Synthesis, Spectroscopic Characterization, and Conformational Properties of Trichloromethanesulfenyl Acetate, $CCl_3SOC(O)CH_3$

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Received: April 24, 2008; Revised Manuscript Received: May 12, 2008

Trichloromethanesulfenyl acetate, $CCl_3SOC(O)CH_3$, belongs to the family of sulfenic esters. This molecule has been characterized by vibrational spectroscopy. The conformational and geometrical properties of this species have been determined by IR and Raman spectroscopy, X-ray diffraction, and quantum chemical calculations. Geometry optimizations of the most stable forms were performed with ab initio (HF, MP2) and density functional theory (B3LYP) methods. According to our data, this compound results in a gauche−syn conformer with C_1 symmetry (gauche orientation around the S−O bond and syn orientation of the C═O double bond with respect to the S−O single bond) for the most stable geometry, and trans−syn conformer with C_s symmetry (trans orientation around the S−O bond and syn orientation of the C═O double bond with respect to the S−O single bond) for the second stable conformer (1.1 and 0.53 kcal/mol higher in energy than the most stable C_1 form according to the matrix FTIR spectroscopy and MP2/6-31G* level of the theory, respectively). The crystalline solid (monoclinic, $P2_1/n$, $a = 8.0152(17)$ Å, $b = 5.7922(13)$ Å, $c = 17.429(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.341(3)°$) consists exclusively of the main form. The geometrical parameters (X-ray diffraction) are $d_{C-Cl} = 1.767(19)$ Å, $d_{C-S} = 1.797(2)$ Å, $d_{S-O} = 1.663(14)$ Å, $d_{C=O} = 1.189(2)$ Å, $d_{O-C} = 1.389(3)$ Å, $d_{C-C} = 1.483(3)$ Å, angles Cl−C−Cl = 110.3(11)°, Cl−C−S = 111.8(12)°, C−S−O = 97.4(8)°, S−O−C = 116.7(11)°, O−C═O = 122.8(19)°, O═C−C = 127.1(2)°, and the main torsion angles are $\delta(CSOC) = 105.9(15)°$ and $\delta(SOC(O)) = 7.6(3)°$. The geometrical data calculated with B3LYP/6-31G++(3df,3pd), B3LYP/6-311G++(3df,3pd), B3LYP/aug-cc-pVTZ, and MP2/6-31G* are in good agreement with diffraction data.

Introduction

One of the most interesting structural properties of disulfides R_1SSR_2, peroxides R_1OOR_2, and sulfenic esters R_1SOR_2 is the dihedral angle around the S−S, O−O, and S−O bonds, respectively. In these families, the p-shape lone pairs of the two chalcogen atoms are perpendicular to each other, and this orientation allows a maximum orbital interaction between these lone pairs and the opposite S−R or O−R σ^* antibonding orbital (anomeric effect, lp(S) → σ^*(S−R) or σ^*(O–R) and anomeric effect, lp(O) → σ^*(O–R) or σ^*(S–R)).[1,2] This is the usual qualitative explanation for the gauche orientation of substituents in peroxides, disulfides, and sulfenic esters. Thus, the dihedral angle depends on the form of the lone pairs, the extension of the anomeric effect, and the steric demand of the substituents. Thioperoxides of the type R_1SOR_2, which are formal derivatives of the sulfenic acid HSOH,[3] are much less stable than peroxides or disulfides, and there is still little known about their structural properties. The parent compound, HSOH,[3] possesses a gauche structure with a dihedral angle ($\delta(HSOH) = 91.3°$) closer to that in disulfide, HSSH[4] ($\delta(HSSH) = 90.76(6)°$), than that in peroxide, HOOH[5] ($\delta(HOOH) = 120.0(5)°$).

In thioperoxides with two formally sp^3-hybridized substituents, CF_3SOCF_3,[6] the dihedral angle is larger than 100° ($\delta(C-S-O-C) = 105°$), and this value is closer to that in disulfide, CF_3SSCF_3[7] ($\delta(C-S-S-C) = 98.2°$), than that in peroxide CF_3OOCF_3,[8] ($\delta(C-O-O-C) = 123.3°$).

Recently, very unexpected conformational properties were determined for two molecules containing S−O bonds, both with one sp^3- and one sp^2-hybridized substituent, $CF_3SOC(O)CH_3$[9] and $CF_3SOC(O)CF_3$.[9] IR (matrix) spectra and GED[9] result in mixtures of gauche−syn and trans−syn conformers. In addition to the expected gauche form for both compounds (dihedral angles of $\delta(C-S-O-C) = 100(4)°$ and $\delta(C-S-O-C) = 101(3)°$, respectively) with a synperiplanar orientation of the

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[#] This work is part of the Ph.D. thesis of M.C.R., who is a doctoral fellow of Regional Program DAAD of Chemistry, Republic of Argentina.

10.1021/jp803609m CCC: $40.75 © 2008 American Chemical Society
Published on Web 08/01/2008

C═O bond relative to the S−O bond, a trans conformation around the S−O bond appears as a second stable form, which is well reproduced by quantum chemical calculations.

The calculated potential functions for internal rotation around the S−O bond for $CF_3SOC(O)CH_3$[9] and $CF_3SOC(O)CF_3$[9] possess a minimum for the trans structure at around 180°, in addition to the minimum near 90° for the gauche structure. In the case of the symmetrically substituted trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)SOC(O)CF_3$,[10] the conjugation between the p-shaped lone pairs of sulfur and oxygen with the π-systems of the two substituents ($CF_3C(O)$) could stabilize a planar trans conformation. However, IR (gas), UV, and ^{13}C NMR spectroscopy predict only the existence of the main conformer, the syn−syn. In $CF_3C(O)SOC(O)CF_3$[10] (δ(C−S−O−C) = 77°) and in $FC(O)SOC(O)CF_3$,[11] (δ(C−S−O−C) = 75(3)°), the dihedral angle around the S−O bond is also smaller than 90°. It is assumed that such small angles are observed in sulfenic esters with two sp^2-hybridized substituents (FC(O) or $C(O)CF_3$). Two trends become apparent from this rather limited number of examples; the dihedral angle (δC−S−O−C) increases as the steric requirements of the substituents for R_1SOR_2 with two sp^3-, one sp^3-, and one sp^2-hybridized substituents are increased and decreases with two sp^2-hybridized substituents.

