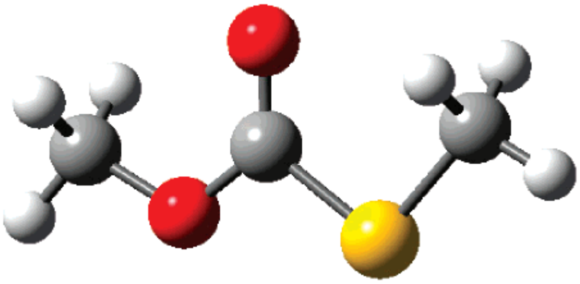
Toward an Intimate Understanding of the Structural Properties and Conformational Preference of Oxoesters and Thioesters: Gas and Crystal Structure and Conformational Analysis of Dimethyl Monothiocarbonate, $CH_3OC(O)SCH_3$

Mauricio F. Erben,[†] Roland Boese,[‡] Carlos O. Della Védova,*[,†,§] Heinz Oberhammer,[||] and Helge Willner[⊥]

CEQUINOR (CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 115 C.C. 962, (B1900AJL) La Plata, Buenos Aires, Argentina, Institut für Anorganische Chemie, Universität GH Essen, Universitätsstr. 5-7, D-45117 Essen, Germany, Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET) Gonnet, Buenos Aires, Argentina, Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-72076 Tübingen, Germany, and Fachbereich C-Anorganische Chemie, Bergische Universität Wuppertal, Gaussstrasse 20, 47097 Wuppertal, Germany

carlosdv@quimica.unlp.edu.ar

Received September 27, 2005



The molecular structure and conformational properties of dimethyl monothiocarbonate, $CH_3OC(O)SCH_3$, have been studied in the gas phase by gas electron diffraction (GED) and vibrational spectroscopy and in the solid state by X-ray crystallography. The experimental investigations were supplemented by quantum chemical calculations at the B3LYP/6-311++G(3df,2p) and MP2/6-311++G(2df,p) levels of approximation. The gaseous molecule exhibits only one conformation having C_s symmetry with synperiplanar orientation of both the C−S and the C−O single bonds relative to the C═O double bond. The following skeletal geometric parameters were derived from the GED analysis (r_{hl} values with 3σ uncertainties): C═O = 1.203(4) Å, C(sp^2)−O = 1.335(5) Å, C(sp^3)−O = 1.437(5) Å, C(sp^2)−S = 1.763(5) Å, and C(sp^3)−S = 1.803(5) Å; O═C−O = 125.9(8)°, O═C−S = 125.7(7)°, O−C−S = 108.4(9)°, and C−O−C = 113.4(15)°. The structure of a single crystal, grown by a miniature zone-melting procedure, was determined by X-ray diffraction analysis at a low temperature. The crystalline solid [monoclinic, $P2_1/n$, $a = 12.6409(9)$ Å, $b = 4.1678(3)$ Å, and $c = 19.940(1)$ Å, $\beta = 98.164(1)°$] exists exclusively as molecules in the synperiplanar conformation and with geometrical parameters that agree with those of the molecule in the gas phase. The results are discussed in terms of anomeric and mesomeric effects and in terms of a natural bond orbital analysis.

Introduction

Structural and conformational properties of oxoesters and thioesters of the type $R_1C(O)XR_2$ can be discussed in terms of two resonance structures shown in Chart 1. From vibrational analyses, it has been concluded that the resonance structure II plays an important role in oxoesters (X = O) but makes only a negligible contribution in thioesters (X = S).[1] The different contributions of this resonance structure strongly correlate with

---

[†] CEQUINOR, Universidad Nacional de La Plata.
[‡] Institut für Anorganische Chemie, Universität GH Essen.
[§] Laboratorio de Servicios a la Industria y al Sistema Científico.
[||] Institut für Physikalische und Theoretische Chemie, Universität Tübingen.
[⊥] Fachbereich C-Anorganische Chemie, Bergische Universität Wuppertal.

(1) El-Assar, A. M. M.; Nash, C. P.; Ingraham, L. L. *Biochemistry* **1982**, *21*, 1972−1976.

10.1021/jo052026k CCC: $33.50

CHART 1. Resonance Structures for $R_1C(O)XR_2$ (X = O and S for Oxoesters and Thioesters, Respectively)

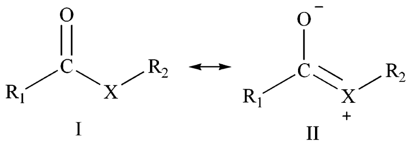
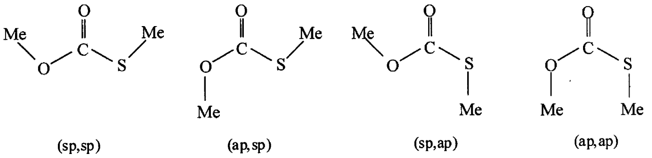


CHART 2. Schematic Representation of the Possible Conformers of $CH_3OC(O)SCH_3$



the much lower reactivity of oxoesters compared with those of the thioesters in nucleophilic acyl transfer reactions.[2] This plays an important role in enzymatic reactions of coenzyme A and cysteine proteases. A quantitative rationalization of the different reactivities of methyl acetate and methyl thioacetate with nucleophiles on the basis of orbital interactions has been given by Yang and Drueckhammer.[3] Orbital interactions of the n_σ and n_π lone pairs of the bridging X atom with antibonding σ^* and π^* orbitals of the C=O bond [$n_\sigma(X) \rightarrow \sigma^*$ (C=O, anomeric effect) and $n_\pi(X) \rightarrow \pi^*$ (C=O, mesomeric effect or conjugation)] can be represented by resonance structure II in Chart 1. According to a natural bond orbital (NBO) analysis, such interactions are considerably stronger in oxoesters and increase the activation energy of acyl transfer reactions compared with that for thioesters. This would give acetyl coenzyme A the driving force for acetylation reactions to form oxygen esters or amides with larger resonance stabilizations.[4]

