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Structures, Energies, and Vibrational Spectra of Several Isomeric Forms of H₂S₂O and Me₂S₂O: An *ab Initio* Study

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High-level *ab initio* MO calculations have been performed to determine the structures, energies, and vibrational spectra of eight isomers (including rotamers) of H₂S₂O and five isomers/rotamers of Me₂S₂O. At the MP2/6-311G**//MP2/6-311G** level of theory, including the zero-point energies (ZPE), the order of decreasing stability of H₂S₂O molecules is *trans*-HOSSH > *cis*-HOSSH > HOS(S)H > *trans*-HSS(O)H > *cis*-HSS(O)H > *trans*-HSOSH > *cis*-HSOSH > HS(O)(S)H. The remarkable stability of the thiono derivative HOS(S)H over the sulfoxide HSS(O)H is explained by the stabilization of the former by an intramolecular OH···S hydrogen bond. The dimethyl derivatives of the more stable H₂S₂O isomers have been calculated at the MP2/6-311G**//HF/6-311G**+ZPE level. The order of decreasing stability is *trans*-MeOSSMe > *cis*-MeOSSMe > *cis*-MeSS(O)Me > *trans*-MeSS(O)Me > MeOS(S)Me. The geometrical parameters of these species agree well with those of related compounds, e.g., MeOSSOMe and RSS(O)R with R = *p*-tolyl.

Introduction

A compound of the composition H₂S₂O is unknown, and if it ever will be prepared, it may turn out to be unstable, as are many other oxyacids of sulfur in its lower oxidation states.[1] However, organic derivatives of H₂S₂O are known, e.g., the well-characterized thiosulfinates RS(O)SR.[2] In the literature, these compounds are also termed thiolsulfinates, disulfane oxides, and thiosulfoxides, although the latter name should be reserved for compounds of the type RS(S)R. Species of the type R₂S₂O may exist as various isomers and/or rotamers. These have never been studied systematically, although *ab initio* MO calculations of two isomers of H₂S₂O[3,4] and of the rotamers of MeS(O)SMe[5] have been published; this work will be discussed below. As part of a systematic study of the oxyacids of sulfur,[6] we have performed extensive *ab initio* MO calculations on eight isomers of H₂S₂O (including rotamers) and on five isomers of Me₂S₂O (also including rotamers). For the molecule of H₂S₂O, nine different connectivities are hypothetically possible, if sulfur and oxygen are allowed to be either two, four, or six valent:
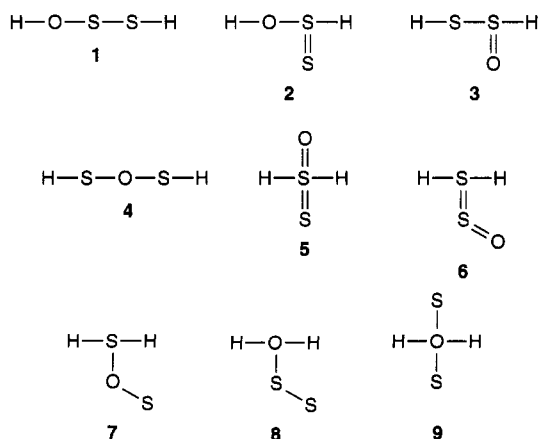
In the present work, we restricted our investigation to the most

reasonable species, **1–5**, which all contain two-valent oxygen and two-, four-, or six-valent sulfur. The hypervalent oxygen compounds **7–9** as well as **6** will be investigated separately. For molecules **1–4**, the energies and vibrational spectra were calculated to support future experimental work, e.g., matrix isolation with spectroscopic detection. In addition, the dimethyl derivatives **1**, **2**, and **3** were studied:
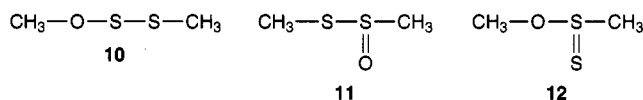
In this context, it should be mentioned that alkylthiosulfinates (e.g., **11**) have been found to possess tumor-inhibiting, antiviral, and antifungal activity and some of them occur naturally.[2,7]

Calculations

All calculations were performed with the GAUSSIAN 92 program package[8] for *ab initio* MO calculations on an IBM/RISC 6000 work station. Molecular structures of the isomers **1–5** were fully optimized at the Hartree–Fock level with the 6-311G** basis set. The optimization was done from different starting geometries toward the rotation around SS and SO bonds. Improved relative energies were obtained by single-point calculations at the valence-electron-correlated MP2 level of theory based on the HF/6-311G**-optimized geometries.[9] The geometries of isomers **1–4** of H₂S₂O were reoptimized at MP2/6-311G** level of theory.