Furthermore, bis(trifluoroaceto) disulfide, $CF_3C(O)OSSOC(O)CF_3$,[12] and diaceto disulfide, $CH_3C(O)OSSOC(O)CH_3$,[13] were studied by photoelectron spectroscopy (PES) and theoretical calculations. The dihedral angles around the S−O bonds were reported computed at δ(S−S−O−C) = 91.8° and δ(S−S−O−C) = 92.3°, respectively. Photoelectron spectroscopy (PES) and quantum chemical calculations were also performed to investigate the first vertical ionization energies of these two compounds, $CCl_3SOC(O)CH_3$,[14] the title molecule, and $CCl_3SOC(O)CF_3$.[14] The dihedral angles of both gauche forms, $CCl_3SOC(O)CH_3$[14] (δ(C−S−O−C) = 107.0°) and $CCl_3SOC(O)CF_3$[14] (δ(C−S−O−C) = 108.5°), were calculated by the B3LYP/6-311+G(3df) method. As far as we know, this is the only antecedent reported for the species under study. This work is part of a systematic study on sulfur−oxygen compounds to obtain more accurate structural information about S−O single bonds. We report here the X-ray structure of $CCl_3SOC(O)CH_3$, its full vibrational characterization, and the geometrical and conformational properties investigated by IR (gas, liquid), Raman (liquid), NMR (^1H, ^{13}C), and UV spectroscopy, with the complement of X-ray diffraction at low temperature and supplemented by quantum chemical calculations.

Experimental Section

Synthesis. Trichloromethanesulfenyl acetate, $CCl_3SOC(O)CH_3$, was prepared using reported methods of the literature,[15] and its purity was checked by IR and ^1H and ^{13}C NMR spectroscopy.

Physical Properties and Spectroscopic Characterization. $CCl_3SOC(O)CH_3$ is a pale-yellow liquid, with the characteristic overpowering trichloromethanesulfenyl odor. In the liquid or gaseous state, $CCl_3SOC(O)CH_3$ is unstable because of its sensitivity to moisture and disproportionation.

The colorless solid sample melts at −20 °C, and the vapor pressure is 0.5 torr at 20 °C. The ^1H NMR spectrum shows only a singlet located at 1.8 ppm that corresponds to the CH_3 group of the molecule. Furthermore, the ^{13}C NMR spectrum shows a singlet signal at 20.1 ppm assigned to the CH_3 group and two singlets at 97.5 and 166.5 ppm, corresponding to the carbon atoms in the CCl_3 and C═O groups, respectively.

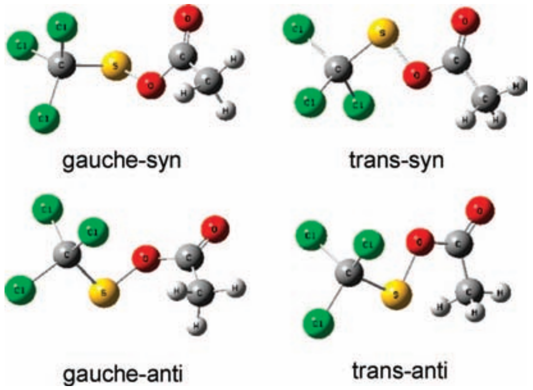

Figure 1. Schematic representation of the four conformers of $CCl_3SOC(O)CH_3$.

TABLE 1: Calculated Relative Energies, Free Energies (kcal mol^{-1}),[a] and ν(C═O) Vibrational Frequencies (cm^{-1}) for $CCl_3SOC(O)CH_3$

conformer[b]	method of caculation	ΔE	$\Delta G°$	$\nu(CH_3C{=}O)$[c]
gauche−syn	HF/6-31G*	0.00	0.00	2066 (307)
	MP2/6-31G*	0.00	0.00	1874 (155)
	B3LYP/6-31++G(3df,3pd)	0.00	0.00	1847 (228)
	B3LYP/6-311++G(3df)	0.00	0.00	1852 (227)
	B3LYP/6-311++G(3df,3pd)	0.00	0.00	1851 (228)
	B3LYP/aug-cc-pVTZ	0.00	0.00	1841 (231)
trans−syn	HF/6-31G*	0.26	0.01	2029 (335)
	MP2/6-31G*	0.90	0.53	1827 (170)
	B3LYP/6-31++G(3df,3pd)	0.17	−0.07	1791 (256)
	B3LYP/6-311++G(3df)	0.15	−0.02	1795 (257)
	B3LYP/6-311++G(3df,3pd)	0.16	−0.05	1795 (258)
	B3LYP/aug-cc-pVTZ	0.01	−0.34	1787 (258)
gauche−anti	HF/6-31G*	6.41	6.95	2078 (423)
	MP2/6-31G*	5.42	5.96	1870 (213)
	B3LYP/6-31++G(3df,3pd)	3.83	4.47	1856 (340)
	B3LYP/6-311++G(3df)	3.77	4.46	1861 (342)
	B3LYP/6-311++G(3df,3pd)	3.77	4.37	1861 (343)
	B3LYP/aug-cc-pVTZ	3.95	4.61	1850 (339)

[a] Includes different multiplicities (m = 1 for trans and m = 2 for gauche). [b] See Figure 1. [c] In parentheses are the calculated IR intensities in km mol^{-1}.

In the mass spectrum of $CCl_3SOC(O)CH_3$, the presence of the molecular ion peak is observed as a low-intensity signal at m/z 208. Other fragments of $CCl_3SOC(O)CH_3$ were also assigned, resulting in peaks at m/z values of 79 (5, $ClCS^+$), 43 (100, CH_3CO^+), 28 (7, CO^+), and 15 (10, CH_3^+); the relative abundance is given in parentheses.

The UV−visible spectrum of $CCl_3SOC(O)CH_3$ exhibits two absorptions at 233 and 283 nm, and the assignment was made by comparison with $CF_3C(O)SOC(O)CF_3$. The band at 233 nm corresponds to the $\pi \rightarrow \pi^*$ transition, which is originated from the C═O chromophore, and the second UV absorption at 283 nm is due to the S−O group.

