

# Structures and Energies of Various Isomers of Dithionous Acid, $\text{H}_2\text{S}_2\text{O}_4$ , and of Its Anion $\text{HS}_2\text{O}_4^-$

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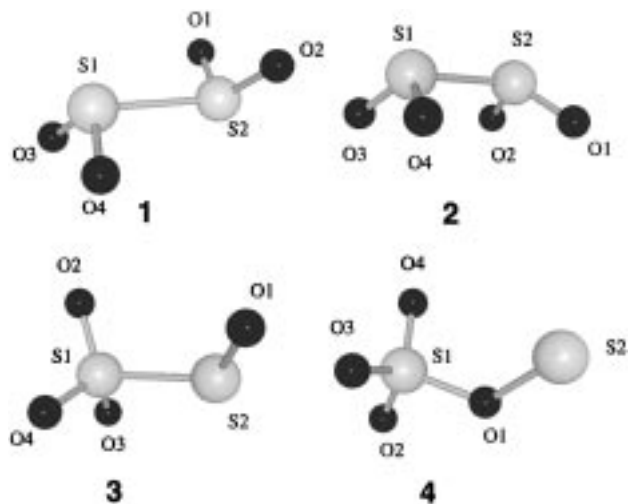
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Ab initio molecular orbital calculations at various, correlated levels of theory have been performed on eight isomers of the  $[\text{H}_2\text{O}_4\text{S}_2]^-$  anion and six forms of  $[\text{H}_2\text{O}_4\text{S}_2]$ . For the former species, the hypothetical  $\text{O}_3\text{SSOH}^-$  (**9**) ion is identified as the lowest energy isomer using second-order Møller–Plesset perturbation theory or the CCSD(T) method, with the protonated dithionite ion,  $\text{O}_2\text{SSO}_2\text{H}^-$  (**6**), being only marginally (less than 5  $\text{kJ mol}^{-1}$  at 25 °C) higher in energy. In contrast, the B3LYP density functional predicts a rather different order of relative stabilities, with  $\text{O}_2\text{SSO}_2\text{H}^-$  (**6**) as the by far most stable ion. **6** is stable with respect to dissociation into  $\text{SO}_2$  and  $\text{HOSO}^-$  or into  $\text{SO}_2^{\bullet-}$  and  $\text{HOSO}^{\bullet}$  (which is more stable than  $\text{HSO}_2^{\bullet}$ ). For the species of composition  $\text{H}_2\text{S}_2\text{O}_4$  the cage-like dithionous acid molecule  $(\text{HO})\text{O}_2\text{SSO}_2(\text{OH})$  (**14**) represents the global minimum at all four levels of theory. However, also for this species, the relative stabilities predicted by the B3LYP approach differ considerably from results obtained from the conventional wave function-based methods. **14** is stabilized by two very strong intramolecular hydrogen bonds (symmetry  $C_2$ ). The homolytic dissociation of **14** at the SS bond is strongly endothermic, but the molecule is unstable with respect to dissociation into  $\text{H}_2\text{SO}_2$  and  $\text{SO}_2$ . The harmonic wavenumbers and infrared intensities of the fundamental vibrations of **6** and **14** are given.

## Introduction

Sodium dithionite is produced on a large scale by reduction of aqueous sulfite and used as a powerful reductant and bleaching agent in dye works, in paper production, and in the printing industry.<sup>3</sup> The structure of the  $\text{S}_2\text{O}_4^{2-}$  anion depends on its environment: in aqueous solution<sup>4,5</sup> and in solid tetraethylammonium dithionite<sup>6</sup> the *trans*- $\text{S}_2\text{O}_4^{2-}$  ion **1** has been observed by vibrational spectroscopy; ab initio MO calculations on the hypothetical dianion in the gas phase (which is, of course, unstable against spontaneous loss of an electron and thus does not exist in the gas phase) have shown<sup>7,8</sup> that the *trans* conformation is the most stable rotamer of  $[\text{O}_2\text{S}-\text{SO}_2]^{2-}$ . This structure is of  $C_{2h}$  symmetry (see Figure 1). Most textbooks of inorganic chemistry give the structure of the dithionite anion as *cis*- $[\text{O}_2\text{S}-\text{SO}_2]^{2-}$  (**2**), which is the conformation found by X-ray structural analyses in the anhydrous sodium,<sup>9</sup> zinc,<sup>10</sup> and tin(II) salts<sup>11</sup> of  $\text{S}_2\text{O}_4^{2-}$ . However, ab initio calculations have revealed that this conformation does not represent a minimum on the potential energy hypersurface of  $\text{S}_2\text{O}_4^{2-}$  but rather corresponds to a saddle point.<sup>7,8</sup> In other words, *cis*- $\text{S}_2\text{O}_4^{2-}$  is stabilized in certain salts by interactions with the cations and does not represent an energetical minimum of the hypothetical free anion. It should be noted in this context that these calculations are only possible because the truncated basis set forces all electrons to remain with the molecule and excludes the energetically favored loss of an electron. In the salt



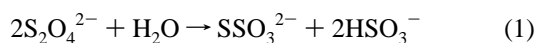
**Figure 1.** Isomers and rotamers of composition  $\text{S}_2\text{O}_4^{2-}$  and numbering of atoms. Species **2** corresponds to a saddle point on the energy hypersurface.

$\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  still another anion conformation has been detected: the two  $\text{SO}_2$  units are rotated against each other by  $56^\circ$ , resulting in a species of  $C_2$  symmetry.<sup>12</sup> Structural data of the various conformations of this anion are given in Table 1.

