

Rotational Isomerism in $\text{CH}_3\text{CH}_2\text{—C(=S)SR}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$): A Combined Vibrational Spectroscopic and *ab Initio* Study

R. Fausto, A. Gabriela Martins, and J. J. C. Teixeira-Dias*

The University Chemical Department, P-3049 Coimbra, Portugal

P. J. Tonge and P. R. Carey

National Research Council of Canada, Division of Biological Sciences, Protein Laboratory (M54), Ottawa, Canada K1A 0R6

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The vibrational and conformational properties exhibited by $\text{CH}_3\text{CH}_2\text{C(=S)SCH}_3$ and $\text{CH}_3\text{CH}_2\text{C(=S)SCH}_2\text{—CH}_3$ were studied by Raman and infrared spectroscopies for the liquid and solid phases, and by *ab initio* calculations for the isolated molecule. It is shown that these molecules tend to adopt nonsymmetric conformations near the C(=S)S group, in contrast to their oxygen analogues whose most stable conformers correspond to structures having a planar skeleton. For the conformers differing by internal rotation about the $\text{C}_\alpha\text{—C}$ bond, the most stable conformer—the *skew* form having the CC—C=S dihedral angle equal to $\pm 100^\circ$ —is more stable than the symmetric *syn* conformer (CC—C=S equal to 0°) by *ca.* 1.0 kJ mol^{-1} . In the annealed solid, $\text{CH}_3\text{CH}_2\text{—C(=S)SCH}_3$ exists in the *skew* conformation, which is also the most stable form in the liquid and isolated molecule. As the liquid is rapid-froze, a glassy state where both conformers exist is obtained, which enables a spectroscopic characterization of the less stable *syn* form, taking advantage of the usual solid-state band-narrowing effect. The conformational dependence of some relevant structural parameters was used to characterize the most important intramolecular interactions present in the various conformers. In addition, the *ab initio* vibrational spectra were calculated and used for the assignment of the experimentally observed bands. In particular, the Raman and IR spectra of the molecules in the liquid and solid phases were assigned and the results were used to explain details of the resonance Raman spectra of methyl dithiopropionate [Ozaki, Y.; Storer, A. C.; Carey, P. R. *Can J. Chem.* **1982**, *60*, 190].

Introduction

The conformational preferences exhibited by simple aliphatic carboxylic alkyl esters are now well established. Unless large branched groups are simultaneously present in both the acyl and the ester moieties, these compounds tend to adopt conformations near the carboxylic group which have a planar skeleton.¹⁻⁵ Indeed, the preferred conformations of the CC—C=O and CO—CC axes are the symmetric *syn* and *anti* conformations (dihedral angles equal to 0 and 180° , respectively).

On the other hand, dithioester molecules exhibit a conformational behavior considerably different from that of their oxygen analogues, in general preferring to adopt nonsymmetric conformations near the C(=S)S group.⁵⁻⁹ In particular, it was shown that a CS—CC dihedral angle of *ca.* 84° is generally slightly more stable than the *anti* conformation for both the isolated molecule and the condensed phases.^{5,6} In turn, the conformational preferences of the CC—C=S axis in dithioesters have been scarcely studied. However, we have recently carried out a series of calculations on dithiopropionic acid, using both molecular mechanics and *ab initio* SCF-MO methods,^{4,7} which point to a *skew* form slightly more stable than the *syn* form. In addition, theoretical studies carried out on $\text{CH}(\text{CH}_3)_2\text{C(=S)SH}$ ⁸ reinforced the idea that the conformations having an α -methyl group *syn* to the thiocarbonyl bond are not favored energetically.

To our knowledge, no studies have been published on the conformational and vibrational properties of ethyl dithiopropionate (EDP). In turn, methyl dithiopropionate (MDP) has been previously studied by Raman spectroscopy,¹⁰ but it was not then possible either to identify the nature of the conformers present in the liquid phase or to determine their relative energies, because the Raman spectra had low signal-to-noise ratios and a sloping

baseline, thus preventing a clear observation of low-intensity bands. Yet, a precise vibrational and conformational characterization of the CC—C=S fragment has a major interest in the context of our biochemical studies on enzyme transient species formed within the active site of cysteine proteases (*e.g.*, papain).¹¹⁻¹³ Thus, in this article, we present the results of a combined vibrational spectroscopic and *ab initio* theoretical study undertaken for MDP and EDP. The main objective of this study is to analyze the internal rotation about the $\text{C}_\alpha\text{—C}$ bond in simple alkyl dithioesters and to determine its relevance to the vibrational spectra of these molecules.

Experimental and Computational Methods

MDP and EDP were synthesized by adding the corresponding alkyl iodide (methyl or ethyl) to $\text{CH}_3\text{CH}_2\text{C(=S)SMgBr}$ in a 1:1 THF:ethyl ether solution. After the addition, the reactive mixture was kept at 283 K for *ca.* 1 h to complete the reaction. Water was then added to the mixture and the dithioester extracted with ether and purified by distillation under low pressure. The purity of the samples was checked by $^1\text{H NMR}$ ($\text{CH}_3\text{CH}_2\text{CSSCH}_3$: CH_2 , qua, δ 2.81, 2; SCH_3 , s, δ 2.29, 3; CCH_3 , t, δ 1.29, 3. $\text{CH}_3\text{—CH}_2\text{CSSCH}_2\text{CH}_3$: SCH_2 , qua, δ 3.24, 2; CCH_2 , qua, δ 3.03, 2; SCH_2CH_3 , t, δ 1.38, 3; CCH_2CH_3 , t, δ 1.33, 3).

Raman spectra were recorded on a Spex 1403 double spectrometer (0.85 m, $f/7.8$), equipped with holographic gratings (1800 grooves/mm, ref. 1800-1SHD) and a thermoelectrically cooled Hamamatsu type R928 photomultiplier tube, controlled by a DM1B microcomputer. The light source was a Spectra Physics Ar⁺ laser (Model 164-05), whose output at 514.5 nm was adjusted to provide 100 mW at the sample position. The slits were adjusted to 160 μm . Samples were sealed in Kimax glass capillary tubes (inner diameter 0.8 mm). The estimated frequency errors are $\pm 1 \text{ cm}^{-1}$. Temperature variation studies were carried

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TABLE 1: Calculated Conformational Energies for Methyl and Ethyl Dithiopropionate

molecule	conformational change	energy difference/kJ mol ⁻¹	
		ab initio ^a	MM ^{4 b}
CH ₃ CH ₂ -C(=S)SCH ₃	<i>syn</i> - <i>skew</i>	0.9 (1.3)	2.1
	<i>skew</i> → <i>syn</i>	2.5	3.1
	<i>skew</i> → <i>skew</i>	9.9	6.4
CH ₃ CH ₂ -C(=S)S-CH ₂ CH ₃	(<i>skew/gauche</i>) - (<i>skew/gauche'</i>)	0.2 (0.2)	
	(<i>skew/anti</i>) - (<i>skew/gauche'</i>)	-0.1 (1.3)	
	(<i>syn/gauche</i>) - (<i>skew/gauche'</i>)	1.0 (1.4)	
	(<i>syn/anti</i>) - (<i>skew/gauche'</i>)	0.8 (2.6)	
	(<i>skew/gauche'</i>) → (<i>skew/gauche</i>)	42	
	(<i>skew/gauche'</i>) → (<i>skew/anti</i>)	2.3	
	(<i>skew/gauche</i>) → (<i>skew/anti</i>)	2.1	
	(<i>syn/gauche</i>) → (<i>syn/anti</i>)	2.3	
	(<i>syn/gauche</i>) → (<i>syn/gauche</i>)	42	

^aSTO-3G calculated values. The values shown in parenthesis were calculated with electron correlation (MP2 level) at the STO-3G optimized geometries. ^bMM, molecular mechanics.

out using a Harney-Miller¹⁴ assembly, the temperature being controlled by a Ventacon (Winchester) Model CAL 9000 controller. Reported band intensities are the average of at least two experiments. Absolute errors in temperature are estimated to be *ca.* 1 K.

