Polysulfite, a hypothetical allotrope of sulfur dioxide? A molecular and periodic quantum investigation of covalent oligomeric and one-dimensional XO_2-based compounds ($X = S, Se$)†

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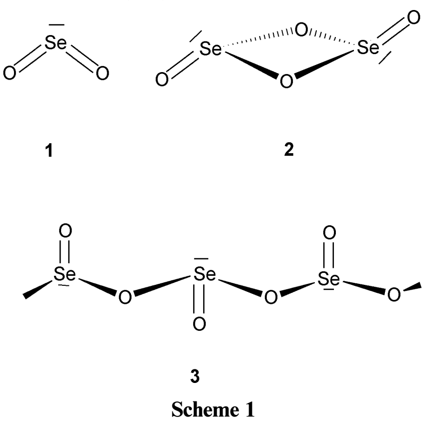
Covalent oligomeric and polymeric phases of SeO_2 and SO_2 have been investigated at high levels of density functional calculations on molecular and periodic models. Polysulfite $[\text{–S(=O)O–}]_x$, a one-dimensional allotropic form of SO_2, is calculated to be energetically less stable than free molecular sulfur dioxide by less than 11 kcal mol^{-1}. This small energy difference δE renders polysulfite a candidate for experimental investigation. Its valence isoelectronic analog, the crystalline downeyite phase with linear $[\text{–Se(=O)O–}]_x$ chains, is more stable than the molecular species SeO_2 by 20 kcal mol^{-1}. Substituting sulfur for selenium in the one-dimensional $[\text{–Se(=O)O–}]_x$ structure containing sp^3 chalcogen atoms slightly favors the 18-valence electron triatomic species. This feature may be related to the s–p energy difference, which diminishes on going down group 16. Finite molecular aggregates such as the four-membered rings X_2O_4 ($X = S$, Se; C_{2v} and C_{2h} symmetry) and S_4O_8 (D_{4h}) are also investigated at the B3LYP level using extended basis sets.

Design of new materials from well-known compounds may be guided by chemical intuition but also by predictive quantum calculations.[1] In this field, various authors have explored theoretically the possibility of the existence of hypothetical oligomers or extended networks made of small stable molecules such as CS,[1a] CNR,[1b] or N_2,[1c] for instance. Pursuing our continuing interest in the search for new allotropic phases of unsaturated species,[2] we decided to investigate the possibility for sulfur dioxide (SO_2) to exist in a polymeric state or as finite aggregates.

How could we figure out other allotropic SO_2 structures? A reasonable way to start such an investigation is to look at characterized covalent finite aggregates and one-dimensional compounds made of 18-valence electron triatomic building blocks, such as selenium dioxide. As shown in Scheme 1, SeO_2 has a bent structure, **1**, with the selenium coordination number (CN) equal to 2 while its dimer **2** presents a four-membered ring with pyramidal selenium atoms (CN = 3).[3] A cyclic trimer and tetramer of thiazyl fluoride, NSF, have also been characterized in which the sulfur atoms are coordinated to two nitrogen and one fluorine atoms (CN = 3 as in **2**).[4] Besides these molecular species, another SeO_2 allotrope, **3**, exists and consists of polymeric chains made of pyramidal –Se(=O)–O– building blocks linked through Se–O single bonds (Scheme 1). Isostructural one-dimensional chains are also encountered in several solid state compounds such as $NaAsO_2$ or AsOF, which possess formally 18-valence electron triatomic units.[3,5]



1

2

3

Scheme 1

Our aim in this work is to calculate the energy of hypothetical SO_2-based compounds in the molecular, **2**, and polymeric, **3**, forms to see whether one of these new sulfur dioxide allotropes may be viable with respect to free SO_2.[6] The valence isoelectronic SeO_2 allotropes **1**–**3** are also investigated for comparison.

Computational details

Molecular approach

DFT computations were carried out with the GAUSSIAN 98 program package.[7] Electron correlation effects were included employing the hybrid Hartree–Fock (HF)/DFT method using the combination of the three-parameter Becke exchange functional with the Lee–Yang–Parr nonlocal correlation functional known as B3LYP.[8] At this level of theory, the triple-ζ plus polarization basis set was used (B3LYP/6-311G* calculations).[9] Harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) were computed for all compounds (local minima) except for the longer $S_7O_{13}F_2$ and $S_8O_{15}F_2$ oligomers, due to computational limitations. The total energies considered in this study were obtained by running single-point calculations on the optimized geometries with the high angular momentum 6-311+G(3df) basis set

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† Electronic supplementary information (ESI) available: B3LYP/6-311G* total energies (hartrees), zero-point vibrational energies (kcal mol^{-1}), geometrical parameters and B3LYP/6-311+G(3df)//B3LYP/6-311G* single point total energies (hartrees) for all molcular compounds discussed in the text and vibrational frequencies for the $(XO_2)_n$ compounds **1**, **2**, **4** and **5**. See http://www.rsc.org/suppdata/nj/b0/b007960j/

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[B3LYP/6-311+G(3df)//B3LYP/6-311G* calculations].[9a] To validate the theoretical approach used in this work, the atomization energies for the free SO and SO_2 molecules have been calculated as the evaluation of this quantity is very sensitive to the level of theory [see electronic supplementary information]. The maximum deviation of 2% between experimental and calculated atomization energies gives some indication as to the accuracy of the level of theory used in this study.

