Synthesis of 1-Methyl-6,10-diphenylheptalene Derivatives

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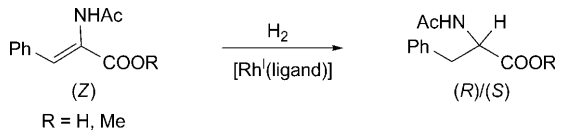
Dedicated to *Manfred Hesse* on the occasion of his 75th birthday

The reduction of heptalene diester **1** with diisobutylaluminium hydride (DIBAH) in THF gave a mixture of heptalene-1,2-dimethanol **2a** and its double-bond-shift (DBS) isomer **2b** (*Scheme 3*). Both products can be isolated by column chromatography on silica gel. The subsequent chlorination of **2a** or **2b** with PCl_5 in CH_2Cl_2 led to a mixture of 1,2-bis(chloromethyl)heptalene **3a** and its DBS isomer **3b**. After a prolonged chromatographic separation, both products **3a** and **3b** were obtained in pure form. They crystallized smoothly from hexane/Et_2O 7:1 at low temperature, and their structures were determined by X-ray crystal-structure analysis (*Figs. 1* and *2*). The nucleophilic exchange of the Cl substituents of **3a** or **3b** by diphenylphosphino groups was easily achieved with excess of (diphenylphospino)lithium (= lithium diphenylphosphanide) in THF at 0° (*Scheme 4*). However, the purification of **4a**/**4b** was very difficult since these bis-phosphines decomposed on column chromatography on silica gel and were converted mostly by oxidation by air to bis(phosphine oxides) **5a** and **5b**. Both **5a** and **5b** were also obtained in pure form by reaction of **3a** or **3b** with (diphenylphosphinyl)lithium (= lithium oxidodiphenylphospanide) in THF, followed by column chromatography on silica gel with Et_2O. Carboxaldehydes **7a** and **7b** were synthesized by a disproportionation reaction of the dimethanol mixture **2a**/**2b** with catalytic amounts of TsOH. The subsequent decarbonylation of both carboxaldehydes with tris(triphenylphosphine)rhodium(1+) chloride yielded heptalene **8** in a quantitative yield. The reaction of a thermal-equilibrium mixture **3a**/**3b** with the borane adduct of (diphenylphosphino)lithium in THF at 0° gave **6a** and **6b** in yields of 5 and 15%, respectively (*Scheme 4*). However, heating **6a** or **6b** in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene, generated both bis-phosphine **4a** and its DBS isomer **4b** which could not be separated. The attempt at a conversion of **3a** or **3b** into bis-phosphines **4a** or **4b** by treatment with *t*-BuLi and Ph_2PCl also failed completely. Thus, we returned to investigate the antipodes of the dimethanols **2a**, **2b**, and of **8** that can be separated on an HPLC *Chiralcel-OD* column. The CD spectra of optically pure (*M*)- and (*P*)-configurated heptalenes **2a**, **2b**, and **8** were measured (*Figs. 4*, *5*, and *9*).

Introduction. – Several years ago, we reported the synthesis of (*P*)- and (*M*)-6,7-bis[(diphenylphosphino)methyl]-8,12-diphenylbenzo[*a*]heptalene [1]. This type of chiral ligands for homogeneous asymmetric catalysis was prepared starting from optically pure diisopropyl (*P*)- and (*M*)-8,12-diphenylbenzo[*a*]heptalene-6,7-dicarboxylate which had been obtained by HPLC separation of the racemate on a semi-prep. *Chiralcel-OD* column. The enantiomers possess a fixed position of the C=C bonds in the heptalene perimeter due to the benzo fusion. Transformation of the two ester groups into (diphenylphosphino)methyl groups gave the new bidentate chiral ligand system. The Rh^I-catalyzed asymmetric hydrogenation reaction of (*Z*)-α-(acetamido)-cinnamic acid in the presence of the new (*P*)-heptalene ligand gave not only (*R*)-*N*-acetylphenylalanine in optical purities up to 77% (*Scheme 1*) but also opened a new

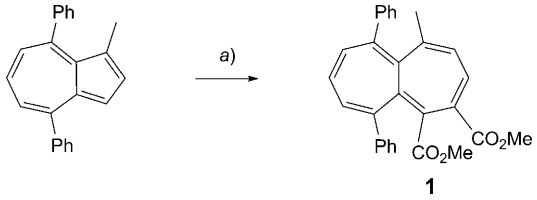
way for applications of heptalenes and induced further investigations of routes to chiral heptalene ligands. In this article, we describe the synthesis of 1-methyl-6,10-diphenylheptalene derivatives and probe their thermal and photochemical double-bond shifts (DBS), which occur according to our earlier investigation with retention of the heptalene configuration [2].

Scheme 1



Results and Discussions. – Heptalene **1** was readily obtained in a reasonable yield from 1-methyl-4,8-diphenylazulene by using a twofold molar excess of ADM (= dimethyl acetylenedicarboxylate = dimethyl but-2-ynedioate) in MeCN at 100° [3] (*Scheme 2*).

Scheme 2



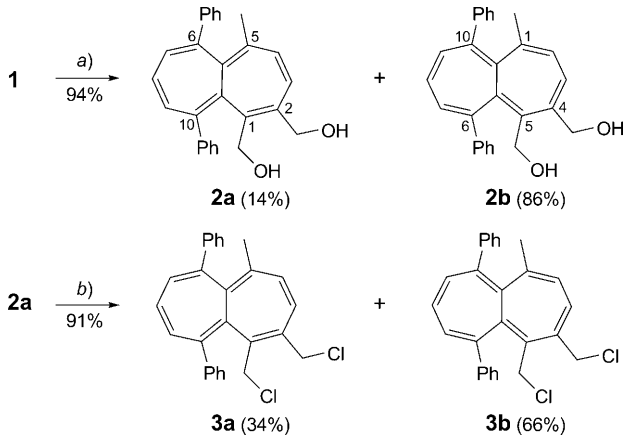
1

a) ADM (3 mol-equiv.), MeCN, 100°, 72 h; 40%.

The reduction of **1** with diisobutylaluminium hydride (DIBAH) in THF at 0° afforded a mixture of heptalene-1,2-dimethanol **2a** and its DBS isomer **2b**. Both products were isolated by column chromatography on silica gel in total yields up to 94% (*Scheme 3*). It should be noted that the thermal DBS equilibrium of the starting diester lies completely on the side of the 4,5-dicarboxylate **1** [3].

The chlorination of **2a** or **2b** with PCl_5 led in both cases to a mixture of 1,2-bis(chloromethyl)heptalene **3a** and its DBS isomer **3b**. After slow chromatography on silica gel with hexane/Et_2O 20:1, both DBS forms **3a** and **3b** were obtained in 31 and 60% yield, respectively. The bis(chloromethyl)heptalenes crystallized smoothly from hexane/Et_2O 7:1 at low temperature as orange (**3a**) and yellow prisms (**3b**), respectively. Both structures could – in addition to their assignment by NMR spectroscopy (see *Tables 1* and *2*) – be confirmed by an X-ray crystal-structure analysis (*Figs. 1* and *2*), which delivered precise geometrical parameters. The *cisoid* angles at the central σ-bond (Θ(C(1)–C(10a)–C(5a)–C(5)) and (Θ(C(6)–C(5a)–C(10a)–C(10)) are 61.2(3) and 60.9(3)°, respectively, for **3a** as well as 66.5(2) and 65.2(2)°, respectively, for **3b**. The torsion angles between the two chloromethyl substituents were found to be 3.6(4)° in the case of **3a** and −23.7(3)° in the case of **3b**. The X-ray crystal structure of **3b** can be compared with that of the starting diester **1** (see Table 1 in [3]), for which the *cisoid* torsion angles at the central σ-bond are 67.0(2) and 68.2(2)°,

Scheme 3



a) 2M DIBAH, hexane, THF, 0° to r.t., 2 h. *b*) PCl_5, CH_2Cl_2, $-60°$, 2 h.

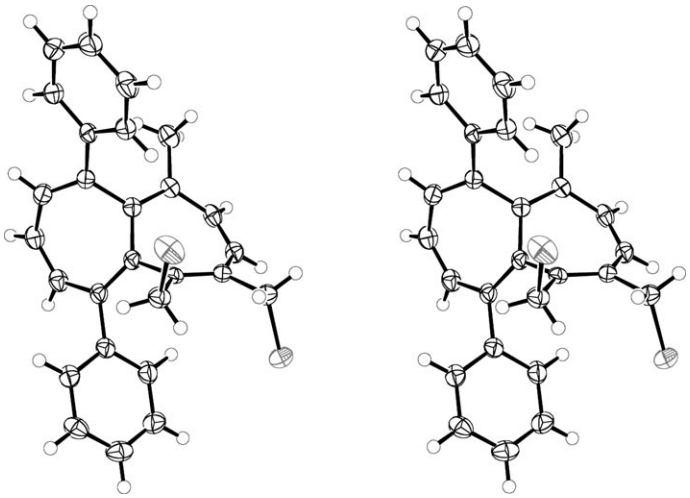


Fig. 1. *Stereoscopic view of the X-ray crystal structure of 1,2-bis(chloromethyl)-5-methyl-6,10-diphenylheptalene* (**3a**) (50% probability ellipsoids)

respectively, and that at the ester substituents, $\Theta(O{=}C{-}C(4){-}C(5){-}C{=}O)$, is $-39.3(2)°$. It is also of interest to note that in both crystal structures, the $Cl{-}CH_2$ bonds are almost perpendicular to the adjacent C=C bonds of the heptalene perimeter: $\Theta(Cl{-}CH_2{-}C(1){=}C(2)) = 80.4(3)°$ and $\Theta(Cl{-}CH_2{-}C(2){=}C(1)) = 97.0(2)°$ for **3a** as well as $\Theta(Cl{-}CH_2{-}C(4){=}C(3)) = 115.7(3)°$ and $\Theta(Cl{-}CH_2{-}C(5){=}C(5a)) = 117.1(2)°$ for **3b**. That these torsion angles are not influenced very much by crystal lattice forces is evident from AM1 calculations which reproduce the experimental molecular structure of **3a** and **3b** nearly perfectly with $\Theta(Cl{-}CH_2{-}C(1){=}C(2)) = 79.2°$ and $\Theta(Cl{-}CH_2{-}C(2){=}C(1)) = 88.2°$ for **3a** as well as $\Theta(Cl{-}CH_2{-}C(4){=}$

Table 1. *^{1}H-NMR Data* ($CDCl_3$) *of the Series* **2a**–**7a** *of Heptalenes.* δ in ppm, J in Hz.

