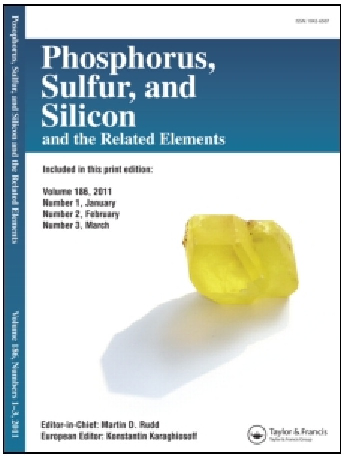

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SPIN DISTRIBUTION IN 3,4-DITHIACYCLOBUTENE (DITHIETE) RADICAL CATION

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SPIN DISTRIBUTION IN 3,4-DITHIACYCLOBUTENE (DITHIETE) RADICAL CATION

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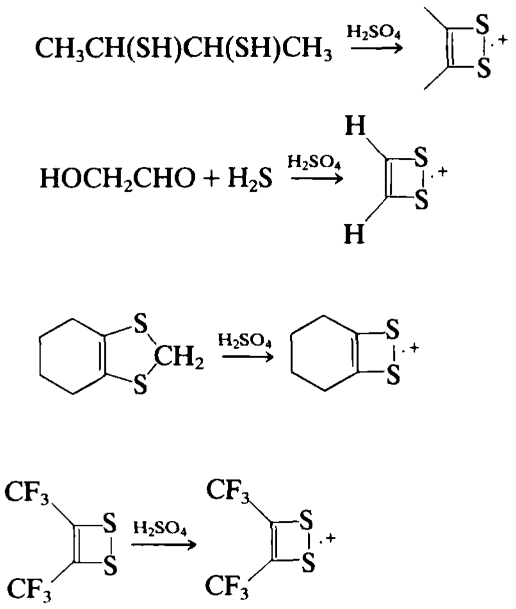
Hückel and *ab initio* (STO-3G) calculations confirm the experimental assignment of the 3,4-dithiacyclobutene (dithiete) radical cation as a π radical with a SOMO symmetric to a plane bisecting the C—C and S—S bonds. However, neither calculation is in good agreement with the low value of $\rho_C \cong 0.1$ observed experimentally.

Dithiete radical cations are reasonable persistent species in H_2SO_4 solution. They are formed by the action of concentrated H_2SO_4 upon certain 1,2-dithiols,[1] upon mixtures of α-hydroxy ketones or aldehydes and H_2S,[2] upon 1,3-dithioles containing hydrogen atoms at C(2),[1] or upon stable 1,2-dithietes.[2,3]



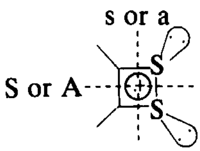
$a^H = 2.19$ g (6H)
$g = 2.0155$

$a^H = 2.76$ G (2H)

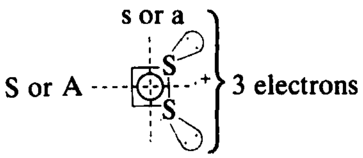
$a^H = 3.04$ G (4H)
$g = 2.0155$

$a^F = 1.35$ G (6F)

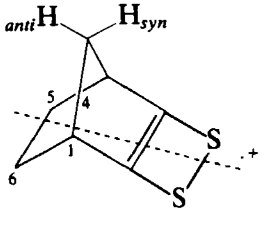
The singly occupied molecular orbital (SOMO) could either be of the π-type involving 5π-electrons in a cyclic array (**1**) or of the σ-type involving unpaired electron density in the plane of the dithiete ring (**2**).[4] The synthesis of **3** by the action of H_2SO_4 and $K_2S_2O_8$ upon an *endo*/*exo* mixture of



1, $\pi(5\pi$ electrons)



2, $\sigma(6\pi$ electrons)

