Molecular and Electronic Structure of δ-Valerothiolactone

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The crystal structure of the six-member heterocyclic δ-valerothiolactone (1-thiocycloalkan-2-one) compound has been determined by X-ray diffraction at low temperature, revealing that its skeleton adopts a half-chair conformation. The conformation around the thioester group is almost planar with an anti orientation of the C=O double bond with respect the S—C single bond [C(2)—S(1)—C(6)—O(1) = 176.26(8)°]. The skeletal parameters, especially valence angles [∠C5—C6—S = 121.19(6)°, ∠O=C6—C5 = 122.25(8)°, ∠C6—S—C2 = 106.80(4)°], differ from those typically found in acyclic thioester compounds, symptomatic of the presence of strain effects. The conventional ring strain energy was determined to be 7.5 kcal/mol at the MP2/6-311++G(d,p) level of calculation within the hyperhomodesmotic model approximation. Moreover, the valence electronic structure was investigated by HeI photoelectron spectroscopy assisted by quantum chemical calculations at the OVGF/6-311++G(d,p) level of theory. The first three bands at 9.35, 9.50, and 11.53 eV denote ionizations related with the n_S, n_O, and $\pi_{C=O}$ orbitals, respectively, demonstrating the importance of the —SC(O)— group in the outermost electronic properties.

1. Introduction

Cyclic compounds containing one or more sulfur atoms are widely used in synthetic, pharmaceutical, and agrochemical products[1] and also more recently have been discovered as compounds with interesting physical properties.[2,3] Thiolactones are very interesting molecules in biological terms, one of the most significant examples being the five-member cyclic homocysteine thiolactone molecule (DL-2-amino-4-mercaptobutyric acid 1,4-thiolactone).[4–6] Moreover, it is well-known that sulfur-containing compounds play an important role in flavor chemistry,[7] and the sensory characteristic of alkyl-substituted thiolactones has been evaluated.[8] In recent years considerable interest has been devoted to this class of compounds and the synthesis of thiolactones has been reviewed by Paryzek and Skiera.[9] The five- and six-member γ-butyrothiolactone[10] and δ-valerothiolactone[11] species, respectively, have been known for several years and a number of the more stable alkyl-substituted compounds derived from both types had already been studied since almost 100 years ago.[12] In particular, polymerization reactions of thiolactones have attracted much attention, and the polymerization of four-member species have been reported earlier.[13] Overberger and Weise polymerized δ-valerothiolactone and ε-caprothiolactone by a base-catalyzed ring-opening reactions to linear, crystalline polythiolesters.[14] Sur-

prisingly, γ-butyrothiolactone does not react under similar conditions. Therefore, the reactivity of the thiolactones toward polymerization is dependent on the ring size in a manner that is analogous to the behavior of lactones. In effect, it is well-known that lactones, except γ-butyrolactone, are fairly reactive and readily convert to their linear counterparts in the presence of catalysts or initiators.[15] The aliphatic polyesters prepared by ring-opening polymerization of lactones are versatile polymers with good mechanical properties that make them helpful for a wide range of applications.[16]

Our research group has quite recently started studies concerning the structural, spectroscopic, and physicochemical properties of simple thiolactones. The nonsubstituted four- and five-member species (β-propiothiolactone[17] and γ-butyrothiolactone,[18] respectively) have been studied by using a combined experimental and quantum chemical approach. Thus, when these molecules are isolated in a low-temperature inert Ar matrix, the UV—visible (200 ≤ λ ≤ 800 nm) induced photochemistry results in the formation of the corresponding ketene species, methyl- and ethylketene, respectively. The valence electronic structure has been also investigated by He(I) photoelectron spectroscopy, and the first three bands for both molecules were assigned to ionizations involving the n_S, n_O, and $\pi_{C=O}$ orbitals. Moreover, the X-ray molecular structure has been elucidated for β-propiothiolactone,[17] and strain energies of 16.4 and 3.8 kcal/mol have been determined at the G2MP2 level for the four- and five-member species, respectively.

In this study, we present an investigation of the structure, electronic, and vibrational properties of the subsequent member of this chemical family, the cyclic six-member δ-valerothiolactone molecule. A comprehensive structural study has been

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accomplished by measuring the low-temperature X-ray diffraction pattern using a laser-induced in situ crystallization method, together with quantum chemical calculations at the B3LYP and MP2 theories employing the 6-311++G(d,p) and aug-cc-pVTZ basis sets. Vibrational spectra have been recorded for the liquid, whereas the gas-phase photoelectron spectrum (PES) has been obtained and interpreted within the orbital valence Green's functional (OVGF) theory. Finally, the strain energy was determined within the s-homodesmotic model at the MP2/6-311++G(p,d) level of approximation.

2. Experimental Section

2.1. Synthesis. δ-Valerothiolactone was prepared by using benzyltriethylammonium tetrathiomolybdate as a sulfur-transfer reagent, together with 5-bromovaleryl chloride, as was previously reported by Bhar et al.[19] The final purity in the liquid phase was carefully checked by reference to its IR, CG−MS, and ^{1}H and ^{13}C NMR spectra.[19]

2.2. Instrumentation. IR absorption spectra in the liquid state were recorded with a resolution of 1 cm^{−1} in the range of 4000−400 cm^{−1} using a Bruker model EQUINOX 55 equipped with DLaTGS detector with a KBr window.

