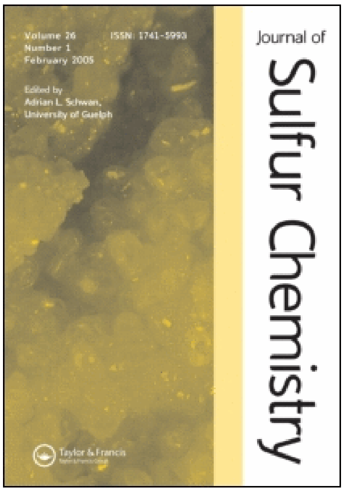

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A conceptual density functional study of structure, bonding, reactivity and the possibility of bond-stretch isomerism in some neutral sulfur clusters, S<i>n</i> (*n*=3-8)

Soma Duley[a]; Arindam Chakraborty[a]; Santanab Giri[a]; Pratim K. Chattaraj[a]
[a] Department of Chemistry and Center for Theoretical Studies, Indian Institute of Technology, Kharagpur, India

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A conceptual density functional study of structure, bonding, reactivity and the possibility of bond-stretch isomerism in some neutral sulfur clusters, S_n (n = 3–8)

Soma Duley, Arindam Chakraborty, Santanab Giri and Pratim K. Chattaraj*

Department of Chemistry and Center for Theoretical Studies, Indian Institute of Technology, Kharagpur 721 302, India

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Geometries of different isomers of various neutral sulfur clusters, S_n ($n = 3$–8) are optimized at the B3LYP/6-311+G* level of theory. Their stability and aromaticity behavior are analyzed in terms of the conceptual density functional theory-based reactivity descriptors and the associated electronic structure principles. The nucleus-independent chemical shift lends additional support. Possibility of bond-stretch isomerism in these clusters is explored.

Keywords: sulfur clusters; conceptual DFT; aromaticity; NICS; electronic structure principle

1. Introduction

The term "allotropy" is generally associated with the elements such as boron, carbon, phosphorus, oxygen, sulfur, silicon and arsenic. However, the element sulfur, S, occupies a unique position in the periodic table with regard to one of the largest numbers of allotropic modifications than any other element. Consequently, a varied number of conformations in open chain-like, closed cyclic or puckered chair/boat forms have been obtained experimentally in the solid, liquid and vapor phases for the sulfur clusters (S_n) (*1–5*). A number of computations at various moderate to higher levels of theory have already been performed to understand the structural and stability aspects of the sulfur clusters. Molecular dynamics and density functional (DF) calculations by Hohl *et al*. (*6*), semi-empirical molecular method calculations by Jug and Iffert (*7*), *ab initio* calculations at HF/3-21G* level by Raghavachari *et al*. (*8*) for small to moderately sized S_n clusters deserve mention. The several plausible isomers of S_3, S_4 and S_5 have been investigated by both *ab initio* (*9*) and Configuration Interaction (CI) approach (*10, 11*). Extensive DF calculations for a number of cationic (S_n^+) (*12*), anionic (S_n^-) (*13*) as well as neutral (S_n) (*14*) sulfur clusters have also been reported.

In this study, we intend to investigate a number of neutral S_n clusters ($n = 3$–8) with the aid of conceptual DF theory (CDFT) (*15–18*). The structural and bonding fascia of all the

*Corresponding author. Emails: pkc@chem.iitkgp.ernet.in; pratim.chattaraj@gmail.com

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possible geometries of the neutral S_n clusters are scrutinized with the aid of various CDFT-based global reactivity descriptors such as electronegativity (χ) (*19–21*), hardness (η) (*22–24*) and electrophilicity (ω) (*25–27*). Many of the neutral S_n isomers for a particular value of n may have a very elusive existence (*28*) and hence may not correspond to the global minimum on the potential energy surface (PES). They will thus correspond to the local minima positions or saddle points on the PES. Thus, a fair possibility of the existence of bond-stretch isomerism (*29–37*) cannot be ruled out for the S_n clusters for a particular n value. Further, for the sulfur clusters, it has been reported that different theoretical methods give varying results (*38*), which lead to an inexact determination of the true global minimum and corresponding saddle points. The CDFT-based global and local reactivity descriptors may also provide valuable insights into the actual global minimum and the respective saddle points on the PES for the sulfur clusters. The nucleus-independent chemical shift calculated at the ring center (NICS(0)) computed by using the procedure suggested by Schleyer *et al.* (*39*) justifies the aromaticity trends and hence the stability aspects of the various isomers of the neutral S_n ($n = 3$–8) clusters.

2. Theoretical background

The actual ground state of a molecular electronic system is generally characterized by its existence at the global minimum position on the PES. However, as quoted earlier, the system may also exist in several other isomeric forms which differ very little in their energy (E) values that occupy the local minima on the PES. The condition of a global minimum may be well justified from the seminal concepts of maximization in the hardness (*40–42*) (η) and minimization in the polarizability (*43, 44*) (α) and electrophilicity (*45, 46*) (ω) values. The above electronic structure principles complement the role played by E in rationalizing the structure and stability of molecular clusters. In an N-electron system, the electronegativity (*19–21*) (χ) and hardness (*22–24*) (η) can be defined as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})}, \tag{2}$$

where E is the total energy of the N-electron system and μ and $v(\vec{r})$ are its chemical potential and external potential, respectively. The electrophilicity (*25–27*) (ω) is defined as:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}. \tag{3}$$

A finite difference approximation to Equations (1) and (2) can be expressed as:

$$\chi = \frac{I + A}{2} \tag{4}$$

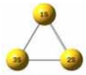
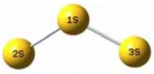
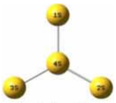
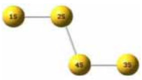
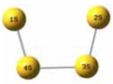
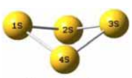
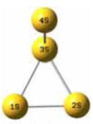
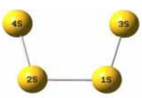
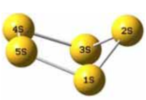
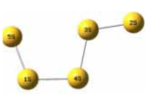
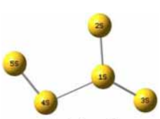
and

$$\eta = I - A, \tag{5}$$

where I and A represent the ionization potential and electron affinity of the system, respectively, and are computed in terms of the energies of the N and $N \pm 1$ electron systems. For an N-electron system with energy $E(N)$, they may be expressed as follows:

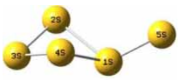
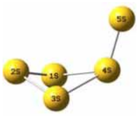
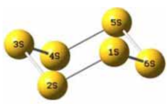
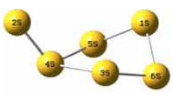
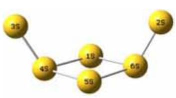
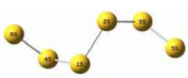
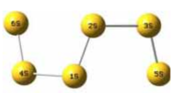
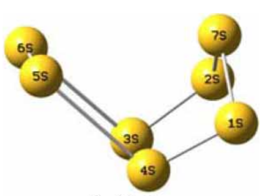
$$I = E(N-1) - E(N) \tag{6}$$

Table 1. The geometrical parameters of the isomers of S_n (n = 3–8) clusters.