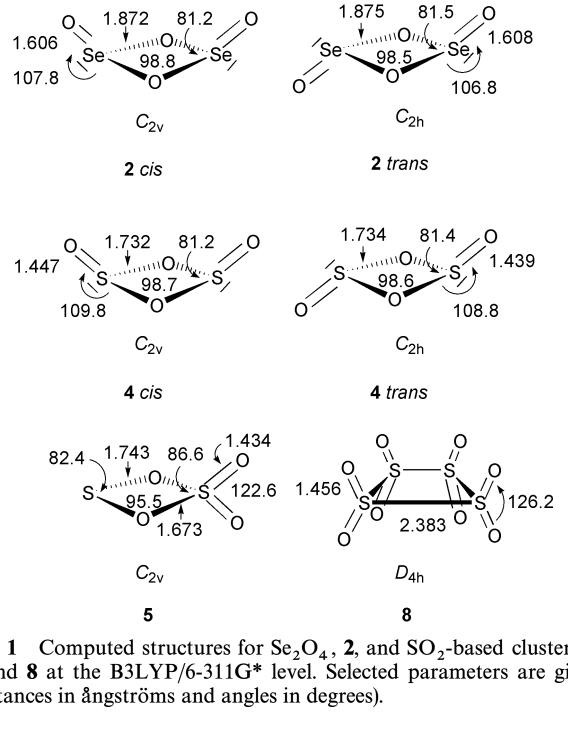
Periodic approach

All periodic calculations were based on density functional methods and were performed using the Vienna *ab initio* simulations program (VASP)[10]. The local functional given by Ceperley and Alder was used in the parametrization of Perdew and Zunger[11a] and the nonlocal exchange-correlation effects are considered in the form of the functional of Perdew *et al.*[11b] These functionals are denoted PW91PL in the text. The DFT method applies a plane wave basis and optimized ultrasoft pseudopotentials. For a detailed description of the theory, we refer to the papers by Kresse *et al.*[10a–c] Typical cut-off energies for the plane wave expansion of the eigenstates can be as low as 540 eV. A spin-restricted approach was used for all compounds. Brillouin zone integration was performed on a grid of 4 × 4 × 4 Monkorst–Pack special *k* points (6 *k* points) for a tetragonal lattice.[12] For the SO_2, SeO_2 and $FS_{n+1}O_{2n+1}F$ ($n = 0$–4) molecular systems, a $10 \times 10 \times 10$ Å^3 cell was used and calculations were performed at the Γ point (1 *k* point).

Results and discussion

Finite covalent aggregates $(XO_2)_n$ (X = S, Se)

Let us start our investigations with the selenium dioxide dimer **2**, which exists in the gas phase. This four-membered ring dimer presents two genuine minima, the *cis* and *trans* forms seen in Fig. 1. The optimized structures show normal Se–O and Se=O distances (1.87 and 1.61 Å, respectively). At our level of theory, the *cis* and *trans* isomers differ in energy by only 0.6 kcal mol^{-1} and *cis*-Se_2O_4 is more stable than two free SeO_2 molecules by 7.7 kcal mol^{-1}. The substitution of S for Se in **2** leads to the hypothetical isoelectronic species **4** shown in Fig. 1. As found for the selenium-based dimer **2**, the S_2O_4 molecule **4** presents two dibridged O=S(μ-O)$_2$S=O local minima that are almost isoenergetic: the C_{2v} *cis* isomer lies 3.0 kcal mol^{-1} below the C_{2h} *trans* one.[13] Their calculated S–O distances (1.73 and 1.44 Å, respectively) are assigned to the expected single and double sulfur–oxygen bonds. The calculations find for the IR active modes a b_u vibration (S=O stretch) with high intensity (354 KM mol^{-1}) at 1259 cm^{-1} for C_{2h} **4** and two S=O stretches at 1261 (b_2, 216 KM mol^{-1}) and 1285 cm^{-1} (a_1, 126 KM mol^{-1}) for the *cis* form. These S=O vibrational frequencies may be a fingerprint to identify the *cis* or *trans* isomers on the basis of an IR study.[14] The *cis*-**4** species is predicted to be less stable than free SO_2 molecules by 12.5 kcal per SO_2. Substituting the selenium atoms in **2** with sulfur atoms (species **4**) destabilizes the dimeric aggregate with respect to the monomer. What is the main reason? First of all, recall that during the formal dimerization process $2\,XO_2 \rightarrow X_2O_4$, a $\pi_{(X-O)}$ bond is broken and a $\sigma_{(X-O)}$ one is created. Thus, in valence bond formalism, an $sp^2 \rightarrow sp^3$ rehybridization occurs for the central atom X. As X goes down group 16 (VIa), the $H_{ss} - H_{pp}$ energy difference decreases, rendering the sp^3 hybridization more accessible [$\Delta E_{s-p}(S) = 9.0$ and $\Delta E_{s-p}(Se) = 6.1$ eV].[15] There are of course other factors (*e.g.* electronegativity, diffuseness of the *ns* and *np* orbitals) that can change with atomic substitution. However, the s–p energy splitting plays a major role in the changes of the X–O bond energy.[16,17] This general trend down a column may be illustrated by looking at well-known 16-valence electron triatomic units: under standard conditions, CO_2 is a linear molecule [C_{sp}, $\Delta E_{s-p}(C) = 10.0$ eV] while SiO_2 is a three-dimensional solid state compound [Si_{sp^3}, $\Delta E_{s-p}(Si) = 8.1$ eV].



