Pergamon

Tetrahedron Letters 41 (2000) 4763–4767

TETRAHEDRON
LETTERS

Non-pentagonal unsaturated dodecahedranes—in-plane delocalized 4C/3e radical cations and σ-bishomoaromatic 4C/2e dications

Andreas Weiler, Edith Quennet, Manfred Keller, Kai Exner and Horst Prinzbach*

Institut für Organische Chemie und Biochemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg i. Br., Germany

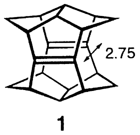
Received 6 April 2000; accepted 29 April 2000

Abstract

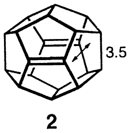
An intriguing route from bissecododecahedrenes to 11,17-disubstituted bishomododecahedrene (**7**) provides access to X-ray crystallographic data (i.e. pyramidalization angle of ca. 22°). Electrochemical oxidation of the parent olefin (**4**, $E_{pc} = 1.46$ V) leads via the bishomododecahedradiene (**3**, $d_{\pi\pi} = 3.0$ Å, $E_{1/2} = 0.84$ V, $E_{pc} = 1.67$ V) to the in-plane delocalized 4C/3e radical cation ($\mathbf{3}^{\bullet+}$, $d_{\pi\pi} = 2.85$ Å) and the σ-bishomoaromatic 4C/2e dication ($\mathbf{3}^{2+}$, $d_{\pi\pi} = 2.71$ Å). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: homododecahedranes; unsaturation; CV-oxidation; in-plane delocalization; σ-bishomoaromaticity.

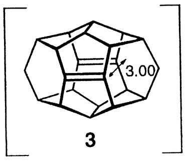
One-electron oxidation of bissecododecahedradiene **1**[1] and dodecahedradiene **2**[2] with their proximate, perfectly *syn*-periplanar C=C double bonds led to the discovery of in-plane delocalized 4C/3e radical cations.[3] 'Proximate', rather persistent $\mathbf{1}^{\bullet+}$ ($d_{\pi\pi} = 2.46$ Å), not, however, 'distant', only in matrix observable $\mathbf{2}^{\bullet+}$ ($d_{\pi\pi}$ ca. 3.4 Å), upon further oxidation allowed the observation of the respective σ-bishomoaromatic 4C/2e dication ($\mathbf{1}^{2+}$).[4] In a study to further define the geometrical prerequisites of the σ-bishomoaromatic bonding motif,[5] the bishomododecahedradiene **3** with its intermediate ππ-distance (calcd $d_{\pi\pi} = 3.00$ Å, B3LYP/6-31G*) became of interest.[4] Yet the recently developed synthetic route to bishomododecahedranes has been blocked for dienes of type **3** by the reactivity of the strongly homoconjugated, significantly bent C=C double bonds (ϕ ca. 20°) towards nucleophiles.[6] In this letter we present a serendipitously discovered variation of this route, allowing access to X-ray structural data for a kinetically stabilized derivative of monoene **4** (≡**7**, Scheme 1) and electrochemical evidence for the generation of the in-plane delocalized 4C/3e



