

# Long-lived [1.1.1.1]- and [2.2.1.1]-‘Isopagodane’ dications: novel 4C/2e $\sigma$ -bishomoaromatic dicationst

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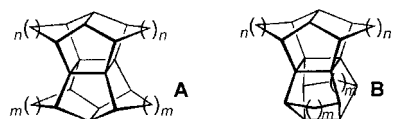
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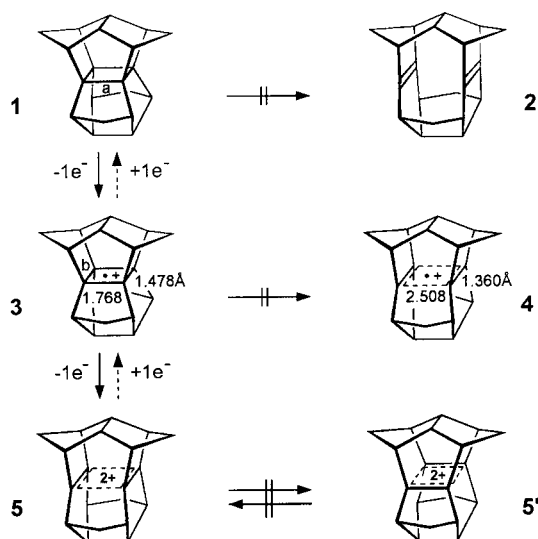
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The dications generated from [1.1.1.1] and [2.2.1.1]isopagodane in  $\text{SbF}_5\text{--SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$  are of  $\sigma$ -bishomoaromatic nature (4C/2e), very similar in geometry, yet chemically different in their properties.

The [1.1.1.1]pagodane (**A**,  $m = n = 1$ ) and functionalized derivatives have received considerable attention as intermediates in the various synthetic routes to pentagonal dodecahedranes.<sup>1</sup> An important theoretical aspect is linked to the central, planar, peralkylated cyclobutane ring: Two-electron oxidations had allowed the experimental verification of  $\sigma$ -homoaromaticity in form of the respective 4C/2e dications.<sup>2,3</sup> In order to gain more insight into the limiting structural and energetic prerequisites of this intriguing phenomenon—and into the intermediate ‘tight’ and ‘extended’ radical cations<sup>4</sup>—structural variations of the pagodane skeleton have been made by homologation<sup>5</sup> and  $90^\circ$  rotation of the two molecular ‘halves’ to give the isopagodanes **B**.<sup>6</sup>



The [1.1.1.1]- and [2.2.1.1]-isopagodanes **1** and **6** had shown rather differing behaviour upon one-electron oxidation: the radical cation of **1** (Scheme 1) was only observable in a Freon



