Electrochemical oxidation of [1.1.1.1]pagodanes, bisseco-, seco- and dodecahedra(di)enes: stability of caged 4c/3e radical cations and 4c/2e dications

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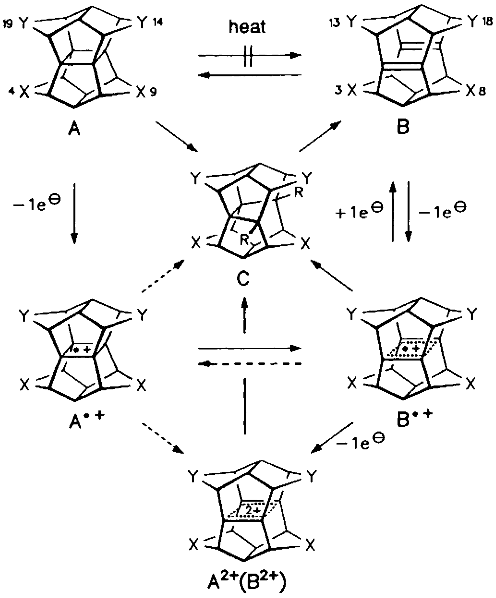
The anodic oxidation of variously functionalized [1.1.1.1]pagodanes **A** and bissecododecahedradienes **B** (π,π-distance, *ca.* 2.8 Å) has been studied by cyclic voltammetry (CV). For nine out of ten pagodanes **A**, independent of their functionalization and of the scan rate, an irreversible two-electron oxidation wave (E_p = 1.20–2.23 V) was observed in line with the sequence $\mathbf{A} \longrightarrow \mathbf{A}^{\bullet +} \longrightarrow \mathbf{B}^{\bullet +} \longrightarrow \mathbf{B}^{2+}$ (ECE) in which the chemical step C is very fast on the CV timescale. For seven of the corresponding valence isomeric dienes **B**, the first one-electron oxidation wave ($\mathbf{B} \longrightarrow \mathbf{B}^{\bullet +}$), was found to be reversible ($E^{\circ\prime}$ = 0.66–1.39 V) whilst the second one-electron oxidation wave ($\mathbf{B}^{\bullet +} \longrightarrow \mathbf{B}^{2+}$) was found to be irreversible (E_p = 1.20–1.80 V). The standard half-wave potentials allowed a thermodynamically meaningful estimate of the conjugative stabilization of the unusually persistent caged, non-classical 4c/3e radical cations $\mathbf{B}^{\bullet +}$ ($\Delta E^{\circ\prime}$ = 0.91 V for the parent diene **B** and the monoene reference) and of the destabilization by various functionalization patterns (0.40–0.73 V). For the secododecahedradienes **D** (π,π-distance *ca.* 2.85/3.2 Å) and the dodecahedradienes **E** (π,π-distance *ca.* 3.5 Å), only irreversible one-electron oxidation waves were recorded [E_p = (0.8)–1.46 V and (1.0)–1.39 V, respectively]. The degree of conjugative stabilization in the increasingly spherical, yet still non-classical 4c/3e radical cations $\mathbf{D}^{\bullet +}$ and $\mathbf{E}^{\bullet +}$ is approximated by ΔE_p = 0.62 and 0.39 V, respectively.

Transformation of the [1.1.1.1]pagodanes **A** (X, Y are one-carbon units) into the bissecododecahedradienes **B** is an essential step in our pagodane ⟶ dodecahedrane scheme.[1] When it was learnt that this 2σ ⟶ 2π valence isomerization cannot be brought about by thermal activation or transition metal catalysis (it turned out to be endothermic in contrast to the original conclusion from force field calculations) two methodological alternatives were pursued:[2] (*i*) halogen addition to the cyclobutane ring followed by ring fragmenting 1,4-halogen elimination (**A** ⟶ **C** ⟶ **B**) and (*ii*) halogen addition or direct isomerization *via* one-electron oxidation followed by (possibly exothermic) cycloreversion of the cyclobutanoid radical cations [$\mathbf{A} \longrightarrow \mathbf{A}^{\bullet +} \longrightarrow \mathbf{B}^{\bullet +} \longrightarrow \mathbf{B}(\mathbf{C})$]. For both strategies literature had offered ample precedence;†[3,4] yet in a very related case, the 'molecular halves' of parent **A** and **B**, the cyclobutanoid radical cation was favoured in the electrochemical oxidation.[5]



The protocol developed for version (*i*) (*via* photobromo-addition, **C**, R = Br) has by now proven to be highly productive not only with the parent pagodane **A** (X = Y = CH_2), but also with a good number of derivatives;[6,7] yet there remained a challenging limitation in that certain functionalization patterns on the pagodane skeleton prevent the bromine addition. Exploratory activities for version (*ii*) with parent pagodane **A** (**1**, Table 1) offered access to the dichloride of type **C** (R = Cl) through treatment with the one-electron oxidant tris(*p*-bromophenyl)aminium hexachloroantimonate[8] in CH_2Cl_2, but did not lead to a direct isomerization route to dienes **B**. The assumption that this addition of chlorine to **1** had occurred *via* the radical cation of type $\mathbf{B}^{\bullet +}$, and hence that the