2 *cis* **2** *trans*

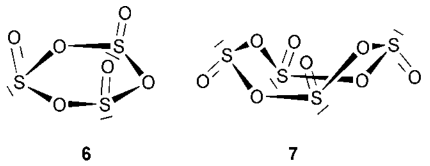
4 *cis* **4** *trans*

5 **8**

Fig. 1 Computed structures for Se_2O_4, **2**, and SO_2-based clusters **4**, **5** and **8** at the B3LYP/6-311G* level. Selected parameters are given (distances in ångströms and angles in degrees).

Also investigated in this research was the S(μ-O)$_2$S(=O)$_2$ structure **5** seen in Fig. 1. **5** lies 28.9 kcal mol^{-1} above *cis*-**4** and 27.0 kcal per SO_2 higher in energy than free sulfur dioxide. The vibrational frequencies are all positive and the b_1 S=O asymmetric vibration is predicted to occur at 1413 cm^{-1} (IR intensity 221 KM mol^{-1}). Besides these localized dimers, the six- and eight-membered rings **6** and **7** in the form of cyclic $(NSF)_x$ ($x = 3, 4$)[4a] have been explored (Scheme 2). At the B3LYP/6-311G* level of theory, S_3O_6, **6**,[13] and S_4O_8, **7**, are both saddle points on the potential energy surfaces and dissociate into free SO_2 molecules.

Let us go further in our hypothetical $(SO_2)_x$ aggregate search by looking at covalent sulfur dioxide clusters made by the linkage of SO_2 building blocks through sulfur–sulfur bonds. Such aggregates with the sulfur coordination number equal to four will contain formally two S=O and one S–S bond per SO_2. The related bond energy sum should be comparable to those in **4** or **3** (sulfur CN = 3; 1 S=O + 2 S–O bonds per SO_2 fragment). For this purpose, the four-membered ring S_4O_8, **8**, was chosen as a prototype[18] and its structure is depicted in Fig. 1.[13] In the D_{4h} symmetry group, **8** is a transition state with an imaginary frequency at 409i cm^{-1} corresponding to S–S stretching vibrations. When the symmetry constraints are released, compound **8** leads to four free SO_2 molecules with a stabilization energy of 23.3 kcal mol^{-1} per SO_2. The long and weak S–S bond (2.383 Å) is comparable to that measured in dithionite $S_2O_4^{2-}$ (2.39 Å), an unstable reducing agent that disproportionates in water.[4b] The unstable four-membered ring **8** is calculated to be 10.8 kcal mol^{-1} per SO_2 higher in energy than *cis*-**4**. Therefore, we will focus this present study on SO_2-extended networks containing S–O single bonds, that is with sulfur CN = 3 as in **3**.



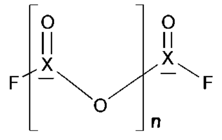
6 **7**

Scheme 2

To close this section, we should recall that, from a bonding topology point of view, a ring-opening polymerization for S_2O_4, **4**, may lead to the hypothetical polysulfite (form **3**) under discussion in the following paragraph.

One-dimensional networks $[-X(=O)O-]_x$ (X = S, Se)

The polymeric SO_2 form isostructural to **3** has been theoretically investigated by using two different modeling approaches, one based on molecular systems, the other coming from periodic calculations on crystalline SeO_2. To illustrate our molecular approach, consider the structures of the $F(S_{n+1}O_{2n+1})F$ oligomers **9** (n = 0–7, Scheme 3 and Fig. 2),[13] which are composed of successive pyramidal –S(=O)O– units saturated by fluorine atoms; the first member of this family is the well-known thionyl difluoride compound SOF_2 (n = 0).



9 (X = S), **10** (X = Se)

Scheme 3

By increasing the number n of SO_2 units in **9**, the one-dimensional network encountered in **3** is described. Moreover, assuming that, for a given n value, E_n is the total energy of the oligomer, the difference function $\Delta E_n = E_{n+1} - E_n$ is expected to tend to the poly-SO_2 energy per SO_2 unit when n becomes large enough. The corresponding $\Delta E_n - E(SO_2)$ energy values denoted δE throughout the text are shown in Fig. 3. For comparison, the evaluation of δE for the polymeric isoelectronic SeO_2 phase **3** has been undertaken by using the same methodological approach on finite selenium dioxide-based oligomers: $F(Se_{n+1}O_{2n+1})F$, **10** (n = 0–3). The detailed structural parameters (B3LYP/6-311G*) and associated energies [B3LYP/6-311+G(3df)] for **9** and **10** are given in the ESI.

