The Energetics of Valence Isomerization in the Norbornadiene−Quadricyclane System

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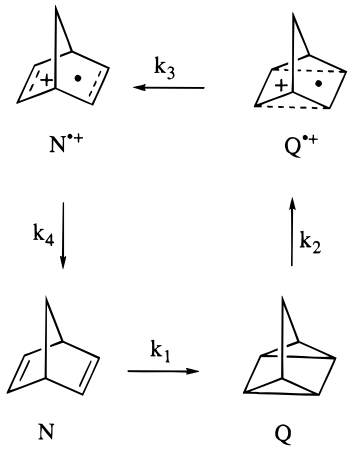
Potential applications of the photochromic valence isomerization of the norbornadiene(N)-quadricyclane(Q) system toward photochemical energy storage[1] and optical memory systems[2] have prompted numerous studies of this overall reaction sequence. While the thermal barrier for reversion of Q to N is relatively high, the energy-releasing conversion of Q to N can be achieved readily via a free-radical-cation chain reaction, initiated by one-electron oxidations (Scheme 1).

Although the existence of two distinct radical cations, $Q^{\bullet+}$ and $N^{\bullet+}$, had been established by chemically induced dynamic nuclear polarization (CIDNP) results,[3] the first direct observation of the quadricyclane radical cation ($Q^{\bullet+}$) by time-resolved ESR (TR-ESR) was reported only recently.[4] A symmetric electronic structure was proposed for this elusive species and a detailed kinetic analysis indicated that its valence isomerization to $N^{\bullet+}$ is relatively slow ($k_3 = \sim 10^6\ s^{-1}$). A key question that remains unanswered in the dynamic interconversion of both the neutral Q−N system and their radical cations is their rates of interconversion.

An earlier theoretical study[5] provided geometries for Q and N that were in excellent agreement with electron diffraction experiments. Geometries were optimized at the HF/6-31G level and single point calculations which included d functions on carbon (6-31G*) and second-order Møller-Plesset perturbation theory with the 6-31G basis were used to give estimated MP2 results with the 6-31G* basis set. Despite the approximations involved in this study, it was clearly a state-of-the-art calculation at that time (121 basis functions). The estimated MP2/6-31G* results for the energy difference between Q and N (26.7 kcal/mol) and $Q^{\bullet+}$ and $N^{\bullet+}$ (10.7 kcal/mol) were both only slightly higher than that observed experimentally (22 ± 1 and 9 kcal/mol).[5,6] Moreover, the estimates for the energy difference between the lower lying triplet state (T_1) and N (60.7 kcal/mol) is in excellent agreement with the results presented below.

As part of a study[7a] on the potential involvement of $Q^{\bullet+}$ in the cytochrome P-450 oxidation of Q,[7b] we had occasion to optimize the geometry of both $Q^{\bullet+}$ and $N^{\bullet+}$. We now report a theoretical prediction of the activation barrier for the conversion of $Q^{\bullet+}$ to $N^{\bullet+}$ and the energy of the triplet state of Q relative to its ground state progenitor. Geometries have been optimized at the MP2/6-31G* level while relative energies that are given have been calculated at the PMP4//MP2/6-31G* and CCSD(T)//MP2/6-31G* levels of theory.

Scheme 1



At the PMP4//MP2/6-31G* level of theory[8] we compute an energy difference between Q and N of 23.59 kcal/mol[9] (Table 1) in good agreement with the average of the experimental values (22 ± 1 kcal/mol).[5,6] The triplet diradical state **2** is predicted to be 57.50 kcal/mol higher than N (Figure 1) in good agreement with an experimental values of 66.4 kcal/mol[11a] and 61.4 kcal/mol.[11b] Compared with the experimental geometries for N[12] and Q,[13] a modest improvement in the corresponding optimized geometries was observed over the HF/6-31G geometries[5] reported previously.[14] Triplet state **2** is slightly distorted to a lower symmetry (C_s) than its parent norbornadiene that has C_{2v} symmetry (Figure 2). The computed S^2 for **2** at the MP2/6-31G* level is 2.007, suggesting that this is a relatively pure spin state with little contamination from other multiplicities.

