Structures and Thermodynamics of the Sulfuranes SF_3CN and $SF_2(CN)_2$ as well as of the Persulfurane $SF_4(CN)_2$ − An ab initio MO Study by the G3(MP2) Method[‡]

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Keywords: Sulfuranes / Sulfur / Cyanides / Fluorides / Transition states / Reaction mechanisms

At the G3(MP2) level of theory the *trans* isomer **1a** of the hypothetical molecule $SF_4(CN)_2$ is more stable than the *cis* isomer **1b** by 8 kJ·mol^{-1}. The isomerization of **1a** to **1b** requires an activation enthalpy of 319 kJ·mol^{-1} at 298 K. The decomposition of *trans*-$SF_4(CN)_2$ to $SF_2(CN)_2$ and F_2 is endothermic (ΔH°_{298} = 395 kJ·mol^{-1}) but the elimination of FCN from *trans*-$SF_4(CN)_2$ is exothermic by −7 kJ·mol^{-1}. The elimination of $(CN)_2$ from *cis*-$SF_4(CN)_2$ is exothermic by −137 kJ·mol^{-1}. The activation enthalpies for the latter two reactions were calculated as 251 and 311 kJ·mol^{-1}, respectively. Thus, $SF_4(CN)_2$ should be a thermally stable compound. In the sulfuranes SF_3CN and $SF_2(CN)_2$ the CN ligands prefer the equatorial positions; mutual exchange of an axial F atom by an equatorial CN group requires a reaction enthalpy of 51 kJ·mol^{-1} [SF_3CN] or 58 kJ·mol^{-1} [$SF_2(CN)_2$].

Introduction

The sulfur fluorides SF_4 and SF_6 are both important industrial products[1] and highly interesting molecules from a theoretical point of view. As so-called hypervalent or − better − hypercoordinate species they have attracted much attention.[2] In addition, numerous mixed derivatives of the types SF_3X and SF_5X have been prepared.[3] Fluorination of either dirhodane $(SCN)_2$ or SF_3CN by elemental fluorine produces SF_5CN, see Equations (1) and (2).[4−6]

$$(SCN)_2 + 5\,F_2 \rightarrow 2\,SF_5CN \qquad (1)$$

$$SF_3CN + F_2 \rightarrow SF_5CN \qquad (2)$$

Evidently, SF_3CN will be an intermediate in Equation (1). According to a combined electron diffraction and microwave spectroscopic investigation the molecule SF_5CN has C_{4v} symmetry in the gas phase.[5] While gaseous SF_5CN is stable up to 350 °C in a flow reactor at low pressures,[4] the related compound $SF_4(CN)_2$ has never been prepared. The same holds for the other members of the series $SF_{6-x}(CN)_x$ with $x > 2$.

To investigate the thermodynamic and the thermal stability of $SF_4(CN)_2$ we have studied for the first time the hypothetical decomposition reactions, presented in Equations (3) to (7) of this molecule using ab initio MO methods.

$$SF_4(CN)_2 \rightarrow SF_2(CN)_2 + F_2 \qquad (3)$$

$$SF_4(CN)_2 \rightarrow SF_3CN + FCN \qquad (4)$$

$$SF_4(CN)_2 \rightarrow SF_4 + (CN)_2 \qquad (5)$$

All the expected decomposition products are experimentally known compounds. SF_3CN and $SF_2(CN)_2$ are accessible by metathesis reactions of SF_4 with Me_3SiCN at low temperatures [Equations (6) and (7)].[7]

$$SF_4 + Me_3SiCN \rightarrow SF_3CN + Me_3SiF \qquad (6)$$

$$SF_3CN + Me_3SiCN \rightarrow SF_2(CN)_2 + Me_3SiF \qquad (7)$$

An earlier report[8] on the synthesis of $SF_2(CN)_2$ according to Equations (6) and (7) was said to be partly in error.[7] SF_3CN is a colorless liquid which is stable at room temperature for a few days but slowly decomposes according to Equation (8).[7]

$$2\,SF_3CN \rightarrow SF_4 + SF_2(CN)_2 \qquad (8)$$

The structure of SF_3CN has been determined by electron diffraction in the gas phase as well as by ab initio MO calculations at the MP2/6-31G* level of theory.[9] The molecule is of C_1 symmetry; its structure can be derived from

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[‡] Sulfur Compounds, 227. Part 226: R. Steudel, *Chem. Rev.* **2002**, *102*, 3905.

