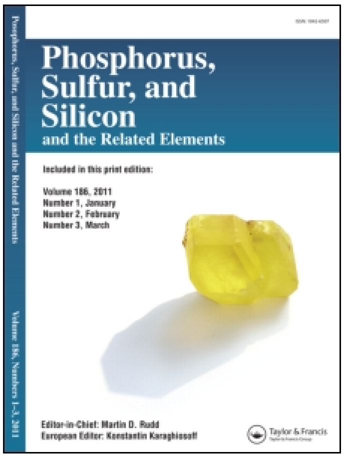

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XII. S-ETHYL α-HETERO-SUBSTITUTED THIOACETATES

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XII. S-ETHYL α-HETERO-SUBSTITUTED THIOACETATES

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The analysis of the ν_{CO} bands in the IR spectra of the S-ethyl α-heterosubstituted thioacetates helped by Molecular Mechanics Calculations indicated the existence of the *cis*/*gauche* rotational isomerism. In the thioacetates series the *gauche* rotamers predominate over the *cis* ones. This has been ascribed to the large stabilization of the π^*_{CO} orbital leading to a stronger π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions and to a larger stabilization of the *gauche* rotamers. The positive carbonyl *cis* shifts ($\Delta\nu_c$) ascribed to the Repulsive Field Effect are smaller than the ones for the heterosubstituted-acetones, -acetophenones, -methyl acetates and -N,N-diethylacetamides. This trend is discussed in terms of the lower carbonyl dipole moment for the thioesters which is mainly due to the $\pi_{CO}/3d_{(S)}$ interaction in the carboxythioethyl group. The larger negative carbonyl *gauche* shifts ($\Delta\nu_g$) for the heterosubstituted thioacetates in relation to the other referred carbonyl compounds along with the higher Non Additivity Effect of the α-methylene carbon chemical shifts for the majority of the title compounds in comparison with the other heterosubstituted carbonyl compounds are further support for the larger contribution of the π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions in the thioesters than the same interactions for the other carbonyl compounds. This has been attributed to a great stabilization of the π^*_{CO} orbital in the carboxythioethyl group of the thioester due to its interaction with a 3d sulfur orbital.

Key words: S-ethyl α-heterosubstituted thioacetates; conformational studies; molecular mechanics calculations; IR spectra; ^{13}C NMR spectra; electronic interactions.

INTRODUCTION

Previous studies from this laboratory by IR, UV, NMR and UPS spectroscopies of some α-heterosubstituted ketones,[1,2,3] amides[4,5] and esters[6] showed the existence of the π_{CO}/σ_{C-X} hyperconjugative interaction for their *gauche* rotamers which is the main controlling factor of the *cis-gauche* rotational isomerism. Moreover our reports on some α-thiosubstituted ketones and their *mono-* and *di*-oxygenated derivatives[7-12] have indicated the occurrence of the π_{CO}/σ^*_{C-S} charge transfer for their *gauche* rotamers besides the π^*_{CO}/σ_{C-S} hyperconjugative interaction.

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It should be pointed out that the IR study[13] of some *mono- di-* and *tri-α*-halo-substituted thioesters mainly with chlorine, bromine and fluorine as α-substituents was already performed long time ago. The authors ascribed the twin overlapped bands observed for the α-monosubstituted thioesters (with chlorine and bromine as substituents) to the rotational isomerism, although they did not understand the origin of the large decrease of the lower frequency carbonyl band in relation to that of the parent thioester.

More recently we have studied[14] the rotational isomerism of the α-(alkylthio)-thioesters by IR spectroscopy which showed that the *cis* rotamer is abnormally less polar than the *gauche* one. This work not only showed that the *gauche* rotamer presents a significant lowering of the carbonyl frequency in relation to the parent compound but also the occurrence of a small lowering of the carbonyl frequency for the *cis* rotamer in relation to the parent compound. Charge transfer from π_{CO} to $3d_{(S)}$ (for the *cis* rotamer) and hyperconjugative π_{CO}/σ_{C-S} interactions (for the *gauche* rotamer) were invoked to explain the obtained results.

In order to improve the understanding of the origin for the anomalies found in the previously studied α-monosubstituted thioesters it became of interest to extend our studies to the α-heterosubstituted thioesters since no systematic work has been performed for the whole series. This paper deals with the study of IR and ^{13}C NMR spectra helped by Molecular Mechanics Calculations of some S-ethyl-α-monosubstituted thioacetates bearing in the α-position representative elements from the first to the fourth rows of the Periodic Table.

RESULTS AND DISCUSSION

Cis-gauche Rotational Isomerism

Table I shows the stretching frequencies and the absorbance ratios of the analytically resolved carbonyl bands for some S-ethyl heterosubstituted thioacetates (**2**)–(**8**) and the carbonyl frequencies for the parent compound (**1**), in n-hexane, carbon tetrachloride (fundamental and 1st overtone transitions) and in acetonitrile. Compounds (**2**), (**3**) and (**7**) show two overlapped carbonyl bands in all solvents. Overlapped triplets are observed for compounds (**5**) and (**6**) in all solvents, except for compound (**5**), in acetonitrile where the middle component disappears. The parent compound (**1**) and compounds (**4**) and (**8**), show a single carbonyl band in all solvents.

The solvent effect[15a] on the components relative intensities of the overlapped bands (**2**), (**3**), (**5**)–(**7**) and the unexpected occurrence of only single bands for compounds (**4**) and (**8**), may not be an evidence of the rotational isomerism. However, the existence of one, two or three carbonyl bands in the first overtone region at frequencies ca. twice those of the fundamental, strongly suggests that a *cis* (**I**)/ *gauche* (**II**) rotational isomerism occurs[16] (Figure 1), except for compounds (**4**) and (**8**) where only a single conformer is present. It may be assumed that for compounds (**2**) and (**3**) the higher frequency band corresponds to the more polar *cis* rotamer (**I**) and the lower frequency band to the less polar *gauche* rotamer (**II**). This condition should also be held for compounds (**5**) and (**6**) where the higher frequency component is the *cis* rotamer and the lower frequency components are

TABLE I

Frequency and intensity ratios of the carbonyl stretching bands in the infrared spectra of S-ethyl α-monosubstituted thioacetates $XCH_2C(O)SEt$.

Compd.	X	$n\text{-}C_6H_{14}$		CCl$_4$				CH$_3$CN	
		ν^a	$\alpha_c/\alpha_g{}^b$		α_c/α_g	ν^c	α_c/α_g	ν	α_c/α_g
(1)	H	1703	-	1695	-	3373	-	1692	-
(2)	F	1720 1694	0.11	1713 1689	0.15	3409 3354	0.18	1707 1690	0.26
(3)	OMe	1716 1695	0.21	1712 1689	0.22	3399 3353	0.18	1704 1686	0.26
(4)	NEt_2^d	1693	-	1687	-	3351	-	1681	-
(5)	Cl	1730 1704^e 1686	0.34(0.29)^f 0.18	1710 1692 1678	0.39(0.31) 0.27	3400 3368 3330	0.29(0.25) 0.18	1700 - 1675	0.88(0.88)
(6)	Br	1714 1696^e 1677	0.59(0.34)^f 0.73	1711 1693 1674	0.55(0.31) 0.75	3403 3369 3325	0.33(0.20) 0.67	1702 1688 1669	0.85(0.37) 1.31
(7)	SEt	1697 1684	0.28	1693 1679	0.27	3370 3332	0.26	1691 1678	0.18
(8)	I^d	1693	-	1688	-	3355	-	1683	-

[a] In cm^{-1}.

