

# Catalysis of the Quadricyclane to Norbornadiene Rearrangement by $\text{SnCl}_2$ and $\text{CuSO}_4$

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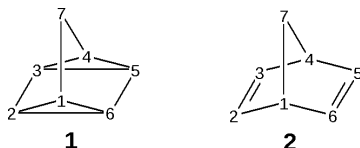
Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70<sup>th</sup> birthday

*Ab initio* and density-functional theory (DFT) calculations have been used to investigate the model rearrangements of quadricyclane to norbornadiene catalysed by single  $\text{CuSO}_4$  and  $\text{SnCl}_2$  molecules. The isolated reactions with the two molecular catalysts proceed *via* electron-transfer catalysis in which the hydrocarbon is oxidised, in contrast to systems investigated previously in which the substrate was reduced. The even-electron  $\text{SnCl}_2$ -catalysed reaction shows singlet-triplet two-state reactivity. Solvation by a single methanol molecule changes the mechanism of the rearrangement to a classical Lewis acid-base process.

**Key words:** *Ab initio* Calculations, Density Functional Calculations, Electron Transfer, Catalysis, Rearrangement

## Introduction

The quadricyclane (**1**) to norbornadiene (**2**) rearrangement [1] has long been of interest as a prominent example of a thermally forbidden, photochemically allowed exothermic process that can be catalysed by many very different species.



Our interest in this rearrangement is strengthened because it represents a very early example of a hole-catalysed [2] reaction. Haselbach *et al.* [3] first observed that the radical cation generated by ionising quadricyclane in a Freon matrix at 77 K, and later Kelsall and Andrews at 4 K [4], rearranged spontaneously under their reaction conditions to the norbornadiene radical cation. Later, Turro and Roth [5] were able to show that the quadricyclane radical cation does have a significant lifetime using CIDNP measurements and later time-resolved ESR spectroscopy.

The rearrangement of  $1^{+\bullet}$  to  $2^{+\bullet}$  is also of considerable theoretical interest as it served as the ma-

ior example that led to our current understanding of hole-catalysed reactions in particular and open-shell pericyclic transformations in general. Soon after Woodward and Hoffmann's original publication of the "HOMO rule" that governs the stereochemistry of electrocyclic reactions [6], Longuet-Higgins pointed out [7] that all radical electrocyclic reactions are Woodward-Hoffmann forbidden. However, his conclusion that these reactions should therefore be slow was revised in Haselbach's seminal paper [3] in which he pointed out that the rearrangement of  $1^{+\bullet}$  to  $2^{+\bullet}$  can take place *via* a very low-lying state crossing, rather than through a continuous change characteristic of an allowed reaction. However, Haselbach's treatment of the symmetrical reaction path, in which the two cyclopropane bonds open simultaneously, neglected the Jahn-Teller effect in the transition state. Bischof [8] pointed out that a classical Jahn-Teller situation exists at the crossing point (because at this point the two "crossing" orbitals are degenerate by definition), so that the  $C_{2v}$  structure suggested by Haselbach is a hilltop, rather than a transition state. Later calculations [9] showed the hilltop to have  $C_2$  symmetry. This structure undergoes Jahn-Teller distortion orthogonal to the reaction path to yield two enantiomeric  $C_1$  transition states. We [9] later described full electronic char-

acteristics of the reaction and calculated the region of the energetic hypersurface that describes the rearrangement, although the reaction had been the subject of earlier *ab initio* calculations [10] and continued to attract attention from theoretically oriented groups [11].

We also pointed out [12] that potentially hole-catalysed reactions (and their radical-anion counterparts) can be catalysed by complexation with a redox-active centre, usually a metal. This electron-transfer catalysis can proceed by either reduction or oxidation of the reacting system and is not necessarily evident in experimental studies because the electron transfer may only occur in the vicinity of the transition state. However, electron-transfer catalysis may be connected with a spin change from low to high spin.

Experimentally, the quadricyclane to norbornadiene rearrangement can be catalysed by many homogeneous and heterogeneous systems. A variety of redox-active homogeneous transition metal-based catalysts [13], Ag(I) [14] and “naked” Li(I) ions [15], cytochrome P450 [16] and some novel heterogeneous catalytic systems such as alkali halide colour centres [17] have been reported to catalyse the rearrangement of quadricyclane to norbornadiene. We will, however, concentrate on the homogeneous catalysis by Cu(II) and Sn(II) compounds and salts [18, 19]. Our reasons are twofold. Firstly, catalysis by divalent metal ions should result in oxidation of the rearranging hydrocarbon moiety, whereas the systems that we have investigated until now are catalysed by one-electron reduction of the reacting ligand [20]. Secondly, experimental activation energies are available for the quadricyclane to norbornadiene rearrangement catalysed by SnCl<sub>2</sub> in homogeneous methanol solution [21] and also under a variety of conditions for the fascinating equivalent reaction in which anhydrous CuSO<sub>4</sub> acts as the heterogeneous catalyst [22–24].

We now report *ab initio* and density-functional theory (DFT) calculations on models for the Sn(II)- and Cu(II)-catalysed rearrangement of quadricyclane to norbornadiene. Our aims are to investigate the catalytic mechanism in the light of the known hole-catalysed nature of the reaction. We emphasise that our intent is not to reproduce the experimental systems, but rather to use simplified models to investigate the nature of any electron-transfer catalysis paths and also to judge the factors that may favour alternative, closed-shell mechanisms. We have therefore not performed calculations at definitive levels of theory, but have rather chosen to check consistency by using very different levels of the-

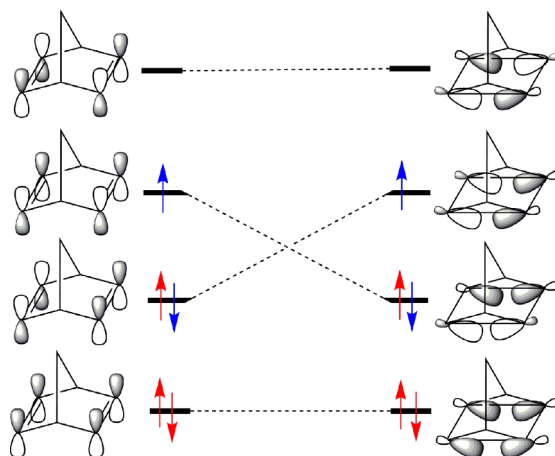
ory (B3LYP, MP2, CCSD and CCSD(T)). In all but one case ( $3^{\ddagger-\bullet}$ ), the results obtained with the different methods are quite consistent, so that we feel confident that our qualitative conclusions are well founded. As discussed below, the special case of  $3^{\ddagger-\bullet}$  is the result of serious spin contamination in the UHF reference wavefunction used for the *ab initio* post Hartree-Fock calculations.

## Results

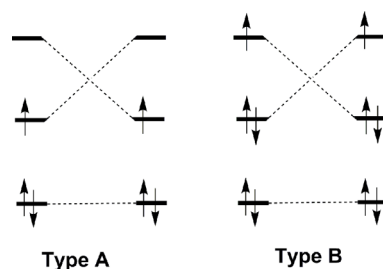
### Qualitative molecular-orbital analysis

Scheme 1 shows the orbitals involved in the rearrangement.

As outlined previously [9], the radical-cation rearrangement occurs *via* an avoided crossing that corresponds to a Type A radical electrocyclic reaction, as defined by Bischof [8], and that of the radical anion to a Type B (Scheme 2).



Scheme 1. The four  $\pi$  molecular orbitals of norbornadiene and the four  $\sigma$  and  $\sigma^*$  orbitals of quadricyclane with which they correlate. The red arrows represent the orbital occupation in the radical cation and the blue ones the additional electrons in the radical anion. The orbital correlations are shown as dashed lines (colour online).



Scheme 2. Schematic diagram of the orbital correlations in Bischof Type A and B radical electrocyclic reactions [8].

Table 1. Relative energies ( $E_{\text{rel.}}$ , kcal mol $^{-1}$ , corrected using the unscaled MP2/6-31G(d) zero-point vibrational energies, ZPE) and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8^{+\bullet}$  structures  $\mathbf{1}^{+\bullet}$ – $\mathbf{3}^{\ddagger+\bullet}$ . Total ( $E_{\text{tot.}}$ , Hartree) and zero-point vibrational energies (ZPE, kcal mol $^{-1}$ , MP2/6-31G(d)) are given in Table S1 of the Supporting Information.

| Species                         | MP2/6-31G(d) |                   | CCSD/6-31G(d)     |                   | CCSD/6-311+G(d,p) |                   | ROCCSD(T)/cc-pVTZ <sup>a</sup> |  |
|---------------------------------|--------------|-------------------|-------------------|-------------------|-------------------|-------------------|--------------------------------|--|
|                                 | $N_i$        | $E_{\text{rel.}}$ | $E_{\text{rel.}}$ | $E_{\text{rel.}}$ | $E_{\text{rel.}}$ | $E_{\text{rel.}}$ |                                |  |
| $\mathbf{1}^{+\bullet}$         | 0            | 0.0               | 0.0               | 0.0               | 0.0               | 0.0               |                                |  |
| $\mathbf{3}^{\ddagger+\bullet}$ | 1            | 14.8              | 10.8              | 9.9               | 11.0              | 11.0              |                                |  |
| $\mathbf{2}^{+\bullet}$         | 0            | −3.4              | −5.1              | −5.5              | −4.8              | −4.8              |                                |  |

<sup>a</sup> At the MP2/6-31G(d)-optimised geometry.

The radical anion of norbornadiene was observed when quadricyclane was reduced in diglyme at  $-96$  K [25] and in methyltetrahydrofuran at  $77$  K [26]. The radical-anion rearrangement therefore has a low barrier, as would be expected from Scheme 2, which shows that an avoided crossing involving the same one-electron excitation leads to the barrier in the rearrangement of the radical cation and anion. We would therefore expect from qualitative ideas that the rearrangements of one-electron-oxidised and -reduced quadricyclane should behave similarly.

#### Radical-cation rearrangement

As pointed out previously [9], the rearrangement of the quadricyclane radical cation  $\mathbf{1}^{+\bullet}$  ( $C_{2v}$ ) to the norbornadiene radical cation  $\mathbf{2}^{+\bullet}$  ( $C_{2v}$ ) proceeds *via* one of the two alternative enantiomeric transition states  $\mathbf{3}^{\ddagger}$  ( $C_1$ ). The transition states are connected by the second-order saddle point (hilltop)  $\mathbf{4}^*$  ( $C_2$ ). The MP2/6-31G(d) potential hypersurface for this reaction was given in ref. [9]. We have re-optimised the minima and transition states at the CCSD/6-311+G(d,p) level and refined the energies using single-point CCSD(T) calculations with the cc-pVTZ basis set and MP2/6-31G(d) calculated zero-point vibrational energies. The results are shown in Fig. 1 and Table 1. The Gaussian Archive entries for the calculations on  $\mathbf{1}$ – $\mathbf{3}$  are given in the Supporting Information (available online only; see note at the end of the article).

The general details reported previously [9] are confirmed. The rearrangement is found to be exothermic by  $-4.8$  kcal mol $^{-1}$ , compared with a value of approx-

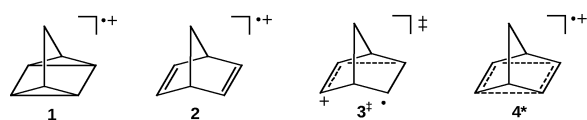


Fig. 1. Structures of quadricyclane radical cation  $\mathbf{1}^{+\bullet}$ , norbornadiene radical cation  $\mathbf{2}^{+\bullet}$ , transition state  $\mathbf{3}^{\ddagger}$ , and hilltop  $\mathbf{4}^*$ .

imately  $-10$  kcal mol $^{-1}$  derived from the experimental heats of formation and ionisation energies of quadricyclane and norbornadiene [27]. The experimental value is uncertain because of the large error bars for the heat of formation of neutral norbornadiene. The activation energy ( $0$  K) is calculated to be  $11.0$  kcal mol $^{-1}$ .

#### Radical-anion rearrangement

The quadricyclane to norbornadiene radical-anion rearrangement is technically difficult to calculate because of the spin contamination in the unrestricted Hartree-Fock reference wavefunction for the transition state. Normally, DFT would be a solution to this problem, but we have shown for the radical cation that B3LYP does not reproduce the Jahn-Teller effect in the transition state correctly [9]. Table 2 shows the results of calculations at different levels for the radical-anion rearrangement.

