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ORIGINAL RESEARCH

Conformational properties of *ortho*-nitrobenzenesulfonamide in gas and crystalline phases. Intra- and intermolecular hydrogen bond

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A combined gas-phase electron diffraction and quantum chemical (B3LYP/6-311+G**, B3LYP/cc-pvtz, MP2/cc-pvtz) study of molecular structure of 2-nitrobenzenesulfonamide (2-NBSA) was carried out. Quantum chemical calculations showed that 2-NBSA has four conformers, two of which are stabilized by intramolecular hydrogen bond. The latter (with the S–N bond in a close to orthogonal position around the phenyl ring and differing from each other by staggered or eclipsed positions of the N–H and S=O bonds in the SO_2NH_2 group) presented in a saturated vapor over 2-NBSA at $T = 433$ (3) K in commensurable amounts. Experimental internuclear distances (Å) for the staggered conformer are (Å): $r_{h1}(C–H)_{av.} = 1.071(9)$, $r_{h1}(C–C)_{av.} = 1.390(4)$, $r_{h1}(C–S) = 1.789(8)$, $r_{h1}(S{=}O)_{av.} = 1.427(6)$, $r_{h1}(S–N) = 1.644(6)$, $r_{h1}(N–O)_{av.} = 1.221(4)$, $r_{h1}(C'–N) = 1.487(8)$, $r_{h1}(N–H)_{av.} = 1.014$. Calculations at B3LYP/cc-pvtz level were performed to determine the structure and the energies of the transition states between conformers. It was shown that the conformer structures of free molecule differ from those of a molecule stabilized by intermolecular hydrogen bonds in a crystal. Influence of a substituent X (X = $–CH_3$, $–NO_2$) on conformational features of the ortho-substituted benzenesulfonamide was established.

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Introduction

At the present time, a synthesis of new, physiologically active compounds derived from sulfonyl-substituted nitrogen-containing aromatic systems is actively developed. The synthesis is based on the high throughput screening (HTS) technologies [1]. To realize a strategy of this and to improve the molecular design methods, information on geometric and electronic structure of arensulfonic acid amides is needed. Benzenesulfonamide and its various substituted derivatives (NO_2–, CH_3–, Cl–) belong to the basic compounds which contain a sulfonamide group $–SO_2NH_2$. Since these compounds are the constituents of most of the precursors for sulfonamide medicines [2, 3], any information concerning the structure and conformational properties is of a great importance for a better understanding the reactive activity in the processes passing with the S–N and N–H bonds cleavage.

In processes with participation of substituted benzenesulfonamides a change of the aggregate state of the latter may occur. This arouses interest in knowledge on structure of molecules in condensed and gaseous phases as well as on those changes in the molecular structure which accompany the crystal-to-gas transition. At present, such information is available only for an unsubstituted benzenesulfonamide (BSA) and its *methyl*-derivatives (MBSA). The crystal structures of BSA [4], *ortho*-MBSA (or 2-MBSA) [5], and *para*-MBSA (or 4-MBSA) [6] were studied by X-ray diffraction (XRD). Earlier, we reported the results of gas-phase electron diffraction (GED) study on the molecular structures of *free* molecules mentioned above [7, 8].

Strong intermolecular hydrogen bonds between O(SO_2) and H(NH_2) atoms occur in crystals of BSA, 2-MBSA, and 4-MBSA. These interactions stabilize a certain conformation of the molecule in a crystal which differs from the molecular geometry in a free state.

Free molecules of unsubstituted and substituted BSA have several conformers. BSA [7] and 4-MBSA [8] have two conformers each: the S–N bond is oriented orthogonally with respect to the benzene ring while the N–H and S=O bonds of the SO_2NH_2 groups either eclipse each other (eclipsed conformers) or are in staggered positions (staggered conformers). Unfortunately, the GED method did not allow to reliably determine a quantitative ratio between the conformers in case of 4-MBSA because of low scattering power of the hydrogen atom in the NH_2 group.

2-MBSA has four conformers [8] differing by as the S–N bond orientation around the benzene ring (orthogonal and planar) as well as by relative orientation of N–H and S=O bonds of the SO_2NH_2 group (eclipsed and staggered).

In contrast to MBSA, no information on free *nitro*-benzenesulfonamides (NBSA) is available in literature. Nevertheless, the structure and packing of molecules in crystalline 2-NBSA [9], 3-NBSA [5], and 4-NBSA [5, 10] is known from XRD measurements. Intermolecular hydrogen bond was found to exist in all these molecules.

In crystalline 4-NBSA [10], the molecules are positioned by a “head-to-tail” scheme forming intermolecular bonds between the hydrogen H(NH_2) atom of one molecule and the oxygen O(NO_2) atom of the next molecule.

In crystalline 3-NBSA [5], the molecules form layers in which the –SO_2NH_2 groups of the adjacent molecules directed toward to each other, and every molecule appears to be connected by two hydrogen bonds with each of the two neighbors. Intermolecular hydrogen bonds are formed between H(NH_2) in one molecule and O(SO_2) of the neighbor and vice versa.

In crystalline 2-NBSA [9], each molecule is bound by hydrogen bonds with four adjacent molecules (see Fig. 1) due to which the layers consisting of alternating mirror isomers of 2-NBSA are formed.

In this study, we report the results of synchronous gas-phase electron diffraction and mass spectrometric (GED/MS) study of saturated vapors of 2-NBSA. This compound is a representative of nitro-substituted benzenesulfonamides in which steric effects between the substituents are expressed most strongly. A composition of saturated vapor over 2-NBSA, conformational properties of free molecule, structural changes in the molecule at the transition from crystal to a free state, and correlations between the nature of ortho-substituent X (X = –CH_3, –NO_2) and conformational properties of the molecules X–C_6H_4–SO_2NH_2 are the subjects of this study.

