Novel rearrangement of conformationally restrained [3.3]orthocyclophanes

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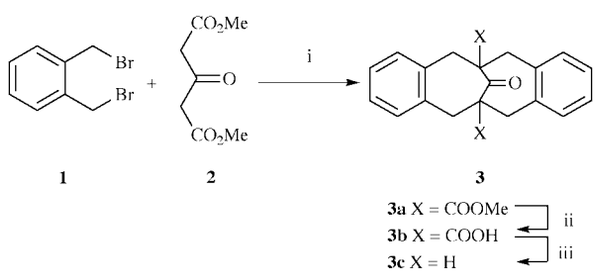
Novel rearrangement of intermediate carbocations generated from rigid, layered [3.3]orthocyclophane-alcohols **4** are presented. The bicyclo[4.4.1]undecane framework of **4** rearranges to either bicyclo[5.4.0]- **5** and/or bicyclo[4.4.0]- **6** or tricyclo[5.4.0.$0^{2,11}$]- ring-system **11**, depending upon the nature of the aryl substituent on the bridging tertiary carbon atom. X-Ray crystal structure analyses have been performed on the rearrangement products.

Introduction

Bisarenobicyclo[4.4.1]undecanones such as **3** are easily prepared by double annelation of 1,2-bis(bromomethyl)arenes such as **1** to dimethyl acetonedicarboxylate **2**, hydrolysis of the diester **3a** and subsequent pyrolysis of the dicarboxylic acid **3b** (Scheme 1).[1,2] The keto functionality can be transformed further. Depending on this last derivatisation the transformed [3.3]orthocyclophanes can show a number of conformations in both the solid state and in solution. These range from a flexible chair-boat conformation in the methylene-bridged compounds to a rigid, tweezer-like topology in the corresponding acetals. In all cases the aromatic units have been found to be nondistorted. [3.3]Orthocyclophanes with rigid, layered structures (Chart 1)[1,2] exhibit interesting properties due to their closely layered π-systems[3] and due to the strain within their bridging [4.4.1]-undecane-subunit. Within the study of π–π interactions in such molecules it was deemed interesting to produce cations from suitable tertiary alcohols **4**, in order to assess their stabilisation by one of the flanking aromatic units and hence their reactivity dependent on this stabilisation. The interaction of the cation with one or both of the aromatic units was predicted to be influenced by the substituent R, both due to electronic and steric effects of R, where the steric demand of R was thought to affect the conformation of the intermediate cation. Rearrangement products produced from the tertiary cations were to provide conclusive evidence on the nature of these cations. The outcome of the rearrangement sequences as described below was indeed dependent on the conformation of the cation formed. Different substituents R led to totally different rearrangement products *via* different rearrangement processes in such a way that R can be considered to be a molecule-inherent reaction switch.



Scheme 1 Synthesis of 3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,9-dien-11-one **3c**. *Reagents and conditions* (*and yields*): *i*, KOH, 5 h (75%); *ii*, KOH, EtOH, reflux, 3 h (92%); *iii*, 320 °C (68%).

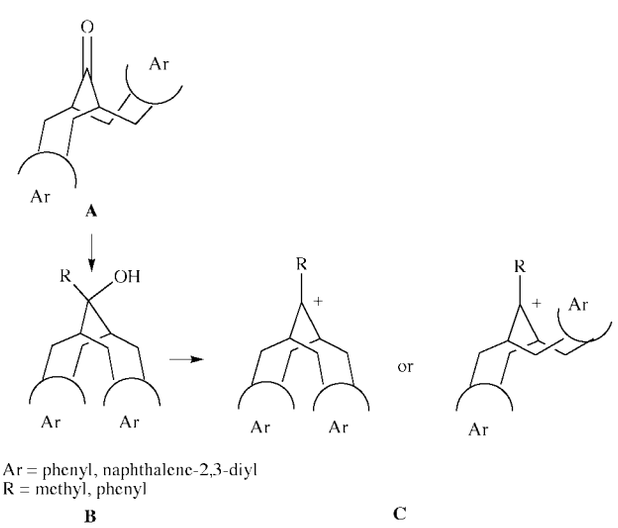


Chart 1 Cation formation from layered [3.3]orthocyclophane alcohols.

Results and discussion

[3.3]Orthocyclophane-alcohols **4a**–**f** were prepared by Grignard reaction of the corresponding ketone **3c**[1a,4] (Scheme 2, Table 1). While the ketone has a flexible structure, the alcohols[1a,5] are locked into position by steric interaction of the aryl and hydroxy groups with the annelated benzo-units. The alcohols can be easily be protonated and dehydrated to the corresponding cations by various acids. The carbocations rearrange, depending on the substituent R of the alcohol precursor, as presented below, and the rearrangement products can be isolated. Alcohols **4a**–**f** were treated with either hydrochloric acid, hydrobromic acid or sulfuric acid at 35–40 °C for 5–48 h.

Table 1 Grignard reaction of **3** and **3-D**

Alcohol	R	Reaction time (*t*/h)	Yield (%)
4a	phenyl	5	82
4b	4-methylphenyl	12	91
4c	4-methoxyphenyl	12	82
4d	2-naphthyl	18	78
4e	2-methylphenyl	10	36
4f	1-naphthyl	15	87
4f-D	1-naphthyl	15	76

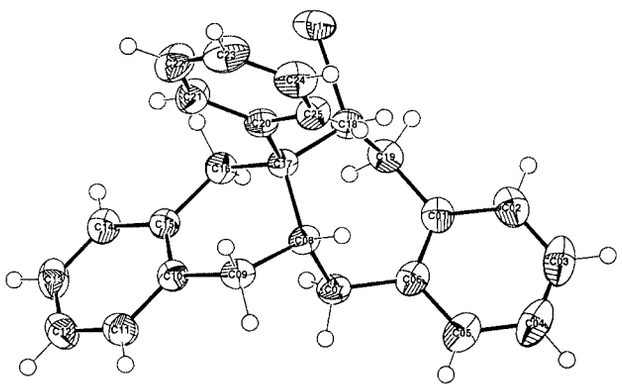
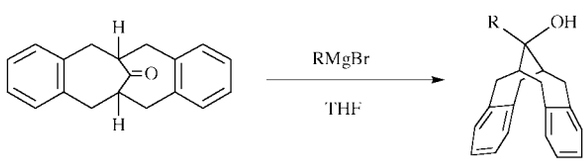


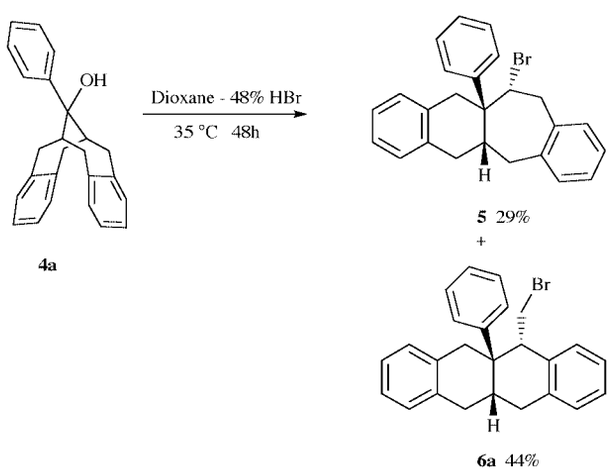
Fig. 1 ORTEP Drawing of **5**.