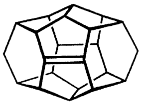
1



2



3



4

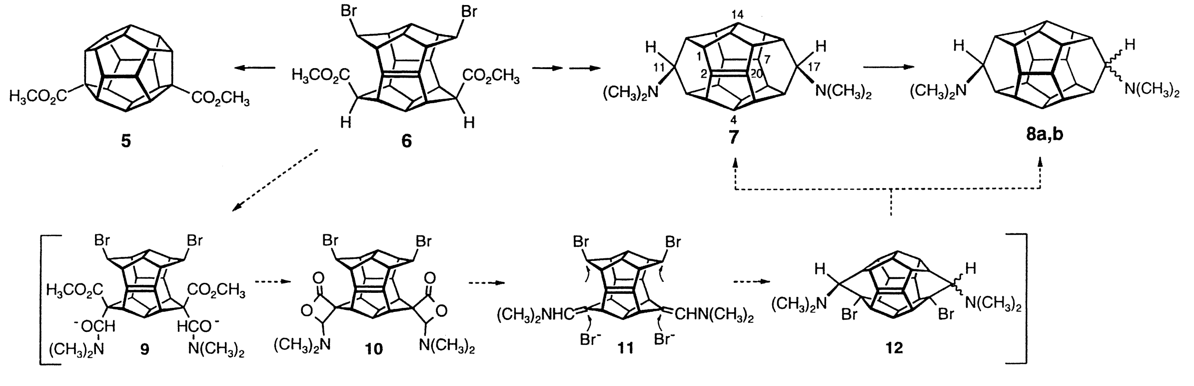
---

* Corresponding author. E-mail: horst.prinzbach@orgmail.chemie.uni-freiburg.de

PII: S0040-4039(00)00721-8

radical cation $\mathbf{3}^{\bullet+}$ and σ-bishomoaromatic 4C/2e dication $\mathbf{3}^{2+}$ via a multistep EC$_n$E process starting from parent monoene **4** (Scheme 2).[7]

Dibromo-bissecododecahedrene-diester **6** is an established precursor of the dodecahedrane-diester **5**.[8] When this normally highly selective 'hydrogenative' cyclization (>90%, CH_3ONa/CH_3OH/THF; Pd/C/H_2) was performed in the presence of dimethylformamide (DMF), besides **5** (ca. 50%), the *syn*-11,17-bis(dimethylamino)-ene **7** and the *syn-*/*anti*-11,17-bis(dimethylamino)-bishomododecahedranes **8a**,**b** were formed in somewhat erratic yields of, at best, 15% besides several in part identified side products.[9] Chromatographically (degassed solvents) the mixture of diamines could be separated; from their solution in degassed CH_2Cl_2/ethyl acetate under careful exclusion of air C_{2v}-symmetrical olefin **7** crystallized in pure form. The highly oxygen sensitive C=C double bond in **7**, efficiently protected by the two *syn*-dimethylamino groups against catalytic hydrogenation, is slowly saturated with diimide to give **8a** (contrary to **7** parent **4** can be catalytically saturated). The symmetry of **7** is expressed in the NMR spectra by the number of ^1H (seven) and ^{13}C (eight) signals, the olefinic ^{13}C shift $\delta = 146.0$ (cf. $\delta = 151.5$ for **1**,[1] $\delta = 170.5$ for **2**[2]) being indicative of a moderately bent double bond.[10] In the MS spectrum, after the loss of one $N(CH_3)_2$ unit, a carbon-by-carbon fragmentation is manifested. The X-crystal structure analysis (Fig. 1)[11] displays an olefinic pyramidalization of ϕ (av.) = 21.8°, expectedly placing **4** between dihydro-**1** (≡**15**, ϕ = 10.3°) and dihydro-**2** (≡**16**, ϕ = 46.2°).[12] For the on first sight intriguing formation of **7** (**8**), addition of DMF to deprotonated **6** (**9**), β-lactone formation (**10**), elimination of CO_2 (**11**), Br^--mediated cyclization (**12**), and hydrogenolytic debromination make up for a plausible sequence (not necessarily parallel in both lateral half-cages). So far, in spite of multiply varied reaction conditions, the share of **7** (**8**) in this very complex reaction scheme could not be enhanced.[13]



Scheme 1.

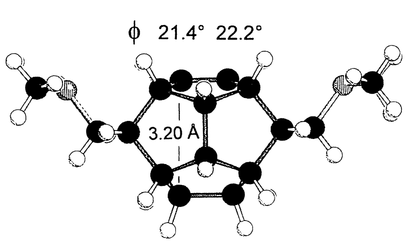


Figure 1. Crystal structure of **7** (Å)

