How Unstable are Thiosulfoxides? An ab Initio MO Study of Various Disulfanes RSSR (R = H, Me, Pr, All), Their Branched Isomers R_2SS, and the Related Transition States[1,2]

Ralf Steudel,*,† Yana Drozdova,† Karol Miaskiewicz,‡ Roland H. Hertwig,§ and Wolfram Koch§

Contribution from the Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Sekr. C2, D-10623 Berlin, Germany, Pacific Northwest Laboratories, K1-96, Richland, Washington 99352, and Institut für Organische Chemie, Technische Universität Berlin, Sekr. C3, D-10623 Berlin, Germany

Received July 12, 1996. Revised Manuscript Received December 3, 1996[⊗]

Abstract: Ab initio MO calculations at the MP2/6-311G** level of theory show that the thiosulfoxide H_2SS is 143 kJ mol^{-1} less stable than the disulfane HSSH, separated by an activation barrier of 210 kJ mol^{-1}. Using much higher levels of theory, these results are only slighty changed, proving the suitability of the economical MP2/6-311G** scheme for the present purpose. At the same level Me_2SS is 84 kJ mol^{-1} less stable than MeSSMe, with the transition state lying 340 kJ mol^{-1} above MeSSMe. Thermal isomerization of HSSH or MeSSMe can therefore be excluded, and H_2SS and Me_2SS should be kinetically stable toward unimolecular isomerization at low temperatures. Vibrational wavenumbers for H_2SS and Me_2SS are given. The allyl methyl thiosulfoxide MeAllSS is 83 kJ mol^{-1} less stable than the disulfane MeSSAll, but isomerization of the latter requires only 110 kJ mol^{-1}. The corresponding RSSR and R_2SS structures for R = Pr and All have been calculated at the HF/6-31G* level. The bimolecular decomposition of dimethyl thiosulfoxide to dimethyl sulfide and S_2 is exothermic but spin-forbidden in the case of triplet S_2, and endothermic but spin-allowed when singlet S_2 is formed. The reactions of Me_2SS with sulfur molecules S_x ($x > 2$) to give Me_2S and S_{x+1} are exothermic.

Introduction

Organic thiosulfoxides R_2SS have never been isolated or directly observed, but numerous times their role as reaction intermediates has been discussed.[3] On the other hand, compounds which formally contain SS double bonds have been known for quite some time: Thiothionyl fluoride $F_2S{=}S$ (**1**), a colorless gas, is more stable thermodynamically than the isomeric difluorodisulfane FSSF (**2**).[4] Disulfur monoxide $S{=}S{=}O$ (**3**) is stable for several days at 20 °C.[5] The cyclic thiosulfite $RO{-}S(=S){-}OR$ (**4**) with R = cyclohexylidene is stable at 20 °C,[6] and several stable thiosulfinylamines $RN{=}S{=}S$ (**5**) have been prepared.[3a] The molecular structures of the species **1**−**5** are known from either microwave spectroscopy (**1**−**3**) or X-ray crystallography (**4**, **5**), and SS bond distances in the range 186−191 pm have been observed. Since the distance of SS single bonds[7] as in S_8 is ca. 205 pm, the species **1**−**5** may be considered as formally containing SS double bonds. It is interesting to note that the SiSi double bonds in disilenes $R_2Si{=}SiR_2$[8] and the PP double bonds in diphosphenes $RP{=}PR$[9] are also ca. 7−10% shorter than the single bonds in the corresponding saturated compounds. It was the aim of this work to find out whether this also holds for organic thiosulfoxides R_2SS versus disulfanes RSSR and for their parent compounds H_2SS and HSSH. In addition, we have calculated for the first time the structures and energies of the transition states for the interconversion of RSSR into R_2SS and vice versa. The relative energies of the two isomers $R{-}S{-}S{-}R$ (**6**) and $R_2S{=}S$ (**7**) have so far only been determined for R = H, OH, and SH. According to an ab initio MO calculation at the MP2/6-311G**//HF/6-311G** + ZPE level of theory, the acyclic parent compound of **4**, $HO{-}S(=S){-}OH$ is only 14 kJ mol^{-1} less stable than the unbranched isomer HOSSOH.[10] At the MP2/6-31G*//HF/4-31G* level the thiosulfoxides H_2SS and $(HS)_2SS$ have been found to be 141 and 132 kJ mol^{-1} less stable than the corresponding sulfanes HSSH and HSSSSH, respectively.[11,12]

To determine the structures and energies of organic thiosulfoxides as well as the activation energies for their formation from disulfanes, we have carried out extensive ab initio MO

† Institut für Anorganische und Analytische Chemie, Technische Universität Berlin.

‡ Pacific Northwest Laboratories.

§ Institut für Organische Chemie, Technische Universität Berlin.

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Sulfur Compounds. 198. Part 197: see ref 2.

(2) Steudel, R.; Kustos, M.; Prenzel, A. *Z. Naturforsch. B* **1997**, *52*, 1.

(3) (a) For an extensive review on S=S bonds see: Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333. (b) Green, M.; Lown, E. M.; Strausz, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 6938.

(4) (a) Seel, F.; Budenz, R. *Chimia* **1963**, *17*, 355. (b) Seel, F.; Gölitz, H. D. *Z. Anorg. Allg. Chem.* **1964**, *327*, 32. (c) Marsden, D. J.; Oberhammer, H.; Lösking, O.; Willner, H. *J. Mol. Struct.* **1989**, *193*, 233.

(5) (a) Schenk, P. W.; Steudel, R. *Z. Anorg. Allg. Chem.* **1966**, *342*, 253. (b) Schenk, P. W.; Steudel, R. *Angew. Chem.* **1964**, *76*, 97; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 61. (c) Tiemann, E.; Hoeft, J.; Lovas, F. J.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5000.