	2a	**3a**	**5a**	**6a**	**7a**
H–C(3)	6.77 (*d*, *J* = 11.6)	6.70 (*d*, *J* = 11.6)	6.35 (*d*, *J* = 10.9)[a])	7.84–6.15[b])	7.12 (*d*, *J* = 11.6)
H–C(4)	6.66 (*d*, *J* = 11.6)	6.64 (*d*, *J* = 11.8)	6.03 (*dd*, *J* = 11.7, 1.6)	7.84–6.15[b])	6.62 (*d*, *J* = 11.8)
H–C(7)	7.00 (*d*, *J* = 6.3)	7.03 (*d*, *J* = 6.3)	6.35 (*d*, *J* = 6.5)[a])	7.84–6.15[b])	7.00 (*d*, *J* = 6.3)
H–C(8)	6.72 (*dd*, *J* = 11.4, 6.3)	6.75 (*dd*, *J* = 11.5, 6.4)	6.45 (*dd*, *J* = 11.4, 6.3)	7.84–6.15[b])	6.73 (*dd*, *J* = 11.5, 6.3)
H–C(9)	6.54 (*d*, *J* = 11.4)	6.55 (*d*, *J* = 11.4)	6.90–6.78[b])	7.84–6.15[b])	6.55 (*d*, *J* = 11.5)
Me–C(5)	1.51 (*s*)	1.49 (*s*)	1.36 (*s*)	1.51 (*s*)	1.51 (*s*)[c])
CH_2–C(1)	3.89 (*d*, *J* = 12.9), 3.82 (*d*, *J* = 12.9)	3.99 (*d*, *J* = 11.8), 3.34 (*d*, *J* = 11.8)	2.90 (*t*, *J* = 17.3), 2.70 (*dd*, *J* = 15.0, 9.0)	4.29 (*t*, *J* = 14.3), 3.31 (*td*, *J* = 14.3, 3.4)	–
CH_2–C(2)	4.35 (*s*)	4.55 (*d*, *J* = 11.3), 4.22 (*d*, *J* = 11.3)	4.00 (*dd*, *J* = 17.3, 10.5), 3.55 (*td*, *J* = 18.0, 4.5)	2.87 (*dd*, *J* = 15.3, 9.9), 3.16 (*dd*, *J* = 15.3, 9.9)	–

[a]) H–C(3) and H–C(8) appear as overlapped peaks. [b]) Hidden in the aromatic *m* signals. [c]) Me–C(1) at 1.91 (*s*).

Table 2. *^{1}H-NMR Data* ($CDCl_3$) *of the Series* **2b**–**7b** *and* **8** *of Heptalenes.* δ in ppm, J in Hz.

	2b	**3b**	**5b**	**6b**	**7b**	**8**
H–C(2)	6.31 (*d*, *J* = 6.0)	6.30 (*d*, *J* = 5.9)	6.15–6.10[a])	n.r.[b])	6.49 (*d*, *J* = 6.9)	6.12 (*d*, *J* = 5.7)
H–C(3)	6.81 (*d*, *J* = 6.0)	6.84 (*d*, *J* = 5.9)	7.11 (br. *s*)	n.r.[b])	7.34 (*d*, *J* = 6.0)	6.45 (*dd*, *J* = 11.4, 5.7)
H–C(7)	6.98 (*d*, *J* = 6.1)	7.03 (*d*, *J* = 6.2)	6.00 (*d*, *J* = 6.0)	6.06 (*d*, *J* = 5.8)	6.98 (*d*, *J* = 6.2)	6.87 (*d*, *J* = 6.2)
H–C(8)	6.74 (*dd*, *J* = 11.4, 6.1)	6.78 (*dd*, *J* = 11.4, 6.2)	6.15–6.10[a])	n.r.[b])	6.73 (*dd*, *J* = 11.5, 6.2)	6.58 (*dd*, *J* = 11.4, 6.2)
H–C(9)	6.53 (*d*, *J* = 11.4)	6.58 (*d*, *J* = 11.4)	6.33 (*d*, *J* = 11.4)	6.46 (*d*, *J* = 10.9)	6.49 (*d*, *J* = 11.3)	6.42 (*d*, *J* = 11.4)
Me–C(1)	1.55 (*s*)	1.56 (*s*)	1.32 (*s*)	1.39 (*s*)	1.60 (*s*)[c])	1.46 (*s*)[d])
CH_2–C(5)	4.19 (*s*)	4.25, 4.21 (2*d*, *J* = 12.2)	3.30 (*d*, *J* = 15.0), 3.16 (*d*, *J* = 12.3)	3.32 (*dd*, *J* = 14.3, 10.7), 2.89 (*t*, *J* = 14.8)	–	–
CH_2–C(4)	4.41, 4.35 (2*d*, *J* = 12.3)	4.78, 4.27 (2*d*, *J* = 12.2)	4.53 (*t*, *J* = 15.1), 3.54 (*t*-like, *J* = 17.5, 16.9)	3.41 (*d*, *J*(H,P) = 11.9)	–	–

[a]) Hidden in the aromatic *m* signals. [b]) n.r. = not recognizable. [c]) Me–C(5) at 1.75 (*s*). [d]) Me–C(5) at 1.42 (*s*).

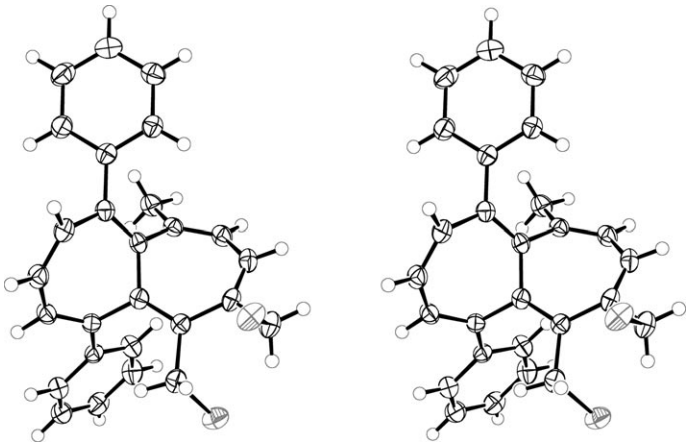


Fig. 2. *Stereoscopic view of the X-ray crystal structure of 4,5-bis(chloromethyl)-1-methyl-6,10-diphenylheptalene* (**3b**) (50% probability ellipsoids)

C(3)) = 119.7° and Θ(Cl–CH_2–C(5)=C(5a)) = 115.4° for **3b**. In other words, there are molecule-inherent effects that determine the orientation of the Cl–CH_2 bonds. We suppose that the main effect is given by an optimal interaction of the empty σ^*(Cl–CH_2) orbital with the filled π-bond, which determines the torsion angles of the Cl–CH_2 bonds. The involved π-bonds all show the same bond lengths (1.353(3)–1.355(3) Å).

When the chlorination reaction was performed in $CHCl_3$ at –60°, the yield of **3a**/**3b** was much lower. Moreover, due to the thermal DBS process that establishes an equilibrium between **3a** and **3b** at temperatures close to room temperature, always the same 1:2 ratio of **3a**/**3b** was formed after workup, independently of the composition of the starting material, *i.e.*, the ratio of **2a**/**2b** (for equilibrium ratios, see *Table 3*).

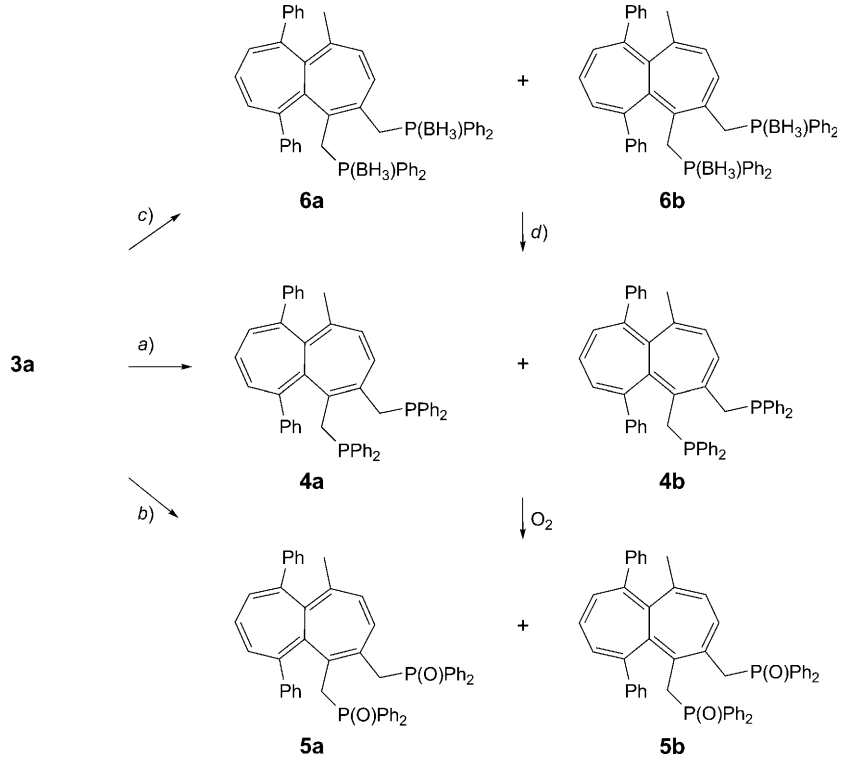
Table 3. *Compositions of the Thermal Equilibrium Mixtures of the Heptalenes*[a])

	2a/2b	**3a/3b**	**5a/5b**	**6a/6b**	**7a/7b**
Approximate ratio	1:2	1:2	1:2	1:2	1:2

[a]) In $CDCl_3$ at r.t.

