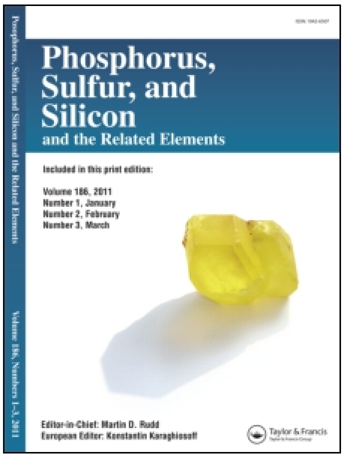

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Olivato, Paulo R. , Wladislaw, Blanka , Guerrero, Sandra A. and Russowsky, Dennis(1985) 'CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS BY I.R. SPECTROSCOPY. III. S-ETHYL α-(ALKYLTHIO)-THIOESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 24: 3, 225 — 233

To link to this Article: DOI: 10.1080/03086648508074233

URL: http://dx.doi.org/10.1080/03086648508074233

Phosphorus and Sulfur, 1985, Vol. 24, pp. 225–233
0308-664X/85/2403–0225/$15.00/0

CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS BY I.R. SPECTROSCOPY. III. S-ETHYL α-(ALKYLTHIO)-THIOESTERS[1]

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(*Received February 28, 1985*)

The carbonyl stretching frequencies and the apparent molar absorptivities are reported for some α-(alkylthio)-thioacetates, thiopropionate and thioisobutyrate, in the fundamental and in the first overtone regions and compared to those for the corresponding unsubstituted thioesters. In the α-(alkylthio)-thioacetate series the data indicate the presence of two rotamers: *cis* and *gauche*. The unusual solvent effect and $\Delta\nu_{CO}$ shifts for the *cis* conformers as compared to other α-hetero-substituted carbonyl compounds are interpreted in terms of a decrease in polarity in relation to the *gauche* conformers. The larger negative $\Delta\nu_{CO}$ values for the *gauche* conformers, which are still more increased by the increased bulkiness of the α-alkylthio group in comparison with the other α-sulfur substituted carbonyl compounds, are attributed to the *gauche* repulsion between two alkylthio-groups. The presence of two *gauche* rotamers in the α-(ethylthio)-thiopropionate and one in the α-(ethylthio)-thioisobutyrate is observed and the $\Delta\nu_{CO}$ values discussed in terms of change in the mechanical coupling and carbonyl angle. Charge transfer from π_{CO} to $3d_{(S)}$ and hyperconjugative σ_{C-S}/π_{CO} interaction are invoked to explain the obtained results.

Previous reports from this laboratory[2,3] showed that, among the hetero-substituted acetones and *N,N*-diethylacetamides, those containing sulfur atom are of particular interest. They exhibit the largest negative frequency shifts of the carbonyl group for the *gauche* conformers, induced by hyperconjugative interaction between σ_{C-S} and π_{CO} orbitals, and, also, the smallest positive shift of the same group for the *cis* conformers.

It is noteworthy that no conformational studies but only carbonyl i.r. frequencies and basicity as well as u.v. measurements were reported for the α-(alkylthio)-thioesters.[4,5] The present work was undertaken in order to fulfil this gap and also because it was expected that the introduction of α-sulfur atom in the —S—CO—C$<$ system could throw some light to the understanding of the relationship between the conformational isomerism and electronic interactions in the α-sulfur substituted carbonyl compounds.

This paper describes the investigation of the rotational isomerism in some S-ethyl α-(alkylthio)thioesters through the study of the i.r. carbonyl stretching vibration data.

