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Theoretical investigation of cationic sulphur carbide clusters C_nS^+ ($n = 1$–23)

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Abstract

C_nS^+ ($n = 1$–23) clusters have been studied using the B3LYP density functional method. The energy calculations show that the linear isomer with the sulphur atom bound to the end of the carbon chain is the most stable geometry up to $n = 17$. The electronic ground state is alternately predicted to be $^2\Sigma^+$ for odd n or $^2\Pi$ for even n when $n \leq 6$ and invariably $^2\Pi$ for $6 < n \leq 17$. Beyond $n = 17$, the most stable geometry is found to be either the S-capped monocyclic ring ($n = 18$, 19) or the linear arrangement of nuclei ($n = 20, 21$) and, following a fourfold periodicity rule, again the cyclic structure for $n = 22, 23$. In the latter cases ($17 < n \leq 23$), however, the linear-cyclic barrier is very low (~a few kcal mol^{-1}). Binding energies have been also computed for all clusters and used to interpret the fragmentation patterns. (Int J Mass Spectrom 181 (1998) 135–149) © 1998 Elsevier Science B.V.

Keywords: Sulphur carbide; Carbon; Clusters; Density functional theory; Interstellar medium

1. Introduction

Carbon clusters where a C atom is substituted by a heteroatom, such as B, N, Si, S or P have attracted much attention in recent years [1–6]. The interest in these species is motivated by the fact that substitution of a foreign atom in a pure carbon cluster results in significant changes on the electronic structure, which may eventually be used to elaborate new types of materials with novel solid-state properties. Quite recently, we have performed a detailed theoretical investigation of the neutral C_nS ($n = 1$–20) clusters [6] by employing the density functional theory (DFT). The main conclusion of this study was that the geometry of the ground state is linear with the sulphur atom in the terminal position of the carbon chain when $n \leq 17$. For $n = 18$, the ground state geometry is a S-capped monocyclic structure but with a low barrier to linearity. $C_{19}S$ and $C_{20}S$ are again unambiguously linear. The calculations have also evidenced a conspicuous odd-even alternation in the stability of the linear clusters from $n = 1$–20 and a fourfold periodicity in the stability of the cyclic structures when $12 \leq n \leq 20$. The present paper will be devoted to a theoretical analysis of the C_nS^+

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Table 1(a)
Structural parameters (distance in Å, angle in degrees), total energies (in Hartree), relative stabilities ΔE (in kcal mol^{-1}) and dipole moments (in debye) of the different C_nS^+ ($1 \leq n \leq 14$) clusters obtained with a DFT/B3LYP/6-311G* method. The symmetry (point group) and the electronic state of the different structures are also given

Isomer	Point group	State	Structural parameters	ΔE^a	μ
CS^+				−435.825 498	
lin 1[b]	$C_{\infty v}$	$^2\Sigma^+$	d = 1.493	0.0	0.58
lin1′	$C_{\infty v}$	$^4\Sigma^-$	d = 1.516	78.2	0.69
C_2S^+				−473.890 784	
lin2	$C_{\infty v}$	$^2\Pi$	d1 = 1.523 d2 = 1.383	0.0	1.11
lin2′	$C_{\infty v}$	$^4\Sigma^-$	d1 = 1.559 d2 = 1.273	1.2	1.35
cyc2	C_{2v}	$^2B_2$	d1 = 1.695 d2 = 1.369 θ = 47.6	28.0	1.16
cyc2′	C_{2v}	$^4A_2$	d1 = 1.817 d2 = 1.300 θ = 41.9	35.1	0.33
C_3S^+				−512.024 484	
lin3	$C_{\infty v}$	$^2\Sigma^+$	d1 = 1.505 d2 = 1.332 d3 = 1.220	0.0	1.13
lin3′	$C_{\infty v}$	$^4\Pi$	d1 = 1.588 d2 = 1.283 d3 = 1.284	65.4	2.12
cyc3	C_{2v}	$^2A_1$	d1 = 1.754 d2 = 1.343 θ1 = 50.8 θ2 = 120.6	53.8	0.07
cyc3′	C_{2v}	$^4A_2$	d1 = 1.935 d2 = 1.338 θ1 = 52.4 θ2 = 114.1	97.4	0.52
S-cycC3	C_{2v}	$^2A_1$	d1 = 1.537 d2 = 1.515 d3 = 1.298 θ = 50.7	34.2	0.90
S-cycC3′	C_{2v}	$^4A_2$	d1 = 1.673 d2 = 1.416 d3 = 1.397 θ = 59.1	62.3	0.79
C_4S^+				−550.111 233	
lin4	$C_{\infty v}$	$^2\Pi$	d1 = 1.523 d2 = 1.312 d3 = 1.258 d4 = 1.340	0.0	1.91
lin4′	$C_{\infty v}$	$^4\Sigma^-$	d1 = 1.542 d2 = 1.285 d3 = 1.294 d4 = 1.250	7.8	1.64
cyc4	C_{2v}	$^2B_2$	d1 = 1.780 d2 = 1.271 d3 = 1.341 θ1 = 86.4 θ2 = 111.3 θ3 = 115.5	100.2	1.37
cyc4′	C_{2v}	$^4B_1$	d1 = 1.767 d2 = 1.375 d3 = 1.253 θ1 = 87.9 θ = 110.2 θ3 = 115.9	93.3	0.96
S-bicycC4	C_{2v}	$^2B_2$	d1 = 1.626 d2 = 1.410 d3 = 1.460 d4 = 1.532 θ1 = 65.8 θ2 = 63.3	51.0	3.05
S-bicycC4′	C_{2v}	$^4A_2$	d1 = 1.669 d2 = 1.414 d3 = 1.372 d4 = 1.522 θ1 = 65.1 θ2 = 67.4	72.7	0.63
C_5S^+				−588.221 137	
lin5	$C_{\infty v}$	$^2\Sigma^+$	d1 = 1.517 d2 = 1.315 d3 = 1.234 d4 = 1.333 d5 = 1.219	0.0	0.91
lin5′	$C_{\infty v}$	$^4\Sigma^-$	d1 = 1.563 d2 = 1.278 d3 = 1.288 d4 = 1.288 d5 = 1.259	41.7	2.22
cyc5	C_{2v}	$^2A_1$	d1 = 1.708 d2 = 1.293 d3 = 1.303 θ2 = 95.5 θ2 = 130.8 θ3 = 110.2 θ4 = 142.4	49.4	0.05
cyc5′	C_{2v}	$^4A_2$	d1 = 1.775 d2 = 1.296 d3 = 1.324 θ1 = 91.2 θ2 = 120.7 θ3 = 147.2 θ4 = 93.0	107.2	1.12
SC-bicycC4	C_{2v}	$^2B_1$	d1 = 1.514 d2 = 1.347 d3 = 1.407 d4 = 1.460 d5 = 1.534 θ1 = 66.1 θ2 = 63.4	47.9	4.30
SC-bicycC4′	C_{2v}	$^4A_2$	d1 = 1.556 d2 = 1.300 d3 = 1.495 d4 = 1.352 d5 = 1.644 θ1 = 66.7 θ2 = 74.8	77.8	1.28
S-bicycC5	C_{2v}	$^2B_2$	d1 = 1.659 d2 = 1.396 d3 = 1.493 d4 = 1.433 d5 = 1.464 θ1 = 63.3 θ2 = 147.8 θ3 = 90.6	155.5	0.52
S-bicycC5′	C_{2v}	$^4A_2$	d1 = = 1.656 d2 = 1.396 d3 = 1.488 d4 = 1.352 d5 = 1.493 θ1 = 64.6 θ2 = 144.9 θ3 = 92.7	123.1	2.04
C_6S^+				−626.316 004	
lin6	$C_{\infty v}$	$^2\Pi$	d1 = = 1.527 d2 = 1.307 d3 = 1.251 d4 = 1.301 d5 = 1.263 d6 = 1.325	0.0	2.79
lin6′	$C_{\infty v}$	$^4\Sigma^-$	d1 = 1.540 d2 = 1.289 d3 = 1.275 d4 = 1.269 d5 = 1.305 d6 = 1.241	15.6	1.59
cyc6	C_{2v}	$^2B_1$	d1 = 1.723 d2 = 1.253 d3 = 1.328 d4 = 1.260 θ1 = 97.1 θ2 = 135.8 θ3 = 140.9 θ4 = 124.7	49.8	1.24

