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Benzo[3.3]benzo[3.3]benzo- and Naphtho[3.3]benzo[3.3]naphtho-Orthocyclophane Bis(alcohol)s. Preparations and Structures.

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***Abstract*: *anti*-Benzo[1,2-*h*;4,5-*h'*]bis(benzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (**7a**) and bis(naphtho[2,3-*c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) derivative **7b** reacted with Grignard reagents (MeMgI and PhMgBr) to give bis(alcohol)s **10-12** or monoalcohols **13** and **14**, depending upon the amount of the reagent used. Similarly, *syn*-bis(alcohol)s **15-17** and *syn*-monoalcohols **18** and **19** were obtained in the reaction of *syn*-benzo[1,2-*h*;4,5-*h'*]bis(benzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (**9**) with the Grignard reagents. The alcohols **10-19** were produced as a mixture of configurational isomers and each isomer was isolated by HPLC. The structures were determined by ^{1}H and ^{13}C NMR spectra, NOE study, and X-ray crystallographic analyses of **12a**, **13**, and **17a**. The triple-layered [3.3][3.3]orthocyclophanes **10-12** take the (twin-chair)/(twin-chair) arrangement and in the structure, the top and the bottom aromatic rings sandwich a central benzo ring. *syn*-Cyclophanes **15-17** exist as an equilibrium mixture of two equivalent (twin-chair)/(chair-boat)- and (chair-boat)/(twin-chair)-conformers in solution. In the solid, the conformation is fixed, as clarified by X-ray crystallographic analysis of **17a**. Because of steric congestion, the central benzene ring in **17a** is not planar. Monoalcohols **13-14** and **18-19** have a rigid and layered twin-chair substructure and a flexible chair-boat part. The existence of a through-space interaction between the three stacked aromatic rings of [3.3][3.3]orthocyclophanes **10-12** was determined on the basis of a long wavelength shift in UV spectra, as compared to the spectra of **13-19** having a double-layered [3.3]orthocyclophane-substructure.

Introduction

Closely layered π-systems in cyclophanes have attracted a lot of attention over the last years.[1,2] They are interesting candidates for the study of non-bonded π–π interactions. Moreover, changing the π-basicity of aromatic ring systems by π–π interactions may alter the chemical reactivity of the aromatic rings and also help tailor host molecules for specific guests. In closely layered para- and metacyclophanes it is not always easy to make a clear distinction between effects due to the deformation of the aromatic rings and effects due to the π–π interaction between the aromatic rings. Recently, more research has been focussed on π-systems that are closely layered and rigidly held in place, but show virtually no deformation due to their specific connection to the rest of the molecule. [3.3]Orthocyclophanes of type **1-6** represent such a class of molecules with virtually non-deformed

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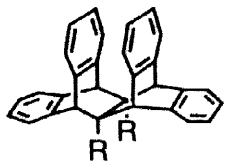
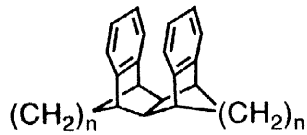
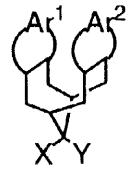
π-systems.[3-6] Nevertheless, different members of these [3.3]orthocyclophanes show different conformational behavior depending on their functionalization on the methylene-bridge, and in multi-bridged systems **5** and **6**, on the relative stereochemistry of the bridges (*syn*- or *anti*-).



1 (R=H, Br)



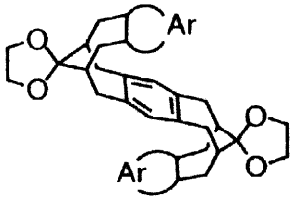
2 (n=1)
3 (n=2)



