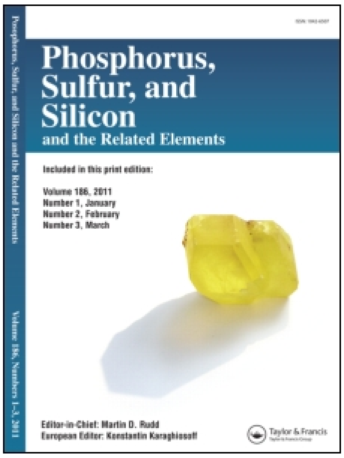

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS BY I.R. SPECTROSCOPY. VII. ETHYL α-(ALKY LTHI0)-ESTERS

Paulo R. Olivato[a]; Fausto Oike[a]; Julio C. D. Lopes[a]
[a] Instituto de Quimica, LISP, São, Paulo, Brazil

To cite this Article Olivato, Paulo R. , Oike, Fausto and Lopes, Julio C. D.(1990) 'CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS BY I.R. SPECTROSCOPY. VII. ETHYL α-(ALKY LTHI0)-ESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 47: 3, 391 — 399

To link to this Article: DOI: 10.1080/10426509008037995
URL: http://dx.doi.org/10.1080/10426509008037995

Phosphorus, Sulfur, and Silicon, 1990, Vol. 47, pp. 391-399

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

PAULO R. OLIVATO,† FAUSTO OIKE and JULIO C. D. LOPES
Instituto de Química, USP, C.P. 20.780, São Paulo, Brazil

(Received June 21 1989; in final form June 22, 1989)

Carbonyl stretching frequencies and apparent molar absorptivities are reported for some α-(alkylthio)-acetates, -propionate and -isobutyrate, in the fundamental and 1st overtone regions and compared to those for the corresponding unsubstituted esters. The I.R. data for α-(alkylthio)-esters indicate the *cis–gauche* rotational isomerism. Both the unusual solvent effect and the $\Delta\nu_{CO}$ frequency shifts for the title compounds indicate that the *cis* rotamers are less polar than the *gauche* ones. The *gauche* rotamer (G_1) for the α-(ethylthio)-propionate corresponds to the *gauche* rotamer (G) for the α-(ethylthio)-acetate while the more crowded *gauche* rotamer (G_2') for the α-(ethylthio)-isobutyrate corresponds to the *gauche* rotamer (G_2) for the α-(ethylthio)-propionate. The larger $\Delta\nu_{CO}$ values for the *cis* (C) and *gauche* (G_2') rotamers of α-(ethylthio)-isobutyrate in comparison to the *cis* (C) and *gauche* (G_1) rotamers of the α-(ethylthio)-propionate are explained in terms of variation in the α-carbonyl angle, changes in mechanical coupling and hybridization. Charge transfer from π_{CO} to $3d_{(S)}$ orbitals and π_{CO}/σ_{C-S} hyperconjugative interaction are also invoked to explain the obtained results.

Key words: Conformational studies, electronic interactions, I.R. spectroscopy, ethyl α-(alkylthio)-esters.

INTRODUCTION

Our previous I.R. conformational study on S-ethyl α-(alkylthio)-thioesters[2] has shown that the *cis* rotamers of the title compounds are abnormally less polar than the *gauche* ones. This behavior has been attributed to the charge transfer from the π_{CO} orbital to a vacant 3d sulfur orbital which occurs in the *cis* conformer, preventing or at least decreasing the normal Field Effect between the C=O and C—S dipoles. Although the $\pi_{CO} \rightarrow 3d_{(S)}$ interaction seems to be generally present in the *cis* rotamers of the α-thiosubstituted carbonyl compounds, in the case of some α-(alkylthio)-acetones[3] and -amides[4] the *cis* rotamers have shown to be more polar than the *gauche* ones. So, it became of interest to investigate the α-(alkylthio)-esters taking into consideration that, similarly to the unsubstituted thioesters, the oxygen basicities[5] and therefore the carbonyl dipole moments of the esters are smaller than those of the majority of the other aliphatic carbonyl compounds. As in the case of the α-(alkylthio)-thioesters, this behavior may cause also in the α-(alkylthio)-esters a lower polarity of the *cis* rotamers in relation to the *gauche* ones.

