Cyclic electron delocalization in hydrocarbon cages (pagodanes, isopagodanes, (bisseco-/seco-)-(dodecahedradienes))

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Abstract. In the polycyclic, rigid [1.1.1.1]/[2.2.1.1] (iso)pagodanes and in the related (bisseco/seco)dodecahedradienes the geometrical and energetical situation for the 4c/3e radical cations and 4c/2e dications produced by loss of one or two electrons from the central cyclobutane/homodiene cores is gradually modified. By spectroscopic (UV, PE, ESR, NMR), cyclovoltammetric, and theoretical investigations the structural prerequisites and the degree of homoconjugational (through-cage) electron delocalization (σ-homoaromaticity) are explored.

CALCULATIONS

A spin-off from our early endeavour (1) to isomerize $C_{20}H_{20}$ pagodane $\underline{1}$ into $C_{20}H_{20}$ dodecahedrane - via carbenium or radical cations - was the discovery of the ("extended") 4c/3e-radical cation $\underline{2}^{\bullet+}$ (2) and the 4c/2e σ-bishomoaromatic dication $\underline{1}^{2+}$ ($\underline{2}^{2+}$) (3). Both ions are impressively persistent, surviving at room temperature for hours. A better insight into the relationship between the geometry of the 4c-core and the stabilization by cyclic electron delocalization was expected from structural modifications along three ways:
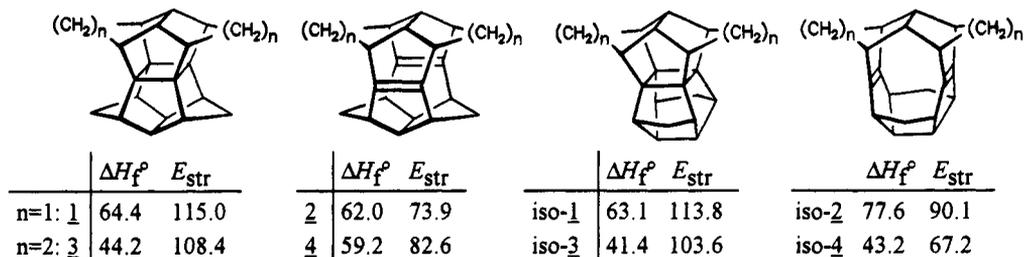

	ΔH_f^o	E_{str}		ΔH_f^o	E_{str}		ΔH_f^o	E_{str}		ΔH_f^o	E_{str}
n=1: $\underline{1}$	64.4	115.0	$\underline{2}$	62.0	73.9	iso-$\underline{1}$	63.1	113.8	iso-$\underline{2}$	77.6	90.1
n=2: $\underline{3}$	44.2	108.4	$\underline{4}$	59.2	82.6	iso-$\underline{3}$	41.4	103.6	iso-$\underline{4}$	43.2	67.2

Fig. 1. ΔH_f^o and E_{str} values (kcal mol^{-1}, MM2) for (iso)pagodanes $\underline{1},\underline{3}$ and bissecodienes $\underline{2},\underline{4}$.

(i): Homologation of the [1.1.1.1]pagodane ($\underline{1} \rightarrow \underline{3}$) and the derived [1.1.1.1]bisseco(dodecahedra)diene ($\underline{2} \rightarrow \underline{4}$) (4). (ii): Rotation (90°C) of one "half" of the structures to give the isopagodanes (iso-$\underline{1},\underline{3}$), iso-bissecodienes (*iso*-$\underline{2},\underline{4}$) (5), and (iii): Lateral C,C bond formation in the bissecodienes $\underline{2}$ ($\underline{2}'$) to give the (seco) dodecahedradienes $\underline{5}(\underline{5}')$ and $\underline{6}(\underline{6}')$, respectively (6).
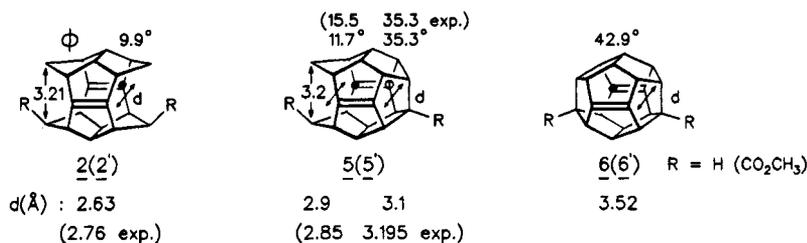
Fig. 2. Selected structural data for bisseco- ($\underline{2}'$), seco- ($\underline{5}'$) and dodecahedradiene diester $\underline{6}'$.

In the sequence of dienes $\underline{2}(\underline{4})$, $\underline{5}$ and $\underline{6}$, the calculated (MM2) transannular distances between the near to perfectly *syn*-periplanar C=C double bonds increase from ca. 2.7 to ca 3.5 Å, the olefinic pyramidalization angle (Φ) from ca. 10 to ca. 43° - in good agreement with X-ray crystallographic data (7). According to the *ab initio* calculations (Table 1), the dienes ($\underline{2},\underline{4}$) are higher in energy than the cyclobutanes ($\underline{1},\underline{3}$) (the MM2 data for proximate dienes are incorrect for known reasons (1)) - with the largest energetic difference ($\Delta\Delta H_f^o$ nearly 45 kcal mol^{-1}) for the pair $\underline{3}/\underline{4}$, the smallest ($\Delta\Delta H_f^o$ ca. 16 kcal mol^{-1}) for the pair iso-$\underline{3}$/iso-$\underline{4}$. Consequently, for the radical cations derived from the former pair (and iso-$\underline{1}(\underline{2})$) a cyclobutane-like ("tight", $\underline{T}$), for the ones from the latter pair (and $\underline{1}(\underline{2})$) a diene-like ("extended", $\underline{E}$) structure is predicted. There are similar energetic relationships with respect to the dications (only one minimum found for each pair). The transannular distance (d) is reduced from ca. 2.75 Å in neutral dienes ((iso) $\underline{2}$, $\underline{4}$)) to ca. 2.5 Å in the corresponding radical cations and to ca. 2.15 Å in the dications.

TABLE 1. PMP2/3 - 21G/3-21G optimized relative energies (E_{rel}, kcal mol^{-1}) and transannular π,π-distances (d,Å) for the parent cages (iso) $\underline{1}$-$\underline{4}$, the radical cations (iso) $\underline{1}^{\bullet+}$ - $\underline{4}^{\bullet+}$ and dications (iso) $\underline{1}^{2+}$, $\underline{3}^{2+}$.