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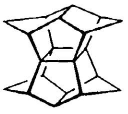
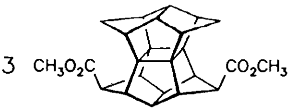
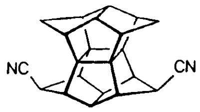
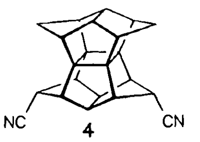
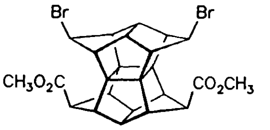
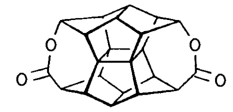
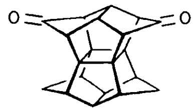
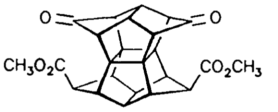
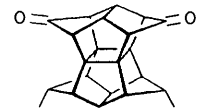
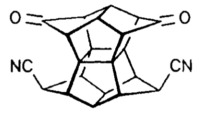
† See particularly the electrochemical functionalization of quadricyclane (A. J. Baggaley, R. Brettle and J. R. Sutton, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1055), the oxidative isomerization of highly strained hydrocarbons *via* the cleavage of cyclobutane subunits [K. Ohta, H. Nakatsuji, H. Kubodera and T. Shida, *Chem. Phys.*, 1983, **76**, 271, *e.g.* of quadricyclanes (Z. Dolejsek, V. Hanus and H. Prinzbach, *Angew. Chem.*, 1962, **74**, 902; E. Haselbach, T. Bally, Z. Lanyiova and P. Baertschi, *Helv. Chim. Acta*, 1979, **62**, 583; H. Weng, X.-M. Du and H.-D. Roth, *J. Am. Chem. Soc.*, 1995, **117**, 135), of (homo)cubanes (X.-Z. Quin, A. D. Trifunac, P. E. Eaton and Y. Xiong, *J. Am. Chem. Soc.*, 1990, **112**, 4565; Y. Takahashi, K. Sato, T. Miyashi and T. Mukai, *Chem. Lett.*, 1984, 1553), of prismanes (K. Raghavachari and H.-D. Roth, *J. Am. Chem. Soc.*, 1989, **111**, 2028)] and the dissimilarity in energy surfaces for neutral valence isomeric hydrocarbons and their radical cations (C. J. Abelt and H.-D. Roth, *J. Am. Chem. Soc.*, 1986, **108**, 6734).

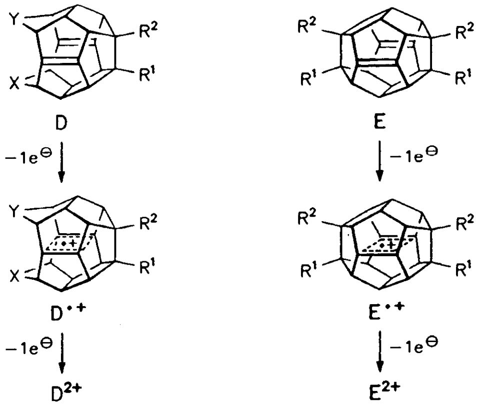
Table 1 Oxidation potentials (E_p/V) of pagodanes **1**–**10**

 **1**	1.20	1.53	 **2**
 **3**	1.70	1.68	 **4**
 **5**	1.89	1.70	 **6**
 **7**	1.81	2.14	 **8**
 **9**	2.23	>2.40	 **10**

opening $\mathbf{A}^{\cdot+}\longrightarrow\mathbf{B}^{\cdot+}$, in contrast to $\mathbf{A}\longrightarrow\mathbf{B}$, is indeed exothermic, was subsequently verified by EPR experiments: for the deeply coloured radical cation generated from parents **A** and **B** and persistent for hours if not for days, the 'extended' non-classical 4c/3e configuration $\mathbf{B}^{\cdot+}$ was established.[9,10] The oxidation of parents **A** and **B** in superacid media to a common dication, and the latter's interception with nucleophiles (R^-) to give derivatives of type **C** meant primarily a theoretically exciting discovery: the dication was identified as the 4c/2e 'in-plane' σ-bishomoaromatic species $\mathbf{B}^{2+}$.[11]

