

# Theoretical Studies on Some S : N Three-Electron Bonded Radical Cations<sup>†,‡</sup>

Ian Carmichael

Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

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*Ab initio* molecular orbital calculations and hybrid density functional theory methods are employed to characterize the structure and properties of some radical cations formed during the radiolysis of aqueous solutions of bifunctional aliphatic sulfide amines.

The theoretical work assists in the assignment and interpretation of transient spectra, experimentally detected by time-resolved pulse-radiolysis/optical detection, resonance Raman, and electron spin resonance techniques.

In particular, results on cyclic species containing the (S : N) linkage are reported. Conformational flexibility in the cyclized transients is probed and the preferred structures, and the pseudorotational paths linking them, are determined. Characteristic vibrational frequencies and optical absorption bands involving the two-center/three-electron S : N bond are predicted.

High-level (coupled-cluster) calculations on model systems (e.g., perhyrido-) are used to assess the reliability of the more approximate computational schemes necessitated in work on the larger species. The usefulness of the hybrid density functional approach for a reliable description of S : N-bonded species is called into question.

As part of a general program of quantum chemical studies of reactive intermediates, carried out at the Notre Dame Radiation Laboratory under the auspices of the United States Department of Energy, we are investigating various theoretical descriptions for the two-center/three-electron S : N bond with a view to providing an accurate and reliable determination of the structure and properties of important species containing this moiety. In particular, pulse radiolysis<sup>1,2</sup> (or flash photolysis<sup>3</sup> in the presence of a suitable electron acceptor) of an aqueous solution of methionine, or related bifunctional sulfur-containing molecules, is thought, under certain conditions (of pH, radiolysis dose and precursor concentration, for example) to lead to radical cations containing the S : N linkage.<sup>1</sup>

Mainly on the basis of kinetic studies of transient optical spectra induced by pulse radiolysis, the cyclized species ( $\lambda_{\max} = 390$  nm) are thought to be formed via intramolecular water elimination from hydroxysulfuranyl radicals ( $\lambda_{\max} = 330$  nm), by analogy with findings in sulfur-containing aliphatic carboxylic acid systems,<sup>4</sup> in which the hydroxysulfuranyl radical is more readily observed. Kinetic evidence for the 330-nm absorbing

precursor has, however, been unequivocally obtained in a recent combined flash photolysis/pulse radiolysis study of aqueous dipeptides.<sup>5</sup> The cyclization reaction is in competition, to a greater or lesser extent, with the formation of sulfur-centered radical cations depending on the availability of protons from the solvent. The sulfur-centered radical cations are believed to deprotonate rapidly to give  $\alpha$ -carbon-centered radicals ( $\alpha$  to sulfur, that is), which have absorption maxima in the vicinity of 285 nm.<sup>1</sup> These carbon-centered radicals are also formed upon direct hydrogen abstraction by the hydroxyl radicals radiolytically generated in the solvent.

Poorly resolved electron spin resonance spectra (ESR) spectra, which do however, show a characteristic triplet pattern due to a <sup>14</sup>N-splitting of about 100 MHz, have been reported<sup>6</sup> in  $\gamma$ -irradiated glassy alkali-metal halide solutions at 77 K, and have been assigned to the cyclic S : N species.

This chemistry is exemplified for 3-(methylthio)propylamine in Fig. 1.

The present theoretical studies were undertaken in conjunction with on-going nanosecond time-resolved resonance Raman experiments at the Radiation Laboratory (G.N.R. Tripathi) aimed at determining the characteristic vibrational patterns associated with the relatively weak S : N bond. The structure and properties of the cyclized species are here determined by means of conventional