The different contributions of these orbital interactions in oxo- and thioesters are also reflected in their ground-state structures. Stronger conjugation and the anomeric effect in methyl acetate, $CH_3C(O)OCH_3$, result in an O$-$C(sp^2) bond [1.360(6) Å] which is shorter by 0.082(9) Å than the O$-$C(sp^3) bond [1.442(6) Å].[5] On the other hand, the two S$-$C bond lengths in methyl thioacetate, $CH_3C(O)SCH_3$, differ by only 0.024(10) Å [S$-$C(sp^2) = 1.781(6) and S$-$C(sp^3) = 1.805(6) Å],[6] demonstrating a minor contribution of resonance structure II. In view of these different structural properties of methyl acetate and thioacetate, we were interested in the molecular structure of dimethyl monothiocarbonate (O,S-dimethyl thiocarbonate or thiocarbonic acid O,S-dimethyl ester), $CH_3OC(O)SCH_3$, which contains both the oxoester group [$-C(O)OCH_3$] and the thioester group [$-C(O)SCH_3$]. In principle, depending on the orientation of the O$-$Me and S$-$Me groups relative to the C=O double bond, which can be synperiplanar (sp) or antiperiplanar (ap), four conformations are feasible for this compound (see Chart 2).

NMR shifts, dipole moments, and vibrational spectra of several monothiocarbonates, $CH_3OC(O)SR$, including the dimethyl derivative (R = CH_3), have been interpreted in terms of a mixture of three conformers. Although these data did not give any definitive guidance on whether ap,sp or sp,ap corresponds to the most stable form, it was concluded that the sp,sp conformer *is clearly the most unstable form* in the liquid phase.[7] This early result is open to question, however, since the conformational preference in both oxoester and thioester molecules has been well-established in the gas phase: synperiplanar orientation around the C$-$O or C$-$S bonds is preferred.[8−10] It is well-known that the conformational preference depends on the molecular environment. Hence, the conformational properties of a given molecule could vary from one phase to another. In this context, the conformational properties of the related $CH_3OC(O)OCH_3$ molecule have been recently reported in the gas and condensed phases.[11] Both sp,sp and sp,ap conformers were identified, with the former being the most stable form. While the enthalpy difference between them was determined to be 3.25(21) kcal/mol in the gas phase, the value decreases to 1.9(1) kcal/mol in the liquid phase (1 kcal/mol ≡ 4.184 kJ/mol).

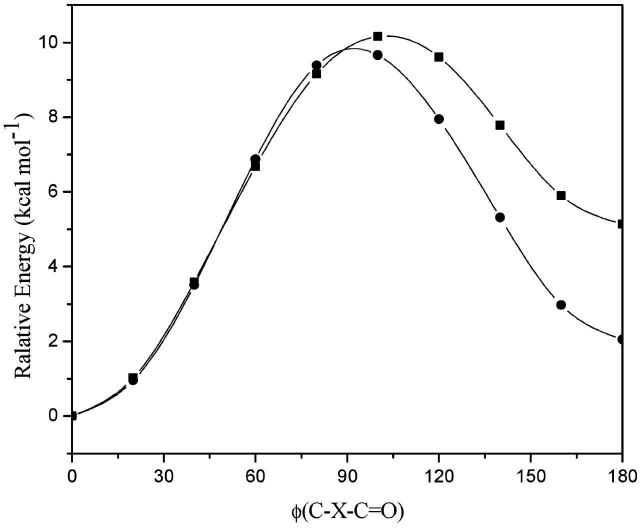


FIGURE 1. Potential energy curves for $CH_3OC(O)SCH_3$ as a function of the oxoester (■) and thioester (●) dihedral angles [ϕ(CX$-$C=O) with X = O and S, respectively] calculated with the B3LYP/6-31+G* approximation.

We have, therefore, studied the structural and conformational properties of $CH_3OC(O)SCH_3$ in the gas phase using FTIR spectroscopy and gas electron diffraction (GED) techniques. The Raman spectrum of the liquid was measured and X-ray analysis was carried out on a single crystal grown in situ by the low-temperature crystallization procedure. Moreover, quantum chemical calculations have been performed to assist the interpretation of the experimental data, and NBO population analyses were applied to rationalize the effect of the electronic interactions on the structural and conformational properties of $CH_3OC(O)SCH_3$.

Quantum Chemical Calculations. In a first step, the potential functions for internal rotation around the C$-$O and C$-$S bonds were calculated (B3LYP/6-31+G*) by geometry optimizations at fixed torsional angles (see Figure 1). Both

---

(2) Castro, E. A. *Chem. Rev.* **1999**, *99*, 3505−3524.

(3) Yang, W.; Drueckhammer, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 11004−11009.

(4) Idoux, J. P.; Hwang, P. T. R.; Hancock, C. K. *J. Org. Chem.* **1973**, *38*, 4239−4243.

(5) Pyckhout, W.; Van Alsenoy, C.; Geise, H. J. *J. Mol. Struct.* **1986**, *144*, 265−279.

