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Molecular structure and conformations of bis(trifluoromethyl)sulfurdiimide

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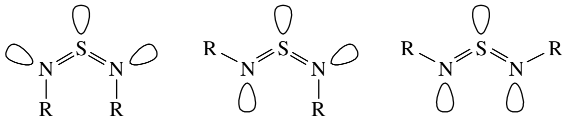
The sterically unfavourable *E*/*Z* and *Z*/*Z* conformers of CF_3N=S=NCF_3, which are present in the gas phase, are stabilised by strong anomeric effects.

The conformational properties of sulfur diimides RN=S=NR have attracted considerable interest by experimentalists and theoreticians. Assuming a planar or nearly planar skeleton, three conformations are feasible: *Z*/*Z*, *E*/*Z* and *E*/*E*. Experimental gas-phase studies have been reported for compounds with electropositive substituents R = H, Me, Bu^t and $SiMe_3$. The parent compound exists as a mixture of *Z*/*Z* and *E*/*Z* forms with slight preference for *E*/*Z*.[1] Only the *E*/*Z* conformer was observed in gas electron diffraction (GED) experiments for R = Me[2] and Bu^t,[3] but a small contribution of the *Z*/*Z* form cannot be excluded for the methyl derivative. The GED intensities of Me_3SiN=S=$NSiMe_3$ were interpreted in terms of a single conformer with non-planar *Z*/*Z* structure and Si–N=S=N dihedral angles of about 40°.[4] The experimental results for R = H, Me and Bu^t are reproduced satisfactorily by quantum-chemical calculations using different computational methods.[3,5,6] *E*/*E* conformers are predicted to be higher in energy by 20 to 30 kJ mol^{-1} and are not expected to be observable. In contrast to experimental results, the B3LYP/6-31G* method predicts a mixture of planar *E*/*Z* and *Z*/*Z* conformers for Me_3SiN=S=$NSiMe_3$ with the *E*/*Z* form strongly prevailing.[7]



Z/*Z* *E*/*Z* *E*/*E*

Here, we report a GED and quantum chemical study of CF_3N=S=NCF_3, a sulfur diimide with electron-withdrawing substituents. Structure optimizations for all three conformers were performed using the MP2 approximation and the B3LYP method with small [6-31G(d)] and large [6-311+(df)] basis sets. A structure possessing C_2 symmetry is derived for the *Z*/*Z* conformer with both CF_3 groups rotated away from the exact staggered orientation relative to the S=N bond. The calculated structure of the *E*/*Z* conformer possesses C_S symmetry with the CF_3 group of the *E*-halve eclipsing and that of the *Z*-halve staggering the vicinal S=N bond (Figure 1). MP2 and B3LYP calculations with small basis sets predict slightly lower energies for the *Z*/*Z* conformer [$\Delta E = E(Z/Z) - E(E/Z) = -4.0$ and –2.1 kJ mol^{-1}, respectively]. However, Gibbs free energies, which are relevant for the experiments, favour the *E*/*Z* form ($\Delta G^0 = 3.2$ and 3.1 kJ mol^{-1}, respectively). Both methods with large basis sets predict higher energies ($\Delta E = 0.9$ and 3.7 kJ mol^{-1}, respectively), as well as higher Gibbs free energies ($\Delta G^0 = 6.3$ and 7.8 kJ mol^{-1}, respectively), for the *Z*/*Z* form. The large differences between ΔE and ΔG^0 are due to different torsional frequencies in the two conformers. The lowest frequency for the *E*/*Z* form is predicted between 10 and 17 cm^{-1} or between 55 and 76 cm^{-1} for the *Z*/*Z* form. This leads to a considerably higher entropy for the *E*/*Z* conformer. The *E*/*E* conformer is calculated to be higher in energy by 14.6 kJ mol^{-1} or more. Vibrational amplitudes and corrections for *E*/*Z* and *Z*/*Z* conformers were derived from B3LYP/6-311+G(df) force fields using the method of Sipachev. [8]

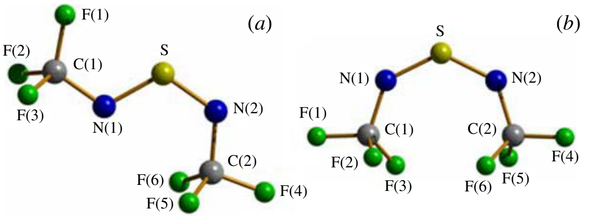


Figure 1 Molecular models for (*a*) *E*/*Z* and (*b*) *Z*/*Z* conformer with atom numbering.

