

BRIEF COMMUNICATIONS

A COMPUTATIONAL EVALUATION OF THE STRUCTURE AND HEAT OF FORMATION OF HALOTRIFLUOROMETHYL- SULFANE COMPOUNDS $\text{XC}(\text{O})\text{SCF}_3$ ($\text{X} = \text{F}$ AND Cl)

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Enthalpies of formation ($\Delta H_{f, 298 \text{ K}}^0$ (g)) are calculated for *syn* and *anti* conformers of $\text{FC}(\text{O})\text{SCF}_3$ and $\text{ClC}(\text{O})\text{SCF}_3$ using the atomization methods with the Gaussian-*n* composite methods for which experimental values do not exist. DFT approaches and MP2 methods are employed to optimize the molecular geometries of $\text{XC}(\text{O})\text{SCF}_3$ ($\text{X} = \text{F}$ and Cl). Excellent results are obtained with the reported experimental data.

Keywords: halotrifluoromethylsulfane, quantum chemistry, *ab initio* calculations, geometric structure, enthalpies of formation.

Introduction. Compounds with the general structure $\text{XC}(\text{O})\text{SY}$ (where X and Y are halogen, CF_3 or NCO) have been synthesized since 1967 by Haas et al. [1] and generated a new family of inorganic compounds that are of great interest in atmospheric chemistry [2, 3]. Compounds such as $\text{ClC}(\text{O})\text{SBr}$ [1], $\text{FC}(\text{O})\text{SNCO}$, $\text{FC}(\text{O})\text{SCF}_3$, $\text{ClC}(\text{O})\text{SCF}_3$, $\text{FC}(\text{O})\text{SBr}$, $\text{FC}(\text{O})\text{SCl}$, and $\text{ClC}(\text{O})\text{SBr}$ [2, 3] have been synthesized by matrix isolation techniques in the gas phase. All these compounds have in common isomeric *syn* and *anti* conformations depending on the spatial orientation of the carbonyl group, as is illustrated in Fig. 1.

The $\text{FC}(\text{O})\text{SCF}_3$ and $\text{ClC}(\text{O})\text{SCF}_3$ compounds have recently been synthesized [7]; geometric structures and conformational properties were studied experimentally by gas electron diffraction. IR spectra, which identified the existence of the *syn* and *anti* conformers, were obtained in the gas phase. Identification was made straightforward by the difference between the CO vibrations of the two conformers [2]. These results obtained by Gobbato [6] and Ulic [7] were compared

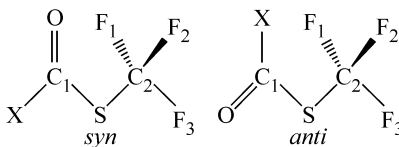


Fig. 1. Atom labeling of *syn* and *anti* conformers of $\text{XC}(\text{O})\text{SCF}_3$ ($\text{X} = \text{Halogen}$).

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with theoretical calculations at different levels of theory. The above properties have only been reported for isomers of *syn* conformation because it is the most stable conformer. For this conclusion Gobbato et al. calculated the theoretical energy differences using HF, MP2, and BPW91 methods with different basis sets for *syn* and *anti* structures. This gave differences between *syn* and *anti* of 0.98-1.24 kcal·mol⁻¹ for the FC(O)SCF₃ compound and 2.96-3.69 kcal·mol⁻¹ for the ClC(O)SCF₃ compound. The gas IR spectrum of FC(O)SCF₃ presents bands at 1846 cm⁻¹ and 1826 cm⁻¹ that correspond to bending C=O for *syn* and *anti* conformers respectively, and at 1801 cm⁻¹ for *syn*-ClC(O)SCF₃. The predictions calculated by Ulic et al. (B3LYP/6-31G*) for the harmonic vibrational frequencies overestimate the experimental values [7].

On the other hand, the high-level Gaussian-*n* (*n* ≤ 3) suite of composite methods (G3 [8], G4 [9], and their derivatives, e.g., G3B3, G3MP2B3 [10], G4MP2, G4MP3 [11]) has been widely benchmarked and employed in the thermochemical study of various compounds with less emphasis on the latest G4, G4MP2, and G4MP3 versions due to these have been developed since 2007.

In the current work, we present the enthalpy of formation ($\Delta H_f^0(g)$) and the Gibbs free energies ($\Delta G_f^0(g)$) at 298.15 K from Gaussian-*n* composite methods via the atomization approach for *syn* and *anti* FC(O)SCF₃ and ClC(O)SCF₃ compounds. Furthermore, we examine the equilibrium structures of the *syn* and *anti* conformers using high-level *ab initio* methods.

