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A Theoretical and Structural Investigation of Thiocarbon Anions

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Received August 3, 2003

Density functional theory energies, geometries, and population analyses as well as nucleus-independent chemical shifts (NICS) have been used to investigate the structural and magnetic evidence for cyclic $C_nS_n^{2-}$ and C_nS_n ($n = 3-6$) electron delocalization. Localized molecular orbital contributions to NICS, computed by the individual gauge for localized orbitals method, dissect π effects from the σ single bonds and lone pair influences. $C_nS_n^{2-}$ ($n = 3-5$) structures in D_{nh} symmetry are minima. Their aromaticity decreases with increasing ring size. $C_3S_3^{2-}$ is both σ and π aromatic, while $C_4S_4^{2-}$ and $C_5S_5^{2-}$ are much less aromatic. NICS(0)$_\pi$, the C−C(π) contribution to NICS(0) (i.e., at the ring center), decreases gradually with ring size. In contrast, cyclic $C_6S_6^{2-}$ prefers D_{2h} symmetry due to the balance between aromaticity, strain energy, and the S−S bond energies and is as aromatic as benzene. The theoretical prediction that $C_6S_6^{6-}$ has D_{6h} minima was confirmed by X-ray structure analysis. Comparisons between thiocarbons and oxocarbons based on dissected NICS analysis show that $C_nS_n^{2-}$ ($n = 3-5$) and $C_6S_6^{6-}$ are less aromatic in D_{nh} symmetry than their oxocarbon analogues.

Introduction

Thiocarbon anions are the heavier analogues of the well-investigated nonbenzenoid aromatic oxocarbons.[1] The continuing interest in their structure and bonding is due partly to the aromaticity[2] of the monocyclic oxocarbon anions $C_nO_n^{2-}$, which are stabilized by the delocalization of the π electrons.[3] There has also been significant interest in thiocarbons and their applications. However, the aromaticity of thiocarbons has not been studied. The thiocarbon anions $C_3S_3^{2-}$ and $C_4S_4^{2-}$ have been synthesized,[4] and $C_4S_4^{2-}$, tetrathiosquarate, is a well-known and versatile ligand in metal complexes.[4b,5] We found no literature pertaining to $C_5S_5^{2-}$ and $C_6S_6^{2-}$. Since Fanghänel's smooth and simple synthesis (Scheme 1),[6] $C_6S_6^{6-}$ hexaanion (**1**) has been used as an electroactive dendrimer core unit[7] and as a component of a variety of electron-rich organic charge-transfer salts [8] and transition metal complexes[9] that sometimes exhibit redox communication between metal centers.[10]

Density-functional computations were used here to investigate the electron delocalization in $C_nS_n^{2-}$ dianions ($n = 3-6$), in their neutral counterparts, and in the more highly reduced C_6S_6 species. Thiocarbons and oxocarbons are compared. The X-ray crystal structure of the C_6S_6 core unit in hydrated $Na_6[C_6S_6]$ was determined.

Results and Discussion

Thiocarbon Dianions $C_nS_n^{2-}$ ($n = 3-5$). Optimized thiocarbon dianion geometries are shown in Figure 1, while computed total energies and zero point energies (ZPE) are summarized in Table 1. As for their oxygen analogues,[3b] $C_nS_n^{2-}$ dianions ($n = 3-5$) favor D_{nh} sym-

