Inductive and Conjugative S→C Polarizations in “Trithiocarbenium Ions” [C(SH)₃]⁺ and [C(SH)₃]⁻²⁺. Potential Energy Surface Analysis, Electronic Structure Motif, and Spin Density Distribution

Rainer Glaser,*¹,² Godwin Sik-Cheung Choy,¹ Grace Shihauy Chen,³ and Hansjörg Grützmacher*¹,⁴

Contribution from the Department of Chemistry, University of Missouri–Columbia, Columbia, Missouri 65211, and Institut für Anorganische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

Received March 22, 1996. Revised Manuscript Received July 9, 1996

Abstract: The formation of [C(SH)₃]⁺ (a) by hydride abstraction from HC(SH)₃ and its oxidation to the radical dication [C(SH)₃]⁺²⁺ (b) were studied to examine the potential of stabilizing carbenium ions via trithio substitution. Potential energy surfaces (PES) were explored at the HF/6-31G* level and energies were refined at the (P)MP4-(full,lsdtq)/6-31G* level without and with annihilation of spin contaminations. The unpaired π-electron in the radical lies below the Fermi level and spin polarization and dynamic electron correlation become important. Open Y-conjugated structures 1 (C₆H₆ or C₄) and their rotamers 2 (C₄) are favored. Four cyclic, S=S connected, distonic, chiral stereoisomers 3b are local minima for the radical dication. The C−S rotational barriers to isomerization via 4 and automerization of 5 (two isomeric TSs) and the high energies of C₆S₅ models 6 indicate stronger S−C π-interactions in the cations 1 and 2 than in the cations. C₆H₆-1b undergoes a Jahn–Teller distortion to C₆H₆-1b⁺ but pseudorotation is facile. The PES analyses suggest two strategies to achieve pyramidalization of the trivalent carbon in heteroatom-substituted carbenium ions via X–X interactions in CₓC₆⁻ or via face-preferential hyperconjugation. The basic approach was found to be successful: The computed hydride affinity of 1a is ΔH = 95.5 kcal/mol lower than for CH₃⁺. ΔHΔ was partitioned into a methane destabilization of 32.0 kcal/mol and a carbenium ion stabilization of 63.5 kcal/mol. Our best estimate for the ionization energy of 1a is IP(1a) = 343.8 kcal/mol (14.9 eV) and results in ΔHΔ(1b) = 541.5 kcal/mol. The cations [C(SH)₃]⁺ and [C(SH)₃]⁻²⁺ show the same unexpected electronic motif. Strong S−C donations occur in the π- and σ-systems and, instead of charge dispersal, large positive SH charges are arranged around a negative C center. The stabilization mechanisms in the S-containing ions and the lighter O homologues are fundamentally different due to the umpolung of the C−X bonds. Oxidation of [C(SH)₃]⁺ removes S−π-electron density and increases the π-acidity of the C atom. The α-spin density is concentrated on the S atoms and carbon is β-spin polarized.

Introduction

Oxidation generally leads to molecular distortions1,² and these are especially large when the HOMO of the non-oxidized molecule is strongly bonding or antibonding. Prominent examples include the pairs CH₂(T₆) and CH₂(T₅) (planar, C₆H₆) as well as C₆H₆(CH₃)₆ (planar) and C₆H₆(CH₃)₆⁻²⁺ (pentagonal pyramid).⁵ To observe the structural effects of twofold oxidation, several donors may be required to achieve sufficient stabilization of the highly charged species as is exemplified by the diamino derivative (Me₂N)₂CC(NMe₂)₂⁺ and [H₂C=CHCH₂]⁺.⁷⁻⁸ We are interested in the stabilizing effects of third or higher row elements on carbenium ions.⁹ In these compounds both σ- and π-donating effects account for stabilization. We have been studying the electronic properties of P analogs¹⁰ I and II of diazonium ions¹¹ and we succeeded in the preparation of methylene phosphonium ions¹² III with different C substituents.


While diazonium ions may be considered as N₂ complexes of R⁺, the P analogs are completely different in that the P₂ group does carry the positive charge. Similarly and in contrast to iminium ions R₂N=CR⁺, the trigonal planar coordinated P center bears a considerable positive charge while the C atom is negatively charged (up to $-0.7$).

As with phosphorus, sulfur is an attractive candidate to stabilize polycations due to its low ionization potential and electronegativity. Related to methyleneophosphonium ions are the thiocarbenium ions IV, Gompper and Kutter described the preparation of $[(MeS)_3C]^+$ by alkylation of $(CH_3)C=CH_2$. Ohl et al. spectroscopically characterized cations of the types $[C(OH)_n(SH)_{3-n}]^+$ ($n = 0$–3) and trisubstituted carbenium ions with $X = OH, SH$, and $NH_2$ also were discussed. The recent discovery that guanidinium ions $(RN)_2N^+$ may play a crucial role in the catalytic activity of a metal free hydrogenase has renewed the interest in these systems. X-ray crystal structures of several dithio- and trithio-substituted carbenium ions were obtained. More recently, evidence was provided for the existence of trithio-substituted silylenium ions and several types of $[S(SX)_3]^+$ ions were described ($X = H, Cl$). There is gas-phase evidence to suggest that S can stabilize carbenium ions better than does oxygen. The stabilization of carbenium ions by adjacent heteroatoms has been discussed for monosubstituted systems and there also have been some studies on the effects of multiple substitution. Recently we could show experimentally and by ab initio calculations (MP2/LANL2DZ+) that the different mechanism of stabilization can be brought to the fore only through consideration of multiple substitution in $[CH_3XR]_{3-n}^+$ ($X = O, S, Se$; $Te$; $R=exp(2.46-1pCR_2CH_2, R_{calc} = H; n = 0-2$). According to our evaluations of $AH$ for the isodesmic reaction $[CH_3(XH)_{3-n}]^+ + nCH_3 \to nCH_3(XH) + CH_3^+$, monosubstituted ions $[CH_2(XH)]^+$ are equally stable for all $X$ while di- and trisubstituted ions $[CH(XH)]_{3-n}^+$ and $[C(XH)]_{3-n}^+$ are considerably more stable for $X = O$ than for the heavier homologs ($X = S, Se, Te$). A particularly noteworthy result of these theoretical studies concerns the discovery of enhanced charge separation in $[C(OH)]^+$ instead of the commonly expected charge delocalization. For this ion $[C(OH)]^+$, natural orbital population (NPA) suggested a positive charge on carbon ($+1.3$) that is larger than unity. The homologous ions $[C(XH)]^+$ ($X = S, Se, Te$) were found to differ greatly and indeed fundamentally in that the carbon center is negatively charged as the result of effective $X \to C$ donation in the $\alpha$- and $\tau$-systems. We will show below that the electronic features suggested by the NPA analysis are fully corroborated.


