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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### ELECTRONIC INTERACTIONS STUDIES OF TRANS-3-(2'-CHLOROCYCLOPENTYLTHIO)- AND E-3-(2'-CHLORO-1'-METHYLPROPEN-1'-YL-THIO)-THIOCHROMONES AND THEIR 3-SULFINYL AND 3-SULFONYL DERIVATIVES

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## ELECTRONIC INTERACTIONS STUDIES OF TRANS-3-(2'-CHLOROCYCLOPENTYLTHIO)- AND E-3-(2'-CHLORO-1'-METHYLPROPEN-1'-YL- THIO)-THIOCHROMONES AND THEIR 3-SULFINYL AND 3-SULFONYL DERIVATIVES

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The analysis of the  $\nu_{\text{CO}}$  bands in the IR spectra of the 3-(2'-chlorocyclopentylthio)- and 3-(2'-chloro-1'-methylpropen-1'-ylthio)-thiochromones and their 3-sulfinyl and 3-sulfonyl derivatives, supported by molecular mechanics calculations of 3-methylthio-, 3-methylsulfinyl- and 3-methylsulfonyl-thiochromones, taken as model compounds, indicates the existence of a single conformer for the whole series except for the case of the 3-(2'-chloro-1'-methylpropen-1'-ylsulfinyl)-thiochromone where three conformers can be observed. The negative carbonyl frequency shifts ( $\Delta\nu$ ) for the 3-sulfinyl- and 3-thio-thiochromone derivatives and the positive carbonyl shifts for the 3-sulfonyl-thiochromone derivatives are interpreted on the grounds of an interplay of the  $\pi_{\text{CO}} \rightarrow 3d_{\text{SO}_n}$  orbital interaction with the inductive and field effects of the 3-substituents. The orbital interaction is responsible for the shorter S...O intramolecular contact observed previously from X-ray data of some 3-thio-thiochromone derivatives. The bathochromically shifted  $n \rightarrow \pi_{\text{CO}}^*$  band for the 3-thio- and 3-sulfinyl-thiochromone derivatives and the slight hypsochromic effect for the 3-sulfonyl-thiochromone derivatives are discussed in terms of the relative energy level stabilization of the  $\pi_{\text{CO}}^*$  orbital (due to the  $\pi_{\text{CO}}^*/3d_{\text{SO}_n}$  orbital interaction) and the  $n_{\text{O(CO)}}$  lone pair (due to the electron-attracting inductive effect of the 3-sulfur-substituent). The IR and UV spectra of thiochroman-4-one show the existence of a mixture of two conformers, the twist-boat being the one where the transannular interaction between the  $3p_{\text{(s)}} \rightarrow \pi_{\text{CO}}^*$  orbitals takes place.

**Key words:** Trans-3-(2'-chlorocyclopentylthio)- and E-3-(2'-chloro-1'-methylpropen-1'-ylthio)-thiochromones and their 3-sulfinyl and 3-sulfonyl derivatives; electronic interactions; conformational studies; molecular mechanics calculations; IR and UV spectra.

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## INTRODUCTION

Our previous IR conformational studies of some  $\alpha$ -thiosubstituted-acetones,<sup>1</sup> -acetamides,<sup>2</sup> -thioesters<sup>3</sup> and -esters<sup>4</sup> have shown that in general there is a decrease of the expected Repulsive Field Effect between the C=O and C—S dipoles in the *cis* rotamers of such compounds. This behavior showed to be more pronounced in the case of the less basic  $\alpha$ -thiosubstituted-thioesters and -esters, causing the *cis* rotamers to be abnormally less polar than the *gauche* ones.

The above behavior has been attributed to charge transfer from the  $\pi_{CO}$  orbital to a vacant 3d sulfur orbital which occurs in the *cis* rotamer of the title compounds preventing, or at least decreasing, the normal Repulsive Field Effect.

It is worth noting that one of us,<sup>5</sup> has recently synthesised several  $\alpha$ -thiosubstituted-thiochromone and -cyclohexenone derivatives. The X-ray crystallographic analysis of trans-3-(2'-chlorocyclopentylthio)-thiochromone and E-2-(2'-chloro-1'-methylpropen-1'-ylthio)-2-cyclohexenone showed the notable feature of shorter intramolecular contacts between the  $\alpha$ -sulfur and the carbonyl oxygen atoms in relation to the sum of their Van der Waals radii. This abnormal behavior has been attributed to the presence of an increased negative charge on the carbonyl oxygen atom in the delocalised valence structure which presumably favours the S...O contact.

Considering that the X-ray analysis indicates that the thiochromone ring of the above mentioned compounds is planar and that the  $\alpha$ -sulfur atom lies in the same plane, it became of interest to perform now the IR and UV studies for the 3-(2'-chlorocyclopentylthio)- and 3-(2'-chloro-1'-methylpropen-1'-ylthio)-thiochromones and their 3-sulfinyl and 3-sulfonyl derivatives (structures I and II, respectively, Figure 1), using the unsubstituted thiochromone (III) as the reference compound.

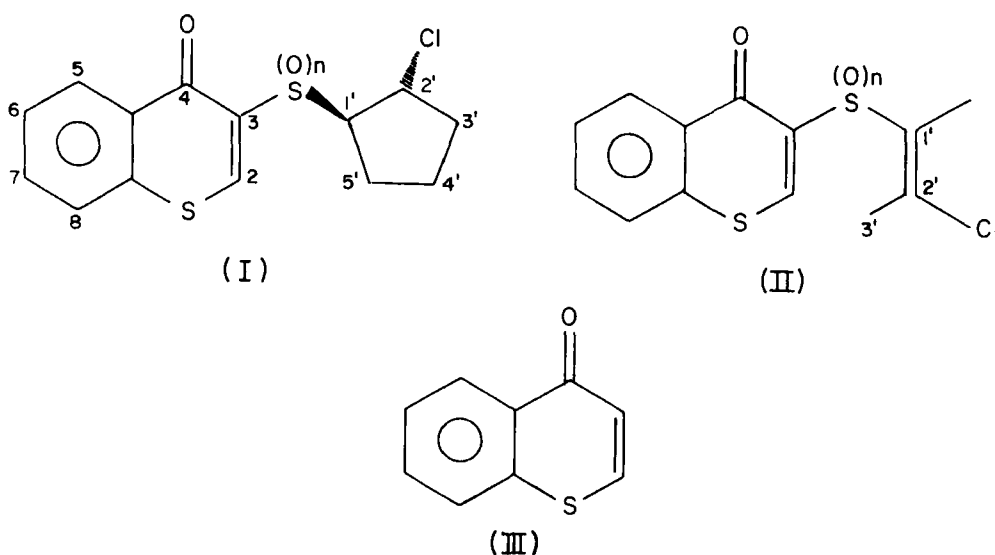


FIGURE 1 Structural formulae of the trans-3-(2'-chlorocyclopentylthio)- (I) and E-3-(2'-chloro-1'-methylpropen-1'-ylthio)- (II) -thiochromone derivatives for  $n = 0, 1$  and  $2$  and of the unsubstituted thiochromone (III).

The aim of this work is to improve our knowledge of the nature of the electronic interactions present when the  $\alpha$ -sulfur and the carbonyl oxygen atoms are nearly coplanar in the *cis* or *equatorial* geometries of the  $\alpha$ -thiosubstituted compounds.

