Molecular Structure and Conformations of Benzenesulfonamide: Gas Electron Diffraction and Quantum Chemical Calculations

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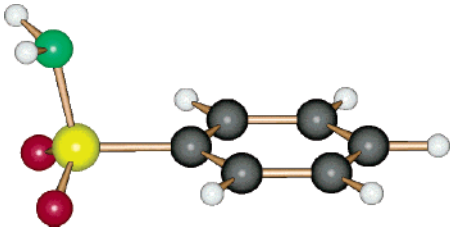

The molecular structure and conformational properties of benzenesulfonamide, $C_6H_5SO_2NH_2$, were studied by gas electron diffraction (GED) and quantum chemical methods (MP2 and B3LYP with different basis sets). The calculations predict the presence of two stable conformers with the NH_2 group eclipsing or staggering the SO_2 group. The eclipsed form is predicted to be favored by about 0.5 kcal/mol. According to GED, the saturated vapor over solid benzenesulfonamide at a temperature of 150(5) °C consists of the eclipsed conformer. The GED intensities, however, possess a very low sensitivity toward the vapor composition, and contributions of the anti conformer of up to 75% (at the 0.05 level of significance) or up to 55% (at the 0.25 level of significance) cannot be excluded. The molecule possesses $C_{s\mathrm{S}}$ symmetry with the S−N bond perpendicular to the ring plane.

Introduction

Derivatives of benzenesulfonamide find wide applications for the synthesis of pharmaceutical products which have bactericidal properties and of various bioactive agents, artificial fibers, dyes, and plasticizers, and the synthesis of high molecular weight substances.[1−3] Knowledge of the molecular structure of benzenesulfonamide and its substituted species is important for explaining their reactivity, in particular for understanding the mechanism of substitution of the hydrogen atoms in the amide group.

Several investigations of the molecular structures of gaseous benzenesulfones, $C_6H_5SO_2X$, have been reported in the past.[4−6] Brunvoll et al. investigated the molecular structure of phenylmethylsulfone (PMS)[4] and benzenesulfonyl chloride (BSC)[5] by gas electron diffraction (GED). It was found that PMS possesses C_s symmetry with perpendicular orientation of the $S-C_{\mathrm{methyl}}$ bond relative to the plane of the benzene ring ($\tau(C_{\mathrm{benz}}-S) = 90°$). For BSC, a structure with C_s symmetry and torsional angle $\tau = 90°$ was found in good agreement with the GED intensities. Slightly better agreement with the experimental radial distribution function, however, was obtained with C_1 symmetry and $\tau = 75.3 \pm 5.0°$.[5] This result was interpreted in terms of an equilibrium structure with C_s symmetry and torsional angle $\tau = 90°$. The C_1 symmetry derived in the GED experiment is the consequence of a large amplitude torsional motion of the sulfonyl group. A similar structure was obtained for pentafluorobenzenesulfonyl chloride by GED.[6] Elongation of C−S and widening of the angle CSCl in comparison with nonfluorinated BSC were observed, and the torsion angle τ was found to be

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(1) Gilbert, E. E., Ed. *Sulfonation and Related Reactions*; Wiley Interscience Publishers: New York, 1965; p 529.

(2) Patai, S., Rappoport, Z., Eds. *The Chemistry of Sulfonic Acids and their Derivatives*; Wiley: Chichester, 1991; p 286.

(3) Gazieva, G. A.; Kravchenko, A. N.; Lebedev, O. V. (Russian) *Adv. Chem.* **2000**, *69*, 239.

(4) Brunvoll, J.; Exner, O.; Hargittai, I.; Kolonits, M., Scharfenberg P. *J. Mol. Struct*. **1984**, *117*, 317.

(5) Brunvoll, J.; Hargittai, I. *J. Mol. Struct*. **1976**, *30*, 361−378.

(6) Vajda, E.; Hargittai, I. *Z. Naturforsch*. **1983**, *38a*, 765−768.