CF_3N=S=NCF_3 was synthesised by the method described previously.[9] Electron diffraction intensities were recorded with a Gasdiffraktograph[10] at 25 and 50 cm nozzle-to-plate distances with an accelerating voltage of about 60 kV. The sample was kept at –26 °C; the inlet system and the gas nozzle were at room temperature. The photographic plates were analysed by usual methods, and molecular intensities in the *s* ranges 2–18 and 8–35 Å^{-1} were derived [$s = (4\pi/\lambda)\sin\theta/2$, where λ is the electron wavelength and θ is the scattering angle]. The radial distribution function (RDF) was calculated by Fourier transformation of the intensities. Figure 2 shows the experimental curve together with calculated functions for the *E*/*Z* and *Z*/*Z* conformers, which differ strongly in the range $r > 2.5$ Å. Comparison between experimental and calculated curves reveals that the *E*/*Z* conformer is prevailing. In the least squares fitting of the molecular intensities, the presence of a mixture of *E*/*Z* and *Z*/*Z* conformers was assumed. The following constraints based on the MP2/6-311+G(df) results were made. For the *E*/*Z* form, C_S overall symmetry and C_{3v} local symmetry for the CF_3 groups with a possible tilt angle between the C_3 axis and the N–C bond direction was assumed. The differences in S=N and N–C bond lengths and in S=N–C angles between the *E*- and *Z*-halve of the molecule were set to calculated values. All C–F bond lengths

Table 1 Experimental and calculated geometric parameters for *E*/*Z* and *Z*/*Z* conformers of $CF_3N{=}S{=}NCF_3$.[a]

Parameter	*E*/*Z*			*Z*/*Z*
	GED[b]	MP2[c]	B3LYP[c]	MP2[c]
S=N(1)	1.547(3)	1.564	1.554	1.551
S=N(2)	1.527(3)[e]	1.544	1.536	1.551
N(1)–C(1)	1.428(7)	1.425	1.417	1.423
N(2)–C(2)	1.434(7)[e]	1.431	1.424	1.423
$(C–F)_{av}$	1.327(2)	1.324	1.337	1.325
C(1)–F(1)	1.344(2)[e]	1.341	1.359	—
N=S=N	114.3(16)	114.1	114.4	128.2
S=N(1)–C(1)	116.1(13)	116.7	119.0	131.7
S=N(2)–C(2)	122.5(13)[e]	123.1	126.6	131.7
$(F–C–F)_{av}$	107.9(4)	108.1	107.7	108.3
tilt[C(1)][d]	4.8(17)	4.0	3.3	2.2
tilt[C(2)][d]	3.2(10)	2.3	2.3	2.2
ϕ[S=N(1)–C(1)–F(1)]	0.0[f]	0.0	0.0	164.0
ϕ[S=N(2)–C(2)–F(4)]	180.0[f]	180.0	180.0	164.0
Contribution (%)	9(4)	8.0	4.0	92.0

[a] Distances in Å, angles in degree. [b] r_a values with 3σ uncertainties; for atom numbering see Figure 1. [c] 6-311+G(df) basis sets. [d] Tilt angles between C_3 axis and N–C bond direction are towards the nitrogen lone pair. [e] Difference to previous parameter constrained to calculated value. [f] Not refined.

were assumed to be equal, except for the C(1)–F(1) bond, which eclipses the S=N bond in the *E*-halve. The difference between this length and the average length was constrained to the calculated difference. The *Z*/*Z* conformer was constrained to C_S symmetry, and all geometric parameters were tied to the respective parameters of the *E*/*Z* form using the calculated differences. The best fit of the experimental molecular intensities (agreement factor $R = 4.29\%$) was obtained for a contribution of 9(4)% of the *Z*/*Z* conformer, corresponding to $\Delta G^0 = 5.8(12)$ kJ mol^{-1}. Experimental and calculated geometric parameters for both conformers are summarised in Table 1, and molecular models with atom numbering are shown in Figure 1. Taking into account that experimentally determined bond distances (r_a values) are systematically longer by about 0.002 to 0.006 Å than calculated equilibrium distances (r_e values), the experimental geometric parameters are reproduced very well by the MP2/6-311+G(df) method, except for the S=N distances, which are predicted slightly too long. The conformational properties are also reproduced correctly by this method.

$CF_3N{=}S{=}NCF_3$ and the other sulfur diimides studied in the gas phase possess unexpected conformational properties. Considering steric interactions, the following sequence of stability is expected: *E*/*E* > *E*/*Z* ? *Z*/*Z*. Experiments and quantum-chemical calculations, however, demonstrate that the *E*/*E* form is by far the least stable conformer and *E*/*Z* and *Z*/*Z* forms possess similar stabilities with the *E*/*Z* conformer slightly favoured. This unexpected sequence of stability can be rationalised on the basis of orbital interactions of sulfur and nitrogen electron lone pairs [lp(S) and lp(N)] with vicinal σ* orbitals. Two types of such anomeric effects can occur in the R–N=S=N–R skeleton, lp(S) → σ*(N–R) and lp(N) → σ*(S=N). These orbital interactions favour strongly the *anti* orientation of lone pair and vicinal bond, *i.e.*, the *Z*/*Z* conformation is strongly favoured. In this conformer, both N–R bonds are *anti* to the sulfur lone pair and both S=N bonds are *anti* to the nitrogen lone pairs. Only two such favourable *trans* arrangements are present in the *E*/*Z* conformer and none in the *E*/*E* form. Natural bond orbital (NBO) analyses of the B3LYP/6-311+G(df) wave functions of $CF_3N{=}S{=}NCF_3$ result in total energies of these orbital interactions of 230, 92 and 33 kJ mol^{-1} for *Z*/*Z*, *E*/*Z* and *E*/*E* conformers, respectively. The high interaction energy in the *Z*/*Z* form compared to that in the *E*/*Z* conformer compensates the much larger steric repulsion, resulting in almost equal total energies for both conformers. The steric repulsion in the *Z*/*Z* form is reflected in an increase of S=N=S and S=N–C angles by 13–14° when going from *E*/*Z* to *Z*/*Z* structure (Table 1).

