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Electrophilic Attack on Sulfur−Sulfur Bonds. 1. Protonation of Various Isomers of the Homoatomic Sulfur Molecules S_n ($n = 2-8$)

Ming Wah Wong,*,[†] Tsz Sian Chwee,[†] and Ralf Steudel[‡]

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, and Institut für Chemie, Technische Universität Berlin, Sekr. C2, D-16023 Berlin, Germany

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The structures and thermodynamic properties of 32 cations of composition $[HS_n]^+$ with $n = 2-8$ have been studied by ab initio methods at the G3X(MP2) level of theory. In the global minimum structures, the proton binds to a single sulfur atom and, except for $n = 2$, this also holds for the less stable isomers. The binding energies at 0 K range from 619.4 kJ mol^{-1} in $[HS_2]^+$ to 835.6 kJ mol^{-1} in $[S_5-SH]^+$, which represents the global minimum structure of composition $[HS_6]^+$. The protonated branched rings are also the global minimum structures in the case of S_7 and S_8, whereas $[HS_5]^+$ is most stable with a five-membered homocycle. The smaller cations $[HS_n]^+$ ($n = 2-4$) are all chainlike with the hydrogen atom at a chain end. Unexpectedly, singlet chainlike structures of $[HS_n]^+$ ($n = 2-8$) with the hydrogen terminating the chain at one end are more stable than the corresponding triplet chains. The protonation of neutral sulfur molecules always takes place at the atom of highest negative charge and the charge transfer to the proton is between 0.77 and 0.86 electrons. The S−H bond lengths are calculated as in the range 135−139 pm. The effect of protonation on the sulfur−sulfur bonds is dramatic, as can be seen in the strong bond length alternation within the cyclic or chainlike structures with the weakest SS bonds originating from the three-coordinate atoms. Hence, there is a pronounced bond activation by protonation. The calculated gas-phase basicities of S_6 and S_8 are in good accord with the experimental values.

1. Introduction

Sulfur−sulfur bonds are important and fairly reactive building blocks in many organic, inorganic, and biological molecules. Although the cleavage of S−S bonds under redox conditions as well as on nucleophilic attack has been extensively studied, the electrophilic attack by cations has received much less attention.[1] This is somewhat surprising because bonds between two-coordinate sulfur atoms are electron-rich systems that should strongly attract electrophilic reagents. The highest occupied molecular orbital (HOMO) in such an S−S bond is the antibonding π* MO originating from the overlap of the two 3p atomic orbitals that are approximately orthogonal to the two neighboring σ bonds and that are fully occupied.[2,3] The gas-phase ionization energies of the cyclic S_n molecules such as S_6 and S_8 containing "normal" SS bonds (−S−S−) with torsion angles close to 90° are approximately 9 eV. However, if one torsion angle is much smaller or larger than 90° (e.g., due to the smaller or larger ring size compared to S_8) the ionization energies are smaller because of the larger overlap of the two mentioned 3p orbitals and the larger energetic splitting between the resulting π and π* MOs. For example, the experimental ionization energy of *cyclo*-S_6 (9.00 eV;[4] torsion angle 73.8° [5]) is slightly smaller than that of *cyclo*−S_8 (9.04 eV;[4] torsion angle 98.5° [6]). In *cyclo*-S_7 one torsion angle has the value 0° [7] resulting in a considerably lower ionization energy of 8.67 eV.[4]

From the above considerations, it follows that removal of electron density from an −S−S− bond should increase the bond strength and change the torsion angle toward a more planar structure. In fact, the radical cations $H_2S_2^{\bullet+}$ [8] and $Me_2S_2^{\bullet+}$ [9] are characterized by trans-planar structural units X−S−S−X (C_{2h} symmetry) with S−S bond lengths of 201.0 and 200.3 pm, respectively, at the MP2/6-31G(d) level of theory. These internuclear distances are by ca. 5 pm shorter than those calculated for the corresponding neutral molecules. The adiabatic ionization energy of dimethyl disulfane Me_2S_2 is 8.18 ± 0.03[9] or 8.20 ± 0.04 eV.[10]

The structures of the monocations S_6^+ and S_7^+ have recently been calculated with the B3PW91 method. The cation S_6^+ (D_{3d} symmetry) adopts a chair conformation[11,12] that is much more flat (torsion angle $\tau = 62.4°$) than in the neutral molecule ($\tau = 73°$). The seven-membered ring of the S_7^+ cation is approximately of C_2 symmetry[11] rather than C_s, as observed[7] and calculated[13] for S_7.

The simplest electrophile to react with a molecule in the gas phase is the proton, and in this context the gas-phase basicity or proton affinity of the species S_n is usually defined as the negative reaction energy, enthalpy, or Gibbs energy of the reaction, as shown in

$$S_n(g) + H^+(g) \rightarrow [HS_n]^+(g) \qquad (1)$$

In real experiments of this type, the structures or conformations of the S_n fragments may be different on both sides of eq 1. However, if the neutral and the protonated forms are derived from the same structure, then the reaction energy is also called the "binding energy" of the proton.

The molecule S_3 is of C_{2v} symmetry in its ground state.[13] It has been reported that the trans-planar cation [HSSS]$^+$ represents the global minimum structure at the QCISD(T)//HF level of

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* To whom correspondence should be addressed. E-mail: chmwmw@nus.edu.sg.

[†] National University of Singapore.

[‡] Technische Universität Berlin.

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theory whereas the cis conformer was found to be slightly less stable, by 5 kJ mol^{-1}. Much less stable are branched and cyclic isomers of $[HS_3]^+$.[14] Protonation of the global minimum structure of S_4 (C_{2v} symmetry[13]) was found to produce a chainlike cation $[HSSSS]^+$ of C_1 symmetry as the global minimum structure at the G2(MP2) level, with the four sulfur atoms in a cis-planar arrangement and the hydrogen atom nearly trans-planar to the sulfur chain. However, three more local energy minima have been identified on the potential energy hypersurface (PES). A trans-planar sulfur-chain structure with the SSSH unit in a gauche conformation was found to be by 7 kJ mol^{-1} less stable than the global minimum structure.[15] In the case of protonated *cyclo*-S_6, two cyclic and three chainlike structures were calculated at the G2(MP2) level with the branched ring $[S_5-S-H]^+$ as the global minimum structure. The protonated six-membered ring $[HS_6]^+$ of C_s symmetry with the proton in an axial position was reported to be by 8 kJ mol^{-1} less stable.[15] Protonation of *cyclo*-S_8 has been studied only at the MP2/6-31G(d)//HF/6-31G(d) level, and the branched ring structure $[S_7-S-H]^+$ was found to be slightly more stable (by 8 kJ mol^{-1}) than the eight-membered ring in octathiocan-1-ium $[HS_8]^+$ and considerably more stable (by 19 kJ mol^{-1}) than the second branched ring isomer of connectivity $[S_6-S-S-H]^+$.[15]

By means of Fourier transform ion cyclotron resonance spectroscopy the protonation of the gaseous homocycles S_6 (D_{3d} symmetry) and S_8 (D_{4d}) has been determined as exothermic by -702 and -783 kJ mol^{-1}, respectively (Gibbs energies of protonation; ± 1 kJ mol^{-1}).[15] Although the structures of the species $[HS_6]^+$ and $[HS_8]^+$ produced in these experiments are unknown, the basicity data obtained are comparable to the protonation enthalpy of H_2S, which has been calculated at the G2 level of theory as -702 kJ mol^{-1} at 298 K,[16] in excellent agreement with previous calculations[17] and with the experimental value of -705 kJ mol^{-1}.[18] To the best of our knowledge, protonation experiments of sulfur rings in solution have not been reported.

