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Synthesis, Properties and Optical Resolution of *rac*-[*n*](1,6)Heptalenophanes

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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Abstract—[*n*](1,6)Heptalenophanes, *rac*-**4a–c**, having a five, six or seven membered methylene bridge, respectively, across the 12 π-perimeter were synthesized from *rac*-1,6-dimethylheptalene (**1**) in two steps. Detailed NMR and UV/vis studies of the new phanes reveal their bridged heptalene moiety to be more twisted than that of the parent heptalene system. Furthermore, the reduction of the [5](1,6)heptalenophane (**4a**) with lithium to its aromatic dianion **10** with 14 π-electrons is presented. NMR spectra of the latter show that its perimeter, although remarkable bent out-of-plane, still exhibits a considerable aromatic ring current. Liquid chromatography with triacetyl cellulose as stationary phase resulted in the optical resolution of racemic [5](1,6)heptalenophane (**4a**).

Introduction

For more than a decade the chemistry of short bridged [*n*]paracyclophanes[1] and their benzoannelated derivatives [*n*](1,4)naphthalenophanes[2] and [*n*](9,10)anthracenophanes[2b,3] has been studied extensively. Apart from benzenoid phanes, the nonbenzenoid [*n*](1,6)- and [*n*](2,6)azulenophanes could recently be synthesized by intramolecular reaction of 4-(ω-cyclopentadienylalkyl)-1-methylpyridinium salts after deprotonation to the corresponding cyclopentadienides.[4] Particularly the properties of severe bent aromatic π-systems are of special interest. Although such systems suffer from remarkable ring strain, partially they maintain their aromatic features.[1b,e] Commonly, their higher reactivity in accordance with a hypothetical cyclohexatriene is taken as a result of the considerable ring strain involved. However, classical aromatic features like e.g. a diamagnetic ring current are present even in highly strained benzene derivatives. Based on numerous contributions to this subject the discussion about the definition and nature of aromaticity has been revived.[1b,d,5]

Contrary to aromatic phanes, little is known about the properties of antiaromatic π-systems forced out-of-plane through a short alkyl bridge. Up to now, solely the synthesis of 6-methyl[5](1,4)cyclooctatetraenophane and their optical resolution was reported in the literature by Paquette et al.[6] Since cyclooctatetraene itself has a 'crown' conformation, this 8π-electron system is not suitable for studying ring deformation effects.

For this reason the so far unknown short bridged heptalenophanes constitute attractive synthetic targets. In addition, preliminary studies in our laboratory indicated that heptalenophanes should be versatile chiral ligands for transition metal complexes, which may serve as chiral catalysts.[7] Herein we report on the synthesis and properties of the first 1,6-bridged heptalenophanes.

rac-1,6-Dimethylheptalene (1) as starting material

rac-1,6-Dimethylheptalene (**1**) proved to be a suitable starting material for the synthesis of [*n*](1,6)heptalenophanes as this hydrocarbon is readily accessible by a multistep pathway starting from bicyclo[3.3.0]octane-3,8-dione in a multigram scale.[8] Due to π-bond fixation of heptalenes in the electronic ground state[9] two nonequivalent bond shift isomers of *rac*-**1** exist.[10] However, at room temperature, only the isomer *rac*-**1a** depicted in Fig. 1 is observed by NMR on the basis of $^1H-^1H$ coupling constants.[8] Less steric interaction across the peri-positions in this π-bond isomer may be the reason for this preferred conformation as the methyl groups of the isomer **1a** are orientated approximately quasi-axial above the plane of the carbocycle. In contrast the methyl groups of **1b** are in a quasi-equatorial position and are situated therefore rather in the plane of the perimeter. Due to this different geometries of the π-bond shift isomers a *n*-alkyl chain connecting the 1- and 6-position of *rac*-**1b**

Keywords: *rac*-[*n*](1,6)heptalenophanes; bent antiaromatics; chiral phanes; aromatic [5](1,6)heptalenophanedianion.

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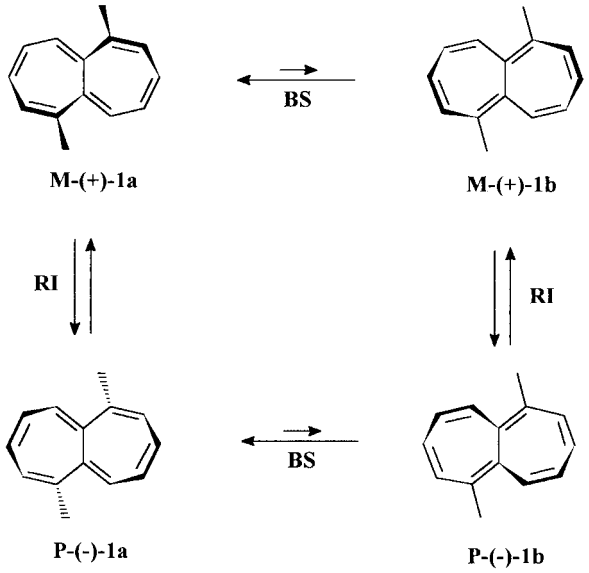


Figure 1. Isodynamic structures of 1,6-dimethylheptalene (**1**) BS: bond shift, RI: ring inversion.

ought to be much longer than in the case of *rac*-**1a**. Since heptalenes suffer from a slight deviation of planarity two more isodynamic structures, the ring inversion isomers of **1a** and **1b** have to be considered. As heptalenes are axial chiral, **1a** and **1b** both represent racemic mixtures of ring inversion isomers. Thus, *rac*-1,6-dimethylheptalene (**1**) should exist as four isodynamic axial chiral structures, which are via bond shifting and ring inversion in a dynamic equilibrium with one another. However, due to the low energy barrier (60 kJ/mol[11]) between ***M*-(+)-1a** and ***P*-(−)-1a** an optical resolution of recemic **1a** at room temperature is impossible. However, provided the alkyl chain between the 1- and 6-position is short enough it should be possible to separate the related 1,6-bridged phanes into their enantiomers which are due to the hindered ring inversion expected to be incapable of racemisation.

In order to synthesize suitable precursors for bridged derivatives of *rac*-**1** it was necessary to investigate its chemical properties. As one result of these studies it turned out that the methyl groups of *rac*-**1** can be deprotonated with LDA in THF/HMPT.[12] The resulting deep violet solution of the lithium salt of the corresponding potentially anti-aromatic anion is rather unstable and has to be maintained below −50°C under a nitrogen atmosphere. It can be trapped with electrophiles by substitution of one of the methyl groups (Fig. 2).

