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4,7,11-Triheterotrishomocubanes – Propeller-Shaped Highly Symmetrical Chiral Molecules Derived from Barrelene

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Dedicated to Professor Paul von R. Schleyer on the occasion of his 75th birthday

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Epoxidation of barrelene (**3**) with a neutralized solution of Oxone® gave the barrelene trisepoxide **6** in 82 % isolated yield, while lead tetraacetate promoted aziridination of **3** with two equiv. of *N*-aminophthalimide gave a mixture of mono-**7** and bis(aziridine) *endo*,*exo*-**8**, which were isolated in 67 and 8 % yield, respectively. Fourfold repetition of this aziridination gave the bis(aziridines) *exo*,*exo*- and *endo*,*exo*-**8** along with the trisaziridine **9** in 21, 8 and 19 % yield, respectively. Epoxidation of **7** and *endo*,*exo*-**8** with buffered *m*-chloroperbenzoic acid furnished the dioxaazatrishomobarrelene **10** and oxadiazatrishomobarrelene **11** in 36 and 62 % yield, respectively. The structures of triheteratrishomobarrelenes **6** and **9** were established by X-ray crystallography. Upon treatment with $BF_3{\cdot}Et_2O$ at –20 °C (for **6**) or with the strongly acidic ion exchange resin Amberlyst 15 at ambient or elevated temperatures (for **9**–**11**), these triheteratrishomobarrelenes rearrange to give the triheteratrishomocubanes *rac*-**12** to *rac*-**15**, as proved by X-ray crystal structure analysis of *rac*-**13**, in 75–100 % yield. The enantiomeric pairs of trioxa-**12** and triazatrishomocubane **13** were separated by preparative HPLC on a chiral column. **12** exhibited specific rotations of $[\alpha]_D^{25}$ = +196 and $[\alpha]_{365}^{25}$ = +652 (*c* = 0.497, $CHCl_3$) for the firstly eluted and $[\alpha]_D^{25}$ = –173 and $[\alpha]_{365}^{25}$ = –608 (*c* = 0.503, $CHCl_3$) for the secondly eluted enantiomer; **13** had $[\alpha]_D^{25}$ = +30 and $[\alpha]_{435}^{25}$ = +501 (*c* = 0.490, $CHCl_3$) for the firstly as well as $[\alpha]_D^{25}$ = –28 and $[\alpha]_{435}^{25}$ = –475 (*c* = 0.501, $CHCl_3$) for the secondly eluted enantiomer. The geometry of *rac*-**13** and the absolute configurations of (–)-**12** and (+)-**13** were determined by X-ray crystal structure analyses. According to this, (–)-**12** and (+)-**13** possess the same (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-configuration. The absolute configuration of the former was also confirmed by DFT computations at the TD-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) level of theory; the computed specific rotation for (–)-**12** was –178. Computations for the elusive (*all-R*)-triazatrishomocubane (*all-R*)-**13**-H without phthalimidyl substituents on the nitrogen atoms disclosed that the sign of rotation is the same for the parent (*all-R*)-**13**-H and (*all-R*)-trioxatrishomocubane (*all-R*)-**12** with the same absolute configuration.

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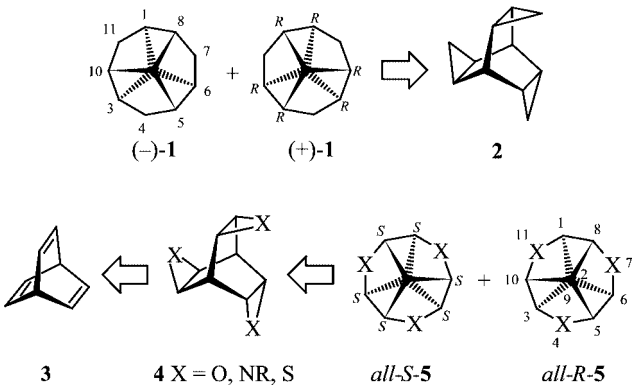
Introduction

The chemistry of strained polycyclic aliphatic molecules continues to be fascinating, and remains a challenging objective for organic chemists to probe various concepts of structure and reactivity.[1,2] Among polycyclic cages, the chiral (D_3)-trishomocubane (pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane) **1**[3] has attracted particular attention with respect to its preparation (in racemic[4] as well as in enantiomerically pure form[5]), its physical[6] and chemical[7] properties as well as the biological activities of some of its derivatives;[8] much less is known about heteroanalogues of **1**. To the best of our knowledge, only 4-oxa-[4a,9] and 4,7,11-trioxatrishomocubanes[10] have been synthesized until now in racemic form in low or moderate yield, respectively (Scheme 1).

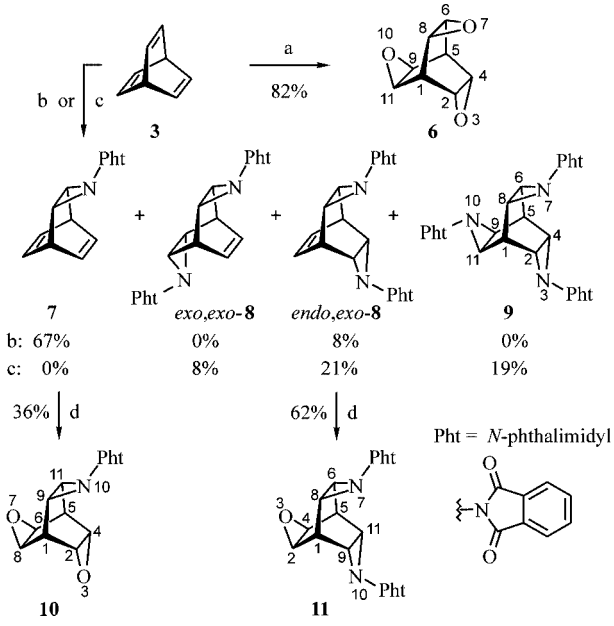


Scheme 1. Propeller-shaped chiral molecules potentially derived from barrelene (**3**).

Formally, (D_3)-trishomocubane **1** is a valence isomer of trishomobarrelene (pentacyclo[3.3.3.$0^{2,4}$.$0^{6,8}$.$0^{9,11}$]undecane, **2**) (Scheme 1). In view of the overall strain energy (SE) of **2** with its three cyclopropane moieties which contribute about 84 kcal mol^{-1} (28.1[11] × 3 = 84.3 kcal mol^{-1}), there should be enough thermodynamic driving force for **2** to rearrange to (D_3)-trishomocubane which has an SE of 39.6 kcal mol^{-1}, as computed at the G3(MP2)/B3LYP-6-31G(d) level of theory.[12] However, under none of the conditions applied in the studies of the chemical properties of **2**[10c,13] and its bridgehead derivatives (cf. ref.[14]) has such a transformation been observed, most probably because appropriate conditions have never been applied (cf. ref.[4e]). Since three-membered heterocycles are more readily activated by acids than cyclopropanes,[15] barrelene trisepoxide **6** (≡ **4**, X = O) (trioxatrishomobarrelene) undergoes this rearrangement upon treatment with boron trifluoride etherate at –20 °C,[10] and bullvalene trisepoxide (trioxatrishomobullvalene) rearranged in the same fashion even upon contact with anhydrous magnesium sulfate.[16] While trioxatrishomobullvalene is a chiral molecule itself, and its enantiomerically pure forms rearrange stereospecifically, **4** is not chiral, but rearranges to chiral (D_3)-trioxatrishomocubane **5** (X = O) (cf. ref.[17]). Since the latter had not been obtained previously in enantiomerically pure form, we set out to separate the racemate of **5** (X = O) and to prepare other heteroanalogues **5** (X = O, NR) by way of the corresponding triheteratrishomobarrelenes **4** and their acid-catalyzed rearrangements (Scheme 1). This would provide new insights into the relationship between structures and optical activities of such molecules.