The harmonic vibrational frequencies were computed analytically at the MP2/6-311G** level for compounds **1–4** and at HF/6-311G** for **10–12**. Following the most recent suggestion by Pople et al.,[10] the vibrational wavenumbers were scaled by a factor of 0.8929 for HF/6-311G** and 0.9427 for MP2//6-311G**. For the values of zero-point energies, these factors are 0.9135 and 0.9646, respectively.[10]

The geometries of isomers **10–12** of Me₂S₂O were optimized at the Hartree–Fock level with the 6-311G** basis set, and single-point calculations at the MP2/6-311G** level were carried out for the optimized structures. The zero-point vibrational energies (ZPEs) and the vibrational wavenumbers were scaled

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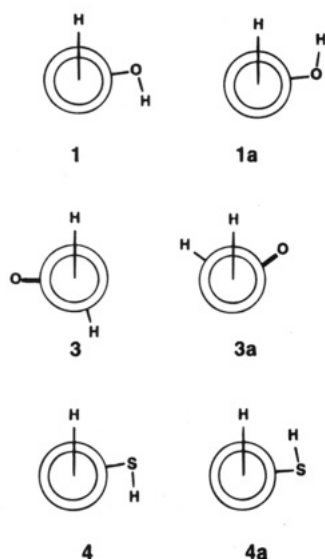⊗ Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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Figure 1. Newman projections of different rotamers of H_2S_2O.
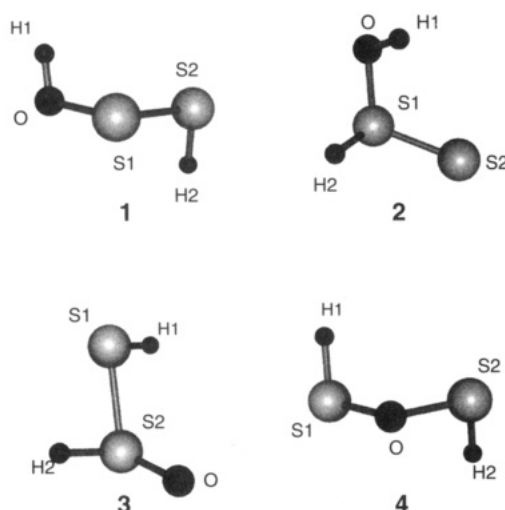
Figure 2. Isomeric forms of H_2S_2O. Numbering of atoms.

TABLE 1: Total Energies (1 hartree = 2625.5 kJ mol^{-1}) of Various Isomers of H_2S_2O and the Corresponding Zero-Point Vibratonal Energies Scaled by 0.9135 for HF/6-311G and by 0.9646 for MP2/6-311G**//HF6-311G** (ZPE in kJ mol^{-1})**

isomer	HF/6-311G**	ZPE	MP2/6-311G**^{a}	MP2/6-311G**^{b}	ZPE
1	−871.082 5608	64.6	−871.545 8236	−871.546 9694	64.1
1a	−871.080 8868	64.4	−871.544 3086	−871.545 4524	64.0
2	−871.044 6948	67.5	−871.509 4023	−871.511 9161	66.1
3	−871.030 0481	59.8	−871.506 7993	−871.508 7719	59.3
3a	−871.030 1593	59.6	−871.505 0910	−871.506 8065	58.7
4	−871.037 1812	56.6	−871.500 4403	−871.501 8793	56.3
4a	−871.036 6167	56.6	−871.500 0968	−871.502 5552	56.4
5	−870.989 9498		−871.465 4324		

^{a} At HF/6-311G**-optimized geometries. ^{b} At MP2/6-311G**-optimized geometries.

TABLE 2: Energies (kJ mol^{-1}) of the Isomeric Structures of H_2S_2O in Relation to the Energy of 1^a

	HF/6-311G**^{b} + ZPE	MP2/6-311G**^{b} + ZPE^c	MP2/6-311G**^{d} + ZPE
1	0	0	0
1a	4.2	3.8	3.9
2	102.3	98.5	94.0
3	133.1	97.7	95.5
3a	132.6	101.9	100.0
4	111.1	111.2	110.5
4a	112.6	112.1	111.5
5	243.2^e	211.1^e	

^{a} The zero-point energies scaled by 0.9135 for HF/6-311G** and by 0.9646 for MP2/6-311G** have been taken into account. ^{b} Geometries optimized at HF/6-311G**. ^{c} ZPE taken from MP2/6-311G** calculations. ^{d} Geometries optimized at MP2/6-311G**. ^{e} Without ZPE.