The main computed structural features for the SO_2-based oligomers **9** are illustrated by looking at $FS_6O_{11}F$ [see Fig. 2(b)]. At the B3LYP/6-311G* level, the calculated sulfur–oxygen bond lengths are between 1.661 and 1.763 Å along the σ chain with inner distances of *ca.* 1.71 Å. The other sulfur–oxygen bond lengths are in the range 1.444–1.454 Å, corresponding to standard S=O double bonds. Besides these expected geometrical parameters, the peculiar structural aspect of these oligomers concerns the relatively short S···O intramolecular distances found in **9** (from 3.027 to 3.480 Å): the sulfur atoms complete their coordination when possible

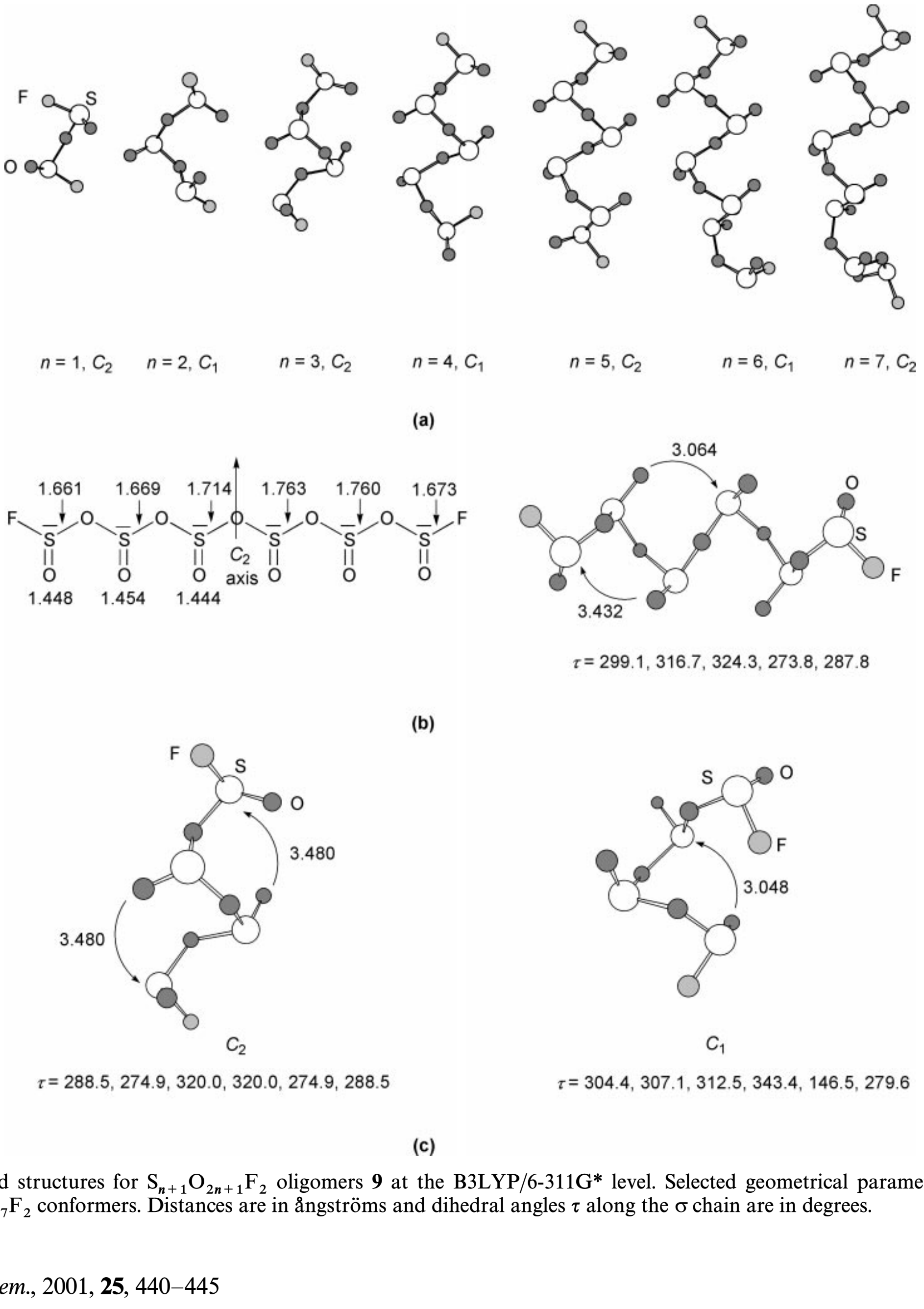


Fig. 2 (a) Computed structures for $S_{n+1}O_{2n+1}F_2$ oligomers **9** at the B3LYP/6-311G* level. Selected geometrical parameters for (b) $S_6O_{11}F_2$ oligomer and (c) $S_4O_7F_2$ conformers. Distances are in ångströms and dihedral angles τ along the σ chain are in degrees.