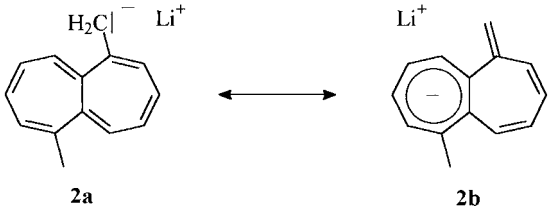


Figure 2. Resonance structures of the lithium salt **2**.

Synthesis of *rac*-[*n*](1,6)heptalenophanes

Reaction of deprotonated *rac*-**1** in THF/HMPT with an excess of α,ω-dibromoalkanes at −60°C leads to the formation of the 1-(ω-bromoalkyl)-6-methylheptalenes *rac*-**3a–c**, which are obtained as red-brown oils. Repeated deprotonation of *rac*-**3** and cyclization under high dilution conditions of the resulting anion by intramolecular nucleophilic substitution afford the expected [*n*](1,6)heptalenophanes *rac*-**4a–c** with *n*=5, 6 or 7 as yellow solids (**4a/b**) and orange oil (**4c**), respectively (Scheme 1).

The new phanes were characterized by elemental analysis as well as by MS, IR, UV and NMR spectral data. In contrast to the unsubstituted heptalene, the bridged derivatives are surprisingly stable at room temperature and insensitive towards air as well as moisture. Besides the *rac*-[7]-(1,6)heptalenophane **4c** two minor products **5** and **6** were isolated. Compound **5** was obviously formed by simple elimination of HBr from **3c** while compound **6** results from an intramolecular cyclization of the deprotonated **3c** with the negative charge located in the seven-membered ring (Fig. 3).

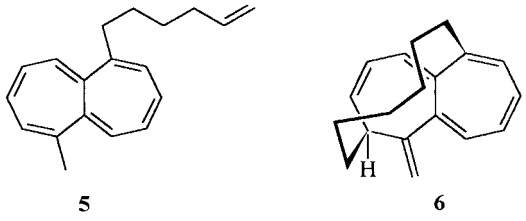
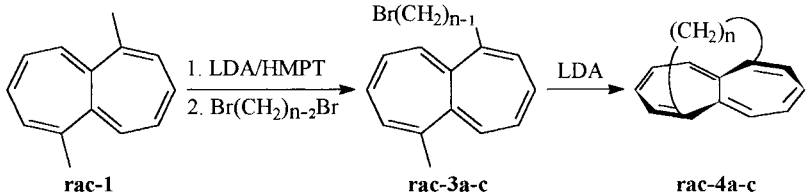


Figure 3. Minor products **5** and **6**.

Spectroscopic features of *rac*-[*n*](1,6)heptalenophanes

Exemplary, the 300 MHz ^{1}H NMR-spectrum of the



a: n = 5, b: n = 6, c: n = 7.

Scheme 1. Synthesis of the [*n*](1,6)heptalenophanes *rac*-**4a–c**.

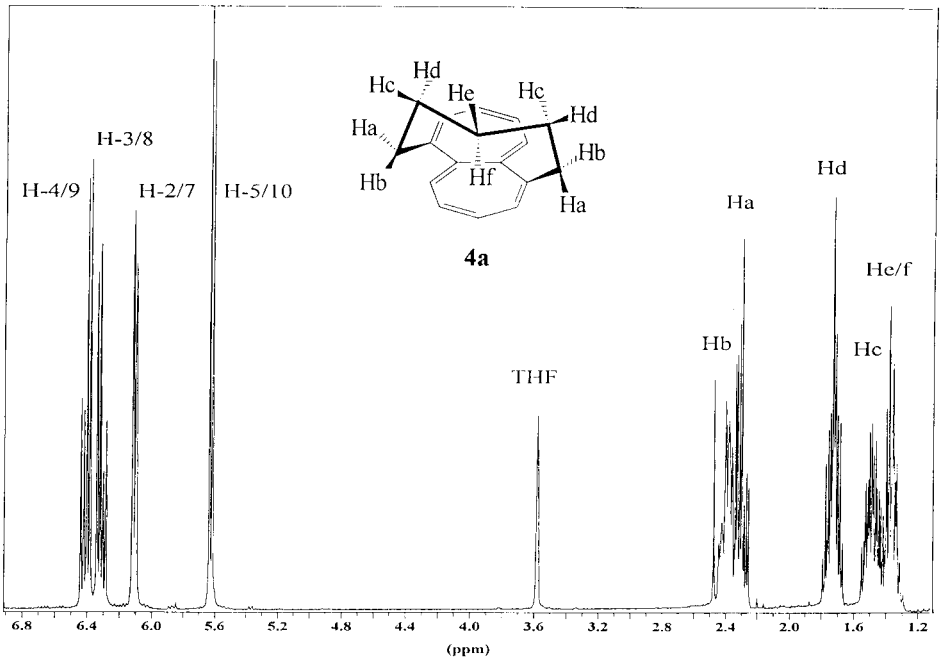


Figure 4. 300 MHz ^{1}H NMR spectrum of *rac*-[5](1,6)heptalenophane (**4a**) in [D_8]THF.

[5](1,6)heptalenophane *rac*-**4a** at room temperature in [D_8]THF is depicted in Fig. 4. The assignment of the NMR signals could be achieved by a combination of 2D NMR techniques (^{1}H–^{1}H-COSY, ^{1}H–^{13}C-COSY, NOESY).

The ^{1}H and ^{13}C NMR spectra of *rac*-**4a** as well as those of *rac*-**4b** and *rac*-**4c** confirm the rigid conformation of the polymethylene bridge and its symmetric orientation with respect to the bicyclic carbocycle. Even at room temperature, a flipping of the methylene bridge of **4a** is frozen so that five signals for the protons (H_a–H_f) are discernable. Coincidentally, H_e and H_f cause almost similar chemical shifts.

No influence of a possible paramagnetic ring current to the central aliphatic protons of the bridge is ascertainable. Position and coupling pattern of the signals of the ring protons of *rac*-**4a** are almost identical with those of the unbridged *rac*-1,6-dimethylheptalene (**1**). In accordance with its symmetrical structure the ^{13}C NMR spectrum of *rac*-**4a** shows six signals belonging to olefinic carbon nuclei and three signals caused by the carbon atoms of the aliphatic bridge.

