Long-lived [1.1.1.1]- and [2.2.1.1]‘Isopagodane’ dications: novel 4C/2e α-bishomoaromatic dications†

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The dications generated from [1.1.1.1] and [2.2.1.1]isopagodane in SbF5–SO2ClF solution at −78 °C are of α-bishomoaromatic nature (4C/2e), very similar in geometry, yet chemically different in their properties.

The [1.1.1.1]isopagodane (A, m = n = 1) and functionalized derivatives have received considerable attention as intermediates in the various synthetic routes to pentagonal dodecahedrane.1 An important theoretical aspect is linked to the central, planar, peralkylated cyclobutane ring: Two-electron oxidations had allowed the experimental verification of homoaromaticity in form of the respective 4C/2e dications.2,3 In ‘halves’ to give the isopagodanes radical cation of rather differing behaviour upon one-electron oxidation: the 

the DFT calculated geometries. Calculated and observed (in brackets) 13 C NMR chemical shifts based on the DFT geometries and a B3LYP/6-31G* optimized structures, experimental and calculated 1030 protection in 10 opening up a sequence of deprotonation (e.g. 11), nucleophilic addition (e.g. 12) and reoxidation of the respective functionalized dienes.

GIAO11 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 13C shifts of the core carbons of 5 and 10 are very similar to those of the reference dications 15 and 16; the 13C NMR chemical shift additivity analysis13 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 theory13 the dications 5 and 10 are of C2v 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 (eight isomers 3, 8; extended isomers 4, 9) there is only one minimum on both dicaticonic hypersurfaces. Evidently, α-bishomoaromaticity provides the energy in dication 5 for the shortening (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 dience]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 respective neutral geometry forbidden neutral [2+2] and radical cationic [2 + 1]cycloaddition energy hypersurfaces.

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Notes and references
5 For the recent synthesis (and one-electron oxidation) of [2.2.2.2]iso pagodanes A/B (m = n = 2) see M. Eltzorn, F. Wahl, M. Keller, H. Prinzbach, F. Barbosa, V. Peron, G. Gescheidt, J. Heinze and R. Herges, J. Org. Chem., 1998, 63, 6080.
9 Chemical shifts are referenced from external acetone-d6, capillary signal (13C shift from CD3 septet at δ29.8; 1H shift from residual CHD2 quintet at δ2.09).
10 Pagodane 7, not, however, 1, underwent 2o → 2π isomerization (8) upon photosensitized electron transfer. M. Eltzorn, Dissertation, University of Freiburg, 1998; D. Heimbach, Diplomarbeit, 1995.

Fig. 1 B3LYP/6-31G* optimized structures, experimental and calculated (in brackets) 13C 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 (Erel) are given in kcal mol−1 and are relative to the more stable isomer.

Scheme 2

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