**TABLE 1: Average Bond Lengths (pm), Valence Angles (deg), and OSSO Torsion Angles  $\tau$  (deg) of the  $S_2O_4^{2-}$  Anion in Various Dithionites As Determined by X-ray Crystallography (for *cis*- $S_2O_4^{2-}$   $\tau = 0^\circ$ ; Site Symmetries Are Given; py = pyridine)**

| cation                              | S-S   | S-O   | O-S-O | S-S-O | $\tau$ (OSSO)            | ref |
|-------------------------------------|-------|-------|-------|-------|--------------------------|-----|
| Na <sup>+</sup>                     | 239.3 | 150.2 | 108.6 | 99.0  | 16 ( $C_2$ )             | 7   |
| Na <sup>+</sup> (2H <sub>2</sub> O) | 229.8 | 150.4 | 109.4 | 97.5  | 56 ( $C_2$ )             | 10  |
| Zn <sup>2+</sup> (py)               | 238.6 | 151.4 | 110.4 | 96.7  | 0 ( $C_s$ )              | 8   |
| Sn <sup>2+</sup>                    | 235.0 | 151.0 | 109.8 | 96.6  | $\approx 0$ ( $C_{2v}$ ) | 9   |

The two most serious problems with the production of sodium dithionite are its high reactivity toward oxygen (O<sub>2</sub>) and its acid-promoted decomposition, which at 20 °C and pH values near 6 proceeds basically according to eq 1 to give thiosulfate and sulfite.<sup>13</sup>



Lowering of the pH results in a rapid decomposition, and therefore, neither the free acid H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> nor its monoprotonated anion HS<sub>2</sub>O<sub>4</sub><sup>-</sup> have ever been observed. However, the strong pH dependence of the dithionite decomposition indicates that the protonated species are reaction intermediates. For this reason, we have performed for the first time extensive ab initio MO calculations on the possible isomers of HS<sub>2</sub>O<sub>4</sub><sup>-</sup> and H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as well as on their possible dissociation products SO<sub>2</sub>, SO<sub>2</sub><sup>•-</sup>, HSO<sub>2</sub><sup>•</sup>, HOSO<sup>•</sup>, HOSO<sup>-</sup>, and HOSOH. The radical HSO<sub>2</sub><sup>•</sup> may also result from protonation of the radical anion SO<sub>2</sub><sup>•-</sup>, which is in equilibrium with dissolved dithionite, eq 2.



ESR spectroscopic and spectrophotometric investigations have shown that the equilibrium 2 is to the left in dilute aqueous dithionite solutions<sup>14</sup> but to the right in polar organic solvents such as DMF, Me<sub>2</sub>SO, and MeCN.<sup>15</sup> Obviously, the ion O<sub>2</sub>SSO<sub>2</sub><sup>2-</sup> is only stable in salts and in polar solvents, under which circumstances a considerable reduction of its negative charge will take place by interaction with either surrounding cations or the positive poles of dipolar molecules.<sup>16</sup> The dissociation 2 is probably the first step in the disproportionation of aqueous dithionite according to eq 1.

Our previous ab initio MO calculations<sup>8</sup> had shown that two isomeric ions of composition S<sub>2</sub>O<sub>4</sub><sup>2-</sup> are more stable than **1**: at the MP2/6-311+G(2d,p)//6-31G\* level of theory the hypothetical ion O<sub>3</sub>SSO<sub>2</sub><sup>2-</sup> (**3**) is by 17 kJ mol<sup>-1</sup> more stable than **1**, while the equally hypothetical ion O<sub>3</sub>SOS<sub>2</sub><sup>2-</sup> (**4**) is by 24 kJ mol<sup>-1</sup> more stable (see Figure 1). Therefore we have investigated all kinds of structures that may be derived from the anions **1–4** by either single or double protonation. The results obtained from the theoretical calculations may help to understand the reaction mechanism of the decomposition of aqueous dithionite.

## Calculations

Standard ab initio MO calculations were performed employing GAUSSIAN 94<sup>17</sup> installed on IBM RS/6000 workstations and a CRAY Y-90 computer. Optimized structures were obtained at the valence electron correlated MP2/6-311++G-(d,p) level of theory. The harmonic vibrational frequencies were computed analytically using the Hartree–Fock approximation and a 6-311G(d,p) basis set. All vibrational wavenumbers and corresponding zero-point energies (ZPE) were scaled by uniform factors of 0.8929 and 0.9135, respectively.<sup>18</sup>

Improved relative energies were obtained at the MP2<sup>19</sup> level by adding an additional set of d-type polarization functions to the non-hydrogen atoms, that is, MP2/6-311++G(2d,p) (method A). For the open-shell species the unrestricted HF and MP2 scheme was used. In these calculations, no severe spin contamination was observed. The  $\langle S^2 \rangle$  expectation value never exceeded 0.77. All energies, enthalpies, and free enthalpies discussed in the following have been corrected for ZPE and thermal contributions and refer to 25°. For a general discussion of the methods and basis sets used, see ref 20.

Improved single-point energies were calculated at the MP2 and the coupled cluster approach (correlated only the valence electrons) with single and double excitations and a perturbative estimation of the triple contributions (CCSD(T)) levels of theory based on a restricted open-shell Hartree–Fock wave function. These were combined with basis sets of the atomic natural orbital (ANO) type designed by Widmark et al. of (8s4p) → [3s2p], (14s9p4d) → [4s3p2d], and (17s12p5d) → [5s4p2d] quality for H, O, and S, respectively.<sup>21</sup> The MP2/ANO and CCSD(T)/ANO levels of approximation will be denoted as method B and method C, respectively, and have been computed utilizing the MOLPRO program package.<sup>22</sup> Since the CCSD-(T) approach is known to cover a much larger fraction of the electron correlation than second-order perturbation theory, method C is expected to represent the most accurate computational strategy and to give the most reliable energetic results. All structural and energetical results mentioned in the following refer to methods A and C, respectively, unless noted otherwise.

Finally the geometries, energies, and vibrational spectra of all the HS<sub>2</sub>O<sub>4</sub><sup>-</sup> and H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> species were calculated with the Becke 3LYP density functionals and 6-311++G\*\* basis sets (method D). Since this particular functional enjoys a lot of popularity as being an economical and at the same time accurate alternative to conventional ab initio MO methods, we included this level of theory in order to study its performance for sulfur-containing neutral and in particular anionic compounds. In the following the letters A–D will be used to refer to these various levels of theory.<sup>23</sup>

## Results and Discussion

### Species SO<sub>2</sub>, SO<sub>2</sub><sup>•-</sup>, HSO<sub>2</sub><sup>•</sup>, HOSO<sup>•</sup>, HOSO<sup>-</sup>, and HOSOH.

