Methoxycarbonyl trifluoromethyl disulfide, $CH_3OC(O)SSCF_3$: synthesis, structure and conformational properties†‡

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Pure methoxycarbonyl trifluoromethyl disulfide, $CH_3OC(O)SSCF_3$, has been prepared quantitatively by the reaction of $CH_3OC(O)SCl$ and $Hg(SCF_3)_2$. The conformational properties of the novel molecule have been studied by vibrational spectroscopy [IR(gas) and Raman(liquid)] and quantum chemical calculations (B3LYP and MP2 methods). The gaseous compound exhibits a conformational equilibrium at room temperature where the most stable form has C_1 symmetry with a synperiplanar (*syn*) orientation of the C=O double bond with respect to the S–S disulfide bond. A second form is observed in the gaseous IR spectra corresponding to a conformer with the carbonyl bond C=O in antiperiplanar (*anti*) position with respect to the S–S single bond. The structure of a single crystal of $CH_3OC(O)SSCF_3$ has been determined by X-ray diffraction analysis at low temperature using a miniature zone melting procedure. The crystalline solid (triclinic, $P\bar{1}$, $a = 6.4698(5)$ Å, $b = 9.0499(8)$ Å, $c = 12.5700(11)$ Å, $\alpha = 97.219(6)^\circ$, $\beta = 93.131(5)^\circ$, $\gamma = 96.888(5)^\circ$ and $Z = 4$) consists exclusively of molecules with the synperiplanar conformation and the usual *gauche* orientation around the disulfide bond [ϕ(CS–SC) = 91.06(15)°] is adopted. The geometrical parameters agree with those obtained from quantum chemical calculations.

Introduction

The tertiary structure of many biological compounds is determined by the structural properties of disulfide bridges.[1] Since a significant fraction of the proteins made in the nature contain disulfide bonds, the molecular structure of disulfides has also attracted much attention. Very recently, Khakshoor and Nowick[2] report the use of disulfide linkages to stabilize a cyclic β-sheet dimer with a well-defined structure. Indeed, changes over time of the structural motifs associated with this bond in different protein folds have been considered to explain their evolution. Catalytic roles have been also attributed to disulfide bonds through mediating thiol–disulfide interchange reactions in substrate proteins. There is rising evidence for a third type of disulfide bond, referred as allosteric disulfides, which can control protein functions by triggering a conformational change when it breaks and/or forms.[3]

The synthesis of symmetrical (RSSR) and unsymmetrical (RSSR′) disulfides has attracted much attention and several outstanding reviews can be found in the chemical literature.[4] Of central interest are efficient methods for the formation of disulfide bonds required for the synthesis of many biologically active compounds, such as peptides and peptide mimetics.[5] A number of disulfide-bridged peptides are of current and potential interest as therapeutic drugs, including oxytocin (childbirth), somatostatin and analogs (anticancer), calcitonin (osteoporosis) and integrelin (anticlotting).[6,7] This may be due to the fact that pairing of cysteine residues to form disulfide bridges represents the principal way for nature to establish covalent crosslinks that can 'lock' conformations, with concomitant effects on structural stabilities[2] and biological activities.[8,9]

Moreover, the knowledge of the structural properties and conformational preference of simple molecules containing disulfide bonds is of prime interest.[10] One of their most important structural properties of symmetric disulfides XSSX is represented by the dihedral angle around the S–S bond [ϕ(X–S–S–X)], with typical values close to 90°. Thus, geometric structures of non-cyclic symmetrical disulfides, XSSX, are characterized by a *gauche* orientation around the S–S bond and S–S bond lengths varying between 1.890(2) Å in FSSF to

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‡ Electronic supplementary information (ESI) available: Experimental and calculated (B3LYP/6-311++G**) vibrational data (cm^{-1}) are given in Table S1. Crystal data and structure refinement for $CH_3OC(O)SSCF_3$ are given in Table S2 and crystallographic details, whole molecular parameters and a list of atomic coordinates and equivalent isotropic displacement coefficients and anisotropic displacement parameters for $CH_3OC(O)SSCF_3$ are given in Tables S3–S7. CCDC reference number 734324. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00382g

2.061(3) Å in HSSH. Recent theoretical calculations predict the strength of the sulfur–sulfur bond energy between 77.7 kcal mol^{-1} for FSSF and only 41.8 kcal mol^{-1} for tetrasulfane, HSS–SSH.[11] The p-shaped lone pairs of the two sulfur atoms are perpendicular to each other with this orientation favored by the anomeric effect, that is, an orbital interaction between these lone pairs and the opposite empty σ* orbital of the S–X bond.[12,13] This effect depends strongly on the relative energies of the two orbitals involved, and can explain the short S–S and long S–F bonds in FSSF[14] with a dihedral angle of 85.2(2)°. Other representative compounds with ϕ(XS–SX) dihedral angle values close to 90° are HSSH[15] (90.76(6)°), ClSSCl[16] (85.2(2)°), FC(O)SSC(O)F[17] (82.2(19)°) and CH_3SSCH_3[18] (85.3(37)°). However, steric repulsions between bulky substituents may lead to larger dihedral angles, such as in CF_3SSCF_3[19] and Bu^tSSBu^t[20] having dihedral angles of 104.4(40) and 128.3(27)°, respectively.