by the topological analysis and, in addition, that this unexpected electronic motif persists even in the dications.

The ability of $S$ to delocalize positive charge even in polycations is reflected in the facile oxidation of $S_2$ to $S_2^{2+}$ by simply dissolving sulfur in concentrated H$_2$SO$_4$. Heterocycles V (SC$_2$H exchange in S$_2$) can be oxidized to dications VI as well. As in $S_2^{2+}$, transannular $S$–$S$ bonds serve to delocalize positive charge thereby inducing excessive structural changes on going from the neutrals to the polycations. Other interesting cations with $S$–$S$ bonds are obtained from electron rich disulfides. Again a considerable change in molecular geometry between the neutral Me$_2$N=S–S=NMMe$_2$ (C$_2$) and its planar radical cation (C$_2$S) is observed. Unsaturated ring systems with $S$ atoms incorporated in the ring or as donor atoms in substituents can be oxidized and their products from redox processes are promising organic materials.

In this context, the question arose as to whether thiogroups SR may contribute to the stabilization of radical dications [C(SR)$_3$]$^{*+}$ which can be derived by further oxidation of the monocations [C(SR)$_3$]$^{*+}$. In this article, we report the results of an ab initio potential energy surface analysis of the monocation [C(SH)$_3$]$^{*+}$ and of the parent radical dication [C(SH)$_3$]$^{2+}$. The degenerate HOMO of [C(SH)$_3$]$^{*+}$ is nonbonding in character and mainly located on the $S$ atoms. Any structural change of molecular geometry upon oxidation is thus not easily predicted. The experimentally determined $S$–$S$ distances in isolated trithiocarbenium ions (2.97–2.99 Å) are significantly less than twice the van der Waals radius of $S$ (3.6 Å) and we have searched for possible three-membered ring structures in which positive charge delocalization might occur via $S$–$S$ bond formation. It is one of the goals of this study to examine whether cyclic distonic radical dication structures may compete energetically with non-distonic open structures. Minima and transition state structures for isomerization and automerization are reported for the monocation and the dication and the activation barriers to rotation provide a probe for the importance of $Y$-conjugation.

Structural and energetic effects of the second ionization of [C(SH)$_3$]$^{*+}$ are evaluated. Topological electron density analysis is employed to analyze the interesting bonding situations in these cations. The electron density relaxation associated with the ionization process [C(SH)$_3$]$^{*+} \rightarrow$ [C(SH)$_3$]$^{*+*}$ has been examined and the ionization energy is reported. The neutral thiocarbonyl HC(SH)$_2$, the precursor for the generation of [C(SH)$_3$]$^{*+}$, has been considered as well and the hydride affinity of [C(SH)$_3$]$^{*+}$ is reported. The mechanism by which the $S$ substituents facilitate the generation of [C(SH)$_3$]$^{*+}$ from HC(SH)$_2$ is analyzed quantitatively and in comparison to the unsubstituted parent system. Optimized structures are compared to available X-ray data of derivatives of these compounds to provide a reference for the adequacy of the reported geometries.

Theory and Computations

Restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock theory (UHF) were employed for the closed- and open-shell systems, respectively. While the wave functions obtained with the UHF formalism are eigenfunctions of the Hamiltonian and the $S$ operators, they are not eigenfunctions of the $S^2$ operator. As a result, the wave functions of the doublet systems are spin contaminated to some extent by admixture of quartet, sextet, and higher spin states. The eigenvalues of the $S^2$ operator are given as a measure of the spin-contamination. Since the projection operator commutes with the charge density operator, the electron density remains unaffected by the projection and effects of spin contamination on the optimized structures are expected to be small. Complete gradient optimizations of geometries were carried out within the point groups specified using the polarized split-valence basis set 6-31G$.^*$. The Hessian matrix and vibrational frequencies were computed to characterize each stationary structure as a minimum or a transition state structure (or a higher-order saddle point) via the number of imaginary frequencies and to obtain vibrational information. The zero-point energies calculated at the HF level were scaled in the usual fashion$^*$ (factor 0.9) when applied to relative energies. Dynamic electron correlation between $\pi$- and $\sigma$-electrons is particularly important in conjugated molecules with a charged $\pi$-system and Borden and Davidson stressed the importance of triple excitations to correctly compute such systems.$^{35}$ In the present study, electron correlation effects on relative stabilities and reaction energies were estimated using full forth-order Möller–Plesset perturbation theory, including core electrons, and using the HF structures, MP4(full,ssd)/6-31G$^*$/HF/6-31G$^*$. For the open shell systems, spin contamination might have significant energetic consequences.$^{46}$ Annihilation of the first higher spin state removes the major part of the spin contamination and projection of the first three unwanted spin states results effectively in complete annihilation. The MP4(s+t)3 energies are reported in a table in the Supporting Information. Pertinent relative energies are summarized in Table 1.