3 **4a - 4f**

Scheme 2

According to the reaction outcome, the alcohols can be classified into three groups. Phenyl-substituted orthocyclophane-alcohol **4a** upon treatment with HBr in 1,4-dioxane gives two rearrangement products, **5** and **6a**, where the formation of **5** can be explained by a Wagner–Meerwein-type rearrangement of the first formed carbocation (Scheme 3). A direct nucleophilic reac-



4a

Scheme 3

tion of the bromide with the first formed tertiary carbocation would result in a layered cyclophane structure with considerable ring strain and thus is disfavored. In **5**, the bromo substituent is exclusively *anti* to the phenyl group as shown in its X-ray crystal structure (Fig. 1).

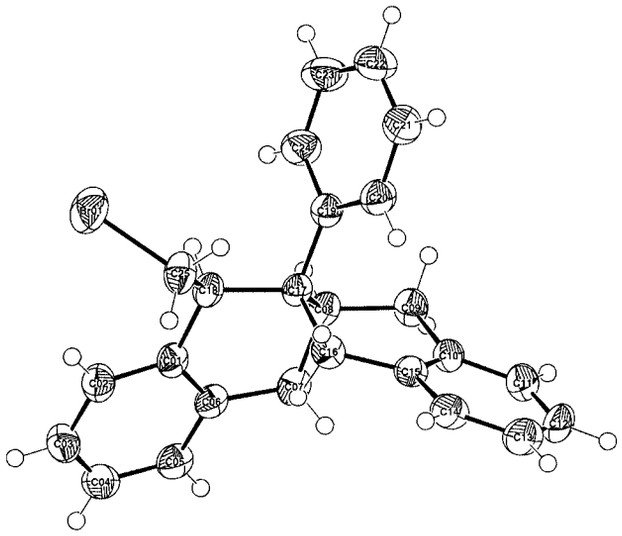
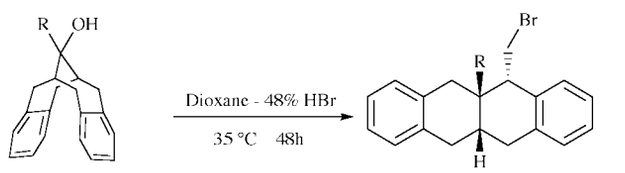


Fig. 2 ORTEP Drawing of **6a**

Alcohols carrying an electron-rich donor, *i.e.* donor-substituted phenyl group or a 2-naphthyl group, rearrange to form *cis*-configurated dibenzo-annelated bromomethyldecalins as the only products, whereas the bromomethyl group is exclusively *anti*-configurated (Scheme 4) as can be seen from the X-ray



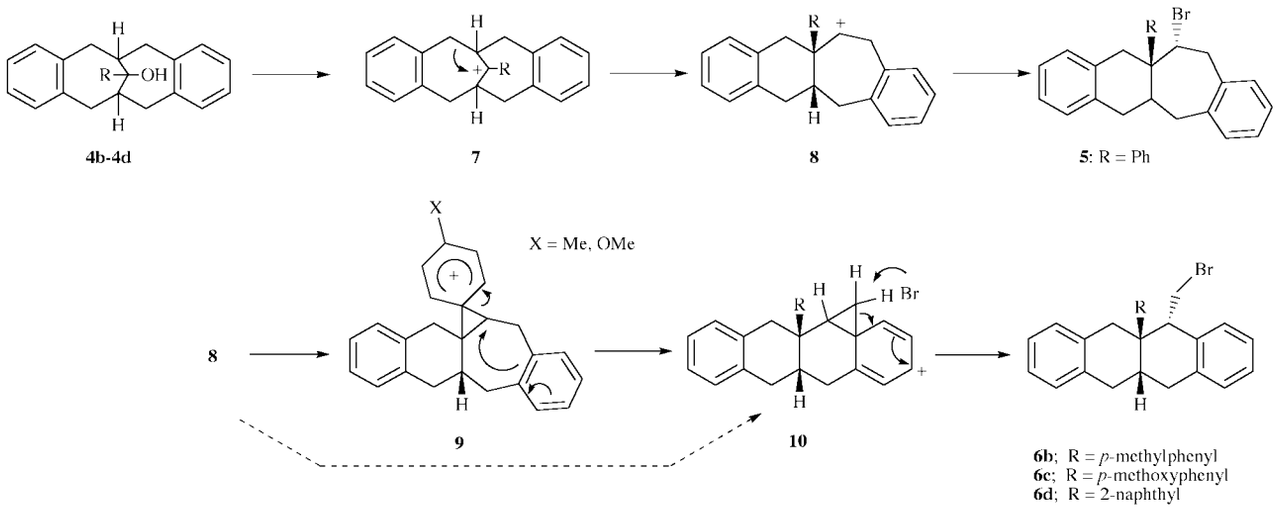
4b - 4d

6b; R = *p*-methylphenyl (58%)
6c; R = *p*-methoxyphenyl (62%)
6d; R = 2-naphthyl (46%)