(6) Harpp, D. N.; Steliou, K.; Cheer, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 825.

(7) Steudel, R. *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

(8) (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) West, R. *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

(9) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(10) Miaskiewicz, K.; Steudel, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2395.

(11) Laitinen, R.; Pakkanen, T.; Steudel, R. *J. Am. Chem. Soc.* **1987**, *109*, 710.

(12) For an earlier MO calculation of HSSH and H_2SS see: Marsden, C. J.; Smith, B. J. *J. Phys. Chem.* **1988**, *92*, 347. At the MP3 level H_2SS was found to be 151.5 kJ mol^{-1} less stable than HSSH. No transition state was calculated.

S0002-7863(96)02402-X CCC: $14.00 © 1997 American Chemical Society

Table 1. Relative Energies (kJ mol^{-1}) of Various Thiosulfoxides R_2SS and Transition States (TS) Compared to the Corresponding Disulfanes RSSR[a]

	H_2SS	TS(H)	Me_2SS	TS(Me)	Pr_2SS	All_2SS	TS(All)	MeAllSS	TS_1	TS_2
MP2/6-31G*//HF/6-31G*	141		82	348	74	78	111			
MP2/6-311G**//HF/6-311G**	145		86	346						
MP2/6-311G**//MP2/6-311G**	143	210	84	340				83	298	110
MP4/6-311G**//MP2/6-311G**	143									

[a] For further data on H_2S_2 see the text.

calculations on $(CH_3)_2S_2$, $(C_3H_7)_2S_2$, $(CH_3)(C_3H_5)S_2$, $(C_3H_5)_2S_2$, and—for comparison—on H_2S_2 (C_3H_5 = 3-allyl).

Methods of Calculation

All geometries were optimized at the Hartree−Fock and, with the exception of the Pr_2S_2 and All_2S_2, also at the valence electron correlated MP2 level of theory, employing 6-31G* and 6-311G** one particle basis sets. The force constant matrices and the harmonic frequencies were computed analytically for each stationary point to characterize it as a minimum or a saddle point and to provide predictions for the vibrational spectra. These calculations were performed at the MP2/6-311G** (H_2S_2, Me_2S_2), the HF/6-311G** ($MeAllS_2$), and the HF/6-31G* (Pr_2S_2, All_2S_2) levels of theory. The HF and MP2 wavenumbers were uniformly scaled by factors of 0.8929 and 0.9427, respectively, while the corresponding zero point energies (ZPE) were scaled by 0.9135 (HF) and 0.9646 (MP2).[13] For assessing the accuracy of the structures and in particular the relative energies that can be expected from the above approach based on single-reference-based MP2 calculations, we performed additional calculations on the H_2S_2 potential energy surface employing more sophisticated theoretical approaches. The geometries were determined at the complete active space SCF (CASSCF)[14] level where all 14 valence electrons were distributed in the 10 orbitals originating from the 3s and 3p atomic orbitals of sulfur and the 1s hydrogen orbital. A generally contracted basis set of the atomic natural orbital (ANO)[15] type of (7s3p)/[3s2p] and (13s10p4d)/[5s4p3d] quality was employed for hydrogen and sulfur, respectively. This set will be denoted as ANO-S. For subsequent energy calculations a considerably larger basis set (H, (8s4p3d)/[3s2p1d]; S, (17s12p5d4f)/[6s5p4d3f] (ANO-L)) was selected. Energies were obtained at second-order multireference perturbation theory based on a CASSCF wave function (CASPT2),[16] by full fourth-order Møller−Plesset perturbation theory (MP4sdtq) and by coupled cluster calculations with single and double excitations and a perturbative estimate of the triple contributions (CCSD(T)).[17] Thus, both dynamic as well as static electron correlation effects are well covered by these methods. Scalar relativistic effects were included in the CASSCF/CASPT2 calculations through the Douglas−Kroll operator.[18] The programs Gaussian 94,[19] MOLCAS-3,[20] GAMESS,[21] and MOLPRO 96[22] as installed on IBM RS/6000 workstations or a CRAY-J90 computer were used.

Results and Discussion

H_2S_2. The relative energies of the three relevant species, i.e., HSSH, H_2SS, and the saddle point connecting these two minima, are collected in Table 1.[23] The energy difference (with ZPE corrections computed at MP2/6-311G**) between the two stable isomers amounts to 113, 115, and 117 kJ mol^{-1} using the ANO-L basis and the CASPT2, MP4, and CCSD(T) approaches, respectively. If instead the smaller 6-311G** or 6-31G* basis sets combined with the MP2 or MP4 treatment are employed, HSSH is predicted to be more stable than H_2SS by 141−145 kJ mol^{-1}. That this difference is indeed a pure basis set effect can be seen by comparing the MP4 results obtained with the 6-311G** and the ANO-L basis set, which amount to 143 and 115 kJ mol^{-1}. As expected, the scalar relativistic effects have hardly any impact on the relative stabilities. The good agreement between the results obtained by three different treatments of electron correlation (CCSD(T), MP4, and CASPT2) demonstrate that this system is "well-behaved" and can be treated with single-determinant-based methods, such as MP2. This is further corroborated by the very small τ_1 diagnostic in the CCSD, which is well below the critical value of 0.02[17] (HSSH, τ_1 = 0.004; H_2SS, τ_1 = 0.006) and by the CASSCF wave function, which is strongly dominated by the HF reference configuration.

