4c/3e Radical Cations Sustained in Hydrocarbon Cages. The [1.1.1.1](Iso)pagodane Cases

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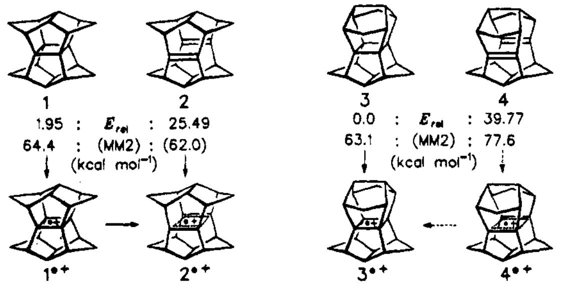
Intriguing 4c/3e cases in the multifaceted story of cyclobutane radical cations[1,2] are the two minima of the reaction coordinate calculated for the synchronous, symmetry forbidden[3] [2 + 1] cycloaddition of ethylene to the ethylene radical cation with imposed D_{2h} symmetry (*ab initio*, UHF 3-21G, Figure 1). Yet, neither the "extended" (π-complex, **E**, $r \cong 2.6$ Å) nor the "tight" (cyclobutane-like, **T**, $r \cong 1.75$ Å) configuration is a true minimum. Without extra stabilization, both structures are bound to open to a linear tetramethylene radical cation;[2] rigid molecular skeletons like that of (iso)pagodanes (e.g., **1** and **3**) and the valence isomeric dienes (e.g., **2** and **4**) indeed provide this stabilization.[4]



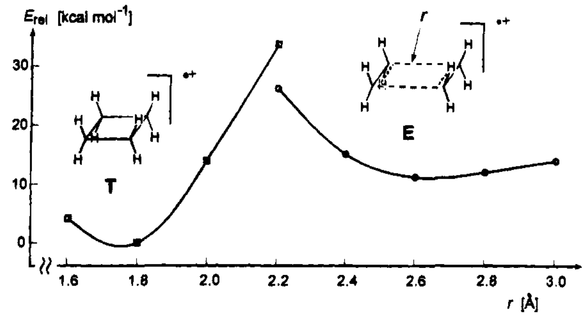


Figure 1. Calculated reaction coordinate for the [2 + 1] cycloaddition of ethylene to the ethylene radical cation in D_{2h} symmetry. Energies are calculated at the PMP2/6-31G* level and are relative to the minimum structure **T**.

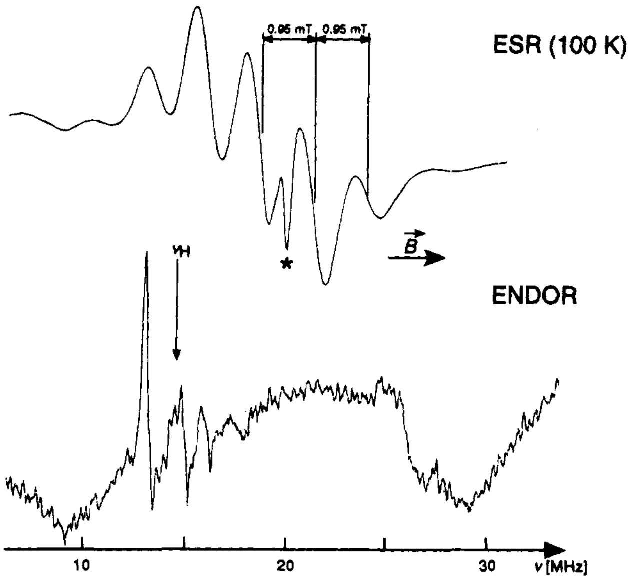


Figure 2. ESR and ENDOR spectrum of **3** (100 K, CFCl$_3$, the peak marked * is a permanent signal in the quartz cell which is induced by the γ-irradiation).

The radical cation produced from the D_{2h} symmetrical [1.1.1.1]pagodane **1**, which was impressively persistent (lifetime at room temperature ca. 2 days, $\lambda_{max} \approx 610$ nm), had been identified by ESR spectroscopy as the rectangular (extended) $\mathbf{2}^{\bullet+}$ (Figure 3), identical with the radical cation analogously prepared from the bissecododecahedradiene **2**.[5] All attempts to directly confirm the intermediacy of the tight ion $\mathbf{1}^{\bullet+}$, e.g., by matrix ESR or "charge-stripping" mass spectroscopy,[6] were not successful. The [1.1.1.1]isopagodane **3** of D_{2d} symmetry was synthesized[7] with the expectation that the inherent skeletal constraints would enforce a tight geometry for the respective radical cation. According to force field (MM2) and *ab initio* calculations ($\mathbf{E}_{rel}$ to **3**, cf. Figure 3), the neutral pagodanes **1** and **3** are of comparable energy and strain, yet diene **4** is clearly higher in energy and strain than diene **2** (MM2 underestimates the π,π repulsion in **2** and (less) in **4**). A similar trend is expected for the corresponding radical cations; the sp^3-like hybridized carbon atoms of tight geometries should be better accommodated by ions derived from **3** (**4**, not available) than by those derived from **1** (**2**).

