



The difference between gas-phase and crystal structures of *ortho*-nitromethylbenzenesulfonate. Conformation variety study of free molecules by electron diffraction and quantum chemistry



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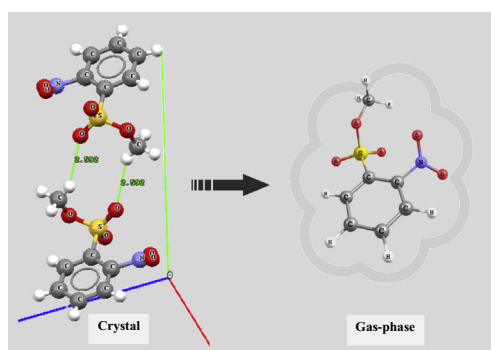
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HIGHLIGHTS

- *Ortho*-nitromethylbenzenesulfonate molecules possess six conformers.
- The structure of each conformer is determined by *ortho*- and *cog wheel* effects and by anomeric effects inside SO₂OCH₃ group.
- According to gas-phase electron diffraction data, the conformer of lowest calculated energy predominates in vapor at 380 K.
- In the crystal the molecular structure is similar to a high energy conformer.

GRAPHICAL ABSTRACT



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ABSTRACT

The conformational composition of the vapor ($T = 380(5)$ K) and the conformer structures of *ortho*-nitromethylbenzenesulfonate (NO₂–C₆H₄–SO₂–OCH₃, 2-NMBS) molecule have been studied by a combined gas-phase electron diffraction and mass spectrometry (GED/MS) method complemented by the results of quantum chemical calculations. According to calculations (MP2/B3LYP, cc-pVTZ), the molecule 2-NMBS possesses six conformers with relative energies $\Delta E = 0/0$; 0.54/1.08; 0.69/0.89; 0.81/1.77; 1.68/2.22 and 2.94/2.91 kcal/mol. The geometrical parameters (Å and degrees) of the prevailing conformer were determined by GED (uncertainties are in parentheses): $r_{h1}(C-C)_{av} = 1.400(5)$, $r_{h1}(C-S) = 1.781(6)$, $r_{h1}(S-O) = 1.588(5)$, $r_{h1}(S=O)_{av} = 1.427(10)$, $r_{h1}(C-N) = 1.469(15)$, $r_{h1}(C-O) = 1.487(16)$, $r_{h1}(N-O)_{av} = 1.236(10)$, $\varphi(C-C-S-O) = -96(7)$, $\varphi(C-S-O-C) = 139(9)$. It is shown that the relative orientation of SO₂–OCH₃ and NO₂ groups in the structure of each of the six conformers is determined by *ortho*- and *cog wheel* effects and by anomeric effects inside the SO₂–OCH₃ group. The reliability of the structure estimation of free 2-NMBS molecules on the base of X-ray data is discussed.

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Introduction

The esters of aromatic sulfonic acids (arenesulfonates) are widely used in substitution and elimination reactions, when a sulfonate-anion ArSO₃[−] is a leaving group. They are known as

alkylation agents and as the precursors for syntheses of many pharmaceuticals, dyes, crop protections and other [1–4]. Aromatic sulfonates are used in monitoring merging of lipids [5]. They have been successfully applied as photoacid generators in a deep-UV resisting system [6]. *Ortho*-nitrobenzenesulfonic group is the best leaving group compared to the tosylate, methanesulfonate or mesylate [7]. Recently the interaction of *p*-nitrobenzenesulfonate

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anions with halides in micellar solutions and ionic liquids was studied [8].

Possessing several non-rigid torsional coordinates, aromatic sulfonates demonstrate structural flexibility. Due to this feature, aromatic sulfonates are promising as building blocks in supramolecular chemistry.

Information about the conformational properties of free molecules of *ortho*-nitrobenzenesulfonic acid methyl ester (*ortho*-nitromethylbenzenesulfonate, 2-NO₂-C₆H₄-SO₂OCH₃, 2-NMBS) is missing in the literature. The Cambridge Structural Database reports the geometric structure of crystalline anhydrous 2-NMBS [9]. However, the conformational properties of the molecule can be masked because the intermolecular interaction in crystal.

Structurally, the 2-NMBS molecule is interesting due to the presence of three non-rigid torsional coordinates in the SO₂OCH₃ fragment that causes a conformational variety and by the presence of two substituents in the benzene ring at *ortho*-position which increases the conformational barriers. In this paper, we report the conformational properties of free *ortho*-nitromethylbenzenesulfonate molecules using gas-phase electron diffraction in combination with quantum chemical calculations and analyze the difference between molecular structures in gas and crystal [9].

Experimental details

Combined GED/MS experiments were carried out using a technique described earlier [10,11] which allow monitoring the vapor composition simultaneously with diffraction patterns recording.

