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Structures and energies of C_nS^+ $(1 \leq n \leq 16)$ and C_nS^- $(9 \leq n \leq 16)$ clusters

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Abstract

The structures and energies of ionic clusters of carbon and sulfur with up to 17 atoms have been investigated by density functional theory using the hybrid B3LYP functional and double-ζ plus polarization basis sets. Geometries are reported for the ground states of all isomeric clusters containing a single sulfur atom. Generally, linear structures, with a terminal sulfur atom, are the energetically favored clusters. (Int J Mass Spectrom 208 (2001) 7–16) © 2001 Elsevier Science B.V.

Keywords: Carbon; Sulfur; Clusters; DFT; Structure

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1. Introduction

During the last decade, much research has been directed toward understanding the structures and properties of small clusters. Small carbon clusters with linear configurations have been of interest for many years, both experimentally and theoretically [1–6]. One reason for this interest results from the involvement of these species in the chemistry of the interstellar medium, where reactivity is minimized by quasicollisionless conditions. Under these conditions, carbon takes the stable, albeit under normal conditions highly reactive, form of linear chains; some of the chains may be terminated by hydrogen atoms or by heteroatoms such as nitrogen, oxygen, or silicon. The heteroatoms provide a means to stabilize the carbon chain. For example, molecules such as C_3O_2, C_3S_2, C_5O_2, and C_5S_2 have been synthesized [7–10], and observed in an argon matrix at 12 K. IR and UV spectra are available and have been assigned by means of quantum-chemical calculations. C_nN_2 clusters were synthesized by an arc discharge, and carbon chains with as many as 20 atoms, stabilized by a noncarbon group on each end, have also been prepared [11,12]. Carbon cluster anions containing a heteroatom, C_nX^- were produced by laser ablation [13]. The ion abundance for these cluster anions exhibited odd/even alternation, which depended the nature of the heteroatom.

The polycarbon sulfides C_nS and their protonated forms are also of interest in interstellar cloud chemistry [14–19]. C_2S and C_3S, in particular, have been identified in interstellar media [14–16]. Ab initio calculations have been reported for these two radicals [20–24]. The earliest ab initio study involving a series of neutral C_nS clusters was coupled with mass spectrometric observations [25]. Subsequently, density

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functional theory (DFT) was used to examine neutral clusters of up to 9 carbon atoms, with a particular focus on the vibrational frequencies [26]. More recently, a broader range of the neutral clusters, C_nS ($1 \leq n \leq 20$), has been studied also using a density functional method [27]. Less is known about the anions and cations of these clusters. The products of the reactions of carbon cluster anions with sulfur containing molecules were observed in an ion cyclotron resonance mass spectrometer. The authors of that study used DFT to explore the structure of the C_nS^- clusters ($2 \leq n \leq 9$) observed in the experiments [28]. There are no previous calculations of the structure of the C_nS cations.

In previous work, one of us has generated sulfur polycarbon hydride and polycarbon sulfides ions by laser ablation of a mixture of sulfur and carbon powder [29]. Sulfur polycarbon hydride cations and anions were investigated experimentally and theoretically by means of collision-induced dissociation and ab initio calculations. The studies indicated that the clusters are all linear when the number of carbons is less than or equal to 20. In this article, we report DFT studies on sulfur polycarbon cluster anions and cations with a single heteroatom and up to 16 carbon atoms. We find that, generally, linear clusters with a terminal sulfur atom are the energetically favored structures.

2. Computational details

All of the reported structure calculations employed the Amsterdam Density Functional suite of programs (ADF 2.3.0) developed by Baerends and co-workers [30,31]. All atomic orbitals were represented by uncontracted double-ζ STO (Slater type orbital) basis sets with single polarization functions (basis set III within ADF; analogous to the 6-31G* basis set). The sulfur 1*s*, 2*s*, 2*p* and the carbon 1*s* orbitals were assigned to the core orbitals and were selected so as to be orthogonal to the valence orbitals. The variational treatment of the wave function is applied only to the valence electrons after the valence basis set has been enlarged by the number of STOs in the core orbitals. The field due to the core is calculated in the first cycle, remains constant and is used in all subsequent cycles. A set of auxiliary *s*, *p*, *d*, *f*, and *g* STO functions, centered on all nuclei, was used to fit the electron density and coulomb and exchange potentials in the SCF cycles. The Vosko-Wilk-Nusair parameterization [32] of the local density approximation was used along with gradient corrections to exchange as proposed by Becke [33] and to correlation as developed by Lee-Yang-Parr [34]. Geometry optimizations were carried out in the absence of symmetry constrains using the unrestricted formalism. The calculation provides atomization energies relative to neutral, ground state, gas phase atoms. Therefore, the bonding energies for anions and cations incorporate the electron affinity and ionization energy, respectively. It is possible, then, that the bonding energy could be negative due to this reference state. Additional ROHF/6-31G* calculations were carried out to study the nature of the molecular orbitals. These results were viewed graphically using MacSpartan.