Computational details. Density functional theory and *ab initio* molecular orbital calculations have been performed using the Gaussian 09 computational package [12]. The molecular geometries of *syn* and *anti* conformers of FC(O)SCF₃ and ClC(O)SCF₃ were fully optimized using the recently developed M06-2X hybrid meta exchange-correlation functional [13] and MP2 levels of theory with the 6-311G(*d,p*) basis set [14].

The thermochemical data ($\Delta H_{f,0\text{K}}^0$ and $\Delta H_{f,298\text{K}}^0$) have been computed using the atomization approach. The total atomization energies $\sum D_0(M)$ are defined from the energy of the molecule and its atoms as

$$\sum D_0(M) = \sum_{\text{atoms}} xE_0(X) - E_0(M) - E_{\text{ZPE}}(M), \quad (1)$$

where $E_0(X)$ and $E_0(M)$ are the energies of the constituent atoms (X) and the whole molecule (M) respectively, and $E_{\text{ZPE}}(M)$ is the scaled ZPE energy of the molecule. The value x is the number of times a particular atom X appears. Then, the enthalpies of formation at 0 K $\Delta H_{f,0\text{K}}^0$ are calculated as

$$\Delta H_{f,0\text{K}}^0(M) = \sum_{\text{atoms}} x\Delta H_{f,0\text{K}}^0(X) - \sum D_0(M), \quad (2)$$

Where $\Delta H_{f,0\text{K}}^0(X)$ are the experimental enthalpies of formation at 0 K of the atoms [15, 16]. To derive the enthalpies of formation at 298.15 K $\Delta H_{f,298\text{K}}^0$, thermal corrections are added so that

$$\Delta H_{f,298\text{K}}^0(M) = \Delta H_{f,0\text{K}}^0(M) + (H_{M,298\text{K}}^0 - H_{M,0\text{K}}^0) - \sum_{\text{atoms}} x(H_{X,298\text{K}}^0 - H_{X,0\text{K}}^0), \quad (3)$$

where the thermal corrections employed for C, H, N, and O are 0.25 kcal·mol⁻¹, 1.01 kcal·mol⁻¹, 1.04 kcal·mol⁻¹, and 1.04 kcal·mol⁻¹ respectively.

The Gibbs free energy $\Delta G_{f,298\text{K}}^0$ also has been computed in this work from $\Delta H_{f,298\text{K}}^0$ obtained by atomization methods.

$$\Delta G_{f,298\text{K}}^0(M) = \Delta H_{f,298\text{K}}^0(M) - 298.15(S_{f,298\text{K}}^0(M) - \sum_{\text{atoms}} x(S_{f,298\text{K}}^0(X))), \quad (4)$$

where $S_{f,298\text{K}}^0(X)$ and $S_{f,298\text{K}}^0(M)$ are the entropy values of the constituent atoms (X) and the whole molecule (M) respectively [17, 18].

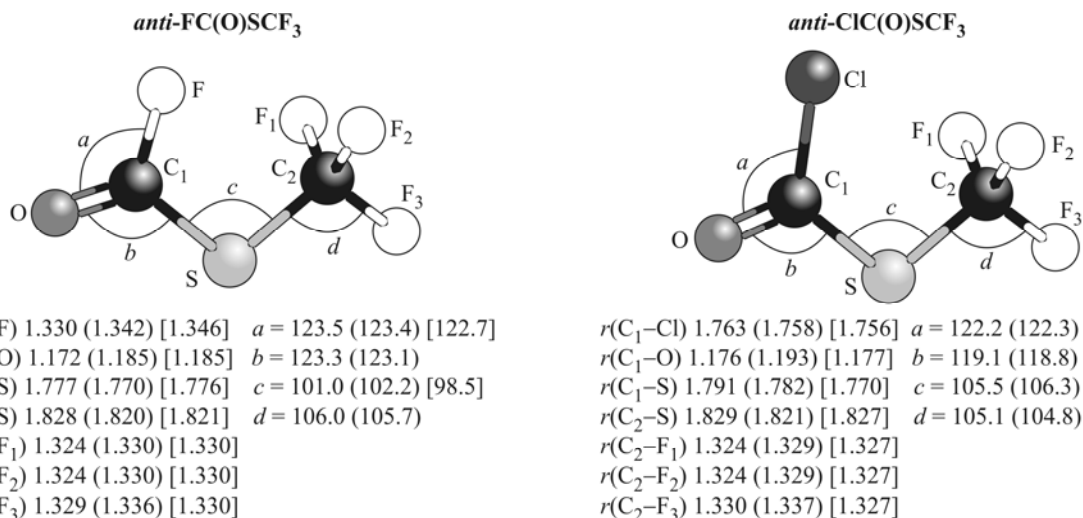


Fig. 2. Geometric parameters of *anti*-conformers of FC(O)SCF₃ and ClC(O)SCF₃ determined from optimizations at the M06-2X/6-311G(*d,p*) (plain text) and MP2/6-311G(*d,p*) (in parentheses) levels and the experimental values reported for *syn*-conformers (in brackets). Bond length units are in angstrom and angles in degrees.

