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# 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,  $2-NO_2-C_6H_4SO_2F$ , 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-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>F each of them possesses  $C_1$  symmetry. Conformer I, in which the S–F bond of the SO<sub>2</sub>F 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 NO<sub>2</sub> 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 NO<sub>2</sub> 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-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>F 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)°), and the torsional angle of the nitro group with respect to the benzene ring  $\phi$ (C–C–N–O) equals 125(4)°.

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

\* Corresponding author. E-mail address: girichev@isuct.ru (G.V. Girichev). 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- $NO_2-C_6H_4SO_2CI$  exists in the crystal phase as single conformer with near perpendicular orientation of the S–CI 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  $NO_2$  and  $SO_2F$  groups in *ortho*-position where strong steric interactions between these groups are expected.

## 2. Experimental

The species  $2-NO_2-C_6H_4SO_2F$  was prepared from a commercial sample of 2-nitrobenzenesulfonyl chloride,  $2-NO_2-C_6H_4SO_2Cl$ . Chlorine was replaced by fluorine by heating  $2-NO_2-C_6H_4SO_2Cl$  in water solution with fivefold molar excess of KF·HF [11]. The  $2-NO_2-C_6H_4SO_2F$  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  $0.6 \times 1.6$  mm size (diameter  $\times$  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 spectrum shown in Table 2 demonstrates that the vapor of the investigated compound consists of only one species with the stoichiometry NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>F 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  $130 \times 15 \text{ mm}^2$  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  $\text{\AA}^{-1}$  and 1.4–16.1  $\text{\AA}^{-1}$  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.

	ortho-Nitrobenz	ortho-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	$1.0 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$		
Scattering angles, $Å^{-1}$	3.0-31.0	1.4-16.1		

#### Table 2

Mass spectrum of the saturated vapour of *ortho*-nitrobenzenesulfonylfluoride, 2-NO<sub>2</sub>- $C_6H_4SO_2F$ , recorded at  $U_{ioniz}$  = 50 V simultaneously with the diffraction pattern registration.

Abundance (relative to [SO <sub>2</sub> ] <sup>+</sup> , %)
100
32.4
63.5
93.2
12.2
4.1
2.0
32.4



**Fig. 1.** Experimental (dots) and theoretical (full line) molecular intensities sM(s) and residuals for *ortho*-nitrobenzenesulfonylfluoride 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<sup>\*\*</sup> and with the *ab initio* approximation MP2/6-31G<sup>\*\*</sup> 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  $\phi$ (C2–C1–S–F) and  $\phi$ (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  $C_1$  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  $\phi$ (C2–C1–S–F) and  $\phi$ (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 ( $\Delta G^{\circ}_{I-II} = 0.60 \text{ kcal/mol}$  (B3LYP/6-311+G\*\*) or 0.64 kcal/mol (MP2/6-31G\*\*), and  $\Delta G^{\circ}_{I-III} = 1.45 \text{ kcal/mol}$  (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



Fig. 2. Molecular models with atom numbering: (a) conformer I; (b) conformer II; (c) conformer III.



**Fig. 3.** Calculated potential energy surface (a), and constant energy contour map (b) with conformers I, II, and III obtained by scanning along torsion angles C2–C1–S–F  $\mu$  C1–C2–N–O3 for *ortho*-nitrobenzenesulfonyl fluoride.

functions of reference [17] were used for calculation of the theoretical molecular intensities. The starting values for bond distances and angles were taken from the B3LYP/6-311+G<sup>\*\*</sup> calculations. Vibrational corrections,  $\Delta r = r_{h1} - r_{a}$ , and the starting values for vibrational amplitudes were derived from the B3LYP/6-311+G<sup>\*\*</sup> force field, using the curvilinear approach of Sipachev (program SHRINK) [18].

#### Table 3

Calculated relative energies and Gibbs free energies (kcal/mol) of the three stable conformers of *ortho*-nitrobenzenesulfonylfluoride.