In this paper a detailed account is given of a cyclic voltammetry (CV) study[12] which had been started with the parents **A** and **B** [**1**, **11** (Table 2)], and which was later extended to variously modified (X, Y) derivatives.[13,14] The assessment of the impact of synthetically relevant functionalities upon the ease of oxidation of the neutrals, upon the relative stability of the radical cations $\mathbf{A}^{\cdot+}$ and $\mathbf{B}^{\cdot+}$ and possibly some insight into the restrictions of version (*i*) were the short term goals. With the realization of the very special nature of the radical cations $\mathbf{B}^{\cdot+}$ and dications $\mathbf{B}^{2+}$ (*inter alia* as 'frozen transition states' of the [2 + 1] and [2 + 0] cycloaddition reactions,[15] respectively) the search for more quantitative information with respect to the relationship between the geometrical situation in the central 4c core of the cage skeletons and the degree of homoconjugational stabilization of these ions was initiated.‡

Under such aspects, the increasingly spherical secododecahedradienes **D** (Table 3) and dodecahedradienes **E** (Table 4) were included in this CV study;[14] in the latter, with transannular π,π-distances of *ca.* 3.5 Å, a limiting situation for a through-space π,π-conjugation and hence for the non-classical nature of the respective radical cations ($\mathbf{E}^{\cdot+}$, $\mathbf{D}^{\cdot+}$) and dications ($\mathbf{E}^{2+}$, $\mathbf{D}^{2+}$) is reached.



Results and discussion

Pagodanes A§

The 10 pagodanes examined (**1**–**10**, Table 1) have been at hand from our preparative-synthetic projects.[1,6,7] A central aspect in the context of affecting their valence isomerization by electrochemical oxidation is the high skeletal strain with typical (calculated, MM2) E_{str} values of 112.0 kcal mol^{-1} for **1** (exp. 95.5 kcal mol^{-1})[16] and 121.5 kcal mol^{-1} for **7**. Their behaviour under the CV conditions is characterized by the cyclic voltammograms (CV) pictured in Fig. 1 for *syn,syn*-diester **2** and bislactone **6**. The former CV is representative of the voltammograms of *syn,syn*-dinitrile **3**, *anti,anti*-dinitrile **4**, *anti,anti*-dibromo-*syn,syn*-diester **5**, diketo-*syn,syn*-diester **8** and *anti,anti*-dimethoxy-diketone **9**, the latter CV of parent hydrocarbon **1** and diketone **7**. Diketo-*syn,syn*-dinitrile **10**, resisted oxidation up to a potential of 2.4 V where oxidation of the solvent (CH_2Cl_2) becomes significant. Both CVs of Fig. 1 represent irreversible oxidation waves, with the difference that for the latter group after reversal of the scan a reduction wave is registered (if only weakly for **1** at 0.62 V, and very weakly for **7** at 1.24 V). By comparison with the CVs of the corresponding dienes (Table 2), these reduction peaks can be safely attributed to the presence of the respective diene radical cations ($\mathbf{B}^{\cdot+}\longrightarrow\mathbf{B}$).

For all nine CVs, the shape of the oxidation wave, steepness and height, give evidence for the operation of an ECE process, interpreted as the sequence of one-electron oxidation $\mathbf{A}\longrightarrow\mathbf{A}^{\cdot+}$, fast cycloreversion $\mathbf{A}^{\cdot+}\longrightarrow\mathbf{B}^{\cdot+}$, one-electron oxidation $\mathbf{B}^{\cdot+}\longrightarrow\mathbf{B}^{2+}$ and moderately fast follow-up reactions.[9,17] For the dication prepared from **1** a lifetime of *ca.* 0.05 s in CH_2Cl_2, somewhat longer in SO_2, has been estimated from measurements under very high scan rates (5–10 V s^{-1}). Still, only on this basis a concerted mechanism $\mathbf{A}\longrightarrow\mathbf{B}^{\cdot+}$ cannot be excluded. There had been early speculation that the special architecture of the pagodane skeleton might kinetically stabilize the cyclobutanoid radical cations $\mathbf{A}^{\cdot+}$ to such an extent as to allow their direct observation. Yet, not even in the CVs

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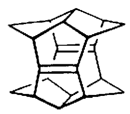
‡ PE spectroscopic investigations with dienes **B** have demonstrated transannular π,π-interactions coming close to classical conjugation: D. Elsässer, H.-D. Martin, B. Mayer, G. Lutz and H. Prinzbach, *Chem. Ber.*, 1991, **124**, 2863.

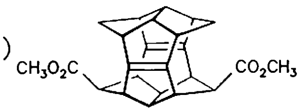
§ Undecacyclo[$9.9.0.0^{1.5}.0^{2.12}.0^{2.18}.0^{3.7}.0^{6.10}.0^{8.12}.0^{11.15}.0^{13.17}.0^{16.20}$]icosane.