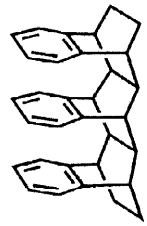
4

Ar^1, Ar^2 = benzo, 2,3-naphtho, 2,3-anthraceno

X, Y = O-$(CH_2)_2$-O ; X = Y = CH_3
X = CH_3, Ph, Y = OH



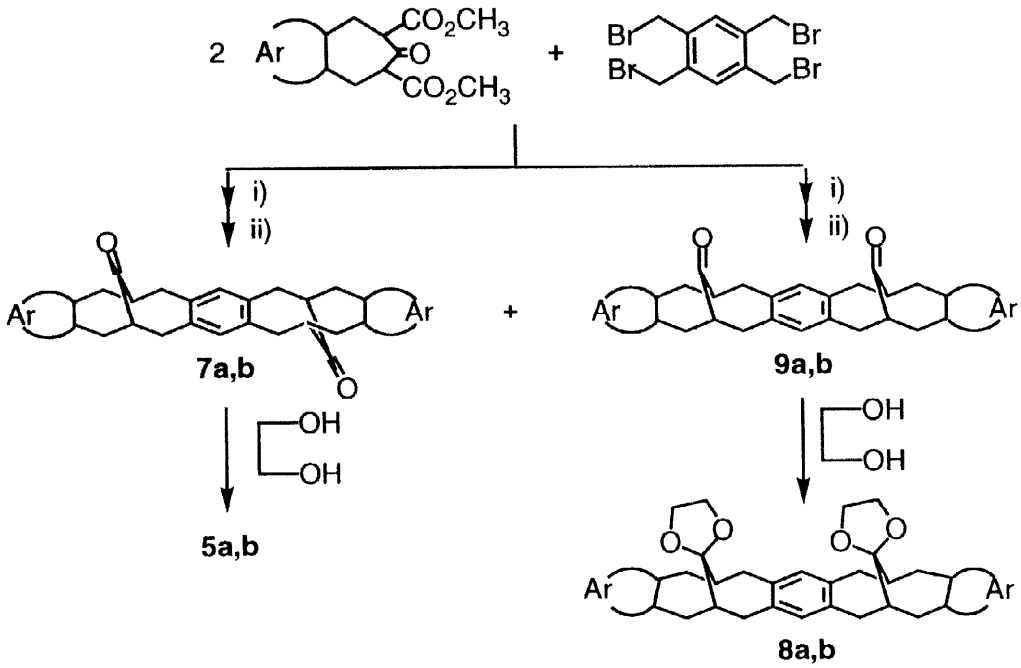
5a,b



6

a : Ar = benzo, **b** : Ar = 2,3-naphtho

As part of the study on these orthocyclophanes, the preparation of the [3.3][3.3]orthocyclophane acetals **5** with rigid triple-layered benzo/benzo/benzo- and naphtho/benzo/naphtho-systems from the *anti*-diketone **7** as



