

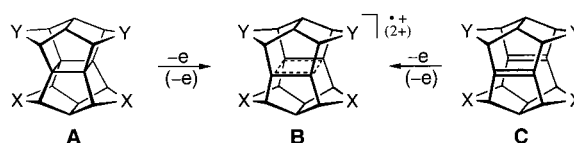
$\rho_{\text{calc}} = 3.040 \text{ g cm}^{-3}$, $\mu = 11.85 \text{ mm}^{-1}$. Crystal size $0.08 \times 0.08 \times 0.2 \text{ mm}^3$. The SMART software was used for data acquisition and the SAINT software for data extraction.^[17a] Unit cell parameters based on 25 reflections ($12^\circ < 2\theta < 30^\circ$). Absorption correction by SADABS,^[17a] structure solved and refined by using the SHELXS-86^[17b] and SHELXTL program systems,^[17c] 1003 independent reflections, 913 with $F > 4\sigma(F_o)$, $R = 0.032/wR2$ (all data) = 0.061; max./min. residual electron density $2.2/-1.3 \text{ e } \text{\AA}^{-3}$ in the vicinity of the U atoms. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411668.

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σ -Bishomoconjugation (σ -Bishomoaromaticity) in 4C/3(2)e Cations—Scope and Limitations**

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The experimental verification of σ -bishomoconjugation (σ -bishomoaromaticity) in the 4C/3e radical cation and the 4C/2e dication **B**, generated by one- and two-electron oxidation of the [1.1.1.1]pagodane **A** ($X = Y = \text{CH}_2$) and of the respective [1.1.1.1]pagodadiene **C** (“biseco-dodecahedradiene”), respectively, was a prominent spin-off from our search for versatile synthetic routes to pentagonal dodecahedranes.^[1] In order to



assess the geometrical prerequisites of these novel bonding motifs,^[2] modification of the cage structures has been pursued in three directions: a) by formal rotation of a molecular “half” ($\rightarrow$ “isopagodanes”),^[3] b) by homologation at the X- and/or Y-positions ($\rightarrow$ [2.2.1.1]/[2.2.2.2](iso)pagodanes),^[3] and c) by bridging the X,Y positions ($\rightarrow$ (homo)dodecahedradienes).^[4] A particularly attractive triad of this latter series consists of the parent biseco-(**1**), seco-(**2**), and 1,16-dodecahedradienes (**3**) (Scheme 1).^[5]

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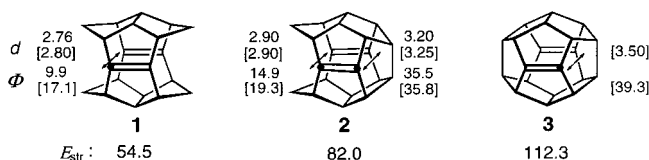
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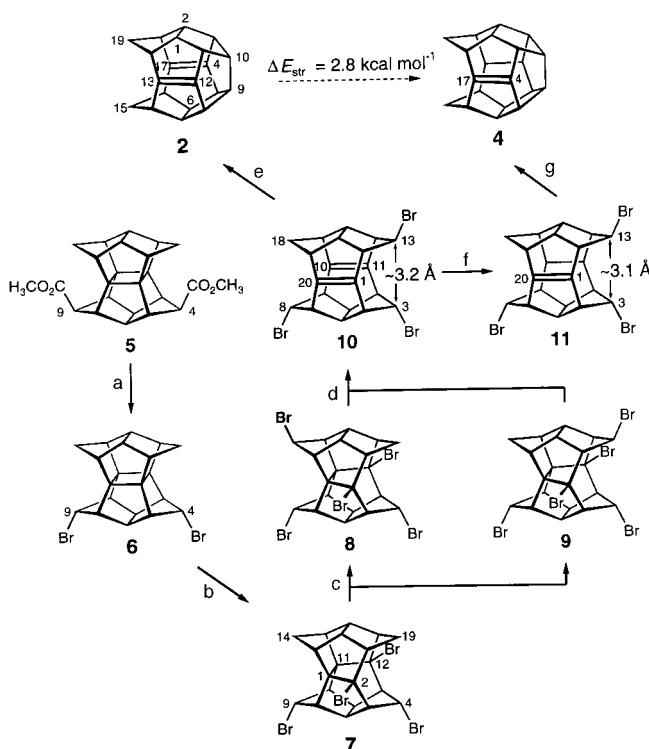
[**] This project has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and BASF AG. We thank A. Kurscheidt and M. Lutterbeck for technical assistance, Dr. D. Hunkler and Dr. J. Wörth for NMR and MS measurements, and Prof. Dr. T. Bally for access to his ⁶⁰Co- γ -irradiation equipment.