TABLE 1. Geometric Parameters for *syn*-FC(O)SCF₃ and *syn*-ClC(O)SCF₃ at the M06-2X and MP2 Levels with the 6-311G(*d,p*) Basis Set. Distances in Å, Angles in deg

<i>syn</i> -FC(O)SCF ₃	M06-2X	MP2	Exp. ^a	<i>syn</i> -ClC(O)SCF ₃	M06-2X	MP2	Exp. ^a
$r(\text{C}_1\text{-F})$	1.333	1.346	1.344	$r(\text{C}_1\text{-Cl})$	1.775	1.773	1.756
$r(\text{C}_1\text{-O})$	1.171	1.184	1.185	$r(\text{C}_1\text{-O})$	1.173	1.189	1.177
$r(\text{C}_1\text{-S})$	1.778	1.769	1.776	$r(\text{C}_1\text{-S})$	1.780	1.774	1.770
$r(\text{C}_2\text{-S})$	1.827	1.820	1.821	$r(\text{C}_2\text{-S})$	1.832	1.824	1.827
$r(\text{C}_2\text{-F}_1)$	1.323	1.328	1.330	$r(\text{C}_2\text{-F}_1)$	1.322	1.328	1.327
$r(\text{C}_2\text{-F}_2)$	1.323	1.328	1.330	$r(\text{C}_2\text{-F}_2)$	1.322	1.328	1.327
$r(\text{C}_2\text{-F}_3)$	1.330	1.336	1.330	$r(\text{C}_2\text{-F}_3)$	1.330	1.337	1.327
$\angle(\text{ClC}_1\text{O})$	123.6	123.5	122.7	$\angle(\text{ClC}_1\text{O})$	123.0	123.1	122.9
$\angle(\text{ClC}_1\text{S})$	107.4	106.8	104.7	$\angle(\text{ClC}_1\text{S})$	109.6	109.3	108.0
$\angle(\text{C}_1\text{SC}_2)$	96.7	97.4	98.5	$\angle(\text{C}_1\text{SC}_2)$	97.2	97.9	98.9
$\angle(\text{SC}_2\text{F}_3)$	106.2	106.1	—	$\angle(\text{SC}_2\text{F}_3)$	106.3	106.1	—
$\angle(\text{F}_1\text{C}_2\text{F}_2)$	108.5	108.5	108.4	$\angle(\text{F}_1\text{C}_2\text{F}_2)$	108.6	108.5	108.8

^aValues taken from [6].

The enthalpies of formation and the Gibbs free energy are calculated by means of the values obtained at a higher level of theory such as composite Gaussian-*n* methods (G3, G3MP2B3, G3B3, G4MP2, and G4 [8-11]), which have an average absolute deviation from the well-known experimental enthalpies of formation of 1.07 kcal·mol⁻¹, 1.25 kcal·mol⁻¹, 1.13 kcal·mol⁻¹, 1.04 kcal·mol⁻¹, and 0.83 kcal·mol⁻¹ respectively.

Results and discussion. Equilibrium structures. The labeling of the atoms is shown in Fig. 1. The bond lengths and bond angles of *syn* and *anti* conformers of FC(O)SCF₃ and ClC(O)SCF₃ are collected in Table 1 and Fig. 2. The optimized M06-2X/6-311G(*d,p*) and MP2/6-311G(*d,p*) geometries are very similar to the experimental values reported by Gobbato et al. for the *syn*-conformers. Our M06-2X and MP2 values tend to have slightly longer bond lengths for ClC(O)SCF₃ than those obtained experimentally; for example, our values for C–Cl bond lengths are 1.775 Å and 1.773 Å at the M06-2X and MP2 levels respectively (Table 1), compared with 1.756 Å obtained experimentally and 1.766 Å obtained

