Structures of the Octahedral Persulfuranes H_4SF_2, H_2SF_4, Me_2SH_4 and Me_2SF_4, and Activation Enthalpies for Their *cis*/*trans* Isomerization[‡]

Yana Steudel[a] and Ralf Steudel*[a]

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Eight hypothetical persulfurane molecules of the type X_2SY_4 (X, Y = H, F, Me) have been studied by ab initio MO calculations at the G3(MP2) level of theory. Depending on the substituents either the *cis* or the *trans* isomers of these octahedral molecules are most stable. While H_4SF_2 is most stable as the *cis* isomer, the global minimum structures of H_2SF_4, Me_2SH_4, and Me_2SF_4 are the *trans* isomers. The enthalpy differences between the corresponding isomers are in the range 7–53 kJ·mol^{-1}. The transition states for the intramolecular *cis* ⇌ *trans* isomerization have been located in all cases. Starting from the global minimum geometries the activation enthalpies ($\Delta H^{\#}_{298}$) for this isomerization are in the range 199–263 kJ·mol^{-1}, indicating rather rigid structures. Therefore, it should be possible to isolate both isomers at low to moderate temperatures.

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Introduction

The persulfurane SF_6 is not only an important industrial product[2] but also one of the most-investigated molecules as far as the bonding properties of so-called hypervalent or hypercoordinate molecules are concerned.[3] Numerous derivatives of the types RSF_5 and R_2SF_4 are known[4,5] but the most simple examples, HSF_5 and H_2SF_4, have never been prepared. While HSF_5 has been investigated by ab initio MO calculations,[6,7] the related molecules H_2SF_4 and H_4SF_2 have not yet been studied at all. We have used these species as model compounds to determine the activation energies for the mutual isomerization of the *cis* and *trans* isomers of octahedral persulfuranes for the first time. To further study the influence of the substituents on these energies the methyl-substituted species Me_2SH_4 and Me_2SF_4 were also included in this investigation. These molecules are also hypothetical species. A theoretical treatment of Me_2SF_4 (at the HF/3-21G* level of theory) has been published before,[8] but no structural data were given and only *trans*-Me_2SF_4 was considered. The formation of Me_2SF_4 from Me_2SF_2 and F_2 was shown to be exothermic.

Calculations

Standard ab initio MO calculations were performed using the Gaussian 98 series of programs.[9] The energies of various equilibrium structures and transition states were examined at the G3(MP2) level of theory.[10] 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 (ZPE) [calculated from HF/6-31G(d) vibrational wavenumbers, scaled by 0.8929] and higher level corrections. It has been shown before that this theoretical method is suitable for hypercoordinate molecules: The reaction enthalpy for the formation of SF_6 from F_2 and SF_4 was obtained as -439.1 kJ·mol^{-1} at 0 K,[1] whereas from the best available experimental enthalpies of formation of these compounds[11] the reaction enthalpy is calculated as -450 ± 20 kJ·mol^{-1} at 0 K. 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 accurately known experimental enthalpy of formation within 7.5 kJ·mol^{-1}.[11]

For all investigated molecules a charge-density analysis, at the MP2(full)/6-31G(d) level, was performed using the natural bond orbital (NBO) approach.[12] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[13] Unless otherwise noted, all relative energies reported in this publication are given as ΔH°_{298} and correspond to the G3(MP2) level, while structural parameters were obtained at the MP2(full)/6-31G(d) level. Since *trans*-Me_2SF_4 (**4a**) does not represent a minimum at the HF/6-31G(d) level of theory, for the calculation of G3MP2 enthalpies and Gibbs energies of **4a**, **4b**, and **TS4** the ZPE and the entropy values obtained from the frequency calculation at the MP2(full)/6-31G(d) level of theory were used.

