Laticyclic conjugated double bonds within the framework of oligocondensed bicyclo[2.2.2]octenes

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The all-*syn* oligocondensed bicyclo[2.2.2]octenes 3, 5, 20 and 29 with two to five etheno bridges show interaction of their π-orbitals by σ-overlap. This laticyclic conjugation reveals itself in the PE and UV spectra of the series as well as in the site selectivity of the Diels–Alder reaction with inverse electron demand found for the dehydro derivatives 11 and 26. As shown in the crystal structures of 3, 5 and 20, the etheno bridges are positioned face to face at a distance which is smaller than the sum of their van der Waals radii.

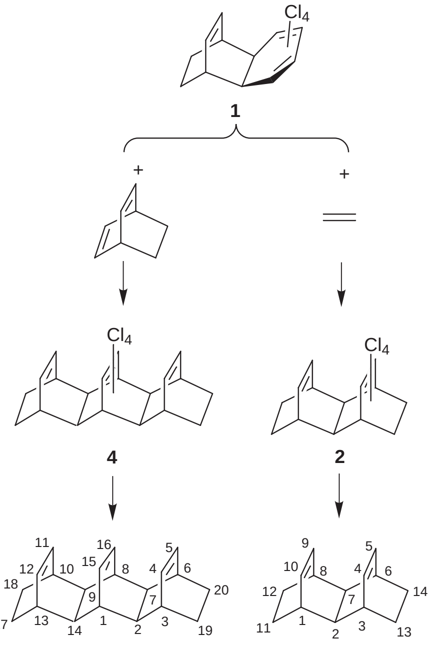
Introduction

The various ways to achieve cyclic delocalization by joining chains of conjugated π-systems were studied in 1971 by Hoffmann and Goldstein.[1] One way they suggested is to arrange the chains face to face at so close a distance that σ-interaction between their termini occurs. This so-called laticyclic conjugation of unsaturated chains can result in an electronic stabilization, but it does not if all the chains are of the same mode. Accordingly, the laticyclic conjugation of ethene units leads to a set of molecular orbitals, bonding and antibonding through space, that are all filled and do not provide a net stabilisation. However, due to their filled 'antibonding' orbitals these systems should show interesting spectroscopic and chemical properties.

Rigid molecules with two double bonds facing each other in close proximity represent the simplest laticyclic conjugated systems. Many of them are known and in, for example, isodrine,[2] *seco*-pagodadiene,[3] hypostrophene,[4] tricyclo-[6.2.2.2^{2,5}]dodeca-1,5-diene[5] and pentacyclo[8.2.1.1^{2,5}.1^{4,7}.1^{8,11}]-hexadeca-1,7-diene[6] the through space interaction has been studied. We have developed a general method for the synthesis of oligocondensed bicyclo[2.2.2]octenes with all-*syn* configuration and here describe a series of them with up to five laticyclic conjugated etheno bridges.

Results and discussion

The common starting compound for the synthesis of all-*syn* condensed bicyclo[2.2.2]octenes is *endo*-tetrachlorotricyclo-[6.2.2.0^{2,7}]dodecatriene **1**, the product of the Diels–Alder reaction of tetrachlorothiophene dioxide (TCTD)[7] with dihydrobarrelene followed by SO_2 extrusion.† The diene unit of **1** is activated for the cycloaddition with inverse electron demand[8] by the chloro substituents and it reacts with unsaturated hydrocarbons if their double bond is easily accessible. This is not the case for the etheno bridge in **1** and therefore it does not add to itself. However, ethene and dihydrobarrelene undergo cycloaddition with **1** below 100 °C under a pressure of 7 kbar (Scheme 1). The resulting condensed bicyclo[2.2.2]octenes **2** and **4** with all-*syn* configuration are dechlorinated with sodium in ethanol or diethylene glycol monoethyl ether to **3** and **5** without the reduction of double bonds. This result differs from that obtained when π-conjugated polyenes bearing chloro substituents are submitted to the same conditions. The triene **1** for example is dechlorinated with loss of a conjugated double bond by sodium in ethanol. The empty antibonding MOs of the π-conjugated diene are responsible for this overreduction.



Scheme 1

This route to *syn*-oligocondensed bicyclo[2.2.2]octenes with laticyclic conjugated etheno bridges was pursued further by using dienophiles with an extended bicyclo[2.2.2]octadiene unit. For the preparation of the next higher homologue with four etheno bridges *syn*-dehydrosesquibicyclo[2.2.2]octene **11** was needed as a dienophile. It was synthesized from the cycloadduct **6**[9] of *p*-benzoquinone to cyclohexadiene in which the carbonyl flanked double bond was saturated with zinc in acetic acid (Scheme 2). The resulting diketone **7** was transformed into tricyclo[6.2.2.0^{2,7}]dodeca-3,6,9-triene **9** *via* the Shapiro reaction[10] of its bis(tosylhydrazone) **8**. Cycloaddition of the acetylene synthon (*E*)-1,2-ditosylethene[11,12] to **9** occurs to the convex side to give **10** which was detosylated with sodium amalgam to the triene **11**.

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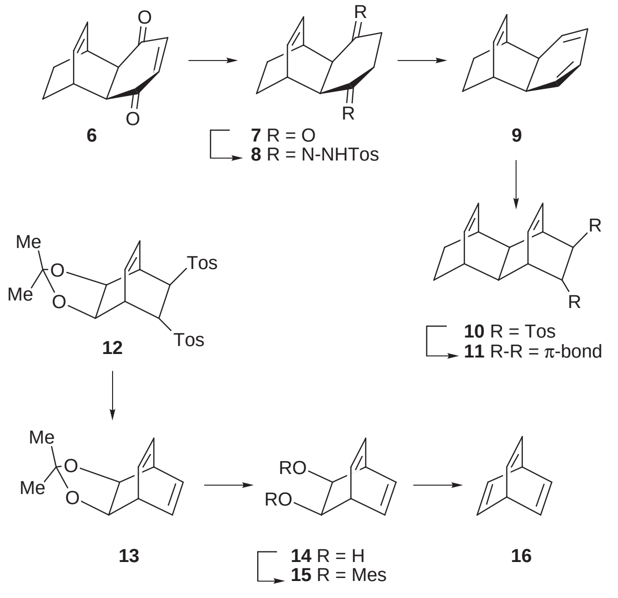
† The term *syn* indicates that the functional groups, here double bonds, are orientated towards each other. Our linear oligocondensed bicyclo-[2.2.2]octenes are all-*syn*; in their angular isomers the double bonds facing each other are marked by numbers, *e.g.* tetraene **17** is 15,16; 19,20;21,22-*syn*. The term *endo* refers to the configuration of Diels–Alder products with the 'maximum accumulation of unsaturation'.



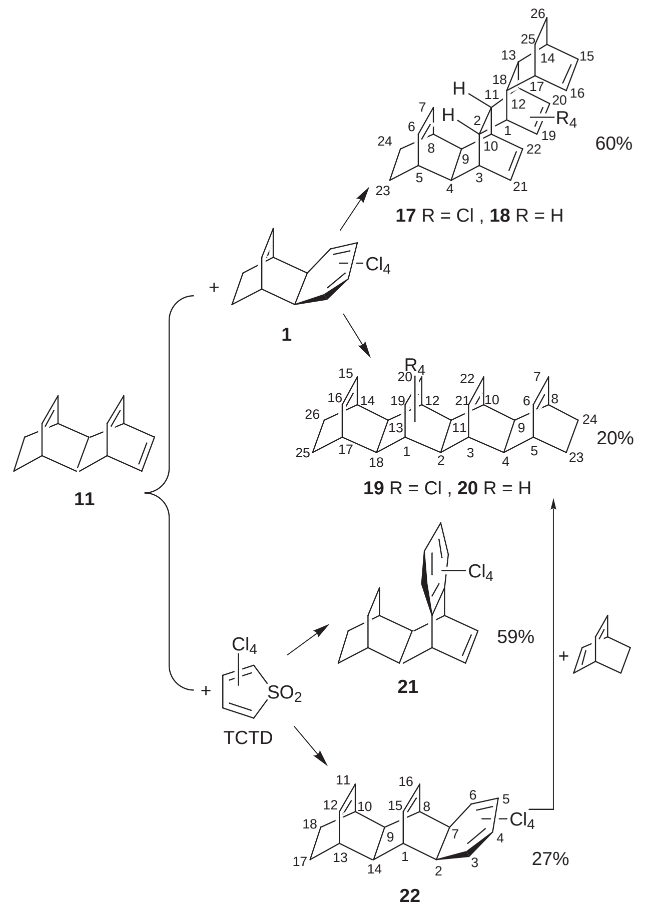
Scheme 2

To synthesize the four-fold *syn*-condensed bicyclo[2.2.2]-octene we planned to add two molecules of the diene **1** to barrelene **16**[13] as the central unit. On our route to barrelene[14] we added in the first step (*E*)-1,2-ditosylethene to dimethyldioxabicyclo[4.3.0]nonadiene[15] to give **12**. After forming the second double bond in the bicyclo[2.2.2]octadiene unit by detosylation with sodium amalgam, the acetonide **13** was hydrolyzed and the resulting diol **14** mesylated. Demesylation[16] of **15** with sodium anthracenide[17] afforded barrelene **16** in a reasonable overall yield.