(6) Della Védova, C. O.; Romano, R. M.; Oberhammer, H. *J. Org. Chem.* **2004**, *69*, 5395−5398.

(7) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1993−1995.

(8) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A* **2002**, *106*, 7235−7244.

(9) Nagy, P. I.; Tejada, F. R.; Sarver, J. G.; Messer, W. S., Jr. *J. Phys. Chem. A* **2004**, *108*, 10173−10185.

TABLE 1. Relative Energies and Free Energies (kcal/mol) and ν(C=O) Vibrational Frequencies (cm^{-1}) with Intensities (km/mol) for the Four Possible Conformers of $CH_3OC(O)SCH_3$

	sp,sp	ap,sp	sp,ap	ap,ap
B3LYP/6-31+G**				
ΔE	0.00[a]	5.14	2.06	14.58
$\Delta G°$	0.00[b]	5.35	2.26	14.40
ν(C=O) [Intensity]	1769 [291]	1795 [403]	1769 [377]	1793 [464]
B3LYP/6-311++G(3df,2p)				
ΔE	0.00[c]	4.65	2.09	not a stable conformer
$\Delta G°$	0.00[d]	4.77	2.20	
ν(C=O) [Intensity]	1764 [270]	1788 [386]	1761 [358]	
MP2/6-31+G**				
ΔE	0.00[e]	5.68	2.09	not a stable conformer
$\Delta G°$	0.00[f]	5.81	2.38	
ν(C=O) [Intensity]	1757 [248]	1775 [325]	1755 [320]	
MP2/6-311++G(2df,p)				
ΔE	0.00[g]	not calculated	2.23	not calculated
$\Delta G°$	0.00[h]	not calculated	2.33	not calculated
ν(C=O) [Intensity]	1762 [237]		1757 [317]	

[a] $E = -666.598037$ hartree. [b] $G° = -666.539658$ hartree. [c] $E = -666.7158243$ hartree. [d] $G° = -666.657471$ hartree. [e] $E = -665.271415$ hartree. [f] $G° = -665.210728$ hartree. [g] $E = -665.588626$ hartree. [h] $G° = -665.528273$ hartree.

curves possess minima for sp {ϕ[CO—C(O)] = ϕ[CS—C(O)] = 0°} and ap {ϕ[CO—C(O)] = ϕ[CS—C(O)] = 180°} orientations. The ap orientation of the O—CH_3 bond corresponds to a considerably higher energy than the ap orientation of the S—CH_3 bond. Full geometry optimizations and frequency calculations for the four feasible conformers have been performed using the B3LYP method and the MP2 approximation with 6-31+G(d,p) basis sets. Additional MP2/6-311++G(2df,p) and B3LYP/6-311++G(3df,2p) calculations have been performed for the two low-energy forms. Relative energies, ΔE, free energies, $\Delta G°$, and frequencies of the ν(C=O) vibration with IR intensities are summarized in Table 1.

The B3LYP method predicts that all four conformers correspond to stable structures with planar molecular skeletons, except for the ap,ap form. In this conformer, the two methyl groups lie, respectively, above and below the molecular plane. This form does not correspond to a stable structure according to the MP2 approximation, and a structure optimization converges toward the sp,ap conformer. All computational methods predict the sp,sp conformer to be lowest in energy, and the predicted geometric parameters are given, together with experimental values, in Table 2. The second most stable conformer, sp,ap, possesses an antiperiplanar orientation of the S—Me group, and its free energy is calculated to be about 2.3 kcal/mol higher than that of the sp,sp form. The other two conformers, ap,sp and ap,ap, are higher in energy by more than 5 and 14 kcal/mol, respectively, and are not expected to be detectable in our experiments. These calculated relative stabilities are in contrast with the conclusions drawn from NMR and vibrational data (see Introduction), according to which the ap,sp and sp,ap conformers are more stable than the sp,sp form.[7]

The calculated maxima for near-perpendicular orientations are similar in both cases, being characterized as torsional transition states (TSs; $N_{imag} = 1$). For the sp,sp → sp,ap transition, the B3LYP/6-311++G(3df,2p) level of approximation predicts a barrier height of 10.0 kcal/mol (corrected for zero-point energies), a value in agreement with reported theoretical estimates for thioesters.[12] The corresponding TS connecting the sp,sp and the ap,sp conformers has a ϕ[CO—C(O)] dihedral angle that is slightly larger than 90° (Figure 1). The fully optimized rotational TS structure is located at 9.3 kcal/mol, with a ϕ[CO—C(O)] dihedral angle of 102.0° [B3LYP/6-311++G(3df,2p)].

TABLE 2. Experimental and Calculated Geometric Parameters for the sp,sp Conformer of $CH_3OC(O)SCH_3$ (Angstroms and Degrees)