(continued)

Table 1(a) (*continued*)

Isomer	Point group	State	Structural parameters	ΔE^a	μ
C_7S^+				−664.417 059	
lin7	$C_{\infty v}$	$^2\Pi$	d1 = 1.533 d2 = 1.297 d3 = 1.262 d4 = 1.286 d5 = 1.272 d6 = 1.282 d7 = 1.311	0.0	3.36
lin7′	$C_{\infty v}$	$^4\Pi$	d1 = 1.552 d2 = 1.287 d3 = 1.284 d4 = 1.271 d5 = 1.297 d6 = 1.270 d7 = 1.341	34.0	3.32
cyc7	C_{2v}	$^2A_2$	d1 =1.717 d2 = 1.245 d3 = 1.318 d4 = 1.287 θ1 = 84.4 θ2 = 157.7 θ3 = 138.6 θ4 = 143.6 θ5 = 115.9	57.6	0.69
C_8S^+				−702.512 166	
lin8	$C_{\infty v}$	$^2\Pi$	d1 = 1.531 d2 = 1.302 d3 = 1.252 d4 = 1.301 d5 = 1.254 d6 = 1.296 d7 = 1.267 d8 = 1.318	0.0	3.73
lin8′	$C_{\infty v}$	$^4\Sigma^-$	d1 = 1.540 d2 = 1.290 d3 = 1.269 d4 = 1.278 d5 = 1.284 d6 = 1.260 d7 = 1.313 d8 = 1.235	13.8	1.36
cyc8	C_{2v}	$^2B_2$	d1 = 1.693 d2 = 1.238 d3 = 1.331 d4 = 1.256 d5 = 1.320 θ1 = 92.9 θ2 = 156.9 θ3 = 150.6 θ4 = 139.1 θ5 = 137.0	45.6	0.71
C_9S^+				−740.609 833	
lin9	$C_{\infty v}$	$^2\Pi$	d1 = 1.534 d2 = 1.296 d3 = 1.260 d4 = 1.289 d5 = 1.266 d6 = 1.282 d7 = 1.273 d8 = 1.282 d9 = 1.307	0.0	4.37
lin9′	$C_{\infty v}$	$^4\Pi$	d1 = 1.549 d2 = 1.288 d3 = 1.277 d4 = 1.276 d5 = 1.288 d6 = 1.266 d7 = 1.294 d8 = 1.271 d9 = 1.327	28.0	4.20
cyc9	C_{2v}	$^2A_1$	d1 = 1.666 d2 = 1.294 d3 = 1.264 d4 = 1.324 d5 = 1.383 θ1 = 97.3 θ2 = 143.2 θ3 = 162.7 θ4 = 156.3 θ5 = 176.2 θ6 = 65.8	79.3	1.27
$C_{10}S^+$				−778.703 410	
lin10	$C_{\infty v}$	$^2\Pi$	d1 = 1.533 d2 = 1.300 d3 = 1.253 d4 = 1.300 d5 = 1.253 d6 = 1.298 d7 = 1.256 d8 = 1.292 d9 = 1.270 d10 = 1.310	0.0	4.72
lin10′	$C_{\infty v}$	$^4\Pi$	d1 = 1.556 d2 = 1.276 d3 = 1.292 d4 = 1.256 d5 = 1.307 d6 = 1.251 d7 = 1.303 d8 = 1.261 d9 = 1.293 d10 = 1.311	21.6	4.49
cyc10	C_{2v}	$^2B_2$	d0 = 1.392 d1 = 1.790 d2 = 1.318 d3 = 1.278 d4 = 1.278 d5 = 1.297 d6 = 1.270 θ = 45.7 θ1 = 200.3 θ2 = 153.9 θ3 = 146.5 θ4 = 147.6 θ5 = 138.9	34.9	1.19
$C_{11}S^+$				−816.798 940	
lin11	$C_{\infty v}$	$^2\Pi$	d1 = 1.536 d2 = 1.295 d3 = 1.259 d4 = 1.291 d5 = 1.264 d6 = 1.286 d7 = 1.269 d8 = 1.279 d9 = 1.274 d10 = 1.282 d11 = 1.304	0.0	5.44
cyc11	C_{2v}	$^2A_2$	d0 = 1.491 d1 = 1.743 d2 = 1.293 d3 = 1.282 d4 = 1.280 d5 = 1.287 d6 = 1.285 θ = 50.7 θ1 = 197.5 θ2 = 158.5 θ3 = 150.9 θ4 = 156.7 θ5 = 134.4 θ6 = 153.5	31.9	0.33
$C_{12}S^+$				−854.891 524	
lin12	$C_{\infty v}$	$^2\Pi$	d1 = 1.536 d2 = 1.297 d3 = 1.254 d4 = 1.299 d5 =1.253 d6 = 1.299 d7 = 1.255 d8 = 1.296 d9 = 1.259 d10 = 1.288 d11 = 1.273 d12 = 1.306	0.0	5.75
cyc12	C_{2v}	$^2A_1$	d0 = 1.470 d1 =1.743 d2 = 1.297 d3 = 1.287 d4 = 1.271 d5 = 1.301 d6 = 1.264 d7 = 1.306 θ = 49.9 θ1 = 201.3 θ2 = 158.6 θ3 = 157.4 θ4 = 153.0 θ5 = 147.9 θ6 = 147.0	41.9	0.54

(continued)

Table 1(a) (*continued*)

Isomer	Point group	State	Structural parameters	ΔE^a	μ
$C_{13}S^+$				−892.985 614	
lin13	$C_{\infty v}$	$^2\Pi$	d1 = 1.538 d2 = 1.293 d3 = 1.259 d4 = 1.292 d5 = 1.261 d6 = 1.288 d7 = 1.266 d8 = 1.283 d9 = 1.271 d10 = 1.278 d11 = 1.274 d12 = 1.282 d13 =1.301	0.0	6.56
cyc13	C_{2v}	$^2B_1$	d0 = 1.395 d1 = 1.768 d2 = 1.325 d3 = 1.257 d4 = 1.300 d5 = 1.269 d6 = 1.292 d7 = 1.283 θ = 46.5 θ1 = 204.7 θ2 = 162.3 θ3 = 155.0 θ4 = 163.0 θ5 = 141.8 θ6 = 162.4 θ7 = 135.1	24.7	1.26
				−931.077520	
$C_{14}S^+$	$C_{\infty v}$	$^2\Pi$	d1 = 1.538 d2 = 1.295 d3 = 1.255 d4 = 1.298 d5 = 1.253 d6 = 1.299 d7 = 1.254 d8 = 1.298 d9 = 1.256 d10 = 1.294 d11 = 1.261 d12 = 1.286 d13 = 1.275 d14 = 1.303	0.0	6.83
cyc14	C_{2v}	$^2B_1$	d0 = 1.388 d1 = 1.778 d2 = 1.329 d3 = 1.249 d4 = 1.311 d5 = 1.250 d6 = 1.313 d7 = 1.250 d8 = 1.314 θ = 45.9 θ1 = 209.2 θ2 = 156.2 θ3 = 166.4 θ4 = 155.3 θ5 = 157.5 θ6 = 150.9 θ7 = 151.4	6.1	1.66

[a] Total energies in hartree.

[b] lin*n* ≡ C_nS^+ isomer, cyc*n* ≡ cyclic C_nS^+ isomer; ′ ≡ quadruplet.