---

† Author to whom all correspondence should be addressed.

TABLE I

Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of ethyl α-(alkylthio)-acetates RC(O)OEt

		n-C_6H_{14}			CH_3CN			$CHCl_3$		
Comp.	R	ν[a]	ε[b]	$\varepsilon_c/\varepsilon_g$[c]	ν	ε	$\varepsilon_c/\varepsilon_g$	ν	ε	$\varepsilon_c/\varepsilon_g$
(1)	Me[d]	1750	681	—	1737	609	—	1731	459	—
(2)	$EtSCH_2$	1746	194		1736	43		—	—	
		1739	401	0.48	1732	375	0.11	1729	404	0
(3)	Bu^iSCH_2	1748	178		1739	23		—	—	
		1738	351	0.51	1732	335	0.07	1729	315	0
(4)	Pr^iSCH_2	1747	183		1737	24		—	—	
		1738	387	0.47	1733	384	0.06	1729	367	0
(5)	Bu^tSCH_2	1751	122		1735	48		—	—	
		1741	406	0.30	1731	352	0.14	1731	367	0

[a] In cm^{-1}.
[b] Apparent molar absorptivity in $l\ mol^{-1}\ cm^{-1}$.
[c] Subscripts c and g indicate *cis* and *gauche* rotamers respectively.
[d] Parent compound.

RESULTS AND DISCUSSION

Carbonyl stretching frequencies and the corresponding apparent molar absorptivities for some α-(alkylthio)-acetates (**2**)–(**5**) measured in the fundamental region in n-hexane, carbon tetrachloride, acetonitrile and chloroform and in the 1st overtone region in carbon tetrachloride are shown in Tables I and II. The corresponding data for the parent unsubstituted ester (**1**) are included for comparison.

TABLE II

Frequencies and intensities of the carbonyl stretching bands in fundamental and in the 1st overtone regions of the ethyl α-(alkylthio)-acetates RC(O)OEt, in CCl_4

		Fundamental			1st overtone		
Comp.	R	ν[a]	ε[b]	$\varepsilon_c/\varepsilon_g$[c]	ν	10ε	$\varepsilon_c/\varepsilon_g$
(1)	Me[d]	1742	715		3466	27	—
(2)	$EtSCH_2$	1741	130 (234)[e]		3463	(13)[e]	
		1733	403	0.32 (0.58)[f]	3444	20	(0.70)[f]
(3)	Bu^iSCH_2	1743	132 (277)		3468	(11)	
		1733	375	0.37 (0.74)	3442	16	(0.68)
(4)	Pr^iSCH_2	1743	160 (234)		3461	(13)	
		1732	377	0.42 (0.62)	3443	20	(0.68)
(5)	Bu^tSCH_2	1746	45 (133)		—[g]		
		1734	407	0.11 (0.32)	3445	29	—

[a] In cm^{-1}.
[b] Apparent molar absorptivity in $l\ mol^{-1}\ cm^{-1}$.
[c] Subscripts c and g indicate *cis* and *gauche* rotamers respectively.
[d] Parent compound.
[e] All intensity data in brackets were estimated at the inflexion point of the unresolved band.
[f] Ratio of the intensities of the high and low frequencies components determined directly on the unresolved bands.
[g] The extensive band overlapping precludes the estimation of the inflexion point.

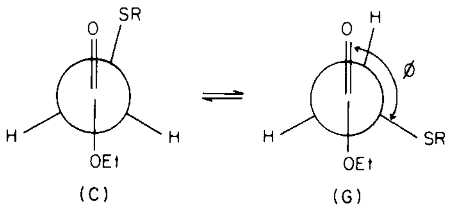

FIGURE 1 Conformations of the α-(alkylthio)-acetates.