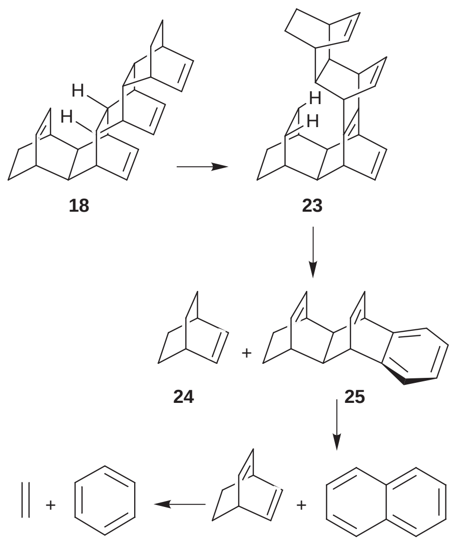
The cycloaddition of diene **1** to *syn*-dehydrosesquibicyclo-[2.2.2]octene **11** cannot be as straightforward as in the case of dihydrobarrelene since the two accessible double bonds in **11** have different surroundings. The reaction under high pressure yielded a mixture of two isomers **17** and **19** (Scheme 3) with the angular adduct prevailing in a ratio of 3:1. This result can be rationalized by the laticyclic conjugation in **11** that enriches one of the double bonds of the bicyclo[2.2.2]octadiene subunit with electrons and favors its addition to the electron poor diene **1**. Both cycloadditions occur exclusively to the convex side of **1** with *endo* stereochemistry. After separation by liquid chromatography, both cycloadducts were dechlorinated with sodium in diethylene glycol monoethyl ether to the tetraenes **18** and **20**, respectively.

The electron poor diene TCTD also discriminates between the two accessible double bonds of **11**, forming at room temperature two isomeric cycloadducts. The main product is the tetrachlorobenzo-condensed tetracyclic diene **21** (59%), that results from cycloaddition to the laticyclic conjugated double bond of **11** followed by extrusion of SO$_2$ and a dyotropic hydrogen shift.[18] The minor product **22** (27%) is a homologue of the tetrachlorodiene **1**. It adds dihydrobarrelene under high pressure to give the laticyclic conjugated tetraene **19** in good yield. This alternative route to **19** offers no advantage as it again includes the addition of an electron poor diene to the wrong double bond of **11**.

In contrast to the all-*syn*-condensed bicyclo[2.2.2]octenes **3**, **5** and **20** that are thermally stable up to 280 °C the angular tetraene **18** decomposes at 214 °C to bicyclo[2.2.2]octene **24**, naphthalene, benzene and ethene (Scheme 4). Monitoring the reaction by sealed-tube NMR showed that the products are formed simultaneously in equal amounts. A proposed mechanism for this fragmentation starts with an intramolecular hydrogen transfer[19] in **18** converting it into its dyotropomer **23**. A rapid cascade of three (4 + 2)-cycloreversions then splits **23** into the observed products with benzodehydrosesquibicyclo-[2.2.2]octene **25** and dihydrobarrelene as intermediates.

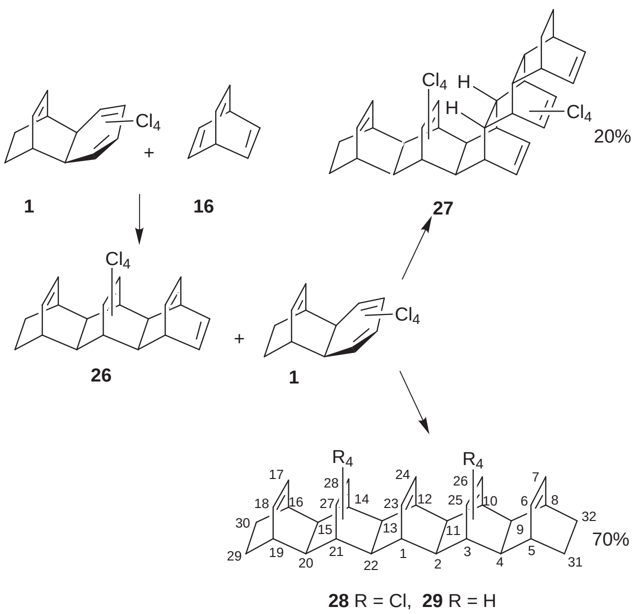


Scheme 3



Scheme 4

The two-fold cycloaddition of **1** to barrelene at 110 °C and 8.1 kbar over 120 h led to the angular and the linear tetra-condensed bicyclo[2.2.2]octenes **27** and **28** in a ratio of 1:3.5 (Scheme 5). The monoadduct **26** formed in the first step is a higher homologue of **11** and again provides a laticyclic conjugated and a terminal double bond for the second addition of the electron poor diene **1**. In this case, however, the terminal double bond is preferred since the four chloro substituents withdraw electrons from the laticyclic system. Dechlorination of the linear tetracondensed bicyclo[2.2.2]octene **28** to **29** was achieved with sodium in diethylene glycol monoethyl ether.



28 R = Cl, **29** R = H

Scheme 5

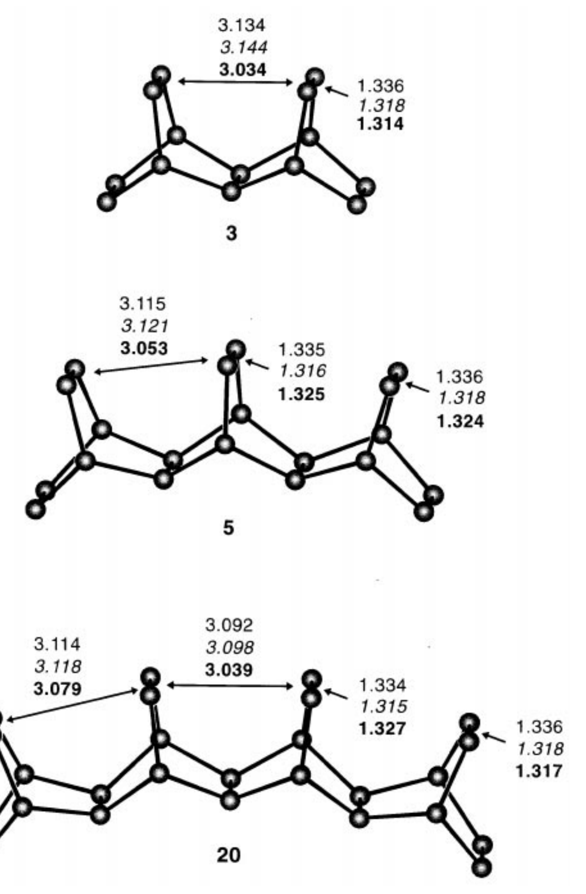


Fig. 1 Computer generated crystal structure (hydrogen atoms omitted) of all-*syn*-condensed bicyclo[2.2.2]octenes **3**, **5** and **20**. Parameters given are from X-ray structural analysis (in bold type) and from calculations at the B3LYP/6-31G* (in normal type) and RHF 6-31G* (in italics) level.

Table 1 Vertical ionization energies $E_{i,v,j}$ of oligocondensed bicyclo-[2.2.2]octenes and calculated orbital energies, $-\varepsilon_j$, using the AM1 and RHF(6-31G*) basis. All values in eV.

