Oxidation Products of Organic Trisulfanes: Molecular Structures and Energies of Various Isomers of the Dimethyltrisulfane Oxides Me_2S_3O and $Me_2S_3O_2$ and of 1,3-$t$$Bu_2S_3O_2$**

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Abstract: Ab initio MO calculations (MP2/6-311G**//HF/6-311G**) have been performed for several isomers (including rotamers) of Me_2S_3O and $Me_2S_3O_2$. MeS(O)SSMe exists as five rotamers; the most stable form (**1a**) has a helical backbone CSSSC with S–S bond lengths of 206.0 ($S^{II}S^{II}$) and 212.4 pm ($S^{II}S^{III}$). The most stable rotamer of MeS-S(O)SMe (**2a**), is less stable than **1a** by 10.7 kJ mol^{-1}; it is of C_1 symmetry, while a rotamer of C_S symmetry (**2b**) is less stable than **2a** by only 1.4 kJ mol^{-1}. Both **2a** and **2b** are stabilized by O ··· H hydrogen bonds. The S–S bond lengths of **2a** are 210.0 and 212.0 pm; the CSSSC chain is not helical (CSSS torsion angles 166.3 and −75.4°). The 1,3-dioxide MeS(O)-SS(O)Me (**3**) has two equivalent chiral centers and exists as diastereomers. The most stable isomer **3a** (*RR*)/(*SS*) is of C_2 symmetry with methyl groups *trans* to each other; the SO bonds form an angle of about 90°. The *meso* form **3b** is less stable than **3a** by 17.2 kJ mol^{-1} and the rotamers **3c** and **3d** are less stable by 25.6 kJ mol^{-1} and 28.4 kJ mol^{-1}, respectively. The trisulfane-1,2-dioxide MeS(O)-S(O)SMe has two nonequivalent chiral centers and exists as five isomers. The most stable form, the (*RS*)/(*SR*) form **4a**, is less stable than **3a** by 21.4 kJ mol^{-1} and is characterized by SS bonds of 220.9 ($S^{III}S^{III}$) and 208.3 pm ($S^{III}S^{II}$). The rotamer **4b** is less stable by 5.9 kJ mol^{-1}. The isomers **4c**, **4d**, and **4e** are all of (*SS*)/(*RR*) configuration and are less stable than **4a** by 6.3, 12.7, and 12.0 kJ mol^{-1}. For comparison, ab initio MO calculations (HF/6-311G*) for *t*BuS(O)SS(O)-*t*Bu yielded two diastereomers of practically identical energy that both contain helical CSSSC backbones. The (*RS*) form is less stable than the (*RR*)/(*SS*) form by 1.8 kJ mol^{-1}.

Keywords
ab initio calculations · rotamers · stereoisomers · sulfane oxides · torsional potentials

Introduction

The oxidation of organic thioethers R_2S by peroxo acids results in sulfoxides and finally in sulfones. In the case of organic disulfanes R_2S_2, a whole series of oxidation products is conceivable, the monosulfoxides RS(O)SR being the first and the disulfones $RS(O)_2S(O)_2R$ the last members of the series. Only very recently have 1,2-disulfoxides RS(O)S(O)R and disulfane-1,1,2-trioxides $RS(O)_2S(O)R$ been observed as intermediates by low-temperature NMR spectroscopy.[1, 2] The peracid oxidation of organic trisulfanes has received relatively little attention. This is surprising, since organic trisulfanes occur naturally[3] and the oxidation to sulfoxides is usually the first step in metabolic degradation reactions. Early work showed that bisalkyl trisulfanes are turned into 1,3-disulfones $RS(O)_2$–S–$S(O)_2R$ on treatment with peroxoacetic acid at 60–70 °C.[4] Under milder conditions (−40 °C) with trifluoroperoxoacetic acid it has been possible to oxidize tri- and tetrasulfanes R_2S_n with R = *t*Bu or 2-naphthyl, first to the 1-sulfoxides and subsequently to the corresponding 1,3- and 1,4-disulfoxides, respectively.[5] By vibrational spectroscopy it was shown that these oxidation products $R_2S_3O_2$ and $R_2S_4O_2$ can be isolated and have the structures of trisulfane-1,3-dioxides R–S(O)–S–S(O)–R and tetrasulfane-1,4-dioxides R–S(O)–S_2–S(O)–R, respectively. Recent NMR spectroscopic studies confirm these findings.[2] However, none of the chain-like trisulfane-1-oxides or the trisulfane-1,3-dioxides has so far been investigated by X-ray crystallography, probably owing to their thermal instability, which hinders the growth of single crystals. Even at 25 °C all of these compounds decompose both in solution and in the solid state to mixtures of sulfones and sulfanes.[5] Only the structures of a number of trisulfane-2-oxides RSS(O)SR and of sulfone derivatives are known. Trisulfane-2-oxides are prepared from thiols by reaction with thionylchloride, and derivatives with R = ClC_6H_4,[6] C_6H_5,[7] $(C_6H_5)_3C$,[8] and *t*Bu[9] have been characterized by X-ray structural analysis. Unsymmetrical trisulfane-2-oxides RSS(O)SR′ are also known.[10] To obtain more structural information on the various organic trisulfane monoxides and dioxides we have carried out extensive ab initio molecular orbital calculations with methyl and *tert*-butyl groups as substituents. Another aim of this work was to find out which of the particular isomers MeS(O)SSMe/MeSS(O)SMe and MeS(O)SS(O)Me/MeS(O)S-(O)SMe is more stable.[11]

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[**] Sulfur Compounds, Part 193; for Part 192 see R. Steudel, *Ind. Eng. Chem. Res.* **1996**, *35*, 1417.

Calculations

All calculations were performed with the GAUSSIAN92 program package [12] for ab initio MO calculations on either an IBM/RISC 6000 workstation or a CRAY YMP-4E supercomputer. The molecular structures of the Me_2S_3O and $Me_2S_3O_2$ isomers were fully optimized at the Hartree–Fock level with the 6-311G** basis set. The optimization was done from different starting geometries with respect to the rotation around the S–S and C–S single bonds. Improved relative energies were obtained by single point calculations taking the electron correlation into account according to second-order Møller–Plesset perturbation theory (MP2) [13]. The starting geometries for all the molecules were taken from the MNDO calculations.

The harmonic vibrational wavenumbers were calculated analytically at the HF/6-311G** level of theory. Following the suggestion of Pople et al. [14] the wavenumbers were scaled by a factor of 0.8929 while the zero-point energies were scaled by a factor of 0.9135. For a general discussion of the basis sets and methods used see ref. [15].

The molecular structures of the tBuS(O)SS(O)tBu isomers were fully optimized at the HF level with the 6-311G* basis set. Because of the size of this molecule neither MP2 energies nor vibrational wavenumbers were calculated.