Scheme 1. Experimental and calculated (B3LYP/6-31G*, in square brackets) π,π -distances d [Å], pyramidalization angles Φ [°], and strain energies E_{str} (MM3, [kcal mol⁻¹]).

For very “proximate” **1**, it had been established that radical cation **1**^{•+} and dication **1**²⁺ are persistent even at room temperature, whilst for “distant” **3** the radical cation **3**^{•+} does exist only in a low temperature matrix and dication **3**²⁺ is not observable at all.^[6] The synthesis of the missing compound **2**—the “hybrid” of **1** and **3** with regard to its π,π -distances d and pyramidalization Φ on the olefinic carbon atoms^[7]—and of monoene **4** as a reference, as well as their response to one-/two-electron oxidation are subject of this Communication.

Prior attempts to prepare parent **2** through defunctionalization of available derivatives^[7, 8] have consistently failed due to the incompatibility of the severely bent C–C double bonds with the respective reaction and separation conditions. Success came with the reaction sequence shown in Scheme 2 (total yield of **2** > 30% with only 5–6% of **1** as impurity),^[9, 10] when a satisfying protocol for the problematic step **10** → **2**—internal competition between reductive C3–C13 bond formation and hydrogenolytic C–Br cleavage—had become



Scheme 2. a) 1) KOH, HOCH₂CH₂OH, 180 °C, 16 h; 2) H₂O, conc. HCl; 3) 2-mercaptopyridine-1-oxide (Na salt), DMAP, BrCCl₃, 120 °C, 30 min; 76%. b) Br₂/CH₂Cl₂ (10/1), RT, *hν* (300 W daylight lamp), 5 min; > 95%. c) Br₂/CH₂Cl₂ (4/1), RT, *hν* (300 W daylight lamp), 5 h; 95%. d) KI, DMF, 180 °C; 70%. e) 1) Li/Hg, THF, –78 °C → RT, 2 h; 2) MeOH, 1 h; 80–85%. f) N₂H₄, 0 °C, 12 h; 95%. g) 1) Li/Hg, THF, –78 °C → RT, 2 h; 2) MeOH/1 h; 80–85%. DMAP = 4-dimethylaminopyridine.

available after intensive experimentation with various metals and electron-transfer agents.

For the hydrogenation of diene **2** to monoene **4**, only a small increase in strain was calculated (+2.8 kcal mol⁻¹); correspondingly, the selective preparation of **4** through hydrogenation of **2** was found to be not possible. Alternatively, **4** was expeditiously obtained by hydrogenation of tribromobiseco-diene **10** to give “hyperstable”^[11] **11** followed by cyclization.

The longest wavelength UV/Vis absorption of **2** at 254 nm ($\epsilon \approx 600$, *n*-hexane), as evidence for transannular π,π -interaction (charge transfer), hardly differs from that of **3** (252 nm, $\epsilon \approx 350$) but significantly from that of **1** (270 nm, $\epsilon = 180$). In the ¹³C NMR spectra, the olefinic shifts of 151.8 and 171.4 ppm reflect the degree of pyramidalization, while $\Delta\delta = 1.47$ for the geminal methylene protons reflects the steric constraint inside the half-cage.^[7]