The nucleophilic exchange of the Cl substituents of **3a** or **3b** by diphenylphosphino groups was facile with excess of (diphenylphosphino)lithium (= lithium diphenylphosphanide) in THF at 0° (*Scheme 4*). However, the purification of the bis-phosphines **4a**/**4b** was very difficult since they decomposed upon column chromatography on silica gel and were converted mostly by oxidation by air to bis(phosphine oxides) **5a** and **5b**. These latter compounds could be obtained in pure form by reaction of **3a** and **3b** with (diphenylphosphinyl)lithium (= lithium oxidodiphenylphospanide) in THF, respectively, followed by column chromatography on silica gel with Et_2O. Due to the poor solubility in Et_2O, the R_f values for both products were very small: 0.11 for **5a** and 0.06 for **5b**.

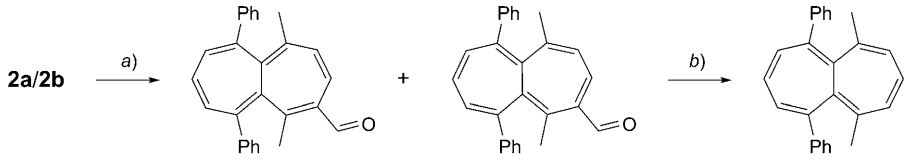
Scheme 4



a) $LiPPh_2$ (3 mol-equiv.), THF, 0° to r.t., 2.5 h. *b*) $LiP(O)Ph_2$ (3 mol-equiv.), THF, 0° to r.t., 2.5 h. *c*) $LiP(BH_3)Ph_2$ (6 mol-equiv.), THF, 0° to r.t., 12 h. *d*) DABCO, toluene, 60°, 4 h.

A mixture of carboxaldehydes **7a**/**7b** was obtained by acid-catalyzed (TsOH) disproportionation of a mixture of **2a**/**2b** in boiling dioxane (*cf.* [4][5]) (*Scheme 5*). Both DBS isomers could be isolated in pure form by chromatography of the mixture **7a**/**7b** on silica gel.

Scheme 5



a) TsOH, dioxane, 100°, 15 h; 77% (**7a**/**7b** 1:2). *b*) $[Rh(Ph_3P)_3]Cl$, toluene, 140°, 3.5 h; quant.

The decarbonylation of both carboxaldehydes with tris(triphenylphosphine)-rhodium(1+) chloride yielded heptalene **8** as a thermally and air-stable compound,

which exists in only one form since the DBS process leads to energetically degenerated structures.

In view of the difficulties of the separation of **4a** and **4b** from their product mixture by column chromatography, BH_3, which could endure oxidation by air, was introduced as a protecting group for the phosphino substituents. The reaction of a thermal-equilibrium mixture **3a**/**3b** with the borane adduct of (diphenylphosphino)lithium (= lithium boranyldiphenylphosphanide) in THF at 0° led to **6a** in 5% yield and **6b** in 15% yield (*Scheme 4*). However, heating **6a** or **6b** with 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene at 60°, followed by extraction of DABCO with 2M aqueous HCl and removal of the solvent after drying, resulted in a mixture of deprotected **6a** and **6b**, *i.e.*, the removal of BH_3 under these conditions caused easy interconversion of the targets **4a** and **4b** which could not be separated as discussed before. We also tried to prepare **4a** and **4b** by reaction of **3a** and **3b** with *t*-BuLi at low temperature, followed by addition of Ph_2PCl (see [6] for similar reactions), but again without success – **4a** and **4b** could not be isolated from the reaction mixture. To avoid any interconversion by DBS, all procedures have to be performed well below room temperature. So, the question is still open how the ligands **4a** and **4b** can be obtained in pure form.

Next, we returned to the thermal equilibrium mixture of the heptalene-dimethanols **2a**/**2b** and studied its chromatographic separation into the two pairs of antipodes (+)- and (−)-**2a** as well as (+)- and (−)-**2b**. Indeed, all 4 isomers were separated on an anal. *Chiralcel OD-H* column with hexane/i-PrOH 19:1 (*Fig. 3*). The separation factor of the antipodes amounted to $\alpha((P)/(M)\text{-}\mathbf{2a}) = 1.14$ and $\alpha((P)/(M)\text{-}\mathbf{2b}) = 1.26$ at room temperature. The separation of the peaks of (*P*)-**2a** and (*M*)-**2b** was further improved on a semi-prep. *Chiralcel-OD* column with hexane/i-PrOH 19:1, which we used for the prep. separation of the 4 isomers. They were all obtained in optically pure form.

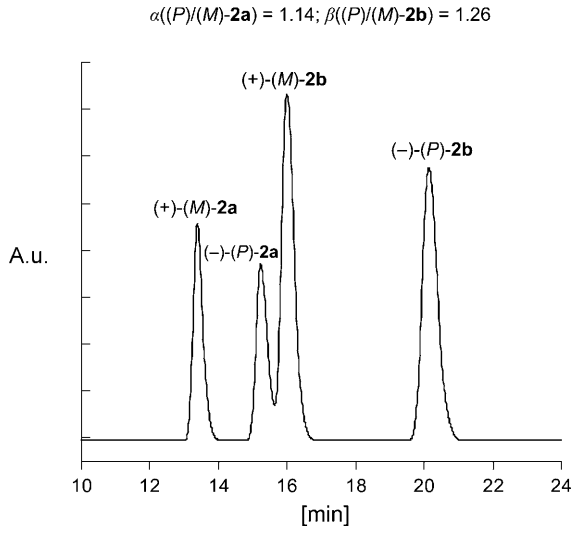


Fig. 3. *Separations of* **2a**/**2b** *on an anal.* Chiralcel-OD-H *column* (eluant hexane/i-PrOH 19:1; flow rate 0.5 ml/min; temp. 20°; detection wavelength 286 nm)

The quantitative CD spectra in hexane of the two pairs of antipodes are displayed in *Figs. 4* and *5*. They correspond very well with the UV/VIS spectra of **2a** and **2b**, which are shown in *Figs. 6* and *7*. The longest-wavelength absorption band, typical for heptalenes, appears in the UV/VIS spectra only as a shoulder at *ca.* 377 (**2a**) and 363 nm (**2b**), respectively. It is found in the CD spectra as a broad maximum or minimum at 388 nm and 378 nm, respectively, for the (*M*)-configured and (*P*)-configured heptalenes **2a** and **2b**. As in all earlier cases (see, *e.g.*, [7]), the heptalene with the larger *cisoid* torsion angles at the central σ-bond exhibits the longest-wavelength absorption at shorter wavelengths than the DBS heptalene with the smaller *cisoid* torsion angles. The difference in the average central torsion angles is 5° according to the crystal structures of **3a** and **3b** and should be similar for **2a** and **2b**.

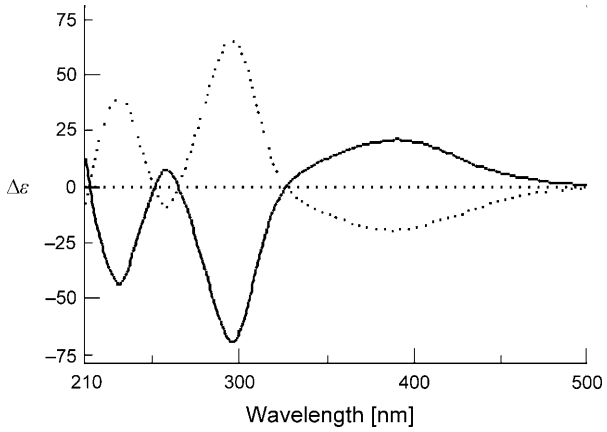


Fig. 4. *CD Spectra* (hexane) *of optically pure (+)-(*M*)-***2a*** (—) and (–)-(*P*)-***2a*** (···)*

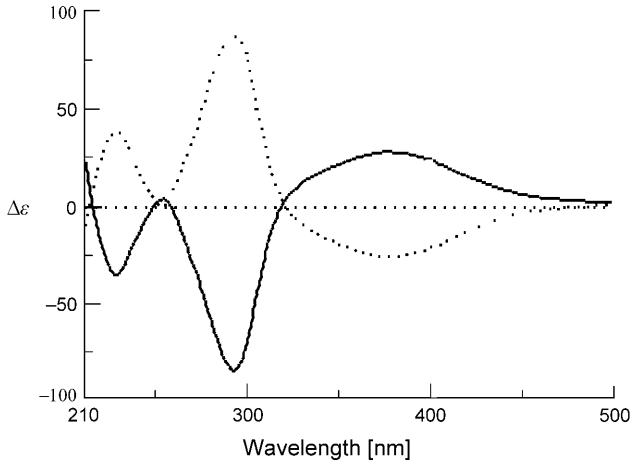


Fig. 5. *CD Spectra* (hexane) *of optically pure (+)-(*M*)-***2b*** (—) and (–)-(*P*)-***2b*** (···)*