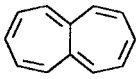
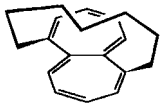
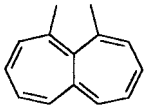
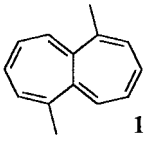
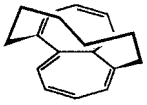
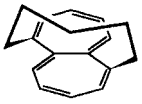
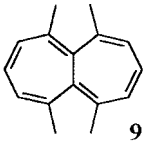
Preliminary studies indicated that the lowest wavelength absorption in the UV/vis spectra of heptalenes is hypsochromically shifted with increasing substitution in the peri-positions of these compounds.[13] This is due to a larger distortion of the bicyclic ring system and therefore a less conjugated π-electron system. For comparison in Table 1 the lowest energy bands of heptalene (**7**),[14] 1,10-dimethylheptalene (**8**)[8,13] 1,6-dimethylheptalene (**1**),[8] the [*n*](1,6)-heptalenophanes **4a**–**c** and the tetrasubstituted heptalene **9**[8,13] are listed.

According to Table 1, the unsubstituted heptalene (**7**) shows the longest absorption wavelength of all examined heptalene derivatives. This indicates an almost planar perimeter of **7** and therefore a larger degree of conjugation of its π-system compared to the other heptalene derivatives. The planarity of heptalenes unsubstituted in the peri-positions could be proven by an X-ray analysis of a 3,8-disubstituted derivative.[15] The longest wavelength absorption of the [7](1,6)heptalenophane (**4c**) exhibits a remarkable hypsochromic shift in comparison with that of heptalene (**7**) indicating a severe out-of-plane deformation of the heptalene perimeter in **4c**. It should be emphasized that the hypsochromic shift of **4c** is however less pronounced than that of the nonbridged 1,6-dimethylheptalene (**1**). This unexpected observation indicates a rather linear conformation of the methylene bridge of **4c** which causes a certain planarisation of the perimeter in comparison to that of **1**. Steric interactions between the methylene units of **4c** should be responsible for this effect. In contrast, twofold substitution in the peri-positions of heptalene e.g. **1** impedes a planarisation of the heptalene unit, as it is shown by its longest wavelength absorption. As expected, the longest wavelength absorptions of the short bridged heptalenes **4a** and **4b** are even more hypsochromically shifted than that of 1,6-dimethylheptalene (**1**), indicating that their heptalene moiety is more twisted than that of **1**. However, the greatest out-of-plane deformation of the heptalene perimeter is observed at the 1,5,6,10-tetramethylheptalene (**9**) with substituents in the four peri-positions. The UV/vis spectra of 1,6-dimethylheptalene (**1**), [5](1,6)heptalenophane (**4a**) and 1,5,6,10-tetramethylheptalene (**9**) are depicted in Fig. 5.

Dilithium salt 10 of the [5](1,6)heptalenophane (4a)

Heptalenes can be reduced by lithium via their radical anions into the dianions with an aromatic 14 π-electron system. NMR studies proved their π-electrons to be delocalized and the perimeter to be flattened.[13,16] Obviously,

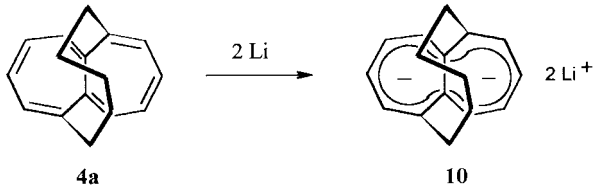
Table 1. UV/Vis data of heptalene derivatives **1**, **4a–c** and **7–9**

Compound	UV/Vis data, λ_{max}nm/(ϵ)	
 **7**	256 (21400)	352 (4140)[a]
 **4c**	254	340[b]
 **8**	250 (21500)	333 (3920)[b]
 **1**	251 (20600)	332 (3890)[b]
 **4b**	251 (18700)	327 (3640)[b]
 **4a**	250 (17900)	319 (3120)[b]
 **9**	251 (22000)	295 sh (2970)[b]

[a] In cyclohexane.
[b] In *n*-hexane.

the stabilization energy associated with the delocalized 14 π-electron system is large enough to compensate for the increased ring strain. However, the chemical shifts of the ring protons of such aromatic dianions are influenced by two opposite effects. On the one hand an upfield shift due to the two extra negative charges may occur. On the other hand the diamagnetic ring current causes a downfield shift of the signals of these protons. Due to these opposite effects an estimation of the degree of π-electron delocalization of such dianions is however difficult.[17]

In this context the generation of a bridged heptalene dianion was of interest since the chemical shifts of the protons of the aliphatic bridge should provide further information.[18] They should be shielded in the case of a significant aromatic ring current of the dianion. No disturbance of the magnetic environment of these protons is expected from the two negative charges of the heptalene moiety. We achieved the generation of the dilithium salt **10** of the [5](1,6)heptalenophane **4a** by reduction of a dry and degassed solution of **4a** in [D_8]THF with lithium in a sealed NMR tube.[13,16] For that, a lithium wire was maintained in the upper part of a NMR tube by a constriction. By inversion of the tube the solution was brought into contact with the metal for controlled periods of time. After a reaction time of 30 min the solution became red and after 24 h the NMR spectrum of the now blood-red solution did not change anymore. As expected the NMR spectrum indicates the formation of the desired dilithium salt **10**, accompanied by a small amount of a so far unknown byproduct. Fortunately, by twodimensional NMR methods a separation of the two absorption patterns was possible, and allowed an unequivocal assignment of the signals of **10** (Scheme 2).



4a **10**

Scheme 2. Formation of **10** by reduction of **4a** with lithium.

The magnetic resonance data of **10** are in accordance with those of a variety of methyl substituted heptalene dianions which have been generated earlier in our group.[13] The signals of 5-H and 10-H are deshielded, whereas all other ring protons are shielded. It should be mentioned that the change of the charge density from the neutral heptalenes to the dianions is almost identical in all investigated cases. Thus, an influence on the proton signals by different charge densities in the respective anions is excluded. This allows to bring the chemical shifts of the ring protons in relation to the extent of the delocalisation of the corresponding π-electron system. Eventually, the degree of the delocalisation of the π-systems depends on the out-of-plane deformation of the heptalene perimeter. Briefly, the magnitude of delocalisation can be estimated by the chemical shifts of the corresponding ring protons. The signals of 3-H and 8-H should be most suitable, since they are not influenced by neighboring methyl groups.