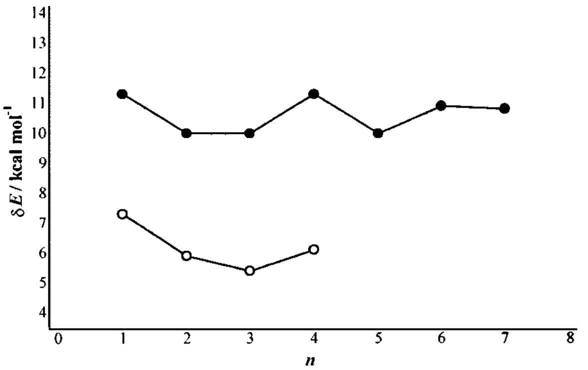


Fig. 3 Plots of $\delta E_n = E[FS_{n+1}O_{2n+1}F] - E[FS_nO_{2n-1}F] - E[SO_2]$ with respect to *n*. Calculations were made at the B3LYP/6-311+G(3df)//B3LYP/6-311G* level (black circles) and VASP PW91PL/pseudopotentials level (white circles).

with longer S···O contacts that are in a few cases less than 3.1 Å, a value slightly shorter than the sum of the S–O van der Waals radii (3.30 Å).[19] To close this structural discussion, note that the helical forms of the acyclic chains (see Fig. 2 and ESI) arise from the starting conformational choice for a given oligomer: in order to avoid energetic alteration in the evaluation of δE due to the conformational changes for the oligomers, the initial S–O–S–O dihedral angles (τ) along the σ chain are set around 320°. Nevertheless, a conformational search was carried out on **9** up to $n = 4$. The associated total energy differences are below 5 kcal mol^{-1}. In Fig. 2(c), the localized FS_4O_7F conformers are shown for illustration, all differing by the relative rotational orientation of their pyramidal SO_3 groups [see the τ values displayed in Fig. 2(c)]. These two conformers differ by only 2.4 kcal mol^{-1}. From these results it is clear that the potential energy surface associated with the conformational fluxionality of oligosulfites **9** is particularly soft and therefore, the conformation of polysulfite in the hypothetical condensed phase may be different from the calculated gas phase helical conformation due to the packing forces; thus, prediction of the conformational structure of poly-$(SO_2)_x$ by using such a molecular modeling approach is not our goal.

Coming back to the energetics, in going from thionyl difluoride SOF_2 to $S_8O_{15}F_2$, the energy per repeat SO_2 unit, δE plotted in Fig. 3, is calculated to be less than that of free SO_2 by an average value of +10.5 kcal mol^{-1}. This incremental δE value has to be compared with that found for the cyclic S_2O_4 molecular compound *cis*-**4** (+12.5 kcal per mol SO_2), showing that the formal ring-opening polymerization does not affect the energetic stability of the extended system. However, on the basis of energetics only, one may conclude that in reality the observation of the one-dimensional polysulfite allotrope is unlikely as the $x\ SO_2 \rightarrow (\text{–}SO_2\text{–})_x$ reaction is slightly endoenergetic. In spite of these observations one should not conclude that aggregates or extended systems made of SO_2 or other stable unsaturated molecules are not feasible. Recently, it has been shown both from high-pressure experiments[20] and computing simulations[21,2b] that carbon dioxide may polymerize to give a high-pressure phase similar to those found in silica (quartz-like structures). Moreover, a value of +19 kcal mol^{-1} has been calculated by using this modeling approach in evaluating the relative stability with respect to free CS_2 for poly-CS_2, the synthesized high-pressure phase of carbon disulfide.[2b]

The isoelectronic analog to polysulfite, poly-SeO_2, **3**, has also been investigated using the same molecular approach. As the main purpose of this paper concerns the allotropic SO_2 phase, the structural and energetic results are given as ESI. From our calculations on the $FSe_{n+1}O_{2n+1}F$ oligomers **10**, the calculated selenium–oxygen distances at the B3LYP/6-311G* level are found to be in the range of the experimental values: *d*(Se–O) = 1.84 and *d*(Se=O) = 1.62 Å. The extrapolated energy δE per SeO_2 unit in poly-SeO_2 is calculated to be −16 kcal mol^{-1} per SeO_2 at the B3LYP/6-311+G(3df) level, illustrating the metastable character of the gas phase monomeric SeO_2 species under normal conditions. This extended network in **3** is 8 kcal mol^{-1} more stable than the dimer **2** (per SeO_2 unit) while both of them contain three-coordinate selenium atoms. This stability difference provides an estimate of the strain energy of Se_2O_4, **2**.

To broaden our investigation we employed another theoretical approach applied to periodic systems: the ground state properties of crystalline poly-SO_2 within the downeyite SeO_2 structure reported in Fig. 4 were calculated by density functional theory methods using a generalized gradient approximation (PW91PL level, see Computational details). A full geometry optimization of both external and internal parameters has been undertaken. Even if this chosen crystalline phase is not the lowest energy structure for polysulfite in the condensed state, such a modeling short-cut might give an upper limit on the relative energetic stability for polymeric *vs.* molecular SO_2. Furthermore, we have shown previously with the molecular approach that the potential energy surface related to the structural conformation of the SO_2-based oligomers is particularly soft: in the solid state, polymorphic structures may exist, differing by a few kcal mol^{-1}.

