The dithiacyclooctane cation (DTCO+): conformational analysis, interconversion barriers and bonding

Ralf Stowasser, Richard S. Glass and Roald Hoffmann *

Departments of Chemistry of Cornell University, Ithaca, New York 14853, USA and University of Arizona, Tucson, AZ 85721, USA
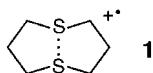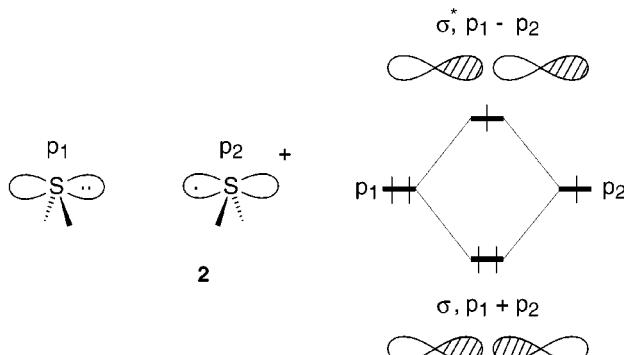
A theoretical conformation analysis of the dithiacyclooctane radical cation (DTCO+) suggests that the lowest energy conformer is a chair-boat, with a partial but significant S–S σ bond. For the ring flip process of this molecule we calculate a barrier of 40 kJ mol⁻¹ and two possible pathways: one involves a boat-boat conformer and an untwisted transition structure, the other a chair-chair conformer and a twisted transition structure.

1 Introduction

The stable dithiacyclooctane radical cation (DTCO+, **1**) has been investigated experimentally by EPR and resonance Raman spectroscopy.[1,2] Both studies suggest the existence of a monomeric species with substantial bonding between the sulfur atoms.

Indeed partial S···S bonding is to be expected in such a radical cation. Consider a hypothetical molecule in which two S p-type lone pairs approach each other, as in **2**. For the four-

electron (neutral) system one would expect no bond, only a repulsive interaction. The dication, configuration (σ²), should have a full S–S single bond. The monocation radical (σ)²(σ*)¹, is expected to have a partial S–S bond.

These expectations will be probed in our calculations. Furthermore, we investigate the interesting question of the equilibrium geometry of the DTCO monocation and its conformational interconversions.

The EPR study suggests a chair-boat (**cb**)-like conformer as the ground state conformation of minimum energy. The related DTCO and DTCO²⁺ compounds, chair-boat (**cb**), and twisted-chair-chair (**tcc**) ground state conformations are observed in X-ray structural studies. These conformations will be illustrated subsequently. MINDO calculations[3] suggested a twisted-chair-chair (**tcc**) as the global minimum DTCO+ conformation.

2 Computational methods

Input geometries were generated by the application of molecular mechanics (MM2) as well as semiempirical SCF (PM3) methods, implemented within the SPARTAN 3.0 program.[4] For the conformational analysis, density functional theory (DFT) was used; specifically the unrestricted spin density approach of the ADF[5–7] program package, using a Becke–Perdew (UBP86) function and the flexible TZVP basis set (type IV). All structures were optimized without geometrical constraints or symmetry restrictions. Interconversion barriers were determined by the calculation of energy differences between transition and ground state structures. The transition structures as well as the global minimum were calculated using the more accurate hybrid B3LYP/6-31G function. Selected points were checked with a larger 6-31G** basis set; no significant change was found. Vibrational frequency calculations were applied to characterize minima and transition structures. Bonding analyses (reduced overlap population, molecular orbitals) were performed *via* single point extended Hückel (EH) calculations (program YAeHMOP 2.0[8]) on DF-calculated global minimum geometries.
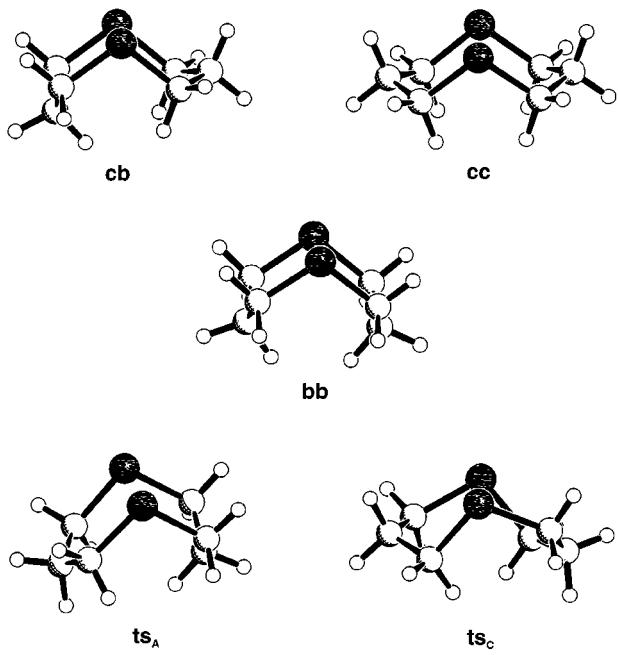
3 Conformational analysis and ground state structures

