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Conformations and Thermodynamic Properties of Sulfur Homocycles. 1. The S_5, S_6, S_7, and S_8 Molecules

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Results of B3LYP/6-311G* and MP2/6-311G* electronic structure calculations provide a comprehensive characterization of all the conformers of the S_5, S_6, S_7, and S_8 homocycles and elucidate their interconversions. The S_5 ring is confirmed to exist exclusively in a highly fluxional C_s conformation. Two conformers of the S_6 homocycle, linked through two transition states, are identified: the D_{3d} structure corresponding to a global energy minimum and the higher-energy species possessing C_{2v} symmetry. The S_7 ring is found to adopt one of two highly fluxional C_s conformations that are separated by a substantial barrier. The complete set of the conformers of the S_8 homocycle, which consists of the C_{2v}, C_2, C_s (and possibly also C_{2h}) structures in addition to the low-energy D_{4d} species, is uncovered.

Introduction

With over 20 known crystalline allotropes,[1−6] all of which are composed of homocyclic rings (homocycles) with as many as 20 atoms, sulfur is unique in its propensity to catenation. The homocycles, which are also constituents of molten sulfur[7−9] and its vapors,[10−13] exhibit reactivities towards organic molecules that are markedly size-dependent.[14−16] Since reactions of elemental sulfur with organic species are of great practical importance due to their role in the formation of undesirable contaminants of fossil fuels,[17] understanding of the factors that determine thermodynamic properties of sulfur allotropes is of much interest to both theoretical and experimental chemists.

During the past decade, a large number of electronic structure studies of sulfur rings have appeared in the chemical literature.[18−29] However, even in the case of the most common S_8 homocycle, none of those studies[18,19,22−24,27−29] has resulted in a definitive characterization of all low-energy conformers and elucidation of their interconversion pathways. Prompted by this lack of data, we have recently carried out extensive quantum-chemical calculations on the S_5, S_6, S_7, and S_8 species. The results of these calculations are presented in the following.

Results and Discussion

The Gaussian 98 suite of programs[30] was employed in all calculations reported in this paper. The stationary points resulting from exhaustive searches within respective potential energy hypersurfaces were characterized by their vibrational frequencies computed at both the B3LYP/6-311G*and MP2/6-311G* levels of theory. The computed standard enthalpies of the interconversion reactions

$$S_8 \rightarrow (8/n)\, S_n, \quad n = 5, 6, \text{and } 7 \qquad (1)$$

are listed in Table 1 together with the previously published theoretical and experimental data.

TABLE 1: Reaction Enthalpies of Sulfur Homocycle Interconversions

method	temp range (K)	reaction enthalpy (kcal/mol) $S_8 \rightarrow {}^8/_5\, S_5$	$S_8 \rightarrow {}^8/_6\, S_6$	$S_8 \rightarrow {}^8/_7\, S_7$
B3LYP/6-311G* [a]	298	28.5	11.7	7.2
MP2/6-311G* [a]	298	29.2	10.5	7.7
HF/DZP[18]	298	28.2	6.3	8.8
MP2/DZP[18]	298	29.1	9.6	7.4
MP3/6-31G*[19,22]	0	29.1	9.2	8.5
HPLC[b] [9]	389−432	n/a	7.1 ± 0.2	5.8 ± 0.2
HPLC[c] [32]	403−428	n/a	7.6	5.7
mass spectrosc[d] [12]	435−625	20.3 ± 3.1[e]	8.3 ± 0.4	6.6 ± 0.4
mass spectrosc[d] [10]	ca. 400	22.9	8.3	6.5
vap.press.[d] [13]	298	17.4	8.1	6.7

[a] Present work. [b] Molten sulfur. [c] CS_2 solution. [d] Vapor. [e] At 565−620 K.

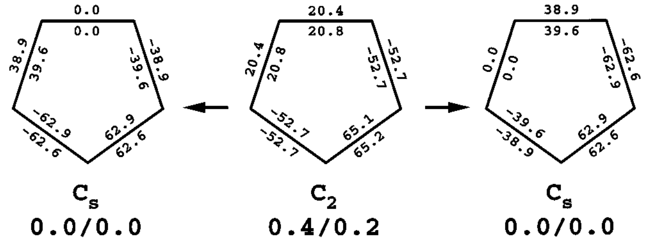

Figure 1. Pseudorotation of the C_s conformer of the S_5 homocycle. The B3LYP/6-311G* and MP2/6-311G* dihedral angles are listed inside and outside the rings, respectively. The B3LYP/6-311G* energies at 0 K (including ZPEs) relative to that of a global minimum are followed by their MP2/6-311G* counterparts.