	GED(r_{h1})[a]		X-ray[b]	MP2[c]	B3LYP[d]
C=O	1.203(4)	*p*1	1.195(2)	1.208	1.202
$(C—O)_{mean}$	1.386(4)	*p*2	1.394(2)	1.390	1.390
ΔCO = (C2—O2) − (C1—O2)	0.102(6)	*p*3	0.113(2)	0.095	0.098
C1—O2	1.335(5)		1.337(1)	1.342	1.341
C2—O2	1.437(5)		1.450(2)	1.437	1.439
$(S—C)_{mean}$	1.783(2)	*p*4	1.775()	1.783	1.795
ΔSC = (S—C3) − (S—C1)	0.040(8)	*p*5	0.032(2)	0.041	0.037
S—C1	1.763(5)		1.759(1)	1.763	1.776
S—C3	1.803(5)		1.791(2)	1.804	1.813
$(C—H)_{mean}$	1.100(9)	*p*6	0.970	1.087	1.087
O1 = C1—O2	125.9(8)	*p*7	125.4(1)	125.3	125.3
O1 = C1—S	125.7(7)	*p*8	126.3(1)	125.9	125.9
O2—C1—S	108.4(9)		108.3(1)	108.8	108.8
C1—O2—C2	113.4(15)	*p*9	115.7(1)	114.0	115.8
C1—S—C3	99.8(8)	*p*10	99.73(9)	99.2	98.9
$(H—C—H)_{mean}$	110.3[f]		109.4	110.3	110.2
C2—O2—C1 = O1	0.0[f]		0.3(2)	0.0	0.0
C3—S—C1 = O1	0.0[f]		1.6(2)	0.0	0.0
H—C2—O2—C1	180.0[f]		177.3(1)	180.0	180.0
H—C3—S—C1	180.0[f]		177.8(1)	180.0	180.0
tilt (CH_3O)[e]	3.4[f]		0.9	3.4	3.4
tilt (CH_3S)[e]	2.8[f]		0.2	2.8	3.1

[a] Error limits are 3σ values. For atom numbering see Figure 4. [b] Mean value for the two molecules in the unit cell. Uncertainties are σ values. [c] 6-311++G(2df,p) basis sets. [d] 6-311++G(3df,2p) basis sets. [e] Tilt angle between the C_3 axis of CH_3 group and the C—O or C—S bond direction, away from the C=O bond. [f] Not refined.

Vibrational Spectra. In an effort to provide an unambiguous basis in support of a methyl thiocarbonate-like structure for paederoside, a natural sulfur-containing iridoid glucoside of *Paederia scandens*, Suzuki et al.[13] have studied the IR spectrum of liquid $CH_3OC(O)SCH_3$. These analyses concentrated on the

---

(10) Jones, G. I. L.; Lister, D. G.; Owen, N. L.; Gerry, M. C. L.; Palmieri, P. *J. Mol. Spectrosc.* **1976**, *60*, 348−360.

(11) Bohets, H.; van der Veken, V. J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1817−1826.

(12) Deerfield, D. W., II; Pedersen, L. G. *THEOCHEM* **1995**, *358*, 99−106.

(13) Suzuki, S.; Hisamichi, K.; Endo, K. *Heterocycles* **1993**, *35*, 895−900.

carbonyl-stretching region, where a band appearing at 1717 cm^{-1} was assigned to the ν(C═O) stretching mode. This is in agreement with the value of 1719 cm^{-1} reported for the compound dissolved in CCl_4.[14,15] To the best of our knowledge, no reports of the IR spectrum of $CH_3OC(O)SCH_3$ vapor exist in the literature. Quantum chemical calculations predict a contribution of about 1.9% [$\Delta G° = 2.33$ kcal/mol, MP2/6-311++G(2df,p)] for the second stable sp,ap form at ambient temperature. Hence, both sp,sp and sp,ap conformers of $CH_3OC(O)SCH_3$ could, in principle, be detected in the gas phase by vibrational spectroscopy. As the conformational behavior of $CH_3OC(O)SCH_3$ can be determined only when the vibrational data have been correctly assigned, we have expanded the previously known data by investigating the vapor IR and liquid-phase Raman spectra. Furthermore, frequency calculations at the MP2/6-311++G** and B3LYP/6-311++G(3df,2p) levels have been performed to support the experimental results.

The IR (gas) and Raman (liquid) spectra are given as Supporting Information (Figure SM1). $CH_3OC(O)SCH_3$ has 30 normal modes of vibration and for the C_s sp,sp conformer, their symmetries are 21 A′ + 9 A″, with all fundamentals being IR and Raman active. A tentative assignment of the observed bands was performed by comparison with the calculated spectrum. The approximate description of the modes is based on the calculated displacement vectors for the fundamentals, as well as on comparison with the spectra of related molecules, especially $CH_3OC(O)OCH_3$[11] and $CH_3SC(O)H$.[10] Experimental and calculated frequencies with their tentative assignments are given as Supporting Information (Table SM1).

The vibrational spectra of gaseous $CH_3OC(O)SCH_3$ can be interpreted on the basis of the presence of only the sp,sp conformer. The calculations predict very small differences between the fundamental modes of the sp,sp and sp,ap conformers, in particular for the ν(C═O) stretching mode, which has been shown to be the most sensitive to the conformational properties of carbonyl compounds.[16−18] From the directions of the bond dipole moments of C═O and C—S in various conformations of $CH_3OC(O)SCH_3$, Oki and Nakanishi[7] have suggested that the wavenumber of the carbonyl absorption of the sp,sp form is the lowest among the conformations. This is contradicted by our calculations which predict ν(C═O) in the sp,sp conformer to be higher by 3 (B3LYP) or 5 cm^{-1} (MP2) than ν(C═O) in the sp,ap form (Table 1). In the IR spectrum of gaseous $CH_3OC(O)SCH_3$, only one band possessing a symmetrical B-type contour is observed in the C═O stretching region (Figure 2), as is expected for the sp,sp conformer, in which the orientation of the dipole derivative vector is almost parallel to the principal axis of inertia, *B*. On the other hand, a hybrid AB-type contour is anticipated for the carbonyl stretching mode of the C_s sp,ap conformer. Any gauche arrangement can be excluded, moreover, because of the lack for a C-type contour of the ν(C═O) band that would be expected for nonplanar forms. Therefore, the well-defined rotational contour observed in the IR spectrum allows an unambiguous assignment of this band to the more stable sp,sp conformer. However, the presence of small amounts (less than 5%) of any other conformer cannot be excluded on the basis of these spectra alone.

