Long-lived [1.1.1.1]- and [2.2.1.1]-'Isopagodane' dications: novel 4C/2e σ-bishomoaromatic dications†

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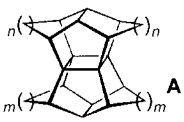
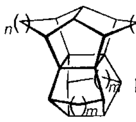
The dications generated from [1.1.1.1] and [2.2.1.1]isopagodane in SbF_5–SO_2ClF solution at −78 °C are of σ-bishomoaromatic nature (4C/2e), very similar in geometry, yet chemically different in their properties.

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.[1] An important theoretical aspect is linked to the central, planar, peralkylated cyclobutane ring: Two-electron oxidations had allowed the experimental verification of σ-homoaromaticity in form of the respective 4C/2e dications.[2,3] 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[4]—structural variations of the pagodane skeleton have been made by homologation[5] and 90° rotation of the two molecular 'halves' to give the isopagodanes **B**.[6]

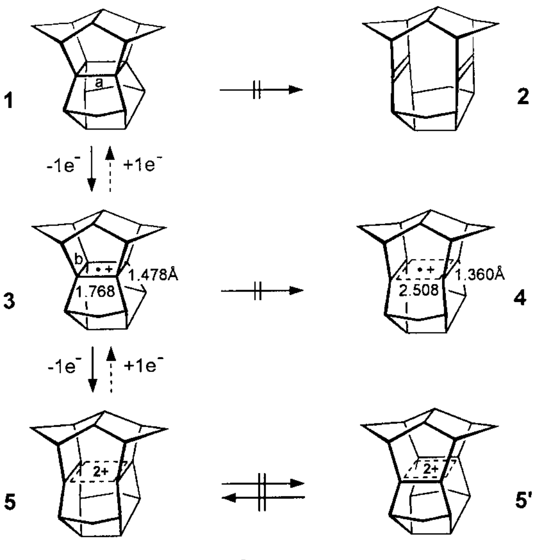


A



B

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 matrix (−196 °C) and was identified as a tight species (**3**, $a = 1.768$ Å),[7] that from **6** was persistent in fluid solution (−40 °C, CH_2Cl_2) and existed, also in the Freon matrix, in an extended configuration (**9**, $a = 2.512$ Å). Under cyclic voltammetry (CV) conditions only for the latter a (reversible) two-electron oxidation wave (ECE) had been recorded.[8] 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 σ-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.



Scheme 1

Upon dissolution of **1** in SbF_5–SO_2ClF at −78 °C (dry ice–acetone bath) the initial dark green–blue color of the paramagnetic solution (**3**[7]) upon prolonged vortex stirring changed into the light yellow of the diamagnetic solution. The 75 MHz ^{13}C NMR spectrum[9] consisted of seven absorptions at δ_C 251.7 (s), 66.8 (d, J_{C-H} 169), 66.5 (t, J_{C-H} 139.6), 63.4 (d, J_{C-H} 149.3), 51.2 (d, J_{C-H} 163.0), 45.3 (d, J_{C-H} 154.3) and 41.7 (t, J_{C-H} 148.8), the 300 MHz ^1H NMR spectrum[9] of seven (two are overlapping) unresolved signals [δ_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),[4] establish the C_{2v} symmetrical σ-bishomoaromatic structure **5** and exclude a rapid equilibration with degenerate **5′**. The lowering of the symmetry from D_{2d} of **1** to C_{2v} of **5** reflects distortion of the central carbon core from square to rectangular. Quenching the ion solution with cold MeOH (at −78 °C) induced two-electron reduction back to pagodane **1** (70% isolated) rather than to the much less stable diene **2** [ΔE_{rel} (**1**–**2**) = 14.68 kcal mol^{-1}, 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.[2]

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

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† 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.

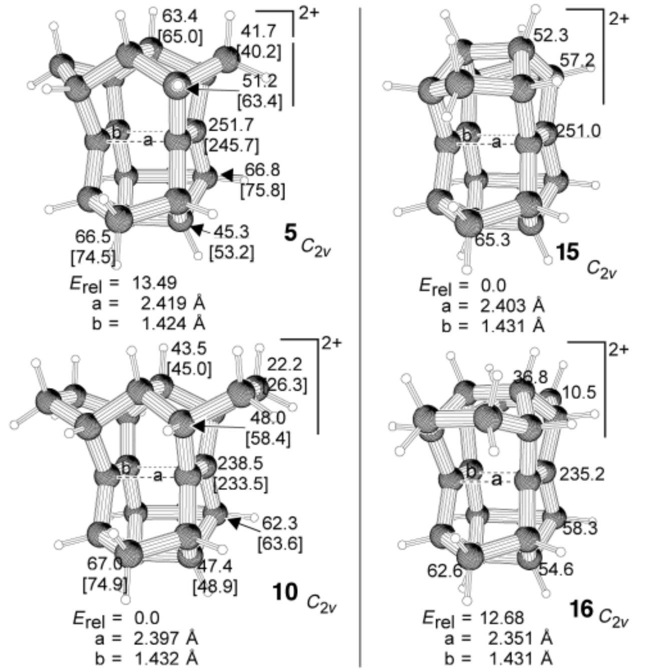
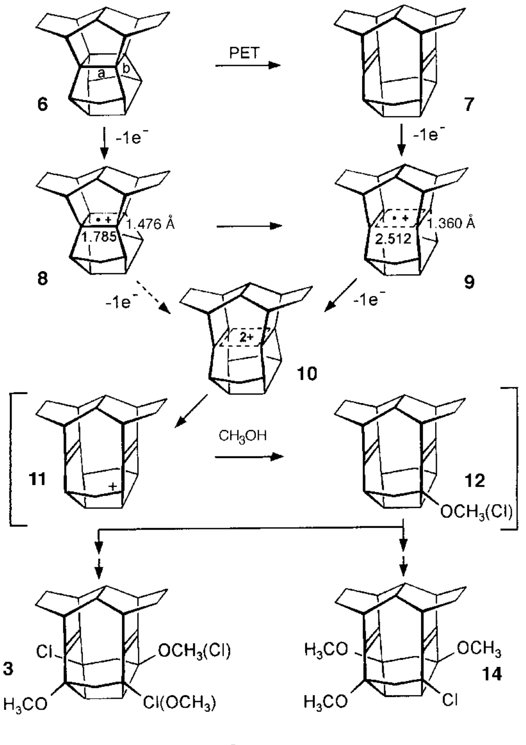


Fig. 1 B3LYP/6-31G* optimized structures, experimental and calculated (in brackets) ^{13}C NMR chemical shifts based on the DFT geometries and a GIAO B3LYP/6-31G* NMR calculation of the dications **3**, **10** (**15**, **16** as references); a and b denote DFT bond lengths; energies (E_{rel}) are given 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[11] 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}C shifts of the core carbons of **5** and **10** are very similar to those of the reference dications **15** and **16**; the ^{13}C NMR chemical shift additivity analysis[12] 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[13] 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, σ-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**].[14] 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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