Table 2 Oxidation potentials [$E^{\circ\prime}$ (r) and E_p] of bisseco(di)enes (**B**) and lactone-bridged analogues



11

0.66(r) 1.06(r)
1.20 1.59



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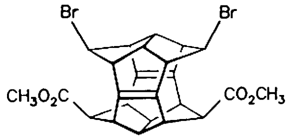
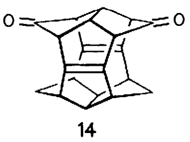
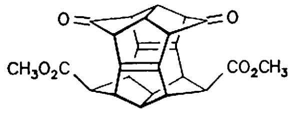


13

1.22(r) 1.24(r)
1.62 1.70

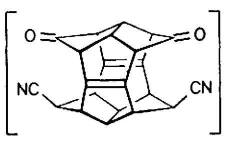


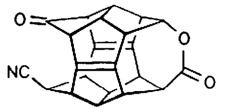
14



15

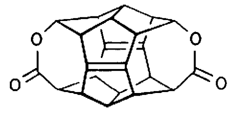
1.38(r)
1.80





16

1.30(r) 1.39(r)
1.80



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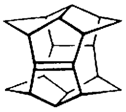

18

1.57(r) 1.90

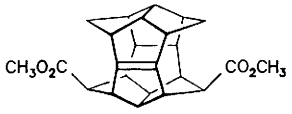

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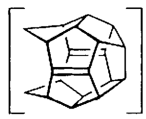
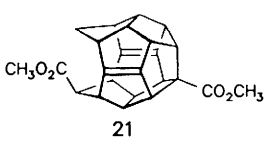
Table 3 Oxidation potentials (E_p) of secododecahedra(di)enes (**D**)



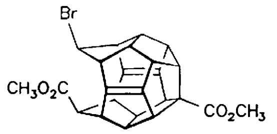
20

(~0.8) 1.22



21

1.46



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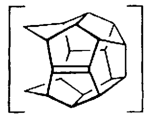

23

(~1.4) 1.84

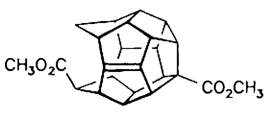

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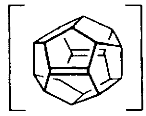
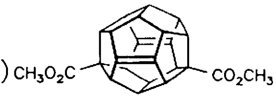
Table 4 Oxidation potentials (E_p) of dodecahedra(di)enes (**E**)

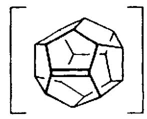


25

(~1.0) 1.39
(1.66)

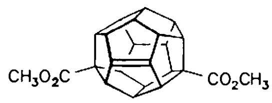


26



27

(~1.4) 1.78



28

registered at very high scan rates and at low temperatures (−60 °C) were any transients observed. In the C-step of the ECE process, the diene radicals $B^{\bullet +}$ are formed at a potential where the diene radical cations themselves are oxidized to the dications B^{2+}. In principle, the chance for their observation on the reversed scan should be better the larger the difference is between the two relevant oxidation potentials.

The oxidation potentials presented in Table 1 are all peak potentials (E_p) measured under kinetic control.[12] Concerning their thermodynamic meaning it is emphasized, that with a rate constant of 10^9 s^{-1} estimated for the transformation $\mathbf{1}^{\bullet +} \longrightarrow \mathbf{11}^{\bullet +}$, a general shift in the cathodic direction of *ca.* 300 mV for the measured values seems reasonable, placing *e.g.* $E^{\circ\prime}$ for **1** at *ca.* 1.5 V. The electron-withdrawing substituents in the derivatives **2**–**10** expectedly shift the E_p potentials to more positive values. The 0.33 and 0.50 V increase for two ester or two cyano groups are in good agreement with the inductive increments reported for these groups γ-positioned in other polycyclic hydrocarbons.[18] The effects are, *cum grano salis*, additive as manifested by the increase in E_p from **1** to **2** to **8** or from **1** to **7** to **8**.

Bissecododecahedradienes B ¶

The seven bissecodienes of Table 2 (**11**–**17**) have been prepared

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¶ **11**: Nonacyclo[$12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}$]icosa-1(20),10-diene.