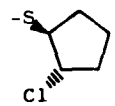
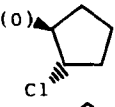
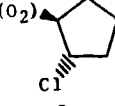
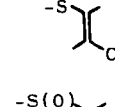
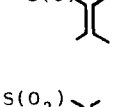
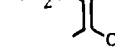
## RESULTS AND DISCUSSION

### Carbonyl and Benzene Ring Stretching Frequencies

Table I shows the carbonyl and benzene ring stretching frequencies and intensities of some 3-sulfur-substituted thiochromones (2)–(7) in the fundamental and first

TABLE I

Frequencies and intensities of the carbonyl and benzene ring stretching bands in the infrared spectra of thiochromone, trans-3-(2'-chlorocyclopentylthio)- and E-3-(2'-chloro-1'-methylpropen-1'-ylthio)-thiochromones and their 3-sulfinyl- and 3-sulfonyl-derivatives

COMPD.	X	CCl <sub>4</sub>					CHCl <sub>3</sub>			
		$\nu^a$	$\epsilon^b$	$\epsilon_1/\epsilon_2^c$	$\nu^d$	10 $\epsilon$	$\epsilon_1/\epsilon_2$	$\nu$	$\epsilon$	$\epsilon_1/\epsilon_2$
(1)	-H <sup>a</sup>	1634 <sup>f</sup> 1594 <sup>g</sup>	966 296	0.31	3258	57		1622 1596	505 197	0.39
(2)		1626 1594	442 155	0.35	3238	48		1616 1590	348 397	1.14
(3)		1620 1592	780 188	0.24	3232	34		1616 1589	458 364	0.78
(4)		1642 1592	700 124	0.18	3264	39		1632 1592	704 330	0.47
(5)		1627 1596	584 220	0.38	3236	39		1615 1592	451 433	0.96
(6)		1643 <sup>f</sup> 1624 <sup>f</sup> 1609 <sup>f</sup> 1592 <sup>g</sup>	447 618 (168) <sup>h</sup> 196	0.72 - 0.27 0.32	3260 3238	(21) 37	0.57	1642 1620 1606 1588	298 487 (277) <sup>h</sup> 317	0.61 - 0.56 0.65
(7)		1644 1591	775 151	0.19	3269	53		1635 1593	796 265	0.33

<sup>a</sup>In cm<sup>-1</sup>.

<sup>b</sup>Apparent molar absorptivity in dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> estimated directly at the absorption maxima or at the inflexion point of the partially overlapped bands.

<sup>c</sup>Intensity ratio between the low and the high frequency bands for all compounds except for compound (6) where the intensity ratio of each component is related to the highest intensity band of the multiplet.

<sup>d</sup>1st overtone; <sup>e</sup>Parent compound.

<sup>f,g</sup>Carbonyl and benzene ring stretching bands, respectively.

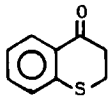
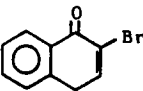
<sup>h</sup>All intensity data in brackets are estimated at the inflexion point of the unresolved doublet.

overtone regions in carbon tetrachloride and chloroform. Corresponding data for the parent unsubstituted thiochromone (1) are included for comparison.

Inspection of Table I shows that in the fundamental region, in carbon tetrachloride, the majority of the 3-sulfur-substituted thiochromones (2)–(5) and (7) as well as the parent thiochromone (1) exhibit two partially overlapped bands, the higher frequency band being significantly more intense than the lower one. It may be noted for these compounds that, on going from carbon tetrachloride to chloroform, there is a decrease of the frequency of the maximum of the higher frequency band which varies from 12 to 4  $\text{cm}^{-1}$ , while the maximum of the lower frequency band changes only slightly in both directions. However, the increasing solvent polarity originates an increase in the intensity of the lower frequency band in relation to the higher one. It should be pointed out that for the whole thiochromone series except for compound (6) (see below), there is only a single band in the first overtone region, at a frequency approximately twice that of the higher frequency band in the fundamental region. This behavior, together with the observed solvent effect on the higher frequency band, strongly suggests that this band corresponds to the carbonyl stretching mode. On the other hand the lower frequency band may be ascribed either to the benzene ring or to the carbon-carbon double bond stretch-

TABLE II

Frequencies and intensities of the carbonyl and benzene ring stretching bands in the infrared spectra of thiochroman-4-one (8) and 3-bromothiochromone (9)

COMPD.	STRUCT.	$\text{CCl}_4$						$\text{CHCl}_3$		
		$\nu^a$	$\epsilon^b$	$\epsilon_a/\epsilon_b^c$	$\nu^d$	$10\epsilon$	$\epsilon_1/\epsilon_2$	$\nu$	$\epsilon$	$\epsilon_1/\epsilon_2$
(8)		1685 <sup>e</sup>	596		3351	91		1680	499	
		1675 <sup>e</sup>	(236) <sup>g</sup>	0.39	3329	(29)	0.32	1670	(469)	0.93
		1594 <sup>f</sup>	164					1596	230	
(9)		1643 <sup>e</sup>	603		3268	53		1630	589	
		1594 <sup>f</sup>	174	0.29				1595	295	0.50

<sup>a</sup>In  $\text{cm}^{-1}$ .

<sup>b</sup>Apparent molar absorptivity in  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$  estimated directly at the absorption maxima or at the inflexion point of the partially overlapped bands.

<sup>c</sup>Intensity ratio between the low and the high frequency components of the overlapped carbonyl bands for compound (8), and the intensity ratio of the low and high frequency bands for compound (9).

<sup>d</sup>1st overtone.

<sup>e,f</sup>Carbonyl and benzene stretching bands, respectively.

<sup>g</sup>All intensity data in brackets are estimated at the inflexion point of the unresolved doublet.

ing mode of the thiochromone moiety of the thiochromone derivatives (Figure 1, structures I–III).

The IR spectrum of thiochroman-4-one (8) (Table II, and Figure 2a), where the conjugated double bond of the thiopyrone moiety of the thiochromone (1) is absent, shows two overlapped carbonyl bands (see below), together with a lower frequency band at practically the same frequency and intensity as that which appears in thiochromone (Figure 2b) and in the thiochromone derivatives, i.e., ca.  $1594\text{ cm}^{-1}$ . This is clear evidence that this latter band corresponds to a benzene ring stretching mode. The  $\nu_{\text{C}=\text{C}}$  mode coupled to the  $\nu_{\text{C}=\text{O}}$  mode in the thiopyrone moiety of the thiochromone molecule seems to be the band of weak or medium intensity which may be seen mainly in chloroform near  $1530\text{ cm}^{-1}$  in the spectra of the thiochromone series (1)–(7) and (9). Figures 2b and 3a and c illustrate this behavior. This band is absent in the spectra of thiochroman-4-one (8), as expected.

Table I shows that the 3-sulfinyl derivative of the thiochromone (6) at the high frequency side of the ring stretching band presents three overlapped bands, the middle component being the most intense, the lowest component showing up as a shoulder in both solvents. Each component shows only a slight decrease in its frequency on going from carbon tetrachloride to chloroform. Additionally, the occurrence of two superimposed bands in the 1st overtone region at frequencies ca. twice those of the two higher components of the triplet in the fundamental region, with approximately the same intensity ratios, throws out the possibility of a Fermi Resonance<sup>6</sup> and rather suggests the occurrence of rotational isomerism (Figures 3a–c). Thus, each component of the triplet must correspond to a particular