(1) For a recent review, see: Bren', V. A.; Dubonsov, A. D.; Minkin, V. I.; Chernoivanov, V. A. *Russ. Chem. Rev.* **1991**, *60*, 451.
(2) Miki, S.; Asako, Y.; Yoshida, Z. *Chem. Lett.* **1987**, 195.
(3) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210. (b) Roth, H. D.; Schilling, M. L. M.; Jones, G., II. *J. Am. Chem. Soc.* **1981**, *103*, 1246.
(4) Ishiguro, K.; Khudyakov, I. V.; McGarry, P. F. Turro, N. J., Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 6933.
(5) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110.
(6) (a) Kabakoff, D. S.; Bunzli, J. G.; Oth, J. M. F. Hammond, W. B.; Berson, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 1810. (b) Rogers, D. W.; Choi, L. S.; Girellini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1510. (c) Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 919.
(7) (a) Bach, R. D.; Mintcheva, I.; Estévez, C. M.; Schlegel, H. B. *J. Am. Chem. Soc.* **1995**, *117*, 10121. (b) Stearns, R. A.; Paul R. Ortiz de Montellano *J. Am. Chem. Soc.* **1985**, *107*, 4081.
(8) Schlegel, H. B. *J. Phys. Chem.* **1988**, *92*, 3075.
(9) All geometries were fully optimized at the MP2/6-31G* level of theory using the Gaussian 94 suite of programs[10a] with gradient optimization.[10b] Analytical frequency calculations on all stationary points were carried out at the MP2/6-31G* level. Relative energies are given at the spin projected MP4 (PMP4) level[8] (including the ZPE correction unless otherwise stated) and the CCSD(T) level[10c] using MP2/6-31G* geometries. All energies cited in the text are at the PMP4/6-31G*//MP2/6-31G* taking into account the zero-point energy unless specified otherwise.
(10) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowki, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andrés, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94, Gaussian, Inc., Pittsburgh, PA, 1995. (b) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (c) Purvis, G. D. Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*,1910. (d) ACES II (Advanced Concepts in Electronic Structure Program System): Bartlett, R. J., Purvis, G. D., III, Fitzgerald, G. B., Harrison, R. J., Rittby, M., Sosa, C., Lee, Y. S., Trucks, G. W., Cole, S. J., Salter, E. A., Pal, S., Watts, J., Laidg, W. D., Magers, D. H., Stanton, J. F., Bernholdt, D.
(11) (a) Allan, M. *J. Electr. Spectrosc. Rel. Phen.* **1989**, *48* 219. (b) Helms, A. M.; Caldwell, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 358.
(12) (a) Burnell, E. E.; Diehl, P. *Can. J. Chem.* **1972**, *50*, 3566. (b) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356.
(13) Mizuno, K.; Fukuyama, T.; Kuchitsu, K. *Chem. Lett.* **1972**, 249.
(14) MP2/6-31G* optimized geometries of quadricyclane and norbornadiene show RMS errors of 0.022 Å for C−C bond lengths and 0.605° for bond angles compared to experiment. HF/6-31G[5] calculations show RMS errors of 0.026 Å and 0.617°.

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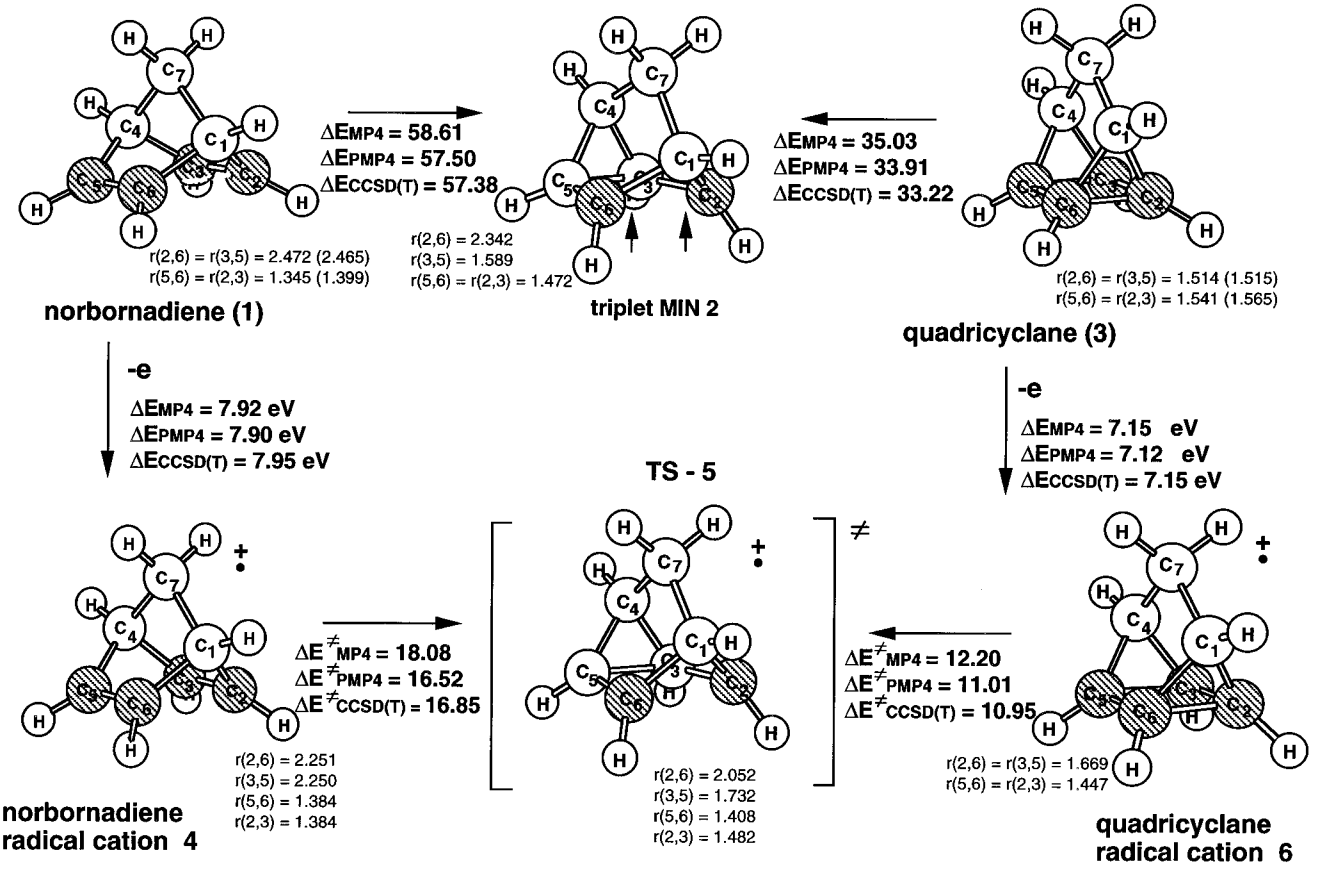