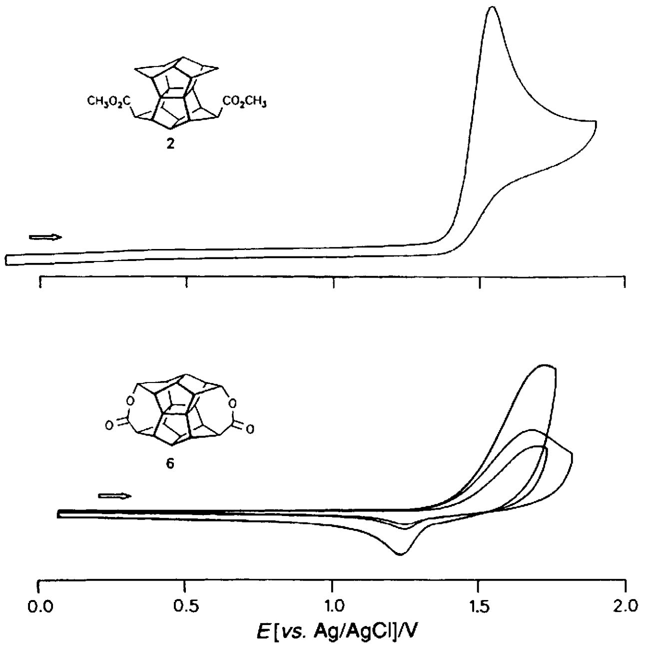

Fig. 1 Cyclic voltammograms of **2** (CH$_2$Cl$_2$/0.1 mol dm^{-3} TBAPF$_6$, −20 °C, v = 100 mV s^{-1}) and **6** (CH$_2$Cl$_2$/0.1 mol dm^{-3} TBAPF$_6$, −40 °C, v = 100, 200, 500 mV s^{-1})

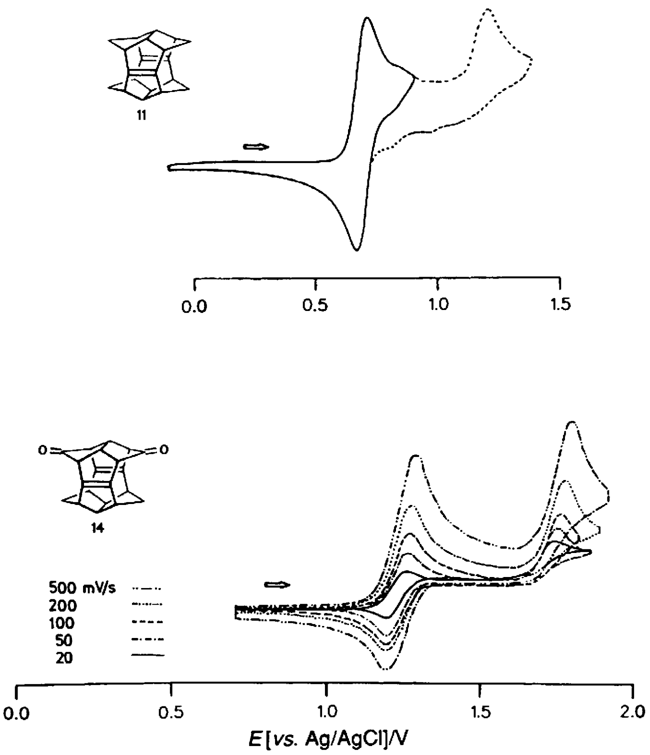

Fig. 2 Cyclic voltammograms of **11** (CH$_2$Cl$_2$/0.1 mol dm^{-3} TBAPF$_6$, −20 °C, v = 50 mV s^{-1}) and **14** (CH$_2$Cl$_2$/0.1 mol dm^{-3} TBAPF$_6$, −65 °C, v = 20–500 mV s^{-1})

from the corresponding pagodanes of Table 1 through the bromine addition/bromine elimination procedure.[2,6] Reference compounds **18** and **19**, hyperstable alkenes,[19] were selectively obtained through hydrogenation (N$_2$H$_2$) of **11** and **12**, respectively, the hydrogenation of the first C=C double bond in the bissecodienes **B** of similar hyperstability is decisively assisted by the concomitant decrease of transannular π,π-destabilization.[1] The two lactone-bridged dienes **16** and **17** are strictly speaking members of the series of (non-pentagonal) secododecahedradienes and dodecahedradienes addressed in the next section, yet are treated here because of their much closer structural relationship (transannular π,π-distance) to the bissecodienes **B**. In Table 2, the data for the dicyanodiketodiene belonging to pagodane **10**, and of special interest in view of the latter's exceptional behaviour,[20] are missing for the trivial reason that no means have been found yet to prepare it from **10**.

To allow for better anticipation of the electrochemical proceedings, a short recollection of the pertinent properties and trends within this series of caged dienes is appropriate: the transannular distance between the *syn*-periplanar C=C double bonds is unusually short with an experimental value of 2.764 Å for the diketodiene-diester **15** and 2.81 Å for bislactodiene **17** (X-ray[21]); the calculated (MM2) skeletal strain energies vary between 74 kcal mol^{-1} for **11** and 84 kcal mol^{-1} for **13**; the experimentally determined alkenic pyramidalization angle (Φ) for **15** and **17** amount to 16° and 18.3°, respectively (10.0° for the monoene **18**). Even these moderately bent dienes are generally sensitive to oxygen, though decreasingly with the degree of the functionalization shown. Short exposure of these compounds to air (seconds) is not very detrimental, their handling under the exclusion of air is nevertheless indicated. Ionic and radical attack occur generally very rapidly with the 2-secopagodyl intermediates enjoying effective through-cage C–C σ bond hyperconjugation (homoconjugation).[22]

