



Synthesis, spectroscopic and structural properties of $\text{CF}_3\text{SO}_2\text{OCCl}_3$

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ABSTRACT

Trichloromethyl trifluoromethanesulphonate, $\text{CF}_3\text{SO}_2\text{OCCl}_3$, was prepared by quantitative reaction between $\text{Ag}(\text{CF}_3\text{SO}_2\text{O})$ and BrCCl_3 . The conformational and structural properties of the gaseous molecule were studied by vibrational spectroscopy (IR (gas, liquid), Raman (liquid) and quantum chemical calculations (DFT and *ab initio* methods)).

Theoretical and experimental vibrational results evidenced the presence of a single conformer with C_1 symmetry. This result is in agreement with the adopted geometry of covalent sulphonates. The conformational preference was studied using the total energy scheme and natural bond orbital partition scheme. Additionally, the total potential-energy has been deconvoluted using six fold decomposition in terms of a Fourier-type expansion.

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1. Introduction

The structural characteristics, conformational preferences and their relation with the reactivity of simple molecules that contain different halogenated substituents are interesting because some covalent sulphonates have a remarkable alkylating agent capacity [1–4], and they are used as precursors in the synthesis of new medicinal drugs of biological interest. Although $\text{CF}_3\text{SO}_2\text{OCH}_3$ [1] is the most commonly used alkylating agent, Taylor and Martin [5] found that $\text{CF}_3\text{SO}_2\text{OCF}_3$ [2] has limited alkylating properties in case of an eventual nucleophilic attack. The $\text{CF}_3\text{SO}_2\text{-R}$ group may exhibit many activities due to its interaction with different intracellular proteins, such as enzymes or receptors [6].

Besides, structural and conformational properties of several sulphonates of the type $\text{CF}_3\text{SO}_2\text{OR}$ [1–4] with $\text{R}=\text{CH}_3$ [1], CF_3 [2], CH_2CH_3 [3], CH_2CF_3 [4] were previously studied in this laboratory. The gas-phase electron diffraction (GED) analyses of methyl triflate, $\text{CF}_3\text{SO}_2\text{OCH}_3$ [1], and trifluoromethyl triflate, $\text{CF}_3\text{SO}_2\text{OCF}_3$ [2], result in structures with *gauche* orientation of the CH_3 and CF_3 groups relative to the CF_3 group, with dihedral angles ϕ (C-S-O-C) $89(7)^\circ$ and $119.5(18)^\circ$, respectively. Quantum chemical calculations reproduced these results closely. For ethyl trifluoromethanesulphonate, $\text{CF}_3\text{SO}_2\text{OCH}_2\text{CH}_3$ [3], and for

2,2,2-trifluoroethyl trifluoromethanesulphonate, $\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_3$ [4], theoretical structural results also showed a *gauche* conformation as the most stable form.

Only in the case of fluorine and chlorine fluorosulphonates, FSO_2OF [7] and FSO_2OCl [7], the B3LYP do calculations result in a second minimum with *trans* orientation, but they are considerably higher in energy than the *gauche* conformer and they were not observed experimentally. These experimental and theoretical studies show the *gauche* orientation preference in covalent sulphonates. However, in order to analyze the influence of the CCl_3 group, we extended the study to $\text{CF}_3\text{SO}_2\text{OCCl}_3$.

$\text{CF}_3\text{SO}_2\text{OCCl}_3$ has been analyzed to obtain information about conformational and vibrational properties. The first synthesis of this compound was reported by Schmeiber et al. [8] in 1969 by reacting $\text{Hg}(\text{CF}_3\text{SO}_2\text{O})_2$ with CXCl_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) but it was characterized only by its boiling point ($122\text{--}123^\circ\text{C}$). Afterwards, Chapman et al. [9] synthesized $\text{CF}_3\text{SO}_2\text{OCCl}_3$ by the reaction of $\text{Ag}(\text{CF}_3\text{SO}_2\text{O})$ and CCl_4 . The product was characterized only by GC and ^{13}C NMR but it could not be isolated. In the present work, we obtained $\text{CF}_3\text{SO}_2\text{OCCl}_3$ by the reaction of $\text{Ag}(\text{CF}_3\text{SO}_2\text{O})$ and CBrCl_3 under milder conditions. In order to complement its characterization, ^{13}C and ^{19}F NMR, infrared and Raman spectra were obtained. The harmonic vibrational wavenumbers and scaled force fields were also calculated for this molecule.