Isomers	Bond distances (Å)	Bond angles (°)
 S_3 (a)_D_{3h}	$R(1,2) = 2.128$ $R(2,3) = 2.128$ $R(1,3) = 2.128$	$A(1,2,3) = 60.00$ $A(2,1,3) = 60.00$ $A(2,3,1) = 60.00$
 S_3 (b)_C_{2v}	$R(1,2) = 1.952$ $R(1,3) = 1.952$ $R(2,3) = 3.351$	$A(2,1,3) = 113.22$
 S_4 (a)_ D_{3h}	$R(1,4) = 1.949$ $R(2,4) = 1.949$ $R(3,4) = 1.949$	$A(1,4,3) = 120.00$ $A(2,4,3) = 120.00$ $A(1,4,2) = 120.00$
 S_4 (b)_ C_{2h}	$R(1,2) = 1.951$ $R(3,4) = 1.951$ $R(2,4) = 2.146$	$A(1,2,4) = 120.23$ $A(2,4,3) = 120.23$
 S_4 (c)_ C_{2v}	$R(1,4) = 1.934$ $R(2,3) = 1.934$ $R(3,4) = 2.226$	$A(1,4,3) = 109.50$ $A(2,3,4) = 109.49$
 S_4 (d)_ D_{2d}	$R(1,2) = 2.168$ $R(2,3) = 2.171$ $R(3,4) = 2.168$ $R(1,4) = 2.166$	$A(2,1,4) = 84.95$ $A(1,2,3) = 84.82$ $A(2,3,4) = 84.81$ $A(1,4,3) = 84.93$
 S_4 (e)_C_s	$R(1,2) = 2.138$ $R(2,3) = 2.233$ $R(1,3) = 2.233$ $R(3,4) = 1.929$	$A(2,3,4) = 116.80$ $A(1,3,4) = 116.80$ $A(1,2,3) = 61.40$ $A(2,1,3) = 61.38$ $A(2,3,1) = 57.22$
 S_4 (f)_ C_{2v}	$R(1,2) = 2.229$ $R(2,4) = 1.394$ $R(1,3) = 1.394$	$A(1,2,4) = 104.57$ $A(2,1,3) = 104.57$
 S_5 (a)_C_s	$R(1,2) = 2.136$ $R(2,3) = 2.136$ $R(3,4) = 2.072$ $R(1,5) = 2.072$ $R(4,5) = 2.255$	$A(1,2,3) = 90.70$ $A(2,3,4) = 100.25$ $A(2,1,5) = 100.27$ $A(1,5,4) = 100.91$ $A(3,4,5) = 100.91$
 S_5 (b)_ C_s	$R(1,5) = 1.966$ $R(1,4) = 2.134$ $R(3,4) = 2.136$ $R(2,3) = 1.959$	$A(2,3,4) = 109.92$ $A(3,4,1) = 101.81$ $A(4,1,5) = 110.49$
 S_5 (c)_ C_s	$R(1,2) = 1.953$ $R(1,3) = 1.955$ $R(1,4) = 2.385$ $R(4,5) = 1.929$	$A(2,1,3) = 125.13$ $A(3,1,4) = 121.69$ $A(1,4,5) = 103.30$ $A(2,1,4) = 110.80$

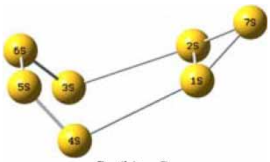
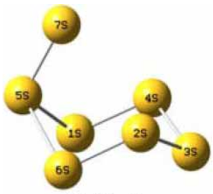
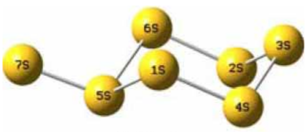
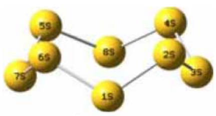
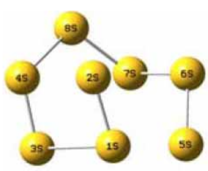
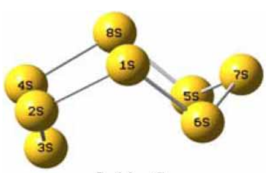
(*Continued*)

Table 1. Continued.

Isomers	Bond distances (Å)	Bond angles (°)
 S_5 (d)_ C_s	$R(1,2) = 2.376$ $R(2,3) = 2.114$ $R(3,4) = 2.115$ $R(1,4) = 2.371$ $R(1,5) = 1.921$	$A(1,2,3) = 81.44$ $A(1,4,3) = 81.52$ $A(2,3,4) = 91.26$ $A(2,1,4) = 79.11$ $A(2,1,5) = 114.83$ $A(4,1,5) = 114.68$
 S_5 (e)_ C_s	$R(1,2) = 2.097$ $R(2,3) = 2.094$ $R(3,4) = 2.406$ $R(1,4) = 2.398$ $R(1,5) = 1.928$	$A(1,2,3) = 91.76$ $A(1,4,3) = 77.56$ $A(2,1,4) = 87.33$ $A(2,3,4) = 87.17$ $A(1,4,5) = 115.75$ $A(2,3,4) = 115.89$
 S_6 (a)_D_{3d}	$R(1,2) = 2.120$ $R(2,3) = 2.120$ $R(3,4) = 2.120$ $R(4,5) = 2.120$ $R(5,6) = 2.120$ $R(1,6) = 2.120$	$A(1,2,3) = 103.13$ $A(2,3,4) = 103.11$ $A(3,4,5) = 103.14$ $A(4,5,6) = 103.12$ $A(5,6,1) = 103.10$ $A(6,1,2) = 103.15$
 S_6 (b)_C_1	$R(2,4) = 1.938$ $R(3,4) = 2.393$ $R(4,5) = 2.344$ $R(1,5) = 2.074$ $R(1,6) = 2.138$ $R(3,6) = 2.052$	$A(2,4,5) = 116.33$ $A(4,5,1) = 103.64$ $A(5,1,6) = 96.21$ $A(1,6,3) = 97.22$ $A(3,4,6) = 103.98$ $A(2,4,3) = 104.18$
 S_6 (c)_ C_{2v}	$R(1,4) = 2.270$ $R(1,6) = 2.270$ $R(4,5) = 2.270$ $R(5,6) = 2.270$ $R(3,4) = 1.938$ $R(2,5) = 1.938$	$A(1,4,5) = 86.89$ $A(4,1,6) = 93.04$ $A(5,6,1) = 86.89$ $A(4,5,6) = 93.04$ $A(3,4,5) = 112.92$ $A(5,6,2) = 112.92$ $A(1,4,3) = 112.92$ $A(1,6,2) = 112.92$
 S_6 (d)_ C_2	$R(1,2) = 2.303$ $R(2,3) = 2.056$ $R(1,4) = 2.056$ $R(3,5) = 1.966$ $R(4,6) = 1.966$	$A(5,3,2) = 114.65$ $A(1,2,3) = 109.57$ $A(2,1,4) = 109.57$ $A(1,4,6) = 114.65$
 S_6 (e)_ C_2	$R(1,2) = 1.986$ $R(2,3) = 2.313$ $R(1,4) = 2.313$ $R(3,5) = 1.942$ $R(4,6) = 1.942$	$A(5,3,2) = 109.91$ $A(1,2,3) = 105.24$ $A(2,1,4) = 105.24$ $A(1,4,6) = 109.91$
 S_7 (a)_C_s	$R(1,7) = 2.108$ $R(2,7) = 2.108$ $R(1,4) = 2.117$ $R(2,3) = 2.117$ $R(4,5) = 3.094$ $R(3,6) = 3.094$ $R(5,6) = 1.952$	$A(4,1,7) = 99.10$ $A(1,4,5) = 104.75$ $A(4,5,6) = 92.09$ $A(5,6,3) = 92.09$ $A(2,3,6) = 104.75$ $A(3,2,7) = 99.10$ $A(2,7,1) = 93.12$

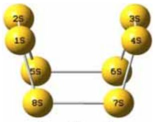
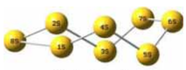
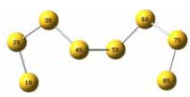
(*Continued*)

Table 1. Continued.