The course of the anodic oxidation of the dienes **11**–**17** is consistent insofar as a first reversible one-electron oxidation wave is (Fig. 2), with the exception of dicyanoketolactone **16**, followed by a second, irreversible one-electron oxidation wave. The first wave remained reversible at low scan rates (50 mV s^{-1}) and at room temperature, the second wave remained irreversible at scan rates as high as 10 V s^{-1} at low temperature (−70 °C). The repeated failure to observe a second oxidation wave for **16** was ascribed to adsorption phenomena rather than to a too high oxidation potential of $\mathbf{16}^{\cdot+}$. In two cases, diene-diester **12** and dibromodiene-diester **13**, at 500 mV s^{-1} additional features were recorded: for **12** a second irreversible reduction wave, for **13** a third irreversible oxidation wave at 1.85 V s^{-1}. The latter, supposedly indicative of a follow-up transformation of $\mathbf{13}^{2+}$, became weaker with increasing scan rates and totally disappeared at 5 V s^{-1}. Oxidation of the bromine substituents with subsequent scission of the C–Br bond is unlikely, since upon scan reversal no bromine reduction ($E^{\circ\prime}$ = 1.6 V *vs.* Ag/AgCl, CH$_3$CN)[23] was noted.

The increase in $E^{\circ\prime}$ of 0.40 and 0.58 V *vs.* **11** caused by the two ester substituents in **12** and the two keto functions in **14**, respectively, runs up to the same order as ΔE_p for the pagodane pairs **1**/**2** and **1**/**7**. In the case of tetrafunctionalization, the increase by 0.56 V for dibromo-diester **13** and by 0.72 V for diketo-diester **15** are smaller than ΔE_p 0.69 and 0.94 V for the pairs of pagodanes **1**/**5** and **1**/**8**, the increase of 0.73 for bislactodiene **17** higher than ΔE_p 0.50 V for the pagodanes **1**/**6**. *In toto*, the thermodynamic destabilization of the respective radical cations ranges from 9 to 15 kcal mol^{-1}. The rate constants for the heterogeneous charge transfer as manifested by ΔE_p of *ca.* 0.08–0.1 V for the oxidation and reduction waves of the $\mathbf{B}/\mathbf{B}^{\cdot+}$ redox pair at low scan rates are generally high and can be taken as an expression of relatively small geometrical changes associated with the oxidation $\mathbf{B} \longrightarrow \mathbf{B}^{\cdot+}$.[12]

Not surprisingly in view of the findings with the pagodanes, all efforts to make the second oxidation process reversible by employing higher rates and lower temperatures, and specifically concentrated on non-deactivated diene **11**, were futile, up to now. There can be no doubt, however, that the peak potentials ranging from 1.20–1.80 V reflect the oxidation $\mathbf{B}^{\cdot+} \longrightarrow \mathbf{B}^{2+}$, the destabilizing impact exerted by substitution (0.39 V for **12** to 0.60 V for **15**) differs expectedly to some degree from that determined for the oxidation $\mathbf{A} \longrightarrow \mathbf{B}^{2+}$.

For the unsubstituted bissecomonoene **18** as reference compound, up to scan rates of 500 mV s^{-1} the process remained irreversible. With increasing rate, though, a reduction wave became discernible and was clearly expressed at 20 V s^{-1} and -20 °C ($\Delta E_p = 0.24$ V). The monoene-diester **19** showed a peak at 1.90 V, for which there was, however, no correspondence after reversal of the scan (2 V s^{-1}). As an explanation for the obviously rather short life-time of $\mathbf{18}^{\cdot +}$ and $\mathbf{19}^{\cdot +}$, the structurally inherent tendency for transannular follow-up reactions could be cited. The potential of **18** comes close to the $E^{\circ\prime}$ values of 1.4–1.6 V reported for the *syn* (*anti*)-sesquinorbornenes having in common with **18** (**19**) the bent bicyclo[3.3.0]oct-1(5)-ene core.[18,24]

With $E^{\circ\prime} = 0.66$ V for **11** and 1.57 V for **18**, the conjugative stabilization of the ion $\mathbf{11}^{\cdot +}$ amounts to 0.91 V (20.9 kcal mol^{-1}). For comparison, the corresponding difference for norbornadiene/norbornene is 0.39[25] (0.48[26]) V, for cyclohexa-1,4-diene/cyclohexene 0.40 V,[26] examples of dominant through-space (TS) and through-bond (TB) interaction (PE).[27] Unfortunately, Wiberg's tricyclododecadiene with probably the most proximate, *syn*-periplanar C=C double bonds (TS and TB contributions are compensating each other in the PE analysis[28]) no electrochemical data are known.