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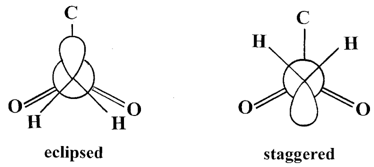
CHART 1



equal to 61.8 ± 1.3°. In contrast to the GED structure, a microwave spectroscopy experiment and CNDO/2 calculations for BSC resulted in a conformation with C_s symmetry and $\tau = 0°$, and the barrier height to internal rotation of the SO_2Cl group is predicted to be 4 kcal/mol.[7] Detailed information about molecular structures of some methyl-substituted benzene sulfonyl halides was obtained by GED and quantum chemical calculations.[8−10] The structure of the sulfonyl group SO_2Hal, with Hal = F, Cl, Br, was studied, and the distortion of the benzene ring depending on the nature of the sulfonyl halide group and on the position the methyl group (ortho or para) was obtained. In the present investigation, we report a study of benzenesulfonamide using GED and quantum chemical calculations. Thus far, no structural data for this compound, neither in the gaseous nor in the solid state, have been reported.

Results

Quantum Chemical Calculations. The conformational properties of benzenesulfonamide were investigated using quantum chemical methods (MP2/6-31G(2df,p) and B3LYP/6-311+G-(2df,p) basis sets). Several conformations are feasible depending on the orientation of the NH_2 group around the S−N bond and on the orientation of the SO_2NH_2 group around the C−S bond. In a first step, geometries with different orientations of the NH_2 group were optimized (see Chart 1). The potential function for internal rotation around the S−N bond possesses minima for the eclipsed orientation (NH_2 group eclipsing both S=O bonds) and for staggered orientation (NH_2 group staggering S−C bond). Each conformer possesses C_s symmetry, and the eclipsed form is predicted to be favored by 1.11 kcal/mol (MP2) and 0.69 kcal/mol (B3LYP). Values of 4.8 and 4.5 kcal/mol were calculated for the barrier to internal rotation around the S−N bond. In the next step, the potential function for internal rotation around the C−S bond was calculated for eclipsed and staggered orientation of the NH_2 group. The potential function for the eclipsed NH_2 group (Figure 1) possesses a single minimum for perpendicular orientation of the S−N bond relative to the plane of the benzene ring (ϕ(C2 = C1−S−N) = 90°). The barrier to internal rotation around the C−S bond occurs for planar orientation and is predicted to be 1.82 kcal/mol (MP2/6-31G**) and 1.68 kcal/mol (B3LYP/6-311+G**). The potential function for the staggered NH_2 group is very similar with a slightly higher barrier to internal rotation. Since both computational methods with small basis sets predict S−C and S=O bond lengths too long by about 0.03 Å, additional B3LYP calculations with large basis sets (6-311++G(2df,p)) were performed for the two stable conformers. According to these calculations, the eclipsed form is favored by $\Delta E = 0.42$ kcal/mol and $\Delta G° = 0.98$ kcal/mol. Geometric parameters of the syn form are listed together with the experimental values. Vibrational corrections, $\Delta r = r_{h1} - r_a$, and vibrational amplitudes were derived from calculated (B3LYP/6-31++G(2df,p)) force fields using the approach of Sipachev incorporated in the program SHRINK.[11] All quantum chemical calculations were performed with the GAUSSIAN 03 program system.[12]

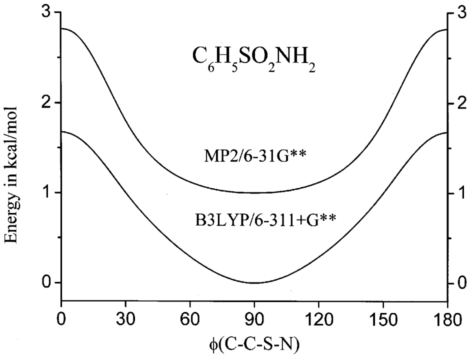


FIGURE 1. Potential function for internal rotation around the C−S bond. MP2 curve is shifted by 1 kcal/mol.

