

# The Quadricyclane to Norbornadiene Radical Cation Rearrangement: an *Ab Initio* and Density Functional Study†

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*Ab initio* and density functional theory have been used to investigate the title reaction. The principles governing radical electrocyclic reactions are summarized and applied to the quadricyclane to norbornadiene radical cation rearrangement. The simple qualitative picture given by this interpretation is then compared with the detailed results of the calculations. In general, the qualitative theories proposed by Bischof and Haselbach provide an excellent conceptual framework for this and other radical electrocyclic reactions. The performance of the different levels of theory is compared and the density functional methods found to underestimate the energy gained from the pseudo-Jahn–Teller distortion away from a symmetrical transition state. Simple BLYP theory fails completely to reproduce this effect and Becke3LYP gives only a small distortion energy. Our best estimate of the activation energy for the rearrangement is  $\leq 10 \text{ kcal mol}^{-1}$ , in agreement with recent calculations by Bach *et al.* This value is about twice as high as the current experimental estimate.

The extremely facile rearrangement of the quadricyclane (tetracyclo[2.2.1.0.2,6<sup>0</sup>3,5]heptane) radical cation to its norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) isomer has exerted a special fascination on many chemists since its discovery in the gas phase in 1962<sup>1</sup> and by Haselbach *et al.* in frozen glasses in 1979.<sup>2</sup> This rearrangement has become the prototype for the so-called ‘hole-catalyzed’ reactions, in which one-electron oxidation leads to an enormous rate acceleration.<sup>3–5</sup> Both the experimental exploitation of such reactions and the interpretation of their mechanisms in terms of orbital symmetry rules have received much attention, although, paradoxically, much of the relevant qualitative theory was proposed long before hole-catalyzed reactions were investigated experimentally. This paper presents *ab initio* and density functional calculations on the title rearrangement and an analysis of the reaction mechanism in terms of state and orbital correlations. Its purpose is twofold; to provide a quantitative picture of the energy hypersurface for the rearrangement and to summarize and collate the somewhat fragmented interpretative theory of hole-catalyzed reactions.

Radical electrocyclic reactions were discussed for the first time by Longuet-Higgins and Abrahamson<sup>6</sup> only six

months after Woodward and Hoffmann’s original communication.<sup>7</sup> They pointed out that the allyl to cyclopropyl radical rearrangement is forbidden and introduced state correlation diagrams as interpretative tools for electrocyclic reactions. Bauld and Cessac<sup>8</sup> later derived rules for the conrotatory/disrotatory stereochemistry of radical electrocyclic reactions, although their predictions have proved remarkably difficult to confirm experimentally. Bischof<sup>9</sup> provided much of the necessary qualitative theoretical framework for the present paper in his treatment of radical electrocyclic reactions in general and of the bicyclo[3.2.0]heptadienyl to cycloheptatrienyl radical rearrangement. His analogy between Jahn–Teller radicals and the state-crossing points for radical rearrangements provides the basis for our current understanding of radical electrocyclic reactions. He also introduced the ‘Type A–C’ nomenclature for radical electrocyclic reactions later adopted by Haselbach<sup>10</sup> in a slightly different form. Haselbach was, however, the first to point out that, although radical electrocyclic reactions are both state- and orbital forbidden, the state-crossing points occur at such low energies for radical cations that activation energies are often extremely low. The companion paper<sup>2</sup> reports semiempirical molecular orbital (MO) calculations on the norbornadiene<sup>+</sup> to quadricyclane<sup>+</sup> rearrangement but, remarkably, does not take Bischof’s

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Jahn–Teller analogy into account. Nevertheless, Haselbach and Bischof's papers<sup>2,9,10</sup> represent a remarkable advance in the qualitative theory of electrocyclic radical reactions. However, apart from Williams' work reported at this conference,<sup>11</sup> progress since 1979 has been remarkably slow. Both experimental studies of radical electrocyclic reactions<sup>12a</sup> and the accurate calculation of radical reaction barriers<sup>12b</sup> proved to be far more difficult than anticipated so that, in contrast with the situation for closed-shell electrocyclic reactions, confirmation of the qualitative theory remained elusive. Borden *et al.*'s high-level calculations<sup>13</sup> on the cyclopropane to propene radical cation rearrangement<sup>14</sup> conclude that the ring-opening barrier is less than  $0.2 \text{ kcal mol}^{-1}$ , but that the reaction occurs via a bifurcation point. Quite generally, the poor performance of *ab initio* levels of theory that would be adequate for closed-shell reactions has hampered work in this field, although recent work<sup>15,16</sup> suggests that density functional theory may provide a solution to this problem. Recently, Bach *et al.*<sup>17</sup> have also used *ab initio* MO-theory to investigate the norbornadiene–quadricyclane system but concentrated on the energetics of the neutral and cation rearrangements, rather than on the interpretation of the cation reaction mechanism. In this paper, the performance of two popular levels of density functional theory (DFT) will also be compared with the conventional *ab initio* results in order to assess the reliability of DFT for radical reaction mechanisms.