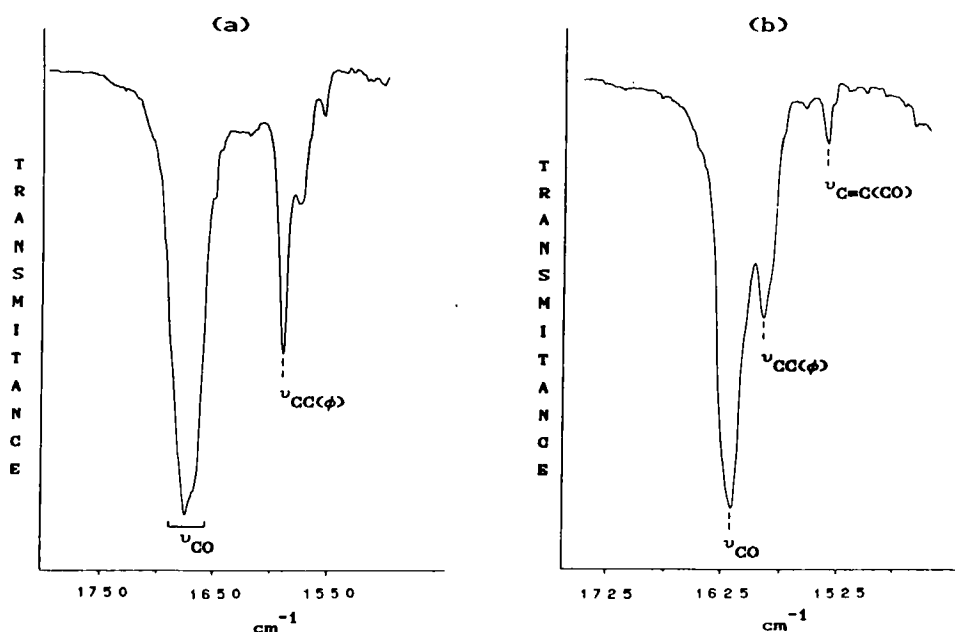


FIGURE 2 IR spectrum of thiochroman-4-one (8), in chloroform, showing the two overlapped carbonyl  $\nu_{\text{CO}}$  and the benzene ring  $\nu_{\text{CC}(\phi)}$  stretching bands (a); and the IR spectrum of thiochromone (1) in chloroform, showing the carbonyl  $\nu_{\text{CO}}$ , benzene ring  $\nu_{\text{CC}(\phi)}$  and the conjugated carbon-carbon double bond  $\nu_{\text{C}=\text{C}(\text{CO})}$  stretching bands of the thiopyrone moiety (b).

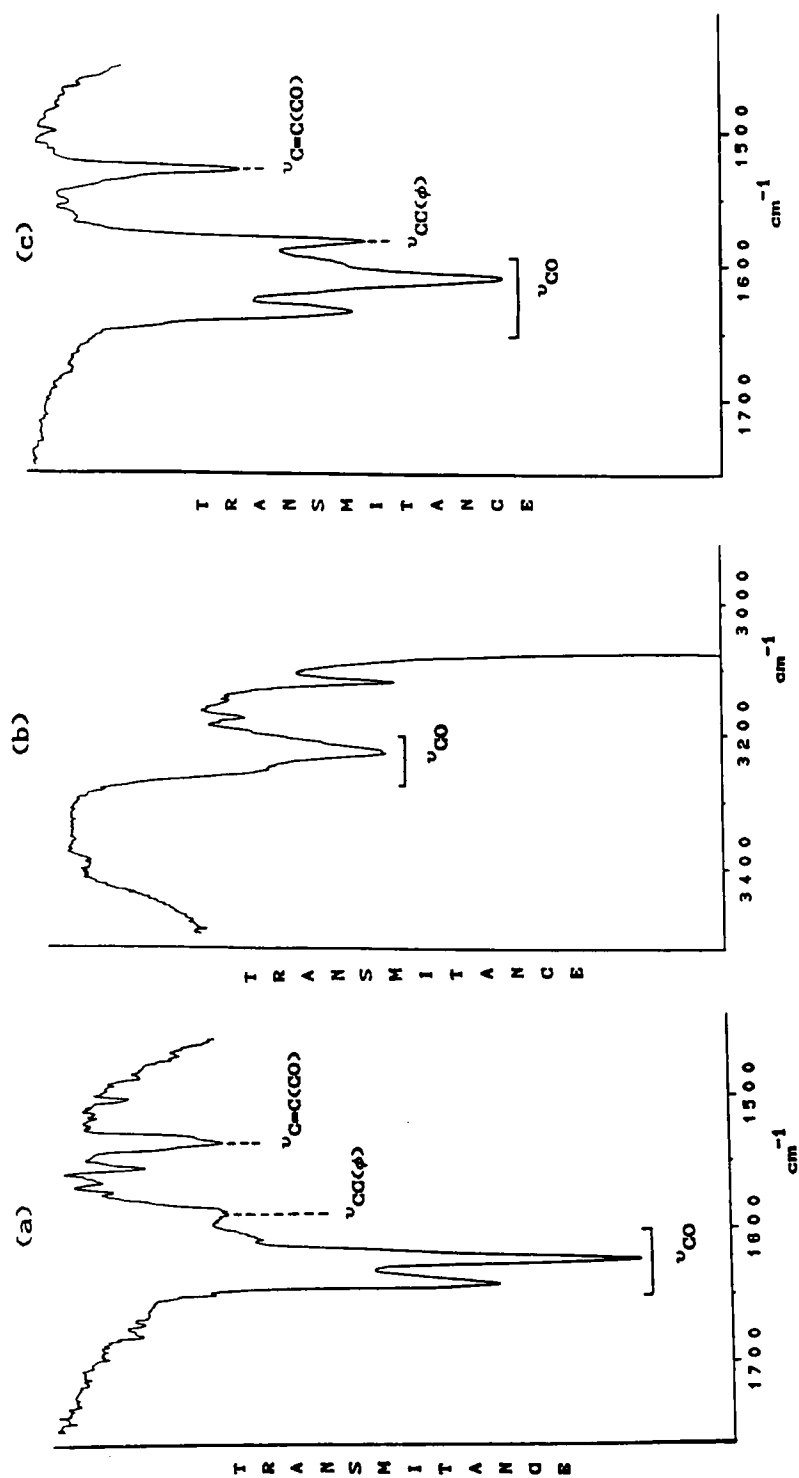


FIGURE 3 IR spectra of the 3-chloro-methylpropenylsulfonethiochromone (6) showing the carbonyl  $\nu_{\text{C=O}}$ , benzene ring  $\nu_{\text{C=C(imp)}}$  and the conjugated carbon-carbon double bond  $\nu_{\text{C=C(CO)}}$  stretching bands in the fundamental region, in carbon tetrachloride (a) and chloroform (c); and the  $2\nu_{\text{CO}}$  bands in the 1st overtone region, in carbon tetrachloride (b).

conformer, the most intense middle component being assignable to the most stable one (see next section).

It should be pointed out that the observed doublet in the carbonyl region of thiochroman-4-one (**8**) (Table II) shows a peculiar behavior. In fact, on going from carbon tetrachloride to chloroform, the shoulder at the lower frequency side of the overlapped bands increases its intensity approximately twice in relation to the higher frequency component, and both bands undergo a shift of ca.  $5\text{ cm}^{-1}$  to lower frequencies. Although the solvent effect may be indicative of a Fermi Resonance, the occurrence of two overlapped bands in the 1st overtone region at frequencies approximately twice those in the fundamental region and with the same intensity ratios rules out this possibility and suggests the occurrence of two conformations<sup>6</sup> for the thiochroman-4-one. From the inspection of a molecular model of this compound it is possible to ascribe the higher frequency carbonyl band in its IR spectra to the non-interacted form, i.e., the conformation where the cycloaliphatic ring of the thiochroman-4-one molecule assumes a twist-chair conformation, maintaining the sulfur atom and the carbonyl group reasonably apart. On the other hand the lower frequency carbonyl band may be attributed to a twist-boat conformation of the cycloaliphatic part, where the sulfur atom approaches the carbonyl carbon favouring the transannular interaction between the  $3p$  sulfur and  $\pi_{\text{CO}}^*$  orbitals, as in the case of 5-thiacyclo-octanone.<sup>7</sup> This interaction originates a decrease in the carbonyl bond order and consequently a lowering in the  $\nu_{\text{CO}}$  frequency of the interacted conformation in relation to that of the non-interacted one.

Table II also presents the IR data of 3-bromothiochromone (**9**). As in the case of the majority of the 3-sulfur-substituted thiochromones (**2**)–(**5**) and (**7**), the analysis of the solvent effect together with the 1st overtone region indicates that the more intense higher frequency band corresponds to the carbonyl stretching mode and the lower one corresponds to a benzene ring stretching mode.