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[a] Institut für Chemie, Technische Universität Berlin, Sekr. C2,
10623 Berlin, Germany
Fax: (internat.) +49-(0)30-31426519
E-mail: steudel@schwefel.chem.tu-berlin.de

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The transition states obtained were characterized by one imaginary vibrational wavenumber whereas the wavenumbers of the structures of minimal energy were all real. The intrinsic reaction coordinates were calculated at the HF/6-31G* level.[14]

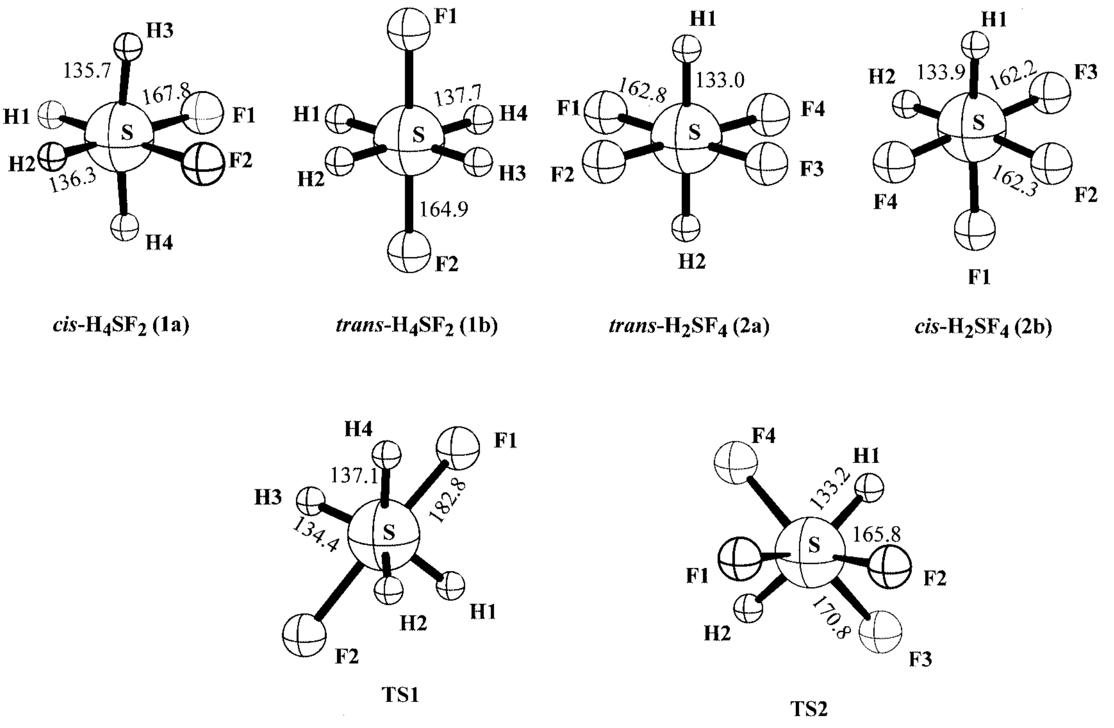
Results and Discussion

Sulfur Hydride Fluorides

The possible isomers of H_4SF_2 (**1**) and H_2SF_4 (**2**) are shown in Figure 1, which also gives the internuclear distances; bond angles are listed in Table 1. The two *trans* isomers are of D_{4h} symmetry with all bond angles either 90° or 180°. The *cis* isomers are of C_{2v} symmetry.

Unexpectedly, the *cis* isomer of H_4SF_2 (**1a**) and the *trans* isomer of H_2SF_4 (**2a**) represent the global minimum structures. The *trans* isomer of H_4SF_2 (**1b**) is 53 kJ·mol^{-1} and the *cis* isomer of H_2SF_4 (**2b**) is 37 kJ·mol^{-1} less stable than the most stable structures **1a** and **2a**, respectively. The origin of these differing stabilities is not evident from the molecular structures. The NBO charges of the sulfur atoms (in atomic units) are +1.29 in **1a**, +1.45 in **1b**, +2.12 in **2a** and +2.13 in **2b**. For comparison, for the octahedral SF_6 molecule we found a charge of +2.85 at the sulfur atom at the same level of theory. It appears that the higher the fluorine content the smaller is the NBO charge on the F atoms (**1a**: −0.62, **1b**: −0.60, **2a**: −0.55, **2b**: −0.53, SF_6: −0.475).