Isomers	Bond distances (Å)	Bond angles (°)
 S_7 (b)_ C_s	$R(1, 7) = 2.134$ $R(2, 7) = 2.134$ $R(1, 4) = 3.563$ $R(2, 3) = 3.563$ $R(4, 5) = 1.994$ $R(3, 6) = 1.936$ $R(5, 6) = 2.212$ $R(1, 2) = 2.118$	$A(2, 1, 7) = 60.23$ $A(1, 7, 2) = 59.54$ $A(1, 2, 7) = 60.23$ $A(3, 4, 5) = 74.43$ $A(3, 4, 6) = 74.43$ $A(3, 6, 5) = 105.58$ $A(4, 5, 6) = 105.57$
 S_7 (c)_ C_s	$R(1, 4) = 2.025$ $R(2, 6) = 2.025$ $R(3, 4) = 2.025$ $R(2, 3) = 2.149$ $R(1, 5) = 2.451$ $R(5, 6) = 2.451$ $R(5, 7) = 1.928$	$A(2, 3, 4) = 102.56$ $A(3, 4, 1) = 107.12$ $A(3, 2, 6) = 107.12$ $A(2, 6, 5) = 97.56$ $A(4, 1, 5) = 97.56$ $A(6, 5, 1) = 91.64$ $A(1, 5, 7) = 105.37$ $A(6, 5, 7) = 105.37$
 S_7 (d)_ C_s	$R(1, 4) = 2.071$ $R(2, 6) = 2.071$ $R(3, 4) = 2.126$ $R(2, 3) = 2.126$ $R(1, 5) = 2.327$ $R(5, 6) = 2.327$ $R(5, 7) = 1.942$	$A(2, 3, 4) = 101.01$ $A(3, 4, 1) = 105.55$ $A(3, 2, 6) = 105.54$ $A(2, 6, 5) = 102.06$ $A(4, 1, 5) = 102.06$ $A(6, 5, 1) = 97.63$ $A(1, 5, 7) = 106.79$ $A(6, 5, 7) = 106.79$
 S_8 (a)_ S_8	$R(1, 2) = 2.108$ $R(2, 3) = 2.108$ $R(3, 4) = 2.108$ $R(4, 6) = 2.108$ $R(1, 6) = 2.108$ $R(6, 7) = 2.108$ $R(7, 5) = 2.108$ $R(5, 8) = 2.108$	$A(1, 2, 3) = 109.13$ $A(2, 3, 4) = 109.12$ $A(3, 4, 8) = 109.13$ $A(4, 8, 5) = 109.12$ $A(5, 8, 7) = 109.13$ $A(1, 6, 7) = 109.13$ $A(5, 7, 6) = 109.12$ $A(2, 1, 6) = 109.12$
 S_8 (b)_ C_2	$R(1, 2) = 1.939$ $R(3, 4) = 1.939$ $R(1, 3) = 2.851$ $R(4, 8) = 2.302$ $R(6, 7) = 2.215$ $R(7, 8) = 2.017$ $R(5, 6) = 2.017$	$A(2, 1, 3) = 100.96$ $A(1, 3, 4) = 88.88$ $A(3, 4, 8) = 109.41$ $A(4, 8, 7) = 104.82$ $A(5, 6, 7) = 105.71$ $A(6, 7, 8) = 105.69$
 S_8 (c)_ C_s	$R(1, 2) = 2.173$ $R(2, 3) = 2.086$ $R(3, 4) = 2.084$ $R(4, 8) = 2.175$ $R(1, 6) = 2.091$ $R(6, 7) = 2.117$ $R(7, 5) = 2.119$ $R(5, 8) = 2.089$	$A(1, 2, 3) = 107.34$ $A(2, 3, 4) = 114.75$ $A(3, 4, 8) = 107.33$ $A(4, 8, 5) = 106.56$ $A(2, 1, 6) = 106.53$ $A(1, 6, 7) = 105.24$ $A(6, 7, 5) = 112.72$ $A(7, 5, 8) = 105.26$

(*Continued*)

Table 1. Continued.

Isomers	Bond distances (Å)	Bond angles (°)
 S_8 (d)_ S_4	$R(1,2) = 2.375$	$A(1,2,5) = 105.34$
	$R(3,4) = 2.375$	$A(2,5,6) = 105.34$
	$R(1,8) = 1.971$	$A(5,6,3) = 105.35$
	$R(2,5) = 1.971$	$A(2,1,8) = 105.34$
	$R(3,6) = 1.971$	$A(1,8,7) = 105.35$
	$R(4,7) = 1.971$	$A(6,3,4) = 105.34$
	$R(5,6) = 2.375$	$A(3,4,7) = 105.34$
	$R(7,8) = 2.375$	$A(4,7,8) = 105.34$
 S_8 (e)_ C_1	$R(2,3) = 1.963$	$A(3,2,1) = 106.12$
	$R(2,1) = 2.310$	$A(2,1,4) = 100.76$
	$R(1,4) = 2.050$	$A(1,4,5) = 106.38$
	$R(4,5) = 2.131$	$A(4,5,6) = 106.72$
	$R(5,6) = 2.117$	$A(5,6,7) = 105.43$
	$R(5,7) = 2.851$	$A(6,7,8) = 112.92$
	$R(7,8) = 1.961$	
 S_8 (f)_ C_s	$R(1,6) = 2.116$	$A(1,4,5) = 102.47$
	$R(6,7) = 2.116$	$A(4,5,2) = 103.71$
	$R(1,4) = 2.123$	$A(5,2,7) = 102.47$
	$R(4,5) = 2.126$	$A(2,7,6) = 103.31$
	$R(2,5) = 2.126$	$A(1,7,6) = 102.94$
	$R(2,7) = 2.123$	$A(4,1,6) = 103.30$
	$R(5,3) = 2.996$	$A(1,4,5) = 102.47$
	$R(3,8) = 1.937$	
 S_8 (g)_ C_1	$R(1,4) = 2.032$	$A(1,4,5) = 102.47$
	$R(1,8) = 3.415$	$A(4,1,6) = 103.30$
	$R(2,8) = 1.946$	$A(1,6,7) = 102.94$
	$R(2,3) = 2.450$	$A(6,7,2) = 103.31$
	$R(3,7) = 1.984$	$A(7,2,5) = 102.47$
	$R(7,6) = 2.283$	$A(2,3,8) = 134.56$
	$R(5,6) = 2.016$	$A(5,3,8) = 118.55$
	$R(4,5) = 2.211$	
 S_8 (h)_ C_2	$R(1,2) = 1.946$	$A(1,2,3) = 108.32$
	$R(2,3) = 2.249$	$A(2,3,4) = 105.60$
	$R(3,4) = 1.985$	$A(3,4,5) = 110.25$
	$R(4,5) = 2.381$	$A(4,5,6) = 110.25$
	$R(5,6) = 1.985$	$A(5,6,7) = 105.60$
	$R(6,7) = 2.249$	$A(6,7,8) = 108.32$
	$R(7,8) = 1.946$	

Note: All the geometries are optimized at the B3LYP/6-311+G* level of theory.

and

$$A = E(N) - E(N+1). \tag{7}$$

The local reactivity descriptor, Fukui function (FF) (*47*) measures the change in electron density at a given point when an electron is added to or removed from a system at constant $v(\vec{r})$. It may be written as:

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\delta \mu}{\delta v(\vec{r})}\right)_N . \tag{8}$$

Condensation of this FF, $f(\vec{r})$ to an individual atomic site k in a molecule gives rise to the following expressions in terms of electron population (*48*) q_k

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{for nucleophilic attack} \tag{9a}$$

$$f_k^- = q_k(N) - q_k(N-1) \quad \text{for electrophilic attack} \tag{9b}$$

$$f_k^o = \frac{q_k(N+1) - q_k(N-1)}{2} \quad \text{for radical attack.} \tag{9c}$$

3. Computational details

The optimization of molecular geometries of the neutral S_n ($n = 3$–8) cluster moieties and their subsequent frequency calculations are carried out at the B3LYP/6-311+G* level of theory with the help of GAUSSIAN 03 program package (*49*). The number of imaginary frequency (NIMAG) values of all the optimized geometries is zero, thereby confirming their existence at the minima on the PES. Single-point calculations are further performed to evaluate the energies of the $(N \pm 1)$-electron systems by adopting the geometries of the corresponding optimized N-electron system. The I and A values are calculated using a ΔSCF technique. The electrophilicity (ω) and hardness (η) are computed using Equations (3) and (5), respectively. A Mulliken population analysis (MPA) scheme is adopted to calculate the atomic charges (Q_k) and FFs ($f(\vec{r})$). The NICS(0) (*38*) values are calculated at the center of the different rings for the various conformers of the neutral S_n ($n = 3$–8) clusters. The frontier molecular orbital (FMO) pictures were obtained through the GAUSSVIEW 03 package (*50*).

