

vestigated here, changes in MCD intensity resulting from population of higher levels leads to nesting of saturation magnetization curves taken at different temperatures<sup>10</sup> as shown in Figure 2A for the FeSD data. Alternatively, plotting the temperature dependence at constant field separates the temperature and field effects (Figure 2B) and shows that in the saturation limit the MCD intensity is field-dependent, unlike the field-independent behavior observed for a Kramers doublet.

Analysis of these curves (Figure 2B) provides insight into the nature of the ground-state splittings in these complexes in terms of an  $S = 2$  spin Hamiltonian with parameters  $D$  and  $E$ , the axial and rhombic zero-field splitting components. The MCD temperature dependence at each field is consistent with thermal population over a pair of levels with no contribution from higher levels, indicating  $D < 0$  which places  $M_s = \pm 2$  lowest. Alternative schemes including  $D > 0$  are not consistent with the observed data or with parallel studies on model complexes.<sup>11</sup> Both the  $M_s = \pm 2$  doublet splitting  $\Delta$  due to rhombic splitting plus the Zeeman interaction and the MCD saturation limit intensity can be obtained by fitting each of the curves in Figure 2B by a Boltzmann population over these two levels.<sup>12</sup> The changes in  $\Delta$  and saturation limit intensity for increasing field for both FeSD and SBL are plotted in Figure 2C.

An explanation of Figure 2C can be obtained in terms of the appropriate spin Hamiltonian matrix for an isolated  $M_s = \pm 2$  doublet:<sup>13</sup>

$$\hat{H} = \begin{array}{c} |2^+\rangle \\ |2^-\rangle \end{array} \begin{bmatrix} +\delta/2 & g\beta H \cos \theta \\ g\beta H \cos \theta & -\delta/2 \end{bmatrix} \quad (1)$$

A rhombic zero-field distortion ( $\delta$ ) removes the degeneracy of this non-Kramers doublet, quenching its angular momentum and eliminating MCD intensity. In a magnetic field, the lowest level can be represented as  $|-\rangle = C_1|+2\rangle - C_2|-2\rangle$ , where the mixing coefficients are  $C_2 = ((\delta/g\beta H \cos \theta)^2 + 1)^{-1/2}$  and  $C_1 = (1 - C_2^2)^{1/2}$ . The change in energy of the levels with increasing field relates to the Zeeman interaction, while the MCD intensity reflects the complex component of the wavefunctions, which change from pure real combinations in the zero field limit to pure imaginary at high fields. Analysis of Figure 2C in terms of the spin Hamiltonian for the ground doublet (eq 1) with orientation averaging<sup>8,9</sup> yields  $g_{\text{eff}} = 8$  and  $\delta = 2.2 \text{ cm}^{-1}$  for FeSD and  $g_{\text{eff}} = 8$ ,  $\delta = 6 \text{ cm}^{-1}$  for SBL. In both proteins a doublet is lowest, indicating  $D < 0$ . The magnitude of  $D$  is most directly obtained from the temperature dependence at a small sampling field<sup>14</sup> (0.5 T for FeSD in Figure 2D). The curve is not very sensitive to the value of  $D$  but we estimate  $D = -7 \pm 2 \text{ cm}^{-1}$ . For SBL no excited-state population is observed but the observed magnitude for  $\delta = 3E^2/D$  of  $6 \text{ cm}^{-1}$  and the fact that  $E/D$  must be between 0 and  $1/3$ <sup>15</sup> requires  $D > -21 \text{ cm}^{-1}$ .

The ground- and excited-state data on FeSD and SBL is best interpreted in terms of correlations with model complexes. Excited-state splittings and energies over 5- and 6-coordination of  $\text{Fe}^{2+}$  by N,O and halide ligands is related to geometry,<sup>16</sup> and, in particular, a single band above  $10^4 \text{ cm}^{-1}$  with a second band at

least  $3000 \text{ cm}^{-1}$  to lower energy implies 5-coordination and approximately square-pyramidal geometry. The presence of two bands near  $10000 \text{ cm}^{-1}$  with a splitting of  $1000 \text{ cm}^{-1}$  implies 6-coordination. A supporting correlation can be made from ground-state parameters:  $D > 10 \text{ cm}^{-1}$  is representative of 6-coordinate iron, while  $D = 2-10 \text{ cm}^{-1}$  is characteristic of 5-coordination.<sup>17</sup> Lower coordination can be ruled out by the energy of the ligand field transitions. From these correlations, we deduce that the most likely coordination number for the SBL ferrous site is six, while the ferrous site in FeSD appears to be 5-coordinate, consistent with the crystallographically determined site structure of  $\text{Fe}^{3+}$  SD<sup>18,19</sup> being retained upon reduction.