The PE spectrum was recorded on a double-chamber UPS-II machine, which was designed specifically to detect transient species, as described elsewhere,[20−22] at a resolution of about 30 meV, indicated by the standard $Ar^+(^2P_{3/2})$ photoelectron band. Experimental vertical ionization energies were calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

An appropriate crystal of δ-valerothiolactone of 0.3 mm diameter was obtained on the diffractometer at a temperature of 188(2) K with a miniature zone-melting procedure using focused infrared laser radiation.[23] The diffraction intensities were measured at low temperature on a Nicolet *R*3*m*/V four-circle diffractometer, the intensities being collected with graphite-monochromatized Mo Kα radiation using the ω-scan technique. The structure was solved by Patterson syntheses and refined by full-matrix least-squares on *F* with the SHELXTL-Plus program.[24] Absorption correction details are given elsewhere. All atoms were assigned anisotropic thermal parameters. Further details as well as atomic coordinates and equivalent isotropic displacement coefficients for heavy and hydrogen atoms and anisotropic displacement parameters ($Å^2 \times 10^3$) for δ-valerothiolactone are given in Tables S1−S4 (Supporting Information). Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). [Enquiries for data can be directed to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K. CB2 1EZ; e-mail, deposit@ccdc.cam.ac.uk; fax, +44 (0) 1223 336033. Any request to the CCDC for this material should quote the full literature citation and the reference number 776608.]

2.3. Quantum Chemical Calculations. The calculations were performed using the Gaussian 03[25] program package. Full geometry optimizations were done by applying ab initio (MP2) and DFT (B3LYP) methods using the 6-311++G(d,p) and aug-cc-pVTZ basis sets. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequencies were found. The vertical ionization energies (Ev) were calculated according to Cederbaum's outer valence Green's function (OVGF) method[26,27] with the 6-311++G(d,p) basis set, based on the B3LYP/6-311++G(d,p)-optimized geometry. The Mülliken population analysis was applied to assign the atomic charges for both neutral and radical−cationic forms. The strain energy of the title compound
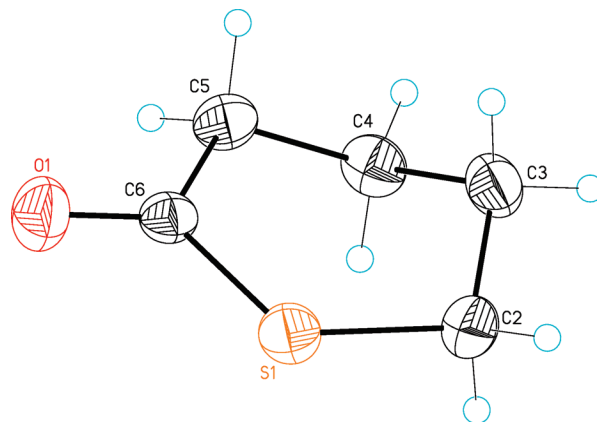

Figure 1. Molecular model (with atom numbering) for the single-crystal structure of δ-valerothiolactone.

has been calculated by applying the s-homodesmotic approach introduced by Zhao and Gimarc.[28] To obtain the energies for all acyclic systems, optimum equilibrium geometries were computed for the singlet ground states of each and every one of the pertinent molecular systems using B3LYP and MP2 methods with the 6-311++G(d,p) basis set. Several conformations were computed in order to ensure that the lowest energy conformation was obtained for every species. In all cases, electronic energies plus the zero-point energy were used to compute the strain energies.

3. Results

3.1. Crystal Structure. Early studies of nonsubstituted monocyclic lactones with different ring sizes showed that they all polymerized except γ-butyrolactone, which is just on the verge of polymerizability. The lack of polymerizability of γ-butyrolactone was attributed to the low strain of the ring, which shows much less geometric distortion in the ester group than δ-valerolactone.[15] Another factor influencing this behavior is the stability of the conformations adopted by the linear counterparts.[29] Thus, the intrinsic correlation between structure and reactivity has led to a better understanding of the chemical reactivity of these cyclic compounds. In this sense, a broader knowledge of the molecular structure of simple thiolactones is of major interest. However, because thiolactones of small ring size are liquids at ambient temperature, the information about their molecular structure is rather scarce. The development of special crystallization techniques has overcome this problem, making possible the extension of the studies to obtain solid-state information. By using the in situ laser-assisted crystallization technique developed by Essen,[23] an appropriate single crystal of δ-valerothiolactone was grown at 188 K. The compound crystallizes in the triclinic system (P 1̄ spatial group), with the following unit cell dimensions: $a = 6.6573(1)$ Å, $b = 6.9608(1)$ Å, $c = 7.2829(1)$ Å, $\alpha = 73.188(1)°$, $\beta = 77.789(1)°$, $\gamma = 62.946(1)°$, and $Z = 2$ (for the full crystallographic data and treatment information, see Table S1 in the Supporting Information).