Infrared spectra were recorded on a Perkin Elmer Model 683 spectrometer, using NaCl cells without spacers. A scan time of 6 min and a noise filter of 2 were selected for data collection, leading to absolute frequency errors of about 2 cm⁻¹.

The *ab initio* SCF-MO calculations were carried out using the *Gaussian 82* program package,¹⁵ running on a VAX 8530 computer, at the STO-3G^{16,17} level. The STO-3G basis set was chosen, considering the number of atoms and electrons in the molecules studied, because this basis set usually yields molecular geometries in reasonable agreement with experimental values. The importance of using reasonably good geometries for the calculation of vibrational spectra from *ab initio* derived force fields has been emphasised by other authors.¹⁸ Molecular geometries were fully optimized, at the STO-3G level, by the force gradient method using Schlegel's algorithm,¹⁹ and they are submitted as supplementary material to this article. The largest residual internal coordinate forces were always less than 3 × 10⁻⁴ hartree bohr⁻¹ (1 hartree = 2625.5001 kJ mol⁻¹; 1 bohr = 5.291 77 × 10⁻¹¹ m) or hartree rad⁻¹, for bond stretches and angle bends, respectively. To obtain the barriers to internal rotation, the geometries were optimized for different fixed internal rotation angles.

Normal coordinate analyses were carried out with a program²⁰ adapted to interface with *Gaussian 82* in order to use the *ab initio* derived force fields. The calculated vibrational frequencies were scaled with a procedure described in ref 6 (see also footnotes of Tables 3 and 4). Local C_s symmetry coordinates were used. The mean and maximum errors in this scaling were 4 and 15%, respectively, the largest percent errors occurring in some low-frequency modes, though the absolute errors in these did not exceed 40 cm⁻¹.

The following conformational nomenclature is adopted herein: *syn*, *anti*, *gauche*, *gauche'*, and *skew*, corresponding to dihedral angles whose reference values are respectively 0, 180, 60, -60, and 120°. In order to label the conformations of the molecules, only the heavy-atom skeleton is considered. Hence, starting at the propionate end common to both MDP and EDP, and following a left-to-right order, two dihedral angles should, in principle, be specified for MDP (CC-C=S, S=C-SC) and three for EDP (CC-C=S, S=C-SC, CS-CC). However, for the S=C-SC axis, the calculated energy difference between the *syn* and *anti* conformers in both molecules is estimated to be larger than 18 kJ mol⁻¹,^{6,21,22} and the energy barriers between these two forms about 45 kJ mol⁻¹.²² Since these energy values are large enough to prevent the experimental detection of the higher energy *s-trans* conformers under the experimental conditions used in the present

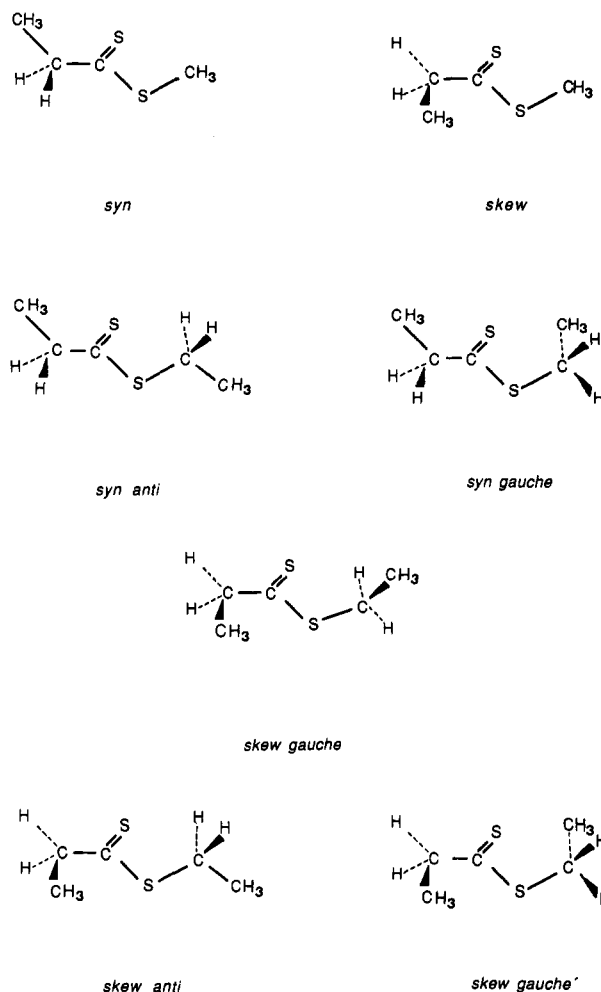


Figure 1. Conformers of MDP and EDP. Numbering of atoms: MDP, C₍₅₎H_(12,13,14)C₍₄₎H_(6,7)C₍₁₎(=S₍₂₎)S₍₃₎C₍₈₎H_(9,10,11); EDP, C₍₅₎H_(12,13,14)-C₍₄₎H_(6,7)C₍₁₎(=S₍₂₎)S₍₃₎C₍₈₎H_(9,10)C₍₁₁₎H_(12,13,14).

study (*kT* at room temperature is ≈ 2.5 kJ mol⁻¹), these structures are not considered herein. Therefore, only a single dihedral angle is specified for MDP (CC-C=S), and two are indicated for EDP (CC-C=S and CS-CC). When a conformation is specified by more than one dihedral angle, as it is in the case for EDP, the above mentioned conformational labels are separated by a slant and a left-to-right order, starting at the propionate end, is followed. Figure 1 represents schematically the relevant conformations of MDP and EDP (the numbering of the atoms, relevant for the tables of structural parameters, is indicated in the caption of Figure 1). Between energy minima (conformers), conformational changes are represented by a minus sign to indicate a difference or by an arrow to represent a barrier height.

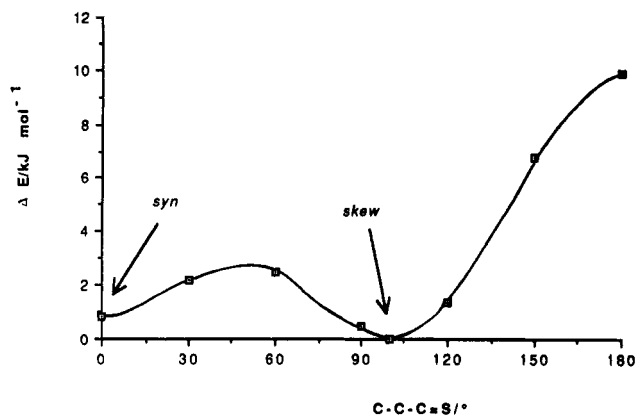


Figure 2. Calculated potential energy profile for internal rotation about the C_α -C bond in MDP.

Results and Discussion

Molecular Energies and Geometries. Table 1 shows the calculated relative conformational energies for the relevant structures of MDP and EDP (see Figure 1). The most stable conformer of MDP, as predicted by the calculations, corresponds to the *skew* conformer. In addition, the two conformers (*skew* and *syn*) have very close energies ($\Delta E_{syn-skew} \approx 1 \text{ kJ mol}^{-1}$). The potential energy profile for internal rotation about the C_α -C bond (Figure 2) shows that the *skew* \rightarrow *syn* energy barrier is only ca. 2.5 kJ mol^{-1} , while the *skew* \rightarrow *skew* energy barrier between the two equivalent-by-symmetry forms is considerably higher ($\approx 10 \text{ kJ mol}^{-1}$).