[b] Ratio of the absorbances of each component of the analytically resolved band and the lowest frequency component; Subscripts c and g indicate *cis* and *gauche* rotamers respectively.

[c] 1st overtone.

[d] Single symetrical band corresponding to the *gauche* rotamer (see text).

[e] The middle component of the triplet may be attributed to another *gauche* rotamer (see text).

[f] All absorbance ratios in components correspond to the quotient between the high frequency component and the sum of the low frequencies of the analytically resolved triplet.

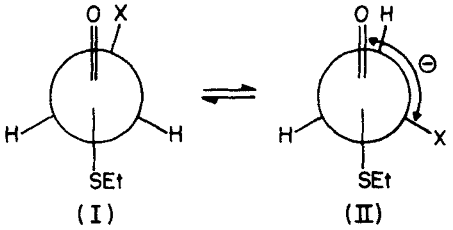


FIGURE 1 *Cis* and *gauche* rotamers of S-ethyl α-heterosubstituted thioacetates.

two *gauche* rotamers (see below). Figure 2 illustrates the analytically resolved triplet of the carbonyl bands for the S-ethyl bromothioacetate (**6**) in the fundamental and in the 1st overtone transitions. The decrease in the intensity ratios for the S-ethyl α-ethylthio-thioacetate (**7**) on going from n-hexane to acetonitrile is in agreement with our previous work,[14] which showed that in the α-alkylthio-thioesters the *cis* rotamer is less polar than the *gauche*. The fact that the frequencies of the single carbonyl bands for compounds (**4**) and (**8**), in all solvents, are decreased by ca. 10 cm^{-1} in relation to the parent compound (**1**) strongly suggests that this band may be ascribed to the less polar *gauche* rotamer (see next section).

As it is impossible to determine the apparent molar absorption coefficients for the pure *cis* and *gauche* rotamers, it was assumed that the molar absorption coefficients for both rotamers were the same. Then the ratio of the two or three rotamers concentrations were estimated from the ratio of the directly measured absorbances

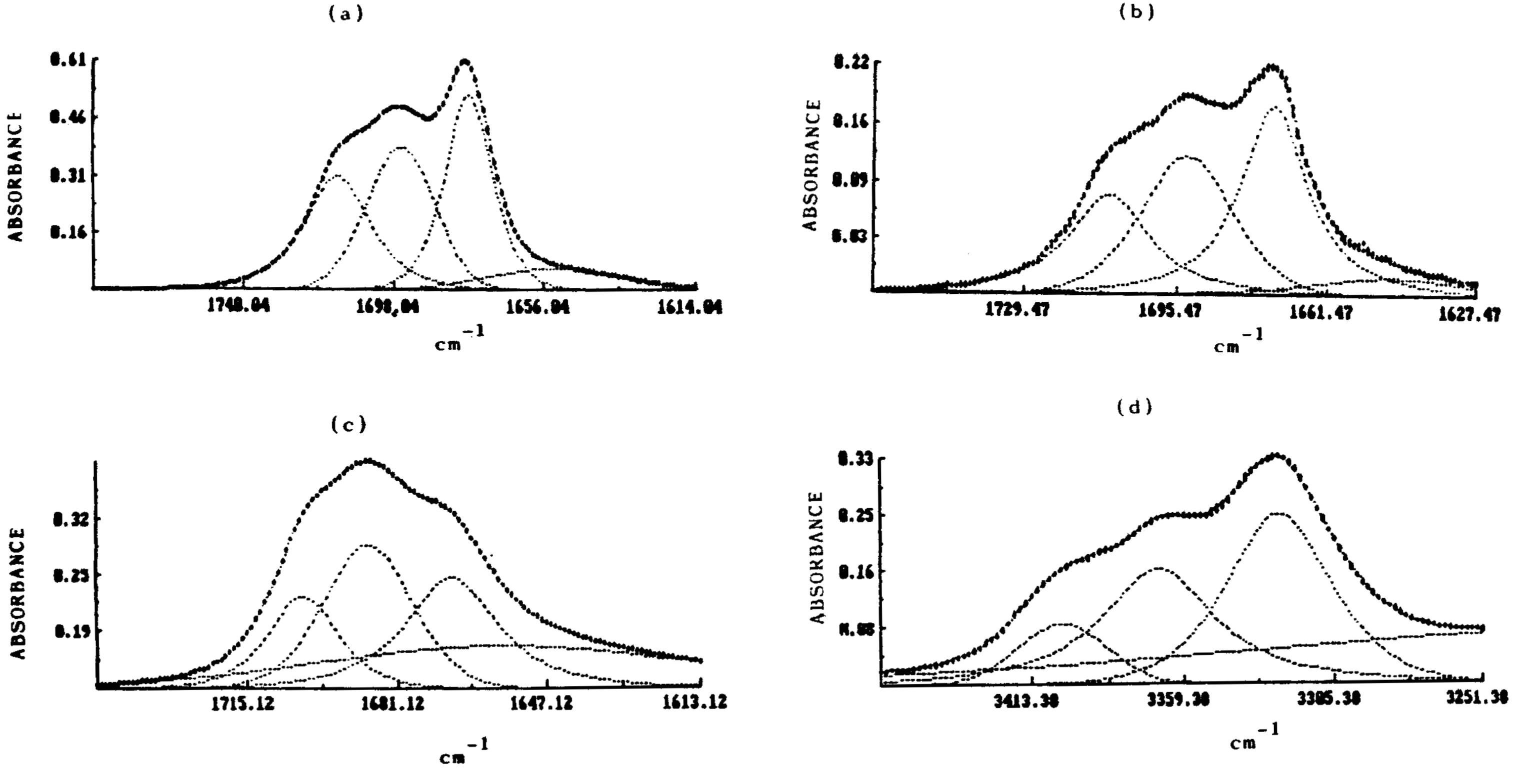


FIGURE 2 I.R. spectra of S-ethyl bromothioacetate (**6**) showing the analitically resolved carbonyl stretching bands in the fundamental region, in n-hexane (a), carbon tetrachloride (b), and acetonitrile (c), and in the 1st overtone region, in carbon tetrachloride (d). The experimental and the simulated spectra are practically superimposed.

at the absorption maxima of the two or three components of the analytically resolved carbonyl band (α_c/α_g).