The spin contamination in the UHF reference wavefunction for the MP2 calculation has the expected effect that the barrier is found to be higher than a qualitative picture suggests it should be. The ROMP2 and B3LYP barriers are of the order expected, and the barrier is comparable to that found in the radical cation. Perhaps the most striking feature of the results shown in Table 2 is that the anion reaction is probably far more exothermic than that of the cation. This is consistent with the fact that the electron affinity of ethylene is  $-1.78$  eV [28], compared with an estimated  $-5.3$  eV for cyclopropane [29]. Even [1.1.1]-propellane, with an electron affinity of  $-2.04$  eV [30] is more difficult to reduce than the  $\pi$  bond in ethylene. Thus the rearrangement of the saturated quadricyclane to olefinic norbornadiene should be favoured thermodynamically by one-electron reduction.

Fig. 2 shows the UMP2- and B3LYP-optimised geometries for the transition state rearrangement. As found for the radical cation [9], the UMP2 geometry displays lower symmetry than that found at B3LYP,

Table 2. Relative energies ( $E_{\text{rel.}}$ , kcal mol<sup>-1</sup>, corrected using the unscaled MP2/6-31G(d) zero-point vibrational energies, ZPE) and number of imaginary vibrations ( $N_i$ ) for the C<sub>7</sub>H<sub>8</sub><sup>-•</sup> structures **1**<sup>-•</sup>–**3**<sup>‡-•</sup>. Total ( $E_{\text{tot.}}$ , Hartree) and zero-point vibrational energies (ZPE, kcal mol<sup>-1</sup>, MP2/6-31G(d) and B3LYP/6-31G(d)) are given in Table S2 of the Supporting Information.

| Species                 | UMP2/<br>6-31+G(d) |                   |                       | ROMP2/<br>6-31+G(d) <sup>a</sup> |                   |  | UB3LYP/<br>6-31+G(d) |                   |                       |
|-------------------------|--------------------|-------------------|-----------------------|----------------------------------|-------------------|--|----------------------|-------------------|-----------------------|
|                         | $N_i$              | $E_{\text{rel.}}$ | $\langle S^2 \rangle$ | $N_i$                            | $E_{\text{rel.}}$ |  | $N_i$                | $E_{\text{rel.}}$ | $\langle S^2 \rangle$ |
| <b>1</b> <sup>-•</sup>  | 0                  | 0.0               | 0.757                 | 0                                | 0.0               |  | 0                    | 0.0               | 0.75                  |
| <b>3</b> <sup>‡-•</sup> | 1                  | 30.3              | 1.359                 | 1                                | 5.0               |  | 1                    | 9.1               | 0.75                  |
| <b>2</b> <sup>-•</sup>  | 0                  | -29.4             | 0.751                 | 0                                | -14.6             |  | 0                    | -34.1             | 0.75                  |

<sup>a</sup> At the UMP2/6-31G(d)-optimised geometry.

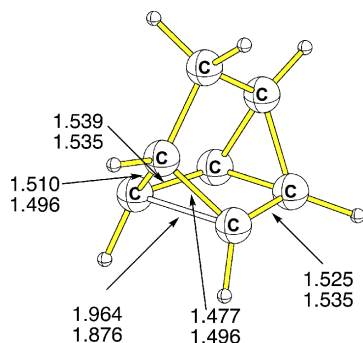


Fig. 2. Optimised geometry MP2/6-31+G\* (top) and B3LYP/6-31+G\* (bottom) of the anionic transition state. Bond lengths are in Å.

which does not reproduce the Jahn-Teller effect properly.

#### The rearrangement catalysed by a single CuSO<sub>4</sub> molecule

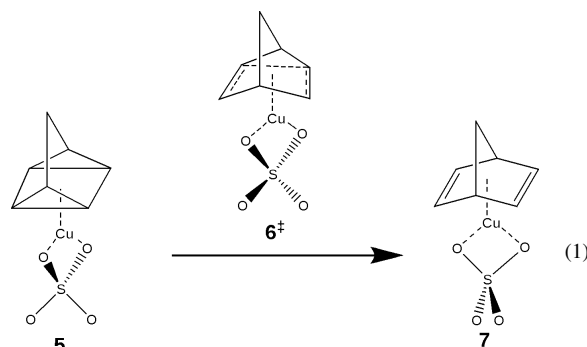
The effect of a single CuSO<sub>4</sub> moiety on the rearrangement was investigated starting from the quadricyclane-CuSO<sub>4</sub> model complex **5**, which rearranges *via* transition state **6**<sup>‡</sup> to give the norbornadiene-CuSO<sub>4</sub> complex **7**. Table 3 shows the calculated energies for this reaction. The Gaussian Archive files for **5**–**7** (Eq. 1) are given in the Supporting Information.

Two geometrical features are especially noteworthy. Firstly, the coordinated sulphate ion rotates by 90° in the course of the rearrangement. We will discuss this effect below, but point out here that the rotation is a consequence of the 90° angle between the nodal planes of the singly occupied molecular orbitals (SOMOs) in the radical cations of **1** and **2**. The second noteworthy point is the resemblance between the geometry of the C<sub>7</sub>H<sub>8</sub> moiety in **6**<sup>‡</sup> and that of the radical-ion transi-

Table 3. Relative energies ( $E_{\text{rel.}}$ , kcal mol<sup>-1</sup>, corrected using the unscaled B3LYP/6-31G(d) zero-point vibrational energies, ZPE) and number of imaginary vibrations ( $N_i$ ) for the C<sub>7</sub>H<sub>8</sub>-CuSO<sub>4</sub> structures **5**–**7**. Total ( $E_{\text{tot.}}$ , Hartree) and zero-point vibrational energies (ZPE, kcal mol<sup>-1</sup>, B3LYP/6-31G(d)) are given in Table S3 of the Supporting Information.

| Species               | CCSD/<br>6-31G(d) <sup>a</sup> |                   | CCSD(T)/<br>6-31G(d) <sup>a</sup> |                   | CCSD(T)/<br>6-31G(d) <sup>a</sup> |                   |
|-----------------------|--------------------------------|-------------------|-----------------------------------|-------------------|-----------------------------------|-------------------|
|                       | $N_i$                          | $E_{\text{rel.}}$ | $E_{\text{rel.}}$                 | $E_{\text{rel.}}$ | $E_{\text{rel.}}$                 | $E_{\text{rel.}}$ |
| <b>5</b>              | 0                              | 0.0               | 0.0                               | 0.0               | 0.0                               | 0.0               |
| <b>6</b> <sup>‡</sup> | 1                              | 2.9               | 16.9                              | 11.5              | 11.5                              | 11.5              |
| <b>7</b>              | 0                              | -36.8             | -34.8                             | -36.7             | -36.7                             | -36.7             |

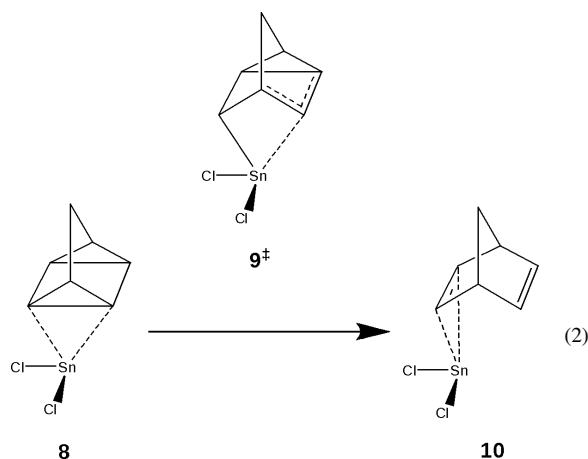
<sup>a</sup> Using the B3LYP/6-31G(d)-optimised geometry.



tion state **3**<sup>‡</sup>. Although the bond lengths in the former four-membered ring are quite different (1.520, 1.518, 1.537, and 2.025 Å for C<sub>2</sub>–C<sub>3</sub>, C<sub>3</sub>–C<sub>5</sub>, C<sub>5</sub>–C<sub>6</sub> and C<sub>6</sub>–C<sub>1</sub>, respectively in **6**<sup>‡</sup>, compared with 1.415, 1.796, 1.476 and 2.055 Å in **3**<sup>‡</sup>, at the B3LYP/6-31G(d) level), both transition states are very unsymmetrical. This is usually indicative of a radical-ion mechanism because of the Jahn-Teller effect in the transition state pointed out by Bischof [8]. The B3LYP activation energy for the rearrangement is only 2.9 kcal mol<sup>-1</sup>, compared with 10.6 kcal mol<sup>-1</sup> for the radical cation and 9.1 kcal mol<sup>-1</sup> for the radical anion at the same level of calculation. However, at the CCSD/6-31G(d) level, the radical cation activation barrier is calculated to be 10.8 kcal mol<sup>-1</sup> and that for the CuSO<sub>4</sub> model 16.9 kcal mol<sup>-1</sup> (11.5 kcal mol<sup>-1</sup> at CCSD(T)/6-31G(d)). However, whereas the UHF reference wavefunctions for **5** and **7** show very little spin contamination, that for **6**<sup>‡</sup> is heavily spin-contaminated ( $\langle S^2 \rangle = 1.392$ ), so that the CCSD and CCSD(T) barriers are likely to be overestimated. The B3LYP  $\langle S^2 \rangle$  for **6**<sup>‡</sup> is 0.771. The reaction is found to be far more exothermic (-36.7 kcal mol<sup>-1</sup>) than that of the uncomplexed radical cation (-4.8 kcal mol<sup>-1</sup>) but of similar exothermicity to the rearrangement of the anion (-34.1 kcal mol<sup>-1</sup> at B3LYP/6-31+G(d)).

### The $\text{SnCl}_2$ -catalysed rearrangement

The  $\text{SnCl}_2$ -catalysed rearrangement of quadricyclane to norbornadiene has been observed in homogeneous methanol solution [21] and at the surface of solid  $\text{SnCl}_2$  [22–24].



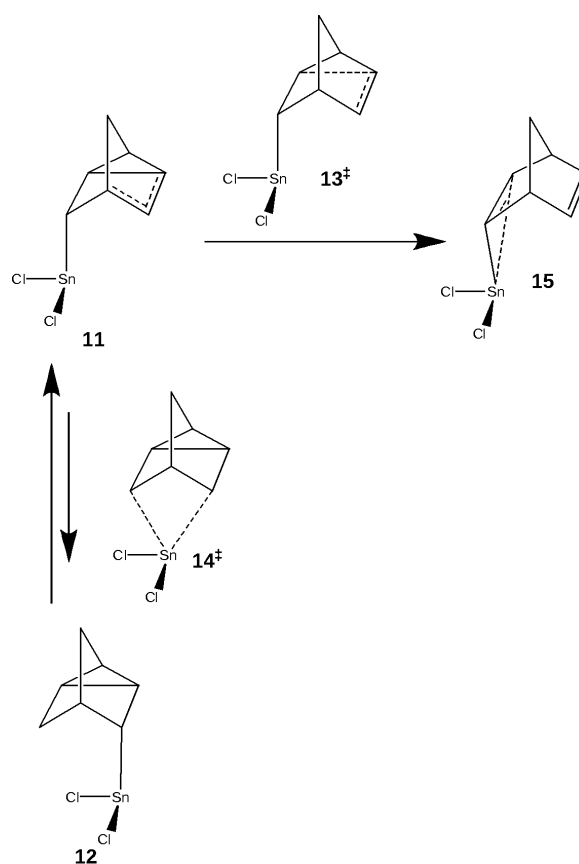
In contrast to the  $\text{CuSO}_4$ -catalysed model reaction, however, that with  $\text{SnCl}_2$  has an even number of electrons, so that the possibility of singlet-triplet two-state reactivity arises [20]. The singlet reaction proceeds from a recognisable quadricyclane complex **8** via transition state **9<sup>‡</sup>** to the unsymmetrical norbornadiene complex **10** (Eq. 2). The triplet reaction is a little more complicated (Scheme 3). We were unable to find a minimum for a quadricyclane complex, but rather found two alternative conformations, **11** and **12**, of a half-open quadricyclane structure analogous to the transition state of the singlet reaction. The product of the rearrangement is the norbornadiene complex **15**, which is connected to **11** by the ring-opening transition state **13<sup>‡</sup>**. **11** and **12** can be interconverted via the transition state **14<sup>‡</sup>**. The energies for **11**–**15** are shown in Table 4.