The electron and spin densities $\rho$ and $\rho^S$ are the sum and the difference, respectively, of the $\alpha$ and $\beta$ electron density functions. We are analyzing both of these density functions without external reference

$$\text{electron density: } \rho = \rho_\alpha + \rho_\beta$$

$$\text{spin density: } \rho^S = \rho_\alpha - \rho_\beta$$

and solely based on properties of the electron density distribution. The topological analysis is based on the properties of the gradient vector field. The collection of all gradient vector field lines originating at a given attractor defines the associated zero-flux surfaces as the boundaries of the atoms in the molecule. Bond critical points occur at the intersection between the zero-flux surfaces and the bond paths. A

Table 1. Relative Energies

<table>
<thead>
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<th>parameter</th>
<th>HF no proj.</th>
<th>AVZPE scaled</th>
<th>MP4 no proj.</th>
<th>MP4 proj.  (x3)</th>
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<td>I-(\text{Pref}1\text{b} \over \text{over} 1\text{b})</td>
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<td>0.11</td>
<td>-2.26</td>
<td>-1.84</td>
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<td>I-(\text{Pref}3\text{b} \over \text{over} 3\text{b}1)</td>
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<td>-0.03</td>
<td>-0.08</td>
<td>0.09</td>
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<td>I-(\text{Pref}3\text{b} \over \text{over} 3\text{b}2)</td>
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<td>0.07</td>
<td>0.73</td>
<td>0.88</td>
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<td>I-(\text{Pref}3\text{c} \over \text{over} 3\text{c}1)</td>
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<td>-0.29</td>
<td>1.17</td>
<td>1.57</td>
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<tr>
<td>I-(\text{Pref}1\text{b} \over \text{over} 3\text{b}2)</td>
<td>46.31</td>
<td>0.85</td>
<td>35.49</td>
<td>42.05</td>
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</table>

*All values for isomer preference energies (\(\text{I-\text{Pref}}\)), activation energies \(E(\text{A})\), ionization energies \(E(\text{I})\), and hydride affinity \(E(\text{HA})\) are in kcal/mol. \(\Delta\text{AVZPE} \) terms calculated at the HF level are scaled (factor 0.9), and they are to be added to the relative energies.

annihilation and electron correlation both are important and Möller–Plesset energy calculations are not sufficient even when carried to full forth-order.\(^{52}\) Unless otherwise noted, relative energies in the following refer to our highest level including projection of spin contamination, MP4\((\text{full, sdtq}/6-31G^*/\text{HF/6-31G^*+\DeltaZPE/6-31G^*})\).

Isomeric Open Structures and Pseudorotation of Jahn–Teller Distorted Dications. The \(\text{C}_3\text{b}\) structures \(\text{Ia}\) and \(\text{Ib}\) both are minima (Figure 1). While this symmetry is expected for \(\text{Ia}\), it is surprising for \(\text{Ib}\) because the \(\pi\)-HOMO of \(\text{Ia}\) is degenerate. Oxidation of \(\text{Ia}\) removes this degeneracy, as shown in Figure 1, and results in an asymmetric wave function for \(\text{Ib}\). Symmetry reduction in the wave function allows for reduction in molecular symmetry and, hence, there might exist a second minimum for \(\text{Ib}\) with lower symmetry due to Jahn–Teller distortion. Indeed, optimization within \(C_3\) symmetry leads to the structure \(\text{Ib}'\). At the UHF level, \(\text{Ib}'\) is preferred over \(\text{Ib}\) by 0.54 kcal/mol. Structure \(\text{Ib}'\) is modestly distorted compared to \(\text{ib}\) in that the two \(C-S\) bonds adjacent to the smallest \(\angle\) (\(S-C-S\)) angle are elongated while the remaining \(C-S\) bond is shortened. The Jahn–Teller distorted structure \(\text{Ib}\) in which one \(C-S\) bond is elongated while the other two bonds are shortened corresponds to the transition state structure for pseudorotation.\(^{53}\) At the MP4 and MP2 levels very similar relative energies were predicted for \(\text{Ib}\) and \(\text{Ib}'\) which indicates that the pseudorotation of \(\text{Ib}'\) is essentially unhindered and there is thus no need to optimize \(\text{Ib}''\).

The valence-MO diagrams of \(\text{Ia}\) and of the isomers \(\text{Ib}\) and \(\text{Ib}'\) are shown in Figure 1. The RHF MOs are for \(\text{Ia}\) and sets of \(\alpha\) and \(\beta\)-spin orbitals are shown for the radicals. For clarity, only the \(\pi\)-electrons are indicated by \(\uparrow\) (\(\alpha\)-spin) and \(\downarrow\) (\(\beta\)-spin). Removal of one electron from the degenerate \(\pi\)-HOMO \((\pi_{C2C3})\) results in a stabilization of the remaining unpaired \(\pi\)-electron \((\pi_{C2C3})\) significantly below the energy of the remaining quasidegenerate \(\pi\)-HOMO \((\pi_{C2C3})\) and \(\beta\)-MO of the radical dication. The energies of the electrons of the all-bonding \(\pi_2\) MO in \(\text{Ia}\) become greatly different in the dication \((\alpha\pi_2; \beta\pi_2)\). Most intriguing is the finding that the unpaired electron is not in the \(\text{HOMO}\) of the dication; instead, sets of spin paired \(\pi\)- and \(\alpha\)-electrons both are higher in energy compared to the \(\text{MO}\) associated with the unpaired \(\pi\)-radical. Dynamic electron correlation becomes so important in this charged radical because of this readily identifiable feature of the molecular orbitals.