RESULTS AND DISCUSSION

Table I shows the carbonyl stretching frequencies and the apparent molar absorptivities for some α-(alkylthio)-thioacetates (2)–(5) in the fundamental and first overtone

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TABLE I

Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of *S*-ethyl α-(alkylthio)thioacetates RC(O)SEt

		Fundamental									First overtone		
		n-C_6H_{14}			CCl_4			$CHCl_3$			CCl_4		
Comp	R	ν^a	ε^b	$\varepsilon_c/^c\varepsilon_g$	ν	ε	$\varepsilon_c/^c\varepsilon_g$	ν	ε	$\varepsilon_c/^c\varepsilon_g$	ν	10ε	$\varepsilon_c/^c\varepsilon_g$
(1)	Me^d	1701	631	—	1693	630	—	1686	398	—	3365	44	—
(2)	$EtSCH_2$	1697	92		1695	70(170)^e		—	—		3364	(16)^e	
		1684	357	0.26	1680	335	0.21(0.51)^f	1675	303	0	3331	33	(0.48)^f
(3)	Bu^iSCH_2	1697	85		1694	71(196)		—	—		3368	(19)	
		1683	368	0.23	1679	355	0.20(0.55)	1676	268	0	3332	36	(0.54)
(4)	Pr^iSCH_2	1696	93		1695	63(197)		—	—		3364	(17)	
		1684	372	0.25	1679	337	0.19(0.56)	1674	357	0	3334	33	(0.51)
(5)	Bu^tSCH_2	1694	108		1696	77(141)		—	—		3360	(15)	
		1682	347	0.31	1678	296	0.26(0.48)	1676	269	0	3333	32	(0.47)

[a] In cm^{-1}.

[b] Apparent molar absorptivity in $l \cdot mol^{-1} \cdot cm^{-1}$.

[c] Subscripts c and g indicate *cis* and *gauche* rotamers respectively.

[d] Parent compound.

[e] All intensity data in brackets are estimated at the inflection point of the unresolved doublet.

[f] Ratio of the high and low frequencies components of the superimposed bands.

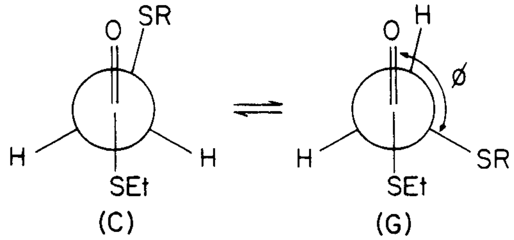

FIGURE 1 Conformations of the α-(alkylthio)-thioacetates.

regions in *n*-hexane, carbon tetrachloride and chloroform. Corresponding data for the parent unsubstituted thioester (1) are included for comparison.

The inspection of the Table I shows that in the fundamental region, in *n*-hexane, all α-(alkylthio)-thioacetates (2)–(5) exhibit two overlapped bands. However, it may be noticed that going to carbon tetrachloride, there is a slight increase in the intensity of the lower frequency component of this doublet in relation to the higher one and when the solvent is chloroform only the lower frequency component is observed. Although, this solvent effect, could be indicative of Fermi resonance,[6a] the occurrence of two superimposed bands for the same compounds, in the first overtone region, at frequencies approximately twice of those in the fundamental one and of the same intensities ratios throws out this possibility and strongly suggests the *cis* (C)–*gauche* (G) rotational isomerism (Figure 1). The decrease in intensity of the higher frequency band corresponding to the *cis* conformer by the increase of solvent polarity, indicating that the lower frequency *gauche* conformer is more polar than the *cis* one, is in disaccord with the solvent effect generally observed in the hetero-substituted carbonyl compounds,[2,3,7] for which the *cis* rotamer was shown to be more polar than the *gauche* one.

This reversal of the polarity in the α-sulfur-substituted thioesters is supported by the carbonyl frequency shifts of the *cis* conformers ($\Delta\nu_c$), in comparison with the unsubstituted thioester (1), in *n*-hexane and carbon tetrachloride (Table II). It may be seen that the $\Delta\nu_c$ values, which, due to the repulsive Field Effect between CO and C—S, should be highly positive,[6b] are negative in *n*-hexane and only slightly positive in carbon tetrachloride. This seems to indicate that there is some other electronic interaction which decreases the electronic density in the π_{CO} orbital, preventing or, at least, decreasing the Field Effect. Such decrease of electronic density in the π_{CO} system could be also responsible for the decrease of the polarity of the *cis* conformer in relation to the *gauche* one (Figure 2). Considering the close spacial proximity of the α-sulfur atom and carbonyl group in the *cis* conformer it seems reasonable to suggest that such decrease of the electronic density on the carbonyl group could be due to an interaction between π_{CO} and $3d_{(S)}$ orbitals (Figure 3).