Table 1 gives a summary of the results for the computed structural parameters and energetics for polysulfite SO_2 and downeyite SeO_2 structures. The calculated SeO_2 structure is in good agreement with the experimental one,[22] even for the long-range distances, that is the van der Waals interactions between chains. From these results and previous works,[25] one may be confident about the accuracy of these first-principles calculations in the structural investigations. Coming back to polysulfite, the calculated sulfur–oxygen bond lengths correspond to the extrapolated distances found in the oligomeric models (S–O = 1.71 *vs.* 1.72 Å and S=O = 1.45 *vs.* 1.45 Å in periodic and molecular models of **9**, respectively). The S···O inter-atomic distances (av. 3.1 Å) in 3D poly-SO_2 are slightly shorter than the sum of the S and O van der Waals radii, 3.30 Å, values which should decrease in the hypothetical polysulfite phase under high pressure. Recall that in our molecular models **9** such stabilizing electrostatic interactions are also present through intramolecular contacts. In order to evaluate the packing forces present in the crystalline compounds, calculations on one XO_2 covalent chain per unit cell (*vide infra*) have been undertaken: this model consists of one $[\text{–}X(=O)\text{–}O\text{–}]_2$ repeating unit ($Z = 2$) per tetragonal cell within the optimized XO_2-based downeyite geometry. SO_2 and SeO_2 polymeric species are stabilized by 4.3 and 10.5 kcal mol^{-1}, respectively, when going from the mimicked gas phase

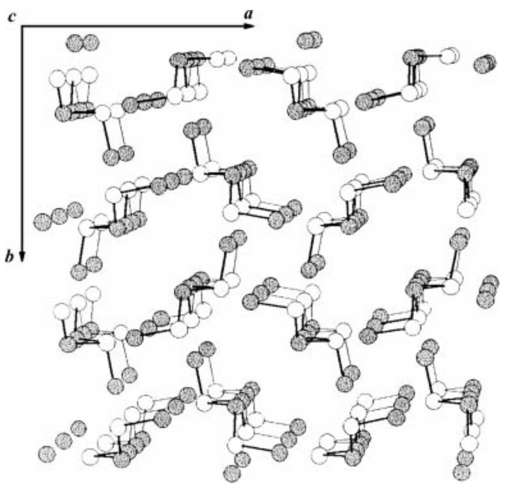


Fig. 4 Representation of the SeO_2 downeyite crystal structure.

Table 1 Structural parameters and relative energies δE^a for the crystalline polymeric[b] and molecular XO_2 phases from periodic first-principles calculations (X = Se, S)

Lattice constants/Å		Internal coordinates	Distances/Å	Angles/°	δE/kcal mol^{-1}
Polymeric SeO_2, **3**					
$a = b = 8.684(8.3622)^c$	$8h^d$ Se	0.131 29(0.133 74); 0.213 15(0.210 19); 0	Se–O: 1.833(1.793)	O–Se–O: 90.5(89.80)	−19.7
$c = 5.206(5.0612)$	8g O	0.138 35(0.138 02); 0.361 65(0.361 98); 1/4	Se=O: 1.635(1.624)	Se–O–Se: 121.8(121.77)	
	8g O	0.945 71(0.9429); 0.181 32(0.175 02); 0	Se···O: 2.800(2.758), 2.978(2.857)		
Molecular SeO_2 **1**					
$a = b = c = 10$			Se=O: 1.620(1.607)	O–Se–O: 115.0(113.5)	
Polymeric SO_2					
$a = b = 8.893$	8h S	0.127 40; 0.236 22; 0	S–O: 1.708	O–S–O: 91.8	+5.5
$c = 4.906$	8g O	0.130 14; 0.369 86; 1/4	S=O: 1.455	S–O–S: 122.4	
	8g O	0.971 96; 0.185 13; 0	S···O: 3.116, 3.143		
Molecular SO_2					
$a = b = c = 10$			S=O: 1.450(1.43)	O–S–O: 119.6(119.5)	

[a] $\delta E = E(\text{polymeric } XO_2)/8 - E(\text{molecular } XO_2)$ with $E(\text{molecular } XO_2) = -16.86$ and -14.75 eV for X = S and Se, respectively. [b] Space group $P4_2/mbc$ (no. 135), number of formula units in the unit cell $Z = 8$. See Fig. 4. [c] The experimental data are given in parentheses. For crystalline polymeric SeO_2, molecular SO_2 and SeO_2, see ref. 22, 23 and 24, respectively. [d] Wyckoff positions.