	E_{rel}	d		E_{rel}	d
$\underline{1}(\underline{2})$	1.95 (25.49)	1.567 (2.702)	iso-$\underline{1}(\underline{2})$	0.00 (39.77)	1.555 (2.805)
$\underline{1}^{\bullet+}$ ($\underline{2}^{\bullet+}$)	1.61 (0.00)	1.789 (2.461)	iso-$\underline{1}^{\bullet+}$ ($\underline{2}^{\bullet+}$)	9.52 (17.27)	1.768 (2.506)
$\underline{1}^{2+}$ ($\underline{2}^{2+}$)	0.00	(2.164)	iso-$\underline{1}^{2+}$ ($\underline{2}^{2+}$)	16.01	(2.167)
$\underline{3}(\underline{4})$	2.25 (47.16)	1.562 (2.767)	iso-$\underline{3}(\underline{4})$	0.00 (16.27)	1.566 (2.794)
$\underline{3}^{\bullet+}$ ($\underline{4}^{\bullet+}$)	12.79 (23.70)	1.770 (2.450)	iso-$\underline{3}^{\bullet+}$ ($\underline{4}^{\bullet+}$)	4.88 (0.00)	1.785 (2.512)
$\underline{3}^{2+}$ ($\underline{4}^{2+}$)	16.10	(2.129)	iso-$\underline{3}^{2+}$ ($\underline{4}^{2+}$)	0.00	(2.174)

Some of the fascination associated with these 4c/3e radical cations and 4c/2e dications constrained into highly rigid molecular skeletons stems from their representation as "frozen" stages on the reaction coordinates for the ethylene/ethylene $^{\bullet+}$ (8) and ethylene$^{\bullet+}$/ethylene$^{\bullet+}$ cycloadditions (9). There was hope that bond-length-isomeric radical cations (e.g. $\underline{3}^{\bullet+}$, $\underline{4}^{\bullet+}$) would become observable (10) (cf. the failure with the classical norbornadiene/quadricyclane case (11)).

PREPARATIVE ASPECTS

For the preparation of the pagodanes ($\underline{1},\underline{3}$, iso-$\underline{1},\underline{3}$) efficient protocols are available (5,6). Distinct reactivity differences between the homologous pairs pose, however, problems for their isomerization into the respective bissecodienes ($\underline{2},\underline{4}$, iso-$\underline{2},\underline{4}$) which are not yet solved for $\underline{4}$ and iso-$\underline{2}$. That the dienes are calculated to be hyperstable and that still one C=C double bond can be readily hydrogenated is a good measure for the inherent π,π-destabilization (12). The (seco) dodecahedradienes $\underline{5}$ and $\underline{6}$ are thermally very stable in spite of their high olefinic strain/pyramidalization - it is only above 200 °C that $\underline{6}'$ undergoes [2+2]-dimerization (13).
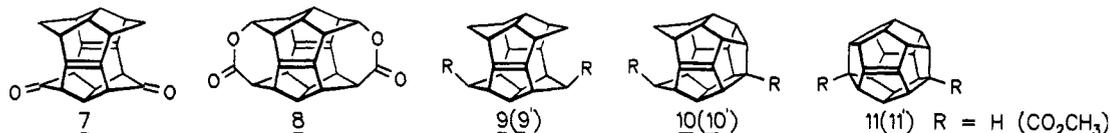
Oxygen sensitivity increases from $\underline{2}$ to $\underline{5}$ to $\underline{6}$ requiring increasingly careful experimentation. In contrast, model dilactonediene $\underline{8}$, a non-pentagonal, flattened (d = 2.81 Å, Φ = 17.4°) dodecahedradiene, is relatively insensitive. Except for $\underline{6}$, X-ray crystallographic data are available (3,7). Recent preparative progress in the pagodane $\rightarrow$ dodecahedrane scheme has dramatically shortened the route to $\underline{5}'$ and $\underline{6}'$ (14). The monoenes $\underline{9}$ - $\underline{11}$ needed as references can be readily obtained by making use of distinct rate differences in the hydrogenation of the bisseco/secodienes.

UV SPECTRA

The long-wavelength UV absorptions of the bissecodiene diesters $\underline{2}',\underline{5}'$ and $\underline{6}'$ (Figure 3, that of $\underline{6}'$ is only qualitative) give evidence for strong π,π-interaction in the very proximate $\underline{2}'$ (maximum at 261 nm (ε =

480), beginning absorption at ca. 330 nm), decreasing to 5' and 6' (blueshifted shoulders at ca. 255 and 240 nm in absorption curves starting at ca. 300 and ca. 270 nm, respectively).(15) The intensive absorption at 226 nm for 6' is understood in terms of high-bending of the C=C double bonds (the HOMO is slightly raised, the LUMO is strongly lowered) (16). Accordingly for dodecahedrene 11' a maximum at 219 nm (ε = 219) is measured (cf. the long-wavelength maxima for strongly bent alkenes 12 and 13) (17) (Table 2).
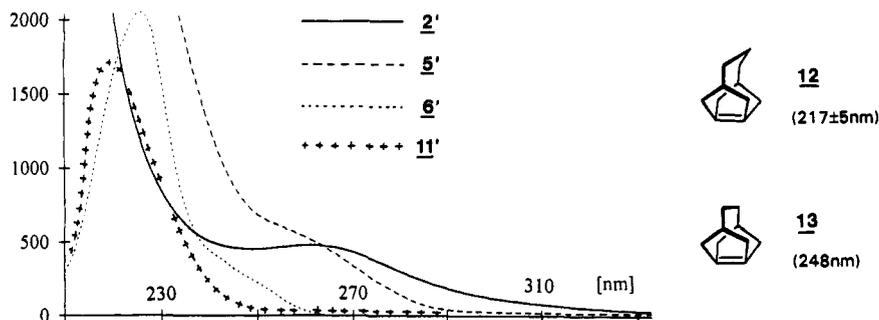
Fig. 3. UV absorption curves of 2', 5', 6' and 11' (CH_3CN).

PE SPECTROSCOPY

The PE spectrum of bissecodiene 2 (Figure 4) exhibits two π-ionization events at 7.12 and 9.03 eV. As frequently demonstrated (18), through-space (TS) and through-bond (TB) transmission was distinguished by the procedure proposed by *Heilbronner* and *Schmelzer* (19) with the result that the split ΔI_π = 1.91 eV is totally ascribed to through-space (TS) π,π-interaction (20). In dienedione 7 the interplay between $\pi_-(b_2)$ and $n_+(b_2)$ raises ΔI_π to a record number of 2.2 eV which comes close to the 2.46 eV of classically conjugated 1,3-butadiene (cf. the split of 0.85 eV (dominant TS) for norbornadiene (21), the split of 1.0 eV (dominant TB) for 1,4-cyclohexadiene (22) and the missing of a split in *Wiberg's* very proximate diene (23)). For secodiene-diester 5' (5 is not yet available) the split is reduced to 1.16 eV, the mean value of 8.25 eV coming close to that of 2. Dodecahedrene 11 shows a well separated π-ionization band with vibrational fine structure (ν = 1300 cm^{-1}). Since the 0.0-transition at 7.94 eV is of highest intensity, this ionization energy is regarded as the reference value for unperturbed π-ionization in the dodecahedrane framework. The addi-
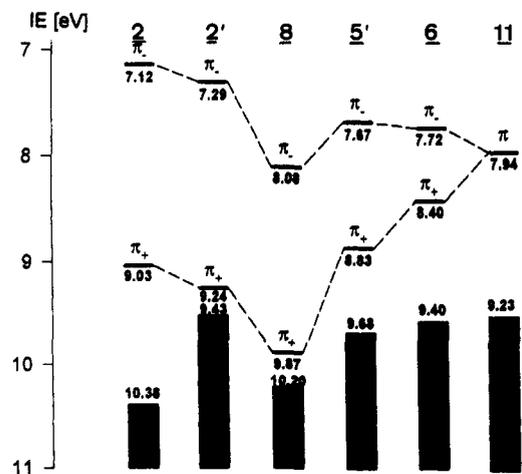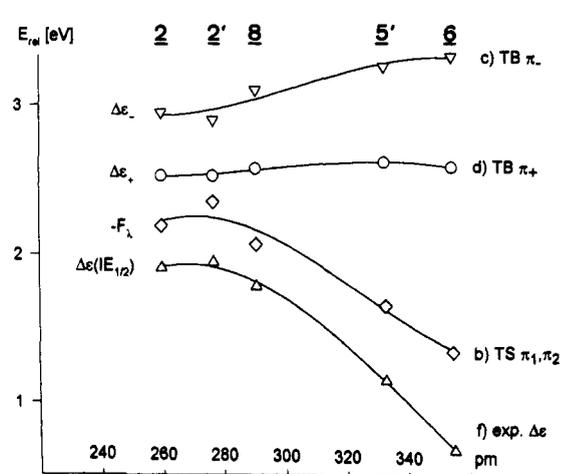