Structure Analysis. According to the mass spectra recorded simultaneously with the diffraction pattern registration (Table 4), the only species was observed in the vapor with the stoichiometry $C_6H_5SO_2NH_2$. A conventional least-squares analysis (LS) of *sM(s)* was carried out using a modified version of the KCED program.[13] Scattering functions and phases of reference[14] were used for calculating the theoretical molecular intensities. According to quantum chemical calculations (see above), two conformers of $C_6H_5SO_2NH_2$, eclipsed (N−H bonds eclipsing the S=O bonds) and staggered (N−H bonds staggering the S−C bond), can exist in the gas phase. Both conformers possess C_s symmetry. According to all calculations (B3LYP and MP2 with different basis sets), the eclipsed form should prevail under the conditions of the GED experiment.

Both conformers can be considered as rather rigid molecules due to a high barrier of internal rotation around the S−N bond.

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(7) Boggia, L. M.; Filgueira, R. R.; Maranon, J.; Sorarraim O. M. *Spectrosc. Lett.* **1978**, *11*, 143. Hargittai, I. Structural Chemistry of Gaseous Sulfoxides and Sulfones. In *The Structural Chemistry of Sulfones and Sulfoxides*; John Wiley & Sons: New York, 1988; pp 33−53.

(8) Petrov, V. M.; Petrova, V. N.; Kislov, V. V.; Ivanov, S. N.; Girichev, G. V.; Noskov, S. Y.; Krasnov, A. V. (Russian). *J. Strukt. Chem.* **1999**, *40*, 4, 654−663.

(9) Petrov, V. M.; Petrova, V. N.; Kislov, V. V.; Ivanov, S. N.; Noskov, S. Y.; Krasnov, A. V.; Bylova, Z. M. (Russian). *J. Strukt. Chem.* **2000**, *40*, 4, 654−663.

(10) Petrov, V. M.; Petrova, V. N.; Chizhova, Z. M. University of Texas at Austin, Austin, TX, 2002; March 3−5.

(11) Sipachev, V. A. *J. Mol. Struct.* **2001**, *67*, 567−568. Sipachev, V. A. *J. Mol. Struct.* **1985**, *121*, 143. Sipachev, V. A. In *Advances in Molecular Structure Research*; Hargittai, I., Hargittai, M., Eds.; JAI Press: New York, 1999; Vol. 5, p 263.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Andersen, B.; Seip, H. M.; Strand, T. G.; Stolevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

(14) Ross, A. W.; Fink, M.; Hildebrandt, R. I. *International Tables of Crystallography C*; Kluwer Academic Publishers: Dordrecht, 1992; p 245.

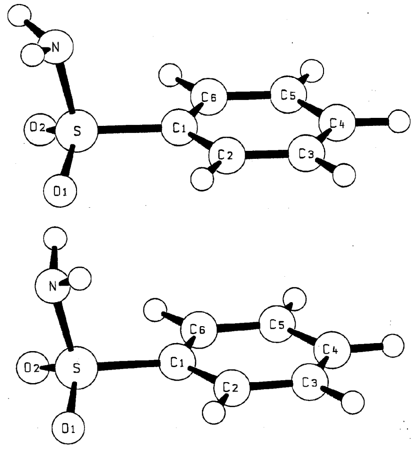

FIGURE 2. Structural models for eclipsed (a) and staggered (b) conformers of benzenesulfonamide, $C_6H_4SO_2NH_2$, with atom numbering.