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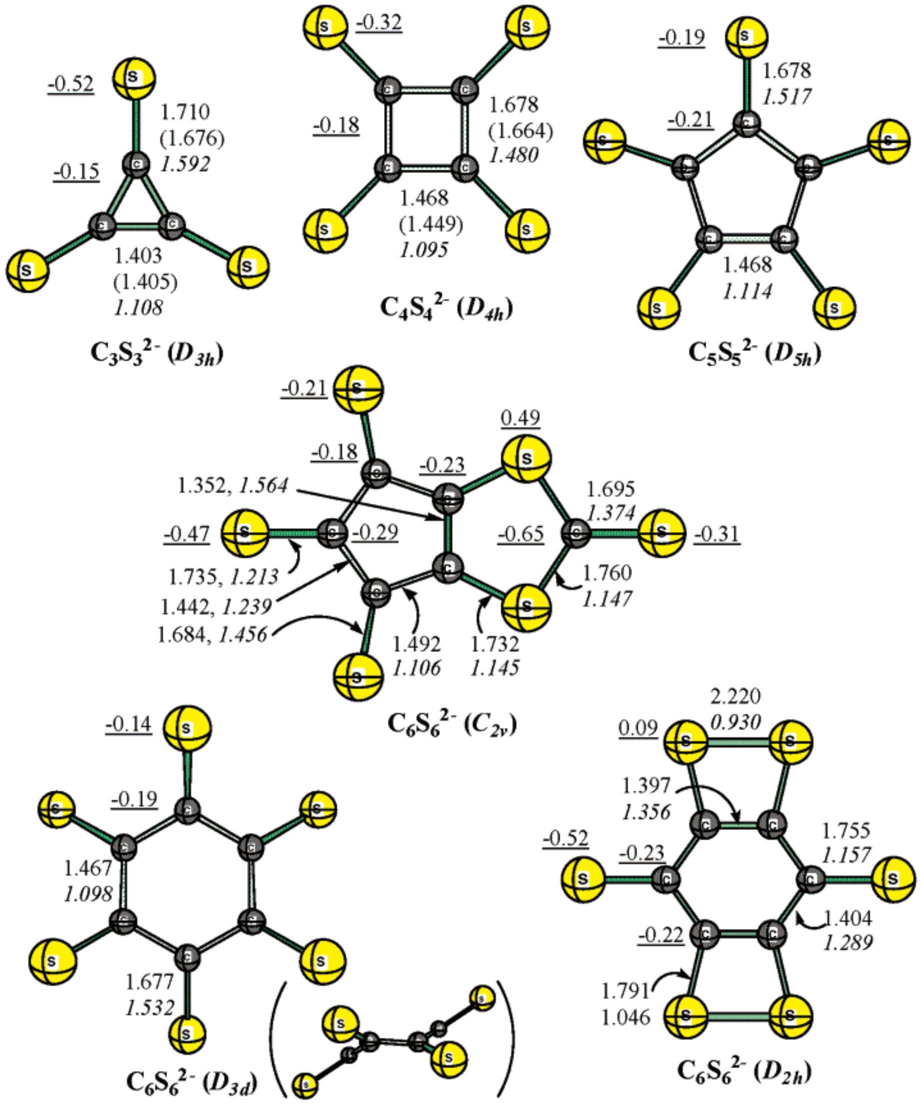
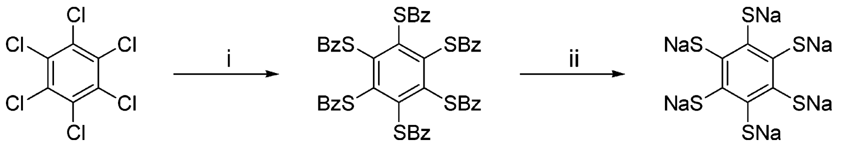


FIGURE 1. B3LYP/6-311+G* bond lengths (in Å) of $C_nS_n^{2-}$ ($n = 3-6$) compared with the X-ray values (in parentheses), Wiberg bond indices (WBI, in italic), and natural charges (q, underlined).

SCHEME 1. Synthesis of Na_6 1: (i) $NaSCH_2Ph$ (6 equiv), DMF; (ii) Na, NH_3 (liquid)



$Bz_6$1

$Na_6$1

metry (Figure 1). The computed bond lengths agree well with the available experimental data for $C_3S_3^{2-}$ [11] and $C_4S_4^{2-}$.[4a] $C_3S_3^{2-}$ has the shortest C−C (1.403 Å) and the longest C−S (1.710 Å) bond length of the set, and the C−C bonds are even shorter than those in $C_3O_3^{2-}$ (1.433 Å at the same level).[3b] The calculated CC Wiberg bond indices (WBI) are 1.108, 1.095, and 1.114 for $C_3S_3^{2-}$, $C_4S_4^{2-}$, and $C_5S_5^{2-}$, respectively, and indicate that the C−C bonds have very little double bond character. However, compared with its higher analogues, the very short C−C bond lengths in the strained $C_3S_3^{2-}$ suggest aromatic stabilization, as is found in cyclopropane.[2a,12] The C−S WBI, which are 1.592 ($C_3S_3^{2-}$), 1.480 ($C_4S_4^{2-}$), and 1.532 ($C_5S_5^{2-}$), also indicate delocalization in the carbon rings. Both the carbon and sulfur atoms in $C_nS_n^{2-}$ have the negative charges.

Among the classical criteria for aromaticity (i.e., structural, energetic (stability), reactivity, and magnetic), nucleus-independent chemical shift (NICS), a magnetic

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TABLE 1. $C_nS_n^{2-}$ (n = 3−6) B3LYP/6-311+G* Zero-Point Energies (ZPE, kcal/mol), Number of Imaginary Frequencies (NImag), Total Energies (au), and Relative Energies (kcal/mol)

molecule	symmetry	ZPE	NImag	E_{tot}	E_{rel} (E_{tot} + ZPE)
$C_3S_3^{2-}$	D_{3h}	11.5	0	−1308.96902	
$C_4S_4^{2-}$	D_{4h}	16.6	0	−1745.34100	
$C_5S_5^{2-}$	D_{5h}	21.4	0	−2181.69003	
$C_6S_6^{2-}$	D_{6h}	25.7	3[a]	[a]	
$C_6S_6^{2-}$	D_{3d}	25.4	0	−2617.98951	2.7
$C_6S_6^{2-}$	D_{2h}	26.1	0	−2617.99496	0.0
$C_6S_6^{2-}$	C_{2v}[b]	25.3	0	−2617.99606	−1.5

[a] Geometry optimization at B3LYP/6-311+G* failed to converge, ZPE given at B3LYP/6-31G(d). [b] Bicyclic structure, see Figure 1.

criterion, has proven to be a simple and efficient aromaticity probe.[13] Thus, it was found that "Oxocarbon acids and their anions are examples where the criteria of aromaticity that use reference systems are unsuccessful, only the NICS criterion gives satisfactory results."[3d] Hence, NICS both at the ring centers, NICS(0), and at 1 Å above ring centers, NICS(1), were computed to analyze the degree of aromaticity (Table 2). Here "dissected NICS", based on Kutzelnigg's individual gauge for localized orbitals (IGLO) method, which reveals the individual contributions to the total shielding of localized orbitals associated with bonds, lone pairs, and core electrons, is employed.