Figure 1. Photoisomerization of norbornadiene (**1**) to quadricyclane (**3**) and the thermal valence isomerization of quadricyclane radical cation **6** to norbornadiene radical cation **4** through transition state TS-**5**. Geometries are at the MP2/6-31G*, and relative energies (kcal/mol) are at the MP4//MP2/6-31G* and CCSD(T)//MP2/6-31G* levels of theory. Experimental geometries are shown in parentheses.

Table 1. Total Energies ar MP2/6-31G*, MP4//MP2/6-31G*, and CCSD(T)//MP2/6-31G* Levels of Theory and Zero-Point Energies at the MP2/6-31G* Level

molecule	MP2/6-31G*	MP4//MP2/6-31G*	PMP4//MP2/6-31G*	CCSD(T)//MP2/6-31G*	ZPE
norbornadiene **1**	−270.553169	−270.644231		−270.644663	0.130565
triplet min **2**	−270.458397	−270.549450	−270.551234	−270.551859	0.129199
quadricyclane **3**	−270.520977	−270.607160		−270.606686	0.131086
radical cation **4**	−270.265918	−270.356990	−270.357650	−270.356474	0.134367
transition state **5**	−270.230937	−270.322227	−270.325382	−270.323681	0.128421
radical cation **6**	−270.256764	−270.343922	−270.345179	−270.343376	0.130671

The calculated adiabatic ionization potential for conversion of N to $N^{\bullet+}$ is 7.90 eV and for Q to $Q^{\bullet+}$ is 7.12 eV in reasonable agreement with the experimental values of 8.37−8.43 and 7.40−7.86 eV, respectively.[15] The predicted S^2 for $N^{\bullet+}$ of 0.7511 and for $Q^{\bullet+}$ of 0.7556 at the MP2/6-31G* level are indicative of a relatively pure doublet state ($S^2 = 0.75$) for both radical cations. The positive charge in $Q^{\bullet+}$ and $N^{\bullet+}$ is uniformly distributed between carbon atoms C_2, C_3, C_5, and C_6. The calculated atomic spin densities of C_2 and C_6 in the triplet (**2**) are 1.202 and the spin density of C_2 in transition state **5** is 1.081. Transition state TS-**5** for the valence isomerization of $Q^{\bullet+}$ to $N^{\bullet+}$ was fully optimized at the MP2/6-31G* level of theory and has only one imaginary frequency (653i cm^{-1}). The calculated activation barrier is predicted to be 11.01 kcal/mol at the PMP4/6-31G*//MP2/6-31G* level. A pulse radiolytic study of the Q−N system suggested an activation barrier of only 20 ± 5 kJ/mol (4.8 ± 1.2 kcal/mol).[16] An activation barrier of ∼40 kJ/mol (9.6 kcal/mol) has been suggested earlier based upon MINDO/3 calculations.[13a] This prompted us to do a single point calculation on TS-**5** at CCSD(T)/6-31G*,[10c,d] which gave a barrier height that was only 0.6 kcal/mol lower in energy (Table 1). The predicted free energy of activation for isomerization of $Q^{\bullet+}$ to $N^{\bullet+}$ is $\Delta G^{\ddagger}_{298} = 10.79$ kcal/mol. This value is considerably higher than the experimental barrier of 4.8 kcal/mol, obtained by Gebicki et al.[16] Transition state theory gives a calculated first-order rate constant $k_3 = 0.76 \times 10^5\ s^{-1}$ ($A = 0.27 \times 10^{14}\ s^{-1}$, $E_a =$ 11.66 kcal/mol) in agreement with the more recent estimate of the experimental rate constant[4] of $k_3 \sim 10^6\ s^{-1}$.