Rotation about one of the \(C-S\) bonds in \(\text{I}\) leads to structures of type 2 for which the highest possible symmetry is \(C_3\). The planar structures \(\text{2a}\) and \(\text{2b}\) are found to be minima. While \(\text{Ia}\) is preferred over \(\text{2a}\) by 1.83 kcal/mol, we find a reversal of stability for the dication: \(\text{Ib}\) is 1.73 kcal/mol less stable than \(\text{2b}\).

The calculated structure of \(\text{Ia}\) can be compared to the X-ray structure of \([\text{C(SR)}_3]^+\) with \(R = 2,4,6\text{-trisopropylphenyl}\) which realizes \(\text{de facto} \text{C}_3\text{b}\) symmetry of the central unit and good agreement is found for the \(C-S\) bond lengths. Ionization of \(\text{Ia}\) hardly elongates the \(C-S\) (0.013 Å) and \(H-S\) (0.008 Å).


\(^{53}\) The situation is closely related to \((\text{H}_2\text{C})_2\text{C}^+\) and \(\text{C}_2\text{H}_4^+\): (a) Trimethylsilylmethane radical cation: Du, P.; Borden W. T. J. Am. Chem. Soc. 1987, 109, 5330. (b) Benzene cation is \(D_6h\) symmetric but fractional and best viewed as \(D_6h\) symmetric: Lindner, R.; Müller-Dethlefs, K.; Wedrum, E.; Haber, K.; Grant, E. R. Science 1996, 271, 1698.
The formation of the distonic radical cation from thiirane radical cations is simply that the total number of unpaired and lone electron pairs is minimized. Distonic radical cations were shown in Scheme 2 to be the most stable isomers of [C(SR)₃]⁺. The electron-deficient trivalent carbon intrinsically prefers trigonal-planar hybridization, yet significant contributions from the open structures. Leading to the distonic radical is thus impeded by the concomitant ring strain. We searched the potential energy surface for such a structure and, indeed, several bridged chiral stereoisomers of 3b were located (Figure 2) and found to be local minima. In both “cis isomers” 3b-c1 and 3b-c2, the endocyclic S–H bonds are cis with regard to each other. While in 3b-c1 both S–H bonds are cis with regard to the exocyclic C–S bond, they are trans in 3b-c2. These “cis isomers” are not simple rotamers about the exocyclic C–S bond, but they have different configurations at the central C atom. In the “trans isomers” 3b-t1 and 3b-t2, the endocyclic S–H bonds are trans to each other. In 3b-t1 and 3b-t2, the ring H that is syn or anti with the exocyclic H–(S) is trans with regard to the exocyclic C–S bond, respectively.

Isomer 3b-t2 is the most stable of these bridged structures. For all practical purposes, the trans structures 3b-t1 and 3b-t2 are isoenergetic. 3b-c2 is 1.22 kcal/mol less stable than 3b-c1. The most stable isomer of 3b, 3b-t2, is 42.90 kcal/mol less stable compared to C₃H₇. The S–S bond formation leading to the distonic radical is thus impeded by the concomitant increase in ring strain. Our results predict that ring structures are thermodynamically disfavored compared to the open structures. The S–S bonds in cis and trans 3b are 2.107 ± 0.004 and 2.098 ± 0.001 Å, respectively. For comparison, the S–S bond in gauche (89.8°) HS–SH is 2.063 Å at the same theoretical level. We optimized the protonated derivative, C₃H₇–SH₂⁺, and an S–S bond length of 2.082 Å was found. The comparisons indicate that the S–S bond in 3b is slightly weakened due to electron deficiency. Significant contributions from II are indicated since the exocyclic C–S bond is rather short, only 1.686–1.693 Å, while the C–S bonds in the ring are long (average 1.776 Å) compared to 1b and 2b. An interesting feature of all ring structures of 3b concerns the substantial pyramidalization at carbon. The electron-deficient trivalent carbon intrinsically prefers trigonal-planar hybridization but the carbon pyramidalization might serve in this case to reduce strain associated with the Cₛ₂ ring.

**Effects of Oxidation on Rotational Isomerizations—Probing C–S Conjugation.** The isomerization between 2 and 1 is suggested. In the case of the dication, the question arises whether this advantage suffices to compensate for the ring strain energy associated with the S–S bond formation.

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involves rotation about the $c$ bond of 2 indicated in Figure 1 and proceeds along enantiotomerically related pathways via the chiral transition state structures 4a and 4b. Rotation about the $a$ or $b$ bonds in 2a or 2b results in automerization via the $C_s$-symmetric transition state structures 5a and 5b (Figure 3). The structures 5 come as isomers 5-w and 5-u depending on whether rotation occurs about the $a$ or the $b$ bond, respectively. The labels “w” and “u” describe the shape of the in-plane $H-S-C$-$H$ fragment. Bond rotation in 1 via 4 or 5 leaves the trigonal-planar carbon sp$^2$ hybridization intact and the $H-C-S$ angles of the “in-plane” SH groups are affected little. The $C_{3v}$ symmetric structures 6a and 6b were optimized to examine the effects of having all $S-H$ bonds in conformations that are not suitable for $S-C$ π-dative bonding. For 6a, three such structures were found. 6a-I is the most stable structure of these, and it exhibits three imaginary frequencies that all are associated with rotations about $C-S$ bonds. The structures 6a-II and 6a-III are second-order saddle points and their $C_{3v}$ units are distinctly pyramidalized (Figure 3) at carbon as the result of the $S-C$ density shift realized in their common electronic configuration. 6a-II and 6a-III differ in that the $H$ atoms and the $C$ atom are on the same or opposite sides, respectively, of the $S_3$ plane. These structures are isoenergetic at the level of optimization and distortions along the $C_{3v}$ inversion coordinate require little energy. The model 6a-90 in which a trigonal-planar $C$ atom was forced gave a slightly higher energy (0.3 kcal/mol) at the level of optimization. In the case of the dication, we also obtained several stationary structures, and we report the structure that is most stable at the level of optimization. This structure 6b (Figure 3) is a transition state with a slight degree of $C$-pyramidalization. These calculations of the model structures 6 suggest an interesting proposition: It might be possible to realize $C$-pyramidalization in carbenium ions by providing an incentive for a face-preference through hyperconjugation.