The X-ray structure of the title compound is shown in Figure 1, where it is clearly observed that the molecule crystallizes in the half-chair conformation, with the thioester group adopting a nearly planar arrangement. Table 1 includes the main geometric parameters derived from the structure refinement, as well as those obtained from quantum chemical calculations.

The molecular structure shows a number of features of interest. First, clearly there are two conflicting geometric

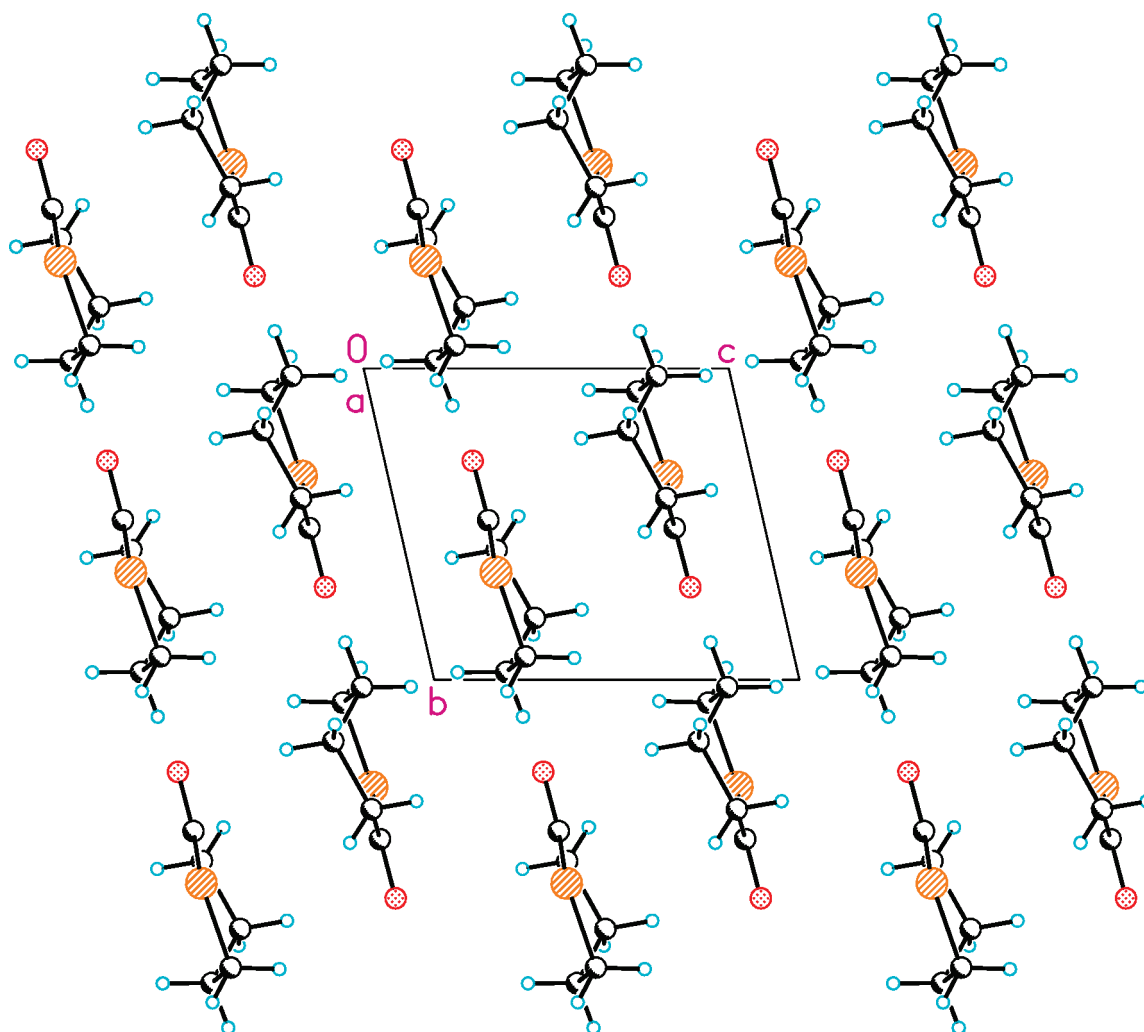**TABLE 1: Experimental and Calculated Geometric Parameters for the δ-Valerothiolactone**

parameter[a]	X-ray[b]	B3LYP 6-311++G(d,p)	B3LYP aug-cc-pVTZ	MP2 6-311++G(d,p)
r(C6−S)	1.7681(8)	1.804	1.798	1.785
r(C2−S)	1.8230(9)	1.851	1.845	1.825
r(O−C6)	1.2048(10)	1.206	1.205	1.216
r(C2−C3)	1.5111(14)	1.523	1.520	1.521
r(C3−C4)	1.5201(13)	1.531	1.527	1.526
r(C4−C5)	1.5215(12)	1.532	1.528	1.527
r(C5−C6)	1.5100(12)	1.521	1.517	1.519
∠C6−S−C2	106.80(4)	106.0	106.3	105.4
∠C3−C2−S	113.33(6)	114.5	114.6	114.3
∠C2−C3−C4	111.18(8)	112.0	112.0	111.0
∠C3−C4−C5	111.83(8)	112.5	112.5	111.5
∠C6−C5−C4	117.26(7)	117.5	117.5	116.8
∠O=C6−C5	122.25(8)	122.2	122.2	121.6
∠O=C6−S	116.47(7)	117.4	117.4	117.7
∠C5−C6−S	121.19(6)	120.3	120.3	120.6