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DOI: 10.1002/ejic.200300027

the structure of SF_4 by replacement of an equatorial fluorine atom by a cyano ligand. $SF_2(CN)_2$ is a colorless solid which rapidly decomposes at room temperature.[7] No structural analysis or theoretical treatment of this molecule has been published yet.

Calculations

Standard ab initio MO calculations were performed by using the Gaussian 98 series of programs.[10] The energies of various equilibrium structures and transition states were examined at the G3(MP2) level of theory.[11] In brief, the G3(MP2) method is a composite procedure which provides an accurate approximation to a high level of theory at QCISD(T)/GTMP2LARGE//MP2(full)/6-31G(d), with the incorporation of zero-point energy [calculated from HF/6-31G(d) vibrational wavenumbers, scaled by 0.8929] and higher level corrections. For small molecules this level of theory is usually within 6 kJ·mol^{-1} of accurate experimental values.[11] In the case of the hypervalent SF_6 molecule the related G2(MP2) method — using the same geometry calculation as in G3(MP2) — reproduced the very accurate experimental enthalpy of formation within 7.5 kJ·mol^{-1}.[12] A charge density analysis, at the MP2(full)/6-31G(d) level, was performed using the natural bond orbital (NBO) approach.[13] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[14] Unless otherwise noted, all relative energies reported in this publication are given as $\Delta H°_{298}$ and correspond to the G3(MP2) level, while structural parameters were obtained at the MP2(full)/6-31G(d) level.

The transition states obtained were characterized by one imaginary vibrational wavenumber (**TS1**: 693i; **TS2**: 264i; **TS3**: 694i; **TS4**: 890i) whereas the wavenumbers of the structures of minimal energy were all real. The intrinsic reaction coordinates were calculated at the HF/6-31G* level.[15]

Results and Discussion

Geometrical Structures

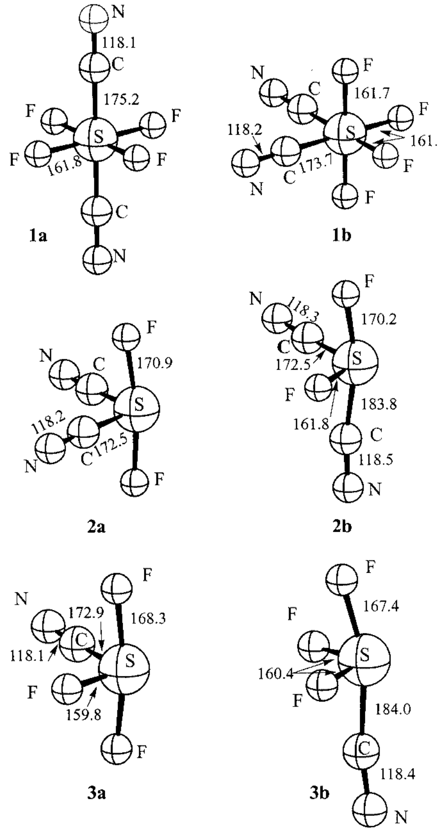


Figure 1. Molecular structures and bond lengths [pm] of two isomers each of the persulfurane $SF_4(CN)_2$ (**1a**, **1b**), the sulfurane $SF_2(CN)_2$ (**2a**, **2b**) and of the sulfurane $SF_3(CN)$ (**3a**, **3b**), calculated at the MP2(full)/6-31G(d) level of theory

To check the accuracy of the G3(MP2) method for the treatment of hypervalent compounds the enthalpies of F_2, SF_4 and SF_6 were calculated and the reaction enthalpy for the formation of SF_6 from F_2 + SF_4 was obtained as −439.1 kJ·mol^{-1} at 0 K. From the best available experimental enthalpies of formation of these compounds[12] the reaction enthalpy is calculated as −450 ± 20 kJ·mol^{-1} at 0 K. This agreement is quite satisfactory.