The geometries and dipole moments as calculated at the MP2/6-311G** level of theory are shown in Table 2 together with the structural data obtained at the CASSCF level with the ANO-S basis set. Also included in Table 2 is the experimental geometry of HSSH as determined by microwave spectroscopy.[24,25] HSSH adopts a helical structure of C_2 symmetry while H_2SS is of C_s symmetry (Figure 1). The MP2/6-311G** geometry of HSSH is in slightly better agreement with the experimental structure than the one obtained at the CASSCF/ANO-S level. In particular the SS bond is overestimated by 2.6 and 5.6 pm at the two levels of theory, respectively. Also the SS bond in H_2SS is probably somewhat overestimated in the calculations (here both methods give almost identical results

(13) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(14) For a review on the CASSCF scheme see: Roos, B. O. In *Lecture Notes in Quantum Chemistry*; Roos, B. O., Ed.; Springer: Berlin, 1992.

(15) (a) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070. (b) Widmark, P.-O.; Persson, B. J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419.

(16) Andersson, K.; Roos, B. O. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Part I.

(17) Lee, T. J.; Scuseria, G. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langnoff, S. F., Ed.; Kluwer Academic Press: Dordrecht, The Netherlands, 1995.

(18) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756. (c) *Ibid*. **1986**, *33*, 3742. (d) Samzov, R.; Hess, B. A. *Chem. Phys. Lett.* **1991**, *184*, 491.

(19) Gaussian 94, Revision B.3: Frisch, M. J.; Trucks, G. W..; Schlegel, H. B..; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(20) MOLCAS-3: Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmquist, P.-A.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., University of Lund, Sweden, 1993.

(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(22) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor.

(23) Total energies, zero point energies, and thermal energies may be obtained from the authors.

(24) Hahn, J.; Schmidt, P.; Reinartz, K.; Behrend, J.; Winnewisser, G.; Yamada, K. M. T. *Z. Naturforsch. B* **1991**, *46*, 1338.

(25) Previous data from electron diffraction and microwave spectroscopy seem to be in error since the angle HSS was found as 91.6 ± 0.3°; see: Winnewisser, G.; Winnewisser, M.; Gordy, W. *J. Chem. Phys.* **1968**, *49*, 3465. Winnewisser, M.; Haase, J. *Z. Naturforsch. A* **1958**, *23*, 56.

Table 2. Bond Distances *d* (pm), Bond Angles α (deg), Torsional Angles τ (deg), and Dipole Moments μ of HSSH, H_2SS, and the Transition State (TS) Calculated at the MP2/6-311G** Level[a]

	HSSH	H_2SS	TS(H)
d(SS)	208.2 [211.2] (205.6)	201.8 [201.7]	219.8 [222.5]
d(SH)	133.6 [135.5] (134.2)	135.1 [133.9]	134.2 [135.7] (H1)
			137.9 [142.3] (H2)
			190.4 [182.3] (S2H2)
α(HSS)	98.1 [98.4] (97.9)	108.6 [107.7]	101.9 [101.2] (H1)
			59.2 [54.8] (H2)
α(HSH)		89.8 [91.7]	94.6 [95.5] (HS1H)
τ(HSSH)	90.4 [90.3] (90.3)		101.1 [99.8] (HSHS)
μ (D)[b]	1.56	5.39	4.35

[a] Data given in brackets refer to calculations at the CASSCF/ANO-S level, while the experimental results for HSSH[24] are given in parentheses. For numbering of atoms see Figure 1. [b] 1 D = 3.336×10^{-30} C m.

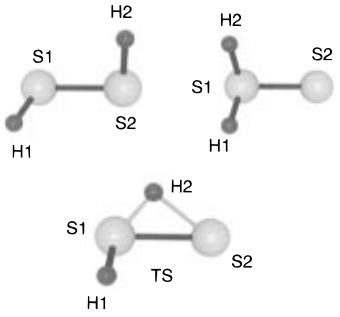


Figure 1. Structures of HSSH, H_2SS, and the transition state (TS) of the interconversion reaction.

of 201.8 and 201.7 pm, respectively), and it can be assumed that the true value of d(SS) for this molecule should be 199 pm. As expected, the dipole moment of H_2SS is much larger (5.39 D at MP2/6-311G** and 4.00 D at CASSCF/ANO-L) than that of HSSH (1.56 and 1.16 D at MP2/6-311G** and CASSCF/ANO-L, respectively). The Mulliken charges on S1 and S2 obtained with the 6-311G** basis amount to +0.34 and −0.49 in H_2SS and to only −0.07 in HSSH.

For the energetically less favorable isomer H_2SS to be experimentally observable, a sizable barrier must prevent the rearrangement back to the more stable form HSSH. Therefore, we have localized the saddle point for the hydrogen migration connecting the two isomers, whose energetical and geometrical data are also included in Tables 1 and 2, respectively. This saddle point is rather high in energy: Including ZPE corrections, its energy computed at MP2/6-311G** is 210 and 67 kJ mol^{-1} above HSSH and H_2SS, respectively. If instead the more elaborate CCSD(T) and CASPT2 approaches combined with the ANO-L basis set are employed, only slightly different barrier heights of 195 kJ mol^{-1} (CCSD(T) and CASPT2) with respect to HSSH and 78 (CCSD(T)) and 82 (CASPT2) kJ mol^{-1} relative to H_2SS are obtained. This, together with the small τ_1 diagnostic of 0.004, indicates that also the saddle point does not require a multireference treatment. Rather, the differences between the MP2/6-311G** data and the results obtained at higher levels of theory are mainly caused by the more flexible one-particle basis set used in the latter as documented by the barrier height of also 196 kJ mol^{-1} computed with the large ANO basis set in the MP2 scheme (the corresponding MP4 number amounts to 194 kJ mol^{-1}). Scalar relativistic effects have an only negligible influence on these data. Hence, it can safely be concluded that the simple MP2 electron correlation treatment is sufficient for a description of the minima and saddle points of the molecules studied in the following. For the present system, the computational data suggest that once H_2SS has been generated at not too high temperatures it should be possible to detect this species, e.g., by vibrational spectroscopy. To assist an experimental identification, the harmonic wavenumbers of the six fundamental vibrations of H_2SS as well as their relative infrared intensities are given in Table 3.