TABLE 2. Calculated Atomization Energies ΣD_0 , Enthalpies of Formation ΔH_f^0 (0 K and 298 K), and Gibbs Free Energies $\Delta G_{f, 298\text{ K}}^0$ for *syn* and *anti* Conformers of FC(O)SCF₃ (in kcal·mol⁻¹)

	<i>syn</i> -FC(O)SCF ₃				<i>anti</i> -FC(O)SCF ₃			
	ΣD_0	$\Delta H_{f, 0\text{ K}}^0$	$\Delta H_{f, 298\text{ K}}^0$	$\Delta G_{f, 298\text{ K}}^0$	ΣD_0	$\Delta H_{f, 0\text{ K}}^0$	$\Delta H_{f, 298\text{ K}}^0$	$\Delta G_{f, 298\text{ K}}^0$
G3	777.1	-238.6	-240.1	-175.1	775.7	-237.2	-238.7	-173.8
G3MP2B3	776.4	-237.9	-239.3	-174.6	775.0	-236.5	-237.9	-173.2
G3B3	776.4	-237.9	-239.3	-174.6	775.1	-236.6	-238.0	-173.3
G4MP2	774.9	-236.4	-237.8	-172.9	773.4	-234.9	-236.4	-171.5
G4	775.2	-236.7	-238.1	-173.3	773.8	-235.3	-236.7	-171.9

TABLE 3. Calculated Atomization E ΣD_0 , Enthalpies of Formation ΔH_f^0 (0 K and 298 K), and Gibbs Free Energies $\Delta G_{f, 298\text{ K}}^0$ for *syn* and *anti* Conformers of ClC(O)SCF₃ (in kcal·mol⁻¹)

	<i>syn</i> -ClC(O)SCF ₃				<i>anti</i> -ClC(O)SCF ₃			
	ΣD_0	$\Delta H_{f, 0\text{ K}}^0$	$\Delta H_{f, 298\text{ K}}^0$	$\Delta G_{f, 298\text{ K}}^0$	ΣD_0	$\Delta H_{f, 0\text{ K}}^0$	$\Delta H_{f, 298\text{ K}}^0$	$\Delta G_{f, 298\text{ K}}^0$
G3	742.2	-193.6	-194.9	-130.3	739.3	-190.7	-192.0	-127.5
G3MP2B3	741.8	-193.2	-194.4	-130.2	738.7	-190.1	-191.3	-127.0
G3B3	741.2	-192.6	-193.8	-129.6	738.2	-189.6	-190.8	-126.5
G4MP2	740.9	-192.3	-193.5	-129.1	737.6	-189.0	-190.2	-125.8
G4	740.5	-191.9	-193.1	-128.7	737.3	-188.7	-189.9	-125.5

by Gobbato, also using the MP2 approach, but with a 6-31G* basis set. However, our M06-2X and MP2 values for *syn*-FC(O)SCF₃ compare reasonably well with those obtained experimentally by Gobbato.

The bond angles obtained for *syn*-XC(O)SCF₃ are very similar to those reported experimentally by Gobbato.

In this work, we reported the geometric parameters for *anti*-FC(O)SCF₃ and *anti*-ClC(O)SCF₃ determined by the same methods as above; the results are presented in Fig. 2. It also contains the experimental values of *syn*-conformers for comparison. The structural parameters obtained for *anti* conformers at the M06-2X and MP2 levels of theory are very close. For example, the values for the C–F bond lengths for the *anti* conformer of 1.330 Å and 1.342 Å at the M06-2X and MP2 levels respectively are compared with the corresponding experimental value of the *syn* conformer of 1.346 Å. We note that they have very good agreement, so we conclude that the bond distances for these compounds are typical and independent of the *syn* or *anti* conformation. Nevertheless, the most noticeable difference between these compounds at a structural level is given by the bond angle $\angle C_1SC_2$ that is slightly greater in *anti* conformers compared to *syn* conformers. The differences between the bond angles $\angle C_1SC_2(\textit{anti}) - \angle C_1SC_2(\textit{syn})$ are approximately 3.0° and 6.0° for *anti*-FC(O)SCF₃ and *anti*-ClC(O)SCF₃ conformers respectively. This is due to the presence of a variable halogen group on the *anti* conformer, which always has a greater repulsive effect on the CF₃ group than the O atom in the *syn* conformation.