The sulfuranes $SF_2(CN)_2$ and SF_3CN as well as the persulfurane $SF_4(CN)_2$ given in Equations (3) to (5) exist as several isomers depending on the axial/equatorial or *cis*/*trans* position of the cyano ligands. The molecular structures and internuclear distances of these six isomers are shown in Figure 1; additional geometrical parameters are listed in Table 1.

In the case of the two octahedral molecules $SF_4(CN)_2$ the isomer with the *trans* position of the two CN ligands (**1a**) is slightly more stable than the *cis* isomer **1b**, by 8 kJ·mol^{-1}. The NBO atomic charges [a.u.] on the fluorine atoms are −0.49 ± 0.01 in these isomers while the carbon atoms bear

Table 1. Selected bond angles of the sulfuranes $SF_2(CN)_2$ and SF_3CN [°], calculated at the MP2(full)/6-31G(d) level of theory

$SF_2(CN)_2$ (**2a**)	$SF_2(CN)_2$ (**2b**)	SF_3CN (**3a**)	SF_3CN (**3b**)
N1−C1−S 175.9	N1−C1−S 170.0	N−C−S 176.3	N−C−S 170.2
N2−C2−S 175.9	N2−C2−S 176.1	F1−S−C86.5	C−S−F1 163.0
F−S−F 170.7	F−S−F 84.7	F3−S−C 103.3	F2−S−F3 112.0
C−S−C 102.9	C−S−C 87.3	F1−S−F2 169.9	F1−S−F2 85.3
F2−S−C1 87.1	F2−S−C1 165.1	F1−S−F2 87.2	F3−S−C 85.3

a small positive charge of 0.07 in **1a** and 0.03 in **1b**. Therefore, the nonbonding F···F interactions must be strongly repulsive while the nonbonding F···C interactions will be weak as far as Coulomb forces are concerned. The sulfur atoms are highly positively charged (+2.31 in both cases) and the nitrogen atoms are slightly negative (−0.22).

Isomer **1a** is of D_{4h} symmetry and **1b** is of C_{2v} symmetry. All bond angles in **1a** are exactly 90 or 180°, i.e. the SCN groups are strictly linear; in **1b** the SCN bond angle is 179.6°. The space requirement of the cyano ligands seems to be slightly larger than that of the fluorine atoms since the C−S−C angle in **1b** is 92.3° while the F−S−F angle in the same plane is only 87.5°. All other bond angles of this molecule are within 0.5° of either 90 or 180°.

The calculated bond lengths of *trans*-$SF_4(CN)_2$ are in fair agreement with the experimental data reported for the related molecule SF_5CN,[5] although ab initio MO calculations at the MP2(full)/6-31G(d) level slightly overestimate the internuclear distances. In addition, the bonds become progressively shorter as the fluorine content of the molecule increases. Thus, the S−F distances in SF_5CN are 155.8 and 156.6 pm compared to 161.8 pm in **1a**. Similarly, the C−N and S−C distances of 115.4 pm and 176.5 pm, respectively, in SF_5CN support our results for the corresponding bonds of **1a** which are 118.1 and 175.2 pm, respectively.

The sulfurane molecules of the type $SF_{4-x}(CN)_x$ can be derived from a trigonal bipyramid in which one corner is empty (or occupied by a lone pair of electrons). In this type of molecule the axial and equatorial positions are not equivalent. Since the electronegativity of the CN group is lower than that of the fluorine atoms the preferred position for the CN ligands in the two sulfuranes $SF_2(CN)_2$ and SF_3CN should be the equatorial plane, as observed in the case of other sulfuranes.[16] In fact, the symmetrical isomer of $SF_2(CN)_2$ (**2a**) with both CN ligands in the equatorial plane is by 58 kJ·mol^{-1} more stable than the less symmetrical form with one CN ligand equatorial and the other in an axial position (**2b**). When we tried to optimize a structure with both CN groups in axial positions (**2c**), the molecule rearranged to isomer **2a**. In the case of SF_3CN the CN ligand is in an equatorial position in the most stable isomer **3a**; the isomer **3b** with an axial CN ligand is by 51 kJ·mol^{-1} less stable than **3a**.