Although, it cannot be excluded that such interaction could be general for the α-thiosubstituted carbonyl systems, it is more pronounced in the α-(alkylthio)-thioesters, which showed to exhibit smaller oxygen basicity[5,8] and, therefore, lower carbonyl dipole moment, in comparison with the majority of the aliphatic carbonyl compounds.

Table II shows that the $\Delta\nu_{CO}$ shifts for the *gauche* conformers ($\Delta\nu_g$) are negative. In analogy to the other α-sulfur-substituted carbonyl compounds[2,3] this decrease of

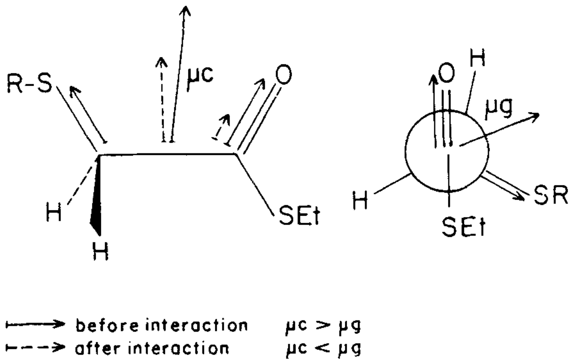

FIGURE 2 The variation of the polarity of the *cis* conformer in relation to that of the *gauche* one.

the force constant of the carbonyl group may be attributed to a hyperconjugative interaction between σ_{C-S} and π_{CO} orbitals (Figure 4).

However it may be noticed that the negative values of the $\Delta\nu_g$, in carbon tetrachloride, for the α-(alkylthio)-thioesters of 13 cm^{-1} are larger than those for the α-alkylthio-*N*,*N*-diethylamides[3] and α-alkylthio-ketones,[2] which were of 9 and 11 cm^{-1} respectively.

Tables I and II show also the dependence of the $\Delta\nu_{CO}$ shifts for the *cis* and *gauche* conformers and of the intensities ratios on the size of the α-SR groups. It may be seen that, in *n*-hexane, going from the ethylthio to the *t*-butylthio-group there is an increase of the absolute $\Delta\nu_{CO}$ values for both components of the doublet, and an increase of the population of the higher frequency component.

It seems reasonable to suggest that the lowering of the carbonyl frequency of the *gauche* conformer, in *n*-hexane, by the increase of the bulkiness of the α-alkylthio group, may be due to a *gauche* repulsion between the ethylthio-carbonyl and α-alkylthio-groups. In order to relieve this strain a decrease of the dihedral angle would occur (Figure 1G) leading to a better overlapping of the σ_{C-S} and π_{CO} orbitals and, therefore, to a decrease in the carbonyl force constant. On the other

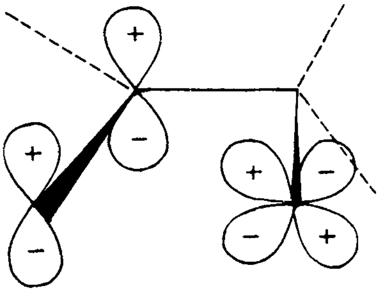

FIGURE 3 Schematic representation of the electronic interaction between the π_{CO} and $3d_{(S)}$ orbitals in the *cis* conformer in the α-(alkylthio)thioacetates.