Fig. 4. Correlation of PE data.

Fig. 5. Dependence on π,π-distance of TS-(b)/TB-(c,d) and experimental interaction (f).

tional C=C double bond of 6 (*in situ* generated in the spectrometer from the bis-β-lactone; 6' could not be vaporized) causes a split of the symmetry-equivalent π-orbitals of $\Delta\varepsilon$ = 0.68 eV. The mean value of 8.06 eV is not significantly higher than IE_π = 7.94 eV of 11. Polar and inductive effects by the increased number of sp^2-hybridized carbon atoms are obviously negligible, most certainly due to the size of the σ-skeleton

"washing" out these multiply documented effects. Standard analysis (19) strongly suggests that TS and TB each contributes ca. 50 % to the total splitting. When transannular π,π-distance was correlated with interaction mechanisms (Figure 5), the curve f displaying the experimental $\Delta\varepsilon$ (IE$_{1,2}$) proved to be in good agreement with the orbital splitting diagram derived for two ethylene molecules approaching each other along an idealized D_{2h}-pathway (STO-3G). The stronger olefinic pyramidalization in $\underline{11}$ with respect to $\underline{2}$ lowers somewhat the ionization energy; with the more meaningful adiabatic ionization potentials this relationship is documented for selected tetraalkyl ethylenes in Table 2. The PE data for the iso compounds have still to be determined.

TABLE 2. Olefinic pyramidalization (Φ, °) and adiabatic ionization potentials for tetraalkyl ethylenes.

	⟨structure⟩	⟨structure⟩	$\underline{9}$	$\underline{12}$	$\underline{11}$	$\underline{13}$
$\Phi(°)$	0	4	11	30(33)	44	48
IP$_a$(eV)	8.27	8.11	7.90	7.8	7.77	7.1-7.3

ELECTROCHEMICAL OXIDATIONS

The electrochemical behaviour (24) of pagodanes (e.g. $\underline{1},\underline{3}$) and bissecodienes (e.g.$\underline{2},\underline{4}$), and of variously functionalized derivatives (2, 25), is characterized by the cyclic voltammograms (CV) pictured for $\underline{1}$ and $\underline{2}$ in Figure 6. CV ($\underline{1}$) is an irreversible oxidation wave, the reduction wave registered after reversal of the scan is not observed for all derivatives. The shape, steepness, and height of the oxidation wave, give evidence to the operation of an ECE process, $\underline{1} \rightarrow \underline{1}^{•+} \rightarrow \underline{2}^{•+} \rightarrow \underline{2}^{2+}$. Not even at very high scan rates was there evi-
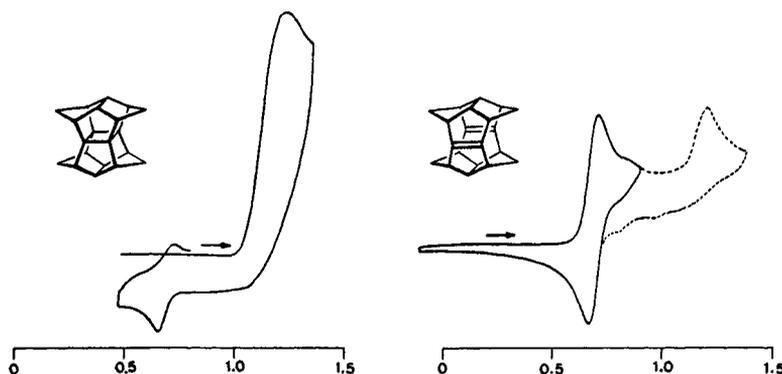
Fig. 6. CV's of $\underline{1}$ and $\underline{2}$ (standard conditions: CH_2Cl_2, 0.1 M TBAF$_6$, $\underline{v}$ = 100 mV/s, vs. Ag/AgCl, r.t.).

dence for the intermediacy of the pagodane ("tight") radical cation. In step C, diene radical cations are formed at a voltage where they themselves are oxidized to the dications, which are known to be unstable under these conditions. Concerning the thermodynamic meaning of Ep values it should be recalled that the chemical step must be extremely fast, with an estimated rate constant of ca. 10^9 s^{-1}; a shift in the negative direction of ca. 300 mV for the measured values seems reasonable, placing the standard potential E$^{o'}$ for $\underline{1}$ at ca. 1.5 V. In CV ($\underline{2}$) the first, reversible one-electron oxidation step is followed by a second, irreversible one. The latter remained irreversible at scan rates as high as 2 V s^{-1} - as noted for $\underline{1}$. From measurements at 10-15 V s^{-1} a half-life of ≤ 0.05 s is estimated for dication $\underline{2}^{2+}$. For bissecomonoene $\underline{9}$ no reversible wave was noted up to rates of 500 mV s^{-1}; reversibility was established (E$_p$ = 1.57 V), though, at 20 V s^{-1} and -20°C, a reduction wave being clearly expressed (1.33 V, ΔE_p = 0.24 V). The peak potential of $\underline{9}$ comes close to E$^{o'}$ (1.4-1.6 V) reported for the syn (anti) - sesquinorbornenes having in common the bent bicyclo [3.3.0]oct-1(5)-ene core (26). Diester $\underline{9}'$ showed a peak at 1.90 V for which there was no correspondence after reversal of the scan. Contrary to the findings with reference $\underline{9}$, the first oxidation wave of bissecodiene $\underline{2}$ remained reversible even at relatively low scan rates at room temperature - the homoconjugative (100 %, PE) stabilization of $\underline{2}^{•+}$ is quantified by $\Delta E^{o'}$ ($\underline{9}$ - $\underline{2}$) = 0.91 V (20.9 kcal mol^{-1}). For comparison, this difference for norbornadiene/norbornene amounts to 0.38 (0.48) V (dominant TS) (27, 28), for 1,4-cyclohexadiene/cyclohexene to 0.40 V (dominant TB) (28).