The lengths of the $C-S$ bonds that are being rotated in 4a and 4b are 1.796 and 1.831 Å and they are much longer than in 1a (by 0.09 Å) and 1b (by 0.11 Å) while the remaining $C-S$ bonds are shortened by $\approx 0.026$ Å in 4a and $\approx 0.042$ Å in 4b. The same is true and slightly more pronounced for 5a and 5b. For 4a and 4b, these are the kinds of structural effect one would expect for a change in conjugation associated with bond rotation. Similarly, one would be tempted to predict longer bond lengths for all $C-S$ bonds in 6a and 6b, but this is only the case for 6a-I and 6b and not for 6a-II and 6a-III. In 6a-II and 6a-III, the $C-S$ bonds are actually shorter than in 1a and this shortening is more pronounced for 6a-III.

Figure 3 shows the great similarities in the structural characteristics of the potential energy surfaces of the cation and the dication. Yet, there are some significant differences in the energetics. Schematic and to scale representations of the potential energy surfaces of the cation $[C(SH)_3]^+$ and the dication $[C(SH)_3]^+\cdot$ are summarized in Figure 4. At the PMP4 level, the activation barriers for the processes 1a $\Rightarrow$ 4a$^+$ and 1b $\Rightarrow$ 4b$^+$ are 9.17 and 3.33 kcal/mol, respectively. These computed rotational barriers are comparable to the activation barriers of 8–14 kcal/mol measured for some disubstituted systems $[R(C(SR)_2)]^+\cdot$ For the automerizations 2a $\Rightarrow$ 5a-u$^-$ $\Rightarrow$ 2a and 2a $\Rightarrow$ 5a-w$^-$ $\Rightarrow$ 2a, the activation barriers are 8.46 and 7.81 kcal/mol, respectively, at the highest level. For the automerizations of 2a via 5b-u$^-$ or 5b-w$^-$, the activation barriers are 4.68 and 7.82 kcal/mol, respectively. One would have expected that the rotational processes in the dication are less hindered than in the monocation. This is true for the isomerizations via 4 and for most automerizations but not for the automerization via 5b-w$^-$. The automerization of 1 involves a sequence of isomerizations to 2 via 4$^+$ and automerizations of 2 via 5$^+$ and the former isomerizations are rate-limiting for the monocation while the latter is rate-limiting for the dication. The relative energies of the models $C_{3v}$–6 as compared to $C_{3v}$-1 are large: The most stable structure of 6a is more than 79 kcal/mol less stable than 1a and 6b is 61 kcal/mol less stable than 1b. The relative stabilities of 6a and 6b are much higher than three times the value of the respective activation barriers to rotation, that is, the loss of one $S-C$ donation in the transition state structure for $C-S$ rotation is effectively counteracted by increased $S-C$ donation in the two other $C-S$ bonds.

Factors Affecting the Hydride Affinity of Trithiocarbenium Ion: Methane Destabilization and Cation Stabilization. While there have been several theoretical studies of the lighter
Figure 3. The transition state structures for isomerization 1 → 4 and automerizations 2 → 5a and 2 → 5b are shown for the monocation (left) and the dication (right). Model structures correspond to higher-order saddle points.
Figure 4. The potential energy surface diagram is shown for the
monocation (solid) and the dication radical (dashed). The potential
energy diagram is represented to scale as computed at the PMP4/6-31G**/HF/6-31G*+∆VZPE level.

Figure 5. The optimized structure of HCSH3 and comparison to the
X-ray structure of HCSR3, with R = 2,4,6-trisopropylphenyl.

homologue, it appears that the neutral molecule HCSH3 has not been studied. We optimized HCSH3 in C3 symmetry with a cisoid
H-C=S-R conformations (Figure 5) and the resulting equilibrium geometry 1-H agrees well with the crystal structure of the analog HCSR3 (R = 2,4,6-iPr3C6H2). The formation of 1a from 1-H via heterolytic C-H bond dissociation (eq 1) requires 261.3 kcal/mol at the RHF/6-31G* level. This

value for the hydride affinity (HA) is expected to be too high since a proper functional description of hydride ion requires
diffuse functions and eq 1 was evaluated also with the
6-31G*+GD2P basis set. At the MP4(full,svdq)/6-31+G**/RHF/6-31G* level and including scaled VZPE(RHF/6-31G*),
HA(1a) becomes 217.7 kcal/mol. The hydride affinity of methyl
cation is HAC(Me3) = 312.2 kcal/mol.51a The difference between the hydride affinities of 1a and CH3+ provides a quantitative measure for the increased propensity of the trithio-


(60) The C3-symmetric structure was considered as a model of the solid state structure of the derivative. The most stable structure of HCSH3 is non-symmetric (C1) and contains two gauche and one anti H-S=C-H arrangements.

substituted system to form the cation and HA(1-H) is about
95.5 kcal/mol lower compared to the respective value for methane.