The SH and SF internuclear distances given in Figure 1 show an interesting pattern. As a reference value the SF



cis-H_4SF_2 (**1a**) *trans*-H_4SF_2 (**1b**) *trans*-H_2SF_4 (**2a**) *cis*-H_2SF_4 (**2b**)

TS1 **TS2**

Figure 1. Molecular structures and bond lengths (pm) of the two persulfuranes H_4SF_2 (**1a**, **1b**) and H_2SF_4 (**2a**, **2b**), as well as of the transition states for the *cis* ⇌ *trans* isomerizations **1a** → **1b** (**TS1**) and **2a** → **2b** (**TS2**)

Table 1. Selected bond angles (degree) of the molecules H_4SF_2 and H_2SF_4 (two isomers each) and of the transition states **TS1** and **TS2** for the *cis* ⇌ *trans* isomerization of these species

Angle	*cis*-H_4SF_2 (**1a**)	*cis*-H_2SF_4 (**2b**)	TS1	TS2
F−S−F	89.4 (F1SF2)	87.0 (F1/F2) 89.9 (F1/F3) 179.7 (F3/F4)	140.6	79.9 (F1/F2) 134.3 (F1/F3) 83.1 (F1/F4) 135.7 (F3/F4)
H−S−F	90.6 (H1/F1) 86.9 (H3/F1) 180.0 (H1/F2)	175.3 (H1/F1) 90.1 (H1/F4) 88.3 (H1/F2)	73.4 (H1/F1) 138.6 (H2/F1) 85.6 (H3/F1) 74.4 (H4/F1)	135.0 (H1/F1) 85.5 (H1/F2) 84.8 (H1/F3) 77.4 (H1/F4)
H−S−H	93.1 (H1/H3) 89.4 (H1/H2)	96.4	94.1 (H1/H2) 115.2 (H1/H3) 134.0 (H1/H4) 88.9 (H2/H4)	131.6

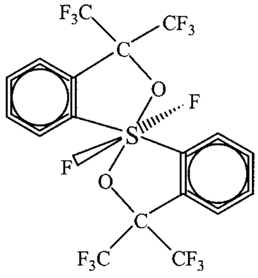
bond length of SF_6 was calculated as 159.3 pm, 3.6 pm (2.2%) longer than the experimental value of 155.7 pm.[15] In **1a** through **2b** the SF distances range from 162.3 to 167.8 pm. With decreasing fluorine content all bonds in the molecules shown in Figure 1 increase substantially in length. Comparing the two pairs of isomers of identical composition (**1a**/**1b** and **2a**/**2b**) one notices that the SH bonds are shortest and the SF bonds are longest in the global minimum structures but the sum of all bond lengths is practically identical in each pair of compounds.

Previous authors have discussed the possibility of so-called *cis*- and *trans*-effects in HSF_5 and related molecules.[6,7] Such effects can partly be seen in the structures investigated in this work as judged from the bond length variation. For the fluorine atoms of H_4SF_2 it is more favorable for them to be *cis* to each other, as in **1a**, while the hydrogen atoms do not show any preference for either *cis* or *trans* positions to each other or to the F atoms. However, the structure of the H_2SF_4 isomer **2b**, with practically identical SH and SF bonds (as judged by the internuclear distances), seemingly rules out any *trans* effect.

The structure of *cis*-H_4SF_2 (**1a**) demonstrates that the formal space requirement of the SH bonds is larger than that of the SF bonds, as expected from the much lower electronegativity of H compared to F. Thus, the H3−S−H4 angle is 171° and the two SH bonds are bent towards the fluorine atoms (see Figure 1). Of course, this effect can also be interpreted as a sign of attractive interactions between the two positively charged hydrogen atoms H3 and H4 (+0.015) and the negatively charged fluorine atoms (−0.62). The hydrogens *trans* to the fluorine atoms (H1 and H2) are slightly negatively charged (−0.04).

