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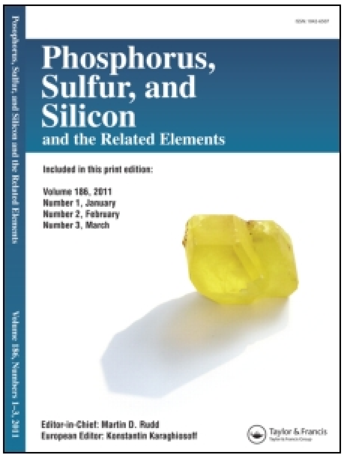

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Conformational and Electronic Interaction Studies of Some 3-Thio-Substituted Thiochromones and Their 3-Sulfinyl and 3-Sulfonyl Derivatives

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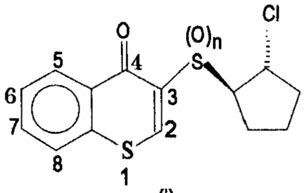
CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF SOME 3-THIO-SUBSTITUTED THIOCHROMONES AND THEIR 3-SULFINYL AND 3-SULFONYL DERIVATIVES.

Paulo R.Olivato[a], Sandra A.Guerrero[a], Julio C.D.Lopes[a], Yoshiyuki Hase[b], Ian W.J.Still[c] and Donna K.T.Wilson. [a]Instituto de Química, Universidade de São Paulo, C.P. 20.780, CEP 01498-970, São Paulo, S.P. - Brazil; [b]Universidade Estadual de Campinas, Brazil; [c]University of Toronto, Canadá.

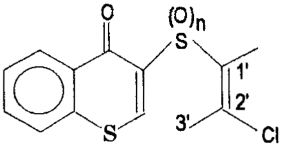
ABSTRACT. The analysis of the carbonyl ($\Delta\nu_{CO}$) and carbon-carbon double bond ($\Delta\nu_{C=C}$) frequency shifts for some 3-thio-substituted thiochromones and their 3-sulfinyl- and 3-sulfonyl derivatives indicated the occurrence of both $\pi_{CO}/3d_{SOn}$ and $n_{O(CO)}/\sigma^*_{C-SOn}$ orbital interactions in the ground state of the title compounds.

INTRODUCTION

This communication reports some additional I.R. results and analysis of the previously studied[1] trans-3-(2'-chlorocyclopentylthio)- (Ia) and E-3(-2'-chloro-1'-methylpropen-1'-ylthio)- (IIa) thiochromones and their corresponding 3-sulfinyl- (Ib,IIb) and 3-sulfonyl- (Ic, IIc) derivatives; and the thiochromone (III).

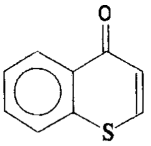


(I)



(II)

n = 0 (a)
n = 1 (b)
n = 2 (c)



(III)

RESULTS AND DISCUSSION

The previous analysis of the ν_{CO} bands in the I.R. spectra of the title compounds supported by Molecular Mechanics Calculations of 3-methyl-, 3-methylsulfinyl- and 3-methylsulfonyl-thiochromones, taken as model compounds, indicated the existence of a single conformer for the whole series except for the case of 3-sulfinyl derivative (IIb), where three conformers were observed.

Table 1 shows the carbonyl stretching frequencies for the most stable conformers of the 3-sulfur-substituted thiochromones I(a,b,c) and II(a,b,c) and their carbonyl frequency shifts in relation to the parent thiochromone (III), in carbon tetrachloride.

The negative frequency shifts ($\Delta\nu_{CO}$) for the 3-sulfinyl- and 3-thio-thiochromone derivatives and the positive carbonyl shifts for the 3-sulfonyl-thiochromone derivatives for series (I) and (II) in relation to the unsubstituted thiochromone have been ascribed to an interplay of the $\pi_{CO}/3d_{SOn}$ orbital interaction with the inductive and field Effects of the 3-substituents.

Taking into account that the carbonyl oxygen lone pair and the α-carbon-sulfur atom lie in the same plane for all the α-sulfur-substituted thiochromone derivatives, it seems reasonable to suggest also the occurrence of the $n_{O(CO)} \rightarrow \sigma^*_{C\text{-}SOn}$ orbital interaction^2 in the title compounds.

TABLE 1. *Carbonyl stretching frequencies[a,b] and the frequency shifts ($\Delta\nu$)[c] for the most stable rotamers of 3-substituted thiochromones.*

Compd.	ν_{CO}	$\Delta\nu_{CO}$
(III)[c]	1634	-
(Ia)	1626	-8
(3)	1620	-14
(Ic)	1642	+8
(IIa)	1627	-7
(IIb)	1624	-10
(IIc)	1644	+10

[a]From reference 1; [b]In cm^{-1}; [c]$\Delta\nu$ refers to the difference: $\nu_{[3\text{-substituted thiochromone}]} - \nu_{[\text{thiochromone}]}$; [c]Parent compound.

From the attachment energy data of the σ^*_{C-SOn} orbital for the Me_2SO_n compounds taken as the reference compounds whose values are: 2.30 eV[3] for Me_2SO, 3.15 eV[4] for Me_2SO_2 and 3.25 eV[5] for the Me_2S, it can be concluded that the σ^*_{C-SO} orbital has the higher electron-affinity and both the $\sigma^*_{C-SO_2}$ and σ^*_{C-S} orbital have the lower ones.