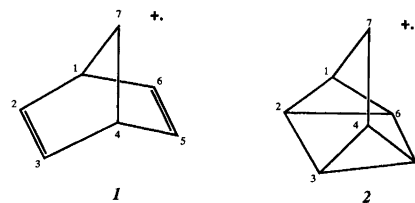
### Computational methods

All calculations used GAUSSIAN 94<sup>18</sup> on Convex C220, Convex SPP-100/CD, Hewlett-Packard 735 and Cray YMP and T90 computers. The 6-31G\* basis set<sup>19</sup> was used throughout. Optimizations were performed without symmetry constraints, except where otherwise noted, and stationary points were characterized by diagonalisation of the Hessian matrix calculated at the level of theory used for the optimization. Single point calculations on the UMP2-optimized geometries used a fourth order Møller–Plesset correction for electron correlation including single, double, triple and quadruple excitations [UMP4sdtq/6-31G\*// (UMP2/6-31G\*)].<sup>20</sup> Density functional calculations used both the Becke<sup>21</sup> and the Becke three-parameter functionals<sup>22</sup> with the Lee–Yang–Parr non-local correction<sup>23</sup> (BLYP/6-31G\* and B3LYP/6-31G\*, respectively). In the latter case, the excess local correlation not provided by the Lee–Yang–Parr expression is calculated using the Vosko, Wilk and Nusair local spin density functional.<sup>24</sup> This is the standard 'Becke3LYP' method implemented in GAUSSIAN94. MP4 energies are also quoted for Schlegel's spin-projected UMP4 method [PMP4sdtq/6-31G\*// (UMP2/6-31G\*)],<sup>25</sup> which has proved to be reliable for other radical applications.<sup>26</sup> Relative energies quoted in the text and tables include zero-point energy corrections. Because the energy hypersurface for the radical cation's

first excited state is of interest, it was calculated approximately using a singles-only configuration interaction using the UHF wavefunction as reference (UCIS/6-31G\*) at the UHF-optimized ground state geometries.

### Results and discussion

*Experimental data.* Experimentally, both the norbornadiene radical cation **1**<sup>9,10,27</sup> and the quadricyclane radical cation **2**<sup>28</sup> are known to be local minima. Their ESR spectra<sup>27–29</sup> suggest symmetrical structures, as do previous *ab initio* calculations<sup>30</sup> (Scheme 1).



Scheme 1.

The activation energy for the **2** → **1** rearrangement is found to be very low, both in frozen glasses<sup>10</sup> and in solution<sup>28</sup> and has been estimated to be  $4.8 \text{ kcal mol}^{-1}$ ,<sup>31</sup> although Bach *et al.*'s calculations suggest a value around  $11 \text{ kcal mol}^{-1}$ .<sup>17</sup> Neutral norbornadiene is  $27.1 \text{ kcal mol}^{-1}$  more stable than quadricyclane ( $\Delta H_f^\circ$  values in the gas phase)<sup>32</sup> and the vertical ionization potentials of the two compounds are 7.86 and 8.43 eV, respectively.<sup>2</sup> These values give an energy difference of about  $14 \text{ kcal mol}^{-1}$  in favor of the norbornadiene radical cation at the vertical geometries.

### Theoretical considerations

The relevant orbitals and their occupancies in norbornadiene<sup>+</sup> and quadricyclane<sup>+</sup> are shown schematically in Fig. 1. According to Haselbach's nomenclature,<sup>10</sup> the rearrangement is a type B forbidden reaction. Simple Marcus theory can be used<sup>33</sup> to estimate the activation energy to be around  $7 \text{ kcal mol}^{-1}$  using the experimental thermochemistry of the reaction and vertical excitation energies of the radical cations.