Instrumentation. ***Vibrational Spectroscopy.*** Infrared (gas, liquid) spectra were recorded on a Bruker Vector 22 FTIR instrument with a resolution of 2 cm^{-1} in the range of 4000−400 cm^{-1} using a gas cell with an optical path length of 200 mm and Si windows (0.5 mm thick). Raman spectra of the liquid substance were measured on a Bruker RFS 100/S FT Raman spectrometer in the region of 3500−100 cm^{-1} with 2 cm^{-1} resolution.

Matrix Isolation. $CCl_3SOC(O)CH_3$ was placed into a small U trap that was mounted in front of the matrix support (a metal

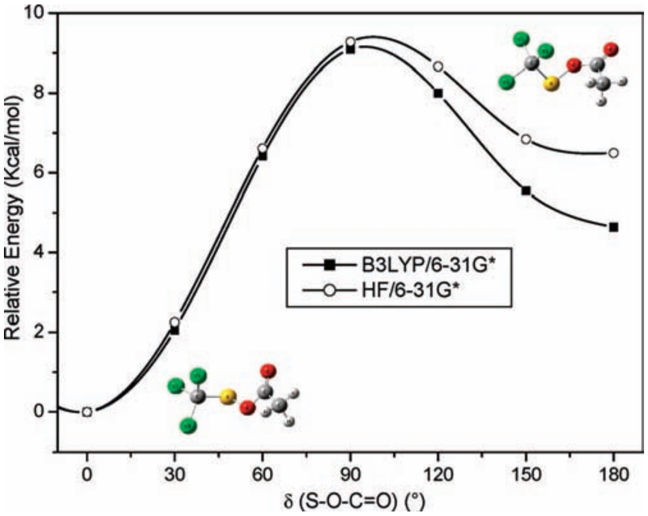

Figure 2. Calculated potential curves for internal rotation around the O−C (sp^2) bond in $CCl_3SOC(O)CH_3$ using HF/6-31G* and B3LYP/6-31G*.

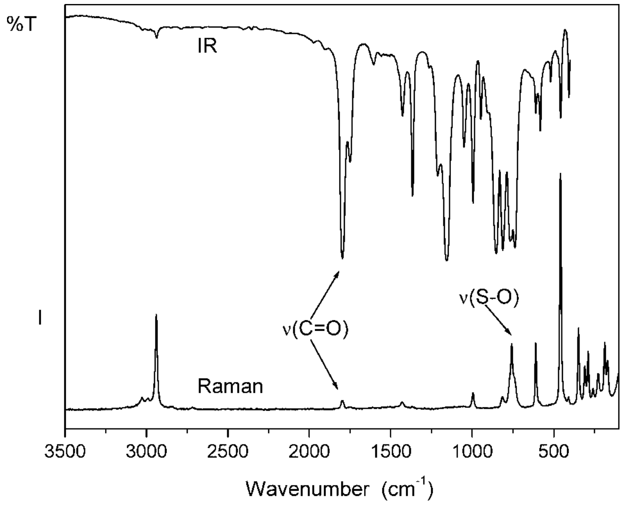

Figure 3. IR and Raman spectra of liquid $CCl_3SOC(O)CH_3$ at room temperature.

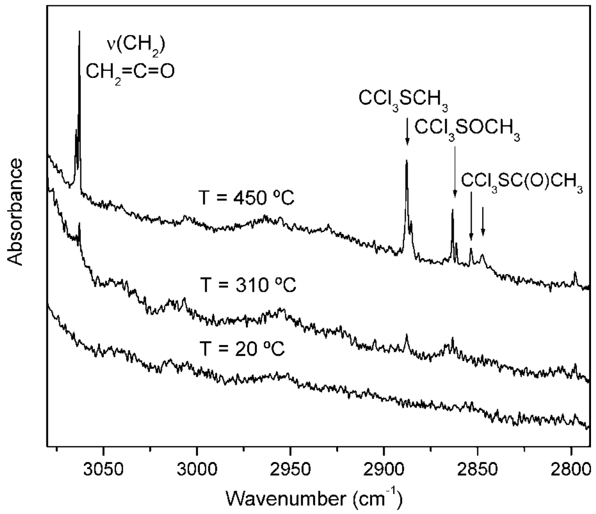

Figure 4. IR spectra in the stretching region of the CH_3 group for $CCl_3SOC(O)CH_3$ isolated in Ar matrixes at 15 K deposited at different temperatures.

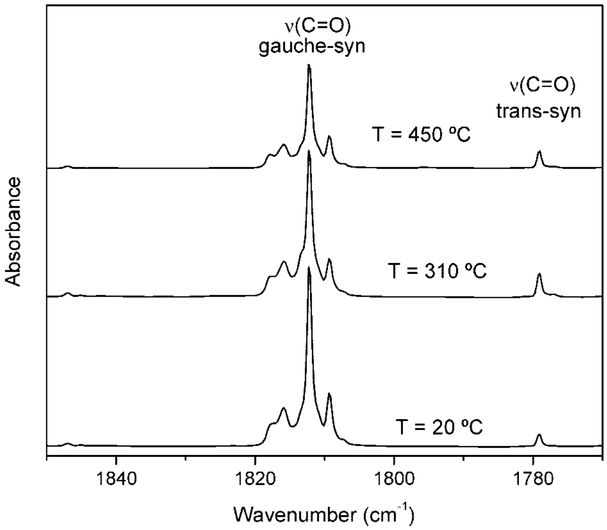

Figure 5. IR spectra in the carbonyl stretching region for $CCl_3SOC(O)CH_3$ isolated in Ar matrixes at 15 K deposited at different temperatures.

mirror) and cooled at −54 °C. A stream of argon gas was passed over the sample in the U trap, and the resulting mixtures of gaseous $CCl_3SOC(O)CH_3$ and argon (≈1:1000) were forced through a quartz tube with a nozzle of 1 mm i.d. that was electrically heated over a length of ≈15 mm. The nozzle was held at temperatures of 20, 210, 310, 400, and 450 °C by deposition onto the matrix support, a rhodium-plated copper mirror cooled at ≈15 K by a He continuous flow cryostat, by the continuous deposition technique. Details of the matrix apparatus have been described elsewhere.[16]

For the photolysis experiments, radiation from a 150 W mercury high-pressure lamp (TQ150, Haereus, Hanau, Germany) with and without a $\lambda = 280-335$ nm cutoff filter (Schott, Mainz, Germany) was used over a period of 5 to 15 min.