Compound	Band	$E_{i,v,j}$	Assignment	$-\varepsilon_j$ (AM1)	$-\varepsilon_j$ (RHF)
3	1	8.1	$b_1(\pi)$	9.1	8.34
	2	9.4	$a_1(\pi)$	10.04	9.84
	3	9.7	$a_2(\sigma)$		10.76
5	1	7.5	$b_1(\pi)$	8.78	7.85
	2	8.6	$a_1(\pi)$	9.57	9.16
	3	9.2	$b_1(\pi)$		10.04
20	1	7.4	$b_1(\pi)$	8.62	7.58
	2	8.3	$a_1(\pi)$	9.24	8.64
	3	9.2	$b_1(\pi)$		9.56

X-Ray structure analyses were performed for the polyenes **3**, **5** and **20** with two to four etheno bridges. They show that their σ-framework is not linear but forms an arc. The etheno bridges face each other more closely than is expected from the sum of their van der Waals radii. The contact between the inner pair of **20** is a little closer (3.04 Å) than that to the terminal bridges (3.08 Å), but compared to the bond alternation in π-conjugated chains the distance between the σ-conjugated double bonds shows little variation. As the four localised π-orbitals are filled and the same is true for the four laticyclic orbitals resulting from their linear combination, the bond order between the etheno bridges is zero. The laticyclic system thus would drift apart were it not kept together by the rigid σ-framework.

In order to assign the ionization potentials of the laticyclic conjugated polyenes we carried out *ab initio*[20] studies on the compounds **3**, **5** and **20**. Calculations were performed with the program GAUSSIAN94[21] on IBM RISC-6000 Model 580. Molecules **3**, **5** and **20** were fully optimized within C_{2v} symmetry constraint using restricted Hartree–Fock theory (RHF) and density functional theory (DFT)[22] applying the hybrid method Becke3LYP[23] together with the 6-31G* basis set. All structures were confirmed to be minima by analytical vibrational frequency calculations.

The optimized structures of **3**, **5** and **20**, together with important structural parameters, are shown in Fig. 1. In general, they agree very well with the corresponding X-ray structures. At the RHF/6-31G* level, all ethene- and σ-bond lengths differ from the corresponding data in the X-ray structures by less than 0.15 Å. All structures show that the σ-framework forms an arc and, furthermore, the degree of bending grows with the number of condensed bicyclo[2.2.2]-octene units. The distances between the etheno bridges decrease with the chain getting longer. The calculated contact between the etheno bridges is 3.14 Å in **3**, 3.12 Å in **5** and 3.10 and 3.12 Å in **20**. As found in the X-ray structure, for compound **20** the contact of the inner pair is predicted to be closer than that of the terminal bridges.

The presence of laticyclic conjugation in the all-*syn*-condensed bicyclo[2.2.2]octenes is demonstrated by their PE spectra. In Table 1 the ionization energies of **3**, **5** and **20** are listed together with the assignment of the individual bands. The latter is based on the results of semi-empirical (AM1)[24] and *ab initio* (RHF/6-31G*) calculations on the ground state assuming the validity of Koopmans' theorem.[25] The first ionization energies decrease from 9.05 eV in the parent bicyclo[2.2.2]octene **24**[26] to 7.4 eV in its three-fold condensed homologue **20**. The second ionization energies also decrease from 9.4 eV in **3** to 8.3 eV in **20** as does the splitting between the two upmost laticyclic MOs. Semi-empirical (AM1) and *ab initio* (RHF/6-31G*) calculations indicate that all the π-MOs of the all-*syn* oligocondensed bicyclo[2.2.2]octenes result from laticyclic conjugation. A detailed analysis by means of the Weinhold natural bond orbital localization procedure[27] applying the method of Imamura and Ohsaku[28] shows large through space interactions and very little through bond contributions. The symmetry of the laticyclic HOMOs and HOMOs-1 in **3**, **5** and **20** is the same as that familiar from the two upmost π-MOs in ethene, the allylic triad and butadiene (Fig. 2).

The UV spectra of the series of all-*syn* oligocondensed bicyclo[2.2.2]octenes show a continuous bathochromic shift of their long wavelength absorption from $\lambda_{max} = 220$ nm for **3** to $\lambda_{max} = 250$ nm for **29** with a broad end absorption (Fig. 3).

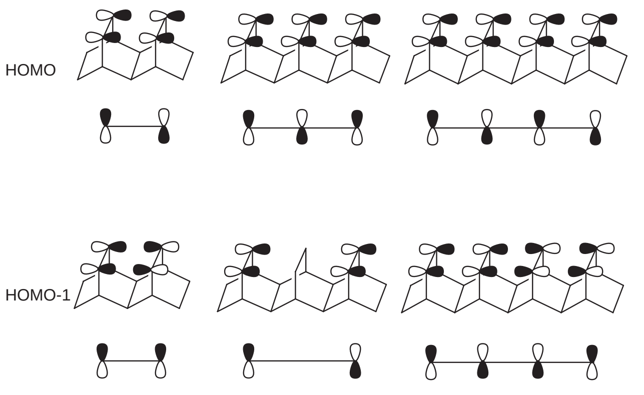


Fig. 2 Orbital symmetry of laticyclic conjugated oligocondensed bicyclo[2.2.2]octenes and of π-conjugated open chains. The HOMO and HOMO-1 of **3**, **5** and **20** are compared with the two upmost π-MOs of ethene, the allylic triad and butadiene.

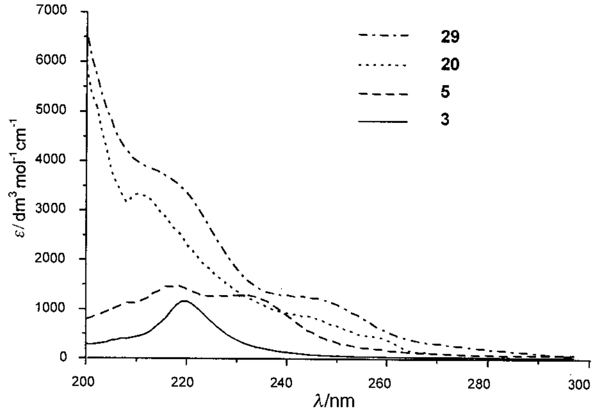


Fig. 3 UV absorption spectra of all-*syn* oligocondensed bicyclo[2.2.2]octenes in *n*-hexane

Additionally, the higher homologues exhibit a second band at shorter wavelengths. In comparison with π-conjugated open chain polyenes[29] the laticyclic systems absorb at lower wavelengths and with extinction coefficients that are smaller by two orders of magnitude. The complete occupation of all laticyclic orbitals resulting from the interaction of the bonding ethene MOs accounts for this effect.

In conclusion, the structural, spectroscopic and chemical properties of the all-*syn* oligocondensed bicyclo[2.2.2]octenes with two to five etheno bridges indicate the presence of laticyclic conjugation. The π-electron configuration of these systems results from perturbation theory in the same way as it does for chains of π-conjugated p-atomic orbitals (AOs). However, in the latter the interaction of singly occupied AOs affords resonance stabilisation whereas the laticyclic interaction of filled π-MOs destabilizes the system.

Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz (^{1}H) and 75.5 MHz (^{13}C) in $CDCl_3$. Chemical shifts are in ppm relative to internal TMS. Signals were assigned by C–H COSY and NOE methods. Multiplicity and position of protons are abbreviated as follows: AA′, BB′ (part of AA′BB′ system at low, high field); AB (AB system centered at the position given); Δ*v* (shift difference of the nuclei of the AB system in Hz); *J* (coupling constant between the nuclei of the AB system in Hz); H_n, H_x (hydrogen atoms in the *endo*- or *exo*-position). UV spectra were obtained using a Perkin-Elmer Lambda 7 spectrometer, IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer, mass spectra on a Finnigan MAT INCOS 50 spectrometer. For preparative GC a Varian Aerograph 90 P was used. Reactions under high pressure were performed in a 10 ml steel autoclave (Nova Swiss, Neu-Isenburg) shielded by a heavy plastic case and heated with an electrical coil. The two stage pressure generator is a product of B. Dieckers, Krefeld. The reaction mixture was sealed into a polytetrafluoroethene (PTFE) cramping tube (10 cm, 0.6 cm diameter). Melting points were determined in open capillaries with a Tottoli apparatus (Büchi, Flawil). For flash chromatography Silitech 32-64 60A (ICN, Eschwege) was used in a column (50 × 3 cm) filled to a third of its height.

endo-3,4,5,6-Tetrachlorobicyclo[6.2.2.0^{2,7}]dodeca-3,4,9-triene 1

Dihydrobarrelene (354 mg, 3.34 mmol) in benzene (2 ml) was added at room temperature to freshly sublimed tetrachlorothiophene dioxide (TCTD, 848 mg, 3.34 mmol). The exothermic reaction that evolves SO_2 was finished by stirring for 1 h. The mixture was evaporated and the residue in hexane was filtered through silica gel (1 cm). Concentration in a rotary evaporator yielded **1** (982 mg, 99%), mp 96–97 °C; δ_H 1.31 (2 H, BB′, 11-H_n, 12-H_n), 1.33 (2 H, AA′, 11-H_n, 12-H_n), 3.13 (2 H, s, 2-H, 7-H), 3.21 (2 H, t, 1-H, 8-H), 6.32 (2 H, q, 9-H, 10-H); δ_C 24.08, 33.68, 48.39, 123.03, 132.60, 133.94; λ_{max}(hexane)/nm 280 (ε/dm^3 mol^{-1} cm^{-1} 2500), 292 (5300), 304 (6300), 318 (4400).

syn-3,4,5,6-Tetrachlorotetracyclo[6.2.2.2.^{3,6}0^{2,7}]tetradeca-4,9-diene 2

1 (296 mg, 1 mmol) in diethyl ether (25 ml) was filled into the glass liner of an autoclave (50 ml). After fitting the vessel with a stopper with a gas inlet and a gas outlet tube it was cooled to −100 °C and ethene (800 ml) was condensed into the solution. The glass liner was placed into the cooled (dry ice) steel autoclave which was closed and heated to 130 °C for 90 h. After cooling to room temperature excess ethene was released and the reaction mixture was concentrated and recrystallized from hexane to afford **2** (310 mg, 95%), mp 84 °C; (Found C, 51.89; H, 4.67. Calc. for $C_{14}H_{14}Cl_4$: C, 51.89; H, 4.35); λ_{max}(hexane)/nm 222sh (ε/dm^3 mol^{-1} cm^{-1} 2200); ν_{max}/cm^{-1} 3052, 2950, 2918, 2902, 2870, 2860, 1595; δ_H 1.19–1.24 (2 H, m, 11-H_n, 12-H_n), 1.44–1.51 (2 H, m, 11-H_x, 12-H_x), 1.90–1.96 (2 H, m, 13-H_n, 14-H_n), 2.10–2.16 (2 H, m, 13-H_x, 14-H_x), 2.36 (2 H, s, 2-H, 7-H), 2.90 (2 H, m, 1-H, 8-H), 6.01–6.03 (2 H, m, 9-H, 10-H); δ_C 25.39 (C-11, 12), 31.65 (C-1, 8), 38.87 (C-13, 14), 52.81 (C-2, 7), 70.74 (C-3, 6), 127.35 (C-4, 5), 129.60 (C-9, 10); *m*/*z* 287 (100%, M − Cl), 251 (82, M − Cl − HCl).

syn-Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene 3

A solution of **2** (130 mg, 0.4 mmol) in anhydrous ethanol (8 ml) was heated to reflux under an argon atmosphere. Sodium (460 mg, 20 mmol) in small pieces was added over 2.5 h to the stirred solution and heating was continued for a further 30 min. After cooling to room temperature the reaction slurry was poured on a mixture of ice and water (20 g) and extracted with hexane (3 × 30 ml). The combined organic layers were washed with water (2 × 30 ml) and brine (1 × 30 ml) and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (hexane) and recrystallized from hexane to yield **3** (52.1 mg, 70%), mp 56 °C; λ_{max}(hexane)/nm 220 (ε/dm^3 mol^{-1} cm^{-1} 1150); ν_{max}/cm^{-1} 3042, 3034, 2973, 2933, 2899, 2875, 2860, 1648, 688; δ_H 1.05–1.09 (4 H, m, 11-H_n, 12-H_n, 13-H_n, 14-H_n), 1.43-1.51 (4 H, m, 11-H_x, 12-H_x, 13-H_x, 14-H_x), 1.93 (2 H, s, 2-H, 7-H), 2.28 (4 H, m, 1-H, 3-H, 6-H, 8-H), 5.74–5.77 (4 H, m, 4-H, 5-H, 9-H, 10-H); δ_C 27.12 (C-11, 12, 13, 14), 35.15 (C-1, 3, 6, 8), 43.69 (C-2, 7), 131.96 (C-4, 5, 9, 10); *m*/*z* 186 (M^+, 44%), 106 (18, M − C_6H_8), 80 (100, $C_6H_8^+$), 78 (24, $C_6H_6^+$); Calc. for $C_{14}H_{18}$: 186.141, Found 186.140 (MS).

all-*syn*-1,8,15,16-Tetrachlorohexacyclo[6.6.2.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]icosa-4,11,15-triene 4

A solution of **1** (424 mg, 1.43 mmol) and bicyclo[2.2.2]octa-2,5-diene (152 mg, 1.43 mmol) in anhydrous tetrahydrofuran (THF, 1.5 ml) together with a crystal of 4-*tert*-butylcatechol was heated for 96 h to 80 °C under a pressure of 7.8 kbar. After cooling to room temperature the solvent was removed under vacuum and the product purified by flash chromatography on silica gel (hexane) and recrystallized from hexane. **4** (486 mg, 85%), mp 198 °C (dec.) (Found: C, 59.86; H, 5.03. Calc. for $C_{20}H_{20}Cl_4$: C, 59.73; H, 5.01%); λ_{max}(hexane)/nm 242sh (ε/dm^3 mol^{-1} cm^{-1} 620); ν_{max}/cm^{-1} 3042, 2953, 2906, 2868, 1654, 1601; δ_H 1.15–1.19 (4 H, m, 17-H$_n$, 18-H$_n$, 19-H$_n$, 20-H$_n$), 1.41–1.48 (4 H, m, 17-H$_x$, 18-H$_x$, 19-H$_x$, 20-H$_x$), 2.30 (4 H, s, 2-H, 7-H, 9-H, 14-H), 2.91–2.92 (4 H, m, 3-H, 6-H, 10-H, 13-H), 5.94–6.00 (4 H, m, 4-H, 5-H, 11-H, 12-H); δ_C 25.54 (C-17, 18, 19, 20), 31.48 (C-3, 6, 10, 13), 54.10 (C-2, 7, 9, 14), 74.89 (C-1, 8), 124.59 (C-15, 16), 130.35 (C-4, 5, 11, 12); *m*/*z* 402 (M$^+$, 20%), 365 (80, M$^+$ − Cl), 329 (60, M − Cl − HCl), 293 (32, M − Cl − 2HCl), 80 (100, $C_6H_8^+$).

all-*syn*-Hexacyclo[6.6.2.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]icosa-4,11,15-triene 5

A solution of **3** (486 mg, 1.21 mmol) in diethylene glycol monoethyl ether (35 ml) was heated to 100 °C under an argon atmosphere. Sodium (1.4 g, 60.5 mmol) was added in small pieces over 3 h to the stirred solution and heating was continued for a further 30 min. After cooling to room temperature the slurry was poured on a mixture of ice and water (50 ml) and was extracted with hexane (5 × 50 ml). The combined organic layers were washed with water (5 × 50 ml) and brine (1 × 50 ml) and dried over $MgSO_4$. After filtration the solvent was removed under vacuum and the residue purified by flash chromatography with hexane. **5** (185.3 mg, 58%), mp 197 °C; λ_{max}(hexane)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 1400), 231 (1200); ν_{max}/cm^{-1} 3050, 2932, 2902, 2881, 2867, 1654, 1618, 686; δ_H 0.99–1.05 (4 H, m, 17-H$_n$, 18-H$_n$, 19-H$_n$, 20-H$_n$), 1.39–1.49 (4 H, m, 17-H$_x$, 18-H$_x$, 19-H$_x$, 20-H$_x$), 1.94 (4 H, s, 2-H, 7-H, 9-H, 14-H), 2.23 (6 H, m, 1-H, 3-H, 6-H, 8-H, 10-H, 13-H), 5.21–5.27 (2 H, m, 15-H, 16-H), 5.64–5.69 (4 H, m, 4-H, 5-H, 11-H, 12-H); δ_C 27.29 (C-17, 18, 19, 20), 34.77 (C-3, 6, 10, 13), 41.28 (C-1, 8), 45.59 (C-2, 7, 9, 14), 130.31 (C-15, 16), 132.28 (C-4, 5, 11, 12); *m*/*z* 264 (M$^+$, 100%), 236 (16, M − C_2H_4), 184 (16, M − C_6H_8), 80 (70, C_6H_8); Calc. for $C_{20}H_{24}$: 264.188, Found 264.188 (MS).