TABLE 3: Bond Distance d (pm), Valence Angles α (deg), and Torsion Angles τ (deg) of the Isomers of H_2S_2O (MP2/6-311G)**

	1	1a	2	3	3	4	4a
d(H1S1)	133.8	133.9	135.3	133.5	133.7	134.0	134.1
d(H2S2)			136.9		136.7		
d(OH)	96.3	96.3	97.0				
d(SS)	205.2	205.4	194.7	217.2	217.1		
d(SO)	167.8	167.8	167.2	147.9	148.1	169.6	169.5
α(HOS)	106.4	106.4	107.0				
α(OSS)	104.9	105.1	111.2	114.1	113.0		
α(HSS)	99.0	99.2	104.8	93.0, 84.1	95.1, 89.2		
α(HSO)			95.3	108.8	107.5	97.8	97.3
α(SOS)						117.5	117.4
τ(HOSS)	85.1	88.7	30.8				
τ(HSSO)	83.6	−89.5	101.9	−88.4	52.2		
τ(HOSH)			−77.3				
τ(HSOS)						80.5	±86.5
τ(HSSH)			163.58	−56.46			

as mentioned above. For the general description of the basis sets and methods used, see the excellent discussion in ref 11.

Results and Discussion

H_2S_2O. The investigation of the various H_2S_2O isomers showed that species **1**, **3**, and **4** can exist as two rotamers each, both of which correspond to energy minima with all the vibrational wavenumbers being real. The rotamers have been termed **1a**, **3a**, and **4a** and Figure 1 shows the corresponding Newman projections. In Figure 2, the geometries of isomers **1**−**4** optimized at the MP2/6-311G** level are shown. In the case of the less stable species **5**, the geometry was optimized at the HF/6-311G** level only. No spectra were calculated for **5**. The total energies of isomers and rotamers at the various levels of theory are given in Table 1, which also contains the zero-point energies as far as available. In Table 2, the relative energies of **1**−**5** with regard to the most stable isomer (**1**) are given. Only the results on the highest level (MP2/6-311G**//MP2/6-311G**+ZPE) will be discussed here unless otherwise noted. The chainlike isomer **1** of trans conformation is the most stable structure of H_2S_2O. This species may be termed either as hydroxydisulfane or as 1-oxatrisulfane. Its structural parameters (Table 3) are of normal value including the two torsional angles of 84° and 85°. Since **1** is chiral, there will be an enantiomer the torsional angles of which are −84° and −85°.

The cis rotamer **1a** is less stable than **1** by 4 kJ mol^{-1}. The geometrical parameters are practically identical to those of **1** except for the two torsional angles of 89° and −90°. These species are relatives of *trans-* and *cis*-trisulfane, H_2S_3.[12]

The finding that the chain structure **1** is the most stable H_2S_2O isomer agrees with previous results on $H_2S_2O_2$ for which the chain has also been found to be more stable than any branched structure.[6b] Unfortunately, no structural data of any organic derivatives of **1** and **1a** are available, although species of the types RSSOR[13] and RSSOH[14] have been prepared. Furthermore, *ab initio* MO calculations have shown that HSOH is more stable than HS(OH).[15]

Isomers **2**−**4** are all of comparable energy, and where rotamers exist, the trans conformation is more stable than the cis form. No rotamers have been found for the thionosulfinic

TABLE 4: Mulliken Atomic Charges and Dipole Moments μ (1D $\approx$ 3.33 $\times$ 10^{-30} C·m) of the Isomers of H₂S₂O (MP2/6-311G**//MP2/6-311G**)^a

	1	1a	2	3	3a	4	4a
H(1)	+0.30	+0.29	+0.31	+0.05	+0.05	+0.01	−0.001
O	−0.55	−0.55	−0.55	−0.67	−0.67	−0.66	−0.65
S(1)	+0.25	+0.24	+0.64	+0.29	+0.28	+0.73	+0.73
S(2)	−0.07	−0.05	−0.46	+0.29	+0.28	−0.15	−0.15
H(2)	+0.08	+0.06	+0.06	+0.05	+0.05	+0.08	+0.075
μ	0.79	2.83	3.39	2.57	1.84	3.35	3.37