The cyclic voltammogram of monoene **4** (Fig. 2a) documents two irreversible oxidation potentials (1.46 V, 1.62 V). As a distinction to the CV's registered for the closely related monoenes **15** and **16**[5c] the reduction wave crosses the oxidation wave, the crossing intensity increasing with increasing temperature and decreasing scan rates (disappears at –60°C/100 mV s^{-1}, –35°C/200 mV s^{-1}, –19°C/500 mV s^{-1}). Thus, the transformation of $\mathbf{4}^{\bullet+}$ into $\mathbf{X}^{\bullet+}$ by an at least two-step chemical process implying its rapid consumption and slow generation of $\mathbf{X}^{\bullet+}$ is indicated. The multisweep experiment (Fig. 2b) establishes a reversible one-electron oxidation/reduction $\mathbf{X} \rightleftarrows \mathbf{X}^{\bullet+}$ with $E_{1/2} = 0.84$ V. The interpretation given in Scheme 2 with **X** = missing bishomododecahedradiene **3** is corroborated by calculations (B3LYP/6-31G*) and comparison with related systems. Thus, E_{pc} $\mathbf{4} \rightarrow \mathbf{4}^{\bullet+} = 1.46$ V nicely fits with $E_{1/2}$ $\mathbf{15} \rightarrow \mathbf{15}^{\bullet+} = 1.57$ V and E_{pc} $\mathbf{16} \rightarrow \mathbf{16}^{\bullet+} = 1.4$ V. That $\mathbf{4}^{\bullet+}$ splits off a proton to give the homoallylic (**13**) rather than the allylic radical (**14**) is in line, inter alia, with the stability of the respective homoallylic cation[14] and the energies calculated for **3** and conjugated diene **17**. $E_{1/2} = 0.84$ V assigned to $\mathbf{3} \rightleftarrows \mathbf{3}^{\bullet+}$ is expectedly somewhat larger than $E_{1/2} = 0.66$ V for more proximate $\mathbf{1} \rightleftarrows \mathbf{1}^{\bullet+}$ and smaller than $E_{pc} = \approx 1.0$ V for more distant $\mathbf{2} \rightarrow \mathbf{2}^{\bullet+}$ (no second oxidation wave). $E_{pc} = 1.62$ V—with due reservation assigned to the oxidation $\mathbf{3}^{\bullet+} \rightarrow \mathbf{3}^{2+}$—is considerably larger than $E_{pc} = 1.20$ V for $\mathbf{1}^{\bullet+} \rightarrow \mathbf{1}^{2+}$ ($\Delta d_{\pi\pi}$ ~0.3 Å).

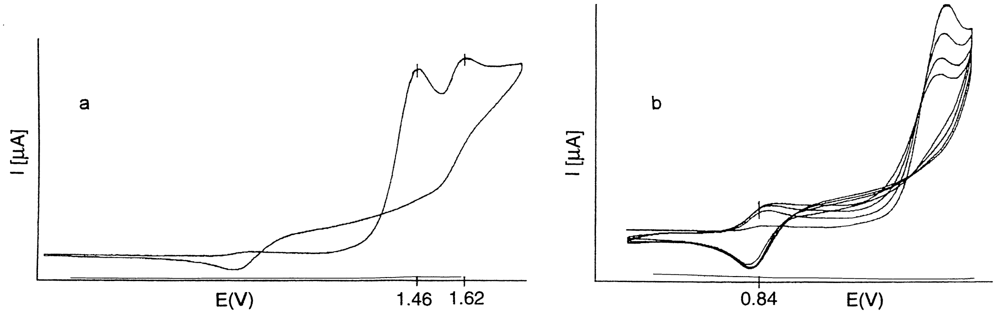
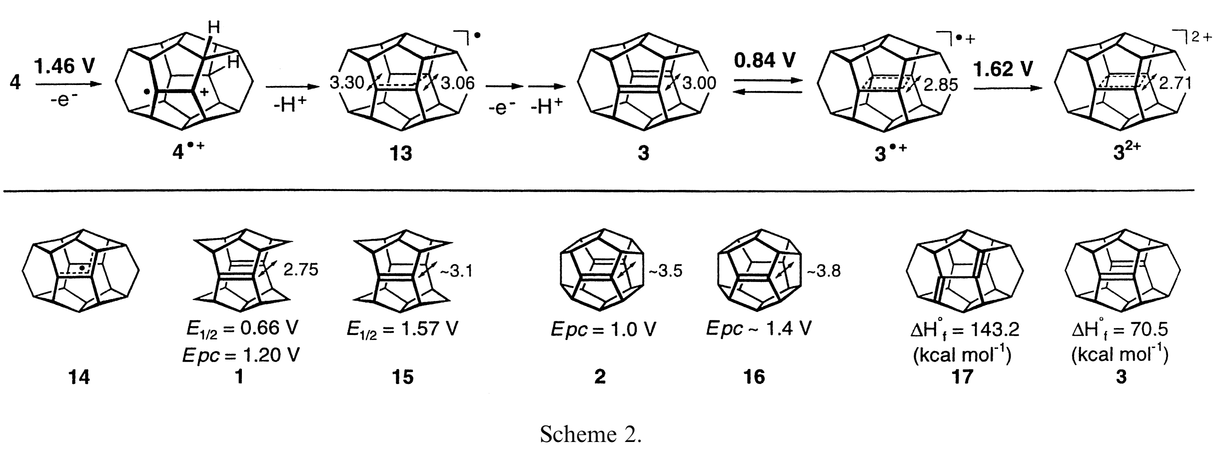