In addition, the energy of the system in relation to the internal rotation around the S-O bond was calculated using several computational approaches and fitted to the six-fold Fourier-type

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expansion. This methodology allowed the analysis of the potential function nature, which explains the preferred conformation of this molecule. The study was complemented with a natural bond orbital (NBO) analysis, to evaluate the significance of hyperconjugative interactions and electrostatic effects on such conformation. In fact, the substitution of the H atom for F or Cl leads to a weakening of the S–O bond together with the strengthening of the next C–O bond. This fact agrees with the major electron occupancy determined in the σ^* S–O orbital of $\text{CF}_3\text{SO}_2\text{OCCl}_3$ and with the increase of the interactions between lone pairs of the sterified oxygen atom with the corresponding σ^* C–X orbital (X = Cl > F > H).

2. Materials and methods

2.1. Synthesis

Trichloromethyl trifluoromethanesulphonate, $\text{CF}_3\text{SO}_2\text{OCCl}_3$, was prepared according to the literature [8,9] with some modifications. Ag ($\text{CF}_3\text{SO}_2\text{O}$) (13 mmol) and BrCCl_3 (17 mmol, Aldrich, 98%) reacted with vigorous agitation for 10 h at 0 °C. The products were separated by trap to trap distillations, keeping traps at –50, –95 and –196 °C. $\text{CF}_3\text{SO}_2\text{OCCl}_3$ was retained in the –95 °C trap with a small amount of BrCCl_3 , which was eliminated by repetitive distillations. Ag($\text{CF}_3\text{SO}_2\text{O}$) was prepared by reaction between Ag_2CO_3 and $\text{CF}_3\text{SO}_2\text{OH}$.

The reaction and the purity of the compound were checked by IR (gas and liquid phases), Raman (liquid phase) and ^{19}F and ^{13}C NMR spectroscopy.

2.2. Instrumentation

2.2.1. General procedure

Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (280E Transducer, Setra, MA USA), three U-traps and valves with PTFE stems (Young, London, U.K.). The IR spectra of gaseous samples were recorded with an IR cell placed in the sample compartment of the spectrometer that followed the course of the reaction and the purification process. The purified compound was stored in flame-sealed glass ampoules under liquid nitrogen in a Dewar vessel. They were opened with an ampoule key in the vacuum line, an appropriate amount for the characterization and were flame-sealed again.

2.2.2. Infrared and Raman spectroscopy

Infrared spectra of $\text{CF}_3\text{SO}_2\text{OCCl}_3$ in the gas and liquid phases were recorded with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} range at room temperature using a LUMEX Infra LUM FT-02 spectrometer. An IR glass cell 100 mm optical path length and 0.5 mm thick Si windows was used to obtain gas phase spectra. AgCl windows were used to record the infrared spectra of liquid substance. Raman spectra of the liquid at room temperature were obtained using a Bruker IFS 66 spectrometer (spectral resolution 4 cm^{-1}). The 1064 nm radiation line of an Nd/YAG laser was used for excitation. The liquid sample was handled in sealed-flame capillaries (4 mm o. d.).

2.2.3. NMR spectra

For ^{13}C and ^{19}F NMR measurements, a pure sample was flame-sealed in thin-walled 4 mm o.d. tubes and placed into 5 mm NMR tubes. The NMR spectra were recorded in a Varian, Mercury Plus 200 spectrometer. The samples were measured at room temperature and CDCl_3 was used as internal lock and reference.