Table 2. Energy (E, au), atomization energy (AE, au), electronegativity (χ, eV), chemical hardness (η, eV) and electrophilicity (ω, eV) of the various isomers of neutral S_n ($n = 3$–8) clusters.

Isomers	E (au)	AE (au)	χ (eV)	η (eV)	ω (eV)
S_2	−796.37989	−0.23679	5.952	6.383	2.774
S_3-(a)	−1194.60893	−0.39428	5.049	8.398	1.518
S_3-(b)	−1194.62225	−0.407599	6.178	6.819	2.799
S_4-(a)	−1592.79877	−0.51257	6.063	6.666	2.758
S_4-(b)	−1592.83087	−0.54467	5.957	6.583	2.696
S_4-(c)	−1592.84260	−0.55639	5.893	6.693	2.594
S_4-(d)	−1592.81190	−0.52570	2.353	12.318	0.225
S_4-(e)	−1592.81704	−0.53084	4.538	14.452	0.712
S_4-(f)	−1592.84256	−0.55636	5.726	6.154	2.663
S_5-(a)	−1991.07118	−0.71343	4.910	7.512	1.604
S_5-(b)	−1991.03740	−0.67964	−9.326	5.082	3.052
S_5-(c)	−1991.01205	−0.65430	5.438	5.578	2.651
S_5-(d)	−1991.02550	−0.66775	4.648	6.233	2.312
S_5-(e)	−1991.02713	−0.66938	5.455	6.245	2.383
S_6-(a)	−2389.30663	−0.87732	5.106	7.885	1.653
S_6-(b)	−2389.27134	−0.84204	5.352	6.670	2.147
S_6-(c)	−2389.22781	−0.79851	5.804	6.239	2.700
S_6-(d)	−2389.24667	−0.81737	6.016	4.400	4.112
S_6-(e)	−2389.24662	−0.81731	5.541	4.085	3.758
S_7-(a)	−2787.45957	−0.95872	4.726	4.919	2.270
S_7-(b)	−2787.45424	−0.95338	5.671	5.346	3.008
S_7-(c)	−2787.50195	−1.00109	5.551	6.917	2.227
S_7-(d)	−2787.49639	−0.99554	5.442	6.504	2.276
S_8-(a)	−3185.76262	−1.19021	5.293	7.859	1.783
S_8-(b)	−3185.73663	−1.16422	5.418	6.715	2.186
S_8-(c)	−3185.74696	−1.17455	4.944	7.088	1.724
S_8-(d)	−3185.73968	−1.16728	5.173	6.854	1.952
S_8-(e)	−3185.68732	−1.11492	5.471	4.294	3.485
S_8-(f)	−3185.69123	−1.11882	5.265	4.775	2.903
S_8-(g)	−3185.72100	−1.14859	5.266	6.104	2.272
S_8-(h)	−3185.68978	−1.11737	5.531	3.697	4.137

4. Results and discussion

The optimized molecular geometries of all the conformations of the neutral S_n ($n = 3$–8) clusters corresponding to the global or local (saddle points) minima positions on the PES and their allied important geometrical parameters like bond distances and associated inter-bond angles are presented in Table 1. Table 2 depicts the ground state energies (E, au), the atomization energies ($AE = E_{S_N} - nE_S, au$) and the essential global DF descriptors such as electronegativity (χ, eV), hardness (η, eV) and electrophilicity (ω, eV) of all the geometric conformations of the S_n clusters. The molecular point groups (PGs) and the NICS(0) values computed for the different rings of the various conformers of the neutral S_n clusters ($n = 3$–8) are composed in Table 3. The atomic charges (Q_k) and FFs of different atomic sites of all the isomers of the corresponding S_n ($n = 3$–8) clusters calculated using MPA are shown in Table 4. A close look at Table 1 reveals that, in general, the number of geometric forms any S_n cluster can adopt increases with an increase in the number of atoms in the cluster unit. Table 2 transpires that the ground state energies (E, au) of the molecular S_n conformers for a particular n value show a slight change upon alteration of the molecular PGs. It, however, becomes further evident that the ground state energies (E, au) of the neutral S_n clusters gradually increase upon increasing molecular weight. A thorough scrutiny of Table 2 further reveals that the hardness (η, eV) and electrophilicity (ω, eV) of all the geometric conformers of the neutral S_n system are positive but do not vary in a regular manner upon increasing cluster size. The electronegativity (χ, eV) values of all the neutral S_n structures are also positive. A positive χ value for almost all the S_n clusters dictates that the

Table 3. Molecular PGs and nucleus independent chemical shift [NICS(0), ppm] of the different isomers of neutral S_n ($n = 3$–8) clusters.

Isomers	PG	NICS (ppm)
S_3-(a)	D_{3h}	−42.271
S_3-(b)	C_{2v}	5.408
S_4-(a)	D_{3h}	252.358 (1,2,3-ring)
S_4-(b)	C_{2h}	−1.559 (1,2,4-ring),
S_4-(c)	C_{2v}	−11.593 (1,2,3,4-ring)
S_4-(d)	D_{2d}	−1.005 (1,2,4-ring)
S_4-(e)	C_s	−35.774 (1,2,3-ring)
S_4-(f)	C_{2v}	−11.666 (1,2,3,4-ring)
S_5-(a)	C_s	−22.073 (1,3,4,5-ring)
S_5-(b)	C_s	−5.047 (1,4,3,5-ring)
S_5-(c)	C_s	−16.139 (1,2,5,4-ring)
S_5-(d)	C_s	1.191 (1,2,4-ring)
S_5-(e)	C_s	3.006 (1,3,4-ring)
S_6-(a)	D_{3d}	4.383 (1,2,4,5-ring)
S_6-(b)	C_1	−23.98 (3,4,5-ring)
S_6-(c)	C_{2v}	−3.887 (1,4,5,6-ring)
S_6-(d)	C_2	−22.344 (1,2,4-ring)
S_6-(e)	C_2	−5.672 (1,2,3,5-ring)
S_7-(a)	C_s	−11.655 (3,4,5,6-ring)
S_7-(b)	C_s	−6.131 (1,2,3,4-ring)
S_7-(c)	C_s	−2.521 (1,4,2,6-ring)
S_7-(d)	C_s	2.405 (1,4,2,6-ring)
S_8-(a)	S_8	−1.481 (2,4,5,6-ring)
S_8-(b)	C_2	−17.589 (2,4,6-ring)
S_8-(c)	C_s	−2.893 (2,4,5,6-ring)
S_8-(d)	S_4	−7.558 (1,2,3,4-ring)
S_8-(e)	C_1	−19.515 (5,6,7-ring)
S_8-(f)	C_s	2.341 (1,4,2,7-ring)
S_8-(g)	C_1	−4.983 (1,3,5-ring)
S_8-(h)	C_2	−28.634 (3,4,5-ring)

Table 4. Atomic charges (Q_k) and FFs (f_k^+, f_k^-) of the isomers of neutral S_n (n = 3–8) clusters.