Scheme 4

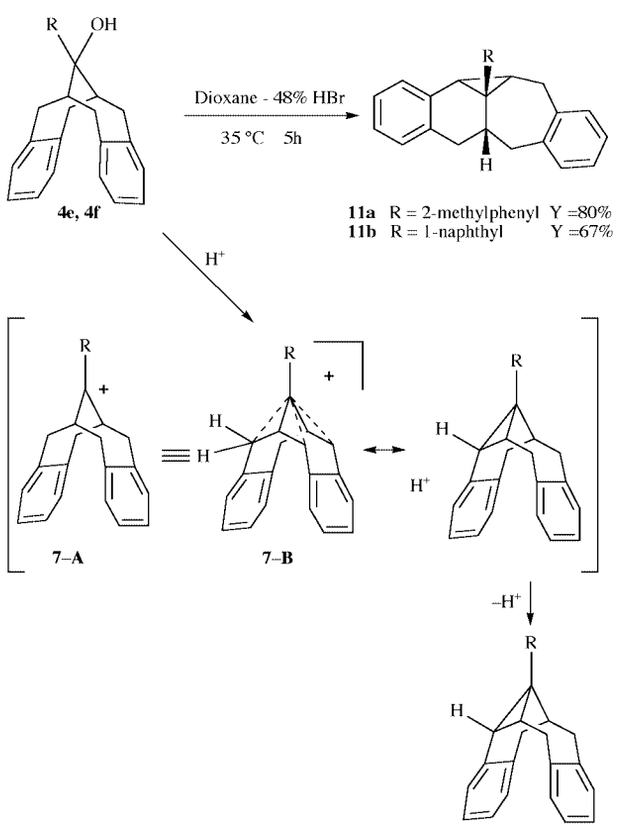
crystal structure of **6a** (Fig. 2). The mechanism of the formation of these products is thought to involve the participation of one of the annelated benzo-units *via* its intramolecular alkylation by the secondary cation produced by Wagner–Meerwein rearrangement. The exclusive formation of *cis*-fused decalins in these cases can be explained by participation of the aryl substituent R. Modelling[5] of the carbocation **8** has shown that due to severe conformational restraint the alignment of the vacant p-orbital of the carbocationic center is not ideal for a good interaction and a subsequent reaction with the annelated benzo group. Conformational and electronic changes involved in a participation of the aryl substituent R *via* a phenonium ion intermediate **9** would allow for a better interaction with the benzo group and a more ready formation of cation **10**. The participation of the aryl group *via* formation of a phenonium ion is more likely with electron-rich substituents R (Scheme 5). It must be added that the secondary cation **8** also exhibits considerable conformational strain.

The third class of orthocyclophane-alcohols is characterised by aryl groups R that are bulky, either by carrying a substituent such as an *ortho*-methyl group or by further ring-annelation as in the case of the 1-naphthyl substituent. These alcohols rearrange exclusively to products **11** with a tricyclo[5.4.0.0^{2,11}]-undecane skeleton, irrespective of the acid used (HBr, HCl, H_2SO_4) (Scheme 6).[6] X-Ray crystallographic analysis has been perfomed on **11b** (Fig. 3). While the cyclopropane formation under these acidic conditions is highly unusual, there is no evidence for ring opening, *e.g.* addition of HBr, under the conditions used, as could be ascertained by subjecting the purified products to the same conditions. That halogenation steps are involved in the mechanism *via* an addition–elimination step



Scheme 5

could be ruled out by the same product formation from **4f** in the case of using sulfuric acid as proton donor. The mechanism of this rearrangement with concomitant cyclopropane formation has not been ascertained to date; however, it is believed that the freely rotating substituent R forces the annelated benzo rings of the primary cation to take a quasi-layered position and that the cation exhibits a conformation similar to that of the alcohols themselves, thus adding strain to the benzylic positions. Bond angles associated with these benzylic positions, as observed in the starting materials by X-ray crystallographic analysis, indicate an appreciable sp^2-character,[7] allowing for the possibility of hyperconjugation in the cation (Scheme 6) if a similar con-



Scheme 6

formation in these cations leading to the tricyclo[5.4.0.$0^{2,11}$]-undecane skeleton is assumed. It is for this reason that a mechanism as drawn in Scheme 6 is likely.

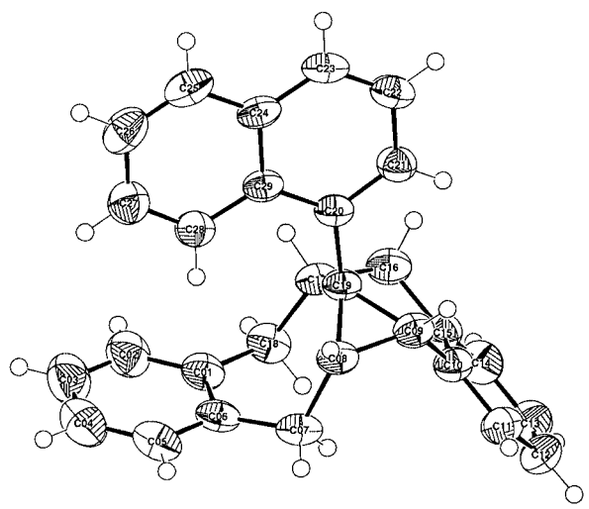
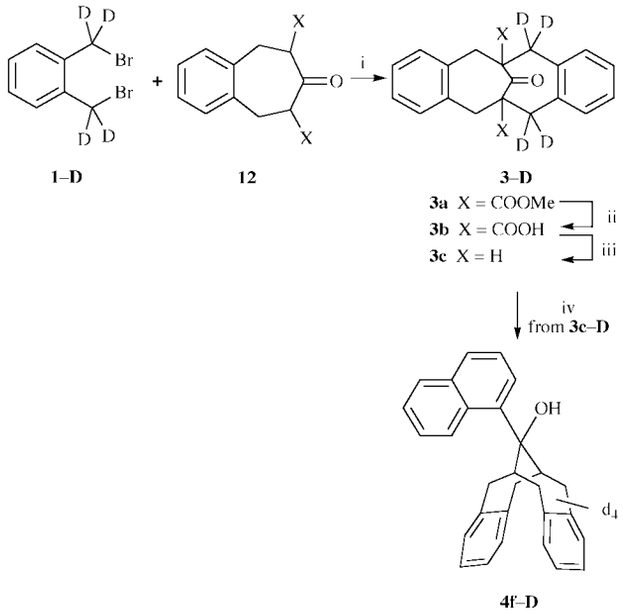


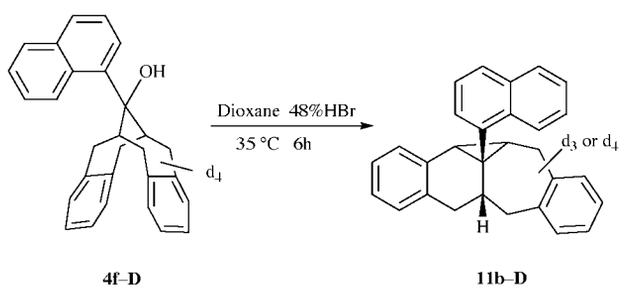
Fig. 3 ORTEP Drawing of **11b** crystallized with one molecule of benzene. Because of better clarity, benzene is not shown in the ORTEP drawing.