[a] See Figure 1 for atom numbering. [b] Uncertainties are σ values.

requirements in this ring system. The thioester moiety, i.e., the −C(2)SC(O)C(5)− group tends to remain planar having the experimental dihedral angle −7.16(10)°. On the other hand, a six-member ring tends also to adopt a chairlike conformation, in order to allow the ethane units to present staggered conformations.[30] As a result of an energetic balance, both molecular bond lengths and angles are substantially distorted in a

compromise to minimize the total energy. The value of the internal ring angles at the carbonyl carbon [∠C5−C6−S = 121.19(6)°] and the alkyl sulfur [∠C6−S−C2 = 106.80(4)°] is considerably opened, as deduced by comparison with the corresponding value of the bond angles of the acyclic related species $CH_3C(O)SCH_3$ with values of 113.8(9)° and 99.2(9)°, respectively, as determined from a gas electron diffraction study.[31] This distortion leads to a substantial strain energy for this conformation, as will be discussed below.

In general, the result of the two methods used in our study to compute both bond lengths and bond angles compares fairly well with the values obtained from the X-ray analysis. Some deviations are found for the bond lengths around the sulfur atom, and even with the large basis sets used in this study (aug-cc-pVTZ), the B3LYP method overestimates the S−C bond length (by up to 0.02 Å for the S−C2 bond and 0.03 Å for the S−C6 bond). Even though these bond parameters are better described by the MP2 method with the modest 6-311++G(d,p) basis set, this level of approximation fails to reproduce the C=O double bond length and the O=C−C bond angle parameters, which are calculated to be 0.01 Å longer and 0.7° smaller than the experimental values, respectively. It is known, however, that in the comparison of crystal and gas-phase structures, systematic differences due to vibrational effects and intermolecular interactions (packing effects) in the solid phase have to be considered, especially for terminal bond lengths.[31b] Thus, considering these

Figure 2. Stereoscopic illustration of the crystal packing of δ-valerothiolactone at 188 K.
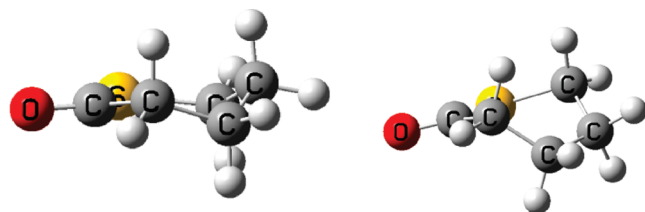
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Half-chair form, $\phi(C3C4\text{-}C5C6)= -54°$ Boat form, $\phi(C3C4\text{-}C5C6)= +64°$

Figure 3. Molecular models computed [MP2/6-311++G(d,p)] for the two main forms of δ-valerothiolactone.

systematic differences and the experimental error limits, experimental and computed MP2/6-311++G(d,p) are very similar.

Moreover, considering that only the gas-phase structure can be reproduced by the optimized molecular geometry, significant packing effects should be absent in solid δ-valerothiolactone as deduced by the comparison between experimental and computed results of Table 1. The overall crystal packing as viewed along the *bc* plane is shown in Figure 2. The crystal packing is governed by weak C−H···O=C interactions that connect molecules into two-dimensional networks. Molecules in the unit cell are arranged forming two parallel chains with the oxygen atoms oriented toward opposite directions, separated by C=O···H−C2 nonbonded distance of 2.65 Å, whereas the distance between molecules within a chain adopts a value of 2.56 Å. Both interchain and intrachain molecular interactions are given by C=O···H−C2 contacts, and in both cases the hydrogen atoms are attached to the carbon atom (C2) bonded to sulfur. This observance is in agreement with the crystal structures of several polythiolactones reported recently.[32] It was found that both tubular and layered assemblies can be formed, depending on the conformation adopted by the molecules.
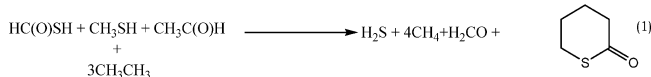
3.2. Conformational Analysis. At this point, the comparison of our results with those reported for the δ-valerolactone molecule becomes interesting. For this species, the presence of two conformers in the gas phase at room temperature, mainly the half-chair and boat forms, was determined by microwave spectroscopy.[33] Both conformers are separated in energy by approximately 0.6 kcal/mol and only the more stable half-chair conformer can be observed in the crystal.[32] Allinger and co-workers[33b] also reported the presence of both conformations in liquid δ-valerolactone by using Raman spectroscopy. In effect, the ring-breathing vibrations appear as prominent signals at 748 and 798 cm^{-1} for the half-chair and boat conformations, respectively.

