Benzo[*a*]heptalenes from Heptaleno[1,2-*c*]furans

Part 2

Formation of Benzo[*a*]heptalenes with Methoxy Groups at the Benzo Part

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It is shown in this 'Part 2' that heptaleno[1,2-*c*]furans **1** react thermally in a *Diels–Alder*-type [4 + 2] cycloaddition at the furan ring with vinylene carbonate (VC), phenylsulfonylallene (PSA), α-(acetyloxy)acrylonitrile (AAN), and (1*Z*)-1,2-bis(phenylsulfonyl)ethene (ZSE) to yield the corresponding 1,4-epoxybenzo[*d*]heptalenes (*cf. Schemes 1, 5, 6,* and *8*). The thermal reaction of **1a** and **1b** with VC at 130° and 150°, respectively, leads mainly to the 2,3-*endo*-cyclocarbonates 2,3-*endo*-**2a** and -**2b** and in minor amounts to the 2,3-*exo*-cyclocarbonates 2,3-*exo*-**2a** and -**2b**. In some cases, the (*P**)- and (*M**)-configured epimers were isolated and characterized (*Scheme 1*). Base-catalyzed cleavage of 2,3-*endo*-**2** gave the corresponding 2,3-diols **3**, which were further transformed *via* reductive cleavage of their dimesylates **4** into the benzo[*a*]heptalenes **5a** and **5b**, respectively (*Scheme 2*). In another reaction sequence, the 2,3-diols **3** were converted into their cyclic carbonothioates **6**, which on treatment with $(EtO)_3P$ gave the deoxygenated 1,4-dihydro-1,4-epoxybenzo[*d*]heptalenes **7**. These were rearranged by acid catalysis into the benzo[*a*]heptalen-4-ols **8a** and **8b**, respectively (*Scheme 2*). Cyclocarbonate 2,3-*endo*-**2b** reacted with lithium diisopropylamide (LDA) at −70° under regioselective ring opening to the 3-hydroxy-substituted benzo[*d*]heptalen-2-yl carbamate 2,3-*endo*-**9b** (*Scheme 3*). The latter was *O*-methylated to 2,3-*endo*-(*P**)-**10b**. The further way, to get finally the benzo[*a*]heptalene **13b** with MeO groups in 1,2,3-position, could not be realized due to the fact that we found no way to cleave the carbamate group of 2,3-*endo*-(*P**)-**10b** without touching its 1,4-epoxy bridge (*Scheme 3*).

The reaction of **1a** with PSA in toluene at 120° was successful, in a way that we found regioisomeric as well as epimeric cycloadducts (*Scheme 5*). Unfortunately, the attempts to rearrange the products under strong-base catalysis as it had been shown successfully with other furan–PSA adducts were unsuccessful (*Scheme 4*).

The thermal cycloaddition reaction of **1a** and **1b** with AAN yielded again regioisomeric and epimeric adducts, which could easily be transformed into the corresponding 2- and 3-oxo products (*Scheme 6*). Only the latter ones could be rearranged with Ac_2O/H_2SO_4 into the corresponding benzo[*a*]heptalene-3,4-diol diacetates **20a** and **20b**, respectively, or with trimethylsilyl trifluoromethanesulfonate ($TfOSiMe_3$/Et_3N), followed by treatment with NH_4Cl/H_2O, into the corresponding benzo[*a*]heptalen-3,4-diols **21a** and **21b** (*Scheme 7*).

The thermal cycloaddition reaction of **1** with ZSE in toluene gave the cycloadducts 2,3-*exo*-**22a** and -**22b** as well as 2-*exo*,3-*endo*-**22c** in high yields (*Scheme 8*). All three adducts eliminated, by treatment with base, benzenesulfinic acid and yielded the corresponding 3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]-heptalenes **25**. The latter turned out to be excellent *Michael* acceptors for H_2O_2 in basic media (*Scheme 9*). The *Michael* adducts lost H_2O on treatment with Ac_2O in pyridine and gave the 3-(phenylsulfonyl)benzo[*d*]heptalen-2-ones **28a** and 3-*exo*-**28b**, respectively. Rearrangement of these compounds in the presence of Ac_2O/AcONa lead to the formation of the corresponding 3-(phenylsulfonyl)benzo[*a*]heptalene-1,2-diol diacetates **30a** and **30b**, which on treatment with MeONa/MeI gave the corresponding MeO-substituted compounds **31a** and **31b**. The reductive elimination of the $PhSO_2$

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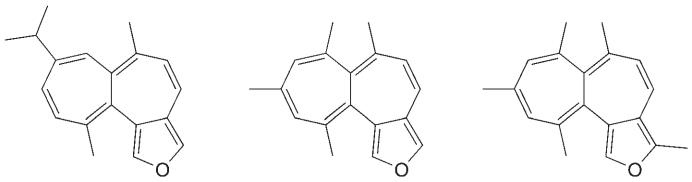
group led finally to the 1,2-dimethoxybenzo[*a*]heptalenes **32a** and **32b**. Deprotonation experiments of **32a** with *t*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmeda) and quenching with D_2O showed that the most acid C–H bond is H–C(3) (*Scheme 9*).

Some of the new structures were established by X-ray crystal-diffraction analyses (*cf. Figs. 1*, *3*, *4*, and *5*). Moreover, nine of the new benzo[*a*]heptalenes were resolved on an anal. *Chiralcel OD-H* column, and their CD spectra were measured (*cf. Figs. 8* and *9*). As a result, the 1,2-dimethoxybenzo[*a*]heptalenes **32a** and **32b** showed unexpectedly new *Cotton*-effect bands just below 300 nm, which were assigned to chiral exciton coupling between the heptalene and benzo part of the structurally highly twisted compounds. The $PhSO_2$-substituted benzo[*a*]heptalenes **30b** and **31b** showed, in addition, a further pair of *Cotton*-effect bands in the range of 275–245 nm, due to chiral exciton coupling of the benzo[*a*]heptalene chromophore and the phenylsulfonyl chromophore (*cf. Fig. 10*).

1. Introduction. – In the preceding part of this study of the transformation of heptaleno[1,2-*c*]furans into benzo[*a*]heptalenes as the underlying core structure of all colchicinoids, we have demonstrated that these furans smoothly undergo thermal [4 + 2] cycloaddition reactions with a number of electron-deficient dienophiles to yield 1,4-epoxybenzo[*d*]heptalenes, which can be rearranged to benzo[*a*]heptalenes with varying substitution patterns at the benzo ring [1]. In the present study, we investigate such dienophiles that would principally allow the introduction of O-functionalities, which will later become MeO substituents at the biologically important 1,2,3-positions of the envisaged benzo[*a*]heptalenes as precursors of colchicinoids. For these experiments, we used our established heptaleno[1,2-*c*]furans **1a** and **1b**. For some control experiments, we included the heptalenofuran **1c** in our investigations. The latter 3-Me-substituted furan was obtained by treatment of the corresponding furan-3(1*H*)-one with *Tebbe* reagent in the usual manner (see [1]).

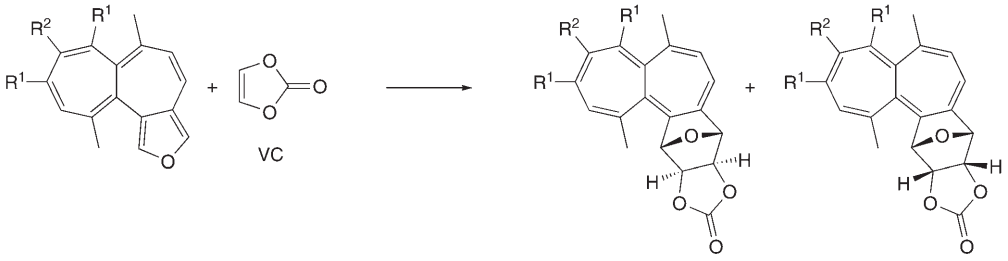


1a **1b** **1c**

2. Cycloaddition Reactions of the Heptaleno[1,2-*c*]furans 1 and Transformations of the Cycloadducts. – 2.1. *Cycloadditions with Vinylene Carbonate.* It is just 50 years ago that vinylene carbonate (=1,3-dioxol-2-one; VC) has been introduced as dienophile by *Newman* and *Addor* [2] (see also [3]). Over the time, it had been treated with numerous dienes (*cf.* [2–5] and lit. cit. therein). It enables *inter alia* the synthesis of *cis*-cyclohexane-1,2-diols and derivatives thereof. *Yur'ev* and *Zefirov* developed on this basis a straightforward synthesis of conduritol C starting with the thermal cycloadditon reaction of furan and VC [6], which has later been extended to the synthesis of other conduritols [7]. In this way, VC would be a suitable reactant for the heptaleno[1,2-*c*]furans, allowing to place two O-functionalities at the right position of the envisaged colchicinoids and with the potential that the third one may come from the 1,4-epoxy bridge.

The cycloaddition reaction of **1a** and **1b** with VC in toluene at 130° and xylene at 150°, respectively, caused no problems (*Scheme 1*). Mixtures of the 2,3-*endo*- and 2,3-*exo*-cycloadducts with relative (*P**)- and (*M**)-configuration were obtained in good yields[2]). Acid- or base-catalyzed rearrangement of the *endo*-cyclocarbonates as such failed in all cases. However, they could easily be saponified to the corresponding diols 2,3-*endo*-**3a** and -**3b**, respectively (*Scheme 2*).

Scheme 1



1a[a])	toluene, 130°/40 h; >70%[b])	2,3-*exo*-**2a** (*ca.* 10%[c]))	2,3-*endo*-**2a** (58%[d]))
1b[a])	xylene, 150°/40 h; 92%[b])	2,3-*exo*-**2b** (29%[e]))	2,3-*endo*-**2b** (48%[f]))

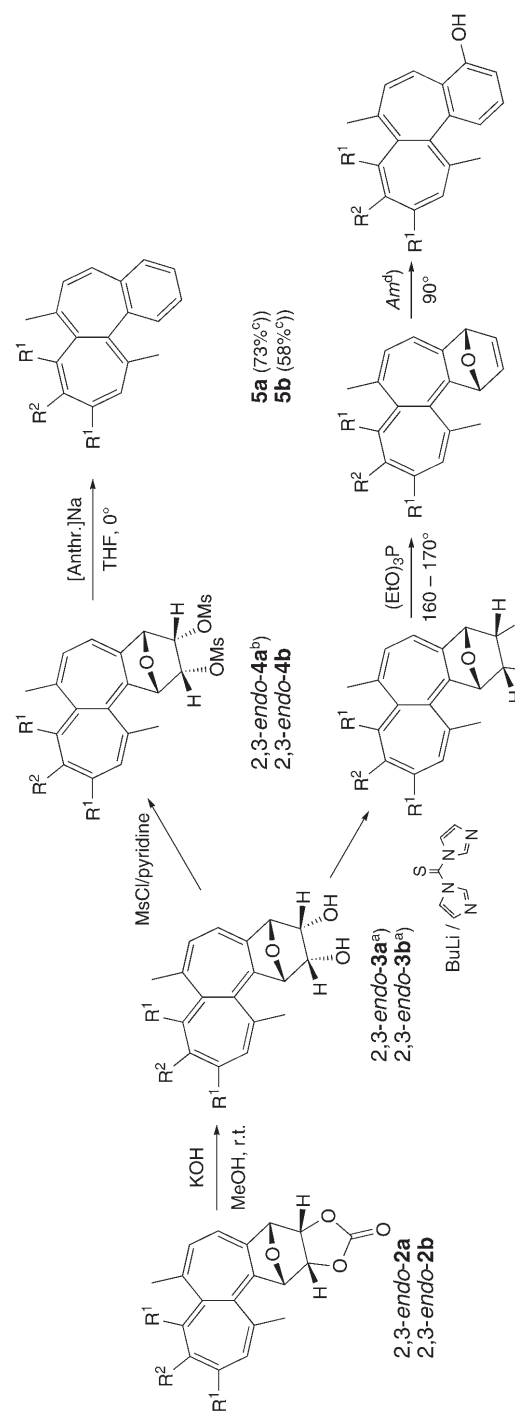
[a]) **a**: $R^1 = H$, $R^2 = {}^i$Pr; **b**: $R^1 = Me$, $R^2 = H$. [b]) Yield of the crude product mixture before chromatography and crystallization. [c]) 2,3-*exo*-(*P**)-**2a** was spectroscopically identified in the mixture, but not isolated. [d]) Yield of the crystallized 2,3-*endo*-(*P**)-**2a**. [e]) Yield of the crystallized 2,3-*exo*-(*P**)- (17%) and 2,3-*exo*-(*M**)-**2b** (12%). [f]) Yield of the crystallized 2,3-*endo*-(*P**)-**2b**.

The structure of 2,3-*endo*-(*P**)-**3a** was established by an X-ray crystal-structure determination (*Fig. 1*). It is of interest to note that in the crystal the OH groups form infinite two-dimensional networks whereby C(2)–OH is linked to the O-atom of C(3′)–OH ($d(H\cdots O) = 186(3)$ pm) of a second molecule and C(3)–OH interacts with the O-atom of the epoxy bridge of another molecule ($d(H\cdots O) = 214(3)$ pm), thus building these networks. The ^{i}Pr group occupies – as in many other heptalene structures – two conformations whereby its methine H-atom is *syn*-oriented to H–C(8) or H–C(10), respectively. In the present case, the occupation factor amounts to *ca.* 75 to 25%.

More than 30 years ago, *Carnahan* and *Closson* [8] reported on the facile reductive cleavage of the dimethanesulfonates of vicinal diols with aromatic radical anions in tetrahydrofuran (THF) to give the corresponding olefins mostly in excellent yields, regardless of the relative configuration or steric constraints in the bicyclic [2.2.1] reactants. The diols 2,3-*endo*-**3a** and -**3b** could easily be transformed into the corresponding dimesylates 2,3-*endo*-**4a** and -**4b**, respectively. When we treated the dimesylates with sodium anthracenide in THF at 0°, we were quite astonished to find that just the benzo[*a*]heptalenes **5a** and **5b** were formed in good yields (*Scheme 2*). Both compounds were obtained in crystalline form. This is by far the most efficient way

[2]) For the assignment of relative configurations, see [1] and the *Exper. Part.*

Scheme 2



[a]) **a**: $R^1 = H$, $R^2 = {}^i$Pr; **b**: $R^1 = Me$, $R^2 = H$. [b]) A thermal equilibrium mixture of the (*P**)- (72%) and (*M**)-epimer (28%) was obtained. [c]) Yields with respect to 2,3-*endo*-**3a** and -**3b**, resp. [d]) *Am* = *Amberlyst 15* in cyclohexane. [e]) Yield of the crystallized (*P**)-epimer. [f]) Mixture of isomers, not further purified. [g]) Mixture of the labile (*P**)- and (*M**)-epimers, just used for the next step. [h]) Yield of HPLC-purified **8a** amounted to 26%. [i]) Yield of crystallized **8b** amounted to 31%.

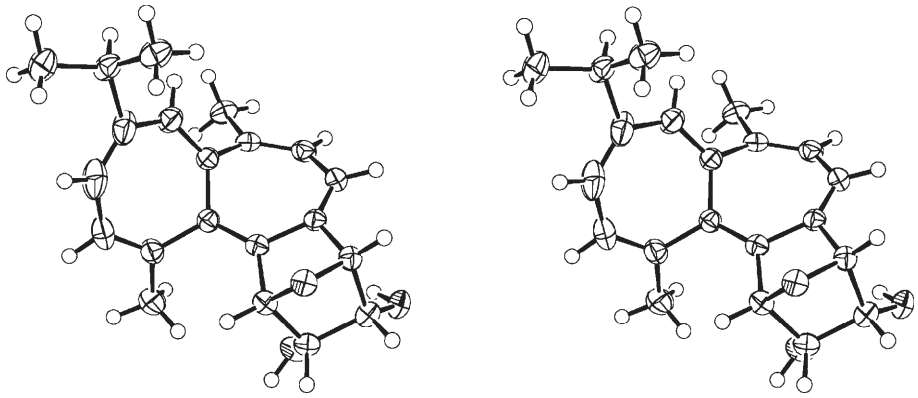


Fig. 1. *Stereoscopic view of the X-ray crystal structure of 2,3*-endo-*(*P**)*-**3a**. The major conformation (75%) of the ^{i}Pr group is shown.

to transform heptalen-4,5- or -1,2-dicarbarboxylates into benzo[*a*]heptalenes with no substituents at the benzo part[3]).

On the other hand, the deprotonated 2,3-*endo*-diols **3a** and **3b** reacted with bis(1*H*-imidazol-1-yl)methanethione (=1,1′-carbonothioylbis[1*H*-imidazole]) to yield the corresponding carbonothioates 2,3-*endo*-**6a** and -**6b**, which could be subjected to the *Corey–Winter* reaction with triethyl phosphite at 160–170° (*Scheme 2*) [10]. The mixture of the epimeric 1,4-dihydro-1,4-epoxy compounds **7a** or **7b** were then rearranged, according to our earlier investigations [1], by acid catalysis into the corresponding benzo[*a*]heptalenols **8a** and **8b**, respectively, with the OH group, as expected, at the biological wrong 4-position. Nevertheless, the formation of **8a** and **8b** represents a further new access to benzo[*a*]heptalenes.

A step forward in view of keeping all three O-functionalities of the cyclocarbonates **2** was the observation that treatment of 2,3-*endo*-(*P**)-**2b** with lithium diisopropylamide (LDA) in THF at −78 to 0° led to a selective ring opening of the cyclocarbonate in such a way that almost exclusively 2,3-*endo*-(*P**)-**9b** was formed (*Scheme 3*). The structure of the product could unequivocally be established by ^{1}H-NMR measurements in $CDCl_3$ (H–C(2) at δ(H) 5.14 (*dd*, $^{3}J(2,1)=5.0$, $^{3}J(2,3)=7.8$), strong ^{1}H-NOE with H–C(1), which itself showed a strong ^{1}H-NOE with Me–C(12); H–C(3) at δ(H) 4.35 (*ddd*, $^{3}J(3,4)=5.0$ and $^{3}J(3,2)=7.8$, $^{3}J(3,OH)=11.4$), strong ^{1}H-NOE with H–C(4), which itself showed a strong ^{1}H-NOE with H–C(5)). It is also of interest to note that the urethane part of 2,3-*endo*-(*P**)-**9b** exhibited a hindered rotation at the O=C–N bond, so that both ^{i}Pr groups showed sharp and clearly separated ^{1}H-NMR signals (for details, see the *Exper. Part*). The AM1-calculated structure of 2,3-*endo*-(*P**)-**9b** is displayed in *Fig. 2*. It exhibits an optimal *anti*-relation of the fragment H–C(3)–O–H with the H-atom of OH pointing inward towards the heptalene core, which well explains its chemical shift (1.66 ppm) and the size of the observed ^{3}J coupling constant with H–C(3).

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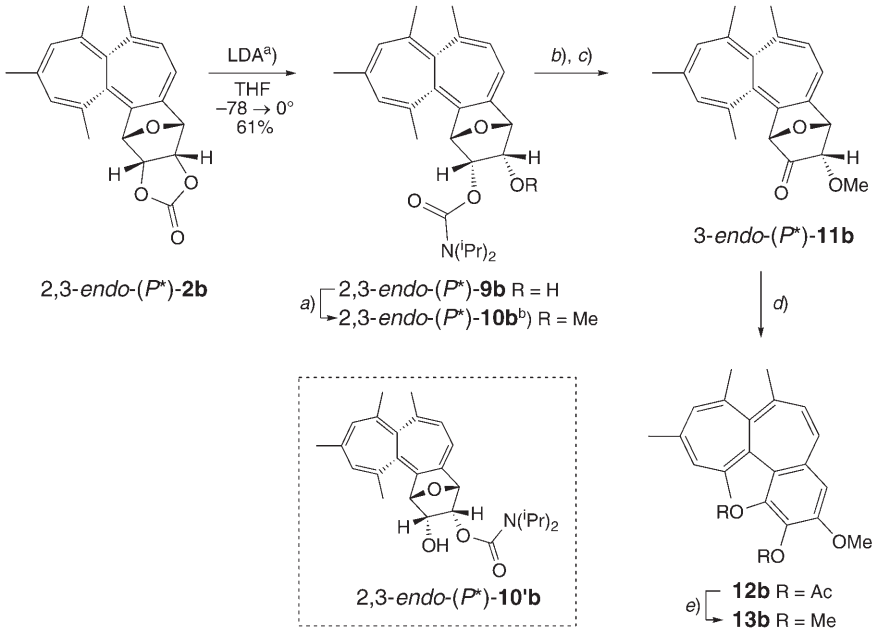
[3]) In a former synthesis of our group, involving the *Bergman* cyclization of a corresponding vicinal diethynylheptalene, **5a** was obtained as an oil [9].

Scheme 3



a) Ag_2O/MeI, r.t. *b*) Acid- and base-catalyzed as well as reductive cleavage of the carbamate group of 2,3-*endo*-(*P**)-**10b** failed. *c*) Periodinane/CH_2Cl_2. *d*) Ac_2O/AcONa. *e*) MeONa/MeI.
[a]) LDA = lithium diisopropylamide. [b]) Traces of 2,3-*endo*-(*P**)-**10′b** were also found.

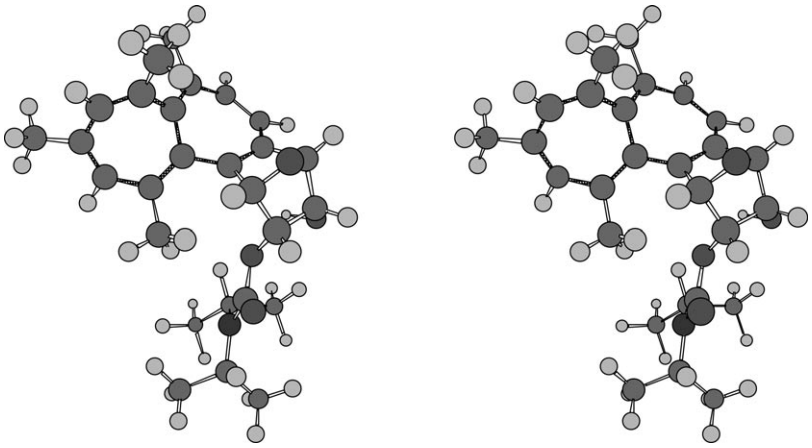


Fig. 2. *Stereoscopic view of the AM1-calculated structure of 2,3-*endo-*(*P**)-**9b**

When we treated 2,3-*exo*-(*P**)-**2b** with LDA under the conditions described above, the yield of the analogous ring-opening product 2,3-*exo*-(*P**)-**9b** amounted only to *ca.* 1%[4]), in sharp contrast to the result with the *endo*-isomer.

Why reacts 2,3-*endo*-(*P**)-**2b** with LDA much better than its *exo*-epimer does? And why do we observe the high selectivity in the ring-opening reaction? The AM1-calculated structures of 2,3-*endo*- and 2,3-*exo*-(*P**)-**2b** allow the following conclusions: In the case of the *endo*-epimer, the *si*-face of the carbonyl group is sterically heavily shielded by the bent heptalene skeleton and its Me-substituent at C(12), so that the nucleophilic attack of the sterically congested LDA can only take place on the corresponding *re*-face. On the other hand, the 1,4-epoxy bridge is relatively close to the *re*-face of the carbonyl group of the *exo*-epimer, so that in this case the nucleophilic attack of LDA should occur on the *si*-face of the carbonyl group. In *Table 1* are listed the AM1-calculated ΔH_f° values of the thus formed 'naked' tetrahedral oxido forms together with those of the respective two ring-opened 2- and 3-oxido structures. Indeed, the primary LDA adduct of the *exo*-epimer displays a lower ΔH_f° value in comparison with that of the *endo*-epimer. Moreover, the ring opened forms exhibit slightly higher ΔH_f° values, which explain quite well the sluggishness of the ring-opening reaction of the LDA adduct of the *exo*-epimer in the given temperature range (*Scheme 3*). On the other side, the ring-opened forms and the LDA adduct of the *endo*-epimer all show almost the same ΔH_f° values, which is in agreement with the ease of the ring-opening reaction. However, the almost equal ΔH_f° values of the ring-opened 2- and 3-oxido forms do not explain the observed high selectivity of the ring-opening reaction, which finally leads, after protonation, to the strongly preferred formation of 2,3-*endo*-(*P**)-**9b**. We assume, therefore, that complexation with the Li^+ ions and solvation effects of THF play the decisive role. The 3-oxido group is farther away from the heptalene backbone and especially from its Me group at C(12), so that it can be much better stabilized by complexation and solvation than the corresponding 2-oxido group of the corresponding regioisomer of 2,3-*endo*-(*P**)-**9b**. As a result, the breakage of the C(3)O–C(O^-)N(^{i}Pr)$_2$ linkage should be favored, resulting finally in the formation of 2,3-*endo*-(*P**)-**9b**.

Table 1. *AM1-Calculated* ΔH_f° *Values* [kcal · mol^{-1}] *of the LDA-Addition Products of 2,3-*endo- *and 2,3-*exo-*(*P**)-***2b** *and Their Corresponding Ring-Opening Products*

Starting isomer	Ring-closed oxido form	Ring-opened 2-oxido form	Ring-opened 3-oxido form
2,3-*endo*-(*P**)-**2b**	– 81.7	– 82.0	– 80.8
2,3-*exo*-(*P**)-**2b**	– 85.5	– 82.5	– 83.5

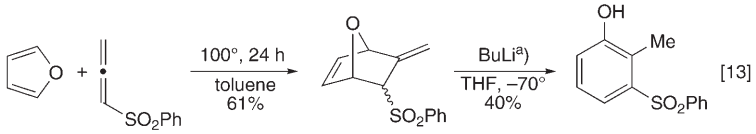
O-Methylation of 2,3-*endo*-(*P**)-**9b** with MeI in the presence of Ag_2O gave the 3-methoxy compound 2,3-*endo*-(*P**)-**10b** in good yield. The further projected steps are shown in *Scheme 3*. Once the urethane moiety is removed, the oxidative dehydrogenation of the corresponding 2-ol with *Dess–Martin* reagent (*cf.* [10]) or under *Swern*

[4]) The ^{1}H-NMR data of this compound, which was isolated only in trace amounts, do not fully exclude the possibility that the urethane moiety is located in *exo*-position at C(3) and, in turn, the OH group in *exo*-position at C(2).

conditions (*cf.* [11]) should yield the 3-methoxy-1,4-epoxybenzo[*d*]heptalen-2-one 2,3-*endo*-(*P**)-**11b**, which then could be rearranged with Ac_2O/AcONa to the 3-methoxybenzo[*a*]heptalene-1,2-diol diacetate **12b** (see below; *Scheme 9*). Finally, cleavage of the diacetate with MeONa/MeOH in the presence of MeI would yield 1,2,3-trimethoxy-6,7,10,12-tetramethylbenzo[*a*]heptalene (**13b**) with the biologically correct position of the three MeO groups at the benzo part. Unfortunately, all our attempts to remove the urethane moiety of 2,3-*endo*-(*P**)-**10b** by base or acid catalysis or reductively with preservation of the essential 1,4-epoxy bridge failed.

2.2. *With Phenylsulfonylallene.* The thermal reaction of furan with (phenylsulfonyl)allene (= phenylsulfonyl)prop-1,2-diene; PSA), which can be prepared easily from propargyl alcohol (= prop-2-yn-1-ol) and benzenesulfenyl chloride [12], has been investigated by *Guildford* and *Turner* [13] (*Scheme 4*)[5]). It was of interest for us to note that the *endo*-adduct could be rearranged with butyllithium (BuLi) in THF to the corresponding phenol. Moreover, the possibility that the 2-methylene group could oxidatively be cleaved into a keto group, the necessary structural feature for a base-catalyzed rearrangement, attracted us too.

Scheme 4



endo/*exo* 19.3

[a]) The pure *endo*-form was rearranged.

Reaction of **1a** with PSA by heating in toluene occurred smoothly and led to the formation of a mixture of 3-*exo*- and 3-*endo*- as well as 2-*exo*-**14a** (*Scheme 5*). Crystallization of the epimers of 3-*exo*-**14a** gave the pure (*P**)-form. The (*M**)-form of 2-*exo*-**14a** was not found in the product mixture. The formation of nearly equal amounts 3-*exo*- and 3-*endo*-**14a** demonstrates that the structurally complex furan **1a** reacts with PSA without preferred stereoselectivity. On the other hand, a clear regioselectivity in favor of the 3-(phenylsulfonyl)-substituted adducts is recognizable.

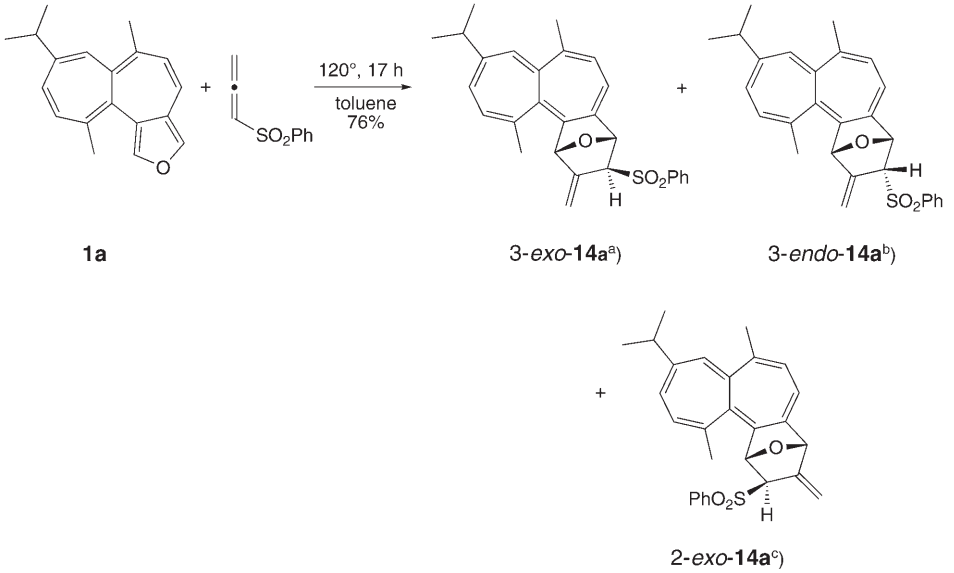
Unfortunately, neither attempts of the base-induced rearrangement of 3-*exo*-**14a** (*cf.* [13][14]) nor those of the ozonolysis of the 2-methylene function were successful. We dropped therefore further experiments with the PSA adducts of **1a**.

2.3. *Cycloaddition with α-(Acetyloxy)acrylonitrile.* α-(Acetyloxy)acrylonitrile (=2-(acetyloxy)prop-2-enenitrile; AAN) as well as α-chloroacrylonitrile and comparable compounds have been proved to be excellent dienophiles and thus to be structural equivalents of ketene in *Diels–Alder* reactions (*cf.* [15] and [16] and lit. cit. therein).

The thermal reaction of heptalenofuran **1a** with 2.4 mol-equiv. of AAN in toluene gave a mixture of the corresponding regioisomeric (acetyloxy)carbonitriles (*Scheme 6*). Column chromatography (CC; silica gel, hexane/Et_2O 3:2) yielded three main fractions, of which the residue of the first two could be crystallized. The third

[5]) For similar reactions with furan and 1,3-bis(phenylsulfonyl)allene, see [14].

Scheme 5



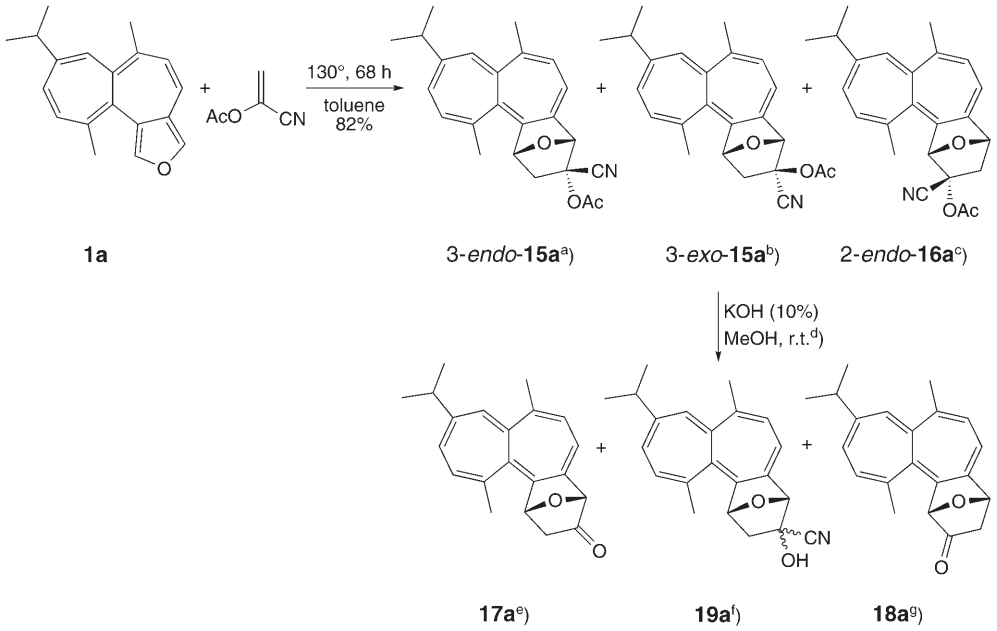
1a 3-*exo*-**14a**[a]) 3-*endo*-**14a**[b])

2-*exo*-**14a**[c])

[a]) 3 : 2 Mixture of the (*P**)- and (*M**)-epimers (34%), from which 11% of the crystalline (*P**)-form were obtained. [b]) 3 : 2 Mixture of the (*P**)- and (*M**)-epimers (27%). [c]) The pure (*P**)-epimer was isolated (14%).

fraction was further purified by prep. HPLC. The ^{1}H-NMR spectra of the two crystalline products showed that both isomers carried the acetyloxy and cyano substituent at C(3), whereas the third product had these substituents at C(2). In solution, the two crystalline products converted slowly into each other. On heating in toluene at 70°, an equilibrium mixture of almost 1 : 1 was established. These experiments demonstrated that the two crystalline products were epimers with respect to their axis of chirality but gave no answer to the question of their relative configuration at C(3), *i.e.*, whether the substituent of higher priority (AcO) occupied the *endo*- or *exo*-position. To clarify the situation, we performed X-ray crystal-structure analyses of both products, which unequivocally showed that both products carried the acetyloxy substituent in *endo*-position at C(3) (*Fig. 3*, *a* and *3*, *b*). The product with the less pronounced UV maximum at 330 nm possessed the relative (*M**)-configuration, in agreement with our former investigations on other (*P**)- and (*M**)-epimers of benzo[*d*]heptalenes [1] (see also below). Since we found no isolable amounts of 3-*exo*-**15a** in the product mixture, we suppose that the thermal reaction of **1a** with AAN took place under kinetic control with respect to the formation of the 3-*endo*-epimers. This is suggested by AM1-calculations which indicate that the (*P**)- as well as the (*M**)-epimer have ΔH_f° values which are by *ca.* 1.6 kcal · mol^{-1} higher than those of 3-*exo*-**15a**. A similar difference (1.2 kcal · mol^{-1}) was found for the AM1-calculated ΔH_f° values of 2-*endo*- and 2-*exo*-**15a**. Since the UV/VIS spectrum of the third, regioisomeric product was almost identical with that of 3-*endo*-(*P**)-**15a**, we assigned the same

Scheme 6



1a 3-*endo*-**15a**[a]) 3-*exo*-**15a**[b]) 2-*endo*-**16a**[c])

17a[e]) **19a**[f]) **18a**[g])

[a]) CC and crystallization gave 13% of the pure (*P**)- and 12% of the pure (*M**)-epimer. [b]) Not found in isolable amounts. [c]) The (*P**)-epimer was isolated as a yellow foam after prep. HPLC of the third CC fraction. [d]) The crude isomer mixture **15a**/**16a** was saponified; yield of product mixture 70%. [e]) Yield after CC, 20% of **17a**, which gave, after recrystallization, 13% of the pure (*P**)-epimer. [f]) Light red oil (17%); relative configuration not determined, presumably (*P**)-configured with OH in *endo*-position. [g]) Obtained as a 2:3 mixture of (*P**)-configured **18a** and **17a**; yield of the mixture 30%.

relative configuration (*P**) to the 2-(acetyloxy)benzo[*a*]heptalene-2-carbonitrile 2-*endo*-**16a** (*Scheme 6*).