In summary, significant differences have been observed in both excited-state spectra and ground-state spin Hamiltonian parameters as obtained through low-temperature MCD spectroscopy, which indicate differences in coordination environments in these two ferrous non-heme iron active sites.

**Acknowledgment.** We acknowledge useful discussions with Mark D. Allendorf, Dr. John D. Lipscomb, and Dr. Vincent B. H. Huynh. This investigation was supported by the National Science Foundation (PCM-81-19844) and Public Health Service (1F32-AM07456-01).

Registry No. SBL, 9029-60-1; FeSD, 9054-89-1; Fe, 7439-89-6.

(17) For example, see: (a) Hodges, K. O.; Wollmann, R. G.; Barefield, E. K.; Hendrickson, D. N. *Inorg. Chem.* 1977, 16, 2746-2751. (b) Supp, R. C. *J. Chem. Phys.* 1959, 30, 326-327.

(18) Ringe, D.; Petsko, G. A.; Yamakura, F.; Suzuki, K.; Ohmori, D. *Proc. Natl. Acad. Sci. U.S.A.* 1983, 80, 3879-3883.

(19) Stallings, W. C.; Powers, T. B.; Patridge, K. A.; Fee, J. A.; Ludwig, M. L., *Proc. Nat. Acad. Sci. USA* 1983, 80, 3884-3888.

## Pagodane Dication, a Unique $2\pi$ -Aromatic Cyclobutanoid System<sup>1</sup>

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The highly symmetrical undecacyclic  $\text{C}_{20}\text{H}_{20}$  hydrocarbon pagodone (**1**) (undecacyclo[9.9.0.0<sup>1,5</sup>.0<sup>2,12</sup>.0<sup>2,18</sup>.0<sup>3,7</sup>.0<sup>6,10</sup>.0<sup>8,12</sup>.0<sup>11,15</sup>.0<sup>13,17</sup>.0<sup>16,20</sup>]icosane) has been recently synthesized by Prinzbach et al.<sup>2</sup> as a potential precursor for its structurally related isomer dodecahedrane (**2**).<sup>3</sup> An isomerization pathway that can be considered would start with pagodane cations prepared under superacidic conditions. Previously we were successful<sup>4</sup> in isom-

(10) Johnson, M. K.; Robinson, A. E.; Thomson, A. J. In "Iron Sulfur Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1979; pp 367-406.

(11) Whittaker, J. W.; Solomon, E. I., unpublished results.

(12)  $A = A_{\text{sat limit}} \tanh(\Delta/2kT)$

(13) Here,  $|2^+\rangle$  and  $|2^-\rangle$  are the symmetric and antisymmetric combinations of the pure spin functions diagonal in zero field,  $\delta$  is the rhombic splitting within the doublet ( $3E^2/D$ ),  $g\beta H \cos \theta$  is the orientation-dependent Zeeman interaction for the doublet, and  $g$  is the effective  $g$  value.

(14) Browett, W. R.; Fucaloro, A. F.; Morgan, T. V.; Stephens, P. J. *J. Am. Chem. Soc.* 1983, 105, 1868-1872.

(15) Blumberg, W. E. In "Magnetic Resonance in Biological Systems"; Ehrenberg, A.; Malmstrom, B. G.; Vänngård, T., Eds.; Pergamon Press: New York, 1983; pp 119-133.