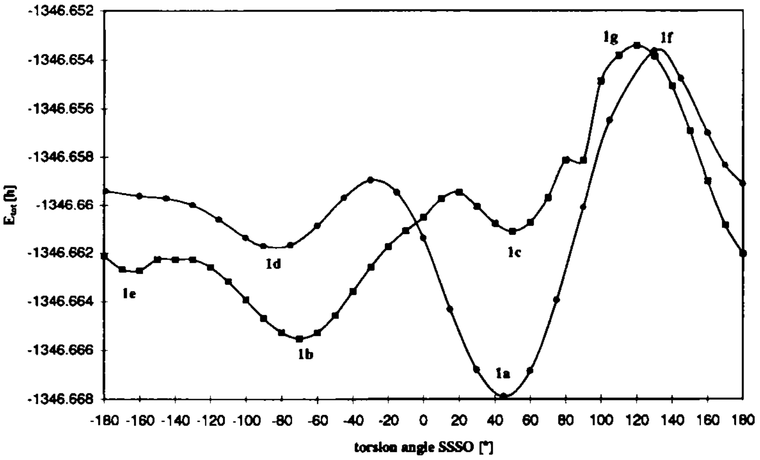

Fig. 2. Energy profiles for the rotamers of dimethyl trisulfane-1-oxides. Starting from the two geometries of minimum energy **1a** and **1b**, the SSSO torsion angle was varied systematically while all other geometrical parameters were optimized by energy minimization. As can be seen from this figure **1d** is a rotamer of **1a**, while **1c** and **1e** are rotamers of **1b** when only rotation about the axis S1–S2 is allowed. Rotation about the axis S2–S3 (followed by optimization) transforms **1a** into **1b**.

Results and Discussion

Methyl derivatives: In the following discussion of the calculations carried out for the methyl trisulfane oxides the energies, geometries, atomic charges and dipole moments, and vibrational wavenumbers of the molecules are described.

Energies: In Figure 1 the five isomeric trisulfane-1-oxides found at minima on the potential hypersurface (no imaginary vibrational frequencies) are shown. This hypersurface has not been fully calculated but instead the torsional potential curves for rotation about the torsional angle SSSO were calculated by fixing this angle to values of between 180° and −180° and optimizing all other geometrical parameters at the HF/6-311G** level of theory (Fig. 2). In the beginning the most likely conformation was inferred from the geometry of the analogous hydrogen compound HS(O)SSH.[16] Starting from this isomer (**1a**) one additional rotamer **1d** was found. The second starting geometry **1b** has also been deduced from the corresponding isomer of H_2S_3O. The torsional potential of this structure shows at least two additional rotamers (**1c** and **1e**) with regard to the axis S1–S2. The shoulder at τ(SSSO) = 85° may indicate another unstable rotamer of **1b**. Since **1a** can be transformed into **1b** by rotation about the S2–S3 axis all five species **1a**–**e** are rotamers of each other. The total energies, relative energies, and zero-point energies of the trisulfane monoxides are listed in Table 1; the geometrical parameters are given in Table 2. The trisulfane-1-oxide **1a** is the most stable structure. It contains a helical CSSSC backbone, while the rotamer **1b** is of *cis* conformation as far as the methyl groups are concerned. Compound **1b** is less stable than **1a** by 13.1 kJ mol^{-1}. The same order of energies has been calculated for the unsubstituted trisulfane-1-oxide: *trans*-H_2S_3O is more stable than *cis*-H_2S_3O by 6.0 kJ mol^{-1}.[16]

In the case of dimethyl trisulfane-2-oxide (**2**), three rotamers have been found. Their structures are shown in Figure 3, the energies are given in Table 1, and the geometrical parameters are given in Table 3. The torsional potential presented in Figure 4 was calculated starting from isomer **2a** and varying the angle τ(C2SSO). All other geometrical parameters were optimized at the HF/6-311G** level of theory. The potential is characterized by a high maximum at τ = 125°, a global minimum at τ = 35°, and an area of almost constant energy despite large variations in the value of τ. In this area a shallow minimum at τ = −43.5° was found corresponding to isomer **2c**. The minimum near τ = −85° corresponds to the enantiomer of **2c**, which is of course of equal energy. Another rotamer (**2b**) was found by restricting the symmetry to C_S. The vibra-

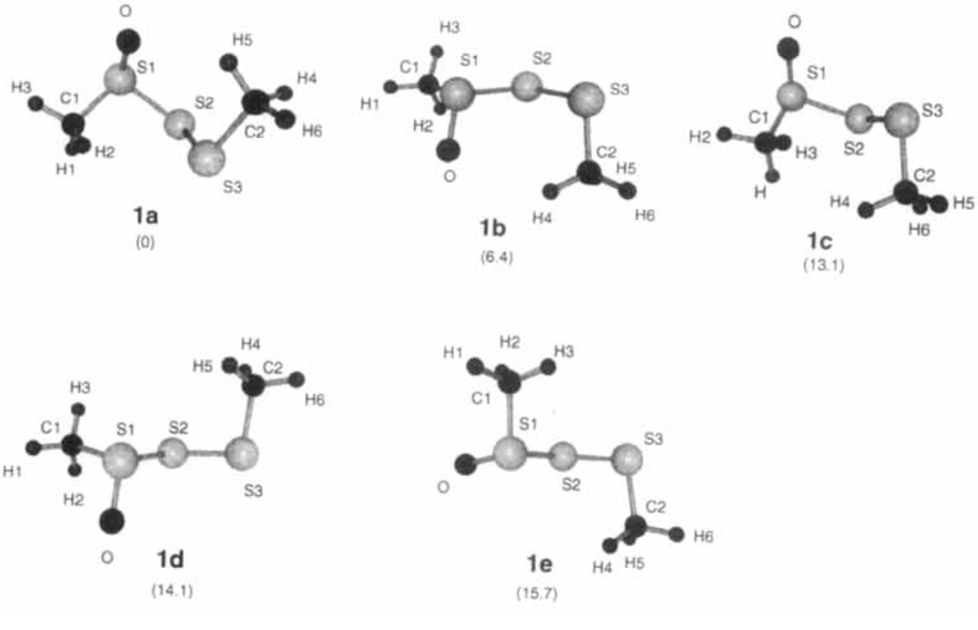

Fig. 1. Molecular structures of the various isomers of dimethyl trisulfane-1-oxides **1a**–**e** and numbering of atoms. The relative energies (kJ mol^{-1}) with respect to the most stable isomer **1a** are given in brackets.

Table 1. Total energies (h = 2625.5 kJ mol^{-1}) of various rotamers of MeS(O)SSMe (**1**) and MeSS(O)SMe (**2**), the corresponding zero-point vibrational energies (kJ mol^{-1}) scaled by 0.9135, and the energies (kJ mol^{-1}) in relation to the energy of **1a** taking the zero-point energies into account (E_{rel}).