After a second run of **1a** and AAN (boiling chlorobenzene, 20 h), the crude product was saponified with KOH/MeOH. CC Separation of the product mixture gave finally pure crystalline (*P**)-**17a** and a 2:3 mixture of (*P**)-**18a** and (*P**)-**17a**. A third fraction contained the cyanohydrine **19a**. Cyanohydrines were not anymore observed when the saponification of the mixture of products was performed in the presence of formaldehyde (*cf.* [17]).

By the same way, the thermal reaction of **1b** with AAN (boiling chlorobenzene, 23 h), followed by saponification, gave a mixture of (*P**)- and (*M**)-**17b**. The 2-keto form **18b** was not found in isolable amounts in the reaction mixture. The epimers **17b** were separated by fractionated crystallization and fully characterized (see the *Exper. Part*).

The acid-catalyzed rearrangements of **17a** and **17b** were performed with the crude product mixtures as they were obtained after saponification (*Scheme 7*). The established condition, Ac_2O/H_2SO_4 at room temperature [18], gave the expected benzo[*a*]heptalene-2,3-diol diacetates **20a** and **20b**, respectively, in acceptable yields if one takes into account that in the case of the reaction of **1a** with AAN also the 1,4-

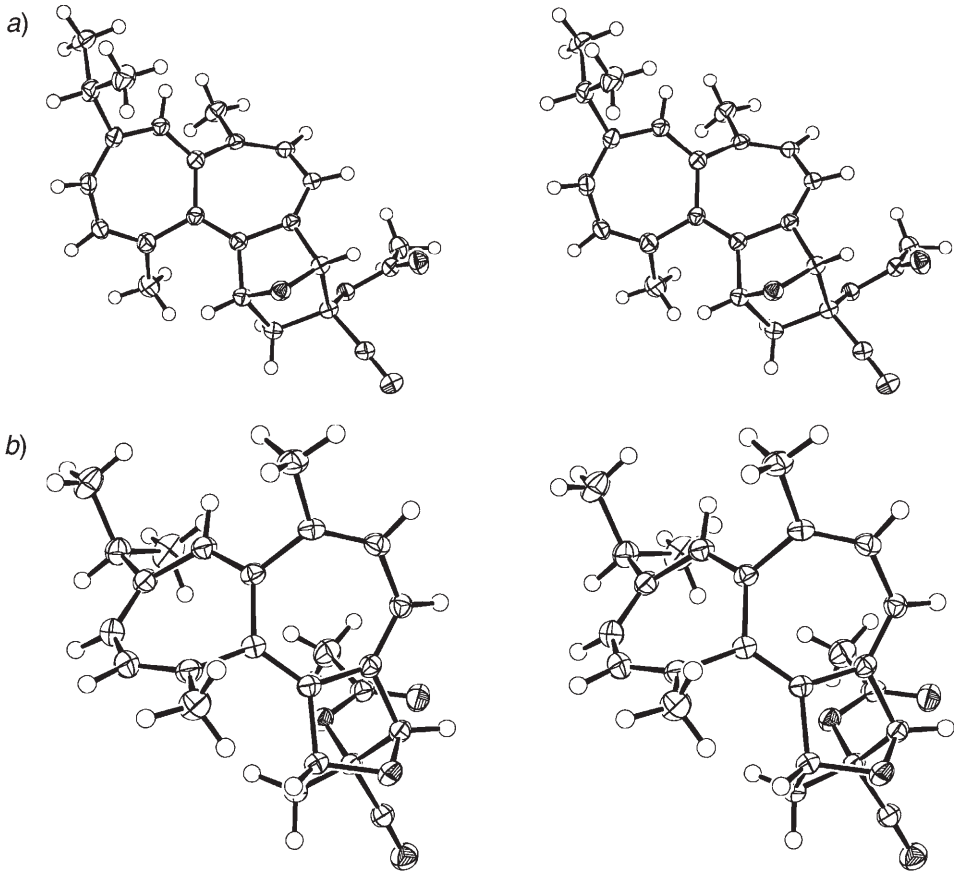


Fig. 3. a) *Stereoscopic view of the X-ray crystal structure of 3*-endo-*(*P**)*-**15a** (the major conformation (90%*)* of the ^{i}Pr group is shown). b) *Stereoscopic view of the X-ray crystal structure of 3*-endo-*(*M**)*-**15a**.

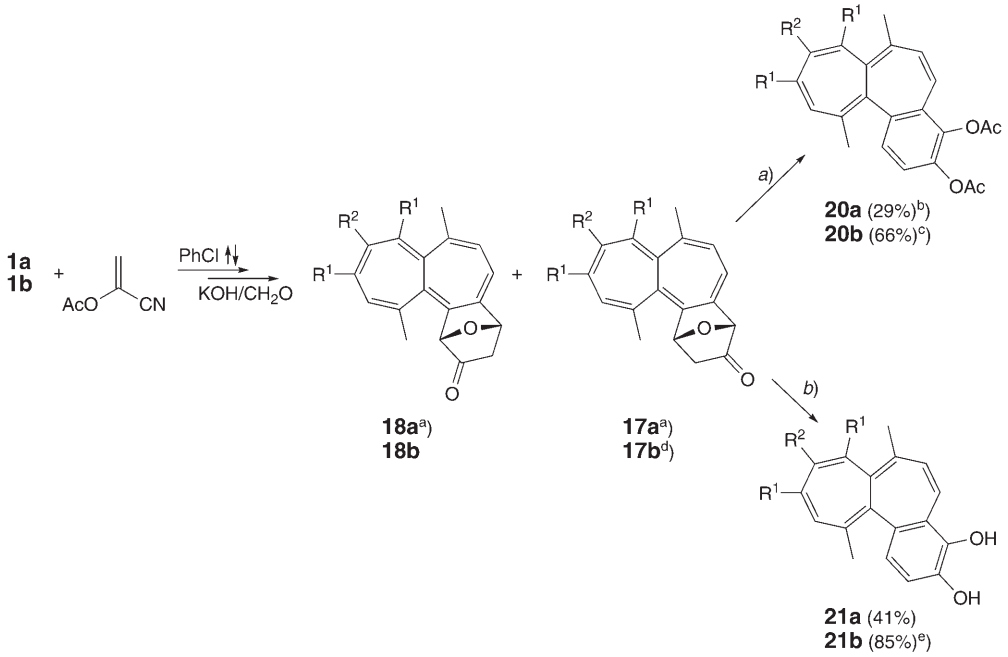
epoxybenzo[*d*]heptalen-2(3*H*)-one **18a** (*ca.* 40%) was formed, which does not rearrange and is mostly destroyed under the reaction conditions.

The free hydroxy forms **21a** and **21b** were obtained when the rearrangement of the oxo product mixtures was performed with trimethylsilyl trifluoromethanesulfonate ($TfOSiMe_3$) in CH_2Cl_2 in the presence of Et_3N (*Scheme 7*), following a procedure of *Vogel* and co-workers [16c].

These experiments demonstrate that AAN is a suitable dienophile for the heptaleno[1,2-*c*]furans **1**. However, mostly the 3-(acetyloxy)-3-carbonitriles **15** are formed and the acid-catalyzed rearrangement of their 3-oxo forms leads to O-functionalities at C(3) and C(4) of the benzo[*a*]heptalenes.

2.4. *Cycloadditions with (1Z)-1,2-Bis(phenylsulfonyl)ethene.* Both diastereoisomers of this ethene have proved to be excellent dienophiles, in particular for furans (*cf.* [19–21] and lit. cit. therein). The thermal reaction of the heptaleno[1,2-*c*]furans **1a**,**b** with (1*Z*)-1,2-bis(phenylsulfonyl)ethene (ZSE) in toluene gave excellent yields of the

Scheme 7

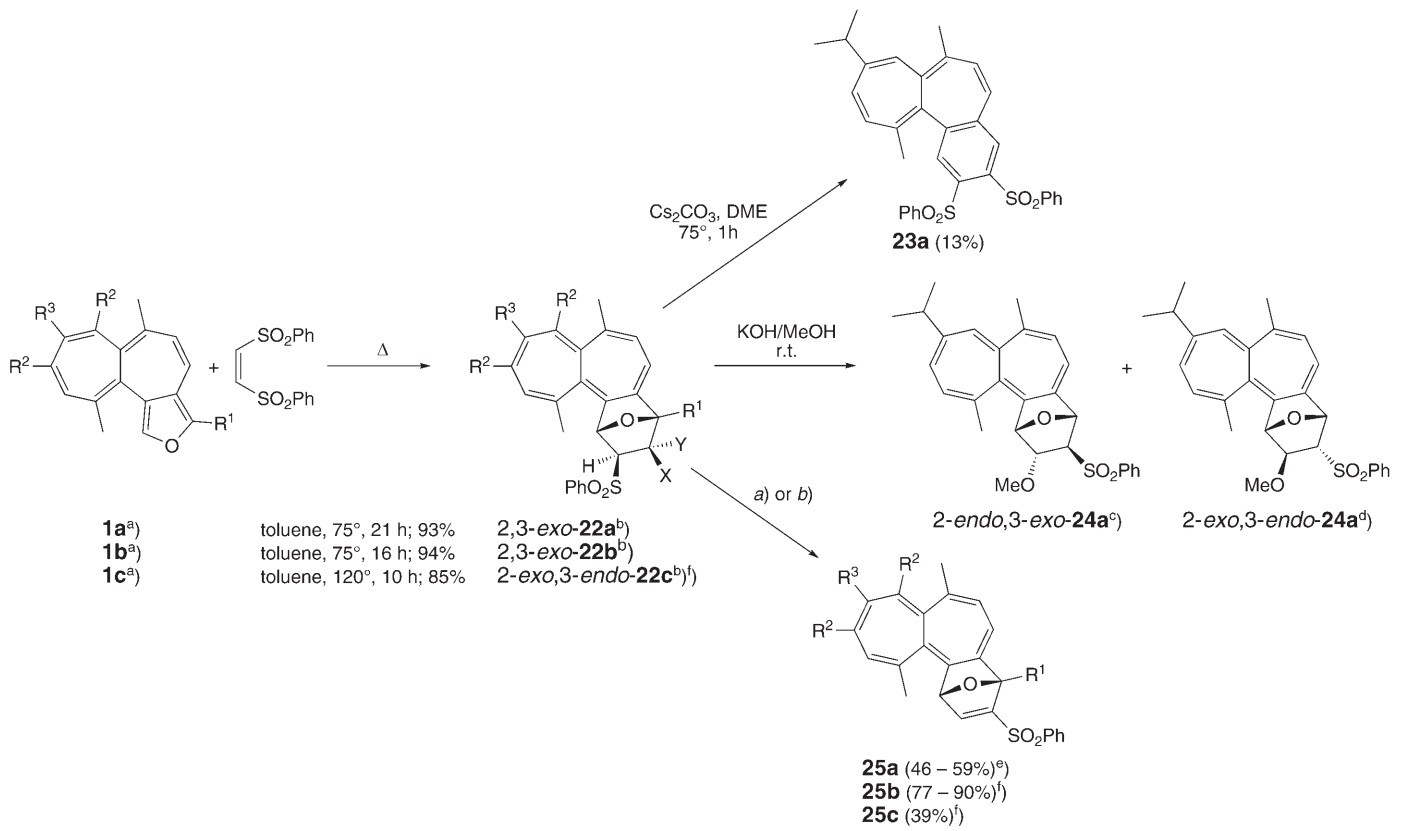


a) Ac_2O/H_2SO_4, r.t. *b*) 1. $TfOSiMe_3/Et_3N/CH_2Cl_2$, r.t. 2. NH_4Cl/H_2O.

[a]) A 1:1 mixture **17a**/**18a** (80%) was obtained and subjected to subsequent reactions without further purification. [b]) After recrystallization 22%. [c]) After crystallization 57%; 12% of **17b** were recovered. [d]) The not further purified mixture of (*P**)- and (*M**)-**17b** (77%) was subjected to subsequent reactions. [e]) Brownish oil, which subsequently crystallized from a $CDCl_3$ solution.

corresponding cycloadducts 2,3-*exo*-**22a** and -**22b** (*Scheme 8*). H–C(2) and H–C(3) appeared in the ^{1}H-NMR spectra as an *AB* system with $J_{AB} = 8.7$ Hz and no further coupling with H–C(1) and H–C(4), respectively, in full agreement with the *exo*-position of the phenylsulfonyl residues at C(2) and C(3). Both compounds exhibited (*P**)-configuration at the axis of chirality since 2,3-*exo*-**22a** showed a strong reciprocal ^{1}H-NOE effect between Me–C(12) and H–C(2), and 2,3-*exo*-**22a** and -**22b** were correlated by their UV/VIS spectra (EtOH), whereby the longest-wavelength band, appearing as a shoulder at 404 and 398 nm, respectively, showed for 2,3-*exo*-**22b** the typical hypsochromic shift due to the higher degree of *peri*-substitution at the heptalene core. The thermal reaction of the heptaleno[1,2-*c*]furan **1c** and ZSE in toluene gave an unexpected result. The CC separation (silica gel, 2% $MeOH/CH_2Cl_2$) of the mixture of products led to two fractions, which turned out to consist of (*M**)- and (*P**)-configured 2-*exo*,3-*endo*-**22c** in a ratio of *ca.* 1:5 (*cf. Scheme 8*). The *trans*-relation of the phenylsulfonyl groups at C(2) and C(3) followed from the observed H,H-coupling constants (5.2 and 4.8 Hz) between H–C(2) and H–C(3). That both epimers possessed indeed the 2-*exo*,3-*endo*-configuration and not the also possible 2-*endo*,3-

Scheme 8



a) Cs_2CO_3, 1,2-dimethoxyethane (DME), 70–80°. *b*) K_2CO_3, dioxane, 70–80°.

[a]) **a**: $R^1=R^2=H$, $R^3={}^i$Pr; **b**: $R^1=R^3=H$, $R^2=Me$; **c**: $R^1=R^2=Me$, $R^3=H$. [b]) **a**, **b**: $X=PhSO_2$, $Y=H$; **c**: $X=H$, $Y=PhSO_2$; the crystalline (*P**)-epimers were obtained in case of **a** and **b**. [c]) The (*P**)-epimer crystallized (21%; before crystallization 54%). [d]) The (*P**)-epimer crystallized (20%; before crystallization 25%). [e]) Procedure *b*) was applied; **23a** (5%) and 2-*exo*,3-*endo*-(*P**)-**22a** (8.5%) were also formed. [f]) The (*M**)-epimer crystallized.

exo-arrangement results from the fact that both compounds showed in their ^{1}H-NMR spectra for H–C(2) and H–C(3) *AB* systems with no further coupling, *i.e.*, H–C(2) must be in *endo*-position to explain the missing of an observable coupling with H–C(1). The (*M**)- and (*P**)-configuration of the two epimers can be derived from the substantial chemical shift differences in $CDCl_3$ of H–C(2) and H–C(3). Whereas in the (*M**)-form, both absorptions are close together (δ(H) 3.78 and 3.76), they are well separated by more than 0.5 ppm in the (*P**)-form (δ(H) 4.03 and 3.47) due to the spatial neighborhood of Me–C(12) and H_{endo}–C(2) in this epimer. We suppose that in the reaction of **1c** and ZSE, also an *exo*-cycloaddition takes place, followed by inversion of the configuration at C(3) due to the steric interference of Me–C(4) with the $PhSO_2$ group in *cis*-relation at C(3). The AM1-calculated enthalpy difference of 2,3-*exo*-**22c** and 2-*exo*,3-*endo*-**22c** amounts to 8 kcal · mol^{-1} for the (*M**)-configured diastereoisomers and 13 kcal · mol^{-1} for the epimeric (*P**)-forms. The mentioned isomerization may have taken place already during the heating period of the reactants; however, we cannot completely exclude the possibility that it happened later on during the CC separation on silica gel. However, the fact that the R_f values of the products on TLC before and after CC were not changed speaks for a thermal isomerization.

Treatment of the cycloadducts **22** with bases opened a potential way to the corresponding benzo[*a*]heptalenes with MeO groups at the biologically correct 1,2,3-positions since the reaction of 2,3-*exo*-**22a** with KOH (3%) in MeOH at room temperature led to a rapid exchange of the $PhSO_2$ group at C(2) by MeO. A mixture of 2-*endo*,3-*exo*- and 2-*exo*,3-*endo*-**24a** was obtained in a ratio of 1:2.2 and a total yield of 79% (*Scheme 8*). CC (silica gel) gave the pure stereoisomers, both with (*P**)-configuration at the heptalene chirality axis according to their UV/VIS spectra (EtOH), whereby the sterically more congested 2-*endo*,3-*exo*-isomer – due to the spatial Me–C(12)/2-*endo*-MeO interaction – showed, in comparison with the 2-*exo*,3-*endo*-isomer, a hypsochromic shift of the two longest-wavelength absorptions (EtOH; 411 *vs.* 421 and 333 *vs.* 340 nm), which are not to be expected for the corresponding two (*M**)-epimers. The *trans*-arrangement of the substituents at C(2) and C(3) followed from the observed small vicinal coupling constants *J*(2,3) of 3.3 and 2.8 Hz, respectively. Moreover, the signal of H–C(2) of 2-*endo*,3-*exo*-**24a** appeared at δ(H) 3.63 ($CDCl_3$) as *dd* with $^3J(2,1) = 4.8$ Hz, whereas 2-*exo*,3-*endo*-**24a** exhibited for H–C(2) solely a *d* signal with $^3J(2,3) = 2.8$ Hz. These observations together with the other recorded ^3J values allowed an unequivocal assignment of the relative configuration of both isomers (see *Exper. Part*). The result demonstrated that a base-catalyzed, selective elimination of the $PhSO_2$ group at C(2) is possible, followed in the present case by a *Michael*-type addition of MeO^- at the intermediately formed C(2)=C(3) bond. The sole formation of the thermodynamically favored '*trans*' products speaks for a reversible addition of MeO^- under the applied conditions[6]).

The treatment of 2,3-*exo*-**22a** with a base under non-nucleophilic conditions (Cs_2CO_3) in 1,2-dimethoxyethane (DME) gave a disappointing result since only the

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[6]) Indeed, AM1 calculations show the ΔH_f° values of the two '*cis*'-isomers lying 6–2.5 kcal · mol^{-1} higher. On the other hand, the $\Delta\Delta H_f^\circ$ between 2-*endo*,3-*exo*- and 2-*exo*,3-*endo*-**24a** predicts for room temperature, assuming $\Delta\Delta S_f^\circ \approx 0$, an equilibrium ratio of *ca.* 1:2.4, which is quite close to the observed ratio of 1:2.2.

rearranged 2,3-bis(phenylsulfonyl)benzo[*a*]heptalene **23a** could be isolated in a low yield from the mixture of products (*Scheme 8*). On the other side, 2,3-*exo*-**22b** delivered under almost the same conditions the expected mono-desulfonylated product **25b** in excellent yields. Even 2-*exo*,3-*endo*-**22c** gave with Cs_2CO_3 in 1,2-dimethoxyethane the desired mono-desulfonylated product **25c**. Finally, it was found that also **25a** was accessible from 2,3-*exo*-**22a** with the weaker base K_2CO_3 in dioxane, however, accompanied by small amounts of rearranged **23a** and epimerized 2-*exo*,3-*endo*-**22a** (*Scheme 8*).

The ease of the formation of the MeO-substituted benzo[*d*]heptalenes **24a** encouraged us to study the base-catalyzed *Michael*-type addition of H_2O_2 at C(2) of the 1,4-dihydro-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalenes **25a** and **25b**. Treatment of (*M**)-**25b** with H_2O_2 in MeOH in the presence of NaOH gave, after heating at 75°, a new crystalline compound, which showed in the IR spectrum (KBr) no absorption above 3300 cm^{-1}, indicating the absence of an OOH group. The missing of a vicinal coupling between H–C(1) (*s* at δ(H) 4.88) and H–C(2) (*s* at δ(H) 3.26) and the position of the *s* of H–C(2) were in agreement with the presence of an *exo*-positioned O-functionality at C(2). Since the ESI-MS indicated a molecular mass just 16 mass units higher than the starting material, we had to conclude that the epoxy derivative 2,3-*exo*-**26b** was formed (*Scheme 9*). This structural assignment was established by an X-ray crystal-structure determination (*Fig. 4*), which also established the (*M**)-configuration at the central heptalene σ-bond. To get access to the primary 2-hydroperoxy *Michael* adduct, we changed the solvent and lowered the reaction temperature. Indeed, the base-catalyzed reaction of (*M**)-**25b** with H_2O_2 in THF at room temperature led to crystalline 2-*exo*,3-*endo*-(*M**)-**27b** in 73% yield (*Scheme 9*).

The presence of the OOH group was indicated in the IR spectrum (KBr) by a strong absorption at 3338 cm^{-1} and a *s* at δ(H) 8.23 in the ^{1}H-NMR spectrum ($CDCl_3$). The fact that the signal of H–C(1) appeared as an *s* in contrast to that of H–C(4), which showed up as a *d*, and the observed $^3J(2,3) = 3.2$ Hz established the *exo*-position of the OOH group at C(2) and the *endo*-position of the $PhSO_2$ substituent at C(3). The expected relative (*M**)-configuration of the heptalene part was evident from the UV/VIS spectrum (EtOH) which showed the longest-wavelength absorption as a shoulder at 384 nm as well as from the missing of an ^{1}H-NOE between Me–C(12) and H–C(2)[7]).

Treatment of 2-*exo*,3-*endo*-(*M**)-**27b** in pyridine with Ac_2O at room temperature gave the 1,4-epoxybenzo[*d*]heptalen-2-one 3-*exo*-(*P**)-**28b** as light yellow crystals in 46% yield (*Scheme 9*). The new compound showed a strong IR band (KBr) at 1770 cm^{-1} and no recognizable coupling between H–C(3),H–C(4), which spoke for the *exo*-position of the $PhSO_2$ group at C(3). We applied the procedure of *Vogel* and co-workers ($TfOSiMe_3/Et_3N$ in CH_2Cl_2; *cf. Scheme 7*) for the rearrangement of 3-*exo*-(*P**)-**28b** hoping to obtain by this way the corresponding benzo[*a*]heptalene-1,2-diol with the $PhSO_2$ group at C(3), in analogy to the rearrangement of the 1,4-

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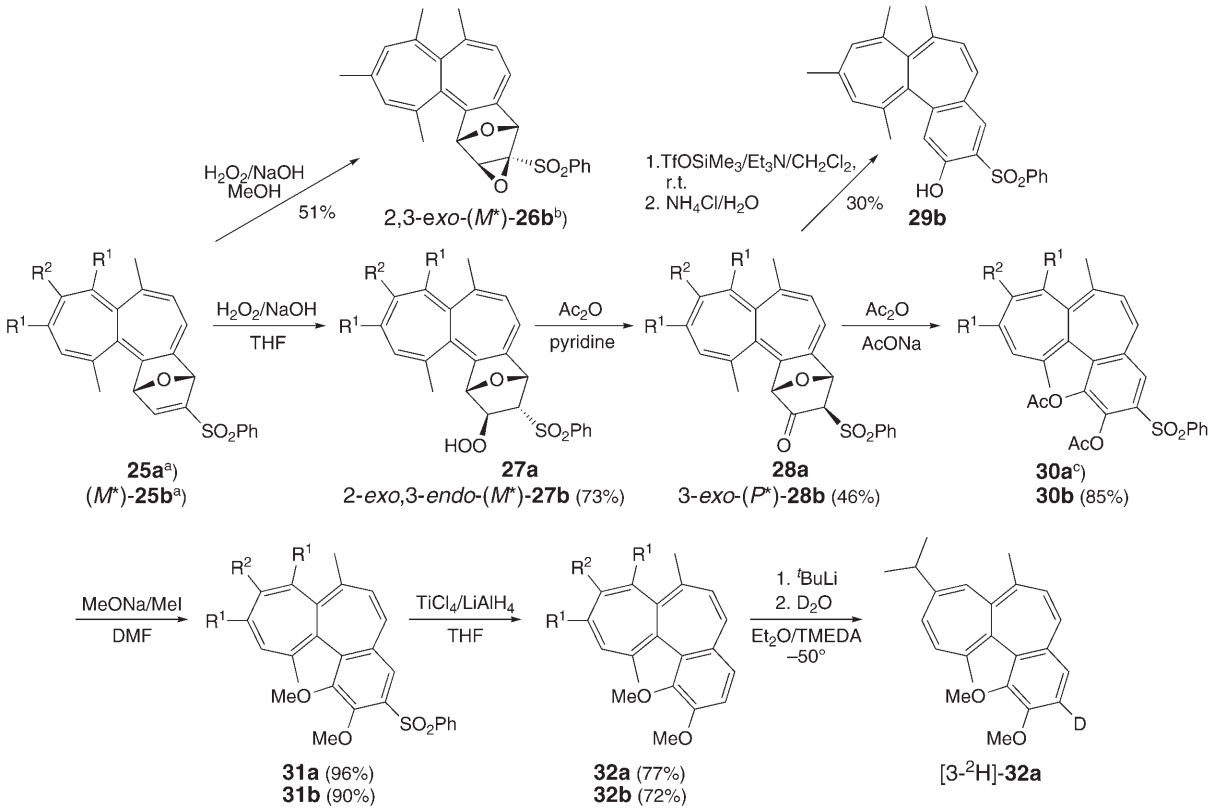
[7]) On standing for several days in $CDCl_3$ solution at room temperature, 2-*exo*,3-*endo*-(*M**)-**27b** decomposed to a *ca.* 3:2 mixture of two compounds with slightly different ^{1}H-NMR spectra (see the *Exper. Part*), which showed no signal in the region of δ(H) 8.23 (HO_2 of 2-*exo*,3-*endo*-(*M**)-**27b**). We suppose that the two new compounds represented the corresponding *meso*- and *rac*-peroxy dimers of the starting material.

Scheme 9



[a]) R^1, R^2 as in *Scheme 8*. [b]) See also *Fig. 4*. [c]) The intermediate products of the reaction sequence **25a** → **27a** → **28a** were not further characterized; overall yield of **30a**: 24%.

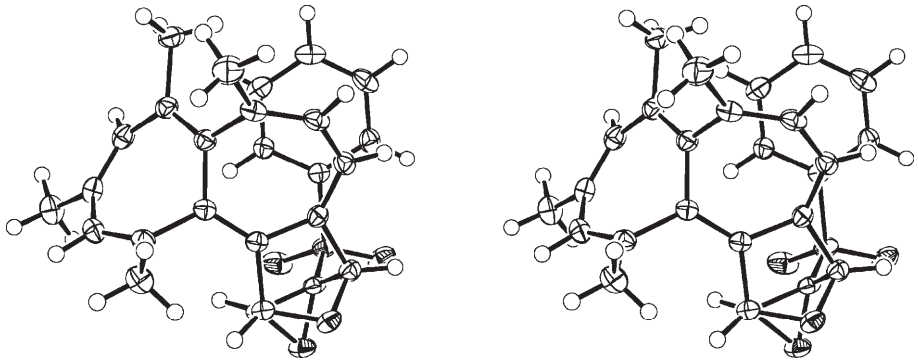


Fig. 4. *Stereoscopic view of the X-ray crystal structure of 2,3*-exo-*(*M**)*-**26b**

epoxybenzo[*d*]heptalen-3-ones **17a** and **17b** (see above, *Scheme 7*). However, in the present case, 7,8,10,12-tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalene-2-ol (**29b**) with loss of the O-atom of the epoxy bridge was obtained in good yield (*Scheme 9*). The structure of **29b** was established unequivocally by its ^{1}H-NMR spectrum ($CDCl_3$).

The chemical shift of the signal of the OH group of **29b** (sharp *s* at δ(H) 9.10) showed that the OH group was involved in H-bonding with the adjacent sulfonyl group. The ^{13}C-shifts ($CDCl_3$) of C(1) (δ(C) 117.97) and C(4) (δ(C) 129.24) were in agreement with the π-donor group (OH) at C(2) and the π/σ-acceptor group ($PhSO_2$) at C(3). ^{1}H-NOE measurements indicated that the *s* for H–C(1) appeared at δ(H) 6.61 and that for H–C(4) at δ(H) 7.59, *prima vista* in contradiction to the electronic properties of the adjacent substituents. However, AM1 calculations showed that the H-bridges of the OH group with the pro-*R* or pro-*S* O-atom of the $PhSO_2$ group (calculated length: 201 and 202 pm, resp.) places the face of its benzene ring close to H–C(4) (d_{av} (C(4)–H$\cdots$C(1)$_{Ph}$/C(2)$_{Ph}$) 344 and 347 pm, resp.), leading to a substantial shielding of H–C(4), so that its *s* signal appears at higher field than that of H–C(1).

More successful, in retaining both O-functionalities in the molecules, proceeded the rearrangement of 3-*exo*-(*P**)-**28b** in Ac_2O at 80° in the presence of dry AcONa (*Scheme 9*). The crystalline 3-(phenylsulfonyl)benzo[*a*]heptalene-1,2-diol diacetate **30b** was obtained in excellent yield. Moreover, the antipodes of **30b** could well be separated on an analytical *Chiralcel-OD-H* capillary column (hexane/^{i}PrOH 4:1; see below). Compound **30b** was fully characterized by spectroscopic means (see the *Exper. Part*). Its almost quantitative transformation into the corresponding 1,2-dimethoxy-3-(phenylsulfonyl)benzo[*a*]heptalene **31b** caused no problems (*Scheme 9*). Since it crystallized well, we performed an X-ray crystal-structure analysis to establish ultimately its 3D structure (*Fig. 5*)[8]).

To get the corresponding 1,2-dimethoxy-3-(phenylsulfonyl)benzo[*a*]heptalene **31a**, 1,4-dihydro-3-(phenylsulfonyl)benzo[*d*]heptalene **25a**, separated by CC from its by-products (see above), was treated without any further purification with H_2O_2/NaOH in

[8]) It is of interest to note that the two Me–O bonds are in a more or less perpendicular orientation with respect to the benzo part and pointing to the same, sterically not shielded side of the ring which is on its opposite side sterically screened by Me–C(12) and $PhSO_2$–C(3). It seems that these orientations are stabilized by a network of weak H-bridges between the *syn*-positioned O-atom of the SO_2 group, MeO–C(2), MeO–C(1), and an H$\cdots\pi$ interaction with C(12)=C(12a) (*cf. Fig. 5*).

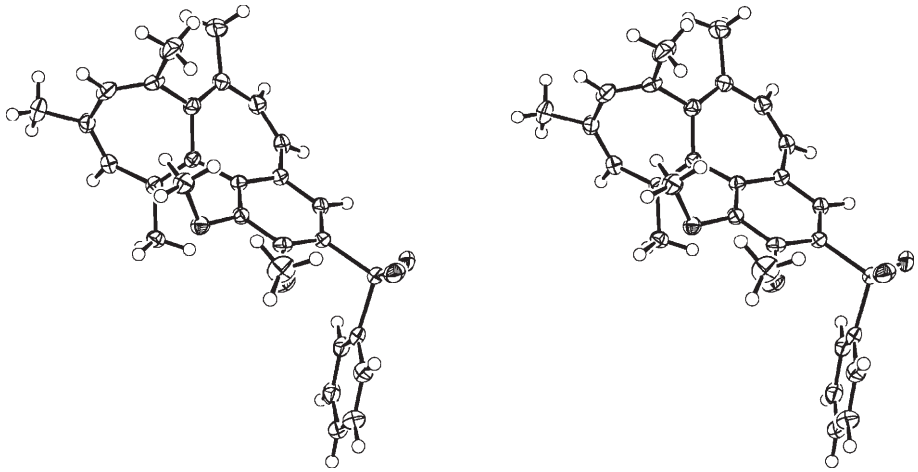


Fig. 5. *Stereoscopic view of the X-ray crystal structure of* **31b**. (*P*)-configuration is shown.

THF. The crude hydroperoxide **27a** was treated with Ac_2O/pyridine to form the corresponding benzo[*d*]heptalen-2(3*H*)-one **28a**, which was isolated and immediately treated with Ac_2O/AcONa at 95–105° to yield, after CC and recrystallization, dark yellow crystalline 3-(phenylsulfonyl)benzo[*a*]heptalene-1,2-diol diacetate **30a** (*Scheme 9*). The reaction of the latter with MeI in DMF in the presence of MeONa gave almost quantitatively **31a**. Characteristic for **30a** and **30b** is the low-field shift of the *s* signal for H–C(4) in their ^{1}H-NMR spectra ($CDCl_3$) at δ(H) 7.94 and 7.95, respectively. As expected, it is slightly shifted to higher field for the corresponding dimethoxy compounds **31a** and **31b** (δ(H) 7.79 and 7.82, resp.).

Reductive elimination of the $PhSO_2$ group of **31a** and **31b** with $LiAlH_4/TiCl_4$ in THF, following our recently published procedure [22], gave the 1,2-dimethoxybenzo[*a*]heptalenes **32a** and **32b**, respectively, in over 70% yield (*Scheme 9*). In both compounds appeared the signals for H–C(3) and H–C(4) as an *AB* system with J_{AB} = 8.5 Hz at δ(H) 6.89, and 7.00 and 7.03, respectively. The antipodes of both compounds could easily be separated on the *Chiralcel* capillary column (see below).

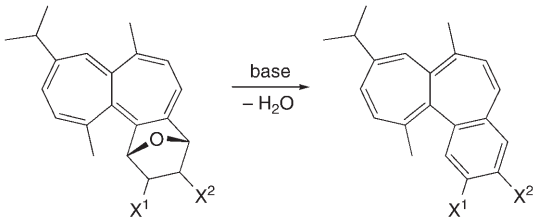
For the introduction of the third MeO group at C(3), we planned metalation at C(3), followed by oxidation with air in the presence of CuBr and methylation of the formed OH–C(3) with MeI/K_2CO_3 in acetone, a procedure based on earlier results of *Razdan et al.* [23] that we had successfully applied in other cases of desulfonylated 1,3-dimethoxybenzo[*a*]heptalenes (*cf.* [24]). Unfortunately, we run short of starting material, so that we could only demonstrate that treatment of **32a** with ^{t}BuLi in Et_2O in the presence of *N*,*N*,*N*′*N*′-tetramethylethanediamine (TMEDA) at −50° gave exclusive metalation at C(3) since quenching of the reaction with D_2O led to [3-^{2}H]-**32a** (*Scheme 9*) as indicated by the disappearance of the signal of H–C(3) and the appearance of H–C(4) as *s* at δ(H) 7.00 in the ^{1}H-NMR spectrum.

3. UV/VIS and CD Spectra of Benzo[*a*]heptalenes. – We have reported already *in extenso* on the UV/VIS and CD spectra of heptalenes [25][26] and of some

benzo[*a*]heptalenes [27][28]. Here, we want to discuss the spectra of this latter class of compounds in more detail, especially with regard to the influence of the benzo fusion on the spectra. In *Table 2* are listed the data of some benzo[*a*]heptalenes and their 1,2,3,4-tetrahydro-1,4-epoxybenzo[*d*]heptalene precursors with the same alkyl substitution pattern at the heptalene part, which guarantees that both series of compounds have almost the same torsion angles at the heptalene chirality axis. Nevertheless, AM1 calculations show that the average *cisoid* torsion angles at C(7a)–C(12a) of the precursors with the bicyclic clamp at C(4a)–C(12b) are slightly smaller than those of the corresponding benzo[*a*]heptalenes (55° *vs.* 60°). As expected, the spectra of all precursors are almost identical. Only the $PhSO_2$- and $PhOSO_2$-carrying compounds exhibit additional shoulders in the region of 270–260 nm, which can be attributed to the isolated side-chain chromophores at C(2) and/or C(3). Most interesting is the fact that the habitus of the spectra above 300 nm is not changed very much in going from the benzo[*d*]heptalenes with the bridged tetrahydrobenzo part to the benzo[*a*]heptalenes with their integrated benzo part, so that we can conclude that this spectral region is determined by the described two heptalene-type electronic transitions [25–28]. The benzo fusion with the σ- and π-acceptor substituents at C(2) and/or C(3) leads to slight bathochromic shifts of 4–10 nm of band I above 400 nm and of 2–15 nm for band II in the region around 340 nm. However, there are two exceptions, namely in the passage of **33a** to **34a** where a marginal shift of 2 nm is observed for band II, which is slightly hypsochromic in case of **39a** to **40a**.