3. Results and discussion

In previous work [13], C_nSH cations and anions were investigated experimentally and theoretically by means of collision-induced dissociation and ab initio calculations, respectively. From the collision-induced dissociation experiment, the structures of $C_nSH^{\pm}$ and $C_nS_2^{\pm}$ clusters were characterized as linear, with the heteroatoms located at the ends of the carbon chain. The experiments indicated that, with the exception of the smallest clusters where the C–S bond is weaker, the weakest bond is the C–C bond adjacent to the sulfur atom. In this article, we report computational results on the structures and energies of C_nS^+ and C_nS^- clusters with up to 16 carbon atoms. In addition to the linear structures, seven different cyclic conformers have been explored for the clusters. These generic structures are shown in Fig. 1. Cyc-1 is a monocyclic structure that includes the sulfur atom in the ring. Cyc-2 is an S-capped, carbon monocyclic configuration. The Cyc-3 structure is a carbon monocyclic ring bound to an external sulfur atom. The

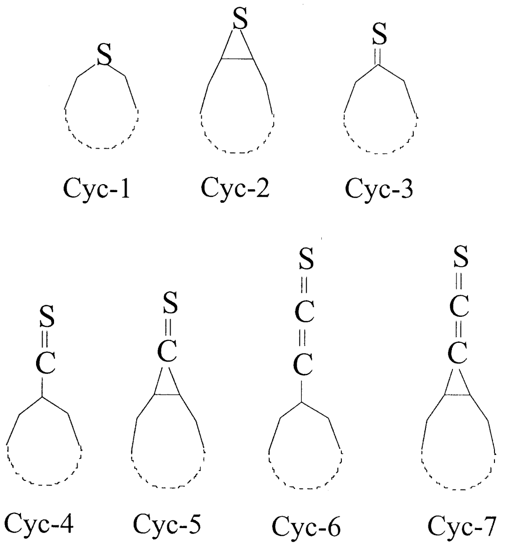

Fig. 1. Schematic geometries for cyclic forms of the C_nS^+, C_nS, and C_nS^- clusters.

Cyc-4 structure is similar to Cyc-3, but the ring has one less carbon and is bound to a –C=S substituent. Cyc-5 is a C=S-capped carbon monocyclic structure. Cyc-6 is a monocyclic carbon ring with a –C–C=S termination and Cyc-7 is a carbon bicyclic ring terminated by a –C=S link. We also investigated other monocyclic and polycyclic structures, but the 7 structures shown were lowest in energy. The calculations indicate that, as a general rule, the energetically favorable clusters have linear structures with the sulfur atom located at the end of the carbon chain. The terminal sulfur atom appears to prevent these clusters from following the trend from chain to cyclic form to cage structures exhibited by pure carbon clusters. As an example of the effect of the terminal sulfur atoms, we may consider $C_2S^{\pm}$. The S-terminated, C-terminated and cyclic forms of both the anion and cation were optimized and the results are shown in Table 1. The S-terminated chains are 4 and 3.5 eV more stable than the C-terminated forms for the anion and cation, respectively. In fact, the cyclic conformers, even with the ring strain, are more stable than the C-terminated chains. Note that this is true, even though the C–S bonds in the cyclic form of the anion are significantly elongated. We now present the details for each set of clusters.

Table 1
Comparison of various structures for C_2S^-

Cluster	E (eV)	r_{CS}	r_{CC}	$<_{\mathrm{CCS}}$ (deg)	$<_{\mathrm{CSC}}$ (deg)
CCS^-	14.79	1.683	1.287		
CSC^-	10.70	1.661			
c-CSC^-	13.34	1.940	1.349	69.65	40.71
CCS^+	1.83	1.553	1.383		
CSC^+	−1.73	1.715			
c-CSC^+	0.70	1.727	1.370	66.64	46.73

3.1. C_nS clusters

The energies and structural parameters for these clusters with up to 20 carbon atoms have recently been reported in the literature by other groups [27]. We, therefore, only provide a brief summary of our results to indicate that our computational structures and molecular properties are consistent with the earlier work and to provide evidence that the theoretical method employed here is reasonable for the C_nS chemical system. Our lowest energy clusters are linear with a terminal sulfur atom. The electronic ground state shows an odd-even alternation with the number of carbon atoms present in the cluster. Those clusters with an odd number of carbon atoms have a $^1\Sigma$ ground state, whereas clusters containing an even number of carbon atoms have a $^3\Sigma$ ground state. The sulfur atom carries a positive charge and the terminal carbon has a negative charge, so that the dipole moment increases with chain length. These observations are consistent with the literature [25–27]. The C=S bond lengths are within ±1% and the C=C bond lengths within 0.2% of those reported in the literature [27]. The bonding, with C=S bond lengths in a small range near 1.585 and the C=C bond lengths in a range near 1.280, is cumulenic.