Table 1(b)

Structural parameters (distance in Å, angle in degrees), total energies (in hartree), relative stabilities ΔE (in kcal mol^{-1}) and dipole moments (in debye) of the different C_nS^+ ($13 \leq n \leq 20$) structures obtained with a DFT/B3LYP/6-31G* method. The symmetry (point group) and the electronic state of the different structures are also given

Isomer	Point group	State	Structural parameters	ΔE^a	μ
$C_{13}S^+$				−892.848 599	
lin13	$C_{\infty v}$	$^2\Pi$	d1 = 1.544 d2 = 1.296 d3 = 1.266 d4 = 1.295 d5 = 1.268 d6 = 1.292 d7 = 1.272 d8 = 1.287 d9 = 1.277 d10 = 1.283 d11 = 1.280 d12 = 1.287 d13 = 1.307	0.0	5.41
cyc13	C_{2v}	$^2B_1$	d0 = 1.402 d1 = 1.771 d2 = 1.327 d3 = 1.265 d4 = 1.304 d5 = 1.277 d6 = 1.297 d7 = 1.289 θ = 46.6 θ1 = 204.4 θ2 = 163.7 θ3 = 152.8 θ4 = 164.8 θ5 = 140.1 θ6 = 164.0 θ7 = 133.7	22.7	1.06
$C_{14}S^+$				−930.931 195	
lin14	$C_{\infty v}$	$^2\Pi$	d1 = 1.543 d2 = 1.299 d3 = 1.262 d4 = 1.302 d5 = 1.260 d6 = 1.303 d7 = 1.260 d8 = 1.302 d9 = 1.262 d10 = 1.298 d11 = 1.266 d12 = 1.291 d13 = 1.280 d14 = 1.309	0.0	5.71
cyc14	C_{2v}	$^2B_1$	d0 = 1.394 d1 = 1.782 d2 = 1.334 d3 = 1.257 d4 = 1.315 d5 = 1.258 d6 = 1.316 d7 = 1.259 d8 = 1.316 θ = 46.1 θ1 = 209.8 θ2 = 154.0 θ3 = 169.3 θ4 = 152.6 θ5 =160.4 θ6 = 149.1 θ7 = 151.9	5.7	0.93
$C_{15}S^+$				−969.015 426	
lin15	$C_{\infty v}$	$^2\Pi$	d1 = 1.545 d2 = 1.295 d3 = 1.267 d4 = 1.295 d5 = 1.268 d6 = 1.293 d7 = 1.270 d8 = 1.290 d9 = 1.274 d10 = 1.286 d11 = 1.278 d12 = 1.282 d13 = 1.279 d14 = 1.288 d15 = 1.309	0.0	6.38
cyc15	C_{2v}	$^2A_1$	d0 = 1.374 d1 = 1.803 d2 = 1.335 d3 = 1.259 d4 = 1.308 d5 = 1.269 d6 = 1.300 d7 = 1.280 d8 = 1.292 θ = 44.8 θ1 = 208.8 θ2 = 159.0 θ3 = 171.0 θ4 = 153.0 θ5 = 166.3 θ6 = 145.7 θ7 = 163.1 θ8 = 141.9	5.2	0.75

(*continued*)

Table 1(b) (*continued*)

Isomer	Point group	State	Structural parameters	ΔE^a	μ $C_{16}S^+$
				−1007.097502	
lin16	$C_{\infty v}$	$^2\Pi$	d1 = 1.545 d2 = 1.297 d3 = 1.264 d4 = 1.300 d5 = 1.261 d6 = 1.303 d7 = 1.260 d8 = 1.303 d9 = 1.260 d10 = 1.301 d11 = 1.263 d12 = 1.297 d13 = 1.268 d14 = 1.289 d15 = 1.281 d16 = 1.307	0.0	6.62
cyc16	C_{2v}	$^2A_2$	d0 = 1.408 d1 = 1.779 d2 = 1.325 d3 = 1.263 d4 = 1.307 d5 = 1.265 d6 = 1.307 d7 = 1.266 d8 = 1.307 d9 = 1.267 θ = 46.6 θ1 = 209.0 θ2 = 161.2 θ3 = 170.1 θ4 = 156.5 θ5 = 162.3 θ6 = 152.7 θ7 = 158.8 θ8 = 153.1	16.9	0.12
$C_{17}S^+$				−1045.180 967	
lin17	$C_{\infty v}$	$^2\Pi$	d1 = 1.547 d2 = 1.294 d3 = 1.267 d4 = 1.294 d5 = 1.267 d6 = 1.294 d7 = 1.269 d8 = 1.292 d9 = 1.272 d10 = 1.289 d11 = 1.275 d12 = 1.285 d13 = 1.278 d14 = 1.282 d15 = 1.279 d16 = 1.289 d17 = 1.303	0.0	7.42
cyc17	C_{2v}	$^2B_1$	d0 = 1.395 d1 = 1.782 d2 = 1.325 d3 = 1.262 d4 = 1.304 d5 = 1.269 d6 = 1.298 d7 = 1.277 d8 = 1.292 d9 = 1.285 d10 θ = 46.1 θ1 = 208.6 θ2 = 168.3 θ3 = 161.9 θ4 = 168.5 θ5 = 154.6 θ6 = 167.6 θ7 = 147.9 θ8 = 166.9 θ9 = 145.1	8.6	0.88
$C_{18}S^+$				−1083.262 656	
lin18	$C_{\infty v}$	$^2\Pi$	d1 = 1.547 d2 = 1.295 d3 = 1.265 d4 = 1.299 d5 = 1.261 d6 = 1.302 d7 = 1.260 d8 = 1.303 d9 = 1.260 d10 = 1.303 d11 = 1.261 d12 = 1.300 d13 = 1.264 d14 = 1.296 d15 = 1.269 d16 = 1.288 d17 = 1.283 d18 = 1.305	4.0	7.62
cyc18	C_{2v}	$^2B_1$	d0 = 1.387 d1 = 1.790 d2 = 1.332 d3 = 1.254 d4 = 1.315 d5 = 1.255 d6 = 1.316 d7 = 1.254 d8 = 1.317 d9 = 1.255 d10 = 1.317 θ = 45.6 θ1 = 211.6 θ2 = 162.1 θ3 = 172.2 θ4 = 160.4 θ5 = 167.9 θ6 = 156.3 θ7 = 163.8 θ8 = 154.6 θ9 = 158.3	0.0	1.20
$C_{19}S^+$				−1121.352 706	
lin19	$C_{\infty v}$	$^2\Pi$	d1 = 1.548 d2 = 1.293 d3 = 1.268 d4 = 1.294 d5 = 1.267 d6 = 1.294 d7 = 1.268 d8 = 1.293 d9 = 1.270 d10 = 1.291 d11 = 1.273 d12 = 1.288 d13 = 1.275 d14 = 1.285 d15 = 1.278 d16 = 1.283 d17 = 1.278 d18 = 1.289 d19 = 1.302	4.5	8.55
cyc19	C_{2v}	$^2A_1$	d0 = 1.369 d1 = 1.810 d2 = 1.333 d3 = 1.256 d4 = 1.308 d5 = 1.265 d6 = 1.301 d7 = 1.272 d8 = 1.295 d9 = 1.280 d10 = 1.288 θ = 44.4 θ1 = 210.8 θ2 = 165.6 θ3 = 172.6 θ4 = 161.1 θ5 = 170.0 θ6 = 156.9 θ7 = 167.2 θ8 = 152.6 θ9 = 165.6 θ10 = 150.8	0.0	0.67
$C_{20}S^+$				−1159.426 935	
lin20	$C_{\infty v}$	$^2\Pi$	d1 = 1.548 d2 = 1.294 d3 = 1.266 d4 = 1.298 d5 = 1.262 d6 = 1.301 d7 = 1.260 d8 = 1.303 d9 = 1.260 d10 = 1.303 d11 = 1.260 d12 = 1.302 d13 = 1.262 d14 = 1.299 d15 = 1.265 d16 = 1.294 d17 = 1.270 d18 = 1.287 d19 = 1.284 d20 = 1.304	0.0	8.67
cyc20	C_{2v}	$^2A_2$	d0 = 1.405 d1 = 1.786 d2 = 1.321 d3 = 1.263 d4 = 1.304 d5 = 1.265 d6 = 1.303 d7 = 1.265 d8 = 1.304 d9 = 1.266 d10 = 1.303 d11 = 1.267 θ = 46.3 θ1 = 210.8 θ2 = 166.8 θ3 = 172.2 θ4 = 162.9 θ5 = 169.5 θ6 = 159.8 θ7 = 166.6 θ8 = 156.6 θ9 = 163.4 θ10 = 158.2	5.3	0.15
$C_{21}S^+$				−1197.509 365	
lin21	$C_{\infty v}$	$^2\Pi$	d1 = 1.549 d2 = 1.292 d3 = 1.268 d4 = 1.294 d5 = 1.267 d6 = 1.295 d7 = 1.267 d8 = 1.294 d9 = 1.269 d10 = 1.293 d11 = 1.271 d12 = 1.291 d13 = 1.273 d14 = 1.288 d15 = 1.276 d16 = 1.285 d17 = 1.278 d18 = 1.283 d19 = 1.278 d20 = 1.290 d21 = 1.301	0.0	9.77