$C_nS_n^{2-}$ (n = 3−5) dissected NICS and ^{13}C shifts are summarized in Table 2. The computed $C_nS_n^{2-}$ carbon-13 chemical shift values agree well with the available experimental values for $C_3S_3^{2-}$ [11] and $C_4S_4^{2-}$.[4a] The σ bonds contribute paramagnetically to NICS(0) for all thiocarbon dianions. The $C_3S_3^{2-}$ dianion C−C(σ) deshielding contribution (6.0 ppm) is exceptionally small compared to the corresponding value in $C_3H_3^+$ (10.2 ppm), in both species carbon atoms are negatively charged, while the C−C(σ) contribution in its oxygen analogue $C_3O_3^{2-}$ and $C_3F_3^+$ are shielding (−11.7 and −9.3 ppm, respectively). This may indicate a hidden σ aromaticity in $C_3S_3^{2-}$ (see below). The relatively small deltathiolate dianion NICS$(0)_\sigma$ may be related to the negative charges on the $C_3S_3^{2-}$ carbon atoms, since, in $C_3O_3^{2-}$ and $C_3F_3^+$, the carbon atoms are positively charged.[3b] The four-membered ring in $C_4S_4^{2-}$ is σ antiaromatic, with abnormally pronounced C−C(σ) contribution (30.4 ppm) compared with its analogues, and much more so than in C_4H_8 (15.2 ppm).[14]

NICS$(0)_\pi$ values decrease with increasing $C_nS_n^{2-}$ (n = 3−5) ring size but are sufficiently diamagnetic that the dianions are classified as π aromatic. For example, the most pronounced C−C(π) shielding in $C_3S_3^{2-}$ (−24.9 ppm) is even stronger than that of benzene (−20.7 ppm)[13c] and just a little less than that of $C_3O_3^{2-}$ (−27.9 ppm).[3b] Thus, aromaticity decreases with increasing $C_nS_n^{2-}$ ring size of n = 3−5, the same as for the $C_nO_n^{2-}$ series.[3b] The NICS results above correlate well with the thiolate dianion structures.

Total NICS(1) values indicate the strong diatropic ring current for $C_3S_3^{2-}$ but weak diatropic currents for $C_4S_4^{2-}$ and $C_5S_5^{2-}$. Generally, the degree decreases with increasing ring size. Dissection shows that NICS$(1)_\sigma$ is negative (−7.0 ppm) for $C_3S_3^{2-}$, confirming its σ aromaticity, analogous to $C_3O_3^{2-}$.[3b] The σ contributions in $C_4S_4^{2-}$ and $C_5S_5^{2-}$ are very small, even negligible, but the π contributions are of a similar magnitude for $C_nS_n^{2-}$ (n = 3−5).

Thiocarbon Dianions $C_6S_6^{2-}$. The lowest-energy isomer of cyclic $C_6S_6^{2-}$ has D_{2h} symmetry, the same as its C_6S_6 neutral analogue.[15] In D_{6h} symmetry, $C_6S_6^{2-}$ is a third-order saddle point (NImag = 3); following the first imaginary mode led to a D_{3d} minimum, 2.7 kcal/mol less stable than the D_{2h} $C_6S_6^{2-}$. A C_2 $C_6S_6^{2-}$ isomer, which is the most favorable structure for $C_6O_6^{2-}$,[3b] has wavefunction instability.

As for C_6S_6,[15,16] the stability of $C_6S_6^{2-}$ is determined by the balance between aromatic stabilization, ring strain, and C−S and S−S bond strength affects. The most stable cyclic $C_6S_6^{2-}$ isomer, like C_6S_6, has D_{2h} symmetry and a strongly delocalized hexagonal carbon ring with C−C bond lengths of approximately the benzene value, 1.40 Å. Hence, the aromatic stabilization adds into the already favorable stability balance of the neutral analogue. In contrast with the nonplanar D_{3d} symmetric minima, the D_{2h} $C_6S_6^{2-}$ isomer has approximately equidistant C−C bond lengths and meets the geometric criteria of aromaticity (also see below).

NICS$(0)_\pi$ analysis shows that the D_{2h} hexathiolate diaanion, the lowest energy cyclic isomer of $C_6S_6^{2-}$, is much more aromatic than its D_{3d} isomer, with a significant shielding π-contribution (−22.4 ppm) , similar to those in $C_3S_3^{2-}$ (−24.9 ppm), while NICS$(0)_\sigma$ values are similar, 7.8 and 9.5 ppm, respectively, for D_{3d} and D_{2h} isomers.

