Structures of the trisulfur oxides S_3O and $S_3O^{\bullet+}$: branched rings, not open chains

Ming Wah Wong*[a] **and Ralf Steudel**[b]

Received (in Cambridge, UK) 23rd May 2005, Accepted 27th May 2005
First published as an Advance Article on the web 15th June 2005
DOI: 10.1039/b507235b

Higher-level *ab initio* calculations showed that the global energy minimum for both S_3O and $S_3O^{\bullet+}$ is a branched, three-membered ring, not an open chain form.

Sulfur is the element with the largest number of binary oxides. Not less than 14 species of composition S_mO_n (m = 1–10, n = 1–4) have been detected experimentally.[1,2] The most recent addition to this collection is the species S_3O, which was prepared by sulfur atom transfer from gaseous COS to the $S_2O^{\bullet+}$ cation, followed by neutralization of the resulting cation $S_3O^{\bullet+}$; S_3O was detected by mass spectrometry:[3]

$$S_2O^{\bullet+} + COS \rightarrow S_3O^{\bullet+} + CO$$

S_3O is likely to be an important species in combustion processes and in interstellar space. The molecular structure of S_3O was examined by the B3LYP density functional method but only a few isomers were considered.[3] It was claimed that the planar, open-chain, *cis*-conformation SSSO was the global energy minimum, with the *trans*-conformer being 17 kJ mol^{-1} (CCSD(T)//B3LYP) less stable. The $S_3O^{\bullet+}$ cation was also reported to have a *cis*-planar chain structure.[3]

We have explored all possible isomers of S_3O and $S_3O^{\bullet+}$ potential energy surfaces (PES).[4] Our previous study of S_4 showed that the stabilities of certain singlet isomers are grossly overestimated by the MP2 theory.[5] Thus, we have examined the structures and energies of several S_3O isomers using two independent methods: G3X(MP2)[6] and CCSD(T)/cc-pVQZ//CCSD(T)//cc-pVTZ.[7] As is evident in Table 1, the G3X(MP2) relative energies of the various singlet S_3O isomers are in good agreement with the CCSD(T) values. This result suggests that the G3X(MP2) theory is sufficiently reliable for the present study. Unless otherwise noted, the structures and relative energies (Table 1) reported in the text correspond to the G3X(MP2) E_o values.

Five isomers (**1a–1e**) are located on the singlet S_3O surface: three chains and two cyclic forms (Fig. 1). Unexpectedly, the branched ring S_3=O (C_s, **1a**) is found to be the global energy minimum. This structure is characterized by a very short S=O bond of length 1.456 Å. In fact, this S=O distance is the shortest of all the sulfur monoxides S_nO (n = 1–9).[1,2,8] The S–S bond (2.156 Å) adjacent to the S=O bond is slightly longer than the other S–S bond (2.118 Å). This structure is in excellent agreement with the collisionally-activated (CA) mass spectrum of S_3O, which is characterized by large peaks due to S_2, SO, and S.[3] It is remarkable that the most stable isomers of the valence-isoelectronic species S_4 (chain),[9] S_3O (cyclic), S_2O_2 (planar "star")[10] and SO_3 (trigonal-planar)[11] have quite different structures. For the sulfur analogue S_4, the branched ring isomer (S_3=S) is 62 kJ mol^{-1} less stable than the *cis*-planar open form. This can be rationalized in terms of the weaker S=S double bond compared to its S=O counterpart in **1a**.