IR (Ar matrix) spectra of the deposits were recorded on an IFS66v FTIR spectrometer in the reflectance mode with a transfer optic. The interferometer was equipped with a globar source, a KBr beam splitter, and a MCT-500 detector. The spectra were recorded with a resolution of 0.5 cm^{-1} in the range of 4000−530 cm^{-1}.

UV Spectroscopy. UV−visible spectra of the gas phase of $CCl_3SOC(O)CH_3$ were recorded using a glass cell (10 cm optical path length) equipped with quartz windows in a Perkin Elmer Lambda EZ210 spectrometer. The measurements were carried out in the spectral region of 200−600 nm.

NMR Spectroscopy. For the ^1H and ^{13}C NMR measurements, neat samples were flame-sealed in thin-walled 4 mm o.d. tubes and placed into 5 mm NMR tubes. The spectra were recorded at low temperature (−30 °C) with a Bruker AC 250 NMR spectrometer using CD_3OD as an external lock and internally referenced to $(CH_3)_4Si$.

X-ray Diffraction. The crystallization was performed on the diffractometer at 247 K with a miniature zone melting procedure using focused infrared laser radiation.[17] The diffraction intensities were measured at low temperatures on a four circle diffractometer. Intensities were collected with graphite-monocromatized Mo Kα radiation using the ω-scan technique. The structure was solved by Patterson syntheses and refined by the full-matrix least-squares method on F^2 with the SHELXTL-Plus program.[18]

TABLE 2: Experimental (IR, Raman) and Calculated Vibrational Wavenumbers of $CCl_3SOC(O)CH_3$

	IR (liquid)^a	Raman (liquid)	IR (Ar matrix)	B3LYP/6-31++G(3df,3pd)^b		
mode	gauche−syn	gauche−syn	gauche−syn	gauche−syn	trans−syn	assignment^c
	3574 vw					$2 \times \nu_4$
ν_1	3025 vw	3028		3157 (4)	3157 (3)	$\nu_{as}(CH_3)$
ν_2	2992 vw	2994		3112 (1)	3113 (2)	$\nu_{as}(CH_3)$
ν_3	2939 vw	2940		3050 (<1)	3050 (<1)	$\nu_s(CH_3)$
ν_4	1796 vs	1796	1812			
	1749 m^e	1749^e	1779^e	1847 (228)	1791 (256)	$\nu(C{=}O)^d$
ν_5				1466 (8)	1467 (9)	$\delta_{as}(CH_3)$
ν_6	1427 w	1432	1432	1463 (11)	1465 (11)	$\delta_{as}(CH_3)$
ν_7	1366 m	1367	1367	1391 (27)	1393 (28)	$\delta_s(CH_3)$
ν_8	1211 m^e		1203^e	1171 (302)	1231 (412)	$\nu(O{-}C)/\nu(C{-}C)/\delta(C{-}C{=}O)/\rho_s(CH_3)$
	1155 vs		1156			
ν_9	1051 w		1045	1060 (6)	1061 (4)	$\rho_{as}(CH_3)$
ν_{10}	993 m	995	989	993 (75)	1010 (64)	$\nu(C{-}C)/\rho_{as}(CH_3)$
ν_{11}	946 w^e					
	852 s	817	856	863 (225)	932 (63)	$\nu(C{-}O)$
ν_{12}	813 s		815	784 (99)	798 (113)	$\nu_s(CCl_3)$
ν_{13}		757	758	755 (37)	757 (23)	$\nu(S{-}O)$
v_{14}	766 s		774	736 (52)	733 (111)	$\nu_{as}(CCl_3)$
ν_{15}	738 s		745	708 (140)	709 (145)	$\nu_{as}(CCl_3)$
ν_{16}	608 vw	610		608 (3)	598 (4)	$\nu(C{-}C)/\delta(C{-}C{=}O)$
ν_{17}	582 w		578	586 (5)	596 (4)	oop $((C{=}O)O)/\rho_s(CH_3)$
ν_{18}	457 w	460		450 (11)	446 (16)	$\nu(S{-}CCl_3)$
ν_{19}		408		398 (12)	392 (7)	$\delta(O{-}C{-}C)$
ν_{20}		348		342 (4)	333 (7)	$\delta_s(CCl_3)$
ν_{21}		309		303 (1)	304 (1)	$\delta_{as}(CCl_3)$
ν_{22}		288		283 (1)	284 (3)	$\delta_{as}(CCl_3)$
ν_{23}		258				
		225^e		250 (2)	228 (<1)	$\rho_s(CCl_3)/\delta(S{-}O{-}C)$
ν_{24}				217 (<1)	199 (1)	$\rho_s(CCl_3)/\delta(C{-}S{-}O))$
ν_{25}		187				
		169^e		177 (1)	172 (7)	$\rho_s(CCl_3)/\delta(S{-}O{-}C)$
ν_{26}				159 (<1)	156 (<1)	$\rho_{as}(CCl_3)$
ν_{27}		85		85 (<1)	83 (1)	$\tau(C{-}C)$
ν_{28}				59 (<1)	68 (2)	$\tau(S{-}O)/\tau(O{-}C)/\tau(C{-}C)$
ν_{29}				51 (1)	41 (1)	$\tau(C{-}S)/\tau(S{-}O)$
ν_{30}				36 (2)	35 (<1)	$\tau(C{-}S)/\tau(S{-}O)/\tau(O{-}C)$

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] In parentheses are the calculated IR intensities in km mol^{-1}. [c] The ν, δ, τ, and ρ represent stretching, deformation, torsion, and rocking modes. [d] Matrix effect (see Figure 5). [e] Bands corresponding to the trans−syn conformer of $CCl_3SOC(O)CH_3$.

Mass Spectrometer. The mass spectra were obtained with a Shimadzu GC-MS QP2010 spectrometer using CH_2Cl_2 as the solvent.

Results

Quantum Chemical Calculations. The calculations were performed using the Gaussian 03[19] sofware package applied with the ab initio (Hartree−Fock (HF) and the MP2 methods) as well as the density functional B3LYP approach. Different basis sets were used to search the possible conformers of $CCl_3SOC(O)CH_3$. All computed stationary points were characterized by evaluating the corresponding harmonic force field. Harmonic vibrational wavenumbers were computed by means of analytic second derivatives at the MP2 and DFT levels.