The  $\text{SnCl}_2$ -catalysed reaction is far more exothermic ( $-26.6 \text{ kcal mol}^{-1}$ ) than that of the uncomplexed radical cation ( $-4.8 \text{ kcal mol}^{-1}$ ) but slightly less so than the anion rearrangement ( $-34.1 \text{ kcal mol}^{-1}$ ). The high complexation energy of the norbornadiene would normally lead to product inhibition of the catalytic reaction, but as the experimental results were obtained in methanol solution, solvation of the Lewis-acidic  $\text{SnCl}_2$  centre should decrease the product complexation energy. The activation energy is calculated to be higher than that found at B3LYP for the  $\text{CuSO}_4$  model, but the agreement between B3LYP, CCSD and CCSD(T)

Table 4. Relative energies ( $E_{\text{rel.}}$ ,  $\text{kcal mol}^{-1}$ , corrected using the unscaled B3LYP/6-31G(d) zero-point vibrational energies, ZPE) and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8\text{-SnCl}_2$  structures **8**–**15**. Total ( $E_{\text{tot.}}$ , Hartree) and zero-point vibrational energies (ZPE,  $\text{kcal mol}^{-1}$ , B3LYP/6-31G(d)) for the  $\text{C}_7\text{H}_8\text{-SnCl}_2$  structures **8**–**15** are given in Table S4 of the Supporting Information.

| Species               | B3LYP/6-31G(d) |                   | CCSD/6-31G(d) <sup>a</sup> |                   | CCSD(T)/6-31G(d) <sup>a</sup> |  |
|-----------------------|----------------|-------------------|----------------------------|-------------------|-------------------------------|--|
|                       | $N_i$          | $E_{\text{rel.}}$ | $E_{\text{rel.}}$          | $E_{\text{rel.}}$ |                               |  |
|                       |                |                   | Singlet                    |                   |                               |  |
| <b>8</b>              | 0              | 0.0               | 0.0                        | 0.0               |                               |  |
| <b>9<sup>‡</sup></b>  | 1              | 16.7              | 19.4                       | 18.1              |                               |  |
| <b>10</b>             | 0              | -23.9             | -25.0                      | -26.6             |                               |  |
|                       |                |                   | Triplet                    |                   |                               |  |
| <b>11</b>             | 0              | 14.7              | 14.5                       | 15.3              |                               |  |
| <b>12</b>             | 0              | 16.0              | 15.2                       | 15.9              |                               |  |
| <b>13<sup>‡</sup></b> | 1              | 23.6              | 26.1                       | 26.3              |                               |  |
| <b>14<sup>‡</sup></b> | 1              | 21.0              | 23.1                       | 23.3              |                               |  |
| <b>15</b>             | 0              | 15.3              | 15.3                       | 15.4              |                               |  |

<sup>a</sup> At the B3LYP/6-31G(d)-optimised geometry.



Scheme 3. Schematic reaction pathway for the triplet reaction.

is good. The energetic results are summarised graphically in Fig. 3, in which the “Reaction Coordinate” axis

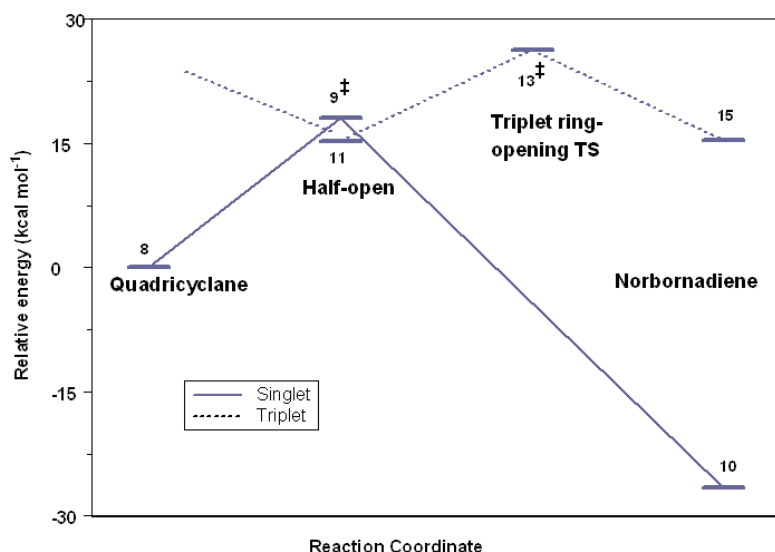


Fig. 3. Schematic reaction profile of the  $\text{SnCl}_2$ -catalysed rearrangement of quadricyclane to norbornadiene. The labels indicate the nature of the stationary points. The energies are given relative to **8** and are those found at the CCSD(T)/6-31G(d)//B3LYP/6-31G(d) level with an unscaled zero-point energy correction calculated at B3LYP/6-31G(d).

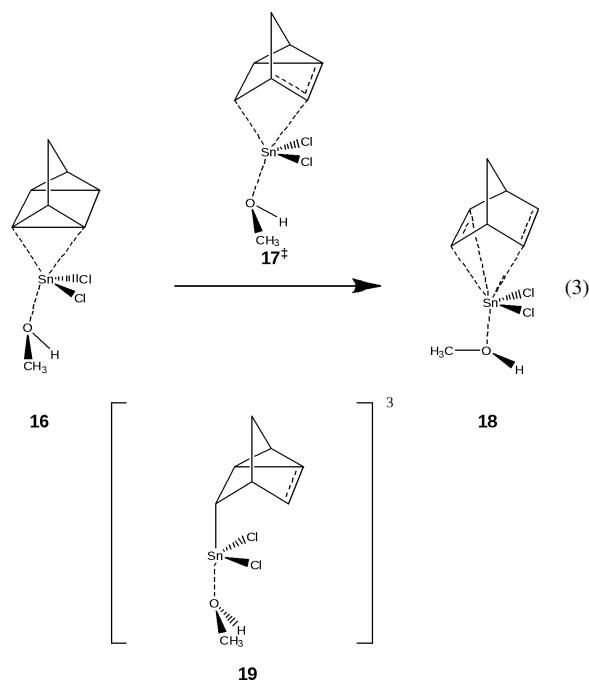
is intended to be descriptive and to define the nature of the stationary points, rather than any specific geometrical parameter.

As expected from the schematic interpretation of electron-transfer catalysis [20], the triplet is calculated to be the ground state at the half-open structure that is the rearrangement transition state for the singlet. In this case, however, the triplet is found to be a minimum. This observation is compatible with the fact that radical cations sometimes adopt geometries equivalent to those of the transition state for a pericyclic reaction of the neutral molecule [31]. The transition state **13**<sup>‡</sup> for opening the second bond in the triplet to give the triplet norbornadiene complex **15** lies significantly higher than the singlet transition state **9**<sup>‡</sup>. However, the lowest-energy path involves two inter-system crossings (ISCs) from the singlet to the triplet in the vicinity of the singlet transition state **9**<sup>‡</sup> and the triplet minimum **11**.

#### The $\text{SnCl}_2$ -catalysed rearrangement solvated by methanol

In order to clarify the role of the methanol solvent in the experimental study [21] of the homogeneous catalysis of the quadricyclane to norbornadiene rearrangement, we used a model in which the species **8**, **9**<sup>‡</sup>, **10**, and **11** are solvated by a methanol molecule to give the three singlet species **16**, **17**<sup>‡</sup> and **18**, and the triplet **19** (Eq. 3).

The effect of the methanol solvent molecule is to stabilise the singlet transition state **17**<sup>‡</sup> far more



strongly than the triplet minimum **19**, so that the two are well separated in energy and no state crossing occurs along the reaction coordinate. A further effect of the solvent is to lower the singlet energy barrier to rearrangement from  $18.1 \text{ kcal mol}^{-1}$  without methanol to only  $6.6 \text{ kcal mol}^{-1}$  when complexed to a single methanol molecule. The heat of reaction ( $-25.3 \text{ kcal mol}^{-1}$ ) is hardly affected by complexation to methanol (Table 5). Note, however, that neither the unperturbed

Table 5. Relative energies ( $E_{\text{rel.}}$ , kcal mol<sup>-1</sup>, corrected using the unscaled B3LYP/6-31G(d) zero-point vibrational energies, ZPE) and number of imaginary vibrations ( $N_i$ ) for the C<sub>7</sub>H<sub>8</sub>-SnCl<sub>2</sub>(CH<sub>3</sub>OH) structures **16**–**19**. Total ( $E_{\text{tot.}}$ , Hartree) and zero-point vibrational energies (ZPE, kcal mol<sup>-1</sup>, B3LYP/6-31G(d)) for the C<sub>7</sub>H<sub>8</sub>-SnCl<sub>2</sub>(CH<sub>3</sub>OH) structures **16**–**19** are given in Table S4 of the Supporting Information.

| Species               | B3LYP/6-31G(d)<br>$N_i$ | B3LYP/6-31G(d)<br>$E_{\text{rel.}}$ | CCSD/6-31G(d) <sup>a</sup><br>$E_{\text{rel.}}$ | CCSD(T)/6-31G(d) <sup>a</sup><br>$E_{\text{rel.}}$ |
|-----------------------|-------------------------|-------------------------------------|---|--|
|                       |                         |                                     | Singlet   |  |
| <b>16</b>             | 0                       | 0.0                                 | 0.0   | 0.0  |
| <b>17<sup>‡</sup></b> | 1                       | 7.6                                 | 13.2  | 6.6  |
| <b>18</b>             | 0                       | -22.3                               | -23.6   | -25.3  |
|                       |                         |                                     | Triplet   |  |
| <b>19</b>             | 0                       | 22.2                                | 22.9  | 23.1   |

<sup>a</sup> Using the B3LYP/6-31G(d)-optimised geometry.

reaction nor that with a single methanol molecule can be compared to the experimental system in methanol solution. As emphasised in the introduction, our purpose is to determine mechanistic features and alternatives based on model systems, not to reproduce experimental results.

## Discussion

Fig. 4 shows the calculated (UB3LYP) spin densities for **5**, **6<sup>‡</sup>**, and **7**. We use both spin densities and atomic charges, because the latter have been shown [32] not to reveal electron transfer in transition-metal complexes, whereas the calculated spin density gives a detailed and accurate picture of the electronic features of reactants, transition states and products. Table 6 shows the calculated NBO [33, 34] charges for the species described above.

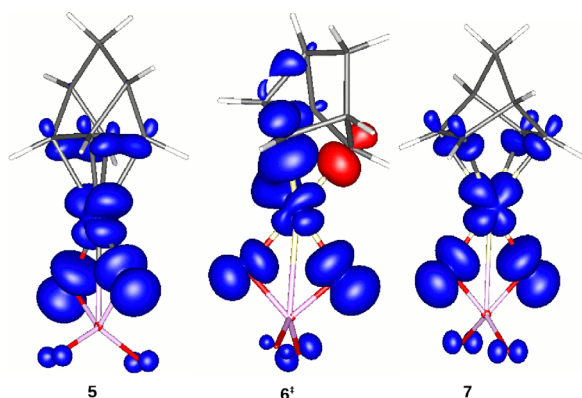
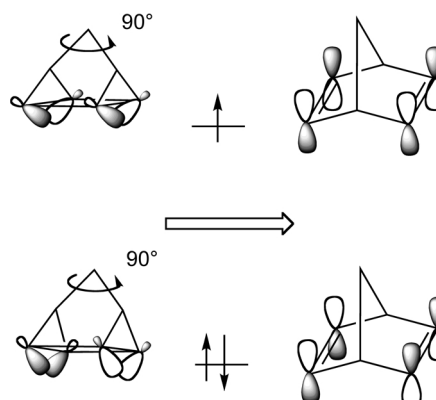


Fig. 4. Calculated spin densities for the C<sub>7</sub>H<sub>8</sub>-CuSO<sub>4</sub> species **5**, **6<sup>‡</sup>**, and **7**. Blue indicates positive ( $\alpha$ ) spin density and red negative ( $\beta$ ) (colour online).