Table 3. Vibrational Wavenumbers (cm^{-1}; Scaled by 0.9427) and Relative Infrared Intensities (in Parentheses) of the Fundamental Harmonic Modes of H_2SS and Me_2SS (C_s Symmetry)

	symmetry species a′	symmetry species a″
H_2SS	2491 (92) ν_{SH}	2491 (8) ν_{SH}
	1168 (100) δ_{HSH}	
	830 (56) δ_{SSH}	793 (6) δ_{SSH}
	464 (46) ν_{SS}	
Me_2SS	3030 (4)/3016 (11) /2908 (51)	3030 (1)/3016 (2)/2908 (8) ν_{CH}
	1391 (43) /1389 (47)	1377 (19)/1373 (17) δ_{CH}
	1322 (17)/1007 (76) /966 (89)	1297 (3)/924 (0) /894 (3)
	676 (27)	710 (10) ν_{CS}
	496 (100) ν_{SS}	
	287 (5) /242 (2)/238 (1)	218 (11)/187 (0)

Table 4. Bond Distances *d* (pm), Bond Angles α (deg), Torsional Angles τ (deg), and Dipole Moments μ (D) of MeSSMe (Experimental Data[27] in Brackets), Me_2SS, and the Transition State (TS) Calculated at the MP2/6-311G** Level[a]

	MeSSMe	Me_2SS	TS(Me)
d(SS)	206.4 [202.9(3)]	200.3	214.2
d(SC)	180.7 [181.6(3)]	180.1	179.1 (C1)
			218.3 (C2S1)
			238.8 (C2S2)
d(CH)	109.0−109.3 [110.5(5)]	109.0−109.3	109.2−109.3
α(CSS)	100.8 [103.2(2)]	105.4	100.3 (C1)
			67.0 (C2)
α(CSC)		97.9	100.5 (S1)
α(S1C2S2)			55.7
τ(CSSC)	83.7 [85(4)]		97.1
μ	2.41	6.14	5.10

[a] For numbering of atoms see Figure 2.

Me_2S_2. The calculated relative energies of MeSSMe[26] and Me_2SS assuming C_2 and C_s symmetry, respectively, are given in Table 1 while the geometrical parameters and dipole moments are compiled in Table 4. The experimental structure of MeSSMe[27] is also given in Table 4. Including ZPE corrections the thiosulfoxide is only 84 kJ mol^{-1} less stable than the disulfane. This energy difference is much smaller than in the case of H_2SS/HSSH (143 kJ mol^{-1}) which may be rationalized as follows. The SS bonds of the thiosulfoxides H_2SS and Me_2SS are highly polar. The charge difference between S1 and S2 is 0.83 e in H_2SS and 0.92 e in Me_2SS; i.e., these bonds are "semipolar". The positive charge on S1 of H_2SS seems to weaken the two adjacent SH bonds, the distances of which are 1.5 pm larger than in HSSH. In contrast, the CS bonds in Me_2SS are 0.6 pm shorter than those in MeSSMe, obviously as a result of the large charge difference of 0.9 e between S1 and the carbon atoms. Thus, the strengthening of the CS bonds of Me_2SS compared to MeSSMe is a result of the negative charge of the carbon atoms (−0.4 e) whereas the hydrogen atoms of HSSH and H_2SS are positively charged (+0.1 e). It therefore seems that the gain in CS bond energy on isomerization of MeSSMe to Me_2SS is at least partly responsible for the relatively low energy needed for this process.

The large negative charge on the terminal sulfur atom of Me_2SS raises the question whether there are intramolecular S···H hydrogen bonds. However, the shortest SH contact in Me_2SS

(26) For previous ab initio MO calculations on MeSSMe using smaller basis sets see: (a) Honda, M.; Tajima, M. *J. Mol. Struct.* **1986**, *136*, 93. (b) Aida, M.; Nagata, C. *Theor. Chim. Acta* **1986**, *70*, 73. (c) Ha, T.-K. *J. Mol. Struct.: THEOCHEM* **1985**, *122*, 225. (d) Li, W.-K.; Chiu, S.-W.; Ma, Z.-X.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1993**, *99*, 8440.

(27) Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1976**, *80*, 618.

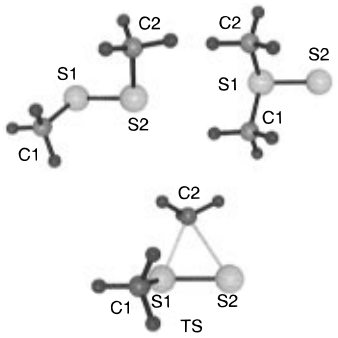


Figure 2. Structures of MeSSMe, Me_2SS, and the transition state (TS) for the interconversion reaction.

is 305.6 pm which is larger than the van der Waals distance. The absence of S···H bonds also holds for Pr_2SS, MeAllSS, and All_2SS discussed below.

The structure of the transition state (TS) for the isomerization of MeSSMe and Me_2SS is shown in Figure 2; the geometrical parameters are listed in Table 4 while the energies at various levels of theory are given in Table 1. TS is characterized by a triangular arrangement of the two sulfur atoms and one methyl carbon atom. Within this triangle all bond lengths are considerably larger than in MeSSMe. These weak bonds must be the main reason that the transition state energy is 340 kJ mol^{-1} higher than the energy of MeSSMe.