In Table 2 the chemical shifts of 3-H and 8-H of a variety of methyl substituted heptalene derivatives before and after the reduction are listed. Obviously, increasing substitution in the peri positions of heptalenes results in an increasing high field shift of the protons in 3- and 8- position, respectively. This phenomenon can be explained by a growing out-of-plane deformation of the corresponding carbocycle which suppresses the diamagnetic ring current. The high-field shift of 3-H and 8-H of **10** amounts to $\Delta\delta = -1.42$ ppm which is even more distinctive than the one observed for the dilithium salt **15** of the 1,5,6,7-tetramethylheptalene ($\Delta\delta = -0.85$ ppm). This indicates a

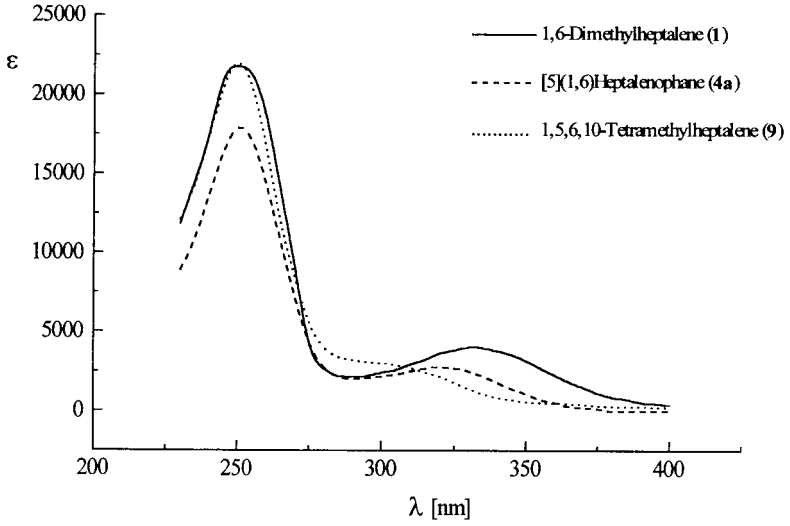


Figure 5. UV/Vis spectra of 1,6-dimethylheptalene (**1**), [5](1,6)heptalenophane (**4a**) and 1,5,6,10-tetramethylheptalene (**9**) in *n*-hexane.

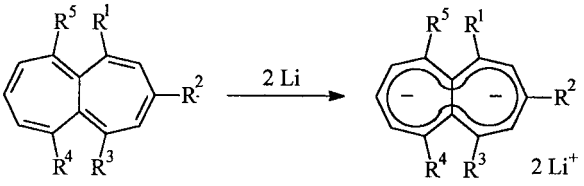
hindered delocalisation of the π-electron system of **10** due to its twisted perimeter.

However, the proton signals of the aliphatic bridge which are not influenced by the negative charges indicate a delocalized π-electron system. In fact, the high field position of the proton signals of the central methylene group of the bridge (δ=0.09 ppm, $\Delta\delta$=−1.28 ppm) of **10** is in accordance with a diamagnetic ring current, i.e. this dianion is delocalized. This is noteworthy, since the perimeter of **10** cannot be planar as shown above.

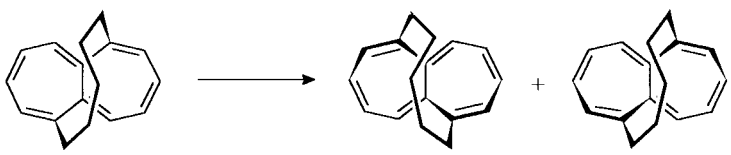
Optical resolution of *rac*-[5](1,6)heptalenophane (4a)

As mentioned above the chiral axial heptalenes are racemic mixtures of four isomers (ring inversion and bond shift isomers). In the case of some steric hindered heptalenes the isolation of all four possible isomers could be achieved and the kinetics of the two isodynamic processes were investigated.[9c,19] However, for the above mentioned reasons an optical resolution of *rac*-**1** at room temperature is not possible. Due to the aliphatic bridges of the racemic phanes **4a**–**c** ring inversion of these compounds should be

Table 2. Chemical shifts of 3- and 8-H of some methyl substituted heptalenes and their dianions in [D_8]THF



Cpd (neutral)	Cpd (dianion)	R^1	R^2	R^3	R^4	R^5	$\delta_{neutral}$	$\delta_{dianion}$	$\Delta\delta$
7	**11**	H	H	H	H	H	5.75	6.13	+0.38
1	**12**	Me	H	H	Me	H	6.01	5.55	−0.46
8	**13**	Me	H	H	H	Me	6.19	5.75	−0.62
11	**14**	Me	Me	Me	H	Me	6.17	5.35	−0.74
9	**15**	Me	H	Me	Me	Me	6.22	5.37	−0.85
4a	**10**	$-CH_2\cdots$	H	H	H	$\cdots CH_2-$	6.39	4.89	−1.42



rac-4a **P-(-)-4a** **M-(+)-4a**

Figure 6. Optical resolution of *rac*-**4a**.

prevented. According to that, we achieved the optical resolution of *rac*-**4a** by chromatography on microcystalline triacetyl cellulose (Fig. 6).

The two enantiomers, i.e. the ring inversion isomers ***M*-(+)-4a** and ***P*-(–)-4a** were obtained with an ee greater than 90%. Racemisation could not be observed (25°C).

The absolute configuration of a (+)-heptalene derivative was determined to be M by a single crystal analysis of a (+)-ephedrin salt of this enantiomer.[9c,19,20] Since the chirality of heptalenes solely derives from the helicity of the π-perimeter all (+)-heptalene derivatives have M-configuration and all (−)-heptalene derivatives have P-configuration, respectively.

Experimental

General

NMR: Bruker WM 300, AC 300, ARX 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz). ^{1}H and ^{13}C NMR spectra were measured with TMS as internal standard. MS: Finnigan MAT 311-A/100 MS. IR: Beckman IR 5A, Perkin–Elmer 125. UV/vis: Beckman DK-2A, UV 5240. Melting points: Kofler apparatus (Reichert, Vienna, Austria), uncorrected values. Elemental analyses: Perkin–Elmer CHN 240 B. Column chromatography: Silica gel [70–230 mesh (ASTM) Macherey-Nagel]. All experiments were performed in anhydrous solvents under nitrogen in flame-dried glassware. Solvents were dried and distilled according to standard procedures.

General procedure for the preparation of *rac*-3 (GP1)

***rac*-1-(4-Bromobut-1-yl)-6-methylheptalene (3a).** A 1.5 M solution of *n*-butyllithium (16.5 mL, 24.75 mmol) in *n*-hexane was added dropwise at 0°C to diisopropylamine (3.47 mL, 24.75 mmol). The reaction mixture was allowed to warm up to room temperature and stirred at this temperature for 30 min. The mixture was then cooled to −50°C and HMPT (4.34 mL, 24.75 mmol) and THF (35 mL) were added. Within 1 h a solution of *rac*-**1** (3.0 g, 16.5 mmol) in THF (50 mL) was then added dropwise at −50°C. The reaction mixture was stirred for 1 h at this temperature to give a deep violet solution of lithium 6-methyl-1-heptalenemethide (**2**). This solution was then added slowly (1.5 h) via a cooled steel tube to a vigorously stirred solution of 1,3-dibromopropane (13.32 g, 66 mmol) in THF (70 mL) at −50°C using a slight nitrogen excess pressure. After 1 h the reaction mixture was allowed to warm up to room temperature and diethyl ether (300 mL) was added. The solution was washed with water (150 mL), saturated aqueous copper sulfate solution (100 mL), water (100 mL), 2 N HCl (100 mL) and finally water. The organic layer was dried with magnesium sulfate and concentrated in vacuo. The resulting brown oil was submitted to column chromatography on silica gel with *n*-hexane.