TABLE 1. Structural Parameters of Benzenesulfonamide, $C_6H_4SO_2NH_2$, from DFT Calculations and GED (Distances in Å, Angles in deg)

	eclipsed		staggered
parameter	GED r_{h1} structure	B3LYP[a] r_e structure	B3LYP[a] r_e structure
C−H	1.092(4)[b] p_1	1.083	1.083
N−H	1.023(4) (p_1)	1.013	1.013
C1−C2	1.403(4) p_2	1.390	1.391
C2−C3	1.402(4) (p_2)	1.389	1.389
C3−C4	1.403(4) (p_2)	1.391	1.391
C1−S	1.775(6) p_3	1.787	1.793
S−N	1.692(5) p_4	1.673	1.663
S−O	1.428(4) p_5	1.445	1.441
∠C2−C1−C6	121.3(2) p_6	121.3	121.1
∠C1−C2−C3	119.1(2) (p_6)	119.1	119.2
∠C2−C3−C4	120.3(6) (p_6)	120.1	120.2
∠C3−C4−C5	120.1(8) (p_6)	120.2	120.2
∠C1−S−N	104.4(7) p_7	103.9	107.1
∠C1−S−O	107.8(4) p_8	107.7	107.6
∠N−S−O	107.0	107.0	105.5
∠H1−N−S	111.0	111.0	113.7
∠H1−N−H2	112.6	112.7	113.6
∠C2−C1−S−N	90.0	90.0	89.5
∠H1−N−S−C1	243.0	243.0	66.7
mol %	100	76	24
R_f, %	2.46		

[a] 6-311++G(2df,p) basis sets. [b] 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).

Molecular models for eclipsed and staggered conformers with atom numbering are shown in Figure 2. On the basis of the results of the quantum chemical calculations, the following assumptions were made to describe the molecular geometry of each conformer in the LS refinement: (1) The conformer has C_s overall symmetry. (2) All atoms of the C_6H_5S entity of both conformers lie in the same plane. (3) All C−H bonds in the ring possess equal lengths and bisect the adjacent C═C═C angles. (4) It has become common use in GED experiments to incorporate structural information from quantum chemical calculations, such as differences between geometric parameters and between vibrational amplitudes or parameters which describe the position of hydrogen atoms in the analysis of experimental intensities. This procedure has been termed MOCED (molecular orbital constrained electron diffraction) and has been tested in great detail in all electron diffraction laboratories.[15] Therefore, the differences between C−H and N−H bond lengths and between C═C bonds and C═C═C angles were constrained to calculated values. (5) The angles S−N−H, H−N−H, and N−S═O were set to calculated values. Refinement of the latter angle caused high correlations with other parameters. With these assumptions, eight independent structural parameters for each conformer were used to define the geometry, five bond distances (C1═C2, C2−H, C1−S, S−N, S═O), and three bond angles (C2═C1═C6, C1−S−N, C1−S═O1). The quantum chemical calculations predict the torsional angle ϕ(C2═C1−S−N) = 90°. All geometrical constructions were made using r_{h1} parameters. A preliminarily LS analysis showed that the agreement factor R_f is quite sensitive toward this torsional angle and the refined value is very close to 90° for both conformers, independent of the starting value. Therefore, this parameter was kept at 90° during the following LS analyses to decrease correlations between refined parameters. The starting values for bond distances and angles were taken from the B3LYP/6-311++G(2df,p) calculations. Similarly, calculated vibrational amplitudes (see above) were used as starting values. In the initial step, it was assumed that the vapor contains only one conformer, eclipsed or staggered, and independent LS refinements were carried out for both conformers. The agreement factors R_f for both refinements were close to each other (2.46% for eclipsed and 2.85% for staggered). The sensitivity of the molecular intensities and of the radial distribution function $f(r)$ toward the presence of different conformers in the vapor is very low.

In the final step, LS analyses were carried out for mixtures of eclipsed and staggered conformers. Eight structural parameters, 11 groups of vibrational amplitudes for the eclipsed conformer, and the vapor composition were refined simultaneously. The geometric parameters of the staggered conformer were tied to those of the eclipsed form using the calculated (B3LYP/6-31++G(2df,p)) differences. Calculated vibrational amplitudes were used for the staggered form. Three correlation coefficients$p_1/p_7 = -0.92$, $p_1/p_8 = 0.77$, $p_4/p_5 = -0.79$ for eclipsed conformer had absolute values larger than 0.7. The best agreement between experimental and calculated *sM(s)* functions was achieved for a contribution of the eclipsed conformer of about 100(70) mol %. The refined geometric parameters (p_1 to p_8) are listed in Table 1 together with calculated values. Experimental and calculated amplitudes, as well vibrational corrections, are collected in the Table 2.