Bischof's theoretical considerations lead us to expect a potential surface in which a conical intersection between the ground and first excited state occurs along the symmetrical ( $C_2-C_3=C_5-C_6$  and  $C_2-C_6=C_3-C_5$ ) reaction path, so that the transition state for the rearrangement should have at most  $C_s$  symmetry. Haselbach *et al.*<sup>10</sup> calculated this conical intersection to lie roughly  $10 \text{ kcal mol}^{-1}$  higher in energy than **2** using MINDO/3<sup>34</sup> and assuming  $C_{2v}$  symmetry along the reaction path. A two-dimensional energy hypersurface was therefore calculated by fixing the  $C_1-C_6$  and  $C_2-C_5$  distances at  $0.1 \text{ \AA}$  intervals between 1.6 and  $2.4 \text{ \AA}$ , but without additional symmetry constraints. Using information gained from this potential surface, four different stationary points, **1**,

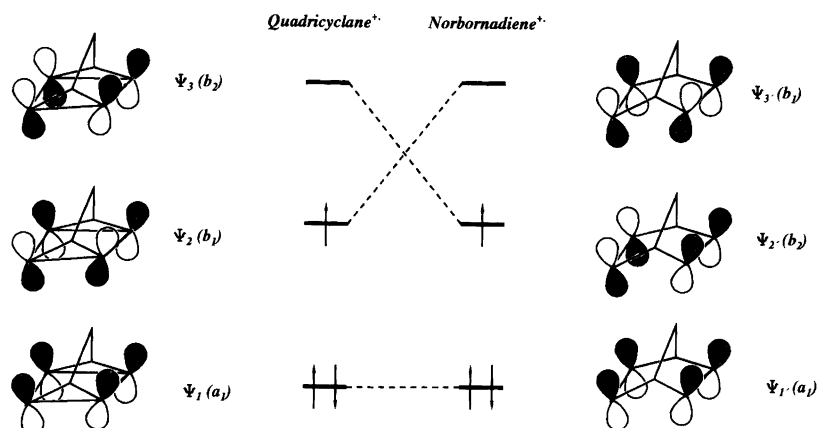
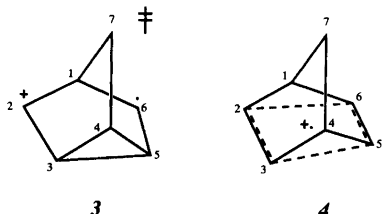


Fig. 1. Schematic MO-occupancy diagram with orbital correlations for the quadricyclane<sup>+</sup> to norbornadiene<sup>+</sup> rearrangement.

2, the rearrangement transition state 3 and the second-order stationary point (hill-top) 4 expected along the symmetrical reaction path were localized and optimized. The second-order stationary point was found by constraining C<sub>2</sub>-C<sub>3</sub> to equal C<sub>5</sub>-C<sub>6</sub> and performing a normal transition state optimization. 1 and 2 were confirmed as minima, 3 as a transition state and 4 to have two imaginary vibrations by calculation of the Hessian matrix at the theoretical level used for the optimization. As described below, however, 4 is found to be a transition state using BLYP (Scheme 2).



Scheme 2.

**Ground state potential surface.** The calculated (UHF/6-31G\*) ground state potential surface is shown as a contour plot in Fig. 2. The calculated energies obtained at the various levels of theory are shown in Table 1. There is good agreement with the qualitative expectations of Bischof's theory.<sup>9</sup> The reaction path is extremely unsymmetrical and one of the opening C-C bonds is actually shorter at the transition state than in the quadricyclane radical cation 2. This is probably the consequence of a simple lever effect caused by the hydrocarbon cage. Opening one of the cyclopropane bonds in the quadricyclane cage causes the other to shorten slightly (Scheme 3).