A comparison of the UV/VIS data of the benzo[*a*]heptalene-2- and -3-sulfonates **38a** and **40a** is quite informative since it demonstrates at a first glance the expected

Table 2. *Comparison of the UV/VIS Data of Some 2- and/or 3-Substituted Benzo[*a*]heptalenes and Their (*P**)-Configured 1,2,3,4-Tetrahydro-1,4-epoxybenzo[*a*]heptalene Precursors*[a])



Substituents		1,4-Epoxybenzo[*a*]heptalene[b])		Benzo[*a*]heptalene	
X^1	X^2	No.	λ_{max} [nm]	No.	λ_{max} [nm]
COOMe	COOMe	**33a**	409 (sh), 336, 252, 214	**34a**	413 (sh), 338, 297 (sh), 257, 224
CN	CN	**35a**	–[c]), 339, 249, 217	**36a**	416 (sh), 355, 303, 260, 226
$PhSO_2$	$PhSO_2$	2,3-*exo*-**22a**	404 (sh), 339[d]), 250, 219	**23a**	414 (sh), 344, 286 (sh), 258, 224
$PhOSO_2$	H	**37a**	404 (sh), 336[e]), 251, 213 (sh)	**38a**	*ca.* 400, 344, 286 (sh), 258, 221
H	$PhOSO_2$	**39a**	406 (sh), 336[f]), 251, 213 (sh)	**40a**	*ca.* 400, 334, 282 (sh), 251, 213 (sh)

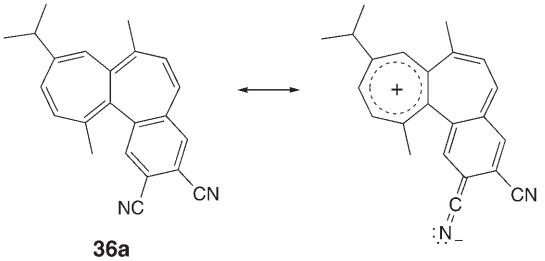
[a]) Data are taken from [1], with the exception of those for **22a** and **23a** (EtOH; see the *Exper. Part*); solvent hexane and 5% ^{i}PrOH/hexane for **35a**, resp.; sh = shoulder. [b]) Substituents in 2-*exo*,3-*exo* position, with the exception **35a** which possesses 2-*exo*,3-*endo* configuration. [c]) Unstructured tailing up to 500 nm. [d]) Further sh at 272, 264, and 258 nm. [e]) Further sh at 273 nm. [f]) Further sh at 274 nm.

similarity of the spectrum of the two positional isomers. However, there is a distinct difference of the position of the heptalene band II, which appears at 334 nm in the case of the phenyl 2-sulfonate **38a** and at 344 nm for the 3-sulfonate **40a**. And this difference is still accentuated in MeCN as solvent, where band II is shifted to 349 and 337 nm, respectively [1]. In other words, the heptalene band II shows a distinctly larger positive solvatochromism for **38a** than for **40a**. This effect of MeCN on the position of band II points to the fact that the excited state shows a stronger charge-transfer contribution than the ground state, whereby π-acceptor substituents at C(2), which are in relative *para*-position of the benzo part with respect to the residual heptalene π-system, stabilize such an excited state better than substituents at C(3), where they occupy a *meta*-position in relation to the residual heptalene π-system, as exemplified for **36a** in *Scheme 10* (*cf.* also [1]).

As a conclusion, it can be said that π-acceptor substituents at the benzene ring stabilize the excited-state band II by stronger charge separation across the heptalene part and its benzo part than in the ground state[9]). Taking as reference the UV/VIS spectrum of 9-isopropyl-7,12-dimethylbenzo[*a*]heptalene (**5a**), which carries no substituent at its benzo part, one can define shift increments for the heptalene band II for π-acceptor substituents at C(2) and/or C(3) (*Table 3*). The increments demonstrate once more that π/σ-acceptor substituents are twice as effective at C(2) than at C(3) on shifting the heptalene band II to longer wavelengths. That the effect of the two COOMe groups of **34a** is much smaller than for the CN or $PhSO_2$ groups of **36a** and **23a**, respectively, can be attributed to the mutual steric hindrance of conjugation of the ester groups in **34a**.

On the other hand, one would expect upon the above arguments that π-donor/σ-acceptor substituents should not effect very much the position of the heptalene band II of benzo[*a*]heptalenes. In *Table 4* are listed the position of the heptalene band II taken

Scheme 10



36a

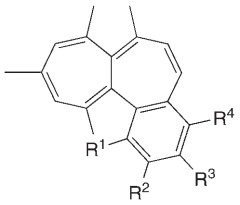
[9]) This is also true for heptalene band I of donor–acceptor 1,4-disubstituted heptalenes, on which the positive solvatochromism is much more expressed [29]. Taking into account that the double-bond shift in heptalenes can be induced thermally as well as photochemically with retention of configuration *via* a transition state with reduced *cisoid* torsion angles of the heptalene parameter [25b], it can be concluded that the two longest-wavelength excited states of heptalenes and benzo[*a*]heptalenes show smaller *cisoid* torsion angles as compared with their ground states, so that intramolecular charge-transfer contributions are more effective in the two excited states than in the ground state.

Table 3. *Increments of π-Acceptor Substituent Effects on Band II of 2- and/or 3-Substituted Benzo[*a*]heptalenes*[a])

Substituent	2,3-COOMe	2,3-CN	2,3-$PhSO_2$	2-$PhOSO_2$	3-$PhOSO_2$
Increment $\Delta\lambda$ [nm][b])	11	28	17	17 (22)	7 (10)

[a]) Reference value: 327 nm (hexane) of 9-isopropyl-7,12-dimethylbenzo[*a*]heptalene (**5a**); for definition of band II, see [26]. [b]) *Cf. Table 2*; solvent hexane; in parentheses, solvent MeCN (*cf.* [1]).

Table 4. *Position of Band II in the UV/VIS and CD Spectra of π-Donor- and π-Donor/σ-Acceptor-Substituted Benzo[*a*]heptalenes*[a])

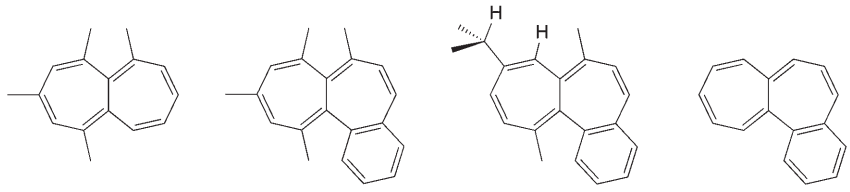


	R^1	R^2	R^3	R^4	Band II position	
					UV/VIS [nm]	CD [nm]
5b	H	H	H	H	321	329
8b	H	H	H	OH	325 (sh)	337
19b	H	H	OH	OH	336	–[b])
20b	H	H	AcO	AcO	322	334
32b	MeO	MeO	H	H	322 (sh)	335
31b	MeO	MeO	$PhSO_2$	H	333 (sh)	344
30b	AcO	AcO	$PhSO_2$	H	338	340
40b[c])	H	COOMe	COOMe	OH	341	–[b])

[a]) UV/VIS Spectra in hexane; **30b** and **31b** in EtOH. CD spectrum of **5b** in hexane, of the others in 2–20% ^{i}PrOH/hexane; for details, see the *Exper. Part.* [b]) Not measured. [c]) For the full data set of **40b**, see [1].

from UV/VIS and CD spectra of some 7,8,10,12-tetramethylbenzo[*a*]heptalenes with π-donor/σ-acceptor substituents at the benzo part. Indeed, the variation of the absorption wavelength of band II is small and increases only with respect to the reference wavelength of **5b** when also π-acceptor/σ-acceptor substituents are present at the benzo part.

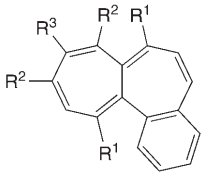
Several years ago, we synthesized 1,3,5,10-tetramethylheptalene (**41**), which forms with its double-bond-shifted isomer 1,3,5,6-tetramethylheptalene, at room temperature, a 1:4 thermal equilibrium mixture [30]. The UV/VIS spectrum of **41** in hexane can be compared with that of **5b**, its benzo-fused analogue, in hexane (*cf. Table 5*). *Fig. 6* shows the structures of **41** and **5b** and the position of heptalene band II, and for further comparisons those of **5a** and benzo[*a*]heptalene (**42**) itself. The difference in wavelength ($\Delta\lambda$) of **41** and **5b** amounts to solely 9 nm. However, the *cisoid* torsion angles at the central σ-bond are larger for **5b** than for **41**, so that the bathochromic shift of 9 nm of band II for benzo[*a*] fusion of heptalenes can only be regarded as the lower



	41	**5b**	**5a**	**42**
Θ [°]	57.7, 58.2	61.4, 63.1	58.5, 59.1	53.0, 54.8
λ_{max} [nm]	312	321	327	347

Fig. 6. *Comparison of torsion angle Θ and wavelength λ_{max} of the heptalene band II of* **41**, **5a**, **5b**, *and* **42**. Θ = AM1-calculated *cisoid* torsion angles at the chirality axis; for **5a**, the displayed lower-energy conformer was calculated. λ_{max} = position of the heptalene band II in hexane; for UV/VIS of **41**, see [30].

Table 5. *UV/VIS and CD Data of Benzo[*a*]heptalenes with Alkyl Substituents at the Heptalene Part*[a])



	R^1	R^2	R^3	UV/VIS		CD	
				λ_{max} [nm]	λ_{min} [nm]	extrema[b]) [nm]	zero [nm]
42	H	H	H	–[c])		–[d])	
				347 (0.24)	314 (0.15)		
				295 (sh, 0.31)			
				259 (1.14)	231 (0.67)		
				215 (1.00)			
5a	Me	H	^{i}Pr	387 (sh, 2.68)	–[c])		
				327 (3.62)	309 (3.55)	335 (– 0.27)	293
				283 (sh, 4.09)		280 (sh, 0.08)	
				258 (4.37)	237 (4.22)	249 (0.87)	
						239 (0.74)	
						229 (1.00)	214
				210 (4.44)		204 (– 0.40)	
5b	Me	Me	H	–[c])		–[c])	
				321 (3.55)	307 (3.52)	329 (– 0.32)	288
				281 (sh, 4.14)		281 (sh, 0.04)	
				248 (4.32)	238 (4.29)	248 (sh, 0.66)	
						231 (1.00)	215
				219 (4.46)		208 (– 0.15)	

[a]) Solvent hexane; data of **42** are taken from [28]. [b]) Relative mdeg with respect to the most intense band (= 1.00) of the (*P*)-configured benzo[*a*]heptalenes. [c]) Unstructured tailing (neg. in CD) up to 450 nm; see Fig. 3 in [28]. [d]) No separation of the antipodes of **42** on an anal. *Chiralcel-OD-H* column in hexane at r.t.

limit of band shift. More realistic seems to be a comparison of the band II position of **41** and **5a**, with *cisoid* torsion angles much closer to those of **41**, but still somewhat larger. A $\Delta\lambda$ value of 15 nm for the bathochromic shift of band II on benzo[*a*] fusion of heptalenes seems, therefore, be more reliable. That alkyl substituents at the heptalene core influence the band position of the UV/VIS spectra of heptalenes almost exclusively by their steric effects, which operate on the degree of the twisting of the π-skeleton, is demonstrated by the position of band II of benzo[*a*]heptalene (**42**) without any alkyl substituent and, therefore, with the smallest central torsion angles (*Fig. 6*).

We separated some of our new benzo[*a*]heptalenes into their antipodes on an anal. *Chiralcel-OD-H* column with hexane or ^{i}PrOH/hexane (*Fig. 7*). Whereas benzo[*a*]-heptalene itself could not be separated with hexane as mobile phase at room temperature, its alkylated forms **5a** and **5b** were separated with comparably high efficiency (*cf. Fig. 7*). In the case of benzo[*a*]heptalenes with polarizing substituents at

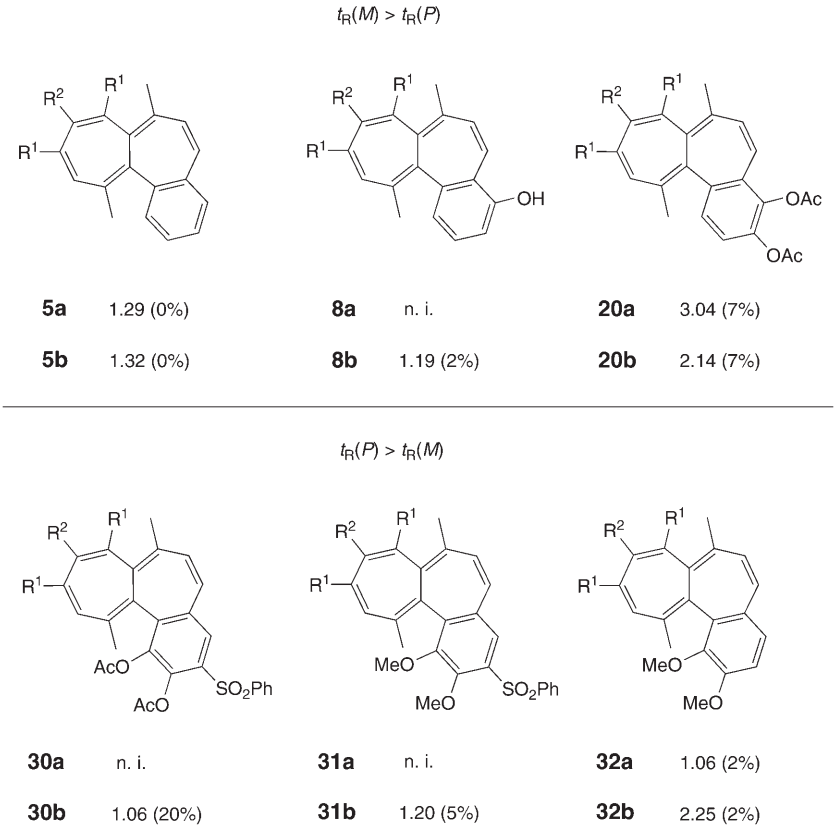


Fig. 7. *Separation factors α for the antipodes, obtained by anal. HPLC* (*Chiralcel-OD-H* column) *at room temperature.* See *Scheme 1* for **a** and **b** series. $\alpha = t_R$ (slow-moving antipode)/t_R(fast-moving antipode), in parentheses, percentage x of eluent x% ^{i}PrOH/hexane; n.i. = not investigated.

the benzo part, we observed hugh differences in the retention time t_R of the antipodes with separation factors $\alpha = 2-3$. Moreover, we found as a rule that the benzo[*a*]heptalenes with substituents at C(1) and C(2) or at C(1), C(2), and C(3) exhibit larger retention times for the (*P*)-enantiomers than for the (*M*)-forms, whereas the reverse is true for benzo[*a*]heptalenes with no substituents at the benzo part or substituents at C(4) or C(3) and C(4) (*Fig. 7*). We assume that this chromatographic differentiation of the enantiomers is mainly the result of the difference of the size of the *cisoid* torsion angles at the axis of chirality, which are on steric grounds distinctly larger for 1- than for 4-substituted benzo[*a*]heptalenes. This is also expressed, as mentioned above, in their UV/VIS spectra.

The UV/VIS and CD data of the benzo[*a*]heptalenes **5a** and **5b** and for comparison those of benzo[*a*]heptalene (**42**) itself are listed in *Table 5*. The CD spectra of (*P*)- and (*M*)-**5b** are displayed in *Fig. 8*,*a*. Above 300 nm, solely the broad *Cotton*-effect (CE) of heptalene band II at 329 nm, negative for the (*P*)-form and positive for the (*M*)-form as for all heptalenes (*cf.* [25][26]), benzo[*a*]heptalenes (*cf.* [27][31] and *Exper. Part*), and heptaleno[1,2-*c*]furans [32], is well determined and slightly shifted by 8 nm to longer wavelength as compared with the corresponding UV absorption band, which appears at 321 nm (see *Table 5*). A comparable observation is made for **5a** and its (*P*)- and (*M*)-antipodes (327 nm → 335 nm; *Table 5*). If this displacement of 8 nm is also applicable to benzo[*a*]heptalene (**42**) itself, one would expect the CE for the heptalene band II at *ca*. 355 nm for hexane as solvent. The heptalene band I, appearing at longer wavelengths, is in almost all cases only visible as an unstructured tailing that ends at *ca.* 450–500 nm (*cf. Figs. 8*,*a–c*, and *9*,*a–c*). Benzo[*a*]heptalene **5a** exhibits in the long-wavelength region of its UV/VIS spectrum a weak shoulder at 387 nm, which can be attributed to the heptalene-band-I absorption. It should appear at slightly shorter wavelengths for the tetramethyl substituted **b** series of benzo[*a*]heptalenes. However, heptalene-band-I is recognizable as a strong asymmetry of the CE of heptalene band II towards longer wavelengths. There are two CD spectra, namely those of **30b** and **31b**, where a faintly recognizable shoulder appears in the range of 368–375 nm (close to the position of heptalene band I in the UV/VIS spectrum of **5a**), which can be attributed to the CE of heptalene band I of **30b** and **31b** (*cf. Figs. 9*,*a* and *b*).

The region below 300 nm of the CD spectra of the benzo[*a*]heptalenes is characterized mainly by two intense CE around 250 nm and 220–230 nm (*cf. Fig. 8*,*a–c* as well as *Table 5* and *Exper. Part* for **20a** and **32a**), which both are positive for all (*P*)-configured and negative for all (*M*)-configured heptalenes and which are not very much dependent on the substitution pattern. The two reference benzo[*a*]-heptalenes **5a** and **5b** show, in addition, a weak CE around 280 nm, only recognizable as a positive shoulder for the (*P*)-configured antipodes and *vice versa* for the (*M*)-configured forms (*cf. Fig. 8*,*a* and *Table 5*). It is of interest to note that this CE changes its sign with π-donor substituents at C(4) (*Fig. 8*,*b*) or at C(3) and C(4) (*Fig. 8*,*c*). Moreover, this CE is well expressed as a clear band appearing just above 300 nm in the case of π-donor substituents at C(1) and C(2), and it is positive again for the (*P*)-configured benzo[*a*]heptalenes, and in turn negative for the (*M*)-configuration (*cf. Fig. 9*,*a–c* and *Exper. Part* for **32a**).

We were quite impressed when we recorded the CD spectra of **30b**–**32b** (*cf. Fig. 9*,*a–c*). Whereas the habitus of the CD spectra of the (*P*)- and (*M*)-enantiomer of

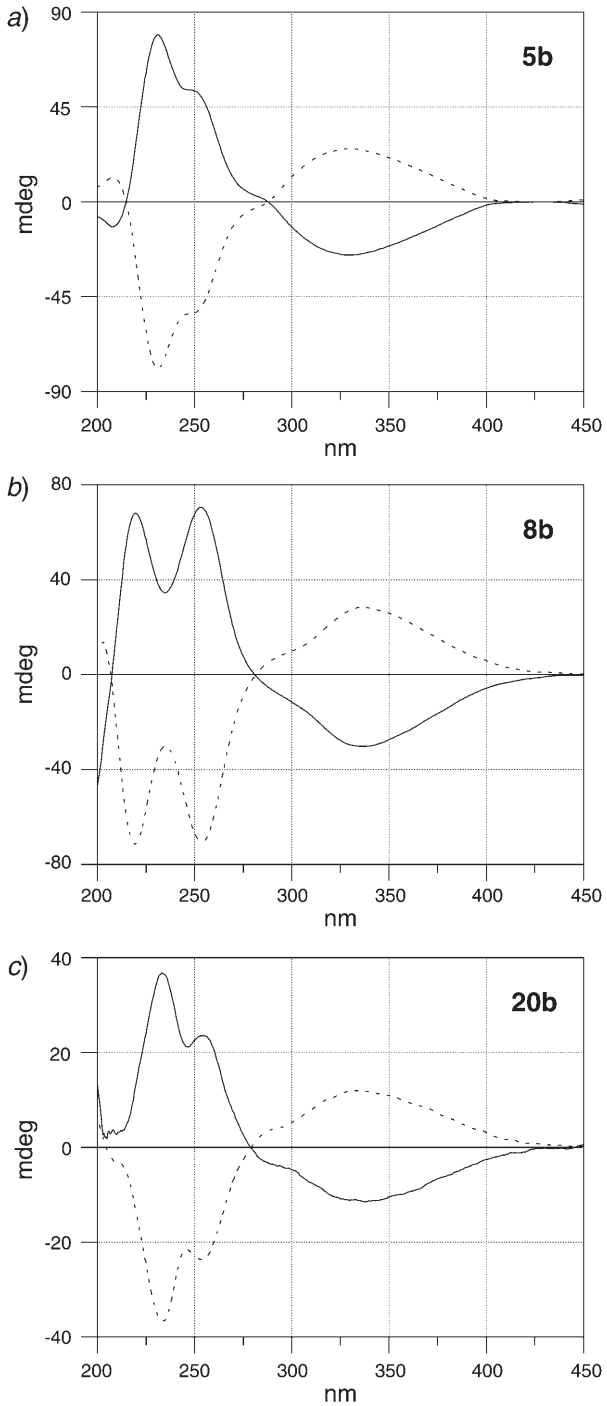


Fig. 8. a) *CD Spectrum* (hexane) *of (*P*)- and (*M*)*-**5b**. b) *CD Spectrum* (2% ^{i}PrOH/hexane) *of (P)- and (*M*)*-**8b**. c) *CD Spectrum* (7% ^{i}PrOH/hexane) *of (*P*)- and (*M*)*-**20b**.

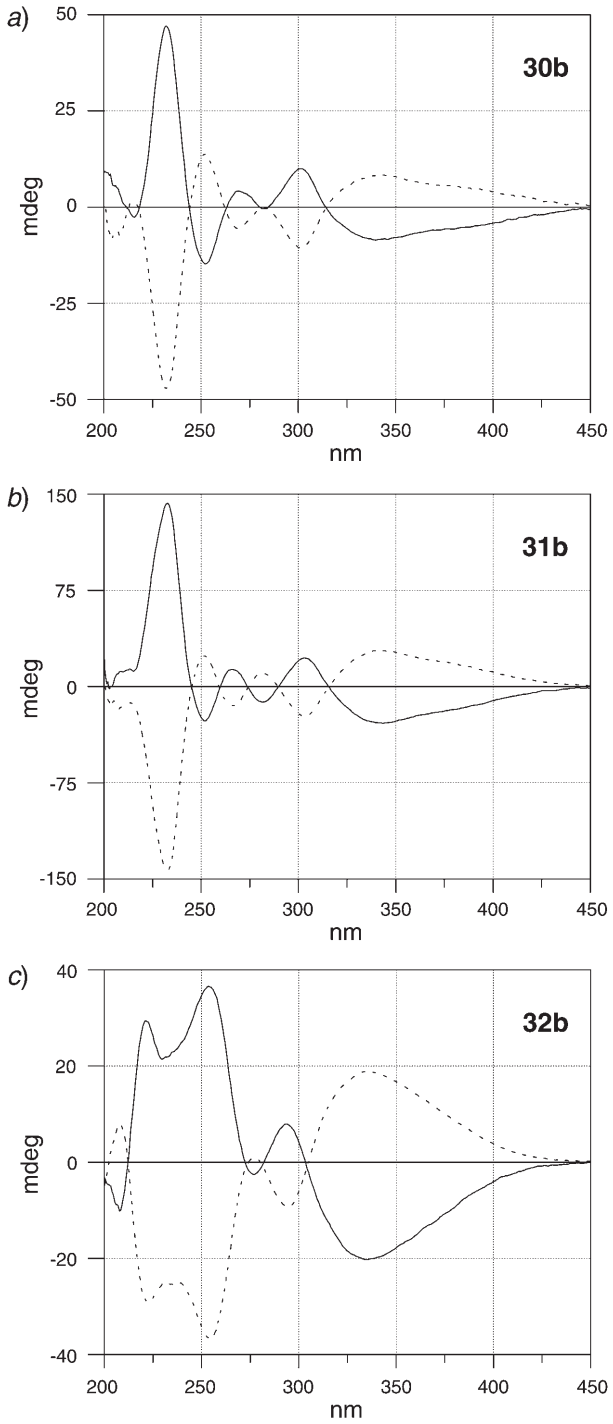
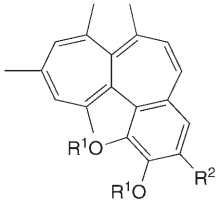


Fig. 9. a) *CD Spectrum* (20% ^{i}PrOH/hexane) *of (P)- and (*M*)*-**30b**. b) *CD Spectrum* (5% ^{i}PrOH/hexane) *of (P)- and (*M*)*-**31b**. c) *CD Spectrum* (2% ^{i}PrOH/hexane) *of (P)- and (*M*)*-**32b**.

the 1,2-dimethoxybenzo[*a*]heptalene **32b** resembled more or less those described above (*cf. Fig. 8*, *a–c,* and *9,* c), with the exception of the region just below 300 nm, where two CE of opposite signs at 294 and 277 nm appear, followed by two strong CE of the same sign at 250 nm and below, which we see in benzo[*a*]heptalenes as well as in heptalenes [25][26], it changed dramatically in the case of the CD spectra of **31b** with an additional $PhSO_2$ substituent at C(3). One recognizes for **31b** as well as for **30b**, which carries AcO instead of MeO groups at C(1) and C(2), two sets of CE of opposite signs in the range of 315–245 nm (*cf. Fig. 9*, *a* and *b*, and *Table 6*) and one very strong CE at 233 nm, which corresponds well with the strong UV-absorption band of **31b** and **30b** at 233 and 231 nm, respectively. We assume that the CE of opposite signs are caused by

Table 6. *Comparison of the Absorption-Band Position in the UV/VIS and CD Spectra of Some 7,8,10,12-Tetramenthylbenzo[*a*]heptalenes*[a])

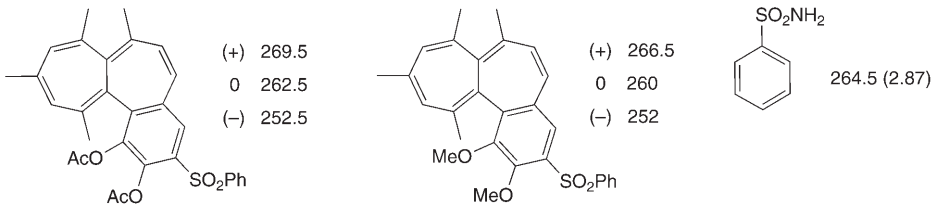


	R^1	R^2	UV/VIS λ_{max} [nm]	CD extrema
32b[b])	Me	H	–[c])	–[c]) (–)
			322 (sh, 3.39)	335 (–)
			291 (3.87)	293.5 (+)
				277 (–)
			250 (4.03)	253.5 (+)
			223 (4.21)	221 (+)
31b[d])	Me	$PhSO_2$	–[c])	*ca.* 368 (sh, –)
			333 (sh, 3.67)	343.5 (–)
			300 (4.23)	303 (+)
				281.5 (–)
			254 (4.52)	266.5 (+)
				252 (–)
			233 (4.56)	233 (+)
			221 (sh)	
30b[e])	Ac	$PhSO_2$	–[c])	*ca.* 375 (sh, –)
			338 (3.67)	339.5 (–)
			297 (4.25)	301.5 (+)
				282 (–)
			253 (4.51)	269.5 (+)
				252.5 (–)
			231 (4.53)	232 (+)
			217 (4.52)	

[a]) UV/VIS: In parentheses log ε; CD: sign of the *Cotton* effect for the (*P*)-form is shown in parentheses; see also *Fig. 9*, *a–c*. [b]) UV/VIS in hexane; CD in 2% ^{i}PrOH/hexane; for details, see the *Exper. Part.* [c]) Unstructured tailing up to 450 nm. [d]) UV/VIS in EtOH; CD in 5% ^{i}PrOH/hexane; for details, see the *Exper. Part.* [e]) UV/VIS in EtOH; CD in 20% ^{i}PrOH/hexane; for details, see the *Exper. Part*.

chiral exciton coupling (*cf.* [33]). Since **32b** possesses also two CE of opposite signs (*vide supra*), which are found in the CD spectra of **30b** and **31b** bathochromically shifted to 303/302 and 282 nm (see *Table 6*), the CE splitting can only be caused by chiral exciton coupling within the twisted benzo[*a*]heptalene system[10]). The chiral coupling effect seems to be dependent on the MeO or AcO groups at C(1) and C(2) and accentuated by the additional $PhSO_2$ group at C(3), since the other benzo[*a*]heptalenes do not exhibit such CE of opposite signs just below 300 nm (*cf. Fig. 8*, *a*–*c*). Indeed, the UV/VIS spectra of the former three benzo[*a*]heptalenes display an absorption band at λ_{max} 297 (**30b**), 300 (**31b**), and 291 nm (**32b**).

The second pair of CE of opposite sign in the range of 275–245 nm is only present in the benzo[*a*]heptalenes **30b** and **31b**, which bear the phenylsulfonyl group at C(3) (*Fig. 9*, *a* and *b*, *Table 6*). It must, therefore, arise from chiral exciton coupling of the heptalene band that appears in **32b** at 250 nm, which shows a strong positive CE at 253.5 nm, and the secondary band (^1L_b) of the $PhSO_2$ group. Indeed, this band is found in benzenesulfonamide (**43**) as a model at 264.5 nm, *i.e.*, just midst of the above mentioned range of CE (*Fig. 10*).



30b **31b** **43**

Fig. 10. Cotton *effects* (λ in nm) *of* **30b** and **31b** (see *Table 6* and *Fig. 9*, *a* and *b*) *due to chiral exciton coupling, as compared to the secondary UV band of* **43** (water + trace of MeOH) [34]

There are two further points worth to be discussed. The two pairs of CE of opposite signs exhibit different intensities of their individual CE within the two pairs, indicating the difference in excitation energy of the two interacting chromophoric systems. The pair of CE at 300 nm and below are highly symmetric and shows a ratio of integrated band intensities of >12:1 (**30b**), 3:1 (**31b**), and 7:1 (**32b**) in favor of the CE appearing at longer wavelengths. We conclude from this effect of substituents at the benzo part of the molecules that the heptalene part interacts chirally by exciton coupling with the benzo part, whereby the CE at longer wavelength possesses more heptalene character and that at lower wavelength more benzo character; in other words, it is the local, slightly higher excitation energy of the benzo part that is modified by the different substituents, so that the excitation energy gap between the two chromophoric systems are smaller (**31b**) or larger (**30b**), with that of **32b** just between those of the two other structures.

The second pair of CE displays the reverse behavior with respect to their intensities. In this case, it is the CE at longer wavelengths that appears with lower intensity in a

[10]) The same is true for **32a**, where the two CE of opposite signs appear slightly bathochromically shifted as compared with **32b** at 297 and 278 nm (for details, see the *Exper. Part*).

ratio of 1:3 (**30b**) and 1:1.5 (**31b**), respectively, in relation to the opposite CE at shorter wavelengths (*Figs. 10* and *9*, *a* and *b*). Moreover, a detailed inspection of the CE at higher wavelengths discloses a slight asymmetry of this band in the case of **30b** and in comparison with that of **31b**. We assume that the inherent higher conformational mobility of the AcO groups of **30b** is responsible for this effect, in a way that thereby the excitation energy of the benzo[*a*]heptalene system is slightly modified, thus changing marginally the chiral exciton coupling between the two chromophors[11]). This reasoning is in agreement with the fact that the CE at lower wavelengths contain more benzo[*a*]heptalene character and that with opposite sign at higher wavelengths more phenylsulfonyl character.

One may ask why does this chiral exciton coupling occur in the discussed benzo[*a*]heptalenes? We suppose that this is a question of the power of twisting of the heptalene part. In *Table 7* are listed some of the crucial torsion angles taken from the X-ray crystal-structure determination of **31b** (*Fig. 5*). All Θ values at the central σ-bond (C(7a)–C(12a)) are around 60° (*cisoid*) or 115° (*transoid*). This means that there exists at the heptalene part in **31b** only a π-system with reduced conjugation, especially between the two seven-membered rings as well as between the not benzo-fused seven-membered ring and the benzo part, so that the excited states of the benzo[*a*]heptalenes can be heptalene- and benzo-centered, resulting in chiral exciton coupling between the (*P*)- or (*M*)-configured heptalene part of the molecules and their benzo part.

Table 7. *Some Torsion Angles Θ of the X-Ray and the AM1-Calculated Structure of 1,2-Dimethoxy-7,8,10,12-tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalene* (**31b**)[a])

Θ [°]	X-Ray	AM1 (I)	AM1 (II)
C(8)–C(7a)–C(12a)–C(12)	63.3(3)	63.2	62.7
C(7)–C(7a)–C(12a)–C(12b)	61.8(3)	64.0	64.1
C(7)–C(7a)–C(8)–C(9)	115.7(3)	114.3	114.9
C(12)–C(12a)–C(12b)–C(1)	– 60.4(3)	– 66.1	– 65.5
C(8)–C(9)–C(10)–C(11)	33.1(4)	33.4	33.3
C(10)–C(11)–C(12)–C(12a)	– 32.5(4)	– 33.7	– 33.8
C(2)–C(3)–S–$C(1)_{Ph}$	65.0(2)	81.3	– 80.2
C(3)–S–$C(1)_{Ph}$–$C(2)_{Ph}$	65.8(2)	100.5	– 99.3
C(3)–S–$C(1)_{Ph}$–$C(6)_{Ph}$	– 119.1(2)	– 81.7	82.6
C(12b)–C(1)–O–CH_3	– 68.3(2)	– 68.3	– 108.3
C(1)–C(2)–O–CH_3	– 68.0(2)	– 78.4	79.3

[a]) Torsion angles of the (*P*)-enantiomer are listed.

A more detailed inspection of the X-ray-determined structure of **31b** reveals that the substituents at the benzo part occupy a spatial arrangement with the two MeO groups pointing in the same direction, their O–Me bonds being nearly perpendicular to the benzo part and with an *anti*-relation of MeO–C(1) and Me–C(12) for obvious

[11]) AM1 Calculations of diverse spatial arrangements of the three substituents at the benzo part of **30b** indicated that the lowest-energy one is comparable with that of **31b** (*cf. Fig. 11*, *b*, below) carrying the AcO moieties in the s-*trans*-conformation. The next higher in energy (by 1.6 kcal · mol^{-1}) bears by the same spatial arrangement AcO–C(2) in the s-*cis*-conformation.

steric reason. The $PhSO_2$ group, on the other hand, takes a spatial position which is in an *anti*-relation with respect to the two MeO groups and with a torsion angle of 65° at the C(3)–S bond and of 66° (–119°) at the $S-C(1)_{Ph}$ bond, respectively (*Table 7*). We were interested to know, in view of the spectral data of **31b**, whether its conformation in the crystals would also be the energetically most favorable in solution. AM1 Calculations with respect to different spatial arrangements of the substituents at C(1), C(2), and C(3) revealed that the energetically most favorable arrangement (AM1 II in *Table 7*) shows the two MeO groups in an *anti*-relation and also MeO–C(2) and $PhSO_2$–C(3), whereby MeO–C(1) has to be in an *anti*-relation to Me–C(12) of the heptalene backbone on steric grounds (*cf. Fig. 11,b*). The second-most-stable arrangement is that found in the crystals (*cf. Fig. 5* and *Fig. 11,a* and AM1 I in *Table 7*). It is by 1.4 kcal · mol^{-1} higher in energy, *i.e.*, *ca.* 8% of **31b** should exist in a dynamic equilibrium with 92% of the most stable conformation (AM1 II) at room temperature. The benzene ring of the $PhSO_2$ group occupies in both arrangements a similar tilted, nearly face-to-face position with respect to the two sides of the benzo[*a*]heptalene backbone, whereby the tilt angle corresponds with the $C(3)-S-C(1)_{Ph}$ bond angle of 102° (X-ray: 106.4(2)°).

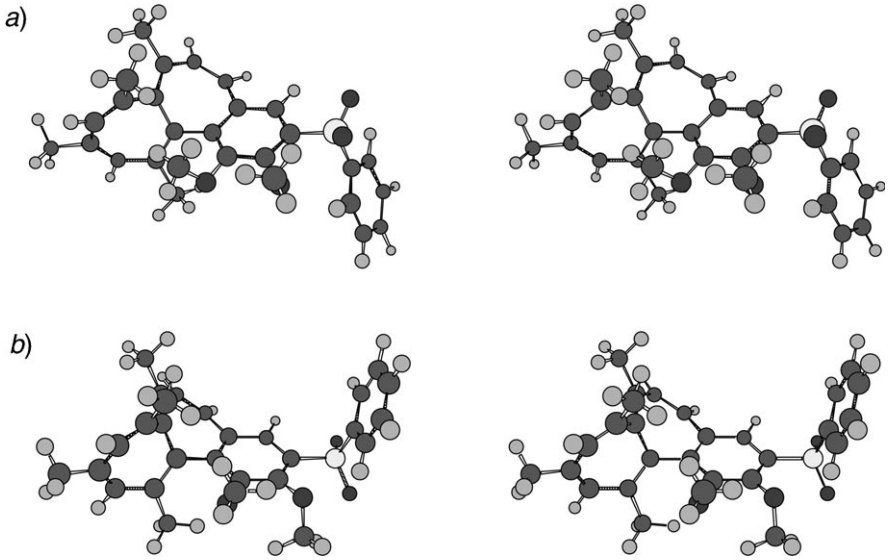


Fig. 11. *Stereoscopic views of the two AM1-calculated lowest-energy conformations* a) *and* b) *of* **31b**. (*P*)-Configuration is shown.