The sample of 2-NMBS was evaporated from a stainless steel (X18H10T) effusion cell with a cylindrical nozzle of 0.6 × 1.8 mm size (diameter × length). The ratio of the evaporation area to the effusion orifice area was above 200. Diffraction patterns were recorded from short, $L = 338$ mm, and long, $L = 598$ mm, camera distances. Six diffraction patterns of gaseous 2-NMBS and two diffraction patterns of polycrystalline standard ZnO were recorded from each camera distance. The main conditions of combined GED/MS experiments are listed in Table 1.

According to the mass spectrometric data [12], 2-NMBS sublimates at $T = 380(5)$ K congruently. The saturated vapor of 2-NMBS consists of monomers. Then heaviest ion detected in the mass spectrum was the parent ion [NO₂C₆H₄SO₂OCH₃]⁺. The most probable dissociative ionization processes are the elimination of OCH₃ fragment resulting the ion [NO₂C₆H₄SO₂]⁺ and the elimination of both substituents resulting the formation of [C₆H_n]⁺ ions. No peaks were detected which indicate any kind of thermal decomposition process or presence of volatile admixtures.

The optical densities of the diffraction patterns were measured by a modified MD-100 (Carl Zeiss, Jena) microdensitometer [13]. The molecular scattering function, $sM(s)$, was calculated as $sM(s) = (I(s)/G(s) - 1)s$, where $I(s)$ is the total electron scattering intensity, $G(s)$ the experimental background.

Quantum chemical calculations

The conformational properties of the 2-NMBS molecule depend on the presence of four non-rigid torsional coordinates and by the *ortho*-position of the nitro-group. Quantum chemical calculations at the theory levels MP2 and DFT/B3LYP with the basis set cc-pVTZ [14] were carried out to estimate starting approximation to the conformational composition of vapor and to the geometric and vibrational parameters of conformers. According to calculations (Gaussian 03 package [15]), the molecule 2-NMBS has six conformers (Fig. 1) with relative energies ΔE (MP2/B3LYP) = 0/0; 0.54/1.08; 0.69/0.89; 0.81/1.77; 1.68/2.22 and 2.94/2.91 kcal/mol.

The QST2 method [16] was used for determination of energy and the structure of transition states between conformers. The NBO-analysis [17] of conformers has been carried out to clarify causes stabilization of certain geometrical configurations. Main attention was paid the donor-acceptor interaction of substituents (NO₂ and SO₂OCH₃) orbitals with the benzene ring orbitals and the orbital interactions into the SO₃CH₃ group. The program ChemCraft [18] was used for visualization of the geometric structure and molecular orbitals.

Structural analysis of GED data

On first stage of the least squares fit (LS) analysis, the structures of conformers from I to V were tested separately. On second stage, the GED structural analysis was carried out taking into account that vapor at experimental conditions consists of four conformers I–IV (Table 2).

The geometric model (Fig. 2) used for the calculation of the theoretical function $sM(s)$ allowed describing the rotation of the SO₂-OCH₃ group about the C–S bond, the rotation of OCH₃ group about the S–O bond, the rotation of CH₃ group about the C–O bond and the rotation NO₂ group about C–N bond, as well as the shift of the sulfur atom from the benzene ring plane. The carbon frame of the benzene ring was assumed to be flat. It was supposed that all C–H bonds in the benzene ring are equivalent and directed along the bisector of corresponding angles C–C–C. The differences between similar parameters of conformers as well as the differences between the same type bond distances and bond angles in each conformer were kept at the values predicted by B3LYP/cc-pVTZ calculations.

The geometric model for the refinement included 19 independent parameters: seven types of internuclear distances (C–H, C–C, S–C, O–S, C–O, N–C, N–O), nine bond angles (C1–C2–C3, S–C1–C2, C1–S–O5, C1–S–O3, O5–S–O4, S–O5–C7, N–C2–C1, O1–N–C2, O1–N–O2) and three torsion angles $\phi(S-C1-C2-C3)$, $\phi(C2-C1-S-O5)$, $\phi(C1-S-O5-C7)$. Other parameters needed for a full description of the structure were tied with independent parameters by differences from quantum chemical calculations according to Table 3.

The LS was carried out by means of a modified KCED-35 program, which is analogous to that described in Ref. [19].

Table 1
Conditions of a simultaneous electron diffraction and mass spectrometric experiment.

Parameters	Nozzle-to-plate distance	
	$L = 338$ mm	$L = 598$ mm
Electron beam current (μ A)	1.40	0.82
Temperature of effusion cell (K)	379(5)	380(5)
Accelerating voltage (kV)	78	80
Exposure time (s) (average)	90	48
Residual gas pressure in diffraction chamber (torr)	$1.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$
Scattering angles (\AA^{-1})	4.4–26.5	1.8–15.4

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