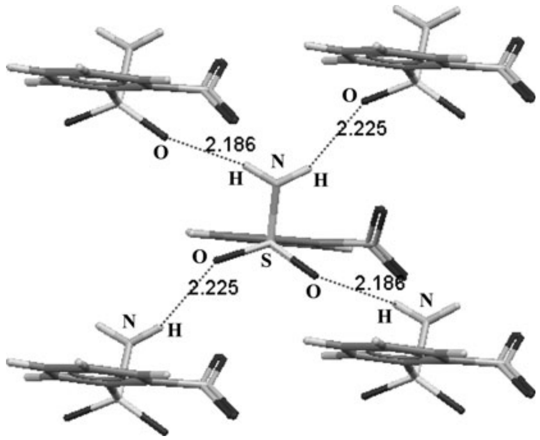


Fig. 1 Intermolecular hydrogen bonds in crystalline structure of 2-NBSA [9]

Experimental

2-NBSA was synthesized from a commercial sample of nitrobenzenesulfonylchloride by interaction with ammonia [11]. The original sulfonylchloride was washed from hydrochloric acid by water. 2-NBSA recrystallized from a solvent (20 vol.% propane-2-ol water solution) till the melting temperature of 465 K (literature: 466 K [12]) has been reached.

The combined GED/MS experiment on saturated vapor over 2-NBSA was carried using a technique described earlier [13, 14] which allows the vapor composition to be in situ monitored during all the diffraction patterns recoding procedure by means the mass spectrometer attached to the GED apparatus. Sublimation of the sample was carried out from a stainless steel (X18H10T) cylindrical effusion cell with the ratio of the cell internal cross section to that of the effusion canal of about 200. The temperature of the sample and nozzle was kept at 433(3) K as measured by a W–Re (5/20) thermocouple. Accurate wavelength of the electrons was calibrated against diffraction patterns of polycrystalline ZnO which were recorded just before and after the exposure of the diffraction patterns series on the gaseous sample. The scattered electrons were collected on Kodak Electron Image films SO-163 of the size 9 × 12 cm^2. The main conditions of the GED/MS experiment are listed in Table 1.

From reproducibility of the electron impact mass spectra recorded during heating the sample one may consider that 2-NBSA sublimes with no decomposition up to the temperature of the GED experiment, 433(3) K. The ion

Table 1 Main conditions of the combined gas-phase electron diffraction and mass spectrometric experiment for 2-NO_2–$C_6H_4SO_2NH_2$

Parameter	Camera distance	
	L = 338 mm	L = 598 mm
Primary beam current (μA)	1.35	0.72
Effusion cell temperature (K)	433(3)	433(3)
Accelerating voltage (kV)	74.3	78.9
Ionizing voltage (V)	50	50
Exposure time (s)	100	90
Residual pressure in the diffraction chamber (torr)	1.3×10^{-6}	3.0×10^{-6}
Scattering angles ($Å^{-1}$)	3.5–26.5	1.2–15.6

Table 2 Electron impact ($U_{\text{ioniz.}} = 50$ V) mass spectrum of saturated vapor over 2-NO_2–$C_6H_4SO_2NH_2$ recorded during the GED/MS experiment

Ion	*m*/*e* a.m.u.	Relative abundance (%)
$[NO_2C_6H_4SO_2NH_2]^+$	202	21
$[NO_2C_6H_4SO_2]^+$	186	100
$[C_6H_3SO_2]^+$	139	4
$[NO_2C_6H_4]^+$	122	2
$[C_6H_4S]^+$	108	5
$[NH_2C_6H_4]^+$	92	12
$[SO_2NH_2]^+$	80	9
$[C_6H_4]^+$	76	17
$[SO_2]^+$	64	43
$[C_4H_2]^+$	50	30

currents recorded simultaneously with the diffraction patterns exposure are given in Table 2 and evidences for presence of the only molecular species in the saturated vapor over 2-NBSA which corresponds to the gross formula of this compound. No associates (dimers, etc.) were detected in the vapor which means that all hydrogen bonds undergo a cleaved at "crystal-to-gas" transition. Moreover, no volatile impurities were found. The mass spectra has a most intensive ion with $m/z = 186$ a.m.u. of a stoichiometry $[NO_2C_6H_4SO_2]^+$, along with a series of lighter ions which are the products of a $NO_2C_6H_4SO_2NH_2$ molecule dissociative ionization processes. Stoichiometry of the latter manifests that under electron impact a predominant cleavage of the bonds takes place between the benzene ring and the substituents, as well as of the bonds within the functional groups.

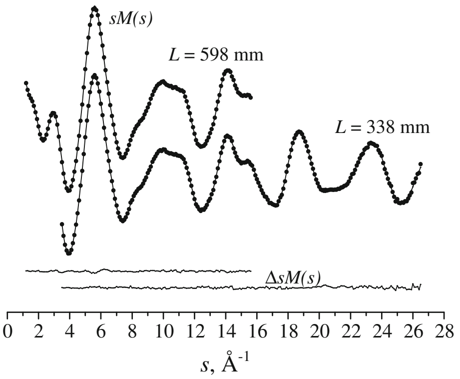
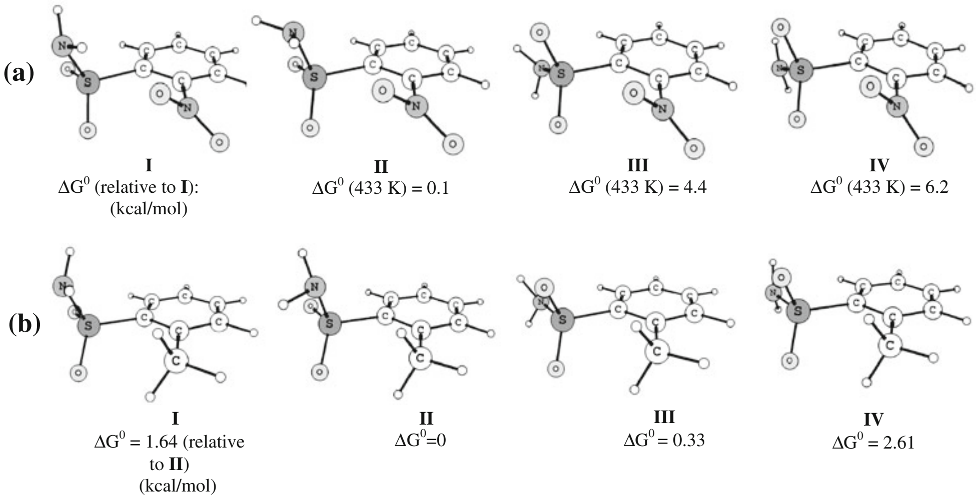