^{a} For the numbering of atoms, see Figure 2.

acid **2**. Most surprisingly, this isomer, formally containing an SS double bond, is more stable (by 1.5 kJ mol^{-1}) than the thiosulfinic acid **3**, which formally contains a SO double bond. This unexpected order of relative stability is probably due to the fact that **2** is stabilized by an intramolecular hydrogen bond not present in **3** and **3a**. The H···S distance between the terminal sulfur atom and the more distant hydrogen of **2** amounts to 288.6 pm, which is well below the sum of the van der Waals radii[16] (300.5 pm). The Mulliken atomic charges of these two atoms (Table 4) are −0.46e for S and +0.31e for H, supporting the idea of an attractive interaction. In **3** and **3a**, the shortest H···O nonbonding distance involving the sulfoxide group amounts to 310.5 pm, which is well above the van der Waals distance of 260 pm. The hydrogen bridge in **2** may be responsible for the finding that no rotamer of **2** exists, in contrast to the two related species **3** and **3a**. The higher stability of **2** over **3** and the existence of two rotamers **3** and **3a** has already been found previously by MO calculations at the MP2/6-31G*/ /HF/6-31G* level.[3] The previous authors did, however, not consider any other isomers nor did they compute vibrational spectra. The data in Table 2 show that the energy difference between **2** and **3** decreases with increasing sophistication of the calculations and becomes almost negligible when the electron correlation is taken into account.

A comparison of the structures of **2** and **3** is most interesting. In **2**, the SO bond distance is normal[17] and practically identical to those in **1** and **1a**. The SS bond (194.7 pm) is much shorter than the formal single bonds of **1** and **1a** (205 pm). In contrast, the SS bonds of **3** and **3a** (217 pm) are much longer than the single bond distance. It is a general observation that formal SS single bonds originating from one sulfur atom of coordination number larger than two are considerably longer than the accepted single bond length of 205 pm.[18]

The chainlike structures **4** and **4a** may be termed 2-oxatrisulfanes. They are less stable than any other chainlike isomer of H₂S₂O. The reduced stability can be seen in the somewhat larger SO bond lengths (169.6 pm) compared to isomer **1** (167.8 pm) and in the unusually large SOS angles of 117.5°, which indicates some repulsion between the two sulfur atoms. The torsional angles of **4** (80.5°/80.5°) and **4a** (86.5°/−86.5°) are normal. Since **4** is chiral, the enantiomer has two negative torsional angles. Species **1**–**3a** are all of C_1 symmetry, while **4** is the C_2 and **4a** of C_s symmetry.

As the data in Table 2 show, the tetrahedral isomer of H₂S₂O (**5**) is by far the least stable H₂S₂O species considered here. Therefore, neither geometry optimization at the MP2/6-311G** level nor vibrational spectra calculations were carried out. At the HF/6-311G** level, the geometrical parameters are S=O, 143.4 pm; S=S, 193.5 pm; S—H, 134.2 pm; H—S=O, 109.0°; H—S=S 107.9°; and O=S=S 122.8°.

Species **7**–**9** containing higher valent oxygen atoms were not calculated. They are relatives of the "thioxonium ylide" H₂OS, which was recently generated in the gas phase.[19]

To confirm that the optimized isomers **1**–**4a** correspond to

minima on the energy hypersurface and to support future experimental work on the generation and detection of these species, we have calculated the vibrational spectra in the harmonic approximation at the MP2/6-311G** level of theory. The scaled wavenumbers of the nine fundamental vibrations and the relative infrared absorption intensities are given in Table 5.

The vibrational assignment presented in Table 5 is straightforward for the vibrations at >500 cm^{-1}. However, in the low wavenumber region due to the low symmetry of these species, considerable coupling between fundamental modes occurs and the description of the modes given should be considered approximate only.

(CH₃)₂S₂O. Of the three dimethyl derivatives of H₂S₂O, two exist as two rotamers each. Their total and relative energies are presented in Table 6. Again the chainlike isomer **10** turns out to be the most stable species. The two rotamers **10** and **10a** differ by 8.2 kJ mol^{-1}. The thiosulfinate **11** is less stable than **10** by 22 kJ mol^{-1} but more stable than the thiosulfoxide structure, **12**, which is by far highest in energy. This is a reversal of the order observed for the unsubstituted species **2** and **3a** (Table 2). The molecular structures optimized at the HF/6-311G** level are shown in Figure 3; the geometrical parameters as well as the dipole moments are given in Table 7. These results may be compared to the available experimental data.