(continued)

Table 1(b) (*continued*)

Isomer	Point group	State	Structural parameters	ΔE^{a}	μ
cyc21	C_{2v}	$^{2}B_{2}$	$d0 = 1.428$ $d1 = 1.776$ $d2 = 1.309$ $d3 = 1.275$ $d4 = 1.289$ $d5 = 1.280$ $d6 = 1.285$ $d7 = 1.283$ $d8 = 1.285$ $d9 = 1.284$ $d10 = 1.285$ $d11 = 1.285$ $\theta = 47.4$ $\theta1 = 211.0$ $\theta2 = 165.9$ $\theta3 = 173.7$ $\theta4 = 164.2$ $\theta5 = 170.6$ $\theta6 = 161.3$ $\theta7 = 167.8$ $\theta8 = 158.0$ $\theta9 = 165.5$ $\theta10 = 156.0$ $\theta11 = 164.5$	4.7	0.96
$C_{22}S^{+}$				−1235.600 147	
lin22	$C_{\infty v}$	$^{2}\Pi$	$d1 = 1.549$ $d2 = 1.293$ $d3 = 1.267$ $d4 = 1.297$ $d5 = 1.263$ $d6 = 1.300$ $d7 = 1.261$ $d8 = 1.302$ $d9 = 1.260$ $d10 = 1.304$ $d11 = 1.259$ $d12 = 1.303$ $d13 = 1.260$ $d14 = 1.302$ $d15 = 1.263$ $d16 = 1.298$ $d17 = 1.266$ $d18 = 1.293$ $d19 = 1.271$ $d20 = 1.286$ $d21 = 1.285$ $d22 = 1.302$	6.0	9.82
cyc22	C_{2v}	$^{2}B_{2}$	$d0 = 1.375$ $d1 = 1.812$ $d2 = 1.323$ $d3 = 1.263$ $d4 = 1.297$ $d5 = 1.273$ $d6 = 1.288$ $d7 = 1.281$ $d8 = 1.282$ $d9 = 1.287$ $d10 = 1.278$ $d11 = 1.290$ $d12 = 1.277$ $\theta = 44.6$ $\theta1 = 211.3$ $\theta2 = 171.9$ $\theta3 = 168.4$ $\theta4 = 171.4$ $\theta5 = 163.6$ $\theta6 = 169.6$ $\theta7 = 160.3$ $\theta8 = 167.8$ $\theta9 = 157.8$ $\theta10 = 165.5$ $\theta11 = 160.2$	0.0	1.47
$C_{23}S^{+}$				−1273.679 369	
lin23	$C_{\infty v}$	$^{2}\Pi$	$d1 = 1.550$ $d2 = 1.292$ $d3 = 1.269$ $d4 = 1.293$ $d5 = 1.267$ $d6 = 1.295$ $d7 = 1.267$ $d8 = 1.295$ $d9 = 1.268$ $d10 = 1.294$ $d11 = 1.269$ $d12 = 1.293$ $d13 = 1.271$ $d14 = 1.291$ $d15 = 1.273$ $d16 = 1.288$ $d17 = 1.275$ $d18 = 1.285$ $d19 = 1.277$ $d20 = 1.284$ $d21 = 1.277$ $d22 = 1.291$ $d23 = 1.300$	4.6	11.14
cyc23	C_{2v}	$^{2}A_{2}$	$d0 = 1.423$ $d1 = 1.784$ $d2 = 1.307$ $d3 = 1.275$ $d4 = 1.288$ $d5 = 1.279$ $d6 = 1.285$ $d7 = 1.281$ $d8 = 1.285$ $d9 = 1.282$ $d10 = 1.284$ $d11 = 1.283$ $d12 = 1.284$ $\theta = 47.0$ $\theta1 = 150.3$ $\theta2 = 171.2$ $\theta3 = 170.1$ $\theta4 = 172.4$ $\theta5 = 164.8$ $\theta6 = 171.1\theta7 = 161.3$ $\theta8 = 169.7$ $\theta9 = 157.8$ $\theta10 = 168.7$ $\theta11 = 157.8$ $\theta12 = 168.2$	0.0	0.00

[a] Total energies in hartree.

cations. The structural parameters of the linear and cyclic isomers, the ionization energies and fragmentation energies are calculated by carrying out the geometry optimization with the DFT(B3LYP) method. Comparison with the corresponding neutral species is also made.

2. Calculation method

All calculations have been carried out using the GAUSSIAN 94 package [7] running in the IBM RS6000 on the Cray C94 and C98 computer of the National Computer Center Idris in Orsay (France). The B3LYP exchange-correlation functional [8] has been used throughout employing a 6-311G* basis set for $1 \leq n \leq 14$ and a 6-31G* basis set for $13 \leq n \leq 23$. This method uses the Lee-Yang-Parr nonlocal correlation functional [8] in conjunction with a three parameter exchange hybrid functional first proposed by Becke [9], the latter being a linear combination of local density approximation, Becke's gradient correction [10] and the Hartree–Fock exchange energy based on Kohn-Sham orbitals [11]. From previous works devoted to application of this method, it is thought that DFT(B3LYP) calculations predict the low-lying structures of pure and heteroatom-doped medium-sized carbon clusters closer to the experimental values than many-body perturbation theory at the second order [MBPT(2)] [12] and at moderate cost compared to any accurate ab initio method in use such as coupled cluster theory with single-double (triple) substitutions [CCSD(T)] [12,13].

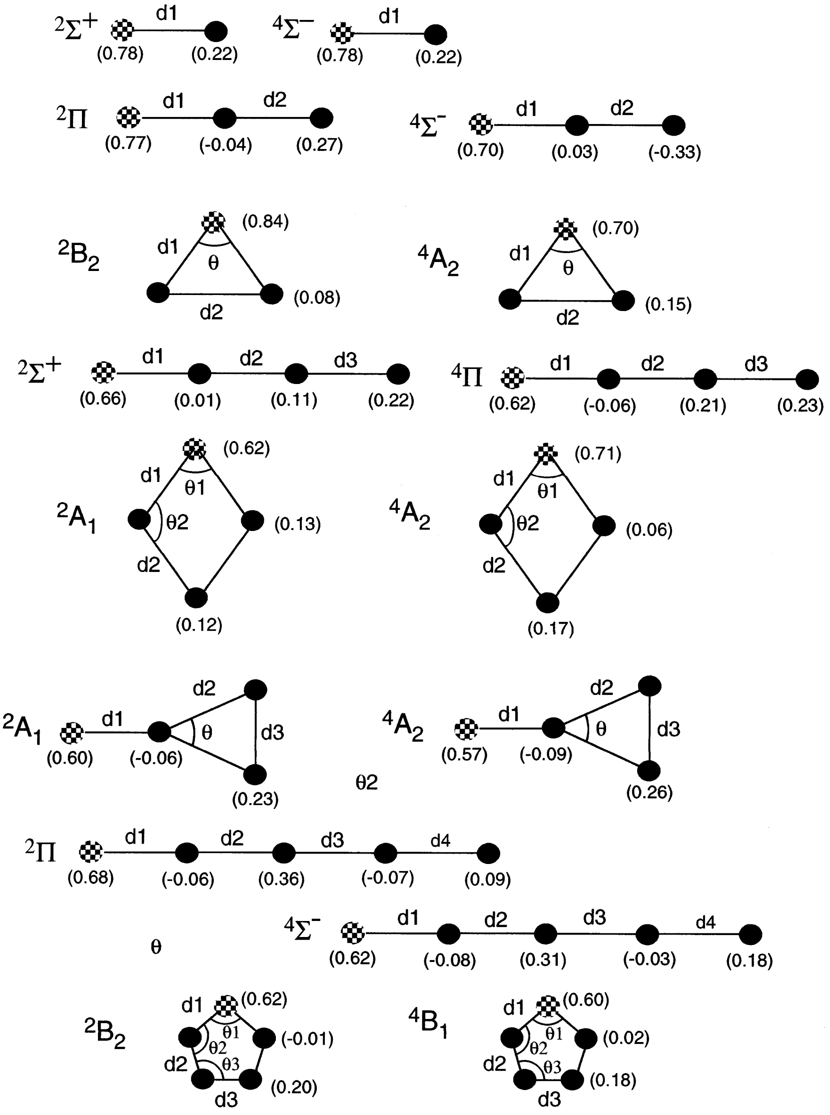

Fig. 1. Equilibrium geometries of energetically low-lying structures of C_nS^+ ($1 \leq n \leq 23$). Mulliken atomic charges (given in parentheses) are given in electron charge unit (e). Structural parameters for these geometries are listed in Tables 1a and 1b.