The σ contributions to NICS(1) are negligible for both D_{2h} and D_{3d} isomers. However, π contributions are still significant. For $C_6S_6^{2-}$(D_{3d}), the NICS$(1)_\pi$ value is similar to those of $C_nS_n^{2-}$ (n = 3−5) (−5.9 vs −5.6 to −6.6 ppm), while $C_6S_6^{2-}$(D_{2h}) exhibits the largest π contributions (−11.0 ppm) in the thiocarbon dianions investigated.

In general, substantial ring currents exist for $C_nS_n^{2-}$ (n = 3−6), all thiocarbon dianions investigated, due to the significant π contribution to both NICS$(0)_\pi$ and NICS$(1)_\pi$.

Neutral Thiocarbons C_nS_n (n = 3−6). For comparison, D_{nh} symmetric C_nS_n (n = 3−6) thiocarbons, the neutral analogues of $C_nS_n^{2-}$ dianions, have been computed. However, the wave functions of all the singlet states are not stable at B3LYP/6-311+G*. While the wave functions of the triplet states are stable for C_nS_n (n = 3−5), both singlet and triplet D_{6h} C_6S_6 states have wavefunction instabilities. Moreover, the triplet states of C_3S_3 (D_{3h}) and C_4S_4 (D_{4h}) are local minimum while the C_5S_5

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TABLE 2. $C_nS_n^{2-}$ ($n = 3-6$), $C_6O_6Li_m$ and $C_6S_6Li_m$ (m = 4, 6) NICS(tot), NICS(σ), NICS(π), NICS(C−S or C−O), and Lone Pair (LP) Contributions at, and 1.0 Å above, Ring Centers[a]

		NICS(x)	NICS(tot)	C−C(σ)	C−C(π)	C−S(O)	LP (S/O)	core	^{13}C NMR
$C_3S_3^{2-}$	D_{3h}	0	−20.9	6.0	−24.9	0.0	−0.6	−1.2	176.9
		1	−10.3	−7.0	−5.6	4.2	−1.5	−0.3	(176.5[b])
$C_4S_4^{2-}$	D_{4h}	0	15.5	30.4	−19.3	5.6	−0.4	−0.4	234.2
		1	−3.1	−1.2	−6.6	6.8	−1.6	0.0	(229.1[c])
$C_5S_5^{2-}$	D_{5h}	0	15.4	23.6	−13.9	6.0	0.0	0.1	207.0
		1	−0.9	1.0	−6.4	5.0	0.0	0.0	
$C_6S_6^{2-}$	D_{3d}	0	1.0	7.8	−9.8	5.8	−2.4	0.0	197.4
		1	−4.8	−1.2	−5.9	5.1	−2.4	0.0	
$C_6S_6^{2-}$	D_{2h}	0	−5.9	9.5	−22.4	7.1	1.0	−0.3	131.1[4];136.9[2]
		1	−5.3	1.1	−11.0	4.5	0.2	0.3	
$C_6O_6Li_4$	D_{2h}	0	13.3	9.4	−0.2	3.4	0.4	1.4	
		1	10.3	1.5	6.7	1.6	−0.4	1.8	
$C_6O_6Li_6$[d]	D_{6h}	0	−17.0	−4.6	−18.7	10.2	−1.9	−2.0	
		1	−12.1	−2.3	−11.3	3.5	−0.4	−1.3	
$C_6S_6Li_4$	C_{2h}	0	13.3	11.0	−0.8	3.0	0.4	−0.2	
		1	7.4	2.0	4.2	1.7	−0.4	0.0	
$C_6S_6Li_6$	D_{6h}	0	−10.0	10.9	−17.2	−0.6	−1.9	−0.8	
		1	−9.6	4.1	−8.8	−2.8	−2.0	−0.4	

[a] Also summarized, $C_nS_n^{2-}$ ($n = 3-6$) ^{13}C chemical shifts (relative to TMS) (experimental values given in the parenthesws, and relative intensities in brackets). [a] GIAO-B3LYP/6-31+G*//B3LYP/6-311+G*. [b] $MePh_3P$ salt, cited from ref 12. [c] Cited from ref 4a. [d] The dissected NICS assignment for $C_6S_6Li_6$ is not clear-cut; however, the contributions from the six electrons are assigned to the C═C bonds.

TABLE 3. C_nS_n ($n = 3-6$) B3LYP/6-311+G* Zero-Point Energies (ZPE; kcal/mol), Number of Imaginary Frequencies (NImag), Total Energies (au), and Relative Energies (kcal/mol)

molecule	symmetry	ZPE	NImag	E_{tot}	E_{rel} (E_{tot} + ZPE)
C_3S_3	D_{3h} (T)	14.2	0	−1308.86578	
C_4S_4	D_{4h} (T)	15.8	0	−1745.21333	
C_5S_5	D_{5h} (T)	20.1	2	−2181.54695	
C_6S_6	D_{2h}	26.9	0	−2617.90670	0.0
C_6S_6	D_{3h}	27.1	0	−2617.89423	7.7
C_6S_6	D_{3d}	25.5	0	−2617.84489	37.4
C_6S_6	C_2	25.6	0	−2617.83907	41.1
C_6S_6	C_{2v}[a]	26.4	0	−2617.91960	−8.6

[a] Bicyclic structure, see Figure 2.