TABLE 3. Oxidation potentials (V, Ep) for (iso) pagodanes, (iso) dienes and references (r: reversible).

	1	1'	3	iso-1	iso-3	2	2'	iso-4	9	9'
Ep	1.20	1.53	1.46	1.72	1.36	0.66 (r)	1.06 (r)	0.84 (r)	1.57 (r)	1.90
					(1.45)	1.20	1.59	1.49 (r)		

		5	5'	6	6'	10	10'
	Ep	(~0.8)	1.22	(0.99)	1.39	(~1.4)	1.84
					[1.6]		

The again irreversible oxidation step of iso-1 (Figure 7) significantly differs from that of 1: The peak potential is higher by ca. 0.5 V, the shape gives no hint for an ECE process. There is rapid change into compounds which even at low temperature (-30°C) and high rate (1 V s^{-1}) can neither be oxidized nor reduced. Stabilization of the "tight" iso-1$^{\bullet+}$ by ways different from the opening iso-1$^{\bullet+} \rightarrow$ iso-2$^{\bullet+}$ is suspected. CV (iso-3) (Figure 7) is exceptional: At -28°C not only is the first oxidation step distinguished, but also the second oxidation step is reversible - iso-4^{2+} (from iso-3^{2+}) turns out to be as yet the most persistent dication of this project (under CV conditions). The comparison in (homoconjugative) stabilization of iso-4$^{\bullet+}$ with 2$^{\bullet+}$ cannot yet be made definitively, the potential for the dihydro reference of iso-4 is not yet at hand. The high rate constants for the heterogeneous charge transfer in 2(2'), iso-4, and iso-4$^{\bullet+}$ (ΔE_{pac} < 0.1 V) indicate relatively small structural changes associated with the one-electron oxidation (*vide infra*).
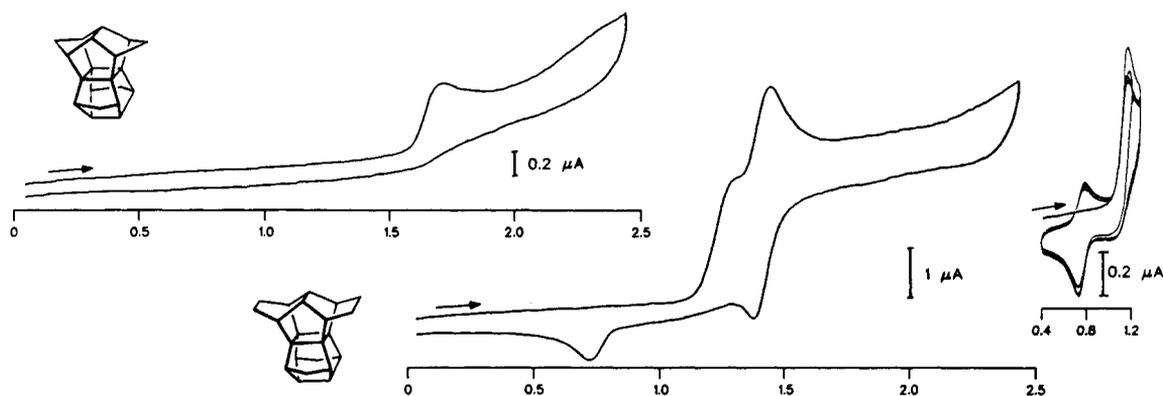
Fig. 7. CV's of iso-1 and iso-3 (CH$_2$Cl$_2$, 0.1 M TBAF$_6$, $\underline{v}$ = 100 mV/s, vs. Ag/AgCl, -30°C).

The oxidation wave of secodiene-diester 5' stays irreversible up to 1 Vs^{-1} scan rate and the peak potential, Ep = 1.22 V, is higher than that of 2' by 0.16 V. With E$_p$ = 1.84 V for reference 10, ΔE_p (10'-5') = 0.62 V manifests - in comparison with ΔE_p (9'-2') = 0.91 V - an expectedly reduced but still remarkable π,π-stabilization (according to the PE analysis (Figure 5) 85 % through-space).

Dodecahedradiene diester 6' is not significantly more persistent than parent 6, yet it is easier to prepare, better to handle and better soluble. The CV results with 6' are still preliminary: In the irreversible oxidation

	2	5	6
ΔE_p (V)	0.91	0.62	0.39
($\Delta\varepsilon$ (eV)	1.91	1.16	0.68

wave the peak at 1.39 V is erratically accompanied by a second one at ca. 1.6 V. *Inter alia* the extrapolation $\underline{2}'$ (1.06 V) → $\underline{5}'$ (1.22 V) → $\underline{6}'$ (1.39) supports the assignment to the formation of $\underline{6}'^{•+}$. The CV of reference $\underline{11}'$ irreversibly peaks at 1.78 V; the decrease of E_p from $\underline{9}'$ to $\underline{10}'$ to $\underline{11}'$ is in line with the increasing olefinic pyramidalization (Table 2). Based on ΔE_p $(\underline{11}'\text{-}\underline{6}')$ = 0.39 V the π,π-stabilization of $\underline{6}'$ is further reduced and with ca. 50 % due to the through-cage interaction (PE, Figure 5) still remarkable, given the 3.5 Å transannular distance.(15)

ESR SPECTROSCOPY - STRUCTURES

The deeply coloured radical cation produced from D_{2h} symmetrical [1.1.1.1]pagodane $\underline{1}$ by chemical (tris (4-bromophenyl) ammoniumyl hexachloroantimonate, $AlCl_3$) or electrochemical oxidation (lifetime at room temperature ca. 2 d, $\lambda_{max} \approx 610$ nm) was identified by the ESR spectrum (Figure 8) as the rectangular ("extended", E) $\underline{2}^{•+}$, identical with the radical cation analogously prepared from D_{2h} diene $\underline{2}$ (2). Attempts to confirm the intermediacy of the cyclobutane-like ("tight", T) ion ($\underline{1}^{•+}$) (29) by "charge-stripping" mass spectroscopy (*H. Schwarz*) (10) were not successful. ESR spectra now recorded after γ-irradiation of $\underline{1}$ (^{60}Co, 77 K) in a $CFCl_3$ matrix reveal (above 130 K) an apparently isotropic hyperfine splitting of ca. 1.5 mT, the same as was detected in the fluid solution between 193 - 293 K. Moreover the irradiated sample at 77 K has the same colour as the fluid solutions in CH_2Cl_2.
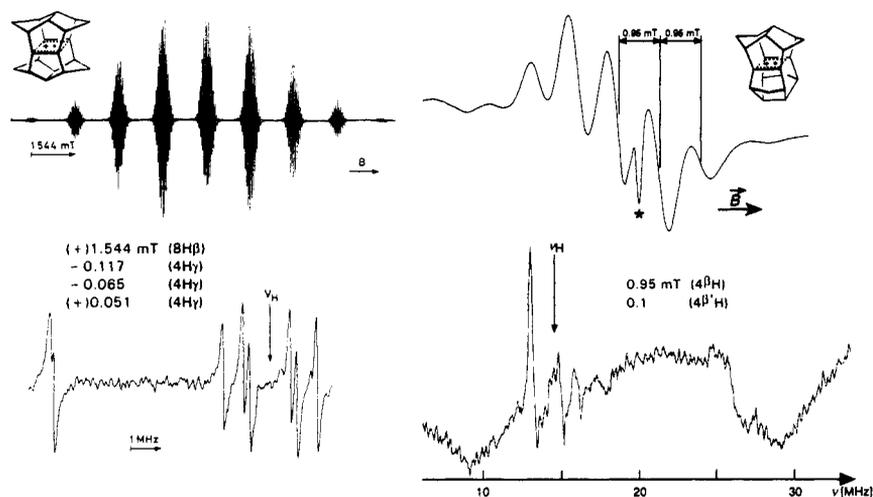