Results and Discussion

Earlier attempts to epoxidize barrelene **3** with buffered *m*-chloroperbenzoic acid led to the trisepoxide **6** in moderate yield (20%), as it was accompanied by the *exo*,*exo*-bis(epoxide), from which **6** had to be separated by preparative gas chromatography.[10a,10b] Even worse were the results of an attempted synthesis of **6** by treatment of barrelene (**3**) with a 0.1 M solution of dimethyldioxirane in acetone[18] at –78 to 20 °C, upon which only a mixture of mono- and bis(epoxides) was obtained. Eventually, the trisepoxide **6** was accessible by treatment of **3** with a buffered solution of Oxone® in a mixture of acetone, dichloromethane and water in 82% isolated yield after recrystallization (Scheme 2). In contrast to the epoxidation of bullvalene, which furnished the trisepoxide in virtually quantitative yield,[16] the trisepoxide **6** was formed as the main, but not the sole product, in fact small fractions of the two diastereomeric bis(epoxides) (*endo*,*exo* and *exo*,*exo*) were also detected in the crude reaction mixture (see Exp. Sect.).



Scheme 2. Preparation of trioxa- (**6**), triaza- (**9**), dioxaaza- (**10**) and oxadiazatrishomobarrelene (**11**) (isolated yields are presented). Reagents and conditions: a) Oxone®, $NaHCO_3$, CH_2Cl_2/acetone/H_2O, 0→20 °C, 3 h; b) *N*-aminophthalimide (2 equiv.), $Pb(OAc)_4$ (2 equiv.), K_2CO_3 (20 equiv.), CH_2Cl_2, 2 h; c) same as in b), but a sixfold excess of reagents was used, and the treatment was repeated three more times; d) *m*CPBA, $KHCO_3$, CH_2Cl_2, 20 °C, 16 h–2 d.

The preparation of the triazatrishomobarrelene **9** (≡ **4**, X = NR) turned out to be more difficult. An attempted direct transformation of all three oxirane into aziridine moieties in **6** according to an established protocol[19] as well as an attempted threefold cycloaddition of (ethoxycarbonyl)-nitrene generated by α-elimination from the anion of *N*-*p*-nitrobenzenesulfonoxyurethane[20] onto barrelene (**3**) both failed. Fortunately, however, aziridination of **3** with phthalimidylnitrene in situ generated by lead tetraacetate oxidation of *N*-aminophthalimide[21] applying two equivalents of reagent led to a mixture of the mono-**7** and the diaziridine *endo*,*exo*-**8**, which were isolated in 67 and 8% yield, respectively, by column chromatography on aluminum oxide (Scheme 2). When this aziridination was repeated four times with an even larger (sixfold) excess of reagents, a mixture of **7** (7%), *endo*,*exo*-**8** (45%), *exo*,*exo*-**8** (19%) and the tris-

adduct **9** (29%) was obtained. From this mixture, the diaziridine *exo*,*exo*-**8** could be isolated by column chromatography in 8% yield, but compounds *endo*,*exo*-**8** and **9** could not be separated. Yet crystallization furnished *endo*,*exo*-**8** and **9** in 21 and 19% isolated product yield, respectively. The diaziridine *endo*,*exo*-**8** has C_s symmetry, and accordingly four signals of the same intensity are observed for its tetracyclic framework in the ^{13}C-NMR spectrum (integrating for 2×CH each, see Exp. Sect.), while the skeleton of its C_{2v} symmetric isomer *exo*,*exo*-**8** should possess only three signals with an intensity ratio of 1:1:2. Epoxidation of mono- **7** and diaziridine *endo*,*exo*-**8** with buffered *m*-chloroperbenzoic acid smoothly led to the dioxaazatrishomobarrelene **10** and the oxadiazatrishomobarrelene **11**, which were isolated in 36 and 63% yield, respectively (Scheme 2).[22]

As the trisepoxide **6** and trisaziridine **9** formed beautifully looking crystals, colorless and yellow, respectively, they were subjected to X-ray structure analysis (Figure 1).[23] In the crystal, the molecules of **6** displayed almost ideal C_{3h} symmetry (τ = 0.2 and Φ = 0.4°, cf. ref.[24]), and the structure virtually corresponds to a superposition of a non-twisted bicyclo[2.2.2]octane skeleton[24] and three oxirane moieties[25] which are fused with a dihedral angle Θ each of 109.1°.

The molecules of **9** in the crystals grown from dichloromethane (**9A** in Figure 2) are located on special positions on a threefold axis. The planes of the phthalimidyl (Pht) groups are parallel to the axis. A similar "perpendicular"[26a] orientation of the substituents with respect to the three-membered rings has been found in all previously studied phthalimidylaziridine derivatives.[26c–26d] Like in other (*N*-phthalimidyl)aziridines,[26c–26d] the C–N and C–C bonds in the three-membered rings of **9** are slightly lengthened and differentiated more significantly in comparison with those in unsubstituted aziridine.[27] The bicyclo[2.2.2]-octane skeleton in **9** is not twisted (i.e. the angles $\tau \approx \Phi \approx$ 0°, cf. ref.[24]), while the interplanar angle between the plane through C1, C2, C4, C5 and that of the aziridine is Θ = 107.3° (Figure 1). The most remarkable feature is the packing of the molecules of **9** in the crystal, where the molecules are arranged in layers, parallel to the *ab*-plane, in such a way that they form hexagonal channels in a honeycomb-like array along the *c*-axis (Figure 2). Each molecule of **9** belongs to three adjacent channels, and at the level of each layer the three phthalimidyl groups form the walls of the channels.

The molecules of **9** in the layer are linked by intermolecular interactions of the distant hydrogen atoms of a phenylene moiety with the carbonyl carbon atoms of adjacent molecule (H···C 2.832 Å); along the channels, numerous (eight per each Pht group) C–H···O contacts (H···O 2.624 and 2.407 Å) hold the molecules together. The channels are filled with disordered solvent molecules. In crystals that were grown from *n*-octane/dichloromethane solution (**B** in Figure 2), both types of solvent molecules are present in the channels. In order to check whether the long molecules of *n*-octane were responsible to some extent for aligning the molecules of **9**, the latter was recrystallized from pure dichloromethane and the crystal structure determined (again **A** in Figure 2). Essentially, the packing of the molecules remained unchanged.

Upon treatment with boron trifluoride–diethyl ether at –20 °C for 1.5 h, the trisepoxide **6** rearranged to give the (D_3)-trioxatrishomocubane *rac*-**12** in virtually quantitative yield (94% after sublimation, Scheme 3). Apparently, barrelene trisepoxide **6** is less sensitive towards acid than bullva-

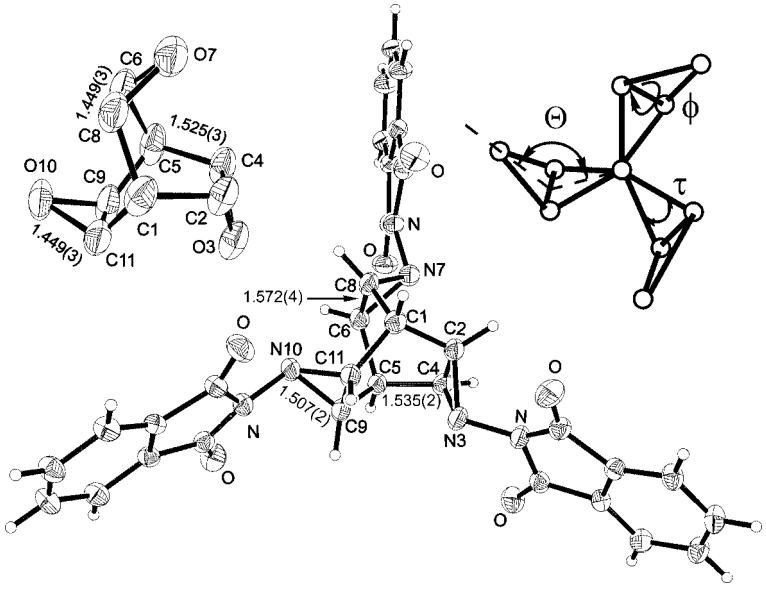


Figure 1. Molecular structures of *endo*,*exo*,*syn*-3,7,10-trioxapentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane [trioxatrishomobarrelene **6**, only one of the two independent molecules in the asymmetric unit is shown] and *endo*,*exo*,*syn*-3,7,10-tris(*N*-phthalimidyl)-3,7,10-triazapentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane [triazatrishomobarrelene, (C_{3h})-**9**] in the crystal.[23] Shown bond lengths [Å] represent mean values; thermal ellipsoids are shown at the 50% probability level.

