Functionalized Enantiomerically Pure [1.1.1]-, [2.1.1]-, [2.2.1]-, and [2.2.2]Triblattanes

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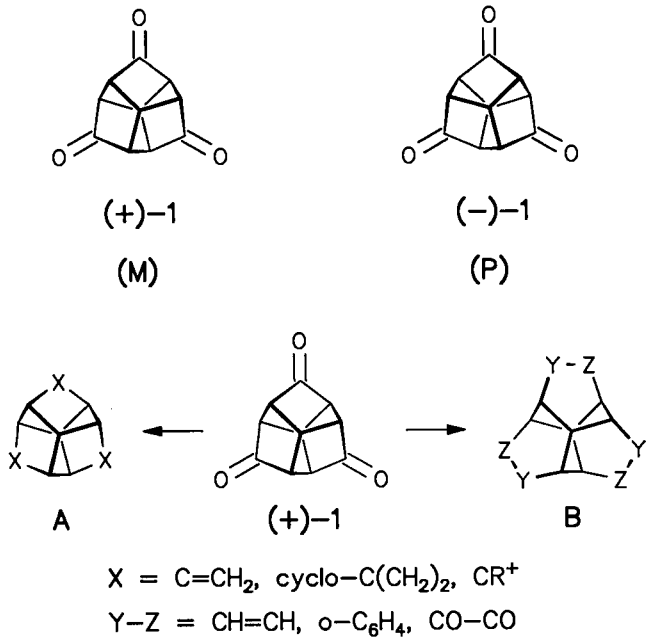
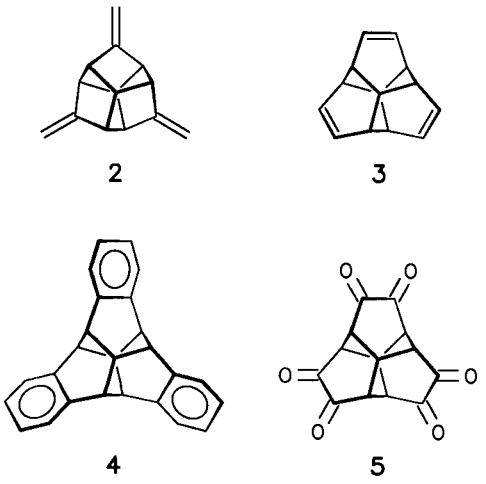
The methylene (**2**, **7**, **10**) and spirocyclopropane derivatives (**8**, **11**, **12**) are made accessible from *rac*-trishomocubane(mono-, di-, tri-)ones and optically pure unsaturated and benzoannulated [2.1.1]- (**19**, **48**), [2.2.1]- (**30**, **53**), and D_3-symmetrical [2.2.2]triblattanes (**3**, **4**) from the enantiomers of these ketones by expeditious (one pot) ring enlargement and olefination procedures. In the case of the central [2.2.2]trienes (+)-**3**/(−)-**3**, novel members of the $(CH)_{14}$ family, optical resolution is advantageously postponed to the stage of the intermediate [2.2.2]triones (**35**, **41**) and effected via their (*R*,*R*)-2,3-butanediol acetals. In the α-diketone series only the [2.1.1]dione (**70**) is sufficiently stable to allow isolation; tetrone **73** and hexone **5** are indirectly identified as quinoxalines **74** and **76**, respectively. Tribenzo[2.2.2]triblattane (−)-**4** is established as the *M*-helical enantiomer by X-ray crystallography. Generally the thermal stabilization pathway of unsaturated and benzoannulated triblattanes is a [4 + 2] cycloreversion with the primary cycloreversion products [e.g. (1α,2α,7α,10α)-tricyclo[8.4.0.0^{2,7}]tetradeca-3,5,9,11,13-pentaene (**78**) from *rac*-**3**] being unstable under the drastic reaction conditions required. The stereochemical course of the perepoxidation of *rac*-**3** is investigated.

In our endeavor to construct novel molecular skeletons that are attractive for preparative or theoretical reasons and that are not (readily) available from natural resources[1], we had detailed a highly efficient synthesis of the appealing D_3-symmetrical, gyrochiral trishomocubanetrione **1** as well as its optical resolution. Since these protocols are readily amenable to large-scale preparations[2,3], the prerequisites were provided for the exploitation of *rac*-**1** and its pure enantiomers as building blocks for a range of cage-type homo- and heteropolycycles, as generalized by formula **A** and **B**. The common topochemical pecularity of these molecular entities is a helical ("gyrochiral") twistane core which is diagonally bridged by various chromophoric units.



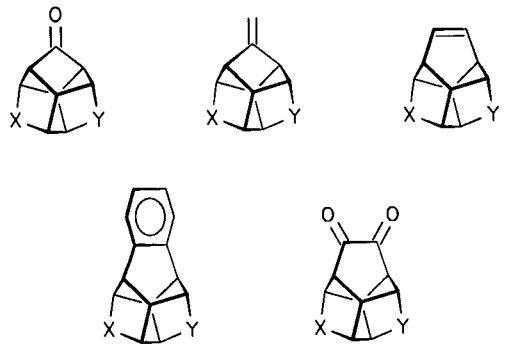
Our interest in these classes of compounds was stimulated primarily by the characteristic relative orientation of functionalities when introduced into the intrinsically chiral D_3-symmetrical parent skeleton[4,5] as represented by the D_3-symmetrical trismethylene compound **2** and its $(CH)_{14}$ isomer [2.2.2]triblattanetriene **3** (tritwistatriene)[6], the tribenzo derivative **4** or the [2.2.2]triblattanehexone **5**. Structural pecularities raised expectations as to providing an entry to novel carbon skeletons, to novel chiral auxiliaries, as to special nonbonded electronic interactions and as to unusual chiroptical properties. While we are presenting here the synthesis, chemistry, and optical resolution of the title compounds, the latter topics were adressed in collaboration with Prof. Gleiter (PE)[7], Prof. Snatzke (CD)[8], Prof. Roth (vapor phase pyrolysis), and Prof. Olah/Prakash (Oxidation to e.g. triscation **A**: X = CR$^+$) and are the subject of following papers.

For the evaluation of potential intramolecular electronic transmissions in systems **2**–**5**, the mono- and *difunctional*-ized [2.1.1]- and [2.2.1]triblattane analogues were also needed as reference compounds. In addition, extensive prior experimentation with such simpler substrates seemed a priori advisable, and proved indeed necessary, since in principle even trivial preparative methodologies like the ring



2 3 4 5

enlargement of cyclic ketones or the benzoannulation of cyclic olefins may indeed pose significant problems when to be effected twice or even three times in the same substrate. Therefore, we have extended our preparative program, which was primarily directed towards the D_3-symmetrical trifunctionalized systems (series C), and included the mono- (series A) and difunctionalized analogues (series B)[9]. Needless to stress the point that all preparations with optically active compounds have been elaborated initially using racemic material. Trishomocubane mono- and diketones (**6** and **9**), which serve as starting materials for the series A and B, are efficiently accessible by literature procedures[10,11]. For a good part of the chemistry involved in this project, extensive precedence exists that has recently been reviewed[4,12].



Series A: X = Y = CH_2

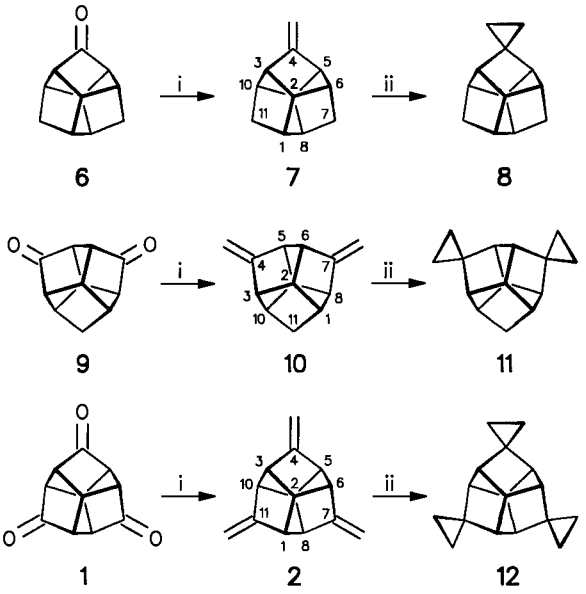
Series B: X = CH_2,
Y = $C{=}CH_2$/C=O/HC=CH/o-C_6H_4/CO–CO

Series C: X = $C{=}CH_2$/C=O/HC=CH/o-C_6H_4/CO–CO,
Y = $C{=}CH_2$/C=O/HC=CH/o-C_6H_4/CO–CO

[1.1.1]Trishomocubanes[13]

For the one-pot threefold Wittig methylenation of triketone **1** to afford the crystalline trismethylene compound *rac*-**2** (Scheme 1), a total yield of 72% was achieved by application of conditions evaluated in the transformations of **6** and **9** to **7** (68%) and **10** (70%), respectively. The two-step threefold cyclopropanation of *rac*-**2**[14], with some optimization using the syntheses of the lower homologues **7** (**8**, 74%) and **10** (**11**, 67%) as models, allowed the ready isolation of 81% of the D_3 trispiro compound *rac*-**12**. The unusual high-field shift of the carbonyl ^{13}C-NMR resonance in the series of mono- to triketone (Table 1) is explicable on the basis of a vector model where the resultant dipol moment should decrease with increasing functionalization. Due to an only minor polarization, this effect can even be traced to sp^3-hybridized *O,O*- or *S,S*-ethylene spiro acetals[13] but is only weakly impressed in the corresponding *exo*-methylene series compounds, however, is again significant for the first two spiro compounds.

Scheme 1. i) $Ph_3P{=}CH_2$/benzene/reflux/3 h/68–72%. – ii) 1. KOH/$CHCl_3$/PTC, 2. Li/NH_3/THF/*tert*-butyl alcohol/ 67–81%



6 7 8 9 10 11 1 2 12

Table 1. Selected ^{13}C-chemical shifts for the [1.1.1]trishomocubanes **1**, **2**, and **6**–**12**

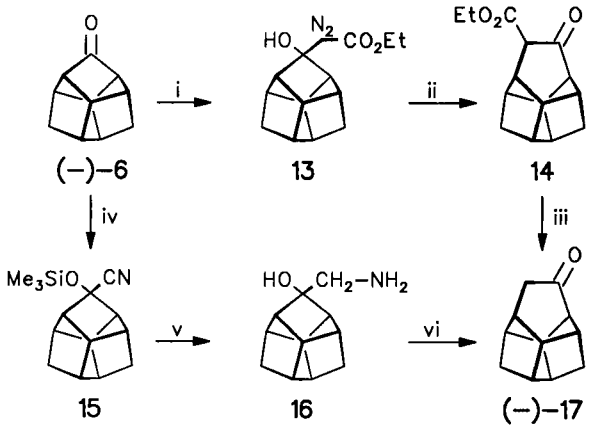
comp.	δ [C-4]	comp.	δ [C-4 (7)]	comp.	δ [C-4 (7, 11)]
6	216.4	**9**	211.4	**1**	205.8
7	157.9	**10**	157.3	**2**	156.6
8	34.2	**11**	30.8	**12**	30.8

[2.1.1]Triblattanes

Ultimate targets of the efforts described in this section are the enantiomerically pure, C_2-symmetrical dimethanotwistenes (–)-**19** and (+)-**19** (Schemes 2 and 3). Their syntheses start with *rac*-**6**[10], which was resolved according to Eaton and Leipzig[15]. The key step en route to (–)-**19**, the ring expansion of (–)-**6** to the [2.1.1]ketone (–)-**17**, had been performed with excessive ethereal diazomethane[16]. Yet, the incontrollable formation of higher homologues necessitated a labour-intensive separation and kept the yield of (–)-**17** below 60%. By taking resort to the two multistep methodologies for C_1 homologization as formulated in Scheme 2, a total yield of 81% according to the modified Tiffeneau-

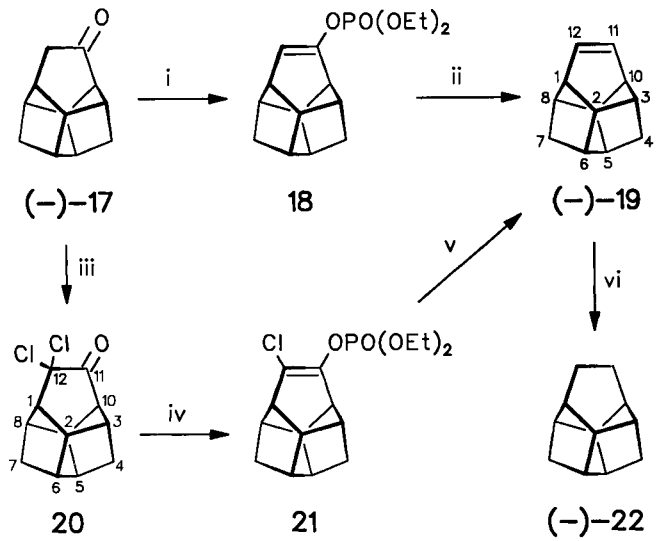
Demjanov procedure via **15**/**16**[17] or even 93% using the Schöllkopf sequence via **13**/**14**[18] was achieved.

Scheme 2. i) N_2HCCO_2Et/*n*-butyllithium/THF/−78 to −30°C/97%. – ii) $C_3H_5Pd(I)Cl$ dimer/CH_2Cl_2/−78 to room temp./96%. – iii) $NaHCO_3/H_2O$/150°C/1 h/100%. – iv) TMSCN/ZnI_2/CH_2Cl_2. – v) $LiAlH_4$/THF. – vi) $NaNO_2/H_2O$/glacial acetic acid/iv–vi: 81%



Several attempts to install the C=C double bond of (−)-**19** by reduction of (−)-**17** followed by acid- or base-catalyzed β- (e.g. – H_2O[19], – HOAc, – HOMes) or thermal *cis*-elimination from the alcohol or a derivate failed or did not produce the olefin in reasonable quantities. Two methodological alternatives to arrive at (−)-**19** by reduction of intermediate enol phosphates (**18**, **21**) proved successful (Scheme 3): The Fetizon route[20] yielded 76% of (−)-**19**. The somewhat lengthier Perkow process[21], which has to compete with the Arbuzov substitution[22] at the stage of dichloroketone **20**, profits here from the nature of the halogen, of the phosphite and the solvent used[23]. The waxy-solid (−)-**19** sublimes at 70°C/13 Torr (m.p. 85–86°C) and is fully characterized by MS, IR, ^{1}H- and ^{13}C-NMR spectra

Scheme 3. i) LDA/THF/$ClPO(OEt)_2$/93%. – ii) Li/NH_3/ether/*tert*-butyl alcohol/82%. – iii) SO_2Cl_2/60°C/14 h/91%. – iv) $P(OEt)_3$/100°C/6 h/96%. – v) cf. ii/79%. – vi) Pd/C/MeOH/H_2/81%



(Figure 1). In an analogous manner, (+)-**19** has been prepared from (+)-**6**.

The absolute configuration of (−)-**19** (*M* helicity) has been secured by correlation with the saturated parent hydrocarbon (−)-**22**[18]. The measured rotation of the latter of $[\alpha]_D^{20} = -279$ is somewhat smaller than the value of −293 extrapolated by Nakazaki, using an optically enriched (55.6%) sample. However, the optical rotation reported for (−)-**6** ($[\alpha]_D^{20} = 88.5$ – again extrapolated from a 55.6% optically enriched sample) is smaller than that of $[\alpha]_D^{20} = -101$ measured by us for the pure enantiomer (^{1}H NMR of a diastereomeric precursor).

[2.2.1]Triblattanes

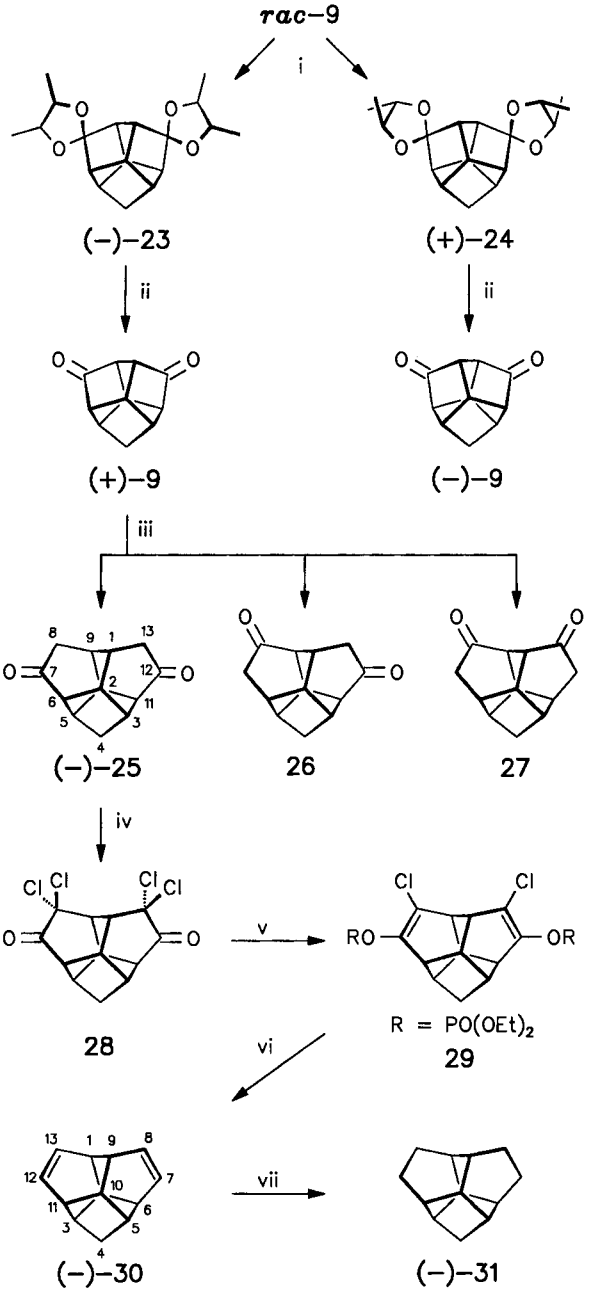
The reaction sequence developped for the synthesis of both enantiomers of C_2-symmetrical methanoditwistadiene **30** is formulated in Scheme 4. The previously unknown optical resolution of *rac*-trishomocubanedione **9** was first attempted with diethyl L-(+)-tartrate; yet, the diastereomeric acetals formed with (*R*,*R*)-2,3-butanediol, **23** and **24**, could be more readily separated by preparative MPLC. The diastereomeric purity of the isolated 60% of **23** and 40% of **24** (crystallized from PE 30/50 at −30°C to remove small amounts of **23**) was conveniently controlled by 400-MHz ^{1}H- and ^{13}C-NMR spectroscopy. Removal of the chiral auxiliary proceeded with very high yield (90% for (+)-**9**, $[\alpha]_D^{20} = +300$ and 97% for (−)-**9**, $[\alpha]_D^{20} = -300$) and afforded the enantiomers with optical rotations of the same absolute value, additional evidence for the high optical purity. For the ring expansion of the two cyclopentanone moieties in the *M*-helical (+)-**9** and *P*-helical (−)-**9**, the Tiffeneau-Demjanow procedure proved superior (75%) to the Schöllkopf alternative (30%)[24]. From its mixture with **26** and **27**, pure C_2 dione (−)-**25** (m.p. 175–176°C, $[\alpha]_D^{20} = -264$, $[\Phi]_D^{20} = -535$) could be isolated chromatographically in 18–20% yield.

Subsequently, isomer **27** (m.p. 183–184°C) was separated from **26** by crystallization. For the analogously prepared (+)-**25**, optical rotations of $[\alpha]_D^{20} = +257$ and $[\alpha]_D^{20} = +520$ were determined.

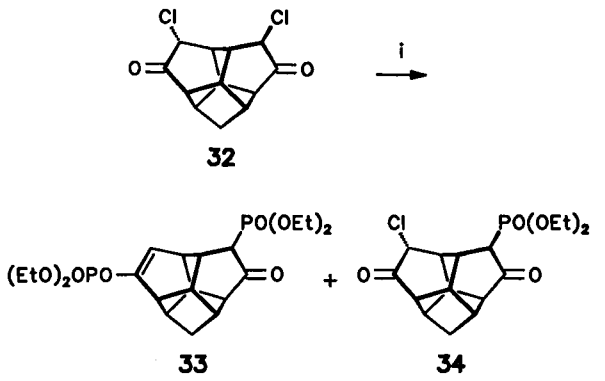
The transformation of dione (−)-**25** into diene (−)-**30** turned out to be a non-trivial task. While the Fetizon approach failed, presumably for the non-occurrence of bisenolate formation, the Shapiro method[25] only ended in a non-acceptable low yield (34%)[24]. Complete chlorination of the two α-ketomethylene groups in (−)-**25** to give the tetrachlorodione intermediate **28** needed for the Perkow sequence could not be brought about under the conditons employed for the chlorination of **17**. With sulfuryl chloride[26], even under forcing conditons, only α,α′-dichlorination to give the symmetrical **32** took place[26,27]. In test experiments with *rac*-**32** and triethyl phosphite, **33** (49%) and presumably (^{1}H NMR) **34** are components of otherwise rather complex reaction mixtures. These products are convincing proof for the predominant Arbusov competition in substrate **32**.

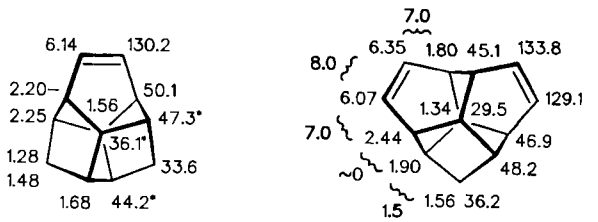
The problem could be solved by taking advantage of the chlorination procedure described by deKimpe[28]. Under

Scheme 4. i) (*R,R*)-2,3-Butanediol/*p*-toluenesulfonic acid/benzene/reflux/8 h/98%. – ii) Glacial acetic acid/H_2SO_4/reflux/15 h/90%. – iii) 1. TMSCN/ZnI_2/CH_2Cl_2, 2. $LiAlH_4$/THF, 3. $NaNO_2$/H_2O/glacial acetic acid/75%. – iv) Cl_2/DMF/80°C/95%. – v) $P(OEt)_3$/100°C/5 h/98%. – vi) Li/NH_3/ether/*tert*-butyl alcohol/85%. – vii) Pd/C/MeOH/H_2/88%

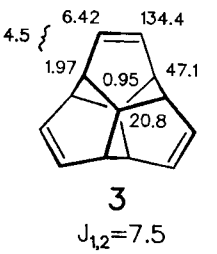


carefully controlled conditions (the temperature in the exothermic reaction must not exceed 80°C), the yield of **28** (m.p. 292–294°C) was 95%. Both the formation of bis(chloroenol phosphate) **29** as well as the one-pot reduction of the four substituents to provide diene (–)-**30** are patterned after the sequence leading from **20** to **19**. For purification, the colorless, crystalline (–)-**30** was sublimed (80°C/13 Torr) and then melts at 47–48°C. Dienes (–)-**30** and (+)-**30** [derived from (+)-**25**] are characterized by spectral (MS, UV, IR, ^{1}H and ^{13}C NMR) and rotational data (Figure 1). Their absolute configuration was established by catalytic hydrogenation to the respective *M*- and *P*-helical parent hydrocarbons (–)-**31** and (+)-**31** with $[\alpha]_D^{20} = -415$ (+422). Based on a rather low 15% optical enrichment, an $[\alpha]_D^{20} = -391$ had previously been extrapolated for (–)-**31**[5]. Under preparative aspects, it is relevant to note that both enantiomers **30** can be produced much more economically without prior separation of the mixture of diones **25–27** to afford an overall yield of 75% for the (three-step) Perkow route.