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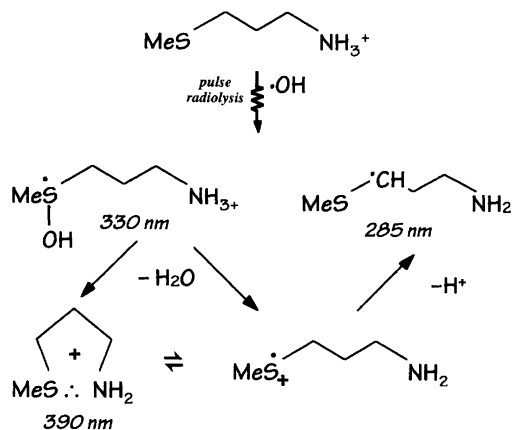


Fig. 1. Mechanism of formation of the cyclic S...N bonded radical cation in the pulse radiolysis of aqueous 3-(methylthio)propylamine and typical absorption bands of similar transients.

self-consistent-field molecular orbital calculations at the unrestricted Hartree-Fock (UHF) level and by density functional theory methods as described below.

The extent of conformational flexibility in the five-membered ring species is investigated. Two distinct stable conformers are found separated by a substantial pseudorotational barrier.

The locations of the lowest optical absorption bands are calculated for both species. Harmonic frequencies are determined at the optimized geometries together with hyperfine properties.

To gauge the validity of the approximations implicit in the density functional treatment, a set of similar calculations is carried out on a related model compound, (dihydridosulfido)trihydridonitrogenyl(1+),  $\text{H}_2\text{SNH}_3^+$ , and the resulting structure and properties compared with the corresponding features revealed by calculations at the quadratic configuration interaction level (QCISD).

## Computational methods

The particular flavor of density functional treatment employed incorporates a non-local hybrid functional, B3LYP, due to Becke<sup>7</sup> which appears to be particularly useful for the computation of optimized molecular geometries<sup>8</sup> and spin densities.<sup>9,10</sup> In addition to local<sup>11</sup> and non-local<sup>12</sup> exchange functionals, the B3LYP model includes a contribution from Hartree-Fock exchange and both local<sup>13</sup> and non-local<sup>14</sup> correlation corrections.

QCISD is a high-level, coupled-cluster-based electron correlation method introduced by Pople and coworkers.<sup>15</sup>

All calculations were performed with a modified version of the GAUSSIAN 94 suite of programs.<sup>16</sup>

For the larger species, basis sets of approximately polarized double- $\zeta$  quality are employed, denoted 6-311G(d,p). These basis sets were originally conceived<sup>17</sup> as triple- $\zeta$  split-valence sets, but were later shown<sup>18</sup> to be better described as double- $\zeta$  in both the core and valence regions, at least for atoms. For more complete

calculations on the smaller model system, supplementary functions, including multiple polarization, diffuse, and higher angular momentum functions, have also been added to this basis to give sets conventionally denoted 6-311++G(3df,2pd).

## Results and discussion

**Conformational structures.** Conformational preferences in the cyclized species derived from 3-(methylthio)propylammonium,  $\text{CH}_3\text{S}(\text{CH}_2)_3\text{NH}_3^+$ , are assessed by calculating a number of envelope structures in which each one of the intra-ring dihedrals is sequentially constrained to be planar. An energy profile for pseudorotational interconversion is thus developed and displayed in the lower part of Fig. 2. Numbering the atoms as S(0), N(1), C(2), and so on around the ring, as indicated in the upper part of Fig. 2 for one particular conformer, shows a double minimum pathway with peaks when either the sulfur or nitrogen is out of the ring plane (structures labeled  ${}^0\text{E}$ ,  $\text{E}_0$ ,  ${}^1\text{E}$  and  $\text{E}_1$ ) and valleys when the carbon, C(3), across the ring from the S...N bond is out of the plane ( ${}^3\text{E}$  and  $\text{E}_3$ ).