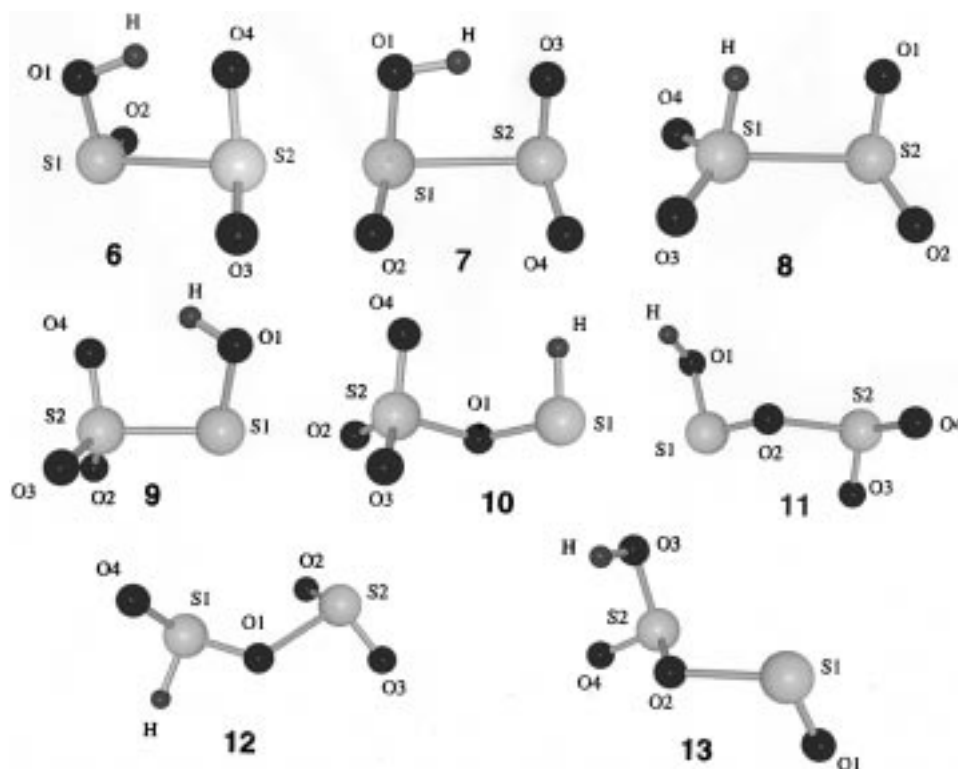
To discuss the thermodynamic stability [ $\Delta G^\circ$ ] of H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and of HS<sub>2</sub>O<sub>4</sub><sup>-</sup> with respect to a similar dissociation as shown in eq 2, it was necessary to calculate the energies and entropies of the possible dissociation products SO<sub>2</sub>, SO<sub>2</sub><sup>•-</sup>, HSO<sub>2</sub><sup>•</sup>, HOSO<sup>•</sup>, HOSO<sup>-</sup>, and HOSOH. The latter molecule had previously been shown to be of C<sub>2</sub> symmetry;<sup>24</sup> its geometrical parameters obtained at the higher level of theory (A) applied in the present work are  $d_{SO} = 166.3$ ,  $d_{OH} = 96.5$  pm,  $\alpha_{OSO} = 102.9^\circ$ ,  $\beta_{OSH} = 108.2^\circ$ , and  $\tau_{HOSO} = 82.5^\circ$ . The thermodynamic data are presented in Table 2. Of the two isomers HSO<sub>2</sub><sup>•</sup> and HOSO<sup>•</sup> (cis-planar) the latter is more stable, in agreement with previous calculations at a lower level.<sup>25</sup>

**Ions of Composition HS<sub>2</sub>O<sub>4</sub><sup>-</sup>.** Dithionous acid is expected to be a relatively weak acid comparable to sulfurous acid, H<sub>2</sub>SO<sub>3</sub>, and as in the case of sulfite ions, protonation of the anion S<sub>2</sub>O<sub>4</sub><sup>2-</sup> may occur at either the sulfur or the oxygen atoms. Hydrogensulfite ions HSO<sub>3</sub><sup>-</sup> exist as both tautomers [HOSO<sub>2</sub><sup>-</sup> and HS(O)<sub>3</sub><sup>-</sup>] in aqueous solution.<sup>26</sup> In Figure 2 three isomeric structures of the hydrogen dithionite anion (**6–8**) are shown, which all correspond to minima on the potential energy hypersurface. In addition, five isomers of composition HS<sub>2</sub>O<sub>4</sub><sup>-</sup> are shown which are derivatives of the isomeric S<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions **3** and **4** (e.g., **9** and **10**) or may originate from protonation of the

**TABLE 2: Total Energies ( $h = 2625.5 \text{ kJ mol}^{-1}$ ), Zero-Point Vibrational Energies (ZPE), Thermal Energies (TE), and Standard Entropies ( $S_{298}^\circ$ ) of  $\text{SO}_2$ ,  $\text{SO}_2^{\cdot-}$ ,  $\text{HSO}_2^\cdot$ ,  $\text{HOSO}^\cdot$ ,  $\text{HOSO}^-$ , and  $\text{HOSO}^\text{H}$** 