Secododecahedradienes D [||] and dodecahedradienes E [**]

Relevant structural changes in going from the bissecodienes **B** to the secodienes **D** and dodecahedradienes **E** are the rise in transannular π,π-distance from *ca.* 2.7 Å in **B** to *ca.* 2.85/3.2 Å in **D** (**22**, X-ray[29]) to *ca.* 3.5 Å in **E** [**25**, (MM2)], in pyramidalization of the alkenic carbons (Φ) from *ca.* 16° to 16°/30° to 43°,[30] with the consequence of a steep increase in strain from the 74 kcal mol^{-1} in **20** to 105.3 kcal mol^{-1} in **25** and particularly in oxygen sensitivity. The loss of functionalization in the course of the cyclizations $\mathbf{B} \longrightarrow \mathbf{D} \longrightarrow \mathbf{E}$ along the S_N2-route,[6,7] together with enormous difficulties in dealing with such 'diradicaloid' species,[31–33] greatly reduced the number of available substrates (Tables 3 and 4). Thus, attempts at reductive elimination of the ester groups in **21** and **24** to give the parent secoalkenes **20** and **23** ended in very complex product mixtures. In the dodecahedral series, the parent diene **25**, surprisingly thermally stable,[††] and generated through vapour-phase pyrolysis of a bis-β-lactone precursor, did not prove amenable to our CV conditions, for whatever deficiencies in the handling. Likewise the efforts to record the cyclic voltammogram of the parent reference monoene **27** were unsuccessful. Diene-diester **26** is not significantly less reactive towards oxygen than the parent **25**, yet is easier to prepare, better to handle and more soluble; it fits into the series of studied diesters made up of **2**, **12**, **19**, **21**, **24** and **28**.

The CVs of the secodiene-diesters **21** and **22** were found to be similar to each other in shape and to differ from that of the corresponding bissecodienes in that they represent strictly irreversible, one-electron oxidation processes, no reduction waves being recognizable at scan rates of 5–10 V s^{-1} and at temperatures as low as -70 °C. There is by now additional support, primarily from PE investigations[34] and *ab initio* calculations,[35] to assign these waves to the oxidations $\mathbf{21} \longrightarrow \mathbf{21}^{\cdot +}$ and $\mathbf{22} \longrightarrow \mathbf{22}^{\cdot +}$.

Secoene-diester **24** showed under analogous conditions an irreversible one-electron oxidation step with $E_p = 1.84$ V. Again, no reduction current was produced by scan rates up to 5 V s^{-1}. With the increments for the ester and bromine groups of Table 2, E_p values for the parent secodiene **20** and secoene **23** of *ca.* 0.8 and *ca.* 1.4 V, respectively, are approximated. Admittedly, $\Delta E_p = 0.62$ V for diene **21** and reference **24** is thermodynamically not as meaningful as $\Delta E^{\circ\prime} = 0.91$ for **11**/**18**, but still can be taken as a measure of the homoconjugation in radical cations of type $\mathbf{D}^{\cdot +}$.

The CV measurements performed with dodecahedradiene-diester **26** at varying scan rates and temperatures, under the best possible exclusion of oxygen and moisture, and with samples of different batches, were somewhat erratic: two irreversible waves peaking at 1.39 and at *ca.* 1.6 V, though in varying relative heights, were registered. There are again good reasons (PE, EPR and *ab initio* calculations)[36] to ascribe the first peak to the oxidation $\mathbf{26} \longrightarrow \mathbf{26}^{\cdot +}$: this E_p value is in the order predicted by the extrapolation $\mathbf{12} \longrightarrow \mathbf{21} \longrightarrow \mathbf{26}$. The second peak is rather attributed to an unknown follow-up (oxidation) product than to the oxidation $\mathbf{26}^{\cdot +} \longrightarrow \mathbf{26}^{2+}$.

The irreversible voltammogram measured for reference dodecahedrene-diester **28** has its one-electron oxidation peak at 1.78 V. The decrease in E_p, if only slight, with respect to the monoenes **24** (1.84 V) and **19** (1.90 V) is in accord with the known consequences of increasing pyramidalization of alkenic carbons upon the HOMO energies.[37] With the increment of 0.4 V for the ester groups, peak potentials of *ca.* 1.0 and *ca.* 1.4 V are extrapolated for the parents **25** and **27**. With $\Delta E_p = 0.39$ V for **26** and **28**, the downhill trend in homoconjugational stabilization from **12**/**19** (0.91 V) to **21**/**24** (0.62 V) is continued by a similar margin.