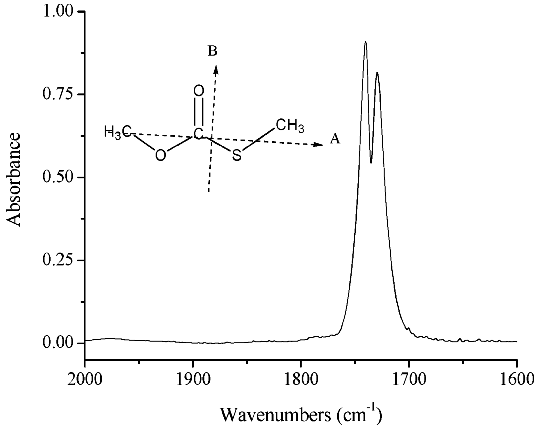


FIGURE 2. C═O stretching region in the IR spectrum of gaseous $CH_3OC(O)SCH_3$ at 5.0 mbar (glass cell, 200-mm optical path length; Si windows, 0.5-mm thick). Molecular model and main axes of inertia for the sp,sp conformer of $CH_3OC(O)SCH_3$ (the *C* axis is perpendicular to the molecular plane).

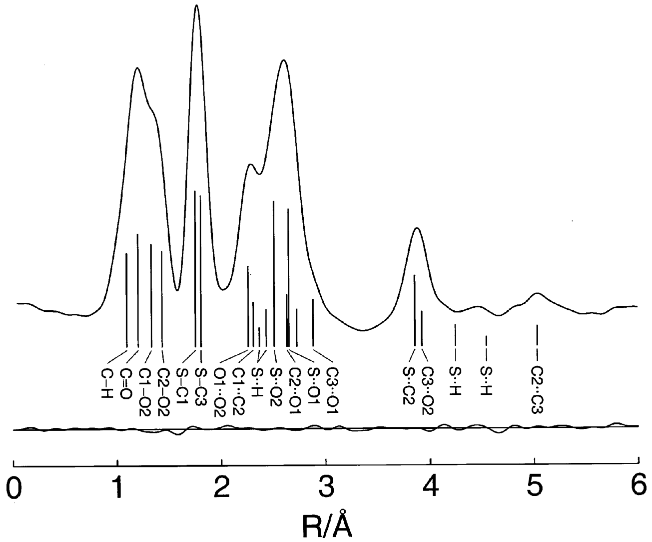


FIGURE 3. Experimental radial distribution function and difference curve. Positions of important distances are shown by vertical bars.

Structure Analysis. Gas-Phase Molecular Structure. The experimental radial distribution function, derived by Fourier transformation of the molecular scattering intensities in the GED experiment, is shown in Figure 3.

This curve can be reproduced reasonably well only by a model with the sp,sp conformation. The following assumptions, which are based on the quantum chemical calculations, were applied in the least-squares fitting of the molecular intensities. (1) Planar molecular skeleton with C_s symmetry. (2) Local C_{3v} symmetry of the two methyl groups with possible tilt angles between the C_3 axis and the O—C and S—C bond directions. The C—H bond lengths and H—C—H bond angles were set to be the same in both methyl groups. The calculated (MP2) distances and angles deviate from the experimental value by only 0.002 Å and 0.5°, respectively. (3) Vibrational amplitudes that were collected in groups according to their calculated values and amplitudes, which caused either high correlation between geometric parameters or bad determinations in the GED analysis,

---

(14) Baker, A. W.; Harris, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 1923−1928.

(15) Barany, G.; Schroll, A. L.; Mott, A. W.; Halsrud, D. A. *J. Org. Chem.* **1983**, *48*, 4750−4761.

(16) Klapstein, D.; Nau, W. M. *J. Mol. Struct.* **1993**, *299*, 29−41.

(17) Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Oberhammer, H.; Parsons, S. *J. Am. Chem. Soc.* **2001**, *123*, 12623−12631.

(18) Erben, M. F.; Della Védova, C. O.; Boese, R.; Willner, H.; Oberhammer, H. *J. Phys. Chem. A* **2004**, *108*, 699−706.

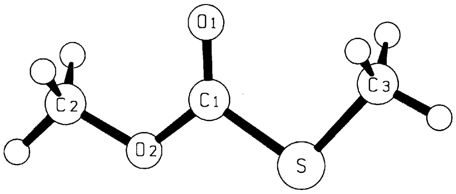


FIGURE 4. Molecular model of the sp,sp conformer of $CH_3OC(O)SCH_3$ with atom numbering.

were not refined. With these assumptions, 10 geometric parameters (*p*1−10) and six vibrational amplitudes (*l*1−6) were refined simultaneously. The following correlation coefficient had an absolute value larger than 0.6: $p7/p8 = -0.84$. The final geometrical parameters determined in this way are listed in Table 2. Vibrational amplitudes are gathered in Supporting Information (Table SM2). Least squares analyses for mixtures of sp,sp and sp,ap conformers did not improve the fit to the experimental intensities; the agreement factor *R* increased for contributions of the sp,ap form of more than 10%.