Finally, there is a last question to be answered, namely, is the sequence of signs of the two pairs of CE in agreement with the (*P*)- and (*M*)-configuration of the benzo[*a*]heptalenes, which are determined for all heptalenes by two negative CE (– CE) above 320 nm for the (*P*)-configured forms and *vice versa* for their antipodes? One finds, in going from longer to shorter wavelengths, for the (*P*)-configured benzo[*a*]heptalenes **32b** (as well as for **32a**) a + CE/ – CE combination for the first pair of bands (*Fig. 9,c*), followed by a second + CE/ – CE combination for the second pair

of bands in the case of **30b** and **31b** (*Fig. 9,a* and *b*) with the additional $PhSO_2$ group at C(3), in agreement with the fact that in moving from the chirally twisted heptalene skeleton to its benzo part and further to the benzene ring of the $PhSO_2$ group in **30b** and **31b**, a helical, clockwise turn is described (*cf. Fig. 11,b* and [33]). Nevertheless, this fully empirical interpretation should be substantiated by corresponding calculations of the CD spectra of benzo[*a*]heptalenes, which have not been performed so far to the best of our knowledge.

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Experimental Part

General. Cf. Part 1 [1].

1. *Cycloaddition Reactions of the Heptaleno[1,2-*c*]furans* **1** *and Transformations of the Adducts.* 1.1. *With Vinylene Carbonate (*VC*).* 1.1.1. *(*P**,1*S**,2*R**,3*S**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Carbonate* (2,3-*endo*-(*P**)-**2a**). A *Schlenk* tube was charged under Ar with heptaleno[1,2-*c*]furan **1a** (0.255 g, 0.965 mmol) and VC (*Aldrich*; 97%; 0.290 g, 3.37 mmol) in toluene (5 ml), sealed, and heated in an oil bath (130°) for 5 days. After evaporation, the residue was filtered through a short column of basic aluminium oxide (act. IV) with CH_2Cl_2. The thus obtained orange solid was recrystallized from Et_2O/hexane to yield pure, microcrystalline 2,3-*endo*-(*P**)-**2a** (0.181 g, 53%). The mother liquor was subjected to CC (SiO_2, ^{t}BuOMe/hexane 3:2), which provided, after recrystallization with Et_2O/pentane, a second crop of 2,3-*endo*-(*P**)-**2a** (16 mg, 5%). Brownish red crystals. M.p. *ca.* 150° (dec.). R_f (^{t}BuOMe/hexane 7:3) 0.30. UV/VIS (hexane): λ_{max} 336 (3.70), 273 (sh, 4.15), 250 (4.34), 213 (4.36); λ_{min} 303 (3.60), 231 (4.17), 207 (4.35). IR (KBr): 2953*s*, 2924*m*, 2866*m*, 1797*s*, 1603*m*, 1460*m*, 1440*m*, 1365*s*, 1338*m*, 1304*m*, 1149*s*, 1084*s*, 995*s*, 835*s*, 762*m*, 617*s*. ^{1}H-NMR (600 MHz, C_6D_6): 5.987 (*dd*, ^3J(10,11) = 6.5, ^4J(11,Me−C(12)) = 1.2, H−C(11)); 5.939 (*d*, ^3J(10,11) = 6.6, H−C(10)); 5.896 (*dd*, ^3J(5,6) = 6.8, ^4J(6, Me−C(7)) = 1.3, H−C(6)); 5.787 (*d*, ^3J(5,6) = 6.8, H−C(5)); 5.655 (br. *s*, H−C(8)); 4.560 (*d*, ^3J(1,2) = 4.5, H−C(1)); 4.306 (*d*, ^3J(3,4) = 4.6, H−C(4)); 3.903 (*dd*, ^3J(2,3) = 8.4, ^3J(3,4) = 4.6, H−C(3)); 3.864 (*dd*, ^3J(1,2) = 4.6, ^3J(2,3) = 8.4, H−C(2)); 2.175 (*sept.*, ^3J = 7.0, Me_2CH−C(9)); 1.933 (br. *s*, Me−C(12)); 1.906 (br. *s*, Me−C(7)); 0.917, 0.905 (2 *d*, ^3J = 7.0, Me_2CH−C(9)); assignments of the signals were verified by NOE. CI-MS (NH_3): 368 (43, $[M+NH_4]^+$), 351 (100, $[M+H]^+$), 307 (34, $[(M+H)-CO_2]^+$), 291 (22, $[(M+H)-(CO_2+O)]^+$), 289 (38, $[(M+H)-(CO_2+H_2O)]^+$).

The HPLC/UV/VIS analysis of the crude material after filtration through aluminium oxide revealed the presence of a second cycloadduct (*ca.* 10%), which exhibited an UV/VIS almost identical with that of *endo*-(*P**)-**2a**. This cycloadduct must, therefore, represent 2,3-*exo*-(*P**)-**2a**.

1.1.1.1. *(*P**,1*S**,2*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol* (2,3-*endo*-(*P**)-**3a**). To a soln. of 10% KOH in MeOH (4 ml) was added *endo*-(*P**)-**2a** (0.135 g, 0.385 mmol). The mixture was stirred at r.t. until a clear soln. resulted (after *ca.* 1 h). The soln. was poured into H_2O and extracted with CH_2Cl_2. The combined extracts were washed with half-conc. brine, filtered through a plug of cotton, and concentrated. The solid residue was recrystallized from AcOEt/hexane, which gave a first crop of 2,3-*endo*-(*P**)-**3a** (79.9 mg) as dark yellow crystals. Recrystallization of the residue of the mother liquor from Et_2O/hexane afforded a second crop of 2,3-*endo*-(*P**)-**3a** (7.0 mg). Total yield: 86.9 mg (70%). M.p. 196.5–197.8°. R_f (AcOEt/hexane 7:3) 0.30. UV/VIS (EtOH): λ_{max} 410 (sh, 2.81), 337 (3.69), 273 (sh, 4.14), 252 (4.31), 214 (4.35); λ_{min} 300 (3.54), 231 (4.16), 208 (4.34). IR (KBr): 3369*s*, 2959*s*, 2870*m*, 1660*w*, 1614*m*, 1442*s*, 1397*s*, 1317*m*, 1148*s*, 1111*s*, 1036*m*, 988*m*, 919*m*, 874*s*, 808*m*, 789*s*, 633*m*. ^{1}H-NMR (600 MHz, C_6D_6): 6.048 (*dd*, ^3J(10,11) = 6.5, ^4J(11,Me−C(12)) = 1.4, H−C(11)); 5.980 (*d*, ^3J(10,11) = 6.5, H−C(10)); 5.824 (*dd*, ^3J(5,6) = 6.6, ^4J(6,Me−C(7)) = 1.3, H−C(6)); 5.786 (*d*, ^3J(5,6) = 6.6, H−C(5)); 5.701 (*d*, ^4J(8,10) = 0.7, H−C(8)); 4.771 (*d*, ^3J(1,2) = 4.9, H−C(1)); 4.502 (*d*, ^3J(3,4) = 5.1, H−C(4)); 3.779 (*ddd*, ^3J(2,3) = 8.1, ^3J(3,4) = 5.1,

^3J(OH–C(3),3) = 8.9, H–C(3)); 3.679 (*ddd*, ^3J(2,3) = 8.0, ^3J(1,2) = 4.9, ^3J(OH–C(2),2) = 5.9, H–C(2)); 2.226 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.131 (br. *s*, Me–C(12)); 1.982 (*d*, ^4J(6,Me–C(7)) = 1.0, Me–C(7)); 1.551 (*d*, ^3J(2, OH–C(2)) = 5.9, OH–C(2)); 1.516 (*d*, ^3J(3, OH–C(3)) = 8.9, OH–C(3)); 0.959, 0.945 (2*d*, ^3J = 6.9, Me_2CH–C(9)); assignments of the signals were verified by NOE. CI-MS (NH_3): 325 (100, $[M+H]^+$), 267 (23, $[(M+H) - HO-C\equiv C-OH$ (or O=CH–HC=O)]$^+$).

The structure of 2,3-*endo*-(*P**)-**3a** was finally established by an X-ray crystal-structure determination (see *Fig. 1* and *Table 8*).

1.1.1.2. *(*P**,1*S**,2*R**,3*S**,4*R**)- and (*M**,1*S**,2*R**,3*S**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Dimethanesulfonate* (2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**4a**). To a soln. of 2,3-*endo*-(*P**)-**3a** (40.0 mg, 0.123 mmol) in pyridine (1 ml), cooled at 0°, was added methanesulfonyl chloride (100 µl). The sealed flask was kept overnight in a refrigerator at 4°. The resultant mixture was poured into H_2O and extracted with Et_2O. The combined extracts were washed with brine and H_2O, dried (Na_2SO_4), and concentrated. The residue was filtered through SiO_2 with ^{t}BuOMe as eluent. The thus obtained orange foam (56 mg, 95%) consisted of the (*P**)- and (*M**)-epimers (by HPLC). Separation by prep. HPLC (*Spherisorb CN* (5 µm, 20 × 250 mm), hexane/(CH_2Cl_2 + 0.5% MeOH) 8:2, 14 ml/min) furnished 9.8 mg of 2,3-*endo*-(*P**)-**4a** and 31.6 mg of 2,3-*endo*-(*M**)-**4a**.

*Data of 2,3-*endo-*(*P**)-**4a***: Light yellow needles from ^{i}PrOH/hexane. M.p. 163.2–164.0°. R_f (AcOEt/hexane 3:2) 0.33. UV/VIS (EtOH): λ_{max} 393 (sh, 3.02), 326 (3.64), 277 (sh, 4.03), 250 (4.30), 212 (sh, 4.34); λ_{min} 311 (3.63), 231 (4.11). IR (KBr): 3034*m*, 2958*m*, 2871*m*, 1621*w*, 1461*m*, 1441*m*, 1412*m*, 1356*s*, 1337*s*, 1171*s*, 1080*s*, 981*s*, 926*s*, 871*s*, 836*s*, 534*s*, 518*s*. ^{1}H-NMR (300 MHz, C_6D_6; some tentative assignments): 6.205 (*d*, ^3J(5,6) = 6.5, H–C(5)); 6.071 (*dd*, ^3J(10,11) = 6.3, ^4J(11,Me–C(12)) = 1.3, H–C(11)); 5.991 (*d*, ^3J(10,11) ≈ 6.0, H–C(10)); 5.973 (*dd*, ^3J(5,6) = 6.3, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.586 (br. *s*, H–C(8)); 5.07, 4.97–4.93 (2*m*, H–C(1), H–C(2), H–C(3), H–C(4)); 2.998, 2.992 (2*s*, 2 $MeSO_2$); 2.408 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.131 (*d*, ^4J(6,Me–C(7)) = 1.2, Me–C(7)); 2.115 (br. *s*, Me–C(12)); 1.073, 1.040 (2*d*, ^3J = 6.9, Me_2CH–C(9)). CI-MS (NH_3): 498 (100, $[M+NH_4]^+$), 481 (81, $[M+H]^+$).

*Data of 2,3-*endo-*(*M**)-**4a***: Orange foam. R_f (AcOEt/hexane 3:2) 0.33. ^{1}H-NMR (300 MHz, $CDCl_3$; some tentative assignments): 6.170 (*d*, ^3J(5,6) = 6.8, H–C(5)); 6.145 (superimposed *dd*, ^3J(10,11) ≈ 6.6, ^4J(11,Me–C(12) = 1.5, H–C(11)); 6.075 (*dd*, ^3J(5,6) = 6.6, ^4J(6,Me–C(7) = 1.4, H–C(6)); 5.979 (br. *d*, ^3J(10,11) ≈ 6.6, H–C(10)); 5.667 (*d*, ^4J(8,10) = 1.2, H–C(8)); 5.12–5.07, 4.90–4.86 (2*m*, H–C(1), H–C(2), H–C(3), H–C(4)); 3.097, 3.035 (2*s*, 2 $MeSO_2$); 2.393 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.153 (*d*, ^4J(6,Me–C(7)) = 1.2, Me–C(7)); 2.042 (br. *s*, Me–C(12)); 1.070, 1.043 (2*d*, ^3J = 6.9, Me_2CH–C(9)).

The thermal equilibrium mixture consisted of 72% of the (*P**)- and 28% of the (*M**)-epimer at r.t.

1.1.1.3. *9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene* (**5a**). Small pieces of Na metal (0.313 g, 13.6 mmol) were added to a soln. of anthracene (2.40 g, 13.5 mmol) in THF (40 ml). The mixture was stirred for 20 min (→ clear dark blue soln. of sodium anthracenide). An aliquot of this soln. (13 ml) was added at 0° to a soln. of crude dimethanesulfonate **4a** (0.330 g, 0.55 mmol) in THF (10 ml). After stirring for 30 min, the mixture was poured into H_2O and extracted with Et_2O. The combined org. layer was dried ($MgSO_4$) and the solvent evaporated. The crude product was purified by CC (SiO_2, hexane/Et_2O 19:1) followed by recrystallization from hexane: **5a** (0.123 g, 66%). Light yellow crystals. M.p. 94.4–95.4° ([9]: light yellow oil). R_f (hexane/Et_2O 9:1) 0.51. UV/VIS (hexane): λ_{max} 387 (sh, 2.68), 327 (3.62), 283 (sh, 4.09), 258 (4.37), 210 (4.44); λ_{min} 309 (3.55), 237 (4.22). HPLC/CD (*Chiralcel-OD-H*, 4.6 × 250 mm, hexane, 0.5 ml/min; $t_R(M)/t_R(P)$ = 1.29); extrema of the (*M*)-enantiomer: 334 (0.30), 293 (0), 280 (sh, −0.08), 249 (−0.88), 239 (−0.75), 229 (−1.00), 214 (0), 203 (0.40). IR (KBr): 3012*m*, 2957*s*, 2913*m*, 2862*m*, 1639*w*, 1576*w*, 1480*m*, 1446*m*, 1372*m*, 1294*w*, 1193*w*, 1033*m*, 1000*m*, 968*m*, 790*s*, 754*s*. ^{1}H-NMR (300 MHz, C_6D_6): 7.19–6.97 (*m*, H–C(1), H–C(2), H–C(3), H–C(4)); 6.820 (*d*, ^3J(5,6) = 11.7, H–C(5)); 6.386 (*d*, ^3J(10,11) = 11.8, H–C(11)); 6.309 (*dd*, ^3J(10,11) = 11.8, ^4J(8,10) ≈ 1, H–C(10)); 6.187 (*d*, ^3J(5,6) = 11.6, H–C(6)); 5.683 (br. *s*, H–C(8)); 2.409 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.632 (*d*, ^4J(6,Me–C(7)) = 0.9, Me–C(7)); 1.608 (*s*, Me–C(12)); 1.083, 1.068 (2*d*, ^3J = 6.9, Me_2CH–C(9)). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.25 (*m*, 3 arom. H, H–C(2), H–C(3), H–C(4)); 7.006 (br. *d*, ^3J(1,2) = 7.4, H–C(1)); 6.840 (*d*, ^3J(5,6) = 11.7, H–C(5)); 6.436 (*d*, ^3J(10,11) = 11.8, H–C(11)); 6.364 (*dd*,

Table 8. *Crystallographic Data for Compounds 2,3*-endo-*(*P**)*-**3a**, *3*-endo-*(*P**)*-**15a**, *3*-endo-*(*M**)*-**15a**, **26b**, *and* **31b**

	2,3-*endo*-(*P**)-**3a**	3-*endo*-(*P**)-**15a**	3-*endo*-(*M**)-**15a**	2,3-*exo*-(*M**)-**26b**	**31b**
Crystallized from	Et_2O/hexane	hexane/CH_2Cl_2	hexane/CH_2Cl_2	hexane/Et_2O	CH_2Cl_2/hexane
Empirical formula	$C_{21}H_{24}O_3$	$C_{24}H_{25}NO_3$	$C_{24}H_{25}NO_3$	$C_{26}H_{24}O_4S$	$C_{28}H_{28}O_4S$
M_r	324.42	375.47	375.47	432.53	460.59
Crystal color, habit	orange, plate	red, prism	orange, prism	yellow, plate	yellow, needle
Crystal dimensions [mm]	0.05 × 0.12 × 0.25	0.17 × 0.20 × 0.25	0.20 × 0.25 × 0.32	0.05 × 0.12 × 0.25	0.02 × 0.05 × 0.25
Temperature [K]	160(1)	160(1)	160(1)	160(1)	160(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2c$ (#15)
Z	4	4	4	4	8
Reflections for cell determination	4170	6109	6244	23344	62903
2θ range for cell determination [°]	4 – 55	4 – 60	4 – 60	4 – 55	4 – 50
Unit cell parameters a [Å]	18.4782(5)	14.1263(2)	14.6726(2)	15.1743(2)	27.1387(3)
b [Å]	9.5121(3)	13.1295(2)	8.0795(1)	8.2236(1)	7.7951(1)
c [Å]	9.8716(3)	11.0883(2)	17.3376(2)	17.2425(3)	25.9228(3)
β [°]	96.182(2)	102.3691(7)	102.3420(5)	97.3742(6)	120.3018(5)
V [Å^3]	1725.01(9)	2008.82(6)	2007.82(4)	2133.85(5)	4734.7(1)
$F(000)$	696	800	800	912	1952
D_x [g·cm^{-3}]	1.249	1.241	1.242	1.346	1.292
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.0820	0.0813	0.0813	0.183	0.169
Scan type	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	55	60	60	55	50
Transmission factors (min, max)	–	–	–	0.930, 0994	0.924, 0.997
Total reflections measured	35610	51715	55695	47232	41445
Symmetry-independent reflections	3947	5870	5859	4872	4179
R_{int}	0.076	0.049	0.047	0.079	0.085
Reflections with $I > 2\sigma(I)$	2729	4349	4686	3558	3091
Reflections used in refinement	3945	5868	5854	4869	4179
Parameters refined	260	323	259	285	305
Restraints	70	177	0	0	0
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0547	0.0458	0.0432	0.0428	0.0418
$wR(F^2)$ (all data)	0.1345	0.1239	0.1191	0.1140	0.1031
Weighting parameters[a]) (a, b)	0.0482, 1.0239	0.0566, 0.5188	0.0563, 0.4413	0.0575, 0.5687	0.0389, 6.3093
Goodness of fit	1.019	1.048	1.043	1.029	1.028
Secondary extinction coeff.	0.012(2)	0.009(2)	0.012(2)	0.006(1)	0.0010(1)
Final Δ_{max}/σ	0.001	0.001	0.001	0.001	0.001
$\Delta\rho$ (max, min) [e Å^{-3}]	0.39, −0.33	0.29, −0.30	0.28, −0.23	0.26, −0.41	0.23, −0.32

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

$^3J(10,11) = 11.8$, $^4J(8,10) = 1.3$, H–C(10)); 6.246 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 5.705 (br. *s*, H–C(8)); 2.560 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 1.715 (*d*, $^4J(6,Me–C(7)) = 0.9$, Me–C(7)); 1.615 (*s*, Me–C(12)); 1.160, 1.146 (2*d*, $^3J = 6.9$, Me_2CH–C(9)). EI-MS: 274 (100, $M^{+\bullet}$), 259 (34, $[M - Me]^+$), 244 (11, $[M - 2\,Me]^{+\bullet}$), 234 (54, $[M - Me - C\equiv CH]^{+\bullet}$), 229 (23), 215 (29), 206 (25, $[M - {}^iPr - C\equiv CH]^{+\bullet}$), 202 (21).

1.1.1.4. *(*P**,1*S**,2*R**,3*S**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Carbonothioate* (2,3-*endo*-(*P**)-**6a**). To a soln. of 2,3-*endo*-**2a** (0.123 g, 0.378 mmol) in THF (4 ml) in an ice bath, *ca*. 2.5M BuLi in hexane (0.30 ml, *ca*. 0.75 mmol) was added in drops. After stirring for 5 min, solid di(1*H*-imidazol-1-yl)methanethione (*Fluka pract.*; 0.110 g, 0.617 mmol) was added. The resulting mixture was heated under reflux for 30 min, then poured into half-conc. brine, and extracted with Et_2O (3×). The combined org. layer was dried ($MgSO_4$) and the solvent evaporated. The residue was filtered through a short column (SiO_2/Et_2O). Pure 2,3-*endo*-(*P**)-**6a** (70.5 mg) was obtained in orange platelets from an Et_2O/hexane soln. The mother liquor yielded, after CC (SiO_2, Et_2O/hexane 4:1) and recrystallization, a second crop of crystals (13.7 mg). Total yield: 84.2 mg (61%). Light red crystals. M.p. 176–177°. R_f (AcOEt/hexane 3:2) 0.47. UV/VIS (EtOH): λ_{max} 410 (sh, 2.93), 337 (3.69), 277 (sh, 4.09), 245 (4.45), 214 (4.38); λ_{min} 307 (3.60), 226 (4.32), 208 (4.37). IR (KBr): 2956*s*, 2868*w*, 1801*w*, 1609*w*, 1445*w*, 1339*s*, 1302*s*, 1268*s*, 1244*s*, 1143*s*, 1046*s*, 1029*s*, 994*m*, 885*m*, 843*m*, 831*m*, 590*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.153 (*dd*, $^3J(10,11) = 6.6$, $^4J(11,Me–C(12)) = 1.3$, H–C(11)); 6.078 (*dd*, $^3J(5,6) = 6.9$, $^4J(6,Me–C(7)) = 1.2$, H–C(6)); 6.053 (*d*, $^3J(5,6) = 6.9$, H–C(5)); 5.994 (*d*, $^3J(10,11) = 6.6$, H–C(10)); 5.678 (br. *s*, H–C(8)); 5.213 (*m*, H–C(2), H–C(3)); 5.160 (*d*, $^3J(3,4) = 3.6$, H–C(4)); 5.008 (*d*, $^3J(1,2) = 3.3$, H–C(1)); 2.394 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.130 (*d*, $^4J(6,Me–C(7)) = 0.8$, Me–C(7)); 2.027 (br. *s*, Me–C(12)); 1.071, 1.043 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments of the signals were verified by NOE. CI-MS (NH_3): 367 (100, $[M + H]^+$), 291 (10).

1.1.1.5. (P**,1*R**,4*S**)- *and* (M**,1*R**,4*S**)-*1,4-Dihydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene* ((*P**)- and (*M**)-**7a**). A *Schlenk* tube was charged under Ar with the carbonothionoate 2,3-*endo*-(*P**)-**6a** (35.4 mg, 0.097 mmol) and triethyl phosphite (0.7 ml), sealed, and heated in an oil bath for 4 d at 165°. After cooling to r.t., the product mixture was directly purified by CC (SiO_2, hexane/^{t}BuOMe 7:3): **7a** (20.7 mg, 74%). Yellow oil consisting of 73% of the (*P**)- and 27% of the (*M**)-epimer (by ^{1}H-NMR, see below).

*Data of (*M**)-***7a***: R_f (*M**) ≈ R_f (*P**)* (^{t}BuOMe/hexane 3:2) 0.47. ^{1}H-NMR (300 MHz, $CDCl_3$; 27% in the mixture): 6.482 (*t*-like, $^3J = 6.8$, H–C(2), H–C(3)); 6.123 (*d*, $^3J(5,6) = 6.6$, H–C(5)); 5.974 (superimposed *dd*, $^3J(10,11) \approx 6.3$, $^4J(11,Me–C(12)) = 1.3$, H–C(11)); 5.922 (superimposed *d*, $^3J(10,11) \approx 6.3$, H–C(10)); 5.974 (superimposed *dq*, $^3J(5,6) \approx 6.6$, H–C(6)); 5.884 (br. *s*, H–C(8)); 5.334, 5.143 (2 br. *s*, H–C(1), H–C(4)); 2.309 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.132 (br. *s*, Me–C(12)); 2.107 (*d*, $^4J(6,Me–C(7)) = 1.1$, Me–C(7)); 1.001, 0.978 (2*d*, $^3J = 6.9$, Me_2CH–C(9)).

*Data of (*P**)-***7a***: IR ($CHCl_3$) of the mixture: 3009*s*, 2968*s*, 2933*m*, 2874*m*, 1705*m*, 1613*m*, 1463*m*, 1376*m*, 1291*m*, 1003*m*, 886*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; 73% in the mixture): 6.606 (*dd*, $^3J(2,3) = 5.5$, $^4J = 1.7$) and 6.556 (*dd*, $^3J(2,3) = 5.6$, $^4J = 1.5$, H–C(2), H–C(3)); 6.087 (*dq*, $^3J(10,11) = 6.5$, $^4J(11,Me–C(12)) = 1.5$, H–C(11)); 5.964 (br. *d*, $^3J(5,6) = 6.7$, H–C(5)); 5.921 (br. *d*, $^3J(10,11) = 6.5$, H–C(10)); 5.840 (*dq*, $^3J(5,6) = 6.7$, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 5.637 (*d*, $^4J(8,10) = 1.2$, H–C(8)); 5.203, 5.177 (2 br. *s*, H–C(1), H–C(4)); 2.362 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.104 (*d*, $^4J(6,Me–C(7)) = 1.3$, Me–C(7)); 2.132 (br. *s*, Me–C(12)); 1.070, 1.044 (2*d*, $^3J = 6.9$, Me_2CH–C(9)). GC-MS: 290 (100, $M^{+\bullet}$), 250 (58, $[M - Me - C\equiv CH]^{+\bullet}$), 235 (42, $[M - (Me + Me - C\equiv CH)]^+$), 222 (42, $[M - {}^iPr - C\equiv CH]^{+\bullet}$).

1.1.1.6. *9-Isopropyl-7,12-dimethylbenzo[*a*]heptalen-4-ol* (**8a**). A *Schlenk* tube was charged under Ar with the above described mixture **7a** (20.7 mg) and *Amberlyst 15* (*Fluka*; H^+-form, 20–50 mesh; 25 mg) in cyclohexane (1 ml), sealed, and heated in an oil bath for 2 h at 90°. After cooling to r.t., the product mixture was filtered and purified by CC (SiO_2, hexane/^{t}BuOMe 3:2): **8a** (9.7 mg, 47%) as a yellow oil. Further purification by prep. HPLC (*Spherisorb CN* (5 μm, 20 × 250 mm), 2% ^{i}PrOH/hexane) furnished spectroscopically clean **8a** (5.3 mg, 26%). Yellow oil. R_f (hexane/^{t}BuOMe 7:3) 0.23. UV/VIS (hexane/EtOH 99:1): λ_{max} 302 (3.96), 255 (4.23), 216 (4.37); λ_{min} 286 (3.88), 238 (4.16). IR ($CHCl_3$): 3596*m*, 3313*w*, 2963*s*, 2928*s*, 2858*m*, 1599*w*, 1565*m*, 1459*s*, 1376*w*, 1277*m*, 988*w*, 848*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.236 (*t*, $^3J = 7.8$, H–C(2)); 7.040 (*d*, $^3J(5,6) = 11.8$, H–C(5)); 6.733 (*dd*, $^3J(2,3) = 7.9$, $^4J(3,OH–C(4)) = 1.1$, H–C(3)); 6.591 (*d*, $^3J(1,2) = 7.7$, H–C(1)); 6.426 (*d*, $^3J(10,11) = 11.8$, H–C(11)); 6.354

(*dd*, $^3J(10,11) = 11.8$, $^4J(8,10) = 1.3$, H–C(10)); 6.325 (*d*, $^3J(5,6) = 11.8$, H–C(6)); 5.712 (br. *s*, H–C(8)); 4.922 (br. *s*, OH–C(4)); 2.551 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 1.707 (*d*, $^4J(6,Me–C(7)) = 0.7$, Me–C(7)); 1.656 (*s*, Me–C(12)); 1.152, 1.140 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 290 (100, $M^{+\bullet}$), 275 (34, $[M - Me]^+$), 250 (53, $[M - Me–C\equiv CH]^{+\bullet}$), 235 (25, $[M - (Me + Me–C\equiv CH)]^+$), 222 (16, $[M - {}^i Pr–C\equiv CH]^{+\bullet}$), 202 (13), 169 (39).

1.1.2. *(*P*,1*S**,2*R**,3*S**,4*R**)-, (*P*,1*S**,2*S**,3*R**,4*R**), and (*M*,1*S**,2*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Carbonate* (2,3-*endo*-(*P**)-, 2,3-*exo*-(*P**)-, and 2,3-*exo*-(*M**)-**2b**). A *Schlenk* tube was charged under Ar with heptaleno[1,2-*c*]furan **1b** (0.106 g, 0.421 mmol) and VC (0.255 g, 2.96 mmol) in *o*-xylene (2.5 ml), sealed, and heated in an oil bath for 40 h at 150°. After evaporation of the solvent, the residue was purified by CC (SiO_2, ^{t}BuOMe/hexane 3:2). A first fraction (32.3 mg) was purified a second time in the same manner, yielding 24.1 mg of crystalline material, which was recrystallized from ^{t}BuOMe/hexane to give finally pure 2,3-*exo*-(*M**)-**2b** (16.6 mg) as orange crystals. A second fraction gave, after recrystallization (Et_2O/hexane), pure 2,3-*exo*-(*P**)-**2b** (23.5 mg) as orange crystals. A third fraction was also purified by recrystallization from Et_2O/hexane to give pure 2,3-*endo*-(*P**)-**2b** (68.0 mg) as yellow crystals. The total yield of crystalline material amounted to 76%, whereby the mother liquor of the first two fractions still contained 14.5 mg of products.

Data of 2,3-exo-*(*P**)*-**2b**: M.p. 251.8–252.7°. R_f (^{t}BuOMe/hexane 7:3) 0.33. UV/VIS (EtOH): λ_{max} 388 (sh, 2.86), 316 (3.64), 276 (sh, 4.02), 257 (4.31), 246 (sh, 4.26); λ_{min} 297 (3.61), 228 (4.12). IR (KBr): 2937*m*, 2915*m*, 1792*s*, 1435*m*, 1366*s*, 1158*s*, 1074*s*, 992*m*, 936*m*, 841*m*, 799*m*, 768*m*, 712*m*, 627*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, some tentative assignments): 6.226 (*d*, $^3J(5,6) = 6.9$, H–C(5)); 6.161 (*dd*, $^3J(5,6) = 6.5$, $^4J(6,Me–C(7)) = 1.0$, H–C(6)); 6.13–6.05 (*m*, H–C(9), H–C(11)); 5.035 (br. *s*, H–C(1)); 4.870 (br. *s*, H–C(4)); 4.716, 4.679 (2*d*, $^3J(2,3) = 6.0$, H–C(2), H–C(3)); 2.00–1.97 (*m*, Me–C(7), Me–C(10), Me–C(12)); 1.711 (*s*, Me–C(8)). CI-MS (NH_3): 354 (100, $[M + NH_4]^+$), 337 (9, $[M + H]^+$). EI-MS: 336 (80, $M^{+\bullet}$), 250 (50, $[M - VC]^{+\bullet}$), 235 (100, $[M - (VC + Me)]^+$), 210 (69, $[M - (VC + Me–C\equiv CH)]^{+\cdot}$), 196 (36), 165 (27).

Data of 2,3-endo-*(*P**)*-**2b**: M.p. 205.5–206.8°. R_f (^{t}BuOMe/hexane 7:3) 0.25. UV/VIS (hexane): λ_{max} 388 (sh, 2.73), 318 (3.62), 256 (4.32), 246 (sh, 4.28), 213 (sh, 4.25), 202 (4.33); λ_{min} 295 (3.57), 229 (4.12). HPLC/UV/VIS (5% ^{i}PrOH/hexane): λ_{max} 319 (0.23; with a long tailing up to >400), 255 (1.00), 216 (0.83); λ_{min} 296 (0.20), 229 (0.69). IR (KBr): 2977*m*, 2934*m*, 2911*m*, 2853*w*, 1793*s*, 1620*w*, 1439*m*, 1361*m*, 1339*m*, 1136*s*, 1078*s*, 909*w*, 835*m*, 608*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.281 (*dd*, $^3J(5,6) = 6.5$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 6.224 (*d*, $^3J(5,6) = 6.5$, H–C(5)); 6.113 (br. *s*, H–C(9)); 6.067 (*quint.*-like, H–C(11)); 5.141 (*d*, $^3J(1,2) = 2.8$, H–C(1)); 5.041 (*t*-like, $^3J(3,4) = 2.5$, $^4J(4,5) \approx 1.2$, H–C(4)); 4.96 (*quint.*-like with sidebands, $^3J(2,3) \approx 8.4$, H–C(2), H–C(3)); 2.008 (*d*, $^4J(11,Me–C(12)) = 1.2$, Me–C(12)); 1.98 (br. *s*, Me–C(7), Me–C(10)); 1.725 (*s*, Me–C(8)). CI-MS (NH_3): 354 (100, $[M + NH_4]^+$), 337 (53, $[M + H]^+$), 293 (41, $[(M + H) - CO_2]^+$), 277 (29, $[(M + H) - (CO_2 + O)]^+$). EI-MS: 336 (100, $M^{+\bullet}$), 250 (43, $[M - VC]^{+\bullet}$), 235 (84, $[M - (VC + Me)]^+$), 210 (63, $[M - (VC + Me–C\equiv CH)]^{+\bullet}$), 196 (39), 165 (16).

Data of 2,3-exo-*(*M**)*-**2b**: M.p. 199.1–200.0°. R_f (^{t}BuOMe/hexane 7:3) 0.38. UV/VIS (hexane): λ_{max} 382 (sh, 2.82), 308 (3.62), 256 (4.240), 249 (4.237), 214 (sh, 4.25), 203 (4.37); λ_{min} 297 (3.61), 252 (4.236), 233 (4.08). IR (KBr): 3010*w*, 2946*m*, 2916*m*, 2862*w*, 1804*s*, 1443*m*, 1363*m*, 1158*s*, 1074*s*, 833*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.335 (*d*, $^3J(5,6) = 6.1$, H–C(5)); 6.113 (*dd*, $^3J(5,6) = 6.1$, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 6.046 (br. *s*, H–C(9)); 6.006 (br. *s*, H–C(11)); 5.041 (*s*, H–C(1)); 4.859, (*s*, H–C(4)); 4.807 (*d*, $^3J(2,3) = 5.9$, H–C(3)); 4.365 (*d*, $^3J(2,3) = 5.9$, H–C(2)); 2.075 (*d*, $^4J(11,Me–C(12)) = 1.2$, Me–C(12)); 2.004 (*d*, $^4J(6,Me–C(7)) = 1.2$, Me–C(7)); 1.976 (*d*, $^4J(9,Me–C(10)) = 1.2$, Me–C(10)); 1.660 (*s*, Me–C(8)); assignments were verified by NOE. CI-MS (NH_3): 354 (100, $[M + NH_4]^+$), 337 (7, $[M + H]^+$), 293 (7, $[(M + H) - CO_2]^+$), 277 (3, $[(M + H) - (CO_2 + O)]^+$). EI-MS: 336 (100, $M^{+\bullet}$), 250 (59, $[M - VC]^{+\bullet}$), 235 (97, $[M - (VC + Me)]^+$), 210 (58, $[M - (VC + Me–C\equiv CH]^{+\bullet}$), 196 (33), 165 (17).

1.1.2.1. *(*P*,1*S**,2*S**,3*R**,4*R**)- and (*M*,1*S**,2*R**,3*S**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol* (2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**3b**). To 5% KOH in MeOH (0.5 ml) was added 2,3-*endo*-(*P**)-**2b** (12 mg, 0.0357 mmol). The mixture was stirred at r.t. until a clear soln. resulted (after *ca.* 30 min). The soln. was poured into H_2O and extracted with Et_2O. The combined Et_2O extracts were washed with half-conc. brine, dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, ^{t}BuOMe/hexane 9:1): yellow oil (10.4 mg, 94%) consisting of 56% of 2,3-*endo*-

(*P**)- and 44% of 2,3-*endo*-(*M**)-**3b** (by ^{1}H-NMR). If the hydrolysis of 2,3-*endo*-(*P**)-**2b** was carried out in a *Schlenk* tube at 80° for 2 h, the same product ratio in the same yield was obtained. Prep. HPLC (*Spherisorb CN* (5 μm, 20 × 250 mm), 4% ^{i}PrOH/hexane) furnished the main epimer 2,3-*endo*-(*P**)-**3b** as light yellow crystals after crystallization from Et_2O/hexane.