#### *Conformations of the $\alpha$ -Sulfur-substituted Thiochromone Derivatives*

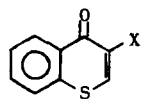
In the present paper it was assumed for all  $\alpha$ -substituted thiochromone derivatives that the  $\alpha$ -heteroatoms lie in the same plane of the thiochromone molecule (see Introduction). In fact Molecular Mechanics Calculations performed for the 3-methylthio- (**10**), 3-methylsulfinyl- (**11**) and 3-methylsulfonyl- (**12**) thiochromones, taken as model compounds for the whole series (**2**)–(**7**), indicate that the  $\alpha$ -sulfur atom lies in the thiochromone plane ( $\theta = 0^\circ$ ) (Table III). Figure 5 shows the single conformer for the methylthio-thiochromone and the most stable conformers for the methylsulfinyl- and methylsulfonyl-thiochromones (Structures VII, VIII and IX, respectively) obtained from Molecular Mechanics Calculations.

Table III and Figure 5 show that the methyl carbon atoms for both the single conformer of  $\alpha$ -methylthio-thiochromone (**10**) and the most stable conformer of  $\alpha$ -methylsulfinyl-thiochromone (**11**) assume a quasi-perpendicular geometry i.e.,  $\phi = 79^\circ$  and  $\phi = 105^\circ$ , respectively. In the case of the virtual single conformer for the  $\alpha$ -methylsulfonyl-thiochromone (**12**), the methyl carbon of the methylsulfonyl group is coplanar with the thiochromone moiety ( $\phi = 0^\circ$ ). It should be noticed that in the more stable conformer of the methylsulfinyl-thiochromone the oxygen atom of the methylsulfinyl group is practically on the opposite side in relation to



TABLE III

Calculated Molecular Mechanics energies, electric dipole moments, dihedral angles for the minimum energy conformations, and the relative rotamer populations of the 3-methylthio-, 3-methylsulfinyl- and 3-methylsulfonyl-thiochromones



COMP.D.	X	$\theta^a$	$\phi^b$	$\mu^c$	$E^d$	$P^f$
(1)	H <sup>g</sup>	0	-	3.853	-	-
(10)	SMe	0	+79	4.280	-	-
(11)	SOMe	0	+105	4.944	0 <sup>e</sup>	0.86
		1	-45	5.849	1.09	0.14
(12)	SO <sub>2</sub> Me	0	0	4.077	0	0.99
		0	180	8.159	2.71	0.01

<sup>a,b</sup>Dihedral angles  $\theta$  and  $\phi$  (in degrees), as defined in Figure 4.

<sup>c</sup>In Debye.

<sup>d</sup>In kcal.mole<sup>-1</sup>

<sup>e</sup>Zero energy corresponds to the minimum energy conformation.

<sup>f</sup>Molar fraction of each rotamer.

<sup>g</sup>Parent compound.

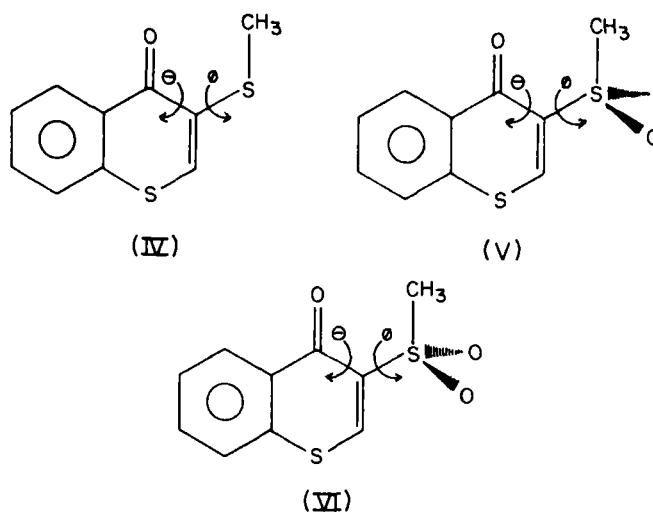


FIGURE 4 Reference conformations ( $\theta = 0^\circ$ ,  $\phi = 0^\circ$ ) for the 3-methylthio-, 3-methylsulfinyl- and 3-methylsulfonyl-thiochromones (Structures IV, V and VI, respectively). The arrows indicate positive torsion angles.

the carbonyl oxygen atom. This geometry originates a lower dipole moment ( $\mu = 4.944$  D) in comparison with that of the less stable conformer ( $\mu = 5.849$  D) where the sulfinyl oxygen atom is near of the carbonyl oxygen atom.

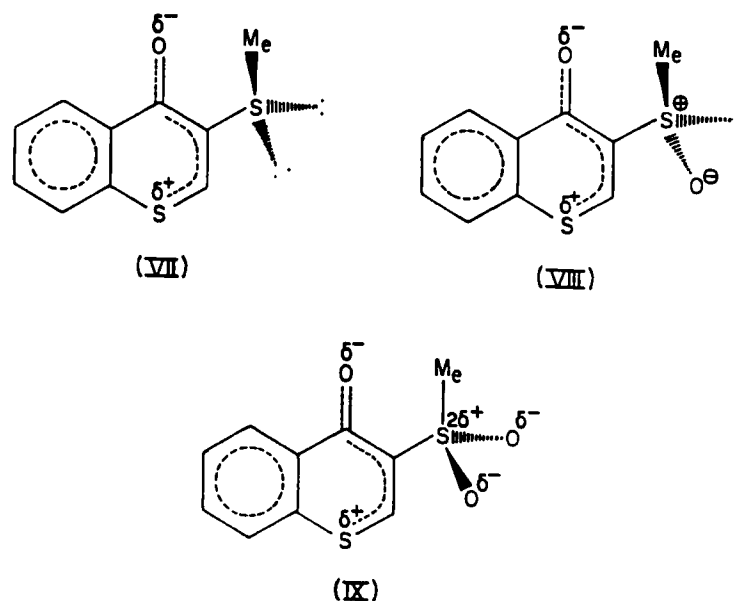


FIGURE 5 The single conformer for the methylthio-thiochromone and the most stable conformers for the methylsulfinyl and methylsulfonyl-thiochromones, Structures VII, VIII and IX, respectively, obtained from Molecular Mechanics Calculations; showing the delocalized valence bond structure of the thiopyrone moiety in the thiochromone rings.

As for the virtual unique conformer for the  $\alpha$ -methylsulfonyl-thiochromone the two oxygen atoms of the methylsulfonyl group lie above and below the thiochromone plane but in the opposite direction in relation to the carbonyl oxygen atom.

It should be noted that the two conformers of the 3-methylsulfinyl-thiochromone (11) obtained from Molecular Mechanics Calculations may well be related to the two higher carbonyl frequency bands of the triplet observed in Table I for the 3-(2'-chloro-1'-methylpropen-1'-ylsulfinyl)-thiochromone. In fact, the highest carbonyl frequency component may be ascribed to the conformation where the sulfinyl oxygen and the carbonyl oxygen atoms are closer, leading consequently to a destabilization of this conformer and to an increase in the carbonyl frequency due to the Repulsive Field Effect<sup>8</sup> between the C=O and S=O dipoles. On the other hand, the more intense middle carbonyl frequency band may be ascribed to the conformation where the sulfinyl and the carbonyl oxygen atoms are further apart and the Repulsive Field Effect is absent. These assignments are supported by the fact that the relative population of the two conformers (Table III) shows approximately the same trend as the intensity ratio of the higher and middle carbonyl bands of the triplet (Table I). It is not possible to attribute the weak shoulder observed at the lowest frequency side of the triplet to any conformer due to the limitations of our chosen simple model compound, where the 2-chlorocyclopentyl and chloro-methylpropenyl groups of the  $\alpha$ -sulfur-substituted thiochromone series (2)–(7) were replaced by the methyl group.

The occurrence of at least two  $\nu_{\text{CO}}$  bands corresponding to the same conformers which have been ascribed to the chloro-methyl propenylsulfinyl-thiochromone (6) should be expected in the IR spectra of the 2-chlorocyclopentylsulfinyl thiochro-

mone (3), by analogy with the chloro-methylpropenylsulfinyl-thiochromone. It seems reasonable, however, to assume from the analysis of Molecular Models that some steric hindrance between the carbonyl oxygen atom and the bulkier cyclopentyl group of compound (3) should exist, thus precluding the occurrence of the higher energy conformer where the carbonyl and the sulfinyl oxygen atoms are closer. In fact, the IR spectra of this compound display only a single carbonyl stretching band (see Table I).