(16) For example, see: (a) Burns, R. G.; Clark, M. G.; Stone, A. J. *Inorg. Chem.* 1966, 5, 1268-1272. (b) Gaffney, E. S., *Phys. Rev.* 1973, 8B, 3484-3486; (c) Riley, D. P.; Merell, P. H.; Stone, J. A.; Busch, D. H., *Inorg. Chem.* 1975, 14, 490; (d) Ciampolini, M.; Nardi, N.; Speroni, G. P., *Coord. Chem. Revs.* 1966, 1, 222-233; (e) Holmes, O. G.; McClure, D. S., *J. Chem. Phys.* 1957, 26, 1686.

(1) Considered Stable Carbocations. 267. University of Southern California. For part 266, see: Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.*, in press.

(2) (a) Fessner, W.-D.; Prinzbach, H.; Rihs, G. *Tetrahedron Lett.* 1983, 5857. (b) Fessner, W.-D. Dissertation, University of Freiburg, 1986. The dihydropagodane **7** ( $X = \text{H}$ ) showed seven peaks in the <sup>13</sup>C NMR spectrum at  $\delta$  <sup>13</sup>C 69.0 (singlet), 60.1 (doublet), 54.9 (doublet), 44.1 (doublet), 39.7 (doublet), 37.0 (triplet), and 34.7 (triplet).

(3) (a) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. J. *Am. Chem. Soc.* 1983, 105, 5446.

(4) Olah, G. A.; Olah, J. A. *Synthesis* 1973, 488.

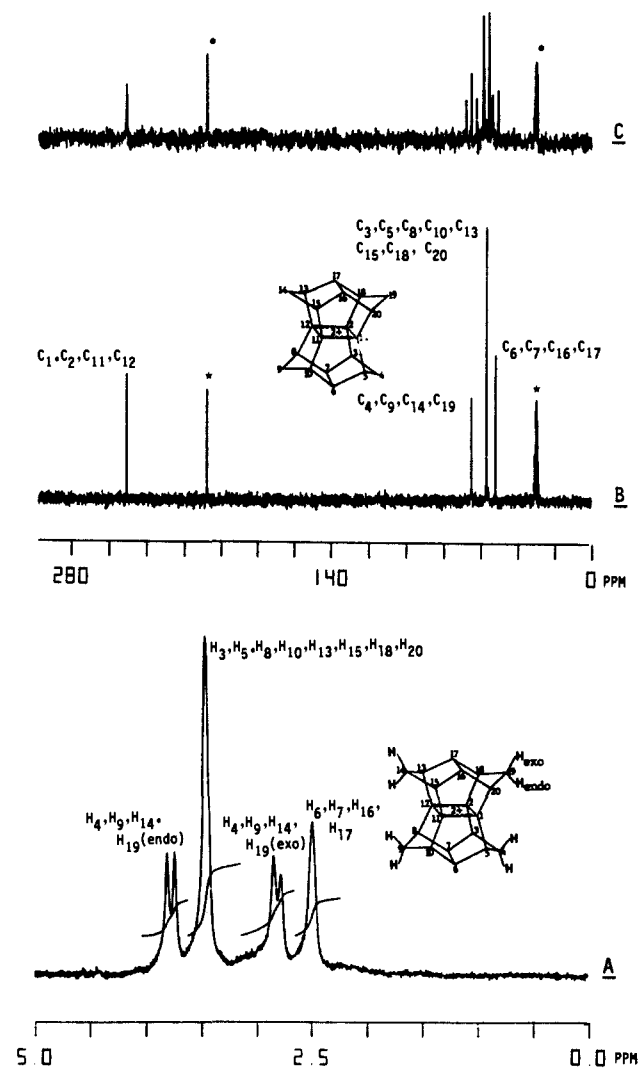
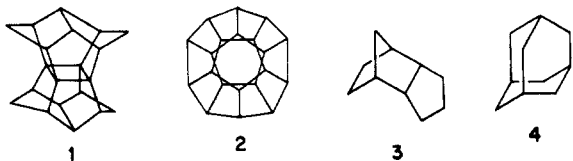


Figure 1. (A) 200-MHz  $^1\text{H}$  NMR spectrum of pagodane dication in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-80^\circ\text{C}$ . (B) 50-MHz proton-decoupled  $^{13}\text{C}$  NMR spectrum. (C) Proton-coupled spectrum (\* peaks due to lock solvent  $(\text{CD}_3)_2\text{CO}$ ).

erizing *endo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane (3) to adamantane 4 in  $\text{HF}:\text{SbF}_5$  medium.