It should be pointed out that it is very difficult to justify the occurrence of three conformers in the case of the chloro- (**5**) and bromo- (**6**) thioacetates. In fact the S-ethyl group position relative to the carbonyl oxygen atom for the α-heterosubstituted thioacetates should be *s-cis* in analogy to the case of the corresponding α-heterosubstituted acetates.[6,17,18] So, it practically rules out the possibility in the chloro- (**5**) and bromo- (**6**) thioacetates that a component of the three overlapped carbonyl bands could be attributed to the occurrence of a *s-trans* rotamer. Thus, in order to clarify this unexpected behavior and to have more precise geometries for the conformations of the S-ethyl α-halosubstituted thioacetates Molecular Mechanics Calculations were performed for the S-methyl α-halothioacetates bearing in the α-position the halogen atoms F, Cl, Br and I.

Table II shows that instead of the only two expected conformers for the S-methyl α-halothioacetates (**10**), (**11**), (**12**), (**13**), there are three minimum energy conformations i.e. one *cis* and two *gauche*. The *cis* (c) rotamers have the dihedral angle θ near 0° while the methyl carbon-sulfur bond are twisted out of the —C(O)—S—

TABLE II

Calculated Molecular-Mechanics energies, electric dipole moments, dihedral angles for the minimum energy conformations, and the relative rotamer populations of S-methyl α-halothioacetates $CH_2XC(O)SMe$.

Compd.	X	Conf.^{a}	θ^b	ϕ^c	μ^d	E^e	P^g	$c/g_1+g_2^h$
(9)	H^i	-	-	55	2.122	-	-	-
(10)	F	c	0	-48	3.034	0^f	0.42	0.72
		g_1	153	+58	1.192	0.35	0.24	$(0.11)^j$
		g_2	150	-76	1.120	0.14	0.34	
(11)	Cl	c	0	-46	3.031	0	0.42	0.72
		g_1	135	+53	2.272	0.43	0.20	(0.29)
		g_2	133	-70	0.892	0.05	0.38	
(12)	Br	c	1	-49	2.946	1.09	0.12	0.14
		g_1	117	+46	2.448	0.45	0.13	(0.34)
		g_2	116	-62	1.128	0	0.75	
(13)	I	c	-1	+53	2.670	1.37	0.06	0.06
		g_1	112	+49	2.292	0.42	0.31	(0)
		g_2	111	-58	1.300	0	0.62	

[a] c, g_1 and g_2, refers to the *cis*, *gauche*$_1$ and *gauche*$_2$ conformations, respectively.

[b,c] Dihedral angles θ and ϕ (in degrees), as defined in structure III, Figure 3.

[d] In Debye.

[e] In kcal·mole^{-1}.

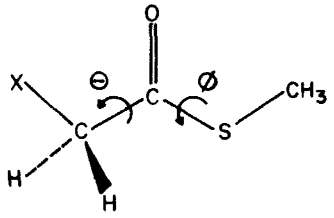
[f] Zero energy corresponds to the minimum-energy conformation.

[g] Molar fraction of each rotamer.

[h] Relative rotamer populations.

[i] Parent compound.

[j] Relative rotamer populations taken from I.R. data, in n-hexane, from Table I.



(III)

FIGURE 3 Reference conformation ($\theta = 0°$, $\phi = 0°$) for the S-methyl α-halothioacetates. The arrows indicate positive torsion angles for the S—C(Me) and C—X bonds in relation to the reference conformation.

plane by an ϕ angle of ca. 50° and, as expected, they have higher electric dipole moments than the corresponding *gauche* rotamers. As for the two *gauche* rotamers (g_1) and (g_2) their dihedral angles θ are very close and their values decrease progressively from fluoro- to the iodo-thioacetate (θ, 150–110°). However, the dihedral angles ϕ of the methyl carbon-sulfur bond are twisted out of the —C(O)—S— plane by ca. +50° for the (g_1) rotamers while for the (g_2) rotamers the ϕ angles are twisted in the opposite direction by ca. −65°. As expected, the (g_1) rotamers with both C—Hal and C—S—C dipole moments pointing practically toward the same direction have the higher dipole moments in relation to the (g_2) rotamers, where the referred dipole moments are nearly in opposition.

Table II also shows that the population ratios between the *cis* and the summing up of the *gauche* rotamers for the halothioacetates obtained by Molecular Mechanics Calculations deviate significantly from the corrresponding values obtained from IR spectra data, in n-hexane, except for the case of the iodo-derivative where both values are practically coincident i.e. ca. zero.

However, the Molecular Mechanics data now support the IR analysis which indicates the existence of three conformers for the chloro- (**5**) and bromo- (**6**) thioacetates. The inspection of Table I shows that as the polarity of the solvent increases for the bromo- (**6**) derivative there is an increasing of the intensity of the higher and the middle frequency components of the triplet in relation to the lower one (Figure 1). In the case of the chloro- (**5**) derivative the increasing polarity of the solvent on going from n-hexane and carbon tetrachloride to acetonitrile augments the intensity of the higher frequency component in relation to the lower one, with the missing of the middle component of the triplet. According to the polarity of each conformer given by Molecular Mechanics Calculations (Table II) it seems reasonable to ascribe for compounds (**5**) and (**6**) the higher frequency component of the triplet to the more polar *cis* rotamer (c), the middle frequency component to the less polar *gauche* rotamer (g_1) and the lower frequency component to the still less polar *gauche* rotamer (g_2), for the reasons outlined below.

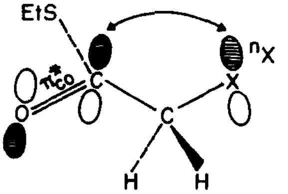
The attribution of the *cis* rotamer to the higher frequency component of the triplet for components (**5**) and (**6**) is supported by the fact that its value is significantly higher than the frequency of the reference compound (**1**), as expected from the Repulsive Field Effect[15b] between the C=O and C—X dipoles; while the frequency of the middle component of the triplet is slightly lower than the one of the reference compound.

The solvent effect analysis in the IR spectra for compound (**6**) (see Figure 1) suggests that the middle component of the triplet is more polar than the lower one, and both should be ascribed according to the Molecular Mechanics dipole moments data (Table II) to the *gauche* rotamers (g_1) and (g_2), respectively. Further support for this attribution can be obtained by a close inspection of the geometries of compounds (**5**) and (**6**) given by Molecular Mechanics Calculations. In fact in the (g_1) conformers there is a Repulsive Field Effect between the C—S—C and C—Hal dipoles desestabilizing this conformation leading as a consequence to a decreasing in its population in relation to the (g_2) conformers, where these dipoles act in cooperation. This behavior is corroborated by the fact that in nonpolar solvents, the middle component of the triplet ascribed to the (g_1) rotamer has a lower intensity than the lower frequency component attributed to the (g_2) rotamer.