endo-Tricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-3,6-dione 6

Cyclohexa-1,3-diene (8.0 g, 0.10 mol) and freshly steam distilled *p*-benzoquinone (11.0 g, 0.10 mol) were boiled in benzene (90 ml) under reflux for 4 h. After concentration in a rotary evaporator the product was recrystallized from ethanol. **6**: (16.2 g, 85%), mp 98 °C; δ_H 1.48 (4 H, AA′BB′, 2 CH_2), 2.92 (s, 2 H), 3.20 (2 H, AA′), 6.15 (2 H, XX′), 6.57 (2 H, s).

endo-Tricyclo[6.2.2.0^{2,7}]dodec-9-ene-3,6-dione 7

Zinc powder (26.1 g, 0.40 mol, <200 mesh) was stirred in 4 M HCl (50 ml) for 2 min, collected on a Büchner funnel and washed with acetic acid. The activated metal was suspended in 95% aqueous acetic acid (250 ml), **6** (12.35 g, 65 mmol) was added and the mixture was stirred vigorously at 70 °C for 3 h. After filtration and washing the filter cake with methylene chloride (3 × 50 ml), the combined filtrates were brought to dryness under vacuum. The residue was taken up in methylene chloride (100 ml), washed consecutively with 2 M HCl (3 × 25 ml), conc. $NaHCO_3$ and brine and dried over $MgSO_4$. After concentration the product was recrystallized from methanol. **7**: (9.7 g, 78%), mp 58 °C; δ_H 1.45 (4 H, AA′BB′, 2 CH_2), 2.48 (4 H, AA′BB′, 2 CH_2), 2.89 (2 H, s), 3.18 (2 H, AA′), 6.20 (2 H, XX′).

endo-Tricyclo[6.2.2.0^{2,7}]dodec-9-ene-3,6-dione bis(tosylhydrazone) 8

The solution of dione **7** (8.6 g, 50 mmol) and tosyl hydrazide (20.7 g, 0.11 mol) in dry methanol (375 ml) was acidified with toluene-*p*-sulfonic acid (0.1 g) and stirred for 2 h at room temperature. The voluminous precipitate was collected on a Büchner funnel, washed with methanol and dried in a desiccator over P_4O_{10}. **8**: (25.2 g, 96%), mp 140 °C (dec.).

endo-Tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9-triene 9

The solution of **8** (18.9 g, 36 mmol) in dry THF (550 ml) was stirred under argon and cooled in an ice bath. *n*-Butyllithium in *n*-hexane (1.6 M, 100 ml, 0.16 mol) was added from a dropping funnel slowly to keep the temperature of the reaction mixture below 5 °C. After stirring at room temperature overnight the mixture was carefully hydrolyzed with conc. NH_4Cl (50 ml), diluted with water (500 ml) and extracted with pentane (5 × 200 ml). The combined extracts were washed with water (6 × 250 ml) and with brine (250 ml) and dried over $MgSO_4$. After concentration in a rotary evaporator at 0 °C and 25 Torr the product was flash chromatographed with pentane and recrystallized from *n*-hexane. **9**: (3.56 g, 63%), mp 57 °C; δ_H 1.24 (2 H, BB′), 1.64 (2 H, AA′), 2.4 (2 H, d), 2.87 (2 H, s), 5.29 (2 H, BB′), 5.42 (2 H, AA′), 6.25 (2 H, q); δ_C 25.95, 35.88, 40.60, 120.55, 129.87, 134.66.

syn-11-*exo*,12-*endo*-ditosyltetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene 10

A solution of *endo*-tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9-triene **9** (2.77 g, 17.5 mmol) and (*E*)-1,2-bis(toluene-*p*-sulfonyl)ethene (5.89 g, 17.5 mmol) in 50 ml toluene was heated to reflux under argon for 24 h. After cooling to room temperature the solvent was removed under vacuum and the residue purified by flash chromatography with hexane–ethyl acetate 3 : 1. **10**: (8.23 g, 95%), mp 178–180 °C (dec.); δ_H 0.99–1.57 (4 H, m, 13-H, 14-H), 2.43 (6 H, br s, 2 CH_3), 1.82–3.21 (6 H, 2 m, 1-H, 3-H, 6-H, 8-H, 2-H, 7-H), 3.44–3.99 (2 H, 2 m, 11-H, 12-H), 5.60–5.94 (4 H, m, 4-H, 5-H, 9-H, 10-H), 7.23–7.39 (4 H, m, 2′-H, 3′-H, 2″-H, 3″-H), 7.55–7.90 (4 H, m, 1′-H, 4′-H, 1″-H, 4″-H).

syn-Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11-triene 11

The ditosylethene adduct **9** (7.42 g, 15 mmol) and sodium dihydrogenphosphate monohydrate (36 g) were suspended under an argon atmosphere in anhydrous methanol (300 ml). The mixture was stirred vigorously for 0.5 h while 2% sodium amalgam (138 g, 0.12 mol Na) was added in small portions and the stirring was continued at room temperature overnight. Mercury and remaining buffer were removed by filtration and the filter cake was washed thoroughly with hexane. To the combined organic filtrates water (300 ml) was added and the aqueous phase was extracted with hexane (3 × 200 ml). The extracts were washed consecutively with water (2 × 200 ml) and brine (1 × 200 ml) and dried over $MgSO_4$. After filtration the solvent was removed under vacuum and the product was purified by flash chromatography with hexane. **11**: (2.07 g, 75%), mp 57 °C (Found C, 91.12; H, 8.74. Calc. for $C_{14}H_{16}$: C, 91.23; H, 8.75%); ν_{max}/cm^{-1} 3048, 2948, 2934, 2893, 2860, 1654, 1618; δ_H 1.11 (2 H, BB′, 13-H$_n$, 14-H$_n$), 1.42 (2 H, AA′, 13-H$_x$, 14-H$_x$), 1.89 (2 H, s, 2-H, 7-H), 2.31 (2 H, m, 3-H, 6-H), 3.32 (2 H, m, 1-H, 8-H), 5.71 (2 H, m, 4-H, 5-H), 5.86 (2 H, m, 9-H, 10-H), 6.38 (2 H, m, 11-H, 12-H); δ_C 27.15 (C-13, 14), 34.92 (C-3, 6), 42.40 (C-1, 8), 43.02 (C-2, 7), 131.45 (C-4, 5), 132.61 (C-9, 10), 136.80 (C-11, 12); *m*/*z* 184 (M$^+$, 0.5%), 57 (100, $C_4H_9^+$); Calc. for $C_{14}H_{16}$: 184.125, Found 184.125 (MS).

4,4-Dimethyl-10,11-ditosyl-3,5-dioxatricyclo[5.2.2.0^{2,6}]undec-8-ene 12[14]

3,3-Dimethyl-2,4-dioxabicyclo[4.2.0]nona-6,8-diene (4.65 g, 30 mmol) and (*E*)-ditosylethene (10.08 g, 30 mmol) in ethyl acetate

(250 ml) were heated to reflux under an argon atmosphere for 48 h. The scarcely soluble dienophile had reacted almost completely after this period. The reaction mixture was filtered and brought to dryness after addition of silica gel (20 g). Flash chromatography of the residue with hexane–ethyl acetate 3 : 1 provided the product **12**. (11.7 g, 80%), mp 166 °C; δ_H 1.21 (3 H, s, CH_3), 1.24 (3 H, s, CH_3), 2.42 (3 H, s, CH_3), 2.43 (3H, s, CH_3), 3.23 (1 H, m), 3.53 (1 H, m), 3.74 (2 H, s), 4.25 (1 H, m), 4.98 (1 H, m), 6.07 (2 H, AB, $\Delta\nu$ 21, *J* 4.1), 7.51 (4 H, AA′BB′), 7.60 (4 H, AA′BB′).