|  | $\text{SO}_2 (C_{2v})$               | $\text{SO}_2^{\cdot-} (C_{2v})$ | $\text{HSO}_2^\cdot (C_s)$ | $\text{HOSO}^\cdot (C_1)$            | $\text{HOSO}^- (C_1)$ | $\text{HOSO}^\text{H} (C_2)$ |
|--|--------------------------------------|---------------------------------|----------------------------|--------------------------------------|-----------------------|------------------------------|
| ZPE <sup>a</sup> (kJ mol <sup>-1</sup> )               | 19.3, <sup>a</sup> 19.1 <sup>b</sup> | 15.6 <sup>a</sup>               | 42.5 <sup>a</sup>          | 43.6, <sup>a</sup> 43.5 <sup>b</sup> | 42.5 <sup>a</sup>     | 76.5 <sup>b</sup>            |
| TE (25 °C) (kJ mol <sup>-1</sup> )                     | 7.9, <sup>a</sup> 7.5 <sup>b</sup>   | 8.1 <sup>a</sup>                | 8.3 <sup>a</sup>           | 9.7, <sup>a</sup> 10.0 <sup>b</sup>  | 9.8 <sup>a</sup>      | 9.6 <sup>b</sup>             |
| (U)MP2/6-311++G(2d,p)//(U)MP2/6-311++G** [A]           | -547.861 92                          | -547.891 18                     | -548.380 96                | -548.418 75                          | -548.455 72           | -549.021 11                  |
| (U)MP2/ANO//(U)MP2/6-311++G** [B]                      | -547.870 43                          |                                 |                            |                                      | -548.481 04           | -549.047 48                  |
| (U)CCSD(T)/ANO//(U)MP2/6-311++G** [C]                  | -547.893 40                          | -547.938 61                     | -548.429 49                | -548.475 46                          | -548.514 58           | -549.087 55                  |
| $S_{298}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ) | 247.0 <sup>b</sup>                   | 255.2 <sup>a</sup>              | 261.8 <sup>a</sup>         | 272.5 <sup>a</sup>                   | 267.2 <sup>a</sup>    | 261.8 <sup>b</sup>           |

<sup>a</sup> Calculated at the HF/6-311G\*\* level of theory. <sup>b</sup> Calculated at the HF/6-311++G\*\* level of theory.

**Figure 2.** Isomers and rotamers of composition  $\text{HS}_2\text{O}_4^-$  as obtained by protonation of the anions shown in Figure 1 (ions 6–10) or by recombination of  $\text{HSO}_2^\cdot$  radicals with  $\text{SO}_2^{\cdot-}$  radical anions (species 11–13).**TABLE 3: Energies of Various Isomers of  $\text{HS}_2\text{O}_4^-$  (6–13) in Relation to the Energy of 9 Taking ZPE and TE into Account, Zero-Point Vibrational Energies (ZPE), Scaled by 0.9135 in kJ mol<sup>-1</sup>, and the Corresponding Thermal Energies (TE, kJ mol<sup>-1</sup>)**

|   | ZPE <sup>a</sup> | TE <sup>a</sup><br>(25 °C) | $E_{\text{rel}}^*$<br>[A] | $E_{\text{rel}}^*$<br>[B] | $E_{\text{rel}}^*$<br>[C] | ZPE<br>[D] | TE<br>(25 °C) [D] | $E_{\text{rel}}^*$<br>[D] |
|---|------------------|----------------------------|---------------------------|---------------------------|---------------------------|------------|-------------------|---------------------------|
| $\text{HO}_2\text{SSO}_2^-$ (6)                 | 72.1             | 16.0                       | 4.1                       | 1.2                       | 4.2                       | 67.1       | 18.0              | -28.9                     |
| $\text{HO}_2\text{SSO}_2^-$ (7)                 | 71.5             | 16.6                       | 13.8                      | 7.4                       | 14.7                      | 66.6       | 18.5              | -15.2                     |
| $\text{O}_2(\text{H})\text{SSO}_2^-$ (8)        | 68.5             | 17.2                       | 63.3                      | 72.3                      | 84.7                      | 62.4       | 19.3              | 62.8                      |
| $\text{O}_3\text{SSOH}^-$ (9)                   | 75.5             | 15.8                       | 0                         | 0                         | 0                         | 72.1       | 17.4              | 0                         |
| $\text{O}_3\text{SOSH}^-$ (10)                  | 70.1             | 15.4                       | 16.1                      | 12.7                      | 12.3                      | 66.1       | 17.1              | 23.8                      |
| $\text{O}_2\text{SOSOH}^-$ (11)                 | 70.0             | 17.9                       | 59.8                      | 48.0                      | 46.3                      | 65.5       | 20.3              | 10.4                      |
| $\text{O}_2\text{SOS}(\text{H})\text{O}^-$ (12) | 66.9             | 17.6                       | 56.4                      | 60.8                      | 67.3                      | 75.0       | 23.6              | 66.9                      |
| $\text{HO}_2\text{SOSO}^-$ (13)                 | 67.1             | 18.9                       | 131.6                     | 124.5                     | 115.6                     | 58.3       | 15.1              | 75.9                      |

<sup>a</sup> Obtained from frequencies calculated at the HF/6-311G\*\* level of theory.

anion  $[\text{O}_2\text{SOSO}]^{2-}$ , which also corresponds to a local minimum.<sup>8</sup> The species 11–13 may be formed by suitable recombination reactions of the radicals  $\text{SO}_2^{\cdot-}$  and  $\text{HSO}_2^\cdot$ .

The relative energies of all eight species of composition  $\text{HS}_2\text{O}_4^-$  are given in Table 3; the geometrical parameters of the more stable anions 6–10 are listed in Table 4. All species shown in Figure 2 are of either  $C_1$  or  $C_s$  symmetry.

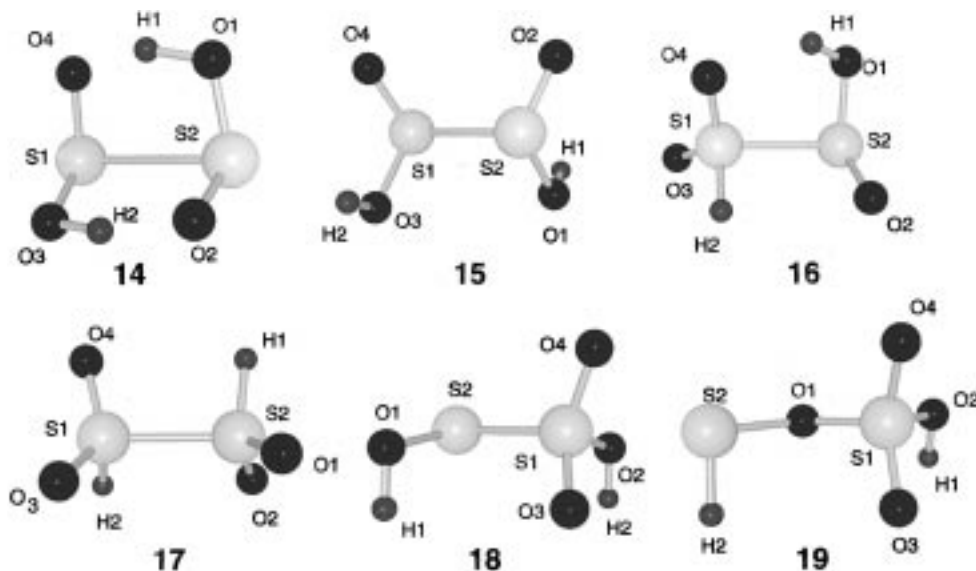
Independent of the method used, the oxygen-protonated anion 6 is the most stable of the three hydrogen dithionite ions. It is of gauche conformation and is stabilized by an intramolecular  $\text{OH}\cdots\text{O}$  hydrogen bond of length 153.6 pm (method A). Its