Table 6. Calculated sum of the NBO charges for the C<sub>7</sub>H<sub>8</sub>-moiety for species **5**–**11**.

| Species                               | B3LYP/6-31G(d) |              | HF/6-31G(d) |              |
|---------------------------------------|----------------|--------------|-------------|--------------|
|                                       | Charge         | Spin density | Charge      | Spin density |
| CuSO <sub>4</sub> -catalysed reaction |                |              |             |              |
| <b>5</b>                              | 0.01           | 0.09         | 0.025       | 0.03         |
| <b>6<sup>‡</sup></b>                  | -0.13          | 0.14         | 0.04        | 0.02         |
| <b>7</b>                              | -0.01          | 0.1          | 0.07        | 0.04         |
| SnCl <sub>2</sub> -catalysed reaction |                |              |             |              |
| <b>8</b>                              | 0.05           |              | 0.03        |              |
| <b>9<sup>‡</sup></b>                  | 0.20           |              | 0.22        |              |
| <b>10</b>                             | 0.09           |              | 0.08        |              |
| <b>311</b>                            | -0.32          | 1.28         | -0.36       | 1.32         |

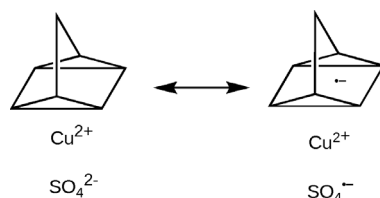


Scheme 4. Schematic orbital-interaction diagram for the three-electron interaction between the copper atom and the C<sub>7</sub>H<sub>8</sub> moiety. The hydrocarbon fragment rotates by 90° on going from quadricyclane (left) to norbornadiene (right).

As expected, the indicated charge transfer is small. Interestingly, however, it occurs in different directions for the two reactions. In the CuSO<sub>4</sub>-complexed transition state **6<sup>‡</sup>**, 0.13 electrons are transferred to the C<sub>7</sub>H<sub>8</sub> moiety by the metal salt and in its SnCl<sub>2</sub>-complexed counterpart **9<sup>‡</sup>** 0.2 electrons in the opposite direction. The triplet minimum that corresponds to the singlet transition state for the latter reaction, **11**, also involves electron transfer from the metal salt to the hydrocarbon (charge on the C<sub>7</sub>H<sub>8</sub> moiety = -0.32).

Fig. 4 illustrates the contribution of the relatively small amount of electron-transfer catalysis. In **5** and **7**, the spin is slightly delocalised onto the C<sub>7</sub>H<sub>8</sub> moiety, but is mostly centred on the copper atom and the two sulphate oxygens directly complexed to it. The three-electron interaction [35] between the singly occupied  $d$  orbital of the copper atom and the unsymmetrical combination of two Walsh orbitals in **5** and two  $\pi$  orbitals of the double bonds in **7** can be seen clearly and is illustrated in Scheme 4.

This interaction results in the rotation of the  $C_7H_8$  moiety by  $90^\circ$  relative to the  $CuSO_4$  unit between the two structures. At the transition state  $6^\ddagger$ , 13% of the spin density has been shifted to the hydrocarbon, indicating some electron-transfer catalysis. This transfer is relatively small, and the strong interaction of the copper atom with  $C_2$  indicates some covalent assistance of the reaction by intermediate formation of a  $C_2-Cu$  bond. Note that the resonance formulation of three-electron bonds [35, 36] is equivalent to the one-electron reduction of the hydrocarbon by the  $CuSO_4$  unit in which the  $Cu^{II}$  ion intervenes between two radical species and can enter into odd-electron bonding with both:



The course of the reaction can thus be described very well as a slight shift of the weights of the two resonance structures from the left to the right as the transition state is approached and back again as the product is formed. The additional covalent participation of the copper atom reduces the B3LYP barrier below that found for the pure radical-cation reaction.

The  $SnCl_2$ -catalysed reaction introduces the possibility of two-state reactivity (TSR) [37] for the rearrangement. In this case, two possible mechanisms, one closed-shell and one involving electron-transfer catalysis and a switch of multiplicity, can be identified. In the absence of solvent, the electron-transfer path *via* the triplet intermediate **11** is favoured slightly over the closed-shell path *via* transition state  $13^\ddagger$ . The B3LYP calculated spin-density for  $13^\ddagger$  is shown in Fig. 5. In this case, there is considerable spin on the  $C_7H_8$  moiety, indicating that one electron has been transferred from the hydrocarbon to the  $SnCl_2$  (*i. e.* in the reverse direction to that found for  $CuSO_4$ ). Thus,  $13^\ddagger$  can be described as a spin-separated triplet complex of  $SnCl_2^{\cdot -}$  and  $C_7H_8^{\cdot +}$ . The closed-shell mechanism *via*  $17^\ddagger$  involves a far more traditional formal two-electron oxidation of the Sn atom in the transition state.

Perhaps not surprisingly, the inclusion of a methanol solvent molecule in the calculations favours the polar, closed-shell mechanism, which at least formally involves a two-electron charge shift, by preferential sol-

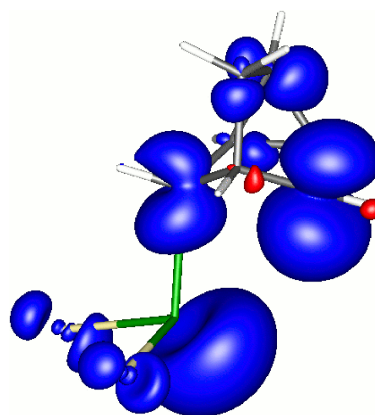


Fig. 5. Calculated spin density for the triplet  $C_7H_8-SnCl_2$  species  $13^\ddagger$ . Blue indicates positive ( $\alpha$ ) spin density and red negative ( $\beta$ ) (colour online).

vation of the tin ion in the transition state  $17^\ddagger$ . Thus, the triplet intermediate **18** is no longer competitive in energy with the closed-shell transition state. This sort of situation, in which a reagent can react alternatively as a one-electron oxidant or as a “two-electron” Lewis acid, is common. However, the direct effect of a single methanol molecule on the mechanism in this case is unusually clear. Patrick and Bechtold [21] proposed what our calculations suggest to be the correct mechanism involving a formal  $Sn(IV)$  structure in methanol solution. Note once more that neither model reaction should reproduce the experimental activation energy, although the model without methanol gives coincidental agreement with experiment.

## Conclusions

The gas-phase calculations show clearly that the quadricyclane to norbornadiene rearrangement can be catalysed by electron transfer from the hydrocarbon to a metal centre. The geometries of the intermediates and transition states, the calculated spin densities and the singlet-triplet two-state reactivity found for the  $SnCl_2$ -catalysed reaction are all consistent with this interpretation. However, inclusion of a single solvent methanol molecule is enough to change the mechanism of the  $SnCl_2$ -catalysed rearrangement to a closed-shell Lewis acid-base process.

## Experimental Section

All calculations on isolated species used the program suite GAUSSIAN09 [38]. Geometries were optimised using density functional theory with the Becke-3-Parameter/Lee-



Yang-Parr hybrid functional [39,40] as implemented in GAUSSIAN09, with a second-order Møller-Plesset correction (MP2) [41] for electron correlation based on the UHF wavefunction and with coupled-cluster theory with single and double excitations (CCSD) [42], also based on the UHF wavefunction. Single-point coupled-cluster calculations with a perturbational correction for triple excitations (CCSD(T)) [43] were performed on the CCSD-optimised geometries. Structures were confirmed as minima, transition states or hilltops by calculating their normal vibrations within the harmonic approximation either at the B3LYP or MP2 levels of theory. The 6-31G(d) [44], 6-311+G(d,p) [45] and cc-pVTZ [46] basis sets were used. For the “6-31G(d)” calculations on Sn-containing species, the Schaefer-Horn-Ahlrichs split-valence basis set [47] with additional polarisation functions was used for Sn as there is no 6-31G(d) basis set for this element.

#### Supporting information

Tables with the total energies, zero-point vibrational energies, and numbers of imaginary vibrations for the  $C_7H_8^{+\bullet}$  structures  $1^{+\bullet}$ – $3^{\ddagger+\bullet}$ , the  $C_7H_8^{-\bullet}$  structures  $1^{-\bullet}$ – $3^{\ddagger-\bullet}$ , the  $C_7H_8$ -CuSO<sub>4</sub> structures **5**–**7**, and the  $C_7H_8$ -SnCl<sub>2</sub> structures **8**–**19**, and Gaussian03/09 Archive entries for all isolated species are provided as Supporting Information online only (<http://www.znaturforsch.com/ab/v65b/c65b.htm>).

#### Acknowledgement

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# **Electron-Transfer Catalysis of the Quadricyclane to Norbornadiene Rearrangement**

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## **SUPPORTING INFORMATION**

- 1. Tables**
- 2. Gaussian03/09 Archive entries for all isolated species**

**Table S1:** Total ( $E_{\text{Tot.}}$ , Hartree), zero-point vibrational energies (ZPE, MP2/6-31G(d)) and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8^{+}$  structures **1<sup>+</sup>**–**3<sup>+</sup>**.

| Species              | MP2/6-31G(d)      |      |       | CCSD/6-31G(d)     | CCSD/6-311+G(d,p) | CCSD(T)/cc-pVTZ <sup>a</sup> |
|----------------------|-------------------|------|-------|-------------------|-------------------|------------------------------|
|                      | $E_{\text{Tot.}}$ | ZPE  | $N_i$ | $E_{\text{Tot.}}$ | $E_{\text{Tot.}}$ | $E_{\text{Tot.}}$            |
| <b>1<sup>+</sup></b> | -270.25676        | 82.0 | 0     | -270.30424        | -270.44763        | -270.66135                   |
| <b>3<sup>+</sup></b> | -270.23094        | 80.6 | 1     | -270.28485        | -270.42957        | -270.64152                   |
| <b>2<sup>+</sup></b> | -270.26592        | 84.3 | 0     | -270.31605        | -270.46003        | -270.67267                   |

<sup>a</sup> Using the CCSD/6-311+G(d,p)-optimized geometry

**Table S2:** Total ( $E_{\text{Tot}}$ , Hartree), zero-point vibrational energies (ZPE, MP2/6-31G(d) and B3LYP/6-31G(d)) and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8^+$  structures **1<sup>+</sup>**–**3<sup>+</sup>**.

| Species              | MP2/6–31+G(d)    |      |       | ROMP2/6–31+G(d)  | B3LYP/6–31+G(d)  |      |
|----------------------|------------------|------|-------|------------------|------------------|------|
|                      | $E_{\text{Tot}}$ | ZPE  | $N_i$ | $E_{\text{Tot}}$ | $E_{\text{Tot}}$ | ZPE  |
| <b>1<sup>+</sup></b> | -270.46920       | 81.1 | 0     | -270.46909       | -271.40143       | 79.3 |
| <b>3<sup>+</sup></b> | -270.43510       | 79.5 | 1     | -270.46107       | -271.38432       | 77.6 |
| <b>2<sup>+</sup></b> | -270.51996       | 82.2 | 0     | -270.49231       | -271.45207       | 76.9 |

<sup>a</sup> Using the MP2/6–31+G(d)-optimized geometry

**Table S3:** Total ( $E_{\text{Tot.}}$ , Hartree), zero-point vibrational (ZPE, B3LYP/6-31G(d)) energies and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8\text{-CuSO}_4$  structures **5–7**.

| Species              | B3LYP/6-31G(d)    |      |       | CCSD/6-31G(d) <sup>a</sup> | CCSD(T)/6-31G(d) <sup>a</sup> |
|----------------------|-------------------|------|-------|----------------------------|-------------------------------|
|                      | $E_{\text{Tot.}}$ | ZPE  | $N_i$ | $E_{\text{Tot.}}$          | $E_{\text{Tot.}}$             |
| <b>5</b>             | -2610.77238       | 92.5 | 0     | -2607.27691                | -2607.35791                   |
| <b>6<sup>‡</sup></b> | -2610.76671       | 91.8 | 1     | -2607.24894                | -2607.33843                   |
| <b>7</b>             | -2610.83165       | 92.9 | 0     | -2607.33301                | -2607.41701                   |

<sup>a</sup> At the B3LYP/6-31G(d)-optimized geometry

**Table S4:** Total ( $E_{\text{Tot.}}$ , Hartree), zero-point vibrational (ZPE, B3LYP/6-31G(d)) energies and number of imaginary vibrations ( $N_i$ ) for the  $\text{C}_7\text{H}_8\text{-SnCl}_2$  structures **8–15** and the  $\text{C}_7\text{H}_8\text{-SnCl}_2(\text{CH}_3\text{OH})$  structures **16–19**.