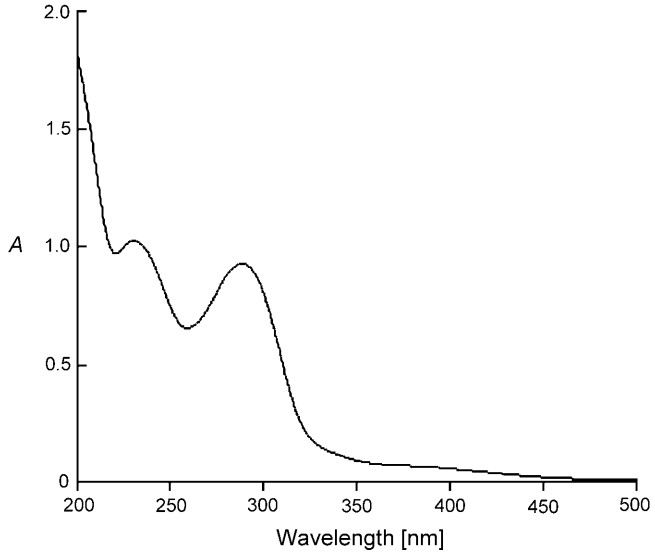


Fig. 6. *UV/VIS Spectrum* (hexane) *of* **2a**

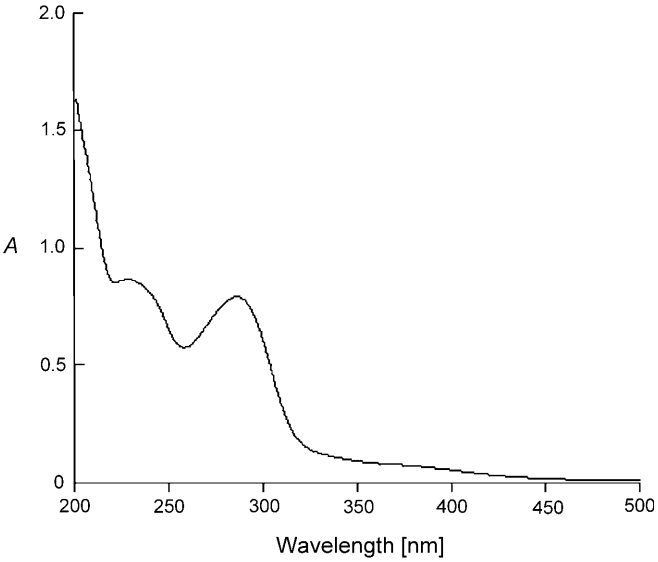


Fig. 7. *UV/VIS Spectrum* (hexane) *of* **2b**

It is also of interest to note that the antipodes of **2a** with torsion angles of *ca.* 0° between the two functional groups (CH_2OH) exhibit smaller retention times and separation factors α on the *Chiralcel-OD-H* column with hexane/i-PrOH mixtures $9:1 \rightarrow 19:1$ than their DBS counterparts **2b** with torsion angles of *ca.* 30° between the two functional groups.

On the other hand, the antipodes of 1,5-dimethyl-6,10-diphenylheptalene (**8**), the product of the decarbonylation of the carboxaldehydes **7a** and **7b**, could be separated on the anal. *Chiralcel-OD-H* column with hexane as mobile phase and the excellent separation factor $\alpha((P)\text{-}\mathbf{8a})/(M)\text{-}\mathbf{8a}) = 1.97$ at room temperature. The qualitative UV/VIS and CD spectra of **8** are displayed in *Figs. 8* and *9*, respectively. As expected, the spectra of **8** strongly resemble those of **2a** and **2b**. The longest-wavelength absorption of **8** appears as a shoulder at *ca.* 381 nm and as a broad CD band at *ca.* 388 nm in the CD spectra of the antipodes. From the data it can be concluded that **8** has similar *cisoid* torsion angles at the central σ-bond as **2a**. Indeed, the AM1 calculation of the structure of **8** gives an average *cisoid* torsion angle at the central σ-bond of 62°, in perfect agreement with that of 61° in the X-ray crystal structure of **3a**.

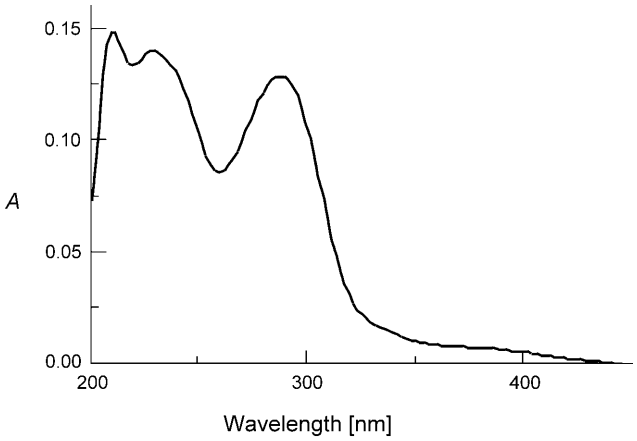


Fig. 8. *Qualitative UV/VIS spectrum* (hexane) *of* **8**

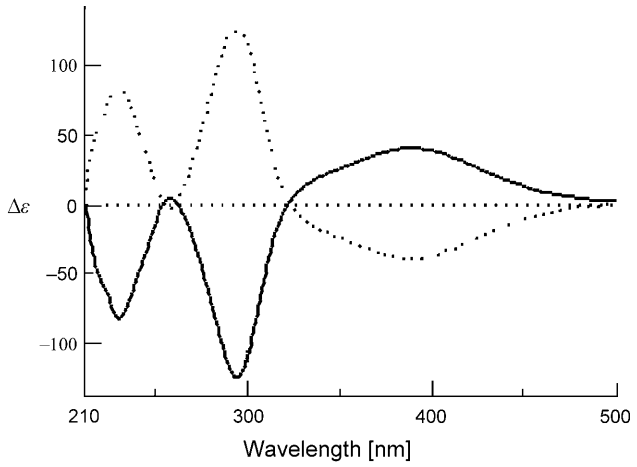


Fig. 9. *Qualitative CD spectra* (hexane) *of optically pure (+)-(*M*)-***8*** (—) and (–)-(*P*)-***8*** (···)*

Concluding Remarks. – A number of new 6,10-diphenylheptalene derivatives were synthesized, and it was demonstrated that such heptalene derivatives could be successfully separated into their antipodes by chromatography on *Chiralcel-OD-H* columns. We were not successful in the synthesis of pure bis[(diphenylphosphino)-methyl] derivatives of the 6,10-diphenylheptalenes since the thermal interconversion of the pure DBS forms takes place slowly even at room temperature.

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Experimental Part

1. *General.* See [1]. HPLC: anal. *Chiralcel-OD-H* column (5 μm; 4.6 × 250 mm) and semi-prep. *Chiralcel-OD* column (10 μm; 20 × 250 mm), from *Daicel Chemical Industries.* CD Spectra: *Jasco* instrument (model *J-715*).

2. *Synthesis of Heptalenes.* 2.1. *5-Methyl-6,10-diphenylheptalene-1,2-dimethanol* (**2a**) *and 1-Methyl-6,10-diphenylheptalene-4,5-dimethanol* (**2b**). To a soln. of heptalene diester **1** (500 mg, 1.15 mmol) [3] in THF (50 ml), 2M DIBAH in hexane (16 ml, 32 mmol) was added at 0°. After 2 h stirring at r.t., the reaction was quenched by addition of H_2O, and the mixture was extracted with AcOEt. The org. phase was washed with 1M H_2SO_4 (3 ×) and sat. aq. soln. of NaCl (1 ×), dried (Na_2SO_4), and concentrated. CC (silica gel (SiO_2), hexane/Et_2O 1:3) yielded **2a** (58 mg, 13.3%) and **2b** (352 mg, 80.7%) as yellow foams. At r.t., **2a**/**2b** were in thermal equilibrium with a ratio of *ca.* 1:2 in $CDCl_3$. The mixture of **2a**/**2b** was determined by HPLC (anal. *Chiralcel-OD-H* column, hexane/i-PrOH 95:5, flow rate 0.5 ml/min, r.t., detection wavelength 286 nm; see also *Fig. 3*). The optically pure agents were isolated by HPLC (semi-prep. *Chiralcel-OD* column, hexane/i-PrOH 95:5): sequential fractions of (+)-(*M*)-**2a**, (−)-(*P*)-**2a**, (+)-(*M*)-**2b**, and, finally, (−)-(*P*)-**2b**.

Data of (±)-**2a**: M.p. 102–103° (hexane/Et_2O). R_f (hexane/Et_2O 1:3) 0.24. UV/VIS ($c = 0.422 \cdot 10^{-4}$ M, hexane): max. 231 (4.83), 288 (4.34), 318 (sh, 3.82), 377 (sh, 3.18); min. 221 (4.36), 259 (4.19). IR (KBr): 3356*m*, 3054*m*, 3010*m*, 2924*s*, 2854*m*, 1596*w*, 1490*m*, 1443*m*, 1179*w*, 1093*w*, 1075*w*, 1027*w*, 999*s*, 758*s*, 725*m*, 701*s*, 531*w*. CD of (+)-(*M*)-**2a** (hexane, r.t., $c = 1.379 \cdot 10^{-5}$ M): 390 (pos. max., +20.5), 327 (+0.2), 295 (neg. max., −70.0), 263 (−0.4), 257 (pos. max., +7.0), 251 (+0.5), 230 (neg. max., −44.6), 213 (−0.7), 206 (pos. max., +25.2). CD of (−)-(*P*)-**2a** (hexane, r.t., $c = 1.379 \cdot 10^{-5}$ M): 385 (neg. max., −20.2), 325 (−0.1), 294 (pos. max., +64.6), 265 (+0.3), 257 (neg. max., −9.9), 250 (−0.7), 230 (pos. max., +39.4), 213 (+0.2), 205 (neg. max., −25.3). ^{1}H-NMR (500 MHz, $CDCl_3$, 243 K; see also *Table 1*): 7.49 (*d*, $^3J = 7.3$, 2 arom. H); 7.40–7.26 (*m*, 5 arom. H); 7.23 (*t*-like, $^3J = 7.2$, 7.3, 1 arom. H); 7.18–7.16 (*m*, 2 arom. H); 7.00 (*d*, $^3J = 6.3$, H−C(7)); 6.77 (*d*, $^3J = 11.6$, H−C(3)); 6.72 (*dd*, $^3J = 11.4$, 6.3, H−C(8)); 6.66 (*d*, $^3J = 11.6$, H−C(4)); 6.54 (*d*, $^3J = 11.4$, H−C(9)); 4.35 (*s*, CH_2−C(2)); 3.89 (*d*, *A* of *AB*, $^2J_{AB} = 12.9$, 1 H, CH_2−C(1)); 3.82 (*d*, *B* of *AB*, $^2J_{AB} = 12.9$, 1 H, CH_2−C(1)); 1.51 (*s*, Me−C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$, 243 K): 142.88 (*s*, C(2)); 139.33 (*s*, 1 arom. C); 138.73 (*s*, 1 arom. C); 136.67 (*d*, C(4)); 135.59 (*s*, C(10)); 135.56 (*s*, C(6)); 134.60 (*s*, C(1)); 134.42 (*s*, C(10a)); 134.10 (*d*, C(3)); 133.28 (*d*, C(9)); 132.02 (*s*, C(5)); 131.22 (*d*, C(8)); 130.00 (*d*, 2 arom. C, C(5a)); 128.72 (*d*, 2 arom. C); 128.34 (*d*, 2 arom. C); 127.88 (*d*, 1 arom. C); 127.32 (*d*, 1 arom. C); 126.18 (*d*, 2 arom. C); 125.66 (*d*, C(7)); 64.56 (*t*, CH_2−C(1)); 63.11 (*t*, CH_2−C(2)); 17.91 (*q*, *Me*−C(5)). CI-MS: 398 (12, $[M + NH_4]^+$), 380 (11, $M^{+\cdot}$), 365 (18, $[M - Me]^+$), 364 (31), 363 (100, $[M - H_2O]^+$), 361 (15), 347 (14). Anal. calc. for $C_{27}H_{24}O_2$ (380.48): C 85.23, H 6.36; found: C 84.77, H 6.73.

