The structure of diethylaminosulfur trifluoride (DAST) — a combined theoretical and nuclear magnetic resonance study [1]

Thomas M. Klapötke, Axel Schulz

Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK

Abstract

The structure of diethylaminosulfur trifluoride (DAST) was computed and fully optimized in C_1 symmetry at the RHF/6-31G** level of theory. In agreement with VSEPR considerations, the isolated molecule adopts the structure of a pseudo trigonal bipyramid (ψ-tbp) with one fluorine atom, the nitrogen atom and the lone pair in the equatorial position; the other two fluorine atoms are in the axial positions. In agreement with earlier work by other authors a ψ-tbp structure was also postulated for the DAST molecule dissolved in non-polar solvents from temperature-dependent solution ^{19}F NMR spectroscopy. The free activation enthalpy for the interconversion was estimated from experimental data to be $\Delta G^{\neq} = 8.5 \pm 0.5$ kcal mol^{-1}. In the ^{14}N NMR spectrum at low temperatures only a significant line broadening but no splitting of the signals was observed. The molecule $(H_2N)SF_3$ was calculated as a model compound for DAST at the same level of theory, and in addition at electron correlated MP2 level. The global minimum (ATM, absolute true minimum) for $(H_2N)SF_3$ is also represented by a ψ-tbp structure with the nitrogen atom and the lone pair in the equatorial position. In addition, a second true minimum (TM) was found with two fluorine atoms and the lone pair in equatorial positions and the nitrogen and one fluorine atom occupying the axial positions. Three transition states (TS) were found for the interconversion of the model compound $(H_2N)SF_3$.

1. Introduction

Diethylaminosulfur trifluoride (DAST) is a widely used and effective fluorinating agent [1,2]. On the basis of the observed and calculated ^{19}F NMR spectra a trigonal bipyramidal structure for DAST has been suggested [3,4]. We now wish to report on a combined experimental NMR and theoretical ab initio study of the molecular structure of the diethylaminosulfur trifluoride molecule.

2. Experimental details

2.1. Materials

$(C_2H_5)_2NSF_3$ (DAST) was prepared by literature methods [3] from the reaction of $(C_2H_5)_2NSi(CH_3)_3$ with SF_4 (Air Products) and purified by fractional distillation under reduced pressure.

2.2. NMR spectra

The NMR spectra (^{14}N, ^{19}F) were recorded in 10 mm NMR tubes in CD_2Cl_2 solution (see Table 1) using a Bruker SY 200 spectrometer operating at 14.462 MHz (^{14}N) or 188.313 MHz respectively. All spectra are reported in ppm in the δ scale and are referred to external $MeNO_2$ (^{14}N) or $CFCl_3$ (^{19}F) respectively. Good ^{14}N spectra could usually be obtained after 5000 scans and a pulse width of 48 µs, ^{19}F spectra after 20 scans and a pulse width of 2 µs. Peak positions appearing downfield (high-frequency) of the reference are reported as plus and those upfield (low-frequency) of the reference are reported as minus.

Table 1
^{14}N NMR data of DAST

T (°C)	δ relative to $MeNO_2$ (ppm)	$\Delta \nu_{1/2}$ (Hz)
+24	−264	870
−30	−258	1720
−50	−276	1950
−80	−267	3900
−90	No resonance found	

2.3. Computational methods

The structure and vibrational data were calculated using the program package Gaussian 94 [5]. For all atoms a standard 6-31G(d, p) basis set was used and the computations were done at the self consistent field level (RHF), and for the model compound H_2NSF_3 in addition at electron correlated MP2 level.