Fully relaxed geometry optimizations in the vicinity of the constrained structures of lowest energy leads to two distinct stable conformers, which will here be labeled ' ${}^3\text{E}$ ' and ' $\text{E}_3$ ' after the envelope forms from which they are

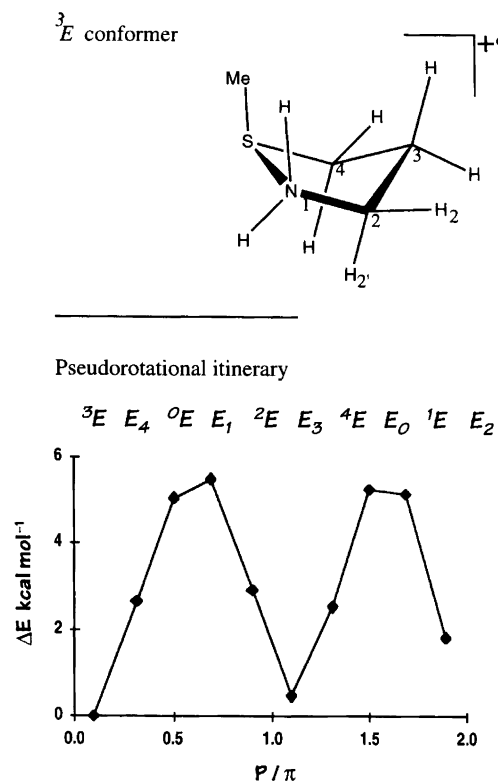


Fig. 2. Numbering scheme for the cyclic S...N bonded radical cation formed in the pulse radiolysis of aqueous 3-(methylthio)propylamine and energy profile along its pseudorotational itinerary.

derived. These conformers are close in energy with the  ${}^3E'$  structure lying about  $0.3 \text{ kcal mol}^{-1}$  below the  $'E_3'$  form and separated from it by a barrier of around  $6 \text{ kcal mol}^{-1}$ . The computed S...N bond lengths in the optimized structures are listed in Table 1. The UB3LYP values for the S...N bond length are noticeably larger than their UHF counterparts. Much smaller increases in the lengths of the bonds from sulfur to the adjacent carbons are found between the UHF and UB3LYP optimizations, as also seen in Table 1.

Vibrational frequencies in both conformers were obtained from conventional harmonic normal-mode analysis at these fully relaxed UHF/6-311G(d,p) and UB3LYP/6-311G(d,p) geometries. The mode dominated by the S...N stretch is given in Table 2. UHF and UB3LYP calculations with a 6-311G(d,p) basis set both indicate that the conformers have observably different fundamentals, split by about  $10\text{--}20 \text{ cm}^{-1}$ . The UB3LYP values are in rough accord with the frequencies assigned to this mode in a preliminary analysis of the resonance Raman data.<sup>19</sup> Calculations at a lower level, UHF/3-21G\*, suggest isotope shifts of about 10 and  $5 \text{ cm}^{-1}$  to lower frequencies for the  ${}^3E'$  and  $'E_3'$  conformers respectively in the *N*-dideuterated species. For example, upon such deuteration, the mode dominated by the S–N stretch in the  ${}^3E'$  structure shifts from  $377 \text{ cm}^{-1}$  to  $365 \text{ cm}^{-1}$  in unscaled UHF/3-21G\* calculations. Crude estimates of solvent effects (self-consistent reaction field in an Onsager cavity of about  $4 \text{ \AA}$ ) suggest only small positive shifts ( $\sim 5 \text{ cm}^{-1}$ ) in the S...N stretching frequency in an aqueous environment. For example in a cavity of  $3.96 \text{ \AA}$ , the mode dominated by the S–N

stretch in the  ${}^3E'$  structure shifts from  $377 \text{ cm}^{-1}$  to  $383 \text{ cm}^{-1}$  in unscaled UHF/3-21G\* calculations. Similar results have also been found in the cyclized species derived from methionine and 3-thiopropylamine and will be reported elsewhere.

*Optical spectra.* Pulse radiolysis with optical detection is an indispensable tool for the investigation of two-center/three-electron bonded transient species, which often possess characteristic optical absorption bands in, or near, the visible. For the above UB3LYP/6-311G(d,p) optimized structures, theoretical estimates of both the location of the lowest absorption bands and an approximate description of the intensity and electronic composition of the transitions were obtained from the CIS (configuration interaction with single excitations) model formulated by Pople and coworkers.<sup>20</sup> Results are given in Table 3, which lists absorption maxima, dipole oscillator strengths, and the component coefficients of largest weight.