TABLE II

Carbonyl frequency shifts[a] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of *S*-ethyl α-(alkylthio)-thioacetates RC(O)SEt

Comp	R	n-C_6H_{14}		CCl_4	
		$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(2)	$EtSCH_2$	−3	−16	2	−13
(3)	Bu^iSCH_2	−4	−17	2	−14
(4)	Pr^iSCH_2	−4	−17	1	−14
(5)	Bu^tSCH_2	−7	−19	3	−15

[a] $\Delta\nu_c$ and $\Delta\nu_g$ in cm^{-1}, refers to the difference: ν[*S*-ethyl α-(alkylthio)-thioacetate]-ν[*S*-ethyl thioacetate].

hand, the increase of the negative value of $\Delta\nu_c$ for the *cis* conformer, going from the ethylthio to *t*-butylthio group, may be attributed to the fact that the bulky group would restrict the rotation of the α-alkylthio-group favouring the planar *trans* conformation in which a better overlapping between π_{CO} and $3d_{(S)}$ orbitals would occur (Figure 5). The increase of the *cis/gauche* ratio is a consequence of the decrease of the stability of the *gauche* conformer in favour of the *cis* one.

It should be mentioned that these i.r. results are in good agreement with the u.v. data, previously reported from this laboratory,[9] which showed a slight hypo- and hypsochromic effects of the $n \rightarrow \pi^*$ transition for the same compounds with the increase of the size of the α-alkylthio-group, indicating a decrease of the population of the *gauche* conformer, responsible for the hyperconjugative interaction between σ^*_{C-S} and π^*_{CO} orbitals.[2]

It became of interest to see whether the replacement of the α-hydrogen atoms in the α-sulfur substituted thioacetate by methyl groups would modify also its conformational aspect. Table III shows the i.r. carbonyl data for the α-(ethylthio)-thiopropionate (7) and α-(ethylthio)-thioisobutyrate (9) in comparison with the parent unsubstituted thioesters (6) and (8). It may be observed that the latter compounds, similarly to the unsubstituted thioacetate (1) (see Table I), show one carbonyl band in all solvents. However the α-(ethylthio)-thiopropionate (7) exhibits a triplet in *n*-hexane and a doublet in carbon tetrachloride and chloroform. The α-(ethylthio)-thioisobutyrate (9) shows only a single symmetrical band for all the solvents used.

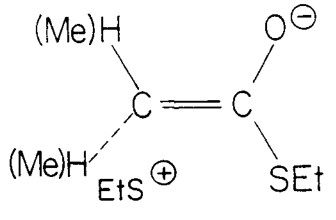

FIGURE 4 Hyperconjugative structure for the *gauche* conformers of the α-ethylthio-(thioesters).

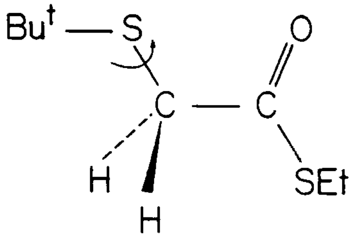

FIGURE 5 Planar *trans* conformation for the α-(*t*-butyl) group.

It may be observed (Table IV) that the carbonyl frequency shift for the higher frequency component of the triplet for (7), in *n*-hexane, is of the same value as that for the *cis* rotamer for the α-(ethylthio)-thioacetate (2) (see Table II). Furthermore, the frequency shift for the middle frequency component of the triplet is practically the same as that for the *gauche* rotamer of (2). Finally, the frequency shift for the lowest component of the triplet shows the carbonyl frequency shift very close to that of the single band of the α-(ethylthio)-thioisobutyrate (9).

Table 4 shows also that the carbonyl frequency shifts for the higher and the lower components of the doublet for the α-ethylthio-thiopropionate (7), in carbon tetrachloride, in the fundamental as well in the first overtone region, correspond approximately to those for the *cis* rotamer of the α-(ethylthio)-thioacetate (2) and to that of the single band of the α-(ethylthio)-thioisobutyrate, respectively (9).