At this point it seems appropriate to comment that the (g_1) conformers are present only for the bromo- (**6**) and chloro- (**5**) thioacetates. In fact, for the fluorothioacetate (**2**) there are the *cis* (c) and *gauche* (g_2) rotamers and for the iodothioacetate (**8**) only the *gauche* (g_2) is present, being missed the *cis* (c) and the *gauche* (g_1) rotamers. The observed differences between the expected and the obtained number of conformers and their relative stabilities within the halothioacetates series may be ascribed to a limitation in the Molecular Mechanics which do not take explicitly into account the different types of orbital interactions, although it considers in their calculations the interactions between non-bonded atoms.

It should be pointed out that in all solvents the *gauche* conformers predominate over the *cis* ones for the whole hetero-substituted thioacetates series, except for the case of the chlorothioacetate (**5**) in acetonitrile (See Table I). In fact in nonpolar solvents (n-hexane and carbon tetrachloride) the α_c/α_g ratios varies in the range (0.0–0.34). Moreover, the α_c/α_g ratios for the α-heterosubstituted thioacetates do not follow the order $F > O > N \simeq Cl > Br > S > I$ which was previously observed for the corresponding α-heterosubstituted-acetates,[6] -acetones[1] and acetophenones.[3] This trend was ascribed to the increasing stabilization of the *gauche* rotamers due to an increasing contribution of the hyperconjugative interaction in these rotamers. However, in the present case on going from fluoro- (**2**) to the iodo- (**8**) thioacetates the *gauche* rotamers are stabilized in such a great extent that any α_c/α_g trend should be masked.

It is well established[19] that the π^*_{CO}/σ_{C-X} hyperconjugative and π^*_{CO}/n_X superjacent (structure IV, Figure 4) orbital interactions are responsible for the stabilization of the *gauche* rotamers, and so is the $n_{O(CO)} \leftrightarrow n_X$ through-bond coupling



(IV)

FIGURE 4 Superjacent interaction between the n_X lone pair and the low-lying π^*_{CO} orbital in the *gauche* rotamers for the α-heterosubstituted thioacetates.

via the σ^*_{C-C} orbital for the stabilization of the *cis* rotamers for the α-heterosubstituted carbonyl compounds.

Thus, it seems appropriate to analyze these interactions in the light of the Molecular Orbital Simple Perturbation Theory[20] in order to rationalize the relative stabilities of the *gauche* rotamers of the α-heterosubstituted thioacetates series.

Table III shows the ionization energies of the $\sigma_{C-X(\text{carbon-heteroatom})}$ and $n_{X(\text{heteroatom})}$ lone pair unperturbed orbitals of the heterosubstituted methanes and Figure 5 shows the qualitative energy levels diagram for the n_X, σ_{C-X} and π^*_{CO} orbitals

TABLE III

The ionization energies[a] for the lone pair n_X[b] and σ_{C-X}[c] orbitals of the heterosubstituted methanes.

Group	n_X	σ_{C-X}
F	>12.5[d]	16.2[i]
OMe	10.04[e]	15.1[j]
NMe_2	8.44[f]	14.4[f]
Cl	11.29[g]	14.4[i]
Br	10.55[g,h] 10.86	13.5[i]
SMe	8.67[e]	13.7[j]
I	9.56[g,h] 10.19	12.5[i]

[a] In eV.

[b] n_X refers to the HOMO.

[c] σ_{C-X} refers to the vertical ionization energy.

[d,e,f,g,i,j] From Reference 21b, 22, 23, 21a, 24, 25, respectively.

[h] Doublet due to spin-orbit coupling.

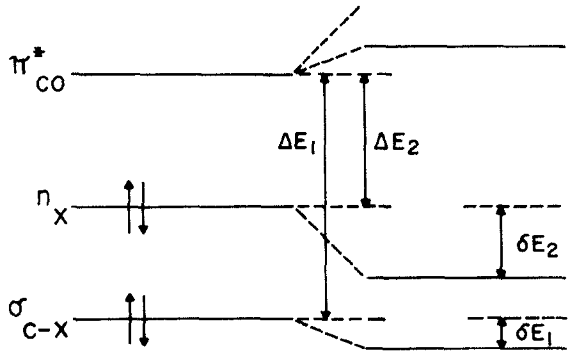


FIGURE 5 Qualitative energy levels diagram for the n_X, σ_{C-X} and π^*_{CO} orbitals, before and after orbital interactions, showing the stabilization of the *gauche* conformers for the α-heterosubstituted thioacetates, due to the π^*_{CO}/n_X superjacent and π^*_{CO}/σ_{C-X} orbital interactions.

(before and after orbital interactions) and the stabilization of the *gauche* conformation due to the π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions. The smaller the bonding character of the σ_{C-X} orbital on going from C—F to C—I bonds, the closer the energy levels (ΔE_1) of the unperturbed σ_{C-X} and π^*_{CO} Molecular Orbitals. Therefore larger interactions between these orbitals will occur leading to a progressive stabilization of the σ_{C-X} orbital by δE_1 (Figure 5). Hence, this π^*_{CO}/σ_{C-X} hyperconjugative interaction should be responsible for the increasing stabilization of the *gauche* rotamers, on going from fluoro-(**2**) to iodo- (**8**) thioacetates. This trend was previously observed for the α-heterosubstituted-acetates,[6] -acetones,[1] and -acetophenones.[3]

On the other hand the π^*_{CO}/n_X superjacent interaction between the n_x lone pair and the low-lying π^*_{CO} orbital in the *gauche* rotamers of the title compounds will be larger than the π^*_{CO}/σ_{C-X} hyperconjugative interaction, taking into account the closer proximity between the π^*_{CO} and n_X lone pair orbitals than that between the π^*_{CO} and σ_{C-X} orbitals.

Now from the point of view of Molecular Orbital Interactions it seems understandable why the diethylamino- (**4**) and the iodo- (**8**) thioacetates display only one *gauche* conformer (see Table I). Thus the lone pair ionization energy of the nitrogen is the lowest of the whole series (Table III), leading to a smallest energy gap (ΔE_2) between the unperturbed π^*_{CO} and n_N orbitals (Figure 5). Therefore, the largest interaction between these orbitals will occur leading to the greatest stabilization of the n_N orbital by δE_2. Consequently, this strong π^*_{CO}/n_N interaction may be responsible for the great stabilization of the single *gauche* rotamer of compound (**4**). On the other hand the ionization energy of the σ_{C-I} orbital is the lowest of the series, therefore, the strongest π^*_{CO}/σ_{C-I} interaction may be responsible for the great stabilization of the single *gauche* rotamer of compound (**8**).

It is worth mentioning that neither the lowest ionization energy of the n_N lone pair is followed by the lowest ionization energy of the σ_{C-N} orbital, nor the lowest ionization energy of the σ_{C-I} orbital is accompanied by the lowest ionization energy of the n_I lone pair (Table III). Therefore it seems evident that the stabilization of the *gauche* rotamers for the whole heterosubstituted thioacetates series depends on the interplay of both π^*_{CO}/n_X and π^*_{CO}/σ_{C-X} orbitals interactions.