In either structure, the lowest energy band is calculated to be described by an essentially one-electron transition between the highest occupied and the lowest unoccupied  $\beta$  molecular orbitals, as evidenced by the weighting coefficients in Table 3. The basis sets used in these calculations ranged from 6-31G\* through 6-311 + G(d,p) with little change in the predicted absorption locations. The effect of solvent was once again considered as above and produced small ( $\sim 8 \text{ nm}$ ) shifts to the red, bringing the computed bands still closer to those observed ( $\sim 390 \text{ nm}$ , see Fig. 1) experimentally.<sup>19</sup>

These calculated band positions lie about  $50 \text{ nm}$  to the red of the corresponding transition energies,  $324 \text{ nm}$  and  $320 \text{ nm}$  for the  ${}^3E'$  and  $'E_3'$  conformers, respectively, computed at the optimized UHF/6-311G(d,p) geometries. The predicted absorption location is thus highly dependent on the underlying structural parameters, in particular, on the length of the S–N bond.

*Hyperfine splittings.* Estimates of the various hyperfine coupling constants were obtained at both the UHF and UB3LYP levels of theory, using the 6-311G(d,p) basis set, with the results presented in Table 4. From the comparison of the UHF results at each geometry, it is apparent that the calculated values are relatively insensitive to the structural parameters. In particular little change is computed in the  ${}^{33}\text{S}$  and  ${}^{14}\text{N}$  couplings despite a

Table 1. Calculated<sup>a</sup> S...N and S–C<sup>b</sup> bond lengths ( $\text{\AA}$ ) in the S...N bonded radical cations derived from 3-(methylthio)propylamine.

Method	UHF	UB3LYP
	Conformer ${}^3E'$	
$r(\text{S...N})$	2.516	2.581
$r(\text{S–C}_4)$	1.822	1.830
$r(\text{S–C}_{\text{ex}})$	1.808	1.819
	Conformer $'E_3'$	
$r(\text{S...N})$	2.537	2.586
$r(\text{S–C}_4)$	1.826	1.837
$r(\text{S–C}_{\text{ex}})$	1.807	1.819

<sup>a</sup>Optimized with the 6-311G(d,p) basis set. <sup>b</sup>C<sub>4</sub> is the adjacent ring carbon, C<sub>ex</sub> is the methyl carbon.

Table 2. Calculated<sup>a</sup> S...N stretching frequency ( $\text{cm}^{-1}$ ) in the S...N bonded radical cations derived from 3-(methylthio)propylamine.

Method	UHF	UB3LYP
Conformer ${}^3E'$	224	256
Conformer $'E_3'$	242	263

<sup>a</sup>6-311G(d,p) basis set.

Table 3. Calculated<sup>a</sup> absorption maxima, strengths and leading composition in the S...N bonded radical cations derived from 3-(methylthio)propylamine.

Conformer	${}^3E'$	$'E_3'$
$\lambda_{\text{max}}/\text{nm}$	372	367
Osc. strength	0.213	0.214
$c[\beta \rightarrow \beta^*]$	0.941	0.935

<sup>a</sup>UCIS/6-311 + G(d,p) at the respective UB3LYP/6-311G(d,p) geometries.

Table 4. Calculated<sup>a</sup> hyperfine splitting (MHz) in the S...N bonded radical cation, conformer <sup>3</sup>E', derived from 3-(methylthio)propylamine.

