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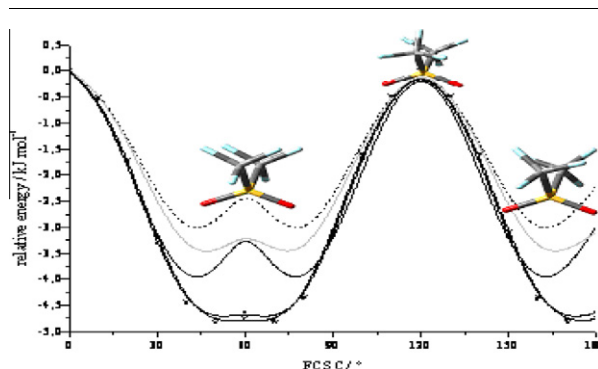
Bis (trifluoromethyl) sulfone, $\text{CF}_3\text{SO}_2\text{CF}_3$: Synthesis, vibrational and conformational properties

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HIGHLIGHTS

- ▶ The compound was characterized by vibrational spectroscopy and quantum chemical calculations.
- ▶ Quantum mechanical calculations indicate the possible existence of two conformers.
- ▶ The total potential energy was deconvoluted using a decomposition in terms of a Fourier expansion.
- ▶ Harmonic vibrational wavenumbers and a scaled force field were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

Bis (trifluoromethyl) sulfone, $\text{CF}_3\text{SO}_2\text{CF}_3$, was obtained as a byproduct in the synthesis of $\text{CF}_3\text{SO}_2\text{SCF}_3$. The compound was characterized by infrared and Raman spectroscopy as well quantum chemical calculations. Quantum mechanical calculations indicate the possible existence of two conformers symmetrically equivalent with C_2 symmetry. The preference for the *staggered* form was studied using the total energy scheme and the natural bond orbital (NBO) partition scheme. Additionally, the total potential energy was deconvoluted using a sixfold decomposition in terms of a Fourier-type expansion, showing that the hyperconjugative effect was dominant in stabilizing the *staggered* conformer. Infrared and Raman spectra of $\text{CF}_3\text{SO}_2\text{CF}_3$ were obtained. Harmonic vibrational wavenumbers and a scaled force field were calculated, leading to a final root mean-square deviation of 7.8 cm^{-1} when comparing experimental and calculated wavenumbers.

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Introduction

The sulfonyl group found large applications in organic and medicinal chemistry, both in sulfonamides, popular as a solid group for the protection of amines, and sulfones [1]. Frequently, sulfones in synthetic systems are inserted to help certain transformations. The use of sulfones, as an auxiliary group, remains

a significant synthetic strategy, especially for the formation of carbon–carbon double bond [2,3]. This functional group can change the polarity of the molecule, as an electron-withdrawing group, to stabilize carbanions or as a leaving group. In recent years the use of sulfones as intermediates in the total synthesis of many natural products has become a classic. The molecular structures of a relatively large series of sulfone derivatives have been determined. For example, the electron diffraction analysis (GED) resulted in C_2 symmetry for the $\text{CCl}_3\text{SO}_2\text{CCl}_3$ molecule, with the two CCl_3 groups rotated 12° in the opposite direction of the C_{2v} position, and tilted away from each other about 5° [4].

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Moreover, the experimental determination of the geometric parameters of $\text{CF}_3\text{SO}_2\text{CF}_3$ by GED in the gas phase was previously reported by Oberhammer [5] in 1981. The resulting symmetry for the molecule is C_2 with $\angle\text{FCF}$ of 109.6° and an effective torsional angle of 14.1° .

In addition, structural and conformational properties of several sulfones of the type $\text{CF}_3\text{SO}_2\text{R}$ with $\text{R} = \text{F}, \text{OH}, \text{NH}_2, \text{CH}_3$ [6] were previously studied in this laboratory.

In this work a complete analysis of the infrared and Raman vibrational recorded spectra for $\text{CF}_3\text{SO}_2\text{CF}_3$ is presented. The harmonic vibrational wavenumbers and scaled force fields are also calculated for this molecule and compared with related compounds [6].

Additionally, the geometric parameters obtained by quantum chemical calculations with different basis sets are compared with experimental data and with results of other sulfones.

Besides, the energy of the system, related to the internal rotation around the C–S bond, is calculated using several computational approaches and fitted to the sixfold Fourier-type expansion. This methodology allowed the characterization of the potential function nature, which explains the preferred conformation of this molecule. The study is complemented by a natural bond orbital (NBO) analysis to evaluate the significance of the hyperconjugative interactions and electrostatic effects on such conformation.

Experimental and theoretical methods

Synthesis

Bis (trifluoromethyl) sulfone, $\text{CF}_3\text{SO}_2\text{CF}_3$, was obtained as a byproduct in the synthesis of $\text{CF}_3\text{SO}_2\text{SCF}_3$, which was carried out following the literature procedure [7] with some modifications [8]. The reaction products were separated by trap to trap distillation. Pure $\text{CF}_3\text{SO}_2\text{CF}_3$ was isolated as a colorless liquid in the -95°C trap.

