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From unsaturated dodecahedranes to C_{40} cages?

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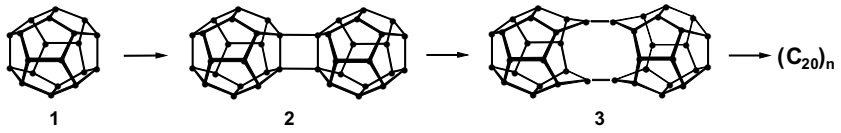
Abstract—(2+2)-Dimerization of unsaturated, highly pyramidalized dodecahedranes ($\Phi = 43-45°$) is explored as a route to C_{40}-cage molecules and non-classical ions derived thereby. The cycloadducts (X-ray structure) formed under vigorous conditions either in solution or in the solid phase above 300 °C did not undergo $2\sigma \rightarrow 2\pi$ isomerization. The MS fragmentation patterns, in line with calculations (B3LYP/6-31G*), suggest the formation of 'open' C_{40} dications.

The coalescence of C_{20}-fullerene **1** in laser desorption experiments to $(C_{20})_k^+$-oligomers ($k = 2–13$) has tentatively been associated with (2+2)-cycloadditions.[1] According to recent calculations,[2] the primary (2+2)-cycloadduct **(2)** spontaneously isomerizes to "open" **3** en route to $(C_{20})_n$-polymers, substances which are of much interest as superconducting carbon materials.[3] With various C_{20}-hydrofullerenes (unsaturated pentagonal dodecahedranes) on hand, we investigated their (2+2)-dimerization as an initial step toward C_{40}-cages and particularly toward novel non-classical caged ions.[4] Noteworthy results are reported in this letter.[5]



Highly bent dodecahedramonoenes **4a** and **b** and diene **12** (olefinic pyramidalization angles $\Phi = 43-45°$, MM2) have been found to undergo various [4+2]-cycloadditions but yet to be very resistant to dimerization, even thermally exceptionally persistent due to H/H repulsions between the allylic hydrogens.[6] In fact, when solid **4a** was heated in a glass ampoule (H_2 atmosphere) it was only at ca. 350 °C that it transformed without any noticeable melting into an amorphous, barely soluble and unseparable mixture of $C_{40}H_{36}$ dimer(s) (**5a**, ca. 75%), $C_{60}H_{54(6)}$ trimers (of unknown structure), and oligomers (MS).[7] In attempts to intercept the 1,4-diradical intermediate by heating an intimate mixture of **4a** and 9,10-dihydroanthracene, mainly **5a** was produced and hydrogen transfer to **4a** provided some dodecahedrane **9** (10%). Bisdodecahedryl **10**, independently prepared from bromide **11**,[7] was not observed. Heating **4a** under an oxygen atmosphere produced trimers or lower oligomers, several $C_{20}H_{18}O/C_{40}H_{36}O_2$ products in addition to **5a** (MS). Heating solid diester **4b** at ca. 350 °C or a saturated (ca. 10^{-2} M) solution in benzene at 140 °C for two days (ampoule) provided amorphous mixtures of dimers (ca. 80%), trimers, and oligomers (MS). Dimers **5b** (C_{2h}, 40%) and **6b** (C_{2v}, 40%) could be isolated by chromatography (CH_2Cl_2/ethyl acetate). Remarkably, when **5b** was boiled in 9,10-dihydroanthracene (bp 302 °C) for 6 h, no change was observed.

Shock heating (ca. 350 °C) of solid diene **12** resulted in the production of polymers. However, from a saturated (ca. 10^{-3} M) benzene/ethyl acetate solution of **12** stirred