3. Results and comments

Tables 1a and 1b present the calculated total and relative energies at optimized structures, reported in Fig. 1, of a number of isomeric forms of C_nS^+ clusters, in both doublet and quadruplet states, and the dipole moments of these species, by employing the B3LYP/6-311G* ($n = 1 - 14$) and B3LYP/6-31G* ($n = 13 - 23$) methods. In Table 2, we list the valence orbital configuration of the linear C_nS^+ ($n = 1 - 5$) clusters. The vibrational frequencies and rotational constants calculated with a 6-311G* basis set for C_nS^+ clusters ($n = 1 - 8$), are respectively listed in Tables 3 and 4. Theoretical investigations on small and medium-sized neutral sulphur carbides have been reported [6,14] but, by contrast and to the best of our knowledge, very little experimental information exists on C_nS^+ cations, except for CS^+ [15]. For the latter

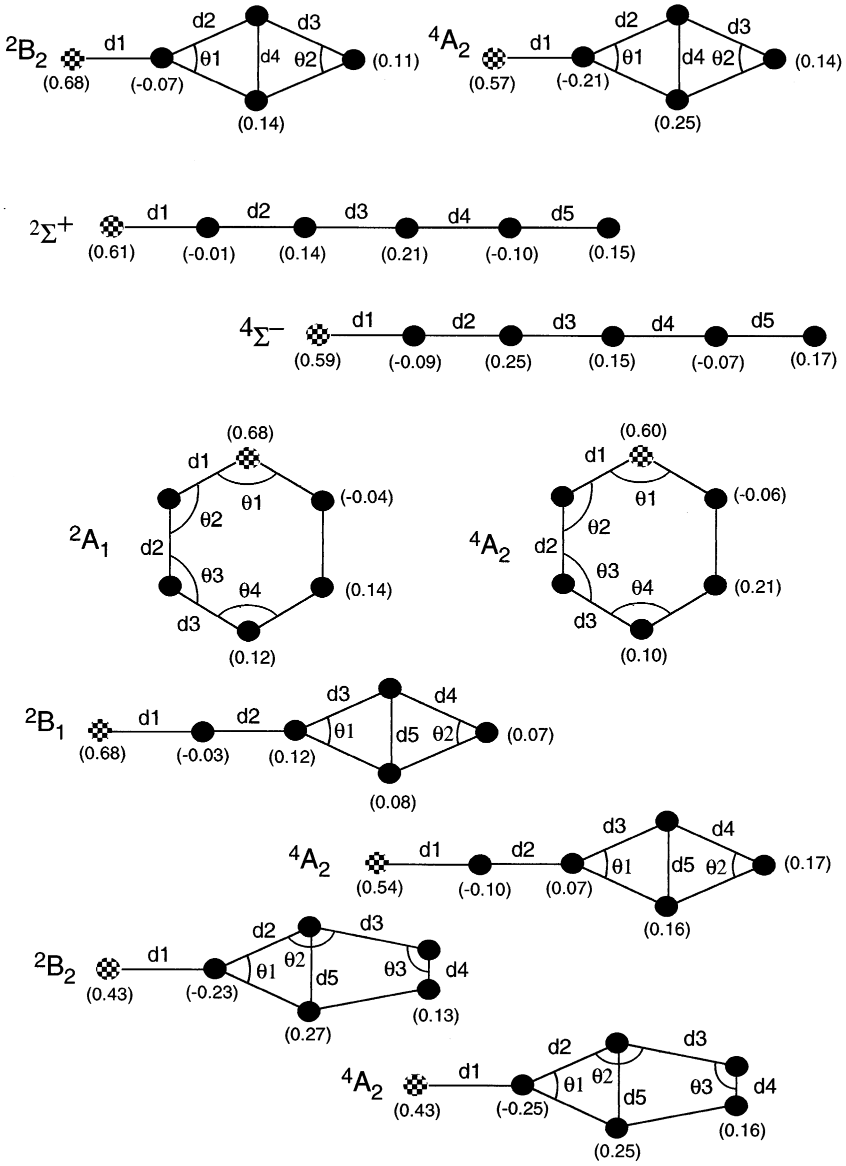

Fig. 1. (*continued*)

molecule the electronic ground state is $^2\Sigma^+$ with a bond length of 1.493 Å.This value coincides with the experimental value [16]. The calculated vibrational frequency is 1417 cm^{-1} in good agreement with the experimental frequency found to be equal to 1376.6 cm^{-1} [16]. More generally, for all the C_nS^+ clusters studied (linear and cyclic), the doublet electronic ground state is lower in energy than the corresponding low-lying quadruplet. Taking into account this fact, we shall only concentrate the discussion on the doublets. First, it is interesting to compare the calculated SC distances in the cations with those of the corresponding neutral isomers. For the linear species, the SC distances are systematically shortened by about 0.04–0.05 Å in the cations with respect to the SC distances in the corresponding neutrals. This is not

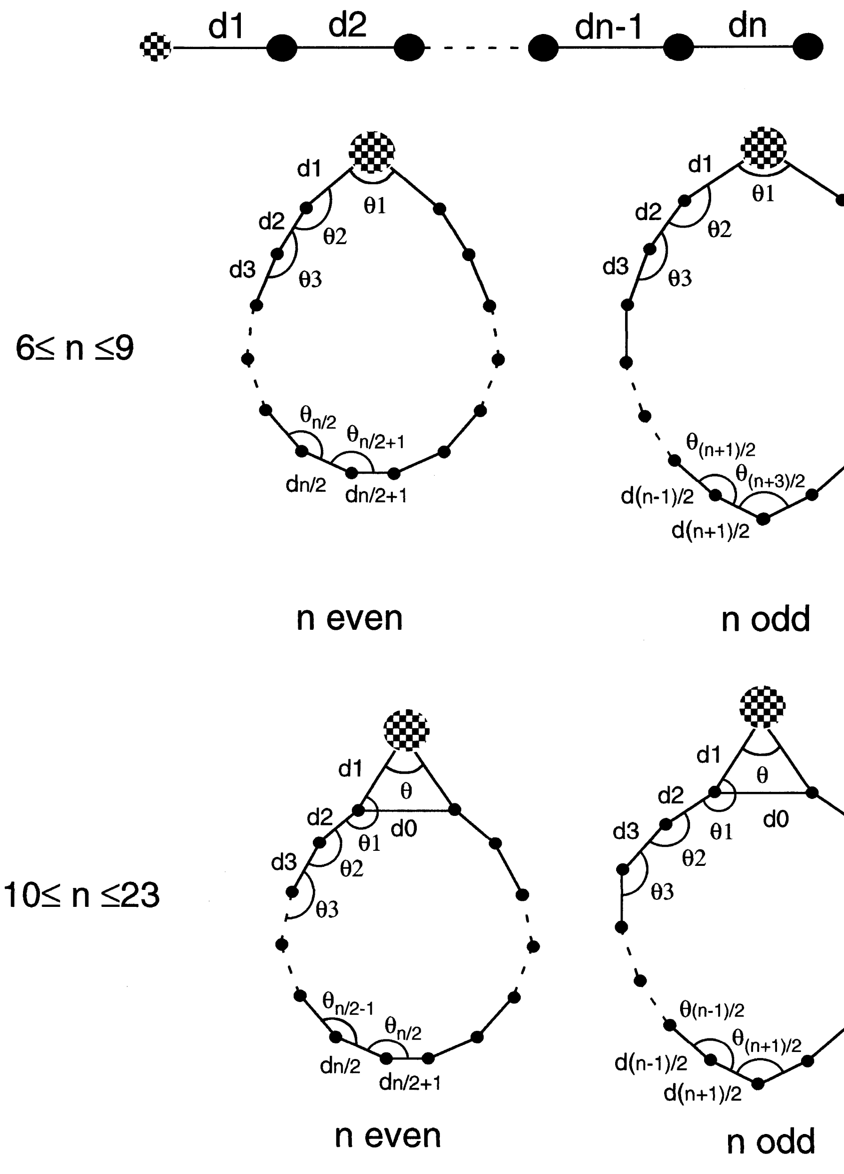

Fig. 1. (*continued*)