Isomers	Q_k	f_k^+	f_k^-
S_3-(a)	0.000, 0.000, 0.000	0.333, 0.333, 0.333	0.216, 0.392, 0.392
S_3-(b)	0.187, −0.093, −0.093	0.220, 0.390, 0.390	0.202, 0.399, 0.399
S_4-(a)	−0.104, −0.104, −0.104, 0.313	0.377, 0.377, 0.377, −0.130	0.358, 0.358, 0.358, −0.074
S_4-(b)	−0.081, 0.081, −0.081, 0.081	0.305, 0.195, 0.305, 0.195	0.426, 0.074, 0.426, 0.074
S_4-(c)	−0.105, −0.105, 0.105, 0.105	0.333, 0.331, 0.170, 0.166	0.373, 0.376, 0.122, 0.129
S_4-(d)	−0.000, 0.000, 0.000, −0.000	0.676, −0.178, 0.677, −0.174	0.257, 0.245, 0.243, 0.255
S_4-(e)	−0.069, −0.069, 0.349, −0.210	0.382, 0.316, 0.123, 0.179	0.338, 0.325, 0.024, 0.313
S_4-(f)	0.105, 0.105, −0.105, −0.105	0.197, 0.197, 0.303, 0.303	0.168, 0.168, 0.332, 0.332
S_5-(a)	0.045, 0.011, 0.045, −0.051, −0.051	0.123, 0.257, 0.123, 0.248, 0.248	0.149, 0.185, 0.148, 0.258, 0.260
S_5-(b)	0.058, 0.058, −0.099, 0.110, −0.127	0.013, 0.712, 0.017, 0.040, 0.218	0.161, 0.340, 0.077, 0.113, 0.309
S_5-(c)	0.095, −0.046, −0.054, 0.093, −0.088	−0.086, 0.244, 0.341, 0.185, 0.315	−0.004, 0.235, 0.302, 0.158, 0.308
S_5-(d)	0.497, −0.186, 0.144, −0.186, −0.269	−0.385, 0.494, 0.028, 0.533, 0.329	0.250, 0.235, 0.224, 0.157, 0.133
S_5-(e)	−0.134, 0.000, −0.136, 0.547, −0.277	0.158, 0.198, 0.183, 0.170, 0.292	0.193, 0.255, 0.194, 0.061, 0.298
S_6-(a)	−0.000, −0.000, 0.000, −0.000, −0.000, 0.000	0.160, 0.133, 0.207, 0.160, 0.132, 0.208	0.167, 0.167, 0.167, 0.167, 0.166, 0.167
S_6-(b)	−0.007, −0.377, −0.188, 0.613, −0.138, 0.097	0.142, 0.278, 0.216, 0.097, 0.106, 0.161	0.166, 0.351, 0.127, 0.056, 0.135, 0.165
S_6-(c)	−0.174, −0.333, −0.333, 0.507, −0.174, 0.507	0.262, 0.291, 0.291, −0.053, 0.262, −0.053	0.171, 0.299, 0.298, 0.030, 0.171, 0.030
S_6-(d)	0.054, 0.054, 0.109, 0.109, −0.163, −0.163	0.083, 0.084, 0.146, 0.146, 0.269, 0.272	0.102, 0.106, 0.101, 0.104, 0.288, 0.298
S_6-(e)	0.046, 0.046, 0.036, 0.036, −0.082, −0.082	0.073, 0.073, 0.169, 0.169, 0.257, 0.258	0.083, 0.083, 0.158, 0.159, 0.259, 0.258
S_7-(a)	−0.185, −0.185, 0.136, 0.136, −0.075, −0.075, 0.247	0.094, 0.094, 0.024, 0.024, 0.308, 0.308, 0.147	0.102, 0.102, 0.073, 0.073, 0.303, 0.302, 0.044
S_7-(b)	−0.069, −0.069, −0.086, −0.086, 0.091, 0.091, 0.128	0.010, 0.011, 0.239, 0.237, 0.181, 0.182, 0.140	0.107, 0.105, 0.166, 0.159, 0.110, 0.114, 0.238
S_7-(c)	−0.219, 0.149, −0.068, 0.149, 0.517, −0.219, −0.308	0.185, 0.088, 0.143, 0.088219, 0.055, 0.185, 0.255	0.154, 0.138, 0.128, 0.137, 0.065, 0.157, 0.221
S_7-(d)	−0.196, 0.069, 0.052, 0.069, 0.440, −0.196, −0.239	0.218, 0.129, 0.101, 0.129, −0.184, 0.218, 0.389	0.085, 0.132, 0.141, 0.132, 0.135, 0.085, 0.290
S_8-(a)	0.000, −0.000, 0.000, −0.000, −0.000, −0.000, 0.000, 0.000	0.105, 0.125, 0.145, 0.125, 0.125, 0.125, 0.145, 0.105	0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125
S_8-(b)	0.214, −0.191, −0.191, 0.214, −0.063, 0.041, 0.040, −0.063	0.087, 0.226, 0.227, 0.087, 0.096, 0.090, 0.090, 0.096	0.050, 0.212, 0.204, 0.053, 0.136, 0.103, 0.103, 0.140
S_8-(c)	−0.040, −0.068, 0.112, −0.070, 0.064, 0.062, −0.020, −0.040	0.085, 0.182, 0.040, 0.183, 0.159, 0.158, 0.108, 0.084	0.152, 0.174, 0.040, 0.173, 0.111, 0.111, 0.089, 0.151
S_8-(d)	−0.001, 0.001, −0.001, 0.001, −0.001, 0.001, −0.001, 0.001	0.134, 0.136, 0.134, 0.136, 0.114, 0.116, 0.114, 0.116	0.114, 0.116, 0.114, 0.116, 0.135, 0.135, 0.135, 0.135
S_8-(e)	0.016, 0.016, −0.071, 0.106, −0.204, 0.278, 0.007, −0.149	0.104, 0.146, 0.181, 0.030, 0.093, 0.025, 0.170, 0.249	0.113, 0.179, 0.183, 0.057, 0.055, 0.038, 0.112, 0.263
S_8-(f)	0.070, −0.246, −0, −0.102, −0.246, 0.355, 0.105, 0.071, −0.007	0.101, 0.074, 0.268, 0.075, −0.016, 0.080, 0.101, 0.316	0.096, 0.072, 0.228, 0.072, 0.030, 0.063, 0.096, 0.343
S_8-(g)	−0.137, 0.397, −0.078, 0.015, 0.141, −0.083, 0.017, −0.272	0.134, −0.042, 0.181, 0.096, 0.082, 0.076, 0.162, 0.311	0.089, 0.040, 0.072, 0.106, 0.086, 0.106, 0.186, 0.316
S_8-(h)	−0.108, 0.060, −0.065, 0.113, 0.113, −0.065, 0.060, −0.108	0.212, 0.147, 0.108, 0.032, 0.032, 0.108, 0.147, 0.212	0.226, 0.121, 0.118, 0.035, 0.035, 0.118, 0.121, 0.226

system might show some tendency to accept electrons upon chemical response. Table 3 shows that the NICS(0) values for the different trigonal and tetragonal rings present in different neutral S_n ($n = 3$–8) clusters are negative in most of the cases, thereby lending some rationale toward stability in terms of aromaticity. However, it may be noted that a mere negative NICS(0) value does not always guarantee an additional stability in terms of energy. For the two conformers of S_3, S_3-(a) and S_3-(b), the latter one is slightly stabilized in terms of energy than the former but