	HF/6-311 G**	ZPE [a]	MP2/6-311 G** [b]	E_{rel}
1a	−1346.66789	213.2	−1347.57406	0
1b	−1346.66552	212.6	−1347.57139	6.4
1c	−1346.66111	212.8	−1347.56892	13.1
1d	−1346.66181	212.2	−1347.56831	14.1
1e	−1346.66276	212.4	−1347.56777	15.7
2a	−1346.65931	212.4	−1347.56966	10.7
2b	−1346.65827	212.4	−1347.56914	12.1
2c	−1346.65491	211.9	−1347.56523	21.9

[a] ZPE taken from HF/6-311 G** calculations. [b] Geometries optimized at HF/6-311 G**.

Table 2. Bond lengths *d* (pm), valence angles α (°), and torsion angles τ (°) of the various rotamers of MeS(O)SSMe (**1**) (HF/6-311 G**).

	1a	**1b**	**1c**	**1d**	**1e**
d(SO)	147.1	146.7	146.4	146.2	146.7
d($S^{II}S^{II}$)	206.0	205.8	206.3	205.8	205.8
d($S^{II}S^{III}$)	212.4	213.0	212.9	213.5	214.5
d(CS)	179.4	179.9	179.5	180.0	179.6
	181.8	181.8	181.6	181.4	181.5
d(CH) [a]	108.0	108.0	108.0	108.0	108.0
α(OSS)	109.4	109.3	110.6	110.7	105.9
α(SSS)	104.5	100.2	106.3	101.6	101.3
α(OSC)	105.4	106.1	105.1	105.8	105.6
α(C2S3S2)	102.3	101.9	102.4	102.2	102.5
α(C1S1S2)	99.7	93.9	100.0	93.5	98.1
α(HCS)	109.6 (H1)	110.2 (H1)	110.2 (H1)	110.3 (H1)	109.9 (H1)
	106.0 (H2)	106.1 (H2)	106.0 (H2)	105.9 (H2)	106.5 (H2)
	109.1 (H3)	109.0 (H3)	108.6 (H3)	109.1 (H3)	108.5 (H3)
	110.1 (H4)	110.2 (H4)	111.8 (H4)	110.9 (H4)	110.8 (H4)
	109.8 (H5)	110.3 (H5)	110.7 (H5)	110.7 (H5)	110.3 (H5)
	105.5 (H6)	105.6 (H6)	105.4 (H6)	105.9 (H6)	106.0 (H6)
τ(SSSO)	46.0	−70.4	50.5	−83.6	−164.78
τ(HCSO)	−174.1 (H1)	−173.1 (H1)	−172.6 (H1)	−176.1 (H1)	−170.5 (H1)
	66.4 (H2)	67.6 (H2)	67.7 (H2)	64.3 (H2)	70.0 (H2)
	−51.9 (H3)	−50.5 (H3)	−49.7 (H3)	−53.4 (H3)	−48.6 (H3)
τ(C1SSS)	−81.0	−179.0	−104.5	168.0	86.4
τ(C2SSS)	−64.2	84.9	59.8	−89.0	86.4

[a] Average value of CH bond lengths.

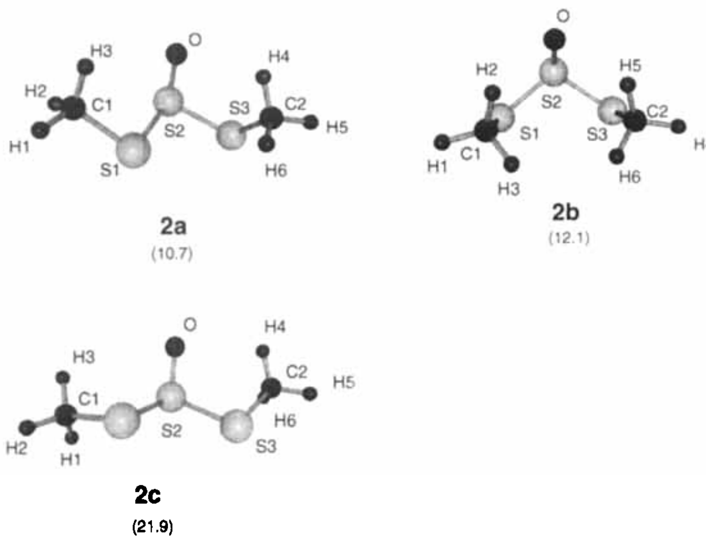

Fig. 3. Molecular structures of the various isomers of dimethyl trisulfane-2-oxides **2a**–**c** and numbering of atoms. The relative energies with respect to the most stable isomer of Me_2S_3O **1a** are given in brackets (kJ mol^{-1}).

Table 3. Bond lengths *d* (pm), valence angles α (°), and torsion angles τ (°) of the various rotamers of MeSS(O)SMe (**2**) (HF/6-311 G**).

	2a	**2b** (*C*$_s$)	**2c**
d(SO)	146.3	146.9	145.8
d($S^{II}S^{III}$)	210.0	211.1	210.1
	212.0	–	212.2
d(CS)	181.6	181.6	181.6
	181.8	–	181.7
d(CH) [a]	108.0	108.0	108.0
α(OSS)	107.0	106.8	110.7
	108.7	–	108.2
α(SSS)	97.4	105.5	92.7
α(CSS)	97.3	101.6	97.7
	99.9	–	97.2
α(HCS)	105.8 (H1)	106.0 (H1)	105.8
	111.1 (H2)	109.0 (H2)	111.1
	109.8 (H3)	111.1 (H3)	110.5
	108.7 (H4)		111.3
	106.0 (H5)		105.5
	110.8 (H6)		109.5
τ(C1SSO)	54.1	−28.9	86.8
τ(C2SSO)	35.5	28.9	−43.5
τ(C1SSS)	166.3	83.2	−162.6
τ(C2SSS)	−75.4	−83.2	−156.3

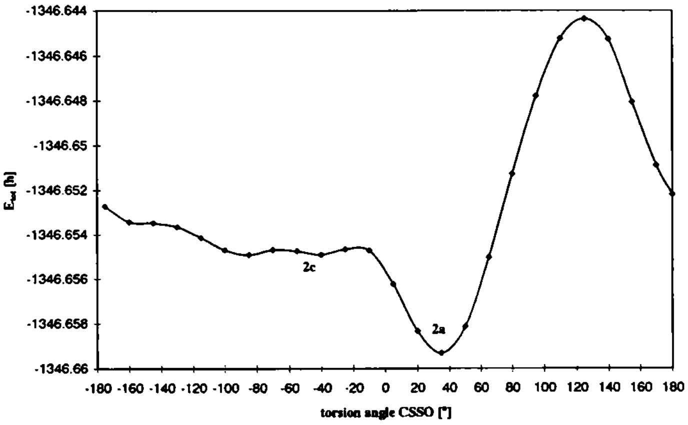

Fig. 4. Torsion potential for dimethyl trisulfane-2-oxide **2**. For each given torsion angle C2SSO the other geometrical parameters were optimized and the energy calculated. This energy profile represents a special path on the energy hypersurface of the molecule.

tional wavenumbers of this structure were all real and its geometry persisted when the symmetry restriction was lifted. When we tried to optimize another symmetrical structure with both methyl groups on one side of the SSS plane and the oxygen atom on the other side the result was rotamer **2b**.