Inspection of Tables I and II shows that in the fundamental region, in *n*-hexane, carbon tetrachloride and acetonitrile, all α-(alkylthio)-acetates (**2**)–(**5**) exhibit two overlapping bands. However, it may be noticed that on going from *n*-hexane to carbon tetrachloride and to acetonitrile there is an increase of the intensity of the lower frequency component in relation to the higher one, while for the chloroform only the lower frequency component is observed. Although this solvent effect on the intensities of the two resolved carbonyl bands suggests the Fermi Resonance,[6a] the occurrence of two superimposed bands, for the title compounds, in the 1st overtone region at frequencies ca. twice those in the fundamental one and with approximately the same intensities ratios practically excludes the Fermi Resonance and strongly suggests the *cis* (C)–*gauche* (G) rotational isomerism[7] (Figure 1).

It should be pointed out that the above solvent effect is in disaccord with that generally observed in α-heterosubstituted carbonyl compounds[3,4,6b,8] for which the *cis* rotamer (the higher frequency band) was shown to be more polar than the *gauche* one (the lower frequency band). Actually, in α-(alkylthio)-acetates (**2**)–(**5**) the increasing of the solvent polarity decreases the intensity of the higher frequency band in relation to the intensity of the lower frequency band. Such behavior already observed for the α-(alkylthio)-thioesters[2] can be rationalized by assigning the higher frequency band to the *cis* rotamer and the lower frequency band to the *gauche* one. This reversal of polarity in the α-sulfur-substituted esters is supported by the carbonyl frequency shifts of the *cis* rotamers in comparison with the unsubstituted ester (see below). Figures 2 and 3 present representative

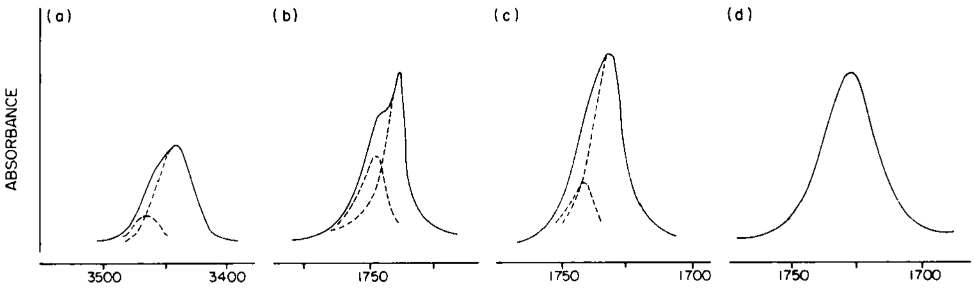

FIGURE 2 I.R. spectrum of ethyl α-(ethylthio)-acetate (**2**) showing the $2\nu_{CO}$ band in CCl_4 (a) and the solvent effect on the ν_{CO} band in n-C_6H_{14} (b), CCl_4 (c) and $CHCl_3$ (d); —— overlapped band, ---- graphically decomposed band.

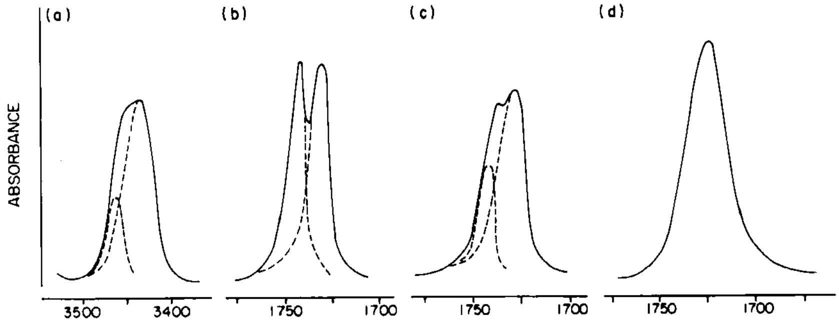

FIGURE 3 I.R. spectrum of ethyl α-(ethylthio)-propionate (**7**) showing the $2\nu_{CO}$ band in CCl_4 (a) and the solvent effect on the ν_{CO} band in n-C_6H_{14} (b), CCl_4 (c) and $CHCl_3$ (d); —— overlapped band, - - - - graphically decomposed band.

spectra of α-ethylthio-esters (**2**) and (**7**) respectively, showing both the overlapped and graphically decomposed carbonyl bands in the 1st overtone region in carbon tetrachloride and in the fundamental region in solvents of increasing polarity.