Fig. 8. ESR and ENDOR spectra of $\underline{1}$ (r.t., CH_2Cl_2) and iso-$\underline{1}$ (100K, $CFCl_3$).

For iso-$\underline{1}$, in contrast to the findings with $\underline{1}$, radical formation could not be detected (UV, ESR) under the established chemical or electrochemical oxidation conditions in fluid solution at temperatures between -90 and +10°C. It was only by γ-irradiation in a $CFCl_3$ matrix (^{60}Co, 77 K) that the well defined ESR and ENDOR spectra (Figure 8) could be obtained. At 100 K the signal becomes apparently isotropic. A quintet splitting of 0.95 mT (due to four equivalent β-protons, verified by the signal at 27.5 MHz ($v_H + a_H$) in the ENDOR spectrum) and a further coupling constant of 0.11 mT detected by the ENDOR technique (signals at 12.9/16.2 MHz; tentatively assigned to the second set of four equivalent β-protons) indicate that the symmetry is reduced from D_{2d} in iso-$\underline{1}$ to C_{2v} in its ion on the hyperfine time scale. Pulsed ESR spectra at 20 K proved to be unresolved. Signal pairs (3.4/26.9 and -2.1/30.1 MHz) in a HYSCORE spectrum (30) representing coupling constants ($a_H\beta$) of 0.8 and 1.2 mT due to two pairs of protons are ascribed to reduction in symmetry by matrix effects (a trapezoidal $\underline{4}^{•+}$ (31) is not in line with calculations). The estimated dihedral angles (θ) between the '$2p_z$'-axis and the C-H^β bonds for "tight" (e.g. iso-$\underline{1}^{•+}$) and "extended" geometries (e.g. iso-$\underline{2}^{•+}$) vary between 10-20° for the "upper" part, between 70-80° for the "lower" part. Since the respective dihedral angles are almost identical, the decrease in the experimental $a_H\beta$ values, particularly the decrease in $a_H\beta$ from the 1.54 mT in $\underline{2}^{•+}$ to 0.95 mT in iso-$\underline{1}^{•+}$, rather mirror an altered pyramidalization of the 4c-core carbon atoms.

According to *ab initio* calculations all the four structures $\underline{1}^{\bullet+}(\underline{T})$, $\underline{2}^{\bullet+}(\underline{E})$, iso-$\underline{1}^{\bullet+}(\underline{T})$, and iso-$\underline{2}^{\bullet+}(\underline{E})$, presented in Figure 9 (geometry optimized at the UHF/3-21G level, energies computed at PMP2/3-21G, $a_H\beta$ - values using the INDO method) represent energetic minima. However, for the ion formed from $\underline{2}$ ($\underline{1}$) it is the "extended" ($\underline{2}^{\bullet+}$), for the ion formed from isopagodane iso-$\underline{1}$ it is the "tight" cyclobutane-like form (iso-$\underline{1}^{\bullet+}$), which is the more stable one by 0.55 and 8.5 kcal mol^{-1}, respectively; the sterically fixed 1,4-radical cation isomers of $\underline{2}^{\bullet+}$ and iso-$\underline{1}^{\bullet+}$ are higher in energy by 4.90 and 4.43 kcal mol^{-1} at PMP2/3-21G/3-21G). In $\underline{2}^{\bullet+}$ the transannular π,π–distance is shortened by ca. 0.35 Å with respect to the ca. 2.8 Å (exp.) in $\underline{2}$, and the olefinic pyramidalization is changed to -3.4°. In iso-$\underline{1}^{\bullet+}$ with deviations of 0.085 and 0.213 Å from the cyclobutane C-C bonds in iso-$\underline{1}$ (1.555 Å, Table 1) a more cyclobutane-like structure is retained. The designation of $\underline{2}^{\bullet+}$ ($\underline{E}$) and iso-$\underline{1}^{\bullet+}(\underline{T})$ as the radical cations obtained from $\underline{1}$ and iso-$\underline{1}$, respectively, is corroborated by comparing calculated (INDO spin density, 3-21G geometry) and experimental ESR proton coupling constants ($a_H\beta$) . There is good agreement with the experimental constants for $\underline{2}^{\bullet+}$ (calc. 1.63 vs. exp. 1.54 mT) and iso-$\underline{1}^{\bullet+}$ (calc. 1.05/0.16 vs. exp. 0.95/0.11 mT), but not for $\underline{1}^{\bullet+}$ (calc. 1.05 vs. exp. 1.54 mT) and iso-$\underline{2}^{\bullet+}$ (calc. 1.63/0.18 vs. exp. 0.95/0.11 mT). $\underline{T}$ and $\underline{E}$ bond-length isomers have different electronic states ($\underline{1}^{\bullet+}$: B_{1u}; $\underline{2}^{\bullet+}$: B_{2u}; iso-$\underline{1}^{\bullet+}$: B_2; iso-$\underline{2}^{\bullet+}$: B_1). The nevertheless extremely rapid isomerization $\underline{1}^{\bullet+} \rightarrow \underline{2}^{\bullet+}$ probably by-passes the concerted route.
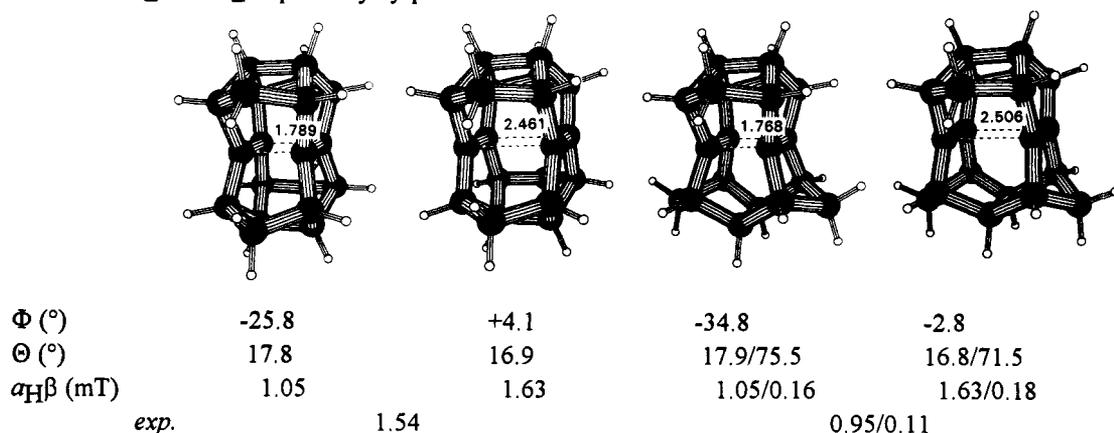