The most stable conformation **2a** is of C_1 symmetry and contains an almost planar CSSS chain, but neither the oxygen atoms nor the second carbon atom are located in this plane. The symmetrical rotamer **2b** is less stable than **2a** by only 1.4 kJ mol^{-1}, while the 2-oxide **2a** is less stable than the 1-oxide **1a** by 10.7 kJ mol^{-1}. The very same results have been found for the unsubstituted trisulfane monoxides: the symmetrical 2-oxide H_2S_3O (C_S symmetry) is less stable than the unsymmetrical rotamer. However, in the case of H_2S_3O the 2-oxide is *more* stable than the 1-oxide (by more than 30 kJ mol^{-1}).[16] At present there is no explanation for this differing behavior of substituted and unsubstituted trisulfane monoxides. The least stable dimethyl trisulfane-2-oxide **2c** is less stable than **2a** by 21.9 kJ mol^{-1}; its CSSS skeleton forms an almost planar zigzag chain.

The various isomers and rotamers found for the dimethyltrisulfane dioxides are shown in Figure 5. The absolute and

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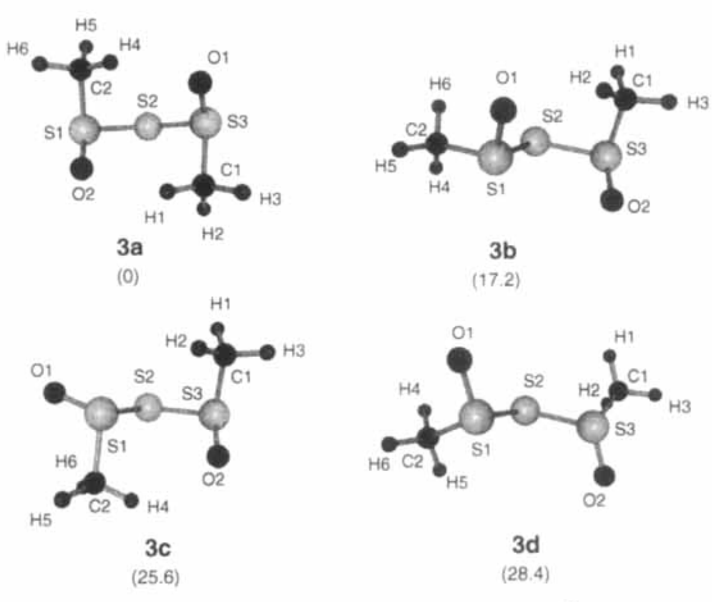


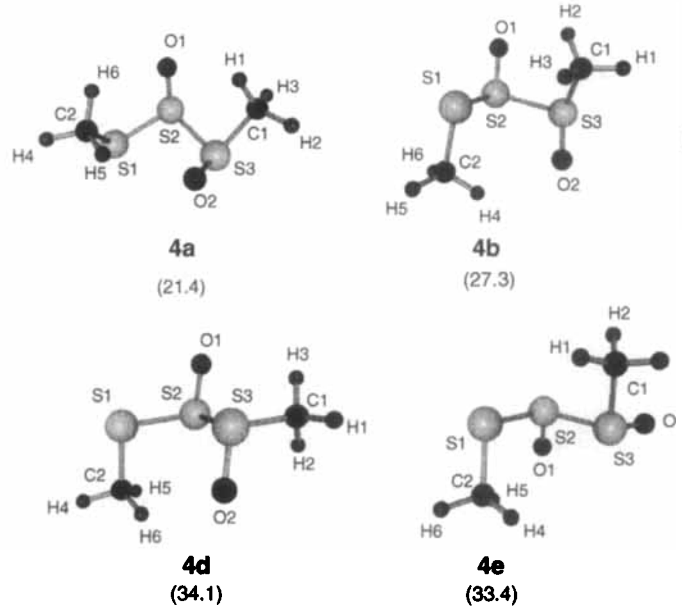


Fig. 5. Molecular structures of the dimethyl trisulfane dioxides **3a**–**4e** and numbering of atoms. The relative energies with respect to the most stable isomer **3a** are given in brackets (kJ mol^{-1}).

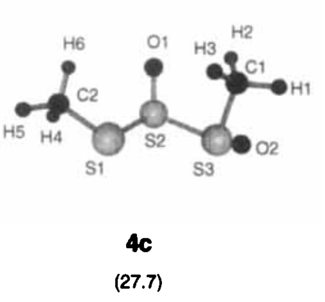
Table 4. Total energies (h = 2625.5 kJ mol^{-1}) of various rotamers of MeS(O)-SS(O)Me (**3**) and MeS(O)S(O)SMe (**4**), the corresponding zero-point vibrational energies scaled by 0.9135 (ZPE in kJ mol^{-1}), and the energies (kJ mol^{-1}) in relation to the energy of **3a** taking the zero-point energies into account (E_{rel}).

	HF/6-311G**	ZPE [a]	MP2/6-311G** [b]	E_{rel}
3a	−1421.48232	212.8	−1422.59823	0
3b	−1421.47843	223.0	−1422.59557	17.2
3c	−1421.47758	222.9	−1422.59227	25.6
3d	−1421.47491	222.3	−1422.59103	28.4
4a	−1421.47168	222.6	−1422.59383	21.4
4b	−1421.47209	221.8	−1422.59128	27.3
4c	−1421.46882	221.7	−1422.59107	27.7
4d	−1421.47092	221.5	−1422.58854	34.1
4e	−1421.46690	221.7	−1422.58892	33.4

[a] ZPE taken from HF/6-311G** calculations. [b] Geometries optimized at HF/6-311G**.

relative energies as well as the zero-point energies are given in Table 4. Since **3** has two equivalent chiral centers there should be two enantiomers and one *meso* form. The most stable structure is the trisulfane-1,3-dioxide **3a**, which is of C_2 symmetry and represents the (*RR*)/(*SS*) form. This molecule has a helical CSSSC backbone with the oxygen atoms on different sides of the SSS plane. Therefore, **3a** may be considered as a derivative of **1a** to which one oxygen atom has been added with otherwise little conformational change. The *meso* form **3b** is less stable than **3a** by 17.2 kJ mol^{-1}. In **3b** the CSSSC chain is no longer helical but the four atoms CSSS are almost coplanar with the second CS bond perpendicular to this plane. The structure **3c** is a rotamer of **3b** and contains a helical CSSSC backbone with both the oxygen atoms and the methyl groups in *anti* positions. This form is less stable than **3a** by 25.6 kJ mol^{-1}. The conformer **3d** is a rotamer of **3a** but less stable by 28.4 kJ mol^{-1}. The Newman-type projections along the S1–S3 axes shown in Figure 6 demonstrate the conformational differences between **3a**, **3b**, **3c**, and **3d**. It is noteworthy that the order of decreasing stability is the same at the HF and MP2 levels (Table 4).