To visualize the low sensitivity of *sM(s)* toward the vapor composition, additional LS analyses with different but fixed compositions were performed. The plot of R_f vs percentage of syn conformer is shown in Figure 3. The Hamilton method[16] at significance levels of 0.05 and of 0.25 demonstrates that the GED method is not very sensitive toward the conformational composition. Figure 4 shows the experimental radial distribution function $f(r)$ and the difference curve for the presence of the eclipsed conformer only.

Discussion

Although the GED method is not very sensitive toward the orientation of the NH_2 group, it clearly demonstrates a prefer-

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(15) . Chiu, N. S.; Ewbank, J. D.; Askari, M.; Schaefer, L. *J. Mol. Struct.* **1979**, *54*, 185.

(16) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

TABLE 2. LS Analysis: Interatomic Distances, Experimental and Calculated Vibrational Amplitudes, and Vibrational Corrections (without Nonbonded Distances Involving Hydrogen Atoms) for Benzenesulfonamide, $C_6H_4SO_2NH_2$ (Eclipsed Conformer)

parameter	r_a	l_{exptl}	l_{calcd}	$\Delta r = r_\alpha - r_a$	no. group
N13−H14	1.018(1)[a]	0.066(2)[a]	0.071	0.005	1
C2−H7	1.087(1)	0.070(2)	0.075	0.005	1
C1−C2	1.401(0.5)	0.049(0.3)	0.046	0.002	2
C2−C3	1.400(0.5)	0.049(0.3)	0.046	0.002	2
C 4-C6	1.402(0.5)	0.049(0.3)	0.046	0.001	2
S12−O16	1.427(0.5)	0.039(0.3)	0.036	0.001	2
S12−N13	1.690(1)	0.059(2)	0.052	0.002	3
C1−S12	1.773(2)	0.061(2)	0.054	0.002	3
C1−C3	2.411(1)	0.059(1)	0.057	0.005	4
C2−C4	2.427(2)	0.058(1)	0.057	0.005	4
C3−C5	2.426(3)	0.059(1)	0.056	0.006	4
C2−C6	2.439(1)	0.059(1)	0.057	0.006	4
N13−O16	2.505(1)	0.098(1)	0.095	0.007	4
O16−O17	2.489(4)	0.064(1)	0.062	0.004	4
C1−O16	2.590(2)	0.083(1)	0.079	0.004	5
C1−N13	2.735(4)	0.095(1)	0.092	0.005	5
C3−S12	2.742(1)	0.075(1)	0.072	0.007	5
C1−C4	2.781(3)	0.068(1)	0.064	0.008	5
C2−C5	2.806(2)	0.068(1)	0.064	0.007	5
C2−O16	2.989(3)	0.179(1)	0.175	−0.041	5
C2−N13	3.485(4)	0.317(3)	0.316	0.049	6
C2−O17	3.787(2)	0.122(2)	0.116	0.058	7
C5−S12	4.036(1)	0.077(2)	0.071	0.014	7
C3−O16	4.352(3)	0.162(3)	0.160	−0.019	8
C4−S12	4.546(3)	0.075(3)	0.072	0.018	8
C3−N13	4.706(5)	0.270(3)	0.268	0.039	8
C3−O17	4.929(2)	0.121(5)	0.115	0.055	9
C4−O16	5.158(4)	0.130(5)	0.124	0.023	9
C4−N13	5.219(6)	0.175(5)	0.170	0.029	9

[a] Standard deviation σ_{LS} (in the units of the last significant digit).