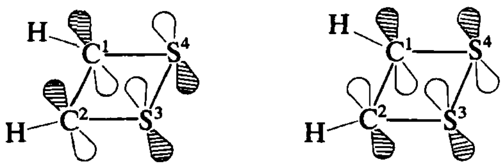


3, $g = 2.0144$

cis-bicyclo[2.2.1]heptene-2,3-dithiols allowed an experimental assignment of the symmetry of the SOMO. In **2**, the σ SOMO would be antisymmetric relative to a plane bisecting the molecule (the horizontal dotted lines in **1–3**) if the three electrons in the two in-plane hybrid sulfur oribtals interact in a π-fashion to form S and A two-center orbitals. For such an antisymmetric SOMO, the bridge hydrogens in **3** (H_{syn}, H_{anti}) would be in a nodal plane and little hyperfine interaction would be expected. Actually, for **3**, a^{H}_{anti} was observed to be 2.75 G with $a^{H}_{syn} \cong 0$ and $a^{H}_{1,4} = a^{H}_{5,6\text{-}exo} = 0.9$ G. The ratio of $a^{H}_{anti}/a^{H}_{5,6\text{-}exo}$ of ~3 is in excellent agreement with other bicyclo[2.2.1]-heptane derivatives containing a symmetric SOMO and not in accord with known derivatives containing an asymmetric SOMO which have a^{H}_{anti}/a^{H}_{syn} in the range of 1–2 and $a^{H}_{anti}/a^{H}_{5,6\text{-}exo} \ll 1$.[1,5] The experimental results thus favor structure **1** in which the SOMO is symmetric (S) relative to the plan bisecting the C—C and S—S bonds.

The symmetry of the SOMO π-orbital is surprising in view of the orbitals of cyclobutadiene, and we would like to present the results of calculations which explain why the sA orbital of **1** is of lower energy (and hence is a filled MO) leaving the aS orbital as the SOMO.

Russell *et al.* have presented a qualitative argument based on the assumption that β(CS) is greater than $[\beta(CC) + \beta(SS)]/2$ and that $\alpha_S > \alpha_C$.[1] With $\alpha_S > \alpha_C$ and $\beta(CC) > \beta(SS)$, the splitting between the C=C and S—S π-orbitals (leading to the sS and aS molecular orbitals) would be greater than the splitting between the corresponding π^* orbitals (leading to the sA and aA molecular orbitals). These restrictions would lead to a situation where the aS orbital would be higher in energy than the sA orbital (Figure 1).



aS sA

FIGURE 1 The aS and sA orbitals of **1**.

TABLE I

The HMO results of dithiocyclobutene

No.	Alpha		Beta			E(aS)-E(sA) in absolute beta	Coefficient of SOMO		Symmetry of SOMO
	C	S	CC	SS	CS		C	S	
1	0	1.5	1	0.4	0.8	0.838	0.610	−0.357	aS
2	0	1.5	1	0.4	0.7	0.694	0.621	−0.339	aS
3	0	1.5	1	0.4	0.6	0.559	0.632	−0.316	aS
4	0	0	1	0.4	0.8	0.309	0.403	−0.581	aS
5	0	0	1	0.4	0.7	0.123	0.389	−0.590	aS
6	0	0	1	0.4	0.6	−0.058	±0.372	±0.602	sA

As a check of the above explanation, we performed Hückel Molecular Orbital (HMO) calculations with different parameters. The results are listed in Table I.

It is apparent that an increase of α_S or β(CS) leads to higher energy of the aS MO relative to the sA MO, agreeing with the view of Russell *et al.*[1] However, this is not the whole story. We see that even when $\alpha_S = \alpha_C$ and $\beta(CS) = [\beta(CC) + \beta(SS)]/2$ (no. 5 in Table I), the SOMO is still aS. Furthermore, β(CS) may not be greater than the average of β(CC) and β(SS), as the A—B bond energy with different atoms A and B is generally less than the average A—A and B—B bond energies.[6]

The main factor leading to the higher energy of the symmetrical (aS) MO is that $\beta(SS) \ll \beta(CC)$, i.e., the magnitude of the interaction between two sulfur atoms is much weaker than the between two carbon atoms. This is shown schematically in Figure 2.