The various conformations of the trisulfane-1,2-dioxides **4** are all less stable than the most stable 1,3-dioxide **3a**, the minimum energy difference being 11.6 kJ mol^{-1}. The most stable 1,2-dioxide **4a** has a remarkable conformation, with all substituents (2 Me, 2 O) on the same side of the SSS plane! Since **4** has two nonequivalent chiral sulfur atoms there should be stereoisomers ((*RR*)/(*SS*) and (*RS*)/(*SR*)) as well as rotamers.



In the following the coordination number of the sulfur atoms will be indicated by a Roman superscript. Rotation around the $S^{III}S^{III}$ and $S^{II}S^{III}$ bonds transforms the (*RS*)/(*SR*) form **4a** into **4b** which is less stable than **4a** by 5.9 kJ mol^{-1}. To generate the

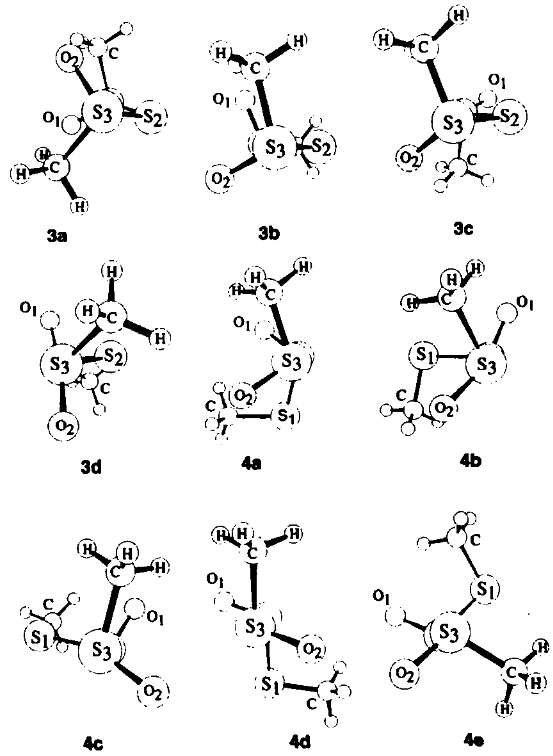


Fig. 6. Molecular structures of the dimethyl trisulfane dioxides **3a**–**4e** as projections in the direction of the S1–S3 axes.

Table 5. Bond lengths d (pm), valence angles α (°), and torsion angles τ (°) of the various rotamers of MeS(O)SS(O)Me (**3a–d**) and of MeSS(O)S(O)Me (**4a–e**) (HF/6-311G**).

	3a (C_2)	**3b**	**3c**	**3d** (C_2)	**4a**	**4b**	**4c**	**4d**	**4e**
d(S1S2)	213.0	213.9	215.5	212.3	220.9	219.6	220.3	218.3	219.5
d(S2S3)	213.0	213.0	211.1	212.3	208.3	209.4	211.6	209.4	210.4
d(SO1)	146.9	146.5	146.4	146.2	146.7	146.9	146.4	146.6	146.1
d(SO2)	146.9	146.7	147.5	146.2	146.9	147.4	146.6	147.4	146.5
d(SC1)	179.9	179.8	179.7	179.9	179.3	179.3	179.2	179.6	179.9
d(SC2)	179.9	180.1	179.2	179.9	182.4	182.1	181.7	182.8	182.0
d(CH) [a]	108.1	108.1	108.1	108.1	108.1	108.1	108.1	108.1	108.1
α(SSS)	107.7	98.9	100.0	96.6	98.0	101.3	91.9	96.7	97.7
α(SSO1)	110.3	109.2	105.8	110.1	109.6/ 107.7	107.2/ 103.4	109.5/ 108.0	107.8/ 103.9	103.9/ 108.2
α(SSO2)	110.3	108.3	108.1	110.1	110.8	106.0	105.5	104.8	105.2
α(SSC1)	100.0	93.3	99.9	95.1	93.4	97.6	97.2	94.0	95.4
α(SSC2)	100.0	98.8	97.6	95.1	100.8	99.2	95.1	98.7	100.2
α(O1SC)	106.2	105.8	106.7	106.1	–	–	–	–	–
α(O2SC)	106.2	106.1	105.6	106.1	106.2	107.8	107.4	106.8	105.7
α(HCS)	109.8/ 109.8	110.1/ 110.2	109.3/ 108.3	109.8/ 109.8	108.5/ 108.6	106.5/ 105.2	109.5/ 110.9	106.8/ 105.1	105.7/ 105.9
	108.8/ 108.8	108.8/ 109.4	109.8/ 106.0	109.4/ 109.4	106.1/ 105.0	108.9/ 110.2	105.4/ 105.7	108.9/ 110.7	109.1/ 108.6
	105.1/ 105.1	105.5/ 105.4	106.0/ 109.0	105.7/ 105.7	110.0/ 110.0	108.4/ 110.6	109.3/ 109.7	109.2/ 110.5	111.0/ 111.0
τ(SSSO1)	−46.5	74.0	162.0	101.8	–	–	–	–	–
τ(SSSO2)	−46.5	33.2	40.3	101.8	−41.7	47.3	155.7	70.1	176.6
τ(OSSO)	–	–	–	–	71.9	158.3	−94.4	−179.6	65.6
τ(C1SSO1)	–	–	–	–	−36.8	47.3	15.3	−71.1	173.5
τ(C2SSO1)	–	–	–	–	−33.9	177.1	53.6	163.3	29.4
τ(C1SSS)	65.1	−77.1	−69.9	−148.9	−150.5	−63.7	−94.6	178.7	−75.5
τ(C2SSS)	65.1	−178.0	−88.2	−148.9	78.2	−84.9	164.8	−89.7	−78.0

[a] Average value of CH bond lengths (range 108.0–108.25 pm).

(RR)/(SS) form **4c** from **4a** requires inversion at the terminal S^{III} atom and rotation about the $S^{II}S^{III}$ bond. This isomer is 6.3 kJ mol^{-1} less stable than **4a**. The least stable structure **4d** is a rotamer of **4c** and is less stable than **4a** by 12.7 kJ mol^{-1}. The species **4e** is another rotamer of **4a** (or of its mirror image as shown in Fig. 5). The projections in Figure 5 and the OSSO torsion angles in Table 5 show that the SO bonds of **4d** are antiparallel, which also holds approximately for **4b**, while in **4a**, **4c**, and **4e** a more perpendicular orientation of the two SO groups is found.