For the title species, computed quantum chemical calculations suggest that three structures are minima in the potential energy hypersurface. In agreement with our results of the X-ray crystal structure, the most stable computed conformation corresponds to the half-chair form, with two energetically equivalent enantiomers. The third conformation, which is 1.41 kcal/mol (ΔE^0, B3LYP/aug-cc-pVTZ) higher in energy, corresponds to the boat form. The calculated molecular structures are shown in Figure 3. The computed (B3LYP/aug-cc-pVTZ) Gibbs free energy difference between the half-chair and boat forms is ΔG^0 = 1.30 kcal/mol, suggesting that a contribution of roughly 10% for the boat form could be expected at room temperature. Even though the theoretical energy difference for the title species is higher than that of the oxygen analog, we carefully analyzed the vibrational data, including the infrared and Raman spectra (see Figure S1 in the Supporting Information) assisted by frequency quantum chemical calculations for both forms. The ring-breathing vibrations are computed (B3LYP/aug-cc-pVTZ) at 853 and 840 cm^{-1} for the half-chair and boat forms,
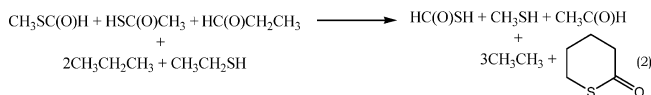
respectively. Only a single medium intensity absorption at 858 cm^{-1} is observed in the infrared spectrum of liquid δ-valerothiolactone in this region, suggesting the presence of one conformation. The carbonyl stretching region shows the presence of a number of broad bands in both spectra. It may be originated by a conformational equilibrium or by association processes. However, clear evidence for the presence of a boat conformation in liquid δ-valerothiolactone is absent. Further studies should be necessary to elucidate the conformational behavior, mainly by using temperature variable experiments.

3.3. Strain Energy. The evaluation of ring strain energies in small cyclic compounds remains a topic of major interest. The precise estimation of the effect that ring strain exerts upon the chemical reactivity and the ground-state energy can be interesting information for a synthetic chemist.[34,35] A detailed understanding of factors affecting the ring-opening polymerization of cyclic esters is the starting point to develop polymer properties relevant to planned applications.[34] The increase of the molecular strain energy as function of the diminution of the ring size in cyclic molecules is well-known.[36] The strain energy of δ-valerothiolactone has been computed within the s-homodesmotic approach[28,37] and compared with the related β-propiothiolactone[17] and γ-butyrothiolactone.[18] The formal reactions needed for computation of the ring strain for the title molecule within this model are given in eqs 1−3.
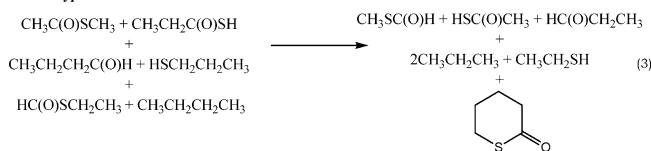
Isodesmic Reaction:

$$HC(O)SH + CH_3SH + CH_3C(O)H \ + \ 3CH_3CH_3 \longrightarrow H_2S + 4CH_4 + H_2CO + \;\; \text{(1)}$$

Homodesmotic Reaction:

$$CH_3SC(O)H + HSC(O)CH_3 + HC(O)CH_2CH_3 \ + \ 2CH_3CH_2CH_3 + CH_3CH_2SH \longrightarrow HC(O)SH + CH_3SH + CH_3C(O)H \ + \ 3CH_3CH_3 + \;\; \text{(2)}$$

Hyperhomodesmotic Reaction:

$$CH_3C(O)SCH_3 + CH_3CH_2C(O)SH \ + \ CH_3CH_2CH_2C(O)H + HSCH_2CH_2CH_3 \ + \ HC(O)SCH_2CH_3 + CH_3CH_2CH_2CH_3 \longrightarrow CH_3SC(O)H + HSC(O)CH_3 + HC(O)CH_2CH_3 \ + \ 2CH_3CH_2CH_3 + CH_3CH_2SH \ + \;\; \text{(3)}$$

The conventional strain energies determined with the B3LYP and MP2 methods including zero-point corrections are given in the Supporting Information (Table S5). As has been recently reported by Ringer and Magers[37] for cyclobutane, homodesmic and hyperhomodesmic models result in similar strain energy values, whereas the isodesmic reaction scheme yields strain values that are definitively too low. These authors also pointed out that the B3LYP method underestimates the strain energy. All of these comments apply for our calculations on the strain energy of δ-valerothiolactone.

The strain energy value calculated at the MP2/6-311++G(d,p) level of approximation is 7.54 kcal/mol, a value much higher than that found for cyclohexane[38] (0.6 kcal/mol)—the "reference" molecule for a six-member cyclic species—and also for cyclohexanone[34] (3.7 kcal/mol). However, the strain energy is lower than that computed for the oxygen analogue δ-valerolactone,[34] which amounts 10.2 kcal/mol. This behavior agrees with the fact that the presence of a carbonyl group has little impact upon the strain energy, but the replacement of a methylene group by an oxygen atom increases the strain of the ring. Thus, the tendency for the strain energy of six-member species related to

TABLE 2: Comparison between the Strain Energy (kcal/mol) of the Thiolactone with Their Respective Lactone Species

	β-propio (ring size = 4)	γ-butyro (ring size = 5)	δ-valero (ring size = 6)
lactone[a]	22.7	7.8	10.2
thiolactone	16.4[b] [17]	3.8[b] [18]	7.5[c]

[a] Calculated values from ref 34 at the CBS-Q level of approximation. [b] G2MP2 values. [c] Calculated with MP2/6-311++G** (this work).

title compound is δ-valerolactone > δ-valerothiolactone > cyclohexanone > cyclohexane.

