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Structure, Bonding, and Spectra of Cyclic Dithia Radical Cations: A Theoretical Study

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Abstract: Ab initio molecular orbital and hybrid density functional theory methods are employed to characterize the structure, bonding and properties of several cyclic dithia radical cation systems, particularly in the context of *intra* molecular *two-center three-electron (2c−3e)* bonding between two sulfur atoms. The calculated results are able to interpret the time-resolved transient optical spectra obtained from pulse radiolysis technique for these positively charged dithia systems in aqueous solution. Visualization of the appropriate molecular orbital (MO) in the systems is able to depict the presence of a 2c−3e bond between two sulfur atoms and its sigma character. Geometry optimizations of these doublet systems are carried out at restricted open shell Becke's half-and-half (BHH) nonlocal exchange and Lee−Yang−Parr (LYP) nonlocal correlation functionals (BHHLYP) with 6-311+G(d,p) basis set including solvent effects adopting Onsager's reaction field model. Hessian calculations are done at the same level to check the nature of the equilibrium geometry. Energy data are further improved by performing MP2/6-311+G(d,p) calculations on these radical cation systems. Excited-state calculations are done following configuration interaction with single-electron excitation (CIS) method and the optical transition wavelength from the highest doubly occupied molecular orbital (HDOMO) to the lowest singly occupied molecular orbital (LSOMO) is seen to correspond and match to the position of the absorption maxima (λ_{max}) obtained from the experimental spectra for all these radical cation systems in aqueous solution. These calculations are able to resolve a long-standing ambiguity in the assignment of *intra* molecular 2c−3e bonding in the case of the 3-methyl-2,4-dithiapentane radical cation system and to provide new insights into bonding features of this odd electron system as well as of other cyclic dithia systems studied.

Introduction

Single-electron oxidation of organic sulfide generates a sulfur-centered molecular radical cation, $-S^{\bullet+}$, with the unpaired electron being located in the sulfur p orbital. This species is known to be highly unstable and has a strong tendency to stabilize by association with a free electron pair of an unoxidized sulfur atom from the same molecule or from a second sulfide molecule by *intra* or *inter* molecular interactions, respectively. The p orbital overlapping results in making a new S−S bond involving three electrons having two electrons in the σ bonding orbital and one electron in the σ^* antibonding orbital. This is also known as $2\sigma/1\sigma^*$ *two-center three-electron* or simply 2c−3e bond and traditionally shown as $-S\therefore S-$.[1−21] Such 2c−3e bonding is also possible with the interaction of a singly occupied sulfur p orbital and lone pairs of O, N, P, or halogen atoms by *intra* or *inter* molecular interactions.[22−28] For *intra* molecular

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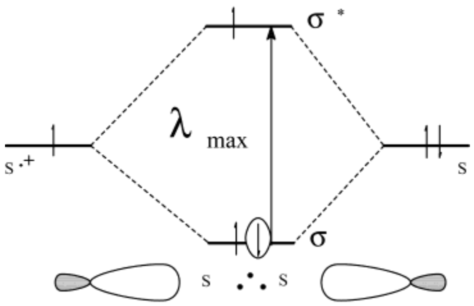
interaction, the two atoms (S and S, O, N, P, or halogens) must be able to adopt a suitable geometry for significant p orbital overlapping to make a short-lived transient of a 2c−3e bonded ion−molecule complex.

The experimental characterization of 2c−3e bonding has often been indirect, and the transient optical absorption maximum ($\lambda_{\max}$) is being used as an indicator for such bonding.[1,8] Sulfur-, nitrogen-, and halogen-centered 2c−3e bonded radical cation complexes are easily formed in aqueous (neutral or acidic, depending on the system) and hydrocarbon solution which give rise to extremely broad and structureless UV/visible absorption band with high extinction coefficient (ϵ) values. Optical absorption spectra, and in particular the position of $\lambda_{\max}$, and lifetimes ($t_{1/2}$) of these bands have been used to provide indirect information on the nature of 2c−3e bonds and the structure of radical cation complexes. However, on many occasions, just by following optical spectra, assignment and characterization of a 2c−2e bonded sulfur-centered radical cation remain ambiguous.[1−2,5,8] Low-temperature matrix isolation and time-resolved pulse radiolysis coupled to optical detection technique has often been used to measure the absorption maximum ($\lambda_{\max}$) in the UV/visible region for many sulfur-centered radical cation systems. $\lambda_{\max}$ is described to correspond the energy gap between the doubly occupied σ bonding orbital and singly occupied σ^* antibonding orbital, and this is often being correlated to the strength of the 2c−3e −S∴S− bond. A $\lambda_{\max}$ value in the blue region has been described to indicate a large separation between the doubly occupied σ and singly occupied σ^* orbitals due to a strong interaction of the corresponding p orbitals resulting in a strong 2c−3e bond and a $\lambda_{\max}$ value in the red region for a small separation between the doubly occupied σ and singly occupied σ^* orbitals due to a weak interaction of the corresponding p orbitals resulting in a weak 2c−3e bond. A direct measurement of the 2c−3e bond strengths has also been made following mass spectroscopic studies of gas-phase ion−molecule association equilibrium to measure the bond enthalpy in *inter* molecular 2c−3e bonded sulfur-centered dimer radical cations.[29−32] However, these studies have been restricted to only a very few systems. Moreover, the question remains to be answered if the complexes studied in those experiments were bound by a 2c−3e bond or not. Electron spin resonance (ESR) has provided valuable information on the nature of bonding in sulfur radical cation systems by probing the degree of localization of the unpaired electron under steady-state flow conditions as well as in low-temperature solid matrixes.[11−13] The strength of the *intra* molecular 2c−3e bond should be sensitive to the details of the geometry, electronic interactions, and substitution patterns. The geometry of the cyclic dithia radical cation systems which allow an interaction between the corresponding p orbitals of two sulfur atoms accounting for steric hindrances due to ring formation leads to the formation of an *intra* molecular 2c−3c bond between two sulfur atoms. As a result, the half-life of the resulting radical cation system increases to a few microseconds from nanosecond for the sulfur-centered radical cation systems which do not form such 2c−3e bonds. The absorption maxima for such 2c−3e bonded sulfur radical cation systems are typically in the range of 400−650 nm with very high extinction coefficient values ($\epsilon \approx 4000$ dm^3 mol^{-1} s^{-1}) compared to the absorption maxima of ~300 nm for sulfur-centered radical cations not bonded by such 2c−3e bonds.[8] Very recently, a real-time probing of a 2c−3e bonded sulfur system has also been performed following femtosecond laser spectroscopy.[19]