[$^2H_4$]-3,4:8,9-Dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one † **3c-D** was prepared in 3 steps from 1,2-bis(bromo[$^2H_2$]methyl)-benzene **1-D**[8] and dimethyl 3-oxo-2,3,4,5-tetrahydro-1*H*-benzocycloheptene-2,4-dicarboxylate[1b] **12**, subsequent hydrolysis of the diester **3a-D** and decarboxylation of the corresponding diacid **3b-D** (Scheme 7). **3c-D** was transformed to 11-hydroxy-11-(1′-naphthyl)-[$^2H_4$]-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene **4f-D** by Grignard reaction as described above. Preliminary studies on the isotope effect of the benzylic position (H/D) in the rearrangement of **4f-D** have given a significant difference in the product distribution **11b-D-d_3**/**11b-D-d_4** (see Scheme 8). The stereochemistry of **4f-D** at C-11 can be established by ^{1}H NMR analyses of this product due to the fact that the naphthyl and hydroxy moieties exert a very different anisotropic effect on the facing proton at C-7/C-10, respectively. Thus it can be verified experimentally that ***syn*-4f-D** and ***anti*-4f-D** form in a ratio close to 50:50 as would be expected. Even if the primarily formed cation **7** (planarity of the cation would lead to C_{2v} symmetry) is non-planar, a small excess of ***anti*-4f-D** *via* memory effect of a non-planar cation **7** should not lead to the large excess of **11b-D-d_3** *vs.* **11b-D-d_4** observed. Rather it seems that the bond breaking C–H(D) in the rate determining step, aided by hyperconjugation, leads to this large isotopic effect. Additional studies on isotopic effects in

† The nomenclature given in this paper for the benzo-faced systems **3**, **4** and **11** is not systematic.



Scheme 7 *Reagents and conditions* (*and yields*): *i*, KOH, 12 h (84%); *ii*, KOH, EtOH, reflux., 3 h (63%); *iii*, 340 °C (90%); *iv*, 1-$C_{10}H_7Br$, Mg, THF, reflux, 15 h (76%).



Entry	d^3 (%)	d^4 (%)	Yield (%)
1	25.64	74.36	68
2	26.18	73.82	62
3	25.38	74.62	66
average	25.73	74.27	

Scheme 8

the rearrangement of suitably deuterated 11-hydroxy-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-dienes are currently underway in order to further probe this mechanistic assumption.

Experimental

Mps were measured on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL EX-270, JEOL LA-395 and LA-600 spectrometer. The chemical shifts are relative to TMS (solvent CD_2Cl_2 unless noted otherwise). *J*-Values are given in Hz. Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV).

3,4 : 8,9-Dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one **3c**,[1] 11-hydroxy-11-phenyl-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene **4a**[1] and dimethyl 3-oxo-2,3,4,5-tetrahydro-1*H*-benzocycloheptene-2,4-dicarboxylate **12**[1b] were prepared according to the literature. Ether refers to diethyl ether.

11-Hydroxy-11-(*p*-methylphenyl)-3,4 : 8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene 4b. Typical procedure A

3c (500 mg, 1.9 mmol) in dry THF (10 mL) was added dropwise within 1 h to the Grignard reagent, prepared from *p*-bromotoluene (520 mg, 3.1 mmol) and Mg (500 mg, 21.0 mmol) in THF (5 mL). The mixture was then refluxed for 12 h. After cooling, 17 wt% aq. NH_4Cl (50 mL) was added. The phases were separated, the aqueous phase was extracted with ether (2 × 15 mL) and the combined phase was dried over anhydrous $MgSO_4$. After evaporation *in vacuo*, the crude was subjected to column chromatography on silica gel (toluene) to yield **4b** (610 mg, 91%) as a colourless solid; mp 200–201 °C; ν_{max}(KBr)/cm^{-1} 3600–3200, 2910, 1495, 1453, 1215 and 748; δ_H(270 MHz) 1.65 (1H, s, OH), 2.31 (3H, s, CH_3), 2.75–2.85 (4H, m), 3.04 (2H, dd, *J* 2.6 and 2.3), 3.18 (2H, br s), 3.91 (2H, d, *J* 14.8), 6.50–6.89 (10H, m), 7.17 (2H, d, *J* 8.3) and 7.55 (2H, d, *J* 8.2); δ_C 20.90, 35.94, 37.61, 39.93, 125.84, 125.93, 126.20, 126.31, 129.59, 130.15, 130.58, 137.20, 139.67, 140.48 and 143.32; *m*/*z* 354 (M^+).

11-Hydroxy-11-(*p*-methoxyphenyl)-3,4 : 8,9-dibenzobicyclo-[4.4.1]undeca-3,8-diene 4c

3c (1.0 g, 3.8 mmol) in dry THF (10 mL) was treated with Grignard reagent [*p*-bromoanisole (1.14 g, 6.1 mmol), Mg (200 mg, 8.3 mmol), THF (5 ml)] according to procedure A (12 h) to yield **4c** (1.16 g, 82%) as a colourless solid, mp 217–218 °C (Found: M^+, 370.1934. $C_{26}H_{26}O_2$ requires *M*, 370.1933); ν_{max}(KBr)/cm^{-1} 3600–3200, 2908, 1517, 1454, 1217 and 748; δ_H(270 MHz) 1.64 (1H, s, OH), 2.75–2.85 (4H, m), 3.03 (2H, dd, *J* 3.0 and 2.9), 3.16 (2H, m), 3.78 (3H, s), 3.87 (2H, dd, *J* 14.8 and 5.9), 6.55–6.93 (10H, m) and 7.56 (2H, dd, *J* 2.3 and 2.0); δ_C 36.20, 37.59, 40.16, 55.60, 114.16, 125.95, 127.80, 130.19, 130.71, 138.56, 139.77, 140.56 and 158.84; *m*/*z* (EI) 370 (M^+).