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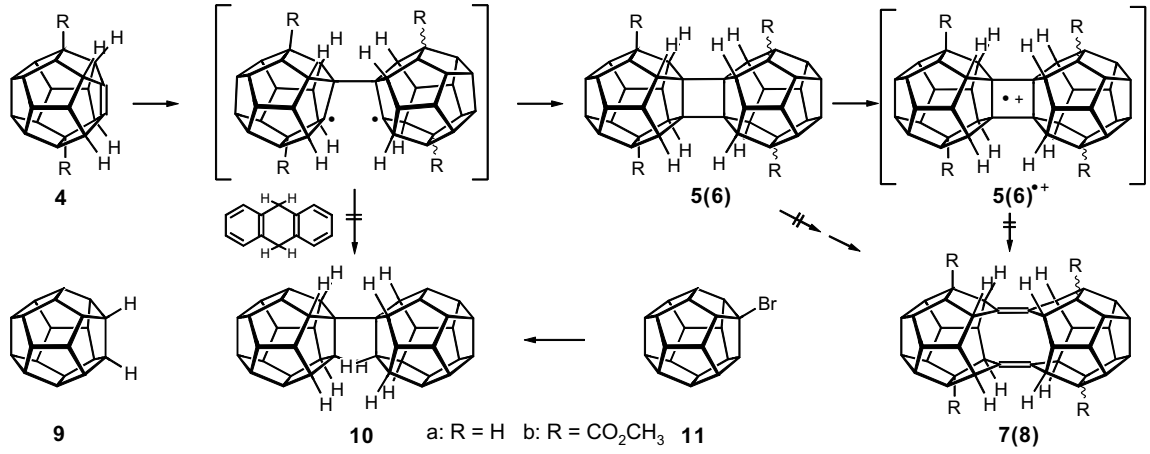
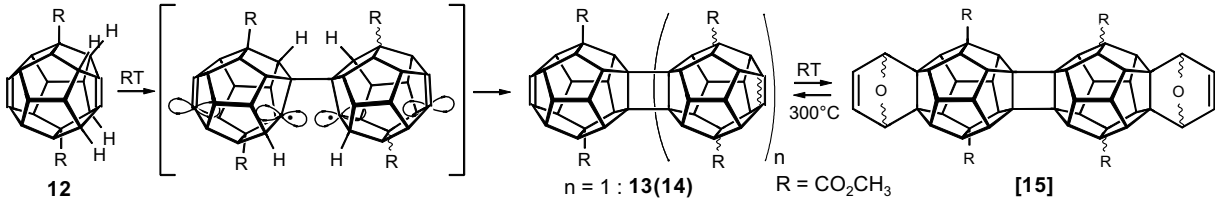


at room temperature for seven days, an amorphous solid precipitated (ca. 80%) which consisted of a ca. 1:2 mixture of the very oxygen-sensitive dimers **13** (C_{2h})/**14** (C_{2v}). By means of crystallization (CH_2Cl_2), **13** was enriched (^{1}H NMR). The through-space electron delocalization in the 1,4-diradical intermediate, demonstrated for the radical cation of the parent diene ($C_{20}H_{16}$),[4d] presumably lowers the barrier for dimerization. The dimers, like **12**,[6] were added to furan at room temperature to give the bisadducts [**15**] (presumably four of six possible isomers, NMR) which upon flash-vacuum pyrolysis (ca. 300 °C, 5×10^{-6} bar) quantitatively returned **13/14**.



Due to their kinetic stability, unsaturated dodecahedranes seemed predisposed for an experimental look into the geometrical environment around such highly bent C=C double bonds. However, only for **4b** could suitable crystals be secured (ether, 0 °C) which while disordered still permitted the assessment of crucial details such as transannular π,π-distance (3.75 Å) and olefinic pyramidalization {Φ ca. 43 °; 43.5° (MM2)}. Crystals of **5b** obtained from CH_2Cl_2/CH_3OH allowed a perfect X-ray structural analysis (Fig. 1).[8] With bond lengths of 1.561(2) and 1.584(2) Å, internal angles of 89.5 and 90.6°, the geometry of the practically planar four-membered ring is close to that recently calculated for dimer **2**.[2,3] The moderate elongation of the connecting bonds brings the former allylic, now pairwise staggered hydrogen atoms not closer than van-der-Waal-distance (2.21 Å).[9]

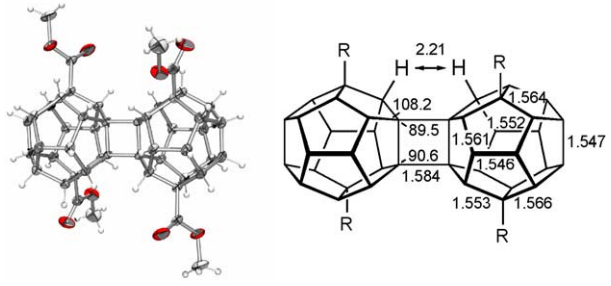


Figure 1. ORTEP-plot and selected structural data for **5b**.