Data of (±)-**2b**: M.p. 91–92° (hexane/Et_2O). R_f (hexane/Et_2O 1:3) 0.18. UV/VIS ($c = 0.406 \cdot 10^{-4}$ M, hexane): max. 228 (4.35), 286 (4.31), 310 (sh, 3.92), 363 (sh, 3.30); min. 221 (4.34), 258 (4.17). IR (KBr): 3315*m*, 3058*m*, 3016*m*, 2956*m*, 2929*m*, 2875*m*, 1635*w*, 1594*w*, 1492*m*, 1444*m*, 1367*w*, 1347*m*, *1255w*, 1157*w*, 1098*w*, 1076*w*, 1061*w*, 1021*s*, 984*s*, 915*w*, 874*w*, 851*m*, 796*w*, 765*s*, 745*s*, 721*s*, 701*s*, 577*w*, 560*w*, 507*w*. CD of (+)-(*M*)-**2b** (hexane, r.t., $c = 2.60 \cdot 10^{-5}$ M): 376 (pos. max., +27.7), 318 (+0.4), 291 (neg. max., −84.9),

257 (−0.3), 253 (pos. max., +2.9), 248 (−0.2), 227 (neg. max., −36.1), 214 (+1.0), 207 (pos. max., +35.3). CD of (−)-(*P*)-**2b** (hexane, r.t., $c = 6.98 \cdot 10^{-5}$ M): 379 (neg. max., −26.7), 319 (−0.3), 291 (pos. max., +87.1), 255 (+0.2), 253 (neg. max., −1.4), 250 (+0.3), 228 (pos. max., +37.7), 213 (−0.5), 206 (neg. max., −26.6). ^{1}H-NMR (500 MHz, $CDCl_3$, 243 K; see also *Table 2*): 7.56 (*d*, $^3J = 7.6$, 2 arom. H); 7.32–7.27 (*m*, 5 arom. H); 7.22 (*t*-like, $^3J = 7.2$, 7.3, 1 arom. H); 7.20–7.18 (*m*, 2 arom. H); 6.98 (*d*, $^3J = 6.1$, H−C(7)); 6.81 (*d*, $^3J = 6.0$, H−C(3)); 6.74 (*dd*, $^3J = 11.4$, 6.1, H−C(8)); 6.53 (*d*, $^3J = 11.4$, H−C(9)); 6.31 (*d*, $^3J = 6.0$, H−C(2)); 4.41 (*d*, *A* of *AB*, $^2J_{AB} = 12.3$, 1 H, CH_2−C(4)); 4.35 (*d*, *B* of *AB*, $^2J_{AB} = 12.2$, 1 H, CH_2−C(4)); 4.19 (*s*, CH_2−C(5)); 1.55 (*s*, Me−C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$, 243 K): 141.60 (*s*, C(4)); 139.36 (*s*, 1 arom. C); 139.18 (*s*, 1 arom. C); 137.14 (*s*, C(5)); 134.03 (*d*, C(9)); 133.89 (*s*, C(10)); 133.83 (*d*, C(3)); 133.55 (*s*, C(1)); 133.42 (*s*, C(6)); 132.84 (*s*, C(10a)); 131.34 (*s*, C(5a)); 131.23 (*d*, C(8)); 129.29 (*d*, 2 arom. C); 128.95 (*d*, 2 arom. C); 128.42 (*d*, C(2)); 127.92 (*d*, 2 arom. C); 127.70 (*d*, 1 arom. C); 127.38 (*d*, 1 arom. C); 125.64 (*d*, 2 arom. C, C(7)); 66.82 (*t*, *C*H_2−C(4)); 59.31 (*t*, *C*H_2−C(5)); 22.19 (*q*, *Me*−C(1)). CI-MS: 398 (12, $[M + NH_4]^+$), 380 (14, $M^{+\cdot}$), 365 (16, $[M - Me]^+$), 364 (22), 363 (100, $[M - H_2O]^+$), 362 (7), 361 (17), 347 (13). Anal. calc. for $C_{27}H_{24}O_2$ (380.48): C 85.23, H 6.36; found: C 84.28, H 6.42.

2.2. *1,2-Bis(chloromethyl)-5-methyl-6,10-diphenylheptalene* (**3a**) *and 4,5-Bis(chloromethyl)-1-methyl-6,10-diphenylheptalene* (**3b**). Dimethanol (±)-**2a** (350 mg, 0.92 mmol) was dissolved in CH_2Cl_2 (50 ml) and cooled to −60°. Simultaneously, PCl_5 (2.5 g) was dissolved in CH_2Cl_2 (25 ml), cooled to 0°, and then added to the soln. of (±)-**2a**, thereby avoiding an increase in temp. (slowly yellow → dark orange mixture). After 1 h, TLC indicated that all (±)-**2a** had been consumed. Then, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ soln. (30 ml). The mixture was extracted with CH_2Cl_2, the extract dried ($MgSO_4$) and concentrated, and the residue purified by CC (prolonged column of SiO_2, hexane/Et_2O 20:1). Pure **3a** (120 mg, 34%) was obtained as orange crystals and **3b** (230 mg, 66%) as yellow crystals. When (±)-**2b** was used as starting material, the yield and the molar ratio of **3a**/**3b** were similar to those obtained from **2a**. At r.t., **3a**/**3b** were in thermal equilibrium with a ratio of *ca.* 1:2 in $CDCl_3$.

Data of **3a**: M.p. 136.2–137.2° (hexane/Et_2O). R_f (hexane/Et_2O 7:1) 0.40. UV/VIS ($c = 0.616 \cdot 10^{-4}$ M, hexane): max. 235 (4.42), 289 (4.37), 327 (sh, 3.72), 370 (sh, 3.24); min. 223 (4.39), 259 (4.26). IR (KBr): 3443*w*, 3014*w*, 2935*w*, 1595*w*, 1492*m*, 1442*m*, 1255*m*, 1073*w*, 1034*w*, 886*w*, 837*w*, 760*m*, 733*m*, 691*s*, 521*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, 243 K; see also *Table 1*): 7.61 (*d* with f.s., $^3J = 7.7$, 2 arom. H); 7.35–7.26 (*m*, 5 arom. H); 7.24 (*t*-like, $^3J = 7.0$, 8.1, 1 arom. H); 7.16–7.14 (*m*, 2 arom. H); 7.03 (*d*, $^3J = 6.3$, H−C(7)); 6.75 (*dd*, $^3J = 6.4$, 11.5, H−C(8)); 6.70 (*d*, $^3J = 11.6$, H−C(3)); 6.64 (*d*, $^3J = 11.8$, H−C(4)); 6.55 (*d*, $^3J = 11.4$, H−C(9)); 4.55 (*d*, *A* of *AB*, $^2J_{AB} = 11.3$, 1 H, CH_2−C(2)); 4.22 (*d*, *B* of *AB*, $^2J_{AB} = 11.3$, 1 H, CH_2−C(2)); 3.99 (*d*, *A* of *AB*, $^2J_{AB} = 11.8$, 1 H, CH_2−C(1)); 3.34 (*d*, *B* of *AB*, $^2J_{AB} = 11.8$, 1 H, CH_2−C(1)); 1.49 (*s*, Me−C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$, 243 K): 139.16 (*s*, C(2)); 138.78 (*s*, 1 arom. C); 138.31 (*s*, 1 arom. C); 137.83 (*d*, C(4)); 137.19 (*s*, C(10)); 136.90 (*s*, C(6)); 135.06 (*s*, C(1)); 133.66 (*d*, C(9)); 132.58 (*s*, C(5), C(10a)); 132.51 (*d*, C(3)); 132.36 (*d*, C(8)); 131.71 (*s*, C(5a)); 130.07 (*d*, 2 arom. C); 128.48 (*d*, 2 arom. C); 128.44 (*d*, 2 arom. C); 128.04 (*d*, 1 arom. C); 127.62 (*d*, 1 arom. C); 127.23 (*d*, 2 arom. C); 125.70 (*d*, C(7)); 43.84 (*t*, *C*H_2−C(1)); 42.71 (*t*, *C*H_2−C(2)); 18.48 (*q*, *Me*−C(5)). EI-MS: 419, 418, 417, and 416 (12, 42, 21, and 62, $M^{+\cdot}$), 383, 382, and 381 (36, 31, and 100, $[M - Cl]^+$), 367 (15, $[M - CH_2Cl]^+$), 346 (32), 345 (32, $[M - 2\ Cl]^+$), 341 (10), 331 (47), 330 (18, $[M - 2\ Cl - Me]^+$), 329 (20), 318 (10), 317 (22), 316 (17), 315 (23), 303 (13), 302 (16), 294 (30), 291 (11), 289 (17), 253 (18), 252 (22), 239 (23), 215 (15), 158 (26), 157 (28), 156 (14), 151 (23), 144 (12). Anal. calc. for $C_{27}H_{22}Cl_2$ (417.37): C 77.70, H 5.31; found: C 76.98, H 5.46.