the case for the cyclic isomers where the SC lengths are mostly similar in both cations and neutral species to within about 0.01 Å, except for C_5S^+ and C_6S^+ where the shortening of the SC length is ~0.03 Å. The CC distances in the neutral linear isomers were found to be ~1.27–1.30 Å confering to these species a clear cumulenic structure [6]. In contrast, the cations appear quasi acetylenic with alternating long (~1.33–1.34 Å) and short (~1.21–1.23 Å) carbon–carbon bonds when $n \leq 6$. Above $n = 6$ the linear structures again appear cumulenic for the cations with CC distances comparable to those found in the neutrals. Atomic charge distributions along the carbon chain are simultaneously represented in Fig. 2 for the neutral, $C_{20}S$, and the cation, $C_{20}S^+$. Comparing the two diagrams shows that, in both cases, neutral and cation, the charge exhibits large-amplitude oscillations, identified with Friedel oscillations, and concentrated at the two extremities "the surface" of the chain. In contrast, the charge beared by each atom forming the middle part of the carbon chain is very weak (smaller than $+0.01\ e$ in the neutral and smaller than $+0.1\ e$ in the cation). But the question can still be reexamined from another point of view. More precisely, summing up the charges over the seven atoms which constitute the middle part of the neutral $C_{20}S$ actually supplies a very weak totalized charge of only $+0.04\ e$. On the contrary, a similar summation performed on $C_{20}S^+$ yields a totalized charge of about $+0.27\ e$ [such a value has to be compared to the totalized charge of the first seven atoms of this cation (sulphur included) and to that of its last seven carbons at the other end, respectively found of the order of $+0.43\ e$ and $+0.30\ e$]. The default of electronic charge in the cation is thus fully delocalized among the chain with $+0.18\ e$ on sulphur and a mean value of about $+0.04\ e$ on each carbon (even though this effect is masked at the two extremities by the very strong oscillations of the charge).

A clear-cut difference between the neutral and cationic linear isomers concerns the odd-even parity. In the neutral linear species, it has been found that the electronic ground state is alternately predicted to be $^1\Sigma^+$ for odd n or $^3\Sigma^-$ for even n with a conspicuous odd-even effect in cluster stability up to $n = 20$ [6]. This odd-even alternation is also apparent on the ionization energies (Fig. 3). On the other hand, all linear cations C_nS^+ are invariably in a $^2\Pi$ electronic ground state, except CS^+, C_3S^+, C_5S^+ which are in a $^2\Sigma^+$ state. Thus, in contrast with what we have found for the neutral C_nS clusters, no parity appearance occurs for large n in the cations, as it is well illustrated by the incremental energy curve which indeed presents a flattening as soon as n is larger than six (Fig. 4). This result is closely related to the filling up of the orbitals [6]. C_nS^+ clusters contains $4n + 5$ valence electrons and two distinct situations can appear. In the first one, the half-filled orbital is a σ orbital and all the π orbitals are fully filled with four electrons. This situation corresponds to CS^+, C_3S^+ and C_5S^+. In this case, excepting CS^+, the C_nS^+ clusters are more stable than their respective $n - 1$ and $n + 1$ congeners. In the second situation, the σ bonding orbitals are fully filled and one π orbital (HOMO) is not fully filled. The latter situation corresponds to all the other cases ($n \neq 1, 3, 5$). Strictly speaking, there nevertheless exists a very small odd-even parity effect even when $n \geq 6$ for the cations, because of the fact that the HOMO, even though not fully filled, is a π bonding orbital for odd n and a π nonbonding orbital for even n, the latter situation being slightly less stable than the former one.

The relative stability of the linear C_nS^+ clusters can also be evaluated within the framework of the fragmentation patterns. The fragmentation reactions $C_nS^+ \rightarrow C_{n-m}^+ + C_m$ with $n = 1, 2$ and 3 are displayed in Fig. 5. A twofold periodicity in stability for C_nS^+ clusters clearly appears on this figure where the fragmentation energies are plotted against n. Clusters with even n easily lose a C atom or a C_3 fragment to becoming $C_{n-1}S^+$ or $C_{n-3}S^+$, i.e. clusters with an odd number of carbons. In other words, the loss of a C atom or a C_3 fragment involves larger energies for odd n clusters than for even n clusters. In contrast, fragmentation with C_2 loss is easier for odd n clusters than for even n clusters, the corresponding

Table 2
Valence orbital configuration of the ground state of the linear C_nS^+ ($1 \leq n \leq 5$) clusters

Isomer	Electronic configuration
CS^+	core $(5\sigma)^2(6\sigma)^2(7\sigma)^1(2\pi)^4$
C_2S^+	core $(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^1$
C_3S^+	core $(7\sigma)^2(8\sigma)^2(9\sigma)^2(10\sigma)^2(11\sigma)^1(2\pi)^4(3\pi)^4$
C_4S^+	core $(8\sigma)^2(9\sigma)^2(10\sigma)^2(11\sigma)^2(12\sigma)^2(2\pi)^4(3\pi)^4(13\sigma)^2(4\pi)^1$
C_5S^+	core $(9\sigma)^2(10\sigma)^2(11\sigma)^2(12\sigma)^2(13\sigma)^2(14\sigma)^2(15\sigma)^1(2\pi)^4(3\pi)^4(4\pi)^4$

Table 3
Vibrational frequencies (in cm^{-1}) and zero-point energy (in kcal mol^{-1}) of the different C$_n$S$^+$ ($1 \le n \le 8$) clusters calculated with a DFT/6-311G* method. Imaginary frequencies indicate a saddle point on the energy surface. The Hessian index is also given