Data of 2,3-endo-*(*P**)-**3b**: M.p. 191.2–192.0°. R_f (^{t}BuOMe/hexane 9:1) 0.25. UV/VIS (EtOH): λ_{max} 381 (sh, 2.80), 319 (3.64), 254 (4.32), 212 (sh, 4.27); λ_{min} 294 (3.58), 230 (4.13). IR (KBr): 3395*s*, 2969*s*, 2937*s*, 2911*s*, 2853*m*, 1656*m*, 1622*m*, 1437*s*, 1376*s*, 1149*s*, 1108*s*, 1033*s*, 981*s*, 918*m*, 840*s*, 794*s*, 607*m*, 575*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.212 (*dd*, $^3J(5,6) = 6.3$, $^4J(6,Me-C(7)) = 1.3$, H–C(6)); 6.165 (*d*, $^3J(5,6) = 6.3$, H–C(5)); 6.091 (br. *s*, H–C(9)); 6.041 (*t*, $^4J(11,Me-C(12)) = 1.3$, H–C(11)); 4.85 (2 superimp. *d* to *t*-like, $\Sigma(^3J(1,2) + {}^3J(3,4)) \approx 7.2$, H–C(1), H–C(4)); 4.09–4.22 (*m*, superimp. signals of H–C(2), H–C(3))[12]); 2.043 (*d*, $^4J(11,Me-C(12)) = 1.3$, Me–C(12)); 2.021 (*d*, $^4J(6,Me-C(7)) = 1.2$, Me–C(7)); 1.968 (*d*, $^4J(9,Me-C(10)) = 1.2$, Me–C(10)); 1.961 (*d*, $^3J = 9.1$, OH–C(2 or 3)); 1.769 (*d*, $^3J = 6.0$, OH–C(3 or 2)); 1.727 (*s*, Me–C(8)). CI-MS (NH_3): 328 (15, $[M + NH_4]^+$), 311 (100, $[M + H]^+$), 251 (24).

Data of 2,3-endo-*(*M**)-**3b**: R_f (^{t}BuOMe/hexane 9:1) 0.25. HPLC/UV/VIS (5% ^{i}PrOH/hexane): λ_{max} 307 (0.24; with a long tailing up to >400), 255 (1.00), 215 (0.88); λ_{min} 297 (0.35), 231 (0.64). ^{1}H-NMR (300 MHz, $CDCl_3$; mixture with 46% of the (*P**)-form): 6.34 (*d*, $^3J(6,5) = 6.2$, H–C(5)); 6.13 (*dd*, $^3J(6,5) = 6.2$, $^4J(6,Me-C(7)) = 1.3$, H–C(6)); 6.12 (br. *s*, H–C(9)); 6.021 (*t*-like, $^4J(11,Me-C(12)) = 1.3$, H–C(11)); 4.97 (*d*, $^3J(1,2) = 5.0$ H–C(1)); 4.78 (*d*, $^3J(4,3) = 4.6$, H–C(4)); 4.05 (center of two *dd*, $^3J(2,3) = 8.3$, H–C(2), H–C(3))[13]); 2.07 (*d*, $^4J(11,Me-C(12)) = 1.2$, Me–C(12)); 2.02 (br. *s*, Me–C(7) of (*M**)- and (*P**)-form); 1.97 (br. *s*, Me–C(10) of (*M**)- and (*P**)-form)); 1.69 (*s*, Me–C(8)); signals of OH–C(2) and OH–C(3) at 2.04–1.95 not clearly assignable.

1.1.2.2. *1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Dimethanesulfonate* (**4b**). A mixture of the isomers of **2b** (96.5 mg, 0.287 mmol) was added to 5% KOH in MeOH (5 ml). The mixture was stirred at r.t. until a clear soln. resulted (after *ca.* 30 min). The usual workup procedure delivered **3b** as a yellow-to-orange foam, which was dissolved in pyridine (2.5 ml). The soln. was cooled to 0°, and methanesulfonyl chloride (150 μl) was added. The mixture was stirred at 0° for 1 h and then poured into H_2O and extracted with Et_2O. The combined extracts were washed with brine and H_2O, dried (Na_2SO_4), and concentrated. The residue was filtered through a short column (SiO_2, Et_2O), which led, after drying *in vacuo*, to a yellow oil of the isomer mixture **4b**. R_f (AcOEt/hexane 3:2) 0.32.

1.1.2.3. *7,8,10,12-Tetramethylbenzo[*a*]heptalene* (**5b**). Sodium anthracenide was prepared as described for **5a** by stirring a soln. of anthracene (1.2 g, 6.73 mmol) in THF (20 ml) and Na metal (0.155 g, 6.73 mmol) for 3 h. An aliquot of this dark blue soln. (5 ml) was added in drops to a cold soln. (0°) of the crude dimethanesulfonate **4b** in THF (3 ml). After stirring for 30 min, the mixture was poured into H_2O and extracted with hexane (3×). The combined org. layer was washed twice with brine and dried ($MgSO_4$), the solvent evaporated, and the residue purified by CC (SiO_2, hexane/Et_2O 19:1) to give a yellow oil which was contaminated by anthracene. Purification by prep. HPLC (*Spherisorb CN* (5 μm, 20 × 250 mm), hexane) furnished **5b** (43.0 mg, 58% rel. to **2b**). The light yellow oil which solidified on standing was recrystallized from pentane at −20°. Light yellow crystals. M.p. 126.5–127.5°. R_f (hexane/Et_2O 19:1) 0.45. UV/VIS (hexane): λ_{max} 321 (3.55), 281 (sh, 4.14), 248 (4.32), 219 (4.46); λ_{min} 307 (3.52), 238 (4.29). HPLC/CD (*cf. Fig. 8*, *a*; *Chiralcel-OD-H* (4.6 × 250 mm), hexane, 0.6 ml/min; $t_R(M)/t_R(P)$ 1.32); extrema of the (*P*)-enantiomer: 329 (−0.32), 288 (0), 281 (sh, 0.04), 248 (sh, 0.66), 231 (1.00), 215 (0), 208 (−0.15). IR (KBr): 3014*m*, 2965*s*, 2936*s*, 2911*s*, 2853*m*, 1645*w*, 1616*w*, 1501*w*, 1475*m*, 1432*s*, 1373*m*, 1025*m*, 1009*m*, 839*s*, 791*s*, 762*s*, 739*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37 (*td*, $J_o = 7.6$, $J_m = 1.3$, H–C(2)); 7.33 (*dd*-like, $J_o = 7.1$, $J_m = 1.5$, H–C(4)); 7.279 (*td*, $J_o = 7.5$, $J_m = 1.3$, H–C(3)); 6.97 (*ddd*-like, $J_o = 7.6$, $J_m = 1.2$, $J_p \approx 0.5$, H–C(1)); 6.871 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.248 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 6.184 (br. *s*, H–C(11)); 6.052 (br. *s*, H–C(9)); 2.029 (*d*, $^4J(Me-C(10),11) = 1.2$, Me–C(10)); 1.924 (*d*, $^4J(Me-C(8),9) = 1.2$, Me–C(8)); 1.742 (*s*, Me–C(7)); 1.594 (*s*, Me–C(12)); assignments were verified by NOESY. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 138.02 (C(10)); 137.64 (C(7a)); 137.57 (C(12b)); 137.25

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[12]) On treatment with D_2O, the two superimposed signals simplified to a *sext.*-like signal with $^3J(2,3) = 8.1$.

[13]) After OH exchange with D_2O in $CDCl_3$.

(C(4a)); 133.76 (C(8)); 132.92 (C(6)); 132.08 (C(5)); 131.17 (C(12a)); 130.78 (C(11)), 130.12 (C(12)); 128.80 (C(2)); 128.49 (C(4), C(9)); 128.31 (C(1)); 126.51 (C(3)); 126.46 (C(7)); 24.98 (*Me*–C(10)); 22.98 (*Me*–C(8)); 19.09 (*Me*–C(12)); 18.14 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 260 (100, $M^{+\cdot}$), 245 (86, $[M-\mathrm{Me}]^+$), 230 (22, $[M-2\,\mathrm{Me}]^{+\cdot}$), 220 (67, $[M-\mathrm{Me}-\mathrm{C}{\equiv}\mathrm{CH}]^{+\cdot}$)), 215 (35, $[M-3\,\mathrm{Me}]^+$), 206 (28), 189 (14).

1.1.2.4. *1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene-2,3-diol Carbonothioate* (**6b**). An isomer mixture **2b** (0.160 g, 0.515 mmol) was dissolved in THF (4 ml), cooled to 0°, and treated with 2.5M BuLi in hexane (0.5 ml). Di(1*H*-imidazol-1-yl)methanethione (0.151 g, 0.845 mmol) was added. The resulting mixture was heated under reflux for 30 min and then worked up as described for 2,3-*endo*-**6a**. Purification of the crude product by CC (SiO_2, AcOEt/hexane 1:1) yielded an isomer mixture **6b** (0.122 g, 67%) as a yellow oil. R_f (AcOEt/hexane 3:2) 0.49.

1.1.2.5. (P*,1R*,4S*)- *and* (M*,1R*,4S*)-*1,4-Dihydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalene* ((*P**)- and (*M**)-**7b**). A *Schlenk* tube was charged under Ar with the crude carbonothioate **6b** (0.122 g) and triethyl phosphite (2 ml), sealed, and heated in an oil bath at 160° for 24 h and then for a further 24 h at 170°. After cooling to r.t., the product mixture was purified by CC (SiO_2, hexane/^{t}BuOMe 7:3): **7b** (65 mg, 68%). Unstable yellow oil, consisting of a 2:1 mixture of the (*P**)- and the (*M**)-epimers (by ^{1}H-NMR).

*Data of (*P**)*-**7b**: HPLC/UV/VIS (hexane/^{i}PrOH 98:2): λ_{max} 313 (0.27), 260 (0.98), 218 (1.00); λ_{min} 302 (0.26), 231 (0.78). ^{1}H-NMR (300 MHz, $CDCl_3$, in presence of 33% of the (*M**)-epimer): 6.653 (*dd*, $^3J(2,3)=5.6$, ^3J(1,2 or 3,4) = 2.1) and 6.596 (*dd*, $^3J(2,3)=5.6$, ^3J(3,4 or 1,2) = 1.6, H–C(2), H–C(3)); 6.134 (*d*, $^3J(5,6)=6.3$, H–C(5)); 6.1–6.0 (*m*, H–C(6), H–C(9), H–C(11)); 5.227 (br. *s*, H–C(1), H–C(4)); 1.98 (*d*, ^4J(11,Me–C(12)) = 1.2, Me–C(12)); 1.96 (*d*-like, Me–C(7), Me–C(10)); 1.708 (*s*, Me–C(8)).

*Data of (*M**)*-**7b**: HPLC/UV/VIS (hexane/^{i}PrOH 98:2): λ_{max} 306 (sh, 0.23), 254 (0.88), 244 (sh, 0.87), 217 (1.0); λ_{min} 229 (0.82). ^{1}H-NMR (300 MHz, $CDCl_3$; in presence of 67% of the (*P**)-epimer): 6.532 (*dd*, $^3J(2,3)=5.6$, ^3J(1,2 or 3,4) = 1.7) and 6.447 (*dd*, $^3J(2,3)=5.6$, ^3J(3,4 or 1,2) = 1.8, H–C(2), H–C(3)); 6.271 (*d*, $^3J(5,6)=6.3$, H–C(5)); 6.1–6.0 (superimp., H–C(6)); 5.931 (br. *s*, H–C(9 or 11)); 5.906 (*quint.*-like, H–C(11 or 9)); 5.346 (*m*, H–C(1 or 4)); 5.176 (br. *s*, H–C(1 or 4)); 2.100 (*d*, ^4J(11,Me–C(12)) = 1.3, Me–C(12)); 2.00 (*d*, ^4J(6,Me–C(7)) = 1.3, Me–C(7)); 1.928 (*d*, ^4J(9,Me–C(10)) = 1.3, Me–C(10)); 1.668 (*s*, Me–C(8)).

1.1.2.6. *7,8,10,12-Tetramethylbenzo[*a*]heptalen-4-ol* (**8b**). A *Schlenk* tube was charged under Ar with the 2:1 epimer mixture **7b** (30 mg, 0.108 mmol) and *Amberlyst 15* (25 mg) in cyclohexane (1.5 ml), sealed, and heated in an oil bath at 80° for 1.5 h. After cooling to r.t., the mixture was purified by CC (SiO_2, hexane/^{t}BuOMe 3:2): **8b** (13.7 mg, 46%). The filthy yellow solid was further purified by recrystallization from pentane/small amounts of Et_2O: brownish-yellow crystals of **8b** (9.3 mg, 31%). M.p. 196–202°. R_f (hexane/^{t}BuOMe 4:1) 0.19. UV/VIS (hexane): λ_{max} 365 (sh, 2.97), 325 (sh, 3.62), 295 (4.10), 252 (4.29), 220 (4.46), 196 (4.36); λ_{min} 279 (4.02), 239 (4.25), 200 (4.33). HPLC/CD (*cf. Fig. 8*, *b*; *Chiralcel-OD-H* (4.6 × 250 mm), 2% ^{i}PrOH/hexane, 0.8 ml/min; $t_R(M)/t_R(P)$ 1.19); extrema of the (*P*)-enantiomer: *ca.* 352 (sh, −0.36), 337 (−0.43), *ca.* 300 (sh, −0.16), 281 (0), 254 (1.00), 235 (0.49), 220 (0.96), 208 (0). IR (KBr): 3520*s* (free OH), 3420*m* (sh, intermolecular bound OH), 2972*m*, 2933*s*, 2913*s*, 2855*m*, 1616*m*, 1596*m*, 1562*m*, 1457*s*, 1372*w*, 1314*s*, 1276*s*, 1259*s*, 1202*m*, 1053*m*, 1027*m*, 988*m*, 846*m*, 775*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.225 (*t*, $^3J \approx 7.8$, H–C(2)); 7.075 (*d*, $^3J(5,6)=11.9$, H–C(5)); 6.735 (*dd*, $^3J(2,3)=6.9$, $^4J=0.9$, H–C(3)); 6.555 (*d*, $^3J(1,2)=7.7$, H–C(1)); 6.325 (*d*, $^3J(5,6)=11.9$, H–C(6)); 6.178 (br. *s*, H–C(11)); 6.036 (br. *s*, H–C(9)); 4.915 (br. *s*, OH–C(4)); 2.025 (*d*, ^4J(9,Me–C(10)) = 1.0, Me–C(10)); 1.919 (*d*, ^4J(Me–C(8),9) = 1.1, Me–C(8)); 1.734 (*s*, Me–C(7)); 1.635 (*s*, Me–C(12)). EI-MS: 276 (100, $M^{+\cdot}$), 261 (86, $[M-\mathrm{Me}]^+$), 246 (42, $[M-2\,\mathrm{Me}]^{+\cdot}$), 236 (75, $[\mathrm{M}-\mathrm{Me}-\mathrm{C}{\equiv}\mathrm{CH}]^{+\cdot}$), 231 (20, $[M-3\,\mathrm{Me}]^+$), 222 (24), 202 (27).

1.1.2.7. *(*P**,1S**,2S**,3S**,4R**)-1,2,3,4-Tetrahydro-3-hydroxy-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalen-2-yl Diisopropylcarbamate* (2,3-*endo*-(*P**)-**9b**). LDA was generated in THF (0.8 ml) at −78° from diisopropylamine (60 mg, 0.593 mmol) and 2.5M BuLi in hexane (70 µl, 0.175 mmol). After 10 min, a soln. of 2,3-*endo*-(*P**)-**2b** (7.2 mg, 0.0214 mmol) in THF (0.5 ml) was added in drops. Stirring at −78° was continued for 1.5 h, then the cooling bath was removed and the temp. slowly raised to 0°. H_2O was added and the mixture extracted with Et_2O. After washing and drying, the residue of the Et_2O phase was

purified by CC (SiO_2, ^{t}BuOMe/hexane 4:1): 2,3-*endo*-(*P**)-**9b** (5.9 mg, 61%). The light yellow oil crystallized on heating at $>100°$. M.p. 178.2–180.4° (Et_2O/pentane). R_f (^{t}BuOMe/hexane 4:1) 0.40. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.21 (*d*, $^3J(5,6)=6.1$, H–C(5)); 6.20 (*dq*-like, $^3J(6,5)=6.1$, $^4J(6,Me–C(7))=1.2$, H–C(6)); 6.10 (br. *s*, H–C(9)); 6.02 (*quint.*-like, H–C(11)); 5.14 (*dd*, $^3J(2,3)=7.8$, $^3J(2,1)=5.0$, H–C(2)); 4.93 (*d*, $^3J(1,2)=5.0$, H–C(1)); 4.81 (*d*, $^3J(4,3)=5.0$, H–C(4)); 4.35 (*ddd*, $^3J(3,OH)=11.4$, $^3J(3,2)=7.8$, $^3J(3,4)=5.0$, H–C(3)); 3.86 (*sept.*-like, Me_2CHN); 3.63 (*sept.*-like, Me_2CHN); 1.98 (*d*, $^4J(Me–C(7),6)=1.0$, Me–C(7)); 1.96 (*d*, $^4J(Me–C(10),9)=1.1$, Me–C(10)); 1.95 (*d*, $^4J(Me–C(12),11)=1.2$, Me–C(12)); 1.73 (*s*, Me–C(8)); 1.66 (*d*, $^3J(OH–C(3),3)=11.4$, OH–C(3)); 1.24, 1.23 (*t*-like, Me_2CHN); 1.08, 1.03 (2*d*, Me_2CHN); assignments according to NOESY, which also indicate that ^{i}Pr(1)–N (3.86, 1.08, and 1.03) is *anti*-oriented with respect to O–C(3) and ^{i}Pr(2)–N (3.63, 1.24, and 1.23) *syn*-oriented. ^{13}C-NMR (150 MHz, $CDCl_3$): 153.46 (C=O, urethane); 138.85 (C(4a)); 137.77 (C(10)); 136.35 (C(12b)); 133.55 (C(12a)); 132.11 (C(12)); 132.08 (C(9)); 131.54 (C(11)); 130.88 (C(7)); 130.21 (C(7a)); 130.07 (C(8)); 126.16 (C(6)); 121.88 (C(5)); 81.65 (C(4)); 78.90 (C(1)); 68.19 (C(3)); 68.02 (C(2)); 46.33 (CH of ^{i}Pr(1)); 45.65 (CH of ^{i}Pr(2)); 25.34 (*Me*–C(10)); 24.75 (*Me*–C(12)); 22.99 (*Me*–C(7)); 20.94, 20.90 (*Me* of ^{i}Pr(1)); 20.52, 20.46 (*Me* of ^{i}Pr(2)); 18.47 (*Me*–C(8)); assignments according to HSQC and HMBC.

When the ring-opening reaction was performed with 2,3-*exo*-(*P**)-**2b** and LDA, the yield of 2,3-*exo*-(*P**)-**9b** amounted only to 1%. Yellow oil (2 mg) after chromatography. R_f (^{t}BuOMe/hexane 4:1) 0.51. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.20 (*d*, $^3J(5,6)=6.6$, H–C(5)); 6.15 (*dd*, $^3J(6,5)=6.5$, $^4J(6,Me–C(7))=1.4$, H–C(6)); 6.08 (br. *s*, H–C(9)); 6.05 (*quint.*-like, H–C(11)); 4.81 (br. *s*, H–C(4)); 4.79 (*d*, $^3J(2,3)=5.8$, H–C(3)); 4.74 (*d*, $^4J(1,4)=1.6$, H–C(1)); 4.08 (*dd*, $^3J(3,2)=5.7$, $^3J(3,OH–C(3))=9.2$, H–C(3)); 3.92 (very br. *s*, $(Me_2CH)_2N$); 2.25 (*d*, $^3J(OH–C(3),3)=9.4$, OH–C(3)); 2.03 (*d*, $^4J(Me–C(12),11)=1.2$, Me–C(12)); 2.00 (*d*, $^4J(Me–C(7),6)=1.2$, Me–C(7)); 1.97 (*d*, $^4J(Me–C(10),9)=1.2$, Me–C(10)); 1.70 (*s*, Me–C(8)); 1.24 (br. *d*, $^3J=6.8$, $(Me_2CH)_2N$).

1.1.2.8. *(*P**,1S*,2*R**,3S*,4*R**)- and (*M**,1S*,2*R**,3S*,4*R**)-1,2,3,4-Tetrahydro-3-methoxy-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]heptalen-2-yl Diisopropylcarbamate* (2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**10b**) *and (*P**,1S*,2*R**,3*R**,4*R**)-1,2,3,4-Tetrahydro-2-hydroxy-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]-heptalen-3-yl Diisopropylcarbamate* (2,3-*endo*-**10′b**). *O*-Methylation experiments were performed with crystalline 2,3-*endo*-(*P**)-**9b** or with oily mixtures of 2,3-*endo*-(*P**)- and 2,3-*endo*-(*M**)-**9b**, whereby 2,3-*endo*-(*M**)-**10b** was obtained as fine, pale yellow needles and 2,3-*endo*-(*P**)-**10b** as orange needles. In one experiment, a chromatographic fraction consisted of *ca.* 75% of 2,3-*endo*-(*P**)-**10b** and *ca.* 25% of 2,3-*endo*-(*P**)-**10′b**. In a typical experiment, the oily mixture **9b** (0.164 g, 0.39 mmol) was dissolved in MeCN (1.5 ml), and MeI (0.8 ml, 12.8 mmol) and then Ag_2O (0.170 g, 0.73 mmol) were added. The mixture was stirred overnight at 57° under Ar, then cooled, diluted with AcOEt (3 ml), and filtered over *Celite*. CC (silica gel, ^{t}BuOMe/hexane 3:2) gave a yellow oil (0.126 g, 74%), from which, when dissolved in hexane, 2,3-*endo*-(*M**)-**10b** separated in fine, pale yellow needles (24.4 mg, 14%). The residue of the mother liquor (100.9 g, 59%), a yellow oil, consisted mainly of 2,3-*endo*-(*M**)- and 2,3-*endo*-(*P**)-**10b** with *ca.* 5% of 2,3-*endo*-(*P**)-**10′b** according to ^{1}H-NMR.

Data of 2,3-endo-(*M**)-**10b**: M.p. 156.0–156.8° (hexane). R_f (Et_2O/hexane 7:3) 0.38. UV/VIS (hexane): λ_{max} 381 (sh, 2.73), 319 (3.65), 253 (4.34), 213 (sh, 4.27); λ_{min} 293 (3.57), 230 (4.15). IR (KBr): 2988*s*, 2965*s*, 2937*s*, 2826*m*, 1699*vs*, 1624*m*, 1437*s*, 1375*m*, 1351*s*, 1316*s*, 1301*s*, 1276*m*, 1218*m*, 1203*w*, 1176*m*, 1156*s*, 1133*m*, 1101*m*, 1040 and 1048*m*, 1022*m*, 990*m*, 763*m*. ^{1}H-NMR (600 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 6.18 (*dq*-like, $^3J(6,5)=6.2$, $^4J(6,Me–C(7))=1.3$, H–C(6)); 6.13 (*d*, $^3J(5,6)=6.2$, H–C(5)); 6.09 (br. *s*, H–C(9)); 6.01 (*t*-like, H–C(11)); 5.23 (*dd*, $^3J(2,1)=5.2$, $^3J(2,3)=7.5$, H–C(2)); 4.91 (*d*, $^3J(1,2)=5.1$, H–C(1)); 4.85 (*d*, $^3J(4,3)=4.8$, H–C(4)); 3.94 (br. *quint.*-like, Me_2CHN); 3.81 (*dd*, $^3J(3,2)=7.5$, $^3J(3,4)=4.8$, H–C(3)); 3.49 (br. *quint.*-like, Me_2CHN); 3.36 (*s*, MeO–C(3)); 1.98 (*d*, $^4J(Me–C(7),6)=1.2$, Me–C(6)); 1.96 (*d*, $^4J(Me–C(10),9)=1.2$, Me–C(10)); 1.95 (*d*, $^4J(Me–C(12),11)=1.2$, Me–C(12)); 1.72 (*s*, Me–C(8)); 1.27, 1.24 (2*d*, $J=6.7$, 6.8, Me_2CHN); 1.02, 1.00 (2*d*, $J=6.9$, 6.7, Me_2CHN). ^{13}C-NMR (150 MHz, $CDCl_3$; $CDCl_3$ at 77.00): 153.90 (C=O); 139.11 (C(4a)); 137.59 (C(10)); 137.04 (C(12b)); 132.70 (C(12)); 132.09 (C(9)); 131.58 (C(12a)); 131.22 (C(11)); 130.71 (C(7a)); 129.56 (C(8)); 129.11 (C(6)); 121.71 (C(5)); 80.22 (C(4)); 79.06 (C(1)); 78.02 (C(3)); 67.53 (C(2)); 58.92 (*Me*O–C(3)); 46.63 (Me_2CHN; corr. with 3.94); 44.92 (Me_2CHN; corr. with 3.49); 25.34 (*Me*–C(10)); 24.78 (*Me*–C(12)); 23.01 (*Me*–C(7)); 20.59, 20.56 (Me_2CHN); 18.49 (*Me*–C(8)).

EI-MS: 451.4 (M^+, 7), 307.3 ([$M - {}^i\mathrm{Pr_2NCO_2}]^+$), 306.2 ([$M - {}^i\mathrm{Pr_2NCO_2H}]^+$), 250.2 ([$M -$ MeOCH=CHOC(O)N^{i}Pr$_2$]$^+$).

Data of 2,3-endo-*(*P**)*-**10b**: M.p. 175.0–175.7°. R_f (Et_2O/hexane 7:3) 0.45. ^{1}H-NMR (600 or 300 MHz, $CDCl_3$; $CHCl_3$ at 7.260): 6.10 (*dq*-like, $^3J(6,5) = 6.3$ or 6.4, $^4J(6,\mathrm{Me-C(7)}) =$ not obs. or 1.2, H–C(6)); 6.071 (*d*, $^3J(5,6) =$ H–C(5); overlap with H–C(9) at 300 MHz); 6.067 (*s*, H–C(9)); 6.02 (*s* or *quint.*-like, H–C(11)); 5.06 or 5.05 (*d*, $^3J(1,2) = 5.1$ or 5.1, H–C(4)); 4.97 (*dd*, $^3J(3,2) = 7.4$ or 7.4, $^3J(3,4) = 5.2$ or 5.1, H–C(3)); 4.78 (*d*, $^3J(1,2) = 5.0$ or 5.0, H–C(1)); 3.93 (br. *s* or *sept.*, Me_2CHN); 3.86 (*dd*, $^3J(2,3) = 7.4$ or 7.4, $^3J(2,1) = 5.1$ or 5.1, H–C(2)); 3.82 (br. *s* or *sept.*, Me_2CHN); 3.31 (*s*, MeO–C(3)); 2.01 (*s* or *d*, $^4J(\mathrm{Me-C(12),11}) = 1.3$, Me–C(12)); 1.99 (*s* or *d*, $^4J(\mathrm{Me-C(10),9}) = 1.1$, Me–C(10)); 1.95 (*s* or *d*, $^4J(\mathrm{Me-C(7),6}) = 1.2$, Me–C(7)); 1.71 (*s*, Me–C(8)); 1.27 (br. *d* or *d*, $J \approx 6.5$ or 6.7, Me_2CHN); 1.14 (2*d*, superimp. to br. *t*, Me_2CHN).

Data of 2,3-endo-*(*P**)*-**10′b**: ^{1}H-NMR (600 MHz, $CDCl_3$; in a mixture with 75% of 2,3-*endo*-(*P**)-**10b**): 6.11 (*s*, H–C(5), H–C(6)); 6.06 (br. *s*, H–C(9)); 6.05 (*t*-like, H–C(11)); 5.11 (*d*, $^3J(4,3) = 5.0$, H–C(4)); 4.87 (*d*, $^3J(1,2) = 4.9$, H–C(1)); 4.82 (*dd*, $^3J(3,2) \approx 8.9$, $^4J(3,4) \approx 5.5$, H–C(3)); 4.37 (*ddd*, $^3J(2,\mathrm{OH-C(2)}) \approx 9.4$, $^3J(2,3) \approx 8.4$, $^3J(2,1) \approx 5.2$, H–C(2)); 3.94 (*quint.*-like, Me_2CHN); *ca.* 3.84 (br. *s*, MeC*H*N); 2.07 (*d*, $^4J = 1.1$, Me–C(12)); 2.00 (*s*, Me–C(10)); 1.97 ($^4J = 1.1$, Me–C(7)); 1.71 (*s*, Me–C(8)); 1.45 (*d*, $^3J(\mathrm{OH-C(2),2}) \approx 10.5$, OH–C(2)); 1.22–1.16 (2 br. *d*, Me_2CHN).

1.2. *With (Phenylsulfonyl)propa-1,2-diene* (PSA). *(*P**,1*S**,2*R**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-3-methylene-7,12-dimethyl-2-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2-*exo*-(*P**)-**14a**) and *(*P**,1*S**,3*S**,4*R**)-, (*P**,1*S**,3*R**,4*R**)-, and (*M**,1*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-2-methylene-7,12-dimethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (3-*exo*-(*P**)-, 3-*endo*-(*P**)-, and 3-*endo*-(*M**)-**14a**). Heptaleno[1,2-*c*]furan **1a** (0.350 g, 1.324 mmol) and PSA (0.385 g, *ca.* 2.1 mmol; prepared according to [35]) were heated under reflux in toluene (9 ml) for 7 h. The usual workup procedure and CC (SiO_2, hexane/AcOEt 7:3) gave, after drying at 50°/1 mbar, a brownish yellow foam of isomers (0.497 g, 84%). Treatment of the foam with Et_2O/hexane gave a first crop of crystals (0.127 g) consisting of a *ca.* 3:1 mixture of the (*P**)-epimers of 3-*exo*- and 3-*endo*-**14a**. The residue of the mother liquor still contained 3-*endo*-**14a** and 2-*exo*-**14a**. The former could be transformed on treatment with MeONa (Et_2O/MeOH 4:1, 1 ml of 2M MeONa in MeOH, r.t., 30 min) into 3-*exo*-**14a**. CC (SiO_2, hexane/Et_2O 1:1) and crystallization from Et_2O/pentane gave pure 3-*exo*-(*P**)-**14a** as very fine orange crystals (50.4 mg (11%); total yield *ca.* 34%).

Data of 3-exo-*(*P**)*-**14a**: Orange crystals. M.p. 175–177°. R_f (Et_2O/hexane 7:3) 0.33. UV (EtOH): λ_{max} 403 (sh, 2.95), 340 (3.67), 272 (sh, 4.22), 264 (sh, 4.27), 252 (4.31), 219 (4.55); λ_{min} 313 (3.59), 237 (4.25), 207 (4.48). IR (KBr): 3011*w*, 2960*m*, 2936*m*, 2871*w*, 1649*w*, 1611*m*, 1584*w*, 1448*m*, 1322*s*, 1148*s*, 1088*m*, 994*m*, 922*m*, 833*m*, 813*m*, 728*m*, 688*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.850 (*d*-like, H_o of $PhSO_2$); 7.609 (*t*-like, H_p of $PhSO_2$); 7.489 (*t*-like, H_m of $PhSO_2$); 6.092 (*d*, $^3J(5,6) = 6.7$, H–C(5)); 6.054 (*dd*, $^3J(10,11) = 6.5$, $^4J(11,\mathrm{Me-C(12)}) = 1.4$, H–C(11)); 5.966 (*dd*, $^3J(5,6) = 6.7$, $^4J(6,\mathrm{Me-C(7)}) = 1.3$, H–C(6)); 5.901 (*d*, $^3J(10,11) = 6.5$, H–C(10)); 5.632 (*s*, H_{cis}–C(2′)); 5.602 (*d*, $J = 0.8$, H–C(8)); 5.436 (*t*-like, H_{trans}–C(2′)); 5.366 (*s*, H–C(4)); 4.676 (*s*, H–C(1)); 3.764 (*s*, H–C(3)); 2.319 (*sept.*, $Me_2CHC(9)$); 2.096 (*d*, $^4J(6,\mathrm{Me-C(7)}) = 0.9$, Me–C(7)); 1.999 (*s*, Me–C(12)); 1.008, 0.983 (2*d*, $^3J =$ 6.9, Me_2CH–C(9)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 150.52 (C(9)); 143.12 (C(4a)); 140.23 (C(2)); 138.75 (C(12b)); 137.82 (C(7a)); 137.65 (C_{ipso} of $PhSO_2$); 133.98 (C_p of $PhSO_2$); 132.07 (C(7)); 130.97 (C(12a)); 130.61 (C(11), C(12)); 130.21 (C_o of $PhSO_2$); 128.75 (C_m of $PhSO_2$); 126.93 (C(6)); 126.87 (C(8)); 123.83 (C(19)); 120.07 (C(5)); 112.53 (CH_2=C(2)); 82.44 (C(1)); 82.15 (C(4)); 72.88 (C(3)); 36.36 (Me_2CH–C(9)); 25.43 (*Me*–C(7)); 25.10 (*Me*–C(12)); 22.95, 22.71 (Me_2CH–C(9)); assignments by ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 462 (62, [$M + \mathrm{NH_4}]^+$), 445 (100, [$M + 1]^+$), 305 (63, [$(M + 1) - (\mathrm{C_6H_4 + SO_2})]^+$).

Prep. HPLC (*Spherisorb CN* (5 μm, 20 × 250 mm), hexane/(CH_2Cl_2 + 0.5% MeOH) 85:15) of mother liquors, which had not been isomerized by base, gave 3-*endo*-**14a** (in total *ca.* 3%) and 2-*exo*-(*P**)-**14a** (in total *ca.* 14%).

Data of 3-endo-*(*M**)*-**14a**: From HPLC separation, light red crystals (Et_2O/hexane). M.p. 168–170°. CI-MS (NH_3): 445 (100, [$M + 1]^+$), 305 (53, [$(M + 1) - (\mathrm{C_6H_4 + SO_2})]^+$). ^{1}H-NMR (600 MHz, $CDCl_3$; in a mixture with 60% of the (*P**)-epimer): 7.90–7.86 (*m*, H_o of $PhSO_2$); 7.67–7.61 (*m*, H_p of $PhSO_2$); 7.58–7.51 (*m*, H_m of $PhSO_2$); 6.060 (*dd*, $^3J(10,11) = 6.4$, $^4J(11,\mathrm{Me-C(12)}) = 1.3$, H–C(11)); 6.016 (*d*, $^3J(5,6) =$

6.6, H–C(5)); 5.924 (*dd*, $^3J(5,6) = 6.6$, $^4J(6,\text{Me}–C(7) = 1.3$, H–C(6)); 5.901 (*d*, $^3J(10,11) = 6.3$, H–C(10)); 5.635 (*d*, $J = 0.8$, H–C(8)); 5.206 (*s*, H–C(1)); 5.131 (*d*, $^4J(H_{trans},3) = 2.5$, H_{trans}–C=C(2)); 5.046 (*d*, $^4J(H_{cis},3) = 1.8$, H_{cis}–C=C(2)); 4,626 (*d*, $^3J(3,4) = 4.5$, H–C(4)); 4.368 (*quint.*-like, $\Sigma(^3J(3,4) + {}^4J(H_{trans},3) + {}^4J(H_{cis},3)) = 9.4$, H–C(3)); 2.391 (*sept.*, Me_2CH–C(9)); 2.145 (br. *s*, Me–C(12)); 2.139 (*d*, $^4J(6,\text{Me}–C(7)) = 1.0$, Me–C(7)); 1.104, 1.088 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE.

Data of 3-endo-*(*P**)*-**14a**: HPLC/UV/VIS (7% ^{i}PrOH/hexane): λ_{max} 345 (0.16), 266 (sh, 0.60), 313 (1.00); λ_{min} 313 (0.12), 239 (0.58). ^{1}H-NMR (600 MHz, $CDCl_3$; in a mixture with 40% of the (*M**)-epimer): 7.90–7.86 (*m*, H_o of $PhSO_2$); 7.67–7.61 (*m*, H_p of $PhSO_2$); 7.58–7.51 (*m*, H_m of $PhSO_2$); 6.156 (*d*, $^3J(5,6) = 6.8$, H–C(5)); 6.120 (*dd*-like, $^3J(10,11) = 6.5$, $^4J(11,\text{Me}–C(12)) = 1.3$, H–C(11)); 5.951 (*d*, $^3J(10,11) = 6.6$, H–C(10)); 5.876 (*dd*-like, $^3J(5,6) = 6.8$, $^4J(6,\text{Me}–C(7)) = 1.3$, H–C(6)); 5.602 (*d*-like, $^4J(8,10) \approx 0.8$, H–C(8)); 5.345 (*d*, $^4J(H_{trans},3) = 2.3$, H_{trans}–C=C(2)); 5.307 (*d*, $^3J(3,4) = 4.8$, H–C(4)); 5.160 (*d*, $^4J(H_{cis},3) = 1.8$, H_{cis}–C=C(2)); 4.501 (*quint.*-like, $\Sigma(^3J(3,4) + {}^4J(H_{trans},3) + {}^4J(H_{cis},3)) = 8.8$, H–C(3)); 2.354 (*sept.*, Me_2CH–C(9)); 2.075 (*d*, $^4J(11,\text{Me}–C(12)) = 1.0$, Me–C(12)); 2.012 (*s*, Me–C(7)); 1.049, 1.022 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE.