It seems that the methoxymethyldisulfane **10** has not been prepared yet, but the X-ray structural analysis of the related dimethoxydisulfane MeOSSOMe (**13**) is available.[17c] In the solid state, **13** is of trans conformation (C_2 symmetry) and its structure may be compared to that of **10**. The SO bond length of **10** (163.7 pm) compares well with that of **13** (165.7 pm), and the same holds for the CO distance (**10**, 141.1 pm; **13**, 143.7 pm). However, the sulfur—sulfur bond is considerably longer in **10** (204.5 pm) than in **13** (197.0 pm), which may be a result of the inductive effect of the *two* methoxy groups in **13**.[17c] The comparable valence angles of **10** and **13** are very similar, and this also applies to the torsional angle at the SS bond which amounts to 78.7° in **10** and to 81.3° in solid **13**.

The dimethylthiosulfinate **11** (methanesulfinothioic acid S-methyl ester), first prepared in 1947, is a well-characterized compound,[2] but its structure is unknown. However, the X-ray structural analysis of the analogous bis(p-tolyl)thiosulfinate **14** (p-toluenesulfinothioic acid S-tolyl ester) has been published.[20] This molecule contains an almost planar backbone CSSC with a torsional angle of 174° at the SS bond. This value agrees well with the corresponding parameters of both **3** and **11a** for which SS torsional angles of 163.6° and 175.6°, respectively, have been calculated (Tables 3 and 7). It therefore is not surprising that the SS bond distances of **11a** (211.3 pm) and **14** (210.8 pm) are practically identical. Other parameters like the SO and CS bond lengths and the SSO bond angles also agree quite well, showing that the data in Table 7 are reliable.

Both **10** and **11** exist as two rotamers the energies of which differ by about 8 kJ mol^{-1}. Newman projections of these species are shown in Figure 4. However, while in the case of **10** and **10a** the cis conformation is less stable than the trans rotamer (as has also been found for **1/1a**, **3/3a**, and **4/4a**), the opposite ordering is observed for **11** and **11a**. Here the cis form is more stable than the trans rotamer. Previous MO calculations at the HF/6-31G* level[5] had also resulted in a lower energy for the cis rotamer **11**. This preference for the cis conformation may be the result of an intramolecular O···H hydrogen bond: in **11**, the shortest O···H contact distance is 240.5 pm, which is well below the van der Waals distance (all other O···H

**TABLE 5: Harmonic Wavenumbers (cm^{-1}) of the Fundamental Vibrations of the H$_2$S$_2$O Isomers (MP2/6-311G**)^a**

	1, C_1	1a, C_1	2, C_1	3, C_1	3a, C_1	4, C_2	4a, C_s
ν(HO)	3628 (80)	3626 (74)	3552 (31)				
ν(HS)	2612 (4)	2603 (7)	2463 (25)	2641 (1)/H1	2630 (0.5)/H1	2601 (s) (0.5)	2594 (s) (3)
				2356 (54)/H2	2369 (56)/H2	2600 (as) (55)	2591 (as) (75)
ν(SO)	702 (100)	702 (100)	652 (100)	1132 (100)	1127 (100)	588 (s) (21)	591 (s) (24)
						712 (as) (100)	710 (as) (100)
ν(SS)	484 (44)	487 (67)	580 (53)	403 (45)	395 (51)		
δ(SOH)	1109 (41)	1107 (43)	1094 (33)				
δ(SSH)	852 (13)	857 (5)	878 (4)	929 (8)	839 (23)		
				656 (9)	683 (5)		
δ(SOS)						298 (s) (0.2)	304 (s) (3)
δ (SSO)	442 (98)	445 (70)	382 (59)	279 (17)	285 (13)	281 (as) (29)	264 (as) (32)
τ(SO)	378 (38)	368 (14)	227 (10)	247 (1)	209 (5)	192 (s) (53)	212 (s) (24)
τ(SS)	259 (0.1)	261 (1)					
δ(OSH)			975 (27)	1052 (4)	1060 (4)	968 (s) (3)	977 (s) (57)
						962 (as) (43)	969 (as) (5)

^{a} Relative infrared intensities are given in parentheses. Wavenumbers have been scaled by a factor of 0.9427 (ν = stretching, δ = bending, τ = torsional mode; s = symmetric, as = asymmetric).