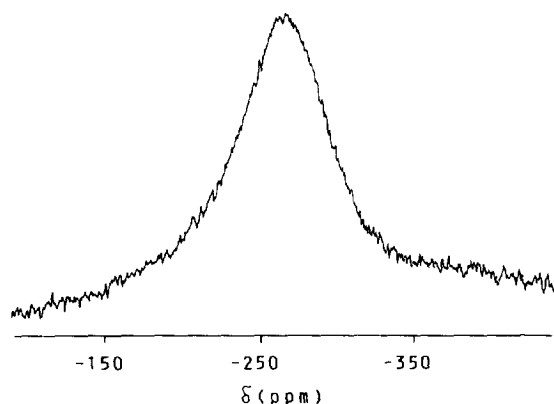Fig. 1. RHF/6-31G** optimized structure of $(C_2H_5)_2NSF_3$. Bond distances in ångströms, angles in degrees: S1–N1 1.625, F1–S1 1.574, F2–S1 1.681, F3–S1 1.668, C1–N1 1.475, C2–N1 1.474; N1–S1–F1 106.0, N1–S1–F2 91.0, N1–S1–F3 90.2, F1–S1–F2 85.9, F1–S1–F3 85.7, F2–S1–F3 171.5, S1–N1–C1 122.6, S1–N1–C2 121.4, C1–N1–C2 115.8; F1–S1–N1–F2 86.0, F1–S1–N1–F3 −85.6, F2–S1–N1–F3 −171.6.
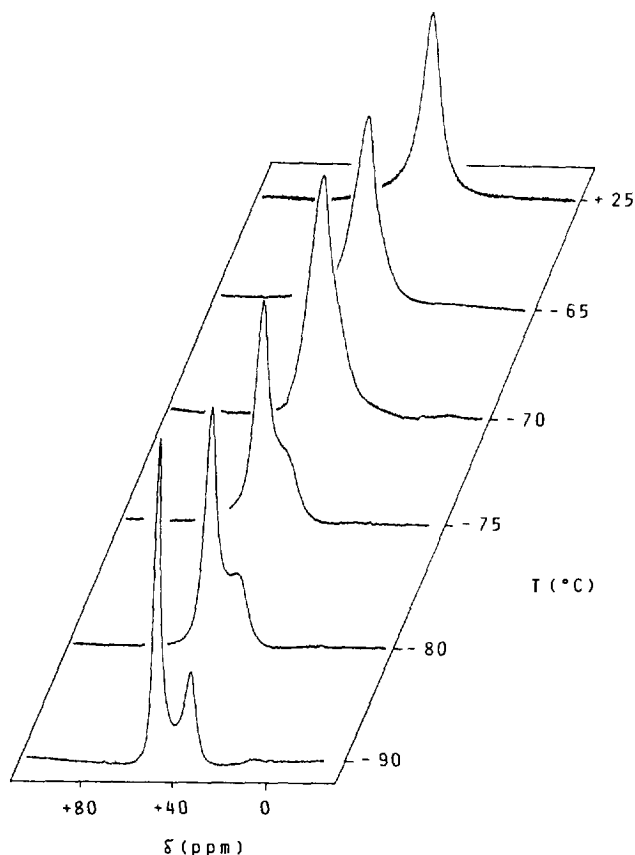

Fig. 2. ^{14}N NMR spectrum of DAST in CD_2Cl_2 solution at 24 °C.

3. Results and discussion

The structure of diethylaminosulfur trifluoride (DAST) was computed and fully optimized in C_1 symmetry at the RHF/6-31G** level of theory (Fig. 1). In agreement with VSEPR considerations [6], the isolated molecule adopts the structure of a pseudo trigonal bipyramid (ψ-tbp) with one fluorine atom, the nitrogen atom and the lone pair in the equatorial position; the other two fluorine atoms are in the axial positions (absolute true minimum ATM, NIMAG = 0).

The experimentally obtained ^{14}N NMR data are summarized in Table 1. Fig. 2 shows the ^{14}N NMR spectrum of DAST at +24 °C and Fig. 3 illustrates the temperature-dependent ^{19}F NMR spectrum of the same molecule. At low temperatures the ^{19}F NMR spectrum shows two resolved resonances at +35.3 and +49.5 ppm in the intensity ratio of 1:2 corresponding to one equatorial and two axial fluorine atoms. At temperatures above the coalescence temperature ($T_c = -63$ °C) only one average signal due to fast exchange at +44.0 ppm was observed. The free activation enthalpy for the interconversion was estimated according to Eq. (1) [7] from the experimental data $T_c = 210 \pm 10$ K and $\Delta \nu = 2674$ Hz to be $\Delta G^\# = 8.5 \pm 0.5$ kcal mol^{-1}:
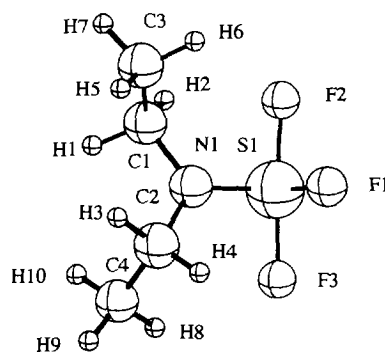