In this work, we have systematically studied the protonation of several isomers of all homoatomic sulfur molecules from S_2 to S_8 at the G3X(MP2) level of theory. The proton is expected to serve as a probe for the location of the maximum electron density within a given molecule.

2. Computational Details

Standard ab initio calculations were carried out with the Gaussian 98 series of programs[19] at the G3X(MP2) level of theory.[20] This theory corresponds effectively to the QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2) theory[21] with three important changes: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large basis set for the second-row atoms at the Hartree−Fock level. All three features are particularly important for the proper description of the sulfur-containing compounds examined in this work. For instance, the geometries and stabilities of several cluster species are poorly predicted by the MP2 theory.[22] Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real, and transition states, with one imaginary frequency. To calculate the Gibbs energy of the proton, a value of 6.197 kJ mol^{-1} was used for the temperature correction ($H_{298} - H_0$) and a value of 108.946 J mol^{-1} K^{-1} was used for the entropy (S_{298}).[23]

For all investigated molecules, a charge density analysis was performed using the natural bond orbital (NBO) approach based on the B3LYP/6-31G(2df,p) wave function.[24] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[25] Unless otherwise noted, all relative energies reported in this publication are given as ΔE_0 and correspond to the G3X(MP2) level.

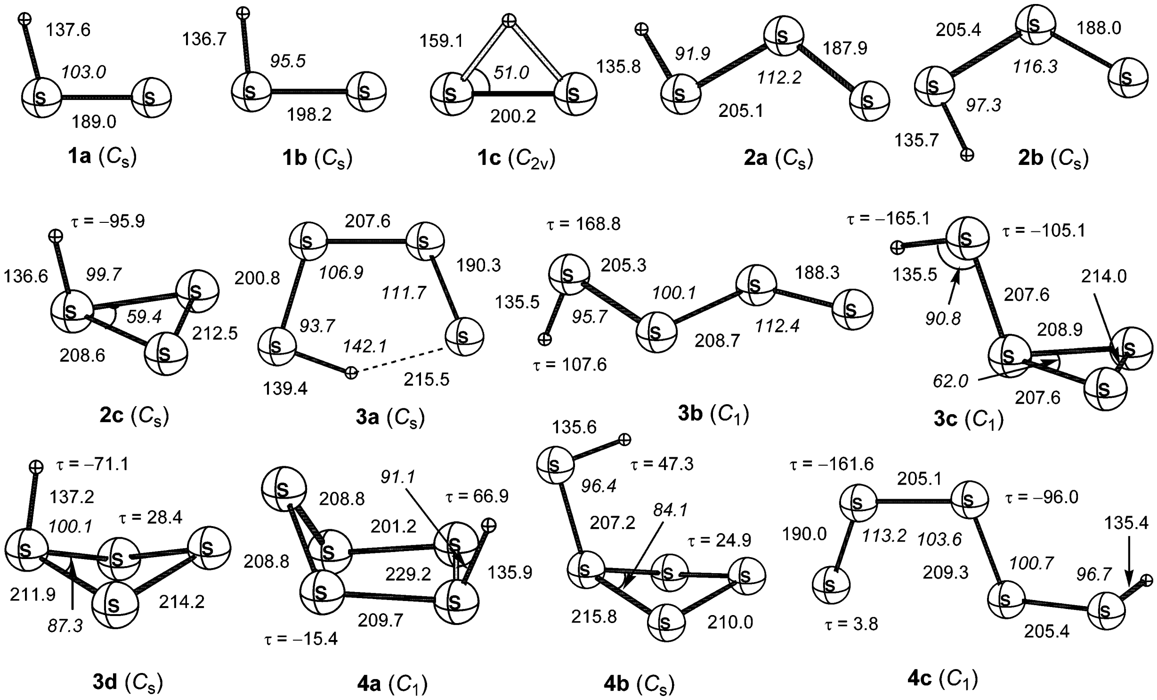
3. Results and Discussion

3.1. Geometrical Structures and Relative Energies. *3.1.1. Disulfur*. In contrast to the triplet ground state of disulfur ($^3S_2$), the protonated form $[HS_2]^+$ favors a singlet ground state (**1a**). The triplet form **1b** lies 46.4 kJ mol^{-1} above the singlet state. This reversal of preference can be rationalized in terms of the greater two-electron stabilization in the singlet state over the one-electron stabilization in the triplet state. The bent singlet cation $[HS_2]^+$ has an S−S bond distance (189.0 pm) shorter than that calculated for $^3S_2$ (191.2 pm) and a bond angle of 103.0° (see Figure 1). Evidently, antibonding electron density is withdrawn from the S_2 unit to form the S−H bond, which is slightly longer (137.6 pm) than in the other species with one-coordinate hydrogen reported below. The NBO atomic charges indicate that 0.80 electrons are transferred from the S_2 unit to the proton, leaving the sulfur atoms with charges of 0.42 (central) and 0.38 (terminal). The binding energies of the singlet and triplet $[HS_2]^+$ are 731.0 and 619.4 kJ mol^{-1}, respectively.

Interestingly, a symmetrical singlet $[HS_2]^+$ structure of C_{2v} symmetry with a bridging hydrogen atom (**1c**) is predicted to be a minimum on the PES, but this structure is considerably less stable than **1a**, by 253.6 kJ mol^{-1} (Table 1). Its geometrical parameters ($d_{SS} = 200.2$ pm, $d_{SH} = 159.1$ pm, $\alpha = 51.0°$) clearly show that the bond energies must be much lower than in the global minimum structure (Figure 1). The charge on the hydrogen atom is nevertheless the same (+0.20).

3.1.2. Trisulfur. The geometry of S_3 is of C_{2v} symmetry. The calculated geometrical parameters (193.9 pm and 118.2°) agree well with the recently determined experimental structure [191.7(1) pm and 117.36(6)°].[26] The NBO charges are 0.32 for the central and -0.16 for the terminal atoms (see Figure 2). Thus, the protonation is expected to take place at one of the terminal atoms. The chainlike trans-planar $[HSSS]^+$ ion **2a** of C_s symmetry (see Figure 1) is calculated to be the global minimum structure, consistent with previous DFT and QCISD(T)//HF calculations by Mineva et al.[14] At the G3X(MP2) level, the cis isomer **2b** is by just 6.4 kJ mol^{-1} less stable than the trans form (Table 1). The cis form is not stabilized by an intramolecular H···S interaction between the two terminal atoms of the chain because the distance between these atoms of 307.7 pm is too large although the HSS angle (89°) is rather small. Furthermore, these atoms both bear a positive charge of 0.20. The very short SS bonds of 188 pm at the chain ends of **2a** and **2b** are remarkable. Protonation at the central atom of S_3 is rather unfavorable. It yields a C_{2v} structure that is 131.7 kJ mol^{-1} higher in energy. For the cyclic S_3 isomer, protonation leads to **2c** (Figure 1), which lies 48.1 kJ mol^{-1} above the global energy minimum (**2a**).