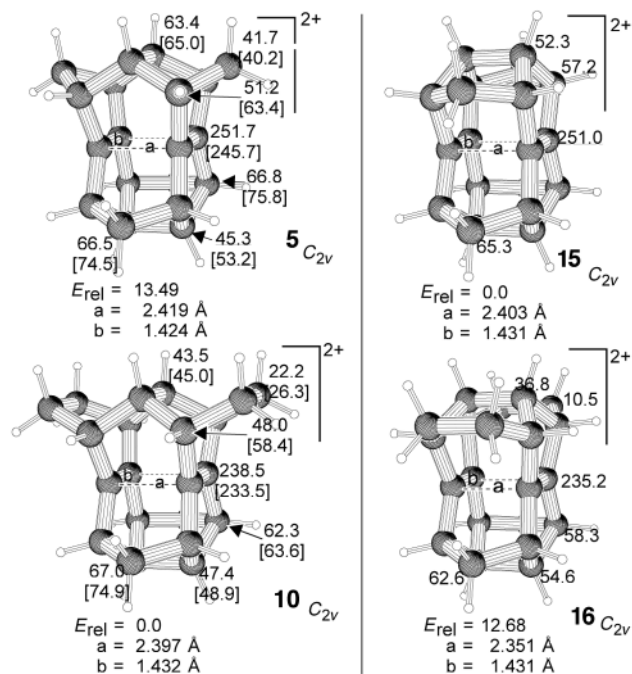
Scheme 1

matrix ( $-196^\circ\text{C}$ ) and was identified as a tight species (**3**,  $a = 1.768\text{ Å}$ ),<sup>7</sup> that from **6** was persistent in fluid solution ( $-40^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2$ ) and existed, also in the Freon matrix, in an extended configuration (**9**,  $a = 2.512\text{ Å}$ ). Under cyclic voltammetry (CV) conditions only for the latter a (reversible) two-electron oxidation wave (ECE) had been recorded.<sup>8</sup> Apparently the iso[1.1.1.1] skeleton does not allow the expansion of tight **3** into extended **4**. Here the question is addressed whether the  $\sigma$ -bishomoaromatic stabilization potentially arising from two-electron oxidation of **1** and **6** would be sufficient to enforce the skeletal changes which are necessary to make the respective cyclically delocalized 4C/2e dications observable.

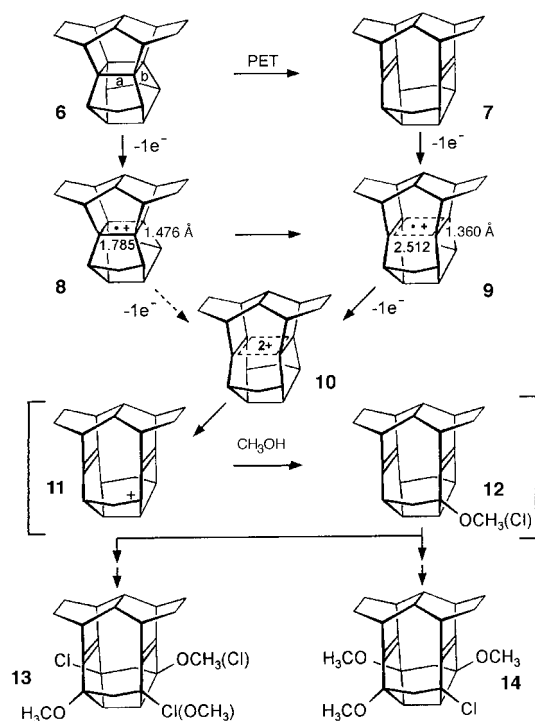
Upon dissolution of **1** in  $\text{SbF}_5\text{--SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  (dry ice–acetone bath) the initial dark green–blue color of the paramagnetic solution (**3'**) upon prolonged vortex stirring changed into the light yellow of the diamagnetic solution. The 75 MHz  $^{13}\text{C}$  NMR spectrum<sup>9</sup> consisted of seven absorptions at  $\delta_{\text{C}}$  251.7 (s), 66.8 (d,  $J_{\text{C-H}}$  169), 66.5 (t,  $J_{\text{C-H}}$  139.6), 63.4 (d,  $J_{\text{C-H}}$  149.3), 51.2 (d,  $J_{\text{C-H}}$  163.0), 45.3 (d,  $J_{\text{C-H}}$  154.3) and 41.7 (t,  $J_{\text{C-H}}$  148.8), the 300 MHz  $^1\text{H}$  NMR spectrum<sup>9</sup> of seven (two are overlapping) unresolved signals [ $\delta_{\text{H}}$  3.35 (br, 4H), 3.3 (br, 2H), 3.2 (br, 4H), 2.76 (br, 4H), 2.27 (br, 2H), 1.84 (br, 2H), 1.72 (br, 2H)]. Number and observed deshielding of carbons and protons relative to neutral **1**, in comparison with isomeric dication **15** (Fig. 1),<sup>4</sup> establish the  $\text{C}_{2v}$  symmetrical  $\sigma$ -bishomoaromatic structure **5** and exclude a rapid equilibration with degenerate **5'**. The lowering of the symmetry from  $D_{2d}$  of **1** to  $\text{C}_{2v}$  of **5** reflects distortion of the central carbon core from square to rectangular. Quenching the ion solution with cold MeOH (at  $-78^\circ\text{C}$ ) induced two-electron reduction back to pagodane **1** (70% isolated) rather than to the much less stable diene **2** [ $\Delta E_{\text{rel}}$  (**1–2**) = 14.68 kcal mol<sup>-1</sup>, Fig. 2]. Particularly 1,4-bisaddition to give the bismethoxy ether was not observed (<5%); in case of reference **15** the corresponding bisether had been the sole product.<sup>2</sup>