In all cases, cyclic structures were higher in energy than the linear forms. No single cyclic structure was generally most stable. For C_3S, C_4S, C_5S, C_6S, C_8S, C_9S, and $C_{13}S$, Cyc-1 is the most stable cyclic form. However, for clusters with the formula C_7S, $C_{11}S$, and $C_{15}S$, Cyc-2 is the lowest energy ring. Finally, for $C_{10}S$ and $C_{14}S$ ($4n + 2$ π electrons), the energetically

Table 2
Energies (eV) and bond distances (Å) for linear C_nS^- clusters (Numbers refer to bonds from left to right)

Cluster	Binding E (eV)	R_{CS}[a]	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}
CS^-	7.32	1.684															
C_2S^-	14.79	1.683	1.287														
C_3S^-	21.48	1.633	1.302	1.303													
C_4S^-	28.69	1.646	1.257	1.335	1.281												
C_5S^-	35.36	1.628	1.278	1.289	1.310	1.289											
C_6S^-	42.35	1.634	1.259	1.317	1.258	1.326	1.281										
C_7S^-	48.99	1.622	1.271	1.294	1.286	1.275	1.313	1.285									
C_8S^-	55.87	1.626	1.262	1.310	1.260	1.310	1.259	1.322	1.281								
C_9S^-	62.49	1.618	1.269	1.296	1.278	1.282	1.291	1.269	1.313	1.283							
$C_{10}S^-$	69.30	1.620	1.263	1.305	1.262	1.304	1.261	1.306	1.259	1.319	1.281						
$C_{11}S^-$	75.92	1.615	1.269	1.295	1.275	1.284	1.284	1.275	1.295	1.266	1.313	1.282					
$C_{12}S^-$	82.69	1.617	1.263	1.305	1.261	1.300	1.263	1.303	1.260	1.306	1.259	1.317	1.280				
$C_{13}S^-$	89.30	1.613	1.269	1.294	1.273	1.286	1.280	1.279	1.287	1.271	1.296	1.265	1.312	1.282			
$C_{14}S^-$	96.03	1.613	1.265	1.300	1.264	1.298	1.264	1.300	1.263	1.300	1.262	1.303	1.260	1.315	1.281		
$C_{15}S^-$	102.64	1.611	1.269	1.294	1.271	1.288	1.276	1.282	1.283	1.276	1.288	1.270	1.296	1.264	1.311	1.283	
$C_{16}S^-$	109.35	1.611	1.267	1.298	1.265	1.296	1.265	1.297	1.264	1.297	1.264	1.300	1.262	1.300	1.260	1.313	1.282

[a] R_{CS} is the carbon–sulfur bond distance.

most favorable cyclic isomers are the Cyc-2 and Cyc-3 conformers, and for the $C_{12}S$ and $C_{16}S$ clusters, the most favorable cyclic isomers are of Cyc-4 structure. In the previous studies [27], the lowest energy cyclic forms were chain size dependent, but only Cyc-1 and Cyc-2 structures were considered.

3.2. C_nS^- clusters

Absolute energies and geometries for the anion clusters with up to 9 carbon atoms have recently been reported [28]. Our optimized geometric parameters for the lowest energy state of the linear isomer ($1 \leq n \leq 16$), are contained in Table 2. Our bond lengths are in good agreement with the earlier geometries, although the previously reported values were reported to less precision and are consistently longer than those from our studies. We have included our results for the smaller clusters to provide data for fragmentation calculations and structural comparisons. The geometries for $n > 9$ have not been previously published. Consistent with the earlier work [28], linear clusters of this series have a terminal sulfur atom and a $^2\Pi$ electronic ground state. The carbon–sulfur bond lengths, with the exception of the smallest members of the series, lie in the range from 1.611 to 1.634, which is within that expected for a double bond between carbon and sulfur, albeit slightly elongated. The typical C–C distance is between 1.262 and 1.326, a range expected for a double bond between two carbon atoms. The carbon–sulfur bonds show significant elongation (~7%) in comparison with the neutral clusters. The carbon–carbon bond lengths are all in the range typically considered as double bonds, but are shorter than was observed in the neutral clusters [26,27]. Coupled cluster single double (triple) [CCSD(T)] calculations [35] of the structures of C_3O and C_4O and their anions, have shown similar changes in structure when the anions are formed. There is an interesting alternation in the lengths of these bonds in the anion clusters, indicating that there is a polyacetylene character to what would be best described as cumulenic bonding. This effect is more significant for the even carbon clusters.