In the photoelectron (PE) spectrum of **2**, the mean value (8.06 eV) of the two π -ionization bands (7.48 and 8.64 eV) turns out to be higher by 0.15 eV than the π -band of **4** (7.91 eV). The π,π -split ($\Delta_{\pi\pi}$) of 1.16 eV is well reproduced by calculations (B3LYP/6-31G*: 1.14 eV; AM1: 1.03 eV). According to Heilbronner–Schmelzer analysis, 87% of the split is caused by through-space (TS) interaction (compare **1**: $\Delta_{\pi\pi} = 1.91$ eV, 100% TS and **3**: $\Delta_{\pi\pi} = 0.68$ eV, 59% TS).^[12]

Cyclovoltammetry (CH₂Cl₂, *n*Bu₄NPF₆, –20 °C, 0.2 V s⁻¹) recorded two irreversible oxidation waves with $E_p = 1.00$ and 1.50 V for **2** and one irreversible wave with $E_p = 1.60$ V for **4** (**1**: $E_{1/2} = 0.66$ V, $E_p = 1.20$ V; **3**: $E_p \approx 1.0$ V). The difference of the peak potential for **2**^{•+} relative to **4**^{•+} ($\Delta E_p = 0.60$ V) as a measure for the homoconjugational stabilization of **2**^{•+} has to be compared with $\Delta E_p = 0.91$ V for **1**^{•+} and $\Delta E_p \approx 0.4$ V for **3**^{•+} relative to the respective monoenes.^[13]

The radical cation **2**^{•+} could not be observed after oxidation of **2** in fluid solution as established for **1** (AlCl₃, tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate, Ti(O₂C–CF₃)₃, electrolysis).^[5] However, as for **3**,^[6] γ -irradiation of **2** and **4** in a CFCl₃ matrix allowed the observation of ESP spectra (Figure 1). The pattern of the ESP spectrum attributed to **2**^{•+} is dominated by a nonet spaced by about 1.5 mT (eight nearly equivalent protons, no differentiation between the β/β' protons). Additional information follows from the polarization pattern of the CIDNP experiment, in which **2**^{•+} was generated by photoinduced electron transfer to chloranil (tetrachloro-*p*-benzoquinone, in CD₂Cl₂). From the intensities of the two emissions lines at 3.28 and 3.48 mT, ¹H hyperfine coupling constants (hfc) of 1.18 and 1.55 mT for the β and β' protons were derived.^[14] These values are in very good agreement with the calculated (B3LYP/6-31G*^[15]) ¹H hfc of 1.49 (β) and 1.59 mT (β'); the very small hfc for the remaining protons (<0.1 mT) are not resolved in experimental spectra.

In the case of **4**^{•+}, the ESP spectrum reveals a pattern due to two pairs of equivalent protons with ¹H hfc of 4.3 and 2.9 mT (Figure 1). According to the calculated values of 3.98 and 2.71 mT, these hfc are attributed to the β and β' protons.

In line with the cyclically delocalized 4C/3e configuration of **2**^{•+}—within the ESP time scale—these hfc are about one half those of **4**^{•+}. According to calculations, in the trapezoidal 4C/3e structure of **2**^{•+} the C_{2v} symmetry of parent

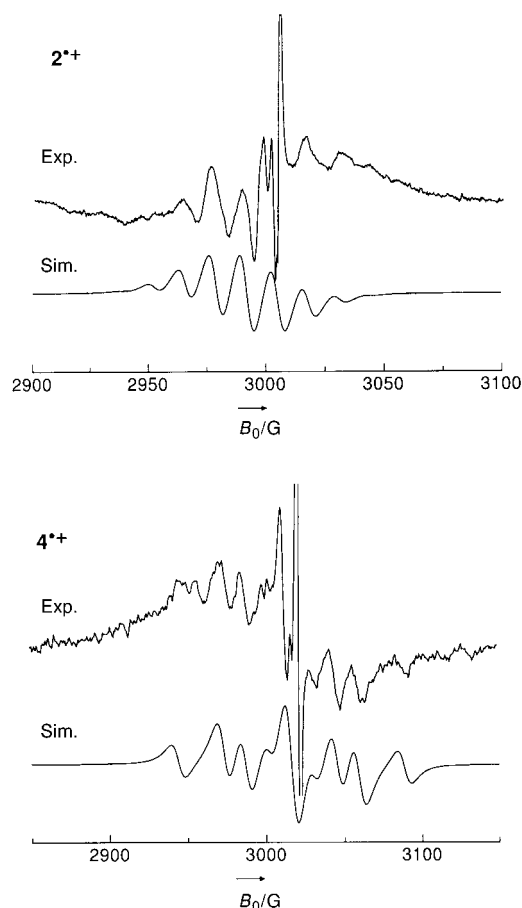
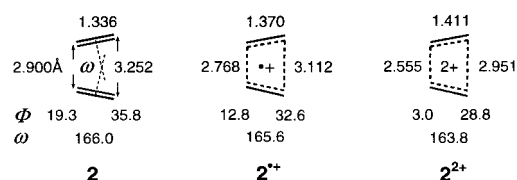