λ_{max}[nm](ε)	210	(1220)	215	(2720)
$\nu_{C=C}$[cm^{-1}]	1620		1610	
$[\alpha]_D^{20}$	-210	(+210)	-264	(+264)
$[\Phi]_D^{20}$	-332	(+332)	-449	(+450)



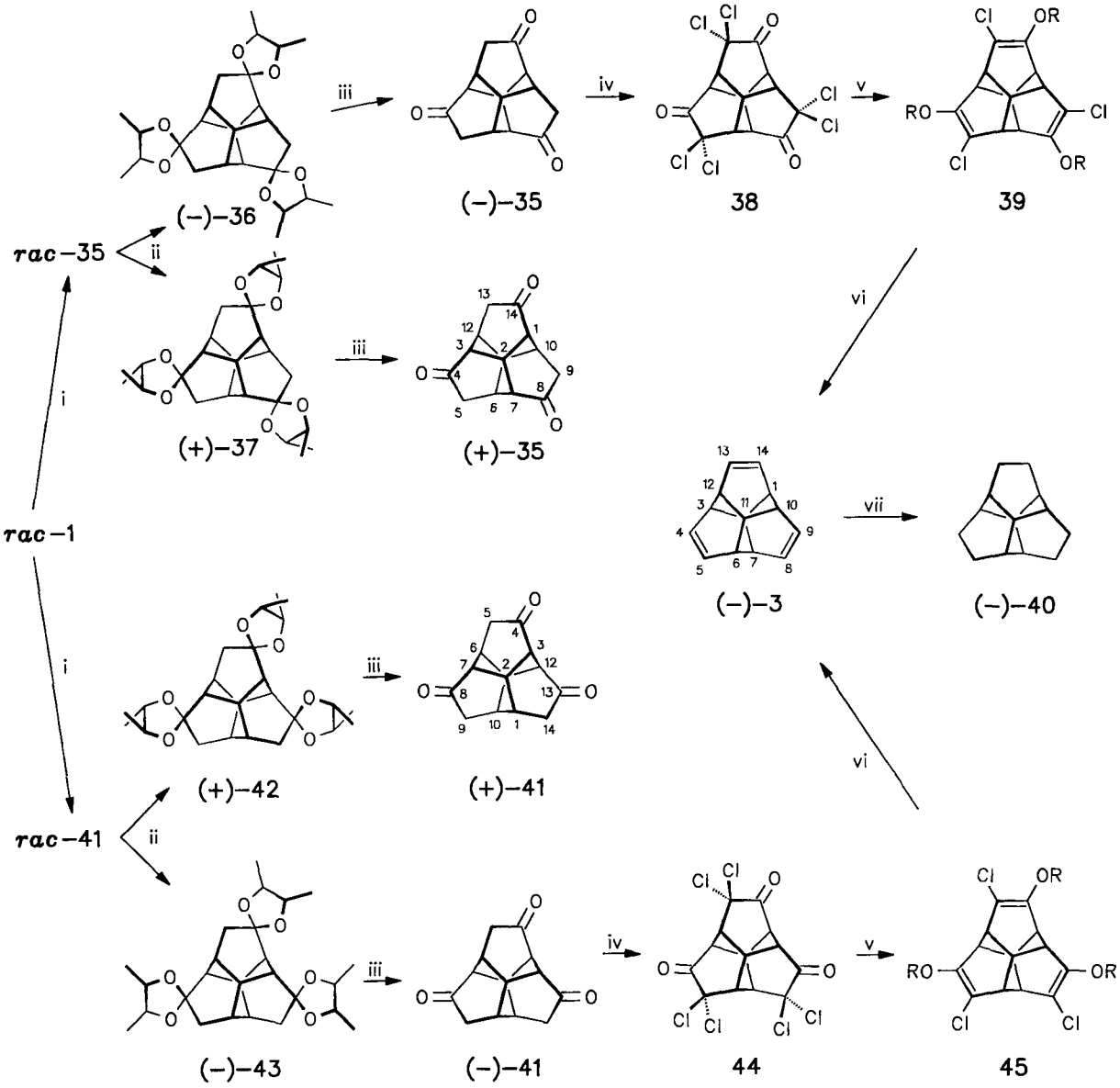
λ_{max}[nm](ε)	216	(4240)
$\nu_{C=C}$[cm^{-1}]	1605	
$[\alpha]_D^{20}$	-414	(+410)
$[\Phi]_D^{20}$	-754	(+747)

Figure 1. ^{1}H- and ^{13}C-NMR [$CDCl_3$, δ, *J* (Hz)], selected UV and IR data and optical rotation values for (–)-/(+)-**19**, (–)-/(+)-**30**, and (–)-/(+)-**3**

[2.2.2]Triblattanes

The design of the route to the (–)- [and (+)-] tritwistatrienes **3** depicted in Scheme 5 completely relied on the

Scheme 5. i) 1. $TMSCN/ZnI_2/CH_2Cl_2$, 2. $LiAlH_4/THF$, 3. $NaNO_2/H_2O$/glacial acetic acid/53%. — ii) (*R,R*)-2,3-Butanediol/*p*-toluenesulfonic acid/benzene/reflux/5 h/96–98%. — iii) Glacial acetic acid/H_2SO_4/reflux/12 h/84–90%. — iv) Cl_2/DMF/80°C/90–91%. — v) $P(OEt)_3$/100°C/5 h/97–100%. — vi) Li/NH_3/ether/*tert*-butyl alcohol/81%. — vii) Pd/C/MeOH/H_2/90%

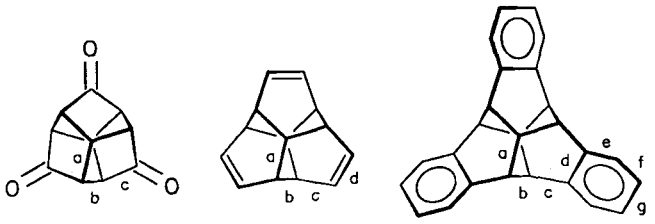


outcome of the threefold ring expansion in trione *rac*-**1** according to the Tieffeneau-Demjanow route as the only method suitable here. Without isolation and characterization of any intermediate, from the crude reaction mixture only a total of 54% of triones was obtained, separable into 17% of C_3-symmetrical *rac*-**35** (m.p. 245–247°C) and 37% of C_1-symmetrical *rac*-**41** (m.p. 236–237°C). For this reason, together with an only ca. 60% yield for the optical resolution of **1**, a total of 68% of optically pure material would have been lost after these transformations. It therefore seemed advisable to postpone the optical resolution to a subsequent stage. It could indeed be satisfactorily effected for the triacetals of *rac*-**35** and *rac*-**41** with (*R,R*)-2,3-butanediol. In case of *rac*-**35**, the separation of triacetals (−)-**36** and (+)-**37** by rapid chromatography turned out to be unproblematic and provided crystalline (−)-**36** and resinous (+)-**37** with a better than 96% diastereomeric purity each (^1H NMR). Their hydrolysis needed exact conditions but nevertheless provided the crystalline triones (−)-**35** and (+)-**35** [m.p. 245–247°C; $[\alpha]_D^{20} = -278$ (+276)] in high yields. In an analogous procedure and with a very similar result, the unsymmetrical trione *rac*-**41** was resolved via the triacetals (+)-**42** and (−)-**43** (diastereomeric purity ≥98%) into its crystalline enantiomers with $[\alpha]_D^{20} = -182$ (+178).

For the threefold olefination of the triketones **35** and **41** to the trienes **3**, the Shapiro method — as observed for **25** and in line with literature reports[29] — was again unsuitable (in a series of experiments at best 15% of **3**[24]). Once more the Perkow procedure proved to be the method of choice: Starting from the optically pure triones (−)-**35** and (−)-**41**,

in three steps via hexachlorotriones **38** (**44**) and tris(chloroenol phosphates) **39** (**45**), triene (−)-**3** became accessible in a total yield of 68%. To achieve this result, a high purity of **38** (**44**) is essential; small amounts of (e.g.) DMF of DMF · HCl caused a drastic reduction in yield. Colorless crystalline (−)-**3** melts at 106−107 °C (pentane) and sublimes at 90 °C/13 Torr. (+)-**35** and (+)-**41** were analogously transformed to (+)-**3**. The NMR spectra, which consist only of three ^1H and ^{13}C signals as demanded by D_3 symmetry, and other spectral data are given in Figure 1. If there is at all a trend in the $\pi \rightarrow \pi^*$ absorption, in the stretching frequencies and the ^{13}C-chemical shifts of the C=C double bonds, when proceeding from **19** via **30** to **3**, the differences are indeed only very small. In the ^1H-NMR spectra, the decreasing shift of the central bridgehead protons reveals an increasing anisotropic shielding by the C=C double bonds. The listed optical rotation values of (−)-**3** and (+)-**3** are derived from samples of (−)-**35** and (+)-**35** having an enantiomeric purity of at least 97−98%; the values of samples derived from (−)-**41** and (+)-**41** differ insignificantly [$[\alpha]_D^{20} = -410$ (+431)]. By hydrogenation of (−)-**3** to (−)-**40** ($[\alpha]_D^{20} = -621$) and of (+)-**3** to (+)-**40** ($[\alpha]_D^{20} = +617$), the absolute configurations at all stages of Scheme 5 were established. The literature value for (−)-**40**[5] of $[\alpha]_D^{20} = -567$ had been extrapolated from the value $[\alpha]_D^{20} = -250$ determined for a sample with 44% optical purity and thus has to be considered to be less reliable.

Triene **3** (pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene) is a novel member of the $(CH)_{14}$ family[30]. Consisting only of fused twisted cyclohexane boat units, it can be considered formally as a twice methyne-bridged (*Z*,*Z*,*Z*)-1,5,9-cyclododecatriene. In fact, the Ni(0) complex of the *E*,*E*,*E*-isomer of the latter is reported to have a topology very similar to that of **3**[31]. From the calculated[32] structure of **3**, as illustrated in Figure 2, and the relevant data for **1** and **4** it can be derived to what extent the nature of the diagonal bridges (C=O, C=C), modifies the twist (aa, quasi torsional angle) of the central bicyclo[2.2.2]octane core and the torsion around its periphery. The trend among the various H/H dihedral angles is nicely reflected in the corresponding vicinal H/H coupling constants. Some contributions to the molecular strain present in **3** can be seen in the appreciable lengthening of the bridging C−C single bonds (a, 1.56 Å) and a twisting of the C=C double bonds (cdc = 9.2°)[33].



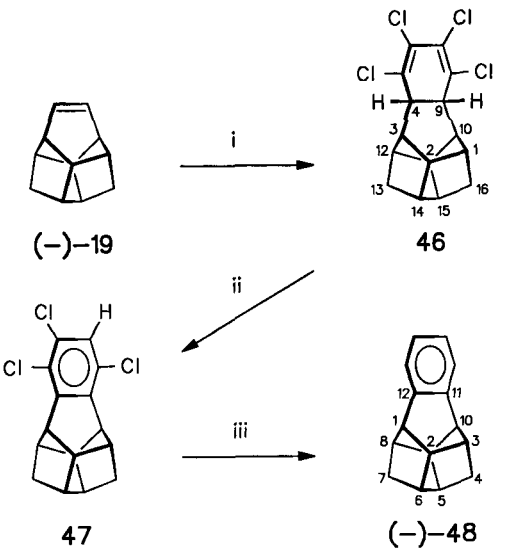
	1	3	4
a [Å]	1.59	1.56	1.55
b [Å]	1.57	1.55	1.55
c [Å]	1.53	1.51	1.51
aa [°]	40.0	25.7	27.8
aba [°]	60.9	40.7	40.4
cdc [°]	-	9.2	7.1
H*a*H [°]	21.6	33.0	33.5
H*b*H [°]	54.3	74.7	75.1
H*c*H [°]	-	2.9	-
H*d*H [°]	-	2.9	-
ΔH_f°	-49.5	78.3	399.1
E_{str}	63.2	47.6	51.3

Figure 2. Selected structural and energetic data (MM2/86, MMPi) of **1**, **3**, and **4**

Benzoannulated [2.1.1]-, [2.2.1]- and [2.2.2]Triblattanes

The enes **19**, dienes **30**, and trienes **3**, now available as pure enantiomers in preparative quantities, were utilized for the construction of the corresponding benzoannulated triblattanes, with the tribenzotritwistatrienes (−)-**4** and (+)-**4** as prominent representatives. The annulation of a benzene ring to a (poly)cyclic olefin can be effected by Diels-Alder methodology with tetrachlorocyclopentadienone acetal[34] or tetrachlorothiophene dioxide (TCTD)[35] as the standard reagents. In addition to being more reactive, the latter has the advantage – especially important for the formation of bis- and trisadducts – of keeping the number of potential isomeric reaction products smaller by cheletropic SO_2 elimination after the initial [4 + 2] addition[36]. TCTD was therefore applied for all annulations described below.

Scheme 6. i) Tetrachlorothiophene dioxide/toluene/110 °C/13 h/92%. – ii) KOH/EtOH/reflux/2 h/100%. – iii) Na/THF/*tert*-butyl alcohol/reflux/91%

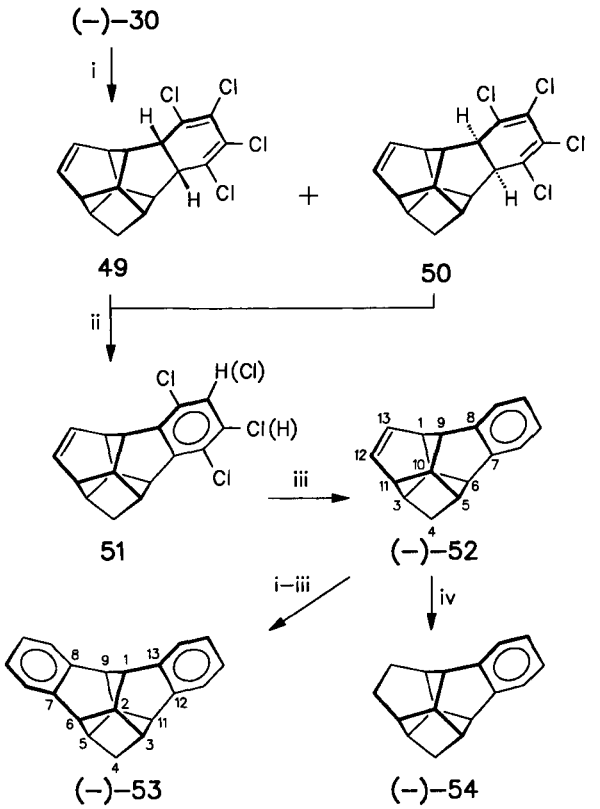


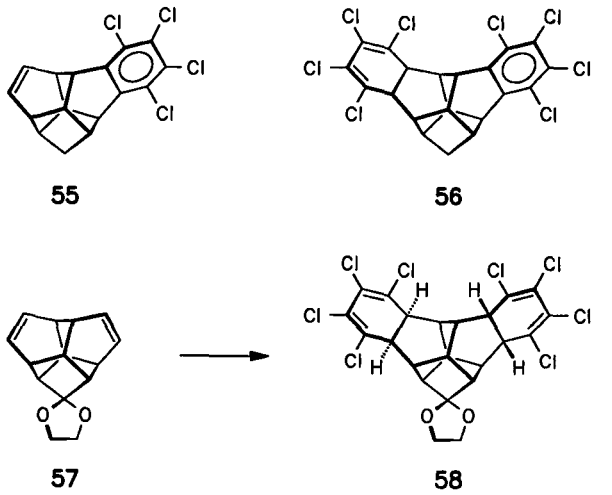
The reaction of TCTD with dimethanotwistenes **19** [(−)-**19** in Scheme 6] required relatively strong thermal activation, but nevertheless furnished cleanly the cyclohexadiene-annulated **46**. Informative in the completely assigned ^1H-NMR spectrum are the two allylic proton absorptions at $\delta = 3.23$ (9-H) and $\delta = 2.99$ (4-H) as well as the coupling constants $J_{2,3} = 6.3$, $J_{4,3} < 0.5$, $J_{4,9} = 13.5$ and $J_{9,10} = 5.0$ Hz. Aromatization by base treatment led selectively to the 1,2,4-

trichloro substitution pattern of **47** in line with earlier findings[37]. Dehalogenation of **47** under Gassman-Pape conditions[38] was straightforward. Based on (−)-**19**, the total yield of isolated benzodimethanotwistene (−)-**48** amounts to 82%. The antipode (+)-**48** was similarly produced from (+)-**19**. After sublimation (75°C/10^{-2} Torr) and crystallization, **48** melts at 100−101°C. Spectral and rotational data are listed in Figure 3. An analytically helpful spectroscopic feature of **48** and other benzoannulated triblattanes is the relatively low-field resonance of the benzylic protons which, in line with the calculated H,H dihedral angles (Figure 2), couple significantly only with the central bridgehead protons.

Diene (−)-**30** (Scheme 7), when exposed to a large excess of TCTD under otherwise identical conditions, added only one equivalent of the reagent. Even at higher reaction temperatures approaching the limit of the thermal stability of TCTD (150°C), no bisaddition took place. The 4:1 mixture of diastereomeric cyclohexadienes **49** and **50** was directly aromatized to an unseparable mixture of isomers **51**, which were reduced to benzomethanotwistadiene (−)-**52** (m.p. 59−60°C; $[\alpha]_D^{20} = -282$; $[\Phi]_D^{20} = -622$; ca. 65% based on (−)-**30**). Its hydrogenation gave (−)-**54** ($[\alpha]_D^{20} = -283$; $[\Phi]_D^{20} = -628$). In contrast to **49**/**50**, (−)-**52** proved to be sufficiently dienophilic to allow the repetition of the sequence consisting of TCTD addition, aromatization, and dehalogenation. By this way the C_2-symmetrical dibenzo-

Scheme 7. i) Tetrachlorothiophene dioxide/toluene/110°C/24 h/68−77%. − ii) KOH/EtOH/reflux/2 h/95−97%. − iii) Na/THF/*tert*-butyl alcohol/reflux/93−98%. − iv) Pd/C/MeOH/H_2/88%





methanotwistadiene (−)-**53** (m.p. 209−210°C) could be isolated in a comparably high total yield (ca. 70%). Analogously, (+)-**52** ($[\alpha]_D^{20} = +280$; $[\Phi]_D^{20} = +617$) and (+)-**53** were procured from (+)-**30**. Noteworthy spectral data and the optical rotation values for both enantiomers **53** are presented in Figure 3.

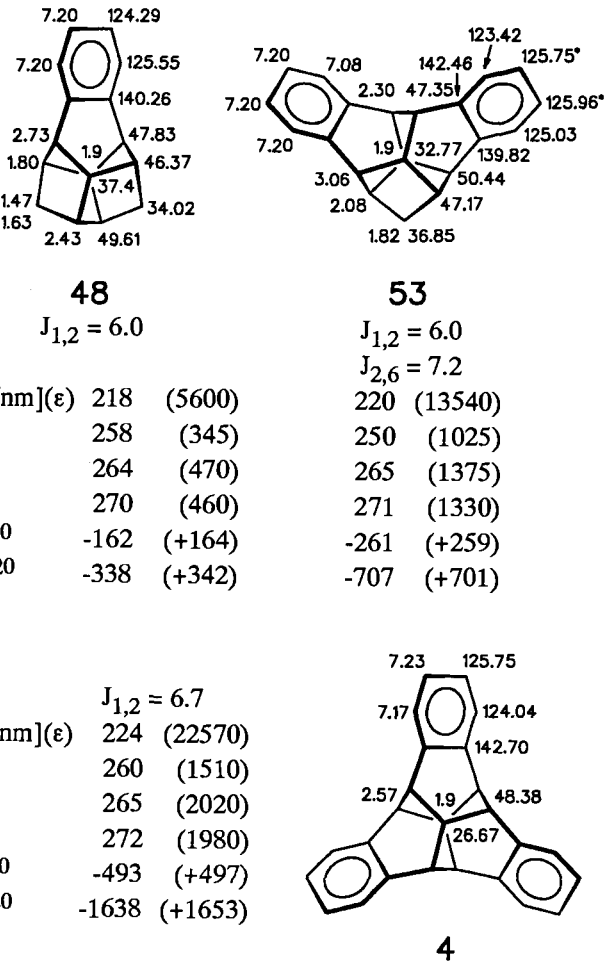
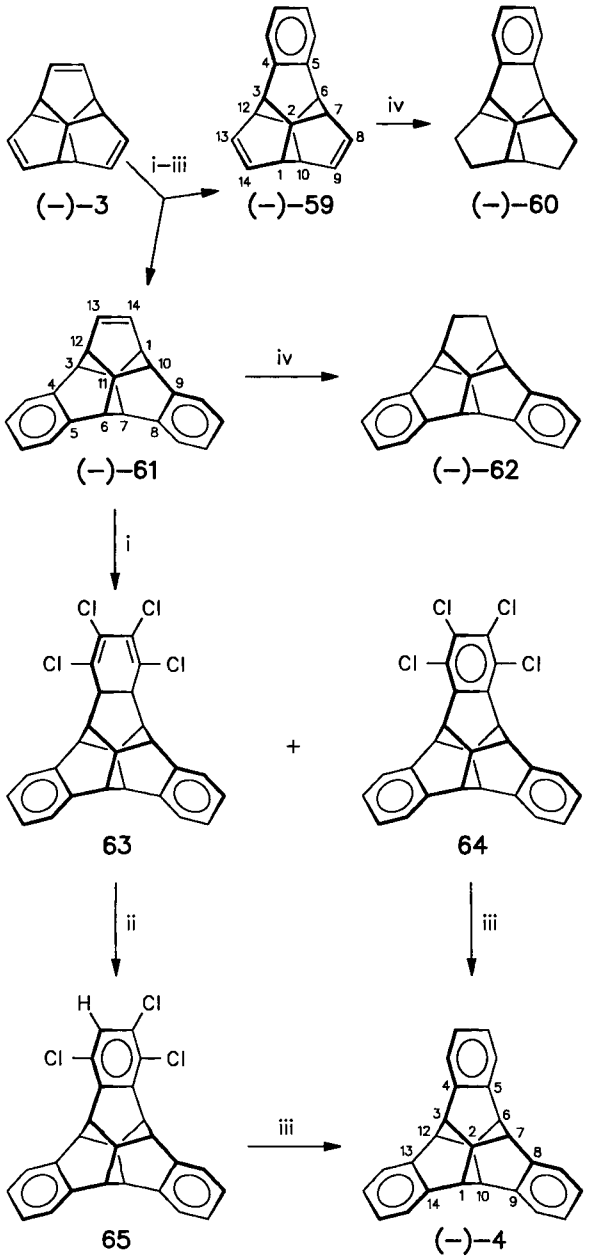


Figure 3. ^{1}H- and ^{13}C-NMR data [$CDCl_3$, δ, *J* (Hz)], UV data (cyclohexane), and optical rotation values of (−)-/(+)-**48**, (−)-/(+)-**53**, and (−)-/(+)-**4**

Two small side products (ca. 2%), which repeatedly appeared in addition to **49**/**50**, were originally suspected to be TCTD bisadducts. They were later identified, however, as **55** and **56**. It is interesting in this context to note that from the reaction of the [2.2.1]dienone acetal *rac*-**57** with TCTD under conditions effecting only monoaddition to [2.2.1]-diene **30**, a stereochemically uniform C_2-symmetrical bisadduct *rac*-**58** emerged in a respectable 75% yield.

In the context of a threefold annulation of (−)- and (+)-tritwistatriene **3** to arrive ultimately at the tribenzotriblattanes **4** [(−)-**4** in Scheme 8], the question a priori was open, whether threefold TCTD addition would occur at all, and to what extent the individual addition steps would be kinetically controllable. It was learned quickly that a trisaddition had no chance and that mono- and bisaddition could not be effected very selectively. Typically, in a run with three equivalents of TCTD and total consumption of **3**, ca. 50% of mono- and biscyclohexadienes in a ca. 1:2 ratio were isolated from polymers. After standard aromatization and dehalogenation of the crude mixture, benzotwistatriene (−)-**59** (oil, $[\alpha]_D^{20} = -463$; $[\Phi]_D^{20} = -1077$) and dibenzotwistatriene (−)-**61** (m.p. 178−179 °C; $[\alpha]_D^{20} = -488$; $[\Phi]_D^{20} = -1320$) were easily separable by column chromatography. (−)-**59** was hydrogenated to (−)-**60** ($[\alpha]_D^{20} = -454$, $[\Phi]_D^{20} = -1073$), and (−)-**61** to (−)-**62** ($[\alpha]_D^{20} = -435$, $[\Phi]_D^{20} = -1238$). Under somewhat more drastic conditions (boiling xylene, 48 h), (−)-**61** adds TCTD again to give a mixture (ca. 70%) of trisannulated **63** and **64**, which were separated and then both transformed independently into tribenzotritwistatriene (−)-**4** (m.p. 215−216 °C). Addition of an excess of (*R*)-1-anthryl-3,3,3-trifluoroethanol to the racemate caused a doubling of the ^{1}H- and ^{13}C-NMR signals for the inner bicyclo[2.2.2]octane core. This splitting had not been observed in the case of *rac*-**3**. Relevant spectral data and optical rotation values for (−)-**4** and for (+)-**4**, which was obtained from (+)-**3**, are presented in Figure 3.

Scheme 8. i) Tetrachlorothiophene dioxide/toluene/110 °C/3 d/69%. – ii) KOH/EtOH/reflux/2 h/95%. – iii) Na/THF/*tert*-butyl alcohol/reflux/80−91%. – iv) Pd/C/MeOH/H_2/79−80%



X-Ray Structure Determination of Tribenzotritwistatriene (−)-4

Compound (−)-**4** crystallized from CH_2Cl_2/PE 30/50 as clear colorless needles which proved suitable for the X-ray structure determination[39] (Figure 4). The molecular parameters measured for the three independent molecules in the asymmetric unit (Table 2) as well as for the chemically equivalent subunits of each molecule (as requested by D_3 symmetry) show such a high agreement that in Table 3 only the averaged values and their scatter are listed. For the comparison with **3** (cf. Figure 2) the data calculated with the MMPi[40] program are also given.