In the pursuit of caged non-classical ions,[4] the response of the dimers **5(6)**, **13(14)**, and of the 'open' isomers such as **7(8)** to one/two electron oxidation was a central aspect. Yet, in case of **5(6)a**,**b** the two-step bromine addition/bromine elimination protocol, established in the pagodane series,[10] was not applicable to their transformation into **7(8)a**,**b**. Even under forcing conditions, bromine did not add to the cyclobutane rings; instead substitution occured in the dodecahedral parts. Neat dimer **5b** was cyclovoltammetrically oxidized (CH_2Cl_2), the peak potential of 1.60 V (vs Ag/AgCl, v = 100 mV/s) of the irreversible oxidation wave coming close to the 1.53 V reported for the [1.1.1.1]pagodane-1*syn*,6-*syn*-diester.[11] As with the latter compound, no second oxidation and, upon reversal of the scan, no reduction waves were observed. Nevertheless, an ECE process (oxidation/isomerization/oxidation) was deemed highly probable. As in the pagodane model, **5b** did not isomerize (to **7b**) when treated with tris(*p*-bromophenyl)hexachloroantimonate or upon irradiation in the presence of triphenylpyrylium tetrafluoroborate. The fragmentation behavior upon electron impact ionization (70 eV MS) provided more information: The cleavages **5(6)a**,**b**$^{\bullet+}$ → **4a**,**b**$^{\bullet+}$ and **13(14)**$^{\bullet+}$ → **12**$^{\bullet+}$ are minor events, doubly charged ions of significant intensity are recorded—$C_{40}H_{36}^{2+}$ for **5(6)a**, $C_{40}H_{30-28}R_{2-0}^{2+}$ for **5(6)b**, and $C_{40}H_{26-24}R_{2-0}^{2+}$ for **13(14)**, elimination of CH_3CO_2(H) units being manifested by singly charged

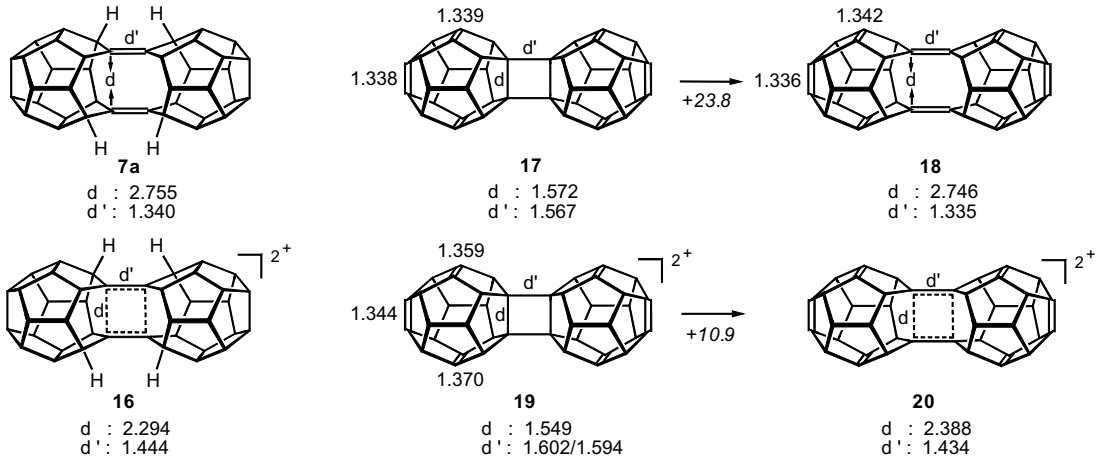


Figure 2. Calculated (B3LYP/6-31G*) distances (Å) and energies (italics, kcal mol^{-1}).

signals of sharply decreasing intensity and partly dominating doubly charged signals. B3LYP/6-31G* calculations[12] for the two-electron oxidation of **5a** and **7a** (Fig. 2) establish the 'extended' 4C/2e dication **16** as the sole minimum configuration. The shortening of the π,π-distance ($\Delta d = -0.461$ Å) and lengthening of the C=C bonds ($\Delta d' = +0.159$ Å) for **7a** → **16** are close to that for the prototypical conversion of [1.1.1.1]pagodadiene into the σ-bishomoaromatic 4C/2e dication (−0.395, +0.087 Å).[13] Taking **19/20** as models for the $C_{40}H_{24}^{2+}$ fragments in the MS spectrum of **13(14)**, the 'tight' form surfaces as more stable by 10.9 kcal mol^{-1}.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.06.072.

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formation of oxygen containing side products (TLC and MS). For experimental and analytical details, see, Supplementary files.

8. CCDC 269185 contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk].
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