The relatively low thermodynamic stability of the S_5 homo cycle, which is formed during photolysis of S_7 in CS_2,[31] may explain the fact that thus far it has not been isolated in a crystalline form. Although the B3LYP/6-311G* and MP2/6-311G* standard enthalpies of the $S_8 \rightarrow (8/5)S_5$ interconversion agree within 0.7 kcal/mol and are very close to the previously published theoretical estimates,[18,19] they are substantially higher than the available gas-phase data. The reasons for this discrepancy are unclear at present.

Only one minimum pertinent to a cyclic S_5 is located at both levels of theory. The envelope-like C_s conformer of S_5, which

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TABLE 2: Geometrical Parameters of the C_s Conformer of the S_5 Homocycle[a]

method	$r_{S_1S_2}$ $r_{S_1S_5}$	$r_{S_2S_3}$ $r_{S_4S_5}$	$r_{S_3S_4}$
B3LYP/6-311G*[b]	2.135	2.071	2.256
MP2/6-311G*[b]	2.084	2.061	2.193
HF/3-21G[19]	2.061	2.066	2.141
HF/DZP[18]	2.066	2.074	2.138

method	$\alpha_{S_1S_2S_3}$ $\alpha_{S_1S_5S_4}$	$\alpha_{S_2S_3S_4}$ $\alpha_{S_3S_4S_5}$	$\alpha_{S_5S_1S_2}$
B3LYP/6-311G*[b]	100.3	100.8	90.7
MP2/6-311G*[b]	99.5	101.3	92.1
HF/3-21G[19]	98.9	102.2	94.1
HF/DZP[18]	99.0	102.3	94.2

method	$\varphi_{S_5S_1S_2S_3}$ $-\varphi_{S_2S_1S_5S_4}$	$\varphi_{S_1S_2S_3S_4}$ $-\varphi_{S_3S_4S_5S_1}$
B3LYP/6-311G*[b]	62.9	−39.6
MP2/6-311G*[b]	62.6	−38.9
HF/3-21G[19]	61.0	−37.6
HF/DZP[18]	60.7	−37.4

[a] All bond lengths in Å, all bond and dihedral angles in deg. [b] Present work.

TABLE 3: Relative Thermodynamic Properties of Various Conformers of the S_6, S_7, and S_8 Homocycles[a]

species	conformer	ΔH (0 K)	ΔH^0	ΔG^0
S_6	D_{3d}	0.0	0.0	0.0
	C_{2v}	11.7/12.9	11.8/13.2	10.4/11.3
S_7	C_s (exo)	0.0	0.0	0.0
	C_s (endo)	3.0/4.0	3.1/4.1	2.1/3.4
S_8	D_{4d}	0.0	0.0	0.0
	C_{2v}	12.7/15.4	12.8/15.9	11.7/13.8
	C_{2h}[b]	13.8	14.0	12.1
	C_2	9.4/9.4	9.5/9.6	7.8/8.0
	C_s	9.0/8.3	9.1 /8.4	7.4/6.8

[a] Present work. The B3LYP/6-311G* data followed by the MP2/6-311G* data, all values in kcal/mol. [b] The C_{2h} conformer is a transition state at the MP2/6-311G* level of theory.

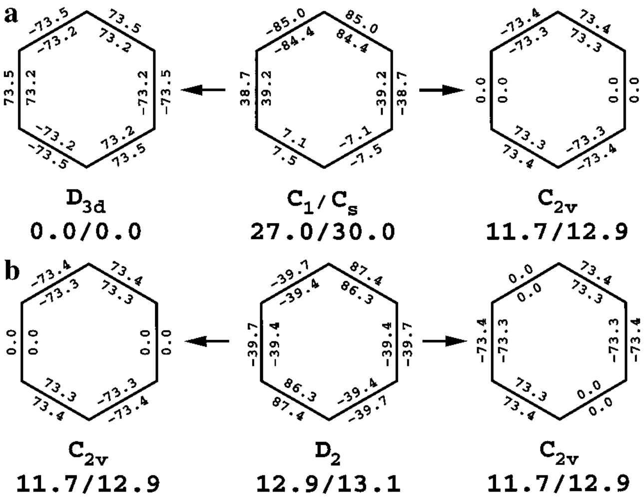

Figure 2. Interconversions among conformers of the S_6 homocycle (see Figure 1 for explanation): (a) the D_{3d}/C_{2v} ring flipping and (b) the C_{2v} pseudorotation.