Fig. 2 Experimental (*dots*) and calculated (*line*) $sM(s)$ functions and their differences $\Delta sM(s) = sM(s)_{\text{exp}} - sM(s)_{\text{theor}}$ for the composition 52% (conformer **I**) and 48% (conformer **II**) of 2-NO_2–$C_6H_4SO_2NH_2$

The optical densities of the diffraction patterns were measured by the MD-100 (Carl Zeiss, Jena) microdensitometer modified in our group earlier as to provide it with a system of computer control [15]. The molecular scattering function, $sM(s)$, was evaluated as $sM(s) = (I(s)/G(s) - 1)s$, where $I(s)$ is the total electron scattering intensity, $G(s)$ the experimental background. The background curves were checked by differentiation to confirm an absence of oscillations with frequencies comparable with those of the experimental $I(s)$ curves. Experimental and theoretical $sM(s)$ curves along with their differences $\Delta sM(s)$ are given in Fig. 2.

Quantum chemical calculations

Since the molecule 2-NBSA possesses three non-rigid torsion vibration coordinates, it may have several rotational conformers. Therefore, prior to the structural analysis a series of quantum chemical calculations were performed to estimate the conformational composition of the vapor under investigation and the geometric and vibrational parameters of the conformers. Two approaches, DFT/B3LYP (basis sets 6-311+G** and cc-pVTZ [16]) and MP2/cc-pVTZ (Gaussian-03 package [17]) were applied. From B3LYP/cc-pVTZ and MP2/cc-pVTZ calculations, we established that 2-NBSA has four conformers (Fig. 3a) differing by rotation angles of the SO_2NH_2 group around the C–S bond, the NH_2 group around the S–N bond and the NO_2 group around the C–N bond. On the other hand, the B3LYP/6-311+G** calculations discovered three conformers only. Torsion angles, relative energies ΔE, and relative Gibbs energies ΔG^0 of the conformers are summarized in Table 3. The latter were calculated using the B3LYP method with 6-311+G** and cc-pVTZ basis sets. In all the calculations performed the conformers **I** and **II** (see Fig. 3a) were found to be the most stable. From this one may consider these two conformers to dominate in the saturated vapor over 2-NBSA at the temperature corresponding to the GED experiment.



(a) **I** ΔG^0 (relative to **I**): (kcal/mol); **II** ΔG^0 (433 K) = 0.1; **III** ΔG^0 (433 K) = 4.4; **IV** ΔG^0 (433 K) = 6.2

(b) **I** ΔG^0 = 1.64 (relative to **II**) (kcal/mol); **II** ΔG^0=0; **III** ΔG^0 = 0.33; **IV** ΔG^0 = 2.61

Fig. 3 Geometric structures and relative Gibbs energies (B3LYP/cc-pVTZ) of the conformers of $2\text{-}NO_2\text{–}C_6H_4SO_2NH_2$ (**a**) and $2\text{-}CH_3\text{–}C_6H_4SO_2NH_2$ (**b**)

Table 3 Calculated geometric parameters (angstroms and degrees), relative energies ΔE and Gibbs energies ΔG^0 (kcal/mol), and estimated mole fractions (%) of the conformers of $2\text{-}NO_2\text{–}C_6H_4SO_2NH_2$

Method/basis	Parameter	Conf. **I** (stag.)	Conf. **II** (eclips.)	Conf. **III** (eclips.)	Conf. **IV** (stag.)
B3LYP/6-311+G**	ϕ(C–C–S–N)[a]	76.2	79.7	21.8	–
B3LYP/cc-pVTZ		76.7	79.9	20.9	24.1
MP2/cc-pVTZ		78.8	82.4	23.9	27.6
B3LYP/6-311+G**	ϕ(C–C–S–O)[a]	1.9	2.8	92.3	
B3LYP/cc-pVTZ		2.7	3.2	91.2	93.8
MP2/cc-pVTZ		5.4	5.8	94.2	96.9
B3LYP/6-311+G**	ϕ(C–S–N–H)	−58.5	−86.9	−130.6	–
B3LYP/cc-pVTZ		−58.1	−88.7	−128.1	−79.2
MP2/cc-pVTZ		−58.1	−88.4	−131.4	−76.3
B3LYP/6-311+G**	ϕ(C–C-N–O)	−40.5	−36.7	−42.4	–
B3LYP/cc-pVTZ		−40.8	−36.5	−41.9	−45.3
MP2/cc-pVTZ		−47.6	−42.8	−48.4	−51.4
B3LYP/6-311+G**	r(C–S)	1.832	1.821	1.824	–
B3LYP/cc-pVTZ		1.825	1.814	1.818	1.825
MP2/cc-pVTZ		1.796	1.786	1.790	1.797
B3LYP/6-311+G**	r(S–N)	1.661	1.674	1.690	
B3LYP/cc-pVTZ		1.652	1.664	1.678	1.652
MP2/cc-pVTZ		1.642	1.653	1.664	1.643
B3LYP/6-311+G**	ΔE	0	−0.008	4.91	–
B3LYP/cc-pVTZ		0	0.26	5.03	7.26
MP2/cc-pVTZ		0	0.23	6.04	7.92
B3LYP/6-311+G**	ΔG^0(298)	0	−0.02	4.20	–
B3LYP/cc-pVTZ		0	0.09	4.36	6.18
MP2/cc-pVTZ[b]		0	0.05	5.36	6.83
B3LYP/6-311+G**	Mole fraction	49.2	50.4	0.4	–
B3LYP/cc-pVTZ		52.3	47.3	0.4	0.0
MP2/cc-pVTZ[b]		51.4	48.5	0.1	0.0