Herein the preparation and characterization of a novel disulfide compound, methoxycarbonyl trifluoromethyl disulfide, $CH_3OC(O)SSCF_3$, are presented. As far as we know, no previous report for this compound exists in the literature. In this study we present an experimental investigation of the structure and vibrational properties of the title compound, which includes the use of vibrational [IR (gas) and Raman (liquid)] and NMR (^1H, ^{19}F and ^{13}C) spectroscopies. Its crystal structure has been also determined at 190 K by X-ray diffraction using an *in situ* crystallization method. The experimental data have been supplemented by using quantum chemical calculations.

Results

Synthesis and characterization

$CH_3OC(O)SSCF_3$ can be synthesized by reacting methoxycarbonylsulfenyl chloride, $CH_3OC(O)SCl$, with bis(trifluoromethylthio)-mercury salt, $Hg(SCF_3)_2$, according the following equation:

$$2CH_3OC(O)SCl + Hg(SCF_3)_2 \rightarrow 2CH_3OC(O)SSCF_3 + HgCl_2$$

This method is adapted from that reported by Haas *et al.*[21,22] used for synthesizing haloformyl(perhaloalkyl)-sulfanes and disulfanes. The new compound is a colorless liquid, with the characteristic overpowering sulfenylcarbonyl odor. The compound is stable at room temperature in vacuum or in an inert atmosphere for a couple of days in the liquid or gaseous state.

The ^1H NMR spectrum only shows a singlet signal located at δ = 3.96 ppm that corresponds to the CH_3O group of the molecule. A similar value of δ = 3.48 ppm was reported for related $CH_3OC(O)SNCO$ molecule.[23] In the ^{19}F NMR spectrum one singlet located at δ = −46.8 ppm is observed. For the trifluoromethyldisulfide group (CF_3SS–) the ^{19}F NMR spectra typically show a resonance at approximately δ = −45 ppm.[24] Besides, the ^{19}F NMR spectrum of $CF_3C(O)SCF_3$ has been recently reported showing a similar singlet at δ = −41.8 ppm assigned to the SCF_3 group. In addition, the uncoupled ^{13}C NMR spectrum of the title compound shows three singlet signals at δ = 56.7, 125.3 and 166.3 ppm, assigned to the carbon atoms of the CH_3, CF_3 and C=O groups, respectively. An extra resonance with very low intensity is observed at δ = 131.6 ppm, possibly due to decomposition products (unidentified). For comparison, the ^{13}C NMR spectrum of the related $CF_3C(O)SCF_3$[25] molecule shows signals at δ = 126.3 and 176.9 ppm attributed to the CF_3 and C=O groups, respectively.

In order to corroborate the purity of the sample, a further GC-MS analysis was carried out. The gas chromatogram of the compound measured in solution of diethyl ether shows a single peak with a retention time of 5.8 min and a purity better than 99%. The molecular ion peak is observed in the mass spectrum as a very low intensity signal at m/z = 192 and several fragments of $CH_3OC(O)SSCF_3$ are assigned. Thus, peaks at m/z = 15 (65, CH_3^+), 59 (100, $CH_3OC(O)^+$), 69 (35, CF_3^+), 79 (35, CH_3SS^+), 133 (20, CF_3SS^+), 148 (15, $CH_3SSCF_3^+$) and 161 (5, $CF_3SSC(O)^+$) are observed in the mass spectrum (relative abundance in parentheses).

Additional evidence for the identity of $CH_3OC(O)SSCF_3$ comes from the analysis of its IR(gas) and Raman(liquid) spectra (see Fig. 1 and Table S1 in the ESI‡). An intense band centered at 1782 cm^{-1} is characteristic for the ν(C=O) group, and the strongest band in the IR(gas) spectrum, centered at 1180 cm^{-1}, is assigned to the ν_{as}(C–O–C) stretching mode. The characteristic disulfide stretching mode[26] is observed in the Raman (liquid) spectrum as a medium intensity signal at 541 cm^{-1}.

Quantum chemical calculations

Several rotamers are possible for $CH_3OC(O)SSCF_3$, mainly depending on the conformations adopted around each of the three O–C, C–S and S–S single bonds in the molecule. Taking into consideration structural studies previously reported for $CH_3OC(O)X$ compounds, the *syn* orientation of the ϕ(CO–C=O) dihedral angle is preferred.[23] Thus, special attention was paid to the ϕ(O=C–CS) and ϕ(CS–SC) dihedral angles. In a first step, the potential function for the internal rotation around the S–S bond was derived by structure