The geometrical parameters calculated for **3a** may be compared with the electron diffraction data of this molecule.[9] The bond lengths [pm] are as follows (calcd./exp. data): $S-F_{eq.}$ 159.8/155.2(4), $S-F_{ax}$ 168.3/165.7(3), S−C 172.9/173.6(8), C−N 118.1/115.9(4). Given the systematic difference between the calculated r_e and the experimental r_a bond lengths the agreement is satisfactory. The NBO atomic charges of **3a** are as follows: $F_{eq.}$ −0.46, F_{ax} −0.59, S +1.85, C +0.01, N −0.21.

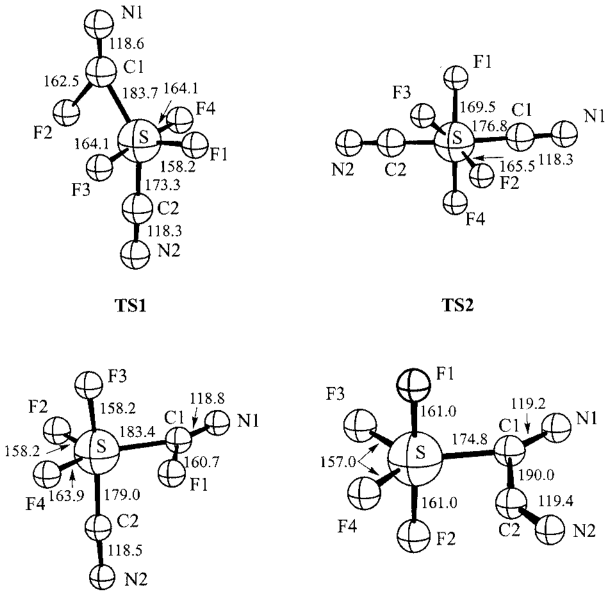
In all sulfurane isomers of the type SF_3CN and $SF_2(CN)_2$ the angles between the two axial S−X bonds are smaller than 180° and these axial bonds are bent away from the formally empty corner of the trigonal bipyramid, i.e. away from the position of the anticipated lone pair at the sulfur atom. The deviation from linearity is 10 ± 1° in the case of **2a** and **3a** but 18 ± 1° in the case of the less stable isomers **2b** and **3b** (see Table 1). This structural feature is well known from SF_4.[2]

The SCN groups are practically linear in the octahedral species **1a** and **1b** (179.8 ± 0.2°) but slightly bent in the various isomers of SF_3CN and $SF_2(CN)_2$: the equatorial SCN groups show bond angles of $\alpha = 176.1 \pm 0.2°$ while the axial SCN groups are more strongly bent ($\alpha = 170.1 \pm 0.1°$).

Transition States and Thermodynamics

The reaction according to Equation (3) is strongly endothermic and therefore can be ruled out for any spontaneous decomposition of $SF_4(CN)_2$ at moderate temperatures. Using the most stable isomers of the reactants, the enthalpy change of reaction shown in Equation (3) is +395 kJ·mol^{-1} at 298 K. Under the same conditions reactions shown in Equations (4) and (5) are exothermic by −137 and −7 kJ·mol^{-1}, respectively. The Gibbs energies ($\Delta G°_{298}$) of the reactions according to Equations (3) to (5) are +341, −187 and −41 kJ·mol^{-1}, respectively, reflecting the increase in entropy during dissociation. From these data it follows that only the reverse reaction according to Equation (3) is a potential route for the synthesis of $SF_4(CN)_2$ at low temperatures.

The transition states for the decomposition reactions according to Equations (4) and (5) have been located on the potential energy hypersurface and their structures are shown in Figure 2. Starting from the most stable isomer **1a** only FCN can be eliminated directly. The corresponding transition state (**TS1**) is shown in Figure 2. The activation



TS1 **TS2**

TS3 **TS4**

Figure 2. Molecular structures and bond lengths [pm] of the transition states for the elimination of FCN from *trans*-$SF_4(CN)_2$ **1a** (**TS1**), for the *cis* $\rightleftarrows$ *trans* isomerization between **1a** and **1b** (**TS2**), for the elimination of FCN from **1b** (**TS3**) and for the elimination of $(CN)_2$ from **1b**, calculated at the MP2(full)/6-31G(d) level of theory

barriers are $\Delta H^{\neq}_{298}$ = 251 kJ·mol^{-1} and $\Delta G^{\neq}_{298}$ = 251 kJ·mol^{-1}.