11-Hydroxy-11-(2-naphthyl)-3,4 : 8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene 4d

3c (1.16 g, 4.4 mmol) in dry THF (10 mL) was treated with Grignard reagent [2-bromonaphthalene (1.72 g, 8.3 mmol), Mg (500 mg, 20.6 mmol), THF (10 ml)] according to procedure A (18 h) to yield **4d** (1.34 g, 78%) as a colourless solid, mp 242 °C (Found: C, 89.11; H, 6.74. $C_{29}H_{26}O$ requires C, 89.19; H, 6.71%); ν_{max}(KBr)/cm^{-1} 3546, 3056, 1497, 1453, 1001, 860 and 748; δ_H(270 MHz) 1.73 (1H, s, OH), 2.90 (4H, m), 3.10 (2H, dd, *J* 3.9 and 3.6), 3.36 (2H, br s), 3.99 (2H, d, *J* 14.4), 6.50–6.88 (8H, m), 7.36–7.50 (2H, m, ArH), 7.78–7.85 (4H, m, ArH) and 8.02 (1H, s, ArH); δ_C 36.15, 37.34, 40.05, 79.36, 124.64, 125.78, 126.01, 126.06, 126.38, 126.54, 127.50, 128.52, 128.69, 130.07, 130.84, 132.59, 133.52, 139.68, 140.49 and 143.78; *m*/*z* (EI) 390 (M^+).

11-Hydroxy-11-(*o*-methylphenyl)-3,4 : 8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene 4e

3c (1.16 g, 4.4 mmol) in dry THF (10 mL) was treated with Grignard reagent [*o*-bromotoluene (1.19 mg, 6.9 mmol), Mg (500 mg, 20.6 mmol), THF (10 mL)] according to procedure A (10 h) to yield **4e** (550 mg, 36%) as a colourless solid, mp 194–196 °C (Found: C, 87.54; H, 7.35. $C_{26}H_{26}O$ requires C, 88.09; H, 7.39%); ν_{max}(KBr)/cm^{-1} 3564, 2912, 1496, 1453, 1000, 942 and 748; δ_H(270 MHz) 1.76 (1H, s, OH), 2.69 (2H, d, *J* 5.6), 2.74 (3H, s, CH_3), 2.75–2.97 (2H, m), 3.06 (2H, dd, *J* 4.0 and 4.0), 3.32–3.34 (2H, m), 4.00 (2H, dd, *J* 2.3 and 2.0), 6.50–8.02 (13H, m); δ_C 20.95, 79.19, 125.89, 125.98, 129.65, 130.20, 130.64, 137.25, 139.73, 140.54, 143.38; *m*/*z* 354 (M^+).

11-Hydroxy-11-(1-naphthyl)-3,4 : 8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene 4f

3c (680 mg, 2.6 mmol) in dry THF (5 mL) was treated with Grignard reagent [1-bromonaphthalene (860 mg, 4.2 mmol), Mg (250 mg, 10.6 mmol), THF (5 mL)] according to procedure A (15 h) to yield **4f** (880 mg, 87%) as a colourless solid, mp 191–192 °C (Found: C, 89.19; H, 6.71. $C_{29}H_{26}O$ requires C, 89.19; H, 6.66%); ν_{max}(KBr)/cm^{-1} 3600–3200br s (OH), 2914, 1495, 994, 804 and 781; δ_H(270 MHz) 1.51 (1H, s, OH), 2.75–3.58 (8H, m), 4.26 (2H, d, *J* 15.2) and 6.60–9.02 (15H, m); δ_C(67.8 MHz)

36.46, 37.02, 41.37, 80.86, 123.83, 124.91, 125.55, 125.80, 127.85, 128.80, 129.04, 129.34, 130.85, 131.30, 135.36, 139.39, 139.77 and 140.90; *m*/*z* (EI) 390 (M^+, 12), 267 (100).

12-Bromo-11a-phenyl-5a,6,11,11a,12,13-hexahydro-5*H*-benzo-[4,5]cyclohepta[1,2-*b*]naphthalene 5 and 5-bromomethyl-5a-phenyl-5,5a,6,11,11a,12-hexahydrotetracene 6a. General procedure B

To **4a** (500 mg, 1.5 mmol) in 1,4-dioxane (60 mL) was added dropwise HBr (48 wt% aq.; 15.5 g, 92.0 mmol) and the resulting two-phase mixture was stirred for 48 h. Then the reaction mixture was extracted with ether (3 × 50 mL), the ether phase was washed successively with sat. aq. Na_2CO_3 (50 mL) and water (2 × 50 mL) and dried over anhydrous Na_2SO_4. After evaporation *in vacuo* the residue was subjected to column chromatography on silica gel (eluent: hexane) to give **5** (170 mg, 29%) as a colourless solid, R_f 0.18; mp 180–187 °C (decomp.) (Found: C, 74.54; H, 5.78. $C_{25}H_{23}Br$ requires C, 74.44; H, 5.75%); ν_{max}(KBr)/cm^{-1} 2924, 1601, 1494, 1454, 1155 and 764; δ_H(270 MHz) 2.11–2.54 (4H, m), 3.15 (1H, dd *J* 10.9 and 10.9), 3.46 (1H, dd, *J* 2.0 and 2.0), 3.76 (2H, s), 4.01 (1H, dd, *J* 12.2, *J* 12.2), 4.68 (1H, dd *J* 2.0 and 2.0) and 6.92–7.42 (13H, m); δ_C 28.88, 38.08, 38.60, 43.58, 44.42, 50.58, 66.20, 126.22, 126.59, 126.84, 127.10, 127.92, 129.25, 130.29, 134.54, 134.59, 138.81, 143.25 and 147.76; *m*/*z* 404 ([^{81}Br]M^+) and 402 ([^{79}Br]M^+), and this was followed by **6a** (260 mg, 44%) as a colourless solid, R_f 0.22; mp 141–144 °C (Found: C, 74.59; H, 5.79%); ν_{max}(KBr)/cm^{-1} 2896, 1600, 1494, 1452, 1121 and 757; δ_H(270 MHz) 2.40 (2H, d, *J* 2.3), 2.74–3.04 (4H, m), 3.24 (1H, d, *J* 17.5), 3.52 (1H, dd, *J* 10.9 and 10.9), 3.68 (1H, dd, *J* 2.6 and 2.3), 3.83 (1H, d, *J* 5.6) and 6.90–7.69 (13H, m); δ_C 29.05, 32.94, 33.06, 33.48, 38.44, 45.96, 52.60, 126.20, 128.93, 129.34, 129.41, 129.88, 134.77, 135.29, 136.44, 136.55, 145.44; *m*/*z* 404 ([^{81}Br]M^+) and 402 ([^{79}Br]M^+).