exhibits a well-pronounced bond alternation (Table 2), undergoes a facile pseudorotation through a C_2 transition state (Figure 1). The computed barrier to this pseudorotation amounts to less than 0.5 kcal/mol, in agreement with the HF/DZP[18] and HF/3-21G*[19] predictions. It should be noted that LDA calculations find the C_2 structure to be a minimum that is almost isoenergetic with its C_s counterpart.[27]

TABLE 4: Geometrical Parameters of the D_{3d} Conformer of the S_6 Homocycle

method	r_{SS} (Å)	α_{SSS} (deg)	φ_{SSSS} (deg)
B3LYP/6-311G*[a]	2.121	102.9	73.2
MP2/6-311G*[a]	2.086	102.8	73.5
HF/DZ[20]	2.253	101.2	76.1
HF/3-21G*[19,22]	2.064	102.5	73.9
HF/3-21G*[21]	2.073	102.4	74.1
HF/DZP[18]	2.070	102.6	73.8
HF/DZP[20]	2.080	102.4	74.1
HF/TZ2P[20]	2.082	102.4	74.1
MP2/DZP[20]	2.085	102.3	74.3
MP2/TZ2P[20]	2.104	102.1	74.6
X-ray[b] [33]	2.068	102.6	73.8
X-ray[34]	2.057	102.2	74.5

[a] Present work. [b] At 180 K.

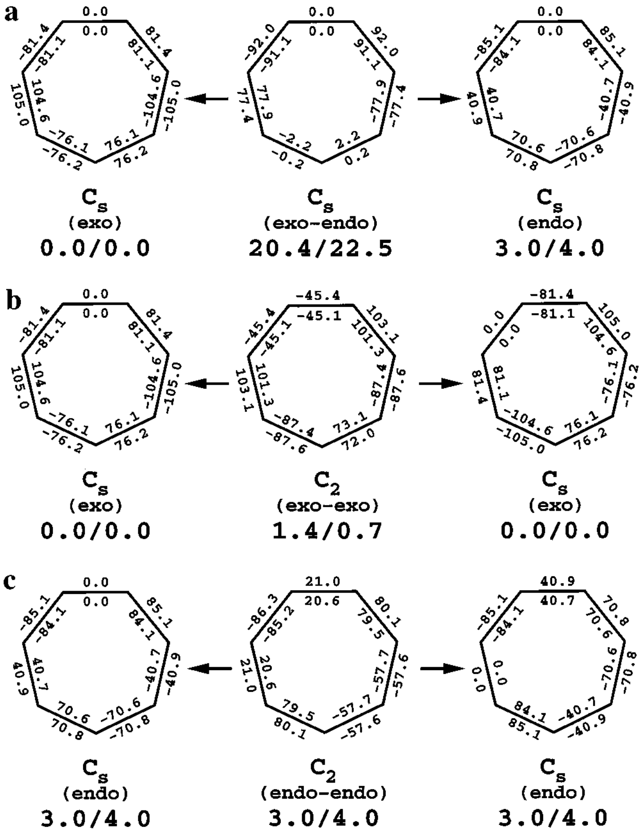

Figure 3. Interconversions among conformers of the S_7 homocycle (see Figure 1 for explanation): (a) the C_s (exo)/C_s (endo) ring flipping, (b) the C_s (exo) pseudorotation, and (c) the C_s (endo) pseudorotation.

Two conformers are found for the S_6 homocycle. The D_{3d} (or chair) structure, which is a global minimum, lies 12−13 kcal/mol below the less stable C_{2v} (or boat) species (Table 3). The $D_{3d} \rightarrow C_{2v}$ interconversion involves a barrier of ca. 30 kcal/mol. Depending on the level of theory, the corresponding transition state possesses either C_1 or C_s symmetry (Figure 2a). The C_{2v} conformer is predicted to readily pseudorotate through a D_2 transition state (Figure 2b), as indicated by the barrier of only ca. 1.2 (B3LYP/6-311G*) and 0.2 kcal/mol (MP2/6-311G*).