[a] Those torsion angles which are close to 90° were measured from the bond C2–C1 (see Fig. 3), i.e., are the angles C2–C1–S–N(or O). Those torsion angles which are close to 0° were measured from the bond C6–C1, i.e., are the angles C6–C1–S–N(or O)

[b] Thermal free energies (B3LYP/cc-pVTZ) were used for calculating ΔG^0(298)

Structural analysis

According to the mass spectrometric data recorded in this study (Table 2) the vapor contains the only molecular species, 2-NBSA, which may, according to the quantum chemical calculations, have four conformers.

The atom numbering of 2-NBSA is given in Fig. 4. For the structural analysis a model was chosen which makes it possible to describe the geometry of any of the four conformers. The model included 23 independent parameters and allowed to take into account the following: (i) an inequivalence of the C–C bonds in the benzene ring; (ii) rotation of the SO_2NH_2 group around the C–S bond; (iii) rotation of the NH_2 group around the S–N bond; (iv) rotation of the nitro-group around the C–N bond; (v) possibility of motion for the S atom out of the benzene ring plane. Eight interatomic distances (C–H, C–C, C–S, S–N, S–O, N–H, C–N, and N–O), nine valence angles (C–C–C, S–C–C, N–S–C, O–S–C, O–S–N, H–N–S, H–N–H, N–C–C, and O–N–C), and six torsion angles ϕ(S–C–C–C), ϕ(N–S–C–C), ϕ(H–N–S–O), ϕ(N–C–C–C), ϕ(O–N–C–C), and ϕ(O3–N–C–O4) were taken as independent parameters.

The model had several constraints:

1. Except the C–H bonds, the lengths of all homotypic bonds (for example, S1–O1 and S1–O2, all bonds in benzene ring, etc.) were refined in corresponding groups. The Δr values which characterized the inequivalence of homotypic bonds were taken from the quantum chemical calculations (B3LYP/6-311+G**) and were not varied in the least-squares analysis. It is to be noted that the calculations with different basis sets give practically the same Δr values.
2. The C–H bonds in the benzene ring were constrained to be equal and to lie along the bisectors of the corresponding C–C–C angles.
3. All carbon atoms of the benzene ring belong to the same plane.
4. The valence angles in the benzene ring were refined in a group.
5. Because of a low scattering power of the hydrogen atoms of the NH_2 groups, the N–H bond lengths, the valence angles H–N–S and H–N–H and the torsion angle ϕ(H–N–S–O1) were not refined being kept at the values given from the quantum chemical calculations.

All geometries were constructed within the r_{h1}-structure. The needed vibrational corrections were calculated with a non-linear relation between Cartesian and internal coordinates taken into account using the program SHRINK [18, 19]. The force field yielded by the B3LYP/6-311+G** calculations was used as an input for this program.

Vibration amplitudes for the terms with close internuclear distances were refined in groups. The terms were sorted into the groups according to belonging to the peaks in the radial distribution function $f(r)$ (see Fig 5; Table 5). The least-squares analysis was carried out using a modified program KCED-35 which is analogical to that described in [20].

The experimental function $sM(s)$ was tested for the fit for conformers **I**, **II**, and **III** of 2-NBSA separately as well as to fit a mixture of the two most stable conformers **I** and **II**. The differences for interatomic distances and for valence angles were kept at the quantum chemical values, whereas the torsional angles ϕ(N–S–C1–C2) and ϕ(O3–N–C2–C1), which determine the position of the substituents with respect to the benzene ring, were refined by turns.

Least-squares results are given in Table 4. Six correlation coefficients exceeded 0.75 in absolute value: $p_{10}/p_{16} = -0.82$, $p_2/p_5 = -0.81$, $p_{12}/p_{13} = 0.78$, $p_9/p_{10} = -0.85$, $l_4/p_{12} = 0.97$, $l_4/p_{13} = 0.76$ (subscript numbering

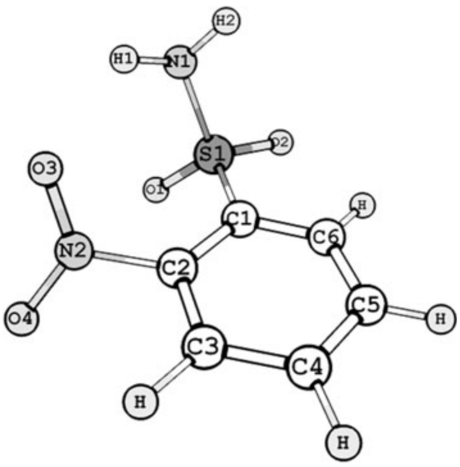


Fig. 4 Atom numbering in the molecule 2-nitrobenzenesulfonamide

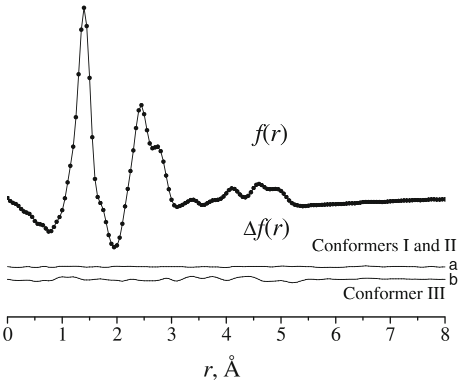


Fig. 5 Experimental (*dots*) and calculated (*line*) radial distribution curves $f(r)$ and their differences $\Delta f(r) = f(r)_{exp} - f(r)_{theor}$ for 2-NO_2–$C_6H_4SO_2NH_2$: (*a*) difference curve when the mixture of conformers **I** (52%) and **II** (48%) are modeled; (*b*) difference curve when conformer III is modeled