The extremely high energy of TS raises doubts whether the isomerization of MeSSMe to Me_2SS in fact proceeds via an intramolecular methyl shift. An alternative pathway would be the homolysis of one CS bond followed by a migration of the CH_3 radical to the second sulfur atom and formation of a new CS bond, enhancing the coordination number of that sulfur atom from 2 to 3. The bond dissociation energies of MeSSMe as given by Benson[28] are $D(H_3CS{-}SCH_3) = 310$ and $D(H_3C{-}SSCH_3) = 238$ kJ mol^{-1}. From these data it follows that the isomerization of MeSSMe to Me_2SS probably takes place by a homolytic dissociation mechanism. Even the calculated activation energy for the reverse reaction $Me_2SS \rightarrow$ MeSSMe (256 kJ mol^{-1}) is higher than $D(H_3C{-}SSCH_3)$. Therefore, the homolytic pathway may also be more favorable here. Once Me_2SS has been formed it is expected to be quite stable kinetically due to these high activation barriers. To detect Me_2SS, for instance by matrix isolation experiments, the vibrational wavenumbers listed in Table 3 may be helpful. The SS stretching vibration at 496 cm^{-1} has the highest infrared intensity.

Strausz et al.[3b] proposed that Me_2SS is formed in the reaction of sulfur atoms with gaseous Me_2S. Depending on the electronic state of the sulfur atoms (^3P or ^1D; generated by photolysis of COS) the thiosulfoxide is formed primarily in an electronically excited triplet state (T_1) or in a vibrationally excited singlet state (S_o). Part of these molecules transform into MeSSMe by an unknown mechanism, but in addition elemental sulfur is formed which was explained by the following bimolecular reactions:[3b]

$$2Me_2SS\ (S_o) \rightarrow 2Me_2S + S_2\ (^3\Sigma_g^-) \qquad (1)$$

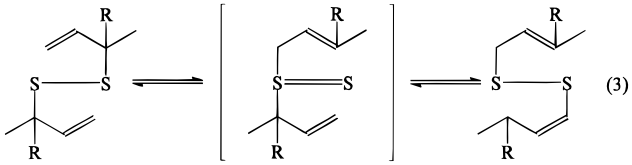
$$Me_2SS + S_x \rightarrow Me_2S + S_{x+1}\ (x = 2, 3, ...) \qquad (2)$$

These processes will be discussed below.

Pr_2S_2 and All_2S_2. The propyl derivatives were investigated to check whether the results obtained for MeSSMe and Me_2SS and in particular the difference from the HSSH/H_2SS pair would persist if the alkyl chain is enlarged. The related allyl compounds have been studied experimentally, and allyl thiosulfoxides have been postulated as intermediates (see below), but no structures are known. Due to the size of these species computations are limited to the HF/6-31G* level. At the MP2 level only single-point energies of PrSSPr, AllSSAll, and their isomeric thiosulfoxides were obtained,[23] and relative energies are given in Table 1; selected geometrical parameters are listed in Table 5 while the structures are shown in Figure 3. The thiosulfoxides Pr_2SS and All_2SS are 74 and 78 kJ mol^{-1} less stable than the related disulfanes. These values are comparable to the 82 kJ mol^{-1} calculated at the same level for Me_2SS versus MeSSMe.

The most stable conformations of PrSSPr and AllSSAll are of C_2 symmetry, but the two thiosulfoxides are of C_1 rather than C_s symmetry. The highly polar nature of the semipolar SS bond results in dipole moments of the thiosulfoxides which are more than twice as large as those of the related disulfanes. Thiosulfoxides should therefore be stabilized by polar environments.

Diallyldisulfane has been isolated from various *Allium* species, and its reactions including thiosulfoxide formation are believed to be responsible for the formation of various derivatives on heat treatment of garlic oil.[29] From the study of the two diallyldisulfanes **8** and **9** comes the only experimental data available in the literature regarding the activation energy of the sigmatropic rearrangement shown in eq 3.



(3)

R = H : **8**

R = CH_3 : **9**

From the temperature dependence of the reaction rate the activation energy in benzene solution has been calculated as 83(4) kJ mol^{-1} for R = H and as 78(4) kJ mol^{-1} for R = CH_3.[30] These low values together with other chemical evidence[31] have been interpreted as indication for the intermediacy of thiosulfoxides in various thermal reactions of diallyldisulfane(s). The sigmatropic rearrangement observed in reaction 3 obviously proceeds via a transition state totally different from the one shown in Figure 2 for Me_2S_2. On the basis of the first-order kinetics and the negative entropy of activation ($\Delta S^{\ddagger}$ ca. −9 J mol^{-1} K^{-1} [23]), a structure with a five-membered C_3S_2 ring has been proposed. We have calculated the geometry and energy of this transition state (TS) at the same level of theory. The results are given in Tables 1 and 5, and the geometry is shown in Figure 3. The energy of TS is 111 kJ mol^{-1} higher than that of AllSSAll and 33 kJ mol^{-1} higher than the energy of All_2SS. The cyclic structure of TS fits the above-mentioned expectations: one allyl group and the two sulfur atoms form an asymmetric puckered ring with a short SS bond (199.1 pm), two CC bonds of similar length (136.7 and 139.3 pm), and two very different and long CS bonds (237.6 and 261.0 pm).

(28) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23. See also: Fournier, R.; DePristo, A. E. *J. Chem. Phys.* **1992**, *96*, 1183.

(29) (a) Review: Block, E. *Angew. Chem.* **1992**, *104*, 1158; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135. (b) Lawson, L. D.; Wang. Z-Y. J.; Hughes, B. G. *Planta Med.* **1991**, *57*, 363.

(30) Höfle, G.; Baldwin, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 6307.

(31) (a) Barnard. D. ; Houseman, T. H.; Porter, M.; Tidd, B. K. *J. Chem. Soc., Chem. Commun.* **1969**, 371. (b) Baechler, R. D.; Hummel, J. P.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 4442.