(D_{5h}) triplet is a second-order saddle point (NIMAG = 2). D_{2h} C_6S_6,[15b,16] the most stable hexathiocarbon, and its D_{3h}, D_{3d}, and C_2 isomers are minima. The C_6S_6 isomer energy order is in agreement with literature reports[15] (Table 3); the D_{2h} structure is lowest in energy, followed by D_{3h} (relative energy 7.7 kcal/mol), D_{3d} (37.4 kcal/mol), and C_2 (41.1 kcal/mol).

The most stable C_6S_6 isomer is not monocyclic but has C_{2v} symmetry and two fused five-membered rings (Figure 2), since the highly strained four-membered sulfur rings are avoided, as in its carbon analogue.[17] This C_{2v} structure is also favored by 1.5 kcal/mol for the C_6S_6 dianion (Table 1 and Figure 1).

Figure 2 presents the B3LYP/6-311+G* structures of the neutral thiocarbons; their total NICS values and the specific contributions are presented in Table 4. Due to the wave function instability of the C_nS_n ($n = 3-5$) singlet states, no reliable NICS values can be computed, only the singlet states of the C_6S_6 cyclic isomers are discussed. The wave function stable C_6S_6 (D_{2h}) is nonaromatic, but C_6S_6 (D_{3h}) is highly aromatic. The nonaromatic D_{2h} isomer is lower in energy than the aromatic D_{3h} isomer. The greater stability of the D_{2h} form is a compromise between the stabilization due to aromaticity and to the strong S−S bonding and the destabilization from the strain energy in the four-membered rings.

More Highly Reduced Forms: Tetraanion and Hexaanion. The existence of the tetraanion $C_6O_6^{4-}$ and hexaanion $C_6O_6^{6-}$ is well established. Experimentally, the tetrapotassium salt of the $C_6O_6^{4-}$ tetraanion has been isolated;[18] $C_6O_6^{6-}$ was synthesized by thermal cyclotrimerization of acetylene diolate salts, which are the first species that can be isolated when the reaction of certain metals with CO is carried out at high temperatures.[19] $C_6S_6^{6-}$ was synthesized by dealkylation of a thioether precursor and has been explored in many experimental studies.[6−10] However, $C_6S_6^{4-}$ has not yet been addressed.

There are formally four and six π electrons, respectively, in $C_6O_6^{4-}$/$C_6S_6^{4-}$ and $C_6O_6^{6-}$/C_6S_6,$^{6-}$ which should, respectively, be antiaromatic and aromatic according to the $4n + 2$ Hückel rule. Is the tetraanion antiaromatic, with a nonplanar structure? Conversely, is the hexaanion aromatic, with a planar structure? To investigate the structure of the tetraanions and hexaanions of C_6O_6 and C_6S_6, avoiding the complication of the Coulomb repulsion, lithium was used as a countercation.

Planar $C_6O_6Li_4$ (D_{2h}) is a true minimum at the B3LYP/6-31G* level. $C_6S_6Li_4$ (D_{2h}), however, is a higher saddle point (NImag = 3); mode following of the first imaginary frequency led to a nonplanar C_{2h} minimum (Figure 3). The hexagonal carbon rings in $C_6O_6^{4-}$ (0.115 Å) and $C_6S_6^{4-}$ (0.09 Å) have strong bond length alternation and the tetraanions are antiaromatic; this is confirmed by the NICS values (Table 2).

In contrast, $C_6O_6Li_6$ and $C_6S_6Li_6$ have highly symmetric D_{6h} minima at the B3LYP/6-31G* level. The CC bond lengths (1.411 and 1.421 Å in $C_6O_6Li_6$ and $C_6S_6Li_6$, respectively) and WBI (1.311 and 1.340, respectively) (Figure 3) indicate their strong electron delocalization in the central carbon rings. According to the NICS analysis, the total NICS(0) and NICS(1) values are −17.0 and −12.1 ppm, respectively, for $C_6O_6Li_6$, and −10.0 and −9.6