The rearrangement reaction is, however, essentially two consecutive C-C bond-breaking processes with the transition state occurring at the completion of the first bond-breaking. The calculated UHF Born-Oppenheimer activation energy is 4.7 kcal mol<sup>-1</sup>. The hill-top 4 lies 7.2 kcal mol<sup>-1</sup> higher in energy than 2, so that the

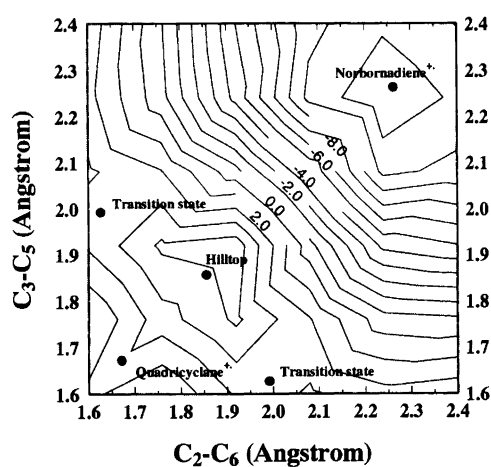
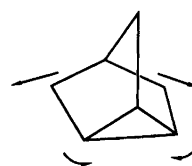


Fig. 2. Contour plot for the Born-Oppenheimer UHF/6-31G\* energy surface for the 1→2 rearrangement. Energies are given in kcal mol<sup>-1</sup> relative to quadricyclane<sup>+</sup>, 2, with contour levels at 1 kcal mol<sup>-1</sup> intervals.



Scheme 3.

distortion energy from the quasi-Jahn-Teller point 4 to the unsymmetrical transition state 3 is about 2.5 kcal mol<sup>-1</sup>. These values are all reduced significantly by the inclusion of the zero point energy corrections (see Table 1).

**Stationary points.** The optimized structures of 1-4 are shown in Table 2. The norbornadiene radical cation 1 is found to be essentially symmetrical at all levels of theory except UHF, for which small deviations from the symmetrical structure are found. The formal C=C bond lengths vary from 1.365 Å at UHF to 1.390 Å with BLYP with UMP2 and B3LYP in fair agreement at

Table 1. Total (a.u.), relative (kcal mol<sup>-1</sup>, in parentheses and with zero-point energy correction) and zero-point energies for 1–4.

	UHF		MP2		BLYP		Becke3LYP		UMP4sdtq <sup>a</sup>		PMP4sdtq <sup>a</sup>	
	Energy <sup>b</sup>	ZPE <sup>c</sup>	Energy <sup>b</sup>	ZPE <sup>c</sup>	Energy <sup>b</sup>	ZPE <sup>c</sup>	Energy <sup>b</sup>	ZPE <sup>c</sup>	Energy <sup>b</sup>	ZPE <sup>c</sup>	Energy <sup>b</sup>	ZPE <sup>c</sup>
1	-269.39579 (-11.6)	85.3 [0]	-270.26592 (-3.4)	84.3 [0]	-271.05363 (-11.4)	78.2 [0]	-271.19066 (-9.1)	80.3 [0]	-270.35699 (-5.9)		-270.35765 (-5.5)	
2	-269.37815 (0.0)	85.8 [0]	-270.25676 (0.0)	82.0 [0]	-271.03475 (0.0)	77.8 [0]	-271.17548 (0.0)	80.7 [0]	-270.34392 (0.0)		-270.34518 (0.0)	
3	-269.37062 (3.7)	84.8 [1]	-270.23094 (14.2)	80.0 [1]	-271.01586 (9.9)	76.2 [1]	-271.15513 (10.9)	78.8 [1]	-270.32227 (11.6)		-270.32538 (10.4)	
4	-269.36661 (5.4)	84.0 [2]	-270.22835 (15.8)	80.0 [2]	-271.01586 (9.9)	76.1 [1]	-271.15473 (10.8)	78.5 [2]	-270.32097 (12.4)		-270.32594 (10.2)	

<sup>a</sup>At the UMP2/6-31G\*-optimized geometry with the UMP2/6-31G\* zero point energy correction. <sup>b</sup>Energies (kcal mol<sup>-1</sup>, including ZPE correction at the level of the geometry optimization) relative to 2 in parentheses. <sup>c</sup>Calculated (unscaled) zero point energy in kcal mol<sup>-1</sup>, number of imaginary frequencies in square brackets.

1.382 ± 0.002 Å. The non-bonded C<sub>2</sub>–C<sub>6</sub> and C<sub>3</sub>–C<sub>5</sub> distances vary between 2.251 Å (MP2) and 2.313 Å (BLYP). The UHF wavefunction is symmetry broken, but this leads to deviations of only about ±0.001 Å from C<sub>2v</sub> symmetry.