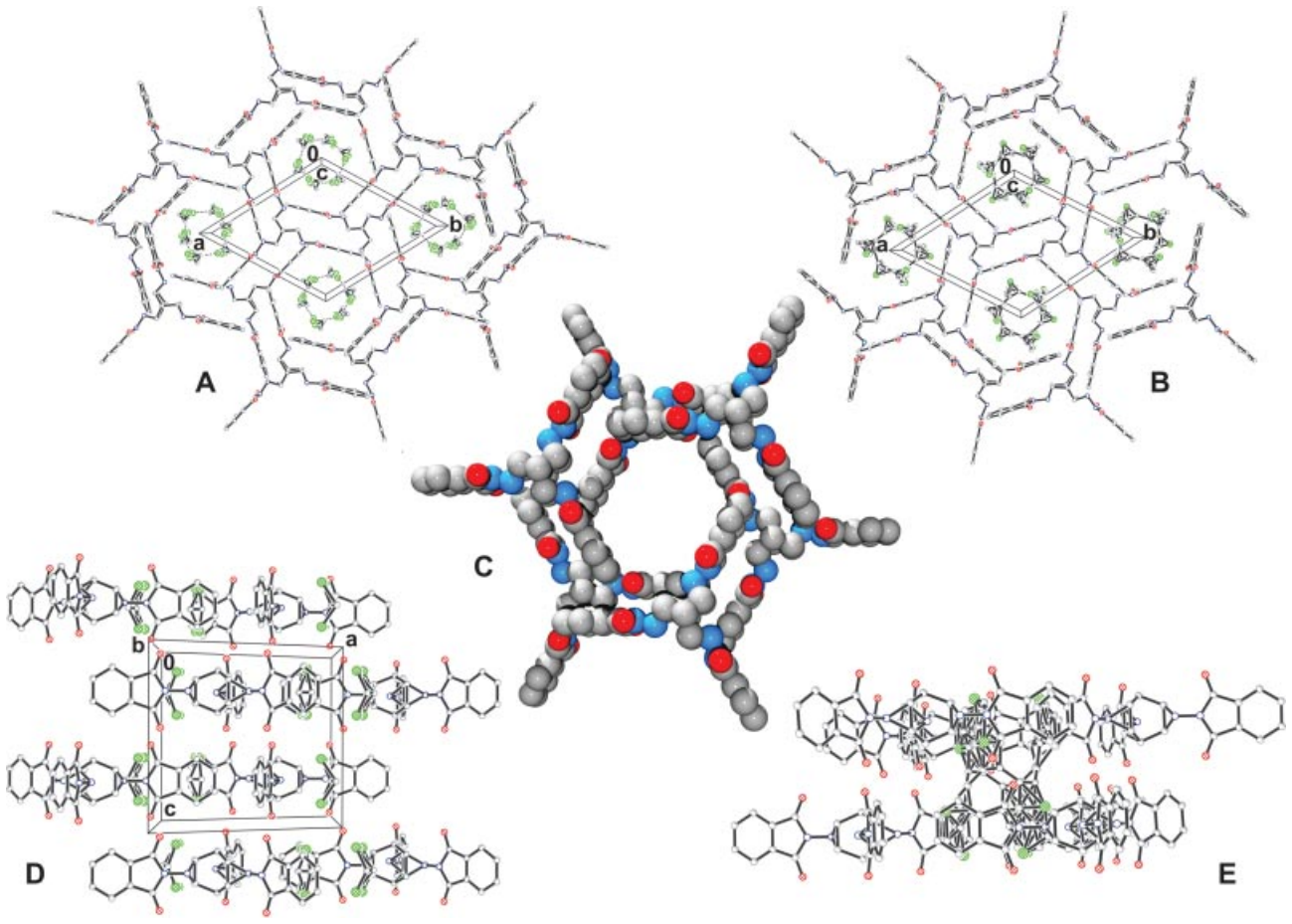
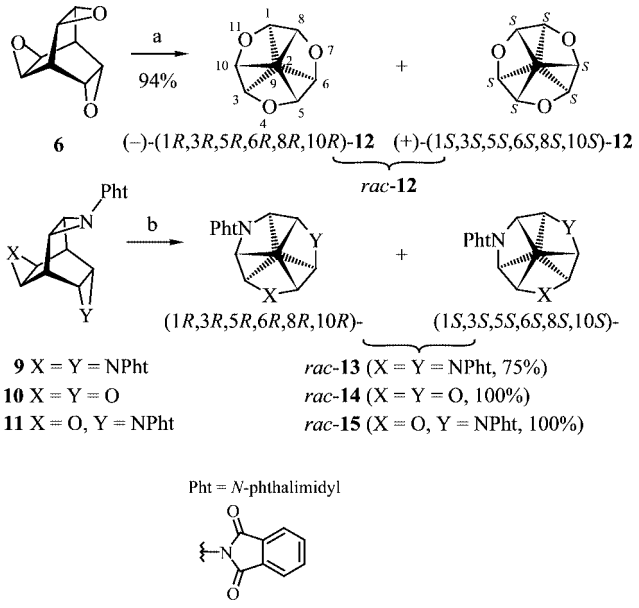


Figure 2. Channels in the crystal packing of **9**: Crystallized from dichloromethane (**A**) and dichloromethane/octane (**B**) (view along the *c* axis; H atoms are omitted for clarity); space-filling model without solvent molecules (**C**); crystal viewed along the *b* axis (**D** and **E**).

lene trisepoxide. Thus, after 15 min the conversion of **6** was only 50%, according to the ^{1}H NMR spectrum, and no rearrangement was observed under the action of anhydrous magnesium sulfate which caused rearrangement of bullvalene trisepoxide.[16]

The enantiomers of *rac*-**12** were eventually separated by preparative HPLC. The firstly eluted (+)-enantiomer had $[\alpha]_D^{25}$ = +196 and $[\alpha]_{365}^{25}$ = +652 (*c* = 0.497, $CHCl_3$); the second, probably less chemically pure, had $[\alpha]_D^{25}$ = –173 and $[\alpha]_{365}^{25}$ = –608 (*c* = 0.503, $CHCl_3$). Thus, the absolute value of the specific rotation of the enantiomerically pure (D_3)-trioxatrishomocubane **12** slightly exceeds that of the parent hydrocarbon (D_3)-trishomocubane **1** ($[\alpha]_D^{20}$ = 155–165 in different solvents, as reported by several research groups[5]). A single crystal of the enantiomerically pure (–)-**12** was subjected to X-ray structure analysis applying Cu-K_α radiation.[28] This revealed the absolute configuration for this enantiomer to be (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*) (Figure 3), and this means at the same time that the (+)-enantiomer possesses (1*S*,3*S*,5*S*,6*S*,8*S*,10*S*)-configuration. Ab initio computations at a reasonably high level of theory (TD-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d),[29–34] see Computational Studies) also predicted the (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-configuration for the (–)-enantiomer with a calculated specific rotation of $[\alpha]_D^{20}$ = –178 in the gas phase. This correlation be-