It is worthy of mentioning that in opposition to our results, a normal solvent effect on the two overlapping carbonyl bands for some α-(ethylthio)-esters has been previously reported by Mori[9] leading therefore to a greater polarity of the *cis* rotamer in relation to the *gauche* one. However, this conclusion is subject to criticism since in such case the two overlapping carbonyl bands were not graphically decomposed and the intensities of the two rotamers were measured directly from the spectrum.

Table III shows the frequency shifts for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of the α-(alkylthio)-acetates (**2**)–(**5**) in comparison to the unsubstituted ester (**1**). It may be seen that the $\Delta\nu_c$ values, both in the fundamental and in the 1st overtone regions, are slightly negative or slightly positive in all solvents, although they should be highly positive due to the repulsive Field Effect between C=O and C—S dipoles.[6b]

So, as in the case of the α-(alkylthio)-thioesters,[2] it is reasonable to suggest that in the *cis* rotamers of the α-(alkylthio)-esters there is, due to the close

TABLE III

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

		Fundamental						1st overtone	
		n-C_6H_{14}		CCl_4		CH_3CN		CCl_4	
Comp.	R	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(**2**)	$EtSCH_2$	−4	−11	−1	−9	−1	−5	−3	−22
(**3**)	Bu^iSCH_2	−2	−12	+1	−9	+2	−5	+2	−24
(**4**)	Pr^iSCH_2	−3	−12	+1	−10	0	−4	−5	−23
(**5**)	Bu^tSCH_2	+1	−9	+4	−8	−2	−6	—	−21

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

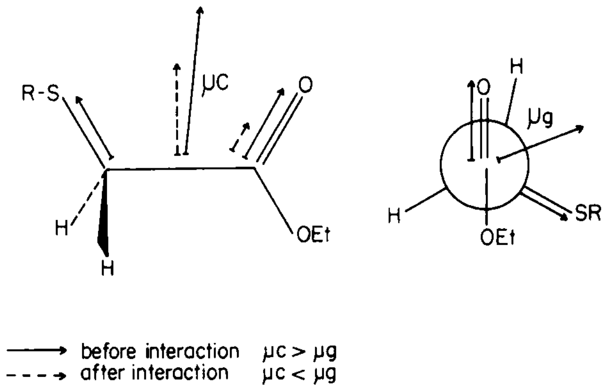

FIGURE 4 The variation of the polarity of the *cis* conformer in relation to that of the *gauche* one.

proximity of the α-sulfur atom and the carbonyl group, a charge transfer from π_{CO} to $3d_{(S)}$ orbitals diminishing the electronic density in the π_{CO} orbitals, leading therefore to a decreasing in the normal Field Effect. As a consequence, such interaction could be responsible for the decrease of the polarity of the *cis* rotamer in relation to the *gauche* one (Figure 4) for the title compounds.

As in the case of other α-sulfur substituted carbonyl compounds[2,3,4] the negative *gauche* shifts ($\Delta\nu_g$) observed for the α-(alkylthio)-acetates (**2**)–(**5**) (Table III) may be ascribed to the hyperconjugative interaction between π_{CO}/σ_{C-S} orbitals (Figure 5) which may occur in the *gauche* rotamers of the title compounds. This interaction should result in a decrease of the carbonyl force constant and consequently in the ν_{CO} frequencies.

In order to improve our knowledge in the above mentioned interactions which occur in the α-(ethylthio)-acetates (**2**)–(**5**), it became of interest to analyse the stereoelectronic effects which could take place by the replacement of α-hydrogen atoms in the α-(ethylthio)-acetate (**2**) by methyl groups.

Tables IV and V show the I.R. carbonyl data for the α-(ethylthio)-propionate (**7**) and α-(ethylthio)-isobutyrate (**9**) in comparison with the parent unsubstituted esters (**6**) and (**8**). It may be observed that while the latter compounds show one carbonyl band in all solvents, in the case of α-(ethylthio)-propionate (**7**), similarly to the α-(ethylthio)-acetate (**2**) (Tables I and II), there are two overlapping carbonyl bands in all solvents except in chloroform where just a single band can be noticed (Figure 3). The α-(ethylthio)-isobutyrate (**9**) presents two overlapping carbonyl bands in all solvents.