The incremental binding energy data obtained for C_nS^- clusters, Fig. 2, indicates that there exists a weak alternation with the even carbon clusters appearing more stable. The negative charge is distributed throughout the cluster. However, the relative distribution is dependent upon the identity of the atom and its position in the cluster. The sulfur atoms have small absolute charges (typically 0.07e), whereas the termi-

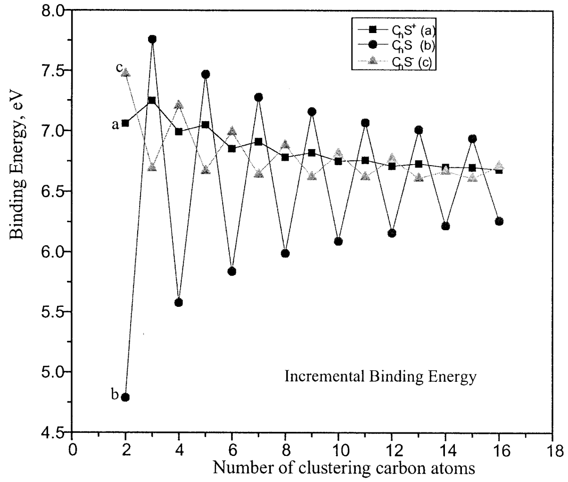

Fig. 2. Incremental binding energies for the (a) C_nS^+, (b) C_nS, and (c) C_nS^- clusters.

nal carbon atoms have charges of the order of $-0.4e$. Relatively large charges, $-0.3e$, are also centered on the carbon atoms adjacent to the sulfur.

Table 3 lists fragmentation energies for various processes involving C_nS^-. Fragmentation energetics did not appear in the earlier study of small cation clusters [28]. For each cluster, we have examined the dissociation into different pairs of products, C_{n-m}^- plus C_mS and $C_{n-m}S^-$ plus C_m, where $m = 0$–2 and $m = 1$–3, respectively, as shown in

$$\Delta E^m_{C^-} = E(C_nS^-) - E(C_{n-m}{}^-) - E(C_mS) \qquad (1)$$

$$\Delta E^m_{S^-} = E(C_nS^-) - E(C_{n-m}S^-) - E(C_m) \qquad (2)$$

With the exception of C_2S^-, the most favorable dissociation pathway is the loss of a CS radical and production of a negatively charged carbon cluster, reaction (1) with $m = 1$. The next most likely dissociation pathway is the loss of a sulfur atom with production of the carbon cluster anion, reaction (1) where $m = 0$.

Table 3
Fragmentation energies (eV) for C_nS^- clusters

Cluster	$\Delta E^0_{C^-}$	$\Delta E^1_{C^-}$	$\Delta E^2_{C^-}$	$\Delta E^1_{S^-}$	$\Delta E^2_{S^-}$	$\Delta E^3_{S^-}$
CS^-	7.94			6.56		
C_2S^-	4.73	7.98		8.58	7.83	
C_3S^-	4.89	3.99	9.87	7.80	9.07	5.05
C_4S^-	4.81	4.67	6.39	8.32	8.81	6.81
C_5S^-	4.74	4.05	6.55	7.78	8.79	6.01
C_6S^-	4.74	4.30	6.25	8.10	8.57	6.31
C_7S^-	4.72	3.95	6.09	7.75	8.54	5.74
C_8S^-	4.74	4.17	6.04	7.99	8.43	5.95
C_9S^-	4.75	3.93	6.00	7.73	8.41	5.58
$C_{10}S^-$	4.75	4.12	5.95	7.92	8.34	5.75
$C_{11}S^-$	4.76	3.94	5.95	7.73	8.34	5.49
$C_{12}S^-$	4.76	4.09	5.92	7.88	8.30	5.64
$C_{13}S^-$	4.77	3.94	5.91	7.72	8.29	5.44
$C_{14}S^-$	4.77	4.07	5.88	7.84	8.25	5.55
$C_{15}S^-$	4.78	3.95	5.89	7.72	8.25	5.39
$C_{16}S^-$	4.78	4.06	5.87	7.82	8.23	5.49

The 7 cyclic structures shown in Fig. 1 have been explored for the anions and the energies are contained in Table 4. For the C_3S, C_4S, C_5S, C_6S, C_8S, and C_9S anionic clusters, Cyc-1 structures, sulfur-containing monocyclic rings, are the most stable cyclic form. For the remaining cyclic C_nS^- clusters, the energetically most favorable isomers are of Cyc-3 structure, a cyclic thio-ketone conformer. A comparison of the energies of the linear and cyclic conformers, shows that linear C_nS^- clusters are more stable, for all n up to 16. The energy differences between the linear structures and any cyclic form are significant (greater than 1 eV).