Crystal Phase Molecular Structure. $CH_3OC(O)SCH_3$ crystallizes in the monoclinic crystal system ($P2_1/n$ space group) with unit cell dimensions of $a = 12.6409(9)$ Å, $b = 4.1678(3)$ Å, and $c = 19.940(1)$ Å, $\beta = 98.164(1)°$, and $Z = 8$ (for more complete information, see Table SM3 in Supporting Information). The molecules are packed as pairs, that is, two nonequivalent molecules are present in the unit cell. Both molecules have similar geometric parameters, the differences being mainly between the C═O and C─O bonds [0.0040(15) and 0.0066(18) Å, respectively] and between the O═C─S and O─C─S bond angles [0.74(15) and 0.65(12)°, respectively]. Only the most stable (sp,sp; Figure 4) conformer is observed in a single crystal at 203 K. The crystal packing, as viewed along the *ac* plane, is shown in Figure 5. This seems to be determined by the intermolecular interactions between three molecules, involving two methyl groups from different molecules and the C═O bond of a third one. The shortest nonbonded contacts feature C═O···H─C distances of 2.640 and 2.680 Å (see Figure 6).

Discussion

According to the GED experiment, the sp,sp form is definitely the prevailing conformer of $CH_3OC(O)SCH_3$. This result contradicts the earlier interpretation of data from NMR, dipole moment, and IR measurements, which concluded that the sp,sp form is the least stable conformer in the liquid phase, which is believed to consist of a mixture of ap,sp and sp,ap conformers. Neither of these forms has been observed, however, in the gas phase. The GED conclusions about the conformational properties are consistent with the IR (gas) spectrum and are wholly in accord with the quantum chemical calculations. In the solid state, moreover, only the sp,sp conformer is present.

Various effects that stabilize the synperiplanar relative to the antiperiplanar conformer of oxoesters and thioesters have been discussed.[19] Dipole−dipole interactions destabilize the sp,ap form of gaseous $CH_3OC(O)SCH_3$. According to B3LYP calculations, the dipole moments of the two forms [μ(sp,sp) = 0.3 D and μ(sp,ap) = 3.7 D] differ markedly. Furthermore, orbital interactions between n_σ and the n_π lone pair orbitals of oxygen and sulfur atoms with opposite σ^* orbitals (the anomeric effect) or π^* orbitals (conjugation) could affect both the conformational and the structural properties.[20,21] According to a NBO analysis of the B3LYP/6-311++G(3df,2p) wave function, the sp orientation of the O─CH$_3$ and S─CH$_3$ bonds is stabilized by $n_\sigma(O) \rightarrow \sigma^*(C{=}O)$ (8.4 kcal/mol) and $n_\sigma(S) \rightarrow \sigma^*(C{=}O)$ (5.7 kcal/mol) donor → acceptor interactions, respectively (anomeric effects). This makes the sp,sp conformer the most stable form. Rotation of the O─CH$_3$ bond from sp to ap orientation leads to a major loss of both anomeric and mesomeric interactions and, consequently, to a much higher energy of the ap,sp conformer. On the other hand, rotation of the S─CH$_3$ bond from sp to ap orientation causes a minor loss of anomeric interaction and a further reduction of conjugation. Thus, $n_\pi(S) \rightarrow \pi^*(C{=}O)$ decreases from 33.1 kcal/mol in the sp,sp form to 32.3 kcal/mol in the sp,ap form. This implies that the sp,ap conformer is the second most stable form of $CH_3OC(O)SCH_3$.

The difference between the two C─O single bond lengths {$\Delta CO = [C(sp^3){-}O] - [C(sp^2){-}O] = 0.102(6)$ Å} is considerably larger than the difference between the two S─C single bond lengths {$\Delta SC = [S{-}C(sp^3)] - [S{-}C(sp^2)] = 0.040(8)$ Å}. These values are very similar in the gaseous and solid state phases [0.102(6) vs 0.113(2) Å and 0.040(8) vs 0.032 (2) Å, see Table 2] and are reproduced satisfactorily by the quantum chemical calculations. Furthermore, the reported gas-phase structure of the O,O- and S,S-dimethyl carbonates, $CH_3OC(O)OCH_3$[22] and $CH_3SC(O)SCH_3$,[23] show similar values for ΔCO and ΔCS (see Table 3). This trend can be rationalized by the NBO analysis. The $CH_3OC(O)SCH_3$ donor → acceptor interaction energies of 33.1 and 49.0 kcal/mol were calculated for the $n_\pi(S) \rightarrow \pi^*(C{=}O)$ and $n_\pi(O) \rightarrow \pi^*(C{=}O)$ resonance interactions, respectively. Similarly, the anomeric effect amounts to 8.4 and 5.7 kcal/mol for the $n_\sigma(O) \rightarrow \sigma^*(C{=}O)$ and $n_\sigma(S) \rightarrow \sigma^*(C{=}O)$ interactions, respectively. Similar values were calculated for the mesomeric and anomeric interactions in the related O,O- and S,S-dimethyl carbonates. Thus, both effects are less important when the donor lone pair orbital is formally located at the sulfur (thioester) rather than at the oxygen atom (oxoester). These differences reflect the greater importance of structure II (Chart 1) for the oxoester compared with that for the thioester group.