The transition states for the *cis*/*trans* isomerization, and vice versa, have been located on the potential energy hypersurfaces; their structures are also shown in Figure 1 (**TS1** and **TS2**). For the *cis* → *trans* isomerization **1a** → **1b** via **TS1** an activation enthalpy of 263 kJ·mol^{-1} is needed ($\Delta G^{\#}_{298}$ = 265 kJ·mol^{-1}). The *trans* → *cis* isomerization **2a** → **2b** via **TS2** requires an activation enthalpy of 199 kJ·mol^{-1} ($\Delta G^{\#}_{298}$ = 196 kJ·mol^{-1}). To the best of our knowledge, neither experimental nor theoretical activation energies for the *cis*/*trans* isomerization of octahedral persulfuranes have been published before, excepting our own recent work on $SF_4(CN)_2$.[1] The data obtained in the present investigation indicate that these molecules are rather rigid, in sharp contrast to the well-known fluxionality of sulfuranes of the type SX_4: in the case of SF_4 the barrier for pseudorotation is only $\Delta H^{\#}_{298}$ = 47 kJ·mol^{-1}.[16] In the case of the persulfurane **A** no *cis*/*trans* isomerization was observed within 254 h at 238 °C under basic conditions. However, the compound isomerized rapidly after addition of a catalytic amount of SbF_5, which cleaved one of the SF bonds, generating a cationic five-coordinate intermediate.[17]

The two transition states **TS1** and **TS2** are of C_2 symmetry and may be regarded as distorted trigonal-prismatic structures. During the isomerization of **1** the F−S−F bond angle changes from 89.4° in **1a** via 140.6° in **TS1** to 180° in **1b**. Similarly, the H−S−H bond angle of **2** decreases from 180° in **2a** via 131.6° in **TS2** to 96.4° in **2b**. The latter value, together with the other bond angles of **2b**, demonstrates once more that the formal space requirement of the SH bonds is larger than that of the SF bonds in these molecules (in **2b** all F−S−F angles are smaller than 90°). This finding is in agreement with the expectations from the VSEPR model of molecular structures[18] but in contrast to the size of the atoms.



A

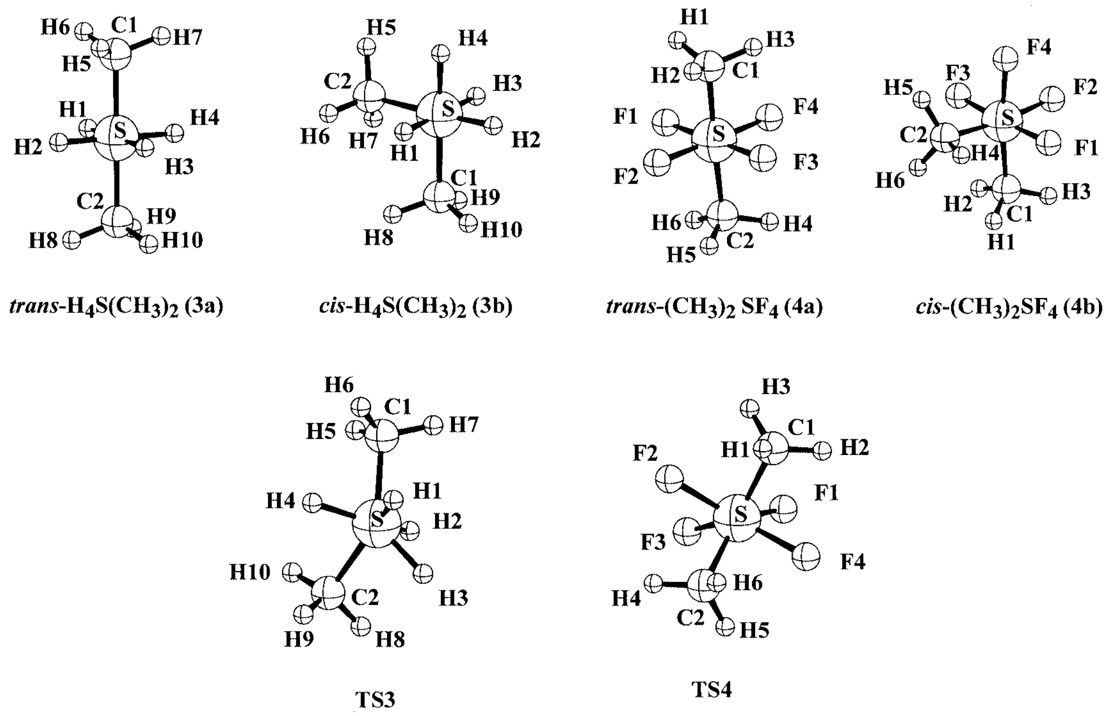
The bond length variations during the isomerization processes are most interesting. For example, the SF bond lengths of H_4SF_2 increase from 167.8 pm in **1a** to 182.8 pm in **TS1** and then decrease to 164.9 pm in **1b**. The SH bonds are much less affected: they change from 135.7/136.3 pm in **1a** via 134.4/137.1 pm in **TS1** to 137.7 pm in **1b**. The corresponding transformation **2a** → **2b** takes the SF bond lengths from 162.8 pm in **2a** via 165.8/170.8 pm in **TS2** to 162.2/162.3 pm in **2b** while the SH bonds change simultaneously only from 133.0 via 133.2 to 133.9 pm. The NBO charges on the sulfur atoms in these transition state structures are slightly lower than in the *cis* and *trans* isomers (**TS1**: +1.18; **TS2**: +2.07).