Scheme 3. Rearrangement of barrelene trisepoxide **6** and its aza analogues **9**–**11** to (D_3)-4,7,11-trioxatrishomocubane *rac*-**12**, (C_{3h})-4,7,11-triazatrishomocubane *rac*-**13**, and their analogues *rac*-**14**, *rac*-**15** as well as their possible configurations. Reagents and conditions: a) $BF_3{\cdot}Et_2O$, CH_2Cl_2, –20 °C, 1.5 h; b) $CHCl_3$, Amberlyst 15, 20–60 °C, 14 h.

tween absolute configuration and sense of rotation for the trioxatrishomocubane **12** is essentially the same as that for the (–)-enantiomer of the parent hydrocarbon **1** for which the absolute configuration had been determined as (1*S*,3*S*,5*S*,6*S*,8*S*,10*S*).[5a,5b] The latter has the same sense of helicity, only the designation differs due to the rules of the *R*,*S*-nomenclature (Scheme 1). The X-ray crystal structure analysis of the trisether (–)-**12** (Figure 3) disclosed almost ideal D_3 symmetry for this molecule in which the six C–C bonds adjacent to the bridgehead atoms C2, C9 [1.559(3) Å] are slightly lengthened as compared to the other three C–C bonds [1.530(3) Å] and to a normal C_{sp^3}–C_{sp^3} bond length (1.536 Å[35]) mostly due to their being incorporated in a polycyclic skeleton.[16,36] The bicyclo[2.2.2]-octane core in **12** is twisted with dihedral angles of Φ = –63.8 and τ = –40.7°.

The rearrangements of the aza analogues **9**–**11** to the 4,7,11-triazatrishomocubane (*rac*-**13**) and its oxa analogues *rac*-**14** and *rac*-**15** were achieved by simply stirring their solutions in chloroform with the strongly acidic ion exchange resin Amberlyst 15 at ambient or elevated temperatures (Scheme 3). The isolated yields of *rac*-**13**, *rac*-**14** and *rac*-**15** ranged from 75–100%. An X-ray crystal structure analysis of the triazatrishomocubane *rac*-**13** (Figure 3) disclosed almost ideal D_3 symmetry for its triazapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane core. However, the configu-

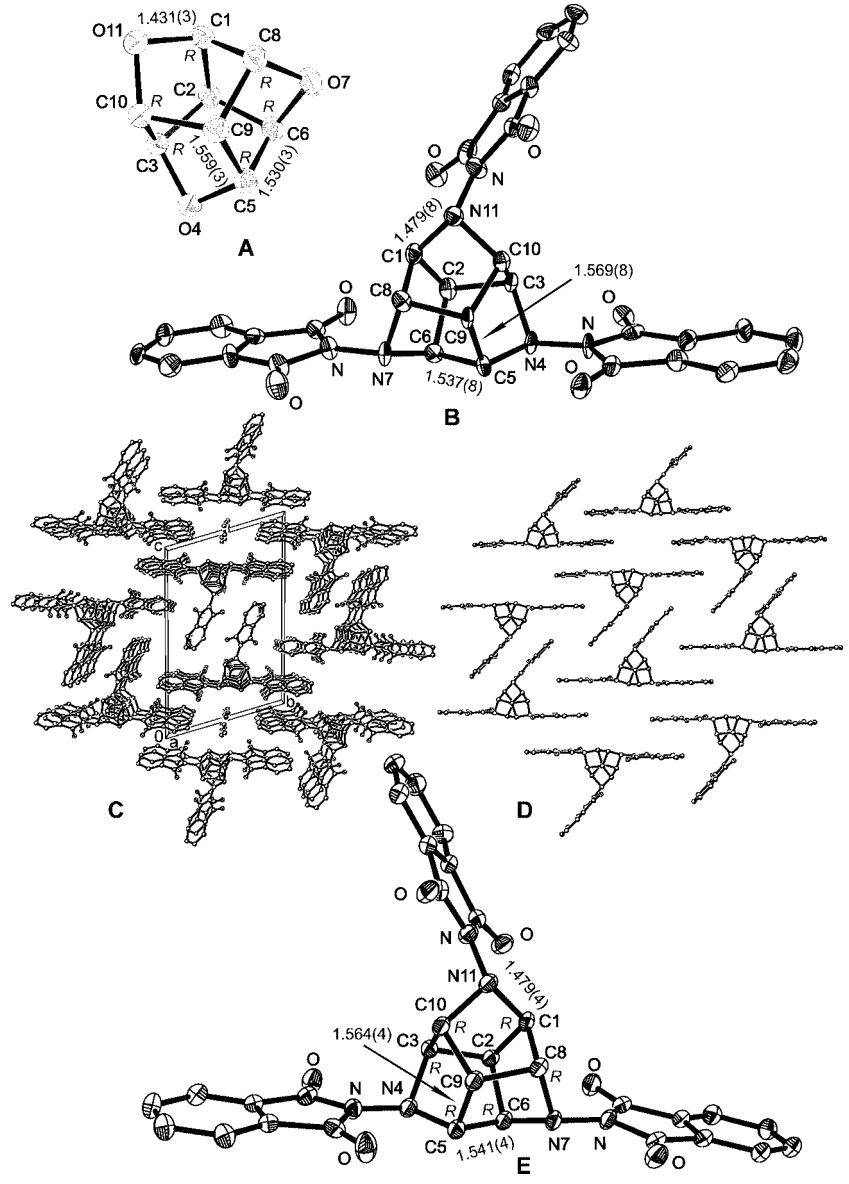


Figure 3. Structure and absolute configuration of (–)-4,7,11-trioxapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**12**] (**A**), structure (**B**) and absolute configuration (**E**) of *rac*- and (+)-4,7,11-tris(*N*-phthalimidyl)-4,7,11-triazapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane [*rac*-**13** and (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**13**] as well as packing (**C** along the b axis, **D** along the phthalimide planes) of *rac*-**13** in the crystal.[23] Bond lengths [Å] represent mean values based on assumed D_3 and C_{3h} symmetry; thermal ellipsoids are shown at the 50% probability level.

ration of the N(4) atom in molecule *rac*-**13** – most probably because of packing effects – in the crystal differs from those of N(7) and N(11), and thus the overall symmetry of the molecule is not D_{3h}. As in the case of **12**, the six C–C bonds adjacent to the bridgehead atoms C2 and C9 [1.569(8) Å] are slightly longer than the other three [1.537(8) Å] and a normal C_{sp^3}–C_{sp^3} bond length (1.536 Å[35]). The bicyclo[2.2.2]octane core in *rac*-**13** is twisted with dihedral angles of $\Phi = 60.7$ and $\tau = 39.2°$. As in the case of **9**, the molecules of *rac*-**13** in the crystal are packed in layers with open channels perpendicular to them. However, the arrangement of the molecules **13** in the layers is determined by π···π interactions between pairs of Pht groups, and not by C–H···π interactions. The C–H···O interactions link the molecules of neighboring layers. The channels in the packing of *rac*-**13** are narrower than those in **9** (about 6 Å across in **13** vs. ca. 10.5 Å in **9**), they have a rhomboid shape and are also filled with disordered solvent molecules.