Data of 2-exo-*(*P**)*-**14a**: From HPLC separation, orange foam. HPLC/UV/VIS (7% ^{i}PrOH/hexane): λ_{max} 341, 252, 219; λ_{min} 313, 237; almost identical with that of 3-*exo*-(*P**)-**10a**. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.88 (*d*-like, H_o of $PhSO_2$); 7.64 (*t*-like, H_p of $PhSO_2$); 7.52 (*t*-like, H_m of $PhSO_2$); 6.122 (*dd*, $^3J(10,11) = 6.6$, $^4J(11,\text{Me}–(12)) = 1.1$, H–C(11)); 5.953 (*d*, $^3J(10,11) = 6.8$, H–C(10)); 5.911 (*s*-like *AB*, H–C(5), H–C(6)); 5.611 (*s*, H–C(8)); 5.461 (*s*, H_{cis}–C=C(3)); 5.327 (*d*-like, $^4J(H_{trans},4) = 1.6$, H_{trans}–C=C(3)); 5.110 (*s*, H–C(1)); 4.903 (*s*, H–C(4)); 3.876 (*s*, H–C(2)); 2.348 (*sept.*, Me_2CH–C(9)); 2.098 (*s*, Me–C(7)); 1.934 (*s*, Me–C(12)); 1.038, 1.010 (2*d*, $^3J = 6.9$, Me_2CH–C(9)).

1.3. *With α-(Acetyloxy)acrylonitrile* (AAN). 1.3.1. *(*M*,1R*,3S*,4R*)- and (*P*,1R*,3S*,4R*)-3-(Acetyloxy)-1,2,3,4-tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-3-carbonitrile* (3-*endo*-(*M**)- and 3-*endo*-(*P**)-**15a**) *and (*P*,1S*,2R*,4S*)-2-(Acetyloxy)-1,2,3,4-tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalene-3-carbonitrile* (2-*endo*-(*P**)-**16a**). A *Schlenk* tube was charged under Ar with heptaleno[1,2-*c*]furan **1a** (0.145 g, 0.548 mmol) and AAN (*Fluka*, *purum*; freshly distilled at 65°/13 Torr; 0.144 g, 1.296 mmol) in toluene (2.5 ml), sealed, and heated in an oil bath at 130° for 68 h. After evaporation of the solvent, the residue was purified by CC (SiO_2, hexane/Et_2O 3:2), which furnished three fractions (in total 169.3 mg, 82%). The first fraction was crystallized from hexane and gave 3-*endo*-(*M**)-**15a** (29.5 mg, 12%) as light red crystals. The second fraction (89.2 mg of crystalline material) was recrystallized from Et_2O/hexane and yielded 3-*endo*-(*P**)-**15a** (26.2 mg, 13%) as light red crystals. The third fraction was an orange foam (50.6 mg), which was subjected to HPLC purification and gave 2-*endo*-(*P**)-**16a** (26.7 mg, 13%) as a stiff yellow foam.

Data of 3-endo-*(*M**)-**15a**: M.p. 150.9–151.6°. R_f (hexane/^{t}BuOMe 3:2) 0.47. UV/VIS (cyclohexane): λ_{max} 405 (sh, 2.82), 330 (3.62), 274 (sh, 3.99), 251 (4.25), 209 (4.29); λ_{min} 300 (3.58), 231 (4.03). IR (KBr): 2953*s*, 2865*m*, 2246*w*, 1758*s*, 1616*m*, 1434*m*, 1365*m*, 1229*s*, 1187*s*, 1113*m*, 1074*s*, 1059*s*, 1034*s*, 902*m*, 845*m*, 834*m*, 813*m*, 621*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.094 (*d*, $^3J(5,6) = 6.5$, H–C(5)); 6.024 (*d*, $^3J(10,11) = 6.3$, H–C(11)); 5.970 (*d*, $^3J(10,11) = 6.4$, H–C(10)); 5.921 (*d*, $^3J(5,6) = 6.6$, H–C(6)); 5.548 (*s*, H–C(8)); 5.458 (*s*, H–C(4)); 5.120 (*d*, $^3J(1,2) = 5.1$, H–C(1)); 2.725 (*dd*, $^2J = 12.8$, $^3J(1,2) = 5.2$, H_{exo}–C(2)); 2.381 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 2.119 (br. *s*, Me–C(7)); 2.094 (br. *s*, Me–C(12)); 1.934 (*s*, AcO–C(3)); 1.860 (*d*, $^2J = 12.8$, H_{endo}–C(2)); 1.046, 1.019 (2*d*, $^3J = 6.8$, Me_2CH–C(9)); assignments were verified by NOESY. CI-MS (NH_3): 393 (81, $[M + NH_4]^+$), 367 (100, $[M + H]^+$), 265 (14, $[(M + H) - CH_2{=}C(OAc)CN]^+$), 215 (5, $[(M + H) - (CH_2{=}C(OAc)CN + Me–C{\equiv}CH)]^+$).

The structure of *endo*-(*M**)-**15a** was finally established by an X-ray crystal-structure determination (see *Fig. 3*, *b* and *Table 8*).

Data of 3-endo-*(*P**)-**15a**: M.p. 162.5–163.7°. R_f (hexane/^{t}BuOMe 3:2) 0.32. UV/VIS (cyclohexane): λ_{max} 415 (sh, 2.76), 339 (3.67), 275 (sh, 4.12), 251 (4.31), 210 (4.32); λ_{min} 303 (3.50), 230 (4.09). IR (KBr): 2964*s*, 2934*m*, 2873*w*, 2241*w*, 1747*s*, 1609*w*, 1443*m*, 1370*m*, 1232*s*, 1219*s*, 1187*s*, 1173*m*, 1061*m*, 1002*s*, 878*m*, 614*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.124 (*dq*-like *dd*, $^3J(10,11) = 6.6$, $^4J(11,\text{Me}–C(12)) = 1.3$, H–C(11)); 5.953 (br. *d*, $^3J(10,11) \approx 7.1$, H–C(10)); 5.908 (*s*-like *AB*, $^3J(5,6) \approx 7.2$, H–C(5), H–C(6)); 5.634 (*d*, $^4J(8,10) = 1.1$, H–C(8)); 5.562 (*s*, H–C(4)); 4.790 (*dd*, $^3J(1,2) = 5.4$, 0.9, H–C(1)); 2.844 (*dd*, $^2J = 13.1$, $^3J(1,2) = 5.5$, H_{exo}–C(2)); 2.369 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.119 (br. *s*, Me–C(7)); 2.087

(*s*, AcO–C(3)); 1.955 (br. *s*, Me–C(12)); 1.934 (superimp. *d*, $^2J \approx 12.5$, H_{endo}–C(2)); 1.062, 1.035 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOESY. CI-MS (NH_3): 393 (64, $[M+NH_4]^+$), 367 (100, $[M+H]^+$), 265 (8, $[(M+H) - CH_2=C(OAc)CN]^+$), 215 (7, $[(M+H) - (CH_2=C(OAc)CN + Me-C\equiv CH]^+$).

The structure of 3-*endo*-(*P**)-**15a** was established by an X-ray crystal-structure determination (see *Fig. 3*,*a* and *Table 8*).

Heating of 3-*endo*-(*M**)-**15a** or 3-*endo*-(*P**)-**15a** in toluene at 70° (1 h) led to an equilibrium mixture with 51% of the (*P**)- and 49% of the (*M**)-epimer.

Data of 2-endo-*(*P**)-**16a**: R_f (hexane/^{t}BuOMe 3:2) 0.24. HPLC/UV/VIS (hexane/^{i}PrOH 95:5): λ_{max} 335 (0.27), 247 (1.0), 219 (0.97); λ_{min} 306 (0.22), 231 (0.83). ^{1}H-NMR (600 MHz, $CDCl_3$): 6.184 (*dd*, $^3J(10,11) = 6.7$, $^4J(11,Me-C(12)) = 1.2$, H–C(11)); 6.043 (*d*, $^4J(5,6) = 6.5$, H–C(5)); 6.001 (superimp. *d*, H–C(6), H–C(10)); 5.676 (*s*, H–C(8)); 5.109 (*s*, H–C(1)); 5.070 (br. *d*, $^3J(3,4) = 3.6$, H–C(4)); 2.46–2.42 (*m*, 2 H–C(3)); 2.396 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.356 (br. *s*, Me–C(12)); 2.143 (*s*, AcO–C(2)); 2.121 (br. *s*, Me–C(7)); 1.066, 1.039 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOESY.

1.3.1.1. *(*P*,*1*S*,*4*S*)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalen-2-one* ((*P**)-**18a**) *and (*P*,*1*R*,*4*R*)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-1,4-epoxybenzo[*d*]heptalen-3-one* ((*P**)-**17a**). The isomer mixture 3-*endo*-**15a**/2-*endo*-**16a** described above was prepared by heating **1a** (0.101 g, 0.383 mmol) and α-(Acetyloxy)acrylonitrile (AAN; 0.090 g, 0.810 mmol) in the presence of small amounts of 3,5-dimethylbenzoic acid (6 mg, 0.040 mmol) in chlorobenzene (0.7 ml) under reflux for 20 h. After evaporation of the chlorobenzene, the residue was dissolved in 10% KOH in MeOH (5 ml), and the mixture was kept for 2 h at r.t. Then the soln. was poured into half-conc. brine and extracted with Et_2O. The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated. After purification of the residue by CC (SiO_2, hexane/^{t}BuOMe 1:1) and drying of the product fractions *in vacuo* (40°/1 mbar), a red oil of **17a**/**18a** and of **19a** (together 116.5 mg, 81%) was obtained. Prep. HPLC (*Spherisorb CN* (5 μm, 20 × 250 mm), 1% ^{i}PrOH/hexane) gave pure (*P**)-**17a** as light red crystals. Isomer (*P**)-**18a** was obtained as a 2:3 mixture with (*P**)-**17a**.

*Data of (*P**)-**18a***: R_f (hexane/^{t}BuOMe 1:1) 0.35. HPLC/UV/VIS (2% ^{i}PrOH/hexane): λ_{max} 332 (0.29; with long tailing up to 400), 329 (0.29), 275 (sh, 0.71), 251 (1.0), 210 (0.99); λ_{min} 325 (0.28), 301 (0.22), 234 (0.82). ^{1}H-NMR (600 MHz, $CDCl_3$; in presence of 60% of (*P**)-**17a**): 6.158 (*dd*, $^3J(10,11) = 6.6$, $^4J(11,Me-C(12)) = 1.4$, H–C(11)); 6.01–5.96 (superimp. *m*, H–C(5), H–C(6), H–C(10)); 5.684 (*s*, H–C(8)); 5.248 (*d*, $^3J(3,4) = 5.4$, H–C(4)); 4.538 (*s*, H–C(1)); 2.582 (*dd*, $^2J = 16.5$, $^3J(3,4) = 5.4$, H_{exo}–C(3)); 2.388 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.125 (*s*, Me–C(7)); 2.080 (*s*, Me–C(12)); 1.933 (superimp. *d*, $^2J = 16.3$, H_{endo}–C(3)); 1.075, 1.047 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOESY. CI-MS (NH_3): 307 (100, $[M+H]^+$).

*Data of (*P**)-**17a***: Light red crystals from hexane/Et_2O. M.p. 124–128°. R_f (hexane/^{t}BuOMe 1:1) 0.35. UV/VIS (cyclohexane): λ_{max} 415 (sh, 2.78), 349 (sh, 3.60), 332 (3.77), 321 (3.75), 278 (sh, 4.12), 252 (4.30), 208 (4.35); λ_{min} 325 (3.74), 300 (3.58), 233 (4.16). IR (KBr): 2967*s*, 2873*m*, 1759*s*, 1612*w*, 1435*m*, 1282*w*, 1139*m*, 1008*m*, 900*m*, 796*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.181 (*d*, $^3J(5,6) = 6.9$, H–C(5)); 6.123 (*dd*, $^3J(10,11) = 6.6$, $^4J(11,Me-C(12)) = 1.3$, H–C(11)); 5.979 (superimp. *d*, H–C(10)); 5.969 (superimp. *dd*, $^3J(5,6) \approx 6.7$, $^4J(6,Me-C(7)) = 1.3$, H–C(6)); 5.663 (*s*, H–C(8)); 5.078 (*dd*, $^3J(1,2) = 5.4$, 0.9, H–C(1)); 4.709 (*s*, H–C(1)); 2.530 (*dd*, $^2J = 16.8$, $^3J(1,2) = 5.4$, H_{exo}–C(2)); 2.388 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.130 (*s*, Me–C(7)); 2.099 (*d*, $^2J = 16.8$, H_{endo}–C(2)); 1.947 (*s*, Me–C(12)); 1.075, 1.047 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOESY. CI-MS (NH_3): 307 (100, $[M+H]^+$), 126 (17).

In a second experiment, **1a** (0.236 g, 0.893 mmol) and AAN (0.150 g, 1.35 mmol) were heated in boiling chlorobenzene (5 ml; 22 h). After evaporation of the solvent and drying, the residue was dissolved in MeOH (8 ml). A 30% aq. formaldehyde soln. (0.3 ml) and dry potassium carbonate (0.120 g) were added, and the mixture was stirred at r.t. for 2.5 h. In this case, **17a** and **18a**, free of any **19a**, were obtained as a 1:1 mixture.

1.3.1.2. *9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-3,4-diol* (**21a**). Trimethylsilyl trifluoromethanesulfonate (*Fluka*; 0.27 ml, 2.02 mmol), dissolved in CH_2Cl_2 (4 ml), was added in drops to an ice-cooled soln. of **17a**/**18a** 1:1 (0.200 g, 0.684 mmol) and Et_3N (0.158 g, 1.56 mmol) in CH_2Cl_2 (4 ml). After the

addition, the mixture was stirred for 30 min at 0° and then at r.t. for 1 h. The CH_2Cl_2 soln. was poured into sat. aq. NH_4Cl soln., followed by two extractions of the aq. phase with CH_2Cl_2. The combined CH_2Cl_2 phases were washed successively with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), filtered, and concentrated to yield a residue, which was purified by CC (SiO_2, CH_2Cl_2/Et_2O 9:1): **21a** (82.0 mg, 41%). Dark brownish foam. R_f (hexane/Et_2O 3:2) 0.14. HPLC/UV/VIS (hexane/^{i}PrOH 9:1): λ_{max} 301 (sh, 0.50), 261 (0.67), 225 (sh, 0.81), 213 (1.00); λ_{min} 257 (0.66). IR (KBr): 3425*s*, 3009*m*, 2959*s*, 2867*m*, 1643*w*, 1611*m*, 1567*w*, 1484*s*, 1460*m*, 1289*s*, 1203*s*, 1061*m*, 962*m*, 947*m*, 809*m*, 787*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.005 (*d*, $^3J(5,6) = 11.8$, H–C(5)); 6.893 (*d*, $^3J(1,2) = 8.2$, H–C(2)); 6.454 (*d*, $^3J(1,2) = 8.2$, H–C(1)); 6.411 (*d*, $^3J(10,11) = 11.8$, H–C(11)); 6.344 (superimp. *d*, H–C(10)); 6.313 (*d*, $^3J(6,5) = 11.9$, H–C(6)); 5.692 (br. *s*, H–C(8)); 5.32 (br. *s*, OH–C(3), OH–C(4)); 2.545 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.702 (*s*, Me–C(7)); 1.663 (*s*, Me–C(12)); 1.147, 1.133 (2*d*, $^3J = 6.8$, Me_2CH–C(9)); assignments were verified by NOESY. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 146.89 (C(9)); 141.70 (C(3)); 140.47 (C(4)); 135.60 (C(11)); 135.01 (C(7a)); 134.98 (C(12a)); 134.10 (C(6)); 132.95 (C(12b)); 130.80 (C(10)); 130.70 (C(12)); 127.37 (C(7)); 125.34 (C(4a)); 124.43 (C(5)); 121.75 (C(8)); 121.05 (C(1)); 116.11 (C(2)); 34.46 (Me_2CH–C(9)); 22.84, 22.78 (Me_2CH–C(9)); 19.75 (*Me*–C(12)); 17.02 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 307 (100, $[M+H]^+$).

1.3.1.3. *9-Isopropyl-7,12-dimethylbenzo[*a*]heptalene-3,4-diol Diacetate* (**20a**). A mixture of **17a** (*ca.* 63%) and **18a** (0.210 g, *ca.* 0.7 mmol) was dissolved in Ac_2O (*puriss.*; 4 ml) and 0.3 ml of a soln. of H_2SO_4 in Ac_2O (0.2 ml of conc. H_2SO_4 in 5 ml of Ac_2O) was added. The mixture was stirred at r.t. for 22 h, then poured into H_2O, and extracted with Et_2O and toluene. The combined org. phases were washed with one portion of aq. sat. $NaHCO_3$ soln., dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, hexane/Et_2O 3:2): starting material (30 mg, mainly **18a**) and **20a** (80.2 mg, 29%) as light yellow crystals. Recrystallization from AcOEt/hexane provided pure **20a** (62.8 mg, 22%). M.p. 162–164°. R_f (hexane/Et_2O 3:2) 0.20. UV/VIS (hexane): λ_{max} 328 (3.61), 287 (sh, 4.13), 259 (4.38), 212 (4.49); λ_{min} 317 (3.60), 239 (4.24), 200 (4.43). HPLC/CD (*Chiralcel-OD-H*, 1.0 ml/min, 7% ^{i}PrOH/hexane; $t_R(M)/t_R(P) = 3.04$); extrema of the (*P*)-enantiomer: 336 (–0.32), 292 (sh, –0.07), 279 (0), 253 (1.00), 240 (0.76), 230 (0.98), 215 (0). IR (KBr): 3013*w*, 2959*s*, 2922*m*, 2865*m*, 1772*s*, 1476*s*, 1372*s*, 1251*s*, 1205*s*, 1156*s*, 1065*m*, 1013*s*, 886*m*, 786*m*, 588*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.214 (*d*, $^3J(1,2) = 8.4$, H–C(2)); 6.875 (*d*, $^3J(1,2) = 8.4$, H–C(1)); 6.753 (*d*, $^3J(5,6) = 11.9$, H–C(5)); 6.421 (*d*, $^3J(10,11) = 11.9$, H–C(11)); 6.372 (*dd*, $^3J(10,11) = 11.9$, $^4J(8,10) = 0.9$, H–C(10)); 6.302 (*d*, $^3J(5,6) = 11.9$, H–C(6)); 5.691 (br. *s*, H–C(8)); 2.549 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.342 (*s*, AcO–C(4)); 2.281 (*s*, AcO–C(3)); 1.684 (br. *s*, Me–C(7)); 1.665 (*s*, Me–C(12)); 1.149, 1.137 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 168.31 (MeO*C*O–C(3)); 167.89 (MeO*C*O–C(4)); 147.23 (C(9)); 141.09 (C(3)); 138.92 (C(4)); 136.80 (C(12b)); 135.58 (C(11)); 135.26 (C(6)); 134.96 (C(7a)); 133.95 (C(12a)); 131.88 (C(4a)); 131.75 (C(12)); 131.50 (C(10)); 127.67 (C(7)); 127.11 (C(1)); 124.19 (C(5)); 123.52 (C(2)); 122.03 (C(8)); 34.50 (Me_2CH–C(9)); 22.84, 22.79 (Me_2CH–C(9)); 20.77 (*Me*OCO–C(3)); 20.40 (*Me*OCO–C(4)); 19.60 (*Me*–C(12)); 17.06 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 390 (100, $M^{+\bullet}$), 348 (27, $[M - CH_2{=}C{=}O]^{+\bullet}$), 306 (22, $[M - 2\,CH_2{=}C{=}O]^{+\bullet}$), 291 (16, $[M - (2\,CH_2{=}C{=}O + Me)]^+$), 266 (25, $[M - (2\,CH_2{=}C{=}O + Me{-}C{\equiv}CH]^{+\bullet}$), 157 (27).

1.3.2. *(*P**,1*R**,4*R**)- and (*M**,1*R**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-1,4-epoxybenzo[*d*]-heptalen-3-one* ((*P**)- *and* (*M**)-**17b**). A mixture of heptalenofuran **1b** (0.307 g, 1.228 mmol) and α-(Acetyloxy)acrylonitrile (0.209 g, 1.88 mmol) in chlorobenzene (5 ml) was heated at reflux for 23 h. After evaporation of the solvent, the residue was dissolved in MeOH (10 ml) and treated with 30% aq. formaldehyde soln. (0.4 ml) and dry K_2CO_3 (0.160 g). After stirring at r.t. for 2 h, the product mixture was poured into half-conc. brine and extracted twice with ^{t}BuOMe. The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated. Purification of the residue by CC (SiO_2, hexane/^{t}BuOMe 7:3) gave **17b** (0.276 g, 77%) as orange semicrystalline material (^{1}H-NMR: (*P**)/(*M**)-**17b** *ca.* 1:1). Considerable signals of the two epimers of benzo[*a*]heptalen-2-one **18b** were not recognized. Recrystallization from Et_2O/hexane gave a conglomerate of yellow and orange crystals (0.194 mg, 54%). Samples of both kinds of crystals could be obtained by manual separation. Recrystallization from Et_2O/pentane afforded anal. pure (*P**)- and (*M**)-**17b**.

*Data of (*P**)*-**17b**: Orange crystals. M.p. 182.7–184.7° (change of the crystal form at *ca.* 150°). R_f (hexane/^{t}BuOMe 3:2) 0.40. UV/VIS (hexane): λ_{max} 392 (sh, 2.80), 330 (sh, 3.72), 319 (sh, 3.76), 307 (sh, 3.70), 276 (sh, 4.05), 257 (4.34), 251 (sh, 4.31), 212 (sh, 4.28), 205 (4.30); λ_{min} 297 (3.62), 232 (4.18). IR (KBr): 2964*m*, 2939*m*, 2913*m*, 2851*w*, 1763*s*, 1435*m*, 1397*w*, 1373*w*, 1284*w*, 988*m*, 848*m*, 819*m*, 775*m*, 613*m*, 587*w*, 553*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.366 (*d*, $^3J(5,6) = 6.5$, H–C(5)); 6.168 (*dd*, $^3J(5,6) = 6.4$, $^4J(6,Me–C(7)) = 1.2$, H–C(6)); 6.115 (br. *s*, H–C(9)); 6.054 (br. *s*, H–C(11)); 5.156 (*d*, $^3J(1,2) = 5.3$, H–C(1)); 4.725 (*s*, H–C(4)); 2.530 (*dd*, $^2J = 16.7$, $^3J(1,2) = 5.4$, H_{exo}–C(2)); 2.074 (*d*, $^2J = 16.7$, H_{endo}–C(2)); 2.007 (br. *s*, Me–C(7)); 1.983 (br. *s*, Me–C(10)); 1.911 (br. *s*, Me–C(12)); 1.717 (*s*, Me–C(8)); assignments were verified by NOE. EI-MS: 292 (100, $M^{+\bullet}$), 277 (6, $[M - Me]^+$), 264 (13, $[M - CO]^{+\bullet}$), 250 (60, $[M - CH_2{=}C{=}CO]^{+\bullet}$), 249 (60, $[M - Ac]^+$), 235 (91, $[M - (CH_2{=}C{=}O + Me)]^+$), 221 (92, $[M - (Ac + CO)]^+$), 206 (65, $[M - (Ac + CO + Me)]^{+\bullet}$), 184 (38), 165 (40).

*Data of (*M*)*-**17b**: Yellow crystals. M.p. 170.4–171.3°. R_f (hexane/^{t}BuOMe 3:2) 0.40. UV/VIS (hexane): λ_{max} 389 (sh, 2.81), 329 (sh, 3.67), 318 (3.73), 309 (sh, 3.69), 276 (sh, 4.03), 258 (sh, 4.24), 250 (4.25), 203 (4.35); λ_{min} 298 (3.65), 232 (4.12). IR (KBr): 3008*m*, 2970*m*, 2913*m*, 2855*m*, 1767*s*, 1657*w*, 1621*m*, 1436*m*, 1404*m*, 1371*m*, 975*m*, 896*m*, 844*m*, 774*m*, 607*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.380 (*d*, $^3J(5,6) = 6.2$, H–C(5)); 6.132 (*dd*, $^3J(5,6) = 6.2$, $^4J(6,Me–C(7)) = 1.2$, H–C(6)); 5.999 (br. *s*, H–C(9)); 5.941 (br. *s*, H–C(11)); 5.316 (*d*, $^3J(1,2) = 5.4$, H–C(1)); 4.547 (*s*, H–C(4)); 2.571 (*dd*, $^2J = 16.5$, $^3J(1,2) = 5.4$, H_{exo}–C(2)); 2.088 (br. *s*, Me–C(12)); 2.028 (br. *s*, Me–C(7)); 1.922 (br. *s*, Me–C(10)); 1.809 (*d*, $^2J = 16.5$, H_{endo}–C(2)); 1.647 (*s*, Me–C(8)); assignments were verified by NOE. EI-MS: 292 (100, $M^{+\bullet}$), 277 (5, $[M - Me]^+$), 264 (11, $[M - CO]^{+\bullet}$), 250 (57, $[M - CH_2{=}C{=}O]^{+\bullet}$), 249 (52, $[M - Ac]^+$), 235 (93, $[M - (CH_2{=}C{=}O + Me)]^+$), 221 (93, $[M - (Ac + CO)]^+$), 206 (64, $[M - (Ac + CO + Me)]^{+\bullet}$), 184 (38), 165 (38).

1.3.2.1. *7,8,10,12-Tetramethylbenzo[*a*]heptalene-3,4-diol* (**21b**). Trimethylsilyl trifluoromethanesulfonate (0.17 ml, 1.26 mmol), dissolved in CH_2Cl_2 (3 ml), was added in drops to an ice-cooled soln. of the mixture (*P**)/(*M**)-**17b** (0.124 g, 0.424 mmol) and Et_3N (0.100 g, 1.0 mmol) in CH_2Cl_2 (3 ml). After the addition, the mixture was stirred for 30 min at 0° and then at r.t. for 1 h. Usual workup and purification by CC afforded **21b** (0.105 g, 85%) as a brown oil. Almost colorless crystals of **21b** were obtained from a $CDCl_3$ soln. M.p. 70–90°. R_f (CH_2Cl_2/EtOH 19:1) 0.32. UV/VIS (hexane): λ_{max} *ca.* 375 (sh, 2.75), *ca.* 336 (sh, 3.45), 295 (4.03), 253 (4.20), 221 (4.34), 211 (4.34); λ_{min} 287 (4.02), 244 (4.18), 215 (4.33), 202 (4.31). IR (KBr): 3406*s*, 2967*m*, 2936*m*, 2912*m*, 2855*m*, 1648*w*, 1613*m*, 1566*w*, 1485*s*, 1454*m*, 1289*s*, 1204*m*, 1180*m*, 1166*m*, 927*m*, 912*m*, 884*m*, 807*m*, 731*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.055 (*d*, $^3J(5,6) = 11.9$, H–C(5)); 6.871 (*d*, $^3J(1,2) = 8.2$, H–C(2)); 6.405 (*d*, $^3J(1,2) = 8.2$, H–C(1)); 6.298 (*d*, $^3J(5,6) = 11.9$, H–C(6)); 6.164 (br. *s*, H–C(11)); 6.028 (br. *s*, H–C(9)); 5.567 (very br. *s*, OH–C(3), OH–C(4)); 2.015 (*d*, $^4J(Me–C(10),11) = 1.0$, Me–C(10)); 1.914 (*d*, $^4J(Me–C(8),9) = 1.1$, Me–C(8)); 1.722 (*s*, Me–C(7)); 1.638 (*s*, Me–C(12)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 141.74 (C(3)); 141.00 (C(4)); 138.56 (C(7a)); 137.89 (C(10)); 133.94 (C(6)); 133.79 (C(12b)); 133.61 (C(8)); 131.03 (C(12a)); 130.89 (C(11)); 129.93 (C(12)); 128.38 (C(9)); 126.53 (C(7)); 125.36 (C(4a)); 125.14 (C(5)); 120.25 (C(1)); 116.34 (C(2)); 25.17 (*Me*–C(10)); 23.19 (*Me*–C(8)); 19.60 (*Me*–C(12)); 18.12 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 292 (100, $M^{+\bullet}$), 277 (57, $[M - Me]^+$), 262 (24, $[M - 2\,Me]^{+\bullet}$), 252 (81, $[M - Me–C{\equiv}CH]^{+\bullet}$), 238 (23, $[M - Me–C{\equiv}C–Me]^{+\bullet}$), 231 (11), 189 (9), 165 (6).

1.3.2.2. *7,8,10,12-Tetramethylbenzo[*a*]heptalene-3,4-diol Diacetate (***20b***)*. To a soln. of the epimer mixture **17b** (0.154 g, 0.527 mmol) in Ac_2O (3.5 ml) was added 0.2 ml of a soln. of H_2SO_4 in Ac_2O (0.2 ml of conc. H_2SO_4 in 5 ml of Ac_2O). The mixture was stirred at r.t. for 1 h, then poured into 50 ml of half-conc. brine, and extracted with ^{t}BuOMe. The combined org. phases were washed with aq. sat. $NaHCO_3$ soln. (2×) and brine (1×), dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, hexane/Et_2O 3:2): **17b** (19 mg, 12%) as a yellow oil and **20b** (0.130 g, 66%) as a light yellow stiff foam. Crystallization from Et_2O/hexane gave pure **20b** (0.114 g, 57%). Light yellow crystals. M.p. 145.7–146.7°. R_f (hexane/Et_2O 3:2) 0.20. UV/VIS (hexane): λ_{max} 322 (3.59), 285 (sh, 4.22), 249 (4.34), 220 (4.53); λ_{min} 316 (3.59), 240 (4.33), 201 (4.38). HPLC/CD (*cf. Fig. 8*, *c*; *Chiralcel-OD-H*, 0.8 ml/min, 7% ^{i}PrOH/hexane; $t_R(M)/t_R(P) = 2.14$); extrema of the (*P*)-enantiomer: 334 (–0.33), 290 (sh, –0.10), 279 (0), 254 (0.64), 246 (0.59), 234 (1.00). IR (KBr): 2976*w*, 2913*m*, 2856*w*, 1762*s*, 1473*m*, 1444*m*, 1371*s*, 1260*s*, 1213*s*, 1178*s*, 1063*m*, 1023*m*, 1011*m*, 940*w*, 910*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.209 (*d*, $^3J(1,2) = 8.4$, H–C(2));

6.838 (*d*, $^3J(1,2) = 8.4$, H–C(1)); 6.789 (*d*, $^3J(5,6) = 12.0$, H–C(5)); 6.298 (*d*, $^3J(5,6) = 12.0$, H–C(6)); 6.166 (br. *s*, H–C(11)); 6.036 (br. *s*, H–C(9)); 2.351 (*s*, AcO–C(4)); 2.283 (*s*, AcO–C(3)); 2.019 (*d*, ^4J(Me–C(10),11) = 0.8, Me–C(10)); 1.943 (*d*, ^4J(Me–C(8),9) = 0.9, Me–C(8)); 1.713 (*s*, Me–C(7)); 1.623 (*s*, Me–C(12)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 168.30 (Me*C*OO–C(3)); 167.87 (Me*C*OO–C(4)); 140.87 (C(3)); 139.01 (C(12b)); 138.44 (C(7a)); 138.41 (C(10)); 137.34 (C(4)); 135.11 (C(6)); 133.73 (C(8)); 131.57 (C(4a)); 130.92 (C(12)); 130.59 (C(11)); 129.62 (C(12a)); 128.58 (C(9)); 126.73 (C(7)); 126.16 (C(1)); 124.42 (C(5)); 123.56 (C(2)); 25.03 (*Me*–C(10)); 25.06 (*Me*–C(8)); 20.78 (*Me*COO–C(3)); 20.42 (*Me*COO–C(4)); 19.25 (*Me*–C(12)); 17.98 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 376 (100, $M^{+\bullet}$), 361 (13, [M – Me]$^+$), 334 (17, [M – CH_2=C=O]$^{+\bullet}$), 319 (29, [M – (CH_2=C=O + Me)]$^+$), 292 (50, [M – 2 CH_2=C=O]$^{+\bullet}$), 277 (48, [M – (2 CH_2=C=O + Me)]$^+$), 252 (56, [M – (2 CH_2=C=O + Me–C≡CH)]$^{+\bullet}$), 238 (16), 221 (12), 202 (13), 189 (16), 165 (12).

1.4. *With (*Z*)-1,2-Bis(phenylsulfonyl)ethene* (ZSE). 1.4.1. *(*P**,1S*,2S*,3R*,4R*)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-2,3-bis(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2,3-*exo*-(*P**)-**22a**). Under Ar, a soln. of heptaleno[1,2-*c*]furan **1a** (0.499 g, 1.888 mmol) and ZSE (*Aldrich*; 98%; 0.680 g, 2.205 mmol) in toluene (13 ml) was stirred at 75° for 21 h. After evaporation of the solvent, the residue was purified by CC (SiO_2, CH_2Cl_2/Et_2O/hexane 94 : 5 : 1), which led to a crude product (1.16 g) as a stiff brown foam. Crystallization from ^{t}BuOMe gave 2,3-*exo*-(*P**)-**22a** (0.687 g, 64%) as light red crystals. Orange crystals from toluene. M.p. 198.2–198.9°. R_f (CH_2Cl_2/MeOH 98 : 2) 0.32. UV/VIS (EtOH): λ_{max} 404 (sh, 2.83), 339 (3.60), 272 (sh, 4.18), 264 (sh, 4.23), 258 (sh, 4.26), 250 (4.28), 219 (4.58); λ_{min} 314 (3.54), 236 (4.20), 207 (4.52). IR (KBr): 3065*w*, 3008*w*, 2965*m*, 1610*w*, 1448*s*, 1342*s*, 1312*s*, 1293*m*, 1274*m*, 1155*s*, 1144*s*, 1087*s*, 999*m*, 820*m*, 808*m*, 755*m*, 688*s*, 601*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.07–8.02 (*m*, H_o of 2 $PhSO_2$); 7.69–7.65 (*m*, H_p of 2 $PhSO_2$); 7.60–7.54 (*m*, H_m of 2 $PhSO_2$); 6.025 (*dd*, $^3J(10,11) = 6.6$, ^4J(11,Me–C(12)) = 1.4, H–C(11)); 5.959 (*d*, $^3J(10,11) = 6.6$, H–C(10)); 5.833 (*dd*, $^3J(5,6) = 6.8$, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.597 (*s*, H–C(8)); 5.592 (superimp. *d*, $^3J(5,6) \approx 5.7$, H–C(5)); 5.348 (*s*, H–C(1)); 5.340 (*s*, H–C(4)); 3.921, 3.753 (2*d*, $^3J(2,3) = 8.7$, H–C(2), H–C(3)); 2.348 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.043 (*d*, ^4J(6,Me–C(7)) = 0.9, Me–C(7)); 1.549 (br. *s*, Me–C(12)); 1.030, 1.000 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 572 (3, $M^{+\bullet}$), 431 (2, [M – SO_2Ph]$^+$), 264 (100, [M – $PhSO_2CH$=$CHSO_2Ph$]$^{+\bullet}$), 249 (31, [M – ($PhSO_2CH$=$CHSO_2Ph$ + Me]$^+$), 224 (25), 196 (30), 165 (20).