The ring strain energy value of the cyclic thioester molecule studied in the present work is compared with their respective cyclic oxoester (lactones) in Table 2, where a good correlation in the trend for both families is observed. The lowest strain energy for both lactone and thiolactone families corresponds to the five-member ring species, the corresponding value for the six-member ring being notably higher. The increase of the number of atoms in the ring allows the carbonyl group and the sulfur atom to adopt bond angle values closer to the geometry expected for the acyclic nonstrained species. However, the conformation requirement imposed by the ring also affects the neighboring methylene groups. These aspects have been clearly discussed in the described molecular structure of the title species.

Experimental and calculated [B3LYP/6-311++G(d,p)] bond angles for lactone and thiolactone species are given in Table 3. With exception of the bond angles around the heteroatom ∠C−X−C(O), similar values are found (±3.5°) when the parameters of both families are compared. The values are higher than 109.5° for this six-member ring, amounting to 117.5° and 115.7° for the ∠C(O)−C−C of δ-valerothiolactone and δ-valerolactone, respectively.

In lactones, the effect of the distortion in the molecular structure was noted in the vibrational spectra reported by Saiyasombat and co-workers.[35] The normal modes related with the lactone group are sensitive toward the strain energy, and an increment in the frequency values of the $\nu(CH_2-O)$ and $\nu(O-C=O)$ stretching modes is noted when the ring size increases. To elucidate whether a similar effect is valid for

thiolactones, the infrared and Raman spectra of δ-valerothiolactone have been measured in liquid phase (Figure S1, Supporting Information), and the results obtained from the theoretical calculations were used to assign these vibrational spectra. The most intense band in the IR spectrum at 1664 cm^{-1} corresponds to the $\nu(C=O)$ and the signal at 601 cm^{-1} (591 cm^{-1} in Raman) can be assigned with confidence to the $\nu(CH_2-S)$ stretching mode of δ-valerothiolactone. The $\nu(S-C=O)$ is absent in the infrared spectrum and observed as a medium intensity signal in the Raman spectrum at 651 cm^{-1}. This last observation is in agreement with the quantum chemical calculations, which compute a very low absorption intensity at 655 cm^{-1} (B3LYP/aug-cc-pVTZ) for this vibrational mode. Vibrational data for the β-propio-[17,39] and γ-butyrothiolactones[18] have already been reported. Relevant vibrational data for these thiolactone species are collected in Table 4. Contrary to the behavior observed in lactones,[35] the frequency values for the $\nu(CH_2-S)$ and $\nu(S-C=O)$ normal modes of vibration slightly decrease when the size of the thiolactone ring increases from β-propio- to δ-valerothiolactone. This difference could be attributed to the fact that ring strain energies (and the geometry distortions) are much higher for the oxygen analog, and thus, the influence exerted by the ring strain is a dominant factor. For thiolactones, other factors also depending on the size of the carbonated chain [for instance, the inductive effect exerted by the $-(CH_2)_n-$ group] seems to influence the force constants of the $-SC(O)-$ moiety.

3.4. He I Photoelectron Spectra. The PE spectrum of δ-valerothiolactone is presented in Figure 4. The experimentally observed ionization energies (IP in eV), calculated vertical ionization energies at OVGF/6-311++G(d,p) (Ev in eV), molecular orbitals, and molecular characters are summarized in Table 5.

Two bands appear overlapped at 9.35 and 9.50 eV; their narrow and sharp contours are characteristic of ionizations from essentially nonbonding orbitals, which suggest that these bands are linked primarily with the ionization process from both sulfur and oxygen lone-pair electrons (n_S, n_O) of the $-SC(O)-$ group, respectively. This assignment is in agreement with the results of ab initio calculations, with respect to the ordering of the orbitals, as shown in Table 5 and Figure 5. The same orbital

TABLE 3: Comparison of the Valence Bond Angles between Lactones (X = O) and Thiolactones (X = S)

	C−X−(C=O)		X(C=O)Cα		(C=O)Cα−Cβ		Cα−Cβ−Cγ		Cβ−Cγ−Cδ		C−C−X	
	calc[a]	exp[b]	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp
β-propiothiolactone	76.4	77.27(5)	94.9	94.55(7)	95.7	95.68(9)					92.9	92.42(7)
β-propiolactone	91.9		94.2		83.9						90.1	
γ-butyrothiolactone	93.1		110.0		108.3		107.3				106.0	
γ-butyrolactone	111.0		109.1		103.7		101.9				105.5	
δ-valerothiolactone	106.0	106.80	120.3	121.19(6)	117.5	>117.26(7)	112.5	111.83(8)	112.0	111.18(8)	114.5	113.33(6)
δ-valerolactone	122.6		118.7		115.7		109.2		109.2		113.7	

[a] Values computed at the B3LYP/6-311++G** level of approximation. [b] Experimental X-ray molecular structure for β-propiothiolactone[17] and δ-valerothiolactone (this work).