The enantiomeric triazatrishomocubanes **13** were separated by preparative HPLC on a chiral column and exhibited specific rotations of $[\alpha]_D^{25} = +30$ and $[\alpha]_{435}^{25} = +501$ (c = 0.490, $CHCl_3$) for the firstly eluted enantiomer as well as $[\alpha]_D^{25} = -28$ and $[\alpha]_{435}^{25} = -475$ (c = 0.501, $CHCl_3$) for the secondly eluted one. The absolute configuration of the enantiomer (+)-**13** (Figure 3) was determined by X-ray crystal structure analysis applying Cu-K_α radiation,[28] and surprisingly turned out to be (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*), i.e. the same as those of (–)-**12**. The two sets of geometrical parameters determined for *rac*-**13** with Mo-K_α radiation and (+)-**13** with Cu-K_α radiation do not differ from one another significantly (Figure 3), in spite of their different crystal systems (triclinic and orthorhombic, respectively). As the molecule **13** with its 68 atoms ($C_{36}H_{20}N_6O_6$) is too large for currently available computer resources, the specific rotations for (*all-R*)-**13** and (*all-S*)-**13** cannot yet be computed. It would certainly be interesting to see whether computations for the gas phase would also reproduce the observed sense of rotation for the two enantiomeric **13**, as they do for the (D_3)-trioxatrishomocubane (*all-R*)-**12** and (*all-S*)-**12**. To clarify this question, we computed the optical rotations for (*all-R*)-triazatrishomocubane (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**13**-H as a hypothetical model without phthalimidyl substituents on the nitrogen atoms. The computations at the B3LYP/6-31+G** level of theory disclosed two possible structures with C_1 and C_3 symmetry which differ in energy by less than 1 kcal mol^{-1}. Their computed specific rotations also were rather similar to each other, namely for (C_1)-**13**-H $[\alpha]_D^{25} = -214.1$ and $[\alpha]_{435}^{25} = -435.9$ and for (C_3)-**13**-H $[\alpha]_D^{25} = -172.4$ and $[\alpha]_{435}^{25} = -341.9$, and thus rather close to those of trioxatrishomocubane (–)-**12**. Most importantly, the signs of the optical rotations remains the same for the triaza- and trioxatrishomocubanes of the same absolute configurations. As a consequence, the three chromophoric phthalimidyl substituents must be responsible for the change in sign of the optical rotations in (all-*R*)-**13** [corresponding to (+)-**13** with three phthalimidyl groups] in comparison with (*all-R*)-trioxatrishomocubane (–)-**12** of same absolute configuration.

Experimental Section

General Remarks: Barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **3**)[37] was prepared according to a previously published procedure. All operations in anhydrous solvents were performed under an argon atmosphere in flame-dried glassware. Dichloromethane and chloroform were dried by distillation from P_4O_{10}. Potassium carbonate was calcinated by heating with a Bunsen burner for 1 h; lead(IV) acetate was dried in a desiccator containing KOH pellets in vacuo for 2 d at ambient temp. All other chemicals were used as commercially available. Organic extracts were dried with $MgSO_4$. IR spectra were recorded with a Bruker IFS 66 (FT-IR) spectrometer as KBr pellets. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AM 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR) instrument in $CDCl_3$. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer), chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual $CHCl_3$ signals. Mass spectra (EI = 70 eV) were measured with a Finnigan MAT 95 spectrometer. Chiral HPLC analysis of *rac*-**12** was performed on a JASCO PU-986 chromatograph equipped with a refractive index (JASCO RI-2031) and a polarimetric (JASCO OR-990) detector using a 25 × 0.46 cm column with Chiralpak AD-H, hexane/2-propanol (90:10, v/v), 0.5 mL min^{-1}, and its preparative separation was conducted on the same HPLC system using a 25 × 2.0 cm column with Chiralpak AD, hexane/2-propanol (90:10, v/v), 10 mL min^{-1}. HPLC separations of *rac*-**13** were performed on a JASCO PU-986 chromatograph equipped with a UV (JASCO MD-2010) and a polarimetric (JASCO OR-990) detector using a 25 × 0.46 cm column for analytical purpose and three 25 × 0.46 cm columns connected in a series for preparative purposes with Chiralpak AD (immobilized type), hexane/chloroform/ethanol (8:10:0.8, v/v/v), 0.5 mL min^{-1}. Optical rotations were measured on a JASCO P-1030 digital polarimeter in a 1- or 2-cm cell for compounds (+)- and (–)-**12** and (+)- and (–)-**13**, respectively. Melting points were determined in a Büchi 510 capillary melting point apparatus, the values are uncorrected.

***endo,exo,syn*-3,7,10-Trioxapentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (Barrelene Trisepoxide, Trioxatrishomobarrelene, 6):** To a vigorously stirred solution of barrelene (**3**) (960 mg, 9.22 mmol) in a mixture of acetone (35 mL) and CH_2Cl_2 (20 mL) was added a neutralized solution of Oxone® [prepared from $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ (Oxone®, 28.29 g, 92.0 mmol SO_5^{2-}), $NaHCO_3$ (11.59 g, 138.0 mmol) in H_2O (150 mL)] at 0 °C over a period of 10 min. After stirring at ambient temp. for an additional 3 h, the reaction mixture was diluted with water (80 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried and concentrated under reduced pressure (20 Torr) at 30 °C to give 1.403 g (100%) of barrelene trisepoxide **6** as a colorless solid which, however, contained impurities of *endo,exo*- and *exo,exo*-bis(epoxides) (ca. 3% each according to a ^{1}H NMR spectrum). Recrystallization from hexane/CH_2Cl_2 gave pure **6** (1.147 g, 82%) with m.p. 223–226 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.20–3.16 (m, 6 H, 6 OCH), 3.09–3.06 ppm (m, 2 H, 2 CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 46.8 (6 CH), 30.4 ppm (2 CH). The structure of **6** was also confirmed by X-ray crystal structure analysis.[23]

Addition of *N*-Phthalimidylnitrene onto Barrelene (3)

General Synthetic Procedure (GP 1): To a vigorously stirred suspension of barrelene (**3**), *N*-aminophthalimide and anhydrous potassium carbonate in anhydrous CH_2Cl_2 (80 mL) was added dropwise a solution of lead(IV) acetate in anhydrous CH_2Cl_2 at –10 °C over a period of 30 min. The reaction mixture was stirred at 0 °C for an additional 0.5 h and at ambient temp. for 1 h, filtered through a

pad of Celite and concentrated under reduced pressure. The product was isolated by rapid column chromatography on aluminum oxide deactivated with water.[38]

3-(*N*-Phthalimidyl)-3-azatricyclo[3.2.2.0^{2,4}]nona-6,8-diene (7) and *endo*,*exo*-3,7-Bis(*N*-phthalimidyl)-3,7-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene (*endo*,*exo*-8): Rapid column chromatography (120 g of aluminum oxide deactivated with 6 mL of water, column 10 × 4.3 cm, CH_2Cl_2) of the residue obtained from barrelene (**3**) (1.041 g, 10.0 mmol), *N*-aminophthalimide (3.243 g, 20.0 mmol), anhydrous K_2CO_3 (27.6 g, 200 mmol) in CH_2Cl_2 (80 mL) and a solution of $Pb(OAc)_4$ (8.87 g, 20.0 mmol) in CH_2Cl_2 (50 mL) according to GP 1 furnished **7** (1.76 g, 67%, R_f = 0.45) and *endo*,*exo*-**8** (340 mg, 8%, R_f = 0.26).

7: Yellow crystals, m.p. 132 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.68 (mc, 2 H, Ar-H), 7.61 (mc, 2 H, Ar-H), 6.60 (dd, J = 2.8, 4.3 Hz, 2 H, 2 =CH), 6.14 (dd, J = 4.3, 7.0 Hz, 2 H, 2 =CH), 4.18 (mc, 2 H, 2 CH), 3.03 ppm (mc, 2 H, 2 NCH). IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2980, 1700, 1360, 1150, 970, 890, 730, 710, 680. $C_{16}H_{12}N_2O_2$ (264.28): calcd. C 72.71, H 4.58, N 10.60; found C 72.97, H 4.62, N 10.11.