i) Hydrolysis, ii) Pyrolysis; **a** : Ar = benzo, **b** : Ar = 2,3-naphtho

Scheme 1

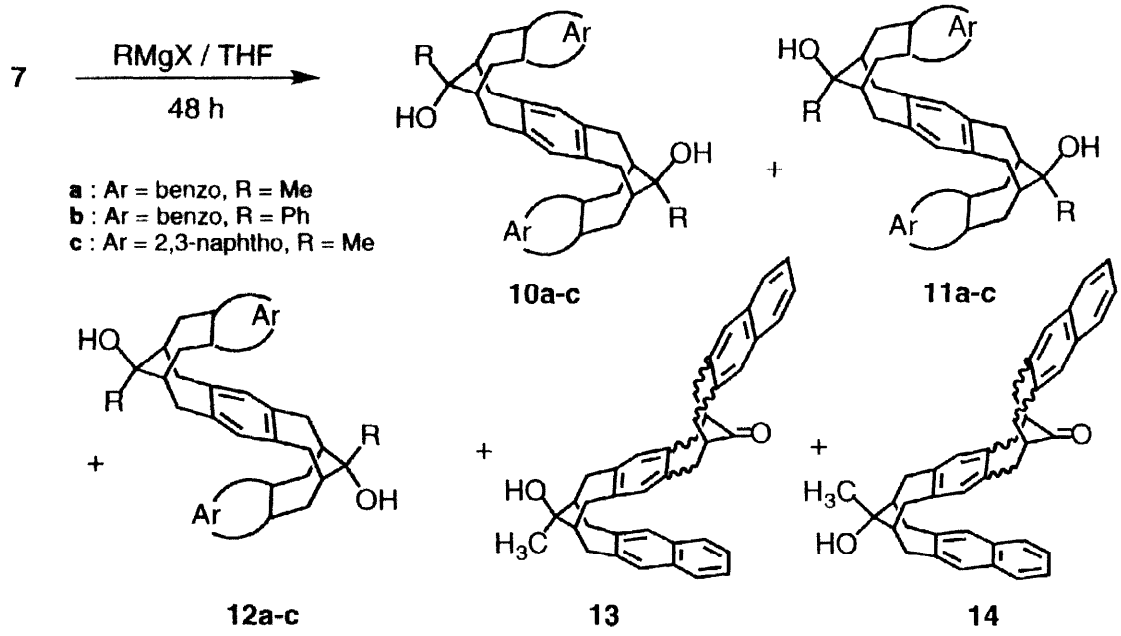
precursor was reported recently (**Scheme 1**).[5] The π–π interaction in these systems has been noted. On the other hand, the corresponding bisacetals **8** of the *syn*-diketones **9** have been found to be flexible and it was supposed that they exist as a quickly equilibrating mixture of conformers, as was indicated in VT-^{1}H NMR studies at a temperature range from -60 °C to rt. Nevertheless, the conformations could not be clarified in detail at that time.

In order to have a better understanding of the conformational behaviour of such structures and in order to have more candidates available for the study of the π–π interaction in the rigid systems, the alcohol derivatives **10-19**, derived from **7** and **9**, have been synthesized. The preparation, structure, conformational behaviour and the spectral properties of these [3.3][3.3]orthocyclophanes are described in this paper. Also, X-ray crystallographic analyses of **12a**, **13**, and **17a** have been provided.

Results and Discussion

Preparation of [3.3][3.3]Orthocyclophane Alcohols

Analogous to the preparation of double-layered [3.3]orthocyclophane alcohols[6a,b], the diketones **7** and **9** were reacted with Grignard reagents to yield **10-19**. As expected, the alcohols were obtained as a mixture of stereoisomers (**Scheme 2-3**). The products **10-19** could be separated by preparative HPLC (**Table 1-2**). Assignment of their configurations will be described later.



Scheme 2

Table 1. Reaction of **7** with Grignard reagents

7	RMgX	RMgX/5 (mol/mol)	Products (Isolated Yield, %)
7a	MeMgI	5	**10a** (21), **11a** (43), **12a** (23)
7a	PhMgBr	15	**10b** (6), **11b** (12), **12b** (19)
7b	MeMgI	10	**10c** (4), **11c** (62), **12c** (12)
7b	MeMgI	5	**13** (64), **14** (21)

In the reaction of *anti*-diketone **7a** with 5 equivalents of MeMgI the expected triple-layered bis(alcohol)s **10a**, **11a**, and **12a** were produced. The ratios of isomers formed of **10a**, **11a**, and **12a** are very close to statistical values. The use of a large excess (15 equiv.) of PhMgBr was necessary to obtain the desired bis(phenylalcohol)s **10b**, **11b**, and **12b**. The corresponding monoalcohol derivatives were not formed, even when a lesser amount of PhMgBr was used. In these cases, a mixture of unchanged diketone **7a** and the bis(alcohol)s **10b**, **11b**, and **12b** were obtained. On the other hand, naphtho derivative **7b** afforded either methylalcohols **13** and **14** or a mixture of bis(alcohol)s **10c**, **11c**, and **12c**, depending upon the amount of MeMgI used. The reaction with 5 equivalents of MeMgI gave a 3:1-mixture of **13** and **14**, while only bis(alcohol)s **10c-12c** were produced in the reaction with 10 equivalents of MeMgI. The first attack of the Grignard reagent on one of the two carbonyl functions of **7b** occurs from the less hindered side to give naphtho/benzo/naphtho-orthophane alcohol **13**, as opposed to **14**. The ORTEP drawing of **13** (**Fig. 1**) gives evidence that the naphthalene rings shield the carbonyl function from attack of the reagent. Thus, the second attack is slowed and the two naphtho units of **7b** may control the direction of the incoming Grignard reagent, leading to the predominant formation of **11c**.