Fraction 1: Removal of the solvent in vacuo yielded 2.70 g of a brown-red oil which was identified to be a 1:1 mixture of 1,3-dibromopropane and 1,6-dimethylheptalene **1** (^{1}H NMR).

Fraction 2: Removal of the solvent in vacuo yielded *rac*-**3a** (865 mg, 17%) as a brown-red oil. ^{1}H NMR ($CDCl_3$): δ=1.65 (m_c, 2H, 2′- or 3′-H), 1.92 (m_c, 2H, 2″ - or 3″ - H), 2.09 (d, J=0.5 Hz, 3H, 6-CH_3), 2.32 (m_c, 1H, 1′-H), 2,52 (m_c, 1H, 1″-H), 3.40 (t, J=6.8 Hz, 2H, 4′-H), 5.60 (d, J=6.5 Hz, 1H, 2-H), 5.66 (d, J=6.5 Hz, 1H, 7-H), 6.00 (m_c, 2H, 5- and 10-H), 6.14 (m_c, 2H, 4- and 9-H), 6.33 (m_c, 2H, 3- and 8-H). ^{13}C NMR ($CDCl_3$): δ=25.2 (6-CH_3), 27.5 (C-2′), 32.3 (C-3′), 33.7 (C-4′), 38.1 (C-1′), 125.2, 125.3 (C-2, C-7), 128.1, 128.4 (C-5, C-10), 129.9, 130.0 (C-4, C-9), 131.4, 131.6 (C-3, C-8), 135.3, 136.8, 139.2, 139.4 (C-1, C-5a, C-6 and C-10a). UV/vis (*n*-hexane): λ_{max}= 251 nm, 335. IR (film): $\tilde{\nu}$=3018 cm^{-1}, 2936, 2854, 1694, 1644, 1435, 1249, 871, 765, 741, 707. MS (70 eV); *m/z* (%): 304/302 (64/64) [M^+], 289/287 (1/1) [M^+-CH_3), 223 (4) [M^+-Br), 197 (16) [$M^+-(CH_2)_2Br$], 181 (100) [$M^+-(CH_2)_3Br$], 165 (82). An analytically pure sample could not be obtained.

***rac*-1-(5-Bromopent-1-yl)-6-methylheptalene (3b).** Using GP1 diisopropylamine (0.42 mL, 3.0 mmol), 2.0 mL (3.0 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane and HMPT (0.53 mL, 3 mmol) were allowed to react with **1** (380 mg, 2.0 mmol) in THF. The resulting deep-violet reaction mixture was then added to a solution of 1,4-dibromobutane (1.72 g, 8 mmol) in 10 mL THF and worked up according to procedure for **3a**.

Fraction 1: Removal of the solvent in vacuo yielded 1.00 g of a red-brown oil which was distilled at 5 mbar and 60°C to give 780 mg (45%) 1,4-dibromobutane. The residue was purified by column chromatography (*n*-pentane, silica gel) to give 100 mg (26%) of unreacted *rac*-**1**.

Fraction 2: Yield 213 mg (32%) of *rac*-**3b** as a red-brown oil. ^{1}H NMR ($CDCl_3$): δ=1.39–1.82 (m, 4H, 2′- and 3′-H), 1.86 (quint, J=6.9 Hz, 2H, 4′-H), 2.08 (br. s, 3H, 6-CH_3), 2.33 (m_c, 1H, 1′-H), 2.47 (m_c, 1H, 1″-H), 3.38 (t, J=6.8 Hz, 2H, 5′-H), 5.60 (d, J=6.3 Hz, 1H, 2-H), 5.65 (d, J=6.3 Hz, 1H, 7-H), 5.97 (br. d, J=6.1 Hz, 1H, 10-H), 6.01 (br. d, J=6.4 Hz, 1H, 5-H), 6.14 (m_c, 2H, 4- and 9-H), 6.35 (m_c, 2H, 3- and 8-H). ^{13}C NMR ($CDCl_3$): δ=25.3 (6-CH_3), 27.8, 28.1 (C-2′ and C-3′), 32.7 (C-4′), 33.8 (C-5′), 38.7 (C-1′), 124.8 (C-7), 125.0 (C-2), 127.2 (C-10), 127.9 (C-5), 129.8, 129.8 (C-4 and C-9), 131.3, 131.4 (C-3 and C-8), 135.1, 136.9, 139.1, 139.9 (C-1, C-5a, C-6 and C-10a). UV/vis (*n*-hexane): λ_{max}=251 nm, 332. IR (film): $\tilde{\nu}$=2920 cm^{-1}, 1640, 1590, 1430, 865, 735, 705. MS (70 eV); *m/z* (%): 318/316 (57/57) [M^+], 303/301 (3/3) [M^+-CH_3), 292/290 (6/6) [$M^+-C_2H_2$), 237 (7) [M^+-Br), 181 (63) [$M^+-(CH_2)_4Br$], 165 (100), 142 (58). An analytically pure sample could not be obtained.

***rac*-1-(6-Bromohex-1-yl)-6-methylheptalene (3c).** Using GP1 diisopropylamine (1.38 mL, 9.9 mmol), 6.60 mL (9.9 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane, HMPT (1.74 mL, 9.9 mmol) and *rac*-**1** (1.20 g, 6.6 mmol) were reacted with 1,5-dibromopentane (6.07 g, 26.4 mmol) in THF. After work up according to **3a** two fractions were obtained.

Fraction 1: Removal of the solvent in vacuo yielded 3.40 g of a brown-red oil which was identified to be a 9:1 mixture of 1,5-dibromopentane and 1,6-dimethylheptalene **1** (^{1}H NMR).