Exposure of **6** (Scheme 2) to similar oxidation conditions ( $-78^\circ\text{C}$ ) produced the deep blue colour of the highly persistent extended radical cation **9**. Only after repeated vortex mixing at higher temperature ( $0^\circ\text{C}$ ) the colour changed into pale yellow. The seven  $^{13}\text{C}$  NMR signals of the diamagnetic solution at  $\delta_{\text{C}}$  238.5 (s), 67.0 (t,  $J_{\text{C-H}}$  142.9), 62.3 (d,  $J_{\text{C-H}}$  138.3), 48.0 (d,  $J_{\text{C-H}}$  148.8), 47.4 (d,  $J_{\text{C-H}}$  130.3), 43.5 (d,  $J_{\text{C-H}}$  150.2), 22.2 (t,  $J_{\text{C-H}}$  140.1) and the  $^1\text{H}$  NMR signals (partially superimposed) at  $\delta_{\text{H}}$  3.26 (br, 6H), 2.88 (br, 6H), 2.66 (br, 4H), 2.08 (br, 4H), 1.4 (br, 4H), 0.82 (br, 4H) are in line with the retention of  $\text{C}_{2v}$  symmetry in going from **6** to the  $\sigma$ -bishomoaromatic dication **10**. The formation of the same dication by the analogous oxidation of [2.2.1.1]isopagodadiene **7**<sup>10</sup> and the comparison with isomeric dication **16** (Fig. 1) provided additional confirmation. After quenching with MeOH ( $-78^\circ\text{C}$ ) from a complex product mixture the dichlorodimethoxy- and chlorotrimethoxydienes **13** (two isomers) and **14** in the ratio  $\sim 1:2$  were separated. Two-electron reduction to either **6** or **7** was not detected. A plausible explanation implies reduced *anti*-Bredt-

† Stable Carbocations, Part 309. For Part 308, see G. K. S. Prakash, V. P. Reddy, G. Rasul, J. Casanova and G. A. Olah, *J. Am. Chem. Soc.*, 1998, **120**, 13 362.



**Fig. 1** B3LYP/6-31G\* optimized structures, experimental and calculated (in brackets)  $^{13}\text{C}$  NMR chemical shifts based on the DFT geometries and a GIAO B3LYP/6-31G\* NMR calculation of the dications **3**, **10** (**15**, **16** as references); a and b denote DFT bond lengths; energies ( $E_{\text{rel}}$ ) are given in kcal mol $^{-1}$  and are relative to the more stable isomer.



**Scheme 2**

protection in **10** opening up a sequence of deprotonation (e.g. **11**), nucleophilic addition (e.g. **12**) and reoxidation of the respective functionalized dienes.

GIAO<sup>11</sup> chemical shift calculations were performed based on the DFT calculated geometries. Calculated and observed chemical shifts agree within the error limit of the method. The  $^{13}\text{C}$  shifts of the core carbons of **5** and **10** are very similar to those of the reference dications **15** and **16**; the  $^{13}\text{C}$  NMR chemical shift additivity analysis<sup>12</sup> with total chemical shift differences of 910 and 905 ppm, respectively, amounts to more than 450 ppm deshielding per unit positive charge in both systems (cf. 460 ppm for **15**, 418 ppm for **16**).

According to *ab initio* calculations at the B3LYP/6-31G\* level of theory<sup>13</sup> the dications **5** and **10** are of  $C_{2v}$  symmetry and the central C4 units have rectangular geometries very similar to the reference dications **15** and **16** (Fig. 1). As opposed to the hypersurface of the neutral species and the radical cations (tight isomers **3**, **8**; extended isomers **4**, **9**) there is only one minimum on both dicationic hypersurfaces. Evidently,  $\sigma$ -bishomoaromaticity provides the energy in dication **5** for the lengthening (shortening) of the a(b)-bonds by 0.651 (0.054) Å with respect to precursor **3** [by 0.857 (0.136) Å relative to **1**], in dication **10** for shortening (lengthening) by 0.115 (0.072) Å with respect to **9** [by 0.484 (0.092) Å relative to diene **7**].<sup>14</sup> The dications **5** and **10** (like **15** and **16**) can be viewed as frozen Woodward–Hoffmann allowed transition states of [1 + 1] cycloadditions of two ethylene radical cations with lengths of the a-bonds which are close to the mean values of the two isomers on the symmetry forbidden neutral [2+2] and radical cationic [2 + 1] cycloaddition energy hypersurfaces.

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