For the stabilization of the *cis* conformers,[19] the through-bond interaction between $n_{O(CO)} \leftrightarrow n_X$ via σ^*_{C-C} orbital is expected to increase in a parallel fashion, but in a lesser extent than it does in the *gauche* rotamers with the π^*_{CO}/n_X and π^*_{CO}/σ_{C-X} orbitals interactions, because of the higher energy of the antibonding σ^*_{C-C} orbital. In fact only in the light of Molecular Orbital interactions, the main controlling factor for the *cis* $\rightleftarrows$ *gauche* equilibrium seems to be the π^*_{CO}/n_X and π^*_{CO}/σ_{C-X} orbital interactions which occurs in the *gauche* rotamers.

In order to explain the lack of selectivity of the α_g/α_c ratios for the heterosubstituted thioacetates series, as mentioned above, it seems of paramount importance to invoke that the unperturbed antibonding π^*_{CO} orbital of the unsubstituted thioester should have a lower energy (or a higher electron affinity) in relation to the same orbital for the other classes of carbonyl compounds. This will originate a smaller gap between the π^*_{CO} and both the n_X, σ_{C-X} unperturbed orbitals (Figure 5) leading consequently to stronger interactions and therefore to a greater stabilization of the *gauche* rotamers for the whole heterosubstituted thioacetates series, thus missing any selectivity of the α_c/α_g ratios.

Carbonyl stretching frequency shifts. Table IV shows the frequency shifts ($\Delta\nu$) in carbon tetrachloride, for the *cis* and *gauche* rotamers of the S-ethyl α-heterosubstituted thioacetates along with the computed carbonyl frequency shifts induced by the hyperconjugative ($\Delta\nu_H$) effects of the substituents of the α-monosubstituted acetones.

The carbonyl frequency shifts for the *cis* rotamers ($\Delta\nu_C$) of compounds (**2**), (**3**) and (**5**), (**6**) are all positive (+18 to +15 cm^{-1}) except for compound (**7**) where this value is negative (−2 cm^{-1}).

The positive *cis* shifts for the above mentioned thioacetates may be attributed to Repulsive Field Effect[15b] between the CO and CX dipoles, combined with the inductive effect of the α-substituent. The slightly negative *cis* shift for the α-ethylthio-thioacetate (**7**) together with the unusual solvent effect (see preceeding section) was already ascribed to the fact that the *cis* rotamers of the α-(alkylthio)-thioesters[14] are less polar than the *gauche* ones. This behavior was attributed to an interaction between the π_{CO} and $3d_{(S)}$ orbitals of the α-alkylthio group in the *cis* rotamers, which decreases the electronic density on the carbonyl group and prevents or at least decreases the Repulsive Field Effect. Although the referred interactions seems to be general in the α-thiosubstituted carbonyl compounds, it is more evident in the α-(alkylthio)thioesters in comparison with the majority of the aliphatic α-(alkylthio)-carbonyl compounds. This was ascribed to the fact that the unsubstituted thioesters show the smaller carbonyl oxygen basicity and therefore lower carbonyl

TABLE IV

Carbonyl frequency shifts[a,b] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of S-ethyl α-monosubstituted thioacetates $XCH_2C(O)SEt$, and the computed carbonyl frequency shifts induced by the hyperconjugative ($\Delta\nu_H$)[c] effects of the substituents in the α-monosubstituted acetones $XCH_2C(O)Me$.

Compd.	X	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_H$
(2)	F	+18	-6	0
(3)	OMe	+17	-6	-2.1
	NMe_2			-4.2
(4)	NEt_2	-	-8	
(5)	Cl	+15	-3 -17	-8.1
(6)	Br	+16	-2 -21	-11.6
(7)	SEt	-2	-16	-15.5
(8)	I	-	-7	-16.2

[a] In CCl_4.

[b] $\Delta\nu_c$ and $\Delta\nu_g$, refers to the difference $\nu_{\text{substituted thioacetate}} - \nu_{\text{parent compound}}$, for the *cis* and *gauche* rotamers, respectively.

[c] From Reference 1.

dipole moment in comparison with the majority of the unsubstituted aliphatic carbonyl compounds.

The lower carbonyl dipole moment of the thioesters which should lead to a lower Repulsive Field Effect between C═O and C—X dipoles is supported by the comparison of the data from Tables IV and V. In fact they show that in general the *cis* shifts of the heterosubstituted thioacetates are smaller than the ones of the heterosubstituted -acetones, -acetophenones, -methyl acetates and -N,N-diethyl-acetamides. (See next section).

The *gauche* shifts ($\Delta\nu_g$) for compounds (**2**)–(**8**) are all negative and vary in the interval -21 to $-2\ \mathrm{cm}^{-1}$ (Table IV) and may be ascribed to a competition between the inductive and hyperconjugative effects. For the α-heterosubstituted acetones the carbonyl frequency shifts induced by the hyperconjugative effect ($\Delta\nu_H$) (Table IV) were previously[1] estimated taking into account that for the fluoroacetone the less polar geometry is *trans*, for which the $\pi^*_{CO}/\sigma_{C—F}$ hyperconjugative interaction should be negligible ($\Delta\nu_H = 0$), and assuming that the carbonyl frequency shift of $+12\ \mathrm{cm}^{-1}$ is due only to the inductive effect of the fluorine atom ($\Delta\nu_I = +12\ \mathrm{cm}^{-1}$). Therefore, the $\Delta\nu_I$ values for the remaining heterosubstituted acetones were computed from the substituents inductive parameters (σ_I), assuming that there is a simple proportionality of both series. Since the frequency shifts for the *gauche* rotamers ($\Delta\nu_g$) should be the result of summing up of the inductive and the hyperconjugative effects ($\Delta\nu_I + \Delta\nu_H$), the $\Delta\nu_H$ values could be obtained, once $\Delta\nu_I$ values were known. As the geometry of the less polar *gauche* rotamer of the S-

TABLE V

Carbonyl frequency shifts[a,b] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of some α-monosubstituted carbonyl compounds $XCH_2C(O)Y$.

X	Y = Me[c]		Y = ϕ[d]		Y = OMe[e]		Y = NEt_2[f]	
	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
F	+28	+12	+24	-4	+27	+2	+31[g]	+4[g]
OMe	+18	+4	+18	-5	+23	-6	+17	-3
NMe_2	+12	-3	+13	+4 -5	+12	- -6	+16	-5
NEt_2			+12	+4 -7				
Cl	+31	+3	+24	+3	+26	-2	+29	+7
Br	+23	-1	+20	-2	+17	-2	+27	+6
SEt	+10	-11	+7	-14	+3	-8	+5	-9
I	+14	-7	+11	-9	+13	-4	-	-11

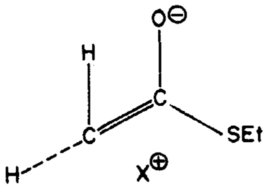
[a] In CCl_4.

[b] $\Delta\nu_c$ and $\Delta\nu_g$, refers to the difference $\nu_{\text{substituted carbonyl compound}} - \nu_{\text{parent compound}}$, for the *cis* and *gauche* rotamers, respectively.