Table 5. Bond Distances *d* (pm), Bond Angles α (deg), Torsion Angles τ (deg), and Dipole Moments μ (D) of Dipropyl- and Diallyldisulfane, the Corresponding Thiosulfoxides, and the Transition State (TS) (All) Calculated at the HF/6-31G* Level[a]

	PrSSPr	Pr_2SS	AllSSAll	All_2SS	TS (All)
d(SS)	205.1	203.2	205.2	203.1	199.1
d(CS)	183.0	181.8 (C1)	183.4	182.5 (C1)	183.2 (C1)
		182.1 (C2)		182.8 (C4)	261.0 (C4)
					237.6 (C6)
α(CSS)	102.9	107.3	103.3	107.3	105.4 (C1)
	102.9	108.1		107.3	90.5 (C4)
					98.5 (C6)
α(CSC)		101.7		100.8	97.6
τ(CSSC)	−89.3		−86.9		−98.7 (C1−C4)
					1.7 (C4−C6)
τ(SCCC)	−68.7	−179.1/−172.4	−111.6	115.4/121.1	65.8 (S2)
τ(CSCC)		−57.4 (C1−C5)		−56.1 (C1−C5)	132.4 (C1−C5)
		−169.9 (C2−C4)		−176.4 (C2−C4)	76.0 (C2−C6)
μ	2.48	5.89	2.42	5.91	4.49

[a] For numbering of atoms see Figure 3.

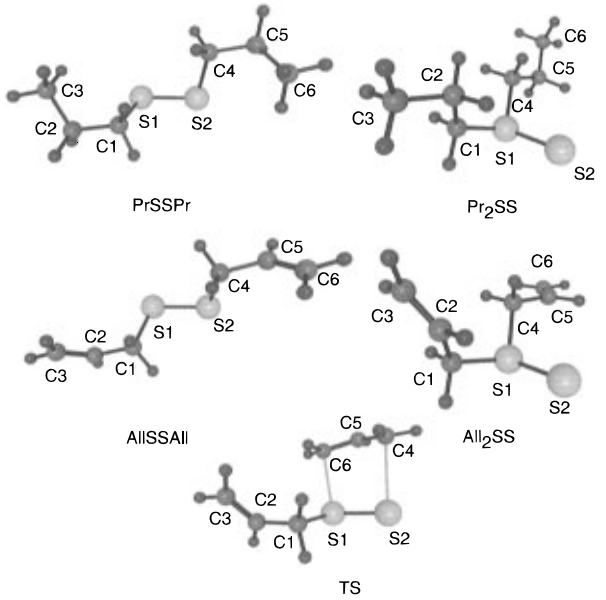


Figure 3. Structures of PrSSPr, Pr_2SS, AllSSAll, All_2SS, and the transition state (TS) for the interconversion reaction (All_2S_2).

The experimental activation energies for the forward reaction (3) of **8** and **9** (80 ± 3 kJ mol^{-1} at 24 °C) are smaller than the calculated energy of TS relative to the energy of AllSSAll (111 kJ mol^{-1}). Even if the thermal energy at 298 K is taken into account, the relative energy of TS is still 106 kJ mol^{-1}. It therefore seems that the transition state is stabilized by interaction with the solvent. To check whether a higher level of theory would result in a lower relative energy of the transition state, we have investigated the thiosulfoxide formation from allylmethyldisulfane, which due to its smaller molecular size can be economically calculated at a higher level.

$MeAllS_2$. The structures of MeSSAll and MeAllSS, optimized at the MP2/6-311G** level of theory, are presented in Figure 4; selected geometrical parameters are compiled in Table 6. The relative energies given in Table 1 are in line with the findings for the dimethyl and diallyl species, the thiosulfoxide MeAllSS being 83 kJ mol^{-1} less stable than the disulfane. Two transition states have been found (see Figure 4). The structure of TS_1 is similar to that of TS(Me): The allyl group faces the disulfane unit of the CH_3SS fragment with only one carbon atom (C2). The atoms C2, S1, and S2 define an unsymmetrical triangle in which the SS bond (214.7 pm) forms the shortest and the C2S2 bond the longest edge (242.7 pm). The energy of TS_1 relative to MeSSAll is 298 kJ mol^{-1} (Table 1), slightly smaller than the relative energy of TS(Me) = 340 kJ mol^{-1} but

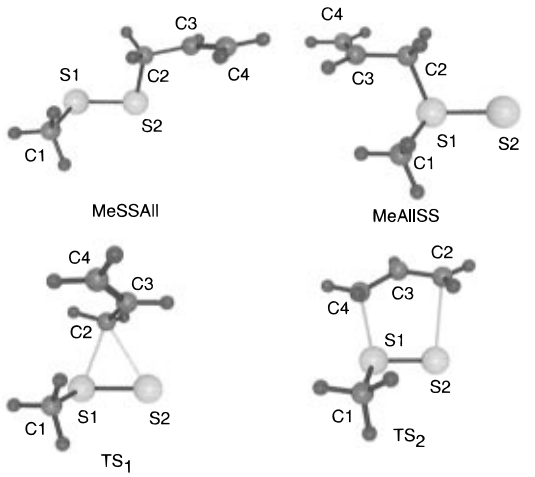


Figure 4. Structures of MeSSAll, MeAllSS, and the transition states of the interconversion reaction. The energy of TS_1 is much higher than the energy of the cyclic TS_2.