TABLE 4: Selected Vibrational Data (in cm^{-1}) for β-Propio-,[17,39] γ-Butyro-,[18] and δ-Valerothiolactones

	β-propiothiolactone[17,39] (ring size = 4)			γ-butyrothiolactone (ring size = 5)[18]			δ-valerothiolactone (ring size = 6)[a]		
	IR[b]	Raman[c]	calc[d]	IR[c]	Raman[c]	calc[d]	IR[d]	Raman[c]	calc[d]
$\nu(C=O)$	1785.0	1759	1855	1704	1702	1793	1663	1663	1754
$\nu(S-CH_2)$	743.6	739	739	685	687	681		651	654
$\nu(S-C=O)$	652.7	662	652	628	632	617	601	591	580

[a] This work. [b] Ar-matrix. [c] Liquid phase. [d] B3LYP/6-311++G** level of approximation.

Structure of δ-Valerothiolactone

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Figure 4. Photoelectron spectrum of δ-valerothiolactone.

Figure 6. Correlation diagram of the ionization potentials of β-propiothiolactone, γ-butyrothiolactone, and δ-valerothiolactone.
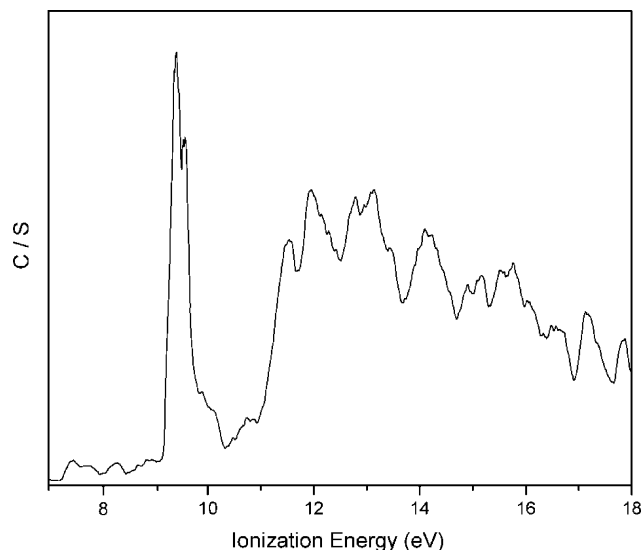
TABLE 5: Experimental Vertical Ionization Energies (IP in eV) and Computed Ionization Energies (Ev in eV) at the OVGF/6-311++G(d,p) Level of Approximation and Molecular Orbital Characters for δ-Valerothiolactone

IP (eV)	Ev (eV)[a]	MO	character
9.35	9.01	(31)	n_S
9.50	9.57	(30)	n_O
11.53	11.29	(29)	π_{CO}
11.96	12.23	(28, 27)	σ_{C4-Hs}
	12.31		
12.79	12.94	(26,25)	σ_{C3-Hs}
13.13	13.19		
14.14	14.31	(24,23)	σ_{C5-Hs}
14.89	14.73		
15.16	15.27	(22,21)	σ_{C2-Hs}
	15.46		

[a] Molecular geometry calculated at the B3LYP/6-311++G(d,p) level of approximation.

trend has been reported for the four- and five-member thiolactone species[17,18,40] and also for related acyclic molecules, for example, thioacetic acid,[41] S-alkyl thioacetates,[42] and XC(O)SCl (X = F[43] and Cl[44]) species. For the first band (n_S), the value observed for the vertical ionization (9.35 eV) is in reasonable agreement with the theoretically predicted value of 9.01 eV [ROVGF/6-311++G(d,p)]. Further calculations [UB3LYP/6-311++G(d,p)] have been performed in order to analyze the nature of the low-lying radical–cation formed in the first ionization process. The adiabatic ionization energy is 8.92 eV
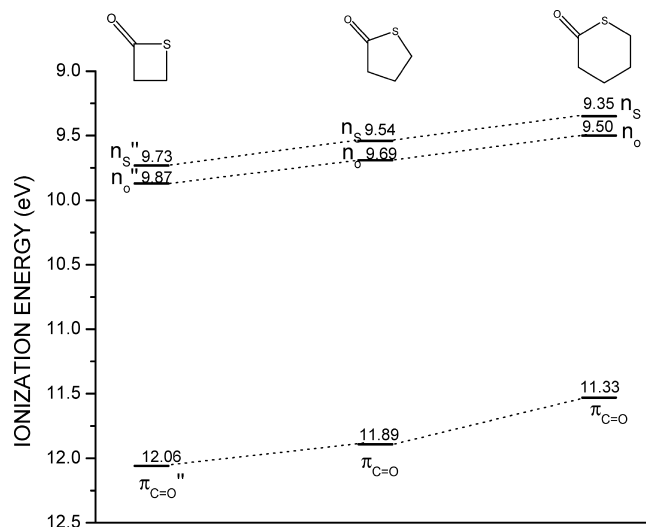
and the atomic charges are mostly delocalized all over the molecule, with an appreciable fraction localized at the −C(O)S− group, as is listed in Table S6 in the Supporting Information. The cyclic planar (C_1) molecular geometry is conserved after the ionization. The C6−S bond length is 0.29 Å longer, while the C=O double bond becomes 0.04 Å shorter in the cationic state.