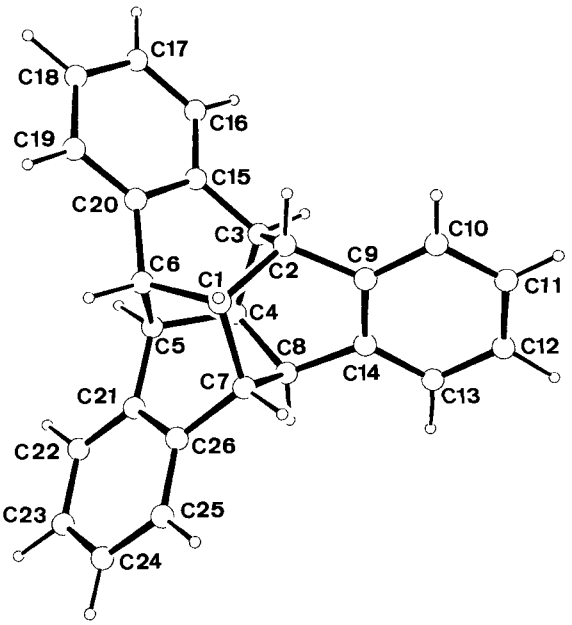


Figure 4. Structure of (−)-**4** with numbering scheme

Table 2. Crystallographic data and refinement parameters of (−)-**4**. Enraf Nonius CAD4 diffractometer, Mo-K_α radiation, graphite monochromator, ω-2Θ scan; structure solution: Multan[41], refinement: full matrix, C atoms anisotropic, H atoms with fixed isotropic temperature parameter: $U_{iso} = 0.02$ Å^2; SDP program system[42] and local programs

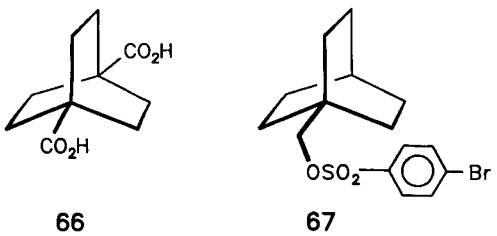
Formula	$C_{26}H_{20}$	T [°C]	-132
Molec. mass	332.4	D_{calc} [Mg·m^{-3}]	1.26
Crystal size [×10^{-1} mm]	4×5×5	(sinΘ/λ) max [Å^{-1}]	0.66
Space group	$P2_1$	Refl. unique	6856
Z	6	Refl. obs [I > 2.5σ (I)]	5338
a [Å]	18.539 (4)	Variables	883
b [Å]	6.308 (1)	*R*	0.045
c [Å]	23.844 (9)	max.Δρ [e·Å^{-3}]	0.27
β [°]	109.58 (2)		

Table 3. Averaged experimental (X-ray) and calculated (MMPi) bond lengths (Å), bond angles, and torsion angles of (−)-**4**. The structural data of three independent molecules and the chemically equivalent subunits of (−)-**4** (according to D_3 symmetry) have been averaged. The esd's are 0.005 Å, 0.3 and 0.4° (C–C–C–C) and 2° (H–C–C–H), respectively. The scatter of the averaging is given in brackets

bond	X-ray [Å]	MMPi [Å]	angle	X-ray [°]	MMPi [°]	angle	X-ray [°]	MMPi [°]
a	1.572 (5)	1.550	*aa*	107.8 (3)	107.9	*aba*	-42.2 (3)	40.4
b	1.578 (5)	1.546	*ab*	103.4 (3)	104.0	*cdc*	-11.0 (13)	7.1
c	1.504 (5)	1.508	*ac*	114.5 (5)	114.9	*cbc*	-161.5 (4)	159.5
d	1.398 (5)	1.397	*bc*	105.0 (5)	103.3	*HbH*	80.0 (3)	75.1
e	1.389 (5)	1.395	*cd*	112.5 (4)	112.3	*HaH*	-35.0 (4)	33.5
f	1.397 (5)	1.400	*ce*	126.7 (6)	127.2			
g	1.385 (5)	1.397	*de*	120.4 (3)	120.3			
			ef	119.0 (4)	119.6			
			fg	120.4 (6)	120.2			

The molecular core of (−)-**4**, the bicyclo[2.2.2]octane unit, is indeed forced into a strongly twisted conformation by the *o*-phenylene groups. The bonds a (Figure 4) parting from the bridgehead atoms C1 and C4, respectively, are twisted by 26.6° [quasi-torsional angle (C2–C1···C4–C3 etc.)]. For comparison, in bicyclooctane derivatives that are not conformationally restricted, the twist is only very small (**66**: 0.2°, after libration correction: 5.9°[43]; **67**: 3°[44]). The strong twisting is also responsible for the large torsion angle aba of −42.2° and for significant shortening of the contacts between the bridgehead atoms (C1···C4 2.557 Å compared with 2.597 Å for **66**[43] and 2.605 Å for **67**[44]). There are further short nonbonded intramolecular contacts (C2···C8 etc. 2.564, C2···C5 etc. 3.151 Å). The bond distances in the bicyclooctane part are especially lengthened (a 1.572, b 1.578 Å), whilst the bond angles are only slightly deformed.

MMPi force field calculations[32,40] essentially reproduce the structural parameters of bond lengths (Δ < 0.01 Å) and bond angles (Δ < 0.6°) with the notable exceptions of bond lengths a (Δ = 0.022 Å) and b (Δ = 0.032 Å), the bond angle bc (Δ = 1.7°), and the torsional angle aba (Δ = 1.8°).



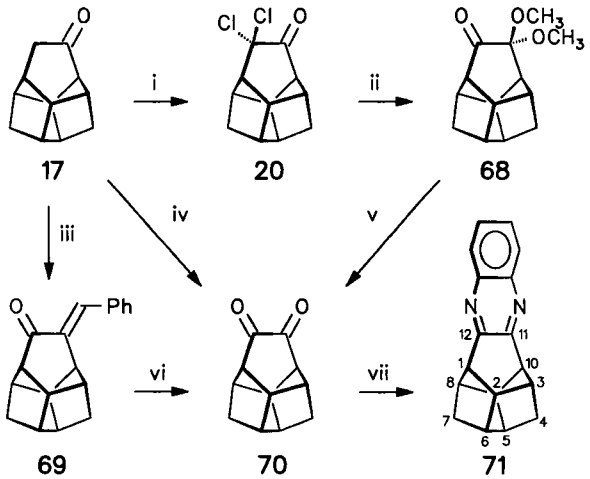
66 **67**

α-Diketotriblattanes

The hexone **5** with its three α-diketo chromophoric subunits[45] was the next and, may be, somewhat naively aspired target on our list of D_3-symmetrical [2.2.2]triblattanes. When the first attempts to prepare **5** by oxidation of the triones **35** and **41** did not even furnish trace amounts of **5**, again recourse was made to the lower homologues.

For the [2.1.1]dione **70**, the ketone **17** and its dichloro derivative **20** were readily available precursors. Even here, standard oxidation procedures (see below) applied to **17** led to complex product mixtures containing, after total conversion, only small quantities of the desired **70**. Clearly, the latter was consumed rapidly under the given reaction conditions. A yield of 14% of **70**, isolated chromatographically from a SeO_2 oxidation run was the best result in a series of experiments. Only slightly better was the result of hydrolysis experiments with **20**; neither $AgOCOCF_3$[46] nor sodium benzoate[47] – otherwise proven catalysts – promoted a selective conversion to **70**. Methanolysis in the presence of a high concentration of methylate ions generated dimethyl acetal **68** in acceptable 67% yield; yet, hydrolysis again caused a significant loss of material (31% dione **70**; 19% based on **20**). In the assumption that the conditions for generating α-diketones from keto ozonides would be better adaptable to highly reactive **70**, ketone **17** was condensed with benzaldehyde and the benzylidene compound **69** (91%) subsequently ozonized at −78°C in methanol solution. After addition of dimethyl sulfide[48] and warming up to room temperature, the oily residue was filtered through a pad of triethylamine-deactivated silica gel. From the yellowish oily fraction of monomers (61%), yellowish, highly labile crystals of **70** (m.p. ≈90–100°C) were obtained by sublimation at

Scheme 9. i) SO_2Cl_2/60°C/14 h/91%. – ii) MeONa/MeOH/reflux/8 h/67%. – iii) PhCHO/KOH/EtOH/91%. – iv) SeO_2/dioxane/H_2O/90°C/15%. – v) H_2SO_4/acetone/31%. – vi) 1. O_3/MeOH/−78°C, 2. CH_3SCH_3/61%. – vii) *o*-Phenylenediamine/MeOH/reflux/>90%

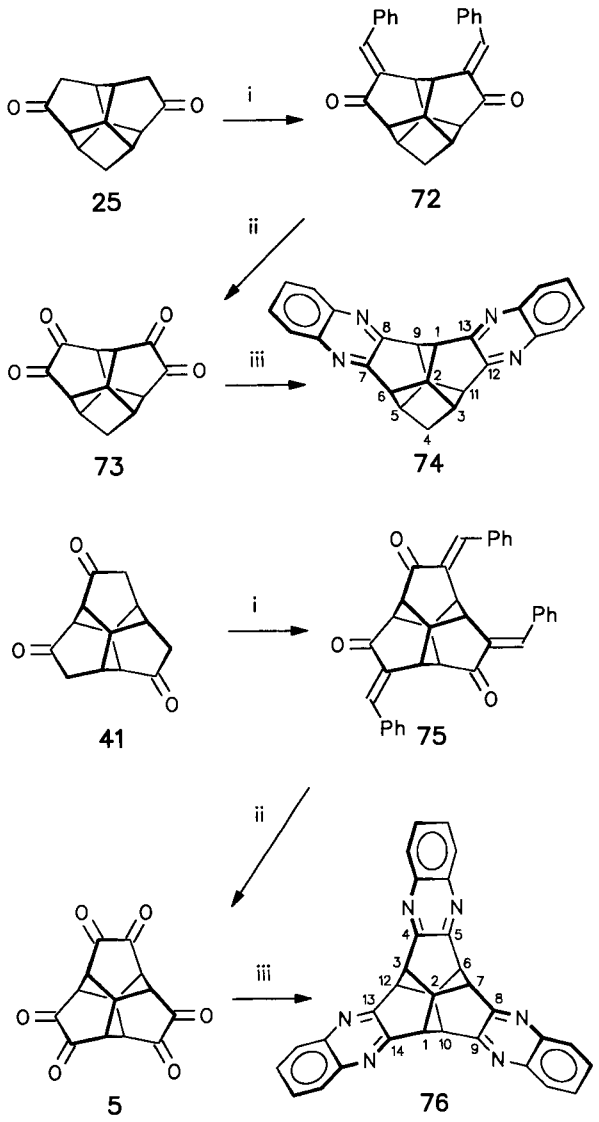


50 °C/10^{-2} Torr, which could not be purified further by crystallization. According to ^{1}H-NMR control, the purity of a freshly prepared sample of **70** was found to be better than 90%. When *o*-phenylenediamine (ca. 1.5 equivalents) was added to the ozonolysis solution directly after dimethyl sulfide quenching, followed by warming to ca. 60 °C, colorless crystalline *rac*-quinoxaline **71** (m.p. 146–147 °C, cf. **48**) was isolated in 95% yield.

[2.2.1]Tetrone **73** was not directly observable along any of the three routes tested for dione **70**, as **73** did not even survive the mild workup procedure following ozonolysis of dibenzylidenedione **72**. This latter C_2-symmetrical isomer was exclusively produced by condensation of **25** with benzaldehyde. As for **69** ($\delta = 7.48$), the chemical shift of the olefinic signal ($\delta = 7.58$) was taken as evidence for the *syn*-orientation of the olefinic hydrogen relative to the carbonyl function. After ozonolysis, reduction, and condensation with *o*-phenylenediamine, the *rac*-diquinoxaline **74** (m.p. 335–337 °C) was obtained in a still acceptable 55% yield.

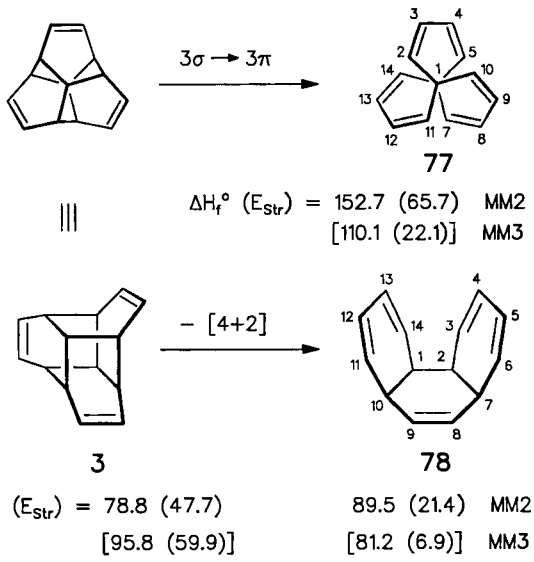
In view of the decreasing stability on going from **70** to **73**, the failure to observe hexone **5** in the above mentioned initial oxidation attempts using **35**/**41** becomes understandable. Problems to even indirectly identify **5** had to be expected. In fact, after ozonolysis of *syn,syn,anti*-tribenzylidenetrione *rac*-**75** in a methanol/CH_2Cl_2 mixture (for solubility reasons) and careful workup, the trisquinoxaline **76** (m.p. >370 °C, cf. **5**) was collected in only very small amounts (9%)[49]. The unsymmetrical *rac*-**75** was the exclusive product (81%) of the condensation of *rac*-**41** with an excess of benzaldehyde.

Scheme 10. i) PhCHO/KOH/EtOH/86% (81%, respectively). – ii) 1. O_3/MeOH/–78 °C, 2. CH_3SCH_3. – iii) *o*-Phenylenediamine/MeOH/reflux/55% (9%)



Thermolysis Studies

A preparative aspect attached early to the synthesis of triene *rac*-**3** was its potential of being a precursor for other members of the $(CH)_{14}$ hydrocarbon family[30,50], e.g. for bicyclo[4.4.4]tetradeca-2,4,7,9,11,13-hexaene (**77**)[51] by a $3\sigma \rightarrow 3\pi$ conversion with participation of the three bisallylic C,C bonds, or for tricyclo[8.4.0.$0^{2,7}$]tetradeca-3,5,8,11,13-pentaene (**78**) by a threefold degenerate [4 + 2] cycloreversion. The notations of **77** as a trisvinylogue of barrelene[52] and of **78** as a vinylogue of *syn-o,o'*-dibenzene[53] or as a special *cis*-bis-σ-homobenzene[54] partly circumscribe their attraction. Yet, as judged by the calculated (enthalpic and strain) energies of **3** (Figure 2), **77**, and **78**, and after closer inspection of the potential reaction pathways, the $3\sigma \rightarrow 3\pi$ isomerization to **77** was not considered to be likely. In contrast, however, the retro Diels-Alder pathway is well documented for lower homologues of the triblattanes, e.g. for basketene[55], homobasketene[56], and ansaradiene[57].



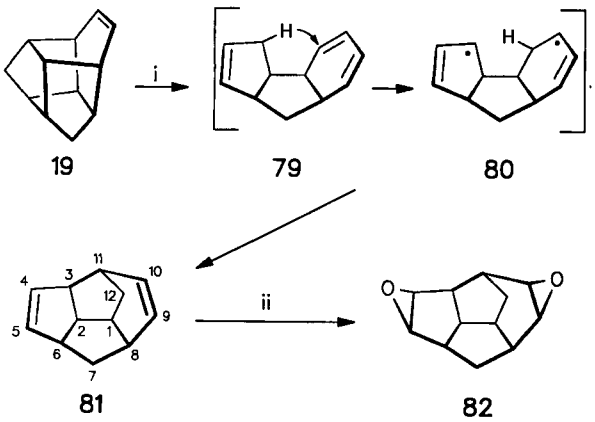
Here, only the results of explorative thermolysis experiments with selected unsaturated and benzoannulated triblattanes are reported. A detailed account of a thermolysis study with triene **3** will be subject of a forthcoming paper[58].

There was rather convincing evidence from the fragmentation patterns in the mass spectra of these triblattanes that

the [4 + 2] cycloreversion pathway should be prevailing generally.

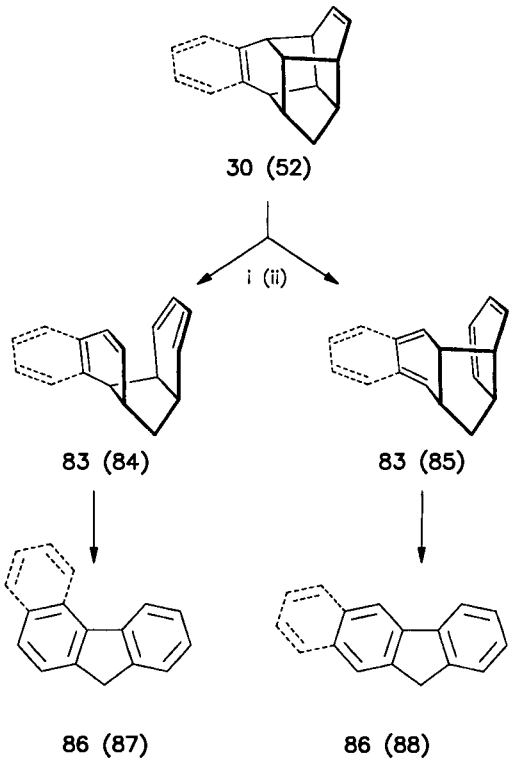
Dimethanotwistene *rac*-**19** (Scheme 11) – *m/z* (%): i.a. 158 (7) [M^+], 129 (12) [$M^+ - C_2H_5$], 117 (16) [$M^+ - C_3H_5$], 92 (100) [C_7H_8, $M^+ - C_5H_6$], 91 (59) [C_7H_7] – remained unchanged when heated to reflux in degassed, ca. 10^{-2} molar benzene solution; at higher temperatures (>150°C), isomerization (complex array of olefinic proton signals) and rapid polymerization set in. Under short-time vapor-phase thermolysis conditions at 420°C (contact time ca. 13 s, 25% conversion), a single isomer (MS) was slowly generated. At 590°C (ca. 90% conversion), 58% of this isomer, which was identified as the tetracyclic diene **81**, and 12% of an unknown component were isolated from polymers (GC/MS). Structure **81** is corroborated by ^{1}H- and ^{13}C-NMR data and further substantiated by the spectral data collected for the exclusively produced *exo,exo*-bisepoxide **82**. For the latter, a full assignment of ^{1}H-NMR signals was made possible by H-H correlated 2D-NMR spectra. A reasonable reaction path from **19** to **81** implies the [4 + 2] cycloreversion to the *syn*-tricyclo[6.4.0.0^{2,6}]dodecatriene **79** followed by an entropically promoted transannular 1,4-hydrogen transfer within the halfcage[56] and the final collaps of the resulting bisallylic diradical **80** in the direction of the most stable isomer of the three possible dienes.

Scheme 11. i) FVP/590°C/58%. – ii) *m*-CPBA/CH_2Cl_2/77%



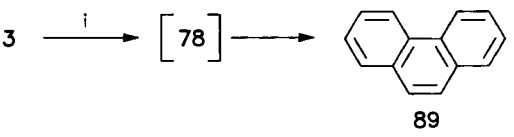
Methanoditwistadiene **30** (Scheme 12) – *m/z* (%): 128 (2), 92 (100) [C_7H_8, $M^+ - C_6H_6$], 91 (64) [C_7H_7]; under CI conditions *m/z* = 171 [$M^+ + 1$] – shows a kinetic stability comparable to that of **19**. At low-conversion (20–25%) thermolysis in degassed, ca. 10^{-2} M benzene solution (ampoule, 200°C) or upon flash vacuum thermolysis, two $C_{13}H_{14}$ isomers of **30** (GC/MS) were produced with ^{1}H multiplets at δ = 5.6–5.7 and 5.85–5.95 (butadiene units?), which are presumably due to **83** and an isomer arising from the latter by internal H shift. With increasing conversion, GC and ^{1}H-NMR monitoring revealed complex mixtures of at least 8 olefinic and benzenoid components. When the experiments were performed in the presence of a Pd/C catalyst known to dehydrogenate 1,2,3,4-tetrahydro-9*H*-fluorene[59], fluorene (**86**) was obtained in high (77%) yield. Under such dehydrogenative conditions (total conversion after 30 h), benzoannulated **52** delivered, in line with the relative stabilities of the intermediates **84** and **85**, an 8:1 mixture of the two annulated fluorenes **87** and **88**. The latter are identified by spectral comparison with commercially available authentic samples. The methylene proton singlets at δ = 4.04 (**87**) and 4.10 (**88**) allow a reliable integration.

Scheme 12. i) Pd/C/benzene/200°C/16 h/77%. – ii) Pd/C/benzene/220°C/30 h/67%



Quite similar to the step from **19** to **30**, the additional double bond in triene **3** (Scheme 13) – *m/z* (%): i.a. 182 (10) [M^+], 128 (12) [$M^+ - C_4H_6$], 104 (100) [$M^+ - C_6H_6$], 91 (94) [$C_7H_7^+$], 78 (38) [$C_6H_6^+$] – does not significantly alter its kinetic stability. Yet, under the dehydrogenative conditions applied to **30** and **52** (Pd/C, benzene, 10^{-2} M solution), phenanthrene (**89**) was formed with high selectivity (74% isolated)[60].

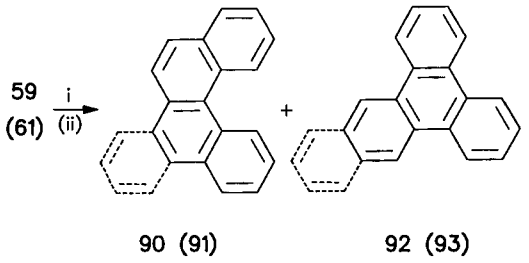
Scheme 13. i) Pd/C/benzene/200°C/20 h/74%



Scheme 14 presents the outcome of the analogously performed thermolysis experiments employing the benzoannulated derivatives **59** and **61**. The 1:4.6 ratio of **90** (chrysene) and **92** (triphenylene)[61] and the 40:1 ratio of **91** (benzo[*g*]chrysene) and **93** (benzo[*b*]triphenylene)[62], respectively, are in line with expectations based on the rel-

ative stability of the primary [4 + 2] cycloreversion products.

Scheme 14. i) Pd/C/benzene/220 °C/24 h/66%. – ii) Pd/C/benzene/260 °C/24 h/46%

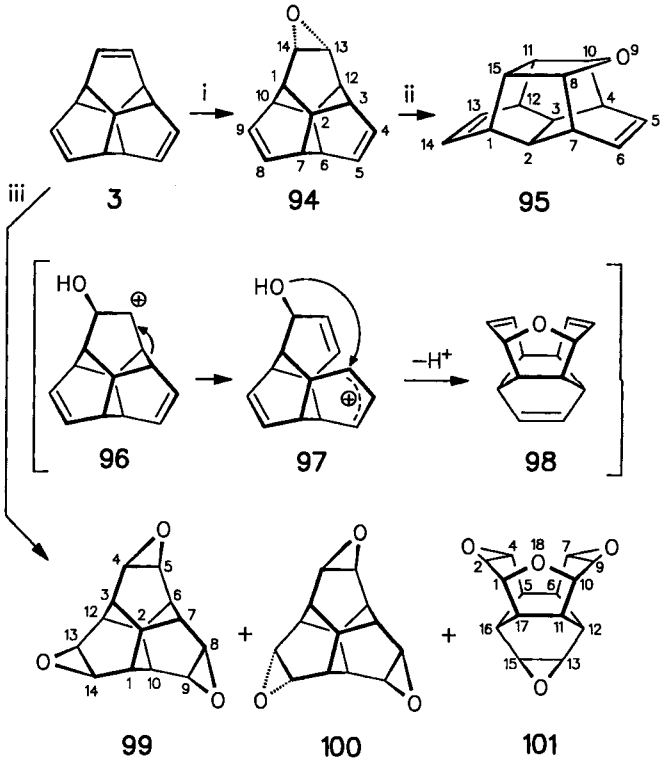


Tribenzotriene **4**, when heated in benzene solution, remained unchanged up to ca. 400 °C; still 40 h are needed for complete conversion under dehydrogenative reaction conditions. The main component (ca. 30%) in a complex product mixture is most probably (^{1}H NMR) naphtho[2,3-*g*]chrysene[63].

Epoxidation of *rac*-3

The epoxides derived from the various unsaturated triblattanes have been prepared[9] as versatile building blocks in the pursuit of directed polyfunctionalization of these skeletons[64]. Here we restrict the discussion to a preliminary oxidation study of triene **3**. We were interested in the selective monooxidation to **94** as a potential entry into an ionic pathway which could ultimately lead to derivatives of hexaene **77**. It was anticipated that the first expoxidation step would be faster than the second and the second faster than the third. As to the stereoselectivity in the formation of di- and trioxides, model-based judgements did not suggest a distinct preference for any one of the isomeric di- and trioxides. Since monooxide **94** turned out to be rather prone to acid-catalyzed rearrangement, benzoylpercarbamic acid[65] had to be employed as the oxidation agent. In a run with 1.4 equivalents of peracid, at 64% conversion of **3** a mixture of mono-, di-, and trioxides was produced (^{1}H NMR), from which 33% of **94** (m.p. 117–118 °C) was separated chromatographically. Until a ca. 30% conversion, **94** remained the only detectable product. The ^{1}H-NMR assignment implies the assumption that of the four allylic hydrogen signals, the conspicuously low-field one ($\delta = 3.18$) belongs to 3-H, which should be exposed to a paramagnetic influence of the epoxide oxygen[66]. In presence of a strongly acidic Amberlyst catalyst[67] or $BF_3 \cdot OEt_2$, **94** remained intact at room temperature, but at reflux temperature slowly and selectively rearranged into a C_s-symmetrical isomer, which was not triene ether **98** – the cationic intermediates **96** and **97** imply a regiospecific epoxide opening – but the diene ether **95**. This latter structure is based on the completely analyzed ^{1}H- and ^{13}C-NMR spectra (Figure 5) and on close similarities of the latter with those of an earlier described analogous $(CH)_{14}$ structure containing a cyclobutane instead of a tetrahydrofuran ring[30d]. The course of its formation is still open to speculation.

Scheme 15. i) Benzoylpercarbamic acid/CH_2Cl_2/room temp./3 h/36%. – ii) Amberlyst 15 (strongly acidic, H^+ form)/CCl_4/70 °C/8 h/77%. – iii) Benzoylpercarbamic acid/CH_2Cl_2/reflux/12 h/61%



The perepoxidation of **3** is expectedly slow and needs a large excess (ca. 5 equiv.) of oxidant to achieve total conversion. Two fractions of products, distinguishable by TLC, were separated by column chromatography and identified as the unsymmetrical trioxide **100** (53%, m.p. 189–190 °C) and a mixture (9%, ca. 1:1) of C_3 trioxide **99** (m.p. 196–198 °C) (Figure 5) and C_s trioxy ether **101** (m.p. 252–254 °C); the two latter compounds could be separated by fractional crystallization from ether/ethyl acetate. It was established by treatment of the corresponding trisepoxides with acids/acidic catalysts that **101** is not derived either from **99** or from **100**. Structure **101**, which can be reasonably imagined as being the sterically preferred trisepoxidation product of **98**, rests mainly on MS and NMR data including a number of vicinal and long-range H,H and C,H couplings.