| Species               | B3LYP/6-31G(d)    |       |       | CCSD/6-31G(d) <sup>a</sup> | CCSD(T)/6-31G(d) <sup>a</sup> |
|-----------------------|-------------------|-------|-------|----------------------------|-------------------------------|
|                       | $E_{\text{Tot.}}$ | ZPE   | $N_i$ | $E_{\text{Tot.}}$          | $E_{\text{Tot.}}$             |
| <b>Singlet</b>        |                   |       |       |                            |                               |
| <b>8</b>              | -1195.33260       | 82.5  | 0     | -1193.25787                | -1193.30749                   |
| <b>9<sup>‡</sup></b>  | -1195.30468       | 81.7  | 1     | -1193.22568                | -1193.27743                   |
| <b>10</b>             | -1195.37152       | 83.0  | 0     | -1193.29854                | -1193.35065                   |
| <b>Triplet</b>        |                   |       |       |                            |                               |
| <b>11</b>             | -1195.30838       | 82.0  | 0     | -1193.23403                | -1193.28235                   |
| <b>12</b>             | -1195.30636       | 82.0  | 0     | -1193.23287                | -1193.28140                   |
| <b>13<sup>‡</sup></b> | -1195.29226       | 80.8  | 1     | -1193.21350                | -1193.26368                   |
| <b>14<sup>‡</sup></b> | -1195.29750       | 81.5  | 1     | -1193.21946                | -1193.26881                   |
| <b>15</b>             | -1195.30664       | 81.5  | 0     | -1193.23189                | -1193.28138                   |
| <b>Singlet</b>        |                   |       |       |                            |                               |
| <b>16</b>             | -1311.07473       | 116.2 | 0     | -1308.65571                | -1308.71189                   |
| <b>17<sup>‡</sup></b> | -1311.06129       | 115.4 | 1     | -1308.63334                | -1308.70009                   |
| <b>18</b>             | -1311.11068       | 116.5 | 0     | -1308.69381                | -1308.75266                   |
| <b>Triplet</b>        |                   |       |       |                            |                               |
| <b>19</b>             | -1311.03789       | 115.3 | 0     | -1308.61778                | -1308.67357                   |

<sup>a</sup> At the B3LYP/6-31G(d)-optimized geometry

1<sup>+</sup>

1\1\FAU-CCC-DERIOCI\FOPT\UMP2-FC\6-31G(D)\C7H8(1+,2)\CLARK\22-Sep-1996\1\# UMP  
2/6-31G\* OPT=Z-MATRIX NAME=CLARK\Quadricyclane+. \|1,2\X\C,1,B1\C,1,B2,2,90.\C,  
1,B1,3,90.,2,180.,0\X,1,B3,2,90.,3,180.,0\X,5,B4,1,90.,2,0.,0\X,5,B4,1,90.,2,18  
0.,0\C,6,B5,5,90.,1,90.,0\C,6,B5,5,90.,1,-90.,0\C,7,B5,5,90.,1,-90.,0\C,7,B5,5,  
90.,1,90.,0\H,3,B6,1,A1,2,-90.,0\H,3,B6,1,A1,2,90.,0\H,4,B7,3,A2,1,180.,0\H,2,B  
7,3,A2,1,180.,0\H,8,B8,9,A3,2,D1,0\H,9,B8,8,A3,2,-D1,0\H,10,B8,11,A3,4,-D1,0\H,  
11,B8,10,A3,4,D1,0\B1=1.1511714\B2=0.99763466\B3=1.17284259\B4=0.73866498\B5=0  
.83478193\B6=1.09377432\B7=1.0863907\B8=1.08490218\A1=125.12739609\A2=123.56488  
068\A3=120.25845219\D1=-116.5921589\Version=Convex-Unix-G94RevC.3\State=2-B2\H  
F=-269.3769631\MP2=-270.2567644\PUHF=-269.380478\PMP2-0=-270.2590748\S2=0.768\S  
2-1=0.756\S2A=0.75\RMSD=3.134e-09\RMSF=1.452e-05\Dipole=-0.6235283,0.,0.\PG=C02  
V [C2(C1),SGV(C2H2),SGV'(H2),X(C4H4)]\@

2<sup>+</sup>

1\1\FAU-CCC-DERIOCI\FOPT\UMP2-FC\6-31G(D)\C7H8(1+,2)\CLARK\21-Sep-1996\1\# UMP  
2/6-31G\* OPT=Z-MATRIX NAME=CLARK\Norbornadien+. C2v\|1,2\X\X,1,r1\C,2,r2,1,a2  
\X,2,r1,3,a2,1,180.,0\C,1,r3,2,90.,3,90.,0\C,1,r3,2,90.,3,-90.,0\C,2,r4,1,90.,3  
,90.,0\C,2,r4,1,90.,3,-90.,0\C,4,r3,2,90.,1,90.,0\C,4,r3,2,90.,1,-90.,0\H,3,r5,  
2,a3,1,0.,0\H,3,r5,2,a3,1,180.,0\H,5,r6,1,a4,2,d1,0\H,6,r6,1,a4,2,-d1,0\H,7,r7,  
2,a5,3,0.,0\H,8,r7,2,a5,3,0.,0\H,9,r6,4,a4,2,-d1,0\H,10,r6,4,a4,2,d1,0\|r1=1.44  
980932\|r2=1.04544028\|r3=0.69221917\|r4=1.1366422\|r5=1.09475717\|r6=1.08623373\|r7=  
1.08860706\|a2=129.07613044\|a3=124.84689879\|a4=127.0531941\|a5=162.69900447\|d1=17  
4.68935816\Version=Convex-Unix-G94RevC.3\State=2-B1\HF=-269.3939563\MP2=-270.2  
659177\PUHF=-269.39667\PMP2-0=-270.2674152\S2=0.761\S2-1=0.751\S2A=0.75\RMSD=4.  
046e-09\RMSF=3.381e-05\Dipole=-0.4530443,0.,-0.3678658\PG=C02V [C2(C1),SGV(C2H2  
,SGV'(H2),X(C4H4)]\@

3<sup>+</sup>‡

1\1\FAU-CCC-DERIOCI\FTS\UMP2-FC\6-31G(D)\C7H8(1+,2)\CLARK\20-Jul-1996\1\# UMP2  
/6-31G\* NAME=CLARK OPT=(Z-MATRIX,TS,READCARTESIANFC)\quadricyclane+. -> norbor  
nadiene+. transition state\|1,2\C\C,1,x1\C,2,r1,1,a1\C,3,x2,2,a2,1,d2,0\C,1,r3,  
2,a3,3,d3,0\C,4,r4,3,a4,2,d4,0\C,6,r5,4,a5,3,d5,0\H,7,r6,6,a6,5,d6,0\H,7,r7,6,a  
7,5,d7,0\H,5,r8,7,a8,6,d8,0\H,6,r9,7,a9,5,d9,0\H,1,r10,5,a10,10,d10,0\H,2,r11,5  
,a11,10,d11,0\H,3,r12,6,a12,11,d12,0\H,4,r13,6,a13,11,d13,0\|r1=1.4815937\|a1=10  
3.57650283\|a2=75.36696725\|d2=-4.0525947\|r3=1.51900488\|a3=53.70089201\|d3=-104.35  
074768\|r4=1.4942922\|a4=47.59251885\|d4=119.22711334\|r5=1.53758256\|a5=103.6318959  
2\|d5=-103.10198668\|r6=1.09333412\|r7=1.09360615\|a6=111.85944555\|a7=112.75703969\  
d6=117.48073272\|d7=-117.90039144\|r8=1.08608062\|a8=123.86616985\|d8=178.97319363\  
r9=1.08728501\|a9=120.80585319\|d9=176.4000767\|r10=1.08281335\|r11=1.08689327\|r12=  
1.08287186\|r13=1.0897975\|a10=127.45932951\|a11=124.03767903\|a12=126.47225807\|a13  
=124.72181191\|d10=-15.3350366\|d11=14.74859689\|d12=-29.86437012\|d13=23.48776685\  
x1=1.73209959\|x2=2.05105665\Version=HP-PARisc-HPUX-G94RevC.3\HF=-269.3707684\M  
P2=-270.2309368\PUHF=-269.3773717\PMP2-0=-270.2358634\S2=0.8\S2-1=0.774\S2A=0.7  
51\RMSD=9.029e-09\RMSF=3.492e-05\Dipole=-0.0683691,-0.7288567,-0.3174191\PG=C01  
[X(C7H8)]\@

1<sup>-</sup>

1\1\KPI-N027\Freq\UB3LYP\6-31+G(d)\C7H8(1-,2)\CLARK\04-Nov-2009\0\#N  
Geom=AllCheck Guess=Read SCRF=Check GenChk UB3LYP/6-31+G(d) Freq\QUAD  
RICYCLANE-. \|1,2\C,-0.0030929142,0.,1.1516668073\C,0.9888634014,0.,0.  
\C,-0.0030929142,0.,-1.1516668073\C,-1.260954838,0.7642643024,0.774568  
3426\C,-1.260954838,-0.7642643024,0.7745683426\C,-1.260954838,0.764264  
3024,-0.7745683426\C,-1.260954838,-0.7642643024,-0.7745683426\H,1.6240



188426,0.8966308386,0.\H,1.6240188426,-0.8966308386,0.\H,0.3267043993,  
0.,-2.1884516248\H,0.3267043993,0.,2.1884516248\H,-1.771240522,1.47111  
00908,1.4198385218\H,-1.771240522,-1.4711100908,1.4198385218\H,-1.7712  
40522,1.4711100908,-1.4198385218\H,-1.771240522,-1.4711100908,-1.41983  
85218\Version=AM64L-G03RevD.02\State=2-B1\HF=-271.40143\S2=0.750151\S  
2-1=0.\S2A=0.75\RMSD=2.526e-09\RMSF=1.722e-05\ZeroPoint=0.1263332\Ther  
mal=0.1311782\Dipole=0.8799244,0.,0.\DipoleDeriv=-0.0720647,0.0000006,  
2.0457403,-0.2260964,0.0082321,0.2932414,0.0682442\Polar=285.4533206,0  
.0001061,4475.7346476,0.0000821,-0.0003508,1196.4606021\PG=C02V [C2(C1  
) ,SGV(C2H2),SGV(H2),X(C4H4)]\NImag=0\0.50172180,0.,0.23290965,0.0760  
475,0.12238293,0.15793971\0.00003550,0.,0.00002452,-0.00001555,0.,0.,  
0000730,-0.00001656,0.00001345,0.00000730,-0.00001656\@

1\1\KPI-N025\Freq\UMP2-FC\6-31+G(d)\C7H8(1-,2)\CLARK\03-Nov-2009\0\#N  
Geom=AllCheck Guess=Read SCRF=Check GenChk UMP2(FC)/6-31+G(d) Freq\Q  
UADRICYCLANE-.\-1,2\C,-0.0031983025,0.,1.1466081125\C,0.9843988573,0.  
,0.\C,-0.0031983025,0.,-1.1466081125\C,-1.2559368141,0.7650310468,0.77  
04379014\C,-1.2559368141,-0.7650310468,0.7704379014\C,-1.2559368141,0.  
7650310468,-0.7704379014\C,-1.2559368141,-0.7650310468,-0.7704379014\H  
,1.6142825876,0.8985431082,0.\H,1.6142825876,-0.8985431082,0.\H,0.3194  
427657,0.,-2.186319829\H,0.3194427657,0.,2.186319829\H,-1.7665907741,1  
.4674992426,1.4206356408\H,-1.7665907741,-1.4674992426,1.4206356408\H,  
-1.7665907741,1.4674992426,-1.4206356408\H,-1.7665907741,-1.4674992426  
,-1.4206356408\Version=AM64L-G03RevD.02\State=2-B1\HF=-269.5432186\MP  
2=-270.4691592\PUHF=-269.5432991\PMP2-0=-270.4691991\S2=0.750604\S2-1=  
0.749996\S2A=0.75\RMSD=6.191e-10\RMSF=5.535e-05\ZeroPoint=0.1292114\Th  
ermal=0.133821\Dipole=0.7381224,0.,0.\DipoleDeriv=-0.0842398,0.0000003  
272645,-0.3511564,0.0159056,-1.1023631,-0.2015653\Polar=278.3964761,0.  
0000004,-2979.1540233,0.0000041,0.0000091,581.9592482\PG=C02V [C2(C1),  
SGV(C2H2),SGV(H2),X(C4H4)]\NImag=0\0.52658863,0.,0.24435420,0.073653  
304,0.09420958,0.12622635,0.16479914\0.00015147,0.,0.00004355,0.0000  
0003198,0.00006546,0.00000493,0.00003198,-0.00006546,0.00000493\@