The DF conformational analysis leads to three energetically favoured *cis*-fused conformers (chair-boat (**cb**), chair-chair (**cc**), boat-boat (**bb**); these are shown in Fig. 1). Interestingly, the twisted *cis*-fused minimum structures (**tcb**, **tcc**, **tbb**) calculated by molecular mechanics and semiempirical MO models are not stable (in a DF framework) with respect to the corresponding non-twisted forms (**cb**, **cc**, **bb**). This result was supported by *ab initio* Hartree–Fock (UHF/6-31G*) calculations, where the same trend (optimization of the twisted conformers to non-twisted minimum structures) was observed. Structures, energies and S–S-bond lengths are summarized in Fig. 1.
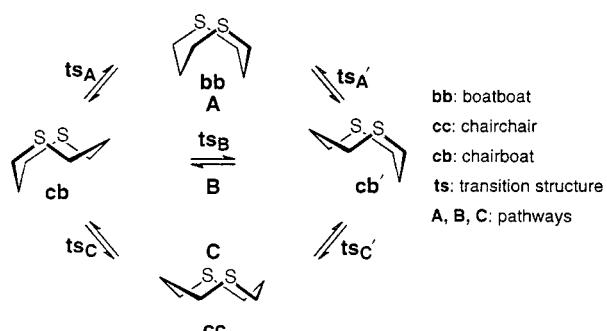
The calculated global minimum is the **cb** conformer. This structure is *ca*. 8 kJ mol⁻¹ more stable than **cc** and **bb** (E_{rel}(**cb**) = 0.0 kJ mol⁻¹, E_{rel}(**cc**) = 7.6 kJ mol⁻¹, E_{rel}(**bb**) = 7.7 kJ mol⁻¹). DTCO+ conformers with a *trans*-fused S–S bond are of dramatically higher relative energy (E_{rel} > 80 kJ mol⁻¹) and they are not further considered in this study.

4 Transition structures and interconversion pathways and barriers

The more demanding and complicated problem of locating the correct transition structures could be solved by switching from the ADF to the GAUSSIAN94[9] transition-state-searching algorithm. It turns out (see Fig. 2) that there is no direct pathway **B** between the **cb** and the **cb′** conformers. We propose (guided by the calculations) for this energy hypersurface two alternative stepwise pathways **A** and **C** (*cf*. Fig. 2).

Conformation	cb	cc	bb	ts_A	ts_C
energy/kJ mol^{-1}	[0.0]	7.6	7.7	37.1	39.9
S–S distance/Å	2.78	2.80	2.76	2.81	2.82

Fig. 1 DF-calculated ground (chair-boat (**cb**), chair-chair (**cc**), boat-boat (**bb**)) and transition structures (untwisted (**ts$_A$**) and twisted (**ts$_C$**)) of DTCO$^+$ with relative energies and S–S bond length.
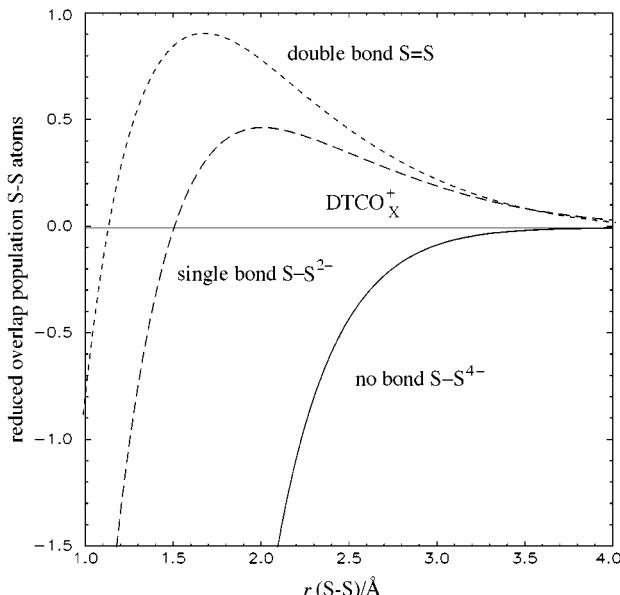