From this frequency shifts analysis and in close analogy to the 3-chlorobutanone-2[10] it seems reasonable to suggest that the α-(ethylthio)-thiopropionate exists, in *n*-hexane, in three conformations (Figure 6), one *cis* (C) and two *gauche* (G_1) and (G_2) and in carbon tetrachloride and chloroform in the *cis* (C) and *gauche* (G_2) conformations. It seems obvious that the single band in the α-(ethylthio)-thioisobutyrate (9) may be assigned to the *gauche* conformer (G_2') which has similar steric environment to (G_2).

It may be observed (Table IV) that the decrease in the carbonyl frequency of the single *gauche* conformer of the α-(ethylthio)-thioisobutyrate (9), in relation to the parent compound (8) shows, in all solvents, an average value which is 1.5 times greater than that of the *gauche* conformer of the α-(ethylthio)-thioacetate (see Table II).

The larger decrease of the carbonyl frequency in (G_2) and (G_2') may be partly explained by a change in the mechanical coupling between C═O, C—C and C—S oscillators, resulting from the increase in the α carbonyl angle,[6c] which should occur in order to relieve the *gauche* strain (Figure 7). However, it seems reasonable to suggest that, although the variation in the hybridization of the carbonyl group is small,[11] it should play also an important role. In fact, with the increase of the α carbonyl angle, the C—O bond becomes longer and, consequently, more polar, thus increasing (in the V.B. terminology) the contribution of the hyperconjugative structure (Figure 4). This effect should produce a decrease of the carbonyl force constant and, thus, a lowering in the carbonyl frequency.

TABLE III

Carbonyl frequencies and intensities of the carbonyl stretching bands in the infrared spectra of *s*-ethyl α-(ethylthio)-thiopropionate and -thioisobutyrate RC(O)SEt

		Fundamental									First overtone		
		n-C_6H_{14}			CCl_4			$CHCl_3$			CCl_4		
Comp	R	ν^a	ε^b	$\varepsilon_c/{}^c\varepsilon_g$	ν	ε	$\varepsilon_c/{}^c\varepsilon_g$	ν	ε	$\varepsilon_c/{}^c\varepsilon_g$	ν	ε	$\varepsilon_c/{}^c\varepsilon_g$
(6)	$MeCH_2$[d]	1702	685	—	1696	652	—	1685	449	—	3367	47	—
(7)	EtSCHMe	1700	136		1694	126(162)[e]		1688	98		3361	(16)[e]	
		1687	121	1.12	–			—			—		
		1677	371	0.37	1673	338	0.37(0.48)[f]	1668	273	0.36	3325	34	(0.47)[f]
(8)	Me_2CH[d]	1699	461	—	1691	557	—	1682	420	—	3360	42	—
(9)	$EtSC(Me)_2$	1677	563	—	1668	493	—	1665	353	—	3316	45	—

[a] In cm^{-1}.

[b] Apparent molar absorptivity, in $l \cdot mol^{-1} \cdot cm^{-1}$.

[c] Subscripts c and g indicate *cis* and *gauche* rotamers respectively.

[d] Parent compound.

[e] All the intensity data in brackets are estimated at the inflection point of the unresolved doublet.

[f] Ratio of the intensities of the high and low frequencies components of the superimposed bands.

TABLE IV

Carbonyl frequency shifts[a] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of *S*-ethyl α-(ethylthio)-thiopropionate and thioisobutyrate RC(O)SEt

		Fundamental						First overtone	
		n-C_6H_{14}		CCl_4		$CHCl_3$		CCl_4	
Comp	R	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(7)	EtSCHMe	−3	−15	−2	—	3	—	−6	—
			−25		−23		−17		−42
(9)	$EtSC(Me)_2$	—	−22	—	−23	—	−17	—	−44

[a] $\Delta\nu_c$ and $\Delta\nu_g$ in cm^{-1}, refers to the difference: ν[S-ethyl α-(ethylthio)thioester]-ν[corresponding unsubstituted *S*-ethyl thioester].