Figure 2. Cyclic voltammograms of **4**: (a) 100 mV s^{-1}; (b) 0.5–1.8 V s^{-1}, CH_2Cl_2/Ag/AgCl; ferrocene, $E_{1/2} = 0.30$ V)



Scheme 2.

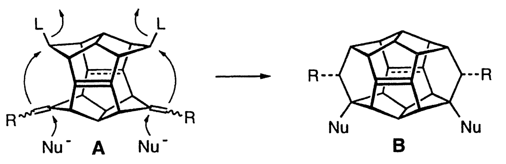
Facit: The difference of 0.62 V for the one-electron oxidation of monoene **4** (irrev.) and diene **3** (rev.) constitutes a thermodynamically meaningful estimate of the minimum stabilization gained by the 4C/3e in-plane delocalization (primarily counterbalanced by the relatively small structural changes involved). For diene **3** with a ππ-distance of 3.0 Å cyclovoltammetric oxidation to the dication is still observable—ΔE_{pc}–$E_{1/2} = 0.78$ V as energetic costs for the oxidation $\mathbf{3}^{\bullet+}\rightarrow\mathbf{3}^{2+}$, versus 0.54 V for $\mathbf{1}^{\bullet+}\rightarrow\mathbf{1}^{2+}$, is suggestive of a nevertheless substantial electron delocalization energy (σ-bishomoaromaticity).[15]

Acknowledgements

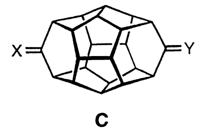
This work has been supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the BASF AG. We thank Dr. D. Hunkler for NMR, Dr. J. Wörth and C. Warth for MS, Dr. H. Trenkle for CV measurements, J. Leonhardt and G. Leonhardt-Lutterbeck for competent technical assistance.

References

1. Murty, B. A. R. C.; Pinkos, R.; Spurr, P. R.; Fessner, W.-D.; Lutz, G.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Chem. Ber.* **1992**, *125*, 1719.
2. Melder, J.-P.; Weber, K.; Weiler, A.; Sackers, E.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Res. Chem. Intermed.* **1996**, *7*, 667.
3. (a) Prinzbach, H.; Murty, B. A. R. C.; Fessner, W.-D.; Mortensen, J.; Heinze, J.; Gescheidt, G.; Gerson, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 457. (b) Weber, K.; Prinzbach, H.; Schmidlin, R.; Gerson, F.; Gescheidt, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 875.
4. Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1988**, *110*, 7764.
5. (a) Gescheidt, G.; Herges, R.; Neumann, H.; Heinze, J.; Wollenweber, M.; Etzkorn, M.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1016. (b) Prinzbach, H.; Gescheidt, G.; Martin, H.-D.; Herges, R.; Heinze, J.; Prakash, G. K. S.; Olah, G. A. *Pure Appl. Chem.* **1995**, *67*, 673. (c) Martin, H.-D.; Mayer, B.; Weber, J.; Prinzbach, H. *Liebigs Ann.* **1995**, 2019. (d) Weber, K.; Lutz, G.; Knothe, L.; Mortensen, J.; Heinze, J.; Prinzbach, H. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1991. (e) Trifunac, A.; Werst, D.; Herges, R.; Neumann, H.; Prinzbach, H.; Etzkorn, M. *J. Am. Chem. Soc.* **1996**, *118*, 9444. (f) Gescheidt, G.; Prinzbach, H.; Davies, A. D.; Herges, R. *Acta Chem. Scand.* **1997** *51*, 174. (g) Etzkorn, M.; Wahl, F.; Keller, M.; Prinzbach, H.; Barbosa, F.; Peron, V.; Gescheidt, G.; Heinze, J.; Herges, R. *J. Org. Chem.* **1998**, *63*, 6080. (h) Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Wollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. *J. Chem. Soc., Chem. Commun.* **1999**, 1029.
6. Sharma, V.; Keller, M.; Weiler, A.; Hunkler, D.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2858. The cyclization step **11**→**12** (Scheme 1) is patterned after the general strategy **A**→**B**.