***endo*,*exo*-8:** Light yellow crystals, which slowly decomposed above 200 °C, m.p. 225–230 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.77–7.73 (m, 4 H, Ar-H), 7.72–7.68 (m, 4 H, Ar-H), 6.18 (dd, J = 3.0, 4.5 Hz, 2 H, 2 =CH), 4.04 (mc, 2 H, 2 CH), 3.07 ppm (mc, 4 H, 4 NCH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 164.8 (2 C), 164.7 (2 C), 134.0 (2 CH), 133.9 (2 CH), 130.2 (4 C), 130.1 (2 CH), 122.9 (2 CH), 122.8 (2 CH), 48.4 (2 CH), 37.6 (2 CH), 31.9 ppm (2 CH). IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 1705, 1370, 1180, 1140, 890, 705. $C_{24}H_{16}N_4O_4$ (424.4): calcd. C 67.92, H 3.80, N 13.20; found C 67.87, H 4.05, N 12.52.

***endo*,*exo*,*syn*-3,7,10-Tris(*N*-phthalimidyl)-3,7,10-triazapentacyclo-[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane [Triazatrishomobarrelene, (C_{3h})-9], *endo*,*exo*-3,7-Bis(*N*-phthalimidyl)-3,7-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene (*exo*,*exo*-8) and *endo*,*exo*-3,7-Bis(*N*-phthalimidyl)-3,7-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (*endo*,*exo*-8):** Rapid column chromatography (120 g of aluminum oxide deactivated with 6 mL of water, column 10 × 4.3 cm, CH_2Cl_2) of the residue obtained from barrelene (**3**) (770 mg, 7.39 mmol), *N*-aminophthalimide (7.19 g, 44.4 mmol), anhydrous K_2CO_3 (61.3 g, 443.7 mmol) in CH_2Cl_2 (80 mL) and a solution of $Pb(OAc)_4$ (19.7 g, 44.4 mmol) in CH_2Cl_2 (70 mL) according to GP 1 furnished 2.5 g of a yellow foam which, according to its ^{1}H NMR spectrum, was essentially a 7:3 mixture of mono-**7** and *endo*,*exo*-bisadduct *endo*,*exo*-**8**. This mixture was treated with the same quantities of reagents three more times according to GP 1, after which a mixture (3.70 g) consisting of **7** (7 mol-%), *endo*,*exo*-**8** (45 mol-%), *exo*,*exo*-**8** (19 mol-%, R_f = 0.39) and trisadduct **9** (29 mol-%, R_f = 0.23) was isolated. Repeated column chromatography (170 g of aluminum oxide deactivated with 9 mL of H_2O, column 18 × 3.8 cm, CH_2Cl_2/Et_2O, 5:1) furnished *exo*,*exo*-**8** (251 mg, 8%, R_f = 0.46) and 2.08 g of a 1:1 mixture of *endo*,*exo*-**8** and **9** (R_f = 0.33). This mixture was taken up with a minimal quantity of CH_2Cl_2 and kept at –20 °C overnight. Still cold, the mixture was quickly filtered to give 1.18 g (19%) of **9** × 3 CH_2Cl_2 (according to X-ray crystal structure analysis) as beautiful yellow crystals which easily loose dichloromethane upon drying under vacuum to give **9** (820 mg, 19%) as a light yellow powder, which slowly decomposed above 260 °C, m.p. 279–281 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 6 H, Ar-H), 7.69–7.64 (m, 6 H, Ar-H), 3.85 (mc, 2 H, 2 CH), 2.98 ppm (mc, 6 H, 6 NCH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 164.7 (6 C), 134.0 (6 CH), 130.2 (6 C), 123.0 (6 CH), 39.8 (6 CH), 25.2 ppm (2 CH). IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 1710, 1460, 1370, 1145, 990, 885, 710, 705. The structure of **9** was also confirmed by X-ray crystal structure analysis.[23]

The mother liquor was concentrated under reduced pressure, and the residue was recrystallized twice from hexane/CH_2Cl_2 to give the bisadduct *endo*,*exo*-**8** (660 mg, 21%).

***exo*,*exo*-8:** Light yellow crystals, which slowly decomposed above 265 °C, m.p. 281 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.70 (mc, 4 H, Ar-H), 7.63 (m, 4 H, Ar-H), 5.61 (mc, 2 H, 2 =CH), 4.05 (mc, 2 H, 2 CH), 3.11 ppm (mc, 4 H, 4 NCH). IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2995, 1705, 1375, 1140, 970, 890, 730, 705. $C_{24}H_{16}N_4O_4$ (424.4): calcd. C 67.92, H 3.80, N 13.20; found C 68.02, H 3.73, N 13.02.

Epoxidation of Azahomobarrelenes 7 and *endo*,*exo*-8

General Synthetic Procedure (GP 2): A mixture of the respective azahomobarrelene, *m*-chloroperbenzoic acid (*m*CPBA, 85%) and $KHCO_3$ in CH_2Cl_2 was vigorously stirred at ambient temp. for the indicated time, then filtered, washed with satd. aq. Na_2CO_3 solution, dried and concentrated under reduced pressure. The product was isolated as indicated below.

***endo*,*exo*,*syn*-10-(*N*-Phthalimidyl)-3,7-dioxa-10-azapentacyclo-[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (Dioxaazatrishomobarrelene, 10):** As the crude product obtained from **7** (528 mg, 2 mmol), *m*CPBA (1.63 g, 8 mmol) and $KHCO_3$ (1.50 g, 15.0 mmol) in CH_2Cl_2 (30 mL) according to GP 2 (2 d reaction time) was contaminated with *endo*,*exo*- and *exo*,*exo*-monoepoxides (22 and 13%, respectively, according to an ^{1}H NMR spectrum), it was taken up with CH_2Cl_2 (20 mL), and the mixture stirred at ambient temp. for 5 h with *p*-toluenesulfonic acid monohydrate (50 mg, 0.26 mmol). The resulting light red solution was washed with satd. aq. Na_2CO_3 solution (5 mL), dried, filtered through a pad of aluminum oxide (2.0 g) and concentrated under reduced pressure to give 215 mg (36%) of **10** as light yellow crystals, m.p. 217–220 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.72 (mc, 2 H, Ar-H), 7.65 (mc, 2 H, Ar-H), 3.29 (mc, 2 H, 2 OCH), 3.24 (mc, 2 H, 2 OCH), 3.16 (mc, 2 H, 2 NCH), 2.76 ppm (mc, 2 H, 2 CH). IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 1705, 1460, 1370, 1140, 960, 895, 705. $C_{16}H_{12}N_2O_4$ (296.28): calcd. C 64.86, H 4.08, N 9.46; found C 64.55, H 4.21, N 9.17.

***endo*,*exo*,*syn*-7,10-Bis(*N*-phthalimidyl)-3-oxa-7,10-diazapentacyclo-[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (Oxadiazatrishomobarrelene, 11):** The residue obtained from *endo*,*exo*-**8** (200 mg, 0.47 mmol), *m*CPBA (205 mg, 1 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in CH_2Cl_2 (5 mL) according to GP 2 (16 h reaction time) was recrystallized from a minimal quantity of $CHCl_3$ to give 128 mg (62%) of **11** as light yellow crystals, m.p. 249–251 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.72 (mc, 4 H, Ar-H), 7.65 (mc, 4 H, Ar-H), 3.56 (mc, 2 H, 2 OCH), 3.27 (mc, 2 H, 2 NCH), 2.91 (mc, 2 H, 2 NCH), 2.82 ppm (mc, 2 H, 2 CH). IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2950, 1710, 1460, 1365, 1140, 990, 890, 830, 700. $C_{24}H_{16}N_4O_5$ (440.4): calcd. C 65.45, H 3.66, N 12.72; found C 65.39, H 3.71, N 12.52.