3.1.3. Tetrasulfur. The cis-planar structure of the free S_4 molecule (C_{2v} symmetry) is now well established theoretically[22] and has recently also been detected in sulfur vapor exposed to an electrical discharge.[27] The central bond [calcd 212.7/exp 217(3) pm] is considerably longer than the two terminal bonds [192.2/189.9(7) pm]. The bond angles [107.4°/103.9(8)°] have



1a (C_s) **1b** (C_s) **1c** (C_{2v}) **2a** (C_s) **2b** (C_s)

2c (C_s) **3a** (C_s) **3b** (C_1) **3c** (C_1)

3d (C_s) **4a** (C_1) **4b** (C_s) **4c** (C_1)

Figure 1. Optimized [B3LYP/6-31G(2df,p)] geometries of the various HS_2^+, HS_3^+, HS_4^+, and HS_5^+ isomers. Selected structural parameters are given, with bond lengths in picometers and bond angles (in italics) and torsional angles in degrees.

TABLE 1: Calculated G3X(MP2) Total Energies (Hartrees) and Relative Energies (kJ mol^{-1}), and Dipole Moments (μ, Debye) of the Ions HS_n^+ ($n = 2-8$)

species	symmetry	total energy	relative energy		μ^a
			ΔE_0	ΔH_{298}	
S_2H^+ bent (singlet) (**1a**)	C_s	−795.74654	0.0	0.0	1.59
S_2H^+ bent (triplet) (**1b**)	C_s	−795.72866	46.4	46.7	1.18
S_2H^+ bridged (**1c**)	C_{2v}	−795.64994	253.6	253.9	0.59
S_3H^+ trans chain (**2a**)	C_s	−1193.54507	0.0	0.0	1.69
S_3H^+ cis chain (**2b**)	C_s	−1193.54261	6.4	6.5	1.11
S_3H^+ 3-ring (**2c**)	C_s	−1193.52673	48.1	47.2	2.13
S_4H^+ cis chain (**3a**)	C_s	−1591.32521	0.0	0.0	1.76
S_4H^+ trans chain (**3b**)	C_1	−1591.31674	22.2	23.5	1.00
S_4H^+ branched (**3c**)	C_1	−1591.30423	55.1	55.8	1.69
S_4H^+ 4-ring (**3d**)	C_s	−1591.28341	109.8	109.0	2.40
S_5H^+ 5-ring (**4a**)	C_1	−1989.09754	0.0	0.0	2.23
S_5H^+ branched (**4b**)	C_1	−1989.06490	85.7	86.7	1.17
S_5H^+ chain (**4c**)	C_1	−1989.09025	19.1	21.1	1.10
S_6H^+ branched (**5b**)	C_1	−2386.87390	0.0	0.0	2.13
S_6H^+ 6-ring (**5a**)	C_s	−2386.86971	11.0	10.1	2.71
S_6H^+ branched (**5c**)	C_1	−2386.86767	16.3	17.6	1.57
S_6H^+ chain (**5d**)	C_1	−2386.85760	42.8	44.5	1.62
S_7H^+ branched (**6b**)	C_1	−2784.64604	0.0	0.0	1.43
S_7H^+ 7-ring (**6a**)	C_1	−2784.64535	1.8	1.5	3.03
S_8H^+ branched (**7c**)	C_1	−3182.42352	0.0	0.0	3.03
S_8H^+ branched (**7b**)	C_1	−3182.42063	7.6	7.2	3.54
S_8H^+ 8-ring (**7a**)	C_s	−3182.41641	18.7	17.6	4.67

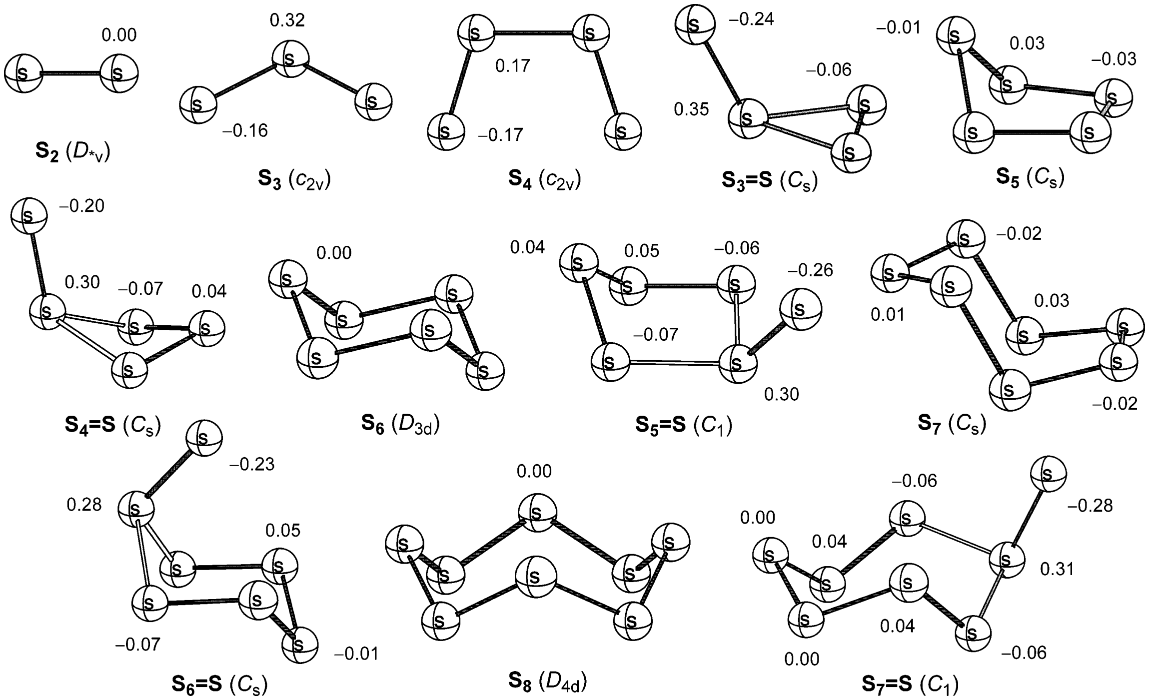
[a] B3LYP/6-31G(2df,p) values.

“normal” values. The NBO charges are +0.17 for the two central and −0.17 for the terminal atoms (Figure 2). On protonation, the cis-planar chainlike ion [HSSSS]$^+$ of C_s symmetry (**3a**) is predicted to be the global minimum structure (Figure 1). However, previous calculations favored a nonplanar cis conformation of the sulfur chain and the hydrogen atom nearly trans-planar to the sulfur atoms.[15] The [HS$_4$]$^+$ structure, as shown in Figure 1, is stabilized by an intramolecular hydrogen bond between the two terminal atoms, separated by only 215.5 pm. Because the hydrogen atom may occupy one of two equivalent positions between the two terminal sulfur atoms, a double minimum potential is to be expected for the energy dependence on the hydrogen atom position. The calculated barrier for the proton transfer is just 5.6 kJ mol^{-1}. The NBO charges of **3a** are presented in Figure 3. The trans isomer (**3b**) is calculated to be 22.2 kJ mol^{-1} less stable than the cis form (Table 1). Interestingly, **3b** is nonplanar, with an SSSH torsion angle of 107.6° (Figure 1).