4,4-Dimethyl-3,5-dioxatricyclo[5.2.2.0^{2,6}]undeca-8,10-diene 13[14]

The suspension of **12** (11.7 g, 24 mmol) and sodium dihydrogenphosphate (57.6 g) in dry methanol (480 ml) was vigorously stirred under an argon atmosphere while 2% sodium amalgam (221 g, 0.192 mol Na) was added over 1 h. After stirring overnight mercury and inorganic salts were filtered off and washed with methylene chloride. The methanol filtrate was diluted with water (300 ml) and extracted with methylene chloride (3 × 300 ml). The combined methylene chloride phases were dried over $MgSO_4$ and concentrated, leaving a colourless oil that crystallized in the refrigerator. **13** (4.06 g, 95%), mp 55 °C; δ_H 1.21 (3 H, s, CH_3), 1.28 (3 H, s, CH_3), 3.79 (2 H, m), 4.18 (2 H, m), 6.25 (2 H, m), 6.32 (2 H, m).

cis-2,3-Dihydroxybicyclo[2.2.2]octa-5,7-diene 14[14]

The ketal **13** (4.06 g, 23 mmol) was dissolved in acetic acid (140 ml) and water was added to the solution until it became turbid. The mixture was heated to 100 °C for 2 h whereafter all volatile components were evaporated at 40 °C and 10 Torr. The residue was flash chromatographed with methylene chloride–acetonitrile 3 : 1 yielding **14** (2.54 g, 80%), mp 60–62 °C; δ_H 2.69 (2 H, br s, OH), 3.77 (4 H, m), 6.20 (2 H, m), 6.41 (2 H, m).

cis-2,3-Bis(methanesulfonyloxy)bicyclo[2.2.2]octa-5,7-diene 15[14]

The solution of diol **14** (2.50 g, 18 mmol) in methylene chloride (100 ml) was treated with triethylamine (6.15 g, 60.9 mmol) and cooled in an ice bath. Freshly distilled methanesulfonyl chloride (4.8 g, 41.9 mmol) was dropped into the solution and stirring was continued for 2 h at 0 °C. The mixture was poured onto ice and water (200 ml) and the organic phase was washed with 2 M HCl, then with 1 M sodium hydrogencarbonate and dried over $MgSO_4$. Concentration in a rotary evaporator left colourless crystals of **15** (4.07 g, 77%), mp 132 °C; δ_H 3.04 (6 H, s, 2 CH_3), 4.12 (2 H, m), 4.68 (2 H, m), 6.35 (2 H, m), 6.48 (2 H, m).

Bicyclo[2.2.2]octa-2,5,7-triene 16[14]

A solution of sodium anthracenide was prepared by stirring anthracene (5.34 g, 30 mmol) in dry THF (100 ml) in an argon atmosphere with finely cut sodium (0.67 g, 30 mmol) for 2 h. The resulting deep blue solution was added dropwise with a syringe to the crystals of dimesylate **15** (2.76 g, 9.4 mmol) that were kept in a two necked flask equipped with a diaphragm and a balloon filled with argon. After addition of 70 ml of the blue anthracenide solution its colour persisted in the reaction flask. The mixture was quenched with a few drops of methanol and the volatile components were condensed at 40 °C and 10 Torr into a trap cooled with liquid nitrogen. The contents of the trap were reduced to 3 ml by fractional distillation over a Vigreux column (30 cm) at 760 Torr. The final separation by preparative GC over 20% reoplex on kieselguhr (1 m, 0.25″, 78 °C, injector and detector 110 °C) yielded barrelene **16** (200 mg, 20.5%).

15,16;19,20;21,22-*syn*-1,12,19,20-Tetrachlorooctacyclo-[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21-tetraene 17 and all-*syn*-1,12,19,20-tetrachlorooctacyclo[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21-tetraene 19 ‡

The solution of **1** (296 mg, 1 mmol) and **11** (184 mg, 1 mmol) in anhydrous THF (2.5 ml) together with a crystal of 4-*tert*-butyl catechol was heated to 80 °C under a pressure of 7.8 kbar for 96 h. The reaction mixture was concentrated under vacuum and the products were separated by twice repeated flash chromatography with hexane followed by fractional recrystallization. **17** (288 mg, 60%), mp 260 °C (dec.); λ_{max}(hexane)/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 2800); ν_{max}/cm^{-1} 3042, 2949, 2869, 1654, 1602; δ_H 1.16 (2 H, m, 25-H$_n$, 26-H$_n$), 1.21 (2 H, m, 23-H$_n$, 24-H$_n$), 1.40–1.46 (4 H, 2 m, 23-H$_x$, 24-H$_x$, 25-H$_x$, 26-H$_x$), 1.53 (2 H, s, 4-H, 9-H), 2.15 (2 H, s, 13-H, 18-H), 2.17 (2 H, s, 2-H, 11-H), 2.41 (2 H, m, 5-H, 8-H), 2.77 (2 H, m, 3-H, 10-H), 2.88 (2 H, m, 14-H, 17-H), 5.95 (2 H, m, 15-H, 16-H), 5.99 (2 H, m, 21-H, 22-H), 6.23 (2 H, m, 6-H, 7-H); δ_C 25.53 (C-25, 26), 27.15 (C-23, 24), 31.52 (C-14, 17), 33.96 (C-5, 8), 36.13 (C-3, 10), 44.44 (C-4, 9), 50.84 (C-2, 11), 54.70 (C-13, 18), 75.09 (C-1, 12), 125.82 (C-19, 20), 130.31 (C-15, 16), 130.48 (C-6, 7), 132.07 (C-21, 22).

19 (96 mg, 20%), mp 252 °C (dec.); λ_{max}(hexane)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 600); ν_{max}/cm^{-1} 3056, 3040, 2952, 2942, 2930, 2913, 2880, 2863, 1634, 1602; δ_H 1.04 (2 H, m, 23-H$_n$, 24-H$_n$), 1.15 (2 H, m, 25-H$_n$, 26-H$_n$), 1.43 (4 H, 2 m, 23-H$_x$, 24-H$_x$, 25-H$_x$, 26-H$_x$), 1.90 (2 H, s, 4-H, 9-H), 2.27 (2 H, s, 13-H, 18-H), 2.32 (2 H, s, 2-H, 11-H), 2.30 (2 H, m, 5-H, 8-H), 2.86 (4 H, m, 3-H, 10-H, 14-H, 17-H), 5.51 (2 H, m, 21-H, 22-H), 5.67 (2 H, m, 6-H, 7-H), 5.94 (2 H, m, 15-H, 16-H); δ_C 25.59 (C-25, 26), 27.05 (C-23, 24), 31.50 (C-14, 17), 34.44 (C-5, 8), 37.86 (C-3, 10), 43.99 (C-4, 9), 54.33, 56.09 (C-2, 11, 13, 18), 74.64 (C-1, 12), 124.68 (C-19, 20), 128.62 (C-21, 22), 130.32 (C-15, 16), 132.29 (C-6, 7).

15,16;19,20;21,22-*syn*-Octacyclo[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21-tetraene 18

Tetrachlorotetraene **17** (200 mg, 0.42 mmol) was dissolved in diethylene glycol monoethyl ether (35 ml) at 100 °C and the stirred solution was kept under argon and treated with finely cut sodium (283 mg, 12 mmol) over the course of 3 h. After another 15 min the mixture was cooled to room temperature and diluted with water (20 ml). The precipitate was collected on silica gel (50 mg) by filtration and washed with water followed by methanol. The coated silica gel was dried under vacuum and subjected to a flash chromatography with hexane. **18** (44.5 mg, 31%), mp 270 °C (dec.); λ_{max}(hexane)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 1100); δ_H 1.00 (2 H, BB′, CH_2), 1.20 (2 H, BB′, CH_2), 1.35 (2 H, s), 1.42 (4 H, 2 AA′, CH_2), 1.74 (2 H, s), 1.78 (2 H, s), 2.12 (4 H, s), 2.20 (2 H, m), 2.32 (2 H, m), 5.24 (2 H, m), 5.65 (4 H, m), 6.21 (2 H, m); δ_C 27.26, 27.43, 34.23, 34.82, 39.67, 41.49 (double intensity), 46.08, 46.25, 129.51, 131.51, 132.27, 134.40; *m*/*z* 342 (M^+, 23%), 262 (50 M − $C_6H_8^{\cdot}$), 234 (97, $C_{18}H_{18}^{\cdot+}$), 128 (90, $C_{10}H_8^{\cdot+}$), 80 (100, C_6H_8).