5-Bromomethyl-5a-(*p*-methylphenyl)-5,5a,6,11,11a,12-hexahydrotetracene 6b

4b (300 mg, 0.85 mmol) in 1,4-dioxane (31 mL) was treated with HBr (48 wt% aq.; 8.5 g, 46.0 mmol) according to procedure B (48 h) to yield **6b** (195 mg, 58%) as a colourless solid, mp 75–79 °C (Found: M^+, 416.1133. $C_{26}H_{25}$[^{79}Br]. $C_{26}H_{25}$[^{79}Br] requires *M*, 416.1140); ν_{max}(KBr)/cm^{-1} 2908, 1514, 1494, 1453, 1116, 810 and 746; δ_H(270 MHz) 2.22–2.53 (3H, m), 2.30 (3H, s, CH_3), 2.74–2.98 (3H, m), 3.20 (1H, d, *J* 17.5), 3.48–3.56 (1H, m), 3.66–3.80 (2H, m), 6.92–7.27 (11H, m, ArH) and 7.66–7.69 (1H, d, *J* 6.9); δ_C 21.00, 29.04, 32.92, 33.06, 33.67, 38.38, 45.59, 52.61, 126.14, 126.29, 126.45, 126.56, 126.77, 127.20, 127.44, 127.51, 129.34, 129.38, 129.59, 129.85, 134.79, 135.40, 136.46, 136.57, 136.64, 142.19; *m*/*z* 416 ([^{79}Br]M^+) and 418 ([^{81}Br]M^+).

5-Bromomethyl-5a-(*p*-methoxyphenyl)-5,5a,6,11,11a,12-hexahydrotetracene 6c

4c (300 mg, 0.81 mmol) in 1,4-dioxane (31 mL) was treated with HBr (48 wt% aq.; 8.5 g, 46.0 mmol) according to procedure B (48 h) to yield **6c** (217 mg, 62%) as a colourless solid, mp 201–203 °C (Found: M^+, 434.1070 and 432.1091. $C_{26}H_{25}BrO$ requires 434.1072 [^{81}Br]M^+ and 432.1089 [^{79}Br]M^+); ν_{max}(KBr)/cm^{-1} 2906, 1494, 1432, 1257, 1257 and 746; δ_H(270 MHz) 2.34–2.40 (3H, m), 2.75–2.94 (3H, m), 3.16–3.22 (1H, d, *J* 17.5), 3.50–3.73 (3H, m), 3.75 (s, 3H, OCH_3) and 6.66–7.69 (12H, m); δ_C 29.27, 32.92, 33.19, 33.44, 38.15, 46.16, 52.15, 114.94, 126.18, 126.31, 126.47, 126.80, 127.49, 128.39, 128.57, 129.36, 129.40, 129.90, 134.81, 135.37, 136.47, 136.65, 137.06 and 158.52; *m*/*z* 432 ([^{79}Br]M^+) and 434 ([^{81}Br]M^+).

5-Bromomethyl-5a-(2-naphthyl)-5,5a,6,11,11a,12-hexahydrotetracene 6d

4d (115 mg, 0.29 mmol) in 1,4-dioxane (12 mL) was treated with HBr (48 wt% aq.; 3.1 g, 16.8 mmol) according to procedure B (24 h) to yield **6d** (60 mg, 46%) as a colourless solid, mp 165–167 °C (Found: C, 77.26; H, 6.10. $C_{29}H_{25}Br$ requires C, 76.99; H, 5.35%); ν_{max}(KBr)/cm^{-1} 2906, 1494, 1432, 1257, 1257 and 746; δ_H(270 MHz) 2.40 (2H, s), 2.79–3.05 (4H, m), 3.39 (1H, d, *J* 17.5), 3.55 (1H, dd, *J* 5.9 and 5.9), 3.71 (1H, dd, *J* 2.6 and 2.3), 3.95 (1H, d, *J* 4.9) and 6.86–7.87 (15H, m); δ_C 29.27, 32.92, 33.19, 33.44, 38.15, 46.16, 52.15, 124.85, 126.23, 126.31, 126.43, 126.47, 126.56, 126.68, 126.88, 127.13, 127.53, 127.69, 127.98, 128.35, 128.95, 129.38, 129.47, 129.90, 132.56, 133.58, 134.73, 135.25 and 136.48; *m*/*z* 454 ([^{81}Br]M^+) and 452 ([^{79}Br]M^+).

1-(*o*-Methylphenyl)-4,5:9,10-dibenzotricyclo[5.4.0.0^{2,11}]undeca-4,9-diene 11a. Typical procedure C for the rearrangement of [3.3]orthocyclophane alcohols with aq. HBr

To **4e** (260 mg, 0.74 mmol) in 1,4-dioxane (30 mL) was added 48 wt% aq. HBr (7.75 g, 45.9 mmol) and the resulting mixture was stirred at 35 °C for 24 h. Thereafter the phases were separated and the aq. phase was extracted with ether (2 × 15 mL). The combined organic phase was washed successively with aq. $NaHCO_3$(2 × 15 mL) and water (2 × 15 mL) and dried over $MgSO_4$. After the solvent had been evaporated *in vacuo*, the residue was recrystallised with benzene to give **11a** (200 mg, 80%) as a colourless solid, mp 164–166 °C (Found: C, 92.79; H, 7.19. $C_{26}H_{24}$ requires C, 92.81; H, 7.15%); ν_{max}(KBr)/cm^{-1} 2924, 1486, 1454, 1116, 1038 and 743; δ_H(270 MHz) 1.42 (3H, s, CH_3), 1.68 (1H, d, *J* 8.5), 2.25–2.53 (6H, m), 2.81 (1H, dd, *J* 8.3 and 8.3), 3.34 (1H, d, ^2J 14.2), 6.94–7.37 (12H, m); δ_C 18.33, 26.25, 29.24, 29.67, 32.03, 35.18, 37.66, 38.15, 125.75, 126.50, 126.65, 126.77, 127.04, 128.14, 129.63, 129.92, 130.60, 130.83, 131.01, 134.91, 137.75, 139.53, 141.87 and 147.29; *m*/*z* 336 (M^+).

1-(1-Naphthyl)-4,5:9,10-dibenzotricyclo[5.4.0.0^{2,11}]undeca-4,9-diene 11b

4f (287 mg, 0.75 mmol) in 1,4-dioxane (30 mL) was treated with HBr (48 wt% aq.; 7.60 g, 45.0 mmol) according to procedure C (5 h) to give **11b** (186 mg, 67%) as colourless plates, mp 244–245 °C (Found: C, 93.40; H, 6.59. $C_{29}H_{24}$ requires C, 93.50; H, 6.49%); ν_{max}(KBr)/cm^{-1} 2898, 1592, 1487, 1453, 1118 and 781; δ_H(270 MHz) 1.81 (1H, dd, *J* 8.9 and 9.2), 2.35–2.68 (6H, m), 2.92 (1H, dd, ^2J 14.3, ^3J 8.6), 3.38 (1H, br d, ^2J 14.3), 6.54 (1H, d, ^3J 8.6), 6.77 (1H, m), 7.14–7.44 (11H, m) and 7.64–7.73 (2H, m); δ_C (100.4 MHz) 25.31, 28.81, 28.93, 31.56, 35.10, 37.16, 38.32, 124.93, 125.05, 125.23, 125.54, 126.31, 126.87, 126.94, 127.25, 127.97, 128.27, 128.32 (2C), 129.63, 130.37, 131.36, 134.00, 134.09, 134.31, 139.20, 140.18, 141.42 and 144.86; *m*/*z* 372 (M^+).