In contrast to the findings with **1**, radical cation formation could not be detected (ESR) when **3** was exposed to the established chemical (tris(4-bromophenyl)ammoniumyl hexachloroantimonate, AlCl$_3$) or electrochemical oxidation conditions

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(1) For experimental investigations of the cyclobutane radical cation, see the recent review: Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 131.

(2) For detailed theoretical investigations of the tetramethylene radical cation hypersurface, see: Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. Ohta, K.; Nakatsuji, H.; Kudobera, H.; Shida, T. *Chem. Phys.* **1983**, *76*, 271. Jungwirth, P.; Carksy, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5776 and references therein.

(3) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(4) Cf. the search for the respective cage dications: Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1986**, *108*, 836. Herges, R.; Schleyer, P. v. R.; Schindler, M.; Fessner, W.-D. *J. Am. Chem. Soc.* **1991**, *113*, 3649.

(5) Prinzbach, H.; Murty, B. A. R. C.; Fessner, W.-D.; Mortensen, J.; Heinze, J.; Gescheidt, G.; Gerson, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 457.

(6) ESR spectra of **1** recorded in a CFCl$_3$ matrix after γ-irradiation (^{60}Co, 77 K) turn apparently isotropic above 130 K and indicate the same $a_{H\beta}$ (ca. 1.5 mT, 8 equivalent protons) as that detected for the radical cation ($\mathbf{2}^{\bullet+}$) generated in fluid solution.[5] Drewello, D.; Fessner, W.-D.; Kos, A. I.; Lebrilla, C. B.; Prinzbach, H.; Schleyer, P. v. R.; Schwarz, H. *Chem. Ber.* **1988**, *121*, 187. Cf. the recent direct characterization of the extremely short-lived quadricyclane radical cation: Ishiguro, K.; Khudyakov, I. V.; McGarry, P. F.; Turro, N.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 6933.

(7) Wollenweber, M.; Pinkos, R.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 117.

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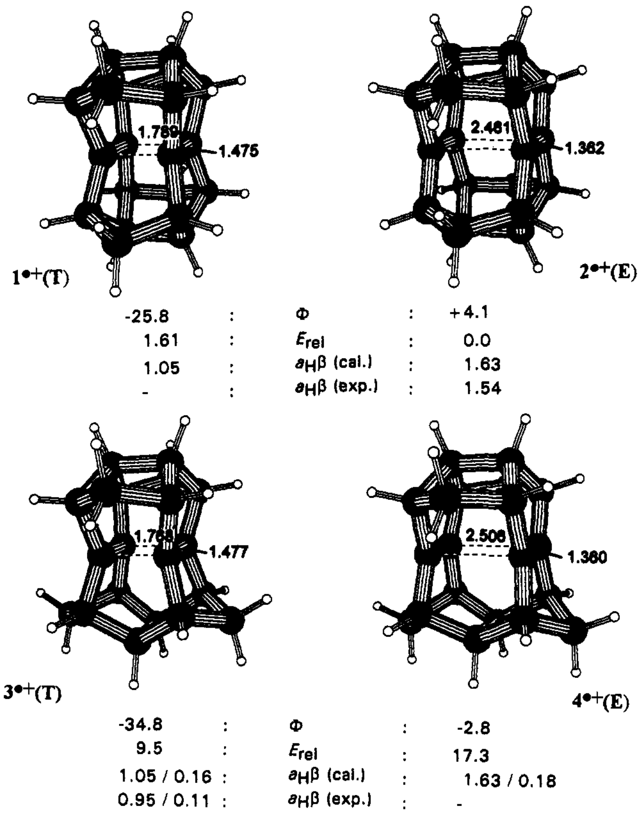

Figure 3. *Ab initio* calculated structures of radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ (UHF/3-21G, bond lengths in angstroms, olefinic pyramidalization Φ in degrees (−)(+) toward in(out)side)) and energies E_{rel} (PMP2/3-21G//3-21G, in kcal mol^{-1} relative to $\mathbf{2}^{\bullet+}$). ESR proton coupling constants $a_H\beta$ (calculated, mT) are based on *ab initio* (UHF/3-21G) calculated geometries and INDO spin densities.