Thermolysis of 15,16;19,20;21,21-*syn*-Octacyclo[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21- tetraene 18

An NMR probe of **18** in [$^2H_{10}$]xylene was deaerated by two freeze–thaw cycles and sealed. The tube was heated in the steam of refluxing *n*-dodecane (bp 214 °C) and the NMR spectrum was taken at intervals of 24 h. After 4 d the NMR analysis indicated that **18** had completely decomposed to equal amounts of bicyclo[2.2.2]octene **24**, naphthalene, benzene and ethene.

all-*syn*-Octacyclo[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21-tetraene 20

A solution of **19** (105 mg, 0.22 mmol) in diethylene glycol monoethyl ether (20 ml) was heated to 100 °C under an argon atmosphere. Sodium (253 mg, 11 mmol) was added in small

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‡ IUPAC names for compounds **17**–**20**, **27**–**29** (excluding stereochemistry) are: **17**–**20**, 1,12,19,20-tetrachlorooctacyclo[10.6.2.2^{3,10}.-2^{5,8}.2^{14,17},0^{2,11}.0^{4,9}.0$^{13.18}$]hexacosa-6,15,19,23-tetraene; **27**–**29**, 3,10,14,21,25,26,29,30-octachlorodecacyclo[10.10.2.2^{3,10}.2^{5,8}.2^{14,21}.2^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]dotriaconta-6,17,23,25,29-pentaene.

pieces over 3 h to the stirred solution and the heating was continued for a further 15 min. The cooled reaction mixture was poured into water (20 ml) and the precipitate was collected on silica gel (50 mg) by filtration. After washing the silica gel with water and a small amount of methanol it was extracted by flash chromatography with hexane. The product fraction was concentrated and recrystallized from $CHCl_3$. **20** (26 mg, 35%), mp 252 °C (dec.); λ_{max}(hexane)/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 600); ν_{max}/cm^{-1} 3042, 2936, 2921, 2905, 2881, 2865, 1619, 683; δ_H 1.01 (4 H, m, 23-H$_n$, 24-H$_n$, 25-H$_n$, 26-H$_n$), 1.42 (4 H, m, 23-H$_x$, 24-H$_x$, 25-H$_x$, 26-H$_x$), 1.91 (4 H, s, 4-H, 9-H, 13-H, 18-H), 1.95 (2 H, s, 2-H, 11-H), 2.15–2.21 (8 H, 2 m, 1-H, 3-H, 5-H, 8-H, 10-H, 12-H, 14-H, 17-H), 5.14 (4 H, m, 19-H, 20-H, 21-H, 22-H), 5.62 (4 H, m, 6-H, 7-H, 15-H, 16-H); δ_C 27.31 (C-23, 24, 25, 26), 34.74 (C-5, 8, 14, 17), 40.97 (C-1, 3, 10, 12), 45.77 (C-4, 9, 18, 19), 47.66 (C-2, 11), 130.67 (C-19, 20, 21, 22), 132.22 (C-6, 7, 15, 16); *m*/*z* 342 (M$^+$, 55%), 262 (100, M − C_6H_8), 80 (71, $C_6H_8^+$); Calc. for $C_{26}H_{30}$: 342.234, Found: 342.234 (MS).

***syn*-3,4,5,6-Tetrachloropentacyclo[6.6.2.2^{10,13}.0^{2,7}.0^{9,14}]octadeca-2,4,6,15-tetraene 21 and *syn-endo*-3,4,5,6-tetrachloropentacyclo[6.6.2.2^{10,13}.0^{2,7}.0^{9,14}]octadeca-3,5,11,15-tetraene 22**

The solution of triene **11** (184 mg, 1 mmol) and tetrachlorothiophene dioxide (253.8 mg, 1 mmol) in benzene (5 ml) was stirred at room temperature for 48 h. After evaporation of solvent the two isomeric cycloadducts were separated by flash chromatography with hexane followed by crystallization from the same solvent. **21** (258 mg, 59%), mp 164 °C; λ_{max}/nm 245sh (ε/dm^3 mol^{-1} cm^{-1} 6300); δ_H 0.43 (2 H, BB′, 11-H$_{in}$, 12-H$_{in}$), 0.93 (2 H, AA′, 11-H$_{out}$, 12-H$_{out}$), 1.45 (4 H, m, CH_2), 1.63 (2 H, s, 10-H, 13-H), 1.91 (2 H, s, 9-H, 14-H), 4.37 (2 H, m, 1-H, 8-H), 6.56 (2 H, m, 15-H, 16-H); δ_C 21.17 (C-11, 12), 29.00 (C-17, 18), 29.18 (C-10, 13), 40.85 (C-9, 14), 43.07 (C-1, 8), 128.30 (C-3, 6), 128.68 (C-4, 5), 136.48 (C-15, 16), 142.78 (C-2, 7); *m*/*z* 374 (M$^+$, 45%), 266 (100, M − C_8H_{12}), 80 (43, $C_6H_8^+$).

22 (118 mg, 27%), mp 131 °C; λ_{max}/nm 269sh (ε/dm^3 mol^{-1} cm^{-1} 2800), 281 (3100), 292 (4300), 305 (4600), 319 (2700); δ_H 1.11 (2 H, BB′, 17-H$_n$, 18-H$_n$), 1.48 (2 H, AA′, 17-H$_x$, 18-H$_x$), 2.02 (2 H, s, 9-H, 14-H), 2.36 (2 H, m, 10-H, 13-H), 3.05 (2 H, m, 1-H, 8-H), 3.12 (2 H, s, 2-H, 7-H), 5.78 (2 H, m, 11-H, 12-H), 5.87 (2 H, m, 15-H, 16-H); δ_C 26.78 (C-17, 18), 34.45 (C-10, 13), 39.68 (C-1, 8), 42.04 (C-9, 14), 50.14 (C-2, 7), 123.21 (C-4, 5), 131.94 (C-15, 16), 132.13 (C-11, 12), 132.28 (C-3, 6).

Alternative route to all-*syn*-1,12,19,20-tetrachlorooctacyclo-[10.6.2.2^{3,10}.2^{5,8}.2^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]hexacosa-6,15,19,21-tetraene 19

The solution of **22** (93.5 mg, 0.25 mmol) and bicyclo[2.2.2]-octadiene (27 mg, 0.25 mmol) in THF (1.5 ml) together with a crystal of 4-*tert*-butylcatechol was heated to 80 °C for 96 h under a pressure of 7.8 kbar. After transferring the reaction mixture with $CHCl_3$ into a flask (10 ml) it was brought to dryness and the product was purified by flash chromatography with hexane. **19** (96.4 mg, 80%).

6,7;23,24;25,26-*syn*-17,18;27,28-*syn*-3,10,14,21,25,26,27,28-Octachlorodecacyclo[10.10.2.2^{3,10}.2^{5,8}.2^{14,21}.2^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]dotriaconta-6,17,23,25,27-pentaene 27 and all-*syn*-3,10,14,21,25,26,27,28-octachlorodecacyclo[10.10.2.2^{3,10}.2^{5,8}.2^{14,21}.2^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]dotriaconta-6,17,23,25,27-pentaene 28

A solution of bicyclo[2.2.2]octatriene **16** (52 mg, 0.5 mmol) and **1** (518 mg, 1.75 mmol) in anhydrous THF (2.5 ml), together with a crystal of 4-*tert*-butylcatechol, was heated to 110 °C for 120 h under a pressure of 8.1 kbar. The reaction mixture was transferred with CH_2Cl_2 into a flask (10 ml) and concentrated under vacuum. The product isomers were separated by flash chromatography on silica gel, first eluting the angular compound **27** with *n*-hexane and then the all-*syn*-isomer **28** with $CHCl_3$. Both products were purified by recrystallization from $CHCl_3$. **27** (69.9 mg, 20%), mp 285 °C (dec.); λ_{max}/nm 236 (ε/dm^3 mol^{-1} cm^{-1} 1450); ν_{max}/cm^{-1} 3047, 2952, 2937, 2908, 2865, 1654, 1600; δ_H 1.12–1.22 (4 H, m, H$_n$ on CH_2), 1.41–1.48 (4 H, m, H$_x$ on CH_2), 1.99 (2 H, s, 13-H, 22-H), 2.17 (4 H, s, 2-H, 4-H, 9-H, 11-H), 2.25 (2 H, s, 15-H, 20-H), 2.88 (2 H, m, 5-H, 8-H), 2.96 (2 H, m, 16-H, 19-H), 3.38 (2 H, m, 1-H, 12-H), 5.93 (2 H, m, 6-H, 7-H), 6.03–6.07 (4 H, 2 m, 17-H, 18-H, 23-H, 24-H); δ_C 25.42, 25.54 (C-29, 30, 31, 32), 31.44 (C-5, 8, 16, 19), 33.52 (C-1, 12), 53.66 (C-13, 22), 49.14, 54.11 (C-2, 4, 9, 11), 54.91 (C-15, 20), 73.07, 74.11 (C-3, 10, 14, 21), 125.61, 126.97 (C-25, 26, 27, 28), 129.54 (C-17, 18), 130.28 (C-6, 7), 131.75 (C-23, 24).

