(Iso)Pagodane Radical Cations in Liquid Hydrocarbons: "Time-Resolved Fluorescence-Detected Magnetic Resonance" Study of Valence Isomeric Radical Cations[†]

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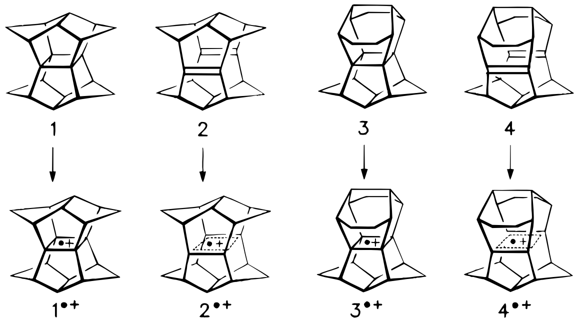
The "tight" (T), cyclobutanoid, and the "extended" (E), π-complex-like, four-centered−three-electron radical cations (4c/3e) derived from (iso)pagodanes and from the valence isomeric (iso)dienes can be viewed as well-separated stationary points on the reaction coordinate for the ethylene/ethylene radical cation [2 + 1]cycloaddition.[1,2] So far, experimentally verified examples (ESR, CV, PE)[3] are the extended [1.1.1.1] ($\mathbf{2}^{\bullet+}$)[4] and *iso*-[2.2.1.1] ($\mathbf{4}^{\bullet+}$) ions,[5] persistent in fluid solution at room temperature, and the tight *iso*-[1.1.1.1]$^{\bullet+}$ [6] and [2.2.1.1]$^{\bullet+}$ ions,[5] observable only in Freon matrix ($CFCl_3$, γ-rays, 77 K).[7] According to calculations, these are the thermodynamically more stable ones of the respective pairs of valence isomers.



Would it be possible to directly observe the thermodynamically unfavorable isomers, specifically the tight ions $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$,[8] even though the activation barrier for the isomerization to the extended $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ should be low? So far, all attempts in this direction had remained unsuccessful.[3,9] According to the ab initio calculations (Table 1, Figure 1),[10] the trapezoidal open (O) structures (eg., $\mathbf{5}^{\bullet+}$) are generally higher in energy and most probably represent the transition states or shallow intermediates in the (symmetry forbidden) valence isomerizations.[11] In this communication the direct observation of tight $\mathbf{1}^{\bullet+}$ and the activation barrier for its isomerization into extended $\mathbf{2}^{\bullet+}$ are reported.

Ionization of **1** under matrix-isolation conditions had not resulted in the trapping of T $\mathbf{1}^{\bullet+}$, in common with radical cations of related strained hydrocarbon cage molecules such as cubane ($C^{\bullet+}$)[12] and quadricyclane ($Q^{\bullet+}$)[13] which were only recently observed with the use of time-resolved ESR methods,[14−16] including fluorescence-detected magnetic resonance (FDMR).[14,15] In the FDMR experiment, fluorescence from recombination of spin-correlated radical ion pairs created by a short electron-beam pulse is modulated at resonant magnetic field by a microwave pulse. The magnetic field dependence of the fluorescence intensity reveals the superimposed ESR spectra of the positive and negative ions present during the microwave pulse. Figure 2 displays the successful application of FDMR to the detection of T $\mathbf{1}^{\bullet+}$ in *n*-hexane solution. The agreement between the experimental (10.2 G) and theoretical coupling constants (10.6 G) for the eight β-hydrogens is excellent.[5] The entire pagodane study consumed less than 50 mg of material,

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Table 1. Ab Initio Calculated Relative Energies (first row PMP2/3-21G//3-21G; second row PMP2/6-31G*//3-21G; kcal mol^{-1}) of the "Tight" (T), "Open" (O), and "Extended" (E) Structures of the [1.1.1.1] Pagodane and [2.2.1.1] *iso*-Pagodane Radical Cations[a–c]

$\mathbf{1}^{\bullet+}$ (T)	$\mathbf{5}^{\bullet+}$ (O)	$\mathbf{2}^{\bullet+}$ (E)	$\mathbf{3}^{\bullet+}$ (T)	(O)	$\mathbf{4}^{\bullet+}$ (E)
0.5	4.9	$\underline{0.0}$	2.9	7.54	$\underline{0.0}$
5.2	10.1	$\underline{0.0}$			—

[a] The relative energies of the experimentally detected species are underlined. [b] The open structures (O) are minima at the Hartree–Fock level. [c] $\langle S^2 \rangle$ of the UHF wave function = 1.756–1.760 for all structures.