The S_4 molecule is known to exist as several isomers in sulfur vapor[22,28] and one of these isomers has been proposed to be a branched three-membered ring $S_3{=}S$.[29] Protonation of this species at the exocyclic atom produces the cation [S_3−SH]$^+$ (**3c**) of C_1 symmetry (Figure 1), which is 55.1 kJ mol^{-1} less stable than **3a**. The S−H group is slightly oriented toward the S−S bond of length 207.6 pm of the S_3 triangle, thus lowering the symmetry from the expected C_s to C_1. Protonation of the unbranched cyclic S_4 isomer results in **3d** (Figure 1), which is significantly higher in energy (109.8 kJ mol^{-1} above **3a**).

3.1.4. Pentasulfur. The S_5 molecule forms a five-membered ring of envelope conformation (C_s symmetry),[13] with a planar arrangement of four atoms (Figure 2). The torsion angle of zero at the unique bond results in a maximum overlap of the nonbonding 3p orbitals of local π-symmetry at this bond, and consequently, the HOMO will be centered at these atoms. In fact, the NBO charges of the corresponding atoms (−0.03) are the most negative in the molecule (Figure 2). Therefore, it is not suprizing that the protonation takes place at one of these two atoms. The lowest energy homocyclic cation [HS$_5$]$^+$ (**4a**) has no symmetry at all (Figure 1). The hydrogen atom occupies an axial position. The increase in coordination number at the protonated atom changes the formerly planar arrangement to a nonplanar structure with an SSSS torsion angle of 15.4°, but the overall conformation of the five-membered ring is still the same as in S_5. The SS bond involving the three-coordinate atom is lengthened from 221.0 to 229.2 pm upon protonation (Figure 1). The atomic charge on the three-coordinate atom is 0.27 and on the hydrogen atom is 0.22 (Figure 3).

A branched four-membered ring isomer [S_4−SH]$^+$ (**4b**) protonated at the exocyclic atom is of C_s symmetry (see Figure

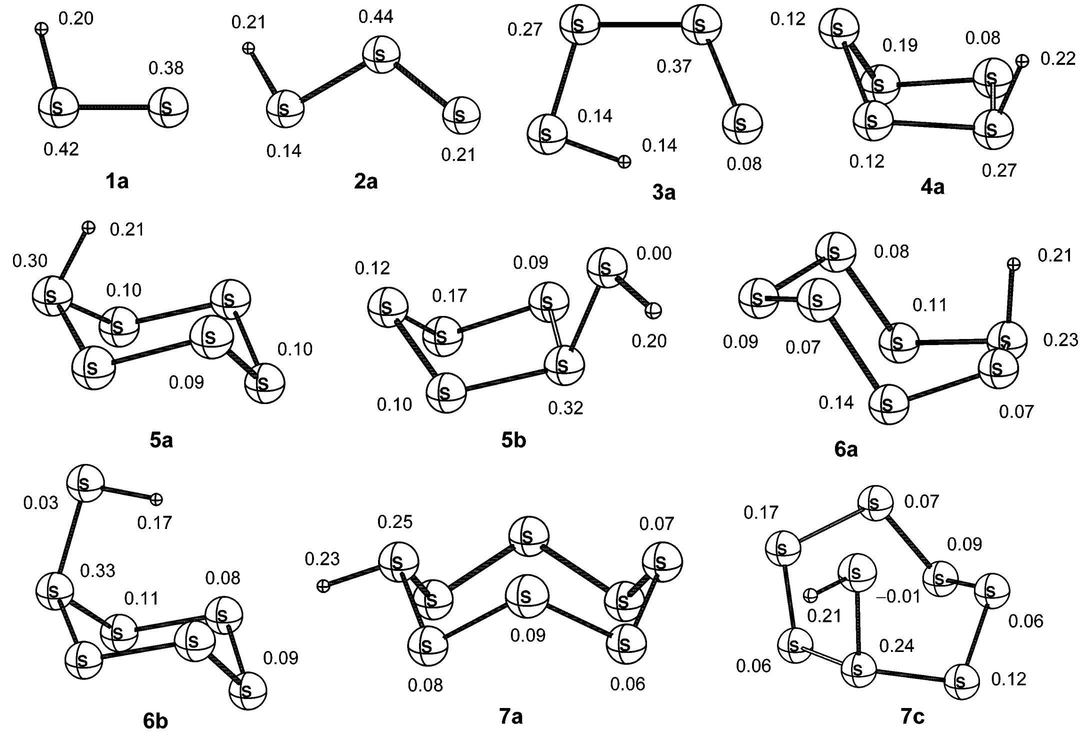


S$_2$ ($D_{\infty v}$) **S$_3$** (C_{2v}) **S$_4$** (C_{2v}) **S$_3$=S** (C_s) **S$_5$** (C_s)

S$_4$=S (C_s) **S$_6$** (D_{3d}) **S$_5$=S** (C_1) **S$_7$** (C_s)

S$_6$=S (C_s) **S$_8$** (D_{4d}) **S$_7$=S** (C_1)

Figure 2. NBO atomic charges [B3LYP/6-31G(2df,p)] of the neutral S$_n$ molecules ($n = 2-8$).



1a **2a** **3a** **4a**

5a **5b** **6a**

6b **7a** **7c**

Figure 3. NBO atomic charges [B3LYP/6-31G(2df,p)] of the ions HS$_n^+$ ($n = 2-8$).

1), but its energy is 85.7 kJ mol^{-1} above the global energy minimum. The S−H bond points toward the rather flat four-membered ring (bond angles within the ring starting at the three-coordinate atom: 84.1°, 87.0°, and 88.7°), but there is no additional S···H interaction. More stable than the protonated branched ring is the singlet open chain isomer **4c** (Figure 1). It has a relative energy of only 19.1 kJ mol^{-1}. In other words, the ring opening reaction of protonated S$_5$ (**4a**) requires an enthalpy of just 19 kJ mol^{-1}! Remarkably, this ring opening takes place on the singlet PES of [HS$_5$]$^+$, in sharp contrast to the ring opening of the S$_5$ molecule which produces a triplet chain.[30] The triplet chain structure of [HS$_5$]$^+$ is much less stable than the singlet chain **4c**, by 67.1 kJ mol^{-1} (Table 2).

3.1.5. Hexasulfur. The formal protonation of the ground-state chairlike structure of *cyclo*-S$_6$ (D_{3d} symmetry) takes place at a single atom rather than bridging a bond. The cation [HS$_6$]$^+$ (**5a**) is of C_s symmetry with an axial arrangement of the SH bond (see Figure 4). The equatorial conformer is by 5.5 kJ mol^{-1} less stable. The preference of the axial form may be rationalized in terms of the stronger lone-pair-lone-pair repulsion in the equatorial form. In **5a**, there is a transfer of 0.79 electrons to the proton (Figure 3). This charge-transfer induces a symmetrical

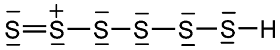
TABLE 2: Calculated G3X(MP2) Relative Energies (ΔE_0, kJ mol^{-1}) of the Branched and Open-Chain HS_n^+ (n = 5−8) Isomers

species	unbranched ring	branched ring	singlet chain	triplet chain
S_4H^+	0.0	−54.7	−109.8	−14.7
S_5H^+	0.0	85.7	19.1	86.2
S_6H^+	0.0	−11.0	31.8	78.0
S_7H^+	0.0	−1.8	45.2	95.8
S_8H^+	0.0	−18.7	50.6	140.2

bond length alternation within the homocycle with the two bonds originating from the three-coordinate atom (213.9 pm) becoming longer, the neighboring bonds shrinking from 209.0 pm in S_6 to 206.8 pm and the two other bonds remaining almost unchanged (208.5 pm). However, this ion with a six-membered ring is not the global minimum structure in the gas phase. Rather, the branched ion $[S_5{-}SH]^+$ (**5b**) is by 11.0 kJ mol^{-1} more stable (Table 1). Although this structure had been found before,[15] our calculated branched cation geometry is quite different, with the longest SS distance of 224.4 pm (see Figure 4) rather than 251.7 pm.[15] Nevertheless, the protonation of the symmetrical homocycle S_6 activates one of the sulfur−sulfur bonds considerably. Remarkably, the hydrogen atom of the axial SH group is turned away from the five-membered ring, which has a similar conformation as in the S_5 molecule. The SH group is connected to the homocycle at the same atom to which the proton is attached in the related cation $[HS_5]^+$ (**4a**). The torsion angle HSSS to the longest bond of the cycle is 108.6°.