The chalcogen−chalcogen bond in bivalent compounds evidences a preference to adopt a gauche conformation with typical dihedral angles of around 90°, which is usually attributed to lone-pair interactions.[20] As was previously reported,[21] compounds of the type R_1SOR_2 and R_1SSR_2 prefer gauche conformations around the S−O or S−S bonds as a result of lone-pair interactions.

Four possible conformers can be predicted for $CCl_3SOC(O)CH_3$, which are gauche−syn, trans−syn, gauche−anti, and trans−anti (Figure 1). The gauche and trans orientations refer to the C−S−O−C dihedral angles of around 90 and 180° respectively, and the syn and anti denote the orientation of the C═O group with respect to the S−O bond.

The geometries of these conformers were optimized with different methods and basis sets, as HF/6-31G*, MP2/6-31G*, B3LYP/6-31++G(3df,3pd), B3LYP/6-311++G(3df), B3LYP/6-311++G(3df,3pd), and B3LYP/aug-cc-pVTZ. The calculated relative energies, free energies, and C═O frequencies of gauche−syn, trans−syn, and gauche−anti conformers are listed in Table 1. According to the MP2/6-31G* calculation the most stable gauche−syn conformer with C_1 symmetry is only slightly more stable (0.53 kcal/mol) than the trans–syn form with C_s symmetry. The calculated energy differences between these conformers are, however, even smaller at the B3LYP level.

To determine the difference between the conformers, a relaxed scan of the potential energy surface was performed by rotating the torsion angle δ(CSOC) and δ(SOC(O)) in steps of 30° at the HF/6-31G* and B3LYP/6-31G* approximations. The resulting potential curves for dihedral angles, δ(SOC(O)), from 0 to 180° are shown in Figure 2. The curve displays a global minimum at around 0° for δ(SOC(O)), associated with the syn orientation of the SOC(O)

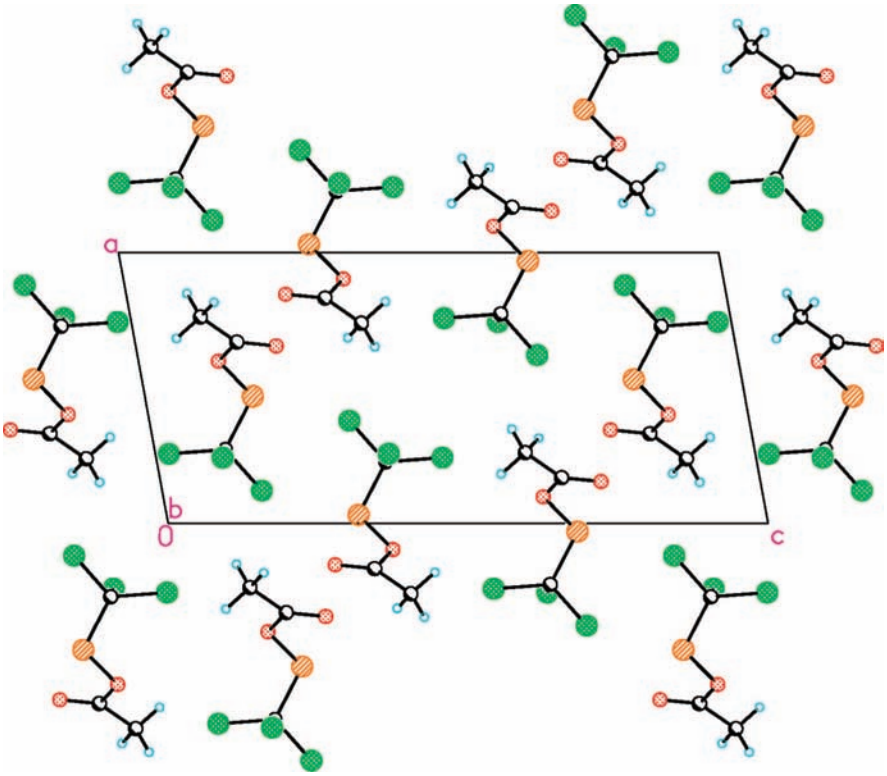

Figure 6. Stereoscopic illustration of the crystal packing of $CCl_3SOC(O)CH_3$ at 233 K.

TABLE 3: Experimental and Calculated Geometric Parameters for the Gauche−Syn Conformer of $CCl_3SOC(O)CH_3$[a]

parameters	X-ray	B3LYP			MP2/6-31G*
		6-31++G(3df,3pd)	6-311++G(3df,3pd)	aug-cc-pVTZ	
S(1)−O(1)	1.663(14)	1.675	1.674	1.685	1.694
S(1)−C(3)	1.797(2)	1.810	1.808	1.813	1.811
Cl(1)−C(3)	1.775(2)	1.790	1.789	1.794	1.775
Cl(2)−C(3)	1.754(3)	1.788	1.787	1.792	1.774
Cl(3)−C(3)	1.767(19)	1.789	1.788	1.793	1.777
C(2)−O(1)	1.389(3)	1.395	1.393	1.393	1.408
C(2)═O(2)	1.189(2)	1.194	1.189	1.191	1.205
C(1)−C(2)	1.483(3)	1.504	1.501	1.501	1.500
O(1)−S(1)−C(3)	97.4(8)	99.6	99.6	99.5	97.4
C(2)−O(1)−S(1)	116.7(11)	118.5	118.6	118.3	116.3
O(1)−C(2)═O(2)	122.8(19)	123.7	123.7	123.7	124.1
C(1)−C2)═O(2)	127.1(2)	127.4	127.4	127.3	128.1
O(1)−C(2)−C(1)	110.0(17)	108.7	108.8	108.8	107.7
Cl(2)−C(3)−Cl(3)	110.7(11)	110.3	110.3	110.0	110.2
Cl(2)−C(3)−Cl(1)	108.5(11)	108.2	108.2	108.2	108.5
Cl(3)−C(3)−Cl(1)	110.3(11)	110.0	110.1	110.3	110.0
Cl(2)−C(3)−S(1)	112.9(12)	113.3	113.3	113.3	112.3
Cl(3)−C(3)−S(1)	102.3(10)	101.4	101.4	101.4	103.4
Cl(1)−C(3)−S(1)	111.8(12)	113.2	113.2	113.2	112.2
S(1)−O(1)−C(2)═O(2)	7.6(3)	4.2	4.4	4.0	4.9
C(3)−S(1)−O(1)−C(2)	105.9(15)	107.5	107.0	107.0	102.5

[a] Distances in angstroms, and angles in degrees. For atom numbering, see Figure 7.

moiety. The potential curve for the dihedral angle δ(CSOC) has been already reported,[14] which shows two minima at around 110 and 180°. The first minimum at 110° corresponds to a gauche orientation and the second minimum at 180° to a trans orientation. Thus, according to different theoretical results, this compound may exist in the gas phase as a mixture of gauche−syn (C_1 symmetry) and trans−syn (C_s symmetry) conformations.