B3LYP/6-311+G**	Conformer I	Conformer II	Conformer III
φ(C2-C1-S-F)	81.8	159.8	45.1
$\phi$ (C1–C2–N–O3)	134.2	27.0	36.3
$\Delta E$ , kcal/mol	0.0	0.73	1.58
$\Delta G^{\circ}$ <sup>a</sup> , kcal/mol	0.0	0.60	1.45
$v_1$ , cm <sup>-1</sup>	46	31	35
MP2/6-31G**			
$\phi$ (C2–C1–S–F)	80.6	156.8	42.4
$\phi$ (C1–C2–N–O3)	137.5	32.8	39.5
$\Delta E$ , kcal/mol	0.0	0.71	1.47
$\Delta G^{\circ}$ <sup>a</sup> , kcal/mol	0.0	0.64	1.40
$v_1$ , cm <sup>-1</sup>	55	45	47

<sup>a</sup> At T = 383 K.

The following assumptions were made to describe the molecular geometry of each conformer: (1)  $C_1$  overall symmetry was assumed for each conformers; (2) all atoms of the N-C<sub>6</sub>H<sub>4</sub>-S fragment lie in the same plane; (3) all C<sub>Ph</sub>-H bonds in the ring possess equal length and bisect the adjacent C-C-C angle; (4) differences between N=O, S=O bond lengths, between C-C bond lengths as well as C-C-C bond angles in the benzene ring, and between O=N-C, O=S-C, O=S-F bond angles are constrained to calculated values; (6) vibrational amplitudes were collected in 11 groups, including two groups for the distances involving the hydrogen atoms. The differences within each group were constrained to calculated values. The molecular structures were constructed with 17 independent structural parameters for three conformers of 2- $NO_2$ -C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>F ( $p_1$  to  $p_{17}$  in Table 4). In the LS-analysis the following parameters were refined independently: 7 bond distances (C1-C2,  $C_{Ph}$ -H, C1–S, C2–N, S–F, S=O, N=O), six bond angles ( $\angle$ C2–C1– C6, ∠C1–S–F, ∠C1–S–O1, ∠O1–S–F, ∠C2–N–O3, ∠C1–C2–N), and four torsion angles for the conformers I and II ( $\phi$ (C2–C1–S–F) and  $\phi$ (C1–C2–N–O3). All parameters of the conformers II and III, excluding the torsion angles, were tied to those of the conformer I using the calculated differences.

On the first step of LS-analysis we assumed that the vapour consisted of only one species – conformer I, or conformer II, or conformer III. The theoretical intensities were calculated separately for each conformer on the base of structural parameters (r, l) fixed in LS-analysis at the values obtained by B3LYP/6-311+G<sup>\*\*</sup>, and the scale-factor was refined only. For each conformer the reasonable agreement between experimental and theoretical functions sM(s)had not been achieved ( $R_f$  = 16.5%, 24.4% and 19.9% for I, II and III conformers correspondingly). Main reason of bad agreement is the large differences between the calculated and experimental S=0, S-F and S-C bond lengths.

#### Table 4

Experimental and calculated structural parameters of ortho-nitrobenzenesulfonylfluoride, 2-NO2-C6H4SO2F, (distances in Å, angles in deg.).