3.3. C_nS^+ clusters

The optimized geometric parameters and binding energies for the lowest energy state of the linear isomers ($1 \leq n \leq 16$), are presented in Table 5(a). For these structures, a carbon chain having a terminal sulfur atom was the lowest energy form and the electronic ground state was $^2\Pi$. With the exception of the smallest molecule, CS^+, the carbon–sulfur bond distances lie in a small range, 1.551–1.566, which indicates C=S bonds (compare to the bond length of 1.55 in CS_2) [36]. The carbon–carbon bond distances are in the range of 1.260–1.319 A°, which are indicative of carbon–carbon double bonds (compare with the bond length of ethylene [36], 1.35). The bonding in these clusters is still cumulenic, but there are changes relative to the neutral clusters. The C=S bond lengths are slightly increased (~2%) and the C=C bond lengths are slightly shortened (~1%).

The incremental binding energy data obtained for

Table 4
Binding energies for linear and cyclic C_nS^- clusters

Cluster	Linear	Cyc-1	Cyc-2	Cyc-3	Cyc-4	Cyc-5	Cyc-6	Cyc-7
CS^-	**7.32**							
C_2S^-	**14.79**	13.34						
C_3S^-	**21.48**	18.39						
C_4S^-	**28.69**	25.09						
C_5S^-	**35.36**	32.51						
C_6S^-	**42.35**	38.78	38.32					
C_7S^-	**48.99**	45.59		46.55				
C_8S^-	**55.87**	53.25	50.57	51.15				
C_9S^-	**62.49**	60.23	59.61	59.67				
$C_{10}S^-$	**69.30**	66.47	66.84	67.43	66.19		66.16	
$C_{11}S^-$	**75.92**	73.68	73.13	74.23	73.80	73.85	73.38	73.80
$C_{12}S^-$	**82.69**	80.75	80.74	80.81	80.17	80.33	80.00	79.82
$C_{13}S^-$	**89.30**	87.66	87.39	87.89	87.23	86.95	87.29	86.11
$C_{14}S^-$	**96.03**	93.72	94.33	95.01	94.06	94.55	94.13	92.30
$C_{15}S^-$	**102.64**	100.94	100.68	101.57	101.28	101.07	101.21	100.40
$C_{16}S^-$	**109.35**	107.94	107.12	108.05	107.91	107.70	108.31	107.26

C_nS^+ clusters, Fig. 2, indicates that with the exception of the smallest clusters, there exists a very weak alternation, with the odd carbon clusters appearing more stable. As expected from the relative electronegativities, the sulfur terminus is more positive and, for larger clusters, the terminal carbon atom has a negative charge. For clusters containing fewer than seven carbon atoms, the terminal carbon atom has a small positive charge.

Table 6 lists energies for fragmentation of C_nS^+. For each cluster, we have examined the dissociation into different pairs of products, C^+_{n-m} plus C_mS ($m = 0$–2) and $C_{n-m}S^+$ plus C_m ($m = 1$–5), as shown in

$$\Delta E^m_{C^+} = E(C_nS^+) - E(C_{n-m}{}^+) - E(C_mS) \qquad (3)$$

$$\Delta E^m_{S^+} = E(C_nS^+) - E(C_{n-m}S^+) - E(C_m) \qquad (4)$$

For all C_nS^+ clusters with $n>6$, the most favorable pathway is the loss of a CS radical, reaction (3) with $m = 1$. The weakest bond in these clusters is the C–C bond adjacent to the sulfur atom, which is reflected in a bond length that is significantly longer than the remaining C–C bonds. The other important dissociation channel is loss of a C_3 radical, reaction (4) where $m = 3$. This channel is similar to that observed for the pure carbon cluster cations and is the preferred dissociation channel for C_3S^+. The C_3 cluster has been shown to be an extremely stable species [37].

The 7 cyclic structures already described in Fig. 1 have also been investigated for the cation clusters. The energies for the cyclic structures are contained in Table 7. We find that linear C_nS^+ clusters are more stable when the number of carbon atoms is less then 15. When the number of clustering carbon atoms is $3 \leq n \leq 10$, the Cyc-1 structure, the monocyclic sulfur-containing ring, is generally more stable than any other cyclic conformer. For $n > 10$, the lowest energy cyclic isomers vary, with small energy differences, in the 0.5 eV range, among the Cyc-1 through Cyc-4 structures. For $C_{15}S^+$ and $C_{16}S^+$, however, the Cyc-4 structures, carbon monocycles with –C=S substituents, are more stable then the linear clusters, by 0.08 and 0.27 eV, respectively. The bond lengths and bond angles for these two cyclic conformers are included in Table 5(b).