The heat of formation ΔHf(1a) can be determined via the reaction enthalpy of the isodesmic reaction shown in eq 2 − ΔHf

CH3+ + 3CH3SH → 3CH4 + [C(SH)3]++ (1a)


Ionization Potential of Trithiocarbenium Ion. Ionization potentials (IP) for the process 1a → 1b + e− were determined using Koopmans’ theorem62 and directly with the energies of

Ionization Potential of Trithiocarbenium Ion. Ionization potentials (IP) for the process 1a → 1b + e− were determined using Koopmans’ theorem62 and directly with the energies of

Figure 5. The optimized structure of HCSH3 and comparison to the X-ray structure of HCSR3, with R = 2,4,6-trisopropylphenyl.
notations, it becomes necessary to employ CS non-connected SH groups. To reflect this electron density feature in Lewis that leads to density accumulation at C at the expense of the shows that there also is a strong polarization in the groups donate π-density to carbon (0.309 each) as suggested (64) For discussions of resonance interactions on Y-conjugated systems, see: (a) Wiberg, K. B. J. Am. Chem. Soc. 1990, 112, 4177. (b) Horn, H.; Ahlrichs, R. J. Am. Chem. Soc. 1990, 112, 2121. (c) Ogorodnikova, N. A. J. Mol. Struct. 1993, 301, 189.

Table 2. Topological Properties of 1a, 1b, and 1b

<table>
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<tr>
<th>atoms</th>
<th>r_a</th>
<th>r_b</th>
<th>F</th>
<th>ρ/Å</th>
<th>λ_1</th>
<th>λ_2</th>
<th>λ_3</th>
<th>ϵ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=S</td>
<td>1.114</td>
<td>0.642</td>
<td>0.634</td>
<td>0.214</td>
<td>-0.297</td>
<td>-0.170</td>
<td>0.357</td>
<td>0.742</td>
</tr>
<tr>
<td>S-H</td>
<td>0.877</td>
<td>0.449</td>
<td>0.661</td>
<td>0.222</td>
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<td>-0.452</td>
<td>0.307</td>
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<tr>
<td>C=S</td>
<td>0.912</td>
<td>0.809</td>
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<td>0.223</td>
<td>-0.347</td>
<td>-0.294</td>
<td>0.061</td>
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<tr>
<td>C=S</td>
<td>0.905</td>
<td>0.817</td>
<td>0.526</td>
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<td>-0.296</td>
<td>0.070</td>
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<td>C-S</td>
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<td>0.651</td>
<td>0.622</td>
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<td>-0.154</td>
<td>0.312</td>
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<td>S-H</td>
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<td>-0.523</td>
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<td>S-H</td>
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<td>0.686</td>
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<td>-0.514</td>
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<td>S-H</td>
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<td>-0.500</td>
<td>-0.469</td>
<td>0.340</td>
<td>0.067</td>
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</table>

1a and 1b. With ϵ(HOMO,1a) = -0.59258 au Koopmans’ theorem predicts IP(1a) = 371.9 kcal/mol (16.1 eV). This approximation neglects the relaxation of the remaining electrons after ionization of 1a and usually represents an upper limit of the true IP although correlation effects counteract. Direct evaluation of the ionization potential at the HF/6-31G* level and considering the ZPE differences these wave functions are used as references in the full forth-order Möller–Plesset treatment. At the PMP4(full,ديدة)/6-31G*/HF/6-31G* level and considering the ZPE differences at the HF level one obtains IP(1a) = 334.8 kcal/mol (14.5 eV). With this best estimate for IP(1a) and with ΔH_f(1a) = 197.7 kcal/mol, we derive ΔH_f(1b) = 541.5 kcal/mol.

Inductive and Conjugative S−C Polarizations in “Trithiocarbenium Ions”. In valence bond theory, the monocation 1a is described by the resonance form that corresponds to the trithio-substituted carbenium ion and by the set of the triply degenerate resonance forms in which the positive charge is delocalized onto S by S-lone pair donation toward C. Based on these formal charges in the Lewis structures describing Y-conjugation,3 one might be inclined to assume that the positive charge is well distributed over all the heavy atoms of 1a. The resonance forms do not reflect actual charges and the topological electron density analysis reveals a different picture. The S atoms are electron-deficient indeed but the sum of the SH group charges of +0.750 far exceeds unity: A negative charge of q(C) = -1.248 is revealed for the “electron-deficient” carbon! The Bader ρ-populations Bρ(ρ) show that the SH groups donate π-density to carbon (0.309 each) as suggested by the respective resonance forms. The electron density analysis shows that there also is a strong polarization in the α-system that leads to density accumulation at C at the expense of the SH groups. To reflect this electron density feature in Lewis notations, it becomes necessary to employ CS non-connected valence bond structures in which the C−S α-bond electron pair

is assigned to C (top row in Scheme 4).4 Clearly, the name “trithiocarbenium ion” does not adequately describe the electronic structure. The electronic structure of 1a indicates that nature tends not only to disperse positive charge to the periphery of the Y-shaped system, but to polarize the C−S bonds in such a way as to create a negative center.5 Apparently, there is an electrostatic advantage associated with placing larger positive charges around a negatively charged center compared to just distributing the positive charge.

Oxidation of 1a removes one electron from one of the π-HOMOs and results in 1b. The HOMOs of 1a are schematically shown in Scheme 5 where the approximate node planes are indicated as dashed lines. The graphical depictions of the electron and spin density distributions (vide infra) show that oxidation occurs for the MO sketched on the left and denoted HOMO’. This oxidation causes a so-called fragment-inequality2b since the equivalence of the SH groups vanishes. The removal of one electron from HOMO’ leaves one SH fragment relatively unchanged (the one on the node or close to it) and there exist three degenerate electronic states for 1b since it is equally probable for each SH fragment to be this least affected SH fragment. In other words, the electronic structure of 1b can be realized in three ways and there also are three structures 1b’ depending on which of the three C−S bonds is elongated. The three states are vibronically coupled and the transitions from one state to another are associated with intramolecular charge and spin transfer between the SH fragments. The potential energy surface analysis shows that the energy gain due to the Jahn−Teller effect in 1b’ is small. Consequently, the pseudorotation between the three 1b’ structures is facile and we will focus on the average properties in our discussion of the integrated properties. The ESR spectra, for example, can be...
expected to describe the average spin density distribution of the three radical dications 1b'. The structural differences between 1b and 1b' are marginal and we examined the electronic structure of the radical dication using the 1b structure.