### Carbonyl Stretching Frequency Shifts

Table IV presents the frequency shifts ( $\Delta\nu$ ), in carbon tetrachloride of the 3-sulfur-substituted thiochromones (2)–(7) and of the 3-bromothiochromone (9) in relation to the parent compound (1). A very similar behavior of the carbonyl frequency shifts for the two classes of  $\alpha$ -sulfur-substituted thiochromones, i.e., for the chlorocyclopentylthio-(2) and chloro-methylpropenylthio-(5)-thiochromones and their *mono*- (3), (6) and *di*- (4), (7) oxygenated derivatives, may be noticed in Table IV. In fact on going from  $\alpha$ -thio to  $\alpha$ -sulfinyl substituents there is an increase of the negative carbonyl frequency shift values. However, in the case of the  $\alpha$ -sulfonyl substituents the  $\Delta\nu$  values become positive.

In the case of the  $\alpha$ -bromo-substituent (9) the observed positive carbonyl frequency shift of  $+9\text{ cm}^{-1}$  is in line with the Normal Repulsive Field Effect<sup>8</sup> which operates between the C=O and C—Br dipoles, leading as a consequence to an increase in the carbonyl bond order and consequently in its frequency.

The carbonyl frequency shifts for the most stable conformers of 3-sulfur-substituted thiochromones (2)–(7) can be rationalized mainly on the grounds of orbital interaction, inductive and field effects, assuming that the geometries of the most stable conformers of 2-chloro-cyclopentylthio- and chloro-methyl propenylthio-

TABLE IV  
Carbonyl frequency shifts<sup>a</sup> for 3-substituted  
thiochromones (2)–(7) and (9)

COMP.D.	$\Delta\nu^b$
(2)	-8
(3)	-14
(4)	+8
(5)	-7
(6)	-10 <sup>c</sup>
(7)	+10
(9)	+9

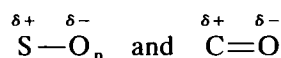
<sup>a</sup>In  $\text{CCl}_4$ .

<sup>b</sup> $\Delta\nu$  in  $\text{cm}^{-1}$ , refers to the difference:  
 $\nu_{[3\text{-substituted thiochromones}]}$   
 $- \nu_{[\text{thiochromone}]}$ .

<sup>c</sup>This frequency shift refers to the more intense component of the multiplet (see Table I).

thiochromones and their *mono*- and *di*-oxygenated derivatives (2)–(7) are close to the most stable conformations for the corresponding methylthio-, methylsulfinyl-, and methylsulfonyl-thiochromones (10)–(12) in relation to the dihedral angles (see Table III and Figure 5). However the influence of some vibrational effect in the  $\nu_{\text{CO}}$  frequencies of the title compounds cannot be ruled out without the help of a Normal Coordinate Analysis.

A progressive increase in the  $\nu_{\text{CO}}$  frequencies on going from —SR to —SOR and to —SO<sub>2</sub>R substituents should be expected from the Attractive Inductive Effect of the  $\alpha$ -substituents in the thiochromone series (2)–(7) as their  $\sigma_{\text{I}}$  values increase in the same direction e.g.,  $\sigma_{\text{I(SMe)}}^9 = 0.23$ ,  $\sigma_{\text{I(SOMe)}}^9 = 0.50$  and  $\sigma_{\text{I(SO}_2\text{Me)}}^9 = 0.59$ . However, while the Repulsive Field Effect is insignificant for the —SR substituent as the C—S—C dipole is perpendicular to the C=O dipole, in the cases of the SOR and SO<sub>2</sub>R substituents the Cooperative Field Effect<sup>10,11</sup> between the



dipoles becomes of importance as the sulfur atoms bear a positive formal charge, and the sulfinyl or sulfonyl oxygen atoms are further apart from the carbonyl oxygen atoms (see Figure 5). This Field Effect should originate an increase in the carbonyl group polarization, decreasing only partially the strong inductive effect of the —SOR and —SO<sub>2</sub>R substituents, thus causing a smaller increase in the  $\nu_{\text{CO}}$  frequencies for the compounds bearing these  $\alpha$ -substituents in relation to the compound with the —SR substituent, but following yet the  $\nu_{\text{CO}}$  order: SO<sub>2</sub>R > SOR > SR.

In the  $\alpha$ -sulfur-substituted thiochromone derivatives the  $\alpha$ -sulfur and the carbonyl oxygen atoms lie in the same plane and are close to each other as in the case of the *cis* rotamers of the aliphatic  $\alpha$ -alkylthio carbonyl compounds.<sup>3</sup> So, it seems quite reasonable to suggest the occurrence of the  $\pi_{\text{CO}}$  and 3d<sub>(S)</sub> through-space orbital interaction in the title compounds, taking into account that the carbonyl oxygen atom bears a significant negative charge in the delocalized valence bond structure<sup>5</sup> of the thiochromone rings which should facilitate this orbital interaction (Figure 5).

As the sulfur atoms of the oxygenated sulfur substituents (—SOR and SO<sub>2</sub>R) bear a positive charge, higher electron-affinities for their 3d sulfur orbitals should be expected in relation to the 3d sulfur orbitals of the SR substituent. This behavior may originate stronger  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO}_n)}$  orbital interactions in the  $\alpha$ -sulfinyl and  $\alpha$ -sulfonyl thiochromone derivatives, leading to a lowering in the  $\pi_{\text{CO}}$  electron density and thus to a larger decrease in the  $\nu_{\text{CO}}$  frequencies of these compounds in relation to the  $\alpha$ -thio-thiochromone derivatives.

Nevertheless in the case of the —SO<sub>2</sub>R group the occurrence of the back-donation from both oxygen atoms lone pairs to the 3d sulfur orbitals decreases the availability of these orbitals preventing at least in part the  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO}_2)}$  orbital interaction. Thus, the probable order of the  $\pi_{\text{CO}} \rightarrow 3d_{\text{SO}_n}$  interaction for the  $\alpha$ -sulfur-substituents in the  $\alpha$ -sulfur-substituted thiochromones is SOR > SO<sub>2</sub>R  $\geq$  SR which should lead to the same order of decrease of the  $\nu_{\text{CO}}$  frequencies for the title compounds.

The largest negative carbonyl frequency shifts for the  $\alpha$ -sulfinyl-thiochromone derivatives (3) and (6), followed by the less negative frequency shifts for the  $\alpha$ -thio-thiochromones (2) and (5), can thus be rationalized as follows. In the  $\alpha$ -

sulfinyl derivatives, the  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO})}$  orbital interaction is stronger in comparison to the same interaction which occur in the  $\alpha$ -thio derivatives. The strongly attracting inductive effect (-I) of the  $\alpha$ -sulfinyl substituents, although attenuated by the Cooperative Field Effect, is yet more pronounced than the -I effect of the  $\alpha$ -thio substituents. Assuming that the orbital interaction prevail over the -I effect for both the  $\alpha$ -sulfinyl and  $\alpha$ -thio derivatives, but to a larger extent for the  $\alpha$ -sulfinyl derivatives, the negative carbonyl frequency shift order is explained. This behavior results in a greater decrease in the carbonyl bond order and thus in a larger lowering of the  $\nu_{\text{CO}}$  frequencies for the  $\alpha$ -sulfinyl derivatives, in comparison to the  $\alpha$ -thio derivatives, in relation to the parent compound.

As for the positive carbonyl frequency shifts for the  $\alpha$ -sulfonyl-thiochromone derivatives (4) and (7) the strong -I effect of the  $\alpha$ -sulfonyl substituent, partially attenuated by the Cooperative Field Effect, prevails over the  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO}_2)}$  orbital interaction, whose extension should be very close to the corresponding orbital interaction taking place in the  $\alpha$ -thio thiochromone derivatives. This behavior increases the carbonyl bond order and therefore the  $\nu_{\text{CO}}$  frequencies of the title compounds in relation to the parent compound.