2<sup>-</sup>

1\1\KPI-N021\Freq\UB3LYP\6-31+G(d)\C7H8(1-,2)\CLARK\04-Nov-2009\0\#N  
Geom=AllCheck Guess=Read SCRF=Check GenChk UB3LYP/6-31+G(d) Freq\NORB  
ORNADIEN-., C2V\|-1,2\C,0.8152992349,0.,2.1118212465\C,0.1190653519,-0  
.6934249346,-0.0372208805\C,0.1190653519,0.6934249346,-0.0372208805\C,  
-0.0175299592,1.1281526139,1.4355752308\C,-0.0175299592,-1.1281526139,  
1.4355752308\C,-1.4309059981,-0.6934249346,1.8716426991\C,-1.430905998  
1,0.6934249346,1.8716426991\H,1.8681907689,0.,1.8018564013\H,0.7281084  
977,0.,3.2059220476\H,-0.1617329845,-1.3412361227,-0.870048187\H,-0.16  
17329845,1.3412361227,-0.870048187\H,0.2639070113,2.1639725605,1.66409  
82356\H,0.2639070113,-2.1639725605,1.6640982356\H,-2.3036424524,-1.341  
2361227,1.767815393\H,-2.3036424524,1.3412361227,1.767815393\Version=  
AM64L-G03RevD.02\State=2-B2\HF=-271.4520668\S2=0.75422\S2-1=0.\S2A=0.7  
50014\RMSD=2.395e-09\RMSF=1.267e-04\ZeroPoint=0.122612\Thermal=0.12805  
37\Dipole=0.4005411,0.,0.3252339\DipoleDeriv=0.1073936,0.0000005,-0.12  
376391,0.0618094,-0.0467567,0.0891789,0.3975384\Polar=150.919483,-0.00  
00014,172.7321502,-20.6080364,-0.0000005,159.5658107\PG=C02V [C2(C1),S  
GV(C2H2),SGV(H2),X(C4H4)]\NImag=0\0.57500907,0.,0.32092773,-0.045319  
0.00276344,0.01620968,-0.01947656,0.01421914\0.00007676,0.,-0.000062  
0000028,0.00002015,-0.00008162,-0.00000028\@

1\1\KPI-N021\Freq\UMP2-FC\6-31+G(d)\C7H8(1-,2)\CLARK\03-Nov-2009\0\#N  
Geom=AllCheck Guess=Read SCRF=Check GenChk UMP2(FC)/6-31+G(d) Freq\N  
ORBORNADIEN-., C2V\|-1,2\C,0.8080025516,0.,2.1058964386\C,0.1182426893  
,-0.695482234,-0.0288293684\C,0.1182426893,0.695482234,-0.0288293684\C  
,-0.0178006658,1.1244154877,1.4353554207\C,-0.0178006658,-1.1244154877  
,1.4353554207\C,-1.4228621554,-0.695482234,1.8691146874\C,-1.422862155

4,0.695482234,1.8691146874\H,1.8598753195,0.,1.7924291435\H,0.71717481  
39,0.,3.1997192702\H,-0.1637749538,-1.3452459192,-0.862156957\H,-0.163  
7749538,1.3452459192,-0.862156957\H,0.2649675349,2.15969312,1.66495936  
64\H,0.2649675349,-2.15969312,1.6649593664\H,-2.2963385719,-1.34524591  
92,1.7641967636\H,-2.2963385719,1.3452459192,1.7641967636\Version=AM6  
4L-G03RevD.02\State=2-B2\HF=-269.5715664\MP2=-270.5179483\PUHF=-269.57  
46083\PMP2-0=-270.5199628\S2=0.770583\S2-1=0.756541\S2A=0.750342\RM  
SD=1.618e-09\RMSF=8.299e-05\ZeroPoint=0.1310751\Thermal=0.1360177\Dipole=  
0.4658018,0.,0.3782247\DipoleDeriv=0.2333283,0.000003,-0.2893996,0.000  
3677,0.4576395,1.2289329,1.6137038,-1.0658815\Polar=-36.3622755,-0.000  
0072,-1313.3069977,228.2864872,0.0000759,-132.1424201\PG=C02V [C2(C1),  
SGV(C2H2),SGV(H2),X(C4H4)]\NImag=0\0.60121990,0.,0.34864314,-0.04139  
361,0.01564014,-0.02210590,0.02500152\0.00003723,0.,0.00003023,-0.000  
0679,0.00000962,0.00002431,0.00000679\@\@

3-\*

1\1\KPI-N025\Freq\UB3LYP\6-31+G(d)\C7H8(1-,2)\CLARK\04-Nov-2009\0\#P  
Geom=AllCheck Guess=Read SCRF=Check GenChk UB3LYP/6-31+G(d) Freq\QUAD  
RICYCLANE-. -> NORBORNADIENE-. TRANSITION STATE\|-1,2\C,1.0192103795,-  
0.4516190376,0.7019537891\C,0.9094945578,-0.4826798038,-0.8096044667\C  
,-0.5779815796,-0.8545057481,-0.8745953706\C,-0.4422205194,-0.81612507  
88,0.9959138483\C,0.9265402643,0.8560705921,-0.0782436571\C,-1.2396364  
037,0.0722483703,0.0949977981\C,-0.4919559914,1.4102469858,0.013452859  
7\H,-0.7768068701,1.9826355105,-0.8802329308\H,-0.646356883,2.01899606  
87,0.9151546231\H,1.7946201594,1.5079249086,-0.154603973\H,-2.32689714  
12,0.07364959,0.1741689215\H,1.8581731146,-0.7123483896,1.3414840291\H  
,1.6482135449,-0.7719585691,-1.5521663308\H,-0.9939438568,-1.770465003  
9,-1.2668778394\H,-0.7948172604,-1.7135988473,1.4818524281\Version=AM  
64L-G03RevD.02\State=2-A\HF=-271.3843163\S2=0.751214\S2-1=0.\S2A=0.750  
001\RM  
SD=5.581e-09\RMSF=1.681e-05\ZeroPoint=0.1237012\Thermal=0.128659  
7\Dipole=-0.314158,0.5999843,-0.0368358\DipoleDeriv=-0.6474129,-0.02613  
,-0.0242356,0.0036417,-0.7509916,-0.132065,0.0436304,-0.4057626\Polar=  
487.92152,59.2652079,200.6699498,61.2654966,19.637024,1345.968376\PG=C  
01 [X(C7H8)]\NImag=1\0.57721268,-0.05249946,0.28957428,0.15918063,-0.  
91528,0.08496945\0.00001649,0.00002763,0.00001207,-0.00000009,0.00000  
.00000410,0.00000119,-0.00001778,0.00000341\@\@

1\1\KPI-N021\Freq\UMP2-FC\6-31+G(d)\C7H8(1-,2)\CLARK\04-Nov-2009\0\#P  
Geom=AllCheck Guess=Read SCRF=Check GenChk UMP2(FC)/6-31+G(d) Freq\Q  
UADRICYCLANE-. -> NORBORNADIENE-. TRANSITION STATE\|-1,2\C,1.006440608  
9,-0.4561909338,0.6987541464\C,0.8883657013,-0.4750774477,-0.803941254  
1\C,-0.6089572305,-0.801622858,-0.9498856593\C,-0.4509784219,-0.779819  
4784,1.0078283518\C,0.9229848352,0.8520204896,-0.0763739718\C,-1.23427  
85931,0.0837605744,0.1014384429\C,-0.4873364216,1.4110218796,0.0189576  
38\H,-0.7756159436,1.9646379089,-0.8817870992\H,-0.6377354798,2.022523  
3111,0.9189317672\H,1.7992948848,1.4921414582,-0.1603960552\H,-2.32258  
77149,0.0951251944,0.172840809\H,1.8464045712,-0.7253018156,1.33508502  
35\H,1.6385944369,-0.7507487948,-1.5370362395\H,-0.9308628186,-1.82780  
29522,-1.082508992\H,-0.7880968995,-1.7561949882,1.3407468214\Version  
=AM64L-G03RevD.02\State=2-A\HF=-269.5187384\MP2=-270.4184928\PUHF=-269  
.5362273\PMP2-0=-270.4351029\S2=1.358533\S2-1=1.295608\S2A=0.779422\RM  
SD=5.274e-09\RMSF=8.020e-05\ZeroPoint=0.1267675\Thermal=0.1314704\Dipo  
le=0.5438088,0.0769092,2.2694768\DipoleDeriv=-4.4910144,-0.0398858,-2.  
-0.7056546,-1.2198767,-0.1591492,0.3665677,0.7689586\Polar=-5959.19570  
44,373.9711335,-867.4890875,1541.7458873,207.0568036,578.836125\PG=C01  
[X(C7H8)]\NImag=1\0.60245824,-0.05581911,0.30092645,0.14716392,-0.15  
94,-0.02640487,-0.10366555,0.05605429\0.00002109,0.00011103,-0.000354  
002297,-0.00001627,0.00000472,0.00002426,-0.00000514,-0.00005540\@\@

5

1\1\FAU-CCC-TCDA04\FOpt\UB3LYP\6-31G(d)\C7H8Cu1O4S1(2)\CLARK\23-Oct-2003\0\# B3LYP/6-31G\* OPT NAME=CLARK SCF=QC\Quadricyclane : Cu(II)\0,2\C,-0.1793511552, 4.0115810561,0.3895715699\C,0.9638709999,3.0896535734,0.0039800915\C,0.44229575 85,1.9148493402,-0.7856691957\C,-1.0624642447,1.8245670322,-0.3856701559\C,-1.2 586092829,2.9624793604,0.5871028128\C,0.8521409242,1.7818956604,0.7474137672\C, -0.6553939073,1.6925147372,1.1371470949\H,-0.4288508998,4.7190770596,-0.4084334 785\H,0.0300784177,4.570069842,1.3081798295\H,1.9554888662,3.4634735069,-0.2286 952362\H,0.9121659259,1.5557575852,-1.695716219\H,-1.871051533,1.373231036,-0.9 509028847\H,-2.2709480093,3.2201671527,0.8800418148\H,1.6952007356,1.3013996118 ,1.2335014139\H,-1.0959356766,1.121438441,1.9475828486\Cu,0.0090167404,-0.12329 60295,-0.0182748202\O,-1.0531482325,-1.6343656569,0.1409601917\S,0.1351166474,- 2.6488975004,-0.2552709019\O,1.2159065757,-1.4694532852,-0.4490020921\O,0.49279 75307,-3.4833439781,0.8878371221\O,-0.1511101501,-3.2918263212,-1.534108944\Ver sion=x86-Linux-G98RevA.11.3\HF=-2610.7723759\S2=0.753205\S2-1=0.\S2A=0.750008\ RMSD=0.000e+00\RMSF=1.687e-05\Dipole=-0.2894297,5.8373816,0.5597053\PG=C01 [X(C 7H8Cu1O4S1)]\@

6

1\1\FAU-RRZE-SNODE060\FTS\UB3LYP\6-31G(d)\C7H8Cu1O4S1(2)\CLARK\05-May-2004\0\# B3LYP/6-31G\* OPT=(TS,CALCF) GUESS=READ SCF=QC NAME=CLARK\Quadricyclane:CuSO4 -> Norbornadiene:CuSO4 TS\0,2\C,-3.7369817862,0.8654550974,-0.1509971786\C,-2 .2469708098,1.2291187623,-0.1335869252\C,-1.5066734308,0.2284040856,-1.01862420 27\C,-2.2663576769,-1.0559595754,-0.6506587821\C,-3.5691254165,-0.6353194044,0. 0110678087\C,-1.5974439475,0.4453838601,0.9907395354\C,-2.3043206754,-0.8932902 131,0.8579038594\H,-4.2220056319,1.1342940561,-1.0959049339\H,-4.2902040924,1.3 228470495,0.6765675016\H,-1.9561572206,2.2732923318,-0.233911443\H,-1.162645437 ,0.4894264822,-2.0204385881\H,-2.123258993,-2.0115723597,-1.1410417151\H,-4.405 7402485,-1.3241258345,0.0715736926\H,-1.247057626,0.893073237,1.9223325785\H,-2 .2060103586,-1.7103415678,1.561595856\Cu,0.0994159389,-0.124602686,0.0543053311 \O,1.629069861,-0.8647371713,0.8049419491\S,2.6708984957,0.0340662637,-0.008118 1161\O,1.4847741031,0.7713818424,-0.838543474\O,3.3370618665,0.9855268768,0.871 5952888\O,3.4694546578,-0.7798254723,-0.9155940618\Version=x86-Linux-G03RevB.0 3\State=2-A\HF=-2610.7667086\S2=0.771287\S2-1=0.\S2A=0.750135\RMSD=0.000e+00\RM SF=3.063e-06\Dipole=-4.8627081,-0.1370242,0.0964088\PG=C01 [X(C7H8Cu1O4S1)]\@