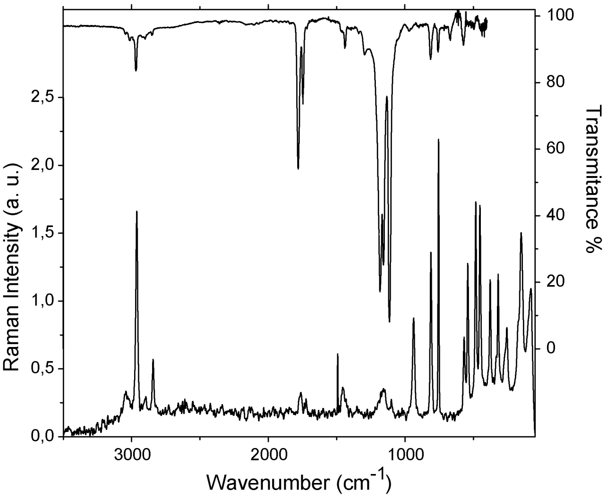

Fig. 1 Gaseous IR spectrum (top) at 7.2 mbar (glass cell, 100 mm optical path length, Si windows, 0.5 mm thick) and liquid Raman spectrum for $CH_3OC(O)SSCF_3$.

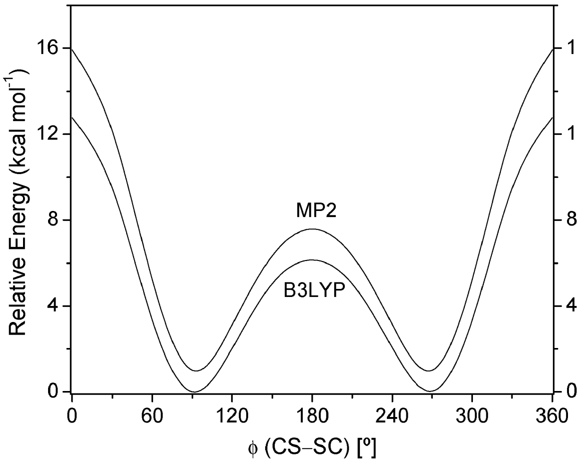

Fig. 2 Calculated (B3LYP and MP2 methods with the 6-31G* basis sets) potential function for internal rotation around the S–S single bond in $CH_3OC(O)SSCF_3$ (MP2 curve is shifted by 1 kcal mol^{-1}).

optimizations at fixed ϕ(CS–SC) dihedral angles (*syn* orientations were supposed around both C–O and C–S single bonds). Potential functions obtained with the B3LYP and MP2 methods and 6-31G* basis sets are shown in Fig. 2. Minima occur at dihedral angles around ±90°, whereas maxima in the region of *syn* and *anti* orientation of the C–S–S–C skeleton are observed, with imaginary frequencies at ϕ(CS–SC) = 0 and 180°.

In addition to the enantiomeric forms that are related by rotation around the disulfide bond, two conformations may occur around the C(O)–S single bond depending on the mutual orientation of the C═O double bond with respect to the S–S single bond. The potential functions for the internal rotation around the CS single bond was calculated (B3LYP/6-31G*) by full geometry optimizations at fixed [ϕ(SS–C═O) in Fig. 3] dihedral angle, supposing *syn* and *gauche* orientations around C(O)–O and S–S single bonds, respectively (see Fig. 3). As expected, two structures correspond to minima in the potential energy curve, the most stable one having *syn* orientation of the C═O with respect to the S–S bond [ϕ(SS–C═O) = 0°] while the *anti* form [ϕ(SS–C═O) = 180°] is located higher in energy by *ca.* 1 kcal mol^{-1}.

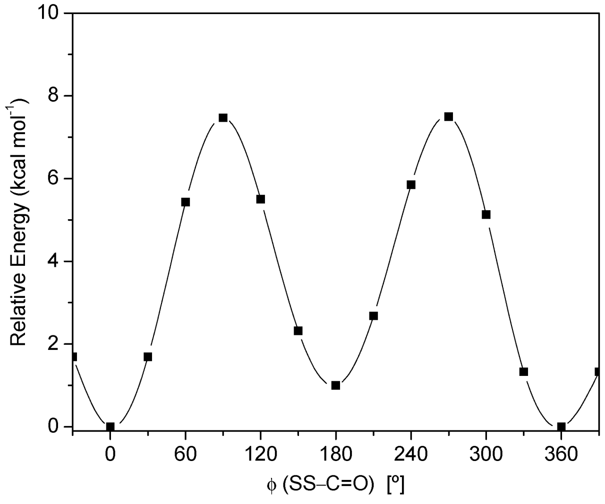

Fig. 3 Calculated potential function (B3LYP/6-31G*) for internal rotation around the C–S single bond in $CH_3OC(O)SSCF_3$.