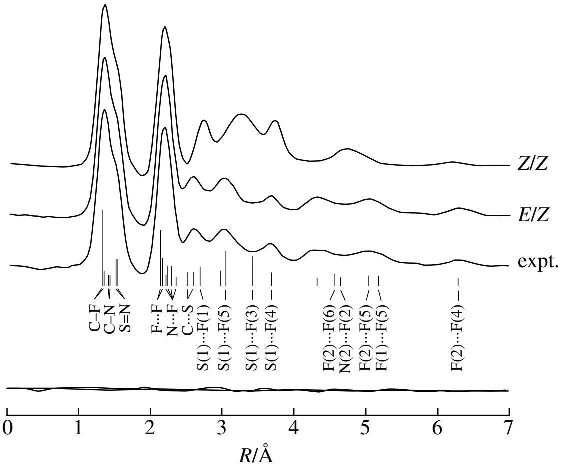


Figure 2 Experimental and calculated radial distribution functions with difference curve. Important distances of the prevailing *E*/*Z* conformer are indicated by vertical bars.

Anomeric effects are also reflected in bond distances. The lp(S) → σ*(N–C) interaction can be represented by the triple-bond-no-bond mesomeric structure $S^+{\equiv}N\ R^-$ leading to shortening of the S=N bond and lengthening of the N–R bond. On the other hand, lp(N) → σ*(S=N) interactions, which can be represented by the triple-bond-single-bond mesomeric structure $N^+{\equiv}S–N^-$, leads to lengthening of the S=N bond in the *E*-halve relative to the bond in the *Z*-halve of the *E*/*Z* conformer. The effect of these interactions on bond distances are too small to be observed in GED experiments, but calculations predict the S=N(2) bond to be shorter by 0.02 Å than S=N(1) and N(1)–C(1) to be slightly shorter than N(2)–C(2). A strong anomeric effect is also present in the N–C–F moiety. All C–F bond lengths in the two CF_3 groups are calculated to be very similar, except for the C(1)–F(1) bond, which eclipses S=N(1) and is *trans* to lp[N(1)]. It is almost 0.02 Å longer than all other C–F bonds. This is in accordance with the double-bond-no-bond mesomeric structure $N^+{=}C\ F^-$ corresponding to the orbital interaction lp[N(1)] → σ*[C(1)–F(1)].

References

1 R. D. Suenram, F. J. Lovas and W. J. Stevens, *J. Mol. Spectrosc.*, 1985, **112**, 482.

2 J. Kuyper, P. H. Isselmann, F. C. Mijlhoff, A. Spelbos and G. Renes, *J. Mol. Struct.*, 1975, **29**, 247.

3 S. L. Hinchley, P. Trickey, H. E. Robertson, B. A. Smart, D. W. H. Rankin, D. Leusser, B. Walfort, D. Stalke, M. Buehl and S. J. Obrey, *J. Chem. Soc., Dalton Trans.*, 2002, 4607.

4 D. G. Anderson, H. E. Robertson, D. W. H. Rankin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 859.

5 H. M. Tuononen, R. J. Suontamo, J. U. Valkonen, R. S. Laitinen and T. Chivers, *Inorg. Chem.*, 2003, **42**, 2447.

6 M. Zahedi, S. Shahbazian and N. S. Weng, *J. Mol. Struct. (Theochem.)*, 2003, **636**, 229.

7 H. Oberhammer, unpublished results.

8 (*a*) V. A. Sipachev, *J. Mol. Struct. (Theochem.)*, 1985, **121**, 143; (*b*) V. A. Sipachev, *Adv. Mol. Struct. Res.*, 1999, **5**, 263; (*c*) V. A. Sipachev, *NATO Science Series II: Mathematics, Physic, Chemistry*, 2002, **68**, 73.

9 M. Geisel and R. Mews, *Z. Anorg. Allg. Chem.*, 1989, **575**, 90.

10 H. Oberhammer, *Molecular Structure by Diffraction Methods*, The Chemical Society, London, 1976, vol. 4, p. 24.

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