1.4.1.1. *9-Isopropyl-7,12-dimethyl-2,3-bis(phenylsulfonyl)benzo[*a*]heptalene* (**23a**). As described in *1.4.1*, **1a** (0.200 g, 0.75 mmol) and ZSE (0.385 g, 1.248 mmol) were heated in toluene (5 ml). CC (SiO_2, 3% MeOH/CH_2O_2) gave the brownish yellow foam of crude 2,3-*exo*-**22a** (0.484 g), which was not further purified. The crude material, dissolved in 1,2-dimethoxyethane (15 ml), and Cs_2CO_3 (1.50 g, 4.60 mmol) were heated for 1 h at 75° under rapid stirring and under Ar. The cooled mixture was diluted with AcOEt (*ca.* 100 ml) and washed twice with half-conc. brine. Drying ($MgSO_4$) and evaporation of the solvent gave a residue, which was purified by CC (SiO_2, ^{t}BuOMe/hexane 7 : 3) to yield a semisolid material, which was crystallized from Et_2O/pentane: **23a** (52.3 mg, 13% with respect to **1a**). Light red crystals. M.p. 230.4–231.3°. R_f (Et_2O/hexane 4 : 1) 0.47. UV/VIS (EtOH): λ_{max} 411 (sh, 3.31), 353 (3.59), 303 (4.31), 258 (4.48), 224 (4.54); λ_{min} 340 (3.57), 287 (4.25), 247 (4.45). IR (KBr): 3026*w*, 2961*m*, 2912*w*, 2863*w*, 1516*w*, 1446*m*, 1320*s*, 1153*s*, 1117*m*, 1084*m*, 790*w*, 728*m*, 717*m*, 687*s*, 599*s*, 580*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.327 (*s*, H–C(4)); 8.080 (*s*, H–C(1)); 8.04–7.92 (H_o of 2 $PhSO_2$); 7.64–7.46 (H_m and H_p of 2 $PhSO_2$); 6.895 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.515 (*d*, $^3J(6,5) = 11.7$, H–C(6)); 6.464 (*s*-like *AB*, H–C(10), H–C(11)); 5.740 (br. *s*, H–C(8)); 2.592 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 1.746 (*s*, Me–C(7)); 1.591 (*s*, Me–C(12)); 1.192, 1.179 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 572 (3, $M^{+\bullet}$), 431 (2, [M – $PhSO_2$]$^+$), 264 (100, [M – $PhSO_2CH$=$CHSO_2Ph$]$^{+\cdot}$), 249 (31, [M – ($PhSO_2CH$=$CHSO_2Ph$ + Me)]$^+$), 224 (25), 196 (30), 165 (20).

1.4.1.2. *(*P**,1S*,2S*,3R*,4R*)- and (*P**,1S*,2R*,3S*,4R*)-1,2,3,4-Tetrahydro-9- isopropyl-2-methoxy-7,12-dimethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2-*exo*,3-*endo*-(*P**)- and 2-*endo*,3-*exo*-(*P**)-**24a**). To an ice-cooled soln. of 2,3-*exo*-**22a** (0.326 g, 0.569 mmol) in MeOH (5 ml) was added 4% KOH in MeOH (15 ml), and the mixture was stirred for 30 min at r.t. The mixture was poured into half-conc. brine and extracted twice with ^{t}BuOMe. The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, Et_2O/hexane 7 : 3): 2-*exo*,3-*endo*-**24a**

(65 mg, 25%) and 2-*endo*,3-*exo*-**24a** (142 mg; 54%) in enriched form. Further purification by crystallization gave pure 2-*exo*,3-*endo*-(*P**)-**24a** (from Et_2O; 50 mg, 20%) and 2-*endo*,3-*exo*-(*P**)-**24a** (from Et_2O/pentane; 55 mg; 21%).

Data of 2-exo,*3*-endo-*(*P**)*-**24a**: Orange crystals. M.p. 155.8–156.5°. R_f (^{t}BuOMe/hexane 4:1) 0.47. UV/VIS (EtOH): λ_{max} 421 (sh, 2.78), 340 (3.57), 253 (4.35), 219 (4.52); λ_{min} 305 (3.57), 235 (4.23), 207 (4.46). IR (KBr): 2938*m*, 1655*w*, 1613*m*, 1444*m*, 1317*s*, 1302*s*, 1152*s*, 1106*s*, 1086*s*, 1006*m*, 750*m*, 723*s*, 692*m*, 617*m*, 596*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.91–7.87 (*m*, 2 H_o of $PhSO_2$); 7.67–7.63 (*m*, H_p of $PhSO_2$); 7.59–7.54 (*m*, 2 H_m of $PhSO_2$); 6.277 (*d*, $^3J(5,6) = 6.8$, H–C(5)); 6.148 (*dd*, $^3J(11,10) = 6.6$, $^4J(11,Me–C(12)) = 1.3$, H–C(11)); 6.089 (*dd*, $^3J(6,5) = 6.9$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 5.944 (*d*, $^3J(10,11) = 6.6$, H–C(10)); 5.656 (*s*, H–C(8)); 5.295 (*d*, $^3J(4,3) = 4.7$, H–C(4)); 4.695 (*s*, H–C(1)); 3.984 (*d*, $^3J(2,3) = 3.3$, H–C(2)); 3.625 (*q*-like *dd*, $\Sigma(^3J(2,3) + ^3J(3,4)) = 8.1$, H–C(3)); 3.099 (*s*, MeO–C(2)); 2.373 (*sept.*, $^3J = 7.1$, Me_2CH–C(9)); 2.168 (*s*, Me–C(7)); 2.067 (*s*, Me–C(12)); 1.066, 1.040 (2*d*, $^3J = 7.1$, Me_2CH–C(9)); assignments were verified by NOE. CI-MS (NH_3): 480 (16, $[M + NH_4]^+$), 463 (100, $[M + H]^+$), 441 (7), 431 (4, $[(M + H) - MeOH]^+$), 388 (15), 371 (15). EI-MS: 462 (60, $M^{+\cdot}$), 321 (58, $[M - PhSO_2]^+$), 264 (100, $[M - PhSO_2CH{=}CHOMe]^{+\cdot}$), 247 (20), 196 (16), 165 (12).

Data of 2-endo,*3*-exo-*(*P**)*-**20a**: Pale yellow crystals. M.p. 131.2–132.8°. R_f (^{t}BuOMe/hexane 4:1) 0.42. UV/VIS (EtOH): λ_{max} 411 (sh, 2.56), 333 (3.63), 270 (sh, 4.13), 251 (4.29), 217 (4.48); λ_{min} 308 (3.56), 234 (4.16), 210 (4.46). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.87–7.85 (*m*, 2 H_o of $PhSO_2$); 7.66–7.62 (*m*, H_p of $PhSO_2$); 7.58–7.54 (*m*, 2 H_m of $PhSO_2$); 6.081 (*dd*, $^3J(11,10) = 6.4$, $^4J(11,Me–C(12)) = 1.2$, H–C(11)); 6.040 (*d*, $^3J(5,6) = 6.5$, H–C(5)); 6.009 (*d*, $^3J(10,11) = 6.3$, H–C(10)); 5.932 (*dd*, $^3J(6.5) = 6.5$, $^4J(6,Me–C(7)) = 1.3$, H–C(6)); 5.702 (*s*, H–C(8)); 5.002 (*s*, H–C(4)); 4.706 (*d*, $^3J(1,2) = 4.8$, H–C(1)); 3.807 (*d*, $^3J(2,3) = 2.8$, H–C(3)); 3.611 (*q*-like *dd*, $\Sigma(^3J(1,2) + ^3J(2,3)) = 7.5$, H–C(2)); 3.186 (*s*, MeO–C(2)); 2.450 (*sept.*, $^3J = 7.1$, Me_2CH–C(9)); 2.144 (*s*, Me–C(7)); 2.127 (*s*, Me–C(12)); 1.140, 1.123 (2*d*, $^3J = 7.1$, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 462 (51, $M^{+\cdot}$), 321 (55, $[M - PhSO_2]^+$), 264 (100, $[M - PhSO_2CH{=}CHOMe]^{+\cdot}$), 247 (25), 196 (19), 165 (19).

1.4.1.3. *1,4-Dihydro-9-isopropyl-7,12-dimethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (**25a**) *and (*P**,1S*,2S*,3S*,4*R**)-1,2,3,4-Tetrahydro-9-isopropyl-7,12-dimethyl-2,3-bis(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2-*exo*,3-*endo*-(*P**)-**22a**). Dry powdered K_2CO_3 (0.950 g) was added to a soln. of 2,3-*exo*-**22a** (0.492 g, 0.859 mmol) in dioxane (18 ml). The mixture was stirred at 70° for 5 h and then at 80° for 1 h. After cooling to r.t., the mixture was diluted with AcOEt and washed twice with half-conc. brine. The org. phase was dried ($MgSO_4$) and concentrated. CC (SiO_2, Et_2O/hexane 7:3) of the residue furnished two fractions. From an Et_2O soln. of the main fraction, crystals of **23a** (25 mg, 5.2%) separated. The residue of the mother liquor consisted mainly of **25a** (0.219 g, *ca.* 59%). It was used in the next step without further purification and characterization. The second minor fraction gave, on crystallization from Et_2O, felted crystals of 2-*exo*,3-*endo*-(*P**)-**22a** (42 mg, 8.5%).

Data of 2-exo,*3*-endo-*(*P**)*-**22a**. M.p. 140–144°. R_f (Et_2O/hexane 7:3) 0.23. UV/VIS (EtOH): λ_{max} 411 (sh, 2.85), 341 (3.68), 272 (sh, 4.24), 264 (sh, 4.30), 256 (sh, 4.33), 253 (4.33), 219 (4.60); λ_{min} 310 (3.57), 236 (4.23), 207 (4.53). IR (KBr): 3063*w*, 2966*m*, 2941*m*, 2868*w*, 1613*w*, 1584*w*, 1447*m*, 1319*s*, 1250*w*, 1153*s*, 1085*m*, 996*m*, 964*w*, 929*w*, 862*m*, 832*m*, 749*m*, 733*m*, 719*m*, 688*m*, 591*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.894 (*dd*, $J_o = 8.4$, $J_m = 1.1$, H_o of $PhSO_2$–C(3)); 7.707 (*t* with fine structure, $J_o = 7.5$, H_p of $PhSO_2$–C(3)); 7.656 (*t* with fine structure, $J_o = 8.5$, H_p of $PhSO_2$–C(2)); 7.595 (*t*-like, H_m of $PhSO_2$–C(3)); 7.590 (*d*, $J_o = 8.5$, H_o of $PhSO_2$–C(2)); 7.500 (*t*-like, $J_o = 7.5$, H_m of $PhSO_2$–C(2)); 6.403 (*d*, $^3J(5,6) = 6.9$, H–C(5)); 6.088 (*dq*-like, $^3J(6,5) = 6.9$, $^4J(6,Me–C(7)) = 1.4$, H–C(6)); 6.054 (*dq*-like, $^3J(11,10) = 6.6$, $^4J(11,Me–C(12)) = 1.4$, H–C(11)); 5.929 (*d*, $^3J(10,11) = 6.6$, H–C(10)); 5.638 (*d*, $^4J = 0.9$, H–C(8)); 5.414 (*d*, $^3J(4,3) = 4.6$, H–C(4)); 5.033 (*d*, $^4J(1,4)) = 1.0$, H–C(1)); 4.132 (*t*-like, $\Sigma(^3J(3,2) + ^3J(3,4)) = 10.1$, H–C(3)); 3.738 (*d*, $^3J(2,3) = 5.4$, H–C(2)); 2.356 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.136 (*d*, $^4J(6,Me–C(7)) = 1.0$, Me–C(7)); 1.660 (br. *s*, Me–C(12)); 1.047, 1.021 (2*d*, $^3J = 6.9$, Me_2CH–C(9)); assignments were verified by NOE. EI-MS: 572 (6, $M^{+\cdot}$), 308 (6, $[PhSO_2CH{=}CHSO_2Ph]^{+\cdot}$), 264 (100, $[M - PhSO_2CH{=}CHSO_2Ph]^{+\cdot}$), 249 (31), 224 (21), 196 (25), 165 (13), 141 (21), 125 (32).

1.4.1.4. *9-Isopropyl-7,12-dimethyl-3-(phenylsulfonyl)-benzo[*a*]heptalene-1,2-diol Diacetate* (**30a**). To a soln. of crude **25a** (*ca.* 4.1 g, max. 9.52 mmol; prepared as described in *1.4.1.3*) in THF (95 ml) was added within 2 min a commercial 30% (*w*/*v*) aq. H_2O_2 soln. (45 ml). To this mixture, cooled by a cold-water bath, was added in drops aq. 6N NaOH (18 ml). The mixture was then allowed to warm to r.t. After

an induction period of *ca.* 1.5 h, the temp. of the mixture raised to *ca.* 30° accompanied by gas evolution. The mixture was cooled again with a cold-water bath until gas evolution ceased. The mixture was then diluted with Et_2O (400 ml) and washed successively with half-conc. brine, twice with 200-ml portions of 3% aq. KI soln., and again with half-conc. brine. The org. phase was dried ($MgSO_4$) and concentrated and the residue purified by CC (SiO_2, Et_2O/hexane 7:3): 3.7 g (*ca.* 84%) of crude hydroperoxide **27a** as an orange foam.

The foam (max. 7.96 mmol) was dissolved in pyridine (75 ml) and treated with Ac_2O (*Fluka*, *puriss.*, *p.a.*; 7.5 ml). The mixture was stirred for 2 h at r.t. (TLC monitoring (silica gel, hexane/AcOEt 3:2): R_f (**28a**) 0.5) and then diluted with Et_2O (700 ml) and washed with half-sat. brine (3×). The org. phase was dried ($MgSO_4$) and concentrated, followed by drying at 45°/1 mbar: crude **28a** (3.25 g, max. 91%) as brownish yellow foam, which was used in the next step without further purification and characterization.

The crude **28a** (max. 7.27 mmol) was dissolved in Ac_2O (175 ml), and dry AcONa (*Riedel de Haen*; dried overnight at 80°/1 mbar; 12 g, 0.146 mol) was added. The mixture was heated at 95° for 6 h. The temp. of the oil-bath was then raised to 105° for 1 h. The mixture was allowed to cool to r.t., poured into H_2O/AcOEt 5:2 (1.4 l) and stirred for a while before the org. phase was separated. A second portion of H_2O (1.0 l) was added. The biphasic mixture was neutralized by addition of solid K_2CO_3. The org. layer was separated, successively washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and concentrated. The residue was crystallized from ^{t}BuOMe: **30a** (0.320 g) as dark yellow crystals. The mother liquor was purified by CC (SiO_2, ^{t}BuOMe/hexane 3:2). The TLC-uniform fraction was recrystallized from Et_2O/pentane to yield a second crop of pure **30a** (0.599 g). Total yield 24% (rel. to **25a**). Dark yellow crystals. M.p. 200–205°. R_f (Et_2O/hexane 7:3) 0.27. UV/VIS (EtOH): λ_{max} 386 (sh, 2.89), 337 (3.68), 291 (4.22), 256 (4.47), 232 (4.51); λ_{min} 320 (3.63), 281 (4.20), 245 (4.43), 223 (4.50). IR (KBr): 3015*w*, 2962*m*, 2933*w*, 2869*w*, 1785*s*, 1584*w*, 1461*m*, 1447*m*, 1370*m*, 1323*s*, 1193*s*, 1168*s*, 1156*s*, 1037*m*, 877*m*, 724*m*, 689*m*, 588*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.935 (*s*, H–C(4)); 7.94 (*dd*-like, H_o of $PhSO_2$); 7.59 (*td*-like, H_p of $PhSO_2$); 7.51 (*td*, H_m of $PhSO_2$); 6.846 (*d*, $^3J(5,6) = 11.8$, H–C(5)); 6.404 (*s*-like *AB*, H–C(10), H–C(11)); 6.333 (*d*, $^3J(6,5) = 11.8$, H–C(6)); 5.657 (br. *s*, H–C(8)); 2.536 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.317 (*s*, AcO–C(2)); 1.949 (*s*, AcO–C(1)); 1.688 (br. *s*, Me–C(7)); 1.581 (*s*, Me–C(12)); 1.130, 1.107 (2*d*, $^3J = 6.9$, Me_2CH–C(9)). EI-MS: 530 (31, $M^{+\bullet}$), 488 (100, $[M - CH_2{=}C{=}O]^{+\bullet}$), 446 (29, $[M - 2\ CH_2{=}C{=}O]^{+\bullet}$), 431 (12, $[M - (2\ CH_2{=}C{=}O + Me)]^+$), 406 (13, $[M - (2\ CH_2{=}C{=}O + Me{-}C{\equiv}CH)]^{+\bullet}$), 358 (7).

1.4.1.5. *9-Isopropyl-1,2-dimethoxy-7,12-dimethyl-3-(phenylsulfonyl)-benzo[*a*]heptalene* (**31a**). In a *Schlenk* tube under Ar, **30a** (0.913 g, 1.72 mmol) was dissolved in dry DMF (15 ml) and treated with MeONa (*Fluka*, *pract.*; 0.250 g, 4.63 mmol). After stirring at r.t. for 15 min, MeI (1.0 ml, 2.28 g, 16.1 mmol) was added to the brown mixture. The *Schlenk* tube was sealed and stirred at r.t. for 2 h. The product mixture was diluted with AcOEt (200 ml), washed with brine (3 × 100 ml), dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, hexane/AcOEt 7:3). The product fraction was dried at 40°/1 mbar to give **31a** (0.785 g, 96%). Stiff bright yellow foam. R_f (hexane/AcOEt 7:3) 0.35. UV/VIS (EtOH): λ_{max} 384 (sh, 3.00), 331 (sh, 3.70), 290 (sh, 4.20), 256 (4.47), 233 (4.52), 218 (4.49); λ_{min} 245 (4.43), 221 (4.49), 213 (4.48). IR (KBr): 3064*w*, 3006*m*, 2958*s*, 2868*m*, 1573*w*, 1467*s*, 1447*s*, 1385*s*, 1317*s*, 1289*s*, 1249*m*, 1151*s*, 1111*m*, 1088*m*, 1066*m*, 1049*s*, 1000*m*, 986*m*, 722*m*, 687*m*, 593*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00 (*dd*-like, $^3J = 8.2$, $^4J = 1.4$, H_o of $PhSO_2$); 7.57 (*td*-like, H_p of $PhSO_2$); 7.52 (*td*-like, H_m of $PhSO_2$); 7.789 (*s*, H–C(4)); 6.844 (*d*, $^3J(5,6) = 11.7$, H–C(5)); 6.442 (*d*, $^3J(11,10) = 11.7$, H–C(11)); 6.376 (*dd*, $^3J(10,11) = 11.8$, $^4J(8,10) = 1.3$, H–C(10)); 6.271 (*d*, $^3J(5,6) = 11.7$, H–C(6)); 5.723 (br. *s*, H–C(8)); 3.786 (*s*, MeO–C(2)); 3.558 (*s*, MeO–C(1)); 2.547 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 1.731 (*d*, $^4J = 0.8$, Me–C(7)); 1.567 (*s*, Me–C(12)). 1.119, 1.113 (2*d*, $^3J = 6.9$, Me_2CH–C(9)). EI-MS: 474 (100, $M^{+\bullet}$), 459 (16, $[M - Me]^+$), 434 (10, $[M - Me{-}C{\equiv}CH]^{+\bullet}$), 431 (7, $[M - {}^i\!Pr]^+$), 419 (10, $[M - (Me{-}C{\equiv}CH + Me)]^+$).

1.4.1.6. *9-Isopropyl-1,2-dimethoxy-7,12-dimethylbenzo[*a*]heptalene* (**32a**). THF (3 ml) was cooled to −70°, and $TiCl_4$ (*Fluka*, *puriss.*; 250 µl, 2.27 mmol) was added in drops *via* a syringe. To the resultant yellow slurry was added in drops a soln. of 1M $LiAlH_4$ in THF (*Aldrich*; *ca.* 6.7 mmol), whereby a black slurry was generated. The temp. of the mixture was allowed to increase to −15° and then again cooled to −70° before a soln. of **31a** (0.107 g, 0.225 mmol) in THF (3 ml) was added in drops. The mixture was allowed to warm gradually to r.t. After stirring for 2 h, the mixture was poured into an ice-cold sat. aq.

NH_4Cl soln., stirred for 1.5 h, and extracted with AcOEt (3×). The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by CC (SiO_2, hexane/AcOEt 7:3): **32a** (57.7 mg, 77%). Light yellow oil after drying at 60°/1 mbar. R_f (hexane/AcOEt 7:3) 0.45. UV/VIS (hexane): λ_{max} 326 (sh, 3.65), 291 (sh, 4.08), 277 (sh, 4.14), 254 (4.30), 219 (4.48); λ_{min} 242 (4.26), 203 (4.42). HPLC/CD (*Chiralcel-OD-H*, 2% ^{i}PrOH/hexane, 0.5 ml/min, $t_R(P)/t_R(M) = 1.06$); extrema of the (*P*)-enantiomer: 337 (−0.46), 307 (0), 297 (0.14), 283 (0), 278 (−0.08), 272 (0), 252 (1.00), 234 (0.72), 221 (0.93), 212 (0). IR ($CHCl_3$): 3009*s*, 2962*s*, 2939*s*, 2870*m*, 2839*m*, 1590*m*, 1556*w*, 1484*s*, 1464*m*, 1451*m*, 1410*m*, 1276*s*, 1112*m*, 1048*m*, 1017*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.997 (*d*, $^3J(4,3) = 8.5$, H−C(4)), 6.888 (*d*, $^3J(3,4) = 8.5$, H−C(3)); 6.783 (*d*, $^3J(5,6) = 11.7$, H−C(5)); 6.445 (*d*, $^3J(11,10) = 11.8$, H−C(11)); 6.369 (*dd*, $^3J(10,11) = 11.8$, $^4J(8,10) = 1.2$, H−C(10)); 6.125 (*d*, $^3J(5,6) = 11.7$, H−C(6)); 5.738 (br. *s*, H−C(8)); 3.869 (*s*, MeO−C(2)); 3.600 (*s*, MeO−C(1)); 2.565 (*sept.*, $^3J = 6.9$, Me_2CH−C(9)); 1.727 (*d*, $^4J = 0.5$, Me−C(7)); 1.587 (*s*, Me−C(12)); 1.143, 1.138 (2*d*, $^3J = 6.9$, Me_2CH−C(9)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 153.92 (C(2)); 146.90 (C(9)); 145.31 (C(1)); 135.79 (C(11)); 133.48 (C(12)); 133.34 (C(7a)); 131.86 (C(4a)); 131.66 (C(12b)); 131.46 (C(5)); 131.21 (C(6)); 130.99 (C(10)); 128.29 (C(7)); 127.56 (C(12a)); 124.26 (C(4)); 122.28 (C(8)); 110.98 (C(3)); 60.77 (*Me*O−C(1)); 56.00 (*Me*O−C(2)); 34.57 (Me_2CH−C(9)); 23.03, 22.81 (Me_2CH−C(9)); 19.24 (*Me*−C(12)); 17.30 (*Me*−C(7)); assignments by ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 335 (100, $[M+H]^+$), 305 (3, $[(M+H) - CH_2{=}O]^+$), 205 (2).

1.4.2. *(*P**,1*S**,2*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-2,3-bis(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2,3-*exo*-(*P**)-**22b**). Under Ar, heptaleno[1,2-*c*]furan **1b** (90.8 mg, 0.363 mmol) and ZSE (0.181 g, 0.587 mmol) in toluene (2.5 ml) were stirred at 75° for 16 h. The soln. was cooled with an ice bath and stirred for 30 min. The precipitated product was collected by filtration, washed with cold toluene and Et_2O, and dried (50°/2 mbar) to afford 2,3-*exo*-(*P**)-**22b** (0.133 g) as dark yellow crystals. The filtrate was concentrated, the residue purified by CC (SiO_2, 3% MeOH/CH_2Cl_2), and the product fraction recrystallized from toluene to yield a second amount of 2,3-*exo*-(*P**)-**22b** (58.6 mg). Total yield 94%. M.p. 213.2–214.0°. R_f (CH_2Cl_2/MeOH 98:2) 0.33. UV/VIS (EtOH): λ_{max} 398 (sh, 2.73), 313 (sh, 3.55), 272 (sh, 4.07), 259 (4.19), 249 (sh, 4.17), 216 (4.54); λ_{min} 236 (4.06). IR (KBr): 3058*w*, 3019*m*, 2976*m*, 2940*m*, 2912*m*, 2854*w*, 1584*w*, 1447*s*, 1332*s*, 1311*s*, 1153*s*, 1136*s*, 1084*s*, 998*m*, 887*m*, 829*m*, 732*s*, 690*s*, 587*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; tentative assignments): 8.11–7.96 (*m*, 4 H of 2 $PhSO_2$); 7.77–7.56 (*m*, 6 H of 2 $PhSO_2$); 6.042 (*d*, $^3J(5,6) = 6.1$, H−C(5)); 5.970 (*m*, H−C(6), H−C(9)); 5.36–5.32 (*m*, H−C(1), H−C(10)); 5.233 (br. *s*, H−C(4)); 4.044 (*d*, $^3J(2,3) = 8.7$, H−C(2)); 3.512 (*d*, $^3J(3,2) = 8.7$, H−C(3)); 1.894 (br. *s*, Me−C(7), Me−C(10)); 1.595 (*s*, Me−C(8)); 1.583 (*d*, ^4J(Me−C(12),11) = 1.0, Me−C(12)). ^{1}H-NMR (300 MHz, C_6D_6; assignments according to those of the adduct of **1b** with dimethyl maleate [1]): 7.85, 7.79 (2*d*-like, H_o of 2 $PhSO_2$); 7.08–6.84 (*m*, 6 H of 2 $PhSO_2$); 5.887 (br. *s*, H−C(9)); 5.824 (*d*, $^3J(5,6) = 6.2$, H−C(5)); 5.734 (superimp. *s*, H−C(11)); 5.724 (superimp. *dd*, H−C(6)); 5.624 (br. *s*, H−C(1)); 5.210 (*t*-like, H−C(4)); 4.017 (*d*, $^3J(2,3) = 8.7$, H−C(2)); 3.598 (*d*, $^3J(3,2) = 8.7$, H−C(3)); 1.767 (*d*, ^4J(Me−C(7),6) = 1.2, Me−C(7)); 1.617 (*d*, ^4J(Me−C(10),9) = 1.2, Me−C(10)); 1.491 (*s*, Me−C(8)); 1.476 (*d*, ^4J(Me−C(12),11) = 1.2, Me−C(12)). EI-MS: 558 (0.5, $M^{+\cdot}$), 250 (18, $[M - PhSO_2CH{=}CHSO_2Ph]^{+\cdot}$), 235 (17, $[M - (PhSO_2CH{=}CHSO_2Ph + Me)]^+$), 210 (9, $[M - (PhSO_2CH{=}CHSO_2Ph + Me{-}C{\equiv}CH)]^{+\cdot}$).

1.4.2.1. *(*M**,1*R**,4*R**)-1,4-Dihydro-7,8,10,12-tetramethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* ((*M**)-**25b**). To a suspension of 2,3-*exo*-(*P**)-**22b** (0.494 g, 0.884 mmol) in hot (80°) 1,2-dimethoxyethane (20 ml) was added in one portion Cs_2CO_3 (1.91 g, 5.86 mmol). The mixture was vigorously stirred under Ar at 80° for 30 min. Subsequently, the cooled mixture was diluted with AcOEt (*ca.* 100 ml) and washed twice with half-conc. brine. The org. phase was dried ($MgSO_4$) and concentrated, the residue purified by CC (SiO_2, 1.5% MeOH/CH_2Cl_2), and the obtained product crystallized from AcOEt/^{t}BuOMe: (*M**)-**25b** (0.284 g, 77%): Light yellow crystals. M.p. 208.1–209.4°. R_f (^{t}BuOMe/hexane 7:3) 0.43. UV/VIS (EtOH): λ_{max} 342 (sh, 3.43), 293 (sh, 3.73), 276 (sh, 3.94), 243 (4.34); λ_{min} 229 (4.30). IR (KBr): 2975*m*, 2947*m*, 2912*m*, 1661*w*, 1622*w*, 1574*m*, 1446*s*, 1373*m*, 1317*s*, 1149*s*, 1087*s*, 920*m*, 842*s*, 724*s*, 689*s*, 642*m*, 613*s*, 591*s*. ^{1}H-NMR (600 MHz, C_6D_6): 7.65 (*d*-like, $J_o = 7.2$, H_o of $PhSO_2$); 6.89 (*tt*-like, $J_o = 7.4$, $J_m \approx 1.2$, H_p of $PhSO_2$); 6.83 (*t*-like, $J_o = 7.5$, H_m of $PhSO_2$); 6.780 (*d*, $^3J(1,2) = 1.9$, H−C(2)); 5.766 (br. *s*, H−C(9)); 5.608 (*dd*, $^3J(6,5) = 6.1$, ^4J(6,Me−C(7) = 1.4, H−C(6)); 5.573 (br. *s*, H−C(11)); 5.543 (*d*, $^3J(5,6) = 6.1$, H−C(5)); 5.284 (*s*, H−C(4)); 5.115 (*t*-like *s*, $^1/2 \cdot {}^3J(1,2) \approx {}^4J(1,4) = 0.9$, H−C(1)); 1.757 (*d*,

^4J(Me–C(7),6) = 1.2, Me–C(7)); 1.749 (*d*, ^4J(Me–C(10),9) = 1.1, Me–C(10)); 1.678 (*d*, ^4J(Me–C(12),11) = 1.2, Me–C(12)); 1.447 (*s*, Me–C(8)); assignments were verified by NOE. EI-MS: 416 (100, $M^{+\cdot}$), 399 (12, $[M-\mathrm{Me}]^+$), 376 (10, $[M-\mathrm{Me-C{\equiv}CH}]^{+\cdot}$), 362 (6, $[M-\mathrm{Me-C{\equiv}C-Me}]^{+\cdot}$), 275 (82, $[M-\mathrm{PhSO_2}]^+$), 260 (21, $[M-(\mathrm{PhSO_2}+\mathrm{Me})]^{+\cdot}$), 215 (22), 193 (31), 178 (20).

1.4.2.2. *(*M**,1*S**,2*S**,3*S**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalen-2-yl Hydroperoxide* (2-*exo*,3-*endo*-(*M**)-**27b**). To a soln. of (*M**)-**25b** (35.7 mg, 0.0857 mmol) in THF (1 ml) was added, at r.t. in drops a commercial 30% (*w*/*v*) aq. H_2O_2 soln. (0.3 ml). After stirring for 1 min, aq. 6N NaOH (0.2 ml) was added in drops, (→ clear soln. after *ca.* 5 min). The soln. was stirred at r.t. for 1 h, then poured into H_2O and extracted with CH_2Cl_2. The combined extracts were successively washed with 3% aq. KI soln. and brine, dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, hexane/AcOEt 1:1) to provide the product as a yellow oil (after drying at 20°/2 mbar: 40.5 mg, 105%). Crystallization from Et_2O gave pure 2-*exo*,3-*endo*-(*M**)-**27b** (28.0 mg, 73%). Light yellow crystals. M.p. 135–145° (dec.). R_f (hexane/AcOEt 7:3) 0.17. UV/VIS (EtOH): λ_{max} 384 (sh, 2.81), 307 (sh, 3.62), 257 (4.26), 250 (sh, 4.25), 216 (sh, 4.43); λ_{min} 233 (4.12). IR (KBr): 3338*s* (OH), 2937*m*, 2911*m*, 1585*w*, 1446*s*, 1406*m*, 1373*m*, 1304*s*, 1218*m*, 1137*s*, 1081*s*, 1027*s*, 975*m*, 836*s*, 728*m*, 645*m*, 607*s*, 584*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.229 (*s*, HOO–C(2)); 7.83–7.78 (*m*, H_o of $PhSO_2$); 7.65–7.50 (*m*, H_m and H_p of $PhSO_2$); 6.232 (*d*, ^3J(5,6) = 6.1, H–C(5)); 6.161 (br. *s*, H–C(9)); 6.087 (*dd*, ^3J(6,5) = 6.1, ^4J(6,Me–C(7)) = 1.4, H–C(6)); 5.985 (br. *s*, H–C(11)); 5.175 (br. *s*, H–C(1)); 4.863 (*d*, ^3J(4,3) = 4.8, H–C(4)); 4.410 (*d*, ^3J(2,3) = 3.2, H–C(2)); 3.591 (*dd*, ^3J(3,2) = 3.2, ^3J(3,4) = 4.7, H–C(3)); 2.079 (*d*, ^4J(Me–C(12),11) = 1.2, Me–C(12)); 2.030 (*d*, ^4J(Me–C(7),6) = 1.0, Me–C(7)); 2.015 (*d*, ^4J(Me–C(10),9) = 1.2, Me–C(10)); 1.733 (*s*, Me–C(8)); assignments were verified by NOE. ESI-MS ($C_{26}H_{26}O_5S$, exact mass 450.15): 489 (63, $[M+\mathrm{K}]^+$), 473 (54, $[M+\mathrm{Na}]^+$), 451 (47, $[M+\mathrm{H}]^+$), 433 (36, $[(M+\mathrm{H})-\mathrm{H_2O}]^+$), 292 (55, $[(M+\mathrm{H})-\mathrm{PhSO_2}]^+$), 291 (100, $[M-\mathrm{PhSO_2}]^+$).

On standing in $CDCl_3$ soln. for several days, 2-*exo*,3-*endo*-(*M**)-**27b** decomposed to a 3:2 mixture of two compounds, which represent presumably the *meso*- and *rac*-form of the dimers of 2-*exo*,3-*endo*-(*M**)-**27b** with a 2,2′-*exo*-peroxy bridge. ^{1}H-NMR (600 MHz, $CDCl_3$; major component, *ca.* 60% of the mixture): 7.802 (*d*, J_o = 7.7, H_o of $PhSO_2$); 7.640 (*t*, J_o = 7.4, H_p of $PhSO_2$); 7.529 (*t*, J_o = 7.7, H_m of $PhSO_2$); 6.225 (*d*, ^3J(5,6) = 6.0, H–C(5)); 6.155 (br. *s*, H–C(9)); 6.08 (*d*, ^3J(6,5) ≈ 6, H–C(6)); 5.982 (br. *s*, H–C(11)); 5.171 (*s*, H–C(1)); 4.855 (*d*, ^3J(4,3) = 4.7, H–C(4)); 4.407 (*d*, ^3J(2,3) = 3.1, H–C(2)); 3.584 (*t*-like, Σ(^3J(3,2) + ^3J(3,4)) = 7.8, H–C(3)); 2.077 (br. *s*, Me–C(12)); 2.029 (br. *s*, Me–C(7)); 2.009 (br. *s*, Me–C(10)); 1.731 (*s*, Me–C(8)); assignments were verified by NOESY. ^{1}H-NMR (600 MHz, $CDCl_3$; minor component, 40% of the mixture): 7.904 (*d*, J_o = 7.4, H_o of $PhSO_2$); 7.652 (*t*, J_o ≈ 7.2, H_p of $PhSO_2$); 7.566 (*t*, J_o = 7.7, H_m of $PhSO_2$); 6.523 (*d*, ^3J(5,6) = 6.4, H–C(5)); 6.308 (br. *d*, ^3J(5,6) = 6.4, H–C(6)); 6.101 (br. *s*, H–C(9)); 6.076 (br. *s*, H–C(11)); 5.369 (*d*, ^3J(3,4) = 4.6, H–C(4)); 4.984 (*s*, H–C(1)); 4.712 (*d*, ^3J(2,3) = 3.7, H–C(2)); 3.584 (*t*-like, Σ(^3J(3,2) + ^3J(3,4)) = 8.4, H–C(3)); 2.05 (br. *s*, Me–C(7), Me–C(12)); 1.961 (br. *s*, Me–C(10)); 1.735 (*s*, Me–C(8)); all assignments were secured by NOESY.