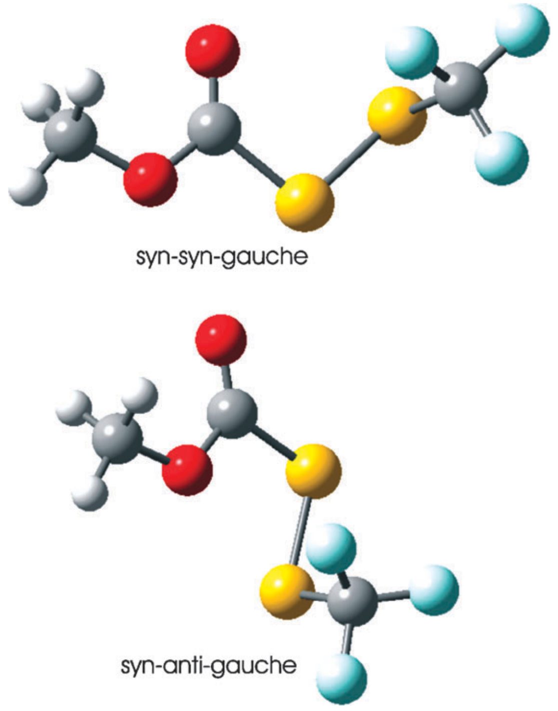

Fig. 4 Molecular models for the two main conformers of $CH_3OC(O)SSCF_3$.

This analysis suggests that two main forms are expected to determine the conformational properties of $CH_3OC(O)SSCF_3$, *syn-syn-gauche* and *syn-anti-gauche*, depending to the orientation around the O–C, C–S and S–S single bonds, respectively. Thus, full geometry optimizations and frequency calculations were performed for each of the most stable structures with the B3LYP method using the 6-31G* and 6-311++G** basis sets as well as with the MP2/6-31G* level of approximation. Structural results obtained from DFT-based methods are often as good as those derived from MP2 calculations.[27] It is well documented that hybrid functionals with large basis sets yield reliable structures and vibrational frequencies for inorganic compounds.[28]

Calculated relative energies (corrected by zero-point energy) and frequencies of the C═O stretching vibrational modes with their IR intensities are collected in Table 1. The optimized molecular structures for the two main conformers of the title molecule are shown in Fig. 4.

Vibrational analysis

The gas phase FTIR spectrum and the Raman spectrum of liquid $CH_3OC(O)SSCF_3$ are shown in Fig. 1. A tentative assignment of the observed bands is performed by comparison with the calculated spectrum, and the approximate description of modes is based on the calculated displacement vectors for the fundamental modes of vibration, and also by comparison with spectra of related molecules, $CH_3OC(O)SNCO$,[23] $CH_3OC(O)SCl$,[29] $CF_3C(O)SCF_3$[25]and $XC(O)SSCF_3$[30] (X = Cl, F). Experimental and calculated (B3LYP/6-311++G**) frequencies for the *syn-syn-gauche*

Table 1 Calculated relative energies (corrected by zero-point energy; kcal mol^{-1}) and vibrational frequency of the C=O stretching mode (cm^{-1}) with IR intensities (Km mol^{-1}, in parentheses) for $CH_3OC(O)SSCF_3$

Conformers	Method of calculation	ΔE°	ν(C=O)
syn-syn-gauche	B3LYP/6-31G*	0.00[a]	1853 (201)
	B3LYP/6-311++G**	0.00[b]	1821 (251)
	MP2/6-31G*	0.00[c]	1839 (160)
syn-anti-gauche	B3LYP/6-31G*	1.01	1823 (265)
	B3LYP/6-311++G**	0.78	1788 (354)
	MP2/6-31G*	1.08	1813 (219)
anti-syn-gauche	B3LYP/6-31G*	6.46	1878 (293)
	B3LYP/6-311++G**	6.44	1847 (355)

[a] $E^\circ = -1362.401432$ hartrees. [b] $E^\circ = -1362.644828$ hartrees. [c] $E^\circ = -1359.835513$ hartrees.

and *syn-anti-gauche* conformers, together with the tentative assignments are given in the ESI (Table S1).‡

As mentioned, quantum chemical calculations reproduce the presence of two conformers of $CH_3OC(O)SSCF_3$ at room temperature, the *syn-syn-gauche* being the most stable form. The presence of two bands in the region of the C=O group in both the IR(gas) and Raman(liquid) spectra is evident. Particularly, as observed in Fig. 5, two intense bands centered at 1782 and 1747 cm^{-1} are observed in the vapor IR spectrum of $CH_3OC(O)SSCF_3$.

The most intense band, located at the higher wavenumber, is assigned to the C=O stretching mode of the most stable *syn-syn-gauche* conformer. A second band centered at 1747 cm^{-1} can be attributed to the C=O stretching mode of the second stable *syn-anti-gauche* form. The well-defined rotational contour observed for this band gives confidence to this assignment. In effect, because of the almost parallel orientation of the carbonyl oscillator with respect to the principal axis of inertia A, an A-type band is expected for the ν(C=O) normal mode of the *syn-anti-gauche* conformer (see Fig. 5). Additionally, the calculated wavenumber difference [B3LYP/6-311++G**] for this mode between the two conformers is +33 cm^{-1} (Table 1), a value in good agreement with the experimentally observed value of +35 cm^{-1} in the gas-phase spectrum. Moreover, the conformational composition was derived from the integrated intensity of both 1782 and 1747 cm^{-1} bands in the vapor IR spectrum and taking into account the computed intensities with the B3LYP/6-311++G** method (Table 1). A composition of 81(5)% of the more stable *syn-syn-gauche* form at room temperature was obtained (the estimated error limit includes uncertainties in the measured areas).

