

Molecular structure and conformations of 2-nitrobenzenesulfonyl fluoride: Gas-phase electron diffraction and quantum chemical calculations study

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ABSTRACT

The molecular structure and conformational properties of 2-nitrobenzenesulfonyl fluoride, 2-NO₂-C₆H₄SO₂F, have been studied by gas-phase electron diffraction (GED) and quantum chemical methods (B3LYP/6-311+G** and MP2/6-31G**). Quantum chemical calculations predict the existence of three conformers for 2-NO₂-C₆H₄SO₂F each of them possesses C₁ symmetry. Conformer I, in which the S–F bond of the SO₂F group is nearly perpendicular to the plane of benzene ring, is predicted to be most favored. Conformer II, in which the S–F bond is situated in opposite direction with reference to the NO₂ group, possesses intermediate energy ($\Delta E_{1-2} = 0.73$ kcal/mol (B3LYP), or 0.71 kcal/mol (MP2)), and conformer III with the S–F bond tilted to the NO₂ group possesses the higher energy ($\Delta E_{1-3} = 1.58$ kcal/mol (B3LYP), or 1.47 kcal/mol (MP2)).

The analysis of the GED intensities was carried out assuming the vapour consists of three conformers. In was obtained the conformer I dominates in vapour over solid 2-NO₂-C₆H₄SO₂F at $T = 383(5)$ K. The conformer III concentration was found to be negligible. In dominant conformer I the S–F bond is bent slightly towards the nitro group ($\phi(C-C-S-F) = 84(8)^\circ$), and the torsional angle of the nitro group with respect to the benzene ring $\phi(C-C-N-O)$ equals $125(4)^\circ$.

The conformation properties were determined by the potential energy surface analysis. The relative stability of conformers is discussed.

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1. Introduction

The reactions of aromatic sulfonyl derivatives, in particular, sulfonyl halides have played an important role in development of many fundamental concepts on which the modern organic chemistry is based, e.g. the reaction mechanisms, the neighboring group effect, the solvent effects on reactivity [1]. The greatest application among sulfonyl halides belongs to sulfonyl chlorides, which widely applied as the initial species for the synthesis of the dyes, detergents, high-temperature polymers and pharmaceutical agents, as the electrophilic reagents and the sources of Ts-radicals, etc. [1,2]. Sulfonyl fluorides, as opposed to chlorides, show the characteristic properties, as low reactivity and stability to the hydrolysis in the water, high volatility, that allows to use them as the volatile forms at the analysis by gas–liquid chromatography. Besides, the sulfonyl fluorides display rather high biological activity as a basis for the enzymatic inhibition. Thus, the different nitro- and

methyl-substituted sulfonyl fluorides find an application as possible therapeutic agents in Alzheimer's disease. The use of these agents in the context of structure/activity relationships is discussed in the literature [3].

Data on the geometrical and electronic structure as well as the conformational properties of this molecule are necessary for deeper understanding the mechanism of enzymatic inhibition under sulfonyl fluorides action, based on the known principle of complementarity substrate/enzyme.

The present study continues a systematic investigation of structural and conformational properties of methyl substituted benzenesulfonyl halides [4–7].

Infrared and NMR spectra of various substituted benzenesulfonyl halides have been reported in the literature [8]. These data, however, do not provide any information about the structural or conformational properties of these compounds. The X-ray studies carried out for 2-nitrobenzenesulfonyl chloride showed that 2-NO₂-C₆H₄SO₂Cl exists in the crystal phase as single conformer with near perpendicular orientation of the S–Cl bond with reference to the plane of benzene ring [9,10].

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The present work is devoted to studying the mutual influence of NO₂ and SO₂F groups in *ortho*-position where strong steric interactions between these groups are expected.

2. Experimental

The species 2-NO₂-C₆H₄SO₂F was prepared from a commercial sample of 2-nitrobenzenesulfonyl chloride, 2-NO₂-C₆H₄SO₂Cl. Chlorine was replaced by fluorine by heating 2-NO₂-C₆H₄SO₂Cl in water solution with fivefold molar excess of KF·HF [11]. The 2-NO₂-C₆H₄SO₂F was washed from hydrochloric acid then filtered, dried and re-crystallized twice from the solvent hexane/propane-2-ol (80/20) until a sample with a melting point of 361.0 (0.5) K was obtained (literature melting point is 362 K [12]). The gas-liquid chromatographic analysis has demonstrated the absence of *meta*- and *para*-isomers.

The electron diffraction patterns were recorded with the apparatus described previously [13]. The effusion cell of molybdenum with a cylindrical nozzle of 0.6 × 1.6 mm size (diameter × length) was used for evaporation of the samples at 383(5) K. The temperature of the effusion cell was measured by a thermocouple W/Re-5/20. The electron wavelength was obtained from diffraction patterns of polycrystalline ZnO. The mass spectra of the vapor were recorded simultaneously with the registration of the diffraction pattern. The heaviest ion was the monomeric parent ion. The details of the combined gas electron diffraction and mass spectrometric experiment (GED/MS) are listed in Table 1. The mass spectrum shown in Table 2 demonstrates that the vapor of the investigated compound consists of only one species with the stoichiometry NO₂-C₆H₄SO₂F and the detectable amount of volatile impurities in the sample is absent.