3. Computational details

Potential-energy curves and geometry optimizations were calculated at the MP2 [10] and DFT (B3LYP [11–13] and mPW1PW91 [14]) levels with different basis sets. DFT methods with Becke's B3 hybrid exchange functional¹¹ and the Lee–Yang–Parr non-local correlation functional (LYP) [12,13] were used. The second DFT method, mPW1PW91 [14], applies a modified Perdew–Wang exchange functional and Perdew–Wang 91 correlation functional [14]. All calculations were spin-restricted and frozen-core.

Vibrational wavenumbers were calculated from analytic second derivatives to check that the optimized structures represented minima on the potential-energy surface. Harmonic force constants calculated at the B3LYP/6-31G (d) level was subsequently used.

The potential energies associated with the CSOC dihedral angle were calculated at the B3LYP, mPW1PW91 and MP2 levels using 6-31G(d), 6-311G(d) and 6-311+G(d) [14–19] basis sets. In such calculations the torsion angle was frozen, whereas all other parameters were relaxed. The total energy curve was scanned in 10° steps using default convergence criteria as implemented in the Gaussian program [20].

Natural bond orbital (NBO) calculations were performed at the B3LYP/6-311+G(d) level using the NBO 3.0 code [21].

The harmonic force field in Cartesian coordinates calculated at the B3LYP/6-31G(d) level was transformed to a set of natural internal (local symmetry) coordinates *via* the B matrix [22], which was obtained using a standard program. Subsequently, an SQM force field was obtained using the scheme of Pulay et al. [23], in which the diagonal force constants are multiplied by scale factors f_i , f_j , ... and the corresponding interaction constants are multiplied by $(f_i \cdot f_j)^{1/2}$, adjusting the scale factors to reproduce the experimental wavenumbers as well as possible. No empirical correction of the theoretical geometry was used. The potential energy distribution was then calculated with the resulting SQM force field. The scaled force field for the *anti* conformer and determination of the potential-energy distribution were performed with the FCARTP program [24]. The atomic displacements for each vibrational mode, given by the Gaussian 03 program, were used to visualize the nature of the molecular vibrations, and were graphically represented using the GaussView program [25].

4. Results and discussion

4.1. Physical properties and spectroscopic characterization

$\text{CF}_3\text{SO}_2\text{OCCl}_3$ is a colorless liquid at room temperature and presents the characteristic odor of sulphonates molecules. This compound is unstable at ambient conditions due to its sensitivity to the temperature and moisture that produce its disproportionation.

The ^{19}F NMR spectrum exhibits one singlet signal at –74.5 ppm, which is located in the same region as compounds with CF_3 groups in their structures [26–28]. The ^{13}C NMR spectrum shows two signals, a quartet signal located at $\delta = 117.9\text{ ppm}$ ($^1J_{\text{CF}_3} = 320.2\text{ Hz}$), which corresponds to the carbon atom of the CF_3 group and assigned in comparison with other CF_3 containing compounds [26–28]. The second signal, a singlet located at $\delta = 67.4\text{ ppm}$, is attributed to the carbon of the CCl_3 group. The last observed signal is quite different from that reported by Chapman et al. (108.7 ppm) [9]. However, the present assignments agree with those derived from quantum chemical calculations (HF/6-311+(2d,p)) ($\delta_{\text{calc}} \text{CF}_3 = 114.26\text{ (q)}$; $\delta_{\text{calc}} \text{CCl}_3 = 70.52\text{ (s)}$). (See Table S1)

Additional evidences for the identity of $\text{CF}_3\text{SO}_2\text{OCCl}_3$ are given by its IR (gas, liquid) and Raman (liquid) spectra (see Fig. 1 and Table 1). The intense characteristic bands in the IR (gas) spectra located at 1455 cm^{-1} and 1143 cm^{-1} are due to the SO_2 group

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