring system with the simple cyclohexenone system is obtained by examining the effects of α- and β-(C-3 and C-2)methyl-substitution. Table 4 shows the remarkably good agreement between the shielding parameters for the thiochromones and the corresponding cyclohexenones. As expected, methyl substitution at C-2 and C-3 exerted little effect on the aromatic carbon atoms. The methyl resonance in 3-methylthiochromone appeared at 4.1 p.p.m. upfield relative to that in the 2-methyl analog. Once again this follows the pattern observed for the 2- and 3-methylthiochromanones in Table 2 and is attributable to the alignment of the 3-methyl substituent in the plane of the carbonyl group (17).

Comparison of the two 2-phenyl substituted compounds in Table 3 with their unsubstituted analogs **8** and **10** reveals that substitution at C-2 (or C-3), as already observed for the methyl derivatives, produces no significant alteration in the chemical shift of any of the aromatic carbon atoms, including C-5*a* and C-8*a*; indeed this consistency was of some assistance in making the given assignments. The (downfield) shift of the C-2 carbon differs considerably, however, being +17.8 for 2-phenyl substitution in the chromone and only +7.8 for the analogous thione. The upfield shift observed at C-3 is almost the same on the other hand, −5.4 and −6.1 respectively. The larger deshielding effect observed for phenyl substitution at C-2 in the ketone may reflect the greater electronegativity of the (carbonyl) oxygen or a greater degree of conjugation in the ketones than in the thiones.

The difference in chemical shift between C-2 and C-3 is, as expected, greater for the chromenethione (**10**) than the thiochromene-thione (**9**) (19.8 *vs.* 6.2 p.p.m.)just as the presumably greater

TABLE 5. Carbon-13 chemical shifts[a] of cyclic sulfoxides

Compound[b]	C-2	C-3	C-4 (C=O)	C-5*a*	C-8*a*	C-5, 6, 7, 8
Thiochromanone 1-oxide, **11**	47.1t	30.7t	191.9s	129.1s	145.6s	128.3d (C-8); 129.7d (C-5); 132.0d (C-6); 134.4d (C-7)
2-Methyl-**11**[c,d]	50.5, 55.8 d	37.1, 40.3 t	191.6, 192.5 s	129.1, 129.3 s	143.3, 146.9 s	127.0, 128.4d (C-8); 129.9, 131.1d (C-5); 132.3d (C-6); 134.6d (C-7)
2,2-Dimethyl-**11**[e]	56.5s	45.7t	192.1s	129.1s	144.0s	128.2d (C-8); 129.1d (C-5); 131.4d (C-6); 134.9d (C-7)
3-Methyl-**11**[f,g]	51.8t	32.1d	195.3s	129.4s	142.5s	129.4d (C-8); 130.4d (C-5); 132.8d (C-6); 134.4d (C-7)
3,3-Dimethyl-**11**[h]	60.7t	43.0s	196.7s	127.9s	147.2s	126.7d (C-8); 129.6d (C-5); 131.1d (C-6); 134.2d (C-7)
2,2,3,3-Tetramethyl-**11**[i]	63.4s	51.2s	197.3s	128.4s	143.3s	127.8d (C-8); 128.8d (C-5); 130.8d (C-6); 134.5d (C-7)
6-Methyl-**11**[j]	46.6t	30.1t	192.4s	129.1s	142.4s	128.9d (C-8); 129.4d (C-5); 135.3d (C-7); 143.1s (C-6)
8-Methyl-**11**[k]	43.5t	27.0t	193.1s	130.2s	141.0s	126.7d (C-5); 132.3d (C-6); 136.5d (C-7); 139.3s (C-8)
6-Methoxy-**11**[l]	46.2t	29.3t	192.4s	131.1s	136.6s	112.6d (C-5); 120.9d (C-7); 131.2d (C-8); 162.7s (C-6)
2-Phenyl-**11**[c] (thioflavanone 1-oxide)	60.1, 66.0 d	34.1, 39.3 t	191.8, 193.5 s	—[p]	143.5, 147.4 s	127.1–133.3[p]; 134.6, 134.8d (C-7)
2-Phenyl-6-methyl-**11**[c,m]	60.4, 66.0 d	34.2, 39.1 t	192.3, 193.9 s	—[p]	140.7, 142.0 s	127.2–135.7[p]; 144.1s (C-6)
3-Bromo-**11**	54.9t	42.1d	186.1s	130.3s	144.2s	129.5d (C-8); 130.5d (C-5); 132.8d (C-6); 135.3d (C-7)
Isothiochromanone 2-oxide, **12**	52.2t[n]	58.8t	188.0s	—[p]	—[p]	128.2–131.6[p]; 135.4d (C-7)