Similar values for $\Delta E_{syn-skew}$ ($(syn/gauche) - (skew/gauche)$, Table 1) are also found for EDP, the energy barrier about C_α -C ($(skew/gauche) \rightarrow (skew/gauche)$, Table 1) also being very

high. Hence, it can be concluded that the two alkyl groups in both molecules interact weakly, at least for a *syn* S=C-SC skeleton. This result reinforces our previous conclusions based on data obtained for methyl and ethyl dithioacetate (MDA, EDA),⁶ which indicated that the two alkyl groups do not interact significantly for conformations having a *syn* axis.

In general terms, the relative energies obtained for conformations differing by internal rotation about the S-CH₂CH₃ bond in EDP follow a trend similar to that obtained for EDA.⁶ In particular, the calculations predict similar energies for the *anti* and *gauche* conformers ($\approx 1 \text{ kJ mol}^{-1}$ at the correlated level), low *gauche* \rightarrow *anti* energy barriers ($\approx 2.3 \text{ kJ mol}^{-1}$), and very high *gauche* \rightarrow *gauche* energy barriers ($> 40 \text{ kJ mol}^{-1}$). In addition, the Hartree-Fock calculations predict the *anti* conformer as being slightly more stable than the *gauche* form as for EDA,⁶ while their relative energies are opposite when electronic correlation is explicitly included in the calculations (Table 1). Consonant with the highest level calculations, the vibrational spectroscopic studies previously undertaken on EDA⁶ clearly indicated that, in the liquid phase, the *gauche* conformation of the CS-CC axis is more stable than the *anti* form, and it is the single form present in the crystal. As seen below, this is also true for EDP.

The conformational behavior exhibited by the geometrical parameters during the S-CH₂CH₃ internal rotation in EDP follows trends similar to those found for EDA.⁶ It was then pointed out that the observed trends can be correlated with important intramolecular interactions involving the C(=S)S and thioester CH₂CH₃ fragments. In particular, both S=C-S and C-S-C angles attain their maximum values for the conformations where the repulsive CH₃...S= and C-H_(methylene)...S= interactions are maximized (energy maxima for CS-CC dihedral angles of 0 and $\pm 120^\circ$, respectively). In addition, methylene

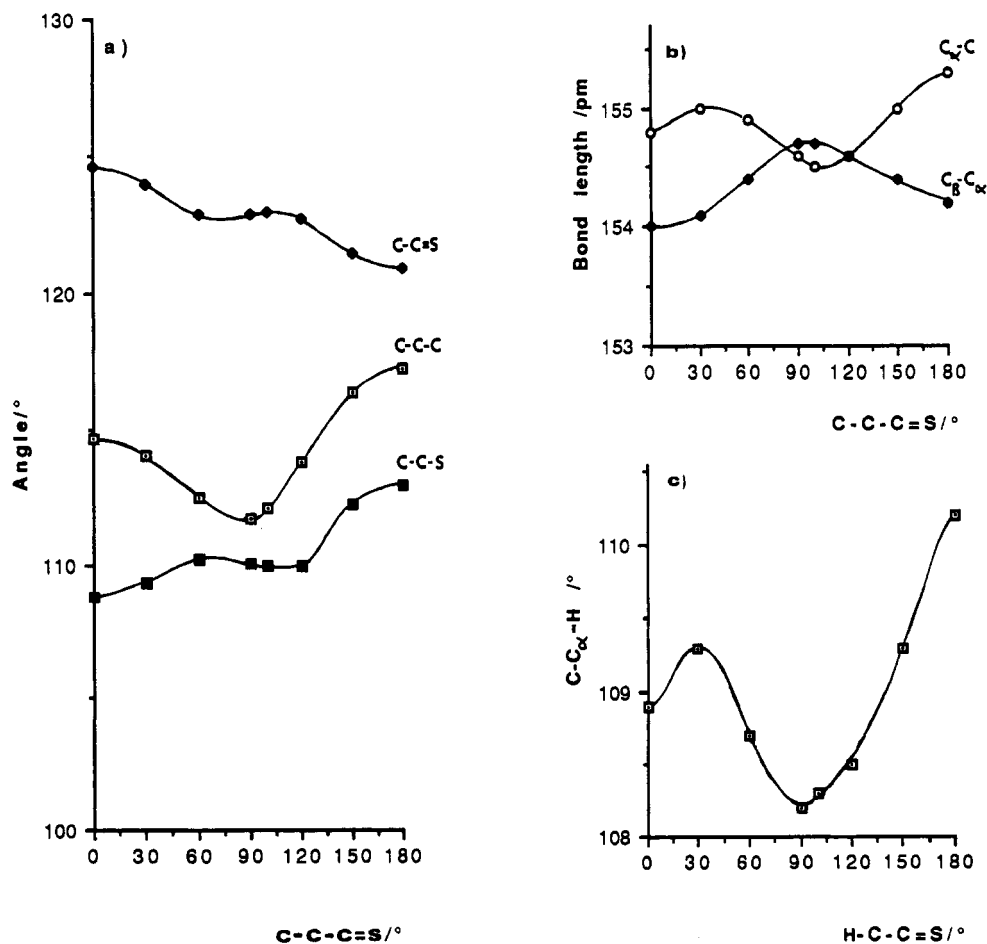


Figure 3. Changes in (a) C-C-C, C-C=S, C-C-S, (b) C_α -C, C_β - C_α , and (c) C-C α -H coordinates vs the C_α -C internal rotation in MDP.