It is worth commenting that the  $\pi_{\text{CO}} \rightarrow 3d_{\text{s}}$  orbital interaction for the  $\alpha$ -thio-substituted thiochromones support the previous X-ray data,<sup>5</sup> being responsible for the shorter S...O intramolecular contact between the  $\alpha$ -sulfur and the carbonyl oxygen atoms in relation to the sum of the Van der Waals radii for compound (2) i.e., trans-3-(2'-chlorocyclopentylthio)-thiochromone and also for a compound which is related to compound (5), i.e., the E-2-(2'-chloro-1'-methylpropen-1'-ylthio)-2-cyclohexenone. It seems quite reasonable to predict for the  $\alpha$ -sulfinyl-thiochromones even shorter S...O contacts between the  $\alpha$ -sulfur and the carbonyl oxygen atoms taking into account that in the  $\alpha$ -sulfinyl-thiochromones (3) and (6) the  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO})}$  orbital interaction should be more pronounced than for the same interaction in the  $\alpha$ -thio derivatives (2) and (5). It is also reasonable to advance for the  $\alpha$ -sulfonyl-thiochromones the same shortening of the S...O intramolecular distance as observed for the  $\alpha$ -thio-substituted thiochromones, since the  $\pi_{\text{CO}} \rightarrow 3d_{(\text{SO}_2)}$  orbital interaction for the  $\alpha$ -sulfonyl-thiochromones (4) and (7) seems to be close to the corresponding orbital interaction in the  $\alpha$ -thio-substituted thiochromones (2) and (5).

#### Carbonyl $n \rightarrow \pi^*$ Transition Energies and Intensities

Table V shows the  $n \rightarrow \pi^*_{\text{CO}}$  transition energies and the corresponding band intensities for the  $\alpha$ -sulfur-substituted thiochromone derivatives (2)–(7) and for thiochroman-4-one (8) in *n*-hexane and methanol. Corresponding data for the parent thiochromone (1) are included for comparison.

The  $n \rightarrow \pi^*$  transition band displays a bathochromic shift for the  $\alpha$ -chlorocyclopentylthio-(2) and  $\alpha$ -chloromethylpropenylthio-(5)-thiochromones in relation to the parent compound (1) which decreases significantly on going to their corresponding  $\alpha$ -sulfinyl derivatives (3) and (6). However, the  $\alpha$ -sulfonyl derivatives (4) and (7) show a slight hypsochromic effect in both solvents except for compound (7) in *n*-hexane where a slight bathochromic shift is observed. In general the  $n \rightarrow$

TABLE V  
UV data for the carbonyl  $n \rightarrow \pi^*$  transition of the 3-substituted  
thiochromones (1)–(7) and thiochroman-4-one (8)

COMPD.	n-C <sub>6</sub> H <sub>14</sub>		MeOH	
	$\lambda^a$	$\log \epsilon^b$	$\lambda$	$\log \epsilon$
(1)	332	4.25	334	3.92
(2)	344	4.06	349	3.98
(3)	338	4.21	340	4.05
(4)	328	3.84	332	4.19
(5)	355	4.00	365	3.85
(6)	338	4.08	339	4.10
(7)	334	3.72	333	3.92
(8)	337	3.52	348	3.38
	238 <sup>c</sup>	4.47	240	4.39

<sup>a</sup>In nm.

<sup>b</sup>Apparent molar absorptivity in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .

<sup>c</sup>Transannular charge transfer transition (for details see text).

$\pi^*$  band intensities of the title compounds (2)–(7) do not change significantly in comparison to the reference compound (1) in both solvents.

The bathochromic effect of the  $\alpha$ -thio and  $\alpha$ -sulfinyl thiochromone derivatives and the slight hypsochromic effect of the  $\alpha$ -sulfonyl thiochromone derivatives may be ascribed to an interplay of the  $\pi_{\text{CO}}^*$  and 3d sulfur orbital interaction (see below) and the inductive effect of the  $\alpha$ -sulfur-substituents and can be visualized by the inspection of Figure 6.

Due to the electron-attracting inductive effect of the  $\alpha$ -sulfur-substituents, which is only partially attenuated for the sulfonyl and sulfinyl groups (see previous section) but should yet follow the order  $\text{SO}_2\text{R} > \text{SOR} \gg \text{SR}$ , the stabilization of the carbonyl lone pair  $n_{\text{O}(\text{CO})}$  should occur to a larger extent than that with the  $\pi_{\text{CO}}^*$  orbital before the interaction of the unperturbed  $\pi_{\text{CO}}^*$  and  $3d_{(\text{S})}$  orbitals.

The previous section suggests that the 3d sulfur orbitals of the sulfinyl group (SOR) should have a higher electron-affinity in relation to the sulfonyl group ( $\text{SO}_2\text{R}$ ), and that the electron-affinity of the 3d sulfur orbitals of the latter group is slightly higher than that of the sulfur substituent (SR).

A larger stabilization of the  $\pi_{\text{CO}}^*$  orbital in relation to that of the carbonyl oxygen lone pair should occur as a consequence of the interaction between the inductively stabilized  $\pi_{\text{CO}}^*$  and the  $3d_{(\text{SO}_n)}$  orbitals for the  $\alpha$ -thio and  $\alpha$ -sulfinyl-thiochromones (see Figure 6). This originates a lowering in the energy gap of the  $n \rightarrow \pi_{\text{CO}}^*$  transition for the title compounds ( $\Delta E_1$  and  $\Delta E_2$ ) in relation to that of the parent thiochromone ( $\Delta E_0$ ), although to a larger extent for the  $\alpha$ -thio derivatives than for the  $\alpha$ -sulfinyl derivatives, i.e.,  $\Delta E_1 < \Delta E_2$ . However, in the case of the  $\alpha$ -sulfonyl-thiochromones a larger stabilization of the carbonyl lone pair in relation to that of the  $\pi_{\text{CO}}^*$  orbital should occur, leading to an increase in the energy gap of the  $n \rightarrow \pi_{\text{CO}}^*$  transition for the title compounds ( $\Delta E_3$ ) in relation to the parent one ( $\Delta E_0$ ).

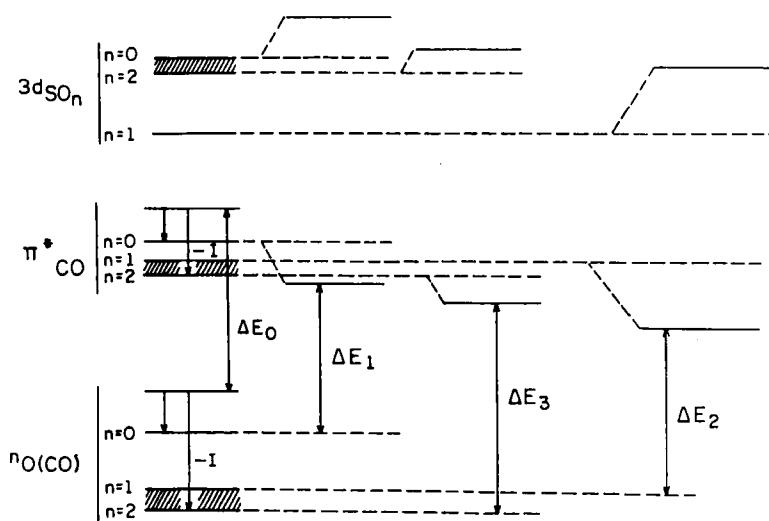


FIGURE 6 Qualitative energy level diagram of the unperturbed  $3d_{(SO_n)}$  ( $n = 0, 1$  and  $2$ ),  $\pi^*_{CO}$  and  $n_{O(CO)}$  orbitals for the  $\alpha$ -thio-,  $\alpha$ -sulfinyl- and  $\alpha$ -sulfonyl-thiochromones, showing the stabilization of the  $\pi^*_{CO}$  and  $n_{O(CO)}$  orbitals by the inductive effect of the  $\alpha$ -substituents, before orbital interaction; and the origin of the bathochromic effect of the  $n \rightarrow \pi^*_{CO}$  transition for the  $\alpha$ -thio- ( $\Delta E_1$ ) and  $\alpha$ -sulfinyl- ( $\Delta E_2$ ) thiochromones and the hypsochromic effect for the  $\alpha$ -sulfonyl-thiochromones ( $\Delta E_3$ ) in relation to the parent compound ( $\Delta E_0$ ), after orbital interaction.