The present findings are in partial disagreement with the published HF/3-21G* studies.[19,21,22] In particular, the D_2 structure is a transition state rather than a minimum at both levels of theory, underlining the importance of inclusion of electron correlation effects in conformational analysis of sulfur homocycles. Moreover, the C_2 structure[21] is not a stationary

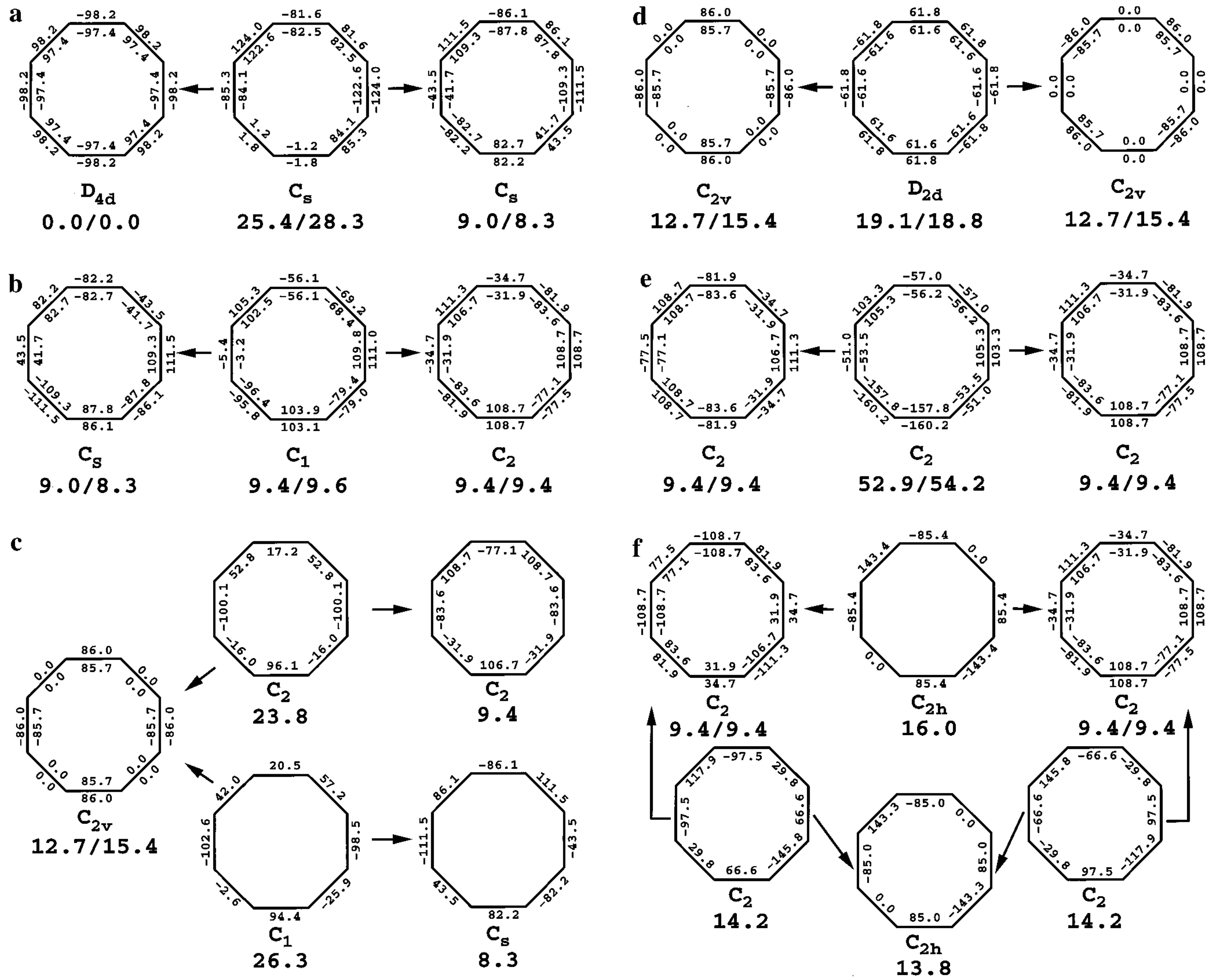

Figure 4. Interconversions among conformers of the S_8 homocycle (see Figure 1 for explanation): (a) the D_{4d} /C_s ring flipping, (b) the C_s /C_2 interconversion, (c) the C_{2v} /C_2 and C_{2v} /C_s interconversions, (d) the C_{2v} pseudorotation, (e) the C_2 pseudorotation, and (f) the C_2 inversion/ pseudorotation.

point at all. The computed geometrical parameters of the D_{3d} conformer are similar to those obtained previously,[18−22] although the MP2/6-311G* S−S bond length is in closer agreement with the experimental data[33,34] than its B3LYP/6-311G* counterpart (Table 4).