Scheme 1



Quantum chemical calculations have played a major role in understanding the nature of such bonding.[33−54] A simple molecular orbital representation of this form of bonding can be described by the potential energy diagram in Scheme 1.

The MO diagram suggests that the 2c−3e bond energy should be approximately half that of a normal *two-center two-electron bond (2c−2e)* and the corresponding bond length should be much longer than a 2c−2e bond as the antibonding orbital is occupied by a single electron. The bond order of such a bond should be 0.5, and thus this type of chemical bond is also known as *hemi* bond.[33] It must be recognized that this is only a nominal description. The actual bond strength of an *intra* molecular 2c−3e bond is expected to depend on the combined effects of structural parameters, substitution patterns, and electronic interactions. The combined effects will control the extent of p orbital interaction that in turn is expected to influence the

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strength of the newly formed bond. However, it was pointed out that the strength of a 2c−3e bond, in general, does not vary linearly with orbital overlap.[34] This is due to the fact that the destabilizing effect of the antibonding σ^* electron becomes increasingly large relative to the stabilizing effect of the two bonding σ electrons for positive overlap integral values. In the valence bond (VB) formalism, the p orbital interaction is depicted as a resonance between two VB structures: $-\mathrm{S}\colon {}^{\bullet}\mathrm{S}^{+}- \leftrightarrow -{}^{+}\mathrm{S}^{\bullet}\colon\ \mathrm{S}-$. The energy of a 2c−3e bond increases with the resonance energy, and the resonance energy is large if the two VB structures are close in energy.[35] Earlier, it was reported that the strongest 2c−3e bond is expected between the systems with the same ionization potential (IP) values, that is, the strongest *inter* molecular 2c−3e bond is expected to be observed in dimer radical cations of the type $(\mathrm{A}\therefore\mathrm{A})^{\bullet+}$.[36] This can be explained as the energy difference between the VB structures may be approximated as the difference between the ionization potentials of two counterparts. Additional insights, based on ab initio MO studies or combined theory and experimental results, toward the understanding of 2c−3e bonding behavior in sulfur systems have been provided.[37−48] However, the analysis of such bonding has been restricted to either the knowledge of bond length or binding energy. The analysis of such odd electron bonding, based on bond length or strength, is not general and fails for many systems. Bond order calculated following semiempirical quantum chemical methods has been found to be a good indicator to test the presence of such a *hemi* bond in halide radical cation systems.[49,50] It has also been shown that ab initio quantum chemical bond order can be used as an index to test the existence of a 2c−3e bond with the exception of a few cases. Localization of the appropriate molecular orbitals has been found to provide the definitive evidence on the presence of a *two-center three-electron σ* bond, and it has been suggested to be considered as the signature of such a *hemi* bond on the basis of the results of a series of radical cation systems studied.[41] Visualization of appropriate localized molecular orbitals in cyclic dithia radical cation systems should be able to provide a more authentic and clear picture on the nature of the interaction between the two sulfur atoms. To address the nature of bonding between two sulfur atoms for cyclic dithia radical cation systems in detail, we have carried out DFT and ab initio molecular electronic structure calculations on selected cyclic dithia radical cation systems. We paid special attention to resolving the ambiguity in characterization of *intra* molecular 2c−3e bonding in the case of the 3-methyl-2,4-dithiacyclopentane radical cation system based on spectral features and kinetic parameters only.[8]

The geometry of the isolated radical cation systems is fully optimized to determine the most stable conformer at restricted open shell (ROHF) correlated nonlocal density functional theory (DFT) with the 6-311G(d,p) basis sets with a polarization function on heavy atoms. These optimized geometries are refined further by including solvent effects following the Onsager reaction field model, and the HDOMOs and the LSOMOs are visualized. The bond order between the two sulfur atoms has also been calculated at this level of theory and reported. The excited-state calculations are performed following configuration interaction calculations with single-electron excitation (CIS) to find out the absorption maximum ($\lambda_{\max}$) which corresponds to the highest doubly occupied σ molecular orbital → lowest singly occupied σ^* molecular orbital with the respective fully optimized geometries. Frequency calculations are performed, and the stretching frequency of the newly formed *inra* molecular $-\mathrm{S}\therefore\mathrm{S}-$ bond is identified in all these radical cation systems and reported here.