Geometries: The bond lengths, valence angles, and torsion angles of **1–4** are given in Tables 2, 3, and 4. The SO bond lengths of the 17 molecules investigated fall in the narrow range 145.8–147.4 pm. By way of contrast, the SS bonds are of widely differing lengths, which vary from 205.8 to 220.9 pm. This parameter clearly depends on the coordination number. The $S^{II}S^{II}$ bonds are calculated in the range 205.8–206.3 pm (**1a**, **1b**), $S^{II}S^{III}$ bonds are longer (208.3–214.5 pm), while the $S^{III}S^{III}$ bonds of **4** are the longest (218.3–220.9 pm). This may explain why compounds of type **4** have not so far been prepared. Recent work shows that a heterolytic cleavage of SS bonds is likely to be the first step in the thermal decomposition of di- and trisulfane monoxides and dioxides.[9, 17] Heterolysis of $S^{II}S^{III}$ bonds followed by recombination will result in scrambling of substituents and thus in racemization at this particular chiral center.

The calculated CS and CH bond lengths and the SSS, SSO, SSC, and OSC bond angles all have unremarkable values and do not require a long discussion. However, the torsion angles are most interesting. The energetically most favorable torsion angle XSSS for an open chain of two-coordinated sulfur atoms is 80–90°, since for this geometry the lone-pair repulsion is at its minimum.[18] However, if one or more sulfur atoms is oxidized the situation changes, since now the angles τ(XSSS) and τ(XSSO) have to have their optimum values. The results for the stable trisulfane monoxides **1a** and **2a** show that the torsion angles involving the oxygen atom (CSSO and SSSO) are always smaller (46.0 and 54.1°) than τ(CSSS), which adopts values of −75.4 and 166.3°. It is obvious that the angle preference changes when sulfur is tricoordinate.

In this context the structures of maximum energy are of interest. In Figure 2 the two highest maxima obtained by rotation about the S1–S2 axis are of similar energy, which is not incidental. The minima in both curves also show some similarities (see **1a** vs. **1c** and **1b** vs. **1d**). The structure corresponding to the maximum **1f** is characterized by the following torsion angles: C1SSS 20.5°, SSSO 130.5°, C2SSS −96.3°. The two methyl groups are on opposite sides of the SSS plane. In the case of **1g** these parameters are: 20.3°, 120.5°, 91.6° with the methyl groups and the oxygen on the same side of SSS plane. The reason for the instability of these conformations is the almost *cis*-planar geometry of C1SSS, which results in a coplanar arrangement of the SO bond and the 3p lone pair at the neighboring sulfur atom and hence in strong repulsion. In the case of **2** the structure corresponding to the highest energy in Figure 3 is characterized by the torsion angles C1SSS 170.7°, C2SSS 13.1°, C1SSO 59.0°, and C2SSO 125.5°. In this structure a strong repulsion between the 3p lone pairs at S1 and S3 and the oxygen lone pairs can be assumed in addition to the C2···S1 repulsion in the almost planar C2-S3-S2-S1 section of the backbone.

In addition to the electronic effects already discussed, the conformations of **1a** and **2** seem to be affected by O···H hydrogen bonds. The shortest O···H contacts are 239 pm in **2b** (H5···O), 245 and 270 pm in **2a** (H4···O and H3···O), and 260 pm in **1a** (H5···O). There are no hydrogen bonds in **1b**. Hydrogen bonds may also determine the relative stability of the trisulfane-1,3-dioxides. In **3a** the two shortest O···H contacts are 229.9 pm (H1···O2 and H4···O1). Considering these interactions as bonds, the molecule forms a kind of cage. In **3b** there is one O···H contact of 245.2 pm (H2···O1) and in **3c** one of 253 pm (H4···O2), while in the case of **3d** only van der Waals O···H distances (280 pm) are found. The torsion angles CSSS show the most reasonable values in **3a** (65.1°) and in **3c** (−69.9° and −88.2°) while the less stable rotamers **3b** and **3d** exhibit large deviations from the 80–90° optimum (−178.0° in **3b**, −148.9° in **3d**). The other torsion angles do not show any systematic behavior, neither for species **3** nor **4**. Equivalent torsion angles of enantiomers have opposite signs. Hydrogen bonds may also be assumed for **4a** with one O···H contact of 246 pm (H1···O1) and another of 251 pm (H4···O1). In **4b** there are two O···H contacts of 250 (H2···O1) and 255 pm (H4···O2), in **4c** these are of length 246 (H2···O1) and 268 pm (H6···O1), and in **4d** of length 242 (H6···O2) and 275 pm (H1···O2). The structure of **4e** shows one short O···H contact of 240 pm (H5···O1).

Atomic charges and dipole moments: The Mulliken atomic charges will not be listed in detail but ranges will be given instead, because similar values have been calculated for comparable atoms in the various trisulfane oxides. The carbon atoms carry a negative charge in the range −0.39 to −0.47 e, while the hydrogen atoms are always positive (+0.13 to +0.21 e). The methyl substituents as groups are slightly positively charged (+0.01 to +0.08 e). The charge on the oxygen atoms amounts to −0.65 to −0.70 e. The two-coordinate sulfur atoms of species **1**, **2**, and **4** are only slightly charged (range +0.04 to −0.13 e) but for the 1,3-oxides **3** the central sulfur atom is somewhat more negative (−0.19 to −0.22 e). The three-coordinate sulfur atoms, as expected, are highly positive (+0.62 to +0.79 e). The charge difference between neighboring sulfur atoms of differing coordination number ranges from 0.65 e in **4a** through 0.74 e in **2a**, 0.84 e in **1a**, ca. 0.94 e in **3a**, **3c**, and **3d** to 1.01 e in **3b**. Heterolytic cleavage of SS bonds should therefore be a possibility. On the other hand, the two neighboring three-coordinate sulfur atoms in **4** both carry positive charges of 0.65 ± 0.05 e resulting in repulsion and instability, as has already been noticed from the long SS bond distances of 218.3–220.9 pm.

In connection with the further oxidation of trisulfane-1-oxides by electrophilic reagents like peroxo acids the charge distribution in the sulfur chain is of interest. For **1a** the central sulfur (−0.12 e) is more negative than the two-coordinate terminal sulfur (±0.00 e). Very similar values have been obtained for **1b**. The dipole moments of **1**–**4** are given in Table 6. The values range from 1.36 (**4b**) to 5.98 D (**4e**).

Table 6. Dipole moments μ ($D = 3.33 \times 10^{-30}$ C m) of the various isomers of Me_2S_3O (**1**, **2**) and of $Me_2S_3O_2$ (**3**, **4**) (HF/6-311G**).