Figure 1. ESR spectra of **2** and **4** (CFCl₃, 100 K, modulation 0.5 mT).

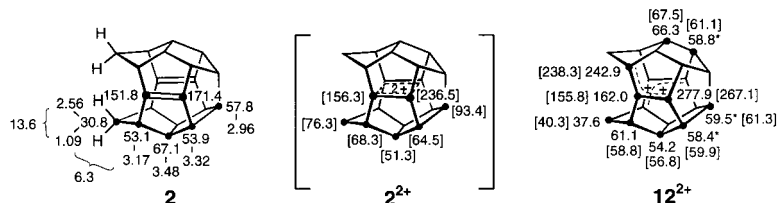
2 is retained, the C–C double bonds are lengthened by 0.034 Å, and the π,π -distances are shortened by 0.132/0.140 Å (Scheme 3).



Scheme 3. Calculated structures of diene **2**, in-plane homoconjugated radical cation **2⁺**, and σ -bishomoaromatic dication **2²⁺** (B3LYP/6-31G*; distances d [Å], pyramidalization angles Φ [°], and angles ω [°]).

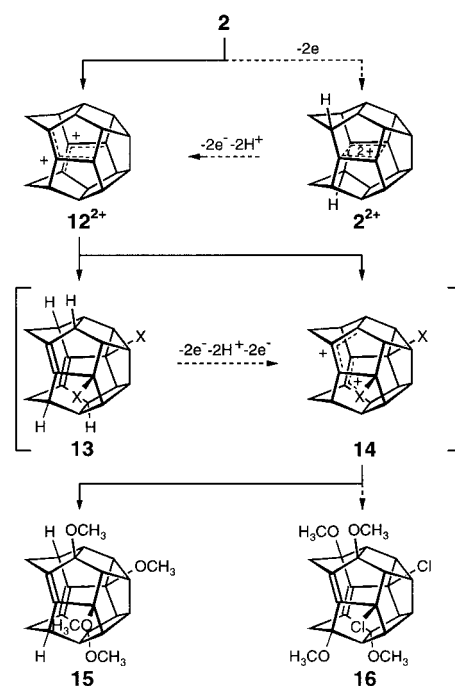
For its two-electron oxidation, **2** was mixed (as a slurry in SO₂ClF at –70 °C) with a six-fold excess of SbF₅ in SO₂ClF at –70 °C. After very slow dissolution (vortex stirrer, –70 °C), a dark yellowish-brown solution developed. At this temperature, the NMR signals were quite broad and indicate some paramagnetic species. Upon warming to –20 °C, however, the peaks sharpened. Whilst the ¹H NMR spectrum was too complex to allow an interpretation, the ¹³C NMR spectrum clearly revealed the presence of one prominent species (>80%, ten intense signals and several weaker ones). The assignment to C₂ symmetrical bisallylic dication **12²⁺**, rather than to the C_{2v} symmetrical 4C/2e dication **2²⁺**, is based on the

number of ¹³C NMR signals (ten rather than seven), the allylic nature of the three olefinic signals (δ = 277.9, 242.9, and 162.0; Scheme 4), and the good agreement with the GIAO-B3LYP/6-31G* calculations.^[16] Additional support comes from