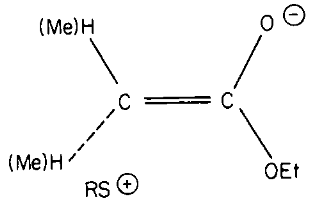

FIGURE 5 Hyperconjugative structure for the *gauche* rotamers of the α-(alkylthio)-esters.

TABLE IV

Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of ethyl α-(ethylthio)-propionate and -isobutyrate RC(O)OEt

		n-C_6H_{14}			CH_3CN			$CHCl_3$		
Comp.	R	ν^a	ε^b	$\varepsilon_c/\varepsilon_g{}^c$	ν	ε	$\varepsilon_c/\varepsilon_g$	ν	ε	$\varepsilon_c/\varepsilon_g$
(6)	$MeCH_2{}^d$	1745	450	—	1733	454		1728	584	—
(7)	EtSCHMe	1746	352		1737	(247)^e		—		
		1734	343	1.02	1730	428	(0.58)^f	1725	553	0
(8)	Me_2CH^d	1744	437	—	1730	423	—	1727	373	—
(9)	$EtSC(Me)_2$	1740	195		1733	115		1725	114	
		1728	474	0.41	1721	406	0.28	1714	368	0.31

[a–f] (See footnotes of Table 2).

TABLE V

Frequencies and intensities of the carbonyl stretching bands in the fundamental and in the 1st overtone regions of the ethyl α-(ethylthio)-propionate and -isobutyrate RC(O)Et, in CCl_4

		Fundamental			1st overtone		
Comp.	R	ν^a	ε^b	$\varepsilon_c/\varepsilon_g{}^c$	ν	10ε	$\varepsilon_c/\varepsilon_g$
(6)	$MeCH_2{}^d$	1739	540		3457	27	
(7)	EtSCHMe	1742	203 (285)^e		3455	(15)^e	
		1729	345	0.59 (0.83)^f	3441	20	(0.75)^f
(8)	Me_2CH^d	1737	523	—	3453	28	—
(9)	$EtSC(Me)_2$	1733	177 (260)		3442	(17)	
		1722	449	0.39 (0.59)	3422	28	(0.60)

[a–f] (See footnotes of Table 2).

TABLE VI

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

		Fundamental						1st overtone	
		n-C_6H_{14}		CCl_4		CH_3CN		CCl_4	
Comp.	R	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(2)	$EtSCH_2$	−4	−11	−1	−9	−1	−5	−3	−22
(7)	EtSCHMe	+1	−11	+3	−10	+4	−3	−2	−16
(9)	$ETSC(Me)_2$	−4	−16	−4	−15	+3	−9	−11	−31

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

Table VI shows that the carbonyl frequency shifts for the higher and lower carbonyl frequency components of the doublet for the α-(ethylthio)-propionate (**7**), both in the fundamental and in the 1st overtone regions, are reasonably close to those of the *cis* (C) and *gauche* (G) rotamers for the α-(ethylthio)-acetate (**2**) respectively. In the case of the α-(ethylthio)-isobutyrate (**9**) the frequency shifts for the higher frequency component of doublet in all solvents, in the fundamental region, are similar to those of the *cis* rotamer for the α-(ethylthio)-acetate (**2**) except in the case of the 1st overtone region where the frequency shift for the higher frequency component of the α-(ethylthio)-isobutyrate (**9**) is significantly

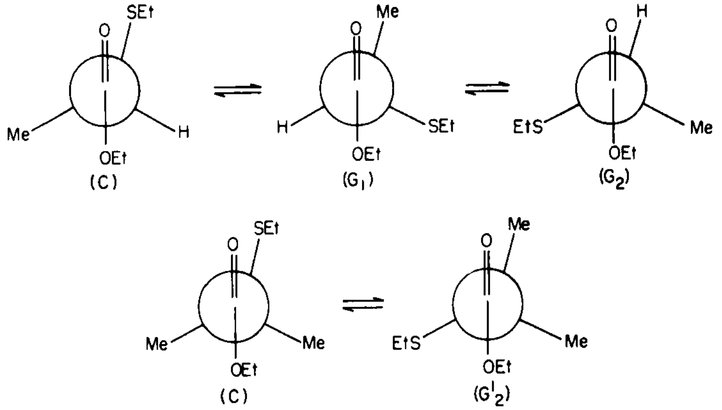

FIGURE 6 Conformations of the α-(ethylthio)-propionate and -isobutyrate.

