Sulphur Compounds. Part 140.[1] Structures and Relative Stabilities of Seven Isomeric Forms of $H_2S_2O_2$

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The ground-state geometries, energies, atomic charges and dipole moments of eight isomeric forms of $H_2S_2O_2$ all containing an SS bond have been calculated at the HF/6-31G* level. The correlation energies have also been included up to the fourth order of Moeller–Plesset perturbation theory (MP4). The four most stable isomers are two rotamers of the chain-like HOSSOH (isomers **1** and **1a**), and the thiosulphurous acids HOS(O)SH **2** and S=S(OH)$_2$ **3** the energies of which differ by less than 40.1 kJ mol^{-1}. The four most stable structures have been refined at the HF/6-311G** level taking into account the correlation energy at level MP2 and zero-point energies, showing **2** to be the most stable isomer followed by **1** (symmetry C_1), **1a** (symmetry C_2) and **3**. The geometries obtained are compared to the known structures of organic derivatives. For isomers **1**, **1a**, **2** and **3** the wavenumbers of the 12 fundamental vibrations are given.

Of the many oxyacids of sulphur[2–4] those of low sulphur oxidation number are particularly unstable and, consequently, little is known about their structures, properties and reactions. This holds, for example, for sulphoxylic acid [hydrogen dioxosulphate(II)], H_2SO_2, and thiosulphurous acid [hydrogen dioxothiosulphate (IV)], $H_2S_2O_2$. While H_2SO_2 has never been observed directly and is known only as derivatives, *e.g.* $(CH_3O)_2S$, the compound $H_2S_2O_2$ has been claimed as an intermediate in the hydrolysis of S_2Cl_2[2,3] and has recently been observed by electron impact (EI) mass spectrometry[5] as a decomposition product of diisopropoxydisulphane, $(Pr^iO)_2S_2$, according to equation (1); Pr^iOSSOH and $H_2S_2O_2$ were observed as molecular ions M^+ with high intensity.

$$(Pr^iO)_2S_2 \xrightarrow[-C_3H_6]{EI} Pr^iOSSOH \xrightarrow[-C_3H_6]{EI} HOSSOH \quad (1)$$

The preparation of pure thiosulphurous acid as a white solid formed from H_2S and SO_2 at −70 °C in CCl_2F_2 has been reported,[6] equation (2). On heating to 20 °C this material

$$H_2S + SO_2 \xrightarrow{-70\,^\circ C} H_2S_2O_2 \quad (2)$$

turned deep yellow and SO_2 was given off, while rapid heating to 100 °C in a vacuum produced S_2O, equation (3). However,

$$H_2S_2O_2 \xrightarrow{100\,^\circ C} S_2O + H_2O \quad (3)$$

no spectra, molecular weight, or structural information of the white solid of composition H:S:O = 1:1:1 are known. Therefore, the existence of thiosulphurous acid in the solid state remains to be demonstrated.

As part of a systematic study of the oxyacids of sulphur[7–10] we have recently investigated the dialkoxypolysulphanes $(RO)_2S_n$ which formally are derivatives of the corresponding oxyacids (or dihydroxides) of sulphur.[5] We succeeded in determining the vapour-phase and solid-state structures[1,11] of $(CH_3O)_2S$ and $(CH_3O)_2S_2$, and in this context the structure of $H_2S_2O_2$ in the vapour phase was of interest. The compound $H_2S_2O_2$ may be an intermediate in the technically important Claus process (conversion of H_2S into elemental sulphur by oxidation with SO_2).

Since at present there seems to be little hope that besides mass spectra any other molecular spectra of gaseous $H_2S_2O_2$ will be measured in the near future, we have performed an extensive *ab-initio* molecular orbital study of this compound to determine its vapour-phase structure as well as the relative stabilities of the likely isomers of $H_2S_2O_2$.