[a]In p.p.m. downfield from TMS; numbering of carbons as in Table 2. [b]In $CDCl_3$ solution. [c]Mixture of diastereoisomers. [d]Methyl, 13.5, 15.4q. [e]Methyls, 19.3, 24.3q. [f]Very small differences in chemical shift indicated a mixture of isomers, with one predominating. [g]Methyl, 14.9q. [h]Methyls, 24.5, 26.9q. [i]Methyls, 15.0, 19.2, 20.0, 20.4q. [j]Methyl, 21.4q. [k]Methyl, 18.9q. [l]Methoxyl, 55.8q. [m]Methyl, 21.3, 21.4q. [n]C-1.
[p]Individual assignments uncertain.

TABLE 6. Carbon-13 chemical shifts[a] of cyclic sulfones

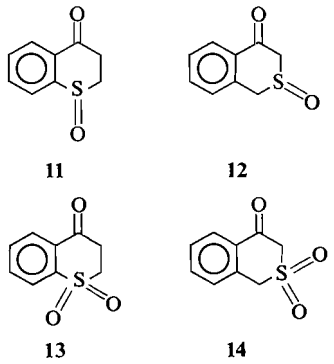
Compound[b]	C-2	C-3	C-4 (C=O)	C-5*a*	C-8*a*	C-5, 6, 7, 8
Thiochromanone 1,1-dioxide, **13**	49.3t	36.8t	190.1s	130.3s	141.5s	123.7d (C-8); 128.8d (C-5); 133.3d (C-7); 134.9d (C-6)
2-Methyl-**13**[c]	54.5d	44.2t	190.4s	130.6s	136.8s	124.2d (C-8); 128.5d (C-5); 133.2d (C-7); 134.9d (C-6)
2,2-Dimethyl-**13**[d]	58.6s	50.5t	190.5s	130.5s	139.1s	124.8d (C-8); 128.1d (C-5); 133.1d (C-7); 135.2d (C-6)
3-Methyl-**13**[e]	55.6t	41.4d	193.2s	129.9s	141.9s	123.4d (C-8); 128.7d (C-5); 133.2d (C-7); 134.7d (C-6)
3,3-Dimethyl-**13**[f]	59.7t	45.1s	196.1s	129.3s	141.9s	123.2d (C-8); 129.3d (C-5); 133.2d (C-7); 134.6d (C-6)
5-Methyl-**13**[g]	48.4t	37.4t	192.0s	129.2s	142.4s	121.9d (C-8); 133.3d (C-7); 137.3d (C-6); 142.6s (C-5)
6-Methyl-**13**[h]	49.4t	36.8t	190.5s	130.2s	138.8s	123.8d (C-8); 129.1d (C-5); 135.5d (C-7); 144.5s (C-6)
7-Methyl-**13**[i]	49.4t	36.7t	189.9s	128.0s	141.3s	121.7d (C-8); 128.9d (C-5); 134.1d (C-6); 146.7s (C-7)
2-Methoxycarbonyl-**13**[j]	64.1d	39.8t	188.1s[k]	130.9s	139.3s	124.1d (C-8); 128.4d (C-5); 133.7d (C-7); 134.7d (C-6)
3-Methoxycarbonyl-**13**[l]	47.5t	93.2s[m]	171.0s[n]	129.8s	138.1s	123.2d (C-8); 127.2d (C-5); 132.3d (C-7); 133.3d (C-6)
2-Phenyl-**13** (thioflavanone 1,1-dioxide)	64.0d	43.1t	190.8s	130.5s	141.5s	124.4–135.0[r]
Isothiochromanone 2,2-dioxide, **14**	55.5t[o]	62.4t	186.5s	130.9s[r]	132.7s[r]	129.9–130.6[r]; 135.6d (C-7)
3,3-Dimethyl-**14**[p]	50.1t[o]	68.2s	192.5s	129.5s[r]	131.1s[r]	129.2–130.4[r]; 134.6d (C-7)