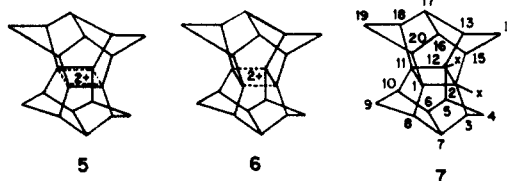


Dissolution<sup>5</sup> of pagodane 1 in 5-fold excess of freshly distilled  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$  resulted in a yellow colored solution, whose 200-MHz  $^1\text{H}$  NMR spectrum indicated a complex spectral pattern in the aliphatic region. However, following several hours at  $-80^\circ\text{C}$ , the solution showed a very clean  $^1\text{H}$  NMR spectrum (Figure 1A);  $\delta^1\text{H}$  3.37 (br, 8H), 3.68 and 2.72 (AX doublets,  $J_{\text{H-H}} = 13.2$  Hz, 8 H),<sup>6</sup> and 2.39 (br, 4 H). The 50-MHz  $^{13}\text{C}$  NMR spectrum of the same solution at  $-80^\circ\text{C}$  (Figure 1B,C) showed only four peaks at  $\delta^{13}\text{C}$ : 251.0 (singlet), 65.3 (triplet,  $J_{\text{C-H}} = 141.9$  Hz), 57.2 (doublet,  $J_{\text{C-H}} = 148.0$  Hz), and 52.3 (doublet,  $J_{\text{C-H}} = 152.8$  Hz). The observed symmetry and the extent of deshielding in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the species in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution when compared to the progenitor

(5) Ten milligrams of pagodane was used. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian Associates Model XL-200 NMR spectrometer. Similar results were also obtained in  $\text{FSO}_3\text{H}:\text{SbF}_5/\text{SO}_2\text{ClF}$  solution.

(6) The AX pattern was confirmed by selective homonuclear proton decoupling.

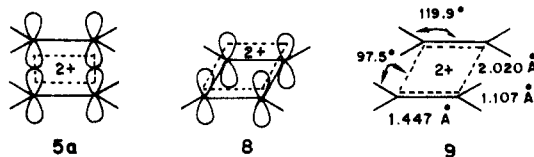
pagodane (1) (Table I) seem to imply that the species is ionic in nature and has the  $D_{2h}$  symmetry of the parent pagodane itself. The ion solution was found to be surprisingly stable.<sup>7</sup> Quenching the ion solution with excess of cold methanol (at  $-78^\circ\text{C}$ ) and usual aqueous  $\text{NaHCO}_3$  workup<sup>8a</sup> provided a white crystalline product. The  $^{13}\text{C}$  NMR spectroscopic analysis of the product in  $\text{CDCl}_3$  solution indicated a simple main product in more than 70% purity, as well as minor byproducts (not yet identified). After repeated recrystallization (from pentane) the major product was isolated.<sup>8b</sup> The product showed eight peaks at  $\delta^{13}\text{C}$ : 101.5 (singlet), 75.2 (singlet), 58.8 (doublet), 49.5 (quartet), 42.8 (doublet), 41.7 (doublet), 35.7 (triplet), and 33.0 (triplet). The 200-MHz  $^1\text{H}$  NMR spectrum of the purified product in  $\text{CDCl}_3$  showed the following absorptions:  $\delta^1\text{H}$  3.14 (singlet, 6 H), 2.62 (br, 4 H), 2.54 (doublet  $J_{\text{AB}} = 13.6$  Hz, 2 H), 2.38 (br, 8 H), 1.79 (doublet,  $J_{\text{AB}} = 11.2$  Hz, 2 H), 1.42 (doublet  $J_{\text{AB}} = 11.2$  Hz, 2 H), and 1.39 (doublet,  $J_{\text{AB}} = 13.6$  Hz, 2 H). The mass spectrometric analysis of the product indicates peaks at  $m/e$  322 (1.4%), 292 (22.9%), and 291 (100%). The parent mass peak at  $m/e$  322 indicates molecular formula of the purified crystalline material to be  $\text{C}_{20}\text{H}_{20}(\text{OCH}_3)_2$ , from which the loss of a  $\text{OCH}_3$  group would give the base peak at  $m/e$  291. Observation of two kinds of methylene in  $^{13}\text{C}$  as well as  $^1\text{H}$  (two AB's) NMR spectra is in accordance with the structure 7 ( $\text{X} = \text{OCH}_3$ ). This assignment