Calculations

The GAUSSIAN 86[12] and GAUSSIAN 88[13] program packages were employed for *ab-initio* calculations on a Convex 220 supercomputer. Molecular structures were fully optimized in the 6-31G* basis set using analytically evaluated energy gradients. The optimization was performed from different starting geometries towards rotations about SS and SO bonds. The geometries and energies presented are for the most stable conformers found. For the optimized 6-31G* structures single-step MP4/6-31G* calculations with the frozen core were performed.

For the four most stable structures of $H_2S_2O_2$ selected at the 6-31G* level, the calculations have been extended using the larger 6-311G** basis set; the geometries were reoptimized at this basis set for the most stable structures from previous 6-31G* calculations, but no rotations about SS and SO bonds were considered. Finally, single-step MP2/6-311G** calculations were done for structures optimized at the 6-311G** basis. The zero-point energies were also included as calculated from 6-311G** frequencies scaled by 0.89 according to the suggestion by Pople *et al.*[14]

Results and Discussion

There are at least ten theoretically possible structural isomers of $H_2S_2O_2$, the seven most likely being shown in Fig. 1. From the structure of H_2SO_4 it follows that the hydrogen atoms in oxyacids of sulphur may be present as OH groups. However, the hydrogensulphite ion, HSO_3^-, exists as two isomers which are in equilibrium in aqueous solution and which contain the H linked to either sulphur or oxygen.[15] Furthermore, the hydrogenthiosulphate ion, $HS_2O_3^-$, has been shown by Raman spectroscopy[7] to be of structure H–S–SO_3^- in solid $NH_4[HS_2O_3]$. Therefore, all isomeric forms of $H_2S_2O_2$ containing an SS bond and the H atoms linked to either sulphur or oxy-

gen have been calculated. Less likely isomers such as HSOOSH, HSOSOH and HSOS(O)H have not been taken into account. The total energies of the seven structures shown in Fig. 1 are given in Table 1, while Table 2 shows the energies relative to the energy of structure **1** which has been set equal to zero. It is very satisfying to notice that with the 6-31G* basis set structure **1** is always the most stable one independent of the level of calculation [Hartree-Fock or Moeller–Plesset (MP)]. This agrees with the finding that $(CH_3O)_2S_2$ is a chain-like molecule of type R–O–S–S–O–R in the solid, liquid and gaseous state.[1,11] In analogy to the rational nomenclature of H_2S_2 (disulphane), S_2Cl_2 (dichlorodisulphane) and $(RO)_2S_2$ (dialkoxydisulphane) the molecule with structure **1** should be termed dihydroxydisulphane.

However, when the larger basis set 6-311G** was used in connection with second-order Moeller-Plesset perturbation theory (MP2) the energy difference between structures **1** and **2** became very small (5.65 kJ mol^{-1}), and inclusion of zero-point energies resulted even in a stabilization of structure **2** over **1** by 1.26 kJ mol^{-1} (Table 2). Therefore, it is most likely that $H_2S_2O_2$ in the vapour phase exists as two or more isomers in equilibrium with each other. In addition, for the chain structure HOSSOH two rotamers of almost equal energy have been found which basically differ only by the sign of one torsional angle about an SO bond (Fig. 2). Structure **1** is of C_1 symmetry and is more stable than **1a** which is of C_2 symmetry. The energy difference between **1** and **1a** amounts to 3.56 kJ mol^{-1} at the HF/6-31G* level, 2.97 kJ mol^{-1} at the MP4/6-31G* level, 4.77 kJ mol^{-1} at HF/6-311G** and 4.44 kJ mol^{-1} at MP2/6-311G**. Inclusion of the zero-point energy reduced the difference to 4.23 kJ mol^{-1}.

Structure **2** represents the true thiosulphurous acid since it is formally derived from sulphurous acid, $(HO)_2SO$,[16] by substitution of one hydroxyl oxygen atom by sulphur. Structure **3** is a second form of thiosulphurous acid derived from $(HO)_2SO$ by substitution of the terminal oxygen atom by sulphur. This

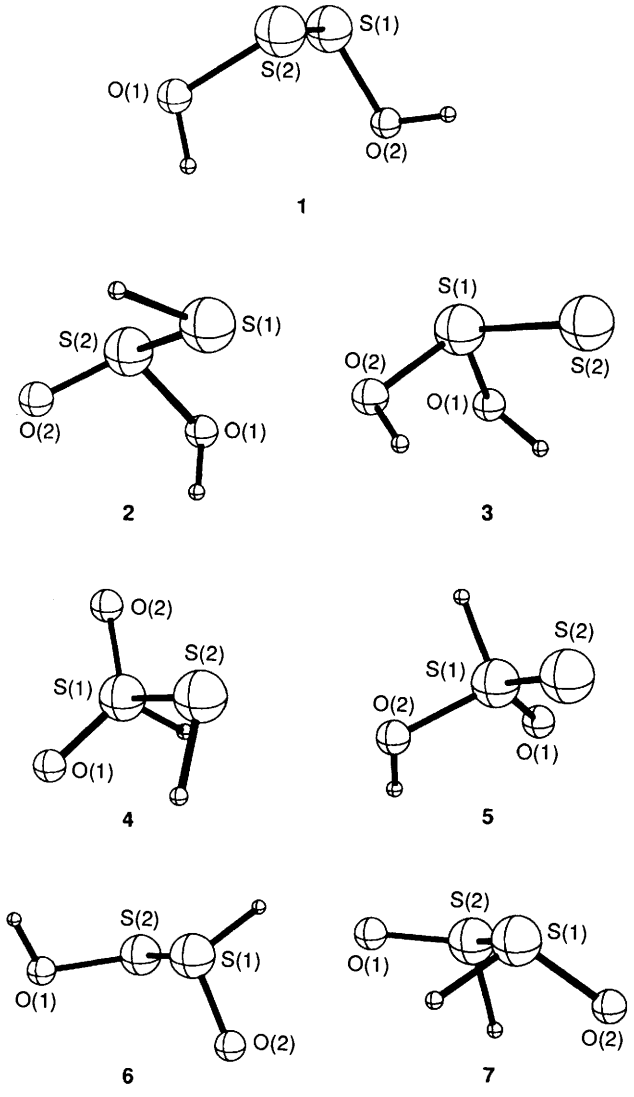


Fig. 1 The seven principal isomers of $H_2S_2O_2$ containing a sulphur–sulphur bond and numbering of atoms

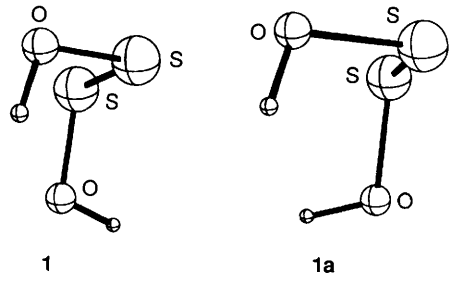


Fig. 2 The two rotamers of chain-like $H_2S_2O_2$: **1** is of C_1 and **1a** of C_2 symmetry

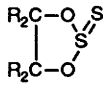
Table 1 Total energies (au = 4.36 × 10^{-18} J) of the seven $H_2S_2O_2$ isomers shown in Fig. 1

Isomer	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	HF/6-311G**	MP2/6-311G**
1	−945.841 162	−946.447 762	−946.469 285	−946.497 448	−945.934 902	−946.596 426
2	−945.826 487	−946.443 09	−946.456 581	−946.492 352	−945.919 655	−946.594 274
3	−945.833 934	−946.443 685	−946.460 833	−946.491 302	−945.926 817	−946.591 797
4	−945.796 494	−946.414 146	−946.421 828	−946.459 997		
5	−945.791 945	−946.407 883	−946.417 35	−946.452 604		
6	−945.782 478	−946.397 212	−946.412 727	−946.448 065		
7	−945.736 506	−946.358 052	−946.367 821	−946.409 409		

Table 2 Energies (kJ mol^{-1}) of the seven $H_2S_2O_2$ isomers of Fig. 1 in relation to the energy of isomer **1**. The zero-point energies (z.p.e.) have been calculated from 6-311G** frequencies scaled by 0.89

Structure	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	HF/6-311G**	MP2/6-311G**	MP2/6-311G** + z.p.e.
1	0	0	0	0	0	0	0
2	38.6	12.3	33.4	13.4	40.1	5.65	−1.26
3	19.0	10.7	22.2	16.2	21.2	12.1	13.2
4	117.4	88.3	124.7	98.4			
5	129.3	104.8	136.5	117.8			
6	154.2	132.8	148.6	129.8			
7	275.0	235.7	266.6	231.3			

molecule is of C_s symmetry and by 12–20 kJ mol^{-1} less stable than the chain-like HOSSOH **1**. The analogous molecule $(HS)_2S{=}S$ has been shown by *ab-initio* molecular orbital (MO) calculations to have a similar structure of C_s symmetry and to be less stable than tetrasulphane, HSSSSH, by 138 kJ mol^{-1}.[17] Compound **3** is also a relative of $F_2S{=}S$, which is more stable than difluorodisulphane, FSSF,[18] and was one of the first compounds containing a double bond between heavier non-metal atoms that could be prepared as a pure substance. The only well established organic derivatives of molecule **3** are two cyclic thiosulphites (R = CH_3 or C_6H_{11})[19] which have also been prepared as pure materials. All non-cyclic species $(RO)_2S_2$[5,20] seem to possess the sulphane structure **1**.



Structures **4** and **5** can be considered as further isomers of thiosulphurous acid derived from the above-mentioned isomeric form of sulphurous acid, $(HO)HSO_2$. Depending on whether a hydroxyl or terminal oxygen atom is replaced by sulphur, structure **4** or **5** will result. Both isomers of $H_2S_2O_2$ are highly unstable and have a negligible chance to exist under equilibrium conditions. The same holds for the last two isomers of $H_2S_2O_2$ (structures **6** and **7**); the disulphoxide **7** is the least-stable isomer regardless of the mathematical approach. This explains the well known instability of organic 1,2-disulphoxides, RS(O)S(O)R.[21]

The bond distances, bond angles, torsion angles and dipole moments of the seven $H_2S_2O_2$ isomers are given in Tables 3–5. Table 3 demonstrates that the OH (94–96 pm) and SH (132–134 pm) bond lengths vary very little. The most dramatic bond distance changes are observed for the SS bond which ranges from 190 to 215 pm. The longest SS bond is observed for the disulphoxide **7** for which unfortunately no experimental data on organic derivatives are available for comparison. As expected, the two shortest SS bonds are found for the isomers **3** and **5** which formally contain SS double bonds.

Molecule **3** with d_{SS} = 196.7 pm may be compared to the organic thiosulphite mentioned above for which d_{SS} = 190.1 pm has been found by X-ray structural analysis.[19] No experimental data are available for comparison with structure **5**. However, it seems reasonable that the SS bond is even shorter than in isomer **3** since the neighbouring SO double bond increases the positive charge on the central S atom and thus stabilizes the SS bond. In a similar fashion it can be explained why the SS bond in the disulphane structure **1** is by 4 pm shorter than the accepted SS single bond distance of 205 pm.[22] The two electronegative OH groups withdraw electrons from the central SS bond which stabilizes this bond by reduced electron repulsion and because of the antibonding nature of the highest occupied molecular orbital (HOMO) in disulphanes.[23] The same effect has been observed for FSSF (d_{SS} = 188.8 pm),[17,24] ClSSCl (d_{SS} = 193.1 pm)[25] and, to a lesser extent, BrSSBr (d_{SS} = 198 pm).[26] The experimental SS bond length of $CH_3OSSOCH_3$ is 196.9 pm,[11] slightly shorter than the 201.3 pm calculated for HOSSOH.

The calculated SO bond distances of the seven $H_2S_2O_2$ isomers are found in the ranges 159–165 or 142.4–147.5 pm depending on whether a formal single or double bond is involved (Table 3). The value d_{SO} = 164.7 pm for structure **1** compares favourably with the average SO bond distance of 165.7 pm determined for solid $CH_3OSSOCH_3$.[11]

The bond angles listed in Table 4 have the expected values and do not deserve further comment. However, the torsional

Table 3 Bond distances (pm) of eight isomeric structures of $H_2S_2O_2$ (6-311G** level for **1**–**3** and 6-31G* level for **4**–**7**; for numbering of atoms see Fig. 1)

Structure	S–S	S–O(1)	S–O(2)	O(1)–H	O(2)–H	S(1)–H	S(2)–H
1	201.3	164.5	164.9	94.3	94.1		
1a	201.3	164.7	164.7	94.3	94.3		
2	213.7	159.8	144.0	95.0		133.0	
3	196.7	159.3	159.3	95.0	95.0		
4	205.8	142.4	142.4			132.5	132.5
5	190.5	143.2	159.1		95.7	132.2	
6	208.1	164.6	146.4	95.0		134.3	
7	214.9	147.5	147.5			134.1	134.1

Table 5 Dipole moments ($\approx$ 3.33 × 10^{-30} C m) of the eight $H_2S_2O_2$ isomers of Figs. 1 and 2 calculated with the HF/6-31G* basis set

Structure	Dipole moment	Structure	Dipole moment
1	2.43	**4**	3.81
1a	2.39	**5**	3.28
2	1.2	**6**	4.91
3	2.24	**7**	0.23

Table 6 Wavenumbers (cm^{-1}) of the 12 fundamental vibrations of the four most stable isomers of $H_2S_2O_2$ calculated at the 6-311G** basis set and scaled by a factor of 0.89 (ν = stretching, δ = bending, τ = torsional mode)

	HO–SS–OH		HO–S(O)–SH	S=S(OH)$_2$
	1	**1a**	**2**	**3**
ν(OH)	3688	3693	3609	3597
ν(OH)	3686	3690	—	3593
ν(SH)	—	—	2562	—
δ(SOH)	1147	1145	1159	1143
δ(SOH)	1138	1127	—	1096
ν(S=O)	—	—	1080	—
δ(SSH)	—	—	800	—
ν(S–O)	758	755	788	811
ν(S–O)	737	734	—	793
ν(SS)	495	502	513	521
δ(SO_2)	—	—	459	457
δ(SSO)	412	413	375	407
δ(SSO)	395	362	294	367
τ(HO–S)	300	306	—	295
τ(HO–S)	249	249	247	231
τ(SS)	131	123	93	—

Table 4 Bond and torsion angles (°) of eight isomers of $H_2S_2O_2$ (6-311G** level for **1**–**3** and 6-31G* level for **4**–**7**; for numbering of atoms see Fig. 1)

Structure	HOS	HSO(1)	HSO(2)	SSO(1)	SSO(2)	OSO	HSS(1)	HSS(2)	HSSO(1)	HSSO(2)	OSSO	HOSS	HOSO	HSSH	HSOH
1	109.5			105.1	105.0						85.7	85.5/85.7			
1a	109.3			105.5	105.5						87.2	95.3			
2	111.9			96.1	105.7	108.7		92.2	−146.7	−35.3		70.0	−38.9		
3	111.9			105.5	105.5	101.4						−21.5	88.4		
4		107.4		107.7	107.7	123.1	94.7	101.7	27.9	162.5				84.8	
5	108.7	109.3	96.9	121.5	110.6	107.1		108.8				124.2	10.2		122.8
6	109.5		107.7	98.9	113.2			88.8	155.1		96.1	91.1			
7			109.1	105.2	105.2			89.6	38.4	38.4	148.1			71.3	

Table 7 Mulliken atomic charges in the $H_2S_2O_2$ isomers of Figs. 1 and 2 as calculated with the basis sets 6-311G** (structures **1–3**) and 6-31G* (structures **4–7**), respectively

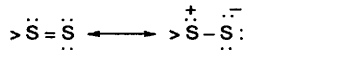
	Isomer							
	1	**1a**	**2**	**3**	**4**	**5**	**6**	**7**
S(1)	+0.25	+0.27	−0.16	+0.89	+1.16	+1.09	+0.68	+0.65
S(2)	+0.27	+0.27	+0.97	−0.49	−0.12	−0.32	+0.28	+0.65
O(1)	−0.55	−0.56	−0.56	−0.52	−0.63	−0.63	−0.77	−0.73
O(2)	−0.56	−0.56	−0.66	−0.52	−0.62	−0.75	−0.70	−0.73
H(1)	+0.31	+0.30	+0.32	+0.32	+0.07	+0.10	+0.48	+0.08
H(2)	+0.30	+0.30	+0.09	+0.32	+0.14	+0.51	+0.04	+0.08

angles are of some interest since it has been known for a long time that the stability of SS bonds in sulphanes depends on the XSSX torsional angle.[22,27–29] The same applies, of course, to SO bonds in XSOX species.[30] Torsional angles of near 90° are most favourable. It is therefore of no surprise that the sulphane structure **1** (C_1 symmetry) exhibits torsional angles HOSS of 85.6° and OSSO of 85.7° (Table 4). In gaseous $CH_3OSSOCH_3$ which is also of C_1 symmetry the COSS and OSSO torsional angles amount to 74 and 91°, respectively.[1] The other molecules contain one or two S atoms of co-ordination number higher than two. In such cases the most favourable conformation with regard to any torsion about SO or SS bonds is more complicated to derive. Consequently, torsional angles of as low as 10° (structure **5**) and as high as 163° (structure **4**) have been calculated.

The $H_2S_2O_2$ isomers **2** and **7** have previously been investigated by *ab-initio* MO calculations at the HF/3-21G* level.[31] The geometrical parameters obtained agree fairly well with ours as far as bond distances and angles are concerned. There are, however, major deviations in the torsional angles. The previous calculations[31] also showed that the energy of three of the $H_2S_2O_2$ isomers increases in the order HOS(O)SH **2** < HS(O)OSH **8** < HS(O)S(O)H **7**. In the vapour phase at 300 K $H_2S_2O_2$ will probably be an equilibrium mixture of isomers **1–3** with **2** being dominant and **1** present as two rotamers. To generate **3** from **1** one OH group has to move from one sulphur atom to the other one which most probably will proceed *via* a triangular transition state. This isomer may then yield **2** by shift of a proton from oxygen to the terminal sulphur atom. The symmetry C_s of isomer **3** explains why only five-membered cyclic thiosulphites of this type have so far been isolated: the *cis* position of the two hydrogen atoms favours a ring formation when H is substituted by carbon.

To support upcoming experimental work on $H_2S_2O_2$ (*e.g.* matrix isolation and molecular spectroscopy) we have calculated the wavenumbers of the 12 fundamental vibrations of structures **1**, **1a**, **2** and **3** using the 6-311G** basis set. Such calculated wavenumbers tend to be too large and scaling by a factor of *ca.* 0.89 is common for sulphur compounds.[32] This factor has therefore also been applied to our data (see Table 6). The assignments given in Table 6 are of course tentative since strong vibrational coupling is to be expected in most of these low-symmetry molecules. The calculated and scaled wavenumbers agree quite well with those of suitable reference compounds like the $HS_2O_3^-$ anion[7] and dimethoxysulphane, CH_3O–S–OCH_3.[1]

Finally, the Mulliken atomic charges given in Table 7 will be discussed. As expected the oxygen atoms are always negatively charged with values in the narrow range −0.52 to −0.77 units. The sulphur atoms are positively charged when linked to at least one oxygen atom, but terminal S atoms as in **3** and **5** as well as the central atom in HSS units as in **2** and **4** are always negatively charged. The bond to the terminal sulphur atoms may therefore be symbolized as shown below.



Hydrogen atoms linked to sulphur as in isomers **2–7** bear a positive charge of between +0.04 and +0.14 units while hydrogen bound to oxygen is charged by +0.30 to +0.48 units. Atom charge values calculated with the 6-311G** basis set were somewhat smaller for identical molecules than those obtained on the 6-31G* level.

Acknowledgements

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