Dimethyl Sulfur Tetrahydride and Tetrafluoride

The *cis* and *trans* isomers of Me_2SH_4 and Me_2SF_4 are shown in Figure 2. The geometrical data are presented in Table 2 (bond lengths) and Table 3 (bond angles).

The *trans* isomer of Me_2SH_4 (**3a**) is of C_{2h} symmetry and is more stable than the *cis* form **3b**, which is of C_s symmetry, by 7 kJ·mol^{-1}. The transition state **TS3** for the *trans*→*cis* isomerization is also shown in Figure 2. The activation enthalpy of 236 kJ·mol^{-1} ($\Delta G^{\#}_{298}$ = 246 kJ·mol^{-1}) is of the same order of magnitude as in the case of the other octahedral molecules studied here and in our recent work on the isomers of $SF_4(CN)_2$.[1] The *trans* isomer of Me_2SF_4 (**4a**; C_{2v} symmetry) is 31 kJ·mol^{-1} more stable than the *cis* isomer **4b** (ΔG°_{298} =38 kJ·mol^{-1}); the transition state for this isomerization (**TS4**; see Figure 2) is 238 kJ·mol^{-1} higher in energy than the *trans* isomer ($\Delta G^{\#}_{298}$ = 252 kJ·mol^{-1}).

The geometry of *trans*-Me_2SH_4 (**3a**) is highly symmetrical (C_{2h}) and all bond angles at the sulfur atom are either 90° or 180°. The atomic charges of this molecule are as follows: S +0.90, C −0.69, H1−H4 −0.14, methyl-H +0.17. Although the electronegativities of sulfur and carbon are usually believed to be more or less identical,[19] and that of



trans-$H_4S(CH_3)_2$ (**3a**) *cis*-$H_4S(CH_3)_2$ (**3b**) *trans*-$(CH_3)_2SF_4$ (**4a**) *cis*-$(CH_3)_2SF_4$ (**4b**)

TS3 **TS4**

Figure 2. Molecular structures and bond lengths (pm) of the two persulfuranes Me_2SH_4 (**3a**, **3b**) and Me_2SF_4 (**4a**, **4b**), as well as of the transition states for the *cis* ⇌ *trans* isomerizations **3a** → **3b** (**TS3**) and **4a** → **4b** (**TS4**); Me: CH_3

Table 2. Internuclear distances (pm) of two isomers each of Me_2SH_4 and Me_2SF_4, as well as of the transition states for the *cis* ⇌ *trans* interconversion of these isomers, **TS3** and **TS4**

Bond	Me_2SH_4 (**3a**)	Me_2SH_4 (**3b**)	Me_2SF_4 (**4a**)	Me_2SF_4 (**4b**)	TS3	TS4
C−S:	185.9	187.5	180.7	181.1	187.8	181.1
S−H:	142.0	140.5/142.0	–	–	144.2/148.0	–
S−F:	–	–	165.9/166.2	164.8/165.1	–	168.3/177.1

Table 3. Selected valence angles (degree) of two isomers each of the sulfuranes Me_2SH_4 and Me_2SF_4 as well as of the transition states **TS3** and **TS4** for the *cis* ⇌ *trans* isomerization