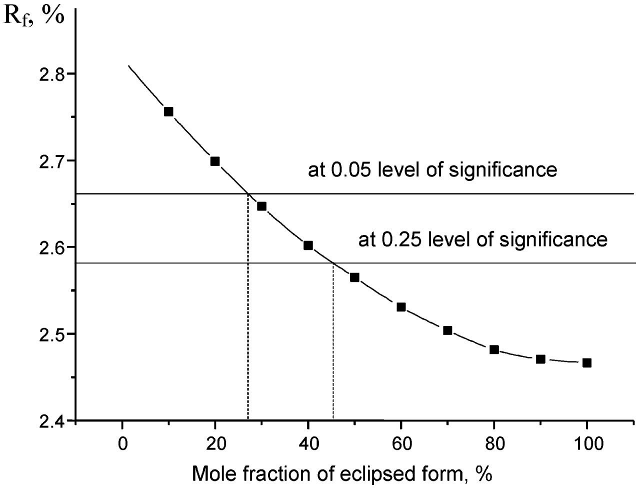

FIGURE 3. Agreement factor R_f for different contributions of eclipsed conformer of benzenesulfonamide, $C_6H_4SO_2NH_2$.

ence for the eclipsed orientation. Intuitively, one would expect a preference for the staggered orientation due to steric interactions. In addition to this, the staggered orientation should be favored by a stabilizing orbital interaction between the nitrogen electron lone pair n_N and the antibonding σ^*(S−C) orbital ($n_N \rightarrow \sigma^*$(S−C), anomeric effect, see Chart 1). Quantum chemical calculations predict eclipsed orientation of the NH_2 group also for the parent sulfonamide, HSO_2NH_2, and this orientation has been rationalized by strong repulsions between nitrogen and oxygen electron lone pairs in the staggered form.[17] On the other hand, in the crystal structure of *N*,*N*-dimethyltoluene-*p*-sulfonamide, *p*-$MeC_6H_4SO_2NMe_2$, the NMe_2 group adopts a staggered orientation,[18] although repulsion between the nitrogen and oxygen lone pairs should have a similar effect in this compound. We suggest that the sterically unfavorable eclipsed orientation of the NH_2 group is stabilized by hydrogen bonds, although the geometric arrangement of the N−H···O entity is not ideal for the formation of such bonds. Indeed, a Mulliken population analysis gives positive values for the H···O contacts (0.008 au from MP2 method), indicating attractive interactions. The experimental structural parameters of benzenesulfonamide are very close to the calculated values, excluding the S═O bond length (Table 1). A very reasonable agreement exists as well between experimental and calculated vibrational amplitudes (Table 2). Table 3 compares important parameters of the SO_2NH_2 group in benzenesulfonamide with those in other benzenesulfonyl derivatives. Since no experimental gas-phase data exist for S(VI)−NH_2 bond lengths, it is not possible to compare our value with those in similar compounds. S−NMe_2 bonds in $ClSO_2NMe_2$ (1.618(5) Å[19]) and $NMe_2SO_2NMe_2$ (1.651(3) Å[20]) are considerably shorter than the S−NH_2 bond in benzenesulfonamide (1.690(5) Å) and depend strongly on the substituent at sulfur. The S═O bond lengths correlate with the donor−acceptor ability of the substituent X in the SO_2X fragment (X = Hal, CH_3, NH_2). A strong correlation between the bond length and the electronegativity of halogen atoms has been pointed out by Petrov et al.[9] The shortest *r*(S═O) bond (1.407(3) Å) was found in 4-$CH_3C_6H_4SO_2F$, where F possesses a strong electron-withdrawing effect. In contrast to this molecule, the S═O bond is significantly longer (1.444(1) Å) in phenylmethyl sulfone where CH_3 is a good donor.[4] In benzenesulfonamide, we found *r*(S═O) = 1.428(4) Å, and this value is in a good agreement with the donor ability of the NH_2 group, which is weaker than that of CH_3.

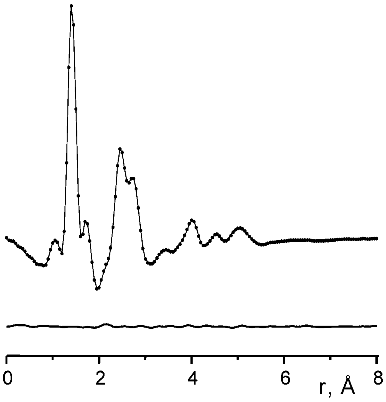

FIGURE 4. Experimental (dotted line) and calculated (solid line) radial distribution functions and residual.