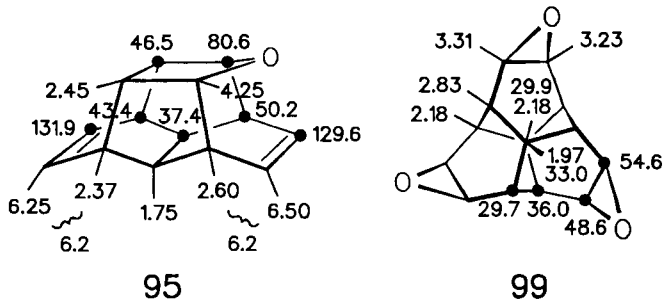
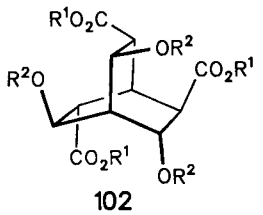


Figure 5. NMR data ($CDCl_3$) of **95** and **99**

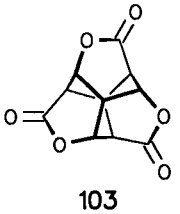
Resumee and Outlook

The primary goal of this project, the construction of novel gyrochiral D_3-symmetrical molecular skeletons with special bonding and chiroptical features, has been realized to a large part. For the – only seemingly trivial – threefold cyclopentanone → cyclohexanone ring expansion in trishomocubanetrione *rac*-**1**, for the optical resolution of the resulting [2.2.2]triones, for the threefold olefination, and for the threefold benzoannulation, expeditious and rather economical procedures have been developped. Thus, the preparation of gram quantities of the respective optically pure [2.2.2]triblattanes (**3**, **4**) is now unproblematic. The same holds true for the unsaturated and benzoannulated [2.1.1]- and [2.2.1]homologues. Of the triblattanes containing α-diketo bridges, though, only the [2.1.1]dione **70** was found to be stable enough to allow its isolation. In the thermolysis of unsaturated or benzoannulated mono-, di- and triblattanes, [4 + 2] cycloreversion is generally the preponderant, if not exclusive, stabilization pathway. Yet, the aspired primary cycloreversion products are kinetically labile under the thermolysis conditions. Further utilization especially of **1** and **3** in synthesis is within sight. Thus, the aim to synthesize a hexa-substituted bicyclo[2.2.2]octane as e.g. **102** is substantiated by a practically quantitative oxidation of **1** to the two possible trislactones, e.g. **103**. Whilst we have not yet found a convenient route leading from **3** to the C_3 trisamine **104**[68], this type of structural manipulation has been realized, however, using the lactone oxime of monoketone **6**, and the amine *rac*-**105** was resolved into the optically pure C_2 bases[9].

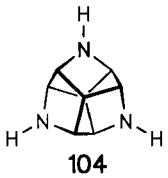
The question of π,π-homoconjugative interaction along the molecular periphery of unsaturated triblattanes as analyzed by PE spectroscopy is subject of the following paper[7]. The π,π* absorptions of the olefins **19**, **30**, and **3** (Figure 1) indeed reveal very small bathochromic shifts not observed for the α band of the corresponding benzoannulated compounds **48**, **53**, and **4** (Figure 3)[69].



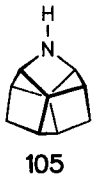
102



103



104



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Experimental

Melting points (m.p.): Bock Monoscop M. – Anal. TLC: Merck silica gel plates with F_{254} indicator. – CC: Silica gel MN 60 from Macherey & Nagel, 0.06–0.20 mm (column dimensions ∅ [mm] × *l* [cm] relatively to separated material if not specified further: 0–100 mg: 15 × 15 or 20, 100–500 mg: 20 × 15 or 30, 500 mg – 2 g: 30 × 30, for flash chromatography 0.04–0.06 mm. – MPLC: Pump Lewa FL 1, refractometer Knauer 5100, Knauer UV-Vis filter photometer 0.4 mm/flux. – GC: Varian 3700, glass capillary column 25 m, SE 30, OV 17, FID; integrator Varian CDS 111. – PE 30/50 = petroleum ether (b.p. 30–50°C). – Optical rotation data: Perkin Elmer 241 polarimeter, cell 10 cm. – IR: Perkin Elmer 457, Philips PU 9706. – UV: Perkin Elmer Lambda 15. – ^{1}H NMR: Bruker AC 250, AM 400. – ^{13}C NMR: Bruker AC 250, AM 400. Chemical shifts relative to TMS (δ = 0), coupling constants in Hz; if not specified differently, the 250-MHz (^{1}H) and 100.6-MHz (^{13}C) spectra in $CDCl_3$ are given; assignments marked by * can be interchanged. – MS: Finnigan MAT 44S, EI 70 eV if not specified differently.

(±)-4-Methylenepentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (*rac*-**7**): To a suspension of methyltriphenylphosphonium bromide (8.7 g, 24.4 mmol) in dry benzene (150 ml) under N_2, a 2.5 M *n*-butyllithium solution in hexane (9.75 ml, 24.4 mmol) is added dropwise within 15 min. After stirring at room temp. for 30 min, followed by refluxing for 30 min, *rac*-**6** (1.50 g, 9.4 mmol) in dry benzene (15 ml) is added dropwise to this solution, followed by further refluxing for 3 h. After cooling to room temp. and addition of water (30 ml), the aqueous phase is extracted with PE 30/50 (2 × 50 ml). The organic phase is washed with NH_4Cl solution, dried ($MgSO_4$), and concentrated in vacuo. The oily residue is triturated in warm PE 30/50 (2 × 50 ml), and the obtained solution is filtered through silica gel. After concentration at 100 Torr and distillation of the residue at 51–54°C/1 Torr, *rac*-**7** is obtained as a colorless oil with a characteristic flavor (1.00 g, 68%). – IR (neat): $\tilde{\nu}$ = i.a. 3060 cm^{-1} (=C–H), 2940 (C–H), 2855 (C–H), 1675 (C=C). – ^{1}H NMR: δ = 1.35 and 1.45 (AB, 7-, 11-H), 2.05 (m, 2-, 9-H), 2.14 (m, 1-, 3-, 5-, 6-, 8-, 10-H), 4.62 (s, 4′-H). – ^{13}C NMR: δ = 34.1 (C-7, -11), 42.6 (C-2, -9), 46.8, 47.4 (C-1, -6, -8, -10), 51.3 (C-3, -5), 97.3 (C-4′), 157.9 (C-4). – $C_{12}H_{14}$ (158.2): calcd. C 91.08, H 8.92; found C 90.72, H 8.73.

(±)-Spiro[cyclopropane-1,4′-pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane] (*rac*-**8**): A mixture of *rac*-**7** (500 mg, 3.2 mmol) and benzyltriethylammonium chloride (50 mg) in $CHCl_3$ (30 ml) and sodium hydroxide solution (50%, 20 ml) is stirred vigorously with ice cooling. After dilution with water (30 ml) and separation of the phases, the aqueous phase is extracted with $CHCl_3$ (50 ml). The organic phase is washed with dild. hydrochloric acid and satd. $NaHCO_3$ solution, dried ($MgSO_4$), and, after filtration through silica gel, concentrated in vacuo. The oily residue is distilled at 106°C/1 Torr and the distillate in dry ether (15 ml) is added within 10 min to a stirred solution of lithium (200 mg, 28.8 mmol) in liquid ammonia (ca. 30 ml, –40°C) with exclusion of moisture. After 2 h, solid NH_4Cl is added until decolorization is achieved and, after evaporation of ammonia, the residue is hydrolysed with water (50 ml). The dried ($MgSO_4$) *n*-pentane extracts are filtered through silica gel and concentrated in vacuo. The residue is distilled at 55–60°C/1 Torr to give *rac*-**8** as a colorless oil (410 mg, 74%). – IR (neat): $\tilde{\nu}$ = i.a. 3055 cm^{-1} (C–H), 2940 (C–H), 2860 (C–H). – ^{1}H NMR: δ = 0.41 (mc, 2-, 3-H), 1.28 (br. d) and 1.37 (m + br. d, 3′-, 5′-, 7′-, 11′-H), 2.01 (m, 2′-, 9′-H), 2.08 (m, 1′-, 8′-H), 2.31 (6′-, 10′-H). – ^{13}C NMR: δ = 5.5 (C-2, -3), 33.5 (C-7′, -11′), 34.2 (C-4′), 42.7, 47.9 (2×) and 54.3 (C-1′, -2′, -3′, -5′, -6′, -8′, -9′, -10′). – $C_{13}H_{16}$ (172.3): calcd. C 90.64, H 9.36; found C 90.47, H 9.49.

(±)-4,7-Bismethylenepentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (*rac*-**10**): (cf. *rac*-**7**). – To a suspension of methyltriphenylphosphonium bromide (6.5 g, 18.2 mmol) in dry benzene (110 ml) under N_2 a solution of 2.5 M *n*-butyllithium in hexane (7.2 ml, 18.0 mmol) is added. After stirring at room temp. and under reflux for 30 min each, *rac*-**9** (600 mg, 3.4 mmol) in dry THF (20 ml) is added dropwise to this solution, and refluxing is continued for another 3 h. After workup, the crude residue is distilled at 55°C/0.8 Torr to give *rac*-**10** as a colorless oil (410 mg, 70%) with characteristic flavor. – IR (KBr): $\tilde{\nu}$ = i.a. 3060 cm^{-1} (=C–H), 2960 (C–H), 2855 (C–H), 1675 (C=C). – ^{1}H NMR: δ = 1.46 (br. s, 11-H), 2.27 (br. s, 1-, 2-, 3-, 5-, 6-, 8-, 9-, 10-H), 4.66 (s,

4′-, 7′-H). – ^{1}H NMR (C_6D_6): δ = 1.26 (br. s, 2H), 2.08–2.20 (m, 6H), 2.29 (m, 2H), 4.75 (s, 4H). – ^{13}C NMR: δ = 34.8 (C-11), 43.4 (C-2, -9), 46.6 (C-1, -10), 50.1, 50.7 (C-3, -5, -6, -8), 98.1 (C-4′, -7′), 157.3 (C-4, -7). – $C_{13}H_{14}$ (170.3): calcd. C 91.71, H 8.29; found C 91.50, H 7.93.

(±)-Dispiro[cyclopropane-1,4′-pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-7′,1″-cyclopropane] (*rac*-**11**): *rac*-**10** (200 mg, 1.2 mmol) and benzyltriethylammonium chloride (50 mg) in $CHCl_3$ (20 ml) are stirred vigorously with sodium hydroxide solution (50%, 20 ml) for 16 h. After workup as above, a solution of the crude product in dry THF (10 ml) is added dropwise to lithium (100 mg, 14.4 mmol) in liquid ammonia (ca. 20 ml) and stirred at −40°C for 2 h. After workup as above and distillation at 94°C/1.5 Torr, *rac*-**11** is obtained as a colorless oil (160 mg, 67%). – IR (KBr): ṽ = i.a. 3055 cm^{-1} (C–H), 2940 (C–H), 2860 (C–H). – ^{1}H NMR: δ = 0.41 (mc, 2-, 3-, 2″-, 3″-H), 1.34 (br. s, 11-H), 1.44 (m, 3′-, 8′-H), 1.67 (m, 5′-, 6′-H), 2.20 (m, 2′-, 9′-H), 2.38 (m, 1′-, 10′-H). – ^{13}C NMR: δ = 5.6 (t, C-2, -2″), 5.8 (t, C-3, -3″), 30.8 (s, C-4′, -7′), 33.7 (t, C-11′), 43.9 (d, C-2′, -9′)*, 48.0 (d, C-1′, -10′)*, 54.27 (d, C-3′, -8′)*, 54.28 (d, C-5′, -6′)*. – $C_{15}H_{18}$ (198.3): calcd. C 90.85, H 9.15; found C 90.89, H 8.98.

(±)-4,7,11-Trismethylenepentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (*rac*-**2**): To a suspension of methyltriphenylphosphonium bromide (8.6 g, 24.1 mmol) in dry benzene (130 ml) under N_2 is added a solution of 2.5 M *n*-butyllithium in hexane (9.6 ml, 24.0 mmol), followed by stirring at room temp. for 30 min and under reflux for another 30 min. After dropwise addition of *rac*-**1** (500 mg, 2.7 mmol) in dry THF (10 ml), the suspension is refluxed for 3 h. Workup as above gives a crude solid (400 mg), which crystallizes in the cold (ethanol) and sublimes at 80°C/15 Torr to give *rac*-**2** as colorless plates (350 mg, 72%), m.p. 53–54°C. – IR (KBr): ṽ = i.a. 3060 cm^{-1} (=C–H), 2965 (C–H), 1675 (C=C). – ^{1}H NMR: δ = 2.41 (br. s, 1-, 2-, 3-, 5-, 6-, 8-, 9-, 10-H), 4.70 (s, 4′-, 4″-, 7′-, 7″-H). – ^{1}H NMR (C_6D_6): δ = 2.31 (br. s, 8H), 4.72 (s, 6H). – ^{13}C NMR: δ = 44.0 (C-2, -9), 50.0 (C-1, -3, -5, -6, -8, -10), 99.0 (C-4′, -7′, -11′), 156.6 (C-4, -7, -11). – $C_{14}H_{14}$ (182.3): calcd. C 92.26, H 7.74; found C 92.21, H 7.65.

(±)-Trispiro[pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,1′:7,1″:11,1‴-triscyclopropane] (*rac*-**12**): *rac*-**2** (360 mg, 1.97 mmol) and benzyltriethylammonium bromide (100 mg) in $CHCl_3$ (60 ml) in an ice bath are mixed with sodium hydroxide solution (50%, 40 ml) and stirred for 20 h while warming up to room temp. After dilution with CH_2Cl_2 (40 ml), the phases are separated, the organic phase is washed with dild. hydrochloric acid and satd. $NaHCO_3$ solution (40 ml each), dried ($MgSO_4$), and concentrated in vacuo. After filtration through silica gel (cyclohexane/ethyl acetate, 9:1, R_f = 0.58), a crude solid (850 mg, 100%) is obtained, which is added together with *tert*-butyl alcohol (4.42 g, 59.7 mmol) in dry ether (30 ml) at −78°C to a solution of lithium (425 mg, 60.7 mmol) in liquid ammonia (ca. 60 ml). After stirring at this temp. for 2 h, NH_4Cl is added until decolorization is achieved, and the ammonia is evaporated by warming to room temp. The residue is hydrolyzed with water (80 ml), the layers are separated, and the aqueous phase is extracted with PE 30/50 (80 ml). The organic phase is washed with water (2 × 80 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue sublimes at 80°C/10^{-2} Torr to give *rac*-**12** as colorless crystals (360 mg, 81%), m.p. 99–100°C. – IR (KBr): ṽ = i.a. 3056 cm^{-1} (C–H), 2982 (C–H), 2954 (C–H), 1462 (CH_2). – ^{1}H NMR: δ = 0.37 (m, 2′-, 2″-, 2‴-H), 0.48 (m, 3′-, 3″-, 3‴-H), 1.75 (m, 1-, 3-, 5-, 6-, 8-, 10-H), 2.39 (m, 2-, 9-H). – ^{13}C NMR: δ = 5.6 (C-2′, -2″, -2‴, -3′, -3″, -3‴), 30.8 (C-4, -7, -11), 44.8 (C-2, -9), 54.3 (C-1, -3, -5, -6, -8, -10). – $C_{17}H_{20}$ (224.3): calcd. C 91.01, H 8.99; found C 90.07, H 8.95.

(M)-Ethyl Diazo(4-hydroxypentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undec-4-yl)acetate [(*M*)-**13**]: A solution of (−)-**6** (1.2 g, 7.5 mmol) and ethyl diazoacetate (860 mg, 7.5 mmol) in dry ether/THF (3:1, 40 ml) under N_2 and with exclusion of moisture is cooled to −78°C. A solution of 2.5 M *n*-butyllithium in hexane (3.0 ml, 7.5 mmol), diluted with ether (5 ml) and cooled to −78°C, is added with stirring within 20 min. The cold bath is taken away, and at −30°C a cooled mixture of glacial acetic acid (450 mg, 7.5 mmol) in ether (10 ml) is added. After warming up to room temp., the precipitated lithium acetate is filtered off and the filtrate concentrated in vacuo. Chromatography of the crude oily product (silica gel, ether) provides pure (^{1}H NMR) (*M*)-**13** as a yellowish oil (2.0 g, 97%). – IR (neat): ṽ = i.a. 3350 cm^{-1} (OH), 2950 (C–H), 2860 (C–H), 2075 (N=N), 1690 (C=O). – ^{1}H NMR: δ = 1.31 (t, 3H, CH_3), 1.33 (br. d, 2H), 1.41 (br. d, 1H), 1.49 (br. d, 1H), 1.97 (m, 1H), 2.03 (m, 1H), 2.18 (m, 3H), 2.27 (m, 2H), 2.76 (m, 1H), 3.40 (br. s, OH), 4.26 (q, 4H, CH_2-CH_3). – $C_{15}H_{18}N_2O_3$ (274.3): calcd. C 65.68, H 6.61, N 10.21; found C 65.53, H 6.68, N 10.50.

(M)-Ethyl 11-Oxopentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecane-12-carboxylate [(*M*)-**14**]: To a stirred solution of (*M*)-**13** (1.0 g, 3.6 mmol) in dry CH_2Cl_2 (100 ml) at −78°C under N_2 is added a catalytic amount of π-allylpalladium(I) chloride dimer. After warming up to room temp. (20 h), the solution is concentrated in vacuo and the brown residue filtered through silica gel (ether). (*M*)-**14** is obtained as a yellowish oil (860 mg, 96%). – IR (neat): ṽ = i.a. 2955 cm^{-1} (C–H), 2865 (C–H), 1720 (C=O), 1965 (C=O). – ^{1}H NMR: δ = 1.20–1.35 (m, 5H), 1.49 (m, 1H), 1.63 (br. d, 1H), 1.96–2.59 (series of m, 8H), 3.28 (d, *J* = 3.3, 1H), 3.37 (d, *J* = 1.5, 1H), 4.15–4.28 (m, 2H). – $C_{15}H_{18}O_3$ (246.3): calcd. C 73.15, H 7.37; found C 73.31, H 7.39.

(1S,2S,3R,5S,6S,8R,9R,10S)-(−)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecan-11-one [(−)-**17**]

From (*M*)-**14**: (*M*)-**14** (1.8 g, 7.3 mmol), $NaHCO_3$ (100 mg), and water (25 ml) are heated with stirring in a glass pressure tube with a safety valve to 150°C for 1 h. From the dried ($MgSO_4$) organic phase as yellowish oil (1.3 g, 100%) is obtained, which crystallizes without solvent. After sublimation at 90°C/15 Torr: colorless crystals of (−)-**17**.

From (−)-**6**: Trimethylsilyl cyanide (TMSCN) (0.70 ml, 554 mg, 5.6 mmol) is added to (−)-pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-4-one [(−)-**6**] (800 mg, 5.0 mmol, $[\alpha]_D^{20}$ = −101 (ref.[15] $[\alpha]_D^{20}$ = −98.8) and dry ZnI_2 (15 mg) in dry CH_2Cl_2 (1 ml) at 0°C under N_2. After stirring at room temp. for 12 h, the solvent and excess of reagent are removed in vacuo, the residue is dissolved in dry THF (15 ml), and this solution is added dropwise at 0°C under N_2 to a stirred suspension of $LiAlH_4$ (300 mg, 7.91 mmol) in dry THF (40 ml). After stirring at reflux temp. for 5 h and cooling to 0°C water (0.8 ml), sodium hydroxide solution (15%, 0.4 ml) and again water (1.2 ml) are added and stirring is continued until decolorization occurs. The solid material is sucked off, washed with CH_2Cl_2, and the combined filtrates are concentrated in vacuo. The residue is dissolved in a mixture of water (50 ml), glacial acetic acid (3 ml), and concd. hydrochloric acid (0.5 ml) and the solution cooled to 0°C. After dropwise addition of $NaNO_2$ (650 mg, 9.42 mmol) in water (15 ml) and warming to room temp. within 12 h, CH_2Cl_2 (100 ml) is added, the layers are separated and the organic phase is washed with satd. $NaHCO_3$ solution (2 × 20 ml). After drying ($MgSO_4$) and concentration in vacuo a yellowish oil (740 mg) is isolated, after distillation at 90°C/13 Torr, 705 mg (81%) of crystalline (−)-**17** is obtained, m.p. 131–132°C (ref.[16] 132–133°C). $[\alpha]_D^{20}$ = −221 (*c* = 0.26 in $CHCl_3$), $[\Phi]_D^{20}$ = −381. – ^{1}H NMR: δ = 1.23 (br. d, 4-H)*, 1.28 (br. d, 7-H)*, 1.47 (br. d, 4′-H)*, 1.61 (br. d, 7′-H)*, 1.85 (m, 1H), 1.93 (br. d, 1H), 2.02 (m, 1H), 2.10 (m, 1H), 2.24 (m, 1H), 2.30 (m, 2H), 2.37 (m, 3H). – ^{13}C NMR: δ = 34.4 (C-4)*, 34.8 (C-7)*, 36.9, 37.6 (C-12), 40.5, 40.6, 41.1, 41.3, 47.7, 48.8, 55.6, 216.7 (C-11).

(1R,2R,3S,5R,6R,8S,9S,10R)-(+)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecan-11-one [(+)-**17**]: $[\alpha]_D^{20}$ = 219 (*c* = 0.47 in $CHCl_3$), $[\Phi]_D^{20}$ = 337.

Diethyl (M)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-en-11-yl Phosphate [(*M*)-**18**]: To a stirred solution of diisopropylamine (300 mg, 3.0 mmol) in dry THF (5 ml) under N_2 and with exclusion of moisture is added a solution of 2.5 M *n*-butyllithium in hexane (1.2 ml, 3.0 mmol) at 0°C, then at −78°C a solution of (−)-**17** (500 mg, 2.9 mmol) in THF (5 ml), followed after 10 min by diethyl chlorophosphate (500 mg, 2.9 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (2 ml). After stirring at room temp. for 16 h, satd. NH_4Cl solution (2 ml) and water (50 ml) are added. After extraction with hexane, the organic phase is washed with cold dild. hydrochloric acid (2 ×) and satd. $NaHCO_3$ solution, dried ($MgSO_4$), concentrated in vacuo, and filtered through silica gel (ether). (*M*)-**18** is obtained by distillation at 150°C/0.4 Torr as a colorless oil, 830 mg (93%). – IR (neat): ṽ = i.a. 2955 cm^{-1} (C–H), 2870 (C–H), 1655 (C=C), 1275 (P=O). – ^{1}H NMR: δ = 1.26–1.40 (m, 8H), 1.46 (br. d, 1H), 1.49 (br. d, 1H), 1.64 (m, 1H), 1.76 (m, 1H), 1.78 (m, 1H), 2.02 (m, 1H), 2.18–2.35 (m, 4H), 5.58 (m, *J* = 2.0, 7.5, 12-H). – $C_{16}H_{23}O_4P$ (310.3): calcd. C 61.93, H 7.47; found C 62.12, H 7.51.

(M)-12,12-Dichloropentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecan-11-one [(*M*)-**20**]: (−)-**17** (500 mg, 2.90 mmol) and SO_2Cl_2 (5 ml) are heated at reflux temp. for 14 h. After cooling, the reagent is evaporated in vacuo, and the residue is filtered through silica gel (cyclohexane/ethyl acetate, 6:1, R_f = 0.47) to give (*M*)-**20** as a colorless solid (640 mg, 91%); an analytically pure sample is obtained by crystallization from ether/PE 30/50, colorless needles, m.p. 106–107°C. – IR (KBr): ṽ = i.a. 2960 cm^{-1} (C–H), 2880 (C–H), 1735

(C=O), 1465 (CH_2), 805 (CCl). – ^{1}H NMR: δ = 1.28 (br. d, 4-H)*, 1.43 (br. d, 7-H)*, 1.60 (br. d, 4′-H), 1.66 (dd, 7′-H)*, 2.18 (br. d, 10-H)**, 2.33–2.57 (m, 6H), 2.70 (m, 1-H)**. – $C_{12}H_{12}Cl_2O$ (243.1): calcd. C 59.28, H 4.97, Cl 29.16; found C 59.03, H 4.68, Cl 28.87.

(M)-12-Chloropentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-en-11-yl Diethyl Phosphate [(*M*)-**21**]: (*M*)-**20** (640 mg, 2.63 mmol) is heated in $P(OEt)_3$ (3 ml) to 100°C for 6 h. Concentration in vacuo leaves (*M*)-**21** as a colorless oil (870 mg, 96%). An analytically pure sample is obtained by distillation at 140°C/0.1 Torr. R_f (cyclohexane/ethyl acetate, 6:1) = 0.04. – IR (neat): ṽ = i.a. 2960 cm^{-1} (C–H), 2870 (C–H), 1675 (C=C), 1280 (P=O), 1030 (P–O). – ^{1}H NMR: δ = 1.37 (m, 8H, 4-, 7-H, and CH_2CH_3), 1.50 (br. d, 4′-, 7′-H), 1.88 (m, 2-, 9-H), 2.07 (m, 1H), 2.16 (m, 1H), 2.25 (m, 2H), 2.42 (br. d, 10-H)*, 2.62 (br. d, 1-H)*, 4.22 (m, 4H, CH_2CH_3). – $C_{16}H_{22}ClO_4P$ (344.8): calcd. C 55.74, H 6.43, Cl 10.28, P 8.98; found C 55.32, H 6.21, Cl 9.45, P 9.18.