The interaction between two sulfur atoms leads to a small energy gap between the antisymmetrical and the symmetrical local SS π-orbitals (Figure 2b), while the gap is much greater in the case of carbon (Figure 2a). When the local orbitals of

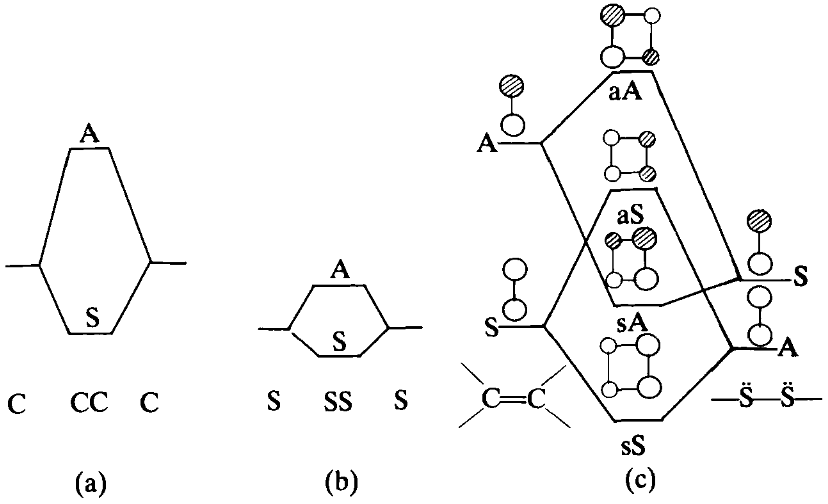


FIGURE 2 Orbital interactions. (a) between two carbons, (b) between two sulfurs, (c) between the local π-orbitals of C=C and —S̈—S̈—.

TABLE II

STO-3G RHF results of π-MOs of the dithiete radical cation[a]

MO energies/Hartree	−0.7325 (sS)	−0.5455 (sA)	−0.3610 (aS)	0.0086 (aA)
Coefficients, C(1), 2p	0.3710	0.2641	0.5402	0.7532
C(2), 2p	0.3710	−0.2641	0.5402	−0.7532
S(3), 3p	0.5081	−0.6880	−0.4937	0.3604
S(4), 3p	0.5081	0.6880	−0.4937	−0.3604

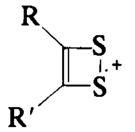
[a] S(3) is bonded to C(2).

the same symmetry interact with each other, the resulting aS MO becomes higher in energy than the sA MO (Figure 2c).

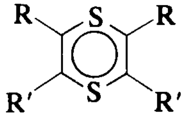
The HMO results in Table I do not reflect all properties of the system due to the shortcoming of the HMO method. As each sulfur atom provides a pair of electrons to the π-system, its α should be rather large. In calculations 1 through 3, it is chosen to be 1.5, the same as suggested by Streitwieser for nitrogen or bromine.[7] A large α value will exaggerate the difference of the coefficients between C and S. Thus, if α_S is set at 0, the coefficients are reversed in magnitude.

We performed *ab initio* calculations to obtain a better description of the MOs. The STO-3G basis set (in which a Stater-type orbital is approximated by a set of three Gaussian functions) is sufficient for qualitative discussion. The usual UHF method for open shell molecules splits the MOs into α and β sets, leading to difficulty in the discussion. We thus employed the restricted Hartree Fock (RHF) method. The geometry optimized by the MNDO method provided by Bock was employed with $d(C—H) = 1.083$ A, $d(C—C) = 1.439$ A, $d(C—S) = 1.659$ A, $d(S—S) = 2.015$ A, $\angle CCH = 131.6°$.[8] The results are listed in Table II. The larger coefficients on C than on S in the SOMO reflect the greater electronegativity of S, which leads to a lower energy π-bonding orbital of $—\ddot{S}—\ddot{S}—$ than of $>C{=}C<$, as shown in Figure 2.