Method	UHF <sup>b</sup>	UHF <sup>c</sup>	UB3LYP <sup>c</sup>
<sup>33</sup> S	125	126	48.0
<sup>14</sup> N	90.1	91.6	70.8
<sup>1</sup> H <sub>1</sub>	-33.5	-39.7	-20.3
<sup>1</sup> H <sub>1</sub> '	-38.4	-41.1	-23.6
<sup>13</sup> C <sub>2</sub>	-19.4	-22.6	-13.2
<sup>1</sup> H <sub>2</sub>	36.7	39.1	69.4
<sup>1</sup> H <sub>2</sub> '	2.9	3.1	0.6
<sup>13</sup> C <sub>3</sub>	1.9	1.2	-3.0
<sup>1</sup> H <sub>3</sub>	-3.8	-4.0	-2.7
<sup>1</sup> H <sub>3</sub> '	-7.9	-8.2	-4.7
<sup>13</sup> C <sub>4</sub>	-21.6	-26.5	-11.2
<sup>1</sup> H <sub>4</sub>	42.6	40.9	41.3
<sup>1</sup> H <sub>4</sub> '	2.9	3.5	0.0
<sup>13</sup> C <sub>ex</sub>	-19.0	-24.6	-10.5
⟨ <sup>1</sup> H <sub>4</sub> ⟩	28.4	28.6	25.0

<sup>a</sup>6-311G(d,p) basis set. <sup>b</sup>UHF/6-311G(d,p) optimized geometry. <sup>c</sup>UB3LYP/6-311G(d,p) optimized geometry.

0.065 Å change in the S–N bond length. This result is somewhat surprising since isotropic splittings are often sharply dependent on bond lengths, for example in some diatomics.<sup>21,22</sup> However, most splittings undergo substantial changes on moving from UHF to UB3LYP suggesting that correlation corrections are often important. Particularly large changes are calculated at the sulfur nucleus. The hydrogens are assigned the numeric indices of the nuclei to which they are attached, see Fig. 2, with the primed hydrogens lying on the opposite side of the ring to that containing the methyl substituent. Without some guidance as to the expected accuracy of the DFT-based values, it is clear that the predicted couplings at this level of theory would be quite uncertain.

*H<sub>2</sub>SNH<sub>3</sub><sup>+</sup> as a model compound.* In an effort to obtain such guidance, similar calculations on a much simpler model compound, H<sub>2</sub>SNH<sub>3</sub><sup>+</sup>, for which an optimized structure can be obtained which also possesses a 2c/3e S–N bond, were compared with results from a more complete quadratic configuration interaction investigation, which includes a thorough treatment of the effects of electron correlation. This particular radical cation has previously been investigated at relatively low levels of theory as part of a comprehensive survey of such odd-electron  $\sigma$ -bonded species.<sup>23</sup>

Table 5 shows the optimized S...N bond lengths obtained at the different levels of theory with the 6-311G(d,p) basis set. Calculations with the much more flexible 6-311G(3df,2pd) basis set lead to UHF and UB3LYP values of the bond length at 2.447 Å and 2.525 Å, respectively, little changed from the tabulated values. The S...N bond is apparently calculated to be too long at UB3LYP, when compared with the presumably more accurate UQCISD value.

For the harmonic vibrational frequency the UB3LYP/6-311G(d,p) calculation predicts a value

Table 5. Calculated<sup>a</sup> structural and bonding parameters in H<sub>2</sub>SNH<sub>3</sub><sup>+</sup>.

Method	UHF	UB3LYP	UQCISD
<i>r</i> (SN)/Å	2.458	2.535	2.439
<i>v</i> (SN)/cm <sup>-1</sup>	334	271	331
<i>D</i> <sup>b</sup> /kcal mol <sup>-1</sup>	8.6, 26.4	34.7, 44.6	28.6, 34.1

<sup>a</sup>6-311G(d,p) basis set at the respective optimized geometries. <sup>b</sup>Bond dissociation energies; first to SH<sub>2</sub>+NH<sub>3</sub><sup>+</sup>, second to NH<sub>3</sub>+SH<sub>2</sub><sup>+</sup>.

60 cm<sup>-1</sup> below the UQCISD result. UHF and UB3LYP results at 326 cm<sup>-1</sup> and 268 cm<sup>-1</sup> respectively, obtained using the much larger basis set, for the SN stretching frequency are also little changed from the values in Table 5. UB3LYP frequencies for this stretch are thus indicated to be too low.