In the case of Equation (5) an intramolecular isomerization has to take place first to generate **1b** in which the two CN ligands are neighboring. Structure **1b** may then decompose with elimination of either FCN or $(CN)_2$. The transition state for the isomerization of **1a** to **1b** (**TS2**) is also shown in Figure 2. The activation enthalpy for this reaction is 319 kJ·mol^{-1} ($\Delta G^{\neq}_{298}$ = 317 kJ·mol^{-1}). The subsequent decomposition of **1b** to SF_3CN + FCN requires an activation enthalpy of 271 kJ·mol^{-1} ($\Delta G^{\neq}_{298}$ = 271 kJ·mol^{-1}) while the elimination of $(CN)_2$ from **1b** can be initiated by an activation enthalpy of 311 kJ·mol^{-1} ($\Delta G^{\neq}_{298}$ = 309 kJ·mol^{-1}). The overall activation barriers starting from the most stable isomer **1a** are consequently $\Delta G^{\neq}_{298}$ = 317 + 271 = 588 kJ·mol^{-1} for the reaction according to Equation (4) and $\Delta G^{\neq}_{298}$ = 317 + 309 = 626 kJ·mol^{-1} for the reaction according to Equation (5). Evidently, these energies are unrealistically high since, for instance, the homolytic dissociation of SF_6 into SF_5 and an F atom requires a reaction enthalpy of only 453 kJ·mol^{-1}.[17] Therefore, one would expect that *trans*-$SF_4(CN)_2$ (**1a**) also breaks down into two radicals rather than isomerizing intramolecularly with subsequent elimination of either FCN or $(CN)_2$ if a Gibbs activation energy of more than 600 kJ·mol^{-1} energy is provided.

The structures of the transition states for the elimination reactions according to Equations (4) and (5) (**TS3** and **TS4**) are shown in Figure 2. Their geometries (C_1 symmetry) are most interesting. In **TS3** a bent FCN unit is connected to the sulfur atom by both a weak S−F bond of length 208.3 pm and a C−S bond of length 183.4 pm; all four atoms are located essentially in one plane with an F−C−N angle of 139.4° (torsion angle N7−C−F2−S: −174°). The other two S−F bonds in that same plane have decreased in length from 161.4 ± 0.3 pm in **1b** to 158.2 and 159.9 pm, respectively, in **TS3**, while the fourth S−F bond has increased in length to 163.9 pm. The structure of **TS4** is characterized by a weak C−C bond of length 190.0 pm, much longer than calculated for isolated $(CN)_2$ (138.1 pm). The two CN units are exactly co-planar. The C−S−C angle is 81.6° but the two C−S bonds are very different with distances of 174.8 and 238.6 pm. In contrast, the two C−N bonds are almost identical with 119.2 and 119.4 pm, slightly longer than in **1b** (118.2 pm) and in $(CN)_2$ (118.5 pm). In other words, it is only *one* CN group which is moving away from the sulfur atom on transformation of **1b** into **TS4**. The other CN group is just bending; its S−C−N angle decreases from 179.6° in **1b** to 145.3° in **TS4**. The SF_4 unit of **TS4** is already very close in geometry to the isolated SF_4 molecule. Despite the low symmetry the S−F bond lengths of **TS4** are pairwise identical and the $F_{ax}-S-F_{ax}$ angle is 174.4°.

We did not succeed in localizing a transition state for the elimination of F_2 from either **1a** or **1b**. This strongly endothermic reaction may proceed without any additional activation energy.

Summarizing, it follows from the above thermodynamic data that the isomerization **1a**→**1b** is highly unfavorable and $SF_4(CN)_2$ is expected to decompose, if at all, with elimination of FCN from the ground state structure **1a**. However, the height of the barriers indicates that $SF_4(CN)_2$ molecules will be quite stable as far as unimolecular dissociation reactions are concerned.

Acknowledgments

We are grateful to Priv.-Doz. Dr. Dieter Lentz for suggesting this investigation to us. This work was supported by the Deutsche Forschungsgemeinschaft, the Verband der Chemischen Industrie and the Konrad-Zuse-Zentrum für Informationstechnik Berlin.

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Received January 13, 2003