Fraction 2: Yield 660 mg (30%) of *rac*-**3c** as a brown–red oil. ^{1}H NMR ($CDCl_3$): δ=1.20–1.64 (m, 6H, 2′-, 3′- and 4′-H), 1.75 (quint, *J*=6.9 Hz, 2H, 5′-H), 2.08 (d, *J*=0.5 Hz, 3H, 6-CH_3), 2.35 (m_c, 1H, 1′-H), 2.52 (m_c, 1H, 1″-H), 3.38 (t, *J*=6.9 Hz, 2H, 6′-H), 5.60 (d, *J*=6.3 Hz, 1H, 2-H), 5.65 (d, *J*=6.3 Hz, 1H, 7-H), 6.00 (br. d, *J*=6.1 Hz, 1H, 10-H), 6.01 (br. d, *J*=6.4 Hz, 1H, 5-H), 6.13 (m_c, 2H, 4- and 9-H), 6.32 (dd, *J*=6.3, 1.8 Hz, 1H, 3- or 8-H), 6.36 (dd, *J*=6.3, 1.8 Hz, 1H, 3- or 8-H). ^{13}C NMR ($CDCl_3$): δ=25.2 (6-CH_3), 28.0, 28.3, 28.7 (C-2′, C-3′ and C-4′), 32.7 (C-5′), 34.0 (C-6′), 38.8 (C-1′), 124.8, 124.9 (C-2 and C-7), 127.1, 127.9 (C-5 and C-10), 129.8, 130.1 (C-4 and C-9), 131.3 (C-3 and C-8), 135.1, 137.0, 139.1, 140.2 (C-1, C-5a, C-6 and C-10a). UV/vis (*n*-hexane): λ_{max}=251 nm, 333. IR ($CHCl_3$): $\tilde{\nu}$=3025 cm^{-1}, 2940, 2858, 1698, 1646, 1602, 1454, 1264, 1104, 1002, 874. MS (70 eV); *m/z* (%): 332/330 (72/72) [M^+], 317/315 (1/1) [M^+-CH_3], 251 (2) [M^+-Br], 195 (9) [$M^+-(CH_2)_4Br$], 181 (75) [$M^+-(CH_2)_5Br$], 165 (100). An analytically pure sample could not be obtained.

General procedure for the preparation of 4 (GP2)

[5](1,6)Heptalenophane (4a). To diisopropylamine (0.58 mL, 4.15 mmol) 2.77 mL (4.15 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane were added dropwise at 0°C. The reaction mixture was allowed to warm up to room temperature and stirred at this temperature for 30 min. The solution was then cooled to −50°C and THF (50 mL) and HMPT (0.74 mL, 4.15 mmol) were added. Subsequently, a solution of *rac*-**3a** (840 mg, 2.77 mmol) in THF (40 mL) was added dropwise within 6 h by using a syringe infusion pump. The resulting deep violet solution was allowed to warm up to 0°C and stirred for further 14 h. After the addition of diethyl ether (100 mL) to the reaction mixture at room temperature the solution was washed with water (50 mL), saturated aqueous copper sulfate solution (50 mL), water (50 mL), 2 N HCl (50 mL) and finally water. The solution was dried with magnesium sulfate and concentrated in vacuo. The resulting oil was separated by column chromatography on silica gel with *n*-hexane. Removal of the solvent in vacuo yielded 162 mg (26%) of *rac*-**4a** as a yellow solid, mp 40–41°C. ^{1}H NMR ($CDCl_3$): δ=1.32–1.39 (m, 2H, 3′-H), 1.43–1.57 (m, 2H, 2′-H), 1.65-1.77 (m, 2H, 2″-H), 2.26–2.35 (m, 2H, 1′-H), 2.35–2.45 (m, 2H, 1″-H), 5.71 (*d*, *J*=5.7 Hz, 2H, 5- and 10-H), 6.14 (d, *J*=5.9 Hz, 2H, 2- and 7-H), 6.39 (dd, *J*=11.2, 5.9 Hz, 2H, 3- and 8-H), 6.50 (dd, *J*=11.2, 5.7 Hz, 2H, 4- and 9-H). ^{13}C NMR ($CDCl_3$): δ=22.9 (C-3′), 29.2 (C-2′), 37.0 (C-1′), 121.9 (C-5 and C-10), 125.9 (C-2 and C-7), 129.6 (C-3 and C-8), 130.3 (C-4 and C-9), 135.3, 137.5 (C-1, C-5a, C-6 and C-10a). UV/vis (*n*-hexane): λ_{max} (lg ϵ)=250 nm (4.25), 319 (3.49). IR ($CHCl_3$): $\tilde{\nu}$=3013 cm^{-1}, 2932, 2866, 1648, 1598, 1514, 1457, 1434, 1443, 1350, 1321, 857, 743, 731, 706. MS (70 eV); *m/z* (%): 222 (100) [M^+], 207 (10) [M^+-CH_3], 193 (22) [$M^+-C_2H_5$], 179 (80) [$M^+-C_3H_7$], 165 (100) [$M^+-C_4H_9$], 152 (36) [$C_{12}H_8$]. $C_{17}H_{18}$ (222.3): calcd C 91.84, H 8.16; found C 91.71, H 8.35.

***rac*-[6](1,6)Heptalenophane (4b).** According to GP2 diisopropylamine (0.35 mL, 2.5 mmol), 1.67 mL (2.5 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane and HMPT (0.48 mL, 2.5 mmol) were allowed to react with *rac*-**3b** (530 mg, 1.67 mmol) in THF. After work up according to **4a** two fractions were obtained.

Fraction 1: Yield 60 mg (15%) *rac*-**4b** as a orange–yellow solid, mp 30°C. ^{1}H NMR ($CDCl_3$): δ=1.24–1.37 (m, 2H, 2′-H), 1.39–1.59 (m, 4H, 2″-, 3′-H), 1.64–1.74 (m, 2H, 3″-H), 2.25–2.34 (m, 2H, 1′-H), 2.56–2.64 (m, 2H, 1″-H), 5.63 (d, *J*=6.1 Hz, 2H, 5- and 10-H), 6.07 (d, *J*=6.1 Hz, 2H, 2- and 7-H), 6.21 (dd, *J*=11.2 Hz, *J*=6.1 Hz, 2H, 3- and 8-H), 6.21 (dd, *J*=11.2, 6.1 Hz, 2H, 4- and 9-H). ^{13}C NMR ($CDCl_3$): δ=24.4 (C-2′), 28.3 (C-3′), 38.4 (C-1′), 123.9 (C-5 and C-10), 127.1 (C-2 and C-7), 129.6 (C-3 and C-8), 130.9 (C-4 and C-9), 138.0, 138.7 (quart. C). UV/vis (*n*-hexane): λ_{max} (lg ϵ)=251 nm (4.27), 327 (3.56). IR ($CHCl_3$): $\tilde{\nu}$=3001 cm^{-1}, 2928, 2862, 1642, 1599, 1459, 1356, 1081, 908, 886, 843. MS (70 eV); *m/z* (%): 236 (100) [M^+], 205 (8), 193 (16), 179 (25), 165 (28). $C_{18}H_{20}$ (236.4): calcd C 91.47, H 8.52; found C 91.58, H 8.67.