Molecule	μ	Molecule	μ
1a	1.94	**3b**	3.63
1b	2.06	**3c**	2.94
1c	5.58	**3d**	1.92
1d	5.19	**4a**	2.09
1e	4.07	**4b**	1.36
2a	1.81	**4c**	4.42
2b	2.89	**4d**	2.12
2c	2.27	**4e**	5.98
3a	1.65		

Vibrational wavenumbers: Owing to the large number of atoms and the low molecular symmetry the vibrational spectra of **1**–**4** are expected to be complex, and in most cases the calculated wavenumbers cannot easily be assigned to particular stretching or bending motions. Therefore, the following discussion will be restricted to the most characteristic modes that might be used to identify the corresponding compounds or derivatives thereof by IR or Raman spectroscopy. In Table 7 the calculated wavenumbers are listed for those fundamentals which occur in the regions typical for SO, CS, and SS stretching vibrations. The SO stretching modes of the species **1a** and **2a** differ by only 5 cm^{-1} despite the differing connectivity; for **2b** a slightly lower value of $\tilde{\nu}_{SO}$ is expected. The various isomers of **3** show wavenumber differences between the two SO stretching modes of between 11 cm^{-1} for **3d** and 34 cm^{-1} for **3c**. The value of 20 cm^{-1} calculated for **3a** is intermediate between these extremes. Similarly, the four species **4** show differences for the two SO modes of between 21 cm^{-1} (**4b**) and 40 cm^{-1} (**4c**); 37 cm^{-1} was obtained for the stable isomer **4a**. These data show that the vibrational coupling between the two SO groups depends on the conformation and, surprisingly, is of similar magnitude in the 1,3- and 1,2-dioxides.

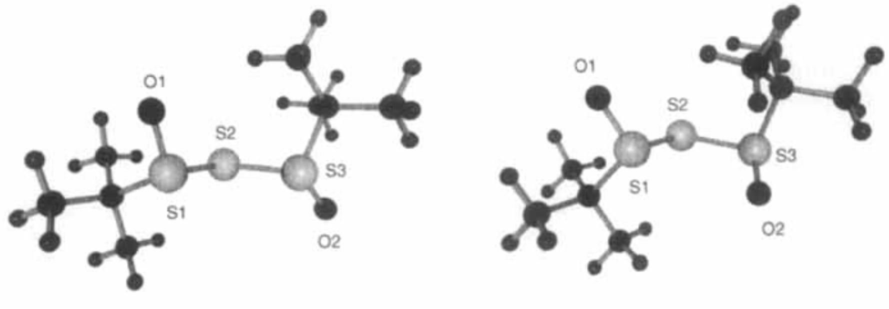
Table 7. Harmonic wavenumbers (cm^{-1}) of the fundamental vibrations in the range 300–800 cm^{-1} and of the stretching vibrations $\tilde{\nu}_{SO}$ of the most stable species of Me_2S_3O (**1a**, **2a**, **2b**) and of $Me_2S_3O_2$ (**3a**, **4a**) (HF/6-311G**). Wavenumbers have been scaled by a factor of 0.8929.

	1a	**2a**	**2b**	**3a**	**4a**
$\tilde{\nu}_{SO}$	1033	1038	1017	1051	1048
				1031	1011
$\tilde{\nu}_{CS}$	682	675	674	671	675
$\tilde{\nu}_{CS}$	669	667	671	670	654
"$\tilde{\nu}_{SS}$"	488	484	476	446	479
	422	467	441	435	440
	388	380	389	402	389
	319	311	333	346	346
				316	320

The CS stretching modes show similar behavior. The equivalent CS bonds of **2a**, **2b**, and **3a** result in two stretching modes near 670 cm^{-1} separated by a maximum of 8 wavenumbers. The wavenumber differences between the two nonequivalent CS bonds of **1a** and **4a** are, however, 13 and 21 cm^{-1}, respectively. SS stretching modes of sulfane derivatives are usually observed in the region 380–530 cm^{-1}. The wavenumbers listed in Table 7 for the 500–300 cm^{-1} region are somehow related to $\tilde{\nu}_{SS}$, but an inspection of the Cartesian displacements shows that strong coupling with bending modes of the SO and CH_3 groups takes place. Only the more stable rotamers/diastereomers have been listed in Table 7. The wavenumbers of the other species are, however, very similar.

***tert*-Butyl derivatives**: None of the methyl compounds investigated in this work has yet been prepared, since trisulfane oxides seem to be relatively stable only with bulky substituents. To check whether a bigger substituent changes the order of stabilities of the various rotamers and diastereomers, we calculated the energies and structures of *t*BuS(O)SS(O)*t*Bu, which we first prepared in 1977. Unfortunately, the size of this molecule requires a somewhat smaller basis set than was applied for the methyl compounds, and the electron correlation had to be ignored when calculating the energy. Comparisons of structural data should therefore be made with caution.

Geometry optimization resulted in only two stereoisomers (**5a** and **5b**; see Fig. 7) which are both of C_1 symmetry and of almost identical energy. Since vibrational wavenumbers could not be calculated for these large molecules, the relative energies given in Table 8 are based on HF/6-311G* energies. The energy



5a (0) **5b** (1.8)

Fig. 7. Molecular structure of the diastereomers of *t*BuS(O)SS(O)*t*Bu (5). The relative energies with respect to the most stable isomer **5a** are given in brackets (kJ mol^{-1}).

Table 8. Total (h = 2625.5 kJ mol^{-1}) and relative (kJ mol^{-1}) energies of the two stereomers of *t*BuS(O)SS(O)*t*Bu **5a** and **5b** calculated at the HF/6-311 G* level of theory.

	HF/6-311 G*	E_{rel}
5a	−1655.72151	0
5b	−1655.72082	1.8

Table 9. Selected bond lengths *d* (pm), valence angles α (°), and torsion angles τ (°) as well as dipole moments μ (D) of the two rotamers of *t*BuS(O)SS(O)*t*Bu (**5a/b**) (HF/6-311 G*).

	5a	**5b**
d(SO)	147.0	147.2
	146.9	147.3
d(SS)	212.3	213.7
	213.2	212.8
d(CS)	184.7	184.7
	185.0	184.9
α(OSS)	108.6	107.5
	107.3	108.3
α(SSS)	96.8	102.2
α(CSO)	106.2	105.8
	106.0	106.5
α(CSS)	99.1	99.9
	100.9	104.4
τ(OSSS)	93.5	31.0
	132.8	123.7
τ(CSSS)	−155.8	−82.2
	−116.5	−126.1
μ	2.17	1.58

difference between the more stable (*RR*)/(*SS*) isomer **5a** and the *meso* form **5b** amounts to only 1.8 kJ mol^{-1}. Selected geometrical parameters and the dipole moments of **5a** and **5b** are compiled in Table 9. The conformations of **5a** and **5b** are similar to those of the methyl derivatives **3a** and **3b** (see Fig. 4). A comparison of the structures **3a/5a** and **3b/5b** (Tables 5 and 9) shows that the substitution of methyl by *tert*-butyl groups has little influence on the SS and SO bond lengths. However, the CS bond lengths, some valence angles, and in particular the torsion angles are quite different. As expected, the CS bonds of **3a/b** (179.9 ± 0.1 pm) are considerably shorter than those of **5a/b** (184.8 ± 0.2 pm). The CSSS torsion angles of **5a** are large (−116.5, −155.8°) and of equal sign, thus minimizing any substituent interaction in the helical (CSSSC) molecule. In **3a** these values are both 65.1°. The SSSO torsion angles of **5a** are also of equal sign (93.5°, 132.8°) and larger than in **3a** (both −46.5°).