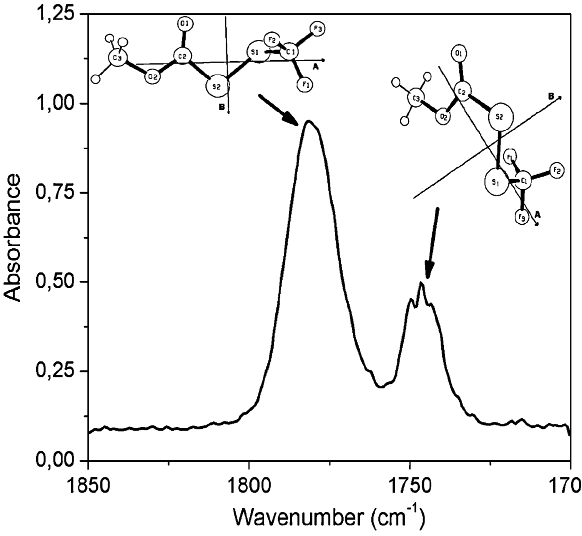

Fig. 5 IR spectrum in the carbonyl stretching region for gaseous $CH_3OC(O)SSCF_3$ at 7.2 mbar. Principal moments of inertia (A and B in the sheet plane) are shown for both *syn-syn-gauche* and *syn-anti-gauche* conformers.

Additional to the C=O normal mode of vibration, it is also important to describe other absorptions. Thus, the most intense gas-phase IR band at 1115 cm^{-1} is assigned to the symmetric stretching mode of the CF_3 group, a value that is in agreement with those reported for related species such as $CF_3C(O)SCF_3$[25] and $XC(O)SSCF_3$[30] (X=Cl, F) with experimental values of 1120, 1116 and 1119 cm^{-1}, respectively. A weak absorption in the IR spectrum observed at 671 cm^{-1} is assigned to the out-of-plane deformation of the –OC(O)S– group, whereas the values reported for this mode in related molecules $CH_3OC(O)SNCO$[23] and $FC(O)SSCF_3$[30] are 681 and 636 cm^{-1}, respectively. It is well-known that the ν(S–S) stretching mode is clearly observed in the Raman spectrum and can be used to characterize disulfide containing compounds. For $CH_3OC(O)SSCF_3$ the medium intensity signal appearing at 541 cm^{-1} is assigned to ν(S–S), in coincidence with reported values for other disulfide compounds [$FC(O)SSCF_3$ (567 cm^{-1}),[30] FC(O)SSC(O)F (555 cm^{-1}),[17] $FC(O)SSC(O)CF_3$ (549 cm^{1})[31] and $FC(O)SSC(O)CF_2Cl$ (535 cm^{-1})[32]].

Crystal structure

By using the *in situ* crystallization technique,[33] an appropriate single crystal of $CH_3OC(O)SSCF_3$ was grown at 190 K with a miniature melting procedure using focused infrared laser radiation. Methoxycarbonyl trifluoromethyl disulfide crystallizes in the triclinic $P\bar{1}$ spatial group with unit cell dimensions of $a = 6.4698(5)$ Å, $b = 9.0499(8)$ Å, $c = 12.5700(11)$ Å, $\alpha = 97.219(6)^\circ$, $\beta = 93.131(5)^\circ$, $\gamma = 96.888(5)^\circ$, and $Z = 4$. The crystal structure has two molecules of $CH_3OC(O)SSCF_3$ in the asymmetric unit. Table 2 includes the main geometric parameters for both independent molecules (named as molecule 1 and molecule 2) derived from the structure refinement, as well as those obtained from quantum chemical calculations. As expected, geometrical parameters for both molecules are quite similar; therefore only the molecular structure of molecule 1 is shown in Fig. 6. In the following discussion, averaged values will be presented.

Only the most stable *syn-syn-gauche* conformer is observed in the single crystal at 190 K, with dihedral angle values for the $CH_3OC(O)S$– group slightly deviating from planarity [ϕ(CO–C=O) = −2.1(4)° and ϕ(SS–C=O) = −0.2(3)°]. The structure adopted for the title compound around the disulfide single bond is definitely *gauche*, with a dihedral angle of ϕ(CS–SC) = 91.06(15)°.

In general, the main geometric parameters obtained by X-ray diffraction analysis are well reproduced by quantum chemical calculations. The main deviations are observed for

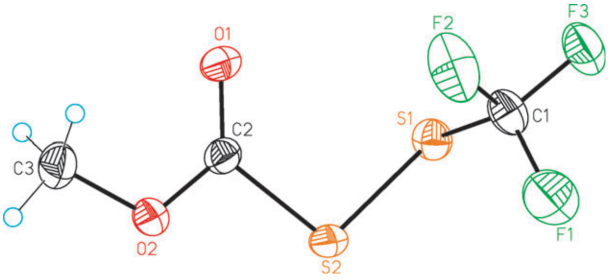

Fig. 6 Molecular model for the single-crystal structure of *syn-syn-gauche* $CH_3OC(O)SSCF_3$ (only molecule 1 in the asymmetric unit is shown).