Φ (°)	-25.8	+4.1	-34.8	-2.8
Θ (°)	17.8	16.9	17.9/75.5	16.8/71.5
$a_H\beta$ (mT)	1.05	1.63	1.05/0.16	1.63/0.18
exp.		1.54	0.95/0.11	

Fig. 9. Calculated geometries and $a_H\beta$ coupling constants of $\underline{1}^{\bullet+}$, $\underline{2}^{\bullet+}$, iso-$\underline{1}^{\bullet+}$, and iso-$\underline{2}^{\bullet+}$.

What about the inverse influence of homologation upon ion geometry as postulated in the introduction? In the [2.2.1.1] series (iso) $\underline{3}/\underline{4}$, ESR experiments are so far limited to the saturated members $\underline{3}$ and iso-$\underline{3}$. The situation is unambiguous: Like $\underline{1}$, iso-$\underline{3}$ is readily oxidized in solution at room temperature to furnish the persistent "extended" ion iso-$\underline{4}^{\bullet+}$ (C_2, from iso-$\underline{3}^{\bullet+}$). From $\underline{3}$, radical cation $\underline{3}^{\bullet+}$ can be produced in fluid solution only at low temperature (Figure 10), but proves somewhat more persistent than iso-$\underline{1}^{\bullet+}$. The differentiation of "extended" and "tight" structures is again based on the comparison of calculated and measured $a_H\beta$ values.
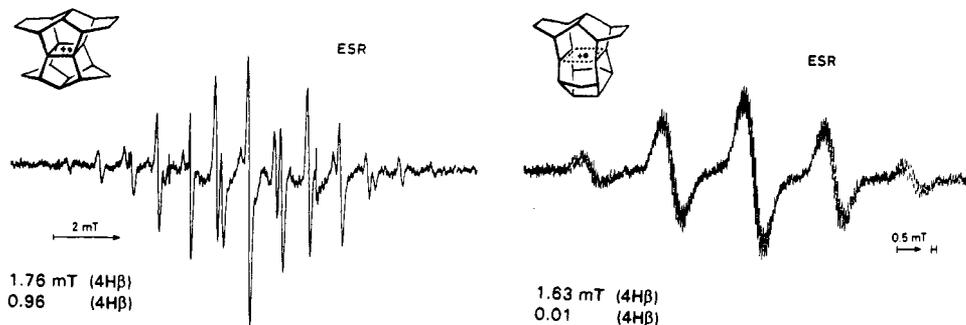

ESR

ESR

1.76 mT (4Hβ)
0.96 (4Hβ)

1.63 mT (4Hβ)
0.01 (4Hβ)

Fig. 10. ESR spectrum of $\underline{3}$ (203 K, CH_2Cl_2) and iso-$\underline{3}$ (r.t., CH_2Cl_2).

For the unparalleled persistence of the "extended" hydrocarbon radical cation $\underline{2}^{\bullet+}$, homoconjugational stabilization, "*anti* - Bredt rule protection" and steric shielding by the β-hydrogens are convincing arguments. The highly labile "tight" isomer iso-$\underline{1}^{\bullet+}$ suffers from higher energy and strain (pyramidalization); at the present time it can only be speculated about the modes of its rapid destruction. In the [2.2.1.1] series the "*anti* - Bredt rule protection" should not be similarly effective.

Can the π,π-homoconjugation as delineated for the rather "distant" dodecahedradiene $\underline{6}$ be "directly seen" for the radical $\underline{6}^{\bullet+}$? This is obviously the case: γ-Irradiation experiments (Figure 11) (32) and calculations - as applied to iso-$\underline{1}$ and $\underline{3}$ - confirmed for the moss-green ion ($t_{1/2}$ 1-2h above 110 K) the D_{2h} symmetry
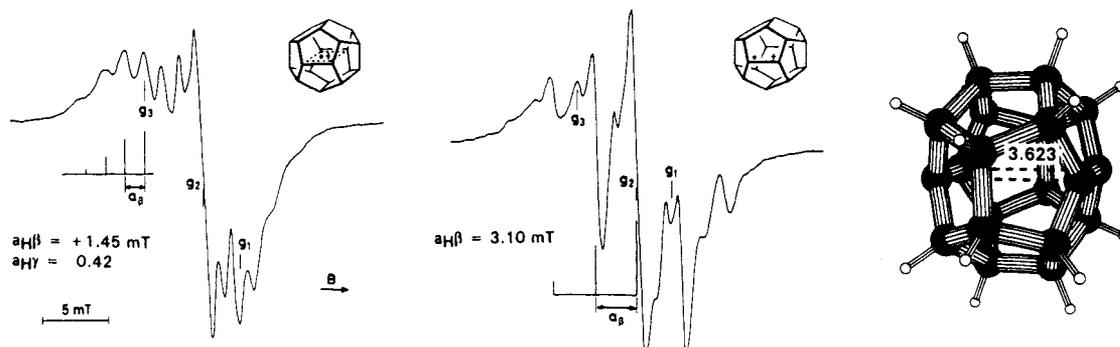

Fig. 11. ESR-spectra of diene $\underline{6}$ and reference $\underline{11}$; calculated geometry of $\underline{6}^{\bullet+}$ (*ab initio* 3-21G).

of its precursor on the hyperfine time scale; $a_H\beta$ = 1.45 mT for the eight symmetry-equivalent β-hydrogens agrees well with the 1.57 mT calculated for the *ab initio* 3-21G structure (Figure 11); in the latter, the transannular π,π-distance as well as the pyramidalization are decreased. Alternative (localized) structures are of higher energy. For reference $\underline{11}^{\bullet+}$, with the spin population distributed over two π-centres, $a_H\beta$ = 3.10 mT (calc. 3.29 mT) practically doubles that of $\underline{6}^{\bullet+}$.