in fluid solution at temperatures between −90 and +10 °C.[8] It was only after γ-irradiation in a CFCl$_3$ matrix (^{60}Co, 77 K)[9] that well-defined ESR and ENDOR spectra were recorded. Above 100 K, the ESR signal becomes apparently isotropic (Figure 2), and its prominent feature is a quintet splitting of 0.95 mT ($a_H\beta$, due to four equivalent β-protons). In addition to this $a_H\beta$ (signal at 27.6 MHz; $\nu_H + {}^1/_2 a_H$), the ENDOR spectrum reveals a signal pair at 12.9/16.2 MHz, manifesting a coupling constant of 0.11 mT (provisionally) ascribed to a second set of four equivalent β-protons, and a signal centered at ν_H mirroring smaller coupling constants (<0.05 mT) of γ-protons. Unlike $\mathbf{2}^{\bullet+}$, where the symmetry (D_{2h}) of the neutral precursors **1** and **2** is preserved, the symmetry is reduced from D_{2d} in **3** to C_{2v} in its ion on the hyperfine time scale.[10] The estimated dihedral angles between the (hypothetical[11]) 2p$_z$ axis and the Cβ−H bonds (θ) for tight ($\mathbf{3}^{\bullet+}$) and extended ($\mathbf{4}^{\bullet+}$) geometries vary between 70 and 80° for the "upper part" and between 10 and 20° for the "lower part" (see formulas). These substantially different dihedral angles for the two sets of four equivalent protons are reflected by the two distinct $a_H\beta$ values of 0.11 and 0.95 mT, respectively. The decrease of $a_H\beta$ from 1.54 mT in $\mathbf{2}^{\bullet+}$ to 0.95 mT in $\mathbf{3}^{\bullet+}$—the respective dihedral angles are nearly the same size—is ascribed to the altered pyramidalization of the "cyclobutanoid carbons" in the latter (an interpretation on the basis of the McConnell equation[12] is not justified).

Ab initio calculations[13] predict that both tight and extended isomers of the radical cations derived from **1** (**2**) and **3** represent energetic minima. However, for pagodane the extended ($\mathbf{2}^{\bullet+}$) and for isopagodane the tight ($\mathbf{3}^{\bullet+}$) forms are more stable by 1.6 and 7.8 kcal mol^{-1}, respectively (the sterically fixed 1,4-radical cation isomers of $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ are energetically unfavorable by 4.9 and 4.4 kcal mol^{-1} at PMP2/3-21G/3-21G). In $\mathbf{2}^{\bullet+}$, the transanular π,π distance is shortened by ca. 0.24 Å with respect to the 2.7 Å (ca. 2.8 Å experimentally[14]) in **2**, and the olefinic pyramidalization is reduced by ca. 10°. In $\mathbf{3}^{\bullet+}$, with deviations of 0.078 and 0.213 Å from the cyclobutane C−C bonds in **3** (1.555 Å, *ab initio* 3-21G), a more cyclobutane-like structure is retained. The designation of $\mathbf{2}^{\bullet+}$ (E) and $\mathbf{3}^{\bullet+}$ (T) as the radical cations obtained from **1** (**2**) and **3**, respectively, is corroborated by comparing calculated (INDO spin density, 3-21G geometry) and experimental ESR proton coupling constants ($a_H\beta$). There is good agreement with the experimental constants for $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ but not for $\mathbf{1}^{\bullet+}$. **T** and **E** isomers have different electronic states ($\mathbf{1}^{\bullet+}$, B$_{1u}$; $\mathbf{2}^{\bullet+}$, B$_{2u}$; $\mathbf{3}^{\bullet+}$, B$_2$; $\mathbf{4}^{\bullet+}$, B$_1$); the nevertheless extremely rapid[6] isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ probably bypasses the concerted route.

Work on further geometrically tuned caged radical cations (homologous [*m.m.n.n*](iso)pagodanes and (seco)dodecahedradienes[15] as particularly extreme points on the [2 + 1] reaction coordinate), is in progress.

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[8] In the electrochemical oxidation (CV), **3** differs from **1** in that the peak potential is significantly higher (1.7 vs 1.2 V, CH$_2$Cl$_2$, −20 °C, v = 1 V s^{-1}, vs Ag/AgCl) and that no reduction wave is registered after reversal of the scan (no ECE process). Wollenweber, M., Dissertation. University of Freiburg, Germany, 1993.

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[10] Symmetry reduction due to trapezoidal geometry of $\mathbf{4}^{\bullet+}$ could not be detected. Whereas pulsed ESR spectra at 20 K were unresolved, the HYSCORE technique (Höfer, P. *J. Magn. Reson.*, in press. Shane, J. J.; Höfer, P.; Reijerse, E. J.; DeBoer, E. J. *J. Magn. Reson.* **1992**, *99*, 596. Höfer, P.; Grupp, A.; Nebenfueh, H.; Mehring, M. *Chem. Phys. Lett.* **1986**, *132*, 279) revealed two different a_H values of 0.8 and 1.2 mT (signal pairs at 3.4/26.3 and −2.1/30.1 MHz, respectively); hyperfine anisotropy within the line width). These data clearly do not correspond to the INDO calculated a_H of 0.3 and 1.4 mT for trapezoidal $\mathbf{4}^{\bullet+}$; they most likely mirror a slight symmetry reduction due to matrix effects, as already noted for the dodecahedra-1,6-diene radical cation (see ref 15).

[11] We define the 2p$_z$ axis as the extension of the longer C···C distance in the cyclobutane moiety.

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