The *meso* form **5b** has also a helical CSSSC backbone (CSSS torsion angles: −82.2 and −126.1°) and the two oxygen atoms on different sides of the SSS plane (SSSO angles: 31.0° and 123.7°). In other words, the OSSSO chain is also of helical structure.

Comparison with experimental work: Since the methyl compounds investigated in this work are still unknown, comparison can be made only to experimental data for trisulfane oxides with other organic substituents. Only chain-like compounds will be considered. Trisulfane-1-oxides have been prepared with R = 2-naphthyl (**6**) and *tert*-butyl (**7**) but only one trisulfane-1,3-dioxide (R = *t*Bu, **5**) has been isolated.[5] The vibrational spectra of these compounds show the SO stretching vibration(s) at 1101 (**6**), 1088 (**7**), and at 1085/1095 cm^{-1} (**5**).[5, 19] Basically these values are in agreement with the data calculated for the methyl derivatives (Table 7) but there is an offset of about 60 cm^{-1} between the latter and the former, showing that the scaling factor of 0.8929 applied to the calculated wavenumbers is somewhat too small. The small wavenumber difference of 10 cm^{-1} observed for the two SO stretching modes of **5**[19] is consistent with a 1,3-dioxide, while for a 1,2-dioxide stronger coupling and thus a somewhat larger difference (> 20 cm^{-1}) would be expected.

Vibrational spectra of trisulfane-1,2-dioxides are not known, but numerous trisulfane-2-oxides have been prepared.[6, 7, 10, 20, 21] For R = *t*Bu the SO stretching mode has been observed at 1108 cm^{-1},[5] 20 cm^{-1} above the value of the isomeric trisulfane-1-oxide but in line with the trends of the data in Table 7.

The molecular and crystal structures of four acyclic trisulfane-2-oxides have been determined by X-ray crystallography (R = C_6H_5 (**9**), ClC_6H_4 (**10**), $(C_6H_5)_3C$ (**11**), *t*Bu (**12**)). All four structures show the CSSSC skeleton to be almost planar with CSSS torsion angles of between 158.5 and 178.7°. The conformation calculated for the most stable methyl compound **2a**, however, is different, with CSSS torsion angles of −75.4 and 166.3°. Obviously, the packing requirements in the crystal lattices of the trisulfane-2-oxides force a rotation around one of the SS bonds to make the CSSSC chain almost planar. This planar zigzag chain geometry of the CSSSC backbone corresponds to the horizontal part of the potential energy curve in Figure 4. For τ(C1 SSO) from −40 to −85° both CSSS torsion angles are calculated as between 154 and 180° (absolute values); this fits the observations in the crystalline trisulfane-2-oxides very well! Since the energy of these conformations are only about 12 kJ mol^{-1} higher than the energy of **2a**, the crystal forces can easily be considered responsible for the deviations from the gas-phase structure of MeSS(O)SMe. However, most of the other molecular parameters calculated for **2a** agree very well with those observed for molecules **9–11**. Only the SS and SO bond lengths of **12** differ substantially from those of **2a** and other trisulfane-2-oxides, as the comparison of data in Table 10 shows.

The formation of two diastereomers of bis(*tert*-butyl)trisulfane-1,3-dioxide **5** has recently been inferred from the ^{13}C NMR spectrum of the product of the oxidation of the corre-

Table 10. Comparison of selected bond lengths (pm) and valence angles (°) of organic trisulfane-2-oxides (data for **9**–**12** from X-ray structural analyses).

R	CH_3 (**2a**)	C_6H_5 (**9**)	ClC_6H_4 (**10**)	Ph_3C (**11**)	*t*Bu (**12**)
d_{SS}	210.0/212.0	212.4	212.5	212.7/211.4	204.4/206.5
d_{SO}	146.3	147.6	144.9	146.9	154.5
d_{CS}	181.6/181.8	177.0	178.0	188.0/188.2	187.1/187.9
α_{SSS}	97.4	88.3	91.3	83.8	89.8
α_{SSO}	107.0/108.7	110.9	108.3/109.2	112.0/112.2	109.4/110.1
α_{CSS}	97.3/99.9	98.0	94.1	104.1	101.1/101.6
ref.	this work	[7]	[6]	[8]	[a]

[a] Calculated from the coordinates given in ref. [9].

sponding monoxide by either *m*-CPBA, peroxoacetic acid, or dimethyldioxirane.[17] The primary and obviously metastable product formed at −40 °C showed a singlet for the tertiary carbon atoms, but on standing at room temperature this signal decreased in intensity while a second, immediately neighboring singlet grew at the expense of the first signal, which disappeared almost completely. This was explained by the conversion of an initially formed "kinetic diastereomer" into a more stable "thermodynamic diastereomer". The latter was assumed to be the *meso* form with the SO groups in an *anti* orientation.[17] However, our results do not support this interpretation. The rather similar conformations of **5a** and **5b** (Fig. 6) do not provide any justification for reasoning that just one of them should be formed in the oxidation of the monoxide *t*Bu−S(O)SS−*t*Bu. In addition, the energies of **5a** and **5b** are so similar that a *complete* conversion of one of them into the other is unlikely. Rather, one would expect that (*RR*)/(*SS*)- and (*RS*)-$tBu_2S_3O_2$ would be formed together when the trisulfane monoxide is oxidized. Thus the identity of the metastable primary oxidation product remains unknown.

Conclusion

Our results show that dimethyl trisulfane oxides have the expected structures with weak S−S bonds at three-coordinated sulfur atoms. The trisulfane-1-oxide Me_2S_3O is more stable than the isomeric 2-oxide, the structure of which is in good agreement with experimental structures of other organic trisulfane-2-oxides. The trisulfane dioxide $Me_2S_3O_2$ is more stable as 1,3-dioxide MeS(O)SS(O)Me than the isomeric 1,2-dioxide. Some of the methyl compounds are stabilized by O ··· H hydrogen bonds. No such hydrogen bonds exist in the di-*tert*-butyl trisulfane-1,3-dioxide, which exists as (*RR*)/(*SS*) and (*RS*)/(*SR*) forms of practically identical energy.

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