TWO-ELECTRON OXIDATIONS - STRUCTURES

The ionic species formed from $\underline{1}$ and $\underline{2}$ in a SbF$_5$/SO$_2$ClF solution at -78°C - and persistent for hours at room temperature - has been identified *(Olah, Prakash, Herges, Schleyer, Schindler, Fessner)* as the rectangular σ-bishomoaromatic 4c/2e dication $\underline{1}^{2+}(\underline{2}^{2+})$. The rapid equilibration of classical 1,4-dication and di(radical cation) structures had been dismissed on the basis of theoretical (i.a. IGLO) investigations (3, 33). The length of the longer side (r = 2.164 Å) of the 3-21G structure (Figure 12) comes very close to the one providing optimum "aromaticity" (stability). Shorter or longer r-bonds cause increasing diradicaloid character (decreasing "aromaticity") - with limiting values for "aromaticity" of ca. 1.9 and 2.3 Å. The [2.2.1.1] dication $\underline{3}^{2+}$ had been found to be less persistent than $\underline{1}^{2+}$ (loss of "anti-Bredt-rule protection"? ,cf. the relative energies in Table 1) (34).
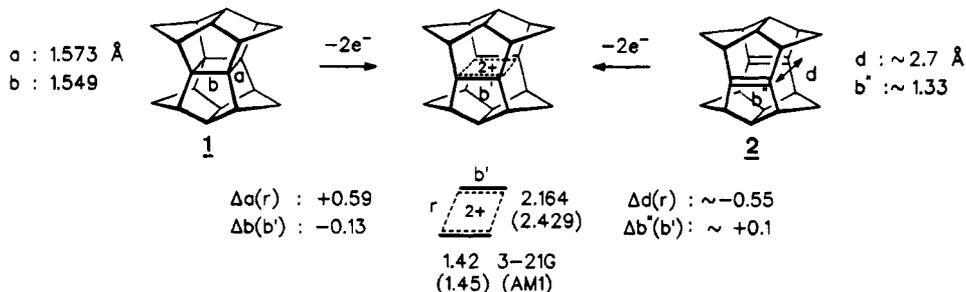

Fig. 12. The prototypical σ-bishomoaromatic dication $\underline{2}^{2+}$.

Very recently the iso-pagodanes iso-$\underline{1}$ (D_{2d}) and iso-$\underline{3}$ (C_2) were oxidized (SbF$_5$/SO$_2$ClF, *Olah, Prakash*). At -80 °C both (σ-bishomoaromatic, IGLO) dications - additional points on the reaction coordinate of the ethylene$^{\bullet+}$/ethylene$^{\bullet+}$ cyclo addition (D_{2h}) (9) - are static localized structures of reduced (iso-$\underline{1}^{2+}$, C_{2v})/ retained symmetry (iso-$\underline{3}^{2+}$, C_2) (provisional NMR assignments, Figure 13). iso-$\underline{3}^{2+}$ is formed much faster (more stable, cf. $\underline{1}^{2+}$) than iso-$\underline{1}^{2+}$ (cf. $\underline{3}^{2+}$).
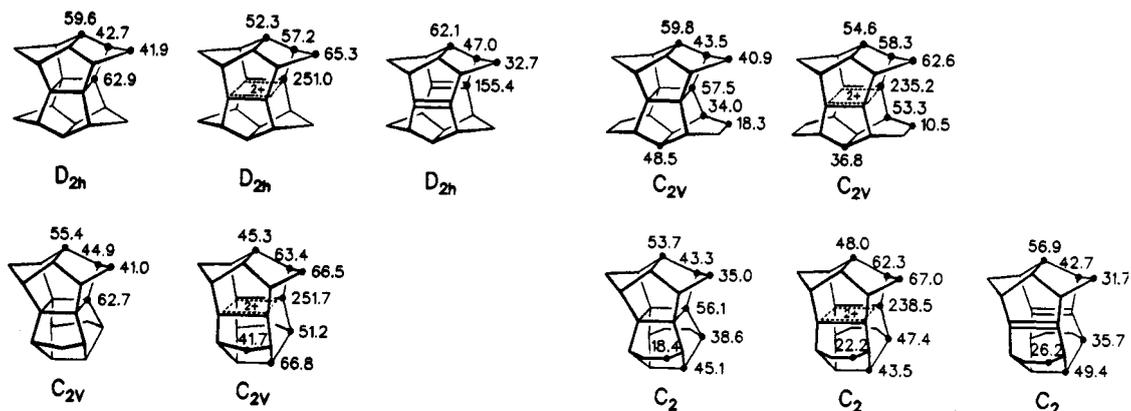

Fig. 13. ^{13}C-NMR comparison of the dications $\underline{2}^{2+}$, $\underline{4}^{2+}$, iso-$\underline{2}^{2+}$, iso-$\underline{4}^{2+}$ and the neutral precursors.

The geometrical limits of the unconventional σ-type of aromaticity should be surpassed with the dication of the rather spherical dodecahedradiene $\underline{6}$. For $\underline{6}^{2+}$, predicted to exhibit a diradicaloid character (34) - cf., though, the homoconjugative interaction in the neutral diene (Figures 3-5) and in the radical cation (Figure 11) - the experimental test is awaited for the near future. Further on the horizon still lies the conversion of the through-cage-delocalized, tetrahomoaromatic 4c/2e and 8c/6e dodecahedral dications $\underline{14}^{2+}$ (35) and $\underline{15}^{2+}$ (36) from paper to reality.
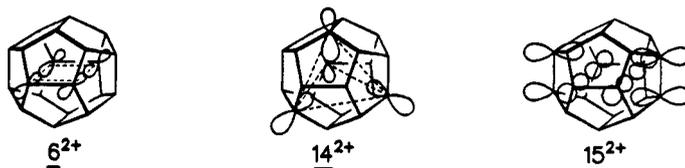
REFERENCES

1. W.-D. Fessner, B.A.R.C. Murty, J. Wörth, D. Hunkler, H. Fritz, H. Prinzbach, W.-D. Roth, P.v.R. Schleyer, A.B. McEwen, W.F. Maier. *Angew. Chem. Int. Ed. Engl.* 26, 452 (1987); G. Lutz, R. Pinkos, B.A.R.C. Murty, P.R. Spurr, W.-D. Fessner, J. Wörth, H. Fritz, L. Knothe, H. Prinzbach. *Chem. Ber.*125, 1741 (1992); Reviews: J.P. Melder, H. Prinzbach, W.-D. Fessner, "Novel Organic Polycycles - an Adventure in Molecular Architecture" in *Organic Synthesis: Modern Trends* (O. Chizhov, Ed.), p. 23-42 Blackwell, Oxford (1987); W-D. Fessner, H. Prinzbach, "The Pagodane Route to Dodecahedrane" in *Cage Hydrocarbons* (Ed. G.A.Olah), chapter 10, p. 353-405 John Wiley & Sons, N.Y. (1990); H. Prinzbach, K. Weber. *Angew. Chem.*, 106, 2329-2348 (1994).

2. H. Prinzbach, B.A.R.C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson. *Angew. Chem. Int. Ed. Engl.* 26, 457 (1987).

3. G.K. Surya. Prakash, V.V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G.A. Olah, W.-D. Fessner, H. Prinzbach. *J. Am. Chem. Soc.* 110, 7764 (1988); R. Herges, P.v.R. Schleyer, M. Schindler, W.-D. Fessner. *J. Am. Chem. Soc.* 113, 3649 (1991).