Infrared and Raman spectroscopy

The infrared spectrum for $\text{CF}_3\text{SO}_2\text{CF}_3$ in the gas phase was recorded in the $4000\text{--}400\text{ cm}^{-1}$ range (spectral resolution of 2 cm^{-1}) at room temperature using a LUMEX Infra LUM FT-02 spectrometer. An IR glass cell 200 mm optical path length and 0.5 mm thick Si windows was used to obtain gas phase spectra. Raman spectra of the liquid at room temperature with a resolution of 2 cm^{-1} 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 flame-sealed tubes (4 mm o.d.).

Computational details

Calculations were performed with the Gaussian 03 [9] package. Potential energy curves were calculated at the B3LYP [10–12] level using the 6-31G(d), 6-311G(d), 6-311+G(d), 6-311G(3df) and 6-311+G(3df) [13–17,10] basis sets, and two minima symmetrically equivalent were identified by rotating the S–C bond. Furthermore, the influence of the level was tested by using the functional mPW1PW91 [18] with the 6-311+G(d) basis set. The *ab initio* Møller–Plesset second order perturbations method (MP2) [19] was employed in the same way, using the 6-311G(3df) and 6-311+G(3df) basis sets. All calculations were performed in such a way, that only the given torsion (FCSC) was fixed and other parameters were allowed to relax. The total energy curve was

constructed in steps of 10° using default convergence criteria as implemented in Gaussian 03.

Geometry optimizations for $\text{CF}_3\text{SO}_2\text{CF}_3$ were performed at the MP2-31G(d) with 6-311G(d), 6-311+G(d) and 6-311G(3df) basis sets and DFT (B3LYP, mPW1PW91) approximation using 6-311G(3df) the basis set.

Additionally we compared the theoretical structures and conformations of $\text{CF}_3\text{SO}_2\text{CF}_3$ with the theoretical and experimental results previously obtained for $\text{CCl}_3\text{SO}_2\text{CCl}_3$, $\text{CBr}_3\text{SO}_2\text{CBr}_3$ [20] and $\text{CH}_3\text{SO}_2\text{CH}_3$ [4].

A natural bond orbital (NBO) calculation was performed at the B3LYP/6-311+G(d) level using the NBO 3.0 [21] code as implemented in the Gaussian 03 package.

A harmonic force field in Cartesian coordinates calculated at the B3LYP/6-311+G(d) level was transformed to a set of natural internal (local symmetry) coordinates *via* the B matrix using a standard program. The scaled quantum mechanical (SQM) force field was obtained using the scheme outlined by Pulay et al. [22], in which the diagonal force constants are multiplied by scale factors f_i, f_j, \dots and the corresponding interaction constants are multiplied by $(f_i \cdot f_j)^{1/2}$, thus adjusting the scale factors to reproduce the experimental wavenumbers as well as possible. An initial set of scale factors was refined to fit the calculated wavenumbers for the experimental data. No empirical correction of the theoretical geometry was used. The potential-energy distribution was then calculated with the resulting SQM force field. The force field for the C_2 conformation, scaling and determination of the potential-energy distribution were performed with the FCARTP program [23]. The atomic displacements given by the Gaussian 03 program for each vibrational mode were used to understand the nature of the molecular vibrations qualitatively. Hence, the corresponding data were represented graphically using the GaussView program [24].

Results/discussion

Quantum chemical calculations

The potential function for internal rotation around the C–S bond was derived by structure optimizations of the C_2 symmetry conformer at fixed FCSC dihedral angles. Potential functions obtained with several combinations of method and basis sets are shown in Fig. 1.

Minima occur at 40° and 80° , which are symmetrically equivalent (*enantiomers*). In these structures the CF_3 groups are allowed to deviate from the *staggered* position (with each other and with the SO_2 group), so that the molecule belongs to C_2 symmetry group. The curves possess two maxima, TS1 with C_s symmetry and TS2 with C_{2v} symmetry. The both conformers have imaginary wavenumbers. The higher energy transition state (TS1) shows both CF_3 groups staggered between them and with respect to the S=O bonds, whereas both CF_3 groups are eclipsed between them and staggered with respect to the S=O bonds in the lower energy transition state (TS2) (Fig. 2).

Predicted and relative energies for the C_2 conformer and the two transition states are collected in Table S1. This table shows that when the set of basis functions is extended, the stability of the *staggered* conformer increases and the energy of the TS1 transition state decreases. However, it is interesting to note that the energy of TS1 is lower at the B3LYP/6-311G(3df) level than at the B3LYP/6-311G+(3df) combination.

The geometries of the C_2 conformer were fully optimized including wavenumber calculations with the MP2 method using 6-31G(d), 6-311G(d), 6-311+G(d) and 6-311G(3df) basis sets and DFT (B3LYP, mPW1PW91) approximation with the 6-311G(3df)

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