The  $\pi^*_{CO}/3d_{(SO_n)}$  orbital interaction may be due to the simultaneous occurrence of: a) the direct interaction of the  $3d$  sulfur orbital of the  $\alpha$ -sulfur-substituent and the stabilized  $\pi^*$  orbital<sup>12</sup> which results from the  $\pi^*_{C=C}$  and  $\pi^*_{CO}$  orbital interaction in the thiopyrone moiety of the thiochromone rings; and b) the through-space interaction between the  $\pi^*_{CO}$  orbital and the  $3d_{(S)}$  orbital of the appropriate symmetry.

Lastly, Table V shows the occurrence of a significant bathochromic shift of the  $n \rightarrow \pi^*_{CO}$  transition for the thiochroman-4-one (**8**) on going from *n*-hexane to methanol. Moreover the UV spectrum of this compound in *n*-hexane displays a new, intense band at 238 nm in the congested part of the spectrum (where the benzene ring transitions appear) which is slightly bathochromically shifted in methanol. This band may be ascribed to charge transfer from the lone pair of the  $3p$  sulfur orbital to the vacant  $\pi^*_{CO}$  orbital, although a more pronounced solvent effect should be expected for this transition.<sup>13</sup> It should be pointed out that this behavior is in line with the IR  $\nu_{CO}$  data for compound (**8**) (see previous section) which suggested the occurrence of a twist-boat conformation in the thiopyranone ring as responsible for the S—CO transannular interaction. This contribution augments on going from a non-polar to a polar solvent at the expense of the twist-chair conformation where the transannular interaction is absent.

## CALCULATIONS

### Molecular-Mechanics Calculations

The MMC for the methylthio-, methylsulfinyl- and methylsulfonyl-thiochromones were performed using the MM2UEC program<sup>14</sup> with the 1989 updated MM2 (87)

parameters.<sup>15-17</sup> To avoid the time-consuming MMP-type calculations the mechanical treatment<sup>18,19</sup> was considered on the thiochromone rings. As the bond stretching parameter ( $k_s$ ) and natural bond length ( $l_0$ ) of a conjugated bond are

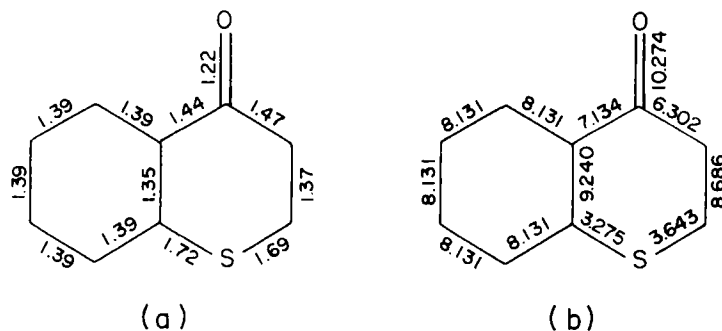


FIGURE 7 Equilibrium distances  $l_0$  (Å) (a) and stretching force constants (mdyn Å<sup>-1</sup>) (b) for the thiochromone rings used in Molecular Mechanics Calculations for the methylthio-, methylsulfinyl- and methylsulfonyl-thiochromones.

TABLE VI  
Parameters used in Molecular-Mechanics Calculations for 3-methylthio-, 3-methylsulfinyl- and 3-methylsulfonyl-thiochromones

Bond	$k_s^a$	$l_0^b$	$\mu^c$	Intervalency angle	$k_b^d$	$\theta_o^e$
2-15 <sup>f</sup>	3.30	1.75		2-2-15 <sup>f</sup>	0.5	120.0
2-17	3.50	1.76		2-2-17	0.5	120.0
2-18	3.50	1.76		2-2-18	0.5	120.0
42-2			1.000	3-2-15	0.5	120.0
				3-2-17	0.5	120.0
				3-2-18	0.5	120.0
				1-15-2	0.7	99.0
				1-17-2	0.8	105.0
				1-18-2	0.8	105.0
				2-17-7	0.6	108.0
				2-18-7	0.6	108.0
				0-2-15	0.05	
				0-2-17	0.05	
				0-2-18	0.05	

<sup>a</sup>Stretching force constant in mdyn Å<sup>-1</sup>.

<sup>b</sup>Equilibrium distance in Å.

<sup>c</sup>Dipole moment in Debye.

<sup>d</sup>Bending force constant in mdyn Å rad<sup>-2</sup>.

<sup>e</sup>Equilibrium intervalency angle in degrees.

<sup>f</sup>Numbers indicate atom type: 1 is sp<sup>3</sup> carbon, 2 is sp<sup>2</sup> carbon, 3 is carbonyl carbon, 5 is hydrogen, 7 is carbonyl oxygen, 15 is >S sulfur, 17 is >SO sulfur, 18 is >SO<sub>2</sub> sulfur and 42 is conjugated sulfur.



TABLE VII  
Out of Plane Torsional Energies<sup>a</sup> used in Molecular-Mechanics  
Calculations for the 3-methylthio-, 3-methylsulfinyl- and 3-  
methylsulfonyl-thiochromones

Dihedral angle	$v_1$	$v_2$	$v_3$
5-1-15-2 <sup>b</sup>	0.0	0.0	0.0
5-1-17-2	0.0	0.0	0.5
5-1-18-2	0.0	0.0	0.5
3-2-2-42	0.0	15.0	0.0
5-2-2-15	0.0	15.0	0.0
5-2-2-17	0.0	15.0	0.0
5-2-2-18	0.0	15.0	0.0
15-2-2-42	0.0	15.0	0.0
17-2-2-42	0.0	15.0	0.0
18-2-2-42	0.0	15.0	0.0
15-2-3-2	0.0	11.1	0.0
15-2-3-7	0.0	11.1	0.0
17-2-3-2	0.0	11.1	0.0
17-2-3-7	0.0	11.1	0.0
18-2-3-2	0.0	11.1	0.0
18-2-3-7	0.0	11.1	0.0
2-2-15-1	0.0	0.0	0.0
3-2-15-1	0.0	0.0	0.0
2-2-17-1	0.0	0.0	0.0
2-2-17-7	0.0	0.0	0.0
3-2-17-1	0.0	0.0	0.0
3-2-17-7	0.0	0.0	0.0
2-2-18-1	0.0	0.0	0.0
2-2-18-7	0.0	0.0	0.0
3-2-18-1	0.0	0.0	0.0
3-2-18-7	0.0	0.0	0.0

<sup>a</sup>In kcal mol<sup>-1</sup>

<sup>b</sup>Numbers indicate atom type as described in Table VI.

related in MMP to the  $\pi$  bond order ( $\rho_\pi$ ) by  $k_s = k_2 - \Delta k (1 - \rho_\pi)$  and  $l_0 = l_2 + \Delta l (1 - \rho_\pi)$ , where  $k_2$  and  $l_2$  are the parameters of the pure double bond and  $\Delta k$  and  $\Delta l$  are the increment factors given in MM2 (87) force field, the parameter  $k_s$  can be estimated without MO calculations by the combined equation  $k_s = k_2 - (\Delta k / \Delta l) \cdot (l_0 - l_2)$  when the value of  $l_0$  is known. In this study, the values  $l_0$  of thiochromone ring were assumed as given in Figure 7 based on the bond lengths from the X-ray diffraction study<sup>5</sup> and the values of  $k_s$  were calculated using the combined equation. The torsional parameters  $V_1$ ,  $V_2$  and  $V_3$  for the ring skeletal bonds were used without modification due to the electron delocalization. Tables VI and VII give the assumed values of the parameters added to complete the MM2 force field to perform the calculations.