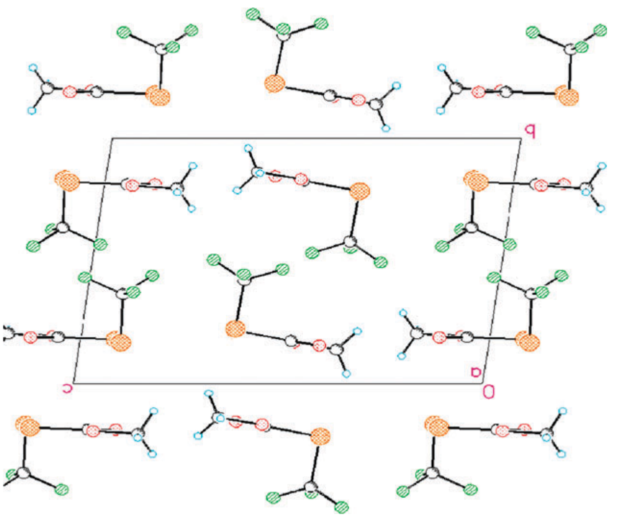

Fig. 7 Packing of molecules in crystalline $CH_3OC(O)SSCF_3$ at 190 K along the *bc* plane.

the bond distances around the disulfide group, which are overestimated especially with the B3LYP method. Thus, even with quite large basis sets (6-311++G**), the B3LYP method predicts the S1–S2, S1–C1 and S2–C2 bonds to be too long by *ca.* 0.06, 0.04 and 0.02 Å, respectively. These parameters are better described by the MP2/6-311++G** method, being the S1–S2 bond length too long by 0.045 Å.

The overall crystal packing of $CH_3OC(O)SSCF_3$ as viewed along the *bc* plane is shown in Fig. 7. Intermolecular interactions dominated by F···F contacts are common for fluorinated molecules where this type of interaction plays an important role in the stabilization of the packing. According to quantum chemical calculations, F···F contacts in aromatic systems can contribute up to 14 kcal mol^{-1} of local stabilization energy.[34] Packing motifs identified in structural studies of perfluorated compounds are characterized by C–F···F–C non-bonded distances of 2.777 and 2.868 Å.[35,36] For the title molecule, the trifluoromethyl group interacts through C–F···F–C contacts with average F···F distances of 2.897 Å. Intermolecular S···O interactions between the disulfide and carbonyl groups are also observed, as can be seen in Fig. 8. The intermolecular non-bonded S1_2···O1_2 distances for molecules 2 (symmetry code $(1 - x, 2 - y, -z)$) are 3.169 Å, a value that is shorter than the sum of the van der Waals radii for sulfur and oxygen atoms (3.3 Å).[37]

The investigation of short non-bonded intramolecular 1,4 S···O contacts in compounds containing sulfur and oxygen atoms has attracted much attention because short S···O distances (typically in the range 2.77–3.16 Å) have been observed in solid phase studies.[38] We have identified such short 1,4 S···O contacts in a series of acyl disulfides, where intramolecular interactions between the C═O and S–S groups may be present.[31,32] For the title compound a 1,4 S···O intramolecular average distance of 3.116 Å defined by the sulfur atom attached to the CF_3 group and the oxygen atom of the carbonyl group is observed (see Fig. 8). Following the study of Burling and Goldstein[39] on non-bonded interactions, the nearly planar conformation of the $CH_3OC(O)SS$– moiety favors the electronic delocalization of non-bonded π electrons of the sulfur atoms, which may result in an increased attractive interaction between the sulfur and oxygen atoms.

Discussion

The conformational properties of sulfenylcarbonyl compounds—with general formula XC(O)SY—have been extensively studied and the preference of a synperiplanar conformation around

Table 2 Experimental and calculated geometric parameters for the *syn-syn-gauche* conformer of $CH_3OC(O)SSCF_3$

	X-ray[b,c]		B3LYP	MP2
Parameters[a]	Molecule 1	Molecule 2	6-311++G**	6-311++G**
S1–C1	1.801(3)	1.803(3)	1.841	1.814
S1–S2	2.0110(15)	2.0116(14)	2.076	2.056
S2–C2	1.806(3)	1.808(3)	1.831	1.804
O1═C2	1.193(4)	1.185(4)	1.193	1.201
O2–C2	1.316(4)	1.326(4)	1.335	1.340
C1–F[d]	1.321(5)	1.326(4)	1.342	1.338
C1–S1–S2	100.26(15)	100.59(13)	101.13	98.90
C2–S2–S1	101.71(14)	102.39(15)	101.41	100.11
F2–C1–S1	113.1(3)	112.8(2)	113.35	113.02
O1═C2–S2	125.9(3)	126.6(3)	126.93	127.25
ϕ(C1S1–S2C2)	92.74(15)	89.37(14)	91.67	88.64
ϕ(S2S1–C1F3)	177.4(2)	51.1(3)	178.80	178.70
ϕ(S1S2–C2═O1)	0.5(3)	−0.9(3)	0.26	0.03
ϕ(C3O2–C2═O1)	−2.4(4)	−1.5(4)	0.07	0.17

[a] For atom numbering see Fig. 6. [b] Distance values in Å and bond angles in degrees. [c] Uncertainties are σ values. [d] Average values of the C–F bond distances.