Theoretical Method

Previous reports have shown that Becke's half-and-half (BHH) nonlocal exchange and Lee−Yang−Parr (LYP) nonlocal correlation functionals (BHHLYP) with the 6-311+G(d,p) basis set under ROHF formalism performs well to describe such open shell systems.[41,51] BHHLYP functional includes 50% Hartree−Fock exchange, 50% Slater exchange, and the additional correlation effects of the LYP functional.[55] A complete search has been performed to determine the geometries of the most stable conformer of different dithia radical cation systems without any symmetry restrictions. The gas-phase geometries are further optimized, including solvent effects following the Onsager reaction field model with the cavity radius calculated on the basis of the gas-phase optimized geometry. To verify the reliability of the computation on such systems, especially in the context of the symmetry-breaking instability problem,[52] the final calculations are also repeated with symmetry restriction, and the absolute energies for the structures with and without symmetry restriction are compared to find the geometries with the lowest energy. Bond order between two atoms has been calculated by following the definition of Mayer.[56] According to this definition the generalized bond order (B_{XY}) between a pair of atoms (X and Y) is given by

$$B_{\mathrm{XY}} = \sum_{\mu\in\mathrm{X}}^{\nu\in\mathrm{Y}}(\mathrm{DS})_{\mu\nu}(\mathrm{DS})_{\mu\nu} + \sum_{\mu\in\mathrm{X}}^{\nu\in\mathrm{Y}}(\mathrm{D^sS})_{\mu\nu}(\mathrm{D^sS})_{\nu\mu}$$

where the one-electron density matrix (ρ) in AO basis has been partitioned into D and $\mathrm{D^s}$; D is the part of the one-electron density due to the core or the doubly occupied orbitals, $\mathrm{D^s}$ is the density due to singly occupied orbitals, and S refers to overlap matrix between two orbitals. Hessian calculations are done at BHHLYP level of theory with BHHLYP/6-311+G(d,p)-optimized geometry to check the nature of stationary geometries and to find the stretching frequency of the newly formed $-\mathrm{S}\therefore\mathrm{S}-$ 2c−3e bond. Single-point energies are recalculated at MP2/6-311+G(d,p)//BHHLYP/6-311+G(d,p) level of theory under restricted open shell (ROHF) formalism to avoid any error in energy due to spin-contaminated wave function. MP2 energy may not be very accurate since electron correlation effects are very strong in such three-electron bonded systems[36,38] However, applying higher levels of theory to such large systems is beyond the scope at present. CIS calculations are performed to find out the excitation wavelength to excite an electron from the highest doubly occupied bonding orbital to the lowest singly occupied antibonding orbital ($\sigma \rightarrow \sigma^*$) of 2c−3e bonded complexes with the BHHLYP/6-311+G(d,p)-optimized geometry. To include the solvent effect in the CIS calculation the optimized geometries and orbitals including solvent effects have been used to find out the absorption maxima ($\lambda_{\max}$) in solution. All these calculations are performed adopting GAMESS suite of program on a PC-based LINUX cluster platform.[57] Visualization of the relevant molecular orbitals are done following MOLDEN program system.[58]

Results and Discussion

The *intra* molecular 2c−3e interactions are studied in single-electron oxidized cyclic dithia systems where the two sulfur

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Table 1. Experimental[a] Absorption Maxima (λ_{max}), Extinction Coefficients (ϵ) in Optical Spectrum and Half Life ($t_{1/2}$) of Selected Cyclic Dithia Radical Cation Systems Including $(H_2S)_2^{\bullet+}$ and (3-Methyl-2,4-dithiapentane)$^{\bullet+}$

system[b]	λ_{max} nm	ϵ_{max} dm^3 mol^{-1} cm^{-1}	$t_{1/2}$ μs
$(H_2S)_2^{\bullet+}$	370	1600	60
(2-methyl-1,3-dithiacyclopentane)$^{\bullet+}$	>650	−	<0.2
(3-methyl-2,4-dithiapentane)$^{\bullet+}$	570	2500	−
(2-methyl-1,3-dithiacyclohexane)$^{\bullet+}$	600	1650	300
(1,4-dithiacyclohexane)$^{\bullet+}$	650	1070	25
(1,4-dithiacycloheptane)$^{\bullet+}$	470	3500	650
(1,5-dithiacyclooctane)$^{\bullet+}$	400	5800	500
(1,6-dithiacyclodecane)$^{\bullet+}$	425	4900	500

[a] References 2 and 8. [b] Cartesian coordinates for the respective molecular structures are provided in Supporting Information.

Table 3. Calculated Vibrational Frequency (ν_i) for the S−S Stretching Mode and the Optical Transition Wave Length (λ_{max}) for the Electronic Transition from the Highest Doubly Occupied σ MO to the Lowest Singly Occupied σ* MO in the Most Stable Equilibrium Geometry in Aqueous Solution

system	ν_i, cm^{-1}	λ_{max}, nm
$(H_2S)_2^{\bullet+}$	215	370
(2-methyl-1,3-dithiacyclopentane)$^{\bullet+}$	301	645
(3-methyl-2,4-dithiapentane)$^{\bullet+}$	277	570
(2-methyl-1,3-dithiacyclohexane)$^{\bullet+}$	270	560
(1,4-dithiacyclohexane)$^{\bullet+}$	320	635
(1,4-dithiacycloheptane)$^{\bullet+}$	285	490
(1,5-dithiacyclooctane)$^{\bullet+}$	273	380
(1,6-dithiacyclodecane)$^{\bullet+}$	253	415[a]

[a] The CI calculation is performed with 6-31+G(d,p) basis set.

centers are separated by a chain of methylene links and where experimental results are available to be compared with the present calculated ones. Table 1 displays the sulfur-centered radical cation systems studied with their experimental absorption maxima (λ_{max}), extinction coefficients (ϵ), and the half-life ($t_{1/2}$) values. Before going to the actual systems of interest at present, let us discuss the results on a well-studied small system, $(H_2S)_2^{\bullet+}$ having *inter* molecular 2c−3e interactions. This small system has been taken up as a model system to obtain guidance for the larger systems to decide on the best cost-effective electron-correlated DFT functional or ab initio method with electron correlation to be adopted to obtain experimental results on the position of absorption maxima. It is to be noted that no imaginary frequency is obtained from the Hessian calculations on any of the equilibrium structures reported at present, showing the reliability of the calculated data.