4. T. Pracht, K. Weber, H. Fritz, L. Knothe, H. Prinzbach. *J. Chin. Chem. Soc. (Taiwan)* 41, 1-26 (1994); cit. lit.

5. M. Wollenweber, R. Pinkos H. Prinzbach. *Angew. Chem. Int. Ed. Engl.* 33, 117 (1994).

6. J.-P. Melder, R. Pinkos, H. Fritz, H. Prinzbach. *Angew. Chem. Int. Ed. Engl.* 29, 95 (1990); J.P. Melder, R. Pinkos, H. Fritz, J. Wörth, H. Prinzbach. *J. Am. Chem. Soc.* 114, 10213 (1992); R. Pinkos, J.-P. Melder, K.

Weber, D. Hunkler, H. Prinzbach. *J. Am. Chem. Soc.* 115, 7173 (1993).

7. H. Irngartinger, U. Reifenstahl, H. Prinzbach, R. Pinkos, K. Weber. *Tetrahedron Lett.* 31, 5459 (1990); M. Keller, K. Scheumann, K. Weber, T. Voss, H. Prinzbach. *Tetrahedron Lett.*, 33, 1531 (1994).

8. H.D. Roth. *Top. Curr. Chem.* 163,131 (1992); N.L. Bauld, D.J. Bellville, R. Pabon, R. Chelsky, G. Green. *J. Am. Chem. Soc.*, 105, 2378 (1983).

9. M.J. Goldstein, R. Hoffmann. *J. Am. Chem. Soc.*, 93, 6193 (1971); R. Hofmann. *Angew. Chem. Int. Ed. Engl.* 21, 711 (1982).

10. T. Drewello, W.-D. Fessner, A.I. Kos, C.B. Lebrilla, H. Prinzbach, P.v.R. Schleyer, H. Schwarz. *Chem. Ber.* 121, 187 (1988).

11. Z. Dolejsek, V. Hanus, H. Prinzbach. *Angew. Chem.* 74, 902 (1962); E. Haselbach, T. Bally, Z. Langiova, P. Baertschi. *Helv. Chim. Acta* 62, 583 (1974); H.-D. Roth, M.L.M. Schilling. *J. Am. Chem. Soc.* 103, 7210 (1981); c.f. K. Ishiguro, I.V. Khudyakov, P.F. McGarry, N.J. Turro, H.-D. Roth, *J. Am. Chem. Soc.* 116, 6933 (1994).

12. B.A.R.C. Murty, R. Pinkos, P.R. Spurr, W.-D. Fessner, G. Lutz, H. Fritz, D. Hunkler, H. Prinzbach. *Chem. Ber.* 125, 1719 (1992).

13. T. Voss, K. Weber, M. Keller, H. Prinzbach. *Angew. Chem.*, in preparation.

14. M. Bertau, J. Leonhardt, R. Pinkos, K. Weber, H. Prinzbach. *Angew. Chem.*, in preparation.

15. K. Weber. Dissertation, Universität Freiburg 1993.

16. D.A. Hrovat, W.T. Borden. *J. Am. Chem. Soc.* 110, 4710 (1988).

17. J.M. Smith, D.A. Hrovat, W.T. Borden. *J. Am. Chem. Soc.* 115, 3816 (1993); J.G. Radzizewski, T.-K. Yin, F. Miyake, G.E. Renzoni, D.A. Hrovat, W.T. Borden, J. Michl. *J. Am. Chem. Soc.* 108, 3544 (1986).

18. H.-D. Martin, B. Mayer. *Angew. Chem. Int. Ed. Engl.* 22, 283 (1983); R. Gleiter, R. Schäfer. *Acc. Chem. Res.* 23, 369 (1990).

19. E. Heilbronner, A. Schmelzer. *Helv. Chim. Acta* 58, 936 (1975).

20. D. Elsässer, H.-D. Martin, B. Mayer, G. Lutz, H. Prinzbach. *Chem. Ber.* 124, 2863 (1991). H.-D. Martin, B. Mayer, K. Weber, H. Prinzbach. In preparation. cf. the 1.70 eV for *trans,trans*-cyclodeca-1,6-diene, a substructure of 2: P. Bischof, E. Heilbronner. *Helv. Chim. Acta* 53, 1677 (1970).

21. P. Bischof, J.A. Hashmall, E. Heilbronner, V. Hornung. *Helv. Chim. Acta* 52, 1745 (1969).

22. R. Hoffmann. *Acc. Chem. Res.* 4, 1 (1971); R. Hoffmann, E. Heilbronner, R. Gleiter. *J. Am. Chem. Soc.* 92, 706 (1970).

23. K.B. Wiberg, R.D. Adams, P.J. Okarma, M.G. Matturo, B. Segmuller. *J. Am. Chem. Soc.* 106, 2200 (1984); E. Honegger, E. Heilbronner, K.B. Wiberg. *J. Electron Spectrosc. Rel. Phenom.* 31, 369 (1983).

24. J. Heinze. *Angew. Chem. Int. Ed. Engl.* 23, 831 (1984); D.H. Evans. *Acc. Chem. Res.* 10, 313 (1977).

25. K. Weber, G. Lutz, L. Knothe, J. Mortensen, J. Heinze, H. Prinzbach. In preparation.

26. F. Gerson, G. Gescheidt, S.F. Nelsen, L.A. Paquette, M.F. Teasly, L. Waykole. *J. Am. Chem. Soc.*, 111, 5518 (1989); S.F. Nelson, D.L. Kapp, R. Akaba, D.H. Evans. *ibid* 108, 6863 (1986); F. Gerson, J. Lopez, R. Akaba, S.F. Nelsen. *ibid* 103, 6716 (1981).

27. P.G. Gassmann, R. Yamaguchi. *Tetrahedron* 38, 1113 (1982).

28. T. Shono, A. Ikeda, I. Hayashi, S. Hakasaki. *J. Am. Chem. Soc.* 97, 4261 (1975).

29. H.D. Roth. *Top. Curr. Chem.* 163, 131 (1992).

30. P. Höfer. *J. Magn. Reson.* In press (1994); J.J. Shane, P. Höfer, E.J. Reijerse, E.J. deBoer. *J. Magn. Reson.* 99, 596 (1992).

31. T. Shida, E. Haselbach, T. Bally. *Acc. Chem. Res.* 17,180 (1984).

32. K. Weber, H. Prinzbach, R. Schmidlin, F. Gerson, G. Gescheidt. *Angew. Chem. Int. Ed. Engl.* 32, 875 (1993).

33. G.K. Surya Prakash, V.V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G.A. Olah, W.-D. Fessner, H. Prinzbach. *J. Am. Chem. Soc.* 108, 836 (1986); G.K. Surya Prakash, W.-D. Fessner, G.A. Olah, G. Lutz, H. Prinzbach. *J. Am. Chem. Soc.* 111, 746 (1989).

34. R. Herges, H. Neumann, W.-D. Fessner, H. Prinzbach, unpublished.

35. M. Bremer, P.v.R. Schleyer, K. Schötz, M. Kausch, M. Schindler. *Angew. Chem. Int. Ed. Engl.* 26, 761 (1987).

36. R. Herges, unpublished. cf.:The early calculations by A.B. McEwen, P.v.R. Schleyer. *J.Org. Chem.* 51, 4357 (1986).