7

1\1\FAU-CCC-TCDA05\FOpt\UB3LYP\6-31G(d)\C7H8Cu1O4S1(2)\CLARK\26-Oct-2003\0\# B3LYP/6-31G\* OPT NAME=CLARK SCF=QC\Norbornadiene : Cu(II)\0,2\C,-0.1507531676, 3.6567021237,-0.0471063813\C,0.2694782735,2.6126872987,1.0325061055\C,1.3076216 714,1.8131428745,0.2093814761\C,0.855550272,1.7781961402,-1.0717578482\C,-0.482 7699907,2.5545185021,-1.0992879364\C,-1.0006321277,1.7287453848,1.0262023302\C, -1.452694528,1.6937794435,-0.2549339168\H,0.6687527483,4.3138633027,-0.35421739 28\H,-1.02172936,4.2520421728,0.2439982124\H,0.6012925453,2.9680121588,2.006891 7636\H,2.2460628628,1.4246857341,0.5888761654\H,1.354942735,1.3558337225,-1.936 5160992\H,-0.8415969481,2.8564447283,-2.0820736869\H,-1.4646255823,1.2890829985 ,1.9019858216\H,-2.3557379988,1.2201552838,-0.6234181188\Cu,-0.0013021555,0.025 4038607,-0.0005755066\O,-1.0479899224,-1.4653359914,0.4088564748\S,0.1044540095 ,-2.525290881,0.0328584435\O,1.1656476329,-1.3837133394,-0.3721178268\O,0.55231 54682,-3.2324914444,1.2283999549\O,-0.2819313114,-3.2983102961,-1.1432129834\Ver sion=x86-Linux-G98RevA.11.3\HF=-2610.831647\S2=0.753328\S2-1=0.\S2A=0.750009\ RMSD=0.000e+00\RMSF=6.275e-06\Dipole=-0.2279129,5.5057368,-0.0716096\PG=C01 [X( C7H8Cu1O4S1)]\@

8

1\1\FAU-RRZE-SNODE054\FOpt\RB3LYP\Gen\C7H8Cl2Sn1\CLARK\05-Nov-2003\0\# B3LYP/6

-31G\* OPT NAME=CLARK EXTRABASIS PSEUDO=READ\\Quadricyclane : SnCl2\\0,1\C,1.439  
2983547,2.4197369502,-0.4832273135\C,0.8983524367,3.8151191472,-0.7449443277\C,  
-0.5727730788,3.4682407484,-0.8759885421\C,-0.9225198557,2.2920178667,0.0184093  
381\C,0.4344066871,1.5999946126,0.3028964632\C,0.6236658202,1.3847774366,-1.225  
006942\C,-0.7393858532,2.0809378814,-1.4721889036\H,2.4954845503,2.2277370882,-  
0.3229101369\H,1.3100444079,4.2518704247,-1.6627727432\H,1.095445316,4.49730210  
1,0.0906099992\H,-1.3265698815,4.2234181504,-1.0758656091\H,-1.8198442915,2.215  
583363,0.6209989394\H,0.7151735735,1.0167460978,1.1728242725\H,1.0815981889,0.5  
849963951,-1.7972002343\H,-1.4717985272,1.8160015566,-2.2257950322\Sn,-0.470906  
425,-1.3446936963,-0.1274435391\Cl,1.8274598406,-2.0498636894,0.0339514235\Cl,-  
0.9745468496,-1.2421314999,2.2279655685\\Version=x86-Linux-G03RevB.03\State=1-A  
\HF=-1195.332603\RMSD=3.324e-09\RMSF=7.480e-06\Dipole=-0.6212377,1.3728039,-1.3  
545696\PG=C01 [X(C7H8Cl2Sn1)]\\@

## 9

1\1\FAU-RRZE-SNODE024\FTS\RB3LYP\Gen\C7H8Cl2Sn1\CLARK\06-Nov-2003\0\# B3LYP/6-  
31G\* OPT=(TS,CALCF) NAME=CLARK EXTRABASIS PSEUDO=READ\\Quadricyclane:SnCl2 ->  
Norbornadiene:SnCl2 TS\\0,1\C,0.6470092303,3.4164248688,-0.3801768554\C,1.03528  
68075,1.9846428218,0.0260977107\C,0.8388442102,1.1488697643,-1.1644105858\C,-0.  
3054611695,1.676378412,-1.8580431658\C,-0.5918440033,3.063774222,-1.1957699666\  
C,-0.2915805797,1.2831814637,0.5189157306\C,-1.2056130048,1.8496130959,-0.59969  
36429\H,1.4235949543,3.9123309115,-0.9735958134\H,0.408327414,4.041393381,0.487  
0671503\H,1.9121242946,1.7924724808,0.6378654778\H,1.3966803215,0.2469882049,-1  
.398920839\H,-0.6995731578,1.3050245312,-2.7920182113\H,-1.1662661376,3.7949109  
696,-1.7547834202\H,-0.4969015833,1.6076282761,1.5483424892\H,-2.2558313655,1.6  
015805916,-0.7065402314\Sn,-0.4021276763,-1.1014157194,0.909375675\Cl,-0.969229  
9754,-1.6397385901,-1.4496283447\Cl,2.0765464536,-1.2878408962,0.7085862446\\Ve  
rsion=x86-Linux-G03RevB.03\State=1-A\HF=-1195.3046766\RMSD=5.517e-09\RMSF=4.295  
e-06\Dipole=-0.5484007,3.3267156,-0.2837851\PG=C01 [X(C7H8Cl2Sn1)]\\@

## 10

1\1\FAU-RRZE-SNODE037\FOpt\RB3LYP\Gen\C7H8Cl2Sn1\CLARK\06-Nov-2003\0\# B3LYP/6  
-31G\* OPT NAME=CLARK EXTRABASIS PSEUDO=READ\\Norbornadiene : SnCl2\\0,1\C,-2.77  
01578277,1.2038061787,1.9660102322\C,-1.8607398523,-0.069540095,1.9557018409\C,  
-0.5214160872,0.6290594678,1.6468348873\C,-0.7889030245,1.6356530099,0.78864805  
75\C,-2.3122559558,1.61126582,0.5271852737\C,-2.3807306201,-0.706402629,0.65228  
19124\C,-2.6517608446,0.2927368745,-0.1969267349\H,-2.4908408628,1.9325044887,2  
.7341969807\H,-3.8376003115,0.9722788803,2.0310433865\H,-1.8598561228,-0.713372  
0646,2.8353858974\H,0.4333970075,0.3624449431,2.0847606954\H,-0.1015845312,2.38  
83885308,0.4172205547\H,-2.7294626523,2.5208884841,0.0931657336\H,-2.4527765382  
, -1.7739775332,0.4838517604\H,-3.0155513959,0.2277176216,-1.2162194537\Sn,0.699  
5836698,-0.1914926331,-1.0577637905\Cl,0.8771130976,-2.2820795633,0.1553381171\  
Cl,2.6988208547,0.8749199483,-0.1914339316\\Version=x86-Linux-G03RevB.03\State=  
1-A\HF=-1195.3715176\RMSD=3.127e-09\RMSF=5.595e-06\Dipole=-2.0506008,0.8861948,  
-0.0926499\PG=C01 [X(C7H8Cl2Sn1)]\\@

## 11

1\1\FAU-RRZE-SNODE033\FOpt\UB3LYP\Gen\C7H8Cl2Sn1(3)\CLARK\05-May-2004\0\# UB3L  
YP/6-31G\* OPT OPTCYC=500 NAME=CLARK EXTRABASIS PSEUDO=READ\\Quadricyclane -> No  
rbornadiene : SnCl2 triplet TS\\0,3\C,-3.2146496405,0.5547077803,1.1182764852\C  
, -1.891069248,1.0345444283,0.4277453883\C,-2.2464494684,0.8518507073,-1.0357291  
46\C,-2.709411461,-0.5498213136,-1.0319725251\C,-3.3307484404,-0.7740398502,0.3  
735992489\C,-0.9880882989,-0.2052459165,0.6597129899\C,-1.9228625473,-1.2511711  
069,0.0767484776\H,-4.0506542441,1.233347094,0.9163436527\H,-3.1084027752,0.433  
1131286,2.2027216402\H,-1.4959556658,1.9994574587,0.7434845043\H,-2.6053185426,  
1.6344408812,-1.6954995807\H,-3.0788941687,-1.0827415671,-1.8999310109\H,-4.148  
1951863,-1.4718442926,0.5209382019\H,-0.6931452113,-0.3771482674,1.7016900055\H  
, -1.6774171247,-2.3060412645,0.0233275928\Sn,0.9479457718,-0.0413347473,-0.4323

876086\Cl,1.8985404777,1.9936941932,0.3724118142\Cl,2.2944224021,-1.7560938507,  
0.5438246513\|Version=x86-Linux-G03RevB.03\State=3-A\HF=-1195.3083824\S2=2.0100  
02\S2-1=0.\S2A=2.000055\RMSD=5.560e-09\RMSF=4.484e-06\Dipole=-2.2036725,-0.2152  
876,-0.5141632\PG=C01 [X(C7H8Cl2Sn1)]\|@

## 12

1\1\FAU-RRZE-SNODE022\FOpt\UB3LYP\Gen\C7H8Cl2Sn1(3)\CLARK\04-May-2004\0\# UB3L  
YP/6-31G\* OPT OPTCYC=500 NAME=CLARK EXTRABASIS PSEUDO=READ\|Quadricyclane -> No  
rbornadiene : SnCl2 triplet TS\|0,3\C,-3.2351367798,0.707736703,0.7975473029\C,  
-1.6804285146,0.9059747308,0.8585005436\C,-1.289434614,0.4274172588,-0.57154548  
46\C,-1.9758491237,-0.9285270662,-0.5228134703\C,-3.2121958459,-0.7497315516,0.  
3388334544\C,-1.2642731617,-0.2964193041,1.6779652216\C,-1.9384031255,-1.382159  
8076,0.9420691112\H,-3.7215256527,1.3784694453,0.0790644565\H,-3.7009951108,0.8  
407029536,1.7802187786\H,-1.3208807137,1.8856118113,1.1692372829\H,-1.632422083  
5,1.0804674109,-1.380814496\H,-1.9448112519,-1.6449034665,-1.3360558547\H,-4.10  
92768316,-1.3359865593,0.169534392\H,-0.9859453703,-0.2959889706,2.7243837579\H  
,-1.8905332052,-2.4304703589,1.2089463612\Sn,0.9349383338,0.2549078699,-0.75587  
86309\Cl,1.8930138386,1.6896774424,0.8930212137\Cl,1.6442685448,-1.9443269449,-  
0.1720755199\|Version=x86-Linux-G03RevB.03\State=3-A\HF=-1195.306365\S2=2.00970  
4\S2-1=0.\S2A=2.000052\RMSD=5.283e-09\RMSF=1.893e-05\Dipole=-1.8519081,0.210799  
2,-0.673955\PG=C01 [X(C7H8Cl2Sn1)]\|@

## 13<sup>‡</sup>

1\1\FAU-CCC-CCDA086\FOpt\UB3LYP\Gen\C7H8Cl2Sn1(3)\CLARK\29-Nov-2004\0\# B3LYP/  
6-31G\* NAME=CLARK EXTRABASIS PSEUDO=READ SCFCYC=200 SCF=QC OPT=MODREDUNDANT\|No  
rbornadiene:SnCl2 triplet TS to open second bond\|0,3\C,-3.2367008838,-0.723761  
4045,-1.0175822086\C,-3.2617200587,0.7037969521,-0.4527534537\C,-1.837086844,1.  
1629426847,-0.4922683709\C,-0.9669719636,-0.0490955579,-0.7100302979\C,-1.95959  
40876,-1.1688716966,-0.2444157705\C,-2.9048410276,0.5148000251,1.0051651855\C,-  
2.322268208,-0.7405916105,1.1688715977\H,-3.1166659026,-0.7555177821,-2.1058397  
403\H,-4.1180388453,-1.3032811748,-0.7235318801\H,-4.0596436698,1.3928305592,-0  
.7220013099\H,-1.516715171,2.1963201612,-0.4693314569\H,-0.6336103684,-0.177631  
6021,-1.7502704805\H,-1.6217143817,-2.1939891276,-0.3982503809\H,-3.1227994468,  
1.2503887552,1.7698825381\H,-1.884068583,-1.1382953607,2.077602271\Sn,0.9342124  
144,0.0636843348,0.4123120267\Cl,2.0953137253,1.8561498811,-0.6421765918\Cl,2.1  
574941621,-1.8944062058,-0.1716928778\|Version=x86-Linux-G03RevB.03\State=3-A\H  
F=-1195.2922652\S2=2.034272\S2-1=0.\S2A=2.000299\RMSD=0.000e+00\RMSF=4.126e-05\  
Dipole=-1.8976248,0.1933655,0.4393166\PG=C01 [X(C7H8Cl2Sn1)]\|@