Integrated properties for 1b were determined both with the UHF and with the PUHF densities (Table 3). Spin projection has only a small effect on the electron density distribution and we will discuss the UHF electron densities as they allow for a clearer presentation. Based on the valence-bond description of 1b, one would expect that oxidation of 1a leads to removal of electron density from the S atoms and this is true to a certain degree. The total charge of all SH groups is increased from 2.25 in 1a to 2.90 in 1b. At the same time, the C population is reduced by 0.35 but the electron deficient in going from 1a to 1b.

The electronic relaxations associated with adiabatic oxidation are clearly manifested in the electron density difference (EDD) function $\Delta \rho$. This function is defined as the difference between $\rho(C(SH)_3)$ and $\rho(C(SH)_3)^-$ as computed with the HF/6-31G* structure of the monocation $C_{16}$-1a. Contour increments are $2 \times 10^{-3}$ e au$^{-3}$ for $\Delta \rho$ in the molecular plane (left) and they are $10^{-3}$ e au$^{-3}$ for the cross section in a plane parallel to the molecular plane and 0.5 Å away from it.

![Figure 6](image-url)  
**Figure 6.** Electron density difference function $\Delta \rho = \rho^{\text{PUHF}}(\text{[C(SH)$_3$]}^-) - \rho^{\text{HF}}(\text{[C(SH)$_3$]})$ as computed with the HF/6-31G* structure of the monocation $C_{16}$-1a. Contour increments are $2 \times 10^{-3}$ e au$^{-3}$ for $\Delta \rho$ in the molecular plane (left) and they are $10^{-3}$ e au$^{-3}$ for the cross section in a plane parallel to the molecular plane and 0.5 Å away from it.

Table 3. Integrated Properties for 1a and 1b

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<tr>
<th>atom</th>
<th>BC (e)</th>
<th>BP(π) (e)</th>
<th>energy</th>
<th>BC (e)</th>
<th>BP(π) (e)</th>
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<th>BC (e)</th>
<th>BP(π) (e)</th>
<th>energy</th>
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<td>0.729</td>
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<td>0.169</td>
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<td>1.000</td>
<td>0.998</td>
<td>-1231.319859</td>
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<td>0.771</td>
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<tr>
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<td>0.987</td>
<td>0.571</td>
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</table>

$^a$ Integrated Bader charge (BC) and Bader populations (BP), spin population (SP), and atom energy ($E = -E_{\text{kin}}$). $^b$ Difference between integrated and directly computed molecular energy for 1a and 1b (UHF) is 0.009 and 0.53 kcal/mol, respectively.

Structural differences describing the S-C π- and σ-donation in which one of the SH groups is singly oxidized (bottom row in Scheme 4). The electronic relaxations associated with adiabatic oxidation are clearly manifested in the electron density difference (EDD) function $\Delta \rho$. This function is defined as the difference between the electron density functions $\rho(C(SH)_3)$ and $\rho(C(SH)_3)^-$ as computed with the HF/6-31G* structure of the monocation $C_{16}$-1a. Contour increments are $2 \times 10^{-3}$ e au$^{-3}$ for $\Delta \rho$ in the molecular plane (left) and they are $10^{-3}$ e au$^{-3}$ for the cross section in a plane parallel to the molecular plane and 0.5 Å away from it.

**Strong Spin Polarization in the σ-System.** While the UHF and PUHF electron density distributions differ only marginally, the associated spin density functions differ greatly and the PUHF electron density functions are clearly manifested in the electron density difference (EDD) function $\Delta \rho$. This function is defined as the difference between the electron density functions $\rho(C(SH)_3)$ and $\rho(C(SH)_3)^-$ as computed with the HF/6-31G* structure of the monocation $C_{16}$-1a. Contour increments are $2 \times 10^{-3}$ e au$^{-3}$ for $\Delta \rho$ in the molecular plane (left) and they are $10^{-3}$ e au$^{-3}$ for the cross section in a plane parallel to the molecular plane and 0.5 Å away from it.
HOMO' of 1a becomes singly occupied in 1b and, consequently, two S atoms show large α-spin densities in the π-system. The C atom is assigned β-spin density due to spin polarization. Interestingly, the unique S does not show α-spin density excess in the π-system. Instead, there occurs a region of α-spin excess in the unique C–S bond region but β-spin density at that S atom. The π-hole causes strong spin polarization in the σ-system as is clearly evidenced in the plot shown to the left in Figure 7. We pointed out above that the MO of the unpaired electron is not the HOMO of the dication but that sets of spin-paired π- and σ-electrons are less bonding than the MO associated with the unpaired π-radical and the strong spin polarization observed therefore comes as no surprise. The C atom shows β-spin density in the σ-system as well. For the SH groups, we find β-spin density in the S lone pair region and in the S core region, and areas of α-spin density in the S–H and S–C bonding regions. The spin density difference function $\Delta \rho = \rho^{\text{UHF}}([\text{C(SH)₃}])^{1+} - \rho^{\text{UHF}}([\text{C(SH)₃}])^{2+}$ of C₃₀-1b also was computed to examine the effects of annihilation of spin contaminants in the UHF density. The resulting plot in the molecular plane greatly resembles the pattern found in the left plot in Figure 7. The function $\Delta \rho$ assumes positive values in all areas in which the spin density indicates β-density and vice versa. This pattern of $\Delta \rho$ shows that the spin projection causes a reduction of spin polarization in this system just like in the methyl and allyl radicals studied previously.¹⁴