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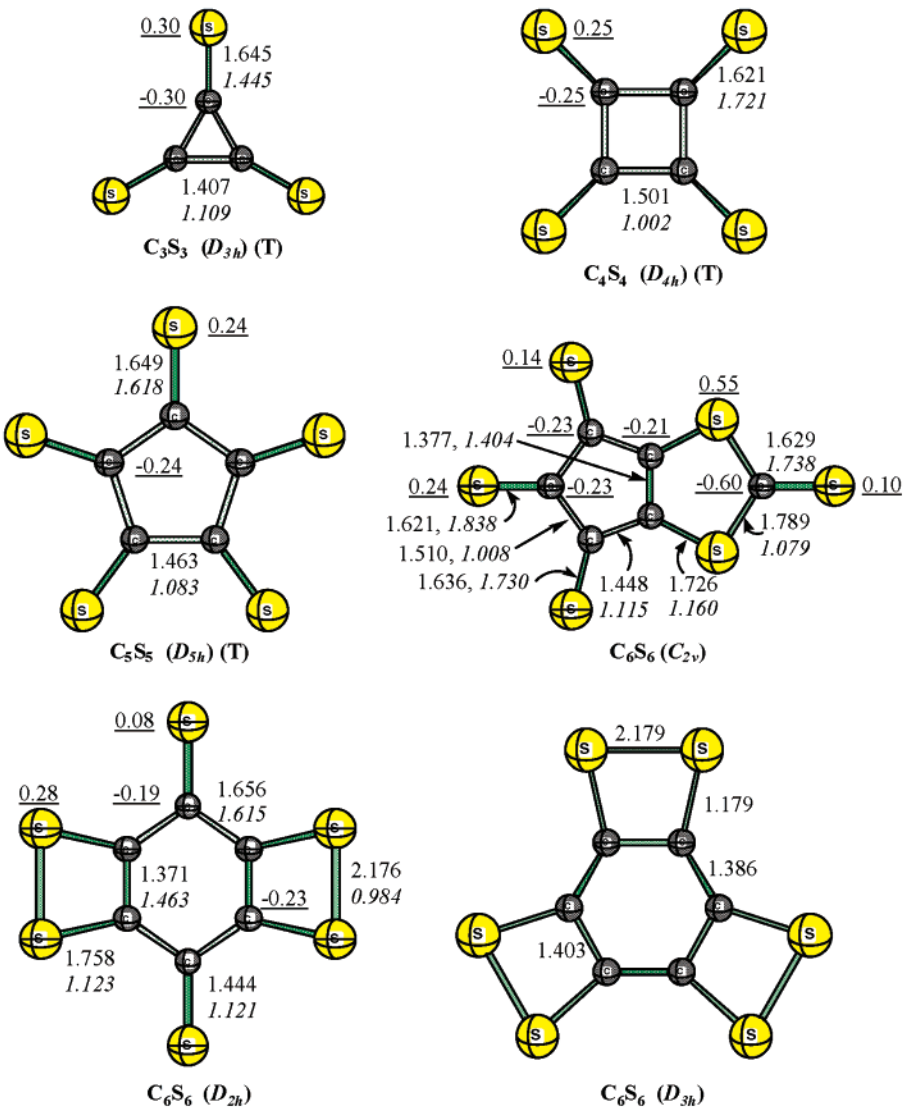


C_3S_3 (D_{3h}) (T)

C_4S_4 (D_{4h}) (T)

C_5S_5 (D_{5h}) (T)

C_6S_6 (C_{2v})

C_6S_6 (D_{2h})

C_6S_6 (D_{3h})

FIGURE 2. B3LYP/6-311+G* bond lengths (in Å), Wiberg bond indices (WBI, in italic), and natural charges (q, underlined) of $C_nS_n^{2-}$ ($n = 3-6$).

TABLE 4. Neutral Thiocarbon C_6S_6 Isomers NICS(tot), NICS(σ), NICS(π), NICS(C−S), and Lone Pair (LP) Contributions at, and 1.0 Å above, Ring Centers

	NICS(x)	NICS(tot)	C−C(σ)	C−C(π)	C−S	LP (S)	core
C_6S_6 D_{2h}	0	11.0	12.2	−4.0	2.2	0.6	−0.4
	1	5.4	2.0	2.6	0.6	−0.2	0.0
C_6S_6 D_{3h}	0	−12.0	6.9	−22.5	2.6	1.3	−0.6
	1	−9.2	0.4	−11.2	0.5	1.7	−0.6