Structure	Vibrational frequencies	Zero-point energy (kcal/mol)	Hessian index
CS+			
lin1[a]	1417(σ)	2.0	0
lin1′	909(σ)	1.3	0
C$_2$S$^+$			
lin2	182(π) 253(π) 857(σ) 1576(σ)	4.1	0
lin2′	360(π)[d] 905(σ) 1701(σ)	4.7	0
cyc2	638i(b2) 857(a1) 1392(a1)	3.2	1
cyc2′	480(b2) 699(a1) 1668(a1)	4.1	0
C$_3$S$^+$			
lin3	192(π)[d] 465(π)[d] 758(σ) 1680(σ) 2189(σ)	8.5	0
lin3′	41(π) 192(π) 201(π) 484(π) 685(σ) 1341(σ) 1961(σ)	7.0	0
cyc3	345(b2) 374(b1) 654(a1) 962(a1) 1030(b2) 1688(a1)	7.2	0
cyc3′	430i(b1) 44i(b2) 279(a1) 533(a1) 1364(b2) 1555(a1)	5.3	2
S-cycC3	276(b2) 380(b2) 420(b1) 665(a1) 1257(a1) 1695(a1)	6.7	0
S-cycC3′	321(b2) 373(b1) 606(a1) 899(b2) 1186(a1) 1426(a1)	6.9	0
C$_4$S$^+$			
lin4	103(π) 120(π) 242(π) 286(π) 369(π) 498(π) 621(σ) 1228(σ) 1726(σ) 2113(σ)	10.4	0
lin4′	133(π)[d] 368(π)[d] 417(π)[d] 625(σ) 1286(σ) 1853(σ) 1914(σ)	10.1	0
cyc4	1002i(b2) 477i(a2) 333(b1) 369(a1) 672(b2) 697(a1) 1369(a1) 1621(b2) 1644(a1)	9.6	2
cyc4′	394(a2) 405(b1) 449(b2) 583(a1) 748(a1) 755(b2) 1232(a1) 1849(a1) 2169(b2)	12.3	0
S-bicycC4	189i(b2) 196(b1) 323(b2) 519(b1) 591(a1) 904(a1) 1062(b2) 1288(a1) 1474(a1)	9.1	1
S-bicycC4′	181(b1) 194(b2) 381(b2) 472(b1) 558(a1) 819(b2) 887(a1) 1490(a1) 1505(a1)	9.3	0
C$_5$S$^+$			
lin5	87(π)[d] 225(π)[d] 425(π)[d] 441(π)[d] 546(σ) 1112(σ) 1724(σ) 2158(σ) 2225(σ)	14.5	0
lin5′	84(π) 87(π) 218(π) 221(π) 364(π) 392(π) 414(π) 433(π) 534(σ) 1060(σ) 1590(σ) 1853(σ) 2019(σ)	13.2	0
cyc5	288(a1) 361(b2) 394(b1) 447(a2) 457(b1) 504(b2) 546(a1) 772(a1) 1252(a1) 1374(b2) 1759(b2) 1769(a1)	14.2	0
cyc5′	273(b1) 276(a2) 381(a1) 528(b1) 534(b2) 566(a1) 615(b2) 711(a1) 1256(a1) 1283(b2) 1546(b2) 1686(a1)	13.8	0
SC-bicycC4	1056i(b1) 148(b2) 151(b1) 388(b1) 401(b2) 536(a1) 633(b2) 9136(a1) 995(b2) 1254(a1) 1420(a1) 1799(a1)	12.3	1
SC-bicycC4′	515i(b1) 131(b2) 162(b1) 394(a1) 414(b1) 417(b2) 537(b2) 661(a1) 1150(a1) 1227(b2) 1513(a1) 1738(a1)	11.9	1
S-bicycC5	881i(b2) 300i(b2) 2041i(b1) 174(b1) 349(b2) 514(a1) 759(b2) 839(a1) 992(a1) 1151(a1) 1336(a2) 1543(a1)	10.9	3
S-bicycC5′	304i(a2) 170(b1) 201(b2) 393(b2) 414(b1) 488(a1) 655(b2) 795(a1) 940(b2) 1088(a1) 1446(a1) 1536(a1)	11.6	1

(continued)

Table 3 (*continued*)

Structure	Vibrational frequencies	Zero-point energy (kcal/mol)	Hessian index
C_6S^+			
lin6	67(π)^{d} 145(π) 151(π) 247(π) 279(π) 321(π) 412(π) 439(π) 479(σ) 557(π) 953(σ) 1415(σ) 1763(σ) 2104(σ) 2133(σ)	16.5	0
lin6′	70(π)^{d} 192(π)^{d} 344(π)^{d} 375(π)^{d} 481(σ) 495(π)^{d} 1486(σ) 1814(σ) 1934(σ) 2060(σ)	15.3	0
cyc6	151(b2) 159(a2) 247(b1) 314(a2) 337(a1) 396(b2) 467(b1) 551(b2) 561(a1) 721(a1) 1192(a1) 1359(b2) 1847(a1) 1900(b2) 1911(a1)	17.3	0
C_7S^+			
lin7	52(π) 54(π) 128(π) 149(π) 231(π) 302(π) 389(π) 418(σ) 439(π) 444(π) 543(π) 616(π) 702(π) 822(σ) 1227(σ) 1586(σ) 1866(σ) 1951(σ) 2092(σ)	20.0	0
lin7′	223i(π) 200i(π) 55(π) 62(π) 125(π) 154(π) 214(π) 248(π) 258(π) 362(π) 408(π) 425(σ) 517(π) 821(σ) 1214(σ) 1529(σ) 1838(σ) 1904(σ) 1993(σ)	17.3	2
cyc7	332i(b1) 152(a2) 188(b1) 252(a2) 289(a1) 307(b1) 362(b2) 435(a1) 496(a1) 512(b2) 596(b2) 668(a1) 1123(a1) 1264(b2) 1610(b2) 1762(a1) 1953(b2) 1960(a1)	19.9	1
C_8S^+			
lin8	44(π) 45(π) 116(π) 136(π) 199(π) 206(π) 332(π) 340(π) 391(σ) 419(π) 454(π) 497(π) 578(π) 627(π) 776(σ) 1157(σ) 1525(σ) 1773(σ) 2057(σ) 2108(σ) 2180(σ)	22.8	0
lin8′	282(π)^{d} 47(π)^{d} 132(π)^{d} 246(π)^{d} 379(π)^{d} 391(σ) 466(π)^{d} 654(π)^{d} 778(σ) 1169(σ) 1555(σ) 2106(σ)	22.3	0
cyc8	467i(b2) 60(a2) 180(b1) 204(b2) 239(a2) 244(a1) 329(b1) 369(a2) 385(b1) 419(a1) 420(b2) 496(a1) 623(b2) 634(a1) 1034(a1) 1197(b2) 1452(a1) 1946(b2) 1947(a1) 2000(b2) 2029(a1)	23.2	1

[a] lin*n* ≡ linear C_nS isomer, cyc*n* ≡ cyclic C_nS isomer; ′ ≡ quadruplet.

reactions giving a fragment (daughter) cluster of the same parity as the original (parent) cluster. Our results equally show that, in the latter situation, the even-odd oscillation of fragmentation energy curve, strongly marked for $n \leq 7$, completely disappears as soon as $n \geq 8$. In any case, for clusters with six or more carbon atoms the dominant channel is C_3 loss with energy dissociation energies ~6 eV. Loss of C_2 fragment is more difficult to realize, involving dissociation energies ~8 eV. This result is consistent with experiments of Gensic et al. [17] and Sowa et al. [18] on pure carbon clusters.

Linear clusters are the most stable isomers up to *n* value equal to 17. Above this value, the cyclic species competes with the corresponding linear. Such a situation was already realized in the case of the neutral C_nS clusters [6]. The SC distances in the cationic cyclic structures, ~1.78–180 Å for $n \geq 14$, are slightly, but systematically, shorter by ~0.05 Å than those found in the corresponding neutral species. The carbon monocycle, here considered as a substructure of C_nS^+ clusters, is cumulenic with strong double bonds with lengths ~–1.35 Å, except for the two carbons bound to the sulphur atom, for which the CC bond distances are found to be ~1.37–1.40 Å. The atomic charge distribution along this monocycle, calculated by a Mulliken analysis, is shown as an illustrative example for C_nS^+ (Fig. 6). The charge strongly oscillates, with variations $\sim\pm 0.6\ e$ along the cycle.

The relative stability of the cationic cyclic structures follows a fourfold periodicity rule (Fig. 4). A similar situation was encountered for the neutrals where $C_{14}S$ and $C_{18}S$ are more stable than their

Table 4
DFT/B3LYP rotational constants (in GHz) for the low-lying C_nS^+ clusters calculated with a 6-311G* basis set for $1 \leq n \leq 8$

Structures	A	B	C
lin1[a]	0.000	25.991	25.991
lin1′	0.000	20.481	20.481
lin2	0.000	6.420	6.420
lin2′	0.000	6.667	6.667
cyc2[a]	44.947	15.338	11.435
cyc2′	49.861	12.807	10.190
lin3	0.000	2.941	2.941
lin3′	0.000	2.822	2.822
cyc3	37.262	6.772	5.731
S-cycC3	49.928	4.373	4.021
lin4	0.000	1.520	1.520
lin4′	0.000	1.539	1.539
lin5	0.000	0.929	0.929
lin5′	0.000	0.916	0.916
cyc5	6.750	4.394	2.661
lin6	0.000	0.598	0.598
lin6′	0.000	0.601	0.601
cyc6	5.283	2.706	1.789
lin7	0.000	0.413	0.413
lin8	0.000	0.298	0.298
lin8′	0.000	0.299	0.299
cyc8	5.366	1.184	0.970

[a] lin*n* ≡ linear C_nS isomer, cyc*n* ≡ cyclic C_nS isomer; ′ ≡ quadruplet.