selected bond lengths (7-OCH<sub>3</sub>): C<sub>1</sub>-C<sub>2</sub> (C<sub>11</sub>-C<sub>12</sub>), 1.540(11) (1.510(11)) Å;  
C<sub>1</sub>-C<sub>11</sub>, 1.600(10) Å; C<sub>6</sub>-C<sub>7</sub> (C<sub>16</sub>-C<sub>17</sub>) 1.580 (12) Å

is supported by comparison with the dihydropagodane 7 ( $\text{X} = \text{H}$ ), which is selectively formed by Pd/C-hydrogenolysis of 1.<sup>2b</sup> Finally the structure 7 ( $\text{X} = \text{OCH}_3$ ) was ascertained by an X-ray crystallographic study<sup>8c</sup> (the important bond distances are shown below the structure). It is suggested that the ionic product derived from pagodane 1 is pagodane dication which is formed by the 2e- $\sigma$ -oxidation of the strained cyclobutane ring and which can be depicted by either of the two  $D_{2h}$  structures 5 or 6.<sup>9</sup> 5 is given preference in view of the product structure 7 ( $\text{X} = \text{OCH}_3$ ) and of the prospective relative strength of the C<sub>1</sub>-C<sub>2</sub>/C<sub>1</sub>-C<sub>11</sub> bonds (the former is longer, by 0.037 Å, in the 4,9-diester of 1).<sup>2a</sup> In addition, according to MM2 calculations of the two dienes derived from 5 and 6 the former is more stable by 48.6 kcal/mol.<sup>2b</sup>

The remarkable stability of the dication 5 can be rationalized as that of a unique 2 $\pi$ -aromatic system. In fact, the dication 5 (see structure 5a) can be considered to be topologically equivalent



to the cyclobutadiene dication 8. The situation is analogous to the transition state for the allowed cycloaddition of ethylene with ethylene dication (mode 2 and mode 0 interaction).<sup>10</sup> The support

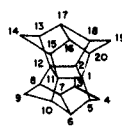
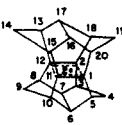
(7) The solution was stable at  $0^\circ\text{C}$  for several hours.

(8) (a) Dichloromethane was used to extract the product; (b) the white crystalline product melted at  $235^\circ\text{C}$  (uncorrected) and showed the following analytical data:  $\text{C}_{22}\text{H}_{20}(\text{OCH}_3)_2$ , mw 322.45. Obsd: C, 81.45; H, 8.10. Calcd: C, 81.94; H, 8.12). (c) A colorless crystal (space group  $Fdd2$ ) of dimension (mm)  $0.23 \times 0.18 \times 0.18$  was used in the X-ray diffraction experiment. The final  $R$  factor is 0.075 for 1220 reflections with  $I > 3\sigma(I)$ . Further structural refinement is in progress. Full structural details of 7-X ( $\text{X} = \text{OCH}_3$ ) will be published elsewhere.

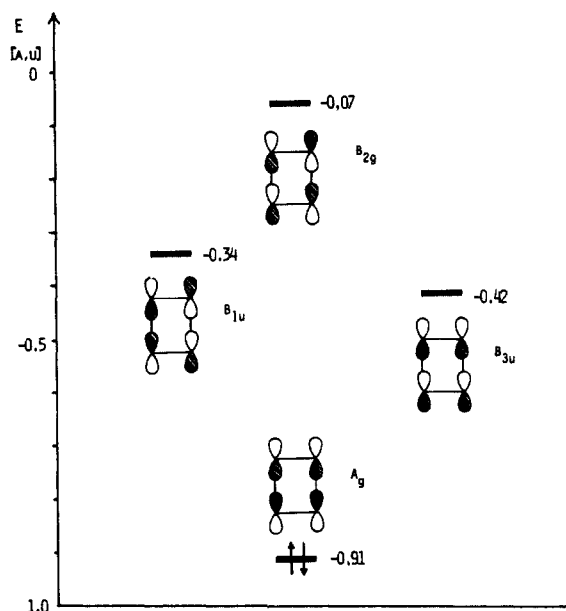
(9) One can also consider the dication as a six-electron system (structure 5  $\leftrightarrow$  6) by delocalizing the additional 4e- electrons. On the basis of ab initio theory at STO-3G level it seems unlikely.