to the crystalline state. This energy difference of 6.2 kcal mol^{-1} may be connected to the diffuseness of the Se orbitals, which can expand in the van der Waals region. But caution has to be taken: recall that the SO_2 crystal geometry is not fully optimized (*e.g.* space group, formula unit in the unit cell) while the SeO_2 one is derived from the experimental structure; another $[\text{–S(=O)–O–}]_x$ crystalline polymorph may exist, lower in energy than our model by *ca.* 5 kcal mol^{-1} if this number, evaluated from the potential energy surface study for molecular **9** at the B3LYP level, is transferable. Our calculations show that poly-SO_2 in the condensed downeyite phase ($Z = 8$) is less stable by only 5.5 kcal mol^{-1} than free SO_2 while the SeO_2 polymeric phase is calculated to be lower in energy than free SeO_2 by 19.7 kcal mol^{-1} (see Table 1). Concerning the electrical properties, both poly-SO_2 and poly-SeO_2 are found to be insulators with a band gap greater than 4 eV.

To summarize, the hypothetical gas phase polysulfite is calculated to be 10.5 and 9.8 kcal per SO_2 less stable than free sulfur dioxide from the so-called molecular (B3LYP level) and periodic (PW91PL level) approaches, respectively, while crystalline poly-SO_2 is only 5.5 kcal mol^{-1} higher in energy than free SO_2. How can we link these results coming from two DFT computational techniques differing in (i) the functionals: *i.e.* B3LYP *vs.* PW91PL,[10] and (ii) the basis sets: extended Gaussian basis set *vs.* ultrasoft pseudopotentials and plane waves? To answer this question, test calculations on molecular $FS_{n+1}O_{2n+1}F$ oligomers **9** (n = 0–4) have been performed using the VASP program and the δE_n values are plotted in Fig. 3. One may see that a correction factor of roughly +4.4 kcal mol^{-1} may be added to the δE_n values calculated from the periodic approach to obtain the δE values evaluated from the molecular approach. Therefore, the corrected δE(PW91PL) relative energies are +14.2 and +9.9 kcal mol^{-1} for the gas and crystalline polysulfite phases, respectively. The δE(PW91PL) − δE(B3LYP) difference of 3.7 kcal mol^{-1} found in the $[\text{–S(=O)–O–}]_x$ gas phase models may be related to the fact that the covalent one-dimensional network is not fully optimized since it has the geometrical structure of a given chain in the optimized crystalline state. Nevertheless, these calculations applied at two levels of theory and on different models reveal the same energetic trends in the evaluation of δE for poly-SO_2 and reinforce our conclusions coming from both the molecular and periodic approaches: the covalent chains $[\text{–S(=O)–O–}]_x$ with three-coordinate sulfur atoms are possible synthetic targets for experimentalists even if the kinetic aspect for the $x\,SO_2 \rightarrow [\text{–S(=O)O–}]_x$ reaction will be a crucial point that is beyond the scope of the present study.

Conclusion

State-of-the-art computational calculations on selenium and sulfur dioxide allotropes made of –X(=O)–O– building blocks have been undertaken to evaluate their stability with respect to molecular 18-valence electron triatomic species. The synthesized crystalline poly-SeO_2 is calculated to be 20 kcal mol^{-1} more stable than the transient gas phase selenium dioxide. The hypothetical polysulfite $[\text{–S(=O)O–}]_x$ and other covalent $(SO_2)_x$ aggregates containing three-coordinate sulfur atoms are calculated to be higher in energy than free SO_2 by less than 12 kcal mol^{-1}. Nevertheless, we believe that polysulfite $[\text{–S(=O)O–}]_x$ is an ideal candidate for high-pressure synthesis, which might overcome the kinetic aspect of the polymerization reaction.

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References and notes

1 The literature is vast. See, for example: (*a*) C. Genin and R. Hoffmann, *J. Am. Chem. Soc.*, 1995, **117**, 328; (*b*) M. J. Bucknum and R. Hoffmann, *J. Am. Chem. Soc.*, 1994, **116**, 11456 and references therein; (*c*) M. N. Glukhovtsev, H. Jiao and P. von Ragué Schleyer, *Inorg. Chem.*, 1996, **35**, 7124 and references therein; (*d*) E. Lewars, *THEOCHEM*, 1996, **363**, 1; (*e*) P. Pyykkö, *Chem. Commun.*, 1999, 495; (*f*) S. Bernard, G. L. Chiarotti, S. Scandolo and E. Tosatti, *Phys. Rev. Lett.*, 1998, **81**, 2092; (*g*) M. Haser, U. Schneider and R. Ahlrichs, *J. Am. Chem. Soc.*, 1992, **114**, 9551; (*h*) P. Kroll and R. Hoffmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2527; (*i*) H. S. Choi and K. S. Kim, *Angew. Chem., Int. Ed.*, 1999, **38**, 2256; (*j*) F. Millich, *Adv. Polym. Sci.*, 1975, **19**, 117; (*k*) C. Kollmar and R. Hoffmann, *J. Am. Chem. Soc.*, 1990, **112**, 8230.

2 (*a*) G. Frapper, C.-X. Cui, J.-F. Halet, J.-Y. Saillard and M. Kertesz, *Chem. Commun.*, 1997, 2011; (*b*) G. Frapper and J.-Y. Saillard, *J. Am. Chem. Soc.*, 2000, **122**, 5367.