$(H_2S)_2^{\bullet+}$. This particular dimer radical cation system have been attempted by several previous theoretical researchers may be due to its small size and the reported gas-phase binding energies ranging from 26.5 to 29.6 kcal/mol.[36−38] The gas-phase S∴S distance is 2.835 Å at the MP2/6-31G(d) level of theory, while the present calculated distance is 2.86 Å at BHHLYP/6-311+G(d,p) level including solvent effects following Onsager's reaction field model with a cavity radius of 3.47 Å. The present calculated MP2 binding energy is 29.7 kcal/mol, and the solvation energy for this *inter* molecular 2c−3e bonded dimer radical cation system is calculated to be 46.0 kcal/mol. The atomic spin population is calculated to be equally distributed over two sulfur atoms, and the values are displayed in Table 2 along with other calculated molecular properties. The computed bond order between two sulfur atoms with 6-31+G(d,p) basis set is same as the intuitive value of 0.50 for a *hemi* bond. It is found that Mayer bond order[56] depends on the size of the basis set and is higher than the intuitive value with larger set of basis functions especially with the addition of diffuse functions. This is explainable as the Mayer bond order is based on a Mulliken-type population analysis. The frequency for the stretching mode of this newly formed 2c−3e bond is calculated to be 215 cm^{-1} at BHHLYP/6-311+G(d,p) level and shown in Table 3. Since the only experimental observation of $(H_2S\therefore SH_2)^+$ is in aqueous solution and the experimental characterization is mainly through absorption maxima (λ_{max}), theoretical calculations have been carried out to predict the position of λ_{max}, including solvent effects. The calculated λ_{max} value corresponding to the transition from the HDOMO to the LSOMO following CIS procedure is 370 nm as displayed in Table 3 and this is the lowest electronic transition for this doublet system. This CIS/6-311+G(d,p) calculation is performed with the solvent-modulated BHHLYP/6-311+G(d,p) optimized geometry and orbitals. The calculated λ_{max} value is exactly same as the reported experimental value[4] and 4 nm lower than the calculated value without solvent-modulated orbitals. Thus, it is concluded that solvent effects should cause a λ_{max} blue-shifted. The previous reported theoretical λ_{max} value for $(H_2S)_2^+$ $4H_2O$ is ∼20 nm lower than the present value and also observed similar solvent effects.[30] However, λ_{max} value does not indicate the presence of a 2c−3e σ bond. Figure 1a displays the HDOMO plot which clearly indicates the head-on mixing of two p orbitals from two sulfur atoms and the formation of an *inter* molecular 2c−3e σ bond. The highest singly occupied MO is displayed in Figure 1b, showing the antibonding nature of the orbital as the two sulfur

Table 2. Calculated Properties of Selected Cyclic Dithia Radical Cation Systems Including $(H_2S)_2^{\bullet+}$ and (3-Methyl-2,4-dithiapentane)$^{\bullet+}$ at Their Most Stable Equilibrium Geometry

			atomic spin population[c]			
systems	r_{SS} (Å)[a]	BO$_{SS}$[b]	S_1	S_2	a$_o$ (Å)[d]	E_{solv} (kcal/mol)[e]
$(H_2S)_2^{\bullet+}$	2.86	0.50	0.49	0.49	3.47	46.0
(2-methyl-1,3-dithiacyclopentane)$^{\bullet+}$	2.62	0.63	0.49	0.49	3.92	41.1
(3-methyl-2,4-dithiapentane)$^{\bullet+}$	2.69	0.51	0.48	0.48	4.42	40.8
(2-methyl-1,3-dithiacyclohexane)$^{\bullet+}$	2.67	0.57	0.48	0.48	4.27	39.4
(1,4-dithiacyclohexane)$^{\bullet+}$	2.70	0.53	0.48	0.48	4.07	40.8
(1,4-dithiacycloheptane)$^{\bullet+}$	2.70	0.56	0.47	0.47	4.20	37.3
(1,5-dithiacyclooctane)$^{\bullet+}$	2.73	0.54	0.46	0.46	4.34	35.9
(1,6-dithiacyclodecane)$^{\bullet+}$	2.76	0.43	0.51	0.54	4.69	35.1

[a] r_{SS} refers to the calculated bond distance between two sulfur atoms. [b] Calculated bond order between the two sulfur atoms with 6-31+G** basis set. [c] These are Mulliken atomic spin population ($\alpha-\beta$) and are ∼0.02 unit larger than the corresponding Lowdin values. [d] Cavity radius calculated with the gas-phase optimized geometry. [e] E_{solv} refers to the energy of solvation calculated at BHHLYP level of theory. This is calculated from the difference in total energy with the optimized geometry with solvent effect and without solvent effect.

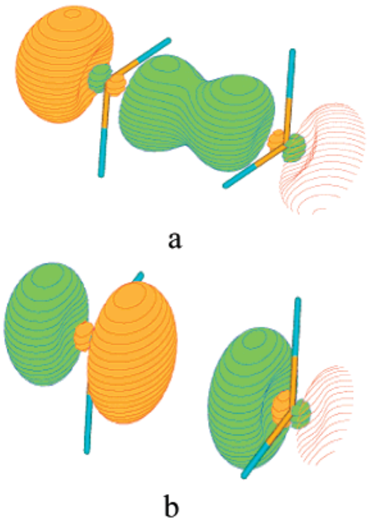

Figure 1. (a) Plot of the HDOMO showing the head-on mixing of two valence p orbitals from sulfur atoms to form a *inter* molecular *two-center three-electron* σ bond between two sulfur atoms with the maximum contour value of 0.1 following MOLDEN visualization program. (b) the plot of the LSOMO showing the antibonding nature of the orbital.

p orbitals oriented toward each other with opposite symmetry. This antibonding orbital causes destabilization on the newly formed 2c−3e bond between the two sulfur atoms and makes the *hemi* bond weak relative to a *two-center two-electron* bond between two sulfur atoms. The present results suggest that the BHHLYP method can be used in combination with Onsager's reaction field model to get the information on the geometry of 2c−3e bonded sulfur systems and that the adopted CIS procedure is excellent to provide information on the lowest electronic transitions for such doublet systems. Moreover, the calculated results provide a definite indication of the presence of a *two-center three-electron* bond in these radical cation systems. We follow the same procedure in the following cyclic dithia radical cation systems to study the bonding and spectral features, and the performance of the adopted method will be examined further.