The quadricyclane radical cation 2, on the other hand, gives symmetrical wavefunctions at all four levels of theory. The cyclopropane C–C bonds that are opened in the rearrangement are calculated to be between 1.670 (MP2) and 1.699 Å (BLYP) with the two density functional methods giving longer bonds than UHF and MP2. Quite generally, for both 1 and 2 the C–C distances are all slightly longer using the density functional method than at UHF.

The transition state 3 has C<sub>1</sub> symmetry and shows strong asymmetry both in the C<sub>2</sub>–C<sub>3</sub> and C<sub>5</sub>–C<sub>6</sub> 'double' bonds (1.482 and 1.409 Å, respectively at UMP2) and in the C<sub>3</sub>–C<sub>5</sub> and C<sub>2</sub>–C<sub>6</sub> 'cyclopropane' distances (2.051 and 1.732 Å, respectively at UMP2). The C<sub>1</sub>–C<sub>7</sub> and C<sub>4</sub>–C<sub>7</sub> bonds to the methylene group are also unsymmetrical with bond lengths of 1.529 and 1.538 Å, respectively at UMP2. The BLYP-optimized structure for the transition state also has C<sub>1</sub> symmetry, but the asymmetry is not as extreme as that found with the other methods. Above all, the shorter of the two opening bonds is now longer (1.909 Å) than the corresponding distance (1.699 Å) in 2. The agreement between the MP2 and the B3LYP geometries for the transition state is, however, particularly gratifying.

Hill-top 4 has approximate C<sub>2</sub> symmetry at all four levels of theory. The C<sub>3</sub>–C<sub>5</sub> and C<sub>2</sub>–C<sub>6</sub> distances (1.921 Å at MP2) are intermediate between those in 2 (1.670 Å) and 1 (2.251 Å). The bond elongation is just over 30% of that found on going from 2 to 1, in accord with the fact that the rearrangement is calculated to be exothermic. The BLYP-optimized structure also has C<sub>2</sub> symmetry but is, however, much closer to that of 3 than is the case for the corresponding UHF, UMP2 and B3LYP structures. This small difference in structure is also reflected in the tiny (0.02 kcal mol<sup>-1</sup>) energy difference between 3 and 4 calculated using BLYP and in the fact that 4 is calculated to be a transition state with BLYP. Experience with UHF symmetry-breaking in other systems<sup>16</sup> might suggest that this feature may be overemphasised on the UHF-calculated energy surface, but Bischof's qualitative MO-considerations and the strong asymmetry found with UMP2 and B3LYP both suggest that the deformation energy from 4 to 3 should be significant. Once again, the good agreement between UMP2 and B3LYP is gratifying. However, the BLYP results for 3 and 4 suggest that this variety of density functional theory is poorly suited for Jahn–Teller distorted radicals and radical reactions. This point will be discussed in more detail below.

The calculated reaction and activation energies vary fairly strongly with the level of calculation. Embarrassingly, but not entirely unexpectedly, the UHF-calculated activation energy (3.7 kcal mol<sup>-1</sup> with ZPE

Table 2. Optimized (6-31G\*) C-C distances (ångström) for the stationary points in the norbornadiene<sup>+</sup> to quadricyclane<sup>+</sup> rearrangement.

Bond	1			2			3			4		
	UHF	MP2	B3LYP	UHF	MP2	B3LYP	UHF	MP2	B3LYP	UHF	MP2	B3LYP
Symm. <sup>a</sup>	C <sub>1</sub>	C <sub>2v</sub>	C <sub>2v</sub>	C <sub>2v</sub>	C <sub>2v</sub>	C <sub>2v</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>
1-2	1.520	1.516	1.538	1.491	1.498	1.516	1.473	1.481	1.501	1.477	1.489	1.494
2-3	1.365	1.384	1.390	1.468	1.477	1.494	1.493	1.482	1.464	1.443	1.429	1.441
3-4	1.520	1.516	1.538	1.491	1.498	1.516	1.525	1.518	1.533	1.514	1.515	1.523
4-5	1.520	1.516	1.538	1.491	1.498	1.516	1.478	1.494	1.508	1.477	1.489	1.494
5-6	1.364	1.384	1.390	1.468	1.477	1.494	1.430	1.409	1.445	1.443	1.429	1.441
1-6	1.520	1.516	1.538	1.491	1.498	1.516	1.518	1.519	1.537	1.515	1.515	1.523
1-7	1.542	1.544	1.568	1.525	1.523	1.544	1.526	1.529	1.553	1.532	1.532	1.541
4-7	1.542	1.544	1.568	1.525	1.523	1.544	1.536	1.538	1.556	1.531	1.532	1.541
2-6	2.263	2.251	2.313	1.672	1.670	1.699	1.627	1.732	1.909	1.856	1.921	1.946
3-5	2.263	2.251	2.313	1.672	1.670	1.699	1.992	2.051	1.983	1.856	1.921	1.928
												1.928