The bond dissociation energies in Table 5 for both S...N bond scissions into either H<sub>2</sub>S+NH<sub>3</sub><sup>+</sup> or H<sub>2</sub>S<sup>+</sup>+NH<sub>3</sub> are calculated from (unscaled) zero-point-energy-corrected total energies with each method at the optimized geometry obtained with that method. The UHF and UB3LYP results for the bond dissociation energies are, once again, essentially unchanged when evaluated with the largest basis set. Thus the present density functional treatment exaggerates the strength of the 2c/3e bond. It is well known the UHF method provides an inadequate description of such three-electron bonds, and Table 5 simply provides a further example.

The lowest optical absorption bands computed at both the UB3LYP/6-311G(d,p) and the UQCISD/6-311G(d,p) optimized geometries are reported in Table 6. The particular values listed are obtained at the UCIS/6-311G+(d,p) level, but little change is found even with a much larger 6-311++G(3df,2pd) basis set. Clearly the location of the optical absorption maximum is sensitive to the molecular geometry, in particular to the length of the SN bond. Agreement obtained between the computed peak position at the optimized UB3LYP geometry and an experimental determination of the peak position would thus be due to a fortuitous cancellation of errors.

Table 7 contains values for the hyperfine coupling constants at each magnetic nucleus, except that only an average value for the coupling at the hydrogens connected to the nitrogen is given, calculated with a 6-311G(d,p) basis set and a range of methods at the optimized structure for each particular method. These

Table 6. Calculated<sup>a</sup> absorption parameters in H<sub>2</sub>SNH<sub>3</sub><sup>+</sup>.

Geometry <sup>b</sup>	UB3LYP	UQCISD
$\lambda_{\max}$ /nm	349	289
<i>f</i> (dip.) <sup>c</sup>	0.366	0.376
<i>c</i> [10a'(β)→11a'(β*)] <sup>d</sup>	0.965	0.957

<sup>a</sup>UCIS/6-311+G(d,p) at the respective optimized geometries.

<sup>b</sup>Geometries optimized with the 6-311G(d,p) basis set.

<sup>c</sup>Dipole oscillator strength. <sup>d</sup>Coefficient of leading component in the transition.

Table 7. Calculated<sup>a</sup> hyperfine splittings (MHz) in H<sub>2</sub>SNH<sub>3</sub><sup>+</sup>.

Method	UHF	UMP2	UB3LYP	UQCISD
$a(^{14}\text{N})$	149	119	105	128
$a(^{33}\text{S})$	130	81	51.6	91.2
$a(^1\text{H}_\text{S})$	-64.2	-45.7	-31.2	-45.9
$\langle a(^1\text{H}_\text{N}) \rangle$	-46.4	-15.0	-21.4	-22.7

<sup>a</sup>6-311G(d,p) basis set at the respective optimized geometries.

results thus reflect both electron correlation and geometrical effects on the spin distribution. The UHF values at the UQCISD/6-311G(d,p) geometry are  $a(^{14}\text{N})=153$  MHz,  $a(^{33}\text{S})=126$  MHz,  $a(^1\text{H}_\text{S})=-64.4$  MHz, and  $\langle a(^1\text{H}_\text{N}) \rangle=-43.2$  MHz showing that structural variations are not as important as the consequences of electron correlation. At the heavy nuclei, the UMP2 correlated treatment overcorrects the UHF values (with respect to results obtained with the more complete UQCISD treatment). The UB3LYP method exaggerates this correction still further. For the sulfur-bound hydrogen atoms similar behavior is evident, except that the UMP2 value fortuitously matches the UQCISD result. The average <sup>1</sup>H-splitting of the ammoniumyl hydrogens at UQCISD and UB3LYP are also fortuitously close. Clearly, the accurate and reliable calculation of hyperfine coupling constants in these S..N containing radical cations will not be achieved at UB3LYP and a more appropriate density functional treatment needs to be developed.

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