[a]In p.p.m. downfield from TMS; numbering of carbons as in Table 2. [b]In $CDCl_3$ solution. [c]Methyl, 11.6q. [d]Methyls, 21.1q. [e]Methyl, 15.2q. [f]Methyls, 26.4q. [g]Methyl, 22.7q. [h]Methyl, 21.6q. [i]Methyl, 21.9q. [j]Methoxyl, 53.9q. [k]Ester C=O, 164.9s. [l]Methoxyl, 52.8q. [m]Enol carbon (see Discussion). [n]Ester C=O, 162.9. [o]C-1. [p]Methyls, 17.7q.
[r]Individual assignments uncertain.

degree of conjugation in chromone (**8**) accounts for a C_β–C_α chemical shift difference of 32.5 p.p.m., compared with 11.3 p.p.m. for thiochromone (*7a*). Chemical shifts of the aromatic carbon atoms in the pair of compounds **8** and **10** and also in *7a* and **9** are generally very similar. The chemical shift difference between the ring fusion positions (C-8*a* – C-5*a*) is, however, much greater in chromone (31.6 p.p.m.) than in the corresponding thione (20.5 p.p.m.), reflecting once more perhaps the greater degree of conjugation in the unsaturated ketones referred to above.

Chemical shift data for the cyclic sulfoxides and sulfones in our study are collected in Tables 5 and 6, respectively. The electron-withdrawing character of the sulfoxide and sulfone functionalities is reflected in the downfield shifts at C-2, relative to thiochromanone itself, of +20.5 p.p.m. in thiochroman-4-one 1-oxide (**11**) and of +22.7 p.p.m. in thiochroman-4-one 1,1-dioxide (**13**). Interestingly, the replacement of the cyclic sulfur atom in thiochroman-4-one by the sulfoxide functionality produces an *upfield* shift at C-3 of −8.8 p.p.m., whereas in the corresponding sulfone the upfield shift at C-3 is only −2.7 p.p.m. The C-4 (carbonyl) carbon is not greatly affected by these changes, showing upfield shifts of −1.9 p.p.m. in the sulfoxide and a further −1.8 p.p.m. in the sulfone. The assignment of the aromatic carbon resonances, including the ring junctions, C-5*a* and C-8*a*, in **11** and **13** was carried out using information obtained from the model compounds in Table 1 and the shielding parameters of aromatic $COCH_3$ substituents (2), as well as by comparison with thiochroman-4-one itself. Our assignments are further supported by the generally good agreement between the observed aromatic resonances in the 6- and 8-methyl- and 6-methoxythiochroman-4-one 1-oxides and in the 5-, 6-, and 7-methylthiochroman-4-one 1,1-dioxides with the values calculated using the known aromatic substituent effects of CH_3 and OCH_3 (2).

In the series diphenyl sulfone, diphenyl sulfoxide, thiobenzophenone (Table 1), and benzophenone (19) the *p*-substituent (deshielding) effects are in the order $SO_2 > C{=}O > C{=}S > S{=}O$, being (+) 4.6, 3.7, 3.3, and 2.4 p.p.m. respectively. In diphenyl sulfide, of course, the *p*-effect is in the opposite sense, although the shift of −1.6 p.p.m. is considerably less than the −3.7 p.p.m. observed in thioanisole (3). A similar reduction in the upfield shift at the *p*-position



11 **12** **13** **14**

is observed in diphenyl ether as compared to anisole. The *o*-effects in the above series (*cf.* Table 1) show much less consistency, being small and in the downfield direction in thiobenzophenone and benzophenone (+0.9 and +1.3 p.p.m., respectively), whereas in diphenyl sulfoxide and diphenyl sulfone they are in the upfield direction, being −3.9 and −1.0 p.p.m., respectively. In diphenyl sulfide, the *o*-effect is +2.4 p.p.m.