Parameter	Conformer I		Conformer II		Conformer III	Conformer III	
	GED r <sub>h1</sub>	B3LYP 6-311+G** r <sub>e</sub>	GED r <sub>h1</sub>	B3LYP 6-311+G** r <sub>e</sub>	GED r <sub>h1</sub>	B3LYP 6-311+G** r <sub>e</sub>	
	structure	structure	structure	structure	structure	structure	
C-H	$1.101(9)^{a} p_{1}$	1.083	$1.101(9)^{a}(p_{1})$	1.082	$1.101(9)^{a}(p_{1})$	1.082	
C1-C2	1.410(3) p <sub>2</sub>	1.399	$1.412(3)(p_2)$	1.401	$1.412(3)(p_2)$	1.401	
C2-C3	$1.398(3)(p_2)$	1.387	$1.399(3)(p_2)$	1.388	$1.400(3)(p_2)$	1.389	
C3-C4	$1.403(3)(p_2)$	1.393	$1.402(3)(p_2)$	1.391	$1.402(3)(p_2)$	1.391	
C4-C5	$1.402(3)(p_2)$	1.391	$1.401(3)(p_2)$	1.390	$1.401(3)(p_2)$	1.390	
C5-C6	$1.404(3)(p_2)$	1.393	$1.405(3)(p_2)$	1.394	$1.405(3)(p_2)$	1.393	
C1-C6	$1.404(3)(p_2)$	1.393	$1.405(3)(p_2)$	1.393	$1.404(3)(p_2)$	1.394	
C–S	$1.757(5) p_3$	1.801	$1.773(5)(p_3)$	1.817	$1.767(5)(p_3)$	1.811	
S–F	$1.527(5) p_4$	1.625	$1.554(5)(p_4)$	1.651	$1.533(5)(p_4)$	1.631	
S-01	$1.410(4) p_5$	1.440	$1.409(4)(p_5)$	1.439	$1.408(4)(p_5)$	1.438	
S-02	$1.414(4)(p_5)$	1.444	$1.409(4)(p_5)$	1.438	$1.415(4)(p_5)$	1.444	
C–N	1.483(8) p <sub>6</sub>	1.484	$1.481(8)(p_6)$	1.481	$1.484(8)(p_6)$	1.484	
N-03	1.212 (3) p <sub>7</sub>	1.221	$1.212(3)(p_7)$	1.221	$1.209(8)(p_7)$	1.218	
N-04	$1.209(3)(p_7)$	1.218	$1.211(3)(p_7)$	1.220	$1.214(10)(p_7)$	1.222	
∠C2-C1-C6	119.5(1) p <sub>8</sub>	119.4	$118.9(1)(p_8)$	118.8	$119.1(1)(p_8)$	119.1	
∠C1-C2-C3	$120.7(1)(p_8)$	120.6	$121.1(1)(p_8)$	121.0	$120.6(1)(p_8)$	120.5	
∠C2-C3-C4	119.3(6) (p <sub>8</sub> )	119.7	$119.4(6)(p_8)$	119.7	119.7(6) (p <sub>8</sub> )	120.0	
∠C3-C4-C5	120.6(9) (p <sub>8</sub> )	120.1	$120.2(9)(p_8)$	119.8	$120.4(9)(p_8)$	119.9	
∠C4–C5–C6	119.8(6) (p <sub>8</sub> )	120.1	$120.1(6)(p_8)$	120.5	119.8(6) (p <sub>8</sub> )	120.1	
∠C1-C6-C5	$120.1(1)(p_8)$	120.1	$120.2(1)(p_8)$	120.2	$120.4(1)(p_8)$	120.3	
∠C1–S–F	98.9(14) p <sub>9</sub>	100.3	$94.6(14)(p_9)$	96.1	$97.0(14)(p_9)$	98.5	
∠C1-S-01	$110.4(5) p_{10}$	110.7	$110.6(5)(p_{10})$	110.8	$113.0(5)(p_{10})$	113.3	
∠C1-S-02	$108.1(5)(p_{10})$	108.3	$111.5(5)(p_{10})$	111.8	$107.1(5)(p_{10})$	107.4	
∠01–S–F	108.6(9) p <sub>11</sub>	108.2	$105.8(9)(p_{11})$	104.4	$108.9(9)(p_{11})$	107.7	
∠02–S–F	$106.5(9)(p_{11})$	105.3	$105.8(9)(p_{11})$	104.5	$106.9(9)(p_{11})$	105.7	
∠01-S-02	121.9(17)	122.5	124.1(17)	124.5	121.0(17)	121.6	
∠C2-C1-S	$124.4(1)(p_8)$	124.4	$122.7(1)(p_8)$	122.6	127.0(1) (p <sub>8</sub> )	126.9	
∠C2-N-O3	116.5(5) p <sub>12</sub>	117.1	116.6(5) (p <sub>12</sub> )	116.6	117.3(5) (p <sub>12</sub> )	117.4	
∠C2-N-O4	116.9(5) (p <sub>12</sub> )	116.6	117.3(5) (p <sub>12</sub> )	117.3	116.4(5) (p <sub>12</sub> )	116.6	
∠03-N-04	126.3(7)	126.3	125.8(7)	125.8	125.8(7)	126.0	
∠C1-C2-N	$123.1(1) p_{13}$	123.0	$122.2(1)(p_{13})$	122.2	123.5(1) (p <sub>13</sub> )	123.4	
∠C2–C1–S–F	83.8(76) p <sub>14</sub>	81.8	147.2(86) p <sub>16</sub>	159.8	45.1	45.1	
∠C1-C2-N-	125.1(41) p <sub>15</sub>	137.0	24.6(168) p <sub>17</sub>	27.0	36.3	36.3	
03							
Mole fraction	0.74(6)	0.66	0.26(10)	0.30	0.0(6)	0.04	
R <sub>f</sub> , %	2.62						

<sup>a</sup> The total error limit in interatomic distances was estimated by formula  $\sigma = ((2.5\sigma_{LS})^2 + (0.002r)^2)^{1/2}$ , total error in the angles was taken to be equal  $3\sigma_{LS}$  (in the units of last significant digit).