4,7,11-Trioxapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(D_3)-4,7,11-Trioxatrishomocubane, *rac*-12]: To a stirred solution of barrelene trisepoxide (**6**) (350 mg, 2.30 mmol) in anhydrous CH_2Cl_2 (30 mL) were added at –25 °C under argon two drops of boron trifluoride etherate. After stirring at –20 °C for an additional 1.5 h, the still cold mixture was poured into 50 mL of a vigorously stirred satd. aq. $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic extracts were dried and concentrated under reduced pressure to give *rac*-**12** (350 mg, 100%) as a colorless powder in essentially pure form. Further purification was achieved by sublimation at 65 °C/0.1 Torr to give 330 mg

(94%) of *rac*-**12** which had m.p. 236–238 °C (decomp.) in a sealed capillary (in an opened capillary this compound slowly sublimes above 220 °C and completely at 226–228 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.75–4.72 (m, 6 H, 6 OCH), 2.47–2.41 ppm (m, 2 H, 2 CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 85.2 (6 CH), 43.5 ppm (2 CH). HPLC analysis on a chiral column (Chiralpak AD-H) proved it to be a 1:1 mixture of two enantiomers with t_R = 20.4 and 29.4 min, respectively, and they were separated by preparative HPLC on a Chiralpak AD column, hexane/2-propanol, 10.0 mL min^{-1}. The firstly eluted enantiomer (1*S*,3*S*,5*S*,6*S*,8*S*,10*S*)-**12** had m.p. 225–227 °C, $[\alpha]_D^{25}$ = +196 and $[\alpha]_{365}^{25}$ = +652 (*c* = 0.497, $CHCl_3$); the second one (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**12** had m.p. 227–230 °C, $[\alpha]_D^{25}$ = –173 and $[\alpha]_{365}^{25}$ = –608 (*c* = 0.503, $CHCl_3$).[39] The structure of (–)-(1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-4,7,11-trioxapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(–)-(1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**12**] as well as its absolute configuration were also proved by an X-ray crystal structure analysis applying Cu-K_α radiation.[23]

Rearrangements of Azatrishomobarrelenes 9–11

General Synthetic Procedure (GP 3): A solution of the respective azatrishomobarrelene in chloroform was vigorously stirred with Amberlyst 15 at the indicated temp. for 14 h. If not otherwise specified, the resulting mixture was filtered through a pad of aluminum oxide and concentrated under reduced pressure.

4,7,11-Tris(*N*-phthalimidyl)-4,7,11-triazapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(C_{3h})-4,7,11-Triazatrishomocubane, *rac*-13]: The reaction mixture obtained from triazatrishomobarrelene (C_{3h})-**9** (185 mg, 0.32 mmol) and Amberlyst 15 (350 mg) in anhydrous $CHCl_3$ (20 mL) according to GP 3 (temp. 60 °C) was cooled and diluted with THF (20 mL) before it was filtered through a pad of aluminum oxide, and then concentrated under reduced pressure. The residue was recrystallized from $CHCl_3$ to give *rac*-**13** (139 mg, 75%) as light-yellow crystals, which slowly decomposed above 270 °C and completely at 310 °C without melting. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.80–7.78 (m, 6 H, Ar-H), 7.72–7.70 (m, 6 H, Ar-H), 4.40 (mc, 6 H, 6 NCH), 3.57 ppm (mc, 2 H, 2 CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 166.1 (6 C), 134.2 (6 CH), 130.0 (6 C), 123.2 (6 CH), 71.8 (6 CH), 46.7 ppm (2 CH). IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 1710, 1365, 1300, 1060, 875, 700. HPLC analysis on a Chiralpak AD-H column proved it to be a 1:1 mixture of two enantiomers with t_R = 9.5 and 14.0 min, respectively, and they were separated by preparative HPLC on a Chiralpak AD × 3 (immobilized-type) column. The firstly eluted enantiomer (1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**13** slowly decomposed above 270 °C, m.p. 288–290 °C (decomp), $[\alpha]_D^{25}$ = +30 and $[\alpha]_{435}^{25}$ = +501 (*c* = 0.490, $CHCl_3$); the second one (1*S*,3*S*,5*S*,6*S*,8*S*,10*S*)-**13** slowly decomposed above 270 °C, m.p. 287–289 °C (decomp.), $[\alpha]_D^{25}$ = –28 and $[\alpha]_{435}^{25}$ = –475 (*c* = 0.501, $CHCl_3$). The structures of *rac*-**13** and (+)-**13** as well as the absolute configuration of (+)-**13** were also proved by an X-ray crystal structure analysis applying Cu-K_α radiation in the latter case.[23]

11-(*N*-Phthalimidyl)-4,7-dioxa-11-azapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(C_s)-4,7,11-Dioxaazatrishomocubane, *rac*-14]: Concentration of the reaction mixture obtained from dioxaazatrishomobarrelene **10** (50 mg, 0.17 mmol) and Amberlyst 15 (50 mg) in $CDCl_3$ (1 mL) according to GP 3 (ambient temp.) furnished 50 mg (100%) of pure *rac*-**14** as light yellow crystals, m.p. 213-215 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.79 (mc, 2 H, Ar-H), 7.71 (mc, 2 H, Ar-H), 4.85 (mc, 2 H, 2 OCH), 4.71 (mc, 2 H, 2 OCH), 4.06 (mc, 2 H, 2 NCH), 2.77 ppm (mc, 2 H, 2 CH). IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 1715, 1360, 1080, 1060, 1040, 880, 705. $C_{16}H_{12}N_2O_4$ (296.28): calcd. C 64.86, H 4.08, N 9.46; found C 65.11, H 3.81, N 9.25.

7,11-Bis(*N*-phthalimidyl)-4-oxa-7,11-diazapentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [(C_s)-4,7,11-Oxadiazatrishomocubane, *rac*-15]: Concentration of the reaction mixture obtained from the oxadiazatrishomobarrelene **11** (20 mg, 0.05 mmol) and Amberlyst 15 (50 mg) in $CDCl_3$ (2 mL) according to GP 3 (ambient temp.) furnished 20 mg (100%) of pure *rac*-**15** as light yellow crystals, m.p. 281–282 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.79 (mc, 4 H, Ar-H), 7.71 (mc, 4 H, Ar-H), 4.90 (mc, 2 H, 2 OCH), 4.26 (mc, 2 H, 2 NCH), 4.21 (mc, 2 H, 2 NCH), 3.17 ppm (mc, 2 H, 2 CH). IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 1710, 1365, 1305, 1060, 1040, 875, 705. $C_{24}H_{16}N_4O_5$ (440.4): calcd. C 65.45, H 3.66, N 12.72; found C 65.21, H 3.91, N 12.48.

Computational Studies: Geometries were optimized using density functional theory (DFT) employing Becke's 3-parameter functional with the Lee–Yang–Parr correlation functional (B3LYP)[31–34] utilizing the 6-31+G(d) basis set[34,40] as implemented in Gaussian 98.[30] All optimized structures were characterized as minima by computing analytical second energy derivatives.[30]

The root mean square (RMS) deviation of the computed geometries from the experimental ones for the C–C and C–O bond lengths were 0.009(0) Å and 0.008(5) Å for (–)-**12** and (+)-**12**, respectively. The maximum deviations were 0.010(4) Å and 0.012(0) Å, respectively. Hence, the computed and experimentally determined geometries are in good agreement. The optical rotations were computed by the sum-over-states method from the circular dichroism data

$$\beta = \frac{c}{3\pi h} \mathrm{Im} \sum_{n \neq 0} \frac{\langle 0 |\boldsymbol{\mu}| n \rangle \langle n |\mathbf{m}| 0 \rangle}{\omega_{n0}^2 - \omega^2}$$

in which μ and **m** are the electric dipole and magnetic dipole operators, respectively; the summation runs over all excitations, and β is the trace of the frequency-dependent electric-dipole magnetic-dipole polarizability tensor.[41]

Only the single excitations of the valence electrons were computed at the time-dependent (TD) DFT level of theory using the B3LYP functional at the respective optimized geometries with the 6-31+G(d,p) basis set[34,40] as implemented in Gaussian 03. The thus obtained optical rotations (ORs) apply to the gas phase while the experimental ORs are measured in solution. In general computed values for the gas phase, sometimes considerably so, overshoot those for the solvated molecules[42] due to interactions with the solvent.