The effects of methyl-substitution at C-2 and C-3 in the sulfide, sulfoxide, and sulfone series (Tables 2, 5, 6) show interesting variations and the data for the three series has been collected in Table 7. Although general trends are difficult to discern, it does appear that substitution of a methyl group at C-2 produces more 'normal' shifts at both C-2 and C-3 than is the case for the corresponding 3-methyl and 3,3-dimethyl series. In fact, downfield shifts at C-3 are generally small, the single exception being in going from the 3-methyl to the 3,3-dimethyl sulfoxide where a change of +10.9 p.p.m. is observed. Once again, in both the sulfoxide and sulfone series, the tendency of α-methyl (C-3) substitution to produce downfield shifts of the C-4 (carbonyl) resonance is just as pronounced as it was for the sulfides in Table 2. The differences in chemical shifts for the methyl resonances themselves at C-2 and C-3, referred to in the discussion of Table 2, are no longer so evident in Tables 5 and 6, not only because of the non-equivalence of methyl groups in 2,2- and (to a lesser extent) 3,3-dimethylthiochroman-4-one 1-oxides, but also no doubt because of the shielding influence, not present in the thiochromanones, of the S=O bond(s) on the C-2 methyls. In general, as was the case for the corresponding sulfides, the effect of C-2 or C-3 methyl substitution on even the closest aromatic (ring-junction) carbon atoms is

not very great, as expected, and is probably attributable to steric crowding of one or both of the polar functionalities at C-1 and C-4, which reaches its maximum expression in 2,2,3,3-tetramethylthiochroman-4-one 1-oxide.

In thioflavanone 1-oxide and thioflavanone 1,1-dioxide, the effect of phenyl substitution at C-2 is to produce downfield shifts of +15.9 (taking the mean value for the two diastereoisomers) and +14.7 p.p.m. respectively. The corresponding shifts so produced at C-3 amount to +6.0 and +6.3 p.p.m., respectively, much the same behavior as was observed in thioflavanone itself. In all three 2-phenyl substituted compounds, the increased complexity of the aromatic region of the ^{13}C n.m.r. spectra prevented the individual assignment of all signals. This problem becomes particularly acute in the case of 2-phenylthiochroman-4-one 1-oxide and 2-phenyl-6-methylthiochroman-4-one 1-oxide owing to the existence of diastereoisomers, since the separation of lines (due to configurational isomerism) becomes quite small for the aromatic carbons which are relatively remote from the chiral centers, leading to much overlapping of neighboring peaks in the relatively narrow region of the spectrum involved. The spectrum of 3-bromothiochroman-4-one 1-oxide reveals that the α-effect produced by replacing hydrogen by bromine is +11.4 and the β-effect +7.8 p.p.m. which, at least as far as the α-effect is concerned, seems to agree well with results quoted by Levy and Nelson (2). The effect of introducing a bromine α to the carbonyl group produces an upfield shift of −5.8 p.p.m. in the resonance due to the C-4 carbon. This compares favorably with the value of −5.3 p.p.m. reported for 3-*endo*-bromocamphor (20). As usual, the signals due to the aromatic carbons were not greatly affected by introduction of the bromine although a general drift downfield of approximately 1 p.p.m. was noted.

The two sulfones which bear an ester functionality in the heterocyclic ring (Table 6) deserve comment. In 2-methoxycarbonylthiochroman-4-one 1,1-dioxide, the α-effect of the ester group is +14.8 p.p.m. and the β-effect +3.0. Very recently, Gordon *et al.* (21) have reported their results from a ^{13}C n.m.r. study of a series of methyl esters in which the α-effect was +15.4 p.p.m. and the β-effect +1.3 p.p.m. for the cyclohexyl system. In our 2-methoxycarbonyl substituted case, the only other significant effect was to produce an upfield shift of −2.0 p.p.m. in the carbonyl carbon (Gordon *et al.* (21) report a γ-effect for simple cyclohexanes of −2.3 p.p.m.). In distinct contrast to the rather routine effects observed in the 2-substituted case, the 3-methoxycarbonylthiochroman-4-one 1,1-dioxide produced a quite unexpected result. It will be noted that this is in fact a β-keto ester and the ^{13}C n.m.r. spectrum indicates quite clearly that in $CDCl_3$ solution at the concentration used (12–15% w/v) enolization is complete. Thus, the C-3 signal appears as a singlet rather than a doublet, as a value of 93.2 p.p.m., far removed from the 36.8 p.p.m. observed in the unsubstituted sulfone, whereas the position of the C-2 signal is altered only slightly. The electron-releasing effect of the enolic OH group, enhanced by the electron-withdrawing effect of the COOMe group, accounts for the unusually high field location for the sp^2 carbon at C-3. As expected, the C-4 carbon shows a chemical shift closer to what one would expect for an sp^2 carbon bonded to oxygen, appearing at 171.0 p.p.m. The methyl and ester carbonyl signals, as well as the signals for the aromatic carbons in the two ester derivatives, are virtually identical.