SS bond is longer than the observed SS distances in dithionite salts (Table 1): method A yields 256.8 pm, while 263.8 pm is obtained by the DFT method D. The species 7 is a rotamer of 6 and is derived from *cis*- $\text{S}_2\text{O}_4^{2-}$  (2) by protonation at oxygen. Due to its unfavorable eclipsed conformation, this ion is less stable than 6 by 10.5 kJ mol<sup>-1</sup>. The short  $\text{OH}\cdots\text{O}$  contact of 151.4 pm in 7 indicates a strong hydrogen bond. The S-protonated anion 8 is higher in energy than 6 by 80.5 kJ mol<sup>-1</sup>; it does not contain a hydrogen bond, although the SH bond and one SO bond are aligned with each other ( $\text{SH}\cdots\text{O}$  distance 254.2 pm, method A).

**TABLE 4: Bond Lengths  $d$  (pm), Valence Angles  $\alpha$  (deg), and Torsion Angles  $\tau$  (deg) of the Various Isomers of  $\text{HS}_2\text{O}_4^-$  (6–10) (MP2/6-311++G\*\*)<sup>a</sup>**

|                      | 6   | 7   | 8   | 9  | 10  |
|----------------------|---|---|---|--|---|
| $d(\text{SS})$       | 256.8   | 266.4   | 264.1   | 219.3  |   |
| $d(\text{SO})$       | 163.9(O1)<br>150.6(O2)<br>150.1(O3)<br>153.1(O4)            | 164.3(O1)<br>150.1(O2)<br>154.0(O3)<br>150.0(O4)          | 149.1(O1)<br>148.8(O2)<br>149.4(O3)<br>149.7(O4)            | 170.5(S1O1)<br>146.8(S2O2)<br>146.7(S2O3)<br>148.2(S2O4) | 167.2(S1O1)<br>175.7(S2O1)<br>146.1(S2O2)<br>146.5(S2O3)<br>147.0(S2O4)                     |
| $d(\text{OH})$       | 102.5   | 103.0   |   | 97.5   |   |
| $d(\text{SH})$       |   |   | 139.3   |  | 134.2   |
| $\alpha(\text{SSO})$ | 85.8(O1)<br>105.0(O2)<br>105.9(O3)<br>89.3(O4)              | 85.0(O1)<br>98.2(O2)<br>88.5(O3)<br>96.9(O4)              | 88.2(O1)<br>105.0(O2)<br>122.7(O3)<br>113.2(O4)             | 96.3(O1)<br>102.0(O2)<br>108.6(O3)<br>98.7(O4)           |   |
| $\alpha(\text{OSO})$ | 110.8(O1–O2)<br>113.7(O3–O4)                                | 111.4(O1–O2)<br>114.6(O3–O4)                              | 115.9(O1–O2)<br>117.4(O3–O4)                                | 115.7(O2–O4)<br>111.0(O3–O4)<br>115.3(O2–O3)             | 104.7(O1–O3)<br>114.8(O3–O4)<br>116.1(O2–O4)<br>98.9(O1–O2)<br>116.2(O2–O3)<br>102.7(O1–O4) |
| $\alpha(\text{SSH})$ |   |   | 87.4  |  |   |
| $\alpha(\text{SOS})$ |   |   |   |  | 116.9   |
| $\alpha(\text{SOH})$ | 106.2   | 106.8   |   | 102.9  |   |
| $\alpha(\text{HSO})$ |   |   | 103.7(O4)<br>104.6(O3)                                      |  | 98.2  |
| $\tau(\text{OSSO})$  | 95.6(O1–O3)<br>–18.9(O1–O4)<br>91.5(O2–O4)<br>–154.0(O2–O3) | 4.0(O1–O3)<br>118.6(O1–O4)<br>–106.9(O2–O3)<br>7.7(O2–O4) | –114.3(O1–O3)<br>95.1(O1–O4)<br>–148.4(O2–O4)<br>3.1(O2–O3) | 155.0(O1–O2)<br>–82.8(O1–O3)<br>36.2(O1–O4)              |   |
| $\tau(\text{HOSS})$  | 16.1  | –8.4  |   | –36.2  |   |
| $\tau(\text{HOSO})$  | –88.4   | 88.4  |   |  |   |
| $\tau(\text{HSOS})$  |   |   |   |  | –72.3   |
| $\tau(\text{HSSO})$  |   |   | –8.6(O1)<br>107.7(O2)                                       |  |   |

<sup>a</sup> The geometrical parameters of species 11–13 are available from the authors on request.



**Figure 3.** Isomers and rotamers of composition  $\text{H}_2\text{S}_2\text{O}_4$  as obtained by 2-fold protonation of the dianions shown in Figure 1.