<sup>a</sup>Optimizations were performed without symmetry constraints. The point groups given are correct within the convergence limits of the geometry optimizer.

correction) is closest to the experimental estimate of 4.8 kcal mol<sup>-1</sup>. All other methods give activation energies in the 10–14 kcal mol<sup>-1</sup> range, in agreement with Bach *et al.*'s CCSD(T)/6-31G\*//UMP2/6-31G\* results.<sup>17</sup> With the exception of UMP2, the correlated *ab initio* methods and both density functional methods give larger energy differences between **2** and **4** and also lower deformation energies from **4** to **3** than UHF, so that the calculated activation energy for the reaction is significantly higher than at UHF. The **4** to **3** deformation energy ranges from 1.7 and 1.6 kcal mol<sup>-1</sup> at UHF and UMP2, respectively, to 0.0 at BLYP and 0.1 at B3LYP. UMP4sdtq also gives a very low value for this deformation energy calculated at the UMP2 geometries, but PMP4sdtq increases it once more to about half that found at UHF and UMP2. We note, however, that the UMP4sdtq/6-31G\*//UHF/6-31G\* energies for **3** and **4** are lower than the UMP4sdtq/6-31G\*//UMP2/6-31G\* values reported in Table 1, whereas the reverse is true for **1** and **2**, so that conclusions based on single point calculations are at best risky for this system. From the above results, however, we can probably conclude that the PMP4 or CCSD(T) activation energy for the rearrangement is  $\approx 10$  kcal mol<sup>-1</sup>. However, finding stationary points **1**–**4** at these levels of theory is currently beyond both our software and hardware capabilities.

*Excited states.* Although simple singles CI calculations (CIS) cannot be expected to reproduce the details of the excited state energy surface for a system of this type quantitatively, they should at least be able to reproduce the main features and trends. Fig. 3 shows a three-dimensional representation of the ground state and first excited state surfaces for the region shown as a contour plot in Fig. 2. There is little resemblance to the qualitative diagram given by Bischof,<sup>9</sup> but this is because of additional state crossings that were not considered. Fig. 4 shows the state energies along the diagonal (symmetrical, C<sub>2v</sub>) reaction path, analogously to the diagram given by Haselbach *et al.*<sup>2</sup> The <sup>2</sup>B<sub>1</sub>–<sup>2</sup>B<sub>2</sub> crossing responsible for the low activation energy for the rearrangement can be seen clearly, as can avoided <sup>2</sup>B<sub>2</sub> and <sup>2</sup>A<sub>1</sub> crossings, the latter being very flat. These crossings lead to <sup>2</sup>B<sub>2</sub> and <sup>2</sup>A<sub>1</sub> minima at vertical excitation energies of approximately 5 and 6 eV, respectively, for the quadricyclane radical cation. The general shape of the <sup>2</sup>B<sub>2</sub> curves is similar to that found with MINDO/3 by Haselbach *et al.*,<sup>2</sup> but the avoided <sup>2</sup>A<sub>1</sub> crossing is only implied in the diagram given by Haselbach *et al.* and would occur at higher energies. Our diagram (Fig. 4) does not contain the second <sup>2</sup>B<sub>1</sub> state that gives the third avoided crossing found by Haselbach *et al.* However, within the bond distance range given in Fig. 4, four different states are involved in the first excited state, so that the complexity of the excited state surface shown in Fig. 3 becomes understandable.