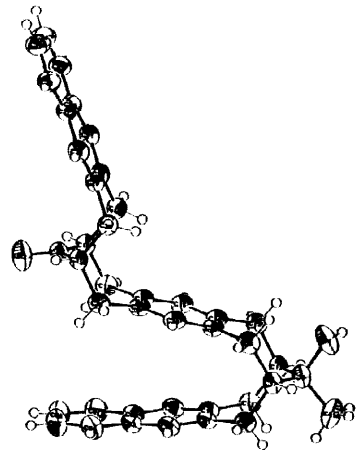
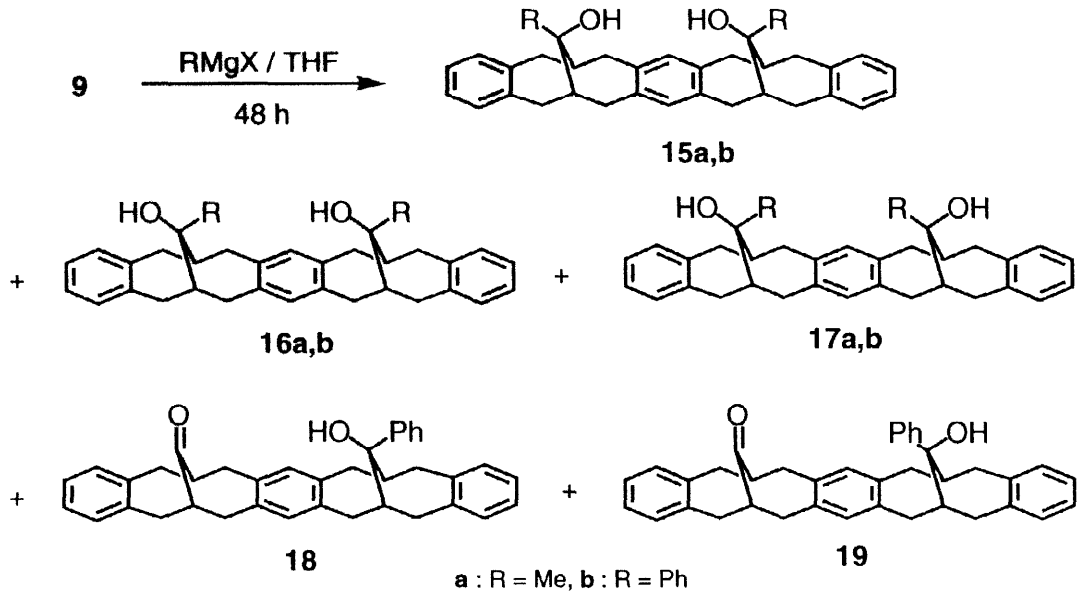


Fig. 1 ORTEP view of **13**



Scheme 3

The reaction of *syn*-diketone **9a** also gives either bis(alcohol)s **15-17** or monoalcohols **18-19**, depending upon the nature of the Grignard reagents and the amount used. In the reaction with MeMgI, bis(alcohol)s **15a**, **16a**, and **17a** were produced in a close-to-statistical ratio. The reaction with PhMgBr proceeded in a diastereoselective manner (**Table 2**), probably due to the fact that a phenyl group is bulkier than a methyl group. When 10 equivalents of PhMgBr were used, bis(alcohol) **16b** was formed as the major product, accompanied by

a small amount of **15b**. Isomer **17b** was not obtained in the reaction. Monoalcohols **18** and **19** were obtained in the reaction using 5 equivalents of PhMgBr. Each of the two monoalcohols was isolated by HPLC, but their structures could not be assigned.