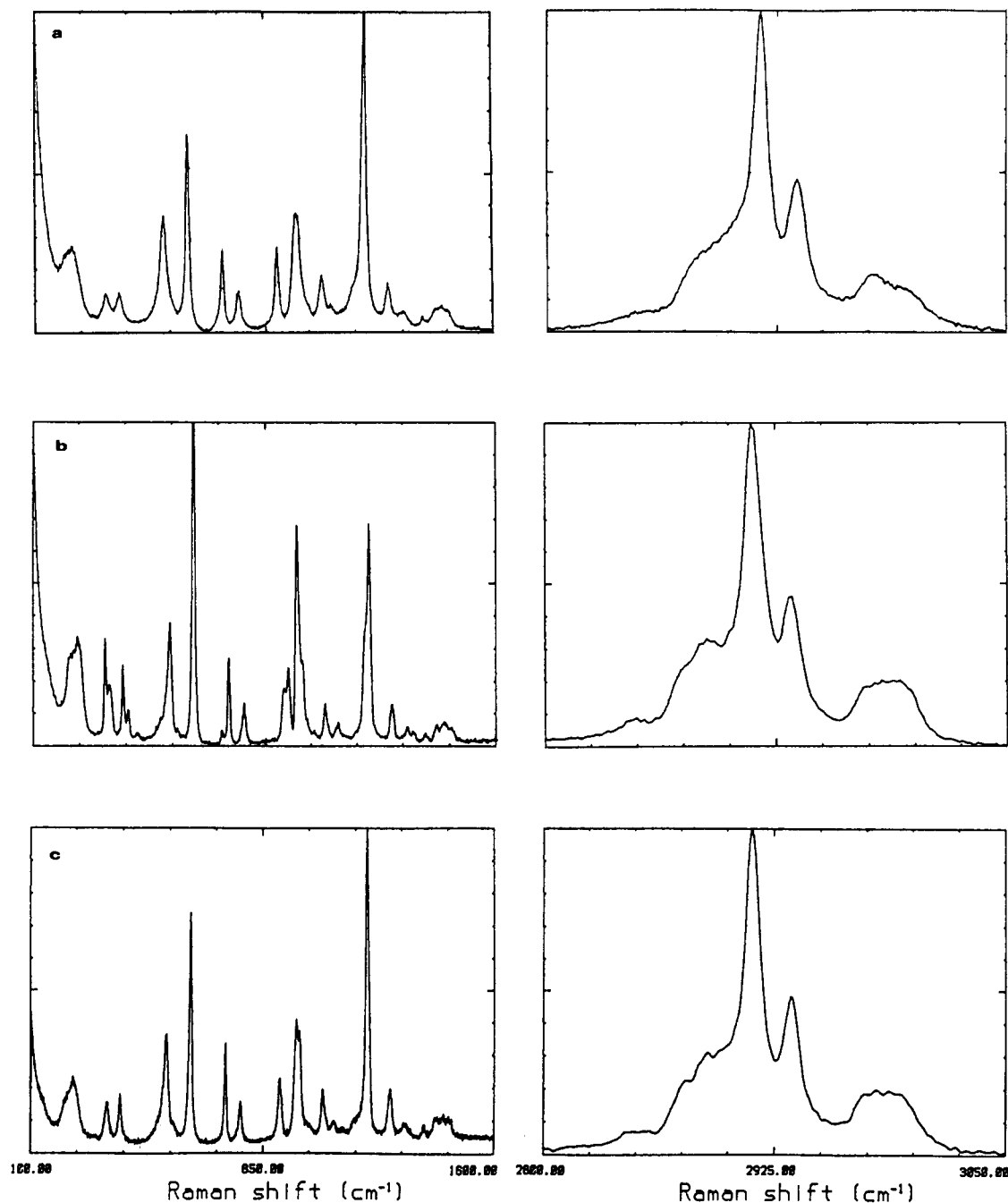


Figure 4. Raman spectra of MDP: (a) pure liquid at room temperature; (b) rapid-frozen solid (glassy state) at *ca.* 133 K; (c) annealed solid.

$\text{S-C-H}_{\text{o.o.p.}}$ angles attain their maximum values for conformations where $\text{C-H}_{\text{(methylene)}}\cdots\text{S=}$ interactions are more important, and S-C-C , $\text{C-C-H}_{\text{o.o.p.}}$, and $\text{C-C-H}_{\text{i.p.}}$ angles depend mainly on the $\text{CH}_3\cdots\text{S=}$ interaction (the S-C-C and $\text{C-C-H}_{\text{o.o.p.}}$ angles systematically decrease with the increase of the CS-CC dihedral angle, whereas the $\text{S-C-H}_{\text{i.p.}}$ angle increases).

In turn, the conformational dependence of the geometrical parameters on the $\text{C}_\alpha\text{-C}$ internal rotation can also be understood in terms of the most important intramolecular interactions involving the C(=S)S and CH_3CH_2 (thioacyl) fragments. In fact, the dependence of the $\text{C}_\alpha\text{-C}$ bond length and those of the C-C-C , C-C-S , and C-C-S angles on the CC-C=S angle (Figure 3) is essentially determined by both $\alpha\text{-CH}_3\cdots\text{S=}$ and $\alpha\text{-CH}_3\cdots\text{S-}$ steric interactions. In particular, the maximum energy of the $\alpha\text{-CH}_3\cdots\text{S-}$ interaction occurs for a CC-C=S dihedral angle of 180° and results in the $\text{C}_\alpha\text{-C}$ bond length and the C-C-C and C-C-S angles having their

maximum values and the C-C-S angle attaining its minimum value (Figure 3).

C=S and C-S bond lengths depend mainly on the mesomerism of the C(=S)S group, and this is mainly dependent on the conformation of the dithioester fragment.⁶ Thus, these bond lengths do not vary appreciably with the $\text{C}_\alpha\text{-C}$ internal rotation. However, slightly shorter C-S bond lengths occur for those conformations where the S= atom is in a staggered conformation with respect to the $\alpha\text{-methyl}$ substituent (mesomerism was also found to be more important in the case of staggered conformations of $\text{CH}_3\text{CH}_2\text{C(=S)SH}^7$).

Finally, the $\text{C}_\alpha\text{-H}$ and $\text{C}_\beta\text{-C}_\alpha$ and $\text{C-C}_\alpha\text{-H}$ coordinates depend mainly on the different degrees of *s* and *p* character of the CH or CC bond, while hyperconjugation can also contribute to the conformational change undergone by $\text{C}_\alpha\text{-H}$ bond lengths leading to larger $\text{C}_\alpha\text{-H}$ out-of-plane bond lengths.^{7,8} Thus, in the two molecules herein studied, $\text{C}_\alpha\text{-H}$ and $\text{C}_\beta\text{-C}_\alpha$ bond lengths reach maxima for HC-C=S or CC-C=S dihedral angles near 90° ,

TABLE 2: Calculated (STO-3G) and Experimental Vibrational Frequencies, and Calculated PED's for Methyl Dithiopropionate (Form *skew*)^a