(10) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* 1971, 93, 6193.

**Table I.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data on Pagodane (**1**) and Pagodane Dication (**5**)

structure	$^1\text{H}$ , $\delta^a$	$^{13}\text{C}$ , $\delta^a$
	$^b$ $\text{H}_4, \text{H}_9, \text{H}_{14}, \text{H}_{19} = 1.58$ (AB, 8 H); $\text{H}_3, \text{H}_5, \text{H}_8, \text{H}_{10}, \text{H}_{13}, \text{H}_{15}, \text{H}_{18}, \text{H}_{20} = 2.24$ (br, 8 H); $\text{H}_6, \text{H}_7, \text{H}_{16}, \text{H}_{17} = 2.60$ (br, 4 H)	$\text{C}_1, \text{C}_2, \text{C}_{11}, \text{C}_{12} = 62.8$ (s); $\text{C}_6, \text{C}_7, \text{C}_{16}, \text{C}_{17} = 59.6$ (d, $J_{\text{C-H}} = 137.8$ Hz); $\text{C}_3, \text{C}_5, \text{C}_8, \text{C}_{10}, \text{C}_{13}, \text{C}_{15}, \text{C}_{18}, \text{C}_{20} = 42.6$ (d, $J_{\text{C-H}} = 140.6$ Hz); $\text{C}_4, \text{C}_9, \text{C}_{14}, \text{C}_{19} = 41.9$ (t, $J_{\text{C-H}} = 129.8$ Hz)
	$^c$ $\text{H}_4, \text{H}_9, \text{H}_{14}, \text{H}_{19} = \text{AX}$ spin system; $\text{H}_{\text{endo}} = 3.68$ (d, $J_{\text{H-H}} = 13.2$ Hz, 4 H); $^d$ $\text{H}_{\text{exo}} = 2.72$ (d, $J_{\text{H-H}} = 13.2$ Hz, 4 H); $^d$ $\text{H}_6, \text{H}_7, \text{H}_{16}, \text{H}_{17} = 2.39$ (br, 4 H); $\text{H}_3, \text{H}_5, \text{H}_8, \text{H}_{10}, \text{H}_{13}, \text{H}_{15}, \text{H}_{18}, \text{H}_{20} = 3.37$ (br, 8 H)	$\text{C}_1, \text{C}_2, \text{C}_{11}, \text{C}_{12} = 251.0$ (s); $\text{C}_4, \text{C}_9, \text{C}_{14}, \text{C}_{19} = 65.3$ (t, $J_{\text{C-H}} = 141.9$ Hz); $\text{C}_3, \text{C}_5, \text{C}_8, \text{C}_{10}, \text{C}_{13}, \text{C}_{15}, \text{C}_{18}, \text{C}_{20} = 57.2$ (d, $J_{\text{C-H}} = 148.0$ Hz); $\text{C}_6, \text{C}_7, \text{C}_{16}, \text{C}_{17} = 52.3$ (d, $J_{\text{C-H}} = 152.8$ Hz)

$^a$  Chemical shifts are in ppm from external capillary tetramethylsilane.  $^b$  In  $\text{CDCl}_3$  solution at 25 °C.  $^c$  In  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at -80 °C.  $^d$  Endo and exo assignments are only tentative. Multiplicities: s = singlet, d = doublet, t = triplet, br = broad.

**Figure 2.** MO diagram of distorted cyclobutane dication.

for such a structure **5** also comes from the MINDO/3 theory. Olah, Schleyer, and Dewar<sup>11</sup> in 1973 rationalized the stability of the related 1,4-bicyclo[2.2.2]octanediyl dication<sup>12a</sup> through such pseudo- $2\pi$  aromatic overlap.