Table 6. Selected Bond Distances *d* (pm), Bond Angles α (deg), and Torsion Angles τ (deg), and Dipole Moments μ (D) of Allylmethyldisulfane, Its Thiosulfoxide, and of Two Transition States (TS) Calculated at the MP2/6-311G** Level[a]

	MeSSAll	MeAllSS	TS_1	TS_2
d(SS)	206.6	200.0	214.7	196.0
d(S−CH_3)	180.7	180.3	179.5	181.0
d(S−All)	182.5	182.8	242.7 (S2)	265.3 (C2-S2)
			231.8 (S1)	215.4 (C4-S1)
d(C−C)	149.7	149.5	145.4	142.3 (C3-C4)
d(C=C)	134.0	134.1	135.2	136.9 (C2-C3)
τ(CSSC)	84.0		94.1 (C1S1S2C2)	−94.0 (C1S1S2C2)
				3.9 (C4S1S2C2)
τ(CCSS)	168.7	170.5	59.8 (C3C2S1S2)	−31.5 (C3C2S2S1)
			−134.6 (C3C2S2S1)	22.8 (C3C4S1S2)
τ(CCCS)	108.3	96.5		-67.1 (S1)/66.3 (S2)
μ	2.40	6.47	5.80	4.59

[a] For numbering of atoms see Figure 3.

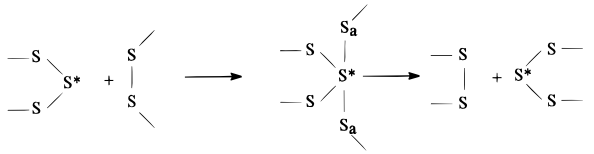
still larger than the CS bond dissociation energy (see Me_2S_2). The second transition state (TS_2) is 110 kJ mol^{-1} less stable than MeSSAll and corresponds to TS of All_2S_2 (see above). While the relative energy of TS_2 is practically identical to the energy of TS(All), the geometry is significantly different. The SS distance of 196.0 pm is even smaller than in the thiosulfoxide (200.0 pm). The allyl group is connected to the disulfane unit through the terminal carbon atoms C2 and C4, forming a nonplanar five-membered heterocycle. However, the distance

C4−S1 (215.4 pm) is much smaller than C2−S2 (265.3 pm). In other words, the original bond All−S of MeSSAll has almost dissolved while the new CS bond is stronger than in the thiosulfoxide. As a consequence, the two CC bonds of the allyl group are of different length (C2−C3 = 136.9, C3−C4 = 142.3 pm) but have changed bond order compared with the disulfane MeSSAll (C2−C3 = 149.7, C3−C4 = 134.0 pm). The torsion angle C2SSC4 is only 3.8°.

Reactions of H_2SS and Me_2SS. Benson[28] has estimated the SS bond dissociation energies of H_2SS and Me_2SS from the enthalpies of formation $\Delta H°$ (kJ mol^{-1} at 298 K) of sulfur atoms (^{3}P; 277.6), H_2S (−20.5), Me_2S (−37.3), HSSH (15.9), and MeSSMe (−24.3) and from an estimate of the activation energy of the reaction of RSSAll with Ph_3P which results in RSAll and Ph_3PS.[24] The SS bond dissociation energies (D) derived are 214 ± 29 kJ mol^{-1} for H_2SS and 222 ± 17 kJ mol^{-1} for Me_2SS. Our results allow a more accurate calculation of these energies from the above $\Delta H°$ values and the relative energies of H_2SS and Me_2SS at 298 K. Taking the thermal energies into account, H_2SS is 144 kJ mol^{-1} less stable than HSSH which leads to a reaction enthalpy $\Delta H°_{298}$ of 97 kJ mol^{-1} for the reaction $H_2SS \rightarrow H_2S + S$ (^{3}P), 117 kJ mol^{-1} less than estimated previously.[28] In an analogous manner the reaction enthalpy for the dissociation of the SS bond of Me_2SS at 298 K is calculated as 181 kJ mol^{-1}, in reasonable agreement with Benson's estimate. The enthalpies of formation $\Delta H°_{298}$ (ideal gas) are calculated from our data and from the values for gaseous HSSH and MeSSMe as 160 kJ mol^{-1} for H_2SS and 60 kJ mol^{-1} for Me_2SS.

The decomposition of Me_2SS according to eq 1 was mentioned earlier. With S_2 molecules in the $^3\Sigma_g^-$ ground state this reaction is spin-forbidden but exothermic by −31 kJ mol^{-1} (calculated using the enthalpy of formation of S_2 as 128.5 kJ mol^{-1} at 298 K[28]). The spin-allowed reaction to give S_2 ($^1\Delta_g$)[32] is endothermic by 37 kJ mol^{-1}. The reaction of Me_2SS with S_2 ($^3\Sigma_g^-$) to give Me_2S and S_3 (eq 2) is spin-forbidden since the ground state of S_3 (and of all larger sulfur species) is a singlet state. Using the enthalpy of formation of gaseous S_3 as $\Delta H°_{298}$ = 141.5 kJ mol^{-1},[33] it is found that reaction 2 is exothermic by −84 kJ mol^{-1} in the case of S_2 ($^3\Sigma_g^-$) and by −153 kJ mol^{-1} in the case of S_2 ($^1\Delta_g$). The analogous reactions of Me_2SS with S_3, S_4, etc. are also exothermic.

Sulfur transfer reactions of this type have been discussed[11,34] as possible pathways for the interconversion of sulfur homocycles which occur at ambient or slightly elevated temperatures. Solid c-S_7 decomposes within hours to c-S_8 and polymeric sulfur. In the case of c-S_6, c-S_9, and c-S_{10} several days are needed for this decomposition.[35] Even c-S_8 is converted into S_6, S_7, S_9, and polymeric sulfur on heating to the melting point (120 °C).[36] A seemingly reasonable pathway included isomerization of c-S_8 to the hypothetical thiosulfoxide S_7═S, followed by a sulfur atom transfer to another S_8 molecule with formation of S_7 and S_8═S and finally isomerization of the latter to c-S_9.[29] However, our present results indicate that the activation energy for the $S_8 \rightarrow S_7$═S reaction is probably too high to allow such a reaction at moderate temperatures. The most likely mechanism for the interconversion is the symmetry-allowed oxidative addition by insertion of an S atom of molecule A into an SS bond of molecule B followed by dissociation to molecules of type A − S and B + S:[11,29]