<sup>b</sup>Errors in determination of the mole fraction are calculated on the basis of analysis criterion Hamilton [19].

On the second step of LS-analysis the theoretical function sM(s) for individual conformers was adjusted to experimental one varying the all mentioned above parameters excluding the torsion angles. The differences between experimental and theoretical functions f(r) were observed in the conformation dependent region 2.45–5.20 Å only. The value  $R_f$  was equal 3.53%, 9.30% and 8.70% for I, II and III conformers correspondently. These calculations testify to the first conformer predominates in the vapour at T = 383 K.

On the third step of LS-analysis the theoretical function *sM*(*s*) was calculated taking into account the contribution of the all three conformers. The coefficients  $\chi 1$ ,  $\chi 2$  and  $\chi 3$  corresponded to conformer mole fractions were changed discretely in the range from 0.60-1.00, 0.00-0.40 and 0.00-0.30 correspondingly, while the structural parameters of conformers were refined in the LS-analysis excepting torsional angles in the conformer III. The minimal  $R_f$  = 2.62% was achieved for the values of mole fractions  $\gamma 1 = 0.76$ ,  $\gamma 2 = 0.24$ ,  $\chi$ 3 = 0.00. Six correlation coefficients had an absolute value larger than 0.7:  $p_2/p_8 = -0.91$ ,  $p_2/p_{14} = 0.74$ ,  $p_4/p_5 = 0.80$ ,  $p_6/p_{17} = -0.70$ ,  $p_{12}/p_{17} = 0.78$ ,  $u_4/p_{11} = 0.94$ . The experimental and calculated geometric parameters of all three conformers are listed in Table 4. The interatomic distances, vibrational amplitudes and vibrational corrections for the prevailing conformer I are listed in Table 5 and those for the minor conformers II and III are given as Supplementary Material (Tables S1 and S2). The experimental radial distribution function, which is derived by Fourier transformation of the experimental intensities, is shown in Fig. 4.

## 5. Discussion

## 5.1. Conformational vapor composition and conformation properties

On diagram in Fig. 5 the refinement of the conformational vapor composition is illustrated. Each point on this diagram corresponds to the solution (refined structures, vapor compositions and  $R_f$ ) obtained by LS-analysis described above as the third step.

The bounded by solid curve points satisfy to Hamilton [19] criteria at the significance level 0.05 (m = 26, n = 429). The best value  $R_f$  = 2.62%, which corresponds to the optimal conformational vapor composition 76% conformer I, 24% conformer II, and 0% conformer III, is given on diagram as the circle.

The standard quantum chemical calculations at the B3LYP/6-311+G\*\* theory level was performed to predict the vapor composition at the temperature 383 K. The vapor composition (in mole fraction)  $\chi_1$  = 0.622,  $\chi_2$  = 0.284 and  $\chi_3$  = 0.094 calculated by Gibbs free energy (Table 3) and marked on the diagram by asterisk, differs significantly from the composition obtained by LS-analysis. The Gaussian 03 program calculates the vibration contribution of the Gibbs free energy at the temperature different from 0 K summing an infinite large progression of vibrational levels of the molecule.

The potential energy surface analysis (see Figs. 3 and 6) suggests that this approach overestimates the relative concentration of conformer III significantly. The more realistic estimation of the

### Table 5

Experimental interatomic distances, experimental and calculated vibrational amplitudes and vibrational corrections (without non-bonded distances involving hydrogen atoms) for *ortho*-nitrobenzenesulfonylfluoride,  $2-NO_2-C_6H_4SO_2F$ , (conformer I).