3.4. Stability and structure of C_nS^+, C_nS, and C_nS^- clusters

Interesting comparisons may be made to carbon clusters and carbon–silicon clusters [38–40]. For C_n^+, when $3 \leq n \leq 9$, linear geometries are most stable [41]. Experiments indicated that linear forms were

Table 5

(a) Energies (eV) and bond distances (Å) for linear C_nS^+ clusters (numbers refer to bonds from left to right); (b) bond distances (Å) and angles for Cyc-4 forms of $C_{15}S^+$ and $C_{16}S^+$ clusters; Carbon 1 is connected to the C=S substituent.

Cluster	Energy (eV)	R_{CS}[a]	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}
CS^+	−5.23	1.673															
C_2S^+	1.83	1.553	1.383														
C_3S^+	9.08	1.566	1.295	1.334													
C_4S^+	16.07	1.551	1.305	1.266	1.319												
C_5S^+	23.12	1.557	1.295	1.273	1.283	1.323											
C_6S^+	29.97	1.554	1.301	1.259	1.294	1.270	1.327										
C_7S^+	36.88	1.560	1.292	1.268	1.280	1.276	1.281	1.318									
C_8S^+	43.66	1.556	1.297	1.260	1.293	1.261	1.290	1.273	1.319								
C_9S^+	50.48	1.561	1.292	1.267	1.283	1.272	1.278	1.286	1.282	1.313							
$C_{10}S^+$	57.23	1.558	1.296	1.261	1.292	1.261	1.290	1.264	1.287	1.275	1.315						
$C_{11}S^+$	63.99	1.562	1.291	1.299	1.285	1.269	1.280	1.274	1.276	1.277	1.282	1.311					
$C_{12}S^+$	70.70	1.561	1.294	1.262	1.291	1.261	1.291	1.263	1.288	1.266	1.284	1.278	1.312				
$C_{13}S^+$	77.43	1.563	1.291	1.267	1.284	1.269	1.282	1.272	1.278	1.276	1.275	1.277	1.282	1.309			
$C_{14}S^+$	84.13	1.563	1.293	1.263	1.291	1.262	1.291	1.263	1.289	1.264	1.287	1.267	1.282	1.278	1.319		
$C_{15}S^+$	90.83	1.563	1.290	1.266	1.285	1.268	1.282	1.271	1.279	1.274	1.276	1.277	1.274	1.277	1.294	1.306	
$C_{16}S^+$	97.51	1.564	1.293	1.263	1.290	1.262	1.291	1.262	1.290	1.264	1.288	1.265	1.285	1.269	1.281	1.281	1.307

(b)

C(1)–C(2)	1.400
C(1)–C(15)	1.382
C(1)–C(14)	1.402
C(2)–C(3)	1.244
C(4)–C(5)	1.261
C(4)–C(3)	1.312
C(5)–C(6)	1.297
C(6)–C(7)	1.275
C(7)–C(8)	1.286
C(8)–C(9)	1.286
C(9)–C(10)	1.274
C(10)–C(11)	1.298
C(11)–C(12)	1.261
C(12)–C(13)	1.312
C(13)–C(14)	1.246
C(15)–S(16)	1.535
C(2)–C(1)–C(15)	118.97
C(2)–C(1)–C(14)	120.11
C(15)–C(1)–C(14)	120.92
C(1)–C(2)–C(3)	157.30
C(1)–C(15)–S(16)	179.00
C(5)–C(4)–C(3)	156.98
C(4)–C(5)–C(6)	158.97
C(5)–C(6)–C(7)	151.02
C(6)–C(7)–C(8)	152.49
C(7)–C(8)–C(9)	148.93
C(8)–C(9)–C(10)	152.69
C(9)–C(10)–C(11)	151.25
C(10)–C(11)–C(12)	158.92
C(11)–C(12)–C(13)	157.93
C(12)–C(13)–C(14)	169.03
C(1)–C(14)–C(13)	155.13
C(2)–C(3)–C(4)	169.31

C(1)–C(2)	1.400
C(1)–C(15)	1.403
C(1)–C(16)	1.370
C(2)–C(3)	1.242
C(3)–C(4)	1.317
C(4)–C(5)	1.251
C(5)–C(6)	1.308
C(6)–C(7)	1.258
C(7)–C(8)	1.306
C(8)–C(9)	1.260
C(9)–C(10)	1.306
C(10)–C(11)	1.257
C(11)–C(12)	1.308
C(12)–C(13)	1.253
C(13)–C(14)	1.317
C(14)–C(15)	1.243
C(16)–S(17)	1.542
C(2)–C(1)–C(15)	114.72
C(2)–C(1)–C(16)	121.49
C(15)–C(1)–C(16)	123.79
C(1)–C(2)–C(3)	163.58
C(2)–C(3)–C(4)	170.20
C(3)–C(4)–C(5)	159.09
C(4)–C(5)–C(6)	160.03
C(5)–C(6)–C(7)	152.38
C(6)–C(7)–C(8)	155.36
C(7)–C(8)–C(9)	152.522
C(8)–C(9)–C(10)	153.43
C(9)–C(10)–C(11)	154.77
C(10)–C(11)–C(12)	153.76
C(11)–C(12)–C(13)	159.89
C(12)–C(13)–C(14)	159.15
C(13)–C(14)–C(15)	170.33
C(1)–C(15)–C(14)	160.82
C(1)–C(16)–S(17)	178.18

[a] R_{CS} is the carbon-sulfur bond distance.