Angle	Me_2SH_4 (**3a**)	Me_2SH_4 (**3b**)	Me_2SF_4 (**4a**)	Me_2SF_4 (**4b**)	TS3	TS4
C−S−C:	180.0	91.7	176.6	97.3	133.3	130.6
H(F)1−S−H(F)3:	180.0	178.8	180.0	175.4	83.2	77.8
H(F)2−S−H(F)4:	180.0	87.9	178.0	84.7	137.0	141.2
H(F)1−S−H(F)4:	90.0	89.8	89.0	87.8	79.7	79.8
H(F)1−S−H(F)2:	90.0	89.3	89.0	88.8	136.7	133.9

hydrogen considerably smaller, our calculated NBO charges show a different picture: The carbon atoms of **3a** are negative, sulfur and the methyl H atoms are positive and the four hydrogen atoms linked directly to the central atom are negatively charged. It has been noted before[19] that the electronegativity of hydrogen is not a constant value and, in general, most electronegativity data are derived from non-hypervalent molecules and may not apply to atoms in species of the type investigated in this work.

The geometry of *trans*-Me_2SF_4 (**4a**) is much less symmetrical (C_{2v}) than that of **3a** although the bond angles at the sulfur atom deviate from the ideal values of 90° and 180° by only 1.0−3.4° (Table 2). The atomic charges of **4a** are as follows: S +2.48, C −0.80, F −0.61, H +0.26. Surprisingly, both the sulfur atom in **4a** is more negative than in H_2SF_4 (**2a**: +2.12) and the two carbon atoms are more negative than in **3a** (−0.69), although one would expect the opposite from the well-known inductive effects of the four fluorine atoms and two methyl groups, respectively. Evidently, the electron-donating properties of methyl groups known from organic chemistry are not active in hypervalent sulfur compounds.

The methyl groups of **3a** and **4a** can be rotated separately about the C−S axis without much change in energy. Scans over 75° in steps of 5° with optimization of all other parameters resulted in absolute energies which differed by less than 0.02 kJ·mol^{-1}.

We now turn to the structures of the less stable isomers. The geometry of *cis*-Me_2SH_4 (**3b**) is of C_2 symmetry with a C−S−C bond angle of 91.7°. As far as possible, the methyl groups are staggered with respect to the hydrogen atoms of the SH_4 group. Thus, the pairwise equivalent torsion angles H8−C1−S−H1/H7−C2−S−H3 are 48.9°, H5−C2−S−H4/H10−C1−S−H2 are +19° and H9−C1−S−H3/H6−C2−S−H1 are −11°. The torsion angles H8−C1−S−C4/H7−C2−S−C1 are −43°. The geometry of *cis*-Me_2SF_4 (**4b**) is also of C_2 symmetry but the orientation of the methyl groups is different since there are evidently attractive non-bonding H···F interactions as a result of the opposite charges on these atoms (H atoms: +0.19−0.22; F atoms: −0.55±0.01). For example, the two pairs of symmetry-related distances H2···F3 and H4···F1 (235 pm) as well as H3···F2 and H5···F4 (233 pm) are shorter than the van der Waals distance of 260 pm between hydrogen and fluorine atoms. The corresponding torsion angles H2−C1−S−F3 and H4−C2−S−F1 are −1° and the C−S−C angle of **4b** is 97.3°.

The transition states **TS3** and **TS4** are of C_1 symmetry but both geometries are very close to C_2 symmetry, the small deviation from the higher symmetry being caused by the methyl groups. The C−S−C angles are 133.3° in **TS3** and 130.6° in **TS4**. The NBO charges of the sulfur atoms are +0.91 in **TS3** and +2.23 in **TS4**. As a result of these differing charges, the C−S bond lengths are considerably longer in **TS3** (187.8 pm) than in **TS4** (181.4 pm), a situation very similar to the one in the stable isomers **3a,b** and **4a,b**.

Summary

We have shown that the most stable structures of several persulfuranes of the type X_2SY_4 (X = H, Me, F; Y = H, F) are in agreement with the predictions made by the VSEPR model. All molecules are approximately octahedral, and the relative stability of the *cis* and *trans* isomers depends on the substituents. An unusual charge distribution has been discovered in these molecules by an NBO analysis. Starting from the most stable of the two isomers, the intramolecular *cis* ⇌ *trans* isomerization is possible only if an activation barrier of $\Delta H^{\#}_{298} \geq 200$ kJ·mol^{-1} can be overcome. Therefore, it should be possible to prepare both isomers separately. The geometries of the transition state structures are all very similar and correspond approximately to a distorted trigonal prism with the sulfur atom at the center.

Acknowledgments

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