[c,d,e,f,g] From Reference 1, 3, 6, 4, 5, respectively.

ethylfluorothioacetate (**1**) is not *trans* but *gauche* $\theta \simeq 150°$ (see Table II), it is not possible to compute the carbonyl frequency shifts induced by the hyperconjugative effect ($\Delta\nu_H$) for the heterosubstituted thioacetates series (**2**)–(**8**) from their $\Delta\nu_g$ values (Table IV). However, it was found that there is a quite reasonable correlation between the carbonyl frequency shifts ($\Delta\nu_g$) for the *gauche* rotamers of the heterosubstituted thioacetates (**2**)–(**7**) and the ($\Delta\nu_H$) frequency shifts for the heterosubstituted acetones ($r = 0.854$; $s = 3.2\ \text{cm}^{-1}$) (the iodo- (**8**) derivative was excluded because it deviates significantly from the correlation). It should be pointed out that as expected there is not any correlation between the carbonyl *gauche* shifts ($\Delta\nu_g$) for the heterosubstituted acetones and the ($\Delta\nu_H$) shifts which were estimated from them. Since $\Delta\nu_g$ corresponds to the summing up ($\Delta\nu_H + \Delta\nu_I$) it seems reasonable to admit that the $\Delta\nu_H$ values for the heterosubstituted thioacetates series should be rather more negative than those computed from the heteroacetones masking significantly their $\Delta\nu_I$ values. Therefore the $\Delta\nu_g$ shifts for the heterosubstituted thioacetates which should have a large contribution of their hyperconjugative parameters $\Delta\nu_H$ correlate with the $\Delta\nu_H$ parameters obtained from the heterosubstituted acetones.

It is worthy of mentioning that the most stable *gauche* rotamers of heterosubstituted thioacetates series (**2**)–(**7**) (Table IV) in general show more negative carbonyl frequency shifts ($\Delta\nu_g$) than those of the corresponding heterosubstituted-acetones, -acetophenones, -methyl acetates and -N,N-diethylacetamides (Table V). This behavior is a further evidence for the greater stabilization of the π^*_{CO} orbital in the heterosubstituted thioacetates series, because both π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X are the main orbital interactions which contribute to the hyperconjugative parameter ($\Delta\nu_H$). In fact the larger stabilization of the unperturbed π^*_{CO} orbital will originate a greater contribution of both π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions (see Figure 5) in the heterosubstituted thioacetates than the same interactions which occur in other classes of the heterosubstituted carbonyl compounds. Thus, this will originate a decreasing in the carbonyl bond order, which in the Valence Bond terminology may be represented by a greater contribution of the dipolar hyperconjugative structure (V) (Figure 6), leading to a decreasing in the carbonyl force constant and in the carbonyl frequencies of the heterosubstituted thioacetates in relation to the parent compound in a larger extent than it does with the other referred heterosubstituted carbonyl compounds. The relative low negative *gauche* shift for the iodothioacetate (**8**) (Table IV) is close to the mean *gauche* shifts value of the other α-iodosubstituted carbonyl compounds (Table V), and it is not in line with the large stabilization of the single *gauche* rotamer present in the iodothioac-



(V)

FIGURE 6 Dipolar hyperconjugative structure for the S-ethyl α-heterosubstituted thioacetates.

etate (see preceding section). It has not been possible to give any explanation for this abnormal behavior up to the present.

Carbon-13 NMR Chemical Shifts. Table VI shows the experimental chemical shifts of the carbonyl and α-methylene carbons, in chloroform, as well as the calculated α-methylene carbon chemical shifts along with the difference (Δδ) between both values i.e. the Non Additivity Effects (NAE) for the S-ethyl α-heterosubstituted thioacetates (**2**)–(**8**). The corresponding chemical shifts for the parent compound (**1**) are also included in this Table for comparison. The mean value of the carbonyl carbon chemical shifts for the title compounds (**2**)–(**8**) (196.5 ppm) was practically the same value of the parent compound (**1**). Table VII shows that this condition is also held by the carbonyl chemical shifts mean values for the heterosubstituted-acetones (201.4 ppm), -acetophenones (192.9 ppm), -methyl acetates (167.9 ppm) and -N,N-diethyl acetamides (165.8 ppm) whose values are close to the carbonyl carbon chemical shifts of their corresponding parent compounds which are presented in Table VIII. It can be seen from Table VIII that as expected from the Resonance involving the heteroatom lone pair (n_X) or the M.O. of the phenyl

TABLE VI

^{13}C NMR chemical shifts[a] for the carbonyl and α-methylene carbons (in —C(O)CH$_2$—) of S-ethyl α-heterosubstituted-thioacetates CH$_2$XC(O)SEt, in CDCl$_3$, and the α effect of the substituent.

Compd.	X	δ_{CO}	α_X[b]	δ_{CH_2}	$\Delta\delta_{CH_2}$[c]
(1)	H[d]	195.5	0	30.3	-
(2)	F	197.8	70.5	89.9 100.8[e]	-10.9
(3)	OMe	199.6	59.5	77.1 89.8	-12.7
(4)	NEt$_2$	202.9	40.1	63.2 70.4	-7.2
(5)	Cl	193.6	31.5	47.7 61.8	-14.1
(6)	Br	192.5	20.0	33.4 50.3	-16.9
(7)	SEt	196.5	18.6	41.7 48.9	-7.2
(8)	I	192.4	-10.5	4.5 19.5	-15.0

[a] In ppm relative to TMS.

[b] From Reference 26.

[c] $\Delta\delta = \delta_{exp.} - \delta_{calc.}$.

[d] Parent compound.

[e] The second entries are those calculated using substituent chemical shifts (see text).

TABLE VII

Carbonyl carbon chemical shifts[a] and Non Additivity Effect[b] of the α-methylene carbon for the monosubstituted carbonyl compounds $XCH_2C(O)Y$, in CCl_4.

X	Y = Me[c]		Y = ϕ		Y = OMe[d]		Y = NEt_2[e]	
	δ_{CO}	$\Delta\delta_{CH_2}$	δ_{CO}[f]	$\Delta\delta_{CH_2}$[g]	δ_{CO}	$\Delta\delta_{CH_2}$	δ_{CO}	$\Delta\delta_{CH_2}$
F	203.5	-13.7	192.5	-12.8	167.0	-13.7	164.8	-11.6
OMe	204.3	-9.8	195.4	-10.0	169.4	-10.5	167.0	-8.2
NMe_2	204.2	-5.1	195.8	-7.9	169.4	-7.8	167.5	-5.8
NEt_2	206.8	-4.3	197.0	-6.1	-	-	-	-
Cl	198.4	-11.6	190.0	-12.6	166.5	-11.4	164.4	-11.6
Br	197.4	-13.9	190.0	-16.3	166.4	-15.2	164.9	-15.1
SMe	200.0	-5.8	-	-	169.2	-6.1	166.6	-7.4
SEt	200.7	-5.8	191.5	-8.4	-	-	-	-
I	197.6	-11.6	191.1	-14.6	167.2	-15.7	165.4	-14.0

[a] In ppm relative to TMS.