There are two C_s conformers of the S_7 homocycle. The C_s (exo) global minimum lies 3−4 kcal/mol below its C_s (endo) counterpart (Table 3). The C_s (exo) conformer possesses the geometry found in the γ-S_7 and δ-S_7 sulfur allotropes,[35,36] the MP2/6-311G* bond lengths, bond angles, and dihedral angles agreeing well with the respective X-ray data (Table 5). The two C_s minima are separated by a barrier of ca. 20 kcal/mol, which is associated with a transition state of C_s symmetry (Figure 3a). Both the C_s (exo) and C_s (endo) conformers are predicted to undergo facile pseudorotations through C_2 transition states, the barrier being only ca. 1 kcal/mol in the former case (Figure 3b) and essentially nil in the latter one (Figure 3c). This prediction is supported by experimental observations.[37,38]

As in the instance of the S_6 homocycle, the present results disagree with those published previously. In variance with the findings at the HF/DZP[18] and HF/3-21G*[19,22] levels of theory, no symmetry breaking is observed for the C_s (exo) structure. Moreover, the C_2 structure[19,21,22] is now identified as the transition state for the pseudorotation of the C_s (endo) conformer.

Among the conformers of the S_8 homocycle, the highly symmetrical D_{4d} structure is found to be a global minimum at both levels of theory (Table 3). This exo−exo conformer, which constitutes the building block of the common crystalline sulfur,[39−43] has been the subject of several electronic structure studies.[18,19,22−24] As in the case of the S_6 and S_7 species, the computed MP2/6-311G* geometrical parameters are in good agreement with their experimental counterparts (Table 6).

Ring flipping in the D_{4d} conformer produces the endo−exo C_s structure with energy higher by ca. 8−9 kcal/mol. The barrier to this process, which involves a C_s transition state, is predicted to be over 25 kcal/mol (Figure 4a). The C_s species undergoes a facile (a barrier of less than 1.5 kcal/mol, Figure 4b) twisting to a less symmetrical C_2 conformer that is only slightly less stable. At the MP2/6-311G* level of theory, the C_s conformer is related to the boat-like C_{2v} structure through a C_1 transition state (Figure 4c), whereas the B3LYP/6-311G* calculations yield a C_2 transition state linking the C_{2v} and C_2 structures (Figure 4c). In either case, the computed barrier to interconversion is quite high.

Both the C_{2v} and C_2 conformers are capable of pseudorotation. The D_{2d} transition state for the former process (Figure 4d) is identical with the previously investigated endo−endo structure.[24] The C_2 pseudorotation is found to proceed through two distinct

TABLE 5: Geometrical Parameters of the C_s(exo) Conformer of the S_7 Homocycle[a]

method	$r_{S_1S_2}$ $r_{S_1S_7}$	$r_{S_2S_3}$ $r_{S_6S_7}$	$r_{S_3S_4}$ $r_{S_5S_6}$	$r_{S_4S_5}$
B3LYP/6-311G*[b]	2.098	2.172	2.027	2.271
MP2/6-311G*[b]	2.070	2.113	2.014	2.207
HF/3-21G*19,22	2.052	2.073	2.018	2.144
HF/3-21G*[21]	2.056	2.083	2.015	2.200
HF/DZP[18]	2.029	2.079	2.060	2.144
X-ray (monoclinic γ-S_7)[c 35]	2.048	2.099	1.998	2.175
X-ray (monoclinic δ-S_7)[d 35,36]	2.050	2.101	1.996	2.181

method	$\alpha_{S_1S_2S_3}$ $\alpha_{S_1S_7S_6}$	$\alpha_{S_2S_3S_4}$ $\alpha_{S_5S_6S_7}$	$\alpha_{S_3S_4S_5}$ $\alpha_{S_4S_5S_6}$	$\alpha_{S_7S_1S_2}$
B3LYP/6-311G*[b]	103.1	107.4	108.8	107.4
MP2/6-311G*[b]	103.0	106.8	108.8	106.8
HF/3-21G*[19,22]	103.0	105.5	109.2	105.8
HF/3-21G*[21]	102.8	105.6	108.8	105.9
HF/DZP[18]	105.5	103.0	106.4	109.5
X-ray (monoclinic γ-S_7)[c 35]	102.1	105.4	107.4	105.0
X-ray (monoclinicδ-S_7)[d35,36]	102.2	105.3	107.1	106.1