The type of ring distortion in monosubstituted benzene compounds depends on the donor−acceptor properties of the substituent.[21] In benzenesulfonamide, the angle C2−C1−C6 is larger by 1.3(2)° than in unsubstituted benzene. This distortion is typical for substituents with acceptor properties.

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(17) Bharatam, P. V.; Amita; Gupta, A. A.; Kaur, D. *Tetrahedron* **2002**, *58*, 1759.

(18) Hakkinen, A. M.; Ruostesuo, P.; Kivekas, R. *J. Chem. Soc., Perkin Trans. 2* **1988**, 815.

(19) Hargittai, I.; Brunvoll, J. *Acta Chem. Scand.* **1976**, *A30*, 634.

(20) Hargittai, I.; Vajda, E.; Szöke, A. *J. Mol. Struct.* **1973**, *18*, 381.

(21) Campanelli, A. R.; Domenicano, A.; Ramondo, F. *J. Phys. Chem. A* **2003**, *107*, 6429.

TABLE 3. Structural Parameters of Benzenesulfone Molecules (Bond Distances in Å, Angles in deg)

structural parameters	$C_6H_5SO_2Cl$ (ref 5)	$C_6F_5SO_2Cl$ (ref 6)	$C_6H_5SO_2C_3$ (ref 4)	4-$CH_3C_6H_4SO_2F$ (ref 9)	4-$CH_3C_6H_4$ SO_2Cl (ref 8)	$C_6H_5SO_2NH_2$ (this work)
r_a ($C_{phen}-S$)	1.764(9)	1.797(3)	1.770(2)	1.753(7)	1.758(6)	1.774(6)
r_a (S=O)	1.417(12)	1.414(1)	1.444(3)	1.407(3)	1.419(3)	1.427(4)
r_a (S−X)[a]	2.047(8)	2.026(2)	1.782(6)	1.546(6)	2.049(5)	1.690(5)
∠C−S-X	100.9(20)	104.8(4)	103.7(5)	95.0(15)	101.3(6)	104.4(7)
∠X−S−O	105.5(18)	105.3(1)	108.2(3)	109.0(9)	106.9(3)	107.0
∠O−S−O	122.5(36)	123.6(7)	118.4(6)	123.6(15)	120.5(9)	121.7(8)
∠τ($C_{phen}-S$)	75.3(50)	61.8(13)	90	89.5(27)	83	90

[a] Where X = F, Cl, CH_3, NH_2.

TABLE 4. Mass Spectra of the Saturated Vapor of Benzenesulfonamide $C_6H_4SO_2NH_2$, Recorded at $U_{Ioniz} = 50V$ Simultaneously with the Diffraction Pattern Registration

ion	*m/e* (amu)	abundance (relative to $[SO_2NH]^+$, %) long camera	abundance (relative to $[SO_2NH]^+$, %) short camera
$[C_6H_4SO_2NH_2]^+$	157	14	17
$[C_6H_5SO_2]^+$	141	9	11
$[C_5H_4S]^+$	96	14	18
$[C_5H_3S]^+$	95	31	37
$[SO_2NH_2]^+$	80	14	16
$[SO_2NH]^+$	79	100	100
$[C_4H_3]^+$	51	62	66
$[C_4H_2]^+$	50	16	22
$[C_3H_3]^+$	39	6	9

TABLE 5. Conditions of the Simultaneous GED/MS Experiments

parameter	value	
nozzle-to-plate distance, mm	338	598
electron beam current, μA	1.20	1.20
accelerating voltage, kV	93.1	91.5
temperature of effusion cell, °C	149(3)	152(3)
ionization voltage, V	50	50
exposure time, s	180	120
residual gas pressure, Torr	5×10^{-6}	5.5×10^{-6}

Experimental Section

A commercial sample of benzenesulfonamide was recrystallized twice from a water−2-propanol mixture (20% alcohol) until a sample with melting point 161.0(0.2) °C was achieved (lit.[22] mp 162 °C).