In recent theoretical studies of S_6,[31,32] a trigonal prism structure was found as a stable isomer of hexasulfur, which lies 51 kJ mol^{-1} above the most stable chair form.[32] On protonation, the prism rearranges to a branched ring structure (**5c**) with an exocyclic SH group in an axial position but with a very long SS bond of length 274 pm between the formal chain end and the atom bearing the SH group (Figure 4). The HSSS torsion angle is −156.6°. This branched form is 16.3 kJ mol^{-1} less stable than the global minimum structure **5b** (Table 1).

Somewhat less stable, by 42.8 kJ mol^{-1} compared to **5b**, is the singlet open chain structure **5d**, which is of C_1 symmetry and which shows a very pronounced bond alternation effect (Figure 4). In this chain, the four torsion angles, starting from the hydrogen atom, are −80.9°, −89.6°, −101.2°, and −1.0°. The bonding in this remarkable ion can approximately be described by the following Lewis structure:



$$\overline{\underline{S}}=\overset{+}{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-\overline{\underline{S}}-H$$

The NBO atomic charges of **5d** are (from left to right): 0.13, 0.38, 0.18, 0.06, 0.07, 0.01, and 0.18.

The thermodynamic data of **5a**−**c** show that the ring opening of $[HS_6]^+$ (**5a**) requires a reaction enthalpy of only 20.8 kJ mol^{-1} and produces a singlet chain (Table 2). Starting from the global minimum structure **5b**, the reaction enthalpy is predicted as 42.8 kJ mol^{-1}. The branched structure **5c** may be an intermediate in the latter reaction. As with $[HS_5]^+$, the triplet chain is significantly less stable than the singlet, by 46.2 kJ mol^{-1} (Table 2). The terminal planar S_4 unit in **5d** is similar to that in **4c**. This cis-planar arrangement of the S_4 unit is prevalent in the longer singlet $[HS_n]^+$ chains as well as in the triplet S_n chains.[30]

3.1.6. Heptasulfur. The *cyclo*-S_7 molecule is of C_s symmetry (Figure 2) with a distinct bond length alternation pattern (starting at the unique atom: 207.1, 212.9, 200.9, and 222.1 pm). As in the case of *cyclo*-S_5, there is a planar arrangement of four atoms with a torsion angle of zero. The HOMO is centered at this S_4 unit. The two atoms forming this bond are negatively charged by −0.02 (Figure 2). The formal protonation of *cyclo*-S_7 takes place at one of the atoms, forming the unique bond with τ = 0°. This bond opens up from 222.1 pm in S_7 to 230.7 pm in $[HS_7]^+$ (**6a**), whereas the SSSS torsion angle increases from

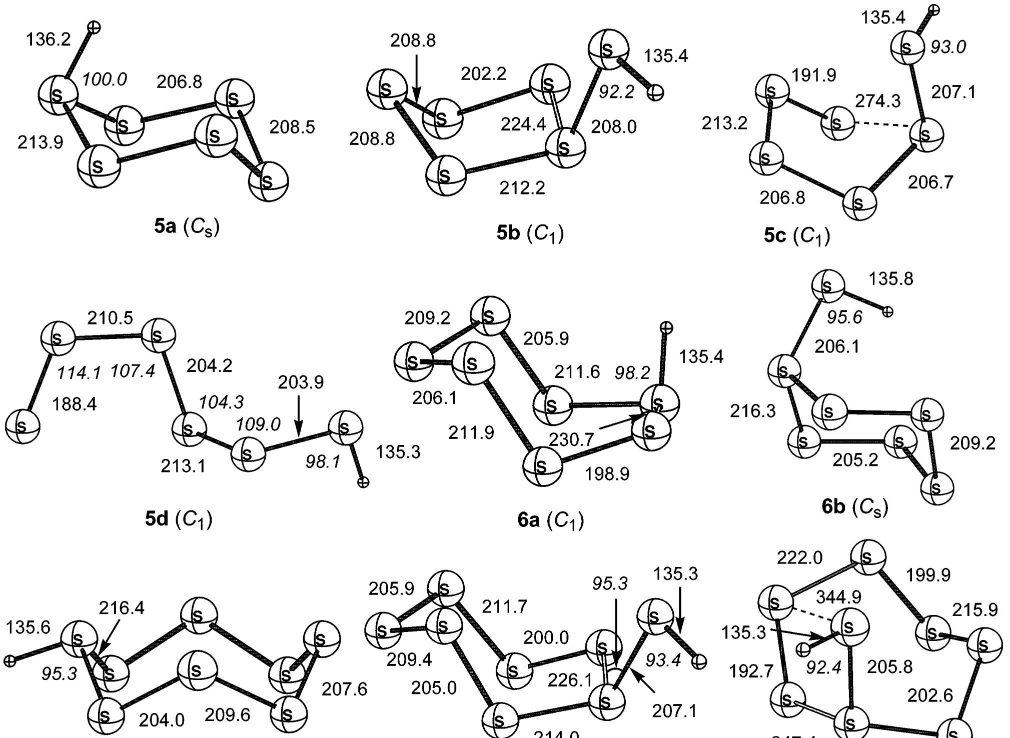


Figure 4. Optimized [B3LYP/6-31G(2df,p)] geometries of the various HS_6^+, HS_7^+, and HS_8^+ isomers. Selected structural parameters are given, with bond lengths in picometers and bond angles (in italics) in degrees.

zero to 4.7° (Figure 4). The other SS bond lengths alternate around the asymmetrical ring, with values between 198.9 and 211.9 pm. This effect is well-known from the X-ray structures of $S_7{=}O$,[33] S_7Br^+,[34] S_7I^+,[35] and S_{19}^{2+} (the last consists of two S_7 rings connected by a chain of five sulfur atoms).[36] The overall chair conformation of the seven-membered rings in S_7 and $[HS_7]^+$ is the same, and the hydrogen atom is in an axial position with the two torsion angles $\tau_{HSSS} = -30.7°$ and 109.7° (Figure 4).

However, the branched isomer $[S_6{-}SH]^+$ (**6b**), as shown in Figure 4, is by 1.8 kJ mol^{-1} more stable than the protonated unbranched ring **6a** and, therefore, represents the global minimum structure (Table 2). This isomer is of C_s symmetry and also exhibits an alternating bond length pattern within the six-membered ring of chair conformation. Because the hydrogen atom is 300.2 pm apart from the two closest sulfur atoms of the ring, there may be a weak attractive interaction between the 3p lone pairs of these atoms (pointing toward the H atom) and the positively charged hydrogen atom (+0.17).