Although the ionization energy datum of the carbonyl oxygen lone pair $n_{O(CO)}$ for the thiochromone moiety is unknown, in the light of the simple M.O. Perturbation Theory[6] stronger $n_{O(CO)} \rightarrow \sigma^*_{C-SOn}$ orbital interaction should be expected with the α-sulfinyl thiochromone derivatives and weaker ones with the α-sulfonyl and α-thio-thiochromone derivatives. i.e. following the order: SOR >> SO_2R > SR.

The $n_{O(CO)} \rightarrow \sigma^*_{C-SOn}$ interaction should originate a great polarization of the carbonyl group leading to a decrease in the ν_{CO} frequency. Thus this orbital interaction should lead to a large decreasing of the ν_{CO} frequency for α-sulfinyl-thiochromone derivatives in relation to the α-sulfonyl- and α-thio-thiochromone derivatives.

The above analysis shows that the attachment energies for the σ^*_{C-SOn} orbitals follow practically the same previously proposed order of the electron-affinities for the $3d_{(SOn)}$ orbitals i.e. SOR > SO_2R > SR, leading to the same sequence for both $n_{O(CO)} \rightarrow \sigma^*_{C-SOn}$ and $\pi_{CO} \rightarrow 3d_{(SOn)}$ orbital interactions in the α-sulfur substituted thiochromone series.

The carbonyl frequency shifts showed in Table 1 can be rationalized as follows.

In the α-sulfinyl-thiochromone derivatives (Ib,IIb) both $\pi_{CO} \rightarrow 3d_{(SO)}$ and $n_{O(CO)} \rightarrow \sigma^*_{C\text{-}SO}$ orbital interactions are stronger in comparison to the same interactions in the α-thio-thiochromone derivatives (Ia,IIa). The -I Effect of the α-sulfonyl substituents is stronger than the -I Effect of the α-thio-substituents. Assuming that the orbital interactions prevail over the -I Effect for both α-sulfinyl- and α-thio- derivatives, but to a larger extent for the α-sulfinyl derivatives, the carbonyl frequency shifts order is explained.

As for the positive carbonyl frequency shifts for the α-sulfonyl thiochromone derivatives (Ic,IIc), the strong -I Effect of the α-sulfonyl substituent prevails over the summing up of both orbital interactions increasing the ν_{CO} frequencies of the title compounds in relation to the parent one.

TABLE 2. Carbon-carbon double bond stretching frequencies[a] and the frequency shifts $(\Delta\nu)^b$ of the enonic system of the thiopyrone moiety of 3-substituted thiochromones, in $CHCl_3$.

Compd.	$\nu_{C=C}$	$\Delta\nu_{C=C}$
(III)[c]	1546	-
(Ia)	1526	-20
(Ib)	1538	-8
(Ic)	1530	-16
(IIa)	1526	-20
(IIb)	1535	-11
(IIc)	1530	-16

[a] In cm^{-1}; $\Delta\nu^b$ refers to the difference: $\nu_{[3\text{-substituted thiochromone}]} - \nu_{[thiochromone]}$; [c] Parent compound.

Table 2 shows the carbon-carbon double bond stretching frequencies of the thiopyrone moiety for the α-substituted thiochromones I(a,b,c) and II(a,b,c) and their frequency shifts in relation to the thiochromone (III), in chloroform. It may be seen that the $\Delta\nu_{C=C}$ values for both α-sulfur substituted thiochromone series are negative.

As expected the decrease of the cooperative vibrational coupling in the carbon-carbon double bond by the substitution of the α-hydrogen atom for the heavier sulfur atom originates a lowering of the $\Delta\nu_{C=C}$ frequency. However, in the case of the title compounds there is also the contribution of the $\pi_{C=C}/3d_{(S)}$ interaction causing further decreasing in the $\nu_{C=C}$ frequency.

Table 2 also shows that the α-sulfinyl derivatives (Ib,IIb) present the less negative frequency shifts in relation to the other α-sulfur derivatives. This trend is opposite to that presented in Table 1 for the carbonyl frequency shifts where the α-sulfinyl derivative showed the more negative shifts in relation to the other α-sulfur derivatives.

This reverse behavior seems to be an evidence of a competition of the interaction between the $n_{O(CO)} \rightarrow \sigma^*_{C-SO}$ orbitals and the interaction between the delocalized enonic π system and the 3d sulfur orbitals (through-space in the case of the π_{CO} orbital and directly in the case of the $\pi_{C=C}$ orbital).

In fact as for the $n_{O(CO)} \rightarrow \sigma^*_{C-S}$ orbital interaction the α-sulfinyl derivatives present the strongest interaction in the α-sulfur thiochromones series leading to a large increase in the charge density of the α-sulfur atom in relation to the α-thio and α-sulfonyl derivatives. Consequently, the electron-affinity of the $3d_{(S)}$ orbital for the α-sulfinyl derivatives should decrease supressing at least in part the $\pi_{C=C}/3d_{(S)}$ interaction, leading to a smaller decrease in the ethenyl frequency shifts for the α-sulfinyl derivatives in relation to the other α-sulfur derivatives.

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