Table 4 Geometric parameters of the conformer **I** of 2-NO_2–$C_6H_4SO_2NH_2$ (angstroms and degrees)

Parameter	GED r_{h1}-structure	B3LYP/6-311+G**	B3LYP/cc-pVTZ	MP2/cc-pVTZ	XRD [9]
C–H	1.071(9)[a] p_1	1.082	1.079	1.080	0.930
C1–C2	1.398(4)[b] p_2	1.401	1.397	1.396	1.386
(C–C)cp.	1.390(4) (p_2)	1.393	1.390	1.392	1.387
C–S	1.789(8) p_3	1.832	1.825	1.796	1.786
S–N1	1.644(6) p_4	1.661	1.652	1.642	1.606
S–O1	1.424(4) p_5	1.452	1.444	1.442	1.433
S–O2	1.430(4) (p_5)	1.458	1.449	1.445	1.432
N1–H1	1.015 p_6	1.015	1.013	1.013	0.883
N1–H2	1.013 (p_6)	1.013	1.011	1.011	0.883
C–N2	1.487(8) p_7	1.481	1.479	1.464	1.466
N–O3	1.226(4) p_8	1.226	1.224	1.231	1.220
N–O4	1.217(4) (p_8)	1.217	1.215	1.226	1.223
∠C2–C1–C6	117.3 (9) p_9	118.4	118.3	118.4	118.4
∠C1–C2–C3	121.5(9) (p_9)	121.3	121.3	121.5	122.0
∠S–C1–C2	125.2(18) p_{10}	125.0	125.0	123.9	124.1
∠N1–S–C1	107.7(32) p_{11}	108.8	108.3	107.4	108.8
∠O1–S–C1	106.3(18) p_{12}	106.3	106.4	106.3	107.7
∠O1–S–N1	108.9(33) p_{13}	108.0	108.1	107.7	108.8
∠H–N–S	112.8 p_{14}	112.7	112.3	111.3	
∠H–N–H	113.5 p_{15}	114.5	114.5	113.8	
∠N2–C2–C1	121.7(21) p_{16}	122.8	122.9	122.3	121.9
∠O3–N2–C2	116.0(3) p_{17}	117.6	117.7	117.4	118.0
ϕS–C1–C2–C3	173(2) p_{18}	172.4	172.6	173.4	
ϕN1–S–C1–C2	74 (8) p_{19}	76.2	76.7	78.8	89.9
ϕ(H–N–S–O1)	56.5 p_{20}	56.4	56.8	56.0	
ϕN–C2–C1–C6	179(6) p_{21}	177.8	177.8	178.2	
ϕO3–N2–C2–C1	−42(6) p_{22}	−40.5	−40.8	−47.6	−47.6
ϕO3–N–C–O4	177.5 p_{23}	176.9	176.9	176.9	
O3(N2)···H1(N1)	2.0(3)	2.128	2.123	2.110	2.578
Mole fraction (%)	52	49.2	52.3	51.4	
R_f (%)	2.48				2.02

See Fig. 4 for atom numbering

[a] Uncertainties were calculated as $[(2.5\sigma_{L-S})^2 + (0.002 \cdot r)^2]^{0.5}$ for internuclear distances, $3\sigma_{L-S}$ for valence angles and σ_{L-S} for torsion angles. The parameters given without uncertainties were fixed in the refinement

[b] p_i parameter refined independently; (p_i) parameter refined in the i-group

of the parameters p and of the root-mean-square amplitudes l are listed in Tables 4 and 5, respectively).

Discussion

Conformers of 2-NBSA

According to the quantum chemical calculations the molecule 2-NBSA has four conformers (Fig. 3a). The distances between the H atom of the NH_2 group and the O atom of the NO_2 group are 2.12 and 2.25 Å, and the angles ∠NH···O are 133.3° and 118.2° in conformers **I** and **II**, respectively (B3LYP/cc-pVTZ). These geometric values indicate that the intramolecular hydrogen bond is formed and stabilizes the conformers **I** and **II** as compared to the conformers **III** and **IV** in which this bond is absent.

In conformers **I** and **II**, the S–N bond is in a position close to orthogonal and deviates from it due to intramolecular hydrogen bond. In this case one of the S=O bonds almost eclipses the C–C bond in benzene ring. In conformers **III** and **IV** the S=O bond is orthogonal to the benzene ring.

Orientation of the NO_2 group about the skeleton is practically the same for all conformers and is probably determined by keeping the longest distances between the

Table 5 Internuclear distances, experimental and theoretical vibration amplitudes and vibrational corrections (excluding the nonbonded atom pairs containing hydrogen atoms) for the conformer **I** of 2-NO_2–$C_6H_4SO_2NH_2$