Enthalpies of formation and Gibbs free energies. The total atomization energy ΣD_0 is the energy needed to dissociate a molecule into its separate atoms. These values also are reported in Tables 2 and 3. As the first step for our results, we estimate the enthalpies of formation of XC(O)SCF₃ conformers at 0K from atomization energies [19]. For this, the enthalpies of formation of F, Cl, C, S, and O atoms at 0 K of 18.47±0.1 kcal·mol⁻¹, 28.59±0.0 kcal·mol⁻¹, 169.98±0.1 kcal·mol⁻¹, 65.66±0.1 kcal·mol⁻¹, and 58.99±0.0 kcal·mol⁻¹ respectively were employed [18]. Then the derived enthalpies of formation at 0 K were transformed afterwards to 298 K using the calculated ZPE and thermal corrections and the sum ($H_{298\text{ K}}^0 - H_{0\text{ K}}^0$) of the contributions for F, Cl, C, S, and O of 1.05 kcal·mol⁻¹, 1.10 kcal·mol⁻¹, 0.25 kcal·mol⁻¹, 1.05 kcal·mol⁻¹, and 1.04 kcal·mol⁻¹ [19] respectively.

The enthalpies of formation estimated for FC(O)SCF₃ and ClC(O)SCF₃ conformers are listed in Tables 2 and 3. We can see that the composite *Gn* methods provide similar values for all the thermochemical data estimated. For example, the $\Delta H_{f, 298\text{ K}}^0$ values obtained for *syn*-FC(O)SCF₃ are $-240.1\text{ kcal}\cdot\text{mol}^{-1}$, $-239.3\text{ kcal}\cdot\text{mol}^{-1}$, $-239.3\text{ kcal}\cdot\text{mol}^{-1}$, $-237.8\text{ kcal}\cdot\text{mol}^{-1}$, and $-238.1\text{ kcal}\cdot\text{mol}^{-1}$ at the G3, G3MP2B3, G3B3, G4MP2, and G4 levels respectively.

Taking an average of the values obtained from the *Gn* composite methods, we obtained the enthalpies of formation of $-238.9\pm 0.9\text{ kcal}\cdot\text{mol}^{-1}$, $-237.5\pm 1.0\text{ kcal}\cdot\text{mol}^{-1}$, $-193.9\pm 0.7\text{ kcal}\cdot\text{mol}^{-1}$, and $-190.8\pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$ for *syn*-FC(O)SCF₃, *anti*-FC(O)SCF₃, *syn*-ClC(O)SCF₃, and *anti*-FC(O)SCF₃ respectively.

With the results presented above, we can expect the FC(O)SCF₃ isomers to be in the same proportions in a mixture due to the energy difference between them being about $1\text{ kcal}\cdot\text{mol}^{-1}$. However, the experiments show that the predominant conformer is *syn*-FC(O)SCF₃ [6].

The Gibbs free energies estimated for FC(O)SCF₃ and ClC(O)SCF₃ conformers are given in Tables 2 and 3; the average of the $\Delta G_{f, 298\text{ K}}^0$ values obtained from G3, G3MP2B3, G3B3, G4MP2, and G4 are $-174.1\pm 0.9\text{ kcal}\cdot\text{mol}^{-1}$, $-172.7\pm 1.0\text{ kcal}\cdot\text{mol}^{-1}$, $-129.6\pm 0.7\text{ kcal}\cdot\text{mol}^{-1}$, and $-126.5\pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$ for *syn*-FC(O)SCF₃, *anti*-FC(O)SCF₃, *syn*-ClC(O)SCF₃, and *anti*-FC(O)SCF₃ respectively.

In view of the difficulties of obtaining experimental values for halotrifluoromethylsulfane compounds, we suggest the above values as a new reference for the enthalpies of formation and Gibbs free energies of the compounds studied here.

Conclusions. High-level *ab initio* calculations have been carried out to study halotrifluoromethylsulfane compounds. Equilibrium structures obtained at the M06-2X and MP2 levels of theory are consistent with the available experimental values.

Accurate enthalpies of formation at 298.15 K have been calculated using Gaussian-*n* theory with atomization methods. After averaging the values obtained from the *Gn* methods at different levels of theory we determine $\Delta H_{f, 298\text{ K}}^0$ of $-238.9\pm 0.9\text{ kcal}\cdot\text{mol}^{-1}$, $-237.5\pm 1.0\text{ kcal}\cdot\text{mol}^{-1}$, $-193.9\pm 0.7\text{ kcal}\cdot\text{mol}^{-1}$, and $-190.8\pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$ for *syn*-FC(O)SCF₃, *anti*-FC(O)SCF₃, *syn*-ClC(O)SCF₃, and *anti*-FC(O)SCF₃ respectively. Therefore, given the difficulties to measure enthalpies of formation for these compounds via direct or indirect methods, we suggest the above values for further reference.

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