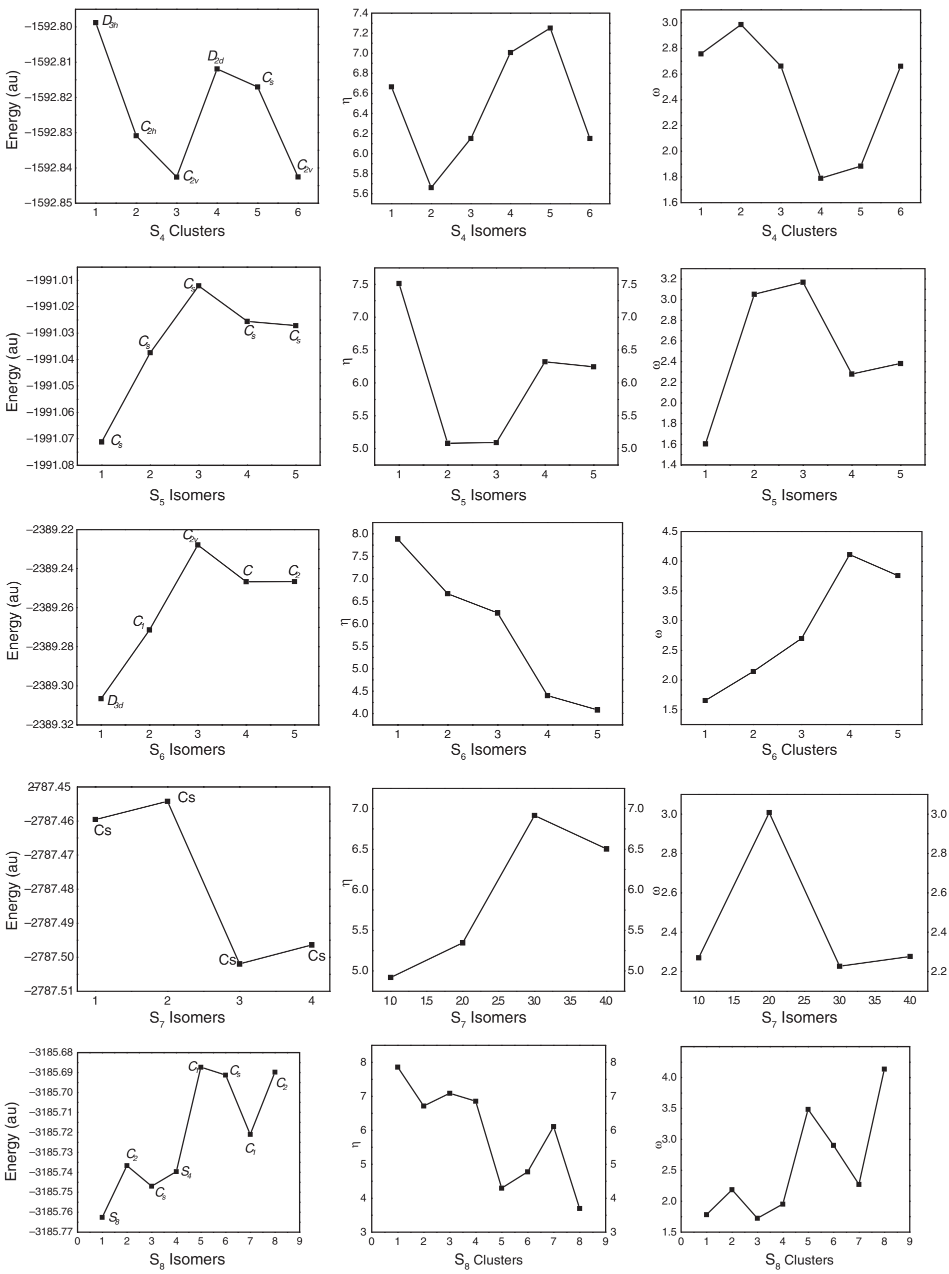


Figure 1. Plots of energy (E), chemical hardness (η) and electrophilicity (ω) of the isomers of neutral S_n clusters.

has got a positive NICS(0) value. On the other hand, the global hardness (η) of S_3-(a) is higher than S_3-(b) as envisaged from Table 2, thereby rendering lesser reactivity and possibly greater stability in terms of aromaticity (negative NICS(0) value). Thus, the stability features of these clusters may be meaningfully justified upon consideration of a subtle interplay of the significant CDFT-based global reactivity descriptors. Further consideration of the aromaticity criterion in terms of NICS(0) values vindicates the associated stability pattern. From Figure 1, it is quite transparent that for the neutral S_n ($n = 5$–7) clusters, the isomer bearing the highest hardness (η) value also possesses the lowest magnitude of electrophilicity (ω). Thus, the hardest species seems to be the least reactive one; a phenomenon well justified from the basic electronic structure principles of maximization of global hardness (MHP) (*40–42*) and minimization of the global

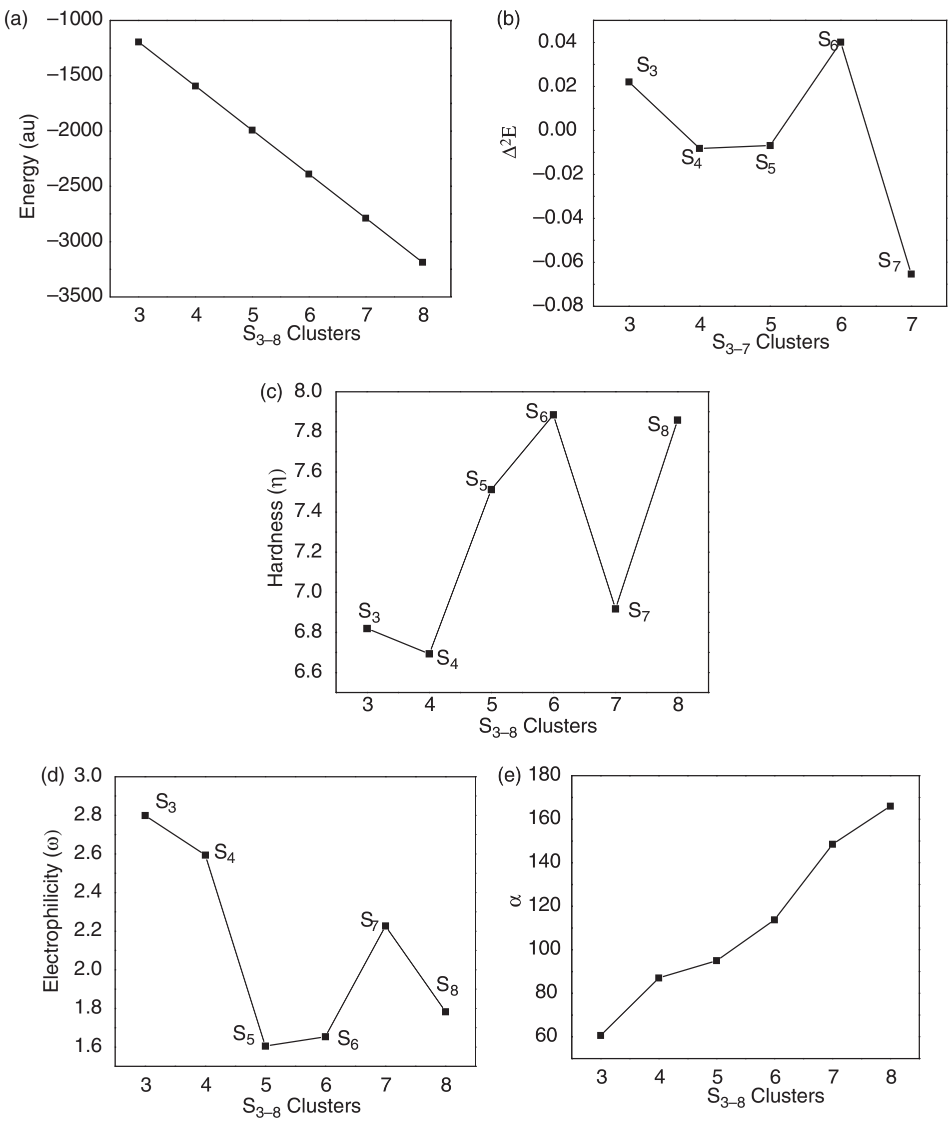


Figure 2. Variation of (a) energy (E), (b) second difference in total energy ($\Delta^2 E$), (c) chemical hardness (η), (d) electrophilicity (ω) and (e) polarizability as a function of sulfur cluster size.