Fig. 3. Temperature-dependent ^{19}F NMR spectrum of DAST in CD_2Cl_2 solution.
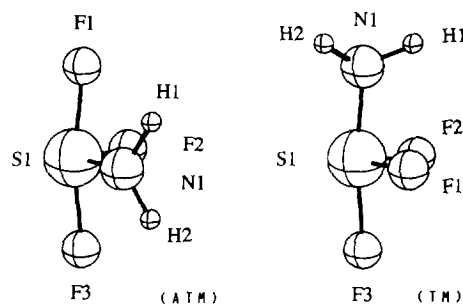

Fig. 4. MP2/6-31G** optimized structures of H_2NSF_3; left ATM (global minimum, N equatorial), right TM (true minimum, N axial), bond distances in ångströms, angles in degrees. ATM (left): S1–N1 1.630, F1–S1 1.705, F2–S1 1.602, F3–S1 1.705; F1–S1–F3 169.3, F1–S1–N1 86.5, F2–S1–N1 108.8, F2–S1–F3 87.2, N1–S1–F3 90.0, F1–N1–F3 −171.8. TM (right): S1–N1 1.704, F1–S1 1.624, F2–S1 1.605, F3–S1 1.710; F1–S1–F3 85.1, F1–S1–N1 92.8, F2–S1–N1 87.1, F2–S1–F3 84.9, N1–S1–F3 −171.5, F1–N1–F3 75.3.

Table 2

Ab initio computed absolute and relative energies for H_2NSF_3

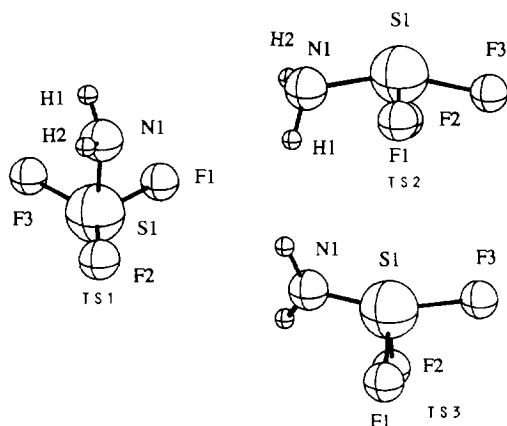|	ATM	TM	TS1	TS2	TS3
E^{RHF} (a.u.)	−751.34592	−751.30436	−751.28520	−751.29937	−751.27782
E^{MP2} (a.u.)	−752.19443	−752.15595	−752.14995	−752.15385	−752.14305
E_{rel}^{MP2} (kcal mol^{-1})	0.0	24.1	27.9	25.5	32.2

Fig. 5. Transition states (NIMAG = 1) for the interconversion of H_2NSF_3: TS1 (tbp with N and lone pair both in axial position); TS2 (quadratic pyramid with the lone pair in apical position); TS3 (tbp with N axial and the lone pair equatorial).

$$\Delta G^{\#}[\text{cal mol}^{-1}]$$

$$= 4.58 T_c[K](9.97 + \log T_c[K]/\Delta \nu T_c[Hz]) \qquad (1)$$

The molecule $(H_2N)SF_3$ was calculated as a model compound for DAST at the same level of theory (RHF), and in addition at electron correlated MP2 level. The global minimum (ATM, absolute true minimum) for $(H_2N)SF_3$ is also represented by a ψ-tbp structure with the nitrogen atom and the lone pair in the equatorial position (Fig. 4). In addition, a second true minimum (TM, higher energy isomer) was found with two fluorine atoms and the lone pair in equatorial positions, and the nitrogen and one fluorine atom occupying

the axial positions (Fig. 4). Three transition states (TS) were found for the interconversion of the model compound $(H_2N)SF_3$ (Fig. 5, Table 2).

Acknowledgements

References

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