There is a relatively large gap between the second and the third band, the last having an ionization energy of 11.53 eV. The calculations predict that this band is associated with an ionization of electron mainly localized on the π_{CO} orbital, as depicted in Figure 5. A group of overlapping bands appears between 12 and 16 eV, which can be assigned to ionizations from several σ-CH$_2$ orbitals, as predicted by the calculations.

3.5. Correlation Diagrams. The first three IP's of the δ-valerothiolactone molecule are correlated with the corresponding values determined for β-propiothiolactone[17] and γ-butyrothiolactone,[18,40] in the diagram shown in Figure 6. The prominent feature is the diminution of the ionization energy of the three outermost orbitals when the ring size increases. Resonance or mesomeric effects in the −C(O)S− group promote a local planar geometry and are dominated by the donor−acceptor interactions from the out-of-plane lone pair n_S orbitals to the vacant $\pi^*_{C=O}$.[45] The nonplanarity of the five- and six-member thiolactones ring would prevent this interaction. Thus, in order to consider the most important intramolecular interactions present in these species, the donor−acceptor interaction energies for β-propio-, γ-butyro-, and δ-valerothiolactone species have
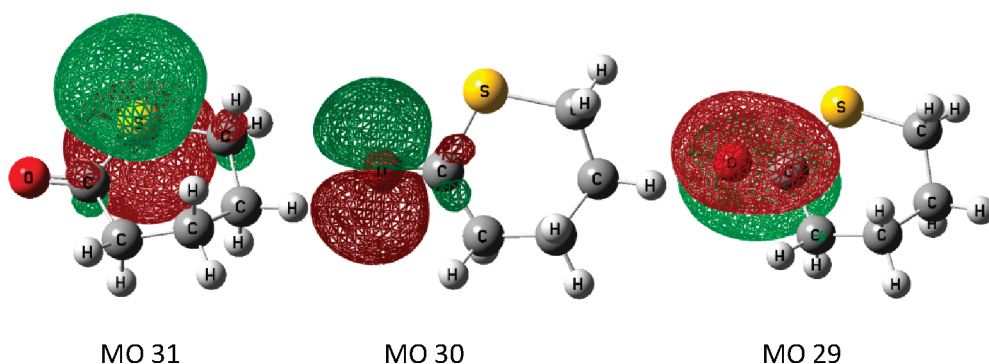

Figure 5. Drawings of three HOMOs (highest occupied molecular orbitals) of δ-valerothiolactone.

been evaluated by using the NBO population analysis. Two energetically relevant interactions around the −SC(O)− group are specially analyzed:[45,46] (a) "mesomeric interaction" or the charge transfer from the lone-electron pair with π symmetry (n''_S) to the $\pi^*_{C=O}$ formally vacant orbital, which serve to commensurate the electronic delocalization within the −SC(O)− fragment, and (b) "anomeric interaction" or the charge transfer from the in-plane p-type lone electron pair of the sulfur atom (n'_S) to the σ^*_{C-C} antibonding orbital.[45] At the B3LYP/6-311++G(d,p) level, the contributions of these interactions amount to 36.2, 36.4, and 34.0 kcal/mol for β-propio-, γ-butyro- and δ-valerothiolactones, respectively. These results suggest that the electronic interaction is not much affected by the nonplanarity of the thiolactone ring. The local planar symmetry around the carbonylic sp^2 carbon atom leads to an efficient electronic conjugation. These results are in agreement with the early suggestion of Chin et al. These authors pointed out that the electronic properties of thiolactones are determined primarily by inductive electronic donations from the alkyl chain.[47] A similar behavior was reported by Isaksson and Lijefors for five-, six-, and seven-member cyclic oxamides.[48]

4. Conclusion

The X-ray molecular structure of δ-valerothiolactone reveals that its skeleton adopts a half-chair conformation with anti orientation of the C=O double bond with respect to the S−C single bond. The skeletal parameters, especially valence angles, differ from those typically found in acyclic thioester compounds, suggesting the presence of strain effects. The conventional ring strain energy was determined to be 7.5 kcal/mol [MP2/6-311++G(d,p)] within the hyperhomodesmotic model. Thus, following the tendency already known for lactone molecules,[29] δ-valerothiolactone is more strained than the five-member species. This nonintuitive behavior can be, however, rationalized on the basis of the molecular structure distortions associated with the ring formation.

Furthermore, the valence electronic structure was investigated by HeI photoelectron spectroscopy. The systematic comparison between thiolactone species can be correlated with the role played by the cycloalkane groups, mainly through inductive donating effects.

Supporting Information Available: Crystallographic data and listing of atomic coordinates and equivalent isotropic displacement coefficients and anisotropic displacement parameters are given in Tables S1−4. Tables S5 and S6 list the computed strain energy and the atomic charge for the neutral and the low-lying cationic state of δ-valerothiolactone, respec-

tively. The FTIR and FT-Raman spectra are shown in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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