To **4f** (547 mg, 1.50 mmol) in 1,4-dioxane (60 mL) was added dropwise aq. HCl (35 wt% aq.; 9.39 g, 90.0 mmol in 5.8 mL) and the resulting mixture was stirred at 35 °C for 20 h. Thereafter the phases were separated and the aq. phase was extracted with ether (2 × 15 mL). The combined organic phase was washed successively with aq. $NaHCO_3$ (2 × 15 mL) and water (2 × 15 mL) and dried over $MgSO_4$. After the solvent had been evaporated *in vacuo*, the residue was recrystallised with benzene to give **11b** (345 mg, 63%).

To **4f** (115 mg, 0.29 mmol) in 1,4-dioxane (12 mL) was added dropwise an H_2SO_4 (98 wt%; 1.76 g, 18.0 mmol in 1.6 mL) and the resulting mixture was stirred at 35 °C for 20 h. Thereafter the phases were separated and the aq. phase was extracted with ether (2 × 15 mL). The combined organic phase was washed successively with aq. $NaHCO_3$ (2 × 15 mL) and water (2 × 15 mL) and dried over $MgSO_4$. After the solvent had been evaporated *in vacuo*, the residue was recrystallised with benzene to give **11b** (68 mg, 62%).

Dimethyl 11-oxo-[2,2,5,5-$^2H_4$]-3,4:8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene-1,6-dicarboxylate 3a-D

To a stirred mixture of tetrabutylammonium bromide (400 mg, 1.20 mmol) in CH_2Cl_2 (12 mL) and KOH (23 wt% aq.; 6 mL)

was added dropwise a solution of 1,2-bis(bromomethyl)-benzene-d_4[8] **1-D** (530 mg, 2.00 mmol) and dimethyl 2,3,4,5-tetrahydro-3-oxo-1*H*-benzocycloheptene-2,4-dicarboxylate[1b] **12** (470 mg, 2.00 mmol) in CH_2Cl_2 (12 mL). The resulting two-phase system was stirred for 24 h at rt. Thereafter the phases were separated, and the organic phase was washed with water (2 × 30 mL) and dried over anhydrous Na_2SO_4. After concentration of the solution *in vacuo* the residue was taken up in methanol (10 mL). The colourless precipitate was filtered off, and recrystallised from methanol to give **3a-D** (650 mg, 84%) as colourless prisms, mp 175–179 °C (Found: M^+, 382.1724. $C_{23}H_{18}D_4O_5$ requires 382.1718); ν_{max}(KBr)/cm^{-1} 3052, 1760, 1685, 1458, 1275 and 752; *m*/*z* 382 (M^+).

11-Oxo-[2,2,5,5-$^2H_4$]-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic acid 3b-D

To a solution of **3a-D** (500 mg, 1.30 mmol) in ethanol (25 mL) was added KOH (1.8 g, 32.0 mmol) and the resulting slurry was refluxed for 3 h. After the mixture had cooled, it was poured into water (100 mL). The solution was acidified with 35 wt% aq. HCl and was kept at rt for 14 h. The precipitate formed was filtered off to give **3b-D** (300 mg, 63%) as a colourless solid (Found: M^+, 354.1412. $C_{21}H_{14}D_4O_5$ requires *M*, 354.1405); ν_{max}(KBr)/cm^{-1} 3309–2600br, 1705, 1410, 1276 and 749; *m*/*z* (FAB, 3-nitrobenzyl alcohol) 355 (MH^+).

[2,2,5,5-$^2H_4$]-3,4:8,9-Dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one 3c-D

3b-D (1.30 g, 3.70 mmol) was heated *in vacuo* (0.2–0.4 mmHg) at 340 °C until the gas evolution ceased. After the reaction mixture had cooled, it was dissolved in CH_2Cl_2 (50 mL). Insoluble material was filtered off. The filtrate was concentrated *in vacuo* and submitted to a column chromatography on silica gel (chloroform) to give **3c-D** (880 mg, 90%) as a colourless solid, mp 130–135 °C (Found: M^+, 266.1605. $C_{19}H_{14}D_4O$ requires *M*, 266.1609); ν_{max}(KBr)/cm^{-1} 3200–2600, 1702, 1449, 1284 and 744; *m*/*z* (FAB, 3-nitrobenzyl alcohol) 266 (M^+).

11-Hydroxy-11-(1-naphthyl)-3,4:8,9-dibenzobicyclo[4.4.1]-undeca-3,8-diene-2,2,5,5-d_4 4f-D (*syn*-4f-D; *anti*-4f-D [1:1])

3c-D (300 mg, 1.3 mmol) in dry THF (2.5 mL) was treated with Grignard reagent [1-bromonaphthalene (370 mg, 1.8 mmol), Mg (100 mg, 4.1 mmol), THF (2.5 mL)] according to procedure A (15 h) to yield a mixture of ***syn***- and ***anti***-**4f-D** (300 mg, 76%) as a colourless solid, mp 187–188 °C (Found: M^+, 394.2234. $C_{29}H_{22}D_4O$ requires *M*, 394.2235); ν_{max}(KBr)/cm^{-1} 3600–3200br (OH), 2914, 1493, 981, 779 and 745; δ_H(600 MHz; $CDCl_3$) [***syn***- and ***anti***-**4f-D** show the same absorptions unless noted otherwise] 1.99 (1H, s, OH), 2.70–2.74 (2H, m), 2.96 (2H [**4f-D-*syn***], br d, ^2J 14.3), 3.50 (2H, m), 4.20 (2H [**4f-D-*anti***], br d, ^2J 15.3), 6.55 (4H, m), 6.77 (4H, m), 7.17 (1H, m), 7.39–7.45 (2H, m), 7.59 (2H, m), 7.76 (1H, d, ^3J 7.9) and 8.94 (1H, d, ^3J 8.6); δ_C‡ (***syn***- and ***anti***-**4f-D** show the same absorptions unless noted otherwise) (150 MHz; $CDCl_3$) 36.46 [**4f-D-*anti***], 37.00 [**4f-D-*syn***], 41.24, 80.88,§ 80.92,§ 123.88, 124.92, 124.96 (2C), 125.60 (2C), 125.84, 127.90, 128.86, 129.03, 129.07, 129.39, 130.88, 130.90, 131.31, 135.39, 139.35, 139.44, 139.75, 139.82 and 140.95; *m*/*z* (FAB, 3-nitrobenzyl alcohol) 394 (M^+).