method	$\varphi_{S_7S_1S_2S_3}$ $-\varphi_{S_2S_1S_7S_6}$	$\varphi_{S_1S_2S_3S_4}$ $-\varphi_{S_5S_6S_7S_1}$	$\varphi_{S_2S_3S_4S_5}$ $-\varphi_{S_4S_5S_6S_7}$
B3LYP/6-311G*[b]	76.1	−104.6	81.1
MP2/6-311G*[b]	76.2	−105.0	81.4
HF/3-21G*[19,22]	77.0	−105.2	81.4
HF/3-21G*[21]	77.7	−105.7	81.3
HF/DZP[18]	76.8	−104.6	81.4
X-ray (monoclinic γ-S_7)[c 35]	76.7	−107.8	83.3
X-ray (monoclinic δ-S_7)[35,36]	75.2	−107.5	84.0

[a] All bond lengths in Å, all bond and dihedral angles in deg. [b] Present work. [c] At 160 K. [d] At 160 K, an average of values for two independent molecules.

TABLE 6: Geometrical Parameters of the D_{4d} Conformer of the S_8 Homocycle

method	r_{SS} (Å)	α_{SSS} (deg)	φ_{SSSS} (deg)
B3LYP/6-311G*[a]	2.110	109.1	97.4
MP2/6-311G*[a]	2.075	108.5	98.2
HF/3-21G*[19,22]	2.052	107.1	99.8
HF/DZ[23]	2.240	104.7	102.4
HF/DZP[23]	2.070	106.8	100.1
HF/DZP[18]	2.060	107.2	99.7
HF/6-311G*[24]	2.069	107.4	n/a
BLYP/6-311G*[24]	2.146	109.8	n/a
X-ray (monoclinic S_8)[b39]	2.045	107.9	n/a
X-ray (monoclinic β-S_8)[c40]	2.050	107.8	98.9
X-ray (monoclinic γ-S_8)[b41]	2.045	107.7	n/a
X-ray (orthorhombic α-S_8)[42]	2.055	108.2	98.5
X-ray (orthorhombic S_8)[d 43]	2.050	108.2	n/a
neutron diff (orthorhombic S_8)[43]	2.046	108.3	n/a

[a] Present work. [b] An average of values for two independent molecules. [c] At 113 K, an average of values for three independent molecules. [d] At 100 K.

pathways. A simple pseudorotation through a C_2 transition state (Figure 4e) is associated with an exceedingly high barrier. On the other hand, pseudorotation to the C_2 enantiomer is much more facile (Figure 4f). At the B3LYP/6-311G* level of theory, such a pseudorotation involves a pair of C_2 transition states that are almost isoenergetic with a chair-like C_{2h} intermediate, which is a transition state according to the MP2/6-311G* calculations.

Conclusions

The present study provides a comprehensive characterization of all the conformers of the S_5, S_6, S_7, and S_8 homocycles and elucidates their interconversions. The results of MP2/6-311G* calculations disagree with those yielded by the B3LYP/6-311G* level of theory only in minor details. Since these two treatments of electron correlation are known to exhibit different sensitivity to the basis set size, such an agreement indicates the adequacy of the levels of theory used. The S_5 ring is confirmed to exist exclusively in a highly fluxional C_s conformation. Two conformers of the S_6 homocycle, linked through two transition states, are identified, the D_{3d} structure corresponding to a global energy minimum and the higher-energy species possessing C_{2v} symmetry. The S_7 ring is found to adopt one of two highly fluxional C_s conformations that are separated by a substantial barrier. The complete set of the conformers of the S_8 homocycle, which consists of the C_{2v}, C_2, C_s (and possibly also C_{2h}) structures in addition to the low-energy D_{4d} species, is uncovered.

The availability of these data is expected to aid experimental research on high-temperature reaction of elemental sulfur with organic and inorganic molecules. In particular, it will allow an accurate estimation of thermodynamic properties of sulfur allotropes and the prediction of their relative reactivities toward various compounds.

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