Scheme 4. Experimental and calculated (GIAO-B3LYP/6-31G*, in square brackets) ¹³C NMR shifts δ for dications **2⁺** and **12²⁺**. For comparison, ¹H and ¹³C shifts and J (H,H) coupling [Hz] for diene **2** (C₆D₆) are given.

quenching the superacid solution with CH₃OH/Na₂CO₃. Two main products could be chromatographically separated from a complex mixture of mostly higher methoxylated dienes (MS, $\approx$ 25%), unequivocally identified as C₂-symmetrical tetramethoxydiene **15** ($\approx$ 30%) and C₂-symmetrical dichlorotetramethoxydiene **16** ($\approx$ 25%). The intermediacy of dienes **13** (X = OCH₃, Cl) and bisallylic dications **14** (X = OCH₃, Cl) is



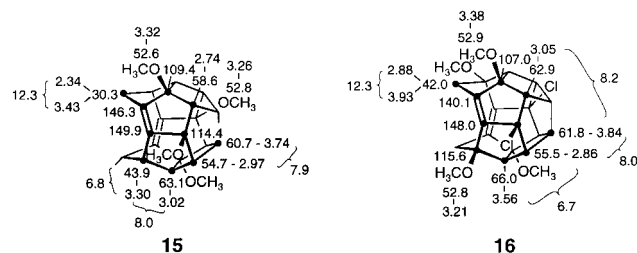
plausible. Correspondingly from DFT calculations, the parent diene structure **13** (X = H), and not **2**, had surfaced as “stabilomer” of the seco-dodecahedradiene family (–3.5 kcal mol^{–1} versus **2**). An intriguing cascade of oxidation/deprotonation/OCH₃-addition steps during the quenching procedure is held responsible for the C₂₀H₄(OCH₃)₁₄ ion in the MS spectrum (m/z = 678, low intensity) and suggests the total substitution of all tertiary hydrogens by CH₃O groups.

The radical cation generated from diene **2** in low temperature matrices (or with very short lifetime in solution, CIDNP), is firmly established as in-plane cyclically delocal-

ized 4C/3e species. Both, the total π,π split (PE) as well as its through-space/through-bond partition, the degree of homo-conjugational stabilization (cyclovoltammetry), and the structural details (DFT) place 2^{++} between 1^{++} and 3^{++} . A limitation of the observability of σ -bishomoaromatic 4C/2e dications is manifested: If 2^{2+} is an intermediate at all on the way from **2** to 12^{2+} , minimization of Coulomb repulsion through “hydride” elimination^[17]—prohibited by the skeleton in 1^{2+} (“anti-Bredt protection”)^[18]—wins over σ -bishomoaromaticity.

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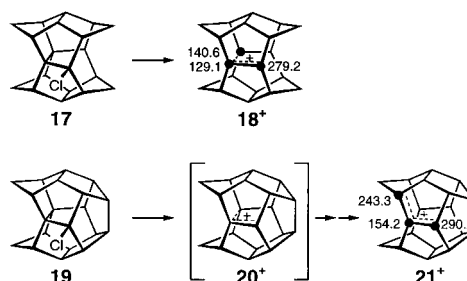
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- [18] The same difference has been established for the behavior of the chlorides **17** and **19** in the superacid medium. Of the σ -homoallylic cations **18**⁺ and **20**⁺, the former is highly persistent,^[19] the latter at -20°C undergoes rapid hydride shifts to give isomeric **21**⁺.



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A Versatile and High-Yield Route to Active and Well-Defined Catalysts [Ru(bisphosphane)(H)(solvent)₃](BF₄)⁺

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Valentin Rautenstrauch*

The well-known and well-defined Rh systems [Rh($\widehat{\text{P}}\text{P}$)(sol)₂]⁺ ($\widehat{\text{P}}\text{P}$ = chiral bisphosphane ligand, sol = weakly O-bound solvent, for example acetone, THF, MeOH)^[1] catalyze a wide variety of reactions, the most prominent of which is the asymmetric hydrogenation of functionalized

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