In summary, the radical cations derived from N and Q both have symmetrical electronic structures. The relative energies of both neutrals and radical cations are predicted in good agreement with experiment. The predicted half life for valence isomerization of $Q^{\bullet+}$ to $N^{\bullet+}$, $\tau_{1/2} = 9.14 \times 10^{-6}$ s at 298 K, is consistent with

(15) (a) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583. (b) Taylor, G. N. Chem. Phys. Lett. **1971**, *10*, 355.

(16) Gebicki, J. L.; Gebicki, J.; Mayer, J. *Radiat. Phys. Chem.* **1987**, *30*, 165.

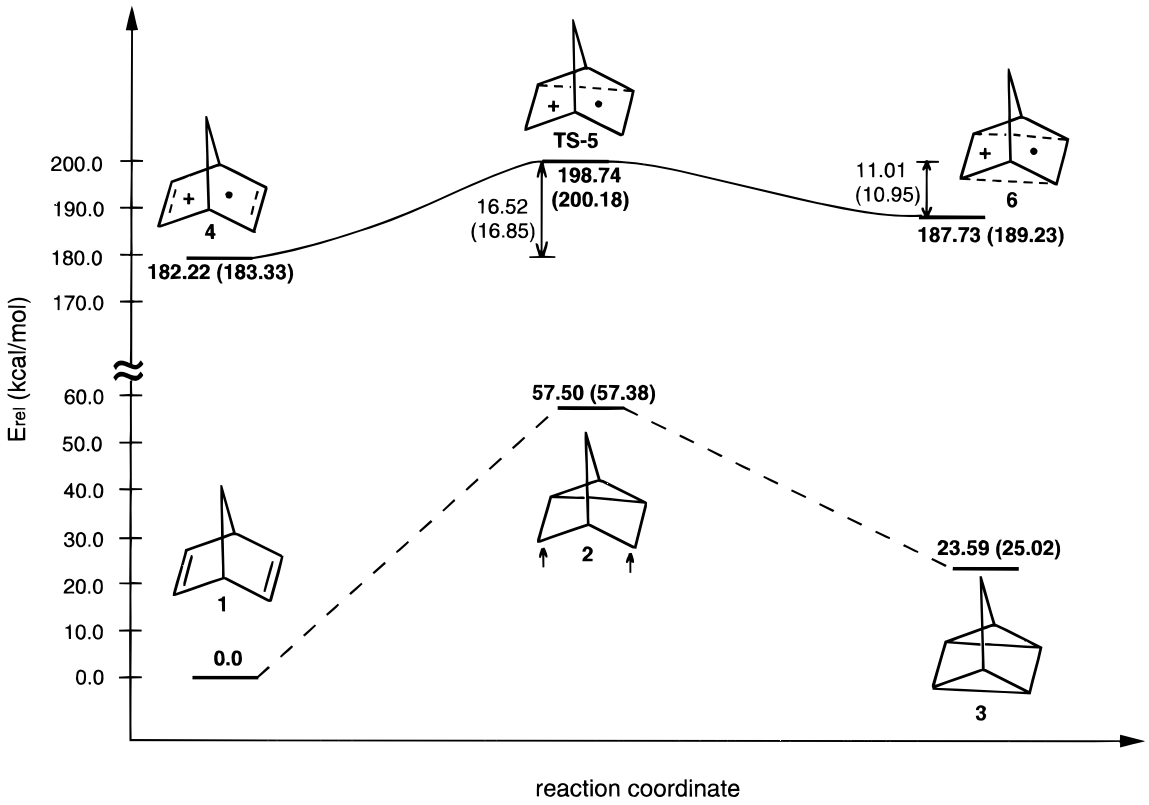

Figure 2. Relative energies (kcal/mol) at the PMP4//MP2/6-31G* level of theory for the photoisomerization of norbornadiene (**1**) to quadricyclane (**3**) and the thermal valence isomerization of quadricyclane radical cation **6** to norbornadiene radical cation **4**. Values in parentheses are at the CCSD(T)//MP2/6-31G* level.

experimental observations where the TR-ESR signal of $Q^{\bullet+}$ decays within microseconds.

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Supporting Information Available: Table of geometries and cartesian coordinates of the six structures optimized at the MP2/6-31G* level of theory are available upon request (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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