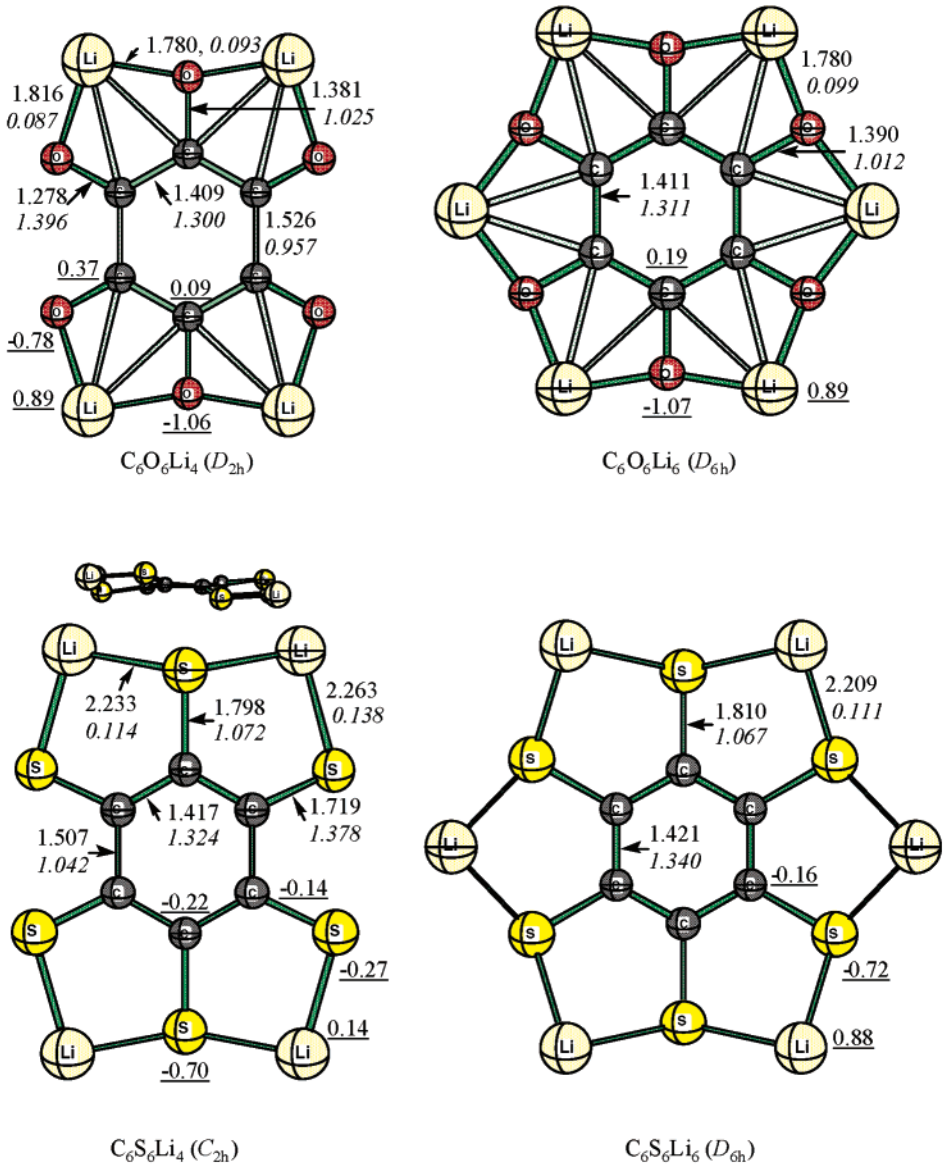
ppm, respectively, for $C_6S_6Li_6$, thus confirming that $C_6O_6^{6-}$ and $C_6S_6^{6-}$ are truly aromatics. The high NICS values are mainly due to the π-electron contributions. All the analyses suggest that $C_6O_6^{6-}$ is more aromatic than $C_6S_6^{6-}$.

X-ray Crystal Structure of $C_6S_6^{6-}$ (as $Na_2C_6S_6H_4$·4NaOH·12H_2O). Encouraged by the prediction of a highly delocalized $C_6S_6^{6-}$ structure, the aesthetically attractive molecule was prepared and its X-ray crystal structure determined.

Crystals grown from aqueous solutions of $Na_6C_6S_6$ (**Na₆1**) adopted the triclinic space group $P\bar{1}$, with a formula best described as $[Na_2H_4C_6S_6]$·4NaOH·12H_2O, taking pK_a considerations into account. (Full details have been submitted to the Crystallographic Structure Database at Cambridge, CCDC 221343.) Figure 4 shows how $C_6S_6^{6-}$ anions form polymeric linear tapes through coordination of para-related sulfur atoms by two η^2-bridging Na^+ ions; the remaining Na^+ ions are contained in cis-edge-sharing octahedra, forming linear polymers of formula $[NaOH(H_2O)_3]_\infty$. The C_6S_6-containing tapes run parallel to the crystallographic a axis, the inorganic polymers along the b axis. Bond lengths lie in typical ranges (see Supporting Information); the benzenoid C atoms are separated by 1.415(3)−1.421(3) Å; C−S distances are 1.770(2)−1.776(2) Å, which agree well with the theoretical predictions. These minimal variations indicate that the low symmetry of the anion's environment has little effect on its structure.

Concluding Remarks

Cyclic D_{nh} $C_nS_n^{2-}$ ($n = 3-5$) structures are minima, whose aromaticity decreases with increasing ring size. While $C_3S_3^{2-}$ is both σ and π aromatic, $C_4S_4^{2-}$ and $C_5S_5^{2-}$



$C_6O_6Li_4$ (D_{2h})

$C_6O_6Li_6$ (D_{6h})

$C_6S_6Li_4$ (C_{2h})

$C_6S_6Li_6$ (D_{6h})

FIGURE 3. B3LYP/6-311+G* bond lengths (in Å), Wiberg bond indices (WBI, in italic), and natural charges (q, underlined) of $C_6O_6Li_4$ (D_{2h}), $C_6S_6Li_4$ (C_{2h}), and $C_6S_6Li_6$ (D_{2h}).