Fraction 2: Removal of the solvent in vacuo yielded 16 mg (3%) of unreacted *rac*-**3b**.

***rac*-[7](1,6)Heptalenophane (4c).** According to GP2 diisopropylamine (0.46 mL, 3.3 mmol), 2.20 mL (3.3 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane and HMPT (0.59 mL, 3.3 mmol) were allowed to react with *rac*-**3c** (730 mg, 2.2 mmol) in THF. After work up according to **4a** four fractions were obtained.

Fraction 1: Yield 21 mg (4%) *rac*-**4c** as a orange oil. ^{1}H NMR ($CDCl_3$): δ=1.20–1.40 (m, 6H, CH_2), 1.63–1.84 (m, 4H, CH_2), 2.20 (dt, *J*=13.1, 2.6 Hz, 2H, 1′-H), 2.75 (br. d, *J*=13.2 Hz, 2H, 1′-H), 5.62 (d, *J*=6.4 Hz, 2H, 5- and 10-H), 5.97 (dd, *J*=6.3, 1.9 Hz, 2H, 2- and 7-H), 6.07 (ddd, *J*=11.2, 6.4, 1.1 Hz, 2H, 3- and 8-H), 6.30 (dd, *J*=11.2, 6.4 Hz, 2H, 4- and 9-H). ^{13}C NMR ($CDCl_3$): δ=20.9, 21.9, 42.8 (CH_2), 37.7 (C-1′), 124.1 (C-5 and C-10), 128.4 (C-2 and C-7), 129.0 (C-3 and C-8), 130.7 (C-4 and C-9), 135.7, 140.0 (quart. C). UV/vis (*n*-hexane): λ_{max}=254 nm, 340. IR ($CHCl_3$): $\tilde{\nu}$=3018 cm^{-1}, 2944, 2925, 2863, 2846, 1643, 1466, 1438, 702. MS (70 eV); *m/z* (%): 250 (100) [M^+], 235 (1) [M^+-CH_3], 221 (3) [$M^+-C_2H_5$], 207 (9) [$M^+-C_3H_7$], 193 (26) [$M^+-C_4H_9$], 178 (30) [$M^+-C_5H_{12}$]. HRMS ($C_{19}H_{22}$): calcd 250.1707; found 250.1722.

Fraction 2: Yield 20 mg (4%) of **6** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ=1.19–1.40 (m, 6H, CH_2), 1.63–1.86 (m, 3H, CH_2), 1.98–2.10 (m, 1H, 6′-H), 2.65 (m_c, 2H, 1′-H), 2.98 (dt, *J*=11.2, 7.7 Hz, 1H, 7-H), 4.69 (br. s, 1H, C=CH_2), 5.05 (*d*, *J*=1.2 Hz, 1H, C=CH'_2), 5.77 (d, *J*=4.5 Hz, 1H, 2-H), 5.90 (dd, *J*=10.6, 4.5 Hz, 1H, 3-H), 6.07 (m_c, 1H, 10-H), 6.29 (m_c, 3H, 4-, 8- and 9-H), 6.44 (m_c, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ=22.8, 24.8, 25.8, 26.4 (CH_2), 29.4 (C-6′), 40.2 (C-1′), 44.6 (C-5), 113.7 (C=*C*H_2), 123.3 (C-7), 124.4 (C-10), 125.5 (C-2), 126.6 (C-3), 128.7,

129.0, 136.9 (C-4, C-8, C-9), 140.0, 140.4, 145.0 (quart. C), 158.4 (*C*=CH_2). UV/vis (*n*-hexane): λ_{max}=250 nm sh, 257, 334. IR ($CHCl_3$): $\tilde{\nu}$=3000 cm^{-1}, 2928, 2360, 2340, 1642, 1600, 1462, 1441, 891. MS (70 eV); *m/z* (%): 250 (83) [M^+], 235 (6) [M^+-CH_3], 221 (8) [$M^+-C_2H_5$], 207 (20) [$M^+-C_3H_7$]. An analytically pure sample could not be obtained.

Fraction 3: Yield 8 mg (1%) of 1-(5-hexen-1-yl)-6-methylheptalene (**5**) as a orange oil. ^{1}H NMR ($CDCl_3$): δ=1.31–1.65 (m, 4H, CH_2), 2.05 (m_c, 2H, CH_2), 2.08 (s, 3H, 6-CH_3), 2.34 (m_c, 1H, C-1′), 2.47 (m_c, 1H, C-1″), 4.90–5.02 (m, 2H, –CH=CH_2), 5.61 (d, *J*=6.4 Hz, 1H, 2-H), 5.66 (d, *J*=6.3 Hz, 1H, 7-H), 5.79 (dm_c, *J*=24 Hz, 1H, –C*H*=CH_2), 5.97 (d, *J*=6.1 Hz, 1H, 10-H), 6.01 (d, *J*=6.4 Hz, 1H, 5-H), 6.15 (m_c, 2H, 4- and 9-H), 6.33 (d, *J*=6.4 Hz, 1H, 3-H), 6.37 (d, *J*=6.3 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$): δ=25.2 (6-CH_3), 28.5 (2×CH_2), 33.7 (CH_2), 38.8 (C-1′), 114.4 (C-6′), 124.7, 124.8 (C-2, C-7), 127.0 (C-10), 127.6 (C-5), 129.8, 129.8 (C-4, C-9), 131.2, 131.3 (C-3, C-8), 135.2, 137.1 (quart. C), 138.8 (C-5′), 139.1, 140.30 (quart. C). UV/vis (*n*-hexane): λ_{max}=230 nm, 253, 303, 333. IR ($CHCl_3$): $\tilde{\nu}$=2931 cm^{-1}, 2855, 1693, 1640, 1601, 1100, 1000. MS (70 eV); *m/z* (%): 250 (100) [M^+], 235 (7) [M^+-CH_3], 181 (61) [$M^+-(CH_2)_3CH=CH_2$], 165 (100). An analytically pure sample could not be obtained.