We also carried out ab initio calculations at the STO-3G level<sup>12b,c</sup> on the parent cyclobutane dication. To simulate the strain, which is imposed by the pagodane framework, the geometry was optimized in a  $D_{2h}$  symmetry. The calculations reveal that the cyclobutane dication has a rectangular structure **9**. The shorter C-C bonds with 1.447 Å in **9** seem to indicate a bond order between C-C single and C-C double bonds, whereas the other two bonds with considerably longer length (2.020 Å) imply a bond order around 0.5 (i.e., less than a C-C single bond). In contrast to the well-known cyclobutadiene dication,<sup>13</sup> the  $\pi$ -orbitals which are delocalized lie in the plane of the cyclobutane ring (structure **5a**). The  $\pi$ -MO's of **9** are shown in Figure 2 with lowest bonding

(11) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829.

(12) (a) The assumed long-lived 1,4-bicyclo[2.2.2]octanediyl dication has been recently reinvestigated and found to be only the monocation monodonor acceptor complex: de Meijere A.; Schallner, O.; Göllitz, P.; Weber, W.; Schleyer, P. v. R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.*, in press. Nevertheless the theoretical argument put forward in ref 11 seems valid in regard to the presently studied pagodane dication: (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPL* **1981**, *13*, 406. Van Kamper, P. N.; Smiths, G. F.; De Leeuw, F. A. M.; Altona, C. *QCPE* **1982**, *14*, 437.

(13) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 6290 and references cited therein. The cyclobutanoid carbons in tetramethylcyclobutadiene dication are observed at  $\delta^{13}\text{C}$  209.7.

MO occupied with 2 electrons which provide the aromatic stabilization.

An accessible experimental test for aromatic system is the detection of a ring current. A ring current effect in the pagodane dication seems to be indicated at positions 6,7 and 16,17. Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts at these positions are shielded compared to pagodane (by 7.3 ppm for carbons and 0.21 ppm for the protons). It is noted that the cyclobutanoid carbons in **5** are much more deshielded than those observed in the isoconjugate tetramethylcyclobutadiene dication<sup>13</sup> (by 41.3 ppm). However, it is improper to compare these chemical shifts in view of the different types of  $\pi$ -bonding. We are continuing our studies to find other examples of  $2\pi$ -aromatic dications in similarly disposed cyclobutane-containing system.<sup>14,15</sup>

**Acknowledgment.** Support of this work at USC by the National Science Foundation is gratefully acknowledged. R.H. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship.

(14) Cyclic voltammetric measurements ( $\text{SO}_2$ , -40 °C, TBA- $\text{PF}_6$ ) reveal an ECE mechanism for the oxidation of **1** to a dication at 1.2 V (vs.  $\text{Ag}/\text{AgCl}$ ). **1** reacts with tris(*p*-bromophenyl)amminium hexachloroantimonate or with bromine ( $\text{CDCl}_3$ , 20 °C) to give exclusively the dichloride **7** ( $\text{X} = \text{Cl}$ ) and the dibromide **7** ( $\text{X} = \text{Br}$ ), respectively. Their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra strongly support the assignment of the dimethoxy/dihydro structures **7** ( $\text{X} = \text{OCH}_3/\text{H}$ ) (Prinzbach, H.; Bulusu, A. R. C. M.; Fessner, W.-D.; Heinze, J.; Mortensen, J., unpublished results).

(15)  $1e^-$  oxidations on strained  $\sigma$ -bonds are known: Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740.

### Gas-Phase Pyrolysis of Isotopically and Stereochemically Labeled $\alpha$ -Pinene: Evidence for a Nonrandomized Intermediate

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Liquid- and gas-phase pyrolysis of  $\alpha$ -pinene leads to dipentene (racemic limonene), allocimine (the 1,5-hydrogen shift product of ocimine, the likely primary product), and enantiomeric  $\alpha$ -pinene. These materials are derived by retro-ene, retro 2 + 2, and 1,3-sigmatropic shift reactions, respectively. The mechanistic question is whether all three are separate, perhaps concerted processes, or if there is a common biradical intermediate.