The structure of **3a** was confirmed by X-ray crystal-structure analysis (see below).

Data of **3b**: M.p. 105.2–105.7° (hexane/Et_2O). R_f (hexane/Et_2O 7:1) 0.38. UV/VIS ($c = 0.766 \cdot 10^{-4}$ M, hexane): max. 285 (4.42), 309 (sh, 4.01), 354 (sh, 3.48); min. 259 (4.30). IR (KBr): 3443*w*, 3017*w*, 2970*w*, 1640*w*, 1595*w*, 1574*w*, 1491*m*, 1456*m*, 1443*m*, 1433*m*, 1372*w*, 1348*w*, 1260 *m*, 1153*w*, 1074*w*, 1023*w*, 965*w*, 912*w*, 886*w*, 838*w*, 825*m*, 789*w*, 763*s*, 735*m*, 717*s*, 698*s*, 689*s*, 673*s*, 649*m*, 624*w*, 606*m*, 568*w*, 515*w*, 483*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, 243 K; see also *Table 2*): 7.57 (*d*, $^3J = 7.4$, 2 arom. H); 7.34 (*t*-like, $^3J = 7.2$, 7.8, 2 arom. H); 7.32–7.26 (*m*, 4 arom. H); 7.23–7.21 (*m*, 2 arom. H); 7.03 (*d*, $^3J = 6.2$, H−C(7)); 6.84 (*d*, $^3J = 5.9$, H−C(3)); 6.78 (*dd*, $^3J = 11.4$, 6.2, H−C(8)); 6.58 (*d*, $^3J = 11.4$, H−C(9)); 6.30 (*d*, $^3J = 5.9$, H−C(2)); 4.78 (*d*, *A* of *AB*, $^2J_{AB} = 12.2$, 1 H, CH_2−C(4)); 4.27 (*d*, *B* of *AB*, $^2J_{AB} = 12.2$, 1 H, CH_2−C(4)); 4.25 (*d*, *A* of *AB*, $^2J_{AB} = 10.7$, 1 H, CH_2−C(5)); 4.21 (*d*, *B* of *AB*, $^2J_{AB} = 12.2$, 1 H, CH_2−C(5)); 1.56 (*s*,

Me–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$, 243 K): 139.33 (*s*, C(1)); 139.17 (*s*, 1 arom. C); 137.91 (*s*, C(4)); 137.33 (*s*, 1 arom. C); 134.97 (*s*, C(5a)); 134.41 (*s*, C(10)); 134.37 (*d*, C(3)); 133.78 (*d*, C(9)); 132.88 (*s*, C(6)); 131.86 (*s*, C(10a)); 131.22 (*d*, C(8)); 129.33 (*d*, 2 arom. C); 128.81 (*s*, C(5)); 128.65 (*d*, 2 arom. C); 127.92 (*d*, 2 arom. C); 127.73 (*d*, 1 arom. C); 127.62 (*d*, C(2)); 127.50 (*d*, 1 arom. C); 126.34 (*d*, 2 arom. C); 125.75 (*d*, C(7)); 48.85 (*t*, CH_2–C(4)); 40.96 (*t*, CH_2–C(5)); 22.22 (*q*, *Me*–C(1)). EI-MS: 419, 418, 417, and 416 (8, 28, 16, and 57, $M^{+\bullet}$), 384, 383, 382, and 381 (6, 26, 26, and 100, $[M-Cl]^+$), 367 (19, $[M-CH_2Cl]^+$), 346 (10), 345 (28, $[M-2\,Cl]^+$), 341 (12), 332 (16), 331 (39), 330 (18, $[M-2\,Cl-Me]^+$), 329 (22), 328 (10), 327 (9), 325 (10), 318 (12), 317 (30), 316 (22), 315 (32), 314 (12), 313 (16), 305 (9), 303 (16), 302 (29), 293 (44), 291 (12), 290 (11), 289 (31), 253 (29), 252 (45), 239 (45), 214 (33), 165 (33), 158 (97), 156 (59), 151 (67), 150 (32), 145 (42), 91 (38), 41 (45). Anal. calc. for $C_{27}H_{22}Cl_2$ (417.37): C 77.70, H 5.31; found: C 77.30, H 5.45.

The structure of **3b** was confirmed by X-ray crystal-structure analysis (see below).

2.3. *[(5-Methyl-6,10-diphenylheptalene-1,2-diyl)bis(methylene)]bis[diphenylphosphine Oxide]* (**5a**) *and [(1-Methyl-6,10-diphenylheptalene-4,5-diyl)bis(methylene)]bis[diphenylphosphine Oxide]* (**5b**). A soln. of (diphenylphosphinyl)lithium in THF (1.5 ml) was prepared by lithiation of diphenylphosphine oxide (0.101 g, 0.50 mmol) with 1.6M BuLi in hexane (0.33 ml, 0.50 mmol) at 0°. The resulting soln. was added dropwise at 0° to a soln. of **3a** (47 mg, 0.11 mmol) in THF (3 ml). After 20 min, the ice bath was removed, and stirring was continued at r.t. for 2.5 h. The mixture was, thereafter, worked up in the usual manner, and purified by CC (SiO_2, Et_2O). Two fractions (**5a**, R_f 0.11; **5b**, R_f 0.06) were obtained as yellow crystals. Total yield of **5a**/**5b**: 52 mg (29%). At r.t., **5a**/**5b** were in thermal equilibrium with a ratio of *ca.* 1:2 in $CDCl_3$.

Data of **5a**: M.p. 268.2–269.2° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$; see also *Table 1*): 8.15–8.09 (*m*, 2 arom. H); 7.95–7.88 (*m*, 2 arom. H); 7.45–7.31 (*m*, 8 arom. H); 7.30–6.99 (*m*, 16 arom. H); 6.90–6.78 (*m*, 2 arom. H, H–C(9)); 6.45 (*dd*, $^3J(8,9)=11.4$, $^3J(8,7)=6.3$, H–C(8)); 6.35 (2*d*, $^3J(3,4)=10.9$, $^3J(7,8)=6.5$, H–C(3), H–C(7)); 6.03 (*dd*, $^3J(4,3)=11.7$, $^4J=1.6$, H–C(4)); 4.00 (*dd*, *A* of *ABX*, $J=17.3$, 10.5, 1 H, CH_2–C(2)); 3.55 (*td*, *B* of *ABX*, $J=18.0$, 4.5, 1 H, CH_2–C(2)); 2.90 (*t*-like, *A* of *ABX*, $J=17.3$, 1 H, CH_2–C(1)); 2.70 (*dd*, *B* of *ABX*, $J=15.0$, 9.0, 1 H, CH_2–C(1)); 1.36 (*s*, Me–C(5)). ESI-MS: 772 (55), 771 (100, $[M+Na]^+$), 749 (65, $[M+1]^+$).

Data of **5b**: M.p. 266.1–266.9° (Et_2O). ^{1}H-NMR (500 MHz, $CDCl_3$, 243 K; see also *Table 2*): 8.05–7.97 (*m*, 4 arom. H); 7.63 (*t*-like, $^3J=6.4$, 7.0, 1 arom. H); 7.57–7.46 (*m*, 6 arom. H); 7.44–7.41 (*m*, 4 arom. H); 7.32–7.29 (*m*, 4 arom. H); 7.25–7.19 (*m*, 7 arom. H); 7.15 (*t*-like, $^3J=7.6$, 7.1, 3 arom. H); 7.11 (br. *s*, H–C(3)); 6.75 (*d*, $^3J=7.3$, 2 arom. H); 6.33 (*d*, $^3J(9,8)=11.4$, H–C(9)); 6.15–6.10 (*m*, H–C(2), H–C(8)); 6.00 (*d*, $^3J(7,8)=6.0$, H–C(7)); 4.53 (*t*, *A* of *ABX*, $^2J_{AB}=^2J_{AX}=15.1$, 1 H, CH_2–C(4)); 3.54 (*t*-like, *B* of *ABX*, $^2J_{AB}=17.5$, $^2J_{BX}=16.9$, 1 H, CH_2–C(4)); 3.30 (*dd*, *A* of *ABX*, $^2J_{AB}=15.0$, $^2J_{AX}=12.3$, 1 H, CH_2–C(5)); 3.16 (*t*-like, *B* of *ABX*, $^2J_{AB}\approx{}^2J_{BX}=14.9$, 1 H, CH_2–C(5)); 1.32 (*s*, Me–C(1)). ^{31}P-NMR (202 MHz, $CDCl_3$, 243 K): 33.09, 28.75 (2*s*, 1:1 ratio). ESI-MS: 772 (50), 771 (100, $[M+Na]^+$), 749 (45, $[M+1]^+$).