3 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, UK, 1984, pp. 714–715.

4 (*a*) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd edn., Butterworth–Heinemann, Oxford, UK, 1998, p. 738; (*b*) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd edn., Butterworth–Heinemann, Oxford, UK, 1998, p. 721.

5 (*a*) A. Astroem, *Acta Chem. Scand.*, 1972, **26**, 3849; (*b*) A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, UK, 1984, pp. 784, 983.

6 Besides these existing 18-valence electron triatomic based-compounds, note that sulfur trioxide presents three different allotropic phases: the gas phase monomer SO_3, the γ-SO_3 phase (*i.e.*

six-membered ring trimeric S_3O_9) and the β-SO_3 phase containing helical polymeric forms. See ref. 4*a*, p. 704.

7 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Rev. A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

8 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

9 (*a*) J. B. Foresman and Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Pittsburgh, PA, 1996; (*b*) http://www.gaussian.com.

10 (*a*) G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251; (*b*) G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15; (*c*) G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169; (*d*) VASP web site: http://cms.mpi.univie.ac.at/vasp/.

11 (*a*) J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048; (*b*) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedersen, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.

12 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

13 During the processing of this paper, a referee brought to our attention, a very recent article[13b] published in early October 2000 on an *ab initio* and density functional study on sulfur oxide oligomers such as cyclic *trans*-**4**, **6**, **8** and acyclic HO[–S(=O)–O–]$_n$H chains with $n = 2$–5. Their results overlap with the present ones for the cyclic $(SO_2)_n$ compounds and both are in agreement. However, they conclude that the higher acyclic chains are either not stationary points on the potential energy surface or are kinetically unstable. Our calculations on $FS_{n+1}O_{2n+1}F$ oligomers mimicking the hypothetical poly-S(=O)O show that these oligomers are local minima on the potential energy surface. This disagreement between their results and the present ones on S(=O)O-based oligomers may come from the choice of the terminal groups: F *vs.* H and OH; (*b*) C. Groves and E. Lewars, *THEOCHEM*, 2000, **530**, 265.

14 For the selenium-based dimers **2**, the calculated vibrational frequencies are at 976 cm^{-1} (b_u, 173 KM mol^{-1}) for the *trans* form, 983 (b_2, 96 KM mol^{-1}) and 993 cm^{-1} (a_1, 63 KM mol^{-1}) for the *cis* one.

15 The ionization potential H_{ii} is a measure of the energy of an orbital. H_{ii} values were collected by S. Alvarez, *Tables of Parameters for Extended Hückel Calculations*, Universitat de Barcelona, Barcelona, Spain, 1993.

16 (*a*) H. A. Bent, *J. Chem. Educ.*, 1960, **37**, 616; (*b*) H. A. Bent, *Chem. Rev.*, 1961, **61**, 275; (*c*) see also in: J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edn., HarperCollins College Publishers, New York, USA, 1993.

17 For recent papers on the influence of s–p mixing in determining the geometrical and electronic structures of isoelectronic compounds, see: (*a*) G. A. Papoian and R. Hoffmann, *Angew. Chem. Int. Ed.*, 2000, **39**, 2409 and references therein; (*b*) D.-K. Seo and R. Hoffmann, *J. Solid State Chem.*, 1999, **147**, 26; (*c*) E. A. Carter and W. A. Goddard III, *J. Phys. Chem.*, 1986, **90**, 998.

18 The compound S_6O_{12}, isoelectronic to the characterized $P_6O_{12}^{6-}$ anion [see ref. 3, p. 858] has also been investigated at the B3LYP/6-311G* level of theory. Starting from the S_6O_{12} D_{3d} structure having a boat-like sulfur skeleton, its optimization without symmetry constraints also leads to six free SO_2.

19 J. Emsley, *The Elements*, Clarendon Press, Oxford, UK, 1989.

20 V. Iota, C. S. Yoo and H. Cynn, *Science*, 1999, **283**, 1510.

21 (*a*) S. Serra, C. Cavazzoni, G. L. Chiarotti, S. Scandolo and E. Tosatti, *Science*, 1999, **284**, 788; (*b*) J. Dong, J. K. Tomfohr and O. F. Sankey, *Phys. Rev. B*, 2000, **61**, 5967.

22 K. Stahl, J. P. Legros and J. Galy, *Z. Kristallogr.*, 1992, **202**, 99.

23 Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, *J. Mol. Spectrosc.*, 1964, **13**, 95.

24 H. Takeo, E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, 1970, **34**, 370.

25 See, for example: (*a*) D. M. Teter, R. J. Hemley, G. Kresse and J. Hafner, *Phys. Rev. Lett.*, 1998, **80**, 2145; (*b*) J. Fürthmüller, J. Hafner and G. Kresse, *Phys. Rev. B*, 1994, **50**, 15606; (*c*) G. Kern, G. Kresse and J. Hafner, *Phys. Rev. B*, 1999, **59**, 8551 and references therein.