Parameter	r <sub>a</sub>	l <sub>exp.</sub>	l <sub>calc.</sub>	$\Delta r = r_{\rm h1} - r_{\rm a}$	No. grou
С3-Н	1.096(4) <sup>a</sup>	0.079(1)	0.075	0.005	1
N-03	1.211(1)	0.042(1)	0.039	0.001	1
N-04	1.208(1)	0.042(1)	0.039	0.001	1
C2-C3	1.396(1)	0.043(0.4)	0.046	0.002	2
$C_{3}-C_{4}$	1.401(1) 1.402(1)	0.043(0.4)	0.045	0.001	2
C1-C6	1.402(1)	0.043(0.4)	0.045	0.001	2
C6-C5	1.403(1)	0.043(0.4)	0.046	0.001	2
C1-C2	1.408(1)	0.044(0.4)	0.046	0.002	2
S-01	1.409(1)	0.033(0.4)	0.036	0.001	2
S-02	1.413(1)	0.033(0.4)	0.036	0.001	2
C2-N	1.481(3)	0.050(0.4)	0.053	0.002	2
5-F C1 S	1.526(1) 1.755(1)	0.046(0.4)	0.048	0.001	2
03-04	2155(1)	0.002(1)	0.033	0.002	4
C2-04	2.292(2)	0.055(2)	0.063	0.004	4
C2-03	2.296(3)	0.056(2)	0.064	0.004	4
F-01	2.383(5)	0.064(2)	0.072	0.004	4
F-02	2.354(5)	0.066(2)	0.074	0.004	4
C2-C4	2.412(3)	0.048(2)	0.056	0.006	4
C6-C2	2.425(2)	0.048(2)	0.056	0.006	4
C5-C5 C6-C4	2.432(3) 2.433(3)	0.048(2)	0.056	0.005	4 4
C1-C5	2.423(3) 2.428(2)	0.048(2)	0.056	0.005	4
C1-C3	2.435(2)	0.048(2)	0.056	0.005	4
C3-N	2.440(3)	0.058(2)	0.066	0.006	4
01-02	2.465(7)	0.051(2)	0.059	0.004	4
C1-F	2.493(9)	0.087(2)	0.095	0.006	4
C1-N	2.538(3)	0.059(2)	0.067	0.007	4
C1-02 C1-01	2.569(3)	0.077(2)	0.085	0.005	4
C6-S	2.004(3)	0.000(2)	0.074	0.004	5
03-01	2.750(34)	0.227(3)	0.235	-0.010	5
C2-C5	2.795(3)	0.055(3)	0.063	0.007	5
C1-C4	2.798(4)	0.056(3)	0.063	0.007	5
C2-S	2.799(1)	0.068(3)	0.076	0.008	5
C6-C3	2.808(3)	0.055(3)	0.063	0.006	5
C8-02	2.815(7)	0.091(3) 0.126(3)	0.098	0.019	5
N-01	2.897(20)	0.107(3)	0.105	0.020	5
C1-03	2.964(9)	0.144(3)	0.152	-0.003	5
F-03	3.065(47)	0.292(1)	0.300	-0.040	6
C2-01	3.100(9)	0.069(1)	0.076	0.016	6
S-03	3.124(19)	0.224(1)	0.232	-0.014	6
N-S	3.214(3)	0.109(1)	0.117	0.007	6
C2-F C6-F	3.310(10)	0.134(1) 0.145(1)	0.142	0.012	6
C3-03	3.359(8)	0.145(1) 0.126(1)	0.133	0.032	6
C1-04	3.409(12)	0.136(1)	0.144	0.032	6
04-01	3.482(40)	0.308(1)	0.317	0.079	6
N–F	3.569(32)	0.178(1)	0.186	0.010	6
C4-N	3.734(3)	0.075(4)	0.067	0.013	7
C6-01	3.797(8)	0.128(4)	0.120	0.003	7
C2-02	3.802(4) 3.881(4)	0.077(4) 0.161(4)	0.069	0.015	7
C5-S	3.998(2)	0.078(4)	0.068	0.014	7
C3-S	4.078(2)	0.084(4)	0.074	0.015	7
S-04	4.068(24)	0.303(4)	0.293	0.059	7
C4-04	4.190(12)	0.151(4)	0.141	0.009	7
C5-02	4.201(6)	0.120(4)	0.110	0.027	7
C5-N	4.268(5)	0.081(4)	0.071	0.016	/
C3-01	4.296(7)	0.143(2) 0.076(2)	0.135	0.005	0 8
C3-F	4.517(12)	0.157(2)	0.167	0.020	8
C5-F	4.519(21)	0.165(2)	0.175	0.025	8
03-02	4.522(19)	0.233(2)	0.243	-0.0001	8
N-02	4.543(7)	0.225(2)	0.235	0.008	8
C4-S	4.542(4)	0.063(2)	0.072	0.018	8
C4-03	4.572(7)	0.116(2) 0.115(2)	0.126	0.031	8 8
F-04	4 640(29)	0.113(2) 0.208(2)	0.125	0.054	8
C5-04	4.900(5)	0.119(3)	0.106	0.024	9
C5-03	4.954(5)	0.119(3)	0.106	0.020	9