28 (240.8 mg, 70%), mp 295 °C (dec.) (Found: C, 55.29; H, 4.09. Calc. for: $C_{32}H_{28}Cl_8$: C, 55.21; H, 4.05%); λ_{max}/nm 256 (ε/dm^3 mol^{-1} cm^{-1} 1030); ν_{max}/cm^{-1} 3056, 2978, 2949, 2934, 2923, 2864, 1654, 1604; δ_H 1.14–1.18 (4 H, BB′, H$_n$ on CH_2), 1.40–1.46 (4 H, AA′, H$_x$ on CH_2), 2.26 (4 H, s, 4-H, 9-H, 15-H, 20-H), 2.28 (4 H, s, 2-H, 11-H, 13-H, 22-H), 2.90 (m, 4 H, 5-H, 8-H, 16-H, 19-H), 3.48 (2 H, m, 1-H, 12-H), 5.78 (2 H, m, 23-H, 24-H), 5.94 (4 H, m, 6-H, 7-H, 17-H, 18-H); δ_C 25.53 (C-29, 30, 31, 32), 31.42 (C-5, 8, 16, 19), 35.01 (C-1, 12), 54.17 (C-4, 9, 15, 20), 54.51 (C-2, 11, 13, 22), 73.97 (C-3, 10, 14, 21), 124.87 (C-25, 26, 27, 28), 127.05 (C-23, 24), 130.30 (C-6, 7, 17, 18).

all-*syn*-Decacyclo[10.10.2.2^{3,10}.2^{5,8}.2^{14,21}.2^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] dotriaconta-6,17,23,25,27-pentaene 29

A solution of **28** (240 mg, 0.35 mmol) in diethylene glycol monoethyl ether (150 ml) was prepared at 110 °C under an argon atmosphere. To the stirred solution sodium (1.6 g, 70 mmol) was added in small pieces over 5 h. Heating was continued for a further 15 min and the cooled reaction mixture was poured on water (100 ml). The precipitate was collected on silica gel (50 mg) by filtration. The silica gel was washed thoroughly with water and a small amount of methanol and continuously extracted with boiling hexane. After 4 d the extract was concentrated and the residue recrystallized from $CHCl_3$. **29** (36.8 mg, 25%), mp 305 °C (dec.); λ_{max}(*n*-hexane)/nm 214sh (ε/dm^3 mol^{-1} cm^{-1} 3800), 250 (1020); ν_{max}/cm^{-1}(KBr) 3047, 2918, 2906, 2883, 2875, 684; δ_H(C_6D_6, 70 °C) 1.15 (4 H, BB′, H$_n$ on CH_2), 1.48 (4 H, AA′, H$_x$ on CH_2), 1.89 (8 H, m, 2-H, 4-H, 9-H, 11-H, 13-H, 15-H, 20-H, 22-H), 2.16 (6 H, m, 1-H, 3-H, 10-H, 12-H, 14-H, 21-H), 2.21 (4 H, m, 5-H, 8-H, 16-H, 19-H), 5.19 (2 H, m, 23-H, 24-H), 5.23 (4 H, m, 25-H, 26-H, 27-H, 28-H), 5.72 (4 H, m, 6-H, 7-H, 17-H, 18-H); *m*/*z* 420 (M$^+$, 5%), 91 (55, $C_7H_7^+$), 80 (85, $C_6H_8^+$), 79 (100, $C_6H_7^+$), 78 (90, $C_6H_6^+$).

Crystal data

3: $C_{14}H_{18}$, $M = 186.28$. Triclinic, $a = 6.268(1)$, $b = 8.387(1)$, $c = 11.135(1)$ Å, $\alpha = 109.09(1)$, $\beta = 90.24(1)$, $\gamma = 111.68(1)°$, $V = 518.91(11)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 0.710\ 69$ Å), space group $P\bar{1}$, $Z = 2$, $D_x = 1.192$ g cm^{-3}. Crystal dimensions: 0.25 × 0.25 × 0.03 mm, μ(Mo-Kα) = 0.96 cm^{-1}.

5: $C_{20}H_{24}$, $M = 264.39$. Triclinic, $a = 6.376(1)$, $b = 10.376(1)$, $c = 11.232(1)$ Å, $\alpha = 97.99(2)$, $\beta = 90.81(2)$, $\gamma = 107.30(2)°$, $V = 701.01(14)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 0.710\ 69$ Å), space group $P\bar{1}$, $Z = 2$, $D_x = 1.253$ g cm^{-3}. Crystal dimensions: 0.30 × 0.30 × 0.20 mm.

20: $C_{26}H_{30}$, $M = 342.50$. Triclinic, $a = 6.385(2)$, $b = 6.398(2)$, $c = 24.947(6)$ Å, $\alpha = 86.11(2)$, $\beta = 86.76(2)$, $\gamma = 60.27(2)°$, $V = 882.7(4)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 0.710\ 69$ Å), space group $P\bar{1}$, $Z = 2$, $D_x = 1.289$ g cm^{-3}. Crystal dimensions: 0.15 × 0.20 × 0.22 mm.

Data collection

CAD4 diffractometer, $\omega/2\delta$ mode with ω scan width =

$0.70 + 0.35 \tan\theta$, ω scan speed 2.2 deg min^{-1}, graphite-monochromated Mo-Kα radiation. **3**: 2257 reflections measured ($2 < \theta < 27°$), giving 1579 with $I > 2\sigma(I)$; **5**: 4070 reflections measured ($2 < \theta < 27°$), giving 3365 with $I > 2\sigma(I)$; **20**: 4943 reflections measured ($2 < \theta < 28°$), giving 2523 with $I > 2\sigma(I)$. Linear and approx. isotropic crystal decay, *ca* 1.6% corrected during processing.

Structure analysis and refinement

After data reduction, the structure was solved by direct methods using the MolEN program package and refined against F_0^2 for all unique reflections using SHELXL-93[30] (C atoms with anisotropic temperature factors and H atoms with isotropic ones). Final R_1 and wR_2 values for reflections $I > 2\sigma(I)$ are **3**: $R_1 = 0.056$ and $wR_2 = 0.123$; **5**: $R_1 = 0.045$ and $wR_2 = 0.118$; **20**: $R_1 = 0.062$ and $wR_2 = 0.159$; $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$, $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2/[\Sigma w(F_o^2)^2]\}^{\frac{1}{2}}$; weighting scheme **3**: $w = 1/[\sigma^2(F_o^2) + (0.053\ P)^2 + 0.162\ P]$; **5**: $w = 1/[\sigma^2(F_o^2) + (0.069\ P)^2 + 0.109\ P]$; **20**: $w = 1/[\sigma^2(F_o^2) + (0.094\ P)^2 + 0.737\ P]$; where $P = (F_o^2 + 2F_c^2)/3$. The calculations were performed at the Regional Computational Center at the University of Cologne. Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Center (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/136.

Photoelectron spectra

The He(I) photoelectron spectra of **3**, **5** and **20** were recorded on a Perkin-Elmer PS18 spectrometer. The recording temperatures were as follows: **3**: 40 °C, **5**: 125 °C, **20**: 160 °C. The calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^3P_{3/2}$ line was obtained.

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