assignment	freq	PED (%) ^c	<i>ab initio</i>				
			scaled ^b freq	experimental			
				R (sol)	R (liq)	IR (liq)	
νCCH_3 as	A''	3756	νCCH_3 as A'' [94]	3006	2990	2990	2989
νCCH_3 as	A'	3754	νCCH_3 as A' [97]	3004	2990	2990	2989
νSCH_3 as	A'	3752	νSCH_3 as A' [100]	3003	2990	2990	2989
νSCH_3 as	A''	3738	νSCH_3 as A'' [100]	2992	2972	2977	n.o.
νCH_2 as		3722	νCH_2 as [97]	2979	2972	2977	n.o.
νCH_2 s		3601	νCH_2 s [99]	2883	2932	2936	2936
νCCH_3 s		3570	νCCH_3 s [100]	2858	2912	2910	2916
νSCH_3 s		3558	νSCH_3 s [100]	2849	2912	2910	2916
δCCH_3 as	A'	1840	δCCH_3 as A' [80]; δCH_2 [15]	1481	1460	1454	1458
δCCH_3 as	A''	1831	δCCH_3 as A'' [100]	1474	1450	1454	1450
δSCH_3 as	A'	1822	δSCH_3 as A' [88]	1467	1440	1433	1434
δSCH_3 as	A''	1811	δSCH_3 as A'' [96]	1458	1420	1410	1416
δCH_2		1810	δCH_2 [93] + δCCH_3 as A' [13]	1457	1420	1410	1416
δCCH_3 s		1730	δCCH_3 s [102]	1394	1374	1374	1372
δSCH_3 s		1699	δSCH_3 s [104]	1369	1310	1313	1310
ωCH_2		1632	ωCH_2 [67] + $\nu\text{C}_\alpha\text{-C}$ [17]	1316	1262	1262	1262
$\nu\text{C}=\text{S}$		1567	twCH_2 [40] + $\nu\text{C}=\text{S}$ [29] + ωCH_2 [13]	1264	1188	1187	1187
twCH_2		1489	$\nu\text{C}=\text{S}$ [22] + twCH_2 [21] + γCCH_3 A'' [20] + γCH_2 [13]	1202	1110	1110	1112
γCCH_3	A''	1348	$\nu\text{C}_\alpha\text{-C}$ [30] + γCH_2 [15] + γCCH_3 A'' [13]	1090	1080	1076	1081
γCCH_3	A'	1271	γCCH_3 A' [47] + $\nu\text{C}_\beta\text{-C}$ [29]	1028	1044	1047	1047
$\nu\text{C}_\beta\text{-C}$		1196	$\nu\text{C}_\beta\text{-C}$ [29] + twCH_2 [16] + $\nu\text{C}=\text{S}$ [14] + γCCH_3 A'' [12]	968	968	964	966
γSCH_3	A'	1177	γSCH_3 A' [83]	954	958	960	960
γSCH_3	A''	1171	γSCH_3 A'' [97]	949	958	960	960
$\nu\text{C}_\alpha\text{-C}$		1097	$\nu\text{C}_\alpha\text{-C}$ [24] + δCCH_3 A'' [21] + $\nu\text{C-S}$ [20] + $\nu\text{C}_\beta\text{-C}$ [15]	890	906	903	903
$\nu\text{S-C}$		959	$\nu\text{S-C}$ [92]	780	728	727	728
γCH_2		926	γCH_2 [61] + γCCH_3 A'' [40]	754	778	789	779
$\nu\text{C-S}$		700	$\nu\text{C-S}$ [36] + $\delta\text{C-C-C}$ [20] + $\gamma\text{C}=\text{S}$ [20] + $\nu\text{C}_\alpha\text{-C}$ [11]	574	616	614	614
$\gamma\text{C}=\text{S}$		619	$\gamma\text{C}=\text{S}$ [53] + $\nu\text{C-S}$ [15] + $\delta\text{C-C-C}$ [13]	510	538	534	535
$\delta\text{S-C-S}$		451	$\delta\text{S-C-S}$ [44] + $\delta\text{C-S-C}$ [43]	376	388	389	n.o.
$\delta\text{C-C-S}$		376	$\delta\text{C-C-S}$ [68] + $\tau\text{C}_\beta\text{-C}$ [11]	316	348	346	n.o.
$\delta\text{C-C-C}$		263	$\delta\text{C-S-C}$ [32] + $\delta\text{C-C-C}$ [31] + $\gamma\text{C}=\text{S}$ [25]	226	233	233	n.o.
$\tau\text{C}_\beta\text{-C}$		238	$\tau\text{C}_\beta\text{-C}$ [39] + $\delta\text{S-C-S}$ [20] + $\delta\text{C-C-C}$ [19] + $\gamma\text{C}=\text{S}$ [17]	206	220	220	n.o.
$\delta\text{C-S-C}$		215	$\tau\text{C}_\beta\text{-C}$ [51] + $\delta\text{C-C-S}$ [20] + $\delta\text{S-C-S}$ [14] + $\delta\text{C-S-C}$ [13]	188	n.o.	n.o.	n.o.
$\tau\text{S-C}$		151	$\tau\text{S-C}$ [101]	137	n.o.	n.o.	n.o.
$\tau\text{C-S}$		95	$\tau\text{C-S}$ [94]	92	n.o.	n.o.	n.o.
$\tau\text{C}_\alpha\text{-C}$		54	$\tau\text{C}_\alpha\text{-C}$ [133] + $\delta\text{C-C-C}$ [12]	60	n.o.	n.o.	n.o.

^a Frequencies in cm^{-1} ; ν , stretching; δ , bending; γ , rocking; ω , wagging; tw , twisting; τ , torsion; s, symmetric; as, asymmetric; n.o., not observed; local C_s symmetry is considered for methyl groups. ^b Scaled using the following relationship: $f_{\text{scaled}} = (0.796) f_{\text{calc}} + 16.7$. ^c PED's smaller than 10% are not presented in the table.

respectively, though the $\alpha\text{-CH}_3\cdots\text{S-}$ repulsion (which leads to the opening of the C-C-C angle, as referred to above) contributes to the significant reduction of the $\text{C-C}_\alpha\text{-H}$ angle observed for the conformation corresponding to a $\text{CC-C}=\text{S}$ angle equal to 180° (Figure 3).

All these trends are in general good agreement with previously reported data for dithiopropionic acid.⁷

Vibrational Results. Methyl Dithiopropionate. In agreement with the results of the calculations, bands due to both the *skew* and *syn* conformers of MDP are expected to be observed in the liquid-phase spectra. The latter conformer belongs to the C_s point group, and its 36 normal modes span the irreducible representations $22 A' + 14 A''$. The *skew* form belongs to the C_1 point group, and all 36 normal modes are totally symmetric (A). The liquid-phase Raman spectrum of MDP at room temperature and the solid-state annealed and rapid-frozen spectra obtained at *ca.* 133 K are shown in Figure 4. The results of the normal-mode analyses based on the STO-3G derived force fields are presented in Tables 2 and 3.

The most interesting observation is that the spectra of the annealed and rapid-frozen samples are significantly different. In fact, in addition to some intensity differences, several bands are only present in the latter spectrum (for instance, bands at 332, 406, 708, 756, 922, and *ca.* 1157 and 1172 cm^{-1}). It is the apparent that in the annealed sample (which corresponds to the crystalline state) one conformer with at least a dominant population should exist, while in the rapid-frozen sample (glass) a mixed conformational population (*skew* + *syn*) is present. In addition, the

results of the normal-coordinate analysis suggest that the form which is present in the crystal should be the *skew* form and that the bands which are present only in the spectrum of the rapid-frozen sample correspond to vibrational modes originating in the *syn* conformer. This is particularly evident if we consider, for example, the pairs of bands at 728/708, 906/922, and 1188/1172 cm^{-1} , which are due to the $\nu\text{S-C}$, $\nu\text{C}_\alpha\text{-C}$, and $\nu\text{C}=\text{S}$ stretching modes, respectively. In all these cases, the first bands are the only ones to remain in the spectrum of the crystal. In turn, the calculations predict that these bands are due to the *skew* form, as the $\nu\text{C}_\alpha\text{-C}$ mode is predicted to have a lower frequency and both $\nu\text{C-S}$ and $\nu\text{C}=\text{S}$ higher frequencies in this conformer, when compared with the *syn* form. Indeed, with a single exception (the pair of bands at 348/332 cm^{-1}), for all the observed doublets, the bands which are absent in the spectrum of the annealed sample occur at frequencies which, in keeping with the calculations, can be unambiguously ascribed to the *syn* form.

The liquid-phase spectra do not exhibit significant changes with temperature within the range of temperatures herein considered (183–298 K). This cannot be due to the presence of a single conformer in this phase, as the rapid-frozen glassy sample must have approximately the same conformational composition of the liquid phase at room temperature (*i.e.* the temperature just before the cooling), and the glassy sample gives rise to spectra in which bands ascribed to the two conformers are clearly observed. On the other hand, the liquid-phase spectra present relatively broad bands, in particular those bands that show a splitting in