Conclusions

The question standing at the beginning of this study is clearly answered: the thermodynamics favouring the [1.1.1.1]pagodanes *vis-à-vis* their valence isomeric dienes ($\mathbf{A} \longleftarrow \mathbf{B}$) are generally reversed for the respective radical cations ($\mathbf{A}^{\cdot +} \longrightarrow \mathbf{B}^{\cdot +}$). Strongly electron-attracting functionalities, which have been installed for synthetic reasons, prohibit neither the oxidation of neutral **A** and **B** nor of the radical cations $\mathbf{B}^{\cdot +}$. Only the pagodane with two carbonyl and two cyano functions cannot be oxidized; without any mechanistic implications, it is the only one of the given series which does not undergo the photoaddition of bromine. How exothermic are the conversions $\mathbf{A}^{\cdot +} \longrightarrow \mathbf{B}^{\cdot +}$? By *ca.* 12 kcal mol^{-1} for the parent ions $\mathbf{1}^{\cdot +} \longrightarrow \mathbf{11}^{\cdot +}$ as calculated from the heats of formation and the adiabatic ionization energies[14] for **1** ($\Delta_f H^\circ = 64.4$ kcal mol^{-1}; $E_i = 7.65$ eV) and **11** ($\Delta_f H^\circ$ *ca.* 70 kcal mol^{-1}; $E_i = 6.86$ eV; MM2 value corrected for the underestimated π,π interaction). The failure to identify electrochemically the pagodane radical cations $\mathbf{A}^{\cdot +}$ as discrete intermediates of the otherwise well documented sequence $\mathbf{A} \longrightarrow \mathbf{A}^{\cdot +} \longrightarrow \mathbf{B}^{\cdot +} \longrightarrow \mathbf{B}^{2+}$ is understood in light of the half-life of 1.2 μs at 193 K (hexane) recently determined for $\mathbf{1}^{\cdot +}$ ($\longrightarrow \mathbf{11}^{\cdot +}$) by the fluorescence-detected magnetic resonance technique (FDMR).[38] It will be checked whether cyclic voltammetry experiments with very fast scans can provide some more insight.

The kinetic and thermodynamic aspects of this study are highlighted by the quantification of the homoconjugative stabilization conferred upon the radical cations $\mathbf{B}^{\cdot +}$, $\mathbf{D}^{\cdot +}$ and $\mathbf{E}^{\cdot +}$.[4] As to the origin of this stabilization it must be recalled that, according to the PE analyses including standard

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[||] **20**: Decacyclo[9.9.0.0$^{2.8}$.0$^{3.10}$.0$^{4.17}$.0$^{5.9}$.0$^{6.16}$.0$^{7.14}$.0$^{8.12}$.0$^{13.20}$]-icosa-4(17),12-diene.

[**] **25**: Undecacyclo[9.9.0.0$^{2.9}$.0$^{3.7}$.0$^{4.20}$.0^{5,18}.0^{6,16}.0$^{8.15}$.0$^{10.14}$.0$^{12.19}$.-0$^{13.17}$]icosa-1,16-diene.

[††] No alkene with this degree of bending has been found before to be persistent enough to allow its isolation at room temperature. That **25** and **27** undergo cyclodimerization only above *ca.* 100 °C is attributed to efficient steric protection of the C=C double bonds by the allylic hydrogens: K. Weber, T. Voss, A. Weiler and H. Prinzbach, to be published.

separation of through-space and through-bond interactions, the π,π-split $\Delta I_\pi = 1.91$ eV for **11** is totally TS in nature, whilst $\Delta I_\pi = 1.16$ eV for **21** and $\Delta I_\pi = 0.68$ eV for **25** include increasing TB contributions.[34] The outstanding persistence of the radical cations **B**$^{\cdot+}$, parent **11**$^{\cdot+}$ is probably the most persistent known hydrocarbon radical cation, is no doubt due to the interplay of the strong electronic stabilization with efficient steric protection against loss of protons ('*anti*-Bredt-rule protection')[18] and dimerization. By making use of structurally modified pagodanes ([2.2.1.1]homologues, [1.1.1.1]/[2.2.1.1]isopagodanes) it has recently been demonstrated how the 'tight' 4c/3e configurations (**A**$^{\cdot+}$) can be made thermodynamically more stable than the extended ones (**B**$^{\cdot+}$).[39,40]

If the rigid cage structures **A** and **B** are ideal hosts for 4c/3e radical cations and 4c/2e dications would they also allow the generation of the corresponding, novel 4c/5e radical anions[41] and 4c/6e σ-bishomoaromatic dianions,‡‡ eventually with assistance of the functionalities which had remarkably destabilized the positive ions? The so far negative answer is not considered as definite.

Experimental

The CV curves were recorded in carefully purified and dried argon purged CH_2Cl_2, or in a few cases SO_2, solutions with tetrabutylammonium hexafluorophosphate as supporting electrolyte (Philips model PM 8271 X-Y-recorder). A three-electrode configuration was employed throughout. The working electrode was a Pt disc (diameter 1 mm) sealed in soft glass, the counter electrode a Pt wire coiled around the glass mantle of the working electrode and the reference electrode an Ag wire on which AgCl had been deposited electrochemically, immersed in the electrolyte solution. Potentials were calibrated against the formal potentials of ferrocene (+0.35 V *vs.* Ag/AgCl) and cobaltocene (−0.94 V *vs.* Ag/AgCl). All manipulations were carried out under an argon atmosphere.

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