Parameter	r_a	l_{exp}	l_{calc}	$\Delta r = r_{h1} - r_a$	Group
N–H1	1.010(1)	0.072(3)	0.071	0.004	1
C–H	1.066(4)	0.076(3)	0.075	0.005	1
N2–O3	1.224(1)	0.045(1)	0.039	0.001	2
C4–C5	1.387(1)	0.051(1)	0.045	0.000	2
C3–C4	1.388(1)	0.051(1)	0.045	0.001	2
S–O1	1.423(1)	0.042(1)	0.036	0.000	2
C2–N2	1.485(3)	0.059(1)	0.053	0.001	2
N1–S1	1.642(2)	0.062(4)	0.050	0.001	3
C1–S1	1.787(3)	0.070(4)	0.058	0.001	3
H–O1	2.315(32)	0.182(2)	0.190	−0.005	4
C2–C6	2.374(5)	0.049(2)	0.057	0.006	4
C3–C5	2.401(2)	0.048(2)	0.056	0.004	4
N1–O2	2.461(17)	0.066(2)	0.074	0.004	4
C1–O2	2.564(10)	0.069(2)	0.077	0.004	4
C1–O1	2.574(10)	0.079(2)	0.087	0.005	4
H1–O1	2.726(21)	0.187(3)	0.180	0.020	5
C2–C5	2.766(3)	0.071(3)	0.064	0.008	5
C3–C6	2.754(7)	0.071(3)	0.064	0.006	5
H–S1	2.771(16)	0.153(3)	0.146	0.011	5
N2–S1	3.215(6)	0.130(9)	0.116	0.006	6
C2–N1	3.501(49)	0.145(9)	0.131	0.010	6
H–O3	3.476(99)	0.257(9)	0.243	−0.014	6
C5–N1	3.734(64)	0.144(4)	0.138	0.017	7
C2–O2	3.880(6)	0.088(4)	0.082	0.015	7
C5–S1	4.026(7)	0.090(2)	0.073	0.015	8
C4–O4	4.130(27)	0.139(2)	0.121	0.012	8
C3–S1	4.097(6)	0.096(2)	0.078	0.015	8
O2–O3	4.441(27)	0.186(2)	0.167	−0.007	9
C4–S1	4.569(4)	0.095(2)	0.077	0.019	9
N2–O2	4.551(8)	0.130(2)	0.112	0.017	9
C3–N1	4.786(39)	0.165(8)	0.153	0.021	10
C5–O4	4.869(35)	0.112(8)	0.099	0.024	10
C3–O2	4.958(6)	0.104(8)	0.092	0.023	10
C4–O2	5.072(11)	0.123(8)	0.111	0.023	10
C4–H1	5.383(24)	0.334(18)	0.271	0.009	11
C4–N1	5.396(19)	0.226(18)	0.163	0.028	11
C4–H2	5.498(27)	0.375(18)	0.313	0.020	11
N1–H(C3)	5.504(61)	0.252(18)	0.189	0.033	11
O2–O4	5.467(31)	0.286(18)	0.223	0.051	11
S1–H(C4)	5.623(6)	0.168(18)	0.105	0.036	11

See Fig. 4 for atom numbering

[a] All parameters given in angstroms. Uncertainties in *parentheses* are the σ_{L-S} values

O(NO_2) atom and the two most adjacent electronegative oxygen and nitrogen atoms (conformers **I** and **II**) or two oxygen atoms (conformers **III** and **IV**) of the sulfonamide group. In all four conformers these distances are 2.87–3.17 Å.

Conformers **I** and **II** differing by mutual orientation of the NH_2 and SO_2 groups may just tentatively be attributed as staggered (conformer **I**) and eclipsed (conformer **II**) since in any of them the NH_2 group turns, due to the intramolecular hydrogen bond formed, that favors the distance between H(NH_2) and O(NO_2) atoms to shorten. The second pair of conformers, **III** and **IV**, also differs mostly by relative positions of the NH_2 group, and the steric factors make the conformer **IV** to be less favorable relative to **III**.

As it may be seen from Table 3, the Gibbs energies of the conformers **I** and **II** are similar, while those of the conformers **III** and **IV** are much higher.

Pathways of conformational transitions

Geometry of the conformers and transition states (TS) between them are shown in Fig. 6. It might be noted that the transition from the staggered to the eclipsed conformer (**I** → **II** or **III** → **IV**) can be realized by as internal rotation of the NH_2 group around the S–N bond, as well as by pyramidal inversion of the N atom around the plane H1H2S. Barriers of the transitions between the conformers are shown in Fig. 7. Apparently, the pyramidal inversion via planar structure of the SNH_2 fragment is the most energetically favorable.

Each of the transition states shown in Fig. 6 is a first-order saddle point on the potential energy surface. Structures of the transition states TS(**I** → **II**) and TS(**III** → **IV**) are characterized by one imaginary frequency each corresponding to the pyramidal inversion motion, while in cases TS(**II** → **III**) and TS(**IV** → **I**) by one imaginary frequency each corresponding to the correlated internal rotation of the NO_2 and SO_2NH_2 substituents. In the TS(**II** → **III**) and TS(**IV** → **I**) structures, the S–N bond lies in a plane of the benzene ring and a plane of the NO_2 group is in either perpendicular or co-planar to the benzene ring position.

The barrier of the transition between the two existing in the gas conformers of 2-NBSA phase, **I** and **II**, exceeds the thermal energy $RT = 0.86$ kcal mol^{-1} which is an evidence of hindered inversion of the N atom in the S-NH_2 fragment. This makes it possible to carry out the structural analysis in a "traditional" way, i.e., without a dynamic model approach.