Optical densities of the plates were measured by a computer controlled MD-100 microdensitometer [14]. For the microphotometric measurements 6 plates for each, long and short camera distance, were used. A rectangular area of about 130 × 15 mm² was scanned along the diagonal of the plates. The data array for the diagonal consisted of 33 lines, 1299 points each. The step width along a scan line was 0.1 mm, and the distance between the lines was about 0.28 mm. The scanning of the plates with ZnO diffraction patterns for calibration of the electron wavelength was done with a step width of 0.0125 mm. The background functions *G*(*s*) for the intensities *I*(*s*) of the long and short camera distances were approximated by smooth lines. The analysis of the first and second order derivatives of the *G*(*s*) functions were used to examine the absence of oscillations in *G*(*s*), which could be close to the oscillations in the *sM*(*s*) function. No elimination of the frequency oscillations was done. The molecular intensities *sM*(*s*) were obtained in the ranges 3.0–31.0 Å⁻¹ and 1.4–16.1 Å⁻¹ for the short and long camera distance, respectively (Fig. 1). The molecular intensity was calculated by the formula

$$sM(s) = \frac{I(s) - G(s)}{G(s)} \cdot s.$$

Table 1
Conditions of the simultaneous GED/MS experiments.

	<i>ortho</i> -Nitrobenzenesulfonyl fluoride	
Nozzle-to-plate distance, mm	338	598
Electron beam current, μA	1.4	0.7
Accelerating voltage, kV	95.2	95.6
Temperature of effusion cell, K	382(5)	384(5)
Ionization voltage, V	50	50
Exposure time, s	90	65
Residual gas pressure, Torr	1.0·10 ⁻⁶	1.2·10 ⁻⁶
Scattering angles, Å ⁻¹	3.0–31.0	1.4–16.1

Table 2

Mass spectrum of the saturated vapour of *ortho*-nitrobenzenesulfonyl fluoride, 2-NO₂-C₆H₄SO₂F, recorded at *U*_{ioniz} = 50 V simultaneously with the diffraction pattern registration.

Ion	m/e a.u.	Abundance (relative to [SO ₂] ⁺ , %)
[SO ₂] ⁺	64	100
[C ₆ H ₄] ⁺	76	32.4
[SO ₂ F] ⁺	83	63.5
[C ₃ H ₄ S] ⁺	96	93.2
[C ₆ H ₄ S] ⁺	108	12.2
[C ₆ H ₄ NO ₂ SO] ⁺	170	4.1
[C ₆ H ₄ NO ₂ SO ₂] ⁺	186	2.0
[C ₆ H ₄ NO ₂ SO ₂ F] ⁺	205	32.4

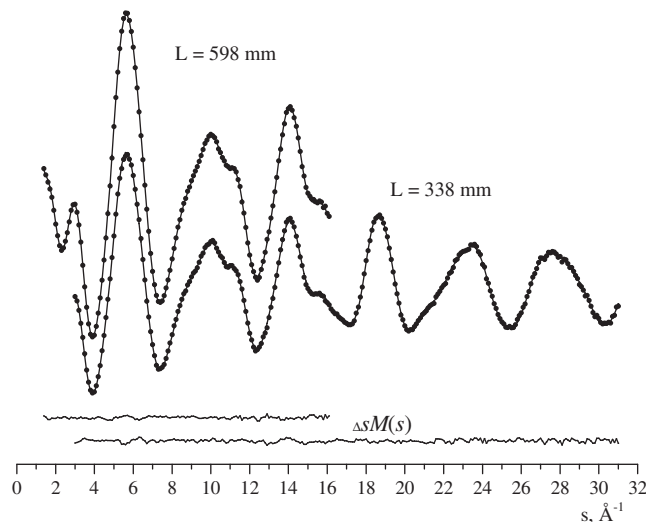


Fig. 1. Experimental (dots) and theoretical (full line) molecular intensities *sM*(*s*) and residuals for *ortho*-nitrobenzenesulfonyl fluoride for the long (a) and short (b) nozzle-to-plate distances.

3. Quantum chemical calculations

The structure optimizations and force field calculations were performed with the DFT method B3LYP/6-311+G** and with the *ab initio* approximation MP2/6-31G** using the GAUSSIAN 03 program system [15]. In the first step the search for all possible stable conformers was performed with the 2-dimensional scan of the ϕ (C2–C1–S–F) and ϕ (C1–C2–N–O) torsional angles in steps of 20° (for atom numbering see Fig. 2). The potential energy surface derived with the B3LYP method (Fig. 3) shows the presence of three conformers, all possessing C₁ symmetry with neither S–F nor N–O bond in the plane of the benzene ring. The structures of these conformers were fully optimized with the B3LYP and MP2 methods (see Fig. 2). The torsional angles ϕ (C2–C1–S–F) and ϕ (C1–C2–N–O), the relative energies and Gibbs free energies and the lowest vibrational frequencies are given in Table 3. The structural parameters of three conformers are included in Table 4.

According to relative Gibbs free energies given in Table 3 ($\Delta G_{I-II}^{\circ} = 0.60$ kcal/mol (B3LYP/6-311+G**) or 0.64 kcal/mol (MP2/6-31G**), and $\Delta G_{I-III}^{\circ} = 1.45$ kcal/mol (B3LYP/6-311+G**) or 1.40 kcal/mol (MP2/6-31G**), conformer I should be prevailing with 62.2 mol.% (B3LYP) or 63.0 mol.% (MP2) and also the concentration of conformer II is significant with 28.4 mol.% (B3LYP) and 27.1 mol.% (MP2). At the temperature of the GED experiment conformer III is predicted to possess an abundance of 9.4 mol.% (B3LYP) or 9.9 mol.% (MP2).

4. Structure analysis

A conventional least squares analysis of *sM*(*s*) was carried out using a modified version of KCED program [16]. The scattering

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