greater than that of the α-(ethylthio)-acetate (**2**). It should be pointed out that the carbonyl frequency shifts for the lower frequency component of the doublet for the α-(ethylthio)-isobutyrate (**9**) are both in the fundamental and in the 1st overtone regions ca. 1.5 times greater than those of the *gauche* rotamer for the α-(ethylthio)-acetate (**2**). It is important to stress that even taking into account the accuracy of the carbonyl frequency values (see Experimental Part), the conclusions drawn from the frequency shift analysis are not affected.

It is worthy of note that in the case of the α-(ethylthio)-propionate similarly to the corresponding thioester,[2] three conformers should be expected: *cis* (C) *gauche* (G_1) and *gauche* (G_2) (Figure 6). From the above frequency shifts analysis and considering that the *cis* (C) and (G_1) rotamers for compound (**7**) (Figure 6) have approximately the same steric environment as those of the *cis* (C) and *gauche* (G) rotamers, respectively, for compound (**2**) (Figure 1), it seems reasonable to admit for the α-(ethylthio)-propionate (**7**), in the fundamental and in the 1st overtone regions, that the higher frequency component corresponds to the *cis* rotamer (C) and the lower frequency component corresponds to the *gauche* one (G_1), being the *gauche* rotamer (G_2) inexistent.

It should be mentioned that the two expected *cis* (C) and *gauche* (G_2') rotamers for the α-(ethylthio)-isobutyrate have respectively similar steric environments as those of the *cis* (C) and *gauche* (G_2) rotamers of the α-(ethylthio)-propionate (Figure 6). So, it is reasonable to suggest for the α-(ethylthio)-isobutyrate, both in the fundamental and in the 1st overtone regions, that the higher frequency component corresponds to the *cis* rotamer (C) and the lower frequency component corresponds to the *gauche* one (G_2').

It may be also noticed in Table VI that in general the carbonyl frequency shifts for the *cis* (C) and *gauche* (G_2') rotamers of the α-(ethylthio)-isobutyrate (**9**) are respectively larger than those for the *cis* (C) and *gauche* (G_1) rotamers of the α-(ethylthio)-propionate (**7**). This trend may be explained as follows.

It is reasonable to admit that in both *cis* (C) and *gauche* (G_2') rotamers of the α-(ethylthio)-isobutyrate an increasing of the α angle may occur in order to relieve the *gauche* steric strain (Figure 7) leading to a change in the mechanical

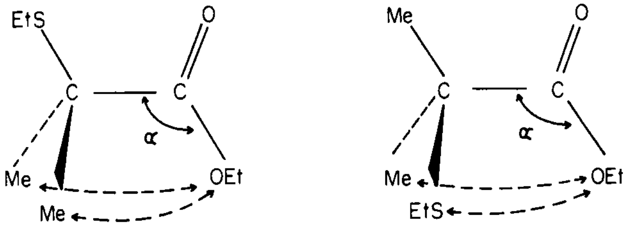

FIGURE 7 *Gauche* strain in the *cis* (C) and *gauche* (G_2') rotamers of the α-(ethylthio)-isobutyrate.

coupling between C═O, C—C and C—O oscillators[6c] and to a variation in the hybridization of the carbonyl group.[10] As a consequence of the latter effect the C—O bond becomes longer and more polar, increasing in the *gauche* rotamer the contribution of the hyperconjugative structure (Figure 5). On the other hand in the *cis* rotamer the increased α angle may also result in a slightly closer proximity between the carbonyl oxygen and the α-sulfur atoms leading consequently to an increase of the $\pi_{CO}/3d_{(S)}$ interaction. Thus, the above effects should produce for both *cis* (C) and *gauche* (G_2') rotamers of the α-(ethylthio)-isobutyrate a decrease of the carbonyl force constant and consequently a lowering of the carbonyl frequencies.