Vibrational Analysis. The vibrational characterization of $CCl_3SOC(O)CH_3$ was performed by infrared and Raman spectroscopy, and the spectra of the liquid are shown in Figure 3. In the IR spectrum, three bands appear in the C−H stretching region at 3025, 2992, and 2939 cm^{-1}, which can be assigned to two $\nu_{as}(CH_3)$ and one $\nu_s(CH_3)$ stretching modes, respectively, by comparison with those assigned in $CH_3OC(O)SCl$[22] and in $CH_3C(O)NCO$.[23] Typical shapes and intensities of the CH_3 group are observed in the Raman spectra, and the bands at 3028, 2994, and 2940 cm^{-1} are attributed to the same modes.

In the IR spectra, two characteristic bands in the region of the C═O stretching mode were observed at 1816 and 1775 cm^{-1}

TABLE 4: S–O Bond Lengths and Dihedral Angles in R_1S-OR_2[a]

R_1S-OR_2	S–O	$\delta(R_1-S-O-R_2)$	method
$HS-OH$[3]	1.662	91.3	CCSD(T)/cc-pCVQZ
CF_3S-OCF_3[6]	1.677	105.0	B3LYP/6-311++G(3df,3pd)
$CF_3S-OC(O)CH_3$[9]	1.659(4)	100(4)	GED
$CF_3S-OC(O)CF_3$[9]	1.663(5)	101(3)	GED
$CCl_3S-OC(O)CH_3$[b]	1.663(14)	105.9(15)	X-ray
$CCl_3S-OC(O)CH_3$[14]	1.675	107.0	B3LYP/6–311+G(3df)
$CCl_3S-OC(O)CF_3$[14]	1.694	108.5	B3LYP/6–311+G(3df)
$FC(O)S-OC(O)CF_3$[11]	1.647(5)	75(3)	GED
$CF_3C(O)S-OC(O)CF_3$[10]	c	77	B3LYP/6-31G*
$CF_3C(O)O-SS-OC(O)CF_3$[12]	1.755	91.8	B3LYP/6-311G*
$CH_3C(O)O-SS-OC(O)CH_3$[13]	1.710	92.3	B3LYP/6-311++G(3df,3pd)

[a] Distances in angstroms; angles in degrees. [b] This work. [c] No data available.

in the gas phase, at 1796 and 1749 cm^{-1} in the liquid, and at 1812 and 1779 cm^{-1} in the Ar matrix. The band at 1816 cm^{-1} is assigned to the gauche–syn conformer (C_1 symmetry), whereas the second C=O stretching at 1775 cm^{-1} is attributed to the trans–syn conformer (C_s symmetry). The location of these C=O bands is in good correlation with related compounds, possessing the OC(O) or SC(O) moiety. This mode is observed in $CF_3SOC(O)CH_3$[9] at 1820 (gauche–syn) and 1761 cm^{-1} (trans–syn), in $CF_3SOC(O)CF_3$[9] at 1839 (gauche–syn) and 1799 cm^{-1} (trans–syn), in $CF_3OOC(O)CF_3$[24] at 1859 cm^{-1} (gauche–syn), and in $CF_3SSC(O)CF_3$[25] at 1768 cm^{-1} (gauche–syn).

The experimentally observed frequency shift $\Delta\nu$(C=O) in the IR spectra are 41 (gas), 47 (liquid), and 33 cm^{-1} (Ar matrix), and the B3LYP/aug-cc-pVTZ method predicts a value of 54 cm^{-1} for the difference between gauche–syn and trans–syn forms and 9 cm^{-1} for the difference between gauche–syn and gauche–anti, which is much smaller than the experimental value. Therefore, the comparison of experimental and calculated $\Delta\nu$(C=O) frequency shift confirms the assignment of the stronger band at 1812 cm^{-1} to the gauche–syn form and the weaker band at 1779 cm^{-1} to the trans–syn conformer. The experimental free-energy difference $\Delta G°$ for these two forms is estimated from the relative ν(C=O) intensities of the matrix infrared bonds to be 1.1 kcal/mol. This value is in fair agreement with the calculated relative free energies of gauche–syn and trans–syn conformers (see Table 1). The free-energy difference of $\Delta G° = 0.53$ kcal/mol was calculated by the MP2/6-31G* method (see Table 1).

The $\nu(CCl_3)$ stretching modes are observed in the infrared spectrum at 813, 766, and 738 cm^{-1} corresponding to $\nu_s(CCl_3)$, $\nu_{as}(CCl_3)$, and $\nu_{as}(CCl_3)$, respectively, and this assignment agrees with reported values for similar molecules containing the CCl_3 group.[26,27]

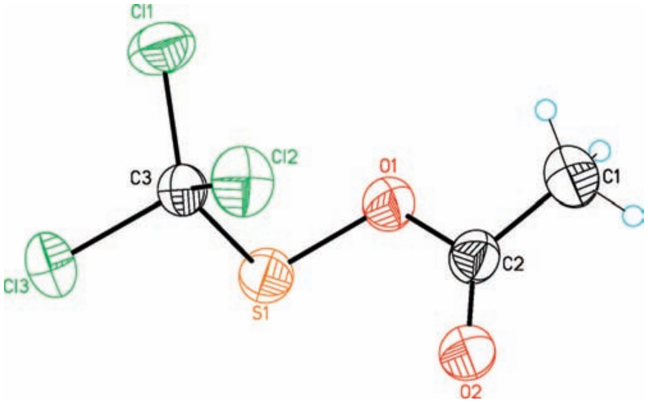

Figure 7. Crystalline structure obtained by X-ray diffraction at low temperatures of $CCl_3SOC(O)CH_3$.