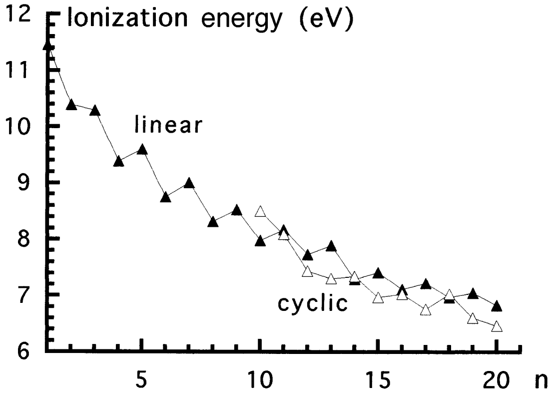

Fig. 3. Ionization energy of the neutral (linear and cyclic) C_nS clusters plotted as a function of n.

respective $n - 1$ and $n + 1$ congeners [6]. In the latter case, however, the fourfold periodicity rule is reminiscent of $4k + 2$ Hückel's rule for neutral C_n ring and explains the particular stability of $C_{14}S$ and $C_{18}S$ [6]. When ionized, the maximum stability for the pure carbon C_n^+ monocycles follows a $4k + 3$ rule with maxima occurring at $n = 15, 19, 23$ [19–21]. surprisingly enough, examining the incremental energy diagram as depicted in Figs. 3 and 7, we can see that the maximum stability is kept at $n = 14, 18, 22$ for positive C_nS^+ clusters as for the neutrals, even though the peaks are not so well marked in the cationic species as for the neutral ones where clear peaks appear for this n value series (Fig 7). This can be reinterpreted by considering the net electric charge carried by the carbon monocycle, this one being taken here as constituent part of the cyclic C_nS^+ clusters. This quantity, displayed in Table 5, is fractional, ~0.6–0.7 e, i.e. intermediary between 0 and +1. In other words, we have thus neither a neutral

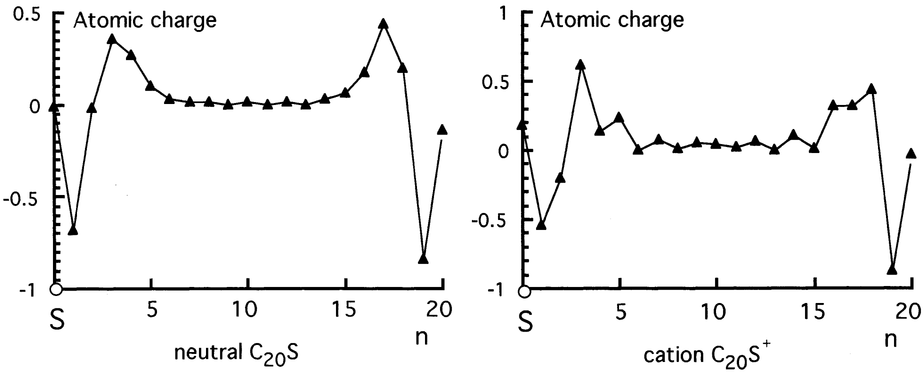

Fig. 2. Atomic charges (in electron charge unit) calculated by means of Mulliken population analysis for the linear neutral $C_{20}S$ and cation $C^{20}S^+$.

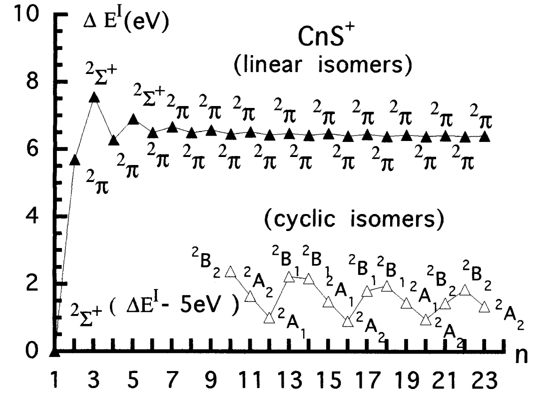

Fig. 4. Incremental binding energies (eV) for the linear and cyclic C_nS clusters vs the number of carbon atoms.

C_n ring nor a cationic C_n^+ ring and the $4k + 2$ (for C_n) or $4k + 3$ (for C_n^+) rules for the maximum stability does not strictly apply, even though a four-fold periodicity rule still subsists. It is worthy to note that the cyclic isomers are more stable than the linear ones when $n = 18, 22$ or $n = 19, 23$, i.e. when $n = 4k + 2$ or $n = 4k + 3$, respectively. It will be very interesting to also consider the C_nS^- and C_nS^{2+} clusters in order to see how the incremental energy diagram would evolve for the cyclic species in the anionic and dicationic cases. This is left for a future work.

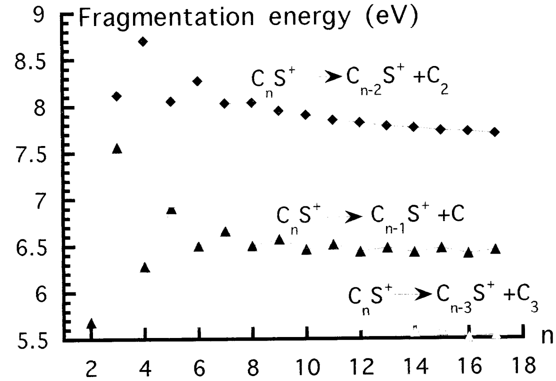

Fig. 5. Fragmentation energy for the C_nS^+ clusters plotted as a function of n.

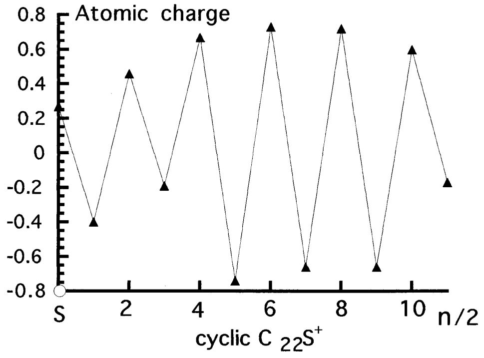

Fig. 6. Atomic charge distribution (in electron charge unit) along the cyclic cation $C_{22}S^+$ (only one half of the carbon monocycle is represented, the other part can be deduced by mirror symmetry).

4. Conclusion

The geometries and energies of small and medium-sized sulphur-containing carbon clusters C_nS^+ ($n = 1 - 23$) have been investigated by the DFT technique. The geometries of the lowest-lying linear and cyclic isomers do not essentially differ from those found for the neutral ones. The linear arrangement of nuclei with the sulphur atom located at one end of the carbon chain, is found to be the most stable isomer for $n = 1 - 17$. $C_{18}S^+$, $C_{19}S^+$, $C_{22}S^+$, $C_{23}S^+$ are found to be cyclic but with a low barrier to linearity. Fragmentation energies have been also calculated for C_nS^+ clusters. It is found that the major fragmentation channel is loss of C_3 neutral and that C_2 fragment is more difficult to remove. The ionization energies relative to the linear neutrals, C_nS,

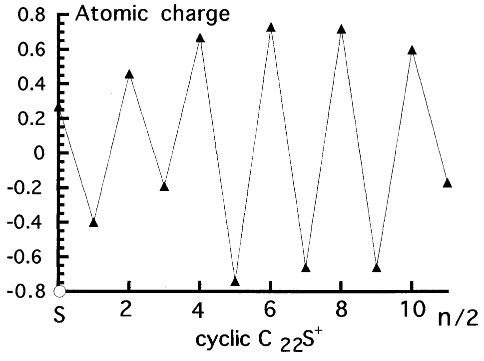

Fig. 7. Comparison of the incremental energies for the cyclic neutral and cationic C_nS species ($10 \leq n \leq 20$).

Table 5
Net electric charge carried by the carbon monocyclic substructure of the cyclic neutral and cationic C_nS clusters ($13 \leq n \leq 23$)

	13	14	15	16	17	18	19	20	21	22	23
Neutral	−0.19	−0.11	−0.12	−0.07	−0.11	−0.11	−0.11	−0.17	· · ·	· · ·	· · ·
Cationic	+0.58	+0.57	+0.67	+0.63	+0.63	+0.62	+0.71	+0.67	+0.65	+0.73	+0.69

have been also computed and the corresponding energies were shown to regularly decrease with size, but with an odd-even oscillation surimposed, from 11.45 eV for $n = 1$ to 8.83 eV for $n = 20$. A very similar result was found for the cyclic neutral species.

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