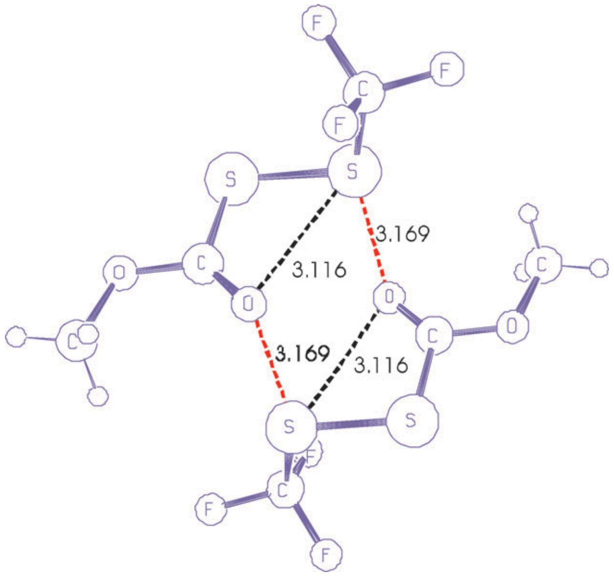

Fig. 8 Illustration of the intermolecular non-bonded S1···O=C distances (3.169 Å) [symmetry code (1 − x, 2 − y, −z)] and 1,4 intramolecular SS1···O=C interaction (3.116 Å) for one of the molecules of $CH_3OC(O)SSCF_3$ observed in the asymmetric unit.

the C–S single bond was well-established.[23,29,40,41] Furthermore, in a few cases, it has been experimentally established that the antiperiplanar conformation appears as a second stable form at ambient temperature.[42,43] In the case that Y is an –SR group, the preferred mutual orientation of the C=O bond with respect to the S–S bond is also synperiplanar.[13,17,30] The presence of an acyl group attached to the disulfide bond, as in FC(O)SSC(O)F,[17] $FC(O)SSCH_3$,[30] $FC(O)SSCF_3$,[44] $FC(O)SSC(O)CF_3$,[31] and $FC(O)SSC(O)CF_2Cl$[32] may lead to the conformational *syn-anti* equilibria. For the title species, $CH_3OC(O)SSCF_3$, the interpretation of the vibrational spectroscopy data suggests that the molecule exists in the gas phase at room temperature as a mixture of two conformers that differ in the relative orientation of the carbonyl group with respect to the S–S single bond, with a prevalence of the *syn* conformer [81(5)%], over the *anti* form. This value is well reproduced by the computational methods, which compute 80(5)% of the molecules in the most stable *syn-syn-gauche* form [ΔG° = 0.83 kcal mol^{-1} (B3LYP/6-311++G**)].

The non-symmetrically substituted disulfides $FC(O)SSCF_3$[30] and $FC(O)SSCH_3$[44] have been studied in the gas phase and possess [ϕ(CS–SC)] dihedral angles of 95.0(27) and 83.5(15)°, respectively. Recently, the molecular structure of two acyldisulfides has been experimentally determined, resulting in dihedral angles [ϕ(CS–SC)] lower than 90°: 84.2(2)° in $FC(O)SSC(O)CF_2Cl$[32] (X-ray) and 77.7(21)° in $FC(O)SSC(O)CF_3$[31] (GED). The last value corresponds to the smallest dihedral angle measured for non-cyclic disulfides in the gas phase so far. Following this trend, the S–S bond length and the [ϕ(CS–SC)] torsion angle in crystalline $CH_3OC(O)SSCF_3$ are 2.0113(15) Å and 91.06(15)°, respectively.

Conclusions

According its vibrational spectra, $CH_3OC(O)SSCF_3$ exists in the gas phase as a mixture of two conformers. At room temperature the most stable *syn-syn-gauche* form is present in a concentration of 81(5)%. This form is present as two independent and similar molecules in a single crystal of $CH_3OC(O)SSCF_3$ at 190(2) K, as deduced form the low temperature X-ray diffraction analysis.