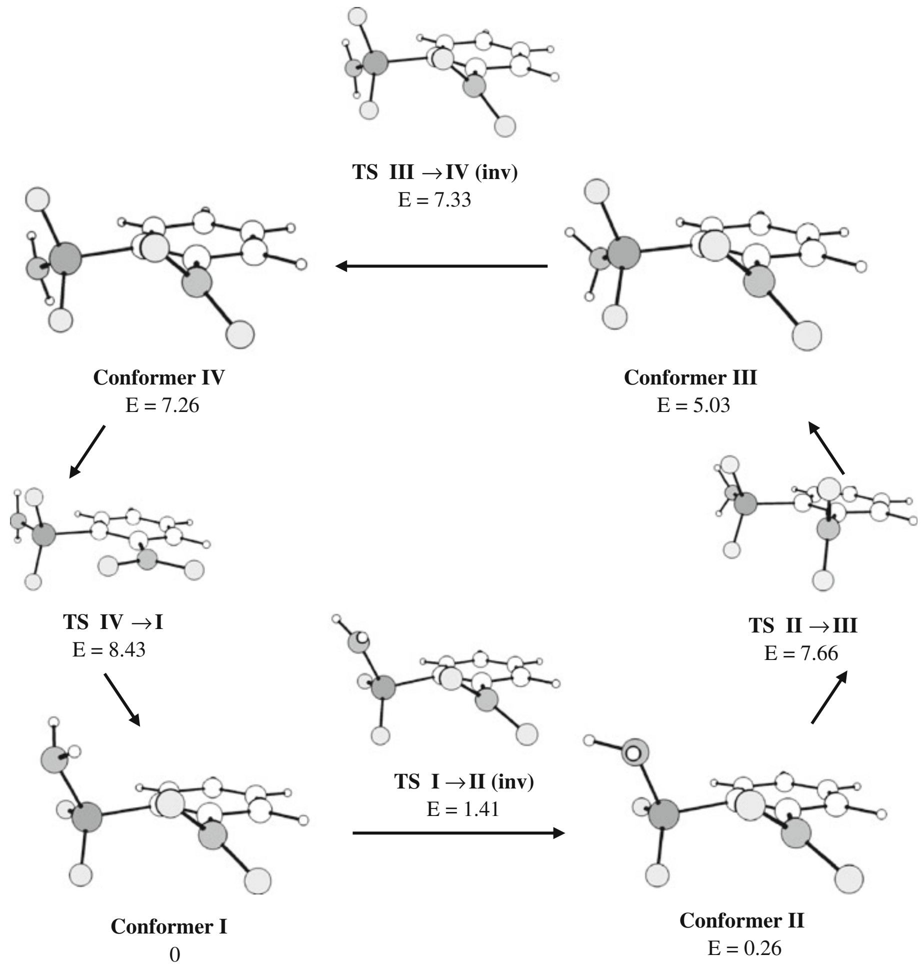


Fig. 6 Geometric structure and relative energies (kcal/mol) of the conformers and transition states for 2-NO_2–$C_6H_4SO_2NH_2$ from theoretical calculations B3LYP/cc-pVTZ

Conformational composition of the saturated vapor. Limitations and abilities of gas electron diffraction

As it may be estimated from the results of the B3LYP/cc-pVTZ calculations, the relative concentrations of the conformers at the temperature of the GED experiment is expected to be 52.3:47.3:0.4:0.0, according to which in a saturated vapor over condensed phase of 2-NBSA the conformers **I** and **II** are to present in comparable amounts, while the conformers **III** and **IV** are to be poorly abundant. These expectations have been supported by the results of the GED data interpretation. Due to low scattering power of the hydrogen atoms of the NH_2 groups an accurate position determination of the N–H and S=O bonds in the SO_2NH_2 group is quite problematic. That, in turn, might bear difficulties in distinguishing between conformers **I** and **II**. Indeed, an attempt to refine the ratio between the abundances of these two conformers yielded 0.44(25) instead of theoretical value 0.52 accompanied by insignificant increase of the disagreement factor R_f.

Nevertheless, the GED method is able to distinguish the conformers **I** and **II** from the conformers **III** and **IV**. Alongside with the hypothesis about predominant presence of conformers **I** and **II** in the saturated vapor (based on the results of quantum chemical calculations) we also tested a possibility to discover a conformer **III** in the gas phase. In this refinement scheme of a least-squares procedure all geometric parameters of the conformer **III** were refined except the torsion angle N–S–C–C which was fixed at the value of −20.9° (B3LYP/cc-pVTZ). Figure 5 and the disagreement factor value of $R_f = 4.5\%$ (which in this case is twice as much as that for the optimal vapor composition) illustrate that a geometry of the conformer **III** does not fit the GED data collected. Thus, the GED experiment supports the theoretical predictions about the maximal stability of the conformers **I** and **II** relative to that of the conformers **III** and **IV**. Experimental and calculated geometries of the conformer **I** are summarized in Table 4, main parameters of the other conformers are given in Table 3. Within error limits, most of the experimental geometric parameters are consistent with those calculated by different methods. The only exceptions are the S=O bond lengths for which the calculated values are larger by ca. 0.02 Å. It is to be noted that only the S–C bond distance is essentially dependent on

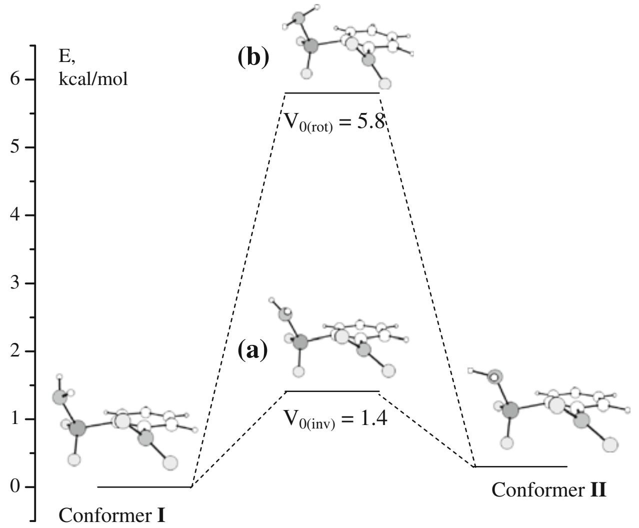


Fig. 7 Barriers of transitions from the 'staggered' conformer **I** to the "eclipsed" conformer **II** of 2-NO_2-$C_6H_4SO_2NH_2$: **a** pyramidal inversion; **b** rotation of the NH_2 group around the N–S bond

the method of calculation—the difference was up to 0.04 Å. The MP2/cc-pVTZ combination reproduces the experimental bond lengths best of all.

Influence of nature of a substituent on conformational properties of ortho-substituted benzenesulfonamide

The non-substituted molecule of benzenesulfonamide, BSA, has two conformers, both with orthogonal position of the S–N bond with respect to the benzene ring plane but differing by staggered and eclipsed orientations of the N–H and S=O bonds in the SO_2NH_2 fragment [7]. When a substituent X (where X = CH_3, NO_2) is introduced into *ortho*-position, the number of conformers increases to four. Along with the conformers of 2-NBSA studied in this work, the conformers of 2-MBSA are also shown in Fig. 3; geometries of the latter were determined in study [8] by GED and quantum chemical methods. Conformers of 2-MBSA are represented in the same sequence determined by orientation of the sulfonamide group as in the case of 2-NBSA.