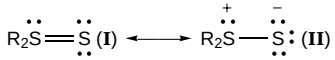
(4)

Table 7. S−S Bond Distances d and Torsion Angles τ at the S−S Bond in Symmetrical Disulfanes RSSR

	d_{SS} (pm)	τ (deg)	ref
HSSH(g)[a]	206.5	90.3	24
MeSSMe(g)	202.9	85	27
R_2NSSNR_2 (s)[b]	202.1	85	38
$CH_3OSSOCH_3$(s)	197.2	81.5	39
BrSSBr(s)	194.8	83.9	40
ClSSCl(s)	194.3	84.8	40
FSSF(g)	189.0	87.7	4c

[a] g = gaseous, s = solid. [b] R = CH_3SO_2.

Bonding in RSSR and R_2SS Molecules. The SS bond in *thiosulfoxides* R_2SS may be considered as either "double" [3a] or "semipolar" [37] depending on the electronegativity of the substituents R:



For R = H the SS bond distance is calculated as 201.8 pm and that for R = Me as 200.3 pm. The experimental value for F_2-SS, derived from microwave spectroscopy,[4c] is 185.6 pm while the thiosulfite R−O−S(═S)−O−R with R = cyclohexylidene contains an SS bond of length 190.1 pm as determined by X-ray crystallography.[6] These data can be rationalized by the inductive effect of R on the easily polarizable sulfur electrons in structures **I** and **II**.

The bond lengths of *disulfanes* RSSR also depend on the electronegativity of R as the data in Table 7 show.[38−40] The values observed range from 206.5 pm for HSSH to 189.0 pm for FSSF. The torsional angles at the SS bonds are all in the usual range of 80−90°. In contrast, the radical ions $HSSH^{\bullet+}$ and $MeSSMe^{\bullet+}$ possess a planar XSSX chain which is explained by the formation of a three-electron π bond.[26d,41] This comparison shows that, in FSSF, for example, with its very short SS bond the reduction in bond length cannot be explained by a simple electrostatic reduction of electron density due to the high electronegativity of the fluorine substituents since this would lead to a planar structure also. Instead, one has to assume a hyperconjugation by which the 3p lone pairs of the sulfur atoms are partly delocalized into σ^* molecular orbitals of those R−S bonds which are located in the same plane. This so-called "gauche effect" has already been discussed for HOOH, FSSF, ClSSCl, and HSSH.[26b,42] In this way two π bonds are created

(32) Singlet S_2 is 68.5 kJ mol^{-1} less stable than triplet S_2: Radzig, A. A.; Smirnov, B. M. *Reference Data on Atoms, Molecules, and Ions*; Springer: Berlin 1985; pp 353−354.

(33) Barin, I. *Thermochemical Data of Pure Substances*, 2nd ed.; VCH: Weinheim, 1993; Part II.

(34) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149.

(35) Steudel, R.; Passlack-Stephan, S.; Holdt, G. *Z. Anorg. Allg. Chem.* **1984**, *517*, 7.

(36) Steudel, R.; Strauss, R.; Koch, L. *Angew. Chem.* **1985**, *97*, 58; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 59.

(37) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(38) Blaschette, A.; Näveke, M.; Jones, P. G. *Z. Naturforsch. B* **1991**, *46*, 5.

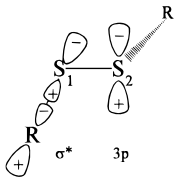
(39) Steudel, R.; Schmidt, H.; Baumeister, E.; Oberhammer, H.; Koritsanszky, T. *J. Phys. Chem.* **1995**, *99*, 8987; Koritsanszky, T.; Buschmann, J.; Luger, P.; Schmidt, H.; Steudel, R. *J. Phys. Chem.* **1994**, *98*, 5416.

(40) Kniep, R.; Koorte, L.; Mootz, D. *Z. Naturforsch. B* **1983**, *38*, 1.

(41) Gillbro, T. *Phosphorus Sulfur* **1978**, *4*, 133. See also: Bonazzola, L.; Michaut, J.-P.; Roncin, J. *J. Phys. Chem.* **1989**, *93*, 639.

(42) Alleres, D. R.; Cooper, D. L.; Cunningham, T. P.; Gerrat, J.; Karadakov, P. B.; Raimondi, M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3357.

in planes almost perpendicular to each other. Since the energy of the σ^* orbital will be lower the more electronegative R is, the increasing strength of these additional π bonds on proceeding from R = H and CH_3 via O, N, Br, and Cl to F (Table 7) is to be expected:



Conclusions

Ab initio MO calculations indicate that the barriers for isomerization of HSSH to H_2SS or vice versa are so high that no thermal isomerization is to be expected at temperatures at which H_2S_2 is stable (<50 °C). Simple organic thiosulfoxides are only 80 ± 5 kJ mol^{-1} less stable than the corresponding disulfanes. In this case a high barrier to isomerization is calculated for alkyl derivatives, while allyl substitutents result in a structurally different transition state which is only 110 kJ mol^{-1} above the energy of the disulfane. The cyclic structure of this transition state corresponds to the previously intuitively assumed intermediates of this "allyl shift". While it should be possible to isolate and identify H_2SS and R_2SS (R = alkyl) in matrix isolation experiments, bulk quantities of these thiosulfoxides will probably decompose in bimolecular reactions to give the monosulfides and elemental sulfur.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, the Verband der Chemischen Industrie, and the Konrad-Zuse-Zentrum für Informationstechnik, Berlin. W.K. thanks B. A. Hess, M. Urban, and V. Kellö for permission to use the Douglas−Kroll relativistic integral code in combination with MOLCAS-3.

JA9624026