Species **9** is derived from protonation of the  $\text{S}=\text{O}$  oxygen in  $\text{O}_3\text{SSO}^{2-}$  (**3**). It represents the global minimum if the conventional methods A, B, and C are used. However, all three levels of theory yield **9** as only slightly more stable than **6**. With the most accurate method, C, an energy difference of only 4.2  $\text{kJ mol}^{-1}$  is predicted, which does not significantly change with method A (4.1  $\text{kJ mol}^{-1}$ ) or method B (1.2  $\text{kJ mol}^{-1}$ ). However, the B3LYP functional employed in method D shows a distinctively different picture. Not only is **6** more stable than **9** by 28.9  $\text{kJ mol}^{-1}$ , even isomer **7** is still predicted to be more stable than **9** by 15.2  $\text{kJ mol}^{-1}$ . It seems that the B3LYP functional,

which works so well in many applications, is apparently not equally well suited for a balanced description of these molecules. The connectivity of **9** corresponds to the monoanion of peroxosulfuric acid  $[\text{O}_3\text{SOOH}]^-$ . The distance  $\text{OH}\cdots\text{O4}$  is 205.7 (A) and 208.3 (D) pm. Species **10** is 12.3  $\text{kJ mol}^{-1}$  less stable than **9** (again, method D gives a much larger energy difference of 23.8  $\text{kJ mol}^{-1}$ ); it originates from **4** by protonation at the terminal sulfur atom. Since this atom bears a higher negative charge ( $-0.80e$ ) than the terminal oxygen atoms ( $-0.61$  to  $-0.67e$ ) it was to be expected that protonation at sulfur would be more favorable. The corresponding O-

**TABLE 5: Energies (kJ mol<sup>-1</sup>) of Various Isomers of H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (14–19) in Relation to the Energy of 14 Taking the Zero-Point Energies into Account, Zero-Point Vibrational Energies (ZPE), Scaled by 0.9135 in kJ Mol<sup>-1</sup> and the Corresponding Thermal Energies (kJ mol<sup>-1</sup>)**

|           | ZPE <sup>a</sup> | TE <sup>a</sup><br>(25 °C) | E <sub>rel</sub><br>[A] | E <sub>rel</sub><br>[B] | E <sub>rel</sub><br>[C] | ZPE<br>[D] | TE<br>(25 °C) [D] | E <sub>rel</sub><br>[D] |
|-----------|------------------|----------------------------|-------------------------|-------------------------|-------------------------|------------|-------------------|-------------------------|
| <b>14</b> | 102.7            | 16.2                       | 0                       | 0                       | 0                       | 96.8       | 17.1              | 0                       |
| <b>15</b> | 99.6             | 18.4                       | 76.6                    | 84.1                    | 63.4                    | 95.0       | 21.5              | 67.7                    |
| <b>16</b> | 101.5            | 16.6                       | 109.8                   | 126.4                   | 119.8                   | 96.1       | 18.3              | 150.6                   |
| <b>17</b> | 105.3            | 17.1                       | 191.8                   | 219.2                   | 226.9                   | 95.7       | 17.8              | 280.6                   |
| <b>18</b> | 105.2            | 17.1                       | 52.8                    | 55.3                    | 39.9                    | 102.5      | 18.9              | 80.0                    |
| <b>19</b> | 100.2            | 16.7                       | 59.8                    | 67.4                    | 50.3                    | 97.1       | 18.3              | 100.9                   |

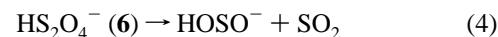
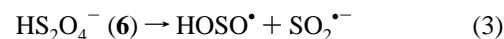
<sup>a</sup> From the frequencies calculated at the HF/6-311++G\*\* level of theory.

protonated anion does not correspond to an energetic minimum but represents a saddle point, as indicated by an imaginary frequency.

The high relative energies of the two species **12** and **13** (>56 kJ mol<sup>-1</sup> above **9**, independent of the method) indicate that they will hardly play a role in dithionite chemistry. Species **11** is also less stable than **9**; method C yields a relative energy of 46.3 kJ mol<sup>-1</sup>, with methods A and B giving similar results of 59.8 and 48.0 kJ mol<sup>-1</sup>, respectively. A different relative stability is only predicted by method D, where **11** is computed to be only 10.4 kJ mol<sup>-1</sup> less stable than **9**.

Since the dithionite ion O<sub>2</sub>SSO<sub>2</sub><sup>2-</sup> is unstable with respect to dissociation in two radical anions SO<sub>2</sub><sup>•-</sup> it was of interest to calculate the reaction energies Δ*U*<sub>298</sub> for the analogous dissociation of (HO)OSSO<sub>2</sub><sup>-</sup> (**6**) according to eqs 3 and 4. Both

reactions are strongly endothermic in the vapor phase, with Δ*U*<sub>298</sub>(3) = 176 kJ mol<sup>-1</sup> and Δ*U*<sub>298</sub>(4) = 193 kJ mol<sup>-1</sup>.



Taking the entropies of **6** (334.3 J mol<sup>-1</sup> K<sup>-1</sup> at 298 K) and of its dissociation products (Table 2) as well as the increase in volume at constant pressure into account one obtains the free reaction enthalpies as follows: Δ*G*<sup>o</sup><sub>298</sub>(3) = 121 and Δ*G*<sup>o</sup><sub>298</sub>(4) = 142 kJ mol<sup>-1</sup>. These high positive values show that a spontaneous dissociation of **6** is unlikely, even in solution since the stabilization of the dissociation products by solvation should be similar to that of **6**.

**Dithionous Acid, H<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.** The various isomers of composition H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> are shown in Figure 3; the corresponding energies are collected in Table 5. The molecules **14**, **15**, and **17** are of C<sub>2</sub> symmetry; the other three species are of C<sub>1</sub> symmetry. All six structures represent minima on the [H<sub>2</sub>O<sub>4</sub>,S<sub>2</sub>] potential energy surface. All four methods of calculation (A–D) unanimously yield species **14** as the global minimum at 25 °C. This molecule is obtained by protonation of the anion O<sub>2</sub>SSO<sub>2</sub><sup>2-</sup> **1** via HO<sub>2</sub>SSO<sub>2</sub><sup>-</sup> (**6**). Second in energy comes HO<sub>3</sub>SSOH (**18**), which is less stable than **14** by 39.9 kJ mol<sup>-1</sup>, followed by **19** and **15**, lying 50.3 and 67.7 kJ mol<sup>-1</sup> above **14**, respectively. The remaining species **16** and **17** are more than 100 kJ mol<sup>-1</sup> less favorable than **14** and are probably chemically irrelevant. Interestingly, while all wave function-based methods (A to C) yield the same qualitative order of stabilities, method D is again