electrophilicity (*45, 46*). The neutral S_4 clusters, however, do not clearly obey the above principles. For the isomers of the neutral S_8 clusters, S_8-(a) possesses the highest hardness (η) value but the electrophilicity (ω) becomes lowest for S_8-(c) and differs very slightly from that of S_8-(a) in magnitude. Both S_8-(a) and S_8-(c) are considered as bond-stretch isomers (*29–37*) having very closely associated structures. Thus, the above electronic structure principles may be presumed to be obeyed approximately for the neutral S_8 conformers. As shown in the supporting information (Figure SI1), the energy per atom and the atomization energy plots mimic that of energy. The variations of energy (E), second difference in the total energy ($\Delta^2 E$), chemical hardness (η) and electrophilicity (ω) as a function of all the neutral S_n ($n = 3$–8) clusters taken together are depicted in Figure 2. The relative stability of cluster assemblies from the perspective of molecular energetics can also be settled by computing the second-order difference in the total energy ($\Delta^2 E$) (*51*) which, for the neutral sulfur clusters in the present case study, may be written as follows:

$$\Delta^2 E = E(S_{n-1}) + E(S_{n+1}) - 2E(S_n), \tag{10}$$

where n signifies the number of S atoms in a particular sulfur cluster. Again the second-order energy difference is mathematically akin to the global hardness (η) from the viewpoint of CDFT. Therefore, a graphical illustration of η and $\Delta^2 E$ as a function of n should produce a similar profile. In Figure 2, the profiles establish S_6 as the system having the highest η and $\Delta^2 E$ values as well. But as far as the electrophilicity (ω) is concerned, the S_5 system possesses the minimum ω values, those of the S_6 moiety being the close second lowest. Thus, it may be inferred that the second-order difference ($\Delta^2 E$) in the total energy (E) of a molecular system mimics the global hardness (η), an energetic parameter and a conceptual DF descriptor serving hands together toward rationalizing molecular stability. It may be noted that $\Delta^2 E$ is the curvature in energy

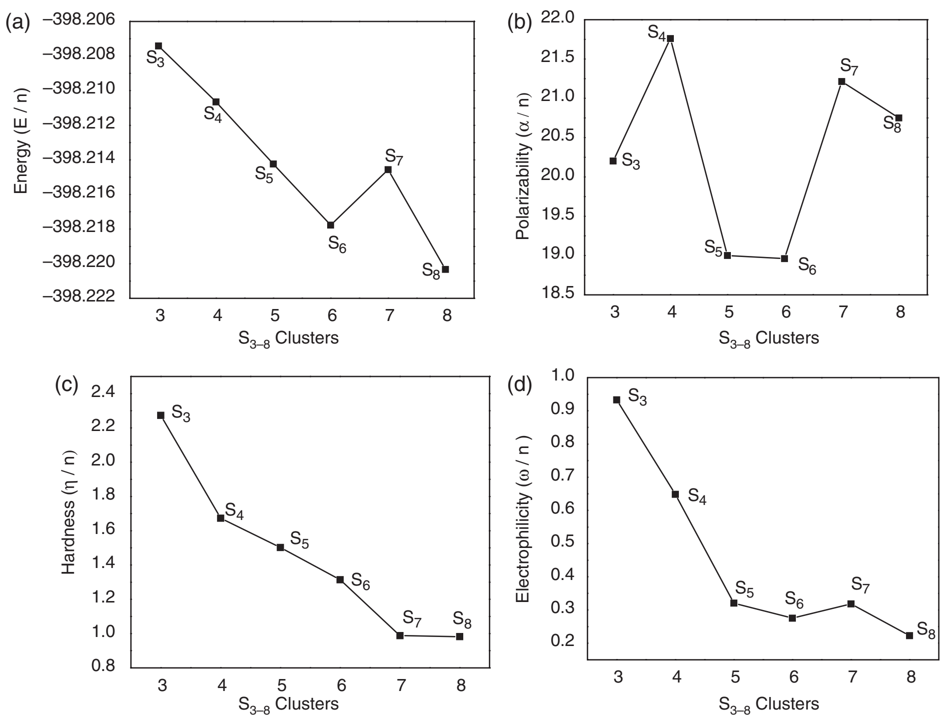


Figure 3. Variation of (a) energy (E/n), (b) polarizability (α/n), (c) chemical hardness (η/n) and (d) electrophilicity (ω/n) per atom as a function of sulfur cluster size.

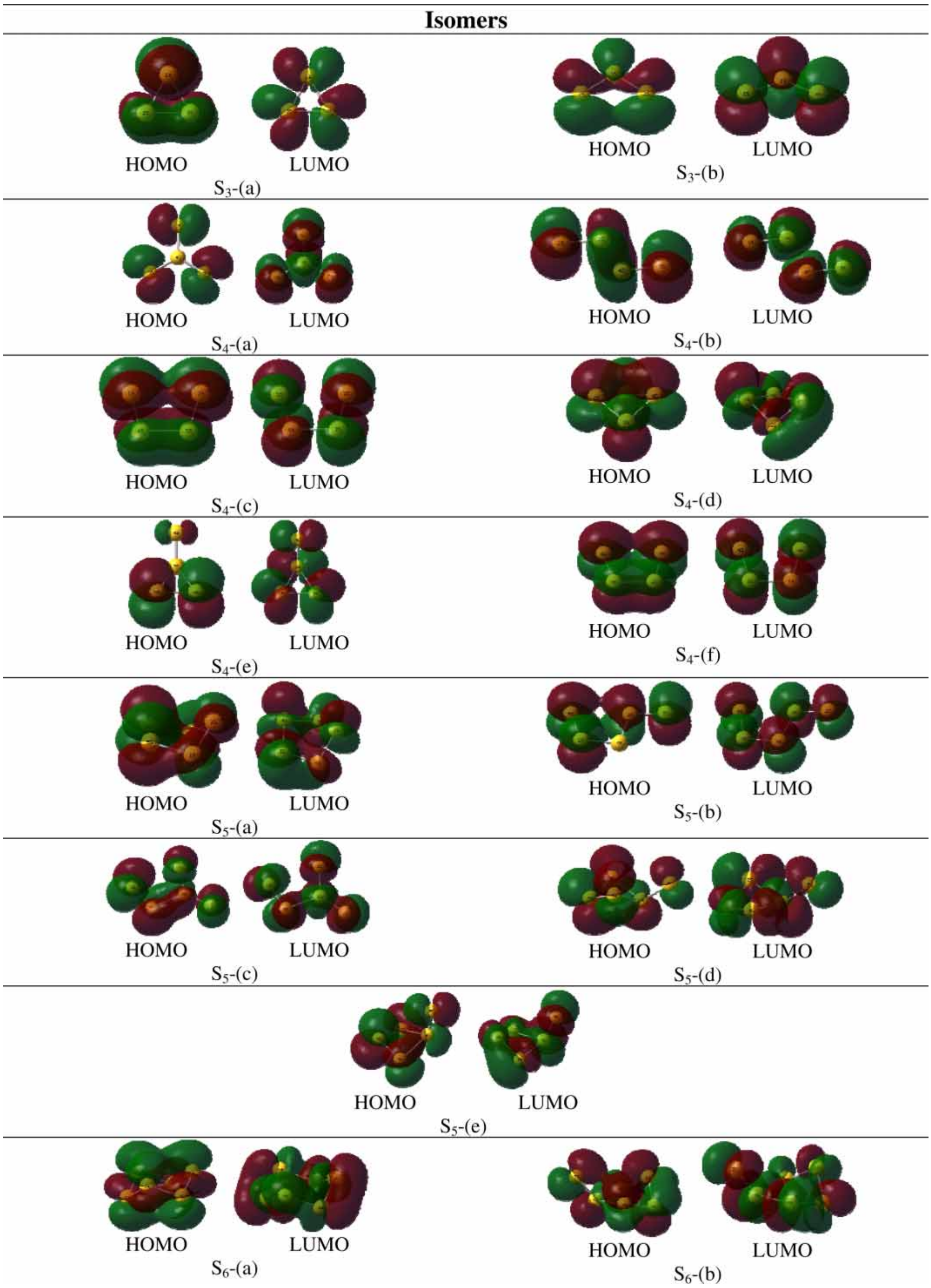


Figure 4. Some FMO pictures of the isomers of neutral S_n ($n = 3$–8) clusters.