TABLE 3: Calculated (STO-3G) and Experimental Vibrational Frequencies, and Calculated PED's for Methyl Dithiopropionate (Form *syn*)^a

assignment	<i>ab initio</i>		scaled ^b	experimental	
	freq	PED (%) ^c	freq	Raman _(sol) ^d	
ν CCH ₃ as	A''	3761	ν CCH ₃ as [100]	3010	2990
ν CCH ₃ as	A'	3756	ν CCH ₃ as [100]	3006	2990
ν SCH ₃ as	A'	3751	ν SCH ₃ as [100]	3002	2990
ν SCH ₃ as	A''	3738	ν SCH ₃ as [100]	2992	2977
ν CH ₂ as	A''	3691	ν CH ₂ as [100]	2955	2954
ν CH ₂ s	A'	3584	ν CH ₂ s [99]	2870	2932
ν CCH ₃ s	A'	3574	ν CCH ₃ s [99]	2862	2912
ν SCH ₃ s	A'	3558	ν SCH ₃ s [100]	2849	2912
δ CCH ₃ as	A'	1833	δ CCH ₃ as [80] + δ CH ₂ [16]	1476	1460
δ CCH ₃ as	A''	1827	δ CCH ₃ as [98]	1471	1450
δ SCH ₃ as	A'	1822	δ SCH ₃ as [88]	1467	1440
δ SCH ₃ as	A''	1812	δ SCH ₃ as [97]	1459	1420
δ CH ₂	A'	1810	δ CH ₂ [103] + δ CCH ₃ as [12]	1457	1420
δ CCH ₃ s	A'	1738	δ CCH ₃ s [92] + ν C β -C [10]	1400	1374
δ SCH ₃ s	A'	1699	δ SCH ₃ s [104]	1369	1310
ω CH ₂	A'	1647	ω CH ₂ [77] + ν C α -C [10]	1327	1262
ν C=S	A'	1549	ν C=S [62] + ν C α -C [25]	1250	1172
twCH ₂	A''	1524	twCH ₂ [64] + γ CCH ₃ [18]	1230	1157
γ CCH ₃	A'	1304	ν C β -C [36] + γ CCH ₃ [30]	1055	1080
γ CCH ₃	A''	1280	γ CCH ₃ [39] + twCH ₂ [32] + γ CH ₂ [25]	1036	1044
ν C β -C	A'	1187	γ CCH ₃ [47] + ω CH ₂ [18] + ν C=S [14] + ν C-S [16] + ν C β -C [13]	962	958
γ SCH ₃	A'	1179	γ SCH ₃ [76]	955	958
γ SCH ₃	A''	1170	γ SCH ₃ [94]	948	958
ν C α -C	A'	1111	ν C α -C [35] + ν C-S [27] + ν C β -C [21]	901	922
ν S-C	A'	957	ν S-C [95]	778	708
γ CH ₂	A''	919	γ CH ₂ [63] + γ CCH ₃ [42]	748	756
ν C-S	A'	721	ν C-S [24] + ν C=S [22] + ν C α -C [21] + δ C-C-C [19]	591	616
γ C=S	A''	490	γ C=S [121] + τ C-S [10]	407	406
δ S=C-S	A'	490	δ C-S-C [28] + δ C-C-C [26] + ν C-S [23] + δ S=C-S [22]	407	406
δ C-C=S	A'	392	δ C-S-C [23] + δ S=C-S [22] + δ C-C-C [14] + δ C-C=S [12]	329	332
δ C-C-C	A'	270	δ S=C-S [28] + δ C-S-C [22] + δ C-C-C [17] + δ C-C=S [15]	232	233
τ C β -C	A''	234	τ C β -C [97]	203	220
δ C-S-C	A'	210	δ C-C=S [43] + δ C-S-C [26] + δ C-C-C [18] + δ S=C-S [14]	184	n.o.
τ S-C	A''	153	τ S-C [102]	138	n.o.
τ C-S	A''	101	τ C-S [107]	97	n.o.
τ C α -C	A''	44	τ C α -C [133] + γ C=S [11]	52	n.o.

^a Frequencies in cm⁻¹; ν , stretching; δ , bend; γ , rock; ω , wagging; tw, twist; τ , torsion; s, symmetric; as, asymmetric; n.o., not observed. ^b Scaled using the following relationship: $f_{\text{scaled}} = (0.796) f_{\text{calc}} + 16.7$. ^c PED's smaller than 10% are not presented. ^d Rapid-frozen sample (glass); an IR band at 1160 cm⁻¹ was also ascribed to this form (see text).

the glassy-phase spectrum where the bands are narrower, thus leading to a much better intrinsic resolution.

For the calculated value of the energy difference between conformers, $\Delta E_{\text{syn-skew}} \approx 1$ kJ mol⁻¹, the *syn/skew* population ratio would be expected to change by *ca.* 7-8% over the range of temperatures studied (298-183 K), a value which would probably give rise to noticeable changes of relative intensities in the spectra. Since no appreciable changes were observed over this range of temperature, it is concluded that the energy difference between conformers for the liquid phase is smaller than the value for the isolated molecule.

In summary, in the annealed solid, MDP exists in the *skew* conformation, which is the most stable form for both the liquid and isolated molecule. As the liquid is rapid-froze, a glassy state where both conformers exist is obtained, enabling a spectroscopic characterization of the less stable *syn* form by taking advantage of the usual solid-state band-narrowing effect.

The most relevant results to the band assignments presented in Tables 2 and 3 are discussed below.

(i) The frequencies of the modes associated with the thioester methyl group are essentially similar to those previously found for MDA,^{6,23} thus indicating that the chemical environment of this group is very similar in the two molecules (*i.e.*, reinforcing once again the idea that the two alkyl groups do not interact significantly with each other). Indeed, the observed frequencies of the SCH₃ stretching, bending, and rocking modes for methyl dithiopropionate (ν SCH₃ 2990, 2972, 2912; δ SCH₃ 1440, 1420, 1310; γ SCH₃ 958 cm⁻¹) compare very closely with those found for MDA (ν SCH₃ 2989, 2962, 2913; δ SCH₃ 1434, 1410, 1309; γ SCH₃ 957 cm⁻¹).

(ii) As in the esters of dithioacetic acid previously studied,⁶ the present results clearly indicate that for the molecules now studied ν S-C is essentially a pure mode, while ν C-S mixes with δ CCC, γ C=S, and ν C α -C. The S-C stretching mode in MDP has a frequency similar to that observed in MDA (728 *vs* 730 cm⁻¹) but considerably higher than those observed in EDA⁶ and ethyl propionate (*ca.* 680 cm⁻¹). In turn, ν C-S occurs at a frequency close to that observed in EDP (616 *vs* 624 cm⁻¹) but much higher than those found for the derivatives of dithioacetic acid (*ca.* 580 cm⁻¹). These results indicate that ν C-S is sensitive to a substitution in the dithioacyl fragment and independent of the dithioester group, while ν S-C exhibits the opposite behavior.

(iii) The modes that are predicted by the calculations to be more sensitive to the internal rotation about the C α -C bond are those involving mainly the CH₂ group and the skeletal modes near the C(=S)S fragment (with the notable exceptions of ν CH₂ and ν S-C; Tables 2 and 3). In keeping with the calculations, all the bands ascribed to the *syn* form (observed clearly in the solid glassy-state spectrum) are ascribed to these modes, and are in agreement (with a single exception) with the predicted order with respect to the same mode in the more stable *skew* form.