(1S,2S,3R,5S,6S,8R,9S,10S)-(–)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]doedec-11-ene [(–)-**19**]: To a solution of lithium (200 mg, 28.9 mmol) in liquid ammonia (ca. 40 ml) at –78°C a solution of (*M*)-**21** (740 mg, 2.15 mmol) [or (*M*)-**18**, 680 mg, 2.20 mmol] and *tert*-butyl alcohol (500 mg, 6.76 mmol) in dry ether (20 ml) is added dropwise. After stirring at this temp. for 2 h, excess lithium is destroyed with NH_4Cl, the ammonia is allowed to evaporate and the residue treated with water (50 ml) and pentane (50 ml). The organic phase is washed with water (3×), dried ($MgSO_4$), and concentrated in vacuo. The colorless oil (290 mg, 85%) is filtered through silica gel to give (–)-**19** as a waxy solid (270 mg, 79%), which sublimes at 70°C/13 Torr, m.p. 85–86°C. $[\alpha]_D^{20} = -210$ (*c* = 0.30 in cyclohexane), $[\Phi]_D^{20} = -332$. – IR (KBr): ṽ = i.a. 3040 cm^{-1} (=C–H), 2950 (C–H), 2870 (C–H), 1620 (C=C), 1460 (CH_2). – UV (*n*-hexane), ^{1}H and ^{13}C NMR: Figure 1. – MS, *m/z* (%): i.a. 158 (7) [M^+], 129 (12) [$M^+ - C_2H_5$], 117 (16) [$M^+ - C_3H_5$], 115 (11) [$M^+ - C_3H_7$], 93 (11) [$M^+ - C_5H_5$], 92 (100) [$M^+ - C_5H_6$], 91 (59) [$M^+ - C_5H_7$]. – $C_{12}H_{14}$ (158.2): calcd. C 91.08, H 8.92; found C 90.99, H 8.84.

(1R,2R,3S,5R,6R,8S,9R,10R)-(+)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-ene [(+)-**19**]: $[\alpha]_D^{20} = 210$ (*c* = 0.23 in cyclohexane), $[\Phi]_D^{20} = 332$.

(1S,2R,3S,5S,6S,8S,9R,10S)-(–)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]doecane [(–)-**22**]: (–)-**19** (40 mg, 0.25 mmol) in dry methanol (5 ml) and a catalytic amount of Pd/C are treated at room temp. with hydrogen (1 atm) with vigorous stirring for 1 h. Then pentane (20 ml) is added, the catalyst is sucked off and the filtrate washed with water (2 × 10 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue is sublimed at 70°C/20 Torr to give (–)-**22** as colorless crystals (33 mg, 81%) with the analytical data known from ref.[16] $[\alpha]_D^{20} = -279$ (*c* = 0.23 in $CHCl_3$), $[\Phi]_D^{20} = -447$.

(1R,2S,3R,5R,6R,8R,9S,10R)-(+)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecane [(+)-**22**]: $[\alpha]_D^{20} = 282$ (*c* = 0.13 in $CHCl_3$), $[\alpha]_D^{20} = 451$.

(1R,2R,3S,5R,6R,8S,9R,10R)-(–)-4,7-Bis[(R,R)-2,3-butylenedioxy]pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(–)-**23**] *and (1S,2S,3R,5S,6S,8R,9S,10S)-(+)-4,7-Bis[(R,R)-2,3-butylenedioxy]pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane* [(+)-**24**]: *rac*-**9** (3.00 g, 17.21 mmol) and *p*-toluenesulfonic acid (300 mg) in dry benzene (100 ml) are heated with (*R,R*)-2,3-butanediol (3.50 ml, 38 mmol) to reflux with use of a Dean-Stark trap for 8 h. After concentration in vacuo, the residue is filtered through silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.50). The partly crystalline material (5.95 g, 98%) is dissolved in hexane/ethyl acetate (7:1, 15 ml). Separation of the diastereomers is achieved by medium-pressure chromatography (hexane/ethyl acetate, 7:1, column: *l* = 50 cm, ∅ = 3.0 cm, *V* = 350 ml, *n* ≈ 7900) at 10–12 bar and a flow of ca. 40 ml/min [retention times: (–)-**23** 30.5 min, (+)-**24** 32.5 min]. 0.3 ml (ca. 120 mg) of the above solution are injected and fractionated (refractive index detector). 1.85 g (60%) of (–)-**23**, 1.60 g (52%) of mixed diastereomers, and 2.35 g (78%) of (+)-**24** are obtained.

(–)-**23**: m.p. 96–97°C, $[\alpha]_D^{20} = -112.5$ (*c* = 2.60 in $CHCl_3$), $[\Phi]_D^{20} = -399$. – IR (KBr): ṽ = i.a. 2960 cm^{-1} (C–H), 2920 (C–H), 2840 (C–H), 1100 (C–O). – ^{1}H NMR (400 MHz): δ = 1.20–1.30 (m, 12H, CH_3), 1.37 (br. s, 11-H), 1.80 (m, 3-, 8-H), 2.10 (m, 5-, 6-H), 2.41 (m, 2-, 9-H), 2.58 (m, 1-, 10-H), 3.57–3.71 (m, 4H, OC*H*RR′). – ^{13}C NMR: δ = 17.3 (CH_3), 17.6 (CH_3), 34.2 (C-11), 40.7, 43.7, 48.4, 51.7, 78.48 (OCHRR′), 78.52 (OCHRR′), 119.0 (C-4, -7). – $C_{19}H_{26}O_4$ (318.4): calcd. C 71.67, H 8.23; found C 71.53, H 8.19.

Crystallization of (+)-**24** (2.35 g, ca. 92% pure) from little PE 30/50 at –30°C provides pure (+)-**24** (1.25 g, 40%), m.p. 97–98°C, $[\alpha]_D^{20} = 104$ (*c* = 1.0 in $CHCl_3$), $[\Phi]_D^{20} = 369$. – IR (KBr): ṽ = i.a. 2970 cm^{-1} (C–H), 2950 (C–H), 2930 (C–H), 2860 (C–H), 1105 (C–O). – ^{1}H NMR (400 MHz): δ = 1.21–1.30 (m, 12H, CH_3), 1.40 (br. s, 11-H), 1.80 (m, 3-, 8-H), 2.12 (m, 5-, 6-H), 2.35 (m, 2-, 9-H), 2.58 (m, 1-, 10-H), 3.53–3.69 (m, 4H, OC*H*RR′). – ^{13}C NMR: δ = 17.1 (CH_3), 17.2 (CH_3), 34.5 (C-11), 40.8, 43.7, 48.3, 51.6, 78.6 (OCHRR′), 78.7 (OCHRR′), 119.0 (C-4, -7). – $C_{19}H_{26}O_4$ (318.4): calcd. C 71.67, H 8.23; found C 71.66, H 8.23.

(1R,2R,3S,5R,6R,8S,9R,10R)-(+)-Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,7-dione [(+)-**9**]: To a solution of (–)-**23** (1.83 g, 5.16 mmol) in glacial acetic acid (40 ml) is added 6 drops of concd. H_2SO_4. After refluxing for 15 h, cooling and dilution with CH_2Cl_2 (200 ml) and water (100 ml), the layers are separated, and the aqueous phase is extracted with CH_2Cl_2 (50 ml). The combined organic phases are washed with satd. $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo. Filtration through silica gel (cyclohexane/ethyl acetate, 1:1) provides colorless crystalline (+)-**9** (810 mg, 90%). The spectral data are in accord with those reported in ref.[11]. $[\alpha]_D^{20} = 300$ (*c* = 1.10 in $CHCl_3$), $[\Phi]_D^{20} = 522$.

(1S,2S,3R,5S,6S,8R,9S,10S)-(–)-Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,7-dione [(–)-**9**]: $[\alpha]_D^{20} = -300$ (*c* = 1.20 in $CHCl_3$), $[\Phi]_D^{20} = -522$.

(1S,2S,3R,5R,6R,9S,10S,11S)-(–)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane-7,12-dione [(–)-**25**], *-7,13-dione* [(*M*)-**26**], and *-8,13-dione* [(*M*)-**27**]: To (+)-**9** (780 mg, 4.48 mmol) and dry ZnI_2 (20 mg) in dry CH_2Cl_2 (10 ml) under N_2, cooled to 0°C, TMSCN (1.3 ml, 10.38 mmol) is added. The mixture is warmed with stirring to room temp. within 24 h. Then excess reagent is condensed into a cold trap at 40°C/15 Torr, the oily residue (1.25 g, 100%) is dissolved in dry THF (10 ml), and this solution is added dropwise under N_2 to an icecold stirred suspension of $LiAlH_4$ (460 mg, 12.1 mmol) in dry THF (60 ml). After refluxing for 3 h and cooling to 0°C, water (1.2 ml), sodium hydroxide solution (0.55 ml, 15%), and again water (1.8 ml) are added. The mixture is heated to 50°C, the inorganic salts are sucked off and washed with warm methanol/CH_2Cl_2 (1:1, 80 ml). Concentration in vacuo affords a colorless, partly crystalline material, which is dissolved in a mixture of water (50 ml), glacial acetic acid (2.3 ml), and concd. hydrochloric acid (0.4 ml, pH ≈ 4.5). After stirring at room temp. for 1 h, the mixture is cooled to 0°C, and a solution of $NaNO_2$ (1.11 g, 16.1 mmol) in water (16 ml) is added slowly. After 16 h at room temp., the solution is heated to 70°C for 1 h, cooled, and diluted with CH_2Cl_2 (40 ml). The layers are separated and the aqueous phase is extracted with CH_2Cl_2 (2 × 25 ml). The combined organic phases are washed twice with satd. $NaHCO_3$ solution (25 ml), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (silica gel, PE 30/50/ethyl acetate, 1:2, R_f = 0.63) provides (–)-**25** (168 mg, 18.5%) and a mixture of (*M*)-**27** and (*M*)-**26** (510 mg, 56.5%, R_f = 0.51). (–)-**25** and (*M*)-**27** crystallize from ether/PE 30/50.

(–)-**25**: m.p. 175–176°C, $[\alpha]_D^{20} = -264$ (*c* = 0.30 in $CHCl_3$), $[\Phi]_D^{20} = -535$. – IR (KBr): ṽ = i.a. 2960 cm^{-1} (C–H), 2930 (C–H), 2900 (C–H), 1710 (C=O). – ^{1}H NMR: δ = 1.58 (br. s, 4-H), 2.18 (m, 1-, 9-H), 2.35 (m, 2-, 3-, 5-, 10-H), 2.43 (dd, *J* = 18.9, 8-, 13-H), 2.45 (m, 6-, 11-H), 2.52 (dd, 8-, 13-H). – ^{13}C NMR: δ = 34.1 (C-2, -10)*, 36.2 (C-4), 38.0 (C-8, -13), 41.5 (C-3, -5)*, 42.2 (C-1, -9), 46.0 (C-6, -11), 212.0 (C-7, -12). – $C_{13}H_{14}O_2$ (202.2): calcd. C 77.20, H 6.97; found C 77.41, H 6.77.

(1R,2R,3S,5S,6S,9R,10R,11R)-(+)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane-7,12-dione [(+)-**25**]: $[\alpha]_D^{20} = 257$ (*c* = 0.25 in $CHCl_3$), $[\Phi]_D^{20} = 520$.

(*M*)-**27**: m.p. 183–184°C. – IR (KBr): ṽ = i.a. 2990 cm^{-1} (C–H), 2950 (C–H), 2890 (C–H), 1700 (C=O). – ^{1}H NMR: δ = 1.68 (br. s, 4-H), 1.93 (m, 6-, 11-H), 2.30 (d, *J* = 3.0, 7-, 12-H), 3.38 (br. d, *J* = 7.5, 1-, 9-H), 2.52 (m, 2-, 10-H), 2.58 (m, 3-, 5-H). – ^{13}C NMR: δ = 35.7 (C-6, -11), 37.7 (C-2, -10)*, 38.7 (C-3, -5)*, 38.8 (C-4), 41.6 (C-7, -12), 57.2 (C-1, -9), 215.0 (C-8, -13). – $C_{13}H_{14}O_2$ (202.2): calcd. C 77.20, H 6.97; found C 77.04, H 7.02.

(±)-8,13-Dichloropentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane-7,12-dione (*rac*-**32**): A solution of *rac*-**25** (200 mg, 0.99 mmol) in SO_2Cl_2 (2 ml) is heated to reflux for 5 h. After concentration in vacuo, the residue is crystallized from ether/CH_2Cl_2 to yield *rac*-**32** as colorless crystals (210 mg, 78%), m.p. 206–208°C. – IR (KBr): ṽ = i.a. 2960 cm^{-1} (C–H), 2950 (C–H), 2880 (C–H), 1730 (C=O), 670 (C–Cl). – ^{1}H NMR: δ = 1.79 (br. s, 4-H), 2.53 (m, 2-, 3-, 5-, 6-, 10-, 11-H), 3.21 (d, *J* = 3.5, 1-, 9-H), 4.20 (d, 8-, 13-H). – $C_{13}H_{12}Cl_2O_2$ (271.1): calcd. C 57.59, H 4.46, Cl 26.15; found C 57.34, H 4.41, Cl 25.81.

Diethyl (±)-12-(Diethoxyphosphoryloxy)-7-oxopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridec-12-en-8-ylphosphonate (*rac*-**33**) *and Diethyl (±)-13-Chloro-7,12-dioxopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecan-8-ylphosphonate* (*rac*-**34**): A so-

lution of *rac*-**32** (150 mg, 0.55 mmol) in $P(OEt)_3$ (1 ml) is heated to 60°C for 5 h. After concentration in vacuo, the residue is separated by chromatography (SiO_2, ether) into 30 mg of a colorless oil ($R_f = 0.42$, inhomogeneous, mainly *rac*-**34** according to ^1H NMR) and 150 mg (57%) of a colorless oil ($R_f = 0.26$), which is further purified by HPLC, *rac*-**33**, colorless liquid (130 mg, 49%). – IR (neat): $\tilde{\nu}$ = i.a. 2970 cm^{-1} (C–H), 1735 (C=O), 1655 (C=C), 1270 (P=O), 1095 (C–O), 1025 (P–O). – ^1H NMR: $\delta = 1.26$ (br. t, 12H, CH_2CH_3), 1.55 and 1.64 (AB, 4-H), 2.07 (m, 2H), 2.18–2.38 (m, 5H), 2.71 (dd, 11-H), 3.23 (m, 8-H), 4.09–4.25 (m, 8H, CH_2CH_3), 5.71 (m, 13-H). – ^{13}C NMR: $\delta = 16.16$ (2 C, CH_2CH_3), 16.22 (2C, CH_2CH_3), 30.7, 32.9, 35.3, 37.5 (dd, $J_{C,P} = 6$ Hz, C-8), 41.1, 45.2, 47.5, 50.3, 54.0, 56.0, 64.6 (2C, CH_2CH_3), 64.7 (2C, CH_2CH_3), 109.2 (C-13), 150.1 (d, $J = 9$ Hz, C-12), 207.7 (C-7). – $C_{21}H_{32}O_8P_2$ (474.4): calcd. C 53.17, H 6.80; found C 53.41, H 6.92.

(M)-8,8,13,13-Tetrachloropentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane-7,12-dione [(*M*)-**28**]: Gaseous chlorine is bubbled through a solution of (–)-**25** (120 mg, 0.59 mmol) in dry DMF (1.2 ml) under N_2, the temp. being kept below 80°C. After total conversion (TLC monitoring), the mixture is heated shortly to 80°C. After concentration in vacuo, the residue is dissolved in CH_2Cl_2/ethyl acetate and filtered through silica gel (ethyl acetate) affording yellowish crystals (190 mg, 95%) ($R_f = 0.63$), which are recrystallized from CH_2Cl_2/ethyl acetate: (*M*)-**28**, colorless crystals (180 mg, 90%), m.p. 292–294°C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 2990 cm^{-1} (C–H), 2980 (C–H), 2900 (C–H), 1740 (C=O), 805 (C–Cl). – ^1H NMR: $\delta = 1.82$ (br. s, 4-H), 2.73 (m, 2-, 10-H), 2.89 (m, 3-, 5-, 6-, 11-H), 3.36 (dd, $J = 5.5$, 1-, 9-H). – $C_{13}H_{10}Cl_4O_2$ (340.0): calcd. C 45.92, H 2.96, Cl 41.71; found C 45.74, H 2.91, Cl 42.22.

(M)-8,13-Dichloropentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene-7,12-diyl Bis(diethyl phosphate) [(*M*)-**29**]: A solution of (*M*)-**28** (180 mg, 0.53 mmol) in $P(OEt)_3$ (0.6 ml) is heated to 100°C for 5 h. After evaporation of the reagent in vacuo, the yellowish oil (287 mg, 100%) is filtered through silica gel [cyclohexane/ethyl acetate, 1:1, $R_f = 0.14$, R_f (ethyl acetate) = 0.42] resulting in a colorless liquid of (*M*)-**29** (280 mg, 98%). – IR (neat): $\tilde{\nu}$ = i.a. 2985 cm^{-1} (C–H), 2900 (C–H), 1675 (C=C), 1280 (P=O), 1200 (=C–O), 1090 (C–O), 1025 (P–O). – ^1H NMR: $\delta = 1.37$ (m, 12H, CH_2CH_3), 1.59 (br. s, 4-H), 1.96 (m, 2-, 10-H), 2.31 (m, 3-, 5-H), 2.60 (d, $J = 7.5$, 6-, 11-H)*, 2.65 (d, $J = 6.8$, 1-, 9-H)*, 4.22 (m, 8H, CH_2CH_3). – $C_{21}H_{30}Cl_2O_8P_2$ (543.3): calcd. C 46.42, H 5.57, Cl 13.05; found C 46.19, H 5.82, Cl 12.74.

(1S,2R,3R,5R,6S,9S,10R,11S)-(–)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(–)-**30**]: (*M*)-**29** (250 mg, 0.46 mmol) and *tert*-butyl alcohol (230 mg, 3.01 mmol) in dry ether (10 ml) are added dropwise to lithium (48 mg, 6.89 mmol) in liquid ammonia (ca. 10 ml) at –78°C, followed by stirring of the mixture at this temp. for 3 h. NH_4Cl is added until the blue color disappears, the ammonia is allowed to evaporate, and to the residue pentane and water (10 ml each) are added. The organic layer is washed with water (2 × 5 ml), dried ($MgSO_4$), and concentrated in vacuo. Filtration of the residue through silica gel (pentane) provides colorless crystalline (–)-**30** (68 mg, 85%), which sublimes at 80°C/13 Torr, m.p. 47–48°C, $[\alpha]_D^{20} = -264$ ($c = 0.71$ in $CHCl_3$), $[\Phi]_D^{20} = -449$. – IR (KBr): i.a. 3040 cm^{-1} (=C–H), 2950 (C–H), 2880 (C–H), 1610 (C=C). – UV (*n*-hexane), ^1H and ^{13}C NMR: Figure 1. – MS (CI), *m/z* (%): i.a. 171 (100) [$M^+ + 1$]. – MS, *m/z* (%): i.a. 165 (1), 152 (1), 141 (2), 128 (2), 115 (3), 92 (100), 91 (64). – $C_{13}H_{14}$ (170.3): calcd. C 91.71, H 8.29; found C 91.48, H 8.14.

(1R,2S,3S,5S,6R,9R,10S,11R)-(+)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(+)-**30**]: $[\alpha]_D^{20} = 264$ ($c = 0.50$ in $CHCl_3$), $[\Phi]_D^{20} = 450$.

(1S,2S,3S,5S,6S,9S,10S,11S)-(–)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane [(–)-**31**]: (–)-**30** (50 mg, 0.29 mmol), dissolved in dry methanol (6 ml), is treated with Pd/C (10 mg) and hydrogen (1 atm) for 2 h. After dilution with pentane (40 ml), the catalyst is sucked off and the organic layer washed with water (3 × 10 ml). Drying ($MgSO_4$) and concentration under reduced pressure followed by sublimation at 85°C/13 Torr yields (–)-**31**, colorless crystals (45 mg, 88%). The spectral data are in accord with those reported in ref.[16] $[\alpha]_D^{20} = -415$ ($c = 0.35$ in $CHCl_3$), $[\Phi]_D^{20} = -723$ (ref.[5] $[\alpha]_D^{20} = -391$ calcd. from $[\Phi]_D^{20} = -58.6$ at 15% optical purity).

(1R,2R,3R,5R,6R,9R,10R,11R)-(+)-Pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane [(+)-**31**]: $[\alpha]_D^{20} = 422$ ($c = 0.26$ in $CHCl_3$), $[\Phi]_D^{20} = 735$.

(±)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,13-trione (*rac*-**41**) *and -4,8,14-trione* (*rac*-**35**): *rac*-**1** (10.0 g, 53.15 mmol) and dry ZnI_2 (600 mg) in dry CH_2Cl_2 (15 ml) under N_2 in an ice bath are treated with TMSCN (25 ml, 19.80 g, 199.5 mmol). After stirring at 0°C to room temp. for 24 h, excess of reagent and the solvent are condensed into a cold trap at 40°C/15 Torr. The colorless oily residue is dissolved in dry THF (300 ml) and the solution added dropwise to a stirred suspension of $LiAlH_4$ (9.55 g, 251.5 mmol) in dry THF (1200 ml) under N_2 at 0°C. After refluxing for 6 h and cooling in an ice bath, water (25 ml), sodium hydroxide solution (11 ml, 15%), and again water (35 ml) are added. The warm (50°C) suspension is sucked off from the precipitate and the latter washed thoroughly with warm methanol/CH_2Cl_2 (1:1). After concentration in vacuo the colorless, partly crystalline oil is dissolved in water (600 ml), glacial acetic acid (50 ml), and concd. hydrochloric acid (10 ml). After stirring at room temp. for 1 h, followed by cooling in an ice bath, a solution of $NaNO_2$ (19.8 g, 287 mmol) in water (300 ml) is added slowly. Stirring at room temp. is continued for 16 h, followed by heating to 70°C for 1 h. The cold reaction mixture is extracted with CH_2Cl_2 (5 × 400 ml), the combined organic layers are washed with satd. $NaHCO_3$ solution (2 × 300 ml), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (SiO_2, ethyl acetate) of the brownish oil provides *rac*-**41** (4.45 g, 36.4%, $R_f = 0.48$) and *rac*-**35** (2.03 g, 16.6%, $R_f = 0.36$). Analytically pure samples are obtained by crystallization from ethyl acetate/PE 30/50.

rac-**35**: Colorless crystals, m.p. 245–247°C. – IR (KBr): $\tilde{\nu}$ = i.a. 2960 cm^{-1} (C–H), 2940 (C–H), 2920 (C–H), 1720 (C=O). – ^1H NMR (400 MHz): $\delta = 2.16$ (d, $J = 6.9$, 1-, 3-, 7-H), 2.32 (dd, $J = 18.0$, 5-, 9-, 13-H), 2.57 (br. s, 6-, 10-, 12-H), 2.57 (m, 11-H), 2.67 (m, 2-H), 2.70 (d, 5′-, 9′-, 13′-H). – ^{13}C NMR: $\delta = 28.9$ (C-11), 31.3 (C-6, -10, -12), 33.9 (C-2), 39.8 (C-5, -9, -13), 48.9 (C-1, -3, -7), 210.6 (C-4, -8, -14). – $C_{14}H_{14}O_3$ (230.2): calcd. C 73.03, H 6.13; found C 73.15, H 6.06.

rac-**41**: Colorless crystals, m.p. 236–237°C. – IR (KBr): $\tilde{\nu}$ = i.a. 2940 cm^{-1} (C–H), 2930 (C–H), 1720 (C=O). – ^1H NMR (400 MHz): $\delta = 2.07$ (m, 10-H), 2.15 (m, 1-H), 2.28 (d, 7-H), 2.39 (mc, 5-, 9-, 14-H), 2.51 (m, 6-H), 2.6–2.7 (m, 5′-, 9′-, 14′-H), 2.6 (m, 3-H), 2.65 (m, 2-H), 2.7 (m, 12-H). – ^{13}C NMR: $\delta = 29.9$ (C-6), 31.0 (C-11), 32.7 (C-2), 34.6 (C-10), 35.3 (C-1), 40.5 (C-9)*, 40.7 (C-14)*, 41.4 (C-5)*, 44.0 (C-3), 45.9 (C-12), 50.4 (C-7), 209.3 (C-8)**, 209.9 (C-13)**, 211.4 (C-4)**. – $C_{14}H_{14}O_4$ (230.2): calcd. C 73.03, H 6.13; found C 72.94, H 6.08.

(1S,3S,6R,7S,10R,12R)-(–)- [(–)-**36**] *and (1R,3R,6S,7R,10S,12S)-(+)-4,8,14-Tris[(R,R)-2,3-butylenedioxy]pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane* [(+)-**37**]: *rac*-**35** (1.83 g, 7.96 mmol), *p*-toluenesulfonic acid (140 mg) and (*R,R*)-2,3-butanediol (2.40 g, 26.51 mmol) in dry benzene (140 ml) are heated to reflux at a Dean-Stark trap for 5 h. Then the reaction mixture is concentrated in vacuo and the residue filtered through silica gel (PE 30/50/ethyl acetate, 1:1, $R_f = 0.63$). The colorless solid foam (3.40 g, 96%) is separated by rapid chromatography (cyclohexane/ethyl acetate, 15:1) into (–)-**36** (colorless solid, $R_f = 0.21$, 1.31 g, 74%), and (+)-**37** (colorless resin, $R_f = 0.17$, 1.26 g, 71%).