The S–O vibration, the characteristic feature of sulfenic esters, is observed at 757 cm^{-1} as a weak band in the Raman spectrum of the liquid, and it was assigned by comparison with $CF_3SOC(O)CH_3$[28] (762 cm^{-1}) and $CF_3SOC(O)CF_3$[28] (765 cm^{-1}). This mode could not be identified in the IR spectra because of its low intensity and the overlapping with the absorptions of the CCl_3 group. However, it was observed in the matrix spectra at 758 cm^{-1}, comparing well with other S–O compounds.[6,10]

When the Ar/$CCl_3SOC(O)CH_3$ mixture was heated at higher temperatures and deposited as a matrix at 15 K, new bands appeared in the IR spectra. They were assigned to CCl_3SOCH_3, CCl_3SCH_3,[29] CCl_3SOH,[30] $CCl_3SC(O)CH_3$,[31] $CH_2C=C=O$,[32] CO_2,[33,34] OCS,[35] and CO.[36] Figure 4, shows the IR spectra in the region of 3070–2700 cm^{-1}, characteristic of the CH_3 group at nozzle temperatures of 20, 310, and 450 °C. Figure 5 shows the 1850–1700 cm^{-1} region deposited at the same temperature. The intensity of the C=O stretching band of the gauche–syn conformer clearly decreases with the increasing of the temperature prior to the deposition. Otherwise, the intensity of the C=O band assigned to the trans–syn conformer scarcely increases relative to those of the main conformer with increasing nozzle temperature. Thus, whereas the photodecarboxylation have been already reported in the literature for similar systems ($CF_3SOC(O)CH_3$[9] and $CF_3SOC(O)CF_3$[9]), the photoevolution and pyroevolution to CO and OCS have not been previously reported.

The assignment of the vibrational modes for $CCl_3SOC(O)CH_3$ was carried out by comparison of the experimental wavenumbers with those of related molecules and with calculated wavenumbers (B3LYP/6-311++G(3df,3pd)). In Table 2, the 30 fundamental vibrations have been fully assigned with the program Asym40[37] for the gauche–syn conformer. The observed absolute wavenumber differences as well as the sign of the shift between the gauche–syn and trans–syn conformer are in perfect agreement with the calculated differences (B3LYP/6-31++G(3df,3pd)) for both conformers.

Crystal Structure. Trichloromethanesulfenyl acetate crystallizes in the monoclinic crystal system ($P2_1/n$ spatial group) with unit cell dimensions of $a = 8.0152(17)$ Å, $b = 5.7922(13)$ Å, $c = 17.429(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.341(3)°$, and $Z = 4$, and only the synperiplanar conformer is observed in a single crystal of $CCl_3SOC(O)CH_3$ at 233(2) K. The crystal packing as viewed along the *ac* plane is shown in Figure 6. It consists of alternating layers of molecules oriented along the *b* axis forming an arrangement such that CCl_3 and $CH_3C(O)$ groups of different layers are face to face, separated by nonbonded $CCl_3\cdots CH_3C(O)$ and $CH_3C{=}O\cdots CH_3C(O)$ distances.

Geometrical parameters of $CCl_3SOC(O)CH_3$ were also obtained by X-ray diffraction at low temperature. The value obtained for the dihedral angle δ(C−S−O−C) is 105.9°, which confirms the gauche conformation. This compound adopts the syn orientation (C═O bond with respect to the S−O bond), and the experimental value of the dihedral angle δ(S−O−C(O)) is 7.6°. Therefore, the molecule presents a gauche−syn conformation with C_1 symmetry. The experimental and calculated geometric parameters by different methods (B3LYP/6-31++G(3df,3pd), B3LYP/6-311++G(3df,3pd), B3LYP/aug-cc-pVTZ, and MP2/6-31G*) are presented in Table 3 for the gauche−syn conformer.

According to X-ray diffraction and quantum chemical calculations, this compound possesses C_1 symmetry. The dihedral angle for the gauche-syn conformer around the S−O bond was compared with different compounds[3,6,9−13] (see Table 4). Furthermore, the experimental value (105.9°) has been compared with the same angle in $CF_3SOC(O)CH_3$[9] (δ(C−S−O−C) = 100°) and that in $CF_3SOC(O)CF_3$[9] (δ(C−S−O−C) = 101°), resulting in a value quite similar to them.

Conclusion

The analysis of the IR (gas, liquid, matrix) and Raman (liquid) spectra of $CCl_3SOC(O)CH_3$ agrees with the presence of the gauche−syn conformer (C_1 symmetry) as the preferred form at room temperature by an experimental free-energy difference of 1.1 kcal/mol. The contribution of a second form with C_s symmetry is evidenced in the gaseous phase, where two bands are clearly identified in the carbonyl stretching region. The weak band at 1775 cm^{-1} can be assigned with confidence to a trans−syn conformer, while the presence of a third gauche−anti conformer at room temperature can be ruled out on the basis of the calculated data.

The existence of a stable trans structure around the S−O bond in addition to the gauche is also predicted by quantum chemical calculations. No such trans structure has been observed so far for any peroxide $R_1O{-}OR_2$ or disulfide $R_1S{-}SR_2$. Also, sulfenic esters such as $CF_3SOC(O)CH_3$[9] and $CF_3S{-}OC(O)CF_3$,[9] whose gas-phase structures have been determined by GED, possess trans−gauche structures. This could suggest that the type of substituents, $R_1 = CF_3$ or CCl_3 and $R_2 = CH_3C(O)$ or $CF_3C(O)$ are responsible for the unusual conformational properties of $CF_3SOC(O)CH_3$, $CCl_3SOC(O)CH_3$, and $CF_3SOC(O)CF_3$. It was observed for these sulfenic esters containing the S−OC(O) group that the stability of them correlates with the electron-withdrawing ability of the C═O group attached to the oxygen atom. The structural properties of S−O-containing compounds could be rather different from those of S−S and O−O derivatives, which have not been reported until now.