(iv) While most of the normal modes associated with the two methyl groups and some skeletal modes involve essentially one symmetry coordinate, ν C-S, ν C=S, ν C α -C, ν C β -C α , and γ CCH₃ are considerably mixed in some vibrations. In addition, δ S=C-S, δ C-S-C, and δ C-C-C were found to mix strongly. These are trends similar to those previously found for both MDA and EDA.⁶

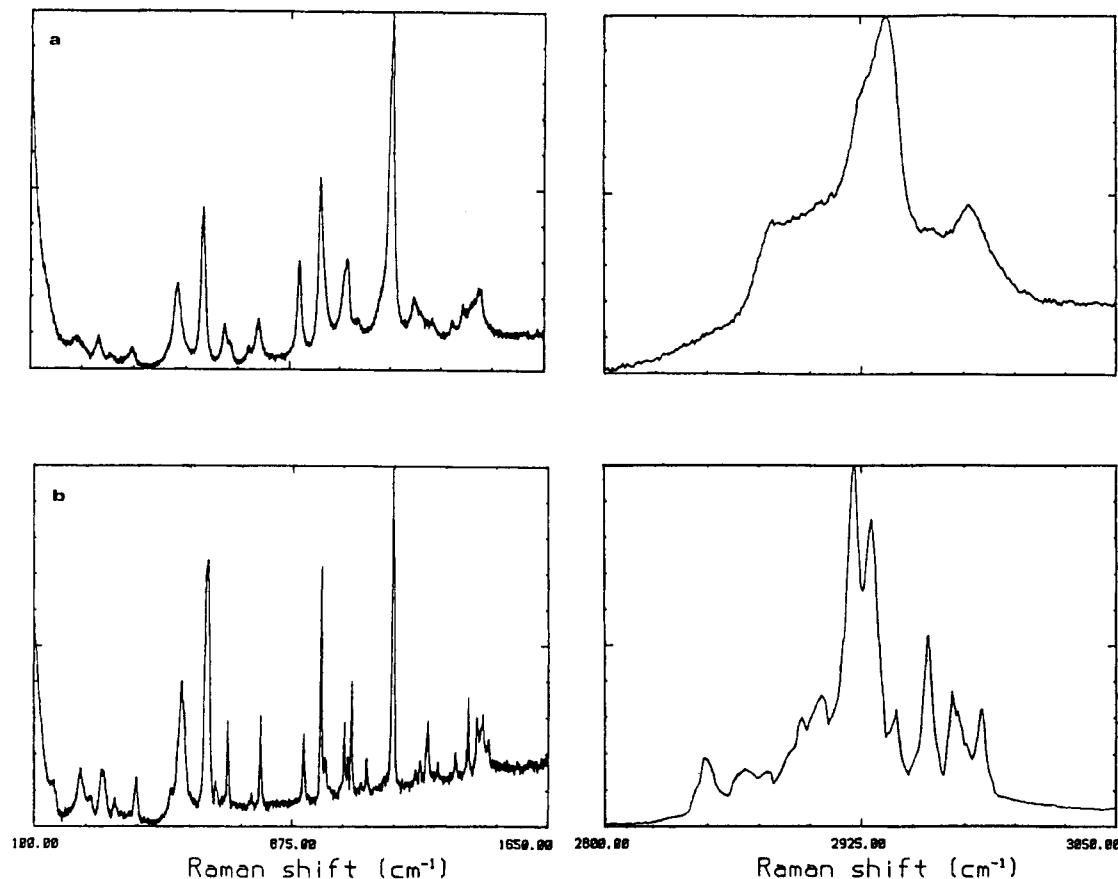
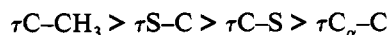


Figure 5. Raman spectra of EDP: (a) pure liquid at room temperature; (b) solid.

(v) The torsional vibrations are predicted to follow the order



in both conformers. The $\tau\text{C-CH}_3$ and $\tau\text{S-C}$ calculated frequencies for the two conformers are essentially the same, while in the *skew* form $\tau\text{C-S}$ occurs at a slightly lower frequency and $\tau\text{C}_\alpha\text{-C}$ at a slightly higher frequency than in the *syn* form. These results may be related respectively with the relative importance of the mesomerism within the C(=S)S group and of the hyperconjugative effect involving the $\text{CH}_2\text{-C(=S)}$ fragment, in the two conformers. Hence, the first effect may be slightly less important and the second effect more important in the *skew* conformer than in the *syn* form. However, these trends do not receive further support from the geometrical parameters (mainly in the case of the C-S bond lengths calculated for the two forms) and are only tentatively proposed herein. The calculated value for $\tau\text{S-C}$ (138 cm^{-1}) is very similar to the value previously obtained for MDA (137 cm^{-1}). In turn, $\tau\text{C-S}$ in this molecule⁶ occurs at the same frequency as in the *syn* form of MDP (98 cm^{-1}), and $\tau\text{C}_\alpha\text{-C}$ has a frequency (116 cm^{-1}) that is approximately twice that of the same mode in MDP (this is essentially due to mass effects, while it has also been pointed out that the hyperconjugative effect involving the C(=S)S and the α -hydrogen atoms is considerably more important in dithioacetic acid than in dithiopropionic acid derivatives⁷).

(vi) Finally, the normal coordinate analysis herein presented enables us also to make a detailed interpretation of the resonance Raman (RR) spectra of the MDP molecule.¹⁰ The RR spectrum shows eight bands which are ascribed to the following modes, which consonant with the present study are those which have substantial character of either $\nu\text{C-S}$, $\nu\text{C=S}$, $\nu\text{C}_\alpha\text{-C}$, or $\nu\text{S-C}$ (*i.e.*, those coordinates mainly involved in the electronic transition associated with the resonance enhancement;¹⁰ Tables 2,3): 1264 cm^{-1} (ωCH_2), 1188 cm^{-1} ($\nu\text{C=S}$), *ca.* 1110 cm^{-1} (twCH_2), *ca.* 1076 cm^{-1} ($\gamma\text{CCH}_3\text{ A}''$), 970 cm^{-1} ($\nu\text{C}_\beta\text{-C}_\alpha$), 728 cm^{-1} ($\nu\text{S-C}$),

615 cm^{-1} ($\nu\text{C-S}$), and 538 cm^{-1} ($\gamma\text{C=S}$). A RR band at *ca.* 906 cm^{-1} , due to the $\nu\text{C}_\alpha\text{-C}$ vibration, should also be expected, but this is certainly underneath the intense solvent band (CH_3CN) at 917 cm^{-1} .

Ethyl Dithiopropionate. With the exception of the *syn/anti* conformer (which belongs to the C_s point group), all the studied conformers of EDP (Figure 1) belong to the C_1 point group, and thus all their 45 normal modes are totally symmetric (A). Figure 5 shows the Raman spectra of this molecule in both the liquid and solid (polycrystalline) phases. The vibrational assignments and the results of the normal mode analysis based on the *ab initio* data for the most stable conformer (*skew/gauche'*) are presented in Table 4.

The main conclusions obtained from the vibrational studies carried out on this molecule can be summarized as follows:

(i) All the vibrations originating in the $\text{CH}_3\text{CH}_2\text{C(=S)S}$ fragment (with the exception of $\delta\text{S=C-S}$) have frequencies very similar to those found for MDP. On the other hand, all the vibrations due to the SCH_2CH_3 group and both $\delta\text{S=C-S}$ and $\delta\text{C-S-C}$ normal modes have frequencies almost identical to those observed for EDA.⁶ These results reinforce once again the idea that in simple unbranched alkyl dithioesters having a *syn* S=C-SC axis the two alkyl groups practically do not interact with each other.⁶ Additionally, the calculations predict that the $\tau\text{C-S}$ in the present molecule has a lower frequency than in both MDA and EDA,⁶ as well as in MDP. However, this is mainly due to a mass effect and does not reflect any substantial change in the electronic properties of the C-S bond.