[b] $\Delta\delta = \delta_{exp.} - \delta_{calc.}$.

[c,d,e,f,g] From Reference 27, 28, 29, 30, 3, respectively.

TABLE VIII

Carbonyl carbon chemical shifts[a] for the carbonyl compounds $MeC(O)Y$, in CCl_4.

Y	δ_{CO}	$\Delta\delta_{CO}$[b]	σ^o_R[c]
Me	203.7	-	-
ϕ	196.8	-6.9	-0.10
SEt	195.5	-8.2	-0.19
OMe	169.3	-34.4	-0.43
NEt_2	164.8	-38.9	-0.57

[a] In ppm relative to TMS.

[b] $\Delta\delta_{CO}$ refers to the difference: $\delta_{MeC(O)Y} - \delta_{MeC(O)Me}$.

[c] Resonance parameters taken from Reference 31.

group (π_ϕ) and the carbonyl π_{CO} orbital of the —C(O)Y group, there is a good correlation between the $\Delta\delta_{CO}$ values (i.e. the difference between carbonyl carbon chemical shifts of other carbonyl compounds and the carbonyl chemical shift of the acetone) and the Resonance parameters σ^0_R of the Y substituents ($r = 0.977$; $s = 4.4$ ppm). In fact in the ester and amide where the π_{CO}/n_X Resonance is more important their carbonyl carbons are significantly upfield shifted in relation to the acetone by ca. 34 and 39 ppm, respectively, while in the thioesters and acetophenones where the Resonance is less important, their carbonyl carbons are only slightly shielded in relation to the acetone by ca. 8 and 7 ppm, respectively.

It is well known that the smaller Resonance in the —C(O)Y group of the thioesters relative to the esters and amides is mainly due to the fact that the overlap between π_{CO} and the sulfur 3p orbital is lower than that which occurs between π_{CO} and 2p lone pair orbitals of the nitrogen and oxygen atoms of the amides and esters, respectively. Moreover, Molecular Mechanics Calculations (see Table II) show that the MeS- group in the S-methyl thioacetate is twisted out of the (—C(O)—S—Me) plane by ca. 55°, decreasing even more the overlap between the sulfur lone pair and the π_{CO} orbital. Therefore these results reinforce what was previously proposed[32] for the thioesters, where the $\pi_{CO}/3d_{(S)}$ interaction should play a significant role in determining both the decreasing basicity of the carbonyl oxygen lone pair and the decreasing of the C=O dipole moment in the referred compounds. (See preceding section).

The calculated α-methylene carbon chemical shifts (Table VI) may be obtained from Equation (**1**) where α_X is the α-effect of the X substituent and α_A is that of the carboxythioethyl group estimated from the acetyl methyl chemical shift of the unsubstituted S-ethyl thioacetate (**1**) and -2.3 is the chemical shift for the methane carbon atom.

$$\delta_{CH_2} = -2.3 + \alpha_A + \alpha_X \qquad (1)$$

The comparison between the experimental and the calculated α-methylene carbon chemical shifts leads to (Δδ) values, i.e. the Non Additivity Effects (NAE), which according to Nesmeyanov[33] may be ascribed to an increase in the double bond character between the α-methylene and the carbonyl carbons due to the π^*_{CO}/σ_{C-X} hyperconjugation. It should be pointed out that the π^*_{CO}/n_X interaction which stabilize the *gauche* conformations and leads to a decrease in the carbonyl bond order, should also cause an increase in the electron density on the α-methylene carbon atom and consequently a higher shielding for the α-methylene carbon.[3,19] This may suggest that the Δδ values should correlate with $\Delta\nu_H$ shifts (see preceding section). However, as the $\Delta\nu_H$ shifts for the S-ethyl α-heterosubstituted thioacetates cannot be estimated (see above), the $\Delta\nu_H$ shifts for the α-heterosubstituted acetones which correlate with the *gauche* shifts $\Delta\nu_g$ of the α-heterosubstituted thioacetates were used instead and a quite reasonable correlation (r = 0.839; 1.43 ppm) was obtained. The ethylthio- (**7**) derivative deviates strongly from the correlation while the diethylamino- (**4**) derivative deviates in a lesser extent from it.

The very low NAE value for the ethylthio-derivative is in agreement with our recent studies[3,7–12] which have indicated that in the α-alkylthiocarbonyl compounds, besides the π^*_{CO}/σ_{C-S} hyperconjugation, the π_{CO}/σ^*_{C-S} interaction also takes place leading to a decrease in the Non Additivity Effect for the SEt substituent. As the Δδ values were obtained from averaged chemical shifts of both rotamers, the existence of only a single *gauche* rotamer for the diethylamino-derivative (see Table I) along with the lack of the $\Delta\nu_H$ datum of the diethylamino substituent may be responsible at least in part for the deviation from the correlation of the dieth-

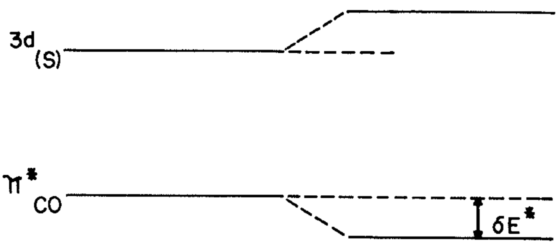


FIGURE 7 Qualitative energy levels diagram showing the interaction between a vacant 3d sulfur orbital and the π^*_{CO} orbital leading to its stabilization δE^* in the carboxythioethyl group for an unsubstituted thioester.

ylamino derivative (the $\Delta\nu_H$ datum of the dimethylamino substituent was used instead of the diethylamino substituent in the correlation).

The comparison of Tables VI and VII shows that the NAE values of the α-methylene carbon chemical shifts for the heterosubstituted thioacetates, excepting the fluoro- (**2**) and ethylthio- (**7**) derivatives are in general higher than the corresponding NAE values for the other classes of the heterosubstituted carbonyl compounds. This behavior is a further support for the fact that the π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions for the α-heterosubstituted thioesters are more important than the same interactions for the α-heterosubstituted-acetones, -acetophenones, -amides and -esters.

Although M.O. studies are in progress it seems reasonable to advance for the unsubstituted thioesters the explanation that the greater stabilization of the unperturbed π^*_{CO} orbital in the carboxythioethyl group in relation to the same orbital for the other classes of the studied unsubstituted carbonyl compounds may be due to the interaction between the π^*_{CO} orbital and a vacant 3d sulfur orbital. This originates the stabilization of the π^*_{CO} orbital (Figure 7) leading as a consequence to a stronger π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions for the α-heterosubstituted thioesters in relation to the same interactions which occur in the other classes of the α-heterosubstituted carbonyl compounds.