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[23] Crystals suitable for X-ray structure analyses were obtained by slow evaporation of their solution in CCl_4 (**6**), CH_2Cl_2 (**9**), octane/CH_2Cl_2 (**9**), octane/Et_2O [(–)-**12**], MeOH/CH_2Cl_2 (*rac*-**13**) or dioxane/water [(+)-**13**]. The X-ray data were collected with

a Bruker SMART CCD 6000 diffractometer at 120.0 K [**9** and *rac*-**13**, Mo-K_α (λ = 0.71073 Å), graphite monochromator, ω-scan, 0.3°/frame, equipped with an Oxford Cryostream LT-device] or with a Bruker SMART CCD 6000 diffractometer at 100.0 K [**6**, (–)-**12** and (+)-**13**, Cu-K_α (λ = 1.54178 Å), φ and ω-scan, 0.5°/frame]. Structures were solved by using direct methods and refined by full-matrix least-squares on F^2 for all data. Non-hydrogen atoms (except the disordered ones) were refined with anisotropic displacement parameters. Disordered atoms were refined with equal site occupation factors of 0.5. **6** ($C_8H_8O_3$, M = 152.14, crystal size 0.40 × 0.30 × 0.10 mm^3) crystallized in the monoclinic space group $C2/c$, a = 18.884(2), b = 10.892(2), c = 11.877(2) Å, $\alpha = \gamma = 90$, β = 127.12(2)°, V = 1947.9(5) Å^3, Z = 12, ρ = 1.556 mg mm^{-3}, μ = 1.008 mm^{-1}. At 100.0(2) K 10380 reflections were collected (θ_{max} = 8.99°, R_{int} = 0.0275). Final R_1 [$I > 2\sigma(I)$] = 0.0417, wR_2 (all data) = 0.1128 for 200 refined parameters and 1398 independent reflections, GOF = 1.092, maximum and minimum residual electron density 0.217 and –0.210 e·Å^{-3}. (–)-(1*R*,3*R*,5*R*,6*R*,8*R*,10*R*)-**12** ($C_8H_8O_3$, M = 152.14, crystal size 0.17 × 0.13 × 0.05 mm^3) crystallized in the tetragonal space group $P4_12_12$, a = 6.801(2), b = 6.801(2), c = 27.548(2) Å, $\alpha = \beta = \gamma = 90°$, V = 1274.2(5) Å^3, Z = 8, ρ = 1.586 mg mm^{-3}, μ = 1.027 mm^{-1}. At 100.0(2) K 17143 reflections were collected: (θ_{max} = 58.80°, R_{int} = 0.0705). Final R_1 [$I > 2\sigma(I)$] = 0.0261, wR_2 (all data) = 0.0667 for 101 refined parameters and 919 independent reflections, GOF = 1.072, maximum and minimum residual electron density 0.125 and –0.119 e·Å^{-3}, absolute structure parameter 0.1(3)[28b]/0.2(2).[28c] A refinement of the inverted structure of (–)-**12** gave the following data: R_1 [$I > 2\sigma(I)$] = 0.0263, wR_2 (all data) = 0.0667, GOF = 1.073, absolute structure parameter = 0.9(3)[28b]/0.8(2),[28c] maximum and minimum residual electron density 0.130 and –0.113 e·Å^{-3}. **9** from octane/CH_2Cl_2 ($C_{32}H_{20}N_6O_6 \times CH_2Cl_2 \times C_8H_{18}$, M = 783.69, crystal size 0.42 × 0.18 × 0.14 mm^3) crystallized in the trigonal space group $P\bar{3}$, a = 13.9411(3), b = 13.9411(3), c = 11.3411(3) Å, $\alpha = \beta = 90$, γ = 120°, V = 1908.88(8) Å^3, Z = 2, ρ = 1.363 mg mm^{-3}, μ = 0.227 mm^{-1}. At 120.0(2) K 18450 reflections were collected: (θ_{max} = 28.50°, R_{int} = 0.0219). Final R_1 [$I > 2\sigma(I)$] = 0.0622, wR_2 (all data) = 0.1760 for 176 refined parameters and 3233 independent reflections, GOF = 1.162, maximum and minimum residual electron density 0.538 and –0.421 e·Å^{-3}. **9** from CH_2Cl_2 ($C_{32}H_{20}N_6O_6 \times 3\ CH_2Cl_2$, M = 839.32, crystal size 0.28 × 0.20 × 0.18 mm^3) crystallized in the hexagonal space group $P6_3/m$, a = 13.6334(1), b = 13.6334(1), c = 11.3890(2) Å, $\alpha = \beta = 90$, γ = 120°, V = 1833.26(4) Å^3, Z = 2, ρ = 1.520 mg mm^{-3}, μ = 0.524 mm^{-1}. At 120.0(2) K 20461 reflections were collected: (θ_{max} = 28.98°, R_{int} = 0.0334). Final R_1 [$I > 2\sigma(I)$] = 0.0576, wR_2 (all data) = 0.1765 for 104 refined parameters and 1709 independent reflections, GOF = 1.082, maximum and minimum residual electron density 0.684 and –0.649 e·Å^{-3}. *rac*-**13** ($C_{32}H_{20}N_6O_6 \times$ MeOH, M = 616.57, crystal size 0.14 × 0.04 × 0.01 mm^3) crystallized in the triclinic space group $P\bar{1}$, a = 5.5789(9), b = 12.634(2), c = 19.548(3) Å, α = 73.36(6), β = 84.34(8), γ = 89.37(7)°, V = 1313.6(4) Å^3, Z = 2, ρ = 1.569 mg mm^{-3}, μ = 0.111 mm^{-1}. At 120.0(2) K 6654 reflections were collected: (θ_{max} = 25.00°, R_{int} = 0.1416). Final R_1 [$I > 2\sigma(I)$] = 0.0676, wR_2 (all data) = 0.1275 for 379 refined parameters and 4590 independent reflections, GOF = 0.704, maximum and minimum residual electron density 0.467 and –0.347 e·Å^{-3}. (+)-**13** ($C_{32}H_{20}N_6O_6 \times 1.5$ dioxane, M = 716.70, crystal size 0.38 × 0.04 × 0.03 mm^3) crystallized in the orthorhombic space group $P2_12_12_1$, a = 5.512(2), b = 23.769(2), c = 24.449(2) Å, $\alpha = \beta = \gamma = 90°$, V = 3204.9(12) Å^3, Z = 4, ρ = 1.485 mg mm^{-3}, μ = 0.900 mm^{-1}. At 100(2) K 42219 reflections were collected: (θ_{max} = 58.99°, R_{int} = 0.0468). Final R_1 [$I > 2\sigma(I)$] = 0.0358, wR_2 (all data) = 0.0837 for 561 refined parameters and 4577 independent reflections, GOF = 1.162, maximum and minimum residual electron density 0.152 and –0.164 e·Å^{-3}, absolute structure parameter 0.1(2)[28b]/0.03(6).[28c] A refinement of the inverted structure of (+)-**13** gave the following data: R_1 [$I > 2\sigma(I)$] = 0.0360, wR_2 (all data) = 0.0839, GOF = 1.165, absolute structure parameter = 1.0(2)[28b]/0.97(6),[28c] maximum and minimum residual electron density 0.151 and –0.163 e·Å^{-3}. CCDC-288512, -288568, -288569, -288513, -288570, and -288514 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[39] Unfortunately, attempted enantioselective rearrangements of the barrelene trisepoxide **6** into the trioxatrishomocubane **12** applying Ipc_2BBr, $IpcBBr_2{\cdot}SMe_2$ or (1*S*)-(–)-camphor-10-sulfonic acid were unsuccessful. We are grateful to Professor Dieter E. Kaufmann, Technical University of Clausthal, for performing these attempts.
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