when number of S atoms in a cluster is varied while η measures the same quantity by changing the number of electrons. Figure 3 presents the variation of energy (E), chemical hardness (η), electrophilicity (ω) and polarizability (α) computed in terms of per atom quantities as a function of the gradual enlargement of the neutral S_n ($n = 3$–8) clusters. The plot of E/n *vs*. n is not linear unlike that of E *vs*. n and produces a small peak at S_7. However, the overall decreasing trend in the total energy, E, with increasing n (cluster size) is followed. The variation of η/n

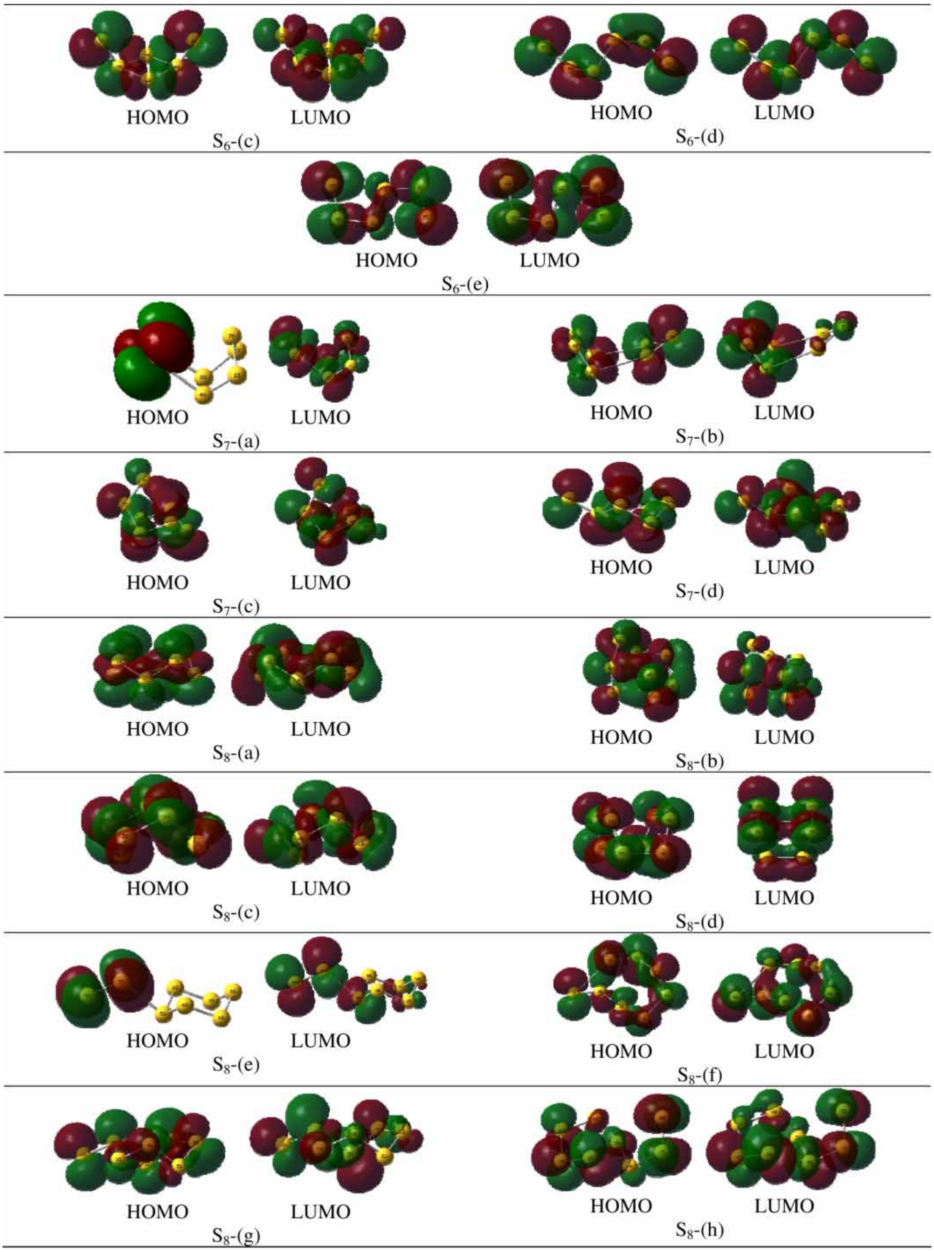


Figure 4. Continued.

and ω/n as a function of cluster size (n) indicates that the neutral S_6 species occupies the local maxima and local minima positions, respectively, with respect to its nearest neighbours (S_5, S_7) as dictated by the principles of maximum hardness and minimum electrophilicity. The α/n values show that S_6 is the least polarizable species. This fact gains further ground from Figure 1 which has already demonstrated S_6 as having the highest η as well as $\Delta^2 E$ values among all under consideration. The ω value of S_6 is close to the corresponding lowest values exhibited by S_5. Thus the possession of S_6 as the least reactive species in terms of CDFT and its several global variants is

Table 5. Ground state energy (E, au), electronegativity (χ, eV), hardness (η, eV) and electrophilicity (ω, eV) of the bond-stretch isomers of neutral S_n ($n = 3$–8) clusters.

Isomers	E (au)	χ (eV)	η (eV)	ω (eV)
S_3-(a), S_3-(b)	−1194.60893, −1194.62225	5.049, 6.178	8.398, 6.819	1.518, 2.799
S_4-(c), S_4-(f)	−1592.84260, −1592.84256	5.893, 5.726	6.693, 6.154	2.594, 2.663
S_5-(d), S_5-(e)	−1991.02550, −1991.02713	4.648, 5.455	6.233, 6.245	2.312, 2.383
S_6-(d), S_6-(e)	−2389.24667, −2389.24662	6.016, 5.541	4.400, 4.085	4.112, 3.758
S_7-(c), S_7-(d)	−2787.50195, −2787.49639	5.551, 5.442	6.917, 6.504	2.227, 2.276
S_8-(a), S_8-(c)	−3185.76262, −3185.74696	5.293, 4.944	7.859, 7.088	1.783, 1.724

quite unequivocal and almost all the electronic structure principles seem to be operative. A close analysis of the important FMOs illustrated in Figure 4 shows the electron delocalization pattern for all the neutral S_n ($n = 3$–8) clusters. The HOMO pictures mostly depict a σ-antibonding nature, whereas conspicuous π-delocalization throughout the entire molecular skeleton is also envisaged in some cases. A potent display of the phenomenon of bond-stretch isomerism, which is defined as the phenomenon whereby molecules of the same spin state, on the same PES, differ only in the length of one or several bonds (*29–37*), can be envisaged among six pairs of the neutral S_n conformers. The ground state energy (E, au) and all the allied global reactivity descriptors for the six bond-stretch isomers are separately presented in Table 5. A comparative study of the geometries and corresponding global quantitative parameters of the bond-stretch isomers infers that one geometric form can be converted to another by simple stretching or flipping. The almost similar magnitudes of the ground state energies (E, au) of every respective isomeric pair further suppose a fairly low barrier height for conversion from one conformation to another. However a substantial reversal of the σ and π characters among the FMOs of the respective bond-stretch isomeric pairs is not distinct. Thus, a relatively fleeting behavior (*28*) and hence the existence of the bond-stretched isomeric pairs at the local minima positions on the PES cannot be ruled out.

5. Conclusion

A vivid analysis of the structure and bonding patterns of some neutral S_n ($n = 3$–8) molecular clusters is presented. The variation in reactivity trends of the different S_n isomers upon changes in the molecular PGs and an increase in cluster size have been analyzed from the viewpoint of CDFT-based global and local descriptors. The existence of the unique phenomenon of bond-stretch isomerism among different pairs of structurally close isomeric species is also carefully scrutinized.

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