Table 6
Fragmentation energies (eV) for linear C_nS^+ clusters

Cluster	$\Delta E^0_{C^+}$	$\Delta E^1_{C^+}$	$\Delta E^2_{C^+}$	$\Delta E^1_{S^+}$	$\Delta E^2_{S^+}$	$\Delta E^3_{S^+}$	$\Delta E^4_{S^+}$	$\Delta E^5_{S^+}$
CS^+	6.49			6.27				
C_2S^+	8.42	6.10		8.17	7.13			
C_3S^+	6.53	8.24	8.56	8.36	9.22	4.91		
C_4S^+	7.35	6.07	10.44	8.10	9.15	6.83	6.89	
C_5S^+	6.58	6.97	8.35	8.16	8.95	6.73	8.87	5.74
C_6S^+	6.68	6.00	9.03	7.96	8.81	6.33	8.67	7.43
C_7S^+	6.49	6.16	8.12	8.02	8.67	6.25	8.23	7.28
C_8S^+	6.38	5.84	8.15	7.89	8.60	5.98	8.02	6.81
C_9S^+	6.26	5.77	7.87	7.93	8.51	5.95	7.79	6.64
$C_{10}S^+$	6.17	5.58	7.73	7.86	8.48	5.79	7.69	6.34
$C_{11}S^+$	6.08	5.50	7.55	7.87	8.42	5.77	7.54	6.25
$C_{12}S^+$	6.00	5.36	7.42	7.82	8.38	5.66	7.47	6.05
$C_{13}S^+$	5.94	5.30	7.30	7.84	8.35	5.64	7.38	6.00
$C_{14}S^+$	5.89	5.21	7.21	7.81	8.34	5.58	7.33	5.88
$C_{15}S^+$	5.84	5.16	7.12	7.81	8.31	5.57	7.27	5.83
$C_{16}S^+$	5.80	5.09	7.05	7.79	8.29	5.52	7.24	5.73

lowest in energy from C_5^+ to C_{10}^+, and that linear and cyclic isomers coexist until $n = 10$. Above C_{10}^+, the preferred geometry changes to ring structures and no linear clusters were observed. The identical trend is observed for the geometry of the carbon anion clusters. Experimentally [42], C_5^- to C_9^- clusters were found to be exclusively linear, but monocyclic structures coexisted with the linear conformers for C_{10}^- through C_{20}^-. Neutral carbon clusters also exhibit a change in geometry, but at $n=10$. Our own calculations using the theoretical method employed in this study led to identical conclusions.

Table 7
Binding energies for linear and cyclic C_nS^+ clusters

Cluster	Linear	Cyc-1	Cyc-2	Cyc-3	Cyc-4	Cyc-5	Cyc-6	Cyc-7
CS^+	**−5.23**							
C_2S^+	**1.83**	0.70						
C_3S^+	**9.08**	6.56						
C_4S^+	**16.07**	13.04						
C_5S^+	**23.12**	21.22						
C_6S^+	**29.97**	27.96	27.30					
C_7S^+	**36.88**	34.33						
C_8S^+	**43.66**	41.67	40.49	41.22				
C_9S*	**50.48**	49.39	48.05	48.24				
$C_{10}S^+$	**57.23**	56.25	56.23	55.94	55.62		54.57	
$C_{11}S^+$	**63.99**	62.64	62.49	63.29	63.31	63.06	61.77	63.30
$C_{12}S^+$	**70.70**	69.67	69.12	69.77	70.39	69.13	69.18	69.80
$C_{13}S^+$	**77.43**	76.95	76.12	76.53	76.53	75.67	76.85	76.16
$C_{14}S^+$	**84.13**	83.70	83.79	83.63	83.67	82.83	83.02	82.35
$C_{15}S^+$	90.83	89.94	90.05	90.77	**90.91**	90.59	89.88	89.51
$C_{16}S^+$	97.51	97.00	96.72	97.33	**97.78**	96.70	96.86	97.22

C_nSi^+ ($n = 4$–15) clusters have been studied by DFT [43]. As a general rule, when $4 \leq n \leq 9$, the energetically most favorable isomers were found to be linear with the silicon atom located at the end of the carbon chain. For $10 \leq n \leq 15$, the linear arrangement is less stable than the Si-capped, carbon monocyclic configuration.