2-Methyl-1,3-dithiacyclopentane$|^{\bullet +}$. On single-electron oxidation of 2-methyl-1,3-dithiacyclopentane in aqueous solution, a very broad weak optical absorption band with red-shifted absorption maxima ($\lambda_{\max}$) > 650 nm was observed following a time-resolved pulse radiolysis experiment.[2] The formation of this weak band was explained on the basis of the rigid nature of the molecule preventing appreciable p orbital overlap to form a S∴S σ bond, and the assignment of this band to a *two-center three-electron* bonded radical cation remained ambiguous.[8] The two sulfur atoms are 2.62 Å apart in the most stable conformer of the fully optimized structures of this radical cation. The atomic spin populations are calculated to be evenly distributed over the two sulfur atoms, and the values are shown in Table 2. The bond order between the two sulfur atoms is calculated to be 0.63 when the expected value is 0.50 for a *hemi* bond. The HDOMO of the fully optimized geometry is depicted in Figure 2a showing only a partial mixing between the two sulfur valence p orbitals. This is due to unfavorable angular orientation of the respective p orbitals because of the rigid nature of this radical cation system. The valence p orbitals over the sulfur atoms are almost perpendicular to the molecular plane of SSC1C2. Moreover, as the S∴S three-electron σ bond (partial) forms, one three-membered and one four-membered ring configurations arise which are not favorable due to high steric constraint. Due to the high steric strain and low orbital overlap, the absorption band arising due to HDOMO → LSOMO electronic transition should be very weak and red-shifted as was observed in pulse radiolysis experiment. The calculated absorption maxima for the transition from the HDOMO to the LSOMO is 645 nm when the experimental reported value was >650 nm. The absorption band is also expected to have a low lifetime due to weak formation of the bond and justifies the reported half-life ($t_{1/2}$) value of less than 2 ns (see Table 1). Frequency for the stretching mode of this partially formed 2c−3e S∴S bond is calculated to be 301 cm^{-1}. The highest singly occupied MO is displayed in Figure 2b, showing the repulsive nature of the two sulfur p orbitals, showing the antibonding behavior. It is worth pointing out that the geometry optimization of this radical cation system was also tried under symmetry restriction, and this led to the geometry of higher energy compared to the present one.

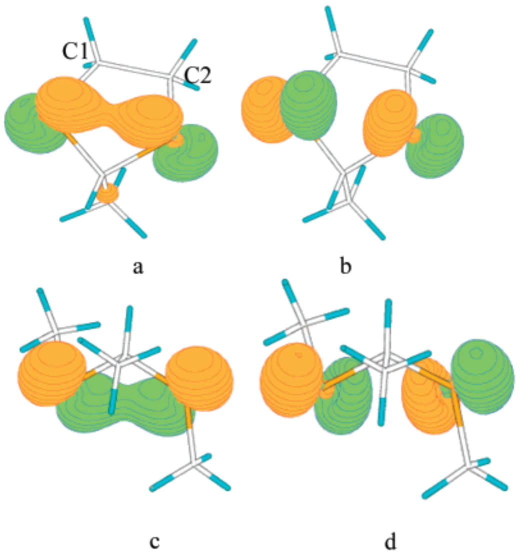

Figure 2. (a) Plot of the HDOMO for the most stable conformer of 2-methyl-1,3-dithiacyclopentane radical cation with the maximum contour value of 0.08 showing the presence of a weak *two-center three-electron* σ bond formation. The plot does not show any mixing of the p orbitals when the contour value cut off is chosen to be 0.1, reflecting only a very weak interaction between the two valence p orbitals under this strained geometrical configuration. (b) Plot of the LSOMO for 2-methyl-1,3-dithiacyclopentane radical cation. (c) Plot of the HDOMO of 3-methyl-2,4-dithiapentane radical cation with the maximum contour value of 0.1 showing the head-on mixing of two valence p orbitals from two sulfur atoms to form a *intra* molecular *two-center three-electron* σ bond. (d) Plot of the LSOMO of 3-methyl-2,4-dithiapentane radical cation.

Now, if the C1−C2 bond is cut, the closed molecular system becomes open-chain and flexible. The fully optimized structure of the new open-chain dithia radical cation system, namely, 3-methyl-2,4-dithiapentane$|^{\bullet +}$ keeps the two sulfur atoms separated by 2.69 Å. Although the S−S distance is longer than the cyclic system by 0.07 Å, the valence p orbitals of the two sulfur atoms oriented more favorably to make a better overlap, and a new S∴S σ bond is formed. This is clearly seen from the HDOMO shown in Figure 2c. The atomic spin population is again equally distributed between the two sulfur atoms, and the calculated bond order for the new 2c−3e bond is 0.51. The present theoretical absorption maximum for the electronic transition of HDOMO → LSOMO is 570 nm, and this is

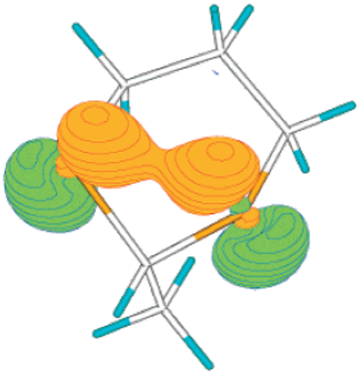

Figure 3. Plot of the HDOMO for the most stable conformer of 2-methyl-1,3-dithiacyclopentane radical cation with the maximum contour value of 0.08 showing the partial mixing of two valence p orbitals from sulfur atoms to form a weak *intra* molecular *two-center three-electron* σ bond between two sulfur atoms. The plot does not show any mixing of the p orbitals when the cut off for the contour value is chosen to be 0.1, reflecting only a weak interaction between the two valence p orbitals.

matched with the reported value based on the pulse radiolysis experiment. The present results support the reported broad absorption band with an appreciable ϵ value of 2500 dm^3 mol^{-1} cm^{-1}. These two systems definitely demonstrate the requirement of proper angular orientation of the valence p orbitals to make a 2c$-$3e σ bond possible. The highest singly occupied MO is displayed in Figure 2d showing the two sulfur p orbitals oriented toward each other with opposite symmetry, indicating the antibonding character of the orbital. It is to be noted that the symmetry constraint geometry optimization was also carried out on this radical cation system, and this produced the geometry of higher energy.