Rearrangement of cation formed from 11-hydroxy-11-(1-naphthyl)-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene-2,2,5,5-d_4 4f-D

To **4f-D** (200 mg, 0.51 mmol) in 1,4-dioxane (21 mL) was added dropwise HBr (48 wt% aq.; 5.3 g, 32.0 mmol) and the resulting mixture was stirred at 35 °C for 24 h. Ether (50 mL) was added and the phases were separated. The organic phase was washed with water (50 mL) and dried over anhydrous Na_2SO_4. After concentration of the solution *in vacuo*, the resulting residue was recrystallised from benzene to give **11b-D** (132 mg, 68%), δ_H (395 MHz; $CDCl_3$) 1.83 (1H, m, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**), 2.37 (1H, dd, ^2J 14.5, ^3J 3.3, **11b-D-*d*$_4$**), 2.43–2.69 (2H [**11b-D-*d*$_4$**], 3H [**11b-D-*d*$_3$**], m), 2.91 (1H, dd, ^2J 14.4, ^3J 8.2, **11b-D-*d*$_3$**), 3.40 (1H, dd, ^2J 6.24, ^3J 6.24, **11b-D-*d*$_4$**), 6.56 (1H, d, ^3J 8.7, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**), 6.79 (1H, m, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**), 7.14–7.50 (11H, m, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**), 7.64 (1H, m, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**), 7.73 (1H, d, ^3J 8.0, **11b-D-*d*$_3$**, **11b-D-*d*$_4$**). The isotopic ratio **11b-D-*d*$_3$** to **11b-D-*d*$_4$** was determined by mass spectrometry. The experiment was repeated twice (see Scheme 8).

X-Ray crystal-structure determination of 5¶

Crystal data. $C_{25}H_{23}Br$, $M = 403.34$, monoclinic, $a = 9.376(2)$ Å, $b = 23.622(3)$ Å, $c = 9.288(2)$ Å, $\beta = 112.03(2)°$, $V = 1906.9(6)$ Å^3, space group $P1\ 21/a$ (No. 14), $Z = 4$, $D_x = 1.405$ g cm^{-3}, colourless prism, crystal size 0.50 × 0.30 × 0.30 mm; μ(Cu-Kα) = 2.950 cm^{-1}.

Data collection and processing. CAD4 FR590 diffractometer, ω–2θ mode with ω scan width = (0.7 + 0.210 tan θ)°, graphite-monochromated Cu-Kα radiation; 4128 reflections were measured ($3.74 \leq \theta \leq 74.42°$). 3889 Unique reflections [merging $R = 0.0411$ after empirical absorption correction (max., min. transmission factor = 0.9988, 0.9017)] were used.

Structure analysis and refinement. The structure was solved by direct methods (SIR92).[9] The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.0704\ P)^2 + 2.1349\ P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final *R*- and R_w-values for 236 parameters are 0.0476, 0.1328. All calculations were performed using MolEN[10] and SHELXL-97.[11]

X-Ray crystal-structure determination of 6a¶

Crystal data. $C_{25}H_{23}Br$, $M = 403.34$, monoclinic, $a = 18.639(4)$ Å, $b = 10.296(2)$ Å, $c = 9.869(2)$ Å, $\beta = 96.77(2)°$, $V = 1880.7(7)$ Å^3, space group $P21/a$ (No. 14), $Z = 4$, $D_x = 1.424$ g cm^{-3}, colourless prism, crystal size 0.20 × 0.20 × 0.20 mm, μ(Cu-Kα) = 2.991 cm^{-1}.

Data collection and processing. CAD4 FR590 diffractometer, ω–2θ mode with ω scan width = (0.5 + 0.380 tan θ)°, graphite-monochromated Cu-Kα radiation; 3953 reflections were measured ($4.51 \leq \theta \leq 74.27°$). 3830 Unique reflections [merging $R = 0.0424$ after empirical absorption correction (max., min. transmission factor = 0.9998, 0.9327)] were used.

Structure analysis and refinement. The structure was solved by direct methods (SIR92).[9] The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.1073\ P)^2 + 1.7062\ P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final *R*- and R_w-values for 236 parameters are 0.0438, 0.1437. All calculations were performed using MolEN[10] and SHELXL-93.[12]

X-Ray crystal-structure determination of 11b¶

Crystal data. $C_{29}H_{24}{\cdot}C_6H_6$, $M = 372$, monoclinic, $a = 12.260(4)$ Å, $b = 19.770(9)$ Å, $c = 10.336(2)$ Å, $\beta = 94.688(2)°$, $V = 2496.9(15)$ Å^3, space group $P1\ 21c/1$ (No. 14.b1), $Z = 4$, $D_x = 1.199$ g cm^{-3}, colourless prism, crystal size 0.24 × 0.24 × 0.18 mm; μ(Cu-Kα) = 0.507 cm^{-1}.

‡ Only the values for the non-deuterated carbons are given.

§ These peaks could not be assigned (***syn***- or ***anti***-**4f-D**); the assignment of the peaks that could be assigned to either ***syn***- or ***anti***-**4f-D** was verified by C–H correlation.

¶ CCDC reference number 207/341. See http://www.rsc.org/suppdata/p1/1999/2101 for crystallographic files in .cif format.

Data collection and processing. CAD4 FR590 diffractometer, ω–2θ mode with ω scan width = (1.3 + 0.280 tan θ)°, graphite-monochromated Cu-Kα radiation; 4817 reflections were measured ($3.62 \leq \theta \leq 68.00°$). 4549 Unique reflections [merging $R = 0.0768$ after empirical absorption correction (max., min. transmission factor = 0.913, 0.903)] were used.

Structure analysis and refinement. The structure was solved by direct methods (SIR92).[9] The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.0732\ P)^2 + 0.7478\ P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final R- and R_w-values for 317 parameters are 0.0569, 0.1317. All calculations were performed using MolEN[10] and SHELXL-93.[12]

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