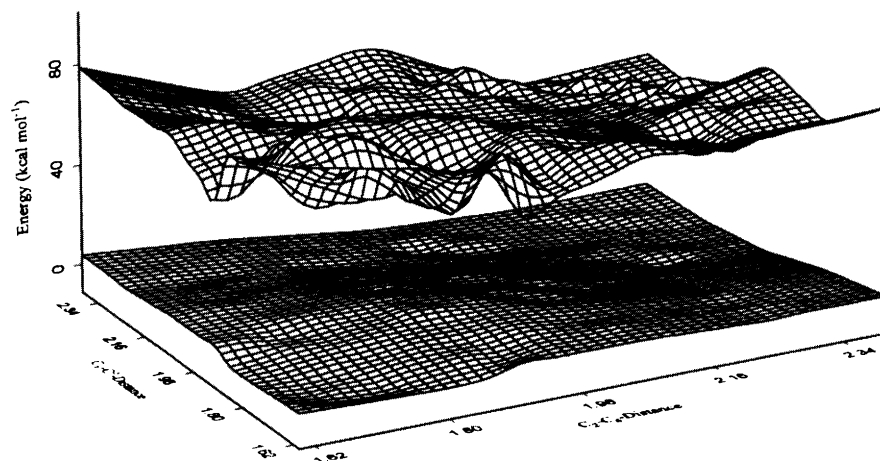


Fig. 3. Three-dimensional representation of the ground and first excited state energy surfaces for the  $2 \rightarrow 1$  rearrangement. The ground state energies are UHF and the first excited state CIS at the ground state geometry.

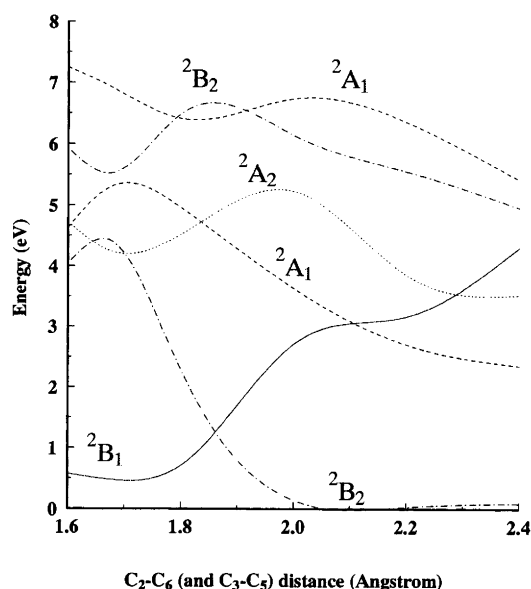


Fig. 4. CIS/6-31G\*//UHF/6-31G\* calculated vertical excitation energies for the norbornadiene<sup>+</sup>-quadricyclane<sup>+</sup> system. Excitation energies are given in eV. Avoided crossings are depicted as real crossings with continuous energy curves for each state. The state symmetries are those that would apply under strict  $C_{2v}$  symmetry.

## Conclusions

The calculations presented here do not give a definitive picture of the quadricyclane to norbornadiene radical cation rearrangement, but, in conjunction with the work of Bach *et al.*,<sup>17</sup> do confirm the low activation energy for the rearrangement (the best current estimate based on our work and that of Bach *et al.* is probably  $\leq 10$  kcal mol<sup>-1</sup>, although UHF does give an activation energy of 3.7 kcal mol<sup>-1</sup>, which is close to the experimental estimate) and give a satisfying qualitative picture of the ground state energy hypersurface. Above all, the ideas of Bischof and Haselbach can be combined to give a consistent interpretational framework for 'hole-cata-

lyzed' reactions, although there is no simple qualitative and predictive picture similar to the Woodward-Hoffmann rules for closed-shell concerted reactions. The question as to exactly how strong the pseudo-Jahn-Teller distortion of the transition states for radical cation rearrangements is cannot be answered definitively from the current calculations, although a deformation energy from the second-order stationary point to the transition state of the order of 1 kcal mol<sup>-1</sup> seems reasonable on the basis of the current results. UHF tends to break symmetry and UMP2 calculations may not be reliable because they are based on the spin-contaminated UHF wavefunction and thus these two methods may overestimate the distortion energy. On the other hand, BLYP density functional calculations give essentially no pseudo-Jahn-Teller distortion and B3LYP reproduces the UMP2 geometries of **3** and **4** well, but gives a very low distortion energy. We suggest these low or non-existent distortion energies to be a consequence of the missing  $\alpha\alpha$  and  $\beta\beta$  correlation in the LYP<sup>23</sup> functional. This is partly corrected by the inclusion of the VWN<sup>24</sup> component in B3LYP, but the distortion energy is still underestimated in comparison with the *ab initio* methods.

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