However, although both the HMO and the STO-3G RHF calculations predict the proper symmetry of the SOMO, the resulting spin densities are not in good agreement with the experimental values of $\rho_C \cong 0.1$, $\rho_S = \frac{1}{2}(1 - 2\rho_C) \cong 0.4$ based on the McConnell relationships for a π-radical using standard values of Q^H_{CH} or $Q^H_{CCH_3}$ which empirically correlate the ESR hyperfine splitting constants of a hydrogen atom with the spin densities of the carbon atom to which the hydrogen atom or methyl group is attached. Very similar spin densities are found for **3** using empirical relationships for long range hyperfine interactions based on the spin distribution in the bicyclo[2.2.1]heptane-2,3-semidione.[3,4] The STO-3G basis set predicts that $\rho_C \cong \rho_S = 0.25$ in **1** whereas experimentally it is obvious that the unpaired electron density must be much higher on S than on C. The discrepancy between the measured value of a^H and the value estimated from the calculated value of ρ_C is puzzling, and it seems doubtful that the use of a larger basis set in the calculation will overcome this discrepancy. It is also puzzling why the hyperfine splitting constants are approximately the same in the dithiete and *p*-dithiin systems.[1,2] Also, the fact that



$R = R' = H$; $a^H = 2.76$ Gauss (2H)
$R = R' = CH_3$: $a^H = 2.19$ Gauss (6H)
$R = H$; $R' = CH_3$; $a^H = 3.31$ (1H), 1.8 (3H)
$g = 2.0155$



$R = R' = H$; $a^H = 2.84$ Gauss (4H)
$R = R' = CH_3$; $a^H = 2.11$ Gauss (12H)
$R = H$; $R' = CH_3$; $a^H = 2.85$ (2H),
$g = 2.0089$

for these systems $Q^{H}_{CCH_3}/Q^{H}_{CH} \simeq 0.75$ is unexpected since this ratio for neutral radicals is approximately 1.3 and is much greater for benzenoid radical cations.[9] Although both systems appear to be π-radical cations with the expected symmetry,[1] the spin and charge are more highly localized on the sulfur atoms than might be expected. This raises the possibility that the dithiete radical cation may indeed be a σ species but with five electrons delocalized in the S—S bond and the two in-plane sulfur hybrid orbitals and with six π-electrons. In such an arrangement, the experimental S-symmetry of the SOMO could be achieved (Figure 3a). Such a structure was considered previously for radical cations of cyclic 1,2-disulfides where aromaticity is not a consideration, such as 2,3-dithiabicyclo[2.2.1]heptane.[1] However, in this case, the SOMO is clearly antisymmetric,[1] as expected for a π-MO involving three electrons in adjacent sulfur 3p orbitals (Figure 3b).

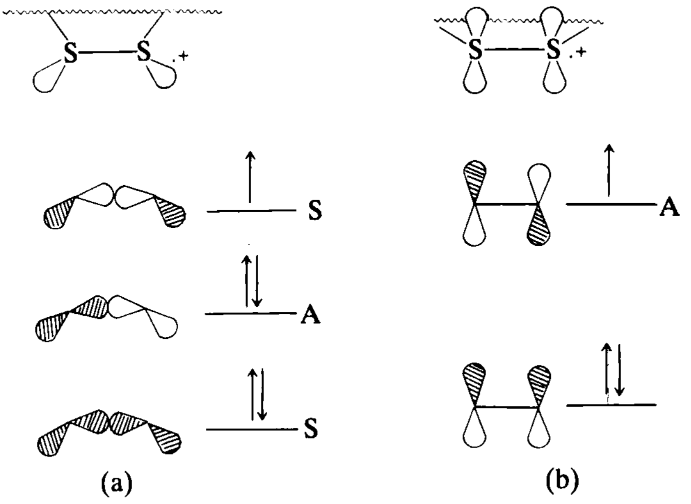


FIGURE 3 Orbital interactions possible for cyclic 1,2-disulfide radical cations. (a) σ-species, excluded for 2,3-dithiabicyclo[2.2.1]heptane. (b) π-species.

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