Fraction 4: Yield 50 mg (7%) of unreacted *rac*-**3c.**

[5](1,6)Heptalenophane dianion (10): A solution of [5](1,6)heptalenophane (*rac*-**4a**) (40 mg, 0.2 mmol) in 0.5 mL degassed and anhydrous [D_8]THF was brought into a prolongated NMR tube, which was constricted at 10 cm from bottom end. Thus, a small reaction vessel in the upper end was made, into which a couple of lithium filings were introduced under an atmosphere of argon. The tube was sealed and a NMR spectrum was recorded before the solution was brought into contact with the lithium filings by simple inversion of the tube. The solution became deep red after 2 h and no further change of the NMR signals could be observed after 24 h reaction time.

[5](1,6)Heptalenophane (4a). ^{1}H NMR ([D_8]THF): δ=1.37 (m_c, 2H, 3′-H), 1.47 (m_c, 2H, 2′-H), 1.73 (m_c, 2H, 2″-H), 2.31 (m_c, 2H, 1′-H), 2.41 (m_c, 2H, 1″-H), 5.63 (d, *J*=5.7 Hz, 2H, 5- and 10-H), 6.11 (d, *J*=5.7 Hz, 2H, 2- and 7-H), 6.31 (dd, *J*=11.2, 5.7 Hz, 2H, 3- and 8-H), 6.41 (dd, *J*=11.2, 5.7 Hz, 2H, 4- and 9-H). ^{13}C NMR ([D_8]THF): δ=22.9 (C-3′), 29.2 (C-2′), 37.0 (C-1′), 121.9 (C-5 and C-10), 125.9 (C-2 and C-7), 129.6 (C-3 and C-8), 130.3 (C-4 and C-9), 135.3, 137.5 (quart. C).

[5](1,6)Heptalenophane dianion (10). ^{1}H NMR ([D_8]THF): δ=0.09 (br. s, 2H, 3′-H), 0.65 (m, 2H, 2′-H), 1.15 (br. s, 2H, 2″-H), 1.52 (m_c, 2H, 1″-H), 2.85 (m_c, 2H, 1″-H), 4.63 (br. s, 2H, 4- and 9-H), 4.89 (m_c, 4H, 2-, 3-, 4- and 8-H), 7.43 (d, *J*=7.2 Hz, 2H, 5- and 10-H). ^{13}C NMR ([D_8]THF): δ=23.7 (C-3′), 29.0 (C-2′), 43.7 (C-1′), 93.6 (C-4 and C-9), 98.8 (C-2 and C-7 or C-3 and C-8), 111.9 (C-2 and C-7 or C-3 and C-8), 114.2 (C-5 and C-10), 125.6 (quart. C), The signal of one of the quart. carbon nuclei is concealed.

Optical resolution of rac-**4a**: 100 mg (0.45 mmol) *rac*-**4a** were subjected to column chromatography (column (400×28 mm); flow rate: 9 mL/h) on triacetyl cellulose with ethanol (96%). 48 fractions à 9 mL were collected, the first ten and the last ten fractions, respectively unified. The solvent was evaporated in vacuum to give 40 mg (40%) of ***P*-(–)-4b** with 98% ee and 20 mg (20%) of ***M*-(+)-4a** with 92% ee. The optical purity was determined by analytical HPLC.

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References

1. For reviews see: (a) Bickelhaupt, F.; de Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988**, 107, 459–478. (b) Bickelhaupt, F. *Pure Appl. Chem.* **1990**, *62*, 373–382. (c) de Wolf, W. H.; Bickelhaupt, F. *Adv. Strain Org. Chem.* **1993**, *3*, 185–227. (d) Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994**, *50*, 4575–4622. (e) Tobe, Y. *Top. Curr. Chem.* **1994**, *172*, 1–40. (f) Bickelhaupt, F.; de Wolf, W. H. *J. Phys. Org. Chem.* **1998**, *11*, 362–376.

2. (a) Hunger, J.; Wolff, C.; Tochtermann, W.; Peters, E. M.; von Schnering, H. G. *Chem. Ber.* **1986**, *119*, 2698–2722. (b) Tobe, Y.; Sakai, S.; Minami, H.; Naemura, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1935–1942. (c) van Es, D. S.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem.* **1995**, *107*, 2728–2730; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2553–2555.

3. (a) Tobe, Y.; Ishii, H.; Kakiuchi, V.; Naemura, K. *J. Am. Chem. Soc.* **1993**, *115*, 11604–11605. (b) Tobe, Y.; Utsumi, N.; Sakai, S.; Naemura, K. *J. Org. Chem.* **1994**, *59*, 5516–5517.

4. Schuchmann, P.; Hafner, K. *Tetrahedron Lett.* **1995**, *36*, 2603–2606.

5. von Ragué Schleyer, P.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209–218.

6. Paquette, L. A.; Trova, M. P. *Tetrahedron Lett.* **1986**, *27*, 1895–1898.

7. Grimm, F. W.; Hafner, K.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 1569–1572.

8. Hafner, K.; Hock, N.; Knaup, G. L.; Meinhardt, K.-P. *Tetrahedron Lett.* **1986**, *27*, 1669–1672.

9. (a) Vogel, E.; Kerimis, D.; Allison, N. T.; Zellerhoff, R.; Wassen, J. *Angew. Chem.* **1979**, *91*, 579–580; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 545–546. (b) Vogel, E.; Königshofen, H.; Wassen, J.; Müllen, K.; Oth, J. F. M. *Angew. Chem.* **1974**, *86*, 777–778; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 732–734. (c) Hafner, K.; Knaup, G. L.; Lindner, H. J.; Flöter, H. C. *Angew. Chem.* **1985**, *97*, 209–213; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 212–214. (d) Hafner, K.; Knaup, G. L. *Tetrahedron Lett.* **1986**, *27*, 1665–1668.

10. The correct and unambiguous nomenclature of the π-bond isomer according to IUPAC-rule A-31.3 is for: **1**: *rac*-2,8-dimethylbicyclo[5.5.0]dodeca-2,4,6,8,10,12-hexaene.

11. Lindner, H. J. Technische Universität Darmstadt, unpublished results.

12. Grimm, F. W. Ph.D Thesis, Technische Hochschule Darmstadt, 1997.
13. Hock, N. Ph.D Thesis, Technische Hochschule Darmstadt, 1991.
14. Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 4659–4660.
15. Stegemann, J.; Lindner, H. J. *Tetrahedron Lett.* **1977**, 2515–2516.
16. Oth, J. F. M.; Müllen, K.; Königshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387–2398.
17. Lazzeretti, P. *Progr. Nucl. Magn. Reson.* **2000**, *36*, 1–88.
18. Müllen, K. *Chem. Rev.* **1984**, *84*, 603–646.
19. Hafner, K.; Knaup, G. L.; Lindner, H. J. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 155–163.
20. Knaup, G. L. Ph.D Thesis, Technische Hochschule Darmstadt, 1985.