As it was mentioned above, a common feature of the conformers of 2-NBSA is that one of the oxygen atoms of the NO_2 group is located at a maximal distance away from the oxygen (or nitrogen) atom of the SO_2NH_2 group. In contrast, for the conformers of 2-MBSA, a tendency to a minimal distance between two H atoms of CH_3 group and O and N (or N) atoms of SO_2NH_2 group was observed. In all four conformers of 2-MBSA one of the bonds (S=O or S–N) of the sulfonamide group eclipses the C–C bond of the benzene ring, in contrast to the conformers of 2-NBSA where one of the bonds (S=O or S–N) strive to occupy an orthogonal position relative to the benzene ring plane (see Table 3). In 2-MBSA, the eclipsed around the bonds (S=O and S–N) conformers **II** and **III** appeared to be more stable than the staggered conformers **I** and **IV**, because the H atoms in the NH_2 group are either most distanced away from the nearest H atoms of the CH_3 group, or from the H atom of the benzene fragment. Effect of a substituent on geometry of the SO_2NH_2 group is reflected in Table 6. Valence angles S–C–C(X) and C–C–X exceed 120° which is due to steric interaction of the substituents and is more expressed in 2-NBSA. The average bond distance C–C in the benzene ring increases as the donor substituent CH_3 is introduced and decreases as the acceptor substituent NO_2 is introduced.

Difference in the ΔG^0 value for the most and the least stable conformers is essentially lower in 2-MBSA than in 2-NBSA.

Change of the hydrogen bond type in 2-NBSA at the transition "crystal-to-gas"

It was mentioned before that in conformers **I** and **II** of free 2-NBSA molecule an intramolecular hydrogen bond exists. According to the X-ray results [9], a crystalline 2-NBSA is

Table 6 Experimental geometries (angstroms and degrees) of the most stable conformers[a] of X–C_6H_4–SO_2NH_2 (X = NO_2, CH_3)

Parameter	2-NBSA, conformer **I** (staggered) X = NO_2, this work	2-NBSA, conformer **II** (eclipsed) X = NO_2, this work	2-MBSA, conformer **II** (eclipsed) X = CH_3, [8]
$(C–C)_{average}$	1.390(4)	1.390(4)	1.406(3)
C–S	1.789(8)	1.778(8)	1.770(7)
S=O	1.424(4)	1.428(4)	1.429(3)
	1.430(4)	1.432(4)	1.430(3)
S–N	1.644(6)	1.657(6)	1.682(5)
C(S)–C(X)	1.398(4)	1.398(4)	1.398(4)
S–C–C(X)	125.2(18)	125.3(18)	121.8(11)
C–C–X	121.7(21)	121.6(21)	123.7(23)

[a] Models of the conformers are shown in Fig. 3

built from alternating layers of mirror isomers. The latter are connected to each other by intermolecular hydrogen bonds (Fig. 1). Each hydrogen atom of the NH_2 group of one molecule forms a hydrogen bond with one of the oxygen atoms of the SO_2 group of the adjacent molecule, and each oxygen atom of the SO_2 group of a first molecule forms a hydrogen bond with one of the hydrogen atoms of the NH_2 groups of the other adjacent molecule. As a result, each molecule in the crystal is connected to four surrounding molecules. By means of the intermolecular hydrogen bonds in the crystal a conformation becomes stabile which may be to some extent considered "orthogonal" as for the position of the S–N bond relative to the benzene ring plane and staggered as for mutual orientation of the S=O and N–H bonds in the SO_2NH_2 group. The configuration stable in the crystal differs from each of the four conformers of free 2-NBSA molecule. Geometric parameters of the molecule in crystal are compared with those of the conformer **I** in Table 4. Most of the bond lengths in the crystal and free molecule are close to each other, except the bond S–N which is shorter in the crystal by 0.04 Å. For C–H and N–H bonds, the differences are caused by large uncertainties in both, GED and XRD, methods. Discrepancies in torsion angles N1–S–C1–C2 and O3–N2–C2–C1 are probably due to the packing effect and due to a tendency to form most strong hydrogen bonds with adjacent molecules in the crystal, while for the free molecule—to form intramolecular hydrogen bonds between SO_2NH_2 and NO_2 groups. A distance between the donor of hydrogen, atom $N(NH_2)$, and its acceptor, $O(NO_2)$ in a free molecule or $O(SO_2)$ of an adjacent molecule in a crystal, is shorter in a free molecule (conformers **I** and **II**) than in a crystal. Nevertheless, the intermolecular hydrogen bonds are, according to our estimations, stronger than the intramolecular ones. This may be connected with favorable mutual bracing of N–H and O=S bonds of two adjacent molecules in a crystal ($\angle N\text{–}H\cdots O = 169°$ and 153°) and less favorable for $N\text{–}H(SO_2NH_2)$ and $O\text{–}N(NO_2)$ in a free molecule ($\angle N\text{–}H\cdots O = 133°$ and 118°) for the conformers **I** and **II**, respectively.

Conclusion

A combined gas-phase electron diffraction and mass spectrometric study showed that 2-nitrobenzenesulfonamide sublimes in vacuo with no decomposition at least up to the temperature of the GED/MS experiment carried out in this work, 433(3) K. The saturated vapor consisted of monomeric molecules and was a mixture of two conformers. Intramolecular hydrogen bond was found to exist in these conformers which connect the H atom of the SO_2NH_2 group and the O atom of the NO_2 group. Geometric parameters of the conformers were determined experimentally and quantum chemical calculations were performed for all possible conformers of this compound, as well as transitions states between those.

It was established that the nature of the *ortho*-substituent in benzenesulfonamides governs not only the geometry but also the conformational vapor composition.

Trends in the geometric structure change of 2-NBSA at the transition "crystal-to-gas" were considered.

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