2-Methyl-1,3-dithiacyclohexane|$^{\bullet+}$. The calculated S$-$S distance in the fully optimized geometry of this cyclic system is 2.67 Å. If a S$-$S three-electron σ bond forms in this substituted chairlike structure, one three-membered and one five-membered ring configurations arise. Thus, steric constraint is expected to be a little less, compared to that of the previous cyclic dithia system as a five-membered ring formation is energetically favorable. Moreover, due to the presence of one more methylene linkage, the system is expected to be less rigid compared to 2-methyl-1,3-dithiacyclohexane radical cation system, making the p orbitals mixing possible. Figure 3 displays the plot of the HDOMO which demonstrates that there is a mixing of the p orbitals from two sulfur atoms but not fully due to restricted angular orientation of the respective orbitals. This supports the experimental estimation of low extinction coefficient. The calculated S$-$S bond order is 0.57, and the atomic spin population is evenly distributed over the two sulfur atoms. Due to less steric strain and better orbital overlap, the lifetime of this 2c$-$3e bonded radical cation system should be higher than that of 2-methyl-1,3-dithiacyclopentane|$^{\bullet+}$, and the reported $t_{1/2}$ value was 300 μs for the present system. Excited-state calculation predicts the position of the absorption maxima ($\lambda_{\max}$) for the transition from the HDOMO to the LSOMO to be 560 nm which is 40 nm smaller than the reported experimental value. The solvation energy for this 2c$-$3e bonded system is calculated to be 39.4 kcal/mol. Hessian calculation and normal-mode analysis predict the frequency of S$\therefore$S stretching mode to be 270 cm^{-1}.

1,4-Dithiacyclohexane|$^{\bullet+}$. The most stable geometry of unoxidized 1,4-dithiacyclohexane is the chair structure where the two bulky sulfur atoms are far apart. This chair structure is more stable than the corresponding boat structure by 10.3 kcal/mol calculated at the MP2/6-311+G(d,p)//BHHLYP/6-311+G-(d,p) level of theory. The conversion of the boat conformer to the corresponding chair conformer is calculated to be barrierless and passes through a *twisted* structure which is more stable than the boat structure by 2.2 kcal/mol. What happens to the structure if an electron is removed from this system? The time-resolved pulse radiolysis study revealed that the corresponding radical cation system has a pronounced absorption at 650 nm with a lifetime ($t_{1/2}$) of 25 μs in aqueous solution and on the basis of these results it was characterized to have a 2c$-$3e σ bond between two sulfur atoms. This is possible only if the two sulfur atoms are in close proximity to make the overlapping of two sulfur valence p orbitals possible, and this can be achieved if the radical cation system takes the boat structure. Energy gained upon 2c$-$3e S$\therefore$S bond formation should be able to make the boat structure stable to be detected. Figure 4a depicts the HDOMO of the fully optimized radical cation in the chair structure, and this clearly indicates that the two valence p orbitals are far off (r_{SS} = 3.42 Å) for mixing and fail to make a *hemi* bond. However, when this charged system is in the boat form, the distance between two sulfur atoms becomes 2.70 Å, and the structure is calculated to be more stable over the corresponding chair structure by 13.2 kcal/mol at MP2/6-311+G-(d,p) level of theory. The conversion of the chair conformer to the corresponding boat conformer is calculated to be barrierless and passes through a *twisted* structure which is more stable than the chair structure by 3.8 kcal/mol. The bond order between two sulfur atoms in the boat configuration is calculated to be 0.53. The atomic atomic spin population is equally distributed over the two sulfur atoms. The HDOMO in the boat configuration is shown in Figure 4b, and this clearly depicts the mixing

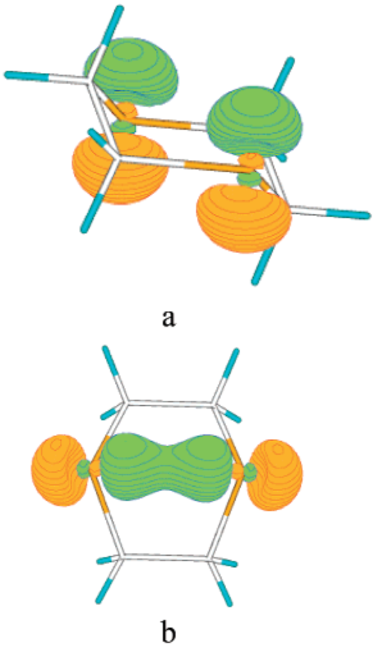

Figure 4. (a) Plot of the HDOMO plot for the most stable chair conformer (*all trans*) of 1,4-dithiacyclohexane radical cation with the cut off contour value of 0.1 showing that the two valence p orbitals from sulfur atoms are far apart to have any interaction. (b) Plot of the HDOMO for the corresponding boat conformer (*all cis*) with the maximum contour value of 0.1 showing the head-on mixing of two sulfur valence p orbitals to form an *intra* molecular 2c$-$3e σ bond in the boat structure.