Experimental Section

(A) Synthesis. $CH_3OC(O)SCH_3$ was synthesized by the method suggested by Baker and Harris,[14] involving the reaction of methyl chlorothioformate with dried methanol, according to the following equation:

$$CH_3SC(O)Cl + CH_3OH \rightarrow CH_3OC(O)SCH_3 + HCl$$

Conventional vacuum techniques were used to condense nearly equimolar quantities (typically 7 mmol) of $CH_3SC(O)Cl$ and CH_3OH (a slight excess of methanol was used) into a 0.2 L glass ampule. This vessel was placed in a 60 °C glycerin bath for about 12 h. After this time, the products were separated by "trap-to-trap" vacuum fractionation through traps maintained at −30, −60, and

---

[19] Pawar, D. M.; Khalil, A. A.; Hooks, D. R.; Collins, K.; Elliott, T.; Stafford, J.; Smith, L.; Noe, E. A. *J. Am. Chem. Soc.* **1998**, *120*, 2108−2112.

[20] Hermann, A.; Trautner, F.; Gholivand, K.; von Ahsen, S.; Varetti, E. L.; Della Védova, C. O.; Willner, H.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 3979−3985.

[21] Erben, M. F.; Della Védova, C. O.; Romano, R. M.; Boese, R.; Oberhammer, H.; Willner, H.; Sala, O. *Inorg. Chem.* **2002**, *41*, 1064−1071.

[22] Mijlhoff, F. C. *J. Mol. Struct.* **1977**, *36*, 334−335.

[23] Auberg, E.; Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1979**, *57*, 95−104.

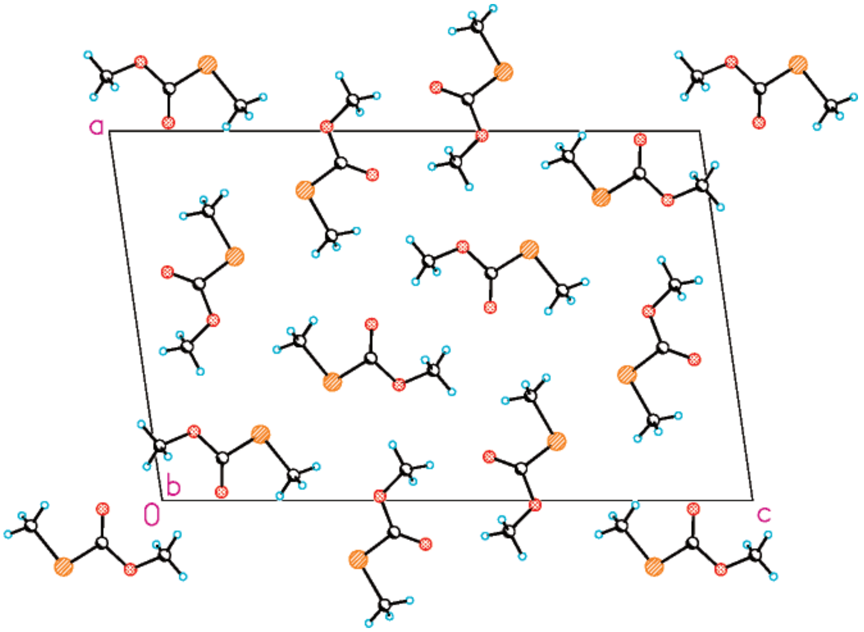


FIGURE 5. Stereoscopic illustration of the crystal packing of $CH_3OC(O)SCH_3$ at 203 K.

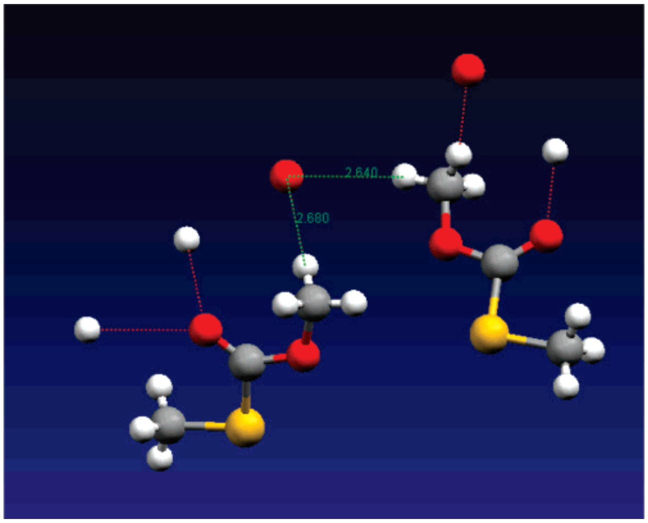


FIGURE 6. Dimeric arrangement of a $CH_3OC(O)SCH_3$ single crystal and the shortest nonbonded distances.

−196 °C. After several cycles of condensation and distillation, pure $CH_3OC(O)SCH_3$ was retained as a colorless liquid in the −30 °C trap. After the reaction finished, as evidenced by the lack of $CH_3SC(O)Cl$ bands in the IR spectrum, an oily residue remained in the reaction vessel. Nonetheless, apart from the HCl generated in the reaction, only small amounts of OCS and CO_2 were observed as byproducts in the −196 °C trap.