Conclusion

The potential energy analysis shows great similarities for the monocation [C(SH)₃]⁺ and its dication radical [C(SH)₃]^{2+}. Open structures 1 and 2 are greatly favored. Cyclic distonic chiral stereoisomers 3b do exist for the radical dication but—at least for the model systems discussed—they all are high in energy. The C–S rotational barriers (4 and 5) and the high energies of the model structures 6 indicate strong π-interactions in 1 and 2. Our best estimates for the rotational barriers of 1a and 1b are 9.2 and 3.3 kcal/mol, respectively, and the activation barriers for the least-energy automerizations of 2a and 2b are 8.5 and 4.7 kcal/mol. The radical dication C₃₀-1b undergoes a Jahn–Teller deformation to form a modestly distorted structure 1b’ with one elongated and two shortened C–S bonds. The energy lowering due to the JT effect is only about 1 kcal/mol and pseudorotation in 1b is essentially unhindered.

Dynamic electron correlation is important for the accurate calculation of the radical dication and the MO analysis shows why that is so. Removal of one electron from one of the degenerate π-HOMOs of 1a results in a stabilization of the remaining π-electron to such an extent that the unpaired electron is not in the HOMO of the dication! Sets of spin-paired π- and σ-electrons both are higher in energy compared to the MO of the unpaired π-radical. Dynamic electron correlation is so important because of this readily identifiable feature of the molecular orbitals. The unpaired π-MO’s “diving below the Fermi level” facilitates strong spin polarization because of energetic proximity with σ-MOs. The combination of annihilation of spin contamination and electron correlation is essential for the determination of relative energies.

Electron-deficient trivalent carbon intrinsically prefers trigonal-planar hybridization. It might be possible, however, to achieve pyramidalization of the trivalent carbon in heteroatom-substituted carbenium ions and our results suggest two strategies. All of the distonic ring structures 3b are substantially pyramidalized at carbon. The pyramidalization might serve to reduce ring strain associated with the S–S interaction and, in effect, the pyramidalization reduces the distances between all three substituents. Hence, it might be possible to achieve C-pyramidalization by design of CX₃ systems that allow for stronger direct interactions between the X-substituents. Also, one could envision cations in which the C–S conformations of 6 are forced by embedding the system in a rigid framework.

Comparison of the hydride abstraction reactions of methane and its trithio derivative shows that the increased propensity for the formation of the trithio-substituted carbenium ion can be attributed to two substituent effects: A destabilization of the substituted methane and a stabilization of the cation formed. The latter effect is about twice as large compared to the former. At our highest level, we find that the computed hydride affinity of 1a is about 95.5 kcal/mol less as compared to the respective experimental hydride affinity of methyl cation. The high magnitude of this value demonstrates in a compelling fashion the success of the basic approach of stabilizing carbenium ions by means of trithio substitution. The heat of formation of 1a...
was determined via the isodesmic reaction $\text{CH}_3^+ + 3\text{CH}_3\text{SH} \rightarrow 3\text{CH}_4 + \text{1a}$ and a value of $\Delta H_f(\text{1a}) = 197.7 \text{ kcal/mol}$ resulted. The heat of formation $\Delta H_f(\text{1-H}) = 14.1 \text{ kcal/mol}$ follows via the hydride abstraction reaction $\text{1-H} \rightarrow \text{H}^- + \text{1a}$. With these enthalpies, the reduction of the heterolytic C–H bond dissociation energies of HC(SH)$_3$ compared to CH$_4$ was partitioned into a methane destabilization of 32.0 kcal/mol and a carbenium ion stabilization of 63.5 kcal/mol. Both effects must be considered in selections of R groups that might further facilitate the preparation of stabilized carbenium ions. Our best estimate for the ionization energy of $\text{1a}$ is $\text{IP(1a)} = 343.8 \text{ kcal/mol}$ (14.9 eV) and results in $\Delta H_f(\text{1b}) = 541.5 \text{ kcal/mol}$.

The trithio-substituted cation and dication radical show the same electronic motif. While one might have expected to find charge dispersal due to $\text{S}^-\text{C} \pi$-donation, a much larger $\text{S}^-\text{C}$ donation actually occurs in both the $\pi$- and $\sigma$-system. The result of the electron density shifts is a motif in which large positive charges are arranged around a negative carbon center. The oxidation of the monocation primarily removes sulfur $\pi$-electron density. The oxidation also removes some electron density from the central carbon and renders this C atom more $\pi$-acidic. The $\alpha$-excess spin density is entirely concentrated on sulfur atoms and the carbon carries some $\beta$-spin density because of spin polarization. The results of the electronic structure analysis show that these S-containing carbenium ions are fundamentally different from the lighter O-homologs due to the umpolung of the C–X bonds. While the electronic structure of oxygen-stabilized carbenium ions is adequately described by the name, the trithio-substituted carbenium ions actually have methanide character associated with the central C atom and the name “sulfuronium ion” would not be inappropriate. Current theoretical and experimental studies are directed at exploring the chemistry suggested by the potential energy surface explorations and by the electronic structure analyses.

Acknowledgment. This research was supported by a NATO Collaborative Research Grant. R.G. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Board of the University of Missouri for additional support. We thank Steve Meyer of the MU Campus Computing Center for excellent systems services.

Supporting Information Available: Total energies and vibrational zero-point energies of all structures (1 page). See any current masthead page for ordering and Internet access instructions.