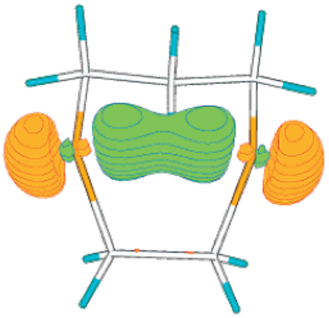

Figure 5. Plot of the HDOMO for 1,4-dithiacycloheptane$|^{\bullet+}$ in the most stable *all cis* configuration (envelope structure) with the maximum contour value of 0.1 showing the head-on mixing of two sulfur valence p orbitals to form an *intra* molecular 2c−3e σ bond in this configuration of one four-membered and one five-membered rings.

of two sulfur valence p orbitals to form an *intra* molecular 2c−3e S∴S σ bond. On the formation of the new *hemi* bond, two four-membered ring configurations arise. Due to the steric strain because of these four-membered ring configurations, this boat configuration is expected to have a low lifetime. In fact, the experimental estimation of $t_{1/2}$ for this system was 25 μs. The calculated absorption maxima (λ_{max}) for the electronic transition from the HDOMO to the LSOMO is 635 nm which is 15 nm smaller than the reported experimental data (see Table 1). From the calculated geometrical parameters (see Supporting Information for geometrical parameters), one can see that the S−C bonds are stretched by 0.4 Å and that the C−C bonds are shortened by 0.3 Å in the boat structure compared to those in the chair structure in this radical cation system. These essentially make the formation of the new *intra* molecular S∴S 2c−3e σ bond possible bringing two sulfur atoms closer.

1,4-Dithiacycloheptane$|^{\bullet+}$. The calculated most stable geometry of 1,4-dithiacycloheptane radical cation is the *all cis* structure where the two bulky sulfur atoms are quite close. This structure is energetically favorable over the *all trans* structures where the two bulky sulfur atoms are far apart by 17.8 kcal/mol. This is possible by the extra stability gained due to the formation of S∴S σ bond in the *all cis* structure. The calculated bond order of 0.56 for S∴S σ bond suggests the formation of a new *hemi* bond. The calculated electron density for the HDOMO is plotted in Figure 5 and the formation of a covalent σ bond between two sulfur atoms by the head-on mixing of two p orbitals is clearly visible. The atomic spin population is also equally distributed over the two sulfur atoms. Table 3 presents the calculated vibrational frequency for the stretching mode of the *hemi* bond to be 285 cm^{-1} which is close to such hemi bonds in the other cyclic dithia radical cation systems. The calculated optical transition wavelength for the electronic transition of HDOMO → LSOMO is 490 nm which 20 nm larger than the reported experimental value. The reported half-life for this 2c−3e bonded system was 650 μs. This high stability may be due to the formation of the new *hemi* bond with one four-membered ring and one energetically favorable five-membered ring configurations. This is also reflected in the calculated stabilization energy of this *all cis* structure over the *all trans* structure.

1,5-Dithiacyclooctane$|^{\bullet+}$. The radical cation of 1,5-dithiacycloheptane prefers an *all cis* (envelope) structure where the two bulky sulfur atoms are close enough to make a significant orbital overlap to form a 2c−3e σ bond. Several attempts were made to get the optimized structure of this radical cation in an *all trans* configuration. However, in all the cases the final fully optimized geometry is the same *all cis* (envelope) structure with S∴S bond distance of 2.73 Å. The formation of the S∴S σ bond is evident from the plot of the HDOMO displayed in Figure 6. Calculated bond order does support the formation of the *hemi* bond. The atomic spin population is also calculated to be distributed equally over the two sulfur atoms. The formation of the new *hemi* bond makes this envelope structure to have two five-membered ring configurations. Due to the proper angular orientation of the two p orbitals, a significant orbital mixing is achieved. These combined effects make this structure quite stable. The reported absorption maxima (λ_{max}) was at 400 nm with a lifetime ($t_{1/2}$) of 500 μs. The calculated absorption maxima (λ_{max}) for the electronic transition HDOMO → LSOMO is 380 nm. The stretching frequency for the *hemi* bond is calculated to be 275 cm^{-1}, and this is in the same range in other radical cation systems.

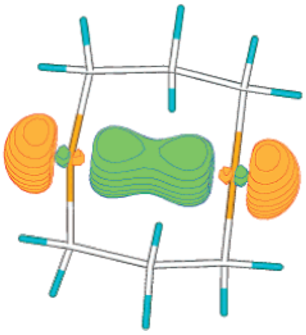

Figure 6. Plot of the HDOMO for the stable *all cis* configuration (envelope structure) of 1,5-dithiacyclooctane radical cation with the maximum contour value of 0.1 showing the formation of an *intra* molecular 2c−3e σ bond with two five-membered ring configurations in the envelope structure.

1,6-Dithiacyclodecane$|^{\bullet+}$. Geometry of 1,6-dithiacycloheptane radical cation system in *all cis* structure is calculated to be more stable over the *all trans* structure by 25.4 kcal/mol at MP2 level. This geometry makes the distance between the two sulfur atoms to be 2.76 Å. The time-resolved pulse radiolysis study revealed that on reaction by OH radicals in aqueous solution it had a pronounced absorption at 425 nm with a lifetime ($t_{1/2}$) of 500 μs. Since the OH radical is known to react by one-electron oxidation, the optical absorption band was assigned to have originated from the formation of 1,6-dithiacycloheptane$|^{\bullet+}$ bound by a 2c−3e S∴S σ bond. The calculated molecular properties do support this interpretation as can be seen from the plot of the HDOMO shown in Figure 7. Again, the calculated S−S bond order is close to that of a *hemi bond*, and the atomic spin population is also distributed more or less equally over the two sulfur atoms. On the formation of the 2c−3e bond, two six-membered ring configurations arise. Due to less steric strain because of six-membered ring configurations, this envelope configuration is expected to have a longer lifetime as was observed in the experiment. The predicted electronic transition wavelength for HDOMO → LSOMO is 415 nm, and the frequency for the stretching mode of S∴S σ bond is 253 cm^{-1}. Due to the large size of the system, this CI calculation is done with the 6-31+G** basis set.