The molecular structure of $CH_3OC(O)SSCF_3$ is characterized by a ϕ(CS–SC) dihedral angle of 91.06(15)°. Previous studies reported for disulfide containing compounds of the type RSSR reveal that dihedral angles smaller than 90° are observed in disulfides attached to two carbon atoms with sp^2 hybridization; if both carbon substituents are sp^3-hybridized, the dihedral angle is larger than 120°.[30–32] An intermediate angle has been observed in $CH_3OC(O)SSCF_3$, which contains both sp^3- and sp^2-hybridized carbon atoms bonded to the disulfide bond.

Experimental section

Hazards. The toxicological activity of $CH_3OC(O)SSCF_3$ has not been investigated so far, but it is know that serious skin burns result from contact with the adduct $Hg(SCF_3)_2$.[45]

Conventional vacuum techniques were used to condense 5.61 mmol of $CH_3OC(O)SCl$ over 2.88 mmol of $Hg(SCF_3)_2$ previously dried in vacuum at low temperatures (near 0 °C). The reaction proceeds at −30 °C with stirring for 15 min, as observed by the vanishing of the pale yellow color (due to $CH_3OC(O)SCl$). Subsequently the products were separated by repeatedly "trap-to-trap" condensation through traps held at −45, −80 and −196 °C. Pure $CH_3OC(O)SSCF_3$ (0.96 g, 89%) was retained as a colorless liquid in the −45 °C trap. The yield was nearly quantitative and only minor quantities of OCS and CO_2 were observed as by-products in the U-trap at −196 °C. $Hg(SCF_3)_2$ was synthesized by reaction of HgF_2 (97% Fluka) with CS_2 (98%, Aldrich) in a metal reactor according to the literature procedure.[45]

Instrumentation

(A) General procedure. Volatile materials were manipulated in a glass vacuum line equipped with PTFE valves (Young, London, UK) and capacitance pressure gauge (680 A, Setra System) for the control of the pressure. The vacuum line had a connection to an IR cell (optical path length 10 cm, Si windows 0.5 mm thick). This arrangement allowed us to observe the course of the reaction by FTIR spectroscopy (EQUINOX 55, Bruker). The pure compound was stored in flame-sealed glass ampoules under liquid nitrogen in a long-term Dewar vessel. The ampoules were opened with an ampoule key on the vacuum line, an appropriate amount was taken out for the experiments and then they were flame-sealed again.[46]

(B) X-Ray diffraction at low temperature. An appropriate crystal of *ca.* 0.3 mm diameter of $CH_3OC(O)SSCF_3$ was obtained on the diffractometer at a temperature of 190(2) K with a miniature zone melting procedure using focused infrared laser radiation.[33] The diffraction intensities were measured at low temperatures on a Nicolet R3m V^{-1} four-circle diffractometer. Intensities were collected with graphite-monochromatized Mo-Kα radiation using the ω-scan technique. The crystallographic data, conditions and some features of the structure are listed in Table S2 (ESI‡). The structure was solved by Patterson syntheses and refined by full-matrix least-squares method on *F* with the SHELXTL-Plus program.[47] Absorption correction details are given elsewhere. All atoms were assigned to anisotropic thermal parameters. Atomic coordinates and equivalent isotropic displacement coefficients are given in Table S3, and anisotropic displacement parameters for $CH_3OC(O)SSCF_3$ are given in Table S4 (ESI‡). X-Ray crystallographic data in CIF format is given as ESI. Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC reference number 734324. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00382g

(C) Vibrational spectroscopy. Gas phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000–400 cm^{-1} on a Bruker EQUINOX 55 FTIR spectrometer. An FT-Raman spectrum of liquid $CH_3OC(O)SSCF_3$ was run with a Bruker 66 with FRA 106 Raman accessory at a resolution of 2 cm^{-1}; the sample in a 3 mm glass capillary was excited with 100 mW of a 1064 nm Nd:YAG laser.

(D) NMR spectroscopy. For the ^1H, ^{13}C and ^{19}F NMR measurements, neat samples were flame-sealed in thin-walled 3 mm o.d. tubes and placed into 5 mm NMR tubes. The spectra were recorded with a Varian Mercury Plus spectrometer operating at 200, 50.3 and 188.2 MHz, respectively. Samples were measured at room temperature using $CDCl_3$ as an external lock and reference.

(E) GC-MS determination. The GC-MS measurements were recorded in a GCMS-QP2010 SHIMADZU instrument using gaseous helium as the mobile phase with the pressure in the column head equal to 100 kPa. The column used was a 19091J-433 HP-5 of 30 m × 0.32 mm × 0.25 mm film thickness. Approximately 1 μL volume of the compound dissolved in $C_2H_5OC_2H_5$ was chromatographed under the following conditions: the injection temperature was 200 °C, the initial column temperature (70 °C) was held for 2 min, then increased to 200 °C at 7 °C min^{-1} and held for 2 min after elevated to 300 °C at 5 °C min^{-1} and held for 2 min more. In the spectrometer the source was kept at 200 °C.

(F) Theoretical calculations. All quantum chemical calculations were performed with the GAUSSIAN03 program package.[48] Full geometry optimizations were done applying *ab initio* (MP2) and DFT (B3LYP) methods using 6-31G* and 6-311++G** basis set. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found.

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