Electron diffraction patterns were recorded using the apparatus at Ivanovo State University of Chemistry and Technology described elsewhere.[23,24] An effusion cell with a cylindrical nozzle of 0.6 × 1.0 mm size (diameter × length) was used for evaporation of the sample at a temperature of 150(5) °C. The mass spectrum of the investigated vapor was recorded simultaneously with the diffraction patterns (Table 4).

The highest mass corresponds to the monomeric parent ion. The experimental set of ions demonstrates the absence of any detectable amount of volatile impurities in the sample. The temperature of the effusion cell was measured by a W/Re-5/20 thermocouple that was calibrated by the melting points of Sn and Al. The electron wavelength was measured by polycrystalline ZnO. Electron image plates were used for the registration of the diffraction patterns at two camera distances. The conditions of the combined gas electron diffraction and mass spectrometric experiments (GED/MS) are shown in Table 5. Optical densities of the plates were measured by the computer-controlled microdensitometer.[25] For the microphotometric measurements, six plates each were selected for the long and short camera distance. A rectangular area of about 130 × 9−15 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 along a scan line was 0.1 mm, and the distance between the lines was about 0.28 mm. The films with ZnO diffraction patterns for calibration of electron wavelength were scanned 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. Analysis of the first and second-order derivatives of the $G(s)$ functions was used to make sure that oscillations of $G(s)$, which could be close to the oscillations of the $sM(s)$ function, were absent. No elimination of high-frequency oscillations was done. The molecular intensities $sM(s)$ in the ranges 3.7−30.9 and 1.6−13.8 Å^{-1} for the short and long camera distance, respectively, are shown in Figure 5.

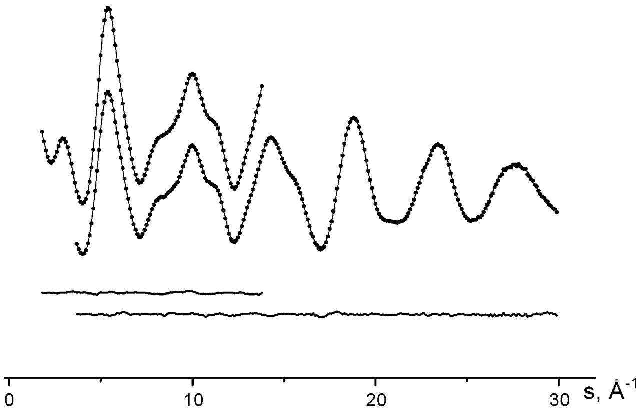

FIGURE 5. Experimental (dotted line) and calculated (solid line) molecular intensities for long (above) and short (below) camera distances and residual.

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Supporting Information Available: Cartesian coordinates and *z*-matrixes of all geometries optimized at all levels of theory referenced, B3LYP, MP2, energies, and number of imaginary vibrational modes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Suter, C. M. *The Organic Chemistry of Sulfur. Tetracovalent Sulfur Compounds*; Winthrop Chemical Co: New York, 1948.

(23) Girichev, G. V.; Utkin, A. N.; Revichev, Yu. F. *Prib. Tekh. Exsp. (Russ.)* **1984**, N2, 187; *Instrum. Exp. Technol.* (*Engl. Transl.*) **1984**, *2*, 457.

(24) Girichev, G. V.; Shlykov, S. A.; Revichev, Yu. F. *Prib. Tekh. Exsp. (Russ.)* **1986**, *N4*, 167; *Instrum. Exp. Technol.* (*Engl. Transl.*) **1986**, *4*, 939.

(25) Girichev, E. G.; Zakharov, A. V.; Girichev, G. V.; Bazanov, M. I. *Izv. VUZ Tekstiln. Prom. (Russ.)* **2000**, *2*, 142.