The remaining compounds for which data are included in Tables 5 and 6 are isothiochromanone 2-oxide (**12**) and isothiochromanone 2,2-dioxide (**14**) and its 3,3-dimethyl derivative. The assignment of the C-1 and C-3 signals in **12** and in **14** as well as in isothiochromanone (**4**) itself was made initially in the expectation that the signal due to C-3, α to the carbonyl, would be downfield from that due to C-1, which is a benzylic methylene, and the assumption that the C-3 signal in particular would not be greatly changed in position from C-3 of thiochroman-4-one. In the sulfoxide (**12**) the C-1 and C-3 signals are shifted downfield by +21.7 and +21.8 p.p.m., respectively, while in the sulfone (**14**) the corresponding shifts are +25.0 and +25.4 p.p.m. These values are very similar to the effects observed at C-2 in the analogous thiochromanones, in proceeding through the series sulfide, sulfoxide, sulfone. Further evidence in support of these assignments comes from a consideration of 3,3-dimethylisothiochromanone 2,2-dioxide (Table 6), where the change in chemical shift at C-3 between this compound and the unsubstituted analog is +5.8 p.p.m., while the corresponding change in chemi-

TABLE 7. Methyl substituent effects[a] at C-2 and C-3

Series	Substituent	Effect at C-2[b]	Effect at C-3[b]
Thiochromanones	2-Methyl	+9.6	+8.1
	2,2-Dimethyl	+17.9	+14.3
	3-Methyl	+6.4	+2.6
	3,3-Dimethyl	+12.5	+1.4
	2,3-Dimethyl[c]	+14.6	+8.3
Thiochromanone sulfoxides	2-Methyl[c]	+6.1	+8.0
	2,2-Dimethyl	+9.4	+15.0
	3-Methyl	+4.7	+1.4
	3,3-Dimethyl	+13.6	+12.3
	2,2,3,3-Tetramethyl	+16.3	+20.5
Thiochromanone sulfones	2-Methyl	+5.2	+7.4
	2,2-Dimethyl	+9.3	+13.7
	3-Methyl	+6.3	+4.6
	3,3-Dimethyl	+10.4	+8.3

[a]In p.p.m.; positive values indicate downfield shifts.
[b]All shifts are related to values for C-2 and C-3 in the parent compounds (**1**, **11**, or **13**), including those for the dimethyl substituted derivatives.
[c]Mean value taken for diastereoisomers.

cal shift at C-3 between thiochroman-4-one 1,1-dioxide and its 3,3-dimethyl analog is +8.3 p.p.m. In general the C-4 (carbonyl) carbon appears at higher field in isothiochromanone and its sulfoxide and sulfone, the differences ranging between 3–4 p.p.m. Once again, however, in the case of 3,3-dimethylisothiochromanone 2,2-dioxide, the characteristic downfield shift in the C-4 (carbonyl) frequency produced by α-methylation is observed. The numerical value of this shift, 6.0 p.p.m., is exactly the same as that observed in 3,3-dimethylthiochroman-4-one 1,1-dioxide. The removal of the electron-withdrawing sulfur group at C-1 in isothiochromanone sulfoxide and sulfone to the C-2 position produces a very marked closing of the gap in chemical shifts between C-5*a* and C-8*a* observed in the analogous thiochromanone sulfoxide and sulfone to about 2 p.p.m. and furthermore greatly reduces the spread in chemical shifts arising from the carbons 5, 6, and 8 to the point at which attempts to make individual assignments become somewhat nebulous.

In Table 7 are gathered data on the effects of methylation at C-2 and C-3 in the thiochromanone and related sulfoxide and sulfone series, calculated from the chemical shifts in Tables 2, 5, and 6. It may be noted that for 2,3-dimethylthiochroman-4-one the total downfield shift observed at C-2 and C-3 approximates quite closely that obtained by simply adding the contributions from the 2-methyl and 3-methyl derivatives. This additivity is not so apparent in 2,2,3,3-tetramethylthiochroman-4-one 1-oxide, where the steric crowding must cause considerable distortion of the heterocyclic ring. Even in this case, however, the relative magnitude of the shifts at C-2 and C-3 is correctly predicted by summing the values from the 2,2-dimethyl and 3,3-dimethyl sulfoxides.

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