2.4. *[(5-Methyl-6,10-diphenylheptalene-1,2-diyl)bis(methylene)]bis[diphenylphosphine Oxide] Adduct with Borane (1:1)* (**6a**) *and [(1-Methyl-6,10-diphenylheptalene-4,5-diyl)bis(methylene)]bis[diphenylphosphine Oxide] Adduct with Borane (1:1)* (**6b**). $LiP(BH_3)Ph_2$ (*cf.* [1]) in THF (4 ml) was prepared from $HPPh_2\cdot BH_3$ (1.139 g, 4.00 mmol) and Li dust (0.056 g, 8.00 mmol) at 0°. After 4 h, *t*-BuCl (0.441 ml, 4.00 mmol) was added, and stirring was continued for further 30 min. The resulting soln. (3.0 ml, 3.00 mmol of $LiP(BH_3)Ph_2$) was added at 0° to a soln. of the thermal-equilibrium mixture **3a**/**3b** (200 mg, 0.48 mmol) in THF (20 ml). Thereafter, the mixture was stirred overnight (*ca.* 12 h) at r.t. The usual workup, followed by CC (SiO_2, hexane/CH_2Cl_2 1:1), gave pure **6a** (19 mg, 5%) and **6b** (55 mg, 15%) as yellow foams. At r.t., **6a**/**6b** were in thermal equilibrium with a ratio of *ca.* 1:2 in $CDCl_3$.

Data of **6a**: R_f (hexane/CH_2Cl_2 1:1) 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$, 243 K; see also *Table 1*): 7.84–6.15 (*m*, 30 arom. H, H–C(3), H–C(4), H–C(7), H–C(8), H–C(9)); 4.29 (*t*-like, *A* of *ABX*, $^2J_{AB}=^2J_{AX}=14.3$, 1 H, CH_2–C(2)); 3.31 (*td*, *B* of *ABX*, $^2J_{AB}=^2J_{BX}=14.3$, $^4J=3.4$, 1 H, CH_2–C(2)); 2.87 (*dd*, *A* of *ABX*, $^2J_{AB}=15.3$, $^2J_{AX}=9.9$, 1 H, CH_2–C(1)); 3.16 (*dd*, *B* of *ABX*, $^2J_{AB}=15.3$, $^2J_{BX}=9.9$, 1 H, CH_2–C(1)); 1.51 (*s*, Me–C(5)), 1.69–0.57 (br. *q*, 2 BH_3). ^{31}P-NMR (121 MHz, $CDCl_3$): 15.28, 13.64 (2*s*, 1:1 ratio).

Data of **6b**: R_f (hexane/CH_2Cl_2 1:1) 0.18. ^{1}H-NMR (300 MHz, $CDCl_3$, 243 K; see also *Table 2*): 7.65–6.49 (*m*, 3 arom. H); 7.47–6.93 (*m*, 26 arom. H); 6.91–6.82 (*m*, 3 arom. H); 6.76–6.23 (*m*, 3 arom. H); 6.46 (*d*, ^3J = 10.9, H–C(9)); 6.06 (*d*, ^3J = 5.8, H–C(7)); 3.41 (*d*, *AX*, $^2J_{AX}$ = 11.9, CH_2–C(4)); 3.32 (*dd*, *A* of *ABX*, $^2J_{AB}$ = 14.3, $^2J_{AX}$ = 10.7, 1 H, CH_2–C(5)); 2.89 (*t*-like, *B* of *ABX*, $^2J_{AB}$ = $^2J_{AX}$ = 14.8, 1 H, CH_2–C(5)); 1.39 (*s*, Me–C(1)), 1.53–0.20 (br. *q*, 2 BH_3). ^{31}P-NMR (121 MHz, $CDCl_3$): 18.25, 15.98 (2*s*, 1:1 ratio).

2.5. *Phosphinylation of* **3a**/**3b**. 2.5.1. *Attempted Reaction of* **3a**/**3b** *with (Diphenylphosphino)lithium.* The reaction of **3a** or **3b** was conducted as described in 1.8.3. of [1]. After workup, a mixture of **4a**/**4b** was recognized by its typical ^{1}H-NMR spectra, where the signals of the CH_2 groups were similar to those of [1]. However, the purification of **4a**/**4b** was really difficult, due to decomposition on CC (SiO_2; 60 cm × 1 cm i.d.). After CC, **5a** and **5b** could be identified in small amounts.

2.5.2. *Attempted Reaction with* t-*BuLi and* Ph_2PCl. The reaction of **3a** or **3b** was conducted as described in 1.4.1. of [6]. It did not afford **4a** or **4b**, either.

2.6. *Deprotection of* **6a**/**6b** *to* **4a**/**4b** *with DABCO.* The reaction of **6a** or **6b** was conducted as described in 1.8.1. of [1]. It led to a mixture **4a**/**4b**, analyzed by ^{1}H-NMR in comparison with their precursor. The mixture could not be purified by CC.

2.7. *1,5-Dimethyl-6,10-diphenylheptalene-2-carboxaldehyde* (**7a**) *and 1,5-Dimethyl-6,10-diphenylheptalene-4-carboxaldehyde* (**7b**). A soln. of the equilibrium mixture **2a**/**2b** (200 mg, 0.52 mmol) and TsOH (10 mg, 0.052 mmol) in 1,4-dioxane (50 ml) was heated at 100° for 15 h (yellow → dark orange). After cooling, the solvent was evaporated and the obtained brown oil subjected to CC (SiO_2, hexane/Et_2O 4:1). The yellow-orange fraction was dried and analyzed by ^{1}H-NMR: 33% of **7a** and 67% of **7b**. Total yield of **7a**/**7b**: 146 mg (77%). The isomers could be separated by CC (long column of SiO_2). At r.t., **7a**/**7b** were in thermal equilibrium in a ratio of *ca.* 1:2 in $CDCl_3$.

Data of **7a**: M.p. 136.9–137.2° (hexane/Et_2O). R_f (hexane/Et_2O 4:1) 0.51. UV/VIS ($c = 0.343 \cdot 10^{-4}$ M, hexane): max. 232 (4.46), 270 (4.32), 290 (4.34), 328 (sh, 3.79), 381 (sh, 3.20); min. 221 (4.40), 256 (4.28), 276 (4.32). IR (KBr): 3442*w*, 3017*w*, 2915*w*, 2867*w*, 1979*w*, 1677*s*, 1634*w*, 1595*w*, 1579*w*, 1490*m*, 1443*m*, 1363*w*, 1306*w*, 1278*w*, 1243*w*, 1231*m*, 1186*w*, 1138*w*, 1076*w*, 1029*w*, 923*w*, 883*w*, 840*w*, 809*m*, 786*m*, 770*m*, 755*m*, 726*m*, 701*s*, 683*w*, 575*w*, 540*w*, 506*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; see also *Table 1*): 10.03 (*s*, CHO); 7.44 (*d* with f.s., ^3J = 7.3, 2 arom. H); 7.29–7.25 (*m*, 5 arom. H); 7.23 (*tt*, *J* = 7.2, 1.1, 1 arom. H); 7.12 (*d*, ^3J = 11.6, H–C(3)); 7.10 (*d*, ^3J = 5.3, 1 arom. H); 7.09 (*d*, ^3J = 7.5, 1 arom. H); 7.00 (*d*, ^3J = 6.3, H–C(7)); 6.73 (*dd*, ^3J(8,9) = 11.5, ^3J(8,7) = 6.3, H–C(8)); 6.62 (*d*, ^3J = 11.8, H–C(4)); 6.55 (*d*, ^3J = 11.5, H–C(9)); 1.91 (*s*, Me–C(1)); 1.51 (*s*, Me–C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$): 190.10 (*d*, CHO), 149.03 (*s*, C(1)); 139.29 (*s*, 1 arom. C); 138.34 (*s*, 1 arom. C); 137.13 (*s*, C(2)); 136.91 (*s*, C(6)); 135.98 (*s*, C(4)); 135.41 (*s*, C(10), C(10a)); 133.93 (*d*, C(9)); 133.41 (*s*, C(5)); 132.00 (*d*, C(8)); 129.65 (*d*, 2 arom. C); 129.09 (*d* and *s*, 2 arom. C, C(5a)); 128.45 (*d*, 2 arom. C); 128.08 (*d*, 1 arom. C); 127.78 (*d*, 1 arom. C); 127.08 (*d*, C(3)); 126.27 (*d*, 2 arom. C); 125.54 (*d*, C(7)); 18.18 (*q*, *Me*–C(5)); 18.15 (*q*, *Me*–C(1)). EI-MS: 363(29, $[M+1]^+$), 362 (100, $M^{+\bullet}$), 348 (7), 347 (26), 334 (11), 333 (26), 329 (10), 320 (7), 319 (28), 318 (15), 317 (8), 305 (10), 304 (14), 303 (16), 302 (15), 294 (23), 293 (9), 289 (11), 280 (14), 279 (13), 278 (9), 276 (9), 260 (17), 241 (11), 239 (17), 217 (7), 216 (8), 215 (17), 202 (11), 157 (7), 152 (16), 151 (19), 145 (9), 91 (8), 86 (15), 71 (10), 57 (58), 56 (27), 55 (9), 43 (38), 42 (16), 41 (35), 39 (8), 32 (10).