EXPERIMENTAL

Materials. All solvents for spectrometric measurements were spectrograde and were used without further purification. Commercial ethyl acetate (**1**), ethyl propionate (**6**) and ethyl isobutyrate (**8**) were purified as described elsewhere.[11] The ethyl α-(ethylthio)-[12] (**2**), α-(isobutylthio)-[12] (**3**), α-(isopropylthio)-[12] (**4**), α-(terc-butylthio)-[13] (**5**) acetates, ethyl α-(ethylthio)-propionate[14] (**7**) and ethyl α-(ethylthio)-isobutyrate[8] (**9**) were prepared by literature procedures.

I.R. Measurements. The conditions for recording the I.R. spectra have already been described for the α-(alkylthio)-thioesters[2] and 4.0–5.0 × 10^{-2} M solutions of the title compounds in *n*-hexane, carbon tetrachloride, acetonitrile and chloroform were employed. In the fundamental region the *cis/gauche* relative concentrations were estimated from the ratio of the apparent molar absorptivities of the two components of the graphically decomposed carbonyl bands,[15] assuming as an approximation the equality of the molar absorptivity of the two rotamers. In the 1st overtone region the *cis/gauche* relative concentrations were estimated from the ratio of the apparent molar absorptivities measured directly at the inflexion point and at the absorption maximum of the superimposed carbonyl band respectively. The spectra were calibrated with polystyrene at 1601.4 and 2850.7 cm^{-1}. The carbonyl frequencies 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 1st overtone region to ±1 and ±2 cm^{-1} respectively.

ACKNOWLEDGMENTS

The authors thank Dr. P. S. Santos for reading the manuscript and for his valuable suggestions. The authors are indebted to the Fundação de Amparo à Pesquisa do Estado de São Paulo for financial support and for scholarship to (F.O. and J.C.D.L.) and to the Conselho Nacional de Pesquisa for a scholarship to (F.O. and J.C.D.L.) and for a grant to (P.R.O.).

REFERENCES

1. Presented at the 12th Symposium on the Organic Chemistry of Sulfur, Nijmegen, Holland, 1986.
2. P. R. Olivato, B. Wladislaw, S. A. Guerrero and D. Russowsky, *Phosphorus and Sulfur*, **24**, 225 (1985).

3. S. A. Guerrero, J. R. T. Barros, B. Wladislaw, R. Rittner and P. R. Olivato, *J.C.S. Perkin Trans* **2,** 1053 (1983).
4. M. P. A. Martins, R. Rittner and P. R. Olivato, *Spectrosc. Lett.*, **14,** 505 (1981).
5. B. Wladislaw, R. Rittner and H. Viertler, *J. Chem. Soc.* (*B*), 1859 (1971).
6. L. J. Bellamy, *Advances in Infrared Group Frequencies,* Chapman and Hall, London 1975 (a) p. 127, (b) p. 141, (c) p. 132.
7. A. Gaset, L. Lafaille, A. Verdier and Lattes, *Bull. Soc. Chim. Fr.*, 4108 (1968).
8. L. J. Bellamy, *The infrared Spectra of Complex Molecules,* Chapman and Hall, London, Third Edition, 1975, p. 159.
9. N. Mori, S. Kaido, K. Suzuki, M. Nakamura and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, **44,** 1858 (1971).
10. D. Chadwick, D. O. Frost and L. Weiler, *Tetrahedron Lett.*, **47,** 4543 (1971).
11. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals,* Pergamon Press, Oxford, 1966.
12. A. Chauvean and R. M. Noel, *Ann. Fac. Sci. Univ., Toulouse, Sci. Math. Sci. Phys.*, **25,** 147 (1963).
13. A. M. Von Leusen and J. Strating, *Recl. Trav. Chim. Pays-Bas.*, **84,** 140 (1965).
14. V. Y. Pochinok and A. P. Limarenko, *Ukrain Khim. Zhur.*, **21,** 628 (1955).
15. M. Horak and A. Vitek, *Interpretation and Processing of Vibrational Spectra,* Wiley, N.Y., 1978, p. 154.