1.4.2.3. *(*M**,1*S**,2*S**,3*S**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-3-(phenylsulfonyl)-1,4:2,3-diepoxybenzo[*a*]heptalene* (=*(*M**,9*R**,9*a*S*,10*a*S,11S*)-9,9a,10a,11-Tetrahydro-1,3,5,6-tetramethyl-9a-(phenylsulfonyl)-9,11-epoxyheptaleno[1′,2′:4,5]benz[1,2-*b*]oxirene*; 2,3-*exo*-(*M**)-**26b**). To a soln. of (*M**)-**25b** (0.149 g, 0.358 mmol) in MeOH (5 ml) at r.t. were added successively a commercial 30% (*w*/*v*) aq. H_2O_2 soln. (1.2 ml) and aq. 6N NaOH (0.8 ml). After stirring at 75° for 1.5 h, the mixture was poured into brine and extracted with AcOEt (2×). The combined extracts were washed with a 3% aq. KI soln. and then half-conc. brine, followed by drying ($MgSO_4$) and removal of the solvent. The solid residue was recrystallized from AcOEt to afford 2,3-*exo*-(*M**)-**26b** (64.4 mg) as light yellow crystals. After CC separation (SiO_2, hexane/AcOEt 3:1) of the residue of the mother liquor, a second crop of 2,3-*exo*-(*M**)-**26b** (14.6 mg) was obtained. Total yield: 51%. M.p. 161–162° (dec.). R_f (hexane/AcOEt 7:3) 0.27. UV/VIS (EtOH): λ_{max} 380 (sh, 2.85), 311 (sh, 3.61), 254 (4.22), 247 (sh, 4.21), 216 (sh, 4.39); λ_{min} 234 (4.11). IR (KBr): 3024*w*, 2938*m*, 2919*m*, 1622*w*, 1447*s*, 1325*s*, 1159*s*, 949*m*, 826*m*, 761*m*, 729*m*, 643*m*, 612*s*, 598*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments in analogy to those of 2,3-*exo*-(*M**)-**2b**): 7.82–7.78 (*m*, H_o of $PhSO_2$); 7.69–7.62 (*m*, H_p of $PhSO_2$); 7.55–7.48 (*m*, 2 H_m of $PhSO_2$); 6.346 (*d*, ^3J(5,6) = 6.2, H–C(5)); 6.125 (br. *s*, H–C(9)); 6.072 (*dq*, ^3J(6,5) = 6.2, ^4J(6,Me–C(7) = 1.5, H–C(6)); 5.925 (br. *s*, H–C(11)); 4.879, 4.868 (2*s*, H–C(1), H–C(4)); 3.265 (*s*, H–C(2)); 2.025 (*d*, ^4J(Me–C(12),11) = 1.2, Me–C(12)); 2.001 (*d*, ^4J(Me–C(7),6) = 1.0, Me–C(7)); 1.931 (*d*, ^4J(Me–C(10),9) = 1.1, Me–C(10)); 1.741 (*s*,

Me–C(8)). ESI-MS ($C_{26}H_{24}O_4S$, exact mass 432.14): 491 (34, $[M+K]^+$), 455 (34, $[M+Na]^+$), 450 (62, $[M+H_2O]^{+\cdot}$), 433 (53, $[M+H]^+$), 292 (80, $[(M+H)-PhSO_2]^+$), 291 (100, $[M-PhSO_2]^+$), 263 (47, $[M-(PhSO_2+CO)]^+$).

The structure of 2,3-*exo*-(*M**)-**26b** was finally established by an X-ray crystal-structure determination (see *Fig. 4* and *Table 8*).

1.4.2.4. *(*P**,1*S**,3*R**,4*R**)-1,2,3,4-Tetrahydro-7,8,10,12-tetramethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalen-2-one* (3-*exo*-(*P**)-**28b**). To a soln. of 2-*exo*,3-*endo*-(*M**)-**27b** (0.185 g, 0.411 mmol) in pyridine (4 ml) was added at r.t. Ac_2O (0.4 ml). The soln. was stirred at r.t. for 1 h, then poured into H_2O and ice and extracted twice with Et_2O. The combined org. phases were washed with half-conc. brine and H_2O, dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, hexane/AcOEt 1:1), and the obtained product (95 mg, 53%) crystallized from AcOEt/hexane: pure 3-*exo*-(*P**)-**28b** (81 mg, 46%). Light yellow crystals. M.p. 166.8–168.3°. R_f (hexane/AcOEt 3:1) 0.38. UV/VIS (EtOH): λ_{max} 409 (sh, 3.30), 336 (3.93), 282 (sh, 4.04), 272 (sh, 4.11), 263 (sh, 4.15), 245 (sh, 4.26), 219 (4.44); λ_{min} 308 (3.86), 213 (4.44). IR (KBr): 2973*m*, 2943*m*, 2913*m*, 2853*w*, 1770*s*, 1653*w*, 1622*w*, 1584*w*, 1446*s*, 1377*w*, 1321*s*, 1155*s*, 1147*s*, 1084*s*, 842*m*, 751*m*, 705*m*, 686*m*, 565*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.91–7.89 (*m*, H_o of $PhSO_2$); 7.68–7.64 (*m*, H_p of $PhSO_2$); 7.56–7.53 (*m*, H_m of $PhSO_2$); 6.401 (*d*, $^3J(5,6)=6.2$, H–C(5)); 6.114 (*dd*, $^3J(6,5)=6.2$, $^4J(6,Me–C(7))=1.4$, H–C(6)); 5.971 (br. *s*, H–C(11)); 5.963 (br. *s*, H–C(9)); 5.602 (*s*, H–C(4)); 4.699 (*s*, H–C(1)); 3.821 (*s*, H–C(3)); 2.019 (*d*, $^4J(11,Me–C(12))=1.2$, Me–C(12)); 1.988 (*d*, $^4J(Me–C(7),6)=1.1$, Me–C(7)); 1.898 (*d*, $^4J(Me–C(10),9)=1.2$, Me–C(10)); 1.642 (*s*, Me–C(8)); assignments were verified by NOE. EI-MS: 432 (100, $M^{+\cdot}$), 417 (29, $[M-Me]^+$), 404 (18, $[M-CO]^{+\cdot}$), 389 (36, $[M-(Me+CO)]^+$), 374 (51, $[M-(2\,Me+CO)]^{+\cdot}$), 286 (36), 263 (70, $[M-(PhSO_2+CO)]^+$), 235 (24).

1.4.2.5. *7,8,10,12-Tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalen-2-ol* (**29b**). (*M**)-**25b** (0.453 g, 1.088 mmol) was transformed into 2-*exo*,3-*endo*-(*M**)-**27b** (0.438 g, 89%) and then in 3-*exo*-(*P**)-**28b** (0.332 g, 79%) as described above.

To an ice-cooled soln. of crude 3-*exo*-(*P**)-**28b** (37.3 mg, 0.0862 mmol) in CH_2Cl_2 (1.2 ml) was added a soln. of trimethylsilyl trifluoromethanesulfonate (0.17 ml, 1.26 mmol) and Et_3N (0.10 g, 1.0 mmol) in CH_2Cl_2 (3 ml). The mixture was stirred for 80 min at 0°. Thereafter, two drops of H_2O were added, and the dark-green mixture was stirred for 5 min, before it was poured into sat. aq. NH_4Cl soln., followed by extraction with CH_2Cl_2 (2×). The combined org. phases were washed successively with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, Et_2O/hexane 4:1), leading to a yellow semicrystalline material (21.6 mg, 60%), which was crystallized from Et_2O: pure **29b** (10.8 mg, 30%). Dark yellow crystals. M.p. 231.2–233.3°. R_f (Et_2O/hexane 4:1) 0.30. UV/VIS (EtOH): λ_{max} 386 (sh, 3.21), 337 (sh, 3.82), 285 (sh, 4.14), 257 (4.54), 233 (4.52), 211 (4.47); λ_{min} 318 (3.76), 243 (4.45), 217 (4.46), 207 (4.46). IR (KBr): 3344*s*, 3061*w*, 2965*m*, 2911*m*, 2854*m*, 1738*w*, 1620*m*, 1604*s*, 1550*m*, 1479*s*, 1448*s*, 1375*m*, 1346*m*, 1295*s*, 1283*s*, 1136*s*, 1087*s*, 996*m*, 732*s*, 693*m*, 622*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 9.099 (*s*, OH–C(2)); 7.99–7.96 (*m*, H_o of $PhSO_2$); 7.64–7.60 (*m*, H_p of $PhSO_2$); 7.593 (*s*, H–C(4)); 7.57–7.53 (*m*, H_m of $PhSO_2$); 6.717 (*d*, $^3J(5,6)=11.7$, H–C(5)); 6.606 (*s*, H–C(1)); 6.159 (*d*, $^3J(6,5)=11.7$, H–C(6)); 6.136 (br. *s*, H–C(11)); 6.016 (br. *s*, H–C(9)); 2.009 (*d*, $^4J(Me–C(10),9)=1.0$, Me–C(10)); 1.898 (*d*, $^4J(Me–C(8),9)=1.1$, Me–C(8)); 1.702 (*s*, Me–C(7)); 1.607 (*s*, Me–C(12)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 156.40 (C(2)); 145.34 (C(12b)); 141.70 (C_{ipso} of $PhSO_2$); 139.19 (C(10)); 136.53 (C(7a)); 134.21 (C(8)); 133.74 (C_p of $PhSO_2$); 132.79 (C(6)); 131.39 (C(12)); 131.04 (C(4a)); 130.40 (C(11)); 130.01 (C(5)); 129.51 (C_m of $PhSO_2$); 129.24 (C(4)); 128.93 (C(12a)); 128.75 (C(9)); 127.24 (C(7)); 126.98 (C_o of $PhSO_2$); 122.23 (C(3)); 117.97 (C(1)); 25.01 (*Me*–C(10)); 22.85 (*Me*–C(8)); 19.24 (*Me*–C(12)); 18.14 (*Me*–C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 416 (100, $M^{+\cdot}$), 401 (76, $[M-Me]^+$), 376 (43, $[M-Me-C\equiv CH]^{+\cdot}$), 362 (26), 260 (24), 245 (13).

1.4.2.6. *7,8,10,12-Tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalene-1,2-diol Diacetate* (**30b**). In a sealed *Schlenk* tube under Ar, a mixture of 3-*exo*-(*P**)-**28b** (50.8 mg, 0.1174 mmol) and dry AcONa (0.145 g) in Ac_2O (3 ml) was heated at 80° for 17 h. The cooled mixture was taken up in AcOEt (70 ml) and washed with a half-sat. aq. $NaHCO_3$ soln. Drying ($MgSO_4$) and concentration of the org. layer afforded a solid residue, which was recrystallized from CH_2Cl_2/^{t}BuOMe to give **30b** (47.9 mg) as light yellow microcrystalline needles. CC (SiO_2, hexane/AcOEt 3:2) of the mother liquor and recrystalliza-

tion from Et_2O gave a second crop of **30b** (3.8 mg). Total yield 85%. M.p. *ca.* 240–248°. R_f (hexane/AcOEt 3:2) 0.33. UV/VIS (EtOH): λ_{max} 338 (3.67), 297 (4.25), 253 (4.51), 231 (4.53), 217 (4.52); λ_{min} 323 (3.63), 281 (4.18), 244 (4.47), 223 (4.52), 213 (4.42). HPLC/CD (*cf. Fig. 9,a*; *Chiralcel-OD-H* (4.6 × 250 mm), hexane/^{i}PrOH 4:1, 0.5 ml/min, $t_R(P)/t_R(M) = 1.06$; extrema of the (*P*)-enantiomer: *ca.* 375sh (faintly visible; −0.12), 340 (−0.18), 314 (0), 302 (0.21), 285 (0), 282 (−0.01), 280 (0), 270 (0.09), 264 (0), 253 (−0.31), 244 (0), 232 (1.00), 219 (0), 216 (−0.06), 212 (0). IR (KBr): 2978*w*, 2921*w*, 1791*s*, 1767*m*, 1448*m*, 1402*m*, 1368*m*, 1391*s*, 1189*s*, 1170*s*, 1153*s*, 1091*m*, 1033*m*, 869*m*, 850*m*, 591*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.96 (*d*-like, $^3J = 7.4$, H_o of $PhSO_2$); 7.948 (*s*, H−C(4)); 7.60 (*t*-like, $^3J = 7.4$, H_p of $PhSO_2$); 7.52 (*t*-like, $^3J = 7.8$, H_m of $PhSO_2$); 6.855 (*d*, $^3J(5,6) = 11.8$, H−C(5)); 6.315 (*d*, $^3J(6,5) = 11.8$, H−C(6)); 6.148 (br. *s*, H−C(11)); 5.964 (br. *s*, H−C(9)); 2.308 (*s*, AcO−C(2)); 1.994 (*d*, ^4J(Me−C(10),9) = 0.6, Me−C(10)); 1.961 (*s*, AcO−C(1)); 1.917 (*d*, ^4J(Me−C(8),9) = 0.6, Me−C(8)); 1.717 (*s*, Me−C(7)); 1.552 (*s*, Me−C(12)); assignments were verified by NOE. ^{13}C-NMR (150 MHz, $CDCl_3$): 167.76 (Me*C*OO−C(1)); 166.93 (Me*C*OO−C(2)); 141.36 (C(2)); 141.23 (C(1)); 141.13 (C_{ipso} of $PhSO_2$); 139.69 (C(10)); 137.41 (C(4a)); 137.38 (C(7a)); 136.34 (C(8)); 136.15 (C(12b)); 135.53 (C(6)); 134.95 (C(12)); 133.59 (C_p of $PhSO_2$); 132.55 (C(3)); 130.28 (C(11)); 130.08 (C(5)); 129.17 (C_m of $PhSO_2$); 129.11 (C(9)); 128.46 (C(7)); 127.81 (C_o of $PhSO_2$); 126.86 (C(4)); 121.41 (C(12a)); 25.22 (Me−C(10)); 22.53 (Me−C(8)); 20.53 (*Me*COO−C(2)); 19.90 (*Me*COO−C(1)); 18.84 (*Me*−C(12)); 18.63 (*Me*−C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 516 (29, $M^{+\cdot}$), 474 (100, $[M - CH_2{=}C{=}O]^{+\cdot}$), 432 (42, $[M - 2\,CH_2{=}C{=}O]^{+\cdot}$), 417 (38, $[M - (2\,CH_2{=}C{=}O + Me)]^+$), 392 (17, $[M - (2\,CH_2{=}C{=}O + Me{-}C{\equiv}CH)]^{+\cdot}$), 276 (10), 202 (10).

1.4.2.7. *1,2-Dimethoxy-7,8,10,12-tetramethyl-3-(phenylsulfonyl)benzo[*a*]heptalene* (**31b**). Under Ar, **30b** (0.217 g, 0.421 mmol) was dissolved in dry DMF (5 ml) and treated with MeONa (70 mg, 1.29 mmol) in a *Schlenk* tube. After stirring at r.t. for 15 min, MeI (0.20 ml, 0.450 g, 3.17 mmol) was added in drops. The *Schlenk* tube was sealed and stirred at r.t. for 2 h. The mixture was then diluted with AcOEt (100 ml), washed with half-conc. brine (3 × 50 ml), dried ($MgSO_4$), and concentrated. The residue was purified by CC (SiO_2, CH_2Cl_2, R_f 0.56) and gave crude **31b** (0.203 g) as stiff yellow foam. Crystallization from Et_2O led to pure **31b** (0.174 g, 90%) as light yellow crystals. Light yellow needles from CH_2Cl_2/hexane. M.p. 199.4–200.2°. R_f (hexane/AcOEt 3:2) 0.43. R_f (CH_2Cl_2) 0.56. UV/VIS (EtOH): λ_{max} 333 (sh, 3.67), 300 (4.23), 254 (4.52), 233 (4.56), 221 (sh, 4.50); λ_{min} 283 (4.20), 245 (4.48), 210 (4.48). HPLC/CD (*cf. Fig. 9,b*; *Chiralcel-OD-H* (4.6 × 250 mm), 5% ^{i}PrOH/hexane, 0.5 ml/min, $t_R(P)/t_R(M) = 1.20$; extrema of the (*P*)-enantiomer): *ca.* 368sh (faintly visible, −0.15), 344 (−0.20), 316 (0), 303 (0.16), 290 (0), 282 (−0.09), 274 (0), 267 (0.09), 260 (0), 252 (−0.19), 245 (0), 233 (1.0). IR (KBr): 2973*w*, 2940*m*, 2914*m*, 2855*w*, 1615*w*, 1573*m*, 1478*s*, 1447*s*, 1385*s*, 1306*s*, 1289*s*, 1255*s*, 1151*s*, 1089*s*, 1042*s*, 1009*s*, 891*m*, 849*m*, 774*m*, 761*m*, 720*m*, 690*m*, 623*m*, 596*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.01 (*dt*-like, $J_o = 8$, H_o of $PhSO_2$); 7.824 (*s*, H−C(4)); 7.578 (*tt*-like, $J_o \approx 7.4$, H_p of $PhSO_2$); 7.507 (*t*-like, $J_o \approx 7.7$, H_m of $PhSO_2$); 6.849 (*d*, $^3J(5,6) = 11.8$, H−C(5)); 6.255 (*d*, $^3J(6,5) = 11.8$, H−C(6)); 6.176 (br. *s*, H−C(11)); 6.039 (br. *s*, H−C(9)); 3.751 (*s*, MeO−C(2)); 3.549 (*s*, MeO−C(1)); 2.021 (*d*, ^4J(Me−C(10),9) = 0.9, Me−C(10)); 1.949 (*d*, ^4J(Me−C(8),9) = 0.9, Me−C(8)); 1.752 (*s*, Me−C(7)); 1.490 (*s*, Me−C(12)); assignments were verified by NOE. ^{13}C-NMR (150. MHz, $CDCl_3$): 151.54 (C(1)); 150.51 (C(2)); 141.87 (C_{ipso} of $PhSO_2$); 139.03 (C(10)); 137.32 (C(7a)); 137.24 (C(12b)); 134.55 (C(4a)); 133.94 (C(8)); 133.75 (C(6)); 133.68 (C(12)); 133.44 (C(3)); 133.04 (H_p of $PhSO_2$); 130.96 (C(5)); 130.79 (C(11)); 129.45 (C(9)); 128.70 (C_m of $PhSO_2$); 128.23 (C_o of $PhSO_2$, C(7)); 124.01 (C(4)); 122.57 (C(12a)); 61.20 (*Me*O−C(2)); 60.44 (*Me*O−C(1)); 25.16 (*Me*−C(10)); 23.25 (*Me*−C(8)); 18.96 (*Me*−C(12)); 18.42 (*Me*−C(7)); assignments by ^{1}H,^{13}C-correlation spectra. CI-MS (NH_3): 478 (100, $[M + NH_4]^+$), 461 (9, $[M + H]^+$).

The structure of **31b** was established by an X-ray crystal-structure determination (see *Fig. 5* and *Table 8*).

1.4.2.8. *1,2-Dimethoxy-7,8,10,12-tetramethylbenzo[*a*]heptalene* (**32b**). Dry THF (3 ml) was cooled to −70°, and $TiCl_4$ (250 µl, 432 mg, 2.27 mmol) was added in drops *via* a syringe. To the yellow slurry, 1M $LiAlH_4$ in THF (*ca.* 6.7 mmol) was added in drops, thus generating a gray-black slurry. The temp. of the mixture was allowed to increase to −10° and was then again cooled to −70°, before a soln. of **31b** (0.107 g, 0.225 mmol) in THF (3 ml) was added in drops. The mixture was allowed to warm gradually to r.t. and stirred for a further 2 h. The mixture was poured into an ice-cold sat. aq. NH_4Cl soln. (50 ml), stirred for 1.5 h, and extracted with AcOEt (3×). The combined org. phases were washed with brine,

dried ($MgSO_4$), and concentrated. The crude product was purified by CC (SiO_2, hexane/AcOEt 7:3). The residue (75.9 mg) thus obtained was dried at 60°/1 mbar and crystallized from pentane at −20° to give pure **32b** (44.2 mg, 72%). Light yellow crystals. M.p. 116.7–119.2°. R_f (hexane/AcOEt 7:3) 0.45. UV/VIS (hexane): λ_{max} 322 (sh, 3.39), 291 (3.87), 250 (4.03), 223 (4.21), 194 (4.10); λ_{min} 273 (3.84), 242 (4.01), 203 (4.10). HPLC/CD (*cf. Fig. 9,c*; *Chiralcel-OD-H* (4.6 × 250 mm), 2% ^{i}PrOH/hexane, 0.6 ml/min, $t_R(P)/t_R(M) = 2.25$; extrema of the (*P*)-enantiomer): 335 (−0.55), 304 (0), 294 (0.22), 280 (0), 277 (−0.07), 273 (0), 254 (1.00), 230 (0.59), 221 (0.80), 212 (0), 208 (−0.28). IR (KBr): 2995*m*, 2911*m*, 2839*m*, 1616*w*, 1589*m*, 1556*w*, 1485*s*, 1444*s*, 1409*s*, 1372*w*, 1279*s*, 1134*m*, 1092*m*, 1042*m*, 1021*m*, 1819*m*, 800*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.033 (*d*, $^3J(4,3) = 8.5$, H−C(4)); 6.893 (*d*, $^3J(3,4) = 8.5$, H−C(3)); 6.790 (*d*, $^3J(5,6) = 11.6$, H−C(5)); 6.188 (br. *s*, H−C(11)); 6.106 (*d*, $^3J(6,5) = 11.7$, H−C(6)); 6.048 (br. *s*, H−C(9)); 3.880 (*s*, MeO−C(2)); 3.603 (*s*, MeO−C(1)); 2.029 (*d*, ^4J(Me−C(10),9) = 1.0, Me−C(10)); 1.972 (*d*, ^4J(Me−C(8),9) = 1.1, Me−C(8)); 1.743 (*s*, Me−C(7)); 1.567 (*s*, Me−C(12)); assignments were verified by NOE. ^{13}C-NMR (150.9 MHz, $CDCl_3$): 153.94 (C(2)); 145.60 (C(1)); 138.16 (C(10)); 137.26 (C(7a)); 133.94 (C(8)); 132.91 (C(12)); 132.40 (C(12b)); 132.06 (C(5)); 132.01 (C(4a)); 131.40 (C(6)); 131.17 (C(11)); 129.12 (C(9)); 127.61 (C(7)); 124.65 (C(4)); 124.01 (C(12a)); 110.96 (C(3)); 60.82 (*Me*O−C(2)); 56.17 (*Me*O−C(1)); 25.34 (*Me*−C(10)); 23.48 (*Me*−C(8)); 19.47 (*Me*−C(12)); 18.63 (*Me*−C(7)); assignments by ^{1}H,^{13}C-correlation spectra. EI-MS: 320 (100, $M^{+\cdot}$), 305 (41, $[M - Me]^+$), 290 (17, $[M - 2\,Me]^{+\cdot}$), 280 (17, $[M - Me - C{\equiv}CH]^{+\cdot}$), 275 (17, $[M - 3\,Me]^+$), 265 (9, $[M - (Me - C{\equiv}CH + Me)]^+$).

1.4.3. *(*P**,1*S**,2*S**,3*S**,4*R**)- and (*M**,1*S**,2*S**,3*S**,4*R**)-1,2,3,4-Tetrahydro-4,7,8,10,12-pentamethyl-2,3-bis(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* (2-*exo*,3-*endo*-(*P**)- and 2-*exo*,3-*endo*-(*M**)-**22c**). Heptaleno[1,2-*c*]furan **1c** (0.100 g, 0.378 mmol) and ZSE (0.170 g, 0.551 mmol) were stirred in toluene (2.5 ml) in a *Schlenk* vessel under Ar at 110° for 21 h. The dark brown soln. was then cooled to 0°, whereby small colorless crystals of ZSE were formed and filtered off (47 mg). The residue of the mother liquor was separated into two fractions by CC (SiO_2, 2% MeOH/CH_2Cl_2). The faster running component was crystallized from Et_2O and gave pure 2-*exo*,3-*endo*-(*M**)-**22c** (28 mg, 13%) as light yellow crystals. The slower moving component represented a light brown foam (155 mg), which contained still some ZSE (*ca.* 15%; *i.e.*, yield of the (*P**)-epimer 62%).

Data of 2-exo,*3*-endo-*(*M**)*-**22c**: Light yellow crystals from Et_2O. M.p. 191.6–192.6°. R_f (1% MeOH/CH_2Cl_2) 0.46. UV/VIS (EtOH): λ_{max} 391 (sh, 2.98), 323 (3.70), 272 (sh, 4.22), 258 (4.39), 219 (4.58); λ_{min} 304 (3.67), 235 (4.29), 210 (4.56). IR (KBr): 3059*w*, 2973*m*, 2937*m*, 2915*m*, 1656*w*, 1616*w*, 1584*w*, 1447*s*, 1397*w*, 1377*w*, 1323*s*, 1309*s*, 1292*m*, 1149*s*, 1085*s*, 847*m*, 822*m*, 739*s*, 689*s*, 614*m*, 600*s*, 588*s*, 574*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; some tentative assignments): 7.87 (*d*-like, H_o of 1 $PhSO_2$); 7.73–7.47 (*m*, 8 H of $PhSO_2$); 6.468 (*d*, $^3J(5,6) = 6.5$, H−C(5)); 6.313 (*dq*-like, $^3J(5,6) = 6.5$, ^4J(6,Me−C(7)) = 1.5, H−C(6)); 6.063 (br. *s*, H−C(11)); 5.978 (*quint.*-like br. *s*, H−C(9)); 4.992 (*s*, H−C(1)); 3.779, 3.761 (*AB*, $^3J_{AB} = 5.2$, H−C(2), H−C(3)); 2.007 (*d*, ^4J(Me−C(12),11) = 1.2, Me−C(12)); 1.948 (*d*, ^4J(Me−C(7),6) = 1.2, Me−C(7)); 1.827 (*s*, Me−C(8)); 1.697 (*s*, Me−C(4)); 1.625 (*d*, $^4J = 1.2$, Me−C(10)). CI-MS (NH_3): 590 (100, $[M + NH_4]^+$), 573 (9, $[M + H]^+$), 326 (43, $[PhSO_2{-}CH{=}CH{-}SO_2Ph + NH_4]^+$), 291 (13, $[(M + H) - (C_6H_5SO_2H + C_6H_4 + SO_2)]^+$), 265 (93, $[(M + H) - PhSO_2{-}CH{=}CH{-}SO_2Ph]^+$).

Data of 2-exo,*3*-endo-*(*P**)*-**22c**: R_f (1% MeOH/CH_2Cl_2) 0.34. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.81–7.50 (*m*, 10 H of 2 $PhSO_2$); 6.231 (*d*, $^3J(5,6) = 6.2$, H−C(5)); 6.124 (br. *s*, H−C(11)); 6.081 (*dd*, $^3J(6,5) = 6.2$, ^4J(6,Me−C(7)) = 1.5, H−C(6)); 5.591 (br. *s*, H−C(9)); 5.112 (*s*, H−C(11)); 4.028, 3.465 (*AB*, $^3J_{AB} = 4.8$, H−C(2), H−C(3)); 1.995 (*d*, ^4J(Me−C(10),9) = 1.0, Me−C(10)); 1.865 (*d*, ^4J(Me−C(7),6) = 1.2, Me−C(7)); 1.815 (*d*, ^4J(Me−C(12),11) = 1.2, Me−C(12)); 1.815 (*s*, Me−C(8)); 1.693 (*s*, Me−C(4)).

1.4.3.1. *(*M**,1*R**,4*R**)-1,4-Dihydro-4,7,8,10,12-pentamethyl-3-(phenylsulfonyl)-1,4-epoxybenzo[*d*]heptalene* ((*M**)-**25c**). The 2-*exo*,3-*endo*-(*P**)-**22c** (0.102 g, *ca.* 0.16 mmol; see *1.4.3.*) was dissolved in 1,2-dimethoxyethane (4 ml) and stirred at 80° in the presence of Cs_2CO_3 (0.26 g, 0.80 mmol) for 1.5 h. The mixture was cooled, and AcOEt (40 ml) was added. After washing and drying, the residue of the org. phase was purified by CC (SiO_2, Et_2O/hexane 4:1). The residue of the main fraction was crystallized from Et_2O/CH_2Cl_2: pure (*M**)-**25c** (25.5 mg, *ca.* 39%). M.p. 187.1–188.0°. R_f (Et_2O/hexane 7:3) 0.45. UV (EtOH): λ_{max} 342 (sh, 3.51), 297 (sh, 3.77), 243 (4.37); λ_{min} 231 (4.33). IR (KBr): 2988*m*, 2965*m*, 2939*m*, 2915*m*, 1659*w*, 1622*w*, 1573*m*, 1446*s*, 1317*s*, 1307*s*, 1158*s*, 1113*m*, 1097*m*, 1026*w*, 954*w*, 836*m*, 724*m*, 687*m*,

606*m*, 597*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.62–7.58 (*dd*-like *m*, H_o of $PhSO_2$); 7.53–7.46 (*tt*-like *m*, H_p of $PhSO_2$); 7.37–7.31 (*t*-like *m*, H_m of $PhSO_2$); 7.127 (*d*, $^3J(2,1) = 1.9$, H–C(2)); 6.013 (br. *s*, H–C(9)); 5.931 (*quint.*-like br. *s*, H–C(11)); 5.863 (*dq*-like, $^3J(5,6) = 6.3$, $^4J(6,Me–C(7)) = 1.5$, H–C(6)); 5.671 (*d*, $^3J(5,6) = 6.3$, H–C(5)); 5.377 (*dd*-like, $^3J(1,2) \approx 1.6$, H–C(1)); 2.058 (*d*, $^4J(Me–C(12),11) = 1.3$, Me–C(12)); 1.977 (*d*, $^4J(Me–C(7),6) = 1.2$, Me–C(7)); 1.928 (*d*, $^4J(Me–C(10),9) = 1.2$, Me–C(10)); 1.703 (*d*-like, $^5J(Me–C(4),5) < 0.5$, Me–C(4)); 1.681 (*s*, Me–C(8)). CI-MS (NH_3): 448 (100, $[M + NH_4]^+$), 431 (62, $[M + H]^+$), 416 (7, $[(M + H) - Me]^+$), 291 (36, $[(M + H) - (C_6H_4 + SO_2)]^+$)), 265 (10, $[(M + H) - PhSO_2 - C{\equiv}CH]^+$)).

2. *X-Ray Crystal-Structure Determinations for Compounds 2,3*-endo-*(*P**)*-**3a**, *3*-endo-*(*P**)*-**15a**, *3*-endo-*(*M**)*-**15a**, *2,3*-exo-*(*M**)*-**26b**, *and* **31b**[14]). All measurements were conducted at low temp. by using a *Nonius-KappaCCD* diffractometer [36] fitted with an *Oxford-Cryosystems-Cryostream-700* cooler. The data collection and refinement parameters are given in *Table 8* and views of the molecules are shown in *Figs. 1*, *3*, *4*, and *5*. Data reduction was performed with HKL Denzo and Scalepack [37]. The intensities were corrected for *Lorentz* and polarization effects, and equivalent reflections were merged. An absorption correction was applied in the case of 2,3-*exo*-(*M**)-**26b** and **31b** and was based on the multiscan method [38]. Each structure was solved by direct methods by using SIR92 [39], which revealed the positions of all non-H-atoms. For 2,3-*endo*-(*P**)-**3a**, the ^{i}Pr substituent was disordered over two conformations. Two sets of positions were defined for the disordered atoms and the site-occupation factor of the major conformation refined to 0.744(5). For 3-*endo*-(*P**)-**15a**, the heptalene ring with the ^{i}Pr substituent was disordered over two conformations. Two positions were defined for ring atoms C(8), C(9), C(10), C(11), and all atoms of the ^{i}Pr substituent. Refinement of the site occupation factors of these two conformations yielded a value of 0.901(2) for the major conformation. For both of the disordered structures, similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered C-atoms, while neighboring atoms within and between each conformation were restrained to have similar atomic displacement parameters. The non-H-atoms of each structure were refined anisotropically. The hydroxy H-atoms in 2,3-*endo*-(*P**)-**3a** were placed in the positions indicated by a difference-electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms in the structures were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in each case. Neutral-atom scattering factors for non-H-atoms were taken from [40], and the scattering factors for H-atoms were taken from [41]. The values of the mass attenuation coefficients were those of [42]. All calculations were performed with the SHELXL97 program [43]. The crystallographic diagrams were drawn by using ORTEPII [44].

REFERENCES

[1] P. Uebelhart, C. Weymuth, H.-J. Hansen, *Helv. Chim. Acta* **2005**, *88*, 1250.
[2] M. S. Newman, R. W. Addor, *J. Am. Chem. Soc.* **1955**, 77, 3789.
[3] M. S. Newman, Z. U. Din, *J. Org. Chem.* **1971**, *36*, 966.
[4] S. V. D'Andrea, J. P. Freeman, J. Szmuszkovits, *J. Org. Chem.* **1990**, *55*, 4356.
[5] K. Afarinkia, J. Berna-Canovas, *Tetrahedron Lett.* **2000**, *41*, 4955.
[6] Y. K. Yur'ev, N. S. Zefirov, *Zh. Obshchei Khim.* **1961**, *31*, 685.
[7] A. Baran, C. Kazaz, H. Seçen, Y. Sütbeyaz, *Tetrahedron* **2003**, *59*, 3643.
[8] J. C. Carnahan Jr., W. D. Closson, *Tetrahedron Lett.* **1972**, *33*, 3447.
[9] K. Abou-Hadeed, *Chimia* **2000**, *54*, 763.

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14) CCDC-265644–265647 and -270037 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif from the *Cambridge Crystallographic Data Centre.*

[10] E. Block, *Org. React.* **1984**, *30*, 457.
[11] K. Omura, D. Swern, *Tetrahedron* **1978**, *34*, 1651; A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165.
[12] S. H. Watterson, Z. Ni, S. S. Murphree, A. Padwa, *Org. Synth.* **1997**, *74*, 115.
[13] A. J. Guildford, R. W. Turner, *J. Chem. Soc.*, *Chem. Commun.* **1983**, 466.
[14] J. R. Bull, N. S. Desmond-Smith, S. J. Heggie, R. Hunter, F.-C. Tien, *Synlett* **1998**, 900.
[15] P. D. Bartlett, B. E. Tate, *J. Am. Chem. Soc.* **1956**, *78*, 2473.
[16] a) S. Ranganathan, D. Ranganathan, A. K. Mehrotra, *Synthesis* **1977**, 289; b) E. Vieira, P. Vogel, *Helv. Chim. Acta* **1982**, *65*, 1700; c) C. Le Drian, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1989**, *72*, 338.
[17] C. Le Drian, P. Vogel, *Tetrahedron Lett.* **1987**, *28*, 1523.
[18] R. W. Baker, T. M. Baker, A. A. Birkbeck, R. G. F. Giles, M. V. Sargent, B. W. Skelton, A. H. White, *J. Chem. Soc.*, *Perkin Trans. 1* **1991**, 1589.
[19] C. O. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron* **1997**, *53*, 14179.
[20] S. Cossu, O. de Lucchi, F. Dilillo, *Gazz. Chim. Ital.* **1989**, *119*, 519.
[21] O. Arjona, F. Iradier, R. M. Mañas, J. Plumet, X. Grabuleda, C. Jaime, *Tetrahedron* **1998**, *54*, 9095.
[22] M. E. A. Fattah, S. E. Rayes, E. S. A. Soliman, A. Linden, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2005**, *88*, 1085.
[23] G. J. Lambert, R. P. Duffley, H. C. Dalzell, R. K. Razdan, *J. Org. Chem.* **1982**, *47*, 3350.
[24] K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2003**, *86*, 4018.
[25] a) W. Bernhard, P. Brügger, J. J. Daly, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985**, *68*, 415; b) W. Bernhard, P. Brügger, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985**, *68*, 429.
[26] A. A. S. Briquet, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1996**, *79*, 2282.
[27] P. Kouroupis, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1247.
[28] J. Guspanová, R. Knecht, M. Laganà, C. Weymuth, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 1375.
[29] Ph. Ott, H.-J. Hansen, *Helv. Chim. Acta* **2001**, *84*, 2670.
[30] P. Uebelhart, A. Linden, H.-J. Hansen, Y. Ustynyuk, O. A. Trifanova, N. G. Akhmedov, V. I. Mstislavsky, *Helv. Chim. Acta* **1999**, *82*, 1930.
[31] A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1993**, *76*, 2906.
[32] P. Uebelhart, P. Mohler, R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1995**, *78*, 1437.
[33] N. Harada, K. Nakanishi, 'Circular Dichroic Spectroscopy – Exciton Coupling in Organic Stereochemistry', Oxford University Press, 1983.
[34] L. Doub, J. M. Vandenbelt, *J. Am. Chem. Soc.* **1947**, *69*, 2714; L. Doub, J. M. Vandenbelt, *J. Am. Chem. Soc.* **1949**, *71*, 2414.
[35] S. H. Watterson, Z. Ni, S. S. Murphree, A. Padwa, *Org. Synth.* **1997**, *74*, 115.
[36] R. Hooft, 'KappaCCD Collect Software', Nonius BV, Delft, The Netherlands, 1999.
[37] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, Macromolecular Crystallography, Part A, Eds. C. W. Carter Jr., and R. M. Sweet, Academic Press, London, 1997, p. 307.
[38] R. H. Blessing, *Acta Crystallogr.*, *Sect. A* **1995**, *51*, 33.
[39] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, 'SIR92', *J. Appl. Crystallogr.* **1994**, *27*, 435.
[40] E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477.
[41] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[42] D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, p. 200.
[43] G. M. Sheldrick, 'SHELXL97', Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.
[44] C. K. Johnson, 'ORTEPII', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.

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