Data of **7b**: M.p. 161.5–162.2° (hexane/Et_2O). R_f (hexane/Et_2O 4:1) 0.44. UV/VIS ($c = 0.430 \cdot 10^{-4}$ M, hexane): max. 233 (4.45), 268 (4.42), 326 (sh, 3.87), 393 (sh, 3.21); min. 221 (4.42), 252 (4.33). IR (KBr): 3441*w*, 3062*w*, 3016*w*, 2922*w*, 2853*w*, 2730*w*, 1675*s*, 1599*m*, 1551*m*, 1511*w*, 1491*w*, 1443*w*, 1366*w*, 1230*w*, 1212*w*, 1160*w*, 1146*w*, 1077*w*, 1031*w*, 946*w*, 905*w*, 882*w*, 844*m*, 781*w*, 763*w*, 750*m*, 725*m*, 699*m*, 655*w*, 571*w*, 513*w*, 467*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; see also *Table 2*): 9.65 (*s*, CHO); 7.50 (*d* with f.s., ^3J = 7.5, 2 arom. H); 7.34 (*d*, ^3J = 6.0, H–C(3)); 7.29–7.25 (*m*, 5 arom. H); 7.21 (*t*-like, ^3J = 7.3, 1 arom. H); 7.13 (*d*, ^3J = 7.4, 1 arom. H); 7.12 (*d*, ^3J = 5.8, 1 arom. H); 6.98 (*d*, ^3J = 6.2, H–C(7)); 6.73 (*dd*, ^3J(8,7) = 6.2, ^3J(8,9) = 11.5, H–C(8)); 6.49 (2*d*, ^3J(9,8) = 11.3, ^3J(2,3) = 6.9, H–C(9), H–C(2)); 1.75 (*s*, Me–C(5)); 1.60 (*s*, Me–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$): 194.15 (*d*, CHO); 147.37 (*d*, C(3)); 145.95 (*s*, C(1)); 143.89 (*s*, C(4)); 139.60 (*s*, 1 arom. C); 138.07 (*s*, 1 arom. C); 135.20 (*s*, C(6)); 135.10 (*s*, C(10)); 133.69 (*d*, C(9)); 132.98 (*s*, C(10a)); 132.34 (*s*, C(5a)); 131.81 (*d*, C(8)); 129.43 (*d*, 2 arom. C); 129.19 (*s*, C(5)); 128.82 (*d*, 2 arom. C); 128.04 (*d*, 2 arom. C); 127.58 (*d*, 1 arom. C); 127.41 (*d*, 1 arom. C); 127.35 (*d*, C(2)); 125.79 (*d*, 2 arom. C); 125.27 (*d*, C(7)); 22.98 (*q*, *Me*–C(1)); 15.09 (*q*, *Me*–C(5)). EI-

MS: 363 (28, $[M+1]^+$), 362 (100, $M^{+\bullet}$), 347 (26), 334 (10),333 (26), 329 (10), 319 (27), 318 (14), 317 (7), 305 (10), 304 (13), 303 (15) 302 (14), 295 (8), 294 (35), 293 (12), 291 (7), 289 (11), 279 (7), 278 (8), 260 (15), 241 (11), 239 (18), 217 (8), 216 (8), 215 (18), 202 (10), 157 (7), 152 (16), 151 (19), 150 (9), 149 (40), 145 (9),138 (7), 123 (19), 105 (16), 97 (11), 95 (7), 91 (14), 85 (9), 83 (14), 81 (10), 77 (9), 71 (16), 70 (9), 69 (20), 57 (29), 56 (11), 55 (20), 44 (21), 43 (24), 41 (20), 32 (22).

2.8. *1,5-Dimethyl-6,10-diphenylheptalene* (**8**). The mixture **7a**/**7b** (48 mg, 0.13 mmol; ratio 1:2) and tris(triphenylphosphine)rhodium(1+) chloride (120 mg, 0.13 mmol) were dissolved in toluene (4.5 ml) in a *Schlenk* vessel. Then, the vessel was flushed with Ar, closed, and heated at 140° for 3.5 h under stirring. After removal of the solvent, CC (SiO_2, hexane/Et_2O 10:1) gave pure **8** (quant.). M.p. 146–147° (hexane/Et_2O). R_f (hexane/Et_2O 10:1) 0.30. UV/VIS (hexane): max. 211, 229, 287, *ca.* 307 (sh), *ca.* 335 (sh), *ca.* 381 (sh); min. 219, 259. IR (KBr): 3441*w*, 3062*w*, 3016*w*, 2922*w*, 2853*w*, 2730*w*, 1675*s*, 1599*m*, 1551*m*, 1511*w*, 1491*w*, 1443*w*, 1366*w*, 1230*w*, 1212*w*, 1160*w*, 1146*w*, 1077*w*, 1031*w*, 946*w*, 905*w*, 882*w*, 844*m*, 781*w*, 763*w*, 750*m*, 725*m*, 699*m*, 655*w*, 571*w*, 513*w*, 467*w*. Qual. CD of (+)-(*M*)-**8** (hexane, r.t.): 388 (mdeg, +39.0), 322 (+0.3), 293 (mdeg, −125.7), 260 (+0.2), 257 (+31), 253 (−0.6), 229 (mdeg, −83.0), 210 (+1.6), 205 (mdeg, +40.8). Qual. CD of (−)-(*P*)-**8** (hexane, r.t.): 390 (mdeg, −39.8), 322 (−0.4), 293 (mdeg, +126.7), 260 (−0.3), 256 (mdeg, −4.6), 253 (+0.7), 229 (mdeg, +81.7), 211 (−1.0), 205 (mdeg, −46.4). ^{1}H-NMR (600 MHz, $CDCl_3$; see also *Table 2*): 7.40 (*d* with f.s., $^3J = 7.4$, 2 arom. H); 7.18–7.13 (*m*, 5 arom. H); 7.10–7.09 (*m*, 3 arom. H); 6.87 (*d*, $^3J = 6.2$, H−C(7)); 6.58 (*dd*, $^3J(8,7) = 6.2$, $^3J(8,9) = 11.4$, H−C(8)); 6.45 (*dd*, $^3J(3,2) = 5.7$, $^3J(3,4) = 11.4$, H−C(3)); 6.42 (*d*, $^3J(9,8) = 11.4$, H−C(9)); 6.41 (*d*, $^3J(4,3) = 11.4$, H−C(4)); 6.12 (*d*, $^3J(2,3) = 5.7$, H−C(2)); 1.46 (*s*, Me−C(1)); 1.42 (*s*, Me−C(5)). ^{13}C-NMR (150 MHz, $CDCl_3$): 140.50 (*s*, 1 arom. C); 139.15 (*s*, 1 arom. C); 136.36 (*s*, C(6)); 135.71 (*s*, C(10a)); 135.51 (*s*, C(1)); 134.73 (*d*, C(4)); 131.92 (*s*, C(5)); 131.08 (*d*, C(8)); 130.45 (*d*, C(3)); 129.70 (*d*, 2 arom. C); 128.86 (*d*, 2 arom. C); 128.40 (*s*, C(5a)); 128.32 (*d*, C(2)); 128.08 (*d*, 2 arom. C); 127.34 (*d*, 1 arom. C); 127.28 (*d*, 1 arom. C); 126.19 (*d*, 2 arom. C); 125.69 (*d*, C(7)); 22.41 (*q*, *Me*−C(1)); 18.17 (*q*, *Me*−C(5)). EI-MS (GC): 334 (100, $M^{+\bullet}$), 319 (46, $[M-\mathrm{Me}]^+$), 304 (27, $[M-2\,\mathrm{Me}]^+$), 280 (9), 252 (5), 232 (76, $[M-\mathrm{Ph-C{=}CH}]^+$), 215 (21), 189 (5), 156 (37), 151 (33), 115 (7), 91 (10), 77 (5).

3. *X-Ray Crystal-Structure Determinations of Compounds* **3a** *and* **3b** (*Table 4* and *Figs. 1* and *2*)[1]). All measurements were conducted on a *Nonius-KappaCCD* area-detector diffractometer [8] with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford-Cryosystems-Cryostream-700* cooler. The data collection and refinement parameters are given in *Table 4*, and the molecules are shown in *Figs. 1* and *2*. Data reduction was performed with HKL DENZO and SCALEPACK [9]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method was applied [10]. Each structure was solved by direct methods with SIR92 [11], which revealed the positions of all non-H-atoms, and the non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C−H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. Refinement of the structure was carried out on F by full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was not applied, only in the case of **3b**. For **3a**, three reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. One large peak of residual electron density (1.10 e Å^{-3}) remained 1.6 Å from C(9) and close to H−C(10). As the position of this peak did not correspond with any chemically logical geometry, it is presumed that it is the result of an artefact in the data. For **3b**, four reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement.

Neutral-atom scattering factors for non-H-atoms were taken from [12a], and the scattering factors for H-atoms were taken from [13]. Anomalous dispersion effects were included in F_c [14]; the values for f' and f'' were those of [12b]. The values of the mass-attenuation coefficients are those of [12c]. All calculations were performed with the teXsan crystallographic software package [15]. The crystallographic diagrams were drawn with ORTEPII [16].

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[1]) CCDC-751407 and -751408 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table 4. *Crystallographic Data of Compounds* **3a** *and* **3b**

	3a	**3b**
Crystallized from	Et_2O/hexane	Et_2O/hexane
Empirical formula	$C_{27}H_{22}Cl_2$	$C_{27}H_{22}Cl_2$
M_r	417.38	417.38
Crystal color, habit	orange, prism	yellow, prism
Crystal dimensions [mm]	$0.12 \times 0.23 \times 0.25$	$0.25 \times 0.25 \times 0.25$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
Z	4	8
Reflections for cell determination	30110	111515
2θ Range for cell determination [°]	4–55	4–55
Unit cell parameters		
a [Å]	10.1670(2)	23.6161(5)
b [Å]	16.0995(3)	9.2406(2)
c [Å]	12.9912(3)	19.8329(5)
α [°]	90	90
β [°]	90.626(1)	99.714(1)
γ [°]	90	90
V [Å^3]	2126.32(8)	4266.0(2)
$F(000)$	872	1744
D_x [g cm^{-3}]	1.304	1.300
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.316	0.315
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(\max)}$ [°]	55	55
Total reflections measured	47026	47860
Symmetry-independent reflections	4871	4863
R_{int}	0.074	0.086
Reflections with $I > 2\sigma(I)$	3420	3364
Reflections used in refinement	–	–
Parameters refined	262	263
R (on F; $I > 2\sigma(I)$ reflections)	0.0530	0.0465
wR (on F; $I > 2\sigma(I)$ reflections)	0.0495	0.0395
wR (on F^2; all indept. reflections)	–	
Weights: p in $w = [\sigma^2 (F_o) + (pF_o)^2]^{-1}$	0.005	0.005
Goodness-of-fit	2.677	2.294
Secondary extinction coefficient	–	$1.6(3) \cdot 10^{-7}$
Final $\Delta_{\max}/\sigma$	0.0001	0.0007
$\Delta\rho$ (max; min) [e Å^{-3}]	1.10; −0.30	0.26; −0.24

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