A **B**

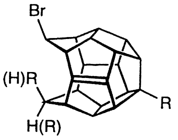


C

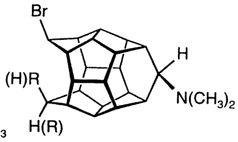
7. Weiler, A. Dissertation, Quennet, E. Diplomarbeit, University of Freiburg, 1997.
8. Pinkos, R.; Melder, J.-P.; Weber, K.; Hunkler, D.; Prinzbach, H. *J. Am. Chem. Soc.* **1993**, *115*, 7173.
9. Of the side products four (**D**, **E**) are identified (MS, NMR). The compounds **4**, **7** and **8a**,**b** have been fully characterized by elemental analysis (or HRMS) and spectra (IR, ^{1}H, ^{13}C NMR, MS). Monoene **4** (undecacyclo-

[10.10.0.0^{2,20}.0^{3,10}.0^{4,19}.0^{5,9}.0^{6,18}.0^{7,15}.0^{8,13}.0^{14,22}.0^{16,21}]docos-2(20)-ene), even more oxygen-sensitive than **7**, was prepared under careful exclusion of air by standard reduction (Li/*tert*-BuOH,/THF) of dibromo-ene **B** (R = H, Nu = Br).

D



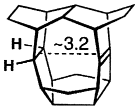
R = CO_2CH_3

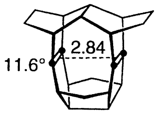


E

10. Borden, W. *Chem. Rev.* **1989**, *89*, 1095. Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385. Dodziuk, H. In *Modern Conformational Analysis*; Dodziuk, H., Ed.; VCH: Weinheim, 1995; Chapter 8.
11. Crystallographic data for **7** have been deposited with the Cambridge Crystallographic Data Centre, Cambridge, UK. Copies of the data can be obtained free of charge (e-mail: deposit@chemcrys.cam.ac.uk) on quoting the deposition number CCDC 405336.
12. Scheme 1 in Melder, J.-P.; Pinkos, R.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1989** *28*, 305.
13. Nevertheless, with **6** available in g-quantities, the transformation of the diamines **8** via the respective diols into 11,17-dione **C** is being pursued. The latter and derivatives are attractive inter alia for the study of defined multiple-path through-bond interactions.
14. Prakash, G. K. S.; Fessner, W.-D.; Olah, G. A.; Lutz G.; Prinzbach, H. *J. Am. Chem. Soc.* **1989**, *111*, 746.
15. This relationship is supported by the analogously conducted multisweep CV experiments with [2.2.1.1]isopagoda(di)enes **F** (**G**) (**F**: $E_{1/2} = 1.52$ V; **G**: $E_{1/2} = 0.83$ V,[5a] $E_{1/2} = 1.49$ V, $\Delta E_{1/2}$ $-E_{1/2} = 0.66$ V) Etzkorn, M., Dissertation, University of Freiburg, 1998. Cf. the $E_{1/2} = 1.27$ V and $E_{cp} = 1.69$ V measured for a structurally related face-to-face diene-anhydride: Grimme, W.; Geich, H.; Lex, J.; Heinze, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1955.

F





G