TABLE 6: Total Energies (1 hartree = 2625.5 kJ mol^{-1}) of Five Isomers of (CH$_3$)$_2$S$_2$O^a

|	HF/6-311G**	ZPE	E_{rel}	MP2/6-311G**	E'_{rel}
10	−949.158 5218	210.5	0	−949.922 1763	0
10a	−949.154 7491	210.0	9.4	−949.918 8485	8.2
11	−949.132 6692	208.4	65.8	−949.912 8974	22.3
11a	−949.130 5971	207.7	70.5	−949.910 0201	29.1
12	−949.132 0974	212.2	71.1	−949.898 0245	65.1

^{a} The corresponding zero-point vibrational energies have been scaled by 0.9135 (ZPE in kJ mol^{-1}). The energies (kJ mol^{-1}) in relation to the energy of **5** are also given. The scaled zero-point energies calculated as the HF/6-311G** have been taken into account in the calculation of E_{rel} and E'_{rel}.
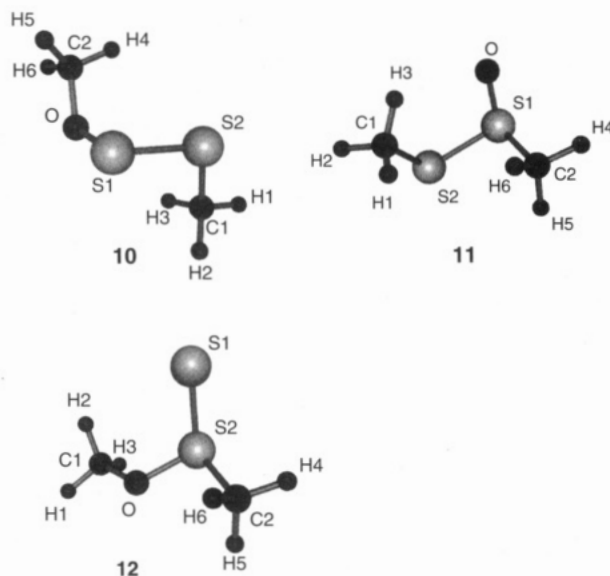
Figure 3. Isomeric forms of Me$_2$S$_2$O. Numbering of atoms.

distances are larger than the van der Waals distance). The charges on the oxygen (−0.69e) and the hydrogen atom H(3) involved (+0.18e) support the assumed attractive interaction. The fact that bis(*p*-tolyl)thiosulfinate **14** adopts the less stable trans form in the solid state is probably due to packing effects. We expect that organic thiosulfinates in the vapor phase as well as in solution are of cis conformation or exist as an equilibrium mixture of both rotamers.

Finally, the structure of the thiono derivative **12** will be addressed. Compounds of this type are still unknown, although a number of related cyclic thionosulfites ROS(S)OR have been prepared;[21,22] these species are stable at 20 °C. However,
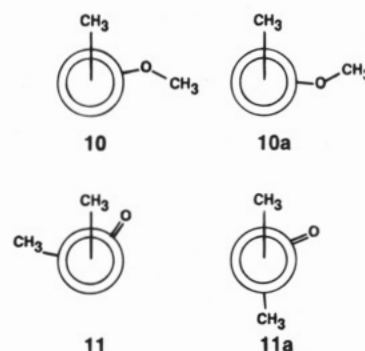
Figure 4. Newman projections of different rotamers of Me$_2$S$_2$O.

chainlike derivatives of the type ROSSOR always adopt the unbranched disulfane structure.[6b,17c] The conformation of **12** is similar to that of **11a**, as can be seen from the corresponding torsional angles of the backbone which are near 176°. No second rotamer of **12** was found.

The Mulliken atomic charges and dipole moments of species **10**−**12** are listed in Table 8. The dipole moment of dimethylthiosulfinate has been determined in benzene solution at 25 °C as 3.14 D.[23] The calculated dipole moments of **11** and **11a** are 3.51 and 3.06 D, respectively (Table 8). The agreement between experimental and theoretical values is satisfactory, but the difference between the values of **11** and **11a** is too small to allow the interpretation of the experimental value to indicate the presence or absence of one or the other rotamer.