As with the smaller $[HS_n]^+$ ions, the cation $[HS_7]^+$ favors a singlet open chain isomer. However, this chain isomer is less competitive in energy (Table 2) compared to the chainlike ions $[HS_5]^+$ and $[HS_6]^+$. It is by 47.0 kJ mol^{-1} less stable than the global minimum **6b**.

3.1.7. Octasulfur. The formal protonation of the *cyclo*-S_8 molecule results in an ion $[HS_8]^+$ (**7a**) of C_s symmetry with the eight-membered ring conformation similar to that of the free S_8 molecule and an hydrogen atom linked to one atom in an equatorial position (see Figure 4). The increased coordination number induces again a symmetrical bond length alternation in **7a** as in the case of $[HS_6]^+$ (**5a**). Compared to the free S_8 molecule, the torsion angle values within the ring are now more scattered, between 94° and 103°, but the arithmetic mean of 99.8° is very close to the value calculated for S_8 (98.0°). The NBO charges of this isomer of $[HS_8]^+$ are +0.23 for the hydrogen atom and +0.25 for the three-coordinate sulfur atom (see Figure 3).

As in the cases of S_6 and S_7, the branched structure $[S_7{-}SH]^+$ (**7b**, Figure 4) is more stable than **7a**, by 11.1 kJ mol^{-1} (Table 1). This finding is in agreement with a previous study at the HF/3-21G(d) level, which also predicted the branched structure $[S_7{-}SH]^+$ as more stable than **7a**.[15] Structure of **7b** is of C_1 symmetry with a strong bond length alternation within the seven-membered ring, with SS bonds of between 200.0 and 226.1 pm. The exocyclic SH group is in an axial position and connected to the ring by a single bond of normal length (207.1 pm). This geometry is very similar to the experimental structure of the S_{19}^{2+} cation with the connectivity [*cyclo*-$S_7{-}S_5$-*cyclo*-$S_7]^{2+}$.[36,37] The latter ion forms on oxidation of S_8 by AsF_5 in solvents of low basicity such as liquid SO_2.[37] It may well be that the first step of this reaction is an isomerization of *cyclo*-S_8 to $S_7{=}S$ under the influence of the strong Lewis acid AsF_5, which is expected to strongly stabilize the branched form by coordination to the exocyclic atom as the proton in **7b** does.

In our previous study of S_8 isomers,[38] a cluster structure of C_2 symmetry was found to be most stable structure besides the crown *cyclo*-S_8. Protonation of this cluster leads to the cation **7c** (Figure 4), which is by 7.6 kJ mol^{-1} more stable than the branched isomer **7b** (Table 1). Thus, **7c** represents the global energy minimum of $[HS_8]^+$. The overall conformational changes are small on going from the neutral to the protonated cluster form. In particular, the planar S_4 unit arising from an $\pi^*{-}\pi^*$ interaction is maintained in **7c**. However, the SS bond lengths within this planar unit are now rather different from those of the neutral cluster, with the longest distance of 344.9 pm being almost identical to the van der Waals distance between sulfur atoms (350 pm). In other words, structure **7c** represents another isomer of connectivity $[S_7{-}SH]^+$. Its connectivity is similar to that of the $S_7{=}O$ molecule.[33]

TABLE 3: Calculated G3X(MP2) Proton Binding Energies and Gas-Phase Basicities (kJ mol^{-1}) of the Branched and Unbranched Molecules S_n with n = 2−8

molecular size (n)	unbranched molecules (S_n)			branched rings ($S_{n-1}{=}S$)		
	$-\Delta E_0$	$-\Delta H_{298}$	$-\Delta G_{298}$	ΔE_0	ΔH_{298}	ΔG_{298}
H_2S	703.7	709.8	678.4			
H_2S_2	724.9	730.1	701.6			
2 (triplet)	619.4	623.9	600.5			
2 (singlet)	731.0	735.8	711.8			
3	742.8	747.7	719.3			
4	775.7	781.0	751.0	782.3	786.8	758.0
5	760.2	765.7	734.1	795.4	800.5	769.3
6	735.1	740.0	714.8	835.6	840.6	809.1
7	754.7	759.6	730.0	814.5	819.2	788.9
8	744.0	748.7	724.5	795.4	799.7	772.6

The singlet chain isomer (**7d**) is predicted to lie 69.3 kJ mol^{-1} above the branched structure (**7c**). As with other $[HS_n]^+$ open-chain isomers, the triplet chain $[HS_8]^+$ is higher in energy, by 89.6 kJ mol^{-1} (Table 2). For comparison, the neutral chainlike S_8 molecule favors the triplet state, which is significantly less stable than the global minium, the crown-S_8, by 151 kJ mol^{-1}.[38]

3.1.8. General Trends in the Geometries and Relative Energies. As with the neutral molecules S_n, the cations $[HS_n]^+$ with n = 2−4 are chainlike, and those with n = 5−8 are cyclic. And as one might have expected, the proton usually binds to the atom of highest negative atomic charge. This statement holds both for the global minimum structures of the sulfur molecules and for their higher energy isomers. In the unbranched homocycles the proton usually binds in an axial or endo position, with the protonated S_8 ring (**7a**) as the only exception. In the branched species $S_n{=}S$, protonation always takes place at the exocyclic atom. With the exception of the disulfur molecule, the protonation leads to an increase in the bond length of the neighboring SS bond(s) and in this way these bonds are activated. To cleave one of these bonds thermally requires much less energy than in the corresponding unprotonated molecules.

In all cases, protonation of the branched isomer is more favorable than the corresponding unbranched structure. For $[HS_6]^+$, $[HS_7]^+$, and $[HS_8]^+$, the differential proton stabilization is sufficiently large that the branched species becomes the global energy minimum. In sharp contrast to the neutral S_n molecules that favor a triplet chain,[30] the ground state of the open-chain ions $[HS_n]^+$ is always a singlet state. The relative stabilities of these singlet chains are significantly smaller than the corresponding neutral (unprotonated) chains. Thus, for $[HS_5]^+$, the singlet chain is just 19.1 kJ mol^{-1} above the global minimum. In summary, the branched ring and chainlike isomers are competitive in energy in the protonated sulfur clusters $[HS_n]^+$.

A common feature of the chainlike species, such as **3a**, **4c**, **5c**, and **5d**, is the planar or almost planar arrangement of the four atoms at the unprotonated chain end. This almost planar S_4 terminal unit is also a characteristic structural feature of the triplet diradicals of S_n (n = 1−10).[30]

3.2. Thermodynamic Properties. The proton affinities (PA) of the various isomers of the S_n and $S_{n-1}{=}S$ molecules (n = 2−8) are summarized in Table 3. The reliability of proton affinities calculated by the G3 and related methods (±5 kJ mol^{-1}) is well established.[20,21,39] For instance, the calculated G3X(MP2) proton affinity (ΔH_{298}) of H_2S (709.8 kJ mol^{-1}) is