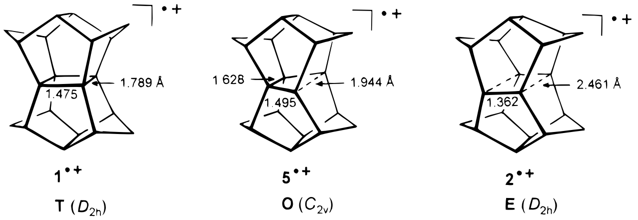

Figure 1. Ab initio UHF/3-21G-optimized geometries of the T, O, and E isomers of the [1.1.1.1] pagodane radical cation.

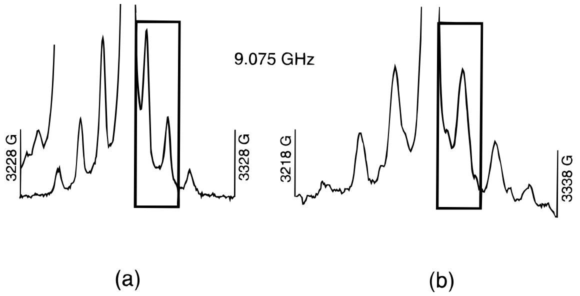

Figure 2. FDMR spectra observed in *n*-hexane solution containing 5 mM **1** and 0.3 mM anthracene-d_{10}: (a) $T = 190$ K, microwave pulse applied from $t = 0$ to $t = 150$ ns; (b) $T = 290$ K, microwave pulse applied from $t = 300$ to $t = 450$ ns. The ionization pulse was a 5 ns electron-beam pulse applied at $t = 0$. The intense central line (off scale) in each spectrum is due to anthracene radical anions.

while a single experimental run required approximately 1 mg of the pagodane compound.

What is the rate of conversion T $\mathbf{1}^{\bullet+} \rightarrow$ E $\mathbf{2}^{\bullet+}$? For $C^{\bullet+}$ and $Q^{\bullet+}$, no product radical cations had been observed either by time-resolved ESR or FDMR, perhaps because isomerization does not occur within the time window of the experiment or because it is slow relative to electron transfer from unoxidized parent molecules to the product radical cation. The study of T $\mathbf{1}^{\bullet+}$ was more informative, since conversion to E $\mathbf{2}^{\bullet+}$ (a(8H) = 15.5 G, compared with 15.4 G ($CFCl_3$) and 16.3 G (calculated)[5]) occurred well within the time window of the FDMR experiment. At room temperature E $\mathbf{2}^{\bullet+}$ was the dominant species after a few hundred nanoseconds (Figure 2).

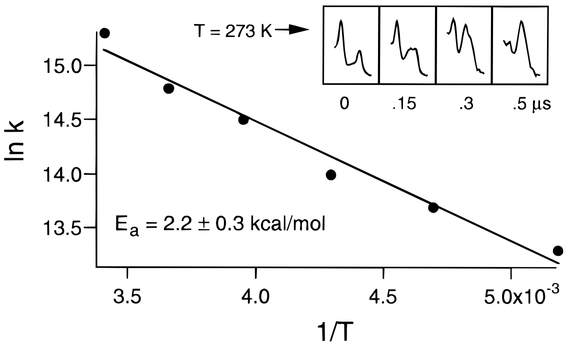

Figure 3. Arrhenius plot for the valence isomerization T $\mathbf{1}^{\bullet+} \rightarrow$ E $\mathbf{2}^{\bullet+}$. The inset shows the evolution of the boxed spectral regions of Figure 2 as a function of microwave pulse delay at 273 K (duration of the pulse was 150 ns).

Thus [1.1.1.1] pagodane **1** is the first example for which the rate of conversion of two valence isomeric radical cations has been directly measured. The half-life for conversion T $\mathbf{1}^{\bullet+} \rightarrow$ E $\mathbf{2}^{\bullet+}$ was approximated by interpolation of data as shown in the inset of Figure 3. The $t_{1/2}$ was taken as the time at which the contributions of the radical cations in the FDMR spectrum were equal. This determination was aided by comparison to computer-simulated absorption curves. The $t_{1/2}$ varied from approximately 1.1 μs at 193 K to approximately 0.15 μs at room temperature. From the Arrhenius plot shown in Figure 3, an activation energy of 2.2 ± 0.3 kcal mol^{-1} was derived.

The isomerization T $\mathbf{3}^{\bullet+} \rightarrow$ E $\mathbf{4}^{\bullet+}$, again predicted to be exothermic (Table 1), could not be followed by spectroscopy. The FDMR spectrum registered for solutions of [2.2.1.1] *iso*-pagodane (**3**), although clearly different from that obtained for E $\mathbf{4}^{\bullet+}$ (a(4H) = 16 G, generated from [2.2.1.1] *iso*-diene **4**) differed significantly from that predicted for T $\mathbf{3}^{\bullet+}$ (analysis not completed). It did, however, conform with the general trend noted throughout the series of pagodanes (and cubane and quadricyclane) that for T radical cations the g-factors are consistently higher than those for E radical cations. Still, to date there is no explanation.

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