Table 5 (continued)

Parameter	r <sub>a</sub>	l <sub>exp.</sub>	l <sub>calc.</sub>	$\Delta r = r_{\rm h1} - r_{\rm a}$	No. group
C3-02	4.980(4)	0.167(3)	0.154	0.020	9
C5-01	4.979(7)	0.139(3)	0.126	0.012	9
C4–F	5.006(13)	0.190(3)	0.177	0.026	9
C4-02	5.099(6)	0.144(3)	0.131	0.027	9
C4-01	5.241(5)	0.120(3)	0.107	0.022	9
04-02	5.314(34)	0.493(3)	0.480	0.073	9

<sup>a</sup>  $\sigma_{\rm LS}$  in brackets.

vapor composition could be derived taking into account the depth of the potential well corresponded to the conformer III.

In Fig. 3b, the extremal for the transition "conformer II  $\rightarrow$  saddle point A  $\rightarrow$  conformer I  $\rightarrow$  saddle point B  $\rightarrow$  conformer III" is shown. In Fig. 6, the profile of potential energy surface along this path II  $\rightarrow$  A  $\rightarrow$  I  $\rightarrow$  B  $\rightarrow$  III is given as the potential function of the internal rotation of group SO<sub>2</sub>F around the bond S–C1. The potential function was calculated scanning the value  $\phi$ (C2–C1–S–F) and refining all other geometrical parameters including torsion angle  $\phi$ (C1–C2–N–O3).

Both computational methods B3LYP/6-311+G\*\* and MP2/6-31G\*\* predict very similar potential function with three minima. The barrier between conformers I and III is 1.79 kcal/mol (B3LYP/6-311+G\*\*) or 1.85 kcal/mol (MP2/6-31G\*\*) and were measured from the energy minima. The barrier between conformers I and II is 2.11 kcal/mol (B3LYP/6-311+G\*\*) or 2.61 kcal/mol (MP2/6-31G\*\*). The conformer I possesses the highest stability. The relative energy of conformer III testifies to its lowest stability. These results don't contradict the conformer concentrations obtained by GED.

The lowest vibrational mode  $v_1$  for all three conformers corresponds to the mixed torsion movement of two groups SO<sub>2</sub>F and NO<sub>2</sub>. The energy of the saddle points A and B exceed the thermal energy RT at the temperature of GED experiment (dots line in Fig. 6) by two times. It means that small relative number of the molecules overcome the potential barriers.

In harmonic approximation the potential well of the conformer III contains only four energy levels of vibrational mode  $v_1$ . If the energy of conformer is higher than the energy barrier  $E_A$ , the vibration state of molecule could be considered as the vibration state of conformer I possessed a very strong anharmonicity rather than as the exited vibrational state of the conformer III.

The conformer composition in equilibrium mixture calculated on the base  $\Delta G^{\circ}$  (383 K) values (Table 3) gives the highest limit of conformer III concentration due to taking into account the infinite large progression of vibrational levels (statistical sum of  $v_1$ mode  $Q_{vib}(v_1) = 7.8$  at T = 383 K). If we keep the statistical sum for other vibrational modes but for mode  $v_1$  take into account four vibrational levels only (the value of  $Q_{vib}(v_1)$  equals 3.1) conformer composition is changed from 62.2/28.4/9.4 to 66.2/29.8/4.0 mol.%. This composition is marked by square on the diagram in Fig. 5 and are close to the conformational composition obtained by GED.

We carried out LS-analysis with the fixed conformer composition 66.2/29.8/4% varying all 17 geometrical parameters and 9 amplitude groups ( $R_f$  = 2.64%). The value of the structural parameters obtained in this refinement are very close to the parameters corresponded to best  $R_f$  equals 2.62% (the discrepancy is about 0.002 Å in bond distances and 0.1–0.2° in bond angles).