## 14<sup>‡</sup>

1\1\FAU-RRZE-SNODE008\FTS\UB3LYP\Gen\C7H8Cl2Sn1(3)\CLARK\01-May-2004\0\# UB3LY  
P/6-31G\* OPT=(TS,CALCFC) NAME=CLARK EXTRABASIS PSEUDO=READ\|Quadricyclane -> No  
rbornadiene : SnCl2 triplet TS\|0,3\C,0.7546627797,3.3010673822,-0.5901032068\C  
,1.0426466726,1.7727424015,-0.4019352653\C,0.3335758492,1.1623866133,-1.6138198  
527\C,-1.0018669712,1.8274309971,-1.4790345395\C,-0.7513720997,3.1706240259,-0.  
8025827588\C,0.0012772427,1.3977732287,0.6497623738\C,-1.223366662,1.9595158011  
,0.0352813348\H,1.2757959461,3.7192958704,-1.4584350355\H,1.0147059357,3.886441  
76,0.2985529456\H,2.0715524926,1.4739078493,-0.2132720347\H,0.8250581844,1.0206  
233789,-2.5738034632\H,-1.8336371952,1.6745675712,-2.1567124908\H,-1.4102988754  
,4.0178242235,-0.9607342081\H,0.1872654583,1.3494695032,1.7190631816\H,-2.20744  
44702,1.9183640702,0.4846651931\Sn,-0.0889795904,-1.0838489284,-0.2141292948\Cl  
,2.1047299551,-1.5340012859,0.7034953037\Cl,-1.5404569448,-1.5493687438,1.69543  
01161\|Version=x86-Linux-G03RevB.03\State=3-A\HF=-1195.2974961\S2=2.020757\S2-1  
=0.\S2A=2.000148\RMSD=6.108e-09\RMSF=7.701e-06\Dipole=-0.3939847,2.3085048,-1.6  
094212\PG=C01 [X(C7H8Cl2Sn1)]\|@

## 15

1\1\FAU-RRZE-SNODE059\FOpt\UB3LYP\Gen\C7H8Cl2Sn1(3)\CLARK\30-Apr-2004\0\# UB3LYP/6-31G\* OPT NAME=CLARK EXTRABASIS PSEUDO=READ\Norbomadiene : SnCl2\0,3\C,-2.5977682205,1.1885834846,1.9308762334\C,-2.3714810855,-0.3472018475,2.0863032615\C,-0.854701264,-0.3675288543,2.0790255222\C,-0.4058703361,0.6855312409,1.1116437265\C,-1.7764041161,1.2682787578,0.6103317662\C,-2.8044557734,-0.8064611874,0.6836667538\C,-2.4671620733,0.1612770365,-0.1846283016\H,-2.1720864754,1.7758664583,2.7518095366\H,-3.650328288,1.4517935535,1.7869011098\H,-2.8499684677,-0.851708301,2.9270119363\H,-0.2170968018,-0.9142928683,2.7629544159\H,0.2758391446,1.436658118,1.5299111724\H,-1.6952673742,2.2387312689,0.1193818446\H,-3.2258857625,-1.7814832857,0.4613326234\H,-2.5797260576,0.1556170236,-1.2640833435\Sn,0.6842915926,-0.4111889334,-0.4560901421\Cl,2.9553365761,-0.4428130685,0.25959254\Cl,0.6662515218,0.8165420636,-2.5051234789\Version=x86-Linux-G03RevB.03\State=3-A\HF=-1195.3066437\S2=2.006467\S2-1=0.\S2A=2.000025\RMSD=7.025e-09\RMSF=1.060e-05\Dipole=-1.6928379,-0.270195,1.156683\PG=C01 [X(C7H8Cl2Sn1)]\@

## 16

1\1\FAU-CCC-SUPERB\SP\RB3LYP\Gen\C8H12Cl2O1Sn1\SHUBINA\17-Jun-2008\0\#P PSEUDO=READ B3LYP/6-31G(D) EXTRABASIS NAME=SHUBINA\Quadricyclane:SnCl2(MeOH)\0,1\C,0,3.383571,1.211714,0.539747\C,0,4.689436,0.476813,0.289696\C,0,4.130188,-0.755123,-0.399982\C,0,2.886938,-0.401042,-1.198324\C,0,2.388459,0.925972,-0.569199\C,0,2.254495,0.227628,0.783911\C,0,2.754517,-1.093882,0.145099\H,0,3.351514,2.177052,1.035748\H,0,5.212811,0.231371,1.222216\H,0,5.369938,1.045204,-0.356729\H,0,4.772367,-1.557351,-0.751521\H,0,2.671228,-0.77076,-2.194594\H,0,1.773878,1.688838,-1.034689\H,0,1.516222,0.337435,1.569909\H,0,2.409147,-2.093995,0.379712\Sn,0,-0.995265,-0.141747,-0.525437\Cl,0,-1.444896,1.953236,0.639398\Cl,0,-1.040855,-1.637896,1.434189\C,0,-4.384948,0.303968,-0.433147\O,0,-3.300717,-0.650225,-0.359409\H,0,-5.337067,-0.224995,-0.334944\H,0,-4.326226,0.764048,-1.420279\H,0,-4.281811,1.073015,0.33615\H,0,-3.321149,-1.117773,0.498366\Version=IA64L-G03RevC.02\State=1-A\HF=-1311.0747229\RMSD=3.244e-09\Dipole=-0.8897093,-0.2239681,-1.1610476\PG=C01 [X(C8H12Cl2O1Sn1)]\@

## 17<sup>‡</sup>

1\1\FAU-CCC-SUPERB\Freq\RB3LYP\Gen\C8H12Cl2O1Sn1\CLARK\12-Jun-2008\0\#N GEOM=ALLCHECK GUESS=READ SCRF=CHECK GENCHK RB3LYP/CHKBAS FREQ\Quadricyclane -> Norbornadiene:SnCl2(MeOH)\0,1\C,1.0431294653,2.197379139,-0.6129312952\C,0.4828727269,3.5473861558,-1.1419485962\C,-0.9576592647,3.0421015946,-1.2674511241\C,-1.1855289704,2.2965583699,0.0188024052\C,0.0649848049,1.8895299309,0.5696894614\C,0.5050459002,1.1812294497,-1.6801919267\C,-0.8101594056,1.7007233525,-1.9130134872\H,2.1090328951,2.1461627222,-0.3880653449\H,0.918738762,3.8402227354,-2.1034206527\H,0.5863069882,4.3653852278,-0.4206272596\H,-1.7500707502,3.6992569993,-1.6206230969\H,-2.1672831714,2.1057916947,0.4358246442\H,0.3089127212,2.0367608941,1.618342168\H,1.11120465,0.8004902435,-2.4999415603\H,-1.6062360405,1.2028013011,-2.454377455\Sn,0.2295537229,-0.4229453231,0.0072718785\Cl,1.6919853008,-2.3946138691,-0.0212020755\Cl,-1.9674087266,-1.4141477423,-0.3790433925\C,0.3443600285,-1.9579698204,3.2153922166\O,-0.4572808042,-1.1973107669,2.2933241351\H,-0.2250635057,-2.1527974767,4.1307404441\H,1.2112360927,-1.340958142,3.4573804838\H,0.6870165775,-2.8952572603,2.7683562994\H,-1.2433084051,-1.7147882878,2.040311358\Version=IA64L-G03RevC.02\State=1-A\HF=-1311.0612939\RMSD=3.825e-09\RMSF=3.348e-06\ZPE=115.3508725\Dipole=-0.0790981,1.5719392,0.978217\DipoleDeriv=0.1387133,0.1720739,-0.0080594,-0.0977757,-0.2270767,0.010400621,-0.014675,0.3760644\Polar=134.133879,-19.480702,198.7731601,7.3737195,-30.1583117,132.7935268\PG=C01 [X(C8H12Cl2O1Sn1)]\NImag=1\0.06138632\0.00000019,-0.00000002,-0.00000251,0.00000082,0.00000055,0.00000123,-0.00000316,-0.00000431,0.00000068,0.00000118,0.00000102\@

## 18

1\1\FAU-CCC-SUPERB\FOpt\RB3LYP\Gen\C8H12Cl2O1Sn1\CLARK\12-Jun-2008\0\0\# B3LYP/6-31G\* NAME=CLARK EXTRABASIS PSEUDO=READ OPT\Norbomadiene:SnCl2(MeOH)\0,1\C,-2.2816437215,1.4612869224,3.3006171736\C,-1.3124152077,0.2671315883,3.0244481452\C,-0.2687993214,1.0247980232,2.1760511951\C,-0.9403999116,1.9158798947,1.4296592585\C,-2.4384083669,1.759075987,1.7748018673\C,-2.2132132811,-0.5335628732,2.0623734787\C,-2.8853398736,0.3537800108,1.3199140352\H,-1.8143101999,2.2809130927,3.8565813876\H,-3.2175619549,1.1583302324,3.7813958116\H,-0.9172955816,-0.2836337104,3.8791095735\H,0.7991421031,0.843378457,2.2029545601\H,-0.5346889203,2.6346895098,0.7263078068\H,-3.0840916329,2.5878156654,1.478683671\H,-2.230335217,-1.6153165029,2.0000263975\H,-3.5877931918,0.1617647538,0.5163260192\Sn,0.0852069056,-0.1908060265,-0.961330205\Cl,0.9589964649,-2.0127577248,0.4686058364\Cl,2.0435699373,1.2809732896,-0.8519268856\C,2.2592833584,-1.0273753154,-3.5001608019\O,1.3218255578,-1.5356559928,-2.5270735281\H,3.0486192441,-0.44557475,-3.0176130687\H,1.6902557746,-0.3812343316,-4.1700506371\H,2.6795424693,-1.8607636858,-4.0711460258\H,1.7755564812,-2.1405694892,-1.9092452936\Version=IA64L-G03RevC.02\State=1-A\HF=-1311.1106805\RMSD=8.470e-09\RMSF=4.478e-06\Dipole=-0.667308,-0.143231,-1.0041361\PG=C01 [X(C8H12Cl2O1Sn1)]\@

## 19

1\1\FAU-CCC-SUPERB\FOpt\UB3LYP\Gen\C8H12Cl2O1Sn1(3)\CLARK\12-Jun-2008\0\0\# B3LYP/6-31G\* NAME=CLARK EXTRABASIS PSEUDO=READ OPT FREQ=NORAMAN\Half-open Quadricyclane:SnCl2(MeOH) triplet\0,3\C,0.8919746932,2.3244506297,-0.8419942348\C,0.637130079,3.2663902059,-2.0727235012\C,-0.8891282497,3.2142557072,-2.020259158\C,-1.2757245063,3.0395853889,-0.5288086439\C,0.0056236294,2.9746652683,0.203066303\C,0.0240828293,1.1085181358,-1.2420400924\C,-1.2754125468,1.8458303035,-1.4848466829\H,1.9321033858,2.1269825627,-0.5852292696\H,1.0496361442,2.8650233997,-3.0059204519\H,1.0377842123,4.2733521074,-1.9098036878\H,-1.5294283562,3.7567401624,-2.7080560728\H,-2.1937912565,3.4586674126,-0.1342586724\H,0.3396963173,3.684443715,0.9525352649\H,0.3987114468,0.5129944367,-2.0821132417\H,-2.1934275717,1.3545301407,-1.7871780938\Sn,-0.1160647558,-0.4575915279,0.4176721573\Cl,2.2098070578,-1.1017983902,0.4870179523\Cl,-1.1158374408,-2.2280049402,-0.9371515529\C,0.4499859898,-2.9640950409,2.982590266\O,-0.5405950039,-2.3850420576,2.118816004\H,0.0204907645,-3.8043531515,3.5404850488\H,0.7450335907,-2.1834550145,3.6857670359\H,1.3321515606,-3.2910369057,2.4233655038\H,-0.819637413,-3.0449229849,1.4586364129\Version=IA64L-G03RevC.02\State=3-A\HF=-1311.0378879\S2=2.012179\S2-1=0.\S2A=2.000075\RMSD=9.354e-09\RMSF=2.199e-05\Dipole=-0.510692,0.9868967,0.6264764\PG=C01 [X(C8H12Cl2O1Sn1)]\@