(B) Instrumentation. General Procedure. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges, three U-traps, and valves with PTFE stems. The vacuum line was connected to an IR cell (optical path length, 200 mm; Si windows, 0.5 mm thick) contained in the sample compartment of an FTIR instrument. This allowed us to observe the purification process and to follow the course of the reaction. The pure compound was stored in flame-sealed glass ampules under liquid nitrogen in a long-term Dewar vessel. Such an ampule was opened with an ampule key on the vacuum line, an appropriate amount was withdrawn for a given experiment, and then the ampule was flame-sealed again.[24]

X-ray Diffraction at Low Temperature. An appropriate crystal of $CH_3OC(O)SCH_3$ about 0.3 mm in diameter was obtained on the diffractometer at a temperature of 203 K with a miniature zone-melting procedure using focused infrared-laser radiation.[25] The diffraction intensities were measured at low temperature on a Nicolet R3m/V four-circle diffractometer, with 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.[26] Absorption correction details are given elsewhere. All but hydrogen atoms were assigned anisotropic thermal parameters. Atomic coordinates and equivalent isotropic displacement coefficients for heavy and hydrogen atoms are given in Tables SM4 and SM5, respectively, and anisotropic displacement parameters ($Å^2 \times 10^3$) for $CH_3OC(O)SCH_3$ are given in Table SM6 (Supporting Information).

Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 1 cm^{-1} in the range 4000−400 cm^{-1}. Raman spectra of the liquid contained in a 4-mm glass capillary were excited with 500 mW of a 1064-nm Nd:YAG laser.

Gas Electron Diffraction. The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[27] at 25- and 50-cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was kept at 15 °C, and the inlet system and gas nozzle were kept at room temperature. The photographic plates were analyzed with a scanner, and the total scattering intensities were obtained with the program SCAN3.[28] Averaged experimental molecular intensities in the ranges $s = 2{-}18$ and $8{-}35$

---

(24) Gombler, W.; Willner, H. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1286−1288.

(25) Boese, R.; Nussbaumer, M. In situ crystallisation techniques. In *Organic Crystal Chemistry*; Jones, D. W., Ed.; Oxford University Press: Oxford, 1994; Vol. 7, pp 20−37.

(26) *SHELTX-Plus*, Version SGI IRIS Indigo; A Complex Software Package for Solving, Refining and Displaying Crystal Structures; Siemens: Germany, 1991.

(27) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(28) Atavin, E. G.; Vilkov, L. V. *Instrum. Exp. Tech.* **2002**, *45*, 27 (in Russian).

TABLE 3. Mean and Difference between C−O and C−S Single Bond Distances (in Å) and Donor → Acceptor Energy Interactions (kcal/mol) for $CH_3XC(O)YCH_3$ (X, Y = O and S) Compounds

compound	$(C-O)_{mean}$	ΔCO	$(C-S)_{mean}$	ΔCS	mesomeric stabilization[a]	anomeric stabilization[b]
X, Y = O	1.383(30)	0.080(42)			99.8	17.8
X, Y = S			1.790(4)	0.025(5)	66.5	11.6
X = O, Y = S	1.386(4)	0.102(6)	1.783(2)	0.024(10)	82.1	14.1

[a] $n_\pi(X/Y) \rightarrow \pi^*(C{=}O)$. [b] $n_\sigma(X/Y) \rightarrow \sigma^*(C{=}O)$ or $lp\sigma(X/Y) \rightarrow \sigma^*[C(sp^2) - Y/X]$ for sp and ap conformations, respectively.

$Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ [$s = (4\pi/\lambda) \sin \theta/2$, where λ is the electron wavelength and θ is the scattering angle] are shown in Figure SM2 (Supporting Information).

Theoretical Calculations. All quantum chemical calculations were performed using the GAUSSIAN 03 program set.[29] MP2 and B3LYP methods employing standard basis sets up to 6-311++G-(3df,2p) and gradient techniques were used for the geometry optimizations and calculations of the vibrational properties. TSs were optimized by the synchronous transit-guided quasi-Newton method implemented by Schlegel et al.,[30] and torsional barrier heights were calculated from the energies of the TSs and the stable structures, taking zero-point vibrational energies into account. All TS structures show only one imaginary frequency, which corresponds to the torsion involved in the conformational transition. Donor → acceptor interaction energies were estimated using a NBO analysis.[31] Vibrational amplitudes and corrections for the sp,sp conformer, which were derived from a calculated (B3LYP/6-31G*) force field using the method of Sipachev,[32,33] are listed together with the experimental values in Table SM2 (Supporting Information).

Acknowledgment. Financial support by the Volkswagen-Stiftung and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. The Argentinean authors thank the ANPCYT-DAAD for the German-Argentinean cooperation Awards (PROALAR). They also thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), República Argentina. They are indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina for financial support. M.F.E. and C.O.D.V. express their gratitude to Holger Pernice, Plácido García, Mike Finze, Stefan Balters, and Stefan von Ahsen for friendship and valuable help in the laboratory work during their stay in Duisburg. C.O.D.V. especially acknowledges the DAAD, which generously sponsors the DAAD Regional Program of Chemistry of the Republic of Argentina, supporting Latin-American Ph.D. students in La Plata.

Supporting Information Available: IR (gas) and Raman (liquid) spectra and calculated vibrational data. X-ray crystallographic data in CIF format, crystal data and structure refinement details, atomic coordinates, equivalent isotropic displacement parameters, and anisotropic displacement parameters. GED-determined interatomic distances, experimental and calculated vibrational amplitudes, and vibrational corrections. Electronic energies (*E*), zero-point energies (ZPE), and the number of imaginary frequencies obtained from DFT and MP2 calculations. Cartesian coordinates of the optimized structures by the DFT and MP2 methods. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052026K

---

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(30) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49−56.

(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(32) Sipachev, V. A. *THEOCHEM* **1985**, *121*, 143−151.

(33) Sipachev, V. A. In *Advances in Molecular Structure Research*; Hargittai, I., Hargittai, M., Eds.; JAI Press: New York, 1999; Vol. 5, p 263.