EXPERIMENTAL

All solvents for spectrometric measurements were spectrograde and were used without further purification. The preparation and purification of the thioesters (1)–(9) have already been described.[5,11]

I.R. Measurements. I.R. spectra were recorded on a Perkin-Elmer model 283 grating spectrometer at room temperature. The spectral slit width was 2.0 cm^{-1} and 3.5 cm^{-1}, in the fundamental and in the first overtone carbonyl frequency regions, respectively. The carbonyl frequencies, in the fundamental region, were measured in the transmittance scale mode for 2.0–3.0 × 10^{-2} M solutions in *n*-hexane, carbon tetrachloride and chloroform, using a pair of 0.50 mm sodium chloride matched cells. In the overtone region, 2.0–3.0 × 10^{-2} M solutions in carbon tetrachloride were measured using a pair of 1.00 cm quartz matched cells. Further dilution did not affect the spectra. The carbonyl frequencies values for the more and less intense components of the doublet were accurated, in the fundamental region to ±0.5 and ±1 cm^{-1}, respectively and in the first overtone region to ±1 and ±2 cm^{-1}, respectively. In the fundamental

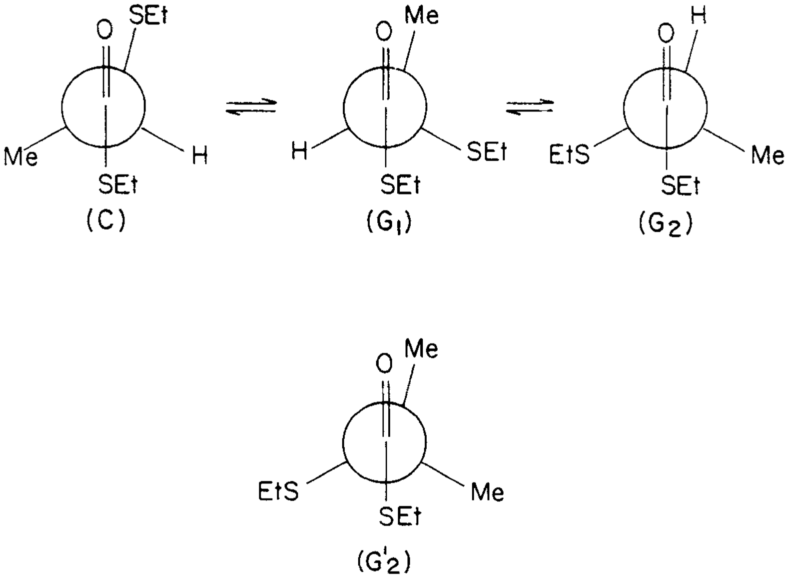

FIGURE 6 Conformations of the α-(ethylthio)-thiopropionate and thioisobutyrate.

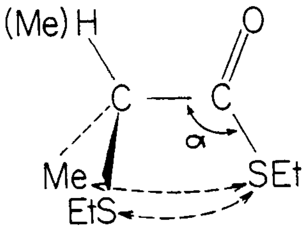

FIGURE 7 *Gauche* strain in the α-(ethylthio)-thiopropionate and thioisobutyrate.

region, the *cis/gauche* ratios were obtained from the spectra recorded in the 1800–1600 cm^{-1} interval, in the absorbance scale mode. The *cis/gauche* relative concentrations were estimated from the ratio of the apparent molar absorptivities of the two components of the graphically decomposed bands,[12] assuming as an approximation equality of the molar absorptivity of the two rotamers. In the first overtone region, the spectra were recorded in the 3600–3200 cm^{-1} interval and due to an extensive overlap of the components of the doublet, the *cis/gauche* relative concentrations were estimated from the ratio of the apparent molar absorptivities measured directly at the inflection point and at the absorptions maxima of the band, respectively.

ACKNOWLEDGMENTS

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo for financial support and for a scholarship (to S.A.G.) and the Conselho Nacional de Pesquisa for a grant (to P.R.O.).

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