#### Rotamer Population Ratios

The rotamer population ratios were determined<sup>20</sup> by the energy difference between them, using the relation:

$$\Delta G^\circ = -RT \ln k$$

where the symbols have their customary meaning. For instance, for the case of the 3-methylsulfinyl-thiochromone at 27°C or 300 K, the equilibrium between the less stable *b* and the more stable *a* conformers has  $\Delta H^\circ = +1.09 \text{ kcal} \cdot \text{mol}^{-1}$  (see Table III). Since there are two enantiomeric rotamers for each conformer the free energy change  $\Delta G^\circ$  is equal to the enthalpy change  $\Delta H^\circ$ , i.e.,  $\Delta G^\circ = \Delta H^\circ$ , as the entropy change  $\Delta S^\circ$  is zero.

Therefore for the  $a \rightleftharpoons b$  equilibrium,  $K = C_b/C_a = 0.164$ . The concentration of each rotamer can be easily determined taking into account that the summing up of the molar fraction of each rotamer is 1.0, i.e.,  $C_a + C_b = 1.0$ . Thus, for the 3-methylsulfinyl-thiochromone the computed concentrations for the two rotamers are:  $C_a = 0.86$  and  $C_b = 0.14$ .

## EXPERIMENTAL

**Materials.** All solvents for spectrometric measurements were spectrograde and were used without further purification.

Commercial (Aldrich) thiochroman-4-one (**8**) was used without further purification. Thiochromone (**1**),<sup>21</sup> and the 3-bromo-(**9**),<sup>22</sup> trans-3-(2'-chlorocyclopentylthio)-(2)<sup>5</sup> and E-3-(2'-chloro-1'-methylpropen-1'-ylthio)-(5)<sup>5</sup> thiochromones were prepared by literature procedures. The 3-sulfinyl (**3**), (**6**) and 3-sulfonyl (**4**), (**7**)-thiochromone derivatives are new compounds and were prepared as outlined below.

**General procedure for the preparation of sulfoxides (**3**) and (**6**):** A solution of the appropriate sulfide (0.33 mmol) in dry dichloromethane (5 ml) was stirred at 0°C under nitrogen. A solution of m-chloroperoxybenzoic acid (m-CPBA) (0.41 mmol) in dichloromethane (5 ml) was added dropwise to the cooled solution. The mixture was stirred at 0°C for 2.5 h and for an additional 30 min while the mixture warmed to 25°C. The reaction mixture was washed thoroughly (10% Na<sub>2</sub>SO<sub>3</sub>, satd. NaHCO<sub>3</sub>, satd. NaCl), and dried (MgSO<sub>4</sub>). Filtration and removal of the solvent gave the crude product, which was then recrystallized (see below).

**Trans-3-(2'-chlorocyclopentylsulfinyl)thiochromone, (**3**):** The crude yellow solid (100%) was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give pale yellow crystals (83%), mp 147–148.5°C; IR (KBr):  $\nu$  1608 (C=O), 1027 (S=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.0 (m, 6H), 4.0 (m, 1H), 4.7 (m, 1H), 7.6 (m, 3H), 8.5 (m, 2H); MS: *m/z* (% rel. int.) 315 (**3**), 313 (**6**), 210 (100), 194 (**6**), 162 (27), 136 (13), 67 (39). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>ClO<sub>2</sub>S<sub>2</sub>: C, 53.75; H, 4.19; Cl, 11.33; S, 20.50. Found: C, 53.61; H, 4.23; Cl, 11.31; S, 20.20.

**E-3-(2'-Chloro-1'-methylpropen-1'-ylsulfinyl)thiochromone, (**6**):** An off-white solid (92%) was obtained and recrystallized from dichloromethane/pentane to yield white needles (82%), mp 187–188°C; IR (KBr):  $\nu$  1618 (C=O), 1048 (S=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.8 (d, *J* ≈ 1 Hz, 3H), 2.7 (d, *J* ≈ 1 Hz, 3H), 7.5 (m, 3H), 8.5 (m, 2H); MS: *m/z* (% rel. int.) 300 (**4**), 298 (**7**), 210 (**41**), 209 (**32**), 194 (**69**), 193 (**100**), 136 (**47**), 108 (**33**), 53 (**51**). Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>ClO<sub>2</sub>S<sub>2</sub>: C, 52.56; H, 3.71; Cl, 11.86; S, 21.46. Found: C, 52.01; H, 3.81; Cl, 11.99; S, 20.82.

**General procedure for the preparation of sulfones (**4**) and (**7**):** A solution of the appropriate sulfide (0.35 mmol) in dry dichloromethane (5 ml) was stirred at 25°C under nitrogen. A solution of m-CPBA (0.79 mmol) in dichloromethane (5 ml) was added dropwise to the solution, which was stirred at 25°C for 20 h. The organic phase was washed thoroughly (10% Na<sub>2</sub>SO<sub>3</sub>, 10% NaHCO<sub>3</sub>, satd. NaCl) before being dried (MgSO<sub>4</sub>). Filtration and subsequent removal of the solvent gave the crude product which was recrystallized as described below.

**Trans-3-(2'-chlorocyclopentylsulfonyl)thiochromone, (**4**):** The crude pale yellow solid was flash chromatographed on silica gel, using dichloromethane as the eluent. The solid (64%) so obtained was recrystallized from ethanol to give white crystals of (**4**), mp 141–142°C; IR (KBr):  $\nu$  1626 (C=O), 1300, 1138 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.2 (m, 6H), 4.5 (m, 2H), 7.6 (m, 3H), 8.6 (m, 1H), 9.0 (s, 1H); MS: *m/z* (% rel. int.) 331 (**1**), 329 (**3**), 226 (**7**), 163 (15), 162 (100), 134 (12), 89 (21), 67 (21). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>ClO<sub>3</sub>S<sub>2</sub>: C, 51.14; H, 3.98; Cl, 10.78; S, 19.50. Found: C, 51.06; H, 3.97; Cl, 10.75; S, 19.51.

**E-3-(2'-Chloro-1'-methylpropen-1'-ylsulfonyl)thiochromone, (**7**):** Recrystallization of the crude white solid (100%) from dichloromethane/petroleum ether (30–60°C) yielded white crystals, mp 145–146°C;

IR (KBr):  $\nu$  1629 (C=O), 1306, 1135 (SO<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.8 (m, 1H), 2.2 (m, 2H), 2.8 (m, 3H), 7.6 (m, 3H), 8.5 (m, 1H), 9.0 (s, 1H); MS: *m/z* (% rel. int.) 316 (0.1), 314 (0.2), 279 (11), 215 (100), 162 (23), 134 (12), 89 (31), 53 (22). Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>ClO<sub>3</sub>S<sub>2</sub>: C, 49.60; H, 3.52; Cl, 11.26; S, 20.37. Found: C, 49.92; H, 3.71; Cl, 11.35; S, 20.19.

**IR and UV measurements.** The conditions for recording the IR carbonyl and benzene ring stretching bands in both fundamental (1750–1500 cm<sup>-1</sup>) and in the  $\nu_{CO}$  first overtone (3400–3100 cm<sup>-1</sup>) regions for ca.  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup> solutions of the thiochromones (1)–(9), in carbon tetrachloride and chloroform, using 0.2 mm calcium fluoride and 1.00 cm quartz matched cells, respectively, have already been described.<sup>23</sup> The  $\nu_{C=O}$  mode of the thiopyrone moiety of the thiochromone derivatives can be easily seen near 1530 cm<sup>-1</sup> in chloroform, but only with uncertainty in carbon tetrachloride, due to the strong absorption of the solvent in this region. The relative rotamer concentrations for compounds (6) and (8) were estimated from the ratio of the apparent molar absorption coefficients measured directly at the maxima or at the inflexion point of the partially overlapped carbonyl bands, assuming as an approximation the equality of the molar absorption coefficients of the two or three rotamers.

The UV spectra of ( $10^{-5}$ – $10^{-4}$  mol dm<sup>-3</sup>) solutions in methanol were recorded in a Beckman DU-70 spectrophotometer as previously described.<sup>1</sup>

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