Previous computational studies of the C_nS clusters also used DFT techniques [26,27]. The results from these two reports are in good agreement (within 1% for the terminal bonds and 0.5% otherwise) and linear structures were reported to be more stable than monocyclic forms up to values of $n = 9$ [27]. For larger values of n, C_nS linear structures remain more stable than cyclic forms, but the energy differences are small, so that the linear and monocyclic structures are expected to coexist. This preference [27] was attributed to the predominately divalent state of the sulfur atom, resulting in double bonds at terminal positions in a linear chain. This linear preference appears to carry over into the structure of both the anion and cation clusters.

The previous DFT studies focused on the smaller anion clusters. The geometry was reported to be cumulenic [28]. Extending this work, our DFT studies indicate that the C_nS^- clusters, where $3 \leq n \leq 16$, are all more stable as linear chains. The energy differences between these linear structures and any cyclic form are all greater than 1 eV, which implies that the C_nS^- clusters should be observed, exclusively, as linear structures. C_nS^+ clusters, when $3 \leq n \leq 14$, are more stable as linear structures. For $C_{15}S^+$ and $C_{16}S^+$, a cyclic carbon structure with a –C=S substituent is more stable than the linear structure, by 0.08 and 0.27 eV, respectively. The energies of the cyclic and linear forms show small differences when $n > 9$, indicating that linear and some cyclic forms may coexist.

The odd-even alternation in stability for neutral and ionic carbon–sulfur clusters, evidenced by the incremental bonding energy, is consistent with the highest occupied molecular orbitals (HOMOs) for the clusters. The nature of the HOMO is strongly depen-

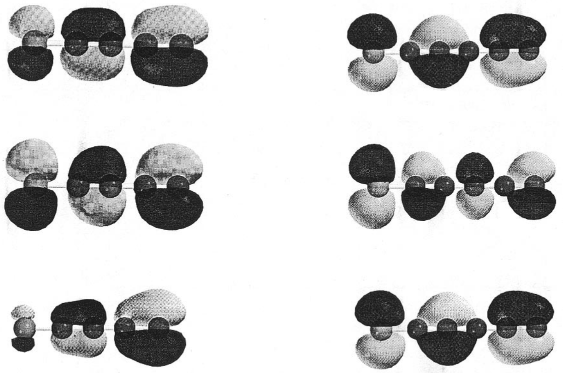

Fig. 3. HOMOs for C_nS, C_nS^-, and C_nS^+ clusters, where $n = 4$ and $n = 5$. Orbitals were obtained from a ROHF/6-31G* calculation.

dent upon the theoretical model used in the calculation. The HOMOs resulting from the DFT calculations used to calculate energies are cluster dependent. In some cases, a σ nonbonding orbital is the highest occupied level, in others π orbitals, of differing origin, are the HOMOs. We have also applied restricted open shell Hartree-Fock (ROHF) calculations, using the optimized DFT geometries, to the investigation of cluster HOMOs. There is a consistency to the results we observe from these calculations. Figure 3 contains the HOMOs for consecutive neutral, cationic and anionic clusters where $n = 4$ or 5. For the neutral clusters, the odd-numbered molecules are more stable than those with an even number of carbons. The MOs in Fig. 3 indicate that this stability may be related to increased delocalization in the HOMO of C_5S as compared with C_4S. A similar argument may be made for the cation clusters. However, in the case of the anionic clusters, for which the even-numbered molecules are more stable, the HOMOs present the opposite characteristics. The odd-numbered cluster HOMO is best described as π nonbonding, while the even-numbered cluster is π bonding. All of the remaining clusters fit the pattern described for $n = 4$ and 5 when ROHF calculations are applied. In the previous report involving the neutral clusters, C_nS, the stability alternation was attributed to filling the highest energy π orbital in the odd-carbon clusters. That analysis is impossible to apply to the ionic clusters, since in both cases, a radical structure exists and the highest energy π orbital is only partially occupied. It appears that, for these clusters, the MO structure provides the best correlation between stability and carbon number.

4. Summary

Density functional calculations for C_nS anion and cation clusters with up to 16 carbon atoms have been carried out at the double-zeta plus polarization basis set level. For both sets of clusters, the electronic ground state is $^2\Pi$. In the case of the anions, linear clusters are the energetically favored structures and are predicted to exist without significant fractions of any cyclic clusters. For the cation clusters, linear structures are preferred up to $n = 14$ and cyclic forms are lower in energy above that threshold. The energy differences between linear and cyclic structures are small, and multiple geometries are predicted to be observed in experimental studies of C_nS^+. All of the linear clusters are cumulenic, but a definite alternation in bond lengths in the case of the even-carbon cluster anions provides evidence of an polyacetylenic contribution to the structure.

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