Table 2. Reaction of **9** with Grignard reagent

9	RMgX	RMgX/**5** (mol/mol)	Products (Isolated Yield)
9a	MeMgI	5	**15a** (23), **16a** (37), **17a** (27)
9b	PhMgBr	10	**15b** (5), **16b** (20)
9b	PhMgBr	5	**18** + **19** (16 + 26)[a]

a) The structures could not be assigned.

Structures

Bis(alcohol)s **10a-c**, **11a-c**, and **12a-c** have two stacked [3.3]orthocyclophane systems and exhibit ^{1}H NMR spectra similar to those of triple-layered [3.3][3.3]orthocyclophanebis(acetals) **5**.[5] The methylene protons on the bridges appear as several sets of double doublets and the methine protons on the bridgehead positions show a multiplet peak. Protons of the stacked aromatic rings show an up-field shift (**Table 3**), as is in the case of the acetals **5**. Due to the anisotropic effects due to the top and the bottom aromatic rings, the protons of the central benzo ring show a remarkable up-field shift.

Table 3. Chemical shifts of the central aromatic-ring protons of **5**, **10**, **11**, and **12**.

Compd	δ ppm	Compd	δ ppm	Compd	δ ppm	Compd	δ ppm
5a	5.91	**10a**	5.97	**10b**	6.31	**10c**	5.71
		11a	6.06	**11b**	6.26	**11c**	5.75
5b	5.86	**12a**	6.12	**12b**	6.02	**12c**	5.78

Of the three stereoisomeric bis(methylalcohol)s **10a-12a**, unsymmetric *exo,endo*-diol **11a** is easily recognisable due to the presence of two different methyl signals in the ^{1}H NMR spectrum. The ^{1}H NMR spectra of **10a** and **12a** reflect the symmetric structures of the two conformers, as the two methyl and the two hydroxyl groups of each conformer are observed as a singlet each, and the methylene protons appear as four sets of double-doublet peaks. A suitable crystal of a 1:1-complex of **12a** with chloroform was obtained and the X-ray crystal analysis confirms the *exo,exo*-configuration (**Fig. 2**), in which the two hydroxyl groups on the methylene bridges are directed to the outer side of the molecule. In this way **10a** could be assigned as *endo,endo*-diol. The NOE spectra (**Fig. 3**) can explain the configurations assigned to **10a-12a** reasonably well. Moreover, the stereochemistry of each isomer

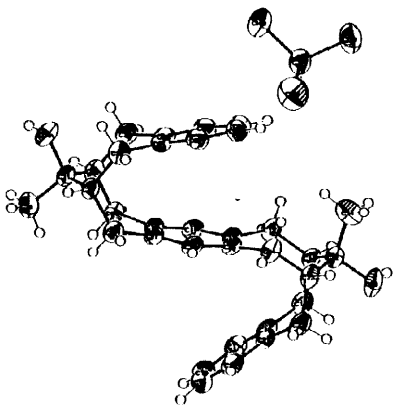


Fig. 2 ORTEP view of **12a**

endo,endo-**10b-c**, *exo,endo*-**11b-c**, and *exo,exo*-**12b-c** could be determined on the basis of NOE experiments (**Fig. 4**).

The bis(twin-chair) conformer seems to be highly improbable in the case of *syn*-bis(alcohol)s **15-17**, because in these imaginary conformers, the two outer rings have to collapse onto the central ring.

A symmetric structure of **15a** seems obvious, as it shows ten signals in the ^{13}C NMR at room temperature. Only one signal for the methyl groups and one for the hydroxyl protons could be observed in the ^{1}H NMR, which shows the methylene protons as four sets of double-doublet peaks. NOE studies on **15** (**Fig. 5**) disclose that the two hydroxyl groups of *endo,endo*-diol **15a** are directed away from

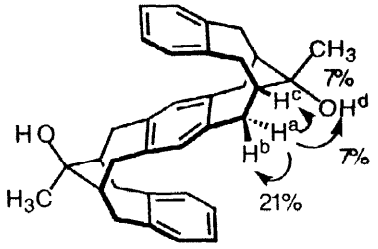