(–)-**36**: m.p. 153–154°C (methanol), $[\alpha]_D^{20} = -192$ ($c = 1.03$ in $CHCl_3$), $[\Phi]_D^{20} = -859$. – IR (KBr): $\tilde{\nu}$ = i.a. 2960 cm^{-1} (C–H), 2930 (C–H), 2850 (C–H), 1105 (C–O). – ^1H NMR (400 MHz): $\delta = 1.21$ and 1.22 (m, 18H, CH_3), 1.67 (dd, 5-, 9-, 13-H), 1.73 (br. q, 11-H), 1.83 (br. d, 1-, 3-, 7-H), 1.89 (br. d, 5′-, 9′-, 13′-H), 1.93 (m, 6-, 10-, 12-H), 2.14 (br. q, 2-H), 3.56 (m, 6H, OC*H*RR′). – ^{13}C NMR: $\delta = 16.7$ and 16.9 (3 C each, CH_3), 28.1 (C-2), 29.2 (C-6, -10, -12), 32.1 (C-11), 37.6 (C-5, -9, -13), 40.8 (C-1, -3, -7), 76.7 and 77.7 (2 C each, OCHRR′), 110.2 (C-4, -8, -14).

(+)-**37**: $[\alpha]_D^{20} = 139$ ($c = 0.74$ in $CHCl_3$), $[\Phi]_D^{20} = 619$. – IR (KBr): $\tilde{\nu}$ = i.a. 2960 cm^{-1} (C–H), 2920 (C–H), 2860 (C–H), 1100 (C–O). – ^1H NMR (400 MHz): $\delta = 1.23$ and 1.25 (m, 18H, CH_3), 1.72 (br. q, 11-H), 1.78 (dd, 5-, 9-, 13-H), 1.89 (br. d, 1-, 3-, 7-H), 1.95 (br. d, 5′-, 9′-, 13′-H), 1.95 (m, 6-, 10-, 12-H), 2.04 (br. q, 2-H), 3.60 and 3.69 (m, 6H, OC*H*RR′). – ^{13}C NMR: $\delta = 17.5$ and 17.7 (3 C each, CH_3), 27.6 (C-2), 28.7 (C-6, -10, -12), 31.9 (C-11), 38.3 (C-5, -9, -13), 40.6 (C-1, -3, -7), 77.8 and 78.6 (2 C each, OCHRR′), 110.1 (C-4, -8, -14).

(1S,3S,6R,7S,10R,12R)-(–)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,14-trione [(–)-**35**]: (–)-**36** (1.22 g, 2.73 mmol) in glacial acetic acid (100 ml) is heated with 5 drops of concd. H_2SO_4 to 110°C for 12 h. The mixture is diluted with water (100 ml), extracted with CH_2Cl_2 (6 × 100 ml), the combined organic layers are washed with satd. $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo. Filtration of the residue through silica gel (ethyl acetate) provides (–)-**35** as colorless crystals (530 mg, 84%), which are recrystallized from CH_2Cl_2/PE 30/50. $[\alpha]_D^{20} = -278$ ($c = 0.84$ in $CHCl_3$), $[\Phi]_D^{20} = -640$.

(1R,3R,6S,7R,10S,12S)-(+)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,14-trione [(+)-**35**]: $[\alpha]_D^{20} = 276$ ($c = 0.77$ in $CHCl_3$), $[\Phi]_D^{20} = 636$.

(1S,2S,3S,6R,7S,10S,11R,12R)-(−)- [(−)-**43**] *and (1R,2R,3R,6S,7R,10R,11S,12S)-(+)-4,8,13-Tris[(R,R)-2,3-butylenedioxy]pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane* [(+)-**42**]: *rac*-**41** (1.22 g, 5.30 mmol) and (*R*,*R*)-2,3-butanediol (1.59 ml, 1.58 g, 17.49 mmol) in dry benzene (70 ml) are heated with *p*-toluenesulfonic acid (70 mg) to reflux at a Dean-Stark trap for 8 h. Most of the solvent is distilled off, and the residue is filtered through silica gel (ethyl acetate). By rapid chromatography of the colorless resin (2.32 g, 98%) on silica gel (cyclohexane/ethyl acetate, 15:1) first (−)-**43** is isolated [R_f (cyclohexane/ethyl acetate, 3:1) = 0.36, after crystallization (PE 30/50) colorless crystals, 870 mg, 73%], then (+)-**42** ($R_f = 0.32$, colorless resin, 800 mg, 67%).

(−)-**43**: m.p. 173−174°C, $[\alpha]_D^{20} = -171$ ($c = 0.68$ in $CHCl_3$), $[\Phi]_D^{20} = -762$. − IR (KBr): $\tilde{\nu}$ = i.a. 2970 cm^{-1} (C−H), 2925 (C−H), 2850 (C−H), 1100 (C−O). − ^{1}H NMR: $\delta = 1.11-1.28$ (m, 18H, CH_3), 1.59−1.76 (m, 3H), 1.81−2.08 (series of m, 11H), 3.48−3.67 (m, 6H, OC*H*RR′). − $C_{26}H_{38}O_6$ (446.6): calcd. C 69.93, H 8.58; found C 69.78, H 8.72.

(+)-**42**: $[\alpha]_D^{20} = 82.3$ ($c = 0.50$ in $CHCl_3$), $[\Phi]_D^{20} = 367$. − IR (KBr): $\tilde{\nu}$ = i.a. 2950 cm^{-1} (C−H), 2920 (C−H), 2850 (C−H), 1100 (C−O). − ^{1}H NMR: $\delta = 1.13-1.36$ (m, 18H, CH_3), 1.69−2.05 (series of m, 14H), 3.52−3.81 (m, 6H, OC*H*RR′). − $C_{26}H_{38}O_6$ (446.6): calcd. C 69.93, H 8.58; found C 69.24, H 9.21.

(1S,2S,3S,6R,7S,10S,11R,12R)-(−)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,13-trione [(−)-**41**]: (−)-**43** (800 mg, 1.79 mmol) is deacetalyzed as described for (−)-**36** to provide (−)-**41**; after crystallization from CH_2Cl_2/PE 30/50, 370 mg (90%). $[\alpha]_D^{20} = -182$ ($c = 0.50$ in $CHCl_3$), $[\Phi]_D^{20} = -419$.

(1R,2R,3R,6S,7R,10R,11S,12S)-(+)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,13-trione [(+)-**41**]: $[\alpha]_D^{20} = 178$ ($c = 0.50$ in $CHCl_3$), $[\Phi]_D^{20} = 411$.

(M)-5,5,9,9,14,14-Hexachloropentacyclo[8.4.0.0.^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,13-trione [(*M*)-**44**]: Gaseous chlorine is bubbled through a solution of (−)-**41** (800 mg, 3.47 mmol) in dry DMF (12 ml) under N_2, whereby the temp. should not raise above 80°C. Then the mixture is heated to 80°C to total conversion (TLC monitoring). After concentration in vacuo, the residue is dissolved in CH_2Cl_2 and filtered through silica gel (ethyl acetate, $R_f = 0.69$) to give a yellowish solid (1.38 g, 91%), which crystallizes from CH_2Cl_2/ethyl acetate. (*M*)-**44**, colorless crystals (1.32 g, 87%), m.p. 303−305°C (sealed tube). − IR (KBr): $\tilde{\nu}$ = i.a. 2980 cm^{-1} (C−H), 1750 (C=O), 830 (C−Cl). − ^{1}H NMR: $\delta = 3.10-3.36$ (m, 1-, 2-, 3-, 10-, 11-H), 3.56 (br. d, 12-H)*, 3.66 (br. d, 7-H)*, 3.69 (br. d, 6-H)*. − $C_{14}H_8Cl_6O_3$ (436.9): calcd. C 38.49, H 1.85, Cl 48.68; found C 38.32, H 1.82, Cl 49.05.

(M)-5,9,14-Trichloropentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,9,13-triene-4,8,13-triyl Tris(diethyl phosphate) [(*M*)-**45**]: A solution of (*M*)-**44** (1.32 g, 3.02 mmol) in $P(OEt)_3$ (8 ml) is heated to 100°C for 6 h. Evaporation of the reagent in vacuo provides a yellowish oil, which is filtered through silica gel (cyclohexane/ethyl acetate, 1:1, $R_f = 0.04$) to yield (*M*)-**45** (2.18 g, 97%) as a colorless liquid. − IR (neat): $\tilde{\nu}$ = i.a. 2980 cm^{-1} (C−H), 2930 (C−H), 2900 (C−H), 1670 (C=C), 1270 (P=O), 1200 (=C−O), 1090 (C−O), 1020 (P−O). − ^{1}H NMR: $\delta = 1.39$ (m, 18H, CH_2CH_3), 1.92 (m, 2-, 11-H), 2.54 (br. d, 3-H)*, 2.57 (br. d, 12-H)*, 2.58 (br. d, 10-H)*, 2.71 (br. d, 1-H)*, 2.80 (br. d, 6-, 7-H)*, 4.24 (m, 12H, CH_2CH_3). − $C_{26}H_{38}Cl_3O_{12}P_3$ (741.9): calcd. C 42.10, H 5.16, Cl 14.34; found C 42.31, H 5.15, Cl 14.02.

(M)-5,5,9,9,13,13-Hexachloropentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,14-trione [(*M*)-**38**]: (−)-**35** (500 mg, 2.15 mmol) in dry DMF (10 ml) is treated as described for (−)-**41**. (*M*)-**38** is obtained as a yellowish solid [850 mg, 90%, R_f (ethyl acetate) = 0.65], which crystallizes from CH_2Cl_2/ethyl acetate (800 mg, 84%), m.p. 327−329°C (sealed tube). − IR (KBr): $\tilde{\nu}$ = i.a. 2965 cm^{-1} (C−H), 1750 (C=O), 830 (C−Cl). − ^{1}H NMR: $\delta = 2.97$ (m, 2-H), 3.13 (dd, $J = 6.0$, 1-, 3-, 7-H), 3.46 (m, 11-H), 3.78 (dd, $J = 6.0$, 6-, 10-, 12-H). − $C_{14}H_8Cl_6O_3$ (436.9): calcd. C 38.49, H 1.85, Cl 48.68; found C 38.71, H 1.70, Cl 49.23.

(M)-5,9,13-Trichloropentacyclo[8.4.0.0^{2,7}0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene-4,8,14-triyl Tris(diethyl phosphate) [(*M*)-**39**]: A solution of (*M*)-**38** (800 mg, 1.85 mmol) in $P(OEt)_3$ (5 ml) is heated to 100°C for 6 h. Evaporation of the reagent in vacuo provides a yellowish oil (1.35 g, 100%), which is filtered through silica gel (ethyl acetate, $R_f = 0.03$) to yield (*M*)-**39** (1.25 g, 92%) as a colorless liquid. − IR (neat): $\tilde{\nu}$ = i.a. 2980 cm^{-1} (C−H), 2930 (C−H), 2900 (C−H), 1670 (C=C), 1270 (P=O), 1190 (=C−O), 1095 (C−O), 1020 (P−O). − ^{1}H NMR: $\delta = 1.40$ (m, 18H, CH_2CH_3), 1.81 (q, 2-H)*, 1.90 (q, 11-H)*, 2.68 (d, $J = 6.0$, 1-, 3-, 7-H)**, 2.71 (d, $J = 6.0$, 6-, 10-, 12-H)**, 4.24 (m, 12H, CH_2CH_3). − $C_{26}H_{38}Cl_3O_{12}P_3$ (741.9): calcd. C 42.10, H 5.16, Cl 14.34; found C 41.79, H 4.88, Cl 14.05.

(1R,3R,6R,7R,10R,12R)-(−)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(−)-**3**]: (*M*)-**39** or (*M*)-**45** (1.25 g, 1.69 mmol) and *tert*-butyl alcohol (2.21 g, 30 mmol) in dry ether (70 ml) are added slowly to a solution of lithium (420 mg, 60 mmol) in liquid ammonia (ca. 70 ml) at −78°C. The mixture is stirred at this temp. for 4 h. Excess lithium is destroyed with NH_4Cl, then the ammonia is allowed to evaporate, and the resulting suspension is dissolved in water and PE 30/50 (50 ml each). The organic layer is washed with water (2 × 25 ml), dried ($MgSO_4$), and concentrated in vacuo. The solid (260 mg) is filtered through silica gel (PE 30/50) to give colorless, crystalline (−)-**3** (250 mg, 81%), which sublimes at 90°C/13 Torr, m.p. 106−107°C (pentane). $[\alpha]_D^{20} = -414$ ($c = 0.68$ in $CHCl_3$) from (−)-**35**, [−410 from (−)-**41**], $[\Phi]_D^{20} = -754$ from (−)-**35** [−746 from (−)-**41**]. − IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (=C−H), 2950 (C−H), 2840 (C−H), 1605 (C=C). − UV (*n*-hexane), ^{1}H and ^{13}C NMR: Figure 1. − MS, *m/z* (%): i.a. 182 (10) [M^+], 128 (12), 104 (100), 91 (94), 78 (38). − $C_{14}H_{14}$ (185.7): calcd. C 92.40, H 7.60; found C 92.19, H 7.53.

(1S,3S,6S,7S,10S,12S)-(+)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(+)-**3**]: $[\alpha]_D^{20} = 410$ ($c = 0.40$ in $CHCl_3$) from (+)-**35**, [401 from (+)-**41**, ee: 97−98%], $[\Phi]_D^{20} = 747$ from (+)-**35**, [731 from (+)-**41**].

(1S,3S,6S,7S,10S,12S)-(−)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane [(−)-**40**]: (−)-**3** (30 mg, 0.16 mmol) in dry methanol (5 ml) is treated with Pd/C (10 mg) and hydrogen (1 atm) for 1 h with vigorous stirring. After dilution with PE 30/50 (30 ml), the catalyst is sucked off, the filtrate washed with water (2 × 20 ml), dried ($MgSO_4$), and concentrated. Sublimation of the residue at 70°C/13 Torr provides colorless crystalline (−)-**40** (28 mg, 90%), whose spectral data correspond to those reported in ref.[5]; $[\alpha]_D^{20} = -621$ ($c = 0.26$ in $CHCl_3$), $[\Phi]_D^{20} = -1169$ (ref.[16] $[\alpha]_D^{20} = -568$, $[\Phi]_D^{20} = -1067$).

(1R,3R,6R,7R,10R,12R)-(+)-Pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane [(+)-**40**]: $[\alpha]_D^{20} = 617$ ($c = 0.15$ in $CHCl_3$), $[\Phi]_D^{20} = 1161$.

(M)-5,6,7,8-Tetrachlorohexacyclo[8.6.0.0^{2,14}.0^{3,12}.0^{4,9}.0^{11,15}]hexadeca-5,7-diene [(*M*)-**46**]: A solution of (−)-**19** (200 mg, 1.26 mmol) and tetrachlorothiophene dioxide (352 mg, 1.39 mmol) in dry toluene (1 ml) is heated under N_2 to 110°C for 13 h. After cooling, the brown reaction mixture is filtered through silica gel (PE 30/50, $R_f = 0.65$) and crystallized from methanol to give (*M*)-**46** as colorless rhombs (404 mg, 92%), m.p. 125−126°C. − IR (KBr): $\tilde{\nu}$ = i.a. 2970 cm^{-1} (C−H), 2950 (C−H), 2910 (C−H), 2880 (C−H), 1610 (C=C), 1460 (CH_2), 750 (C−Cl), 640 (C−Cl), 560 (C−Cl). − ^{1}H NMR (400 MHz): $\delta = 1.13$ and 1.42 (AB, 13-H), 1.21 and 1.45 (AB, 16-H), 1.58 (br. d, $J = 6.3$, 3-H), 1.91 (m, 10-H), 1.95 (m, 2-H), 2.00 (m, 11-H), 2.09 (m, 1-H), 2.20 (m, 12-H), 2.26 (m, 14-H), 2.29 (m, 15-H), 2.99 (d, $J = 13.5$, 4-H), 3.23 (dd, $J = 5.0$, 13.5, 9-H). − ^{13}C NMR: $\delta = 34.7$ (C-16), 34.8 (C-13), 35.0 (C-12), 36.7 (C-11), 37.5 (C-2), 37.8 (C-9), 39.0 (C-1), 40.8 (C-4), 41.2 (C-10), 42.0 (C-3), 47.9 (C-14), 48.1 (C-15), 123.0 (C-7)*, 123.4 (C-6)*, 131.6 (C-8)**, 133.6 (C-5)**. − $C_{16}H_{14}Cl_4$ (348.1): calcd. C 55.21, H 4.05, Cl 40.74; found C 55.44, H 4.04, Cl 39.91.

(M)-3′,4′,6′-Trichloro-11,12-benzopentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-ene [(*M*)-**47**]: (*M*)-**46** (380 mg, 1.09 mmol) and KOH (190 mg, 3.39 mmol) in dry ethanol (50 ml) are heated to reflux for 2 h. After cooling, water (40 ml) is added, and the aqueous phase is extracted with CH_2Cl_2 (2 × 40 ml). The organic layer is washed with water, dried ($MgSO_4$), and concentrated in vacuo. After distillation of the residue (340 mg, 100%) at 120°C/10^{-2} Torr, (*M*)-**47** is obtained as a colorless oil (330 mg, 98%), which slowly crystallizes, m.p. 87−88°C, R_f (PE 30/50) = 0.61. − IR (KBr): $\tilde{\nu}$ = i.a. 3070 cm^{-1} (aryl-H), 2960 (C−H), 2870 (C−H), 1430 (aryl), 1150 (C−Cl). − ^{1}H NMR: $\delta = 1.52$ and 1.64 (AB, 4,4′-, 7,7′-H), 1.74 (m, 3-, 8-H), 1.88 (m, 2-, 9-H), 2.43 (m, 5-, 6-H), 3.17 (d, 10-H)*, 3.26 (d, 1-H)*, 7.34 (s, 5′-H). − $C_{16}H_{13}Cl_3$ (311.6): calcd. C 61.67, H 4.20, Cl 34.13; found C 61.80, H 4.24, Cl 33.93.

(1S,2S,3R,5S,6S,8R,9S,10S)-(−)-11,12-Benzopentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-dodec-11-ene [(−)-**48**]: To (*M*)-**47** (300 mg, 0.96 mmol) and *tert*-butyl alcohol (710 mg, 9.60 mmol) in dry THF (10 ml) small pieces of sodium (223 mg, 9.60 mmol) are added against a stream of N_2. Then the mixture is heated to reflux until the sodium pieces form a clotted mass. Excess of sodium is destroyed with methanol, then water and PE 30/50 are added (50 ml each). After separation of the layers, the organic phase is washed with water (3 × 20 ml),

dried ($MgSO_4$), and concentrated in vacuo. The residue is filtered through silica gel (PE 30/50, $R_f = 0.45$). (−)-**48** is obtained as colorless solid (184 mg, 91%), which sublimes at 75°C/10^{-2} Torr, m.p. 100−101°C, $[\alpha]_D^{20} = -162$ ($c = 0.37$ in cyclohexane), $[\Phi]_D^{20} = -338$. − IR (KBr): $\tilde{\nu}$ = i.a. 3010 cm^{-1} (aryl-H), 2950 (C−H), 2860 (C−H), 1480 (aryl), 1450 (CH_2), 745 (aryl-H), 735 (aryl-H). − UV (*n*-hexane): Figure 3. − ^1H NMR (400 MHz): Figure 3; $J_{4,4'} = J_{7,7'} = 10$. − ^{13}C NMR: Figure 3. − MS, *m/z* (%): i.a. 208 (17) [M^+], 143 (16) [$M^+ - C_5H_5$], 142 (100) [$M^+ - C_5H_6$], 141 (36) [$M^+ - C_5H_7$], 128 (26) [$M^+ - C_6H_8$]. − $C_{16}H_{16}$ (208.3): calcd. C 92.26, H 7.74; found C 92.38, H 7.64.

(1R,2R,3S,5R,6R,8S,9R,10R)-(+)-11,12-Benzopentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-ene [(+)-**48**]: $[\alpha]_D^{20}$ = 164 ($c = 0.45$ in cyclohexane), $[\Phi]_D^{20}$ = 342.

(M)-5,6,7,8-Tetrachlorohexacyclo[8.7.0.0^{2,15}.0^{3,12}.0^{4,9}.0^{11,16}]heptadeca-5,7,13-triene (Stereoisomers) [(*M*)-**49** and (*M*)-**50**]: A solution of (−)-**30** (450 mg, 2.64 mmol) and tetrachlorothiophene dioxide (900 mg, 3.24 mmol) in dry toluene (1 ml) under N_2 is heated to 110°C for 24 h. After cooling, the reaction mixture is brought directly onto a silica gel column. With cyclohexane, besides (*M*)-**49**/(*M*)-**50** (647 mg, 68%, $R_f = 0.43$) (*M*)-**55** (20 mg, 2%, $R_f = 0.48$) and (*M*)-**56** (24 mg, 1.6%, $R_f = 0.37$) are eluted. GC analysis of (*M*)-**49**/(*M*)-**50**: column 250°C, injector 280°C, detector 280°C, retention times: 8.46 min (22.87%), 9.84 min (77.13%). An analytically pure sample of (*M*)-**49**/(*M*)-**50** is obtained by sublimation at 170−180°C/10^{-2} Torr, m.p. 144−151°C. − IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (=C−H), 2940 (C−H), 2870 (C−H), 1610 (C=C), 765 (C−Cl), 685 (C−Cl). − ^1H NMR: δ = 1.30 (AB, 1H), 1.43−1.64 (m, 2H), 1.66−1.87 (m, 3H), 2.01 (m, 1H), 2.21 (m), 2.36 (m), 2.43−2.56 (m), 2.68 (dd), 3.10 (br. d, 1H), 3.30 and 3.36 (2 dd, 1H each), 6.01−6.12 (m, 14-H), 6.21−6.35 (m, 13-H). − $C_{17}H_{14}Cl_4$ (360.1): calcd. C 56.70, H 3.92, Cl 39.38; found C 56.73, H 3.85, Cl 39.38.

(M)-3′,4′,5′,6′-Tetrachloro-7,8-benzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(*M*)-**55**]: From CH_2Cl_2/PE 30/50 colorless crystals, m.p. 133−134°C. − IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (=C−H), 2950 (C−H), 2880 (C−H), 1630 (C=C), 1160 (C−Cl), 685 (=C−H). − ^1H NMR: δ = 1.55−1.84 (m, 5H), 1.94 (m, 5-H), 2.11 (m, 3-H), 2.63 (dd, 11-H), 2.85 (d, 9-H), 3.48 (dd, 6-H), 6.22 (dd, 12-H), 6.37 (ddd, 13-H). − MS, *m/z*: i.a. 360 [$M^+ + 2$], 358 [M^+], 356 [$M^+ - 2$], 303, 266, 264. − $C_{15}H_{12}Cl_4$ (358.1): calcd. C 57.02, H 3.38, Cl 39.60; found C 56.79, H 3.49, Cl 39.42.

(M)-5,6,7,8,3′,4′,5′,6′-Octachloro-13,14-benzohexacyclo[8.7.0.0^{2,15}.0^{3,12}.0^{4,9}.0^{11,16}]heptadeca-5,7,13-triene [(*M*)-**56**]: From CH_2Cl_2/PE 30/50 colorless crystals, m.p. 263−266°C. − IR (KBr): $\tilde{\nu}$ = i.a. 2950 cm^{-1} (C−H), 2930 (C−H), 2920 (C−H), 2880 (C−H), 2840 (C−H), 1605 (C=C), 1190 (aryl-Cl), 1065 (aryl-Cl), 735 (vinyl-Cl), 720 (vinyl-Cl). − ^1H NMR: δ = 1.52−1.61 (m, 2H), 1.80 (dd, J = 10.9, 17-H), 2.04 (m, 3H), 2.13 (ddd, 1H), 2.57 (m, 1H), 3.30 (d, J = 12.6, 9-H), 1.39−1.49 (m, 4-, 12-H), 3.56 (d, 15-H). − MS, *m/z*: i.a. 552 [$M^+ + 4$], 550 [$M^+ + 2$], 548 [M^+], 546 [$M^+ - 2$], 544 [$M^+ - 4$]. − $C_{21}H_{12}Cl_8$ (548.0): calcd. C 46.03, H 2.21, Cl 51.76; found C 45.97, H 2.45, Cl 52.32.

(−)-(1R,2R,3S,5S,6R,9R,10R,11R)-7,8-Benzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(−)-**52**]: (*M*)-**49**/(*M*)-**50** (600 mg, 1.66 mmol) and KOH (800 mg, 14.3 mmol) in dry ethanol (80 ml) are heated to reflux for 2 h. After dilution with water (80 ml) and extraction with CH_2Cl_2 (80 ml), the organic phase is washed with water, dried ($MgSO_4$), and concentrated in vacuo. The colorless oil (535 mg, 99.5%) is filtered through silica gel (cyclohexane, $R_f = 0.51$) to afford an oil (510 mg, 95%), which is dissolved in dry THF (30 ml) under N_2 together with *tert*-butyl alcohol (1.16 g, 15.9 mmol). To this solution sodium (370 mg, 16.0 mmol) is added in small pieces, followed by refluxing until the remaining sodium forms a clotted mass. Excess sodium is destroyed with methanol, then PE 30/50 (140 ml) and water (70 ml) are added. The organic layer is washed with water (3 × 70 ml), dried ($MgSO_4$), and concentrated in vacuo. After filtration through silica gel (PE 30/50, $R_f = 0.28$) the colorless oil (340 mg, 98%) crystallizes slowly. For analytical purposes the crystals are sublimed at 60°C/10^{-2} Torr, m.p. 59−60°C, $[\alpha]_D^{20} = -282$ ($c = 0.55$ in $CHCl_3$), $[\Phi]_D^{20} = -622$. − IR (KBr): $\tilde{\nu}$ = i.a. 3030 cm^{-1} (aryl-H), 2950 (C−H), 2870 (C−H), 1480 (aryl), 745 (aryl-H), 735 (aryl-H). − ^1H NMR (400 MHz): δ = 1.62 (m, J = 6.0, 2-, 10-H), 1.65 and 1.71 (AB, 4-H), 1.80 (dd, J = 6.8, 1-H), 1.93 (m, 5-H), 2.06 (m, 3-H), 2.30 (d, 9-H), 2.58 (dd, J = 6.8, 11-H), 2.93 (br. d, 6-H), 6.18 (ddd, J = 6.8, 12-H), 6.39 (ddd, 13-H), 7.10−7.19 (m, 3′-, 4′-, 5′-, 6′-H). − ^{13}C NMR: δ = 30.9 (C-2)*, 31.5 (C-10)*, 36.5 (C-4), 43.9 (C-1), 46.6 (C-11), 47.4 (C-5), 48.0 (C-3), 49.1 (C-9), 50.8 (C-6), 123.4 (C-3′)**, 124.8 (C-4′)**, 125.6 (C-5′)**, 125.7 (C-6′)**, 129.7 (C-12), 133.5 (C-13), 139.9 (C-7)***, 143.2 (C-8)***. − MS, *m/z* (%): i.a. 220 (3) [M^+], 143 (15) [$M^+ - C_6H_5$], 142 (100) [$M^+ - C_6H_6$], 141 (32) [$M^+ - C_6H_7$], 127 (20) [$M^+ - C_7H_7$], 128 (28) [$M^+ - C_7H_8$]. − $C_{17}H_{16}$ (220.3): calcd. C 92.68, H 7.32; found C 92.49, H 7.16.