**TABLE 6: Bond Lengths *d* (pm), Valence Angles α (deg), and Torsion Angles τ (deg) of the Various Isomers of H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (14–19) (MP2/6-311++G\*\*)**

|               | <b>14</b> (C <sub>2</sub> ) | <b>15</b> (C <sub>2</sub> ) | <b>16</b> (C <sub>1</sub> ) | <b>17</b> (C <sub>2</sub> ) | <b>18</b> (C <sub>1</sub> ) | <b>19</b> (C <sub>1</sub> ) |
|---------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| <i>d</i> (SS) | 270.3                       | 237.4                       | 234.8                       | 224.6                       | 213.4                       |                             |
| <i>d</i> (SO) | 157.8(S2O1)                 | 166.4                       | 162.4(O1)                   | 144.8(O1.O3)                | 166.3(O1)                   | 164.8(O1S1)                 |
|               | 157.8(S1O3)                 | 147.4                       | 147.5(O2)                   | 145.5(O2.O4)                | 162.5(O2)                   | 170.9(O1S2)                 |
|               | 152.1(S2O2)                 |                             | 145.4(O3)                   |                             | 144.9(O3)                   | 159.9(O2S1)                 |
|               | 152.1(S1O4)                 |                             | 147.2(O4)                   |                             | 143.7(O4)                   | 144.1(O3S1)                 |
| <i>d</i> (SH) |                             |                             | 137.2                       | 136.5                       |                             | 143.0(O4S1)                 |
| <i>d</i> (OH) | 106.9                       | 97.1                        | 98.7                        |                             | 96.7(H1)                    | 133.9                       |
|               |                             |                             |                             |                             | 96.9(H2)                    | 96.8                        |
| α(SSO)        | 85.8(SSO4)                  | 92.4(O(H))                  | 89.2(O1)                    | 110.1(O1.O3)                | 98.0(O1)                    |                             |
|               | 83.2(SSO3)                  | 105.6                       | 96.2(O2)                    | 104.2(O2.O4)                | 96.8(O2)                    |                             |
|               |                             |                             | 119.3(O3)                   |                             | 106.9(O3)                   |                             |
|               |                             |                             | 101.0(O4)                   |                             | 112.9(O4)                   |                             |
| α(SOS)        |                             |                             |                             |                             |                             | 116.5                       |
| α(SOH)        | 109.7                       | 110.0                       | 111.5                       |                             | 108.0(H1)                   | 109.6                       |
|               |                             |                             |                             |                             | 108.9(H2)                   |                             |
| α(SSH)        |                             |                             | 92.4                        | 96.8                        |                             |                             |
| α(OSO)        | 110.7                       | 110.5                       | 113.0(O1SO2)                | 125.1                       | 122.8(O3O4)                 | 95.5(O1O2)                  |
|               |                             |                             | 123.1(O3SO4)                |                             | 105.4(O2O4)                 | 106.7(O2O4)                 |
|               |                             |                             |                             |                             | 108.9(O2O3)                 | 107.7(O1O3)                 |
|               |                             |                             |                             |                             |                             | 110.4(O1O4)                 |
|               |                             |                             |                             |                             |                             | 110.4(O2O3)                 |
| τ(HOSS)       | -6.2                        | -73.1                       | -27.1                       |                             | 83.4(H2O2)                  |                             |
|               |                             |                             |                             |                             | 80.8(H1O1)                  |                             |
| τ(OSSO)       | 4.9(O1O4)                   | 55.5(O2O4)                  | 129.8(O3O2)                 | -119.1(O3O2)                | -158.9(O1O2)                |                             |
|               | 4.9(O2O3)                   | -80.3(O1O3)                 | 21.3(O1O4)                  | -119.1(O1O4)                | 91.2(O1O4)                  |                             |
|               | -106.5(O2O4)                | 167.6(O1O4)                 | -117.1(O1O3)                | 17.3(O1O3)                  | -46.8(O1O3)                 |                             |
|               | 116.3(O1O3)                 | 167.6(O2O3)                 | -91.8(O2O4)                 | 104.5(O2O4)                 |                             |                             |
| τ(HOSO)       | 76.7                        | 34.5                        | 69.3                        |                             | -27.1(O3)                   | -38.8(H1O3)                 |
|               |                             |                             |                             |                             | -160.6(O4)                  | -174.4(H1O4)                |
|               |                             |                             |                             |                             |                             | 72.4(H1O1)                  |
|               |                             |                             |                             |                             |                             | 82.6                        |
| τ(HSOS)       |                             |                             | 128.5                       | -6.4(H2O1)                  |                             |                             |
| τ(HSSO)       |                             |                             | 15.4                        | -6.4(H1O4)                  |                             |                             |
|               |                             |                             |                             | 130.0(H2O2)                 |                             |                             |
|               |                             |                             |                             | 130.0(H1O3)                 |                             |                             |

**TABLE 7: Harmonic Fundamental Vibrations of the Hydrogen Dithionite Anion **6** and of Dithionous Acid **14** (Wavenumbers Scaled by 0.8929; in cm<sup>-1</sup>; Infrared Intensities Given)**

| HS <sub>2</sub> O <sub>4</sub> <sup>-</sup> ( <b>6</b> ) | H <sub>2</sub> S <sub>2</sub> O <sub>4</sub> ( <b>14</b> ) | assignment |
|--|--|------------|
| 3235 vs  | 3340 (A) vs<br>3338 (B) vs                                 | } ν(OH)    |
| 1296 s   | 1223 (A) vvw<br>1193 (B) vs                                |            |
| 1121 vs  | 1096 (A) vs  | } ν(SO)    |
| 1055 vs  | 1089 (B) vvs   |            |
| 987 vvs  | 846 (A) s  |            |
| 780 vs   | 820 (B) vs   |            |
| 714 vs   | 632 (A) vs<br>604 (B) s                                    |            |
| 526 s  | 527 (B) s  |            |
| 465 m  | 419 (A) m  |            |
| 451 m  | 395 (B) m  |            |
| 374 w  | 362 (A) m  |            |
| 286 w  | 327 (A) vvw  |            |
| 224 w  | 273 (B) w  |            |
| 181 w  | 273 (A) m  |            |
| 80 w   | 83 (A) vvw   |            |

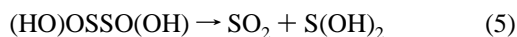
out of line. Rather than **18**, species **15** is computed as being the second most stable isomer, with **18** and **19** following. Both are computed to be roughly twice as much less stable with method D than with method C (80.0 and 100.9 kJ mol<sup>-1</sup> versus 39.9 and 50.3 kJ mol<sup>-1</sup>, respectively). Thus, the rather poor performance of the B3LYP functional observed above for the anions does also apply to these neutral species.