According to the X-ray diffraction, the gauche−syn structure is present in a single crystal of $CCl_3SOC(O)CH_3$ at 233(2) K. Theoretical MP2/6-31G* studies of this compound also result in a gauche−syn form with C_1 symmetry for the most stable geometry and the trans−syn conformer with C_s symmetry for the less stable conformer (0.53 Kcal/mol). Diffraction data of the main torsion angle is δ(CSOC) = 105.9(15)°; this relatively high value becomes evident when it is compared with similar compounds such as $CF_3SOC(O)CH_3$[9] (δ(C−S−O−C) = 100°) and $CF_3SOC(O)CF_3$[9] (δ(C−S−O−C) = 101°).

Acknowledgment. The authors thank the DAAD (Deutscher Akademischer Austauschdienst, Germany), Agencia Nacional de Promoción Científica y Técnica (ANPCYT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Comisión de Investigaciones de la Provincia de Buenos Aires (CIC), Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), and Chinese Academy of Sciences for financial support. S.E.U also thanks the Departamento de Ciencias Básicas de la Universidad Nacional de Luján for financial support. M.C.R. acknowledges the Deutscher Akademischer Austauschdienst (DAAD) award. C.O.D.V. especially acknowledges the DAAD, which generously sponsors the DAAD Regional Program of Chemistry for the República Argentina supporting Latin-American students to make their Ph.D. in La Plata.

References and Notes

(1) Alleres, D. R.; Cooper, D. L.; Cunningham, T. P.; Gerratt, J.; Karadakov, P. B.; Raimondi, M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3357.

(2) Kirby, J. *The Anomeric Effect and Related Stereochemical Effects at Oxygen*; Springer: Berlin, Germany, 1983.

(3) Winnewisser, G.; Lewen, F.; Thoswirth, S.; Behnke, M.; Hahn, J.; Gauss, J.; Herbst, E. *Chem.—Eur. J.* **2003**, *9*, 5501.

(4) Marsden, C. J.; Smith, B. J. *J. Phys. Chem.* **1988**, *92*, 347.

(5) Redington, R. L.; Olson, W. B.; Cross, P. C. *J. Chem. Phys.* **1962**, *36*, 1311.

(6) Ulic, S. E.; von Ahsen, S.; Willner, H. *Inorg. Chem.* **2004**, *43*, 5268.

(7) Meyer, C.; Mootz, D.; Bäck, B.; Minkwitz, R. *Z. Naturforsch. B* **1997**, *52*, 69.

(8) Marsden, C. J.; Bartell, L. S.; Diodati, F. P. *J. Mol. Struct.* **1977**, *39*, 253.

(9) Ulic, S. E.; Kosma, A.; Leibold, C.; Della Védova, C. O.; Oberhammer, H. *J. Phys. Chem. A* **2005**, *109*, 3739.

(10) Ulic, S. E.; Della Védova, C. O.; Hermann, A.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **2002**, *41*, 5699.

(11) Ulic, S. E.; Kosma, A.; Della Védova, C. O.; Willner, H.; Oberhammer, H. *J. Phys. Chem. A* **2006**, *110*, 10201.

(12) Zeng, X.; Ge, M.; Sun, Z.; Wang, D. *J. Phys. Chem. A* **2006**, *110*, 5685.

(13) Du, L.; Yao, L.; Ge, M. *J. Phys. Chem. A* **2007**, *111*, 11787.

(14) Du, L.; Yao, L.; Zeng, X.; Ge, M.; Wang, D. *J. Phys. Chem. A* **2007**, *111*, 4944.

(15) Haas, A.; Lieb; M.; Zhang, Y. *J. Fluorine Chem.* **1985**, *29*, 297.

(16) Schöckel, H.; Willner, H. *Matrix-Isolated Molecules*; VCH: Weinheim, Germany, 1994; p 297.

(17) Boese, R.; Nussbaumer, M. In *Correlations, Transformations and Interactions in Organic Crystal Chemistry*; Jones, D. W., Katrusiat, A., Eds.; Oxford University: Oxford, U.K., 1994; Vol. 7, p 20.

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

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. 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.; Bakken, V.; 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 D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(20) Steudel, R.; Schmidt, H.; Baumeister, E.; Oberhammer, H.; Koritsanszky, T. *J. Phys. Chem.* **1995**, *99*, 8987.

(21) Snyder, J. P.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, *99*, 2931.

(22) Erben, M. F.; Della Védova, C. O.; Romano, R. M.; Boese, R.; Oberhammer, H.; Willner, H.; Sala, O. *Inorg. Chem.* **2002**, *41*, 1064.

(23) Della Védova, C. O.; Mack, H.-G.; Ben Altabef, A. *J. Raman Spectrosc.* **1993**, *24*, 621.

(24) DesMarteau, D. D.; Bernstein, P. A.; Hohorst, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 3882.

(25) Burton, C. A.; Shreeve, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 6545.

(26) Ulic, S. E.; Di Napoli, F.; Hermann, A.; Mack, H.-G.; Della Védova, C. O. *J. Raman Spectrosc.* **2000**, *31*, 909.

(27) Della Védova, C. O.; Aymonino, P. J. *J. Raman Spectrosc.* **1986**, *17*, 485.

(28) Unpublished results.

(29) Fernandez, L. E.; Ben Altabef, A.; Varetti, E. L. *J. Mol. Struct.* **1998**, *444*, 227.

(30) Beckers, H.; Esser, S.; Metzroth, T.; Behnke, M.; Willner, H.; Gauss, J.; Hahn, J. *Chem.—Eur. J.* **2006**, *12*, 832.

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

(32) Moore, C. B.; Pimentel, G. C. *J. Chem. Phys.* **1963**, *38*, 2816.

(33) Svensson, T.; Nelander, B.; Karlström, G. *Chem. Phys.* **2001**, *265*, 323.

(34) Abe, H.; Takeo, H.; Yamada, K. M. T. *Chem. Phys. Lett.* **1999**, *311*, 153.

(35) Hawkins, M.; Almond, M. J.; Downs, A. J. *J. Phys. Chem.* **1985**, *89*, 3326.

(36) Dubost, H. *Chem. Phys.* **1976**, *12*, 139.

(37) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **2000**, *203*, 82.

JP803609M