(1S,2S,3R,5R,6S,9S,11S)-(+)-7,8-Benzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(+)-**52**]: $[\alpha]_D^{20}$ = 280 ($c = 0.33$ in $CHCl_3$), $[\Phi]_D^{20}$ = 617.

(1R,2S,3S,5R,6S,9S,10S,11S)-(−)-7,8-Benzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridec-7-ene [(−)-**54**]: (−)-**52** (24.5 mg, 0.11 mmol), dissolved in dry methanol (5 ml), is treated with a catalytic amount of Pd/C and hydrogen (1 atm) for 1 h. After dilution with PE 30/50 (20 ml), filtration, and washing with water (2 × 10 ml), the filtrate is dried ($MgSO_4$) and concentrated in vacuo. The residue is sublimed at 60°C/10^{-2} Torr to give crystalline (−)-**54** (22 mg, 88%), m.p. 58−59°C, $[\alpha]_D^{20} = -283$ ($c = 0.17$ in $CHCl_3$), $[\Phi]_D^{20}$ = 628. − IR (KBr): $\tilde{\nu}$ = i.a. 3012 cm^{-1} (aryl-H), 2936 (C−H), 2836 (C−H), 1480 (aryl), 1441 (CH_2), 742 (aryl-H), 732 (aryl-H). − ^1H NMR: δ = 0.98 (m, 1H), 1.47 (br. d, 4-H), 1.59−1.96 (m, 9H), 2.28 (m, 1H), 2.85 (br. d, 9-H)*, 2.90 (br. d, 6-H)*, 7.04−7.18 (m, 4H). − ^{13}C NMR: δ = 19.4 (C-12)*, 21.9 (C-13)*, 34.8, 35.2, 37.4 (C-4), 38.5, 39.5, 39.8, 41.7, 46.3 (C-9), 50.0 (C-6), 122.6, 125.1, 125.4, 125.5, 141.0 (C-7)**, 144.1 (C-8)**. − $C_{17}H_{18}$ (222.3): calcd. C 91.84, H 8.16; found C 91.61, H 7.87.

(1S,2R,3R,5S,6R,9R,10R,11R)-(+)-7,8-Benzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridec-7-ene [(+)-**54**]: $[\alpha]_D^{20}$ = 274 ($c = 0.15$ in $CHCl_3$), $[\Phi]_D^{20}$ = 610.

(1R,2R,3R,5R,6S,9R,10R,11S)-(−)-7,8;12,13-Dibenzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(−)-**53**]: A solution of (−)-**51** (290 mg, 1.31 mmol) and tetrachlorothiophene dioxide (370 mg, 1.45 mmol) in dry toluene (1 ml) is heated under N_2 to 110°C for 3 d. After cooling to room temp., the reaction mixture is poured onto a column (SiO_2, $R_f = 0.21$). With cyclohexane a colorless solid (415 mg) is eluted which is heated together with KOH (500 mg, 8.89 mmol) in dry ethanol (50 ml) at reflux for 2 h. After addition of water (50 ml) and extraction with CH_2Cl_2 (2 × 50 ml), the organic layer is washed with water, dried ($MgSO_4$), and concentrated in vacuo. To the residue and *tert*-butyl alcohol (711 mg, 9.68 mmol) in dry THF (20 ml) under N_2 sodium (227 mg, 9.8 mmol) is added in small pieces, followed by refluxing until the remaining sodium forms a clotted mass. Excess sodium is destroyed with methanol, the resulting solution is diluted with PE 30/50 (140 ml) and water (70 ml) and the organic layer washed thoroughly with water. After drying ($MgSO_4$) and concentration in vacuo, the residue is filtered through silica gel (cyclohexane, $R_f = 0.23$) to give (−)-**53** as a colorless solid (242 mg, 68%), which sublimes at 120°C/10^{-2} Torr: colorless crystals, m.p. 209−210°C (CH_2Cl_2/PE 30/50), $[\alpha]_D^{20} = -261$ ($c = 0.29$ in $CHCl_3$), $[\Phi]_D^{20} = -707$. − IR (KBr): $\tilde{\nu}$ = i.a. 3010 cm^{-1} (aryl-H), 2940 (C−H), 2910 (C−H), 2880 (C−H), 1480 (aryl), 740 (aryl-H), 735 (aryl-H). − UV (*n*-hexane), ^1H NMR (400 MHz), and ^{13}C NMR: Figure 3. − MS, *m/z* (%): i.a. 270 (6) [M^+], 143 (12), 142 (100) [$M^+ - C_{10}H_8$]. − $C_{21}H_{18}$ (270.4): calcd. C 93.29, H 6.71; found C 93.21, H 7.04.

(1S,2S,3S,5S,6R,9S,10S,11R)-(+)-7,8;12,13-Dibenzopentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene [(+)-**53**]: $[\alpha]_D^{20}$ = 259 ($c = 0.27$ in $CHCl_3$), $[\Phi]_D^{20}$ = 701.

(1R,2S,3R,6R,7R,10R,11S,12R)-(−)-4,5-Benzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(−)-**59**] *and (1R,2R,3R,6R,7R,10R,11R,12R)-(−)-4,5;8,9-Dibenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene* [(−)-**61**]: A solution of (−)-**3** (200 mg, 1.10 mmol) and tetrachlorothiophene dioxide (840 mg, 3.30 mmol) in dry toluene (0.8 ml) is heated under N_2 to 110°C for 30 h. The reaction mixture is diluted with CH_2Cl_2 (30 ml), washed with water (2 × 20 ml), and dried ($MgSO_4$). A solution of the crude product (ca. 490 mg) in dry ethanol (60 ml) is heated with KOH (710 mg, 12.7 mmol) to reflux for 2 h. After cooling, CH_2Cl_2 (100 ml) and water (50 ml) are added, the organic layer is washed with water, dried ($MgSO_4$), and concentrated in vacuo. To the residue (ca. 370 mg) and *tert*-butyl alcohol (950 mg, 12.89 mmol) in dry THF (50 ml) under N_2 sodium (300 mg, 12.9 mmol) is added in small pieces, followed by refluxing until the sodium forms a clotted mass. Excess sodium is destroyed with methanol and, after dilution with water (60 ml) and PE 30/50 (120 ml), the organic layer is washed with water (50 ml), dried ($MgSO_4$), and concentrated in vacuo. Chromatography of the brownish residue (SiO_2, cyclohexane) provides liquid (−)-**59** ($R_f = 0.37$, 55 mg, 22%, sublimes at 85°C/10^{-2} Torr) and colorless crystalline (−)-**61** ($R_f = 0.18$, 140 mg, 46%, sublimes at 160°C/10^{-2} Torr).

(−)-**59**: Oil, $[\alpha]_D^{20} = -463$ ($c = 0.39$ in $CHCl_3$), $[\Phi]_D^{20} = -1077$. – IR (neat): $\tilde{\nu}$ = i.a. 3050 cm^{-1} (=C−H), 2950 (C−H), 1615 (C=C), 1480 (aryl), 760 (aryl-H), 740 (aryl-H), 675 (=C−H). – UV (*n*-hexane): λ_{max} (ε) = 222 nm (8160), 260 (460), 266 (625), 272 (605). – ^{1}H NMR (400 MHz): δ = 1.27 (ddd, J = 6.4, 2-, 11-H), 1.90 (dd, 7-, 12-H), 2.12 (dd, 1-, 10-H), 2.50 (d, 3-, 6-H), 6.44 (ddd, J = 6.5, 8-, 13-H), 6.48 (ddd, 9-, 14-H), 7.17 (br. s, 3′-, 4′-, 5′-, 6′-H). – ^{13}C NMR: δ = 22.8 (C-2, -11), 45.2 (C-1, -10), 46.7 (C-7, -12), 50.4 (C-3, -6), 123.8 (C-3′, -6′), 125.3 (C-4′, -5′), 133.6 (C-8, -13), 134.4 (C-9, -14), 143.8 (C-4, -5). – MS, *m/z* (%): i.a. 233 (11) [M^+ + 1], 232 (49) [M^+], 217 (22) [M^+ − CH_3], 191 (39) [M^+ − C_3H_5], 178 (25) [M^+ − C_4H_6], 165 (19) [M^+ − (C_5H_7], 153 (22) [M^+ − C_6H_7], 152 (20) [M^+ − C_6H_8], 141 (73) [M^+ − C_7H_7], 128 (100) [M^+ − C_8H_8]. – $C_{18}H_{16}$ (232.3): calcd. C 93.06, H 6.94; found C 92.87, H 7.03.

(−)-**61**: Colorless crystals, m.p. 178−179°C (CH_2Cl_2/PE 30/50), $[\alpha]_D^{20} = -488$ ($c = 0.42$ in $CHCl_3$), $[\Phi]_D^{20} = -1320$. – IR (KBr): $\tilde{\nu}$ = i.a. 3060 cm^{-1} (aryl-H), 3035 (=C−H), 3005 (C−H), 2990 (C−H), 2970 (C−H), 2925 (C−H), 1605 (C=C), 1450 (aryl), 745 (aryl-H), 735 (aryl-H). – UV (*n*-hexane): λ_{max} (ε) = 228 nm (9380), 260 (980), 265 (1220), 272 (1070). – ^{1}H NMR (400 MHz): δ = 1.57 (ddd, J = 6.5, 6.5, 2-, 11-H), 2.05 (1-, 12-H), 2.42 (d, 6-, 7-H), 2.63 (d, 3-, 10-H), 6.51 (m, 13-, 14-H), 7.10 (m, 3′-, 6″-H), 7.15 (m, 6′-, 3″-H), 7.22 (m, 4′-, 4″-, 5′-, 5″-H). – ^{13}C NMR: δ = 24.7 (C-2, -11), 44.9 (C-1, -12), 48.6 (C-6, -7), 50.0 (C-3, -10), 123.8 (C-3′, -6″), 124.0 (C-6′, -3″)*, 125.6 (C-5′, -4″)*, 125.7 (C-4′, -5″)*, 133.7 (C-13, -14), 142.9 (C-5, -8)**, 143.5 (C-4, -9)**. – MS, *m/z* (%): i.a. 283 (25) [M^+ + 1], 282 (100) [M^+], 267 (40) [M^+ − CH_3], 265 (23) [M^+ − CH_4], 178 (26) [M^+ − C_8H_8], 167 (28) [M^+ − C_9H_7], 165 (23) [M^+ − C_9H_9]. – $C_{22}H_{18}$ (282.4): calcd. C 93.58, H 6.42; found C 93.47, H 6.61.

(1S,2R,3S,6S,7S,10S,11R,12S)-(+)-4,5-Benzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(+)-**59**]: Colorless crystals, m.p. 91−92°C, $[\alpha]_D^{20} = 457$ ($c = 0.39$ in $CHCl_3$), $[\Phi]_D^{20} = 1062$.

(1S,2S,3S,6S,7S,10S,11S,12S)-(+)-4,5;8,9-Dibenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene[(+)-**61**]: $[\alpha]_D^{20} = 490$ ($c = 0.40$ in $CHCl_3$), $[\Phi]_D^{20} = 1325$.

(1S,2S,3S,6S,7R,10S,11S,12R)-(−)-4,5-Benzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradec-4-ene [(−)-**60**]: (−)-**59** (25 mg, 0.11 mmol) in dry methanol (8 ml) is treated with Pd/C (10 mg) and hydrogen (1 atm) with vigorous stirring for 1.5 h. After filtration, concentration in vacuo, and distillation of the residue at 130°C/10^{-1} Torr in a kugelrohr apparatus (−)-**60** is isolated as a colorless oil (20 mg, 79%), $[\alpha]_D^{20} = -454$ ($c = 0.34$ in $CHCl_3$), $[\Phi]_D^{20} = -1073$. – IR (neat): $\tilde{\nu}$ = i.a. 3060 cm^{-1} (aryl-H), 3034 (aryl-H), 3010 (aryl-H), 2918 (C−H), 2858 (C−H), 1474 (aryl), 764 (aryl-H), 731 (aryl-H). – ^{1}H NMR: δ = 1.08 (m, 7-, 12-H), 1.60−1.89 (m, 12H), 2.90 (br. d, J = 6.3, 3-, 6-H), 7.06 (m, 2H), 7.10 (m, 2H). – ^{13}C NMR: δ = 22.4 (C-9, -14)*, 22.9 (C-8, -13)*, 30.6 (2 C), 32.7 (2 C), 38.6 (2 C), 40.4 (2 C), 123.0 (2 C), 125.2 (2 C), 144.5 (C-4, -5). – $C_{18}H_{20}$ (236.4): calcd. C 91.47, H 8.53; found C 91.38, H 8.60.

(1R,2R,3R,6R,7S,10R,11R,12S)-(+)-4,5-Benzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradec-4-ene [(+)-**60**]: $[\alpha]_D^{20} = 446$ ($c = 0.47$ in $CHCl_3$), $[\Phi]_D^{20} = 1053$.

(1R,2R,3S,6R,7R,10S,11R,12R)-(−)-4,5;8,9-Dibenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8-diene [(−)-**62**]: (−)-**61** (19.8 mg, 0.07 mmol) in dry methanol (5 ml) is treated with a catalytic amount of Pd/C and hydrogen (1 atm) with vigorous stirring for 1.5 h. The catalyst is sucked off, the filtrate concentrated in vacuo, and the residue sublimed at 150°C/10^{-2} Torr to give (−)-**62** as colorless crystals (16 mg, 80%), m.p. 160−161°C, $[\alpha]_D^{20} = -435$ ($c = 0.10$ in $CHCl_3$), $[\Phi]_D^{20} = -1238$. – IR (KBr): $\tilde{\nu}$ = i.a. 3014 cm^{-1} (aryl-H), 2922 (C−H), 2854 (C−H), 1476 (aryl), 1458 (CH_2), 750 (aryl-H), 734 (aryl-H). – ^{1}H NMR: δ = 1.26 (m, 1-, 12-H), 1.82−1.96 (m, 2-, 11-, 13-, 14-H), 2.41 (br. d, 6-, 7-H), 3.07 (br. d, 3-, 10-H), 7.06 (m, 3′-, 6″-H), 7.11−7.20 (m, 6H). – ^{13}C NMR: δ = 22.3 (C-13, -14), 29.8, 39.4, 40.1, 47.6 (C-6, -7), 124.0, 125.6, 125.7, 143.2 (C-4, -9)*, 143.8 (C-5, -8)*. – $C_{22}H_{20}$ (284.4): calcd. C 92.91, H 7.09; found C 92.46, H 7.53.

(1S,2S,3R,6S,7S,10R,11S,12S)-(+)-4,5;8,9-Dibenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8-diene [(+)-**62**]: $[\alpha]_D^{20} = 431$ ($c = 0.11$ in $CHCl_3$), $[\Phi]_D^{20} = 1226$.

(M)-5,6,7,8-Tetrachloro-13,14;17,18-dibenzohexacyclo[8.8.0.0^{2,15}.0^{3,12}.0^{4,9}.0^{11,16}]octadeca-5,7,13,17-tetraene [(*M*)-**63**] *and (M)-3′,4′,5′,6′-Tetrachloro-4,5;8,9;13,14-tribenzopentacyclo[8.4.0.0.^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene* [(*M*)-**64**]: A solution of (−)-**61** (120 mg, 0.42 mmol) and tetrachlorothiophene dioxide (130 mg, 0.51 mmol) in dry xylene (0.5 ml) is heated to 135°C for 48 h. After cooling, the reaction mixture is put onto a silica gel column. With cyclohexane first colorless crystalline (−)-**64** (R_f = 0.21, 23 mg, 12%), then colorless crystalline (−)-**63** (R_f = 0.16, 115 mg, 57%) is eluted.

(*M*)-**63**: m.p. 273−275°C (CH_2Cl_2/PE 30/50). – IR (KBr): $\tilde{\nu}$ = i.a. 3020 cm^{-1} (aryl-H), 2940 (C−H), 1610 (C=C), 1460 (aryl), 760 (aryl-H), 750 (aryl-H). – ^{1}H NMR: δ = 1.62 (d, J = 6.8, 10-H), 1.87 (d, J = 5.1, 3-H), 2.08 (m, 2-, 11-H), 2.49 (m, 2H), 3.05 (d, 1H), 3.36 (d, 1H), 3.40 (dd, J = 14.3, 9-H), 3.60 (dd, 4-H), 7.08 (m, 2H), 7.19 (m, 6H). – $C_{26}H_{18}Cl_4$ (472.2): calcd. C 66.13, H 3.84, Cl 30.03; found C 65.89, H 4.17, Cl 29.61.

(*M*)-**64**: m.p. > 350°C (CH_2Cl_2/PE 30/50). – IR (KBr): $\tilde{\nu}$ = i.a. 3030 cm^{-1} (aryl-H), 2980 (C−H), 2930 (C−H), 1480 (aryl), 1460 (aryl), 1030 (aryl-Cl), 760 (aryl-H), 750 (aryl-H). – ^{1}H NMR: δ = 1.97 (dd, 2-, 11-H), 2.57 (d, 1-, 10-H)*, 2.61 (d, 7-, 12-H)*, 3.11 (m, 2H), 7.17 (m, 2H), 7.30 (m, 6H). – $C_{26}H_{16}Cl_4$ (470.2): calcd. C 66.41, H 3.43, Cl 30.16; found C 66.38, H 3.07, Cl 30.12.

(M)-3′,4′,6′-Trichloro-4,5;8,9;13,14-tribenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]-tetradeca-4,8,13-triene [(*M*)-**65**]: A solution of 115 mg (0.24 mmol) of (*M*)-**63** and 122 mg (2.18 mmol) of KOH in 15 ml dry ethanol is heated to reflux for 2 h. After dilution with water and CH_2Cl_2 (15 ml each), the organic layer is washed with water (10 ml), dried ($MgSO_4$), and concentrated in vacuo. Filtration of the residue through silica gel (cyclohexane, R_f = 0.24) provides a colorless solid (100 mg, 95%), which crystallizes from CH_2Cl_2/PE 30/50, m.p. 298−300°C. – IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (aryl-H), 2950 (C−H), 1490 (aryl), 1470 (aryl), 1440 (aryl), 1020 (aryl-Cl), 760 (aryl-H). – ^{1}H NMR: δ = 1.94 (m, 2H), 2.53 (d, 1H), 2.56 (d, 1H), 2.60 (d, 2H), 3.03 (d, 1H), 3.12 (d, 1H), 7.20 (m, 4H), 7.27 (m, 4H), 7.41 (s, 5′-H). – $C_{26}H_{17}Cl_3$ (435.8): calcd. C 71.66, H 3.93, Cl 24.41; found C 71.85, H 4.21, Cl 23.82.

(1R,3R,6R,7R,10R,12R)-(−)-4,5;8,9;13,14-Tribenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(−)-**4**]

From (*M*)-**65**: To (*M*)-**65** (100 mg, 0.23 mmol) and *tert*-butyl alcohol (170 mg, 2.3 mmol) in dry THF (15 ml) sodium (54 mg, 2.34 mmol) is added in small pieces against a stream of N_2, followed by heating to reflux until the remaining sodium forms a clotted mass. Then methanol is added carefully and, after total conversion, water (10 ml). The aqueous layer is extracted with cyclohexane (40 ml), the extract is washed with water (10 ml), dried ($MgSO_4$), and concentrated in vacuo. Filtration through silica gel (cyclohexane, R_f = 0.12) gives (−)-**4** as a colorless solid (70 mg, 91%), which crystallizes in needles from CH_2Cl_2/PE 30/50.

From (*M*)-**64**: (*M*)-**64** (23 mg, 0.05 mmol) and *tert*-butyl alcohol (36 mg, 0.49 mmol) in dry THF (10 ml) are treated with sodium (13 mg, 0.57 mmol) as described above to yield (−)-**4** (13 mg, 80%), m.p. 215−216°C, $[\alpha]_D^{20} = -493$ ($c = 0.15$ in $CHCl_3$), $[\Phi]_D^{20} = -1638$. – IR (KBr): $\tilde{\nu}$ = i.a. 3080 cm^{-1} (aryl-H), 3060 (aryl-H), 3040 (aryl-H), 2960 (C−H), 1490 (aryl), 1465 (aryl), 765 (aryl-H), 745 (aryl-H). – UV (*n*-hexane), ^{1}H NMR (400 MHz), and ^{13}C NMR: Figure 3. – MS, *m/z* (%): i.a. 333 (35) [M^+ + 1], 332 (100) [M^+], 317 (23) [M^+ − CH_5], 229 (15) [M^+ − C_8H_7], 228 (54) [M^+ − C_8H_8], 216 (19) [M^+ − C_9H_8], 215 (42) [M^+ − C_9H_9], 203 (18) [M^+ − $C_{10}H_9$], 202 (32) [M^+ − $C_{10}H_{10}$], 128 (21). – $C_{26}H_{20}$ (332.4): calcd. C 93.94, H 6.06; found C 93.78, H 6.19.

(1S,3S,6S,7S,10S,12S)-(+)-4,5;8,9;13,14-Tribenzopentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene [(+)-**4**]: $[\alpha]_D^{20} = 497$ ($c = 0.16$ in $CHCl_3$), $[\Phi]_D^{20} = 1653$.

(±)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecane-11,12-dione 11-Dimethyl Acetal (*rac*-**68**): *rac*-**20** (200 mg, 0.82 mmol) is added to a freshly prepared solution of sodium methanolate in methanol (20 ml, from 200 mg (8.7 mmol) sodium), followed by heating to reflux for 8 h. Then water (50 ml) and CH_2Cl_2 (100 ml) are added, the organic layer is washed with water (2 × 40 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue is filtered through silica gel (cyclohexane/ethyl acetate, 3:1, R_f = 0.36), the brownish oily eluate is distilled at 80°C/10^{-2} Torr to give *rac*-**68** (130 mg, 67%) as a colorless oil. – IR (neat): $\tilde{\nu}$ = i.a. 2960 cm^{-1} (C−H), 2880 (C−H), 2840 (C−H), 1735 (C=O), 1470 (CH_2), 1120 (C−O). – ^{1}H NMR: δ = 1.19 (br. d, 4-H)*, 1.28 (dd, 7-H)*, 1.50 (dd, 4′-H)*, 1.59 (dd, 7′-H)*, 1.94 (d, J = 6.3, 10-H)**, 2.03 (d, J = 6.3, 1-H)**, 2.15−2.46 (m, 5H), 2.51 (m, 1H), 3.28 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3). – $C_{14}H_{18}O_3$ (234.3): calcd. C 71.77, H 7.74; found C 71.05, H 7.68.

(±)-11-Benzylidenepentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecan-12-one (*rac*-**69**): *rac*-**17** (500 mg, 2.90 mmol) and benzaldehyde (340 mg, 3.20 mmol) in dry ethanol (20 ml) are stirred with KOH (50 mg, 0.89 mmol) at room temp. for

14 h. The reaction mixture is diluted with ether and water (80 ml each), the organic layer is washed twice with water (30 ml), dried ($MgSO_4$), and concentrated in vacuo to give *rac*-**69** as colorless crystals (690 mg, 91%), m.p. 108–109°C (methanol). – IR (KBr): $\tilde{\nu}$ = i.a. 3070 cm^{-1} (aryl-H), 3020 (=C–H), 2940 (C–H), 2870 (C–H), 1690 (C=O), 1620 (C=C), 1485 (aryl), 1440 (CH_2). – ^1H NMR: δ = 1.31 (br. d, J = 10.5, 4-, 7-H), 1.53 (br. d, 4′-H)*, 1.65 (br. d, 7′-H)*, 2.11 (m, 1H), 2.18 (br. d, 1-H), 2.28 (m, 2H), 2.36–2.50 (m, 3H), 2.95 (br. d, $J_{9,10}$ = 6.8, 10-H), 7.28–7.42 (m, 5H), 7.48 (s, =C*H*Ph). – $C_{19}H_{18}O$ (262.4): calcd. C 86.99, H 6.92; found C 87.21, H 6.73.

(±)-Pentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecane-11,12-dione (*rac*-**70**)

From rac-**68**: A solution of *rac*-**68** (120 mg, 0.51 mmol) in acetone (5 ml) and 2 M H_2SO_4 (2.5 ml) is stirred at room temp. for 20 h. Then, after dilution with water and CH_2Cl_2 (50 ml each), the organic layer is washed with satd. $NaHCO_3$ solution (30 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue is filtered through silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.30) to yield *rac*-**70** as a yellow oil (30 mg, 31%).