The geometrical parameters of **14**–**19** are listed in Table 6. The structure of the cage-like dithionous acid molecule (HO)OSSO(OH) (**14**) is very interesting. On one hand, it contains two very short but asymmetric OH...O hydrogen bonds of length 140.0 pm. On the other hand, the SS bond of **14** (270.3 pm) is extremely long and even longer than in the related anions HS<sub>2</sub>O<sub>4</sub><sup>-</sup> (**6**) (256.8 pm) and S<sub>2</sub>O<sub>4</sub><sup>2-</sup> (**1**) (Table 1). It therefore seems that the two halves of molecule **14** are held together mainly by the hydrogen bonds! Interestingly, the conformation of **14** is similar to that of the unstable *cis*-S<sub>2</sub>O<sub>4</sub><sup>2-</sup> (**2**), the smallest OSSO torsion angle being 4.9°. However, in contrast to **2** the homolytic dissociation of **14** into two radicals HOSO• is endothermic by Δ*U*<sub>298</sub><sup>o</sup> = 114 kJ mol<sup>-1</sup> and the equilibrium **14** ⇌ 2HOSO• is on the left: Δ*G*<sub>298</sub><sup>o</sup> = 51 kJ mol<sup>-1</sup>. The harmonic vibrational wavenumbers of **14** and its monoanion **6** are given in Table 7.

Many fundamentals have high infrared intensities and should help to identify these species.

The other conformer of (HO)OSSO(OH) (**15**) is 67.7 kJ mol<sup>-1</sup> less stable than **14**. Its SS bond (237.4 pm) is much shorter compared to **14**, but the shortest OH...O distances are much larger: 264.0 pm (within the SO<sub>2</sub>H groups). In other words, there are no hydrogen bonds in this molecule. The two SO<sub>2</sub> groups of **15** are practically trans to each other, as in the dithionite dianion **1**.

We have also investigated the possibility of double protonation of S<sub>2</sub>O<sub>4</sub><sup>2-</sup> at one SO<sub>2</sub> group, as in O<sub>2</sub>SS(OH)<sub>2</sub>. However, on attempts to optimize its geometry this molecule dissociated into SO<sub>2</sub> and S(OH)<sub>2</sub>. This result raises the question whether the species **14** and **15** are also unstable thermodynamically with respect to dissociation into SO<sub>2</sub> and S(OH)<sub>2</sub>, eq 5.



For the acid **14** the reaction energy Δ*U*<sub>298</sub><sup>o</sup>(5) = +43 kJ mol<sup>-1</sup> is obtained from the energies of SO<sub>2</sub> and H<sub>2</sub>SO<sub>2</sub> (Table 2). Using the entropy of **14** (*S*<sub>298</sub><sup>o</sup> = 327.6 J mol<sup>-1</sup> K<sup>-1</sup>) and

its dissociation products (Table 2) and taking the increase in volume into account, one obtains Δ*G*<sub>298</sub><sup>o</sup>(5) = -9 kJ mol<sup>-1</sup>. The same thermodynamic instability is then to be expected for **15**. The decomposition of **14** according to eq 5 just requires the shift of one proton within its hydrogen bond from one minimum into the neighboring minimum, whereupon spontaneous dissociation will occur. Since the barrier of such a proton shift within a short hydrogen bond is known to be low, the decomposition of **14** by this route should be possible without much activation energy.

The two S-protonated species **16** and **17** (Figure 3) are also isomers (tautomers) of dithionous acid but are much less stable than **14**. There is another conformer of [O<sub>3</sub>SSO(OH)]<sup>-</sup> (not shown) which is less stable than **6**. S protonation stabilizes the sulfur-sulfur bond, as can be seen from the much shorter SS bond of **17** (224.6 pm) compared to that of **14** (270.3 pm). The two SHO<sub>2</sub> groups of **17** are almost eclipsed but rotated against each other: the smallest HSSO torsion angle amounts to -6.4°, while the torsion angle HSSH is 117.3°.

## Conclusions

We have calculated the geometries and energies of 25 molecules, anions, and radicals of type H<sub>x</sub>S<sub>y</sub>O<sub>z</sub> with *x* = 0–2 using various levels of ab initio theory. The cage-like dithionous acid (HO)OSSO(OH) (**14**) is the most stable molecule on the potential energy hypersurface [H<sub>2</sub>O<sub>4</sub>S<sub>2</sub>], but **14** is thermodynamically unstable with respect to dissociation into SO<sub>2</sub> and H<sub>2</sub>SO<sub>2</sub>. At the CCSD(T) and MP2 levels of approximation, the monoanion O<sub>3</sub>SSOH<sup>-</sup>, which is generated by O protonation of the hypothetical O<sub>3</sub>SSO<sup>2-</sup> and is isoelectronic to the monoanion of peroxosulfuric acid, O<sub>3</sub>SOOH<sup>-</sup>, represents the global minimum on the [H<sub>2</sub>O<sub>4</sub>S<sub>2</sub>]<sup>-</sup> potential energy surface. However, the anion O<sub>2</sub>SSO(OH)<sup>-</sup> (**5**) derived from **14** is computationally predicted to be only 4 kJ mol<sup>-1</sup> less stable. This anion is stable against dissociation into HOSO• + SO<sub>2</sub><sup>-</sup> and into HOSO<sup>-</sup> + SO<sub>2</sub> by more than 100 kJ mol<sup>-1</sup>. The popular B3LYP density functional shows a surprisingly poor performance as compared to our most accurate CCSD(T) results. For the [H<sub>2</sub>O<sub>4</sub>S<sub>2</sub>]<sup>-</sup> anion, **6** is predicted as the global minimum, with **9** being almost 30 kJ mol<sup>-1</sup> higher in energy. Also in the neutral [H<sub>2</sub>O<sub>4</sub>S<sub>2</sub>] system, the B3LYP calculations lead to a different order of relative stabilities.

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