## 5.2. Structural parameters of conformers

The calculated structural parameters of three conformers are very close to the experimental parameters excluding bond lengths involving sulphur, especially the S–F and S=O bonds. It is well known that calculations with relatively small basis sets



Fig. 4. Experimental (dots) and theoretical (full line) radial distribution function for *ortho*-nitrobenzenesulfonyl fluoride and residual curve for optimal mixture.



**Fig. 5.** The ternary diagram of conformer composition. The bounded by solid curve points satisfy to Hamilton criteria at the significance level 0.05. The circle corresponds to best value  $R_f = 2.62\%$ . The asterisk and the square mark the vapor compositions calculated using standard and corrected vibrational statistical sum correspondingly (see the text).

overestimate S–X bond lengths if X is an electronegative element. The addition of diffuse functions to the basis set makes the agreement between theory and experiment closer but does not solve the problem completely (Table 4). A reasonable agreement was obtained between the experimental and calculated values of vibrational amplitudes (Table 5 and Supplementary materials S1 and S2).

The NBO-analyses was carried out studying the orbital and steric interactions, which affect the stability of conformers. It was found the interaction between  $\pi$ (C–C) bonding orbitals and  $\sigma$ \*(S–F) and  $\sigma$ \*(S–O) antibonding orbitals occur.

The conformer I possesses the largest value of orbital effect  $(\pi(C-C) + \sigma^*(S-F) = 7.09 \text{ kcal/mol})$ . In conformer I the torsion angle between S–F bond and the plane of benzene ring is about 82°, and it leads to remarkable orbital interaction.

In conformer II the orbital interaction exists between  $\pi(C-C) \rightarrow \sigma^*(S-O2)$  and  $\pi(C-C) \rightarrow \sigma^*(S-O1)$ . The energy of these interactions (2.55 kcal/mol and 1.42 kcal/mol correspondingly) correlate with the value of torsion angles O2–S–C–C  $\approx$ 90°, and O1–S–C–C  $\approx$ 51°.



**Fig. 6.** Calculated potential functions for internal rotation around the C1–S bond in *ortho*nitro-benzenesulfonylfluoride.

In conformer III no one bond of group SO<sub>2</sub>F lies in near perpendicular plane to benzene ring. The larges torsion angle O1–S–C–C is equal 69°. The energy of  $\pi$ (C–C)  $\rightarrow \sigma$ \*(S–O1) interaction is 2.94 kcal/mol is lower than sum of similar interactions mentioned above in conformer II. But in conformer III the strong interaction of  $\pi$ (C–C)  $\rightarrow \sigma$ \*(S–F) with energy 4.0 kcal/mol occur in spite of the torsion angle F–S–C–C value in 45° only.

Thus the analysis of the orbital interactions between  $\sigma^*$  orbitals of SO<sub>2</sub>F fragment and  $\pi$ -system of benzene ring allow to conclude the conformer I can be more stable in comparison with the conformers II and III, but can't say about any preference for II in comparison with conformer III.

Besides the orbital interaction the steric interaction between groups  $SO_2F$  and  $NO_2$  was studied in each conformer. The steric interaction was found to be higher in conformer II.

The analysis of C1–C2, C1–S and C2–N bond order shows the C1–C2 bond order are the same in all conformers while the bond C1–S is stronger in conformer I, and the bond C2–N1 is stronger in conformer II.

Perhaps the prevailing of conformer II over conformer III is connected with lower angle strain C2–C1–S in conformer II due to the value of this bond angle is close to 120°, whereas this bond angle in conformer III equals to 127°.

According to the calculations all conformers are flexible and possess approximately equal electric dipole moments ( $\mu_I$  = 7.37 D,  $\mu_{II}$  = 7.59 D,  $\mu_{II}$  = 7.24 D; B3LYP/6-311+G\*\*), but they have different distribution of electrostatic potentials and steric accessibility of O and F atoms of SO<sub>2</sub>F group. Probably these factors affect the reactivity difference of the conformers. Due to the low values of conformational

barriers the molecule can adjusted to surrounded space shaping the energetic preferable configuration.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.12.005.

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