From rac-**17**: *rac*-**17** (500 mg, 2.90 mmol) in dioxane/water (10 ml, 10:1) is treated with SeO_2 (400 mg, 3.60 mmol) at 90°C for 7 h, whereby amorphous selenium slowly precipitates and is sucked off. The filtrate is diluted with water (50 ml) and CH_2Cl_2 (80 ml) and the organic layer washed twice with water, dried ($MgSO_4$), and concentrated in vacuo. Chromatography (SiO_2) gives besides other components a fraction of a yellowish oil (80 mg, 15%), which consists to about 90% of *rac*-**70** (^1H NMR).

From rac-**69**: Ozone is bubbled through a solution of *rac*-**69** (230 mg, 0.88 mmol) in dry methanol (15 ml) at –78°C for 6 min, whereupon a yellow color appears. Then 5 drops of dimethyl sulfide is added, and the solution is allowed to warm to room temp. After concentration in vacuo, the residue is filtered through silica gel (deactivated with NEt_3, cyclohexane/ethyl acetate, 1:1, R_f = 0.30) to yield a yellow oil (100 mg, 61%), which sublimes at 50°C/10^{-2} Torr to give *rac*-**70** as yellow, rapidly decomposing crystals, m.p. ≈ 90–100°C. – IR (KBr): $\tilde{\nu}$ = i.a. 2980 cm^{-1} (C–H), 2880 (C–H), 1740 (C=O), 1710 (C=O). – ^1H NMR: δ = 1.39 (br. d, 4-, 7-H), 1.75 (br. d, 4′-, 7′-H), 2.42 (br. d, 1-, 10-H), 2.49–2.63 (m, 2-, 3-, 5-, 6-, 8-, 9-H).

(±)-11,12-[2′,3′]Quinoxalinopentacyclo[6.4.0.0^{2,6}.0^{3,10}.0^{5,9}]dodec-11-ene (*rac*-**71**): *rac*-**69** (290 mg, 1.11 mmol) is treated with ozone as described above. The reaction mixture is immediately heated to 60°C (preheated bath), and *o*-phenylenediamine (180 mg, 1.66 mmol) in dry methanol (3 ml) is added. After stirring at this temp. for 2 h, the solution is concentrated in vacuo and the residue filtered through silica gel (cyclohexane/ethyl acetate, 3:1, R_f = 0.48). The brownish solid is sublimed at 150°C/10^{-2} Torr to give *rac*-**71** as colorless crystals (260 mg, 95%), m.p. 146–147°C. – IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (aryl-H), 2960 (C–H), 2940 (C–H), 2870 (C–H), 1500 (aryl), 1465 (CH_2), 1400 (C=N), 1340 (C=N). – ^1H NMR: δ = 1.59 and 1.74 (AB, 4,4′-, 7,7′-H), 2.08 (m, 3-, 8-H), 2.21 (ddd, 2-, 9-H), 2.56 (m, 5-, 6-H), 3.06 (d, 1-, 10-H), 7.69 (m, *m*-H), 8.05 (m, *o*-H). – ^{13}C NMR: δ = 34.6 (C-4, -7), 37.9 (d, C-2, -9), 45.1 (d, C-3, -8), 49.3 (d, C-1, -10), 50.1 (d, C-5, -6), 128.4 (2 C_m), 128.6 (2 C_o), 142.3 (2 C_{ipso}), 156.8 (C-11, -12). – $C_{18}H_{16}N_2$ (260.3): calcd. C 83.05, H 6.19, N 10.76; found C 82.87, H 6.16, N 10.78.

(±)-8,13-Dibenzylidenepentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]tridecane-7,12-dione (*rac*-**72**): *rac*-**25** (230 mg, 1.14 mmol) and benzaldehyde (260 mg, 2.45 mmol) in ethanol (30 ml) are treated with KOH (80 mg, 1.43 mmol) at room temp. for 1 d. The reaction mixture is dissolved in CH_2Cl_2 (100 ml), the solution washed with water (2 × 50 ml), dried ($MgSO_4$), and concentrated in vacuo. The solid residue crystallizes from methanol to give *rac*-**72** as colorless crystals (370 mg, 86%), m.p. 272–274°C. – IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (aryl-H), 3020 (=C–H), 2980 (C–H), 2950 (C–H), 1690 (C=O), 1615 (C=C), 1490 (aryl). – ^1H NMR: δ = 1.68 (br. s, 4-H), 2.45 (m, 3-, 5-H), 2.57–2.69 (m, 2-, 6-, 10-, 11-H), 3.34 (br. d, 1-, 9-H), 7.30–7.45 (m, 10H), 7.58 (s, 2H, =C*H*Ph). – $C_{27}H_{22}O_2$ (378.5): calcd. C 85.69, H 5.86; found C 85.43, H 5.98.

(±)-7,8;12,13-Bis([2′,3′]quinoxalino)pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene (*rac*-**74**): Ozone (2 mmol) is bubbled through a solution of *rac*-**72** (350 mg, 0.92 mmol) in methanol/CH_2Cl_2 (30 ml, 1:2) at –78°C. After 15 min at –78°C, dimethyl sulfide (0.5 ml) is added. Then the reaction mixture is immediately heated to 60°C, followed by addition of *o*-phenylenediamine (300 mg, 2.77 mmol) in methanol (5 ml) in one portion. Stirring is continued for 2 h at this temp., then the mixture is concentrated in vacuo and the solid residue filtered through silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.15). The now colorless *rac*-**74** (190 mg, 55%) crystallizes from CH_2Cl_2/PE 30/50, m.p. 335–337°C. – IR (KBr): $\tilde{\nu}$ = i.a. 3050 cm^{-1} (aryl-H), 2980 (C–H), 2880 (C–H), 1500 (aryl), 1400 (C=N), 1380 (C=N). – ^1H NMR: δ = 2.12 (br. s, 4-H), 2.50–2.64 (m, 2-, 3-, 5-, 11-H), 3.03 (br. d, J = 6.8, 1-, 9-H), 3.59 (br. d, J = 6.8, 6-, 11-H), 7.75 (m, 4H), 8.07 (m, 2H), 8.12 (m, 2H). – ^{13}C NMR: δ = 33.8, 37.7 (C-4), 45.6, 47.0, 52.3, 128.8 (4 C_m), 128.98 (2 C_o), 129.0 (2 C_o), 142.2 (2 C_{ipso}), 142.6 (2 C_{ispo}), 155.8 (C-7, -12)*, 155.9 (C-8, -13)*. – $C_{25}H_{18}N_4$ (374.4): calcd. C 80.19, H 4.85, N 14.96; found C 79.76, H 4.71, N 15.23.

(±)-5,9,14-Tribenzylidenepentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane-4,8,13-trione (*rac*-**75**): *rac*-**41** (600 mg, 2.61 mmol) and benzaldehyde (1.08 g, 10 mmol) in dry ethanol (50 ml) are treated with KOH (100 mg, 1.79 mmol) at room temp. for 2 d. After dilution with CH_2Cl_2 and water (100 ml each), the organic layer is washed with water (2 × 80 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue crystallizes from methanol to yield *rac*-**75** as colorless crystals (1.05 g, 81%), m.p. 233–234°C. – IR (KBr): $\tilde{\nu}$ = i.a. 3050 cm^{-1} (aryl-H), 3020 (=C–H), 2940 (C–H), 1700 (C=O), 1625 (C=C), 1490 (aryl). – ^1H NMR: δ = 2.68 (br. d, 3-H)*, 2.85 (br. d, 12-H)*, 2.91–3.02 (m, 2-, 7-, 11-H), 3.31 (br. d, 6-H)**, 3.41 (br. d, 1-H)**, 3.57 (br. d, 10-H)**, 7.24–7.45 (m, 15H), 7.50 (s, 1H, =C*H*Ph), 7.52 (s, 1H, =C*H*Ph), 7.62 (s, 1H, =C*H*Ph). – $C_{35}H_{26}O_3$ (494.6): calcd. C 85.00, H 5.30; found C 84.97, H 5.81.

(±)-4,5;8,9;13,14-Tris([2′,3′]quinoxalino)pentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8,13-triene (*rac*-**76**): Ozone is bubbled through a solution of *rac*-**75** (1.0 g, 2.02 mmol) in methanol/CH_2Cl_2 (50 ml, 1:3) at –78°C until a blue color appears. Stirring is continued for 15 min, followed by addition of dimethyl sulfide (2 ml). The reaction vessel is brought into a bath at 60°C, and immediately *o*-phenylenediamine (1.0 g, 9.25 mmol) in dry methanol (8 ml) is added. After 3 h at 60°C, the solvent is evaporated in vacuo and the residue filtered through silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.09) to provide a mixture of 140 mg *rac*-**76** and *o*-phenylenediamine, which is dissolved in CH_2Cl_2 (50 ml), washed twice with 0.5 M HCl, dried ($MgSO_4$), and concentrated in vacuo to give colorless crystals of *rac*-**76** (90 mg, 9%), m.p. >370°C (CH_2Cl_2/PE 30/50). – IR (KBr): $\tilde{\nu}$ = i.a. 3060 cm^{-1} (aryl-H), 2940 (C–H), 1500 (aryl), 1395 (C=N), 1380 (C=N), 1325 (C=N). – ^1H NMR: δ = 2.87 (br. q, 2-, 11-H), 3.34 (dd, 1-, 3-, 6-, 7-, 10-, 12-H), 7.80 (m, 6H, *m*-H), 8.11 (m, 6H, *o*-H). – ^{13}C NMR: δ = 28.2 (C-2, -11), 47.4 (C-1, -3, -6, -7, -10, -12), 129.1 (6 C_m), 129.6 (6 C_o), 142.2 (6 C_{ispo}), 155.5 (C-4, -5, -8, -9, -13, -14). – $C_{32}H_{20}N_6$ (488.6): calcd. C 78.67, H 4.13, N 17.20; found C 78.45, H 3.87, N 17.60.

(±)-Tetracyclo[6.4.0.0^{2,6}.0^{3,11}]dodeca-4,9-diene (*rac*-**81**): *rac*-**19** (370 mg, 2.34 mmol) is sublimed at 0.4 Torr by slight warming within 10 min through a 20 cm long quartz tube filled with quartz Raschig rings, preheated to 590°C. The condensate (cold trap, liquid N_2) consisting of starting material and 2 products [GC analysis: injector 150°C, SE 30 column 110°C, detector 150°C, retention times: *rac*-**19** 18.60 min (11%), unknown byproduct 18.90 min (13%), *rac*-**81** 19.30 min (58%)], is filtered through silica gel (hexane) to provide *rac*-**19** (27 mg, 7%, R_f = 0.56) and a mixture of the byproduct and *rac*-**81** (170 mg, 63%, ca. 1:4, GC). The latter is separated by column chromatography (SiO_2, hexane, 70 cm/20 mm, R_f = 0.42) with analysis of the fractions by GC, *rac*-**81** (30 mg), m.p. 148–149°C, sublimes at 60–70°C/65 Torr. – IR (KBr): $\tilde{\nu}$ = i.a. 3034 cm^{-1} (=C–H), 3014 (=C–H), 2928 (C–H), 2850 (C–H), 1634 (C=C), 1605 (C=C), 1441 (CH_2). – ^1H NMR (400 MHz): δ = 1.45 and 1.70 (AB, 7-H), 1.77 and 1.82 (AB, 12-H), 2.35 (m, 1-H), 2.64 (m, 8-, 11-H), 2.98 (m, 6-H), 3.02 (m, 2-H), 3.46 (m, 3-H), 5.21 (m, 4-H), 5.41 (dd, 10-H)*, 5.55 (dd, 9-H)*, 5.62 (dd, 5-H). – ^{13}C NMR: δ = 34.6 (C-7), 38.2 (C-12), 40.2 (C-8)*, 42.5 (C-11)*, 45.2 (C-1), 47.6 (C-6), 53.7 (C-2), 60.4 (C-3), 130.8 (C-9)**, 132.9 (C-4), 133.6 (C-10)**, 135.4 (C-5). – $C_{12}H_{14}$ (158.2): calcd. C 91.08, H 8.92; found C 90.89, H 8.74.

(±)-(rel-1R:4R,9R)-4,5;9,10-Bisepoxytetracyclo[6.4.0.0^{2,6}.0^{3,11}]dodecane (*rac*-**82**): *m*-CPBA (90 mg, 70%, 63 mg, 0.37 mmol) is added with vigorous stirring to a solution of *rac*-**81** (25 mg, 0.16 mmol) in CH_2Cl_2 (10 ml) and 0.5 M $NaHCO_3$ solution (20 ml). After 2 h, the mixture is diluted with CH_2Cl_2 (50 ml) and satd. $NaHCO_3$ solution (20 ml). The organic layer is washed with satd. $NaHSO_3$ solution (10 ml) and satd. $NaHCO_3$ solution (20 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue is filtered through silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.32) to give *rac*-**82** (22 mg, 77%) as a colorless solid, m.p. 194–195°C, which sublimes at 80°C/10^{-2} Torr. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1} (C–H), 2924 (C–H), 1447 (CH_2), 1257 (C–O), 900 (C–O), 808 (C–O). – ^1H NMR (400 MHz): δ = 1.25 (ddd, J = 4.8; 4.8; 12.0, 12-H), 1.64 (br. d, 7-H), 2.01 (ddd, J = 7.5, 10.1, 14.3, 7′-H), 2.18 (br. d, 12′-H), 2.29 (ddd, 1-H), 2.47 (dd, 8-H), 2.63 (m, 11-H), 2.67–2.74 (m, 2-, 9-H), 2.79 (dd, J = 8.3, 6-H), 2.87 (dd, J = 6.8; 9.6, 3-H), 3.18 (dd, J = 4.4; 4.4, 10-

H), 3.40 (d, $J = 2.2$, 5-H), 3.59 (d, 4-H). – ^{13}C NMR: δ = 28.8, 33.5, 35.1, 39.0, 44.9, 45.2, 49.6, 53.3, 53.8, 55.4, 59.3, 64.3. – $C_{12}H_{14}O_2$ (190.2): calcd. C 75.76, H 7.42; found C 75.68, H 7.40.

The following thermolysis reactions are generally carried out in a sealed glass ampoule. The starting material and hydrogen acceptor (Pd/C) are filled in as solids, benzene is added and the tube is evacuated several times in a cooled (liquid N_2) Schlenk tube and vented with N_2. Then the tube is sealed and heated in a furnace with a homogeneous temperature distribution.

*Thermolysis of rac-***30**: *rac-***30** (28 mg, 0.16 mmol) and Pd/C (38 mg) in dry benzene (2 ml) are heated to 200°C for 16 h. The reaction mixture consisting of one monomeric component besides polymers is filtered through silica gel (PE 30/50, $R_f = 0.25$): after concentration 21 mg (77%) of fluorene (**86**, identified by comparison of the ^{1}H-NMR spectrum with one of an authentic sample).

*Thermolysis of rac-***52**: *rac-***52** (53 mg, 0.24 mmol) and Pd/C (95 mg) in dry benzene (ca. 2 ml) are heated to 220°C for 30 h. The resulting suspension is stirred in CH_2Cl_2 (20 ml) for 1 h, the Pd/C is sucked off and the solution filtered through silica gel (cyclohexane, $R_f = 0.16$) to give a colorless solid (35 mg, 67%), a 8:1 mixture of **87** and **88** (^{1}H NMR, comparison with spectra of authentic samples).

*Thermolysis of rac-***53**: *rac-***53** (25 mg, 0.09 mmol) and Pd/C (38 mg) in benzene (ca. 1 ml) are heated to 380°C for 2 d. The suspension is stirred in CH_2Cl_2 (10 ml) for 1 h, the Pd/C is sucked off and the solution concentrated in vacuo. Filtration of the brownish residue through silica gel (cyclohexane) yields a yellowish crystalline solid (11 mg, 44%), a 1:1 mixture of naphthalene and 2-methylnaphthalene (^{1}H NMR, comparison with the known spectra[170]).

*Thermolysis of rac-***3**: *rac-***3** (25 mg, 0.14 mmol) and Pd/C (50 mg) in dry benzene (ca. 2 ml) are heated to 200°C for 20 h. The reaction mixture consisting of one monomeric component (TLC) is filtered through silica gel (PE 30/50, $R_f = 0.27$); after concentration 18 mg (74%) of **79** (^{1}H NMR, comparison with an authentic sample).

*Thermolysis of rac-***59**: *rac-***59** (34 mg, 0.15 mmol) and Pd/C (59 mg) in dry benzene (ca. 1.5 ml) are heated to 220°C for 24 h. The reaction mixture is stirred with CH_2Cl_2 for 1 h, sucked off from the Pd/C, and concentrated in vacuo. The solid residue is filtered through silica gel (cyclohexane) to give a nearly colorless solid material (22 mg, 66%), a 1:4.6 mixture of **90** and **92** (^{1}H NMR, comparison with the known spectra[61]).

*Thermolysis of rac-***61**: *rac-***61** (60 mg, 0.21 mmol) and Pd/C (150 mg) in dry benzene (3 ml) are heated to 260°C for 24 h. The reaction mixture is stirred with CH_2Cl_2 (50 ml) for 1 h, filtered, and the filtrate concentrated in vacuo. The brown residue is filtered through silica gel (cyclohexane/ethyl acetate, 50:1, $R_f = 0.30$) to give a colorless solid (27 mg, 46%), a 40:1 mixture of **91** and **93** (^{1}H NMR, comparison with the known spectra[62]).

*Thermolysis of rac-***4**: *rac-***4** (40 mg, 0.12 mmol) and Pd/C (80 mg) in dry benzene (2 ml) are heated to 400°C for 40 h. The reaction mixture is extracted in a soxhlet apparatus with ethyl acetate for 6 h. After concentration in vacuo, the residue is filtered through silica gel (cyclohexane/ethyl acetate, 50:1, $R_f = 0.18$) to provide a yellowish solid (11 mg, 28%), which is most probably naphtho[2,3-*g*]chrysene (^{1}H NMR, comparison with a calculated spectrum[63]).

(±)-(13R,14S)-13,14-Epoxypentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradeca-4,8-diene (*rac-***94**): Benzoylpercarbamic acid (350 mg, 1.92 mmol) is added within 3 h at room temp. to *rac-***3** (250 mg, 1.37 mmol) in dry CH_2Cl_2 (5 ml). The reaction mixture is filtered through silica gel (PE 30/50) to separate *rac-***3** (90 mg, 36%). Further eluation (ethyl acetate) gives a mixture (190 mg) of mono-, bis-, and trisepoxides, from which *rac-***94** (90 mg, 33%, $R_f = 0.59$), m.p. 117–118°C (ether/PE 30/50) can be separated by chromatography through silica gel (cyclohexane/ethyl acetate 9:1). A further fraction contains a colorless solid (60 mg, not uniform, bisepoxides, 250-MHz ^{1}H NMR).

*rac-***94**: IR (KBr): $\tilde{\nu}$ = i.a. 3042 cm^{-1} (=C–H), 2992 (C–H), 2936 (C–H), 1611 (C=C), 1259 (C–O), 896 (C–O), 782 (C–O), 667 (=C–H). – ^{1}H NMR: δ = 1.43 (m, 2-, 11-H), 1.64 (dd, 12-H), 1.76 (dd, 1-H), 1.89 (dd, 7-H)*, 2.06 (dd, 6-H)*, 2.38 (dd, 3-H), 3.18 (dd, 10-H), 3.39 (dd, 14-H), 3.60 (dd, 13-H), 6.17 (dd, 9-H), 6.27 (dd, 4-H), 6.36 (m, 5-, 8-H). – ^{13}C NMR: δ = 24.5, 25.5, 33.2, 37.9, 43.4, 43.9, 46.0, 47.3, 51.6 (C-13)*, 55.4 (C-14)*, 132.1 (C-5)**, 132.9 (C-8)**, 134.8 (C-4)**, 135.1 (C-9)**. – $C_{14}H_{14}O$ (198.3): calcd. C 84.81, H 7.12; found C 84.47, H 6.83.

9-Oxahexacyclo[6.6.1.0^{2,7}.0^{3,12}.0^{4,10}.0^{11,15}]pentadeca-5,13-diene (**95**): *rac-***94** (30 mg, 0.15 mmol) in dry CCl_4 (1 ml) under N_2 is treated with amberlyst 15 (100 mg, H^+ form, 20–50 mesh, evaporated several times with benzene and dried in vacuo at 80°C) at 70°C for 8 h. After filtration and concentration in vacuo, the residue is filtered through silica gel (cyclohexane/ethyl acetate, 9:1, $R_f = 0.18$) to give **95** as a colorless oil (23 mg, 77%), which is distilled at 80°C/10^{-2} Torr. – IR (neat): $\tilde{\nu}$ = i.a. 3040 cm^{-1} (=C–H), 2964 (C–H), 2885 (C–H), 1621 (C=C), 1101 (C–O), 674 (=C–H). – ^{1}H NMR: Figure 5, $J_{1,13} = J_{4,6} = 3.2$. – ^{13}C NMR: Figure 5. – $C_{14}H_{14}O$ (198.3): calcd. C 84.81, H 7.12; found C 84.03, H 7.56.

(±)-(4R,5S,8R,9S,13S,14R)-4,5;8,9;13,14-Trisepoxypentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane (*rac-***99**), *(±)-(4R,5S,8R,9S,13R,14S)-4,5;8,9;13,14-Trisepoxypentacyclo[8.4.0.0^{2,7}.0^{3,12}.0^{6,11}]tetradecane* (*rac-***100**), *and endo, endo,exo-3,8,14,18-Tetroxaoctacyclo[8.7.0.0^{2,4}.0^{5,16}.0^{6,12}.0^{7,9}.0^{11,17}.0^{13,15}]octadecane* (*rac-***101**): Benzoylpercarbamic acid is added at 40°C to *rac-***3** (135 mg, 0.74 mmol), dissolved in dry CH_2Cl_2 (20 ml), until all starting material has reacted (TLC monitoring, ca. 690 mg, 3.81 mmol, within 12 h). After addition of silica gel (1.5 g), the solvent is evaporated, the residue put onto a silica gel column, and eluted with cyclohexane/ethyl acetate (1:1) to give colorless crystalline *rac-***100** (90 mg, 53%, $R_f = 0.24$) in the first fraction, which can be recrystallized from ether for analytical purposes. The second fraction (15 mg, 9%) contains a mixture of *rac-***99** and *rac-***101** (1:1, 250-MHz ^{1}H-NMR spectrum), which can be separated by fractional crystallization from ether/ethyl acetate mixtures.

*rac-***99**: m.p. 196–198°C (ether). – IR (KBr): $\tilde{\nu}$ = i.a. 2994 cm^{-1} (C–H), 2914 (C–H), 1254 (C–O), 798 (C–O). – ^{1}H and ^{13}C NMR: Figure 5. – $C_{14}H_{14}O_3$ (230.3): calcd. C 73.03, H 6.13; found C 72.68, H 5.96.

*rac-***100**: m.p. 189–190°C (ether). – IR (KBr): $\tilde{\nu}$ = i.a. 2994 cm^{-1} (C–H), 2918 (C–H), 1258 (C–O), 803 (C–O). – ^{1}H NMR: δ = 1.94 (dd, 12-H), 1.99–2.15 (m, 2-, 3-, 6-, 11-H), 2.90 (dd, 1-H)*, 2.98 (dd, 7-H)*, 3.03 (dd, 10-H)*, 3.12 (dd, 4-, 5-H)**, 3.24 (dd, 8-H)**, 3.28 (dd, 9-H)**, 3.42 (dd, 13-H)**, 3.46 (dd, 14-H)**. – ^{13}C NMR: δ = 29.9, 30.6 (2 C), 30.7, 31.6, 34.9, 35.4, 35.7, 49.0 (C-4)*, 49.2 (C-5)*, 49.5 (C-8)*, 54.13 (C-9)*, 54.2 (C-13)*, 54.5 (C-14)*. – $C_{14}H_{14}O_3$ (230.3): calcd. C 73.03, H 6.13; found C 72.69, H 6.11.

*rac-***101**: m.p. 252–254°C (ether). – IR (KBr): $\tilde{\nu}$ = i.a. 3026 cm^{-1} (C–H), 2986 (C–H), 2954 (C–H), 2918 (C–H), 1266 (C–O), 790 (C–O). – ^{1}H NMR: δ = 2.37 (m, 11-, 17-H), 2.57 (m, 5-, 6-, 12-, 16-H), 3.16 (m, 2-, 9-H), 3.24 (m, 13-, 15-H), 3.43 (m, 4-, 7-H), 4.50 (m, 1-, 10-H). – ^{13}C NMR: δ = 23.6 (2 C, $J_{C,H} = 141$), 30.2 (2 C, $J_{C,H} = 138$), 35.8 (2 C, $J_{C,H} = 142$), 49.5 (2 C, $J_{C,H} = 186$), 52.7 (2 C, $J_{C,H} = 177$), 53.4 (2 C, $J_{C,H} = 177$), 74.1 (C-1, -10, $J_{C,H} = 157$). – MS (CI, isobutane), *m/z* (%): 247 (100) [$M^+ + 1$], 229 [$M^+ - H_2O$], 201 [$M^+ - H_2O$, – CO], 183 [$M^+ - 2\,H_2O$, – CO]. – $C_{14}H_{14}O_4$ (246.3): calcd. C 68.28, H 5.73; found C 67.58, H 6.10.

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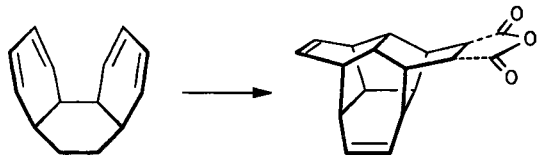

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