TABLE 4: Calculated B3LYP/6-31G(2df,p) Vibrational Frequencies (cm^{-1}) and Infrared Intensities ($km\ mol^{-1}$) of the Protonated S_n species

species	frequency (infrared intensity)
HS_2^+ (**1a**)	2483 (16.6), 953 (0.6), 708 (0.1)
HS_3^+ (**2a**)	2621 (35.2), 878 (11.3), 711 (36.4), 506 (34.3), 378 (18.4), 222 (2.7)
HS_4^+ (**3a**)	2153 (16.0), 925 (2.5), 678 (37.3), 550 (14.0), 433 (7.8), 341 (12.1), 336 (0.1), 198 (0.1), 153 (1.6)
HS_5^+ (**4a**)	2593, (29.0), 816, (2.4), 733, (7.7), 532, (2.0), 484, (1.7), 423, (1.1), 342, (0.1), 289, (0.1), 282, (0.8), 251, (1.7), 195, (5.2), 130, (3.5)
HS_6^+ (**5a**)	2556, (19.5), 839, (6.8), 689, (7.9), 484, (0.0), 467, (0.8), 449, (0.7), 438, (0.9), 348, (1.0), 303, (0.0), 301, (4.7), 249, (0.9), 184, (0.6), 175, (0.0), 154, (1.9), 135, (0.2)
HS_6^+ (**5b**)	2647, (37.2), 889, (2.0), 534, (0.8), 496, (14.4), 474, (8.3), 409, (0.6), 334, (4.3), 312, (0.1), 302, (11.7), 270, (4.8), 246, (0.6), 241, (11.4), 201, (1.1), 133, (0.9), 65, (1.4)
HS_7^+ (**6a**)	2622, (28.9), 827, (3.2), 625, (11.0), 538, (6.9), 492, (0.5), 470, (0.9), 429, (0.4), 387, (3.6), 361, (1.1), 273, (0.9), 262, (2.9), 237, (6.1), 234, (2.8), 192, (2.7), 158, (0.8), 154, (0.3), 102, (0.6), 50, (1.3)
HS_7^+ (**6b**)	2593, (3.7), 875, (7.2), 496, (10.1), 477, (3.4), 475, (1.0), 445, (2.5), 430, (1.1), 342, (0.4), 320, (0.4), 304, (1.5), 264, (1.9), 256, (18.4), 216, (1.3), 197, (8.6), 168, (0.2), 159, (1.7), 104, (1.7), 74, (0.6)
HS_8^+ (**7a**)	2611, (59.7), 827, (2.8), 645, (10.1), 487, (2.8), 481, (1.4), 478, (0.2), 462, (0.0), 420, (0.2), 383, (2.2), 363, (0.1), 328, (0.0), 240, (1.8), 237, (0.1), 216, (0.2), 200, (0.4), 192, (4.2), 161, (4.7), 135, (0.8), 128, (0.3), 68, (1.1), 67, (0.0)
HS_8^+ (**7c**)	2651, (47.0), 866, (3.2), 631, (20.6), 541, (2.0), 521, (8.0), 497, (3.9), 382, (0.3), 349, (2.6), 320, (0.6), 304, (0.1), 286, (2.4), 248 (1.1), 231, (1.3), 205, (3.5), 177, (4.1), 161, (6.0), 144, (1.1), 136, (2.9), 103, (0.3), 90, (0.8), 58, (0.3)

in pleasing agreement with the experimental value of 705.0 kJ mol^{-1}.[18] Among all the S_n cluster species, the maximum proton affinity is obtained for $S_6{=}S$ (835.6 kJ mol^{-1}) and the minimum for triplet S_2 (619.4 kJ mol^{-1}). For the unbranched molecules S_3 to S_8, the predicted proton affinities lie in the range 731−776 kJ mol^{-1}. These values are slightly larger than those of H_2S (703.7 kJ mol^{-1}) and H_2S_2 (724.9 kJ mol^{-1}) (Table 3). The PA values of the branched species are expectedly higher than those of the related unbranched rings because of the high negative charge on the exocyclic atom (see Figure 2). The odd-numbered rings S_5 and S_7 with their planar arrangement of four atoms have higher PA values than S_6 and S_8 with their torsion angles of 73−90°; torsion angles near 0° result in a larger splitting between the π and π^* molecular orbitals and consequently in a higher HOMO energy. The following trend of the proton binding energies of the unbranched species is predicted:

$$S_4 > S_5 > S_7 > S_8 \approx S_3 > S_6 > {}^1S_2 \gg {}^3S_2$$

The gas-phase basicities ($-\Delta G$) of the unbranched homocycles S_6 and S_8 at 298 K are calculated as 714.8 and 724.6 kJ mol^{-1}, respectively, and for the branched rings as 809.2 and 772.6 kJ mol^{-1} (Table 3). The experimental values are 702 kJ mol^{-1} (S_6) and 783 kJ mol^{-1} (S_8), respectively (absolute Gibbs energies of protonation determined by FTICR spectroscopy at 298 K, ±1 kJ mol^{-1}).[15] Thus, the experimental S_6 value agrees well with the PA value predicted for the formation of the unbranched protonated ring **5a**. In the case of S_8, the observed value is in accord with the formation of the branched protonated homocycle, i.e., $[S_7{-}SH]^+$ (**7c**), in the reported experiment.

Because the proton affinities of the neutral sulfur molecules S_n are similar in value to those of H_2S (see Introduction) and H_2S_2 (718 kJ mol^{-1}),[16] it should be possible to prepare solid compounds of composition $[HS_n]X$ (n = 6−8; X: univalent anion of low basicity) in a fashion similar to that of the crystalline salts $[H_3S][SbF_6]$,[40] $[H_3S_2][AsF_6]$,[41] and $[H_3S_2][SbF_6]$,[41] which have been prepared from H_2S and H_2S_2, respectively, by protonation in the superacidic mixtures HF/AsF_5 and HF/SbF_5. Access to the species $[HS_n]X$ with n = 2−5 may be more difficult. To facilitate the future experimental observation, the predicted fundamental vibrations of the most stable $[HS_n]^+$ ions (n = 2−8) and their infrared intensities have been compiled in Table 4.

Because sulfur transfer reactions are very common between neutral and ionic sulfur molecules, we have calculated the reaction energies of the following disproportionation reactions between the most stable isomers of each composition. As can be seen below, these reactions are partly endothermic and partly exothermic:

$$2[HS_3]^+\ (\mathbf{2a}) \rightarrow [HS_2]^+\ (\mathbf{1a}) + [HS_4]^+\ (\mathbf{3a}) \qquad \Delta E_0 = +48.3\ \text{kJ mol}^{-1} \quad (2)$$

$$2[HS_4]^+\ (\mathbf{3a}) \rightarrow [HS_3]^+\ (\mathbf{2a}) + [HS_5]^+\ (\mathbf{4a}) \qquad \Delta E_0 = +20.5\ \text{kJ mol}^{-1} \quad (3)$$

$$2[HS_5]^+\ (\mathbf{4a}) \rightarrow [HS_4]^+\ (\mathbf{3a}) + [HS_6]^+\ (\mathbf{5b}) \qquad \Delta E_0 = -10.6\ \text{kJ mol}^{-1} \quad (4)$$

$$2[HS_6]^+\ (\mathbf{5b}) \rightarrow [HS_5]^+\ (\mathbf{4a}) + [HS_7]^+\ (\mathbf{6b}) \qquad \Delta E_0 = +11.1\ \text{kJ mol}^{-1} \quad (5)$$

$$2[HS_7]^+\ (\mathbf{6b}) \rightarrow [HS_6]^+\ (\mathbf{5b}) + [HS_8]^+\ (\mathbf{7c}) \qquad \Delta E_0 = -14.0\ \text{kJ mol}^{-1} \quad (6)$$