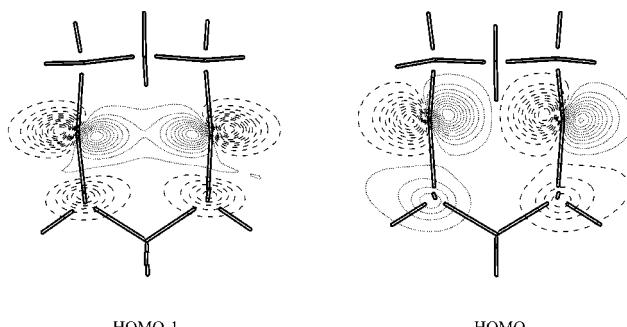**Fig. 2** Possible pathways for the ring flip process in DTCO$^+$.

Path **A** traverses transition structure **ts$_A$** and goes through the **bb** conformer into the **cb'** minimum conformation traversing **ts'$_A$**. Process **A** is associated with a calculated activation barrier $\Delta E = E_{ts_A} - E_{cb} = 37.1$ kJ mol^{-1}. The alternative pathway goes through transition structure **ts$_C$**, the **cc** minimum conformer and the transition structure **ts$_C$'**, ending in **cb'**. The activation barrier $\Delta E = E_{ts_C} - E_{cb} = 39.9$ kJ mol^{-1} of process **C** is close to the barrier of pathway **A**. However the transition structures (*cf*. Fig. 1) are quite different. The path **A** transition structure is not twisted (and identical with the linear transit between **cb** and **bb**), while transition structure **ts$_C$** is twisted.[10]

5 Bonding in DTCO$^+$

An extended Hückel (EH) calculation on the global minimum structure of DTCO$^+$ results in a Mulliken reduced overlap population (OP) of 0.08 between the sulfur atoms. This is obtained by calculating the OP's for S^{2-} ions approaching each other (no bond), two S$^-$ (yielding a single bond) and two neutral S (a model for a double bond). From Fig. 3 we see that the computed 0.08 reduced overlap population falls exactly in between the overlap population range of a single bond and no bond.

Fig. 3 Reduced overlap population between S atoms *vs*. S–S distance in S$_2$, S$_2^{2-}$, S$_2^{4-}$, and DTCO$^+$.

Fig. 4 Contour plots of the HOMO and HOMO-1 orbital of DTCO$^+$, which show the σ and σ^* bond.

The DF calculated S–S bond lengths for DTCO$^+$ of 2.7–2.8 Å, (*cf*. Fig. 1), are between the non-bonded S–S distance in DTCO-type molecules *e.g.* 3.23 Å in naphtho[1,8-*b*,*c*][1,5]-dithiocine[11] and the single bond distance of 2.12 Å in DTCO^{2+}.[12] Calculations on the dication will be reported separately.

The analysis of the EH MO's shows that the S–S σ-orbital (formed by overlap of two p orbitals) is nicely localized in the HOMO-1, and the S–S σ^*-orbital in the HOMO (*cf*. Fig. 4; in the case of DTCO$^+$ the HOMO is identical with the SOMO). The calculated energy difference ΔE (HOMO–(HOMO-1)) = 2.30 eV is in reasonable agreement with an experimentally measured electronic transition at 405 nm (ΔE = 3.06 eV), which has been ascribed to the σ–σ^* excitation.[2] The calculated results are also in agreement with the literature.[13] The authors ascribe the 405 nm transition to an excitation from an orbital that has σ lone pair (perpendicular to the S–S axis) character to one that has p lone pair (parallel to the S–S axis) character. The former type is localized in the HOMO-1, which also shows σ S–S bond character; the latter one can be found in the HOMO (= SOMO).

6 Summary

Computations on DTCO$^+$ confirm the existence of significant S–S σ bonding. As the minimum energy conformation of DTCO$^+$ we find the chair-boat conformer. The calculated inter-conversion barrier for the ring flip process is significant, nearly 40 kJ mol^{-1}. For this interconversion we find two possible pathways. One involves the boat-boat conformer and an

untwisted transition structure, the other a chair-chair conformer and a twisted transition structure.

References

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