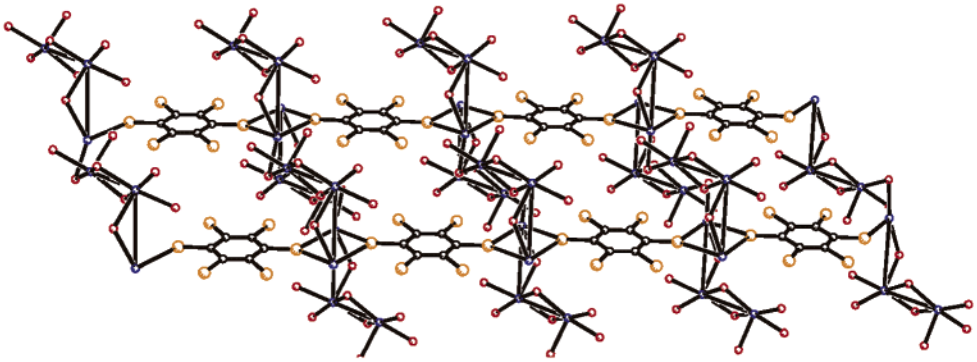


FIGURE 4. Crystal structure of $Na_2C_6S_6H_4{\cdot}4NaOH{\cdot}12H_2O$.

are much less aromatic. Detailed dissected IGLO NICS analysis reveals the localized orbital contributions to the NICS shieldings. While NICS(0)$_\pi$ obtained from dissected NICS computations shows a gradual decrease with ring size, NICS(1)$_\pi$ is nearly constant for these three thiocarbon dianion systems. Cyclic $C_6S_6^{2-}$, which prefers D_{2h} symmetry, exhibits pronounced aromatic character comparable to benzene and represents a nice balance between aromaticity, strain energy, and strong S−S bonding. Computations predict $C_6S_6^{6-}$ (D_{6h}) to be a minimum. Its crystal structure recorded for the first time is in accord with the theoretical calculations. We hope to prepare crystals containing the $C_6O_6^{6-}$ core and to investigate the electrochemical oxidation of the $C_6S_6^{6-}$ system in future.

Computations

The geometries of $C_nS_n^{2-}$ and C_nS_n ($n = 3-6$) were optimized first at B3LYP/6-31G* and then at B3LYP/6-311+G* levels of density functional theory as implemented in the Gaussian98 program.[20] Frequency calculations, carried out at B3LYP/6-311+G*, determined the nature of the stationary points and gave the ZPE.[21] Optimized and frequency analysis have been performed at B3LYP/6-31G* level for $C_6O_6Li_4$ and $C_6O_6Li_6$ and $C_6S_6Li_4$ and $C_6S_6Li_6$. Wave-function stability was checked at the B3LYP/6-311+G* level of theory for dianion and neutral species and at the B3LYP/6-31G* for higher reduced oxocarbons and thiocarbons.

NICS and their dissected localized molecular orbital contributions, so-called dissected NICS, were computed using the IGLO method and Pipek−Mezey localization procedure,[22] as implemented in the deMon NMR program.[23] Dissected NICS reveal the individual contributions of bond, lone pairs, and core electrons to the total shielding. The IGLO calculations employed the Perdew−Wang-91 functional in conjunction with the IGLO-III TZ2P basis set. B3LYP/6-311+G** optimized dianion and neutral species geometries were used, while B3LYP/6-31G* geometries were used for higher reduced oxocarbons and thiocarbons.

Experimental Section

Synthesis of $Na_6$1. The procedure described by Fanghänel was employed (see Scheme).[6] **$Bz_6$1** was synthesized at 0 °C in DMF containing freshly prepared sodium benzylthiolate, to which hexachlorobenzene was added. The colorless suspension turned yellow very quickly and the product precipitated as a yellow powder in less than 1 h. This was recrystallized from 3:1 v/v MeOH/$CHCl_3$ to give lustrous yellow fibers. **$Bz_6$1** was then dealkylated in refluxing liquid NH_3 by the action of sodium metal for 30 min. The reaction was quenched with MeOH, and the NH_3 was allowed to boil off. Following washing with N_2-purged Et_2O, the white residue was taken up in the minimum quantity of N_2-purged water at room temperature. The resulting yellowish solution cooled to 0 °C and yielded large, slightly gray crystals, which were amenable to X-ray crystallographic structure solution. Both the intermediate **$Bz_6$1** and **$Na_6$1** gave analytical data in agreement with those previously reported.

Acknowledgment. This work was supported by the Alexander von Humboldt Stiftung (Z.C., L.R.S.), Deutsche Forschungsgemeinschaft, the University of Georgia, and the U.S. National Science Foundation (Grant CHE-0209857). We thank Dr. Wolfgang A. Donaubauer and Dr. Frank Hampel for crystal structure measurement.

Supporting Information Available: *Gaussian98* archive entries for the optimized structures and crystal data for $Na_2C_6S_6H_4 \cdot 4NaOH \cdot 12H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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