The vibrational spectra of species **10**−**12** are given in Table 9. Major differences between the spectra of the molecules are to be expected in the region 500−1100 cm^{-1}. In this region, the strongest bands in the infrared spectrum are expected, as can be seen from the intensities given in Table 9. Although MeSS(O)Me has been prepared a long time ago, its vibrational spetrum has never been reported in detail; just the SO stretching vibration is known. It has been observed[24] at 1097 cm^{-1} in CCl$_4$ and at 1075 cm^{-1} in CHCl$_3$. The calculated wavenumbers of 1023 cm^{-1} for the cis rotamer and 1041 cm^{-1} for the trans form (both scaled by 0.8929) are in fair agreement with the observed values.

As has already been pointed out above, due to the low symmetry of these molecules, the vibrations in the region below 1000 cm^{-1} are strongly coupled, and only tentative assignments can be made as long as no normal-coordinate analysis is available. Therefore, we did not try to specify the vibrational modes expected at wavenumbers of <400 cm^{-1}. The SO and CS vibrations of **12** are particularly strongly coupled since the two oscillators have one atom in common.

Spectra of Isomeric Forms of H₂S₂O and Me₂S₂O

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TABLE 7: Bond Distances d (pm), Valence Angles α (deg), and Torsion Angles τ (deg) of the Five Most Stable Isomers (Including Rotamers) of $(CH_3)_2S_2O$ (HF/6-311G**)

	10	10a	11	11a	12
d(SS)	204.5	204.7	211.1	211.3	198.5
d(CS)	(C1S2) 181.6	181.8	(C1S2) 181.7	181.6	(C2S2) 179.0
			(C2S1) 179.7	179.6	
d(SO)	(S1O) 163.7	163.5	(S1O) 147.4	146.8	(S2O) 162.6
d(CO)	(C2O) 141.1	140.8			(C1O) 142.0
d(CH)^a	108.1	108.1	108.1	108.1	108.1
α(CSS)	(C1S2S1) 102.4	104.1	(C1S2S1) 100.2	97.4	(C2S2S1) 106.3
			(C2S1S2) 99.7	94.8	
α(COS)	(C2OS1) 117.2	118.2			(C1OS2) 116.8
α(OSS)	(OS1S2) 104.3	105.7	(OS1S2) 108.4	109.4	(OS2S1) 110.0
α(HCS)	(H1C1S2) 106.5	105.9	(H1C1S2) 106.5	106.2	(H4C2S2) 108.3
	(H2C1S2) 110.6	111.5	(H2C1S2) 111.4	111.0	(H5C2S2) 107.8
	(H3C1S2) 110.0	110.6	(H3C1S2) 108.5	109.6	(H6C2S2) 107.0
			(H4C2S1) 109.6	110.2	
			(H5C2S1) 109.6	106.2	
			(H6C2S1) 106.4	108.6	
α(HCO)	(H4C2O) 106.3	106.4			(H1C1O) 105.6
	(H5C2O) 110.9	110.9			(H2C1O) 110.5
	(H6C2O) 110.8	111.1			(H3C1O) 110.6
α(CSO)			(C2S1O) 105.1	106.4	(C2S2O) 94.1
τ(HCSS)	(H1C1S2S1) 181.3	−171.8	(H1C1S2S1) −153.1	−176.0	(H4C2S2S1) −174.3
			(H4C2S1S2) −60.7	60.8	
τ(CSSO)	78.7	−95.5	33.2	66.4	
τ(SSOC)	83.3	83.7			−73.6
τ(CSSC)			−76.4	175.6	
τ(HCSO)			(H4C2S1O) −172.9	172.7	−62.0
τ(CSOC)					177.4
τ(HCOS)	(H4C2OS1) 175.8	168.8			186.3

TABLE 8: Mulliken Atomic Charges and Dipole Moments μ (1D $\simeq$ 3.33 $\times$ 10^{-30} C·m) of Three Isomers of $(CH_3)_2S_2O$ (HF/6-311G**)^a

	10	10a	11	11a	12
S(1)	+0.24	+0.24	+0.71	+0.73	−0.48
S(2)	−0.02	+0.01	−0.08	−0.07	+0.6
O	−0.57	−0.56	−0.69	−0.69	−0.58
C(1)	−0.38	−0.39	−0.41	−0.42	+0.01
H(1)	+0.13	+0.13	+0.15	+0.14	+0.12
H(2)	+0.14	+0.13	+0.13	+0.14	+0.14
H(3)	+0.15	+0.14	+0.18	+0.16	+0.10
C(2)	+0.03	+0.03	−0.42	−0.45	−0.38
H(4)	+0.10	+0.11	+0.14	+0.14	+0.14
H(5)	+0.10	+0.09	+0.14	+0.15	+0.17
H(6)	+0.09	+0.09	+0.15	+0.16	+0.16
μ	1.14	3.44	3.51	3.06	4.61

^{a} For the numbering of Atoms, see Figure 3.