In case of *inter* molecular 2c−3e bonding in the H_2S dimer radical cation, the bond distance between two sulfur atoms is 2.86 Å which is the longest among all these studied (see Table 2), suggesting the weakest interaction between the two valence

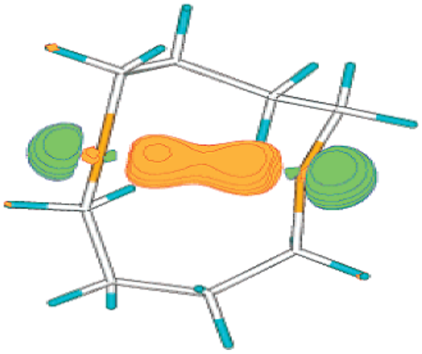

Figure 7. Plot of the HDOMO for the most stable *all cis* configuration of 1,6-dithiacyclodecane radical cation with the maximum contour value of 0.1 showing the formation of an *intra* molecular 2c−3e σ bond in this envelope structure with two six-membered ring configurations following MOLDEN visualization program.

p orbitals from two sulfur atoms among all the systems studied at present. However, the experimental blue-shifted λ_{max} value suggests a strong interaction. In fact, this dimer radical cation system is expected to have the highest $-S\therefore S-$ bond strength due to the optimum p orbital overlap because of the flexibility in the molecular structure. The calculated strength for this three-electron bond is ~30.0 kcal/mol. The calculated bond distance between two sulfur atoms is 2.62 Å in the case of 2-methyl-1,3-dithiacyclopentane$|^{\bullet+}$, and this is the shortest among all the cyclic dithia radical systems studied including $(H_2S)_2^{\bullet+}$, suggesting a strong interaction between the two valence p orbitals from two sulfur atoms. However, in reality it is seen to have only a partial formation of 2c−3e bonding from the plot of the HDOMO. This is because of the fact that the angular orientations of the two p orbitals are not suitable to have an optimum overlap due to the rigid structure. This is tested further from the results on the open chain system of 3-methyl-2,4-dithiapentane$|^{\bullet+}$ with a longer $S\therefore S$ bond distance of 2.69 Å. Thus, the calculated bond distances between the two sulfur atoms do not suggest conclusively the presence of a *intra* molecular 2c−3e bonds in these radical cation systems. The atomic spin population is distributed equally over the two sulfur atoms in all the radical cation systems studied. This index is able to suggest the presence of a 2c−3e σ bond between the two sulfur atoms but fails to give any indication about the extent of the formation of such bond. The C−S bonds are symmetrically stretched to ~1.82 Å in all *all cis* cyclic structures from the distance of ~1.78 Å in *all trans* structures to make a three-electron bond formation possible, bringing two sulfur atoms closer. In all these cases, the ab initio bond order is found to be close to the intuitive value, indicating the presence of a *hemi* bond. However, the calculated bond order shows a large positive deviation with the larger sets of basis functions. The calculated stretching frequency of the *hemi* bonds shows that the *hemi* bond in case of 1,4-dithiacycloheptane$|^{\bullet+}$ is the strongest among the cyclic dithia systems. However, the calculated blue-shifted λ_{max} value in the case of 1,4-dithiacyclooctane$|^{\bullet+}$ indicates that the interaction of the doubly occupied p orbital (lone pair) of one sulfur directed toward the singly occupied orbital of the second sulfur is the strongest, making a large separation between the highest doubly occupied σ MO and the lowest singly occupied σ^* MO, indicating no definite trend of calculated bond energy or experimental λ_{max} value with each methylene linkage addition. In the case of *intra* molecular bonding, the geometrical parameters which decide an optimal p orbital interaction play the decisive role in the stability and optical properties of the three-electron bonded species. In other words, the *intra* molecular *two-center three-electron* bond strength in cyclic dithia systems is a compensation between the extent of the interaction of p orbitals and the steric repulsion of the two bulky sulfur atoms.

Conclusions

The nature of *intra* molecular bonding between the sulfur atoms in several mono positively charged cyclic dithia systems are studied. Visualization of the highest doubly occupied molecular orbital in the equilibrium geometries of 2c−3e bonded systems suggest that the sulfur valence p orbitals are mixed head-on, resulting in sigma character of the newly formed $S\therefore S$ bond. Calculated bond order between the two sulfur atoms in these systems is close to the intuitive value of 0.5 for a *hemi* bond, and atomic spin populations are equally distributed over two sulfur atoms. The frequencies of the stretching mode for *intra* molecular 2c−3e $S\therefore S$ bond in these cyclic systems are calculated to be ~300 cm^{-1}. The optical transition wavelengths from the HDOMO to the LSOMO are calculated on the basis of CIS procedure and found to be very close to the experimental solution phase λ_{max} values with the only exception in the case of 2-methyl-1,3-dithiacyclohexane$|^{\bullet+}$ with a difference of 40 nm. Becke's half-and-half (BHH) nonlocal exchange and Lee−Yang−Parr (LYP) nonlocal correlation functionals (BHHLYP) have been found to describe 2c−3e bonded systems well under the restricted open shell formalism. It is concluded that in the case of *intra* molecular bonding, structural parameters of radical cation systems which decide the angular orientation and the extent of overlapping of the valence p orbitals play the decisive role in the stability and optical properties of the three-electron bonded species. The *intra* molecular three-electron bond strengths in cyclic dithia systems are the compensation between the interactions of the p orbitals and the steric repulsions of the two bulky sulfur atoms.

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Supporting Information Available: Tables of *xyz* coordinates, absolute energies at different methods for all the stationary point geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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