4. Summary

Protonation of gaseous neutral sulfur molecules S_n (n = 2−8) results in dramatic structural changes, and a large number of isomers of comparable energies including branched rings and singlet chains are predicted to exist as stable structures on the corresponding potential energy surfaces. Strong bond length alternation effects are predicted with the longest SS bonds originating from the three-coordinate atoms. The global minimum structures have the following connectivities and symmetries (by increasing numbers of sulfur atoms): $[HSS]^+$ (C_s), [*trans*-HSSS]$^+$ (C_s), [*cis*-HSSSS]$^+$ (C_s), [*cyclo*-HS_5]$^+$ (C_1), [*cyclo*-$S_5{-}SH$]$^+$ (C_1), [*cyclo*-$S_6{-}SH$]$^+$ (C_s), [*cyclo*-$S_7{-}SH$]$^+$ (C_1). All chainlike cations $[HS_n]^+$ (n = 2−8) are more stable in the singlet rather than the triplet state. The proton binding energies of the unbranched sulfur molecules are predicted to decrease in the following order: $S_4 > S_5 > S_7 > S_8 \approx S_3 > S_6 > {}^1S_2 \gg {}^3S_2$ (range: 619−776 kJ mol^{-1}). The binding energies of the branched rings with n = 4−8 are larger than those of the unbranched isomers because of the negative charge on the exocyclic atoms. The experimental protonation of gaseous S_6 and S_8 studied by Abboud et al.[15] using FTICR spectroscopy is shown to lead to the six-membered homocyclic cation $[HS_6]^+$ (**6a**) and to the branched ring $[S_7{-}SH]^+$ (**7c**), respectively.

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References and Notes

(1) (a) *Elemental Sulfur and Sulfur-Rich Compounds*; Steudel, R. Ed.; Topics in Current Chemistry, Vols. 230 and 231; Springer: Heidelberg, 2003; Parts I and II. (b) Steudel, R. *Chem. Rev.* **2002**, *102*, 3905−3945. (c) Davis, R. E. *Survey Prog. Chem.* **1964**, *2*, 189−238. (d) Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583−628.

(2) Steudel, R. *Angew. Chem.* **1975**, *87*, 683−692; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655−664.

(3) For calculated and experimental electron density maps of molecules containing divalent sulfur atoms, see ref 6 and: Brown, A. S.; Smith, V. H. *J. Chem. Phys.* **1993**, *99*, 1837−1843.

(4) Berkowitz, J.; Lifshitz, C. *J. Chem. Phys.* **1968**, *48*, 4346−4350.

(5) Steidel, J.; Pickardt, J.; Steudel, R. *Z. Naturforsch. Part B* **1978**, *33*, 1554−1555.

(6) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760−766.

(7) Steudel, R.; Steidel, J.; Schuster, F.; Pickardt, J.; Reinhardt, R. *Z. Naturforsch. Part B* **1980**, *35*, 1378−1383.

(8) Cheng, B.-M..; Eberhard, J.; Chen, W.-C.; Yu, C.-H. *J. Chem. Phys.* **1997**, *107*, 5273−5274.

(9) Li, W.-K.; Chiu, S.-W.; Ma, Z.-X.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1993**, *99*, 8440−8444.

(10) Chiang, S.-Y.; Ma, C.-I.; Shr, D.-J. *J. Chem. Phys.* **1999**, *110*, 9056−9063.

(11) Krossing, I.; Passmore, J. *Inorg. Chem.* **2004**, *43*, 1000−1011.

(12) Cioslowski, J.; Szarecka, A.; Moncrieff, D. *Int. J. Quantum Chem.* **2002**, *90*, 1049−1054.

(13) Wong, M. W. *Top. Curr. Chem.* **2003**, *231*, 1−29.

(14) Mineva, T.; Russo, N.; Sicilia, E.; Toscano, M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3309−3312.

(15) Abboud, J.-L. M.; Essefar, M.; Herreros, M.; Mó, O.; Molina, M. T.; Notario, R.; Yánez, M. *J. Phys. Chem. A* **1998**, *102*, 7996−8003.

(16) Otto, A. H.; Steudel, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2063−2068.

(17) (a) Harris, N. J.; Ohwada, T.; Lammertsma, K. *J. Comput. Chem.* **1998**, *19*, 250−257. (b) Markham, G. D.; Bock, C. W. *J. Phys. Chem.* **1993**, *97*, 5562−5569. (c) Del Bene, J. L.; Shavitt, I. *J. Phys. Chem.* **1990**, *94*, 5514−5518. (d) Botschwina, P.; Zilch, A.; Werner, H.-J.; Rosmus, P.; Reinsch, E.-A. *J. Chem. Phys.* **1986**, *85*, 5107−5116.

(18) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413−656.

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

(20) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108−117.

(21) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. *J. Chem. Phys.* **1999**, *110*, 4703−4709.

(22) Wong, M. W.; Steudel, R. *Chem. Phys. Lett.* **2003**, *379*, 162−169.

(23) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, M. W., Ed.; National Institute of Standards and Technology: New York, 1998.

(24) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(25) Messerschmidt, M.; Wagner, A.; Wong, M. W.; Luger, P. *J. Am. Chem. Soc.* **2002**, *124*, 732−733.

(26) McCarthy, M. C.; Thorwirth, S.; Gottlieb, C. A.; Thaddeus, P. *J. Am. Chem. Soc.* **2004**, *126*, 4096−4097.

(27) McCarthy, M. C., Thorwirth, S.; Gottlieb, C. A.; Thaddeus, P. *J. Chem. Phys.* **2004**, *121*, 632−635.

(28) Steudel, R. *Top. Curr. Chem.* **2003**, *230*, 117−134.

(29) (a) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1992**, *96*, 6579. (b) Boumedien, M. S.; Corset, J.; Picqenard, E. *J. Raman Spectrosc.* **1999**, *30*, 463.

(30) (a) Steudel, R.; Steudel, Y.; Wong, M. W. *Top. Curr. Chem.* **2003**, *230*, 117−134. (b) Wong, M. W.; Steudel, R. To be published.

(31) Hunsicker, S.; Jones, R. O.; Ganteför, G., *J. Chem Phys.* **1995**, *102*, 5917−5936.

(32) Wong, M. W.; Steudel, Y.; Steudel, R. *J. Chem. Phys.*, in press.

(33) (a) Steudel, R.; Reinhardt, R.; Sandow, T. *Angew. Chem.* **1977**, *89*, 757−758; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 716−717. (b) R. Steudel, *Top. Curr. Chem.* **2003**, *231*, 203−230.

(34) Passmore, J.; Sutherland, G.; Whidden, T. K.; White, P. S.; Wong, C.-M. *Can. J. Chem.* **1985**, *63*, 1209−1214.

(35) Passmore, J.; Sutherland, G.; White, P. S. *Inorg. Chem.* **1982**, *21*, 2717−2723.

(36) Faggiani, R.; Gillespie, R. J.; Sawyer, J. F.; Vekris, J. E. *Acta Crystallogr.* **1989**, *C45*, 1847−1853.

(37) Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423−1432.

(38) Wong, M. W.; Steudel, Y.; Steudel, R. *Chem. Phys. Lett.* **2002**, *364*, 387−392.

(39) Curtiss, L. A.; Ragavachari, K. *Theor. Chim. Acta* **2002**, *108*, 61−70.

(40) Christe, K. O. *Inorg. Chem.* **1975**, *14*, 2230−2233.

(41) Minkwitz, R.; Kornath, A.; Sawodny, W.; Hahn, J. *Inorg. Chem.* **1996**, *35*, 3622−3625.