Conclusion

It is shown that the sulfur oxyacid H_2S_2O can exist as eight isomers at least (including rotamers); the order of decreasing stability is *trans*-HOSSH > *cis*-HOSSH > HOS(S)H > *trans*-HSS(O)H > *cis*-HSS(O)H > *trans*-HSOSH > *cis*-HSOSH > HS(O)(S)H.

The vibrational spectra of the first seven species have been calculated and assigned; different connectivities result in sufficiently different spectra to allow detection of these still unknown species by, for example, matrix isolation infrared spectroscopy. The stability of the corresponding dimethyl derivatives decreases in the order *trans*-MeOSSMe > *cis*-MeOSSMe > *cis*-MeSS(O)Me > *trans*-MeSS(O)Me > MeOS-(S)Me. The calculated spectra await the preparation and vibrational spectroscopic investigation of these species of which only MeSS(O)Me is known.

TABLE 9: Harmonic Wavenumbers (cm^{-1}) of the Fundamental Vibrations of the $(CH_3)_2S_2O$ Isomers (HF/6-311G**)^a

	10	10a	11	11a	12
ν(CH)	2945 (4)	2942 (6)	2951 (3)	2947 (1)	2965 (0.1)
	2930 (3)	2928 (5)	2945 (1)	2946 (2)	2956 (1)
	2927 (15)	2926 (17)	2938 (4)	2939 (1)	2953 (8)
	2896 (19)	2889 (25)	2936 (4)	2934 (4)	2918 (12)
	2851 (12)	2852 (15)	2855 (16)	2855 (13)	2862 (3)
	2834 (24)	2830 (21)	2853 (6)	2852 (3)	2843 (23)
δ (CH₃)	1450 (5)	1449 (5)	1435 (7)	1432 (6)	1454 (7)
	1438 (5)	1439 (5)	1422 (5)	1417 (6)	1436 (6)
	1427 (2)	1425 (3)	1413 (11)	1415 (3)	1426 (2)
	1426 (5)	1423 (6)	1396 (4)	1399 (4)	1409 (5)
	1414 (3)	1414 (5)	1329 (1)	1326 (4)	1400 (4)
	1326 (4)	1328 (4)	1320 (7)	1321 (2)	1327 (2)
ϱ(CH₃)^b	1167 (1) (O)	1166 (1) (O)	966 (10)	979 (0.5)	1167 (3) (O)
	1143 (2) (O)	1140 (2) (O)	961 (11)	958 (2)	1142 (2) (O)
	962 (4) (S)	957 (5) (S)	949 (3)	947 (9)	974 (6) (S)
	955 (2) (S)	950 (1) (S)	946 (21)	935 (7)	960 (43) (S)
ν_{CO}	1037 (100)	1044 (100)			1043 (100)
ν(CS)	678 (1)	676 (1)	682 (8) (S^{IV})	681 (1) (S^{II})	705 (19)^c
			672 (6) (S^{II})	676 (6) (S^{IV})	
ν(SO)	700 (32)	699 (40)	1023 (100)	1041 (100)	682 (32)^c
ν(SS)	489 (5)	486 (6)	450 (41)	471 (27)	496 (23)
δ and τ	374 (1)	370 (1)	389 (5)	354 (7)	382 (3)
	308 (3)	286 (5)	321 (8)	311 (3)	315 (4)
	214 (2)	234 (1)	245 (2)	257 (1)	238 (1)
	169 (1)	163 (0.3)	228 (2)	201 (0.1)	213 (1)
	148 (0.1)	141 (0.3)	196 (3)	163 (3)	195 (2)
	105 (2)	95 (0.3)	143 (1)	145 (0.2)	148 (1)
	75 (2)	66 (1)	85 (5)	38 (5)	71 (4)

^{a} Relative infrared intensities are in parentheses. Wavenumbers have been scaled by 0.8929 (ν = stretching, δ = bending, τ = torsional, ϱ = rocking mode). ^{b} The atom to which the methyl group is linked is given in parentheses. ^{c} ν(CS) and ν(SO) are strongly coupled with each other.

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