(ii) It is only possible to observe clearly one band ascribed to conformers having an *anti* CS-CC axis: the band at 696 cm^{-1} (in the liquid-phase spectra), assigned to $\nu\text{S-C}$ in these forms. From the temperature dependence of the relative intensity of this band and the band at 682 cm^{-1} , due to those forms having a *gauche* CS-CC axis, the enthalpy difference between these axes is estimated to be $1.9 \pm 0.2\text{ kJ mol}^{-1}$. As expected, this value is

TABLE 4: Calculated (STO-3G) and Experimental Vibrational Frequencies, and Calculated PED's for Ethyl Dithiopropionate (Form *skew-gauche*)^a

assignment	<i>ab initio</i>		scaled ^b freq	experimental			
	freq	PED (%) ^c		R (sol)	R (liq)	IR (liq)	
ν C'CH ₃ as	A''	3756	ν C'CH ₃ as A'' [96]	3006	2983	2980	2978
ν CCH ₃ as	A''	3756	ν CCH ₃ as A'' [94]	3006	2983	2980	2978
ν CCH ₃ as	A'	3754	ν CCH ₃ as A' [97]	3005	2983	2980	2978
ν C'CH ₃ as	A'	3749	ν C'CH ₃ as A' [99]	3001	2970	n.o.	2978
ν CH ₂ (C) as		3722	ν CH ₂ (C) as [95]	2979	2957	n.o.	n.o.
δ CH ₂ (S) as		3722	ν CH ₂ (S) as [96]	2979	2957	n.o.	n.o.
ν CH ₂ (C) s		3601	ν CH ₂ (C) s [99]	2885	2942	2942	n.o.
ν CH ₂ (S) s		3603	ν CH ₂ (S) s [100]	2885	2930	2935	2930
ν CCH ₃ s		3570	ν CCH ₃ s [100]	2858	2921	n.o.	2921
ν C'CH ₃ s		3569	ν C'CH ₃ s [100]	2858	2905	2905	2905
δ CCH ₃ as	A'	1840	δ CCH ₃ as A' [80] + δ CH ₂ (C) [15]	1481	1471	n.o.	1465
δ C'CH ₃ as	A'	1835	δ C'CH ₃ as A' [62] + δ C'CH ₃ as A'' [31]	1477	1452	1458	1455
δ CCH ₃ as	A''	1831	δ CCH ₃ as A'' [99]	1474	1436	1436	1436
δ C'CH ₃ as	A''	1831	δ C'CH ₃ as A'' [68] + δ C'CH ₃ as A' [29]	1474	1436	1436	1436
δ CH ₂ (C)		1810	δ CH ₂ (C) [94] + δ CCH ₃ as A' [14]	1457	1425	1425	1427
δ CH ₂ (S)		1787	δ CH ₂ (S) [108]	1439	1408	1408	1404
δ C'CH ₃ s		1731	δ C'CH ₃ s [96]	1394	1370	1376	1372
δ CCH ₃ s		1730	δ CCH ₃ s [99]	1394	1317	1314	1330
ω CH ₂ (S)		1612	ω CH ₂ (S) [63] + ω H ₂ (C) [20]	1300	1285	1276	1275
ω CH ₂ (C)		1636	ω CH ₂ (C) [51] + ν C α -C [15] + ω CH ₂ (S) [14] + ν C=S [11]	1319	1264	1257	1255
ν C=S		1564	twCH ₂ (C) [39] + ν C=S [26]	1262	1182	1189	1185
twCH ₂ (S)		1532	twCH ₂ (S) [56] + γ C'CH ₃ A'' [17]	1236	1154	1150	1150
twCH ₂ (C)		1487	ν C=S [23] + twCH ₂ (C) [20] + γ CCH ₃ A' [20] + γ CH ₂ (C) [13]	1200	1103	n.o.	1110
γ CCH ₃	A''	1346	ν C α -C [30] + γ CH ₂ (C) [15] + γ CCH ₃ A'' [14]	1088	1084	1087	1084
γ CCH ₃	A'	1273	γ CCH ₃ A' [34] + ν C β -C [19]	1030	1058	1054	1052
γ C'CH ₃	A'	1267	γ C'CH ₃ A' [42] + ν C'-C [26]	1025	1047	1049	1045
γ C'CH ₃	A''	1261	γ CCH ₃ A'' [35] + twCH ₂ (S) [30] + γ CH ₂ (S) [16]	1020	1036	n.o.	1036
ν C β -C		1195	ν C β -C [30] + twCH ₂ (C) [15] + ν C=S [14] + ω CH ₂ (C) [12]	968	978	971	980
ν C'-C		1190	ν C'-C [44] + γ C'CH ₃ A' [21] + δ S-C [13] + γ CH ₂ (S) [12]	934	964	971	964
ν C α -C		1096	ν C-C [24] + γ CCH ₃ A' [21] + ν C-S [21] + ν C α -C [15]	889	912	906	906
γ CH ₂ (C)		928	γ CH ₂ (C) [61] + γ CCH ₃ A'' [41]	756	780	789	776
γ CH ₂ (S)		897	γ CH ₂ (S) [36] + ν S-C [33] + γ C'CH ₃ A'' [23]	731	750	750	748
ν S-C		877	ν S-C [43] + γ CH ₂ (S) [35] + γ C'CH ₃ A'' [16]	715	681	682	679
ν C-S		700	ν C-S [35] + γ C=S [21] + δ C-C-C [20]	574	624	617	613
γ C=S		616	γ C=S [53] + ν C-S [17] + δ C-C-C [12]	507	534	540	535
δ S=C-S		470	δ C-S-C [37] + δ S=C-S [34] + δ S-C-C [17]	391	406	407	n.o.
δ C-C=S		386	δ C-C=S [53] + δ S-C-C' [15] + δ S=S-S [12]	324	359	341	n.o.
δ S-C-C'		346	δ S-C-C' [54] + δ C-C=S [14]	292	310	306	n.o.
δ C-S-C		284	τ C'-C [37] + δ C-S-C [21] + δ S-C=C [14]	243	267	247	n.o.
δ C-C-C		244	δ C-C-C [45] + C=S [38] + τ C-S [14]	211	248	240	n.o.
τ C β -C		227	τ C β -C [75] + τ C'-C [15]	197	236	240	n.o.
τ C'-C		200	τ C'-C [40] + δ C-S-C [30] + δ S=C-S [11]	176	204	n.o.	n.o.
τ S-C		82	τ S-C [102]	82	119	n.o.	n.o.
τ C-S		63	τ C-S [95]	67	n.o.	n.o.	n.o.
τ C α -C		54	τ C α -C [121] + δ C-C-C [13]	60	n.o.	n.o.	n.o.

^a Frequencies in cm⁻¹: ν , stretching; δ , bending; γ , rocking; ω , wagging; tw, twisting; τ , torsion; s, symmetric; as, asymmetric; n.o. not observed; local C_s symmetry is considered for methyl groups. ^b Scaled using the following relationship:⁶ $f_{\text{scaled}} = (0.796) f_{\text{calc}} + 16.7$. ^c PED's smaller than 10% are not presented in the table.

equal to that found for EDA (1.9 ± 0.2 kJ mol⁻¹ ⁶), within the experimental error.

(iii) On the other hand, as it was found for MDP, it was not possible to detect any changes in the spectra of the liquid EDP with temperature which could be related to the CC-C=S *skew* \rightarrow *syn* isomerization. It should be noted that while in MDP we were able to identify, in the liquid-phase IR spectrum, one band ascribed to the *syn* form (ν CH₂ at ca. 1160 cm⁻¹; see Table 3), in EDP this was not possible, as there are several vibrations which give rise to bands at the frequency where it is expected this band would appear (for example, ν CH₂(S) originating from the most stable conformer).

(iv) The calculated spectrum for the *skew/gauche* conformer is essentially the same as that of the most stable form (*skew/gauche*). In turn, the calculated frequency shifts due to internal rotations about the CC-C=S and CS-CC axes are very similar to those found for MDP and EDA,⁶ respectively (complete results—calculated frequencies and PED's for the less stable forms of EDP—are available from the authors upon request).

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Supplementary Material Available: A figure of the conformers of MDP and EDP and Tables 1 and 2 listing calculated geometries of conformers of ethyl and methyl dithiopropionate (3 pages). Ordering information is given on any current masthead page.

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