CALCULATIONS

Molecular-Mechanics Calculations. The MMC for the S-methyl α-halothioacetates and S-methyl thioacetate were performed on a IBM-PC/XT compatible computer by means of the MM2UEC program using MM2(87) force field with OCT/89 updated parameter set by Allinger.[34,35] Some parameters not found in Allinger's list were transferred from similar ones and are listed in Table IX.

Rotamer Population Ratios. The rotamer population ratios were determined[36] by the energy difference between them, using the relation:

$$\Delta G^\circ = RT \ln K$$

where the symbols have their customary meaning. For the case of the S-methyl α-halothioacetates the equilibrium:

$$cis(c) \rightleftarrows gauche_1(g_1) \rightleftarrows gauche_2(g_2)$$

TABLE IX

Parameters used in Molecular-Mechanics Calculations for S-methyl α-halothioacetates $CH_2(X)C(O)SMe$ and S-methyl thioacetate $CH_3C(O)SMe$.

Bond	k_S[a]	l_o[b]	μ[c]	Intervalency angle	K_b[d]	θ_0[e]
C(=O)-S	3.300	1.750	1.000	C-C(=O)-S	0.500	120.0
				O=C-S	0.500	120.0
				C(Me)-S-C(=O)	0.700	99.0

Dihedral angle	V_1[f]	V_2[f]	V_3[f]
H-C-C(=O)-S	0.0	0.0	0.5
F-C-C(=O)-S	0.0	0.0	0.5
Cl-C-C(=O)-S	0.0	0.0	0.5
Br-C-C(=O)-S	0.0	0.0	0.5
I-C-C(=O)-S	0.0	0.0	0.5

[a] Stretching force constant in mdyn Å^{-1}.
[b] Equilibrium distance in Å.
[c] Dipole moment in Debye.
[d] Bonding force constant in mdyn Å rad^{-1}.
[e] Equilibrium intervalency angle in degree.
[f] Out of plane torsion energy in kcal·mol^{-1}.

may be determined, considering that there are two enantiomers for the *cis* and two enantiomers for each *gauche* (g_1 and g_2) rotamers for the entropy of mixing. For instance for the fluorothioacetate at 27°C or 300 K, the *cis*/*gauche*$_1$ and the *cis*/*gauche*$_2$ equilibria have $\Delta H° = +0.35$ and $+0.14$ kcal·mol^{-1}, respectively (see Table II). Since there are two enantiomeric rotamers for each conformer the free energy change $\Delta G°$ for each equilibrium is equal to the enthalpy change $\Delta H°$, i.e., $\Delta G° = \Delta H°$, as the entropy change $\Delta S°$ is zero. Therefore for the *cis* ⇄ *gauche*$_1$ equilibrium, $K = C_{g_1}/C_c = 0.79$ and for the *cis* ⇄ *gauche*$_2$ equilibrium, $K = C_{g_2}/C_c = 0.56$. 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. $C_c + C_{g_1} + C_{g_2} = 1.0$. Thus, for the fluorothioacetate the computed concentrations for the three rotamers are: $C_c = 0.42$, $C_{g_1} = 0.24$ and $C_{g_2} = 0.34$.

EXPERIMENTAL

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

The S-ethyl thioacetate (**1**),[37] S-ethyl fluoro- (**2**),[38] chloro- (**5**),[39] bromo- (**6**)[40] and ethylthio- (**7**)[37]-thioacetates were prepared by the literature[37] procedure i.e. by the reaction of the corresponding acid chlorides and ethanethiol. The S-ethyl methoxythioacetate (**3**) b.p. 78–79°/25 Torr was obtained by the same method: ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3H, $J = 7.3$ Hz, CH_3); 2.91 (q, 2H, $J = 7.4$ Hz, CH_2S);

3.48 (s, 3H, CH_3O), 4.07 (s, 2H, CH_2). Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H; 7.51. Found: C, 45.08; H, 7.21. S-ethyl iodothioacetate (**8**), b.p. 56°/4.5 Torr was prepared by an adaptation of the procedure described for the iodoacetone[41] i.e. by the reaction of S-ethyl chlorothioacetate and potassium iodide in anhydrous acetone: ^1H NMR ($CDCl_3$): δ 1.27 (t, 3H, J = 7.5 Hz, CH_3); 2.95 (q, 2H, J = 7.5 Hz, CH_2S); 3.99 (s, 2H, CH_2). Anal. Calcd. for C_4H_7IOS: C, 20.88: H, 3.07. Found: C, 21.24; H, 3.12. Although compounds (**3**) and (**8**) have already been described in the literature[42] their physical constants have not been presented. S-ethyl N,N-diethylaminothioacetate (**4**), b.p. 90–91°/9 Torr, is a new compound and was obtained by an adaptation of the procedure described for the diethylaminoacetophenone[43] i.e. by the reaction of an ethereal solution of diethylamine and S-ethyl bromothioacetate in the 2:1 molar ratio: ^1H NMR ($CDCl_3$): δ 1.02 (t, 6H, J = 7.0 Hz, CH_3); 1.19 (t, 3H, 7.5 Hz, CH_3); 2.59 (q, 4H, J = 7.0 Hz, CH_2N), 2.77 (q, 2H, J = 7.5 Hz, CH_2S); 3.26 (s, 2H, CH_2). Anal. Calcd. for $C_8H_{17}NOS$: C, 54.81; H, 9.77; N, 7.90. Found: C, 55.00; H, 9.84: N, 7.99.

I.R. Measurements. The conditions for recording the I.R. carbonyl stretching bands in both fundamental (1800 – 1600 cm^{-1}) and in the first overtone (3600 – 3200 cm^{-1}) regions for 4.0×10^{-2} M solutions of the thioesters (**1**)–(**8**), in n-hexane, carbon tetrachloride and acetonitrile, using 0.5 mm sodium chloride and 1.00 cm quartz matched cells, respectively, have already been described.[3]

The overlapped carbonyl stretching bands were deconvoluted computationally by means of a curve fitting program based on the unrestricted Cauchy-Gauss sum function of the program developed by Jones and Pitha.[44a,44b,45] Minor Modifications were introduced[46] by using the half band width and the Cauchy-Gauss shape ratio as the input parameters. The non linear base line was optimized[46] by introduction of another component having a Gaussian profile and a very large half-width. For evaluation of the accuracy of the band envelope fit the root mean square of the residuals (DIS) was used. All the carbonyl bands analysed showed DIS values less than 0.02 transmittance units. The program was run a IBM-PC/XT compatible computer.

The carbonyl frequencies are accurate in the fundamental and in the 1st overtone regions to ±0.5 and ±1 cm^{-1}, respectively.

This *cis/gauche* ratios for the S-methyl heterosubstituted thioacetates (**2**)–(**8**) were estimated from the absorbances ratio of the two or three components of the computationally resolved bands measured directly at their absorption maxima assuming equality of the molar absorption coefficients of the two or three rotamers (see text).

^1H and ^{13}C NMR spectra of 0.5 M solutions of the title compounds in $CDCl_3$ were obtained as previously described.[47]

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