The planar chain structures **1b** (*cis*) and **1c** (*trans*) are respectively 12 and 28 kJ mol^{-1} higher in energy than **1a**. These chain structures resemble those of the two most stable isomers of

Table 1 Calculated relative energies (kJ mol^{-1}) for S_3O, $S_3O^{\bullet+}$ and related species using single-reference methods (TS = transition state)

		ΔE°			
Species	Symmetry	CCSD(T)[a]	G3X(MP2)[b]	ΔH°_{298}[c]	ΔG°_{298}[c]
Branched ring-S_3O (**1a**)	C_S	0.0	0.0	0.0	0.0
Cis-planar-S_3O (**1b**)	C_S	12.0	12.3	12.8	10.7
Trans-planar-S_3O (**1c**)	C_S	29.2	28.2	29.1	26.2
Planar branched-S_3O (**1d**)	C_{2v}	48.8	44.6	44.0	46.4
Puckered ring-S_3O (**1e**)	C_S	167.3	173.3	173.0	174.0
Triplet *trans*-planar-S_3O, $^3A'$ (**1f**)	C_S	60.0	64.6	66.8	55.7
Triplet *cis*-planar-S_3O, $^3A'$ (**1g**)	C_S	63.5	68.1	70.1	59.5
Triplet branched-S_3O, $^3A''$ (**1h**)	C_S	—	159.5	159.9	155.8
TS: **1a** → **1b** (**1i**)	C_1	107.9	112.5	111.9	112.1
Branched ring-$S_3O^{\bullet+}$, $^2A''$ (**2a**)	C_S	—	0.0	0.0	0.0
Cis-planar-$S_3O^{\bullet+}$, $^2A''$ (**2b**)	C_S	—	57.4	58.1	5.9
TS: **2a** → **2b**, ^2A (**2c**)	C_1	—	106.4	105.6	106.3

[a] CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ + ZPE(CCSD(T)/cc-pVTZ) level. The CCSD(T)/cc-pVQZ energy of **1a** is −1268.38767 Hartree. [b] The calculated G3X(MP2) E_o energies of **1a** and **2a** are −1268.39641 and −1268.07197 Hartree respectively. [c] G3X(MP2) level.

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[a] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: chmwmw@nus.edu.sg; Fax: 65 67791691; Tel: 68744320*
[b] *Institut für Chemie, Technische Universität Berlin, Sekr. C2, D-10623, Berlin, Germany. E-mail: steudel@sulfur-research.de; Fax: 49 30 31426519; Tel: 49 30 31422707*

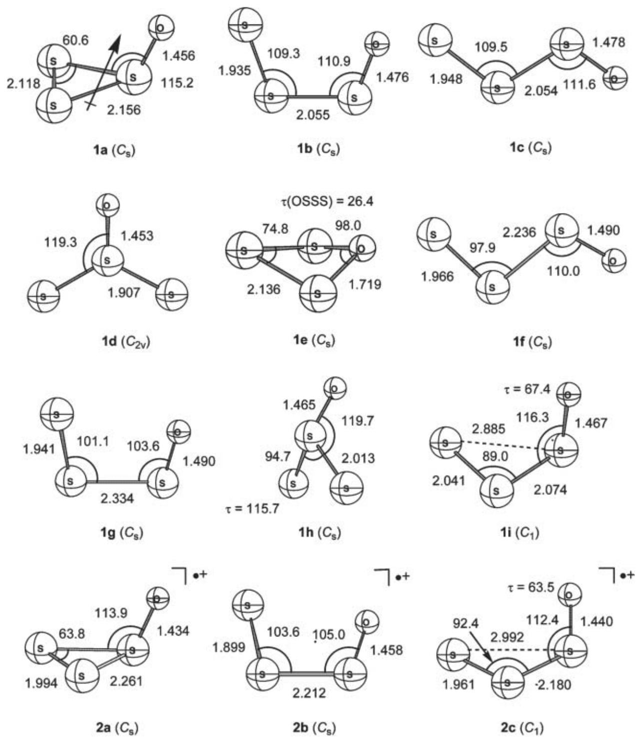

Fig. 1 The optimized [B3LYP/6-31G(2df)] geometries of S_3O, $S_3O^{\bullet+}$ and related species (bond lengths in Å and angles in °). The dipole moment vector of **1a** is also given.

the related molecule S_4.[5] The corresponding triplet chains **1f** and **1g** are much less stable. The planar branched isomer (**1d**, C_{2v}), an analogue of SO_3, is 45 kJ mol^{-1} higher in energy than **1a**. This structure is characterized by relatively short S–O and S–S bonds (1.453 and 1.907 Å, respectively), indicating that the π bond is strongly delocalized. The four-membered heterocyclic ring (**1e**, C_s) is the least stable of the singlet S_3O isomers (Table 1). The branched ring structure does not exist on the triplet PES. Upon geometry optimization, it collapses to a non-planar, branched form (**1h**, C_s) which is 160 kJ mol^{-1} less stable than **1a**.

It is important to note that there is a very low-lying lowest unoccupied molecular orbital (LUMO: a″, −4.2 eV) for both of the singlet chain isomers **1b** and **1c**. As a consequence, an unrestricted Kohn–Sham based method leads to a lower energy structure with a significantly spin-contaminated wave function ($\langle S^2 \rangle = 0.54$ and 0.67 for **1b** and **1c** respectively). Strong multireference character is also calculated for the transition state **1i** ($\langle S^2 \rangle = 1.01$). Hence, we have also examined the relative stabilities of **1a**, the four open-chain isomers (**1b**, **1c**, **1d** and **1e**) and **1i** using the complete active space SCF (CASSCF)[12] approach. This is expected to provide a proper description of the degeneracy problem involved. An active space of four electrons in four orbitals, *i.e.* CASSCF(4,4), was chosen to provide a balanced description for all the species. Full CASSCF geometry optimizations were carried out with the cc-pVTZ basis set. The A′ state is preferred over the A″ state for all open-chain singlet and triplet isomers. Dynamic electron correlation effects were included by second-order multireference perturbation (CASPT2)[13] and multiconfiguration reference configuration interaction (MRCI)[14] single-point energy calculations, in conjunction with the aug-cc-pVTZ basis set, based on the CASSCF-optimized geometries. Our best relative energies correspond to the MRCI + Q level (Table 2). For all four open-chain isomers, the calculated relative energies are in close agreement with those obtained by the single reference methods CCSD(T) and G3X(MP2) (Table 1), with a slightly larger discrepancy for **1c**. However, the relative energy of **1i** is substantially lower, by 40 kJ mol^{-1}, compared to the CCSD(T) value (Table 1). This large error is due to the very strong multireference character of **1i**, and is strongly reflected in the two dominant configurations, which have almost equal weight (0.663, −0.662). In summary, the multireference calculations confirm that the branched ring is the lowest energy structure of S_3O. It is of interest to note that CASPT2 strongly favours the diradicalic chain structures. This is not unexpected as the convergence of the perturbation method is generally poor for systems with strong spin contamination.

Table 2 Calculated relative energies (kJ mol^{-1}) of S_3O isomers using mulitreference methods[a]

Level	1a	1b	1c	1f	1g	1i
CASSCF	0.0	17.9	34.1	49.2	62.3	72.7
CASPT2	0.0	−30.9	−21.1	23.1	29.5	43.3
MRCI	0.0	13.0	27.3	62.2	73.3	81.9
MRCI + Q[b]	0.0	10.9	21.0	58.3	69.1	68.4

[a] CAS(4,4) active space with aug-cc-pVTZ basis set, based on CASSCF(4,4)/cc-pVTZ optimized geometry. [b] MRCI with Davidson correction, including ZPE correction.

As with the neutral S_3O, the branched ring structure, **2a**, is the global energy minimum on the $S_3O^{\bullet+}$ PES. In this case, the *cis*-planar form, **2b**, is significantly less stable (57 kJ mol^{-1}) compared to the neutral analogue (Table 1). Remarkably, the S=O bond in **2a** (1.433 Å) is even shorter than that in **1a**. Accordingly, the positive charge of **2a** is localized on the three sulfur atoms. The geometrical features and charge distribution indicate that the S=O bond is stabilized in the cationic form. The spin densities of **2a** are located exclusively on the two sulfur atoms adjacent to the S=O bond. A strong bond alternation is noticed in the structure of **2b**. In particular, it has a particularly long S–S central bond (2.212 Å). Other $S_3O^{\bullet+}$ isomers are predicted to be higher in energy: *trans*-planar chain (68 kJ mol^{-1}), 4-membered homocycle (118 kJ mol^{-1}) and planar branched isomer (126 kJ mol^{-1}).

Finally, we examined the unimolecular rearrangement of the open-chain isomer, **1b**, to the branched ring form, **1a**. This rearrangement, *via* transition structure **1i**, is inhibited by a moderate barrier of 68 kJ mol^{-1} (MRCI + Q/aug-cc-pVTZ value, Table 2). So, the observation of the chain form of S_3O is not straightforward to explain. For the $S_3O^{\bullet+}$ radical cation, the corresponding interconversion process **2b** → **2a**, *via* transition structure **2c**, has a smaller activation barrier of 49 kJ mol^{-1}. This result suggests that the observation of **2b** is unlikely, particularly in a high-energy process like CAD mass spectrometry. Hence, we conclude that the observed CA and neutralization–reionization mass spectra by Cacace *et al.*[3] correspond to the branched ring structure. It is important to note that **2a** and **2b** are expected to have similar fragmentation patterns. In other words, it is not possible to deduce the structure of $S_3O^{\bullet+}$ with certainty from the CA mass spectrum alone.

S_3O and $S_3O^{\bullet+}$ are the first experimentally-detected molecules containing a three-membered sulfur homocycle. The parent species

Table 3 Calculated properties for ground-state S_3O (**1a**)

Property	Value
Dipole moment[a]/Debye	1.421
Rotational constants/GHz[a]	6.0324 (A), 3.3671 (B) 2.4090 (C)
IR/Raman spectra[a,b]/cm^{-1}	1214 a′ (193, 14), 554 a′ (23, 31), 443 a′ (21, 8), 369 a″ (23, 7), 306 a′ (3, 10), 230 a″(0, 9)
UV-visible spectrum[c]	191 (0.033), 210 (0.032), 223 (0.004), 253 (0.002), 453 (0.002) nm
Enthalpy of formation[d]/kJ mol^{-1}	-4.8 ($\Delta H_f{}^o{}_0$), -13.7 ($\Delta H_f{}^o{}_{298}$)
Ionization energy[d]/eV	8.83 (adiabatic), 9.20 (vertical)
Proton affinity[d]/kJ mol^{-1}	752.5
Dissociation energies[d]/kJ mol^{-1}	$S_3O \rightarrow S_2\ (^3\Sigma_g^-) + SO\ (^3\Sigma^-)$: $\Delta H^\circ_{298} = 143.3$ $S_3O \rightarrow O\ (^3P) + S_3\ (^3A_2)$: $\Delta H^\circ_{298} = 475.7$

[a] B3LYP/6-31G(2df) value. [b] IR (km mol^{-1}) and Raman (A^4 amu^{-1}) intensities are given in parentheses, frequencies scaled by 0.99. [c] CIS/aug-cc-pVTZ level, oscillator strength is given in parenthesis. [d] G3X(MP2) value.

S_3 is of C_{2v} symmetry,[15] and the cyclic D_{3h} isomer is 23–31 kJ mol^{-1} higher in energy (depending on the level of theory).[16] *Ab initio* calculations indicate that coordination of S_3 to certain metal complexes stabilizes the homocycle,[17] but such species have not yet been prepared. However, this observation supports our findings that withdrawal of electron density from the S_3 unit (*e.g.*, by an electronegative oxygen atom) favours the ring isomer, explaining the homocyclic structure of S_3O. To assist future experimental characterization of the ground-state of trisulfur oxide, the predicted dipole moment, rotational constants, IR, Raman and UV-visible spectra, enthalpy of formation, ionization energy and proton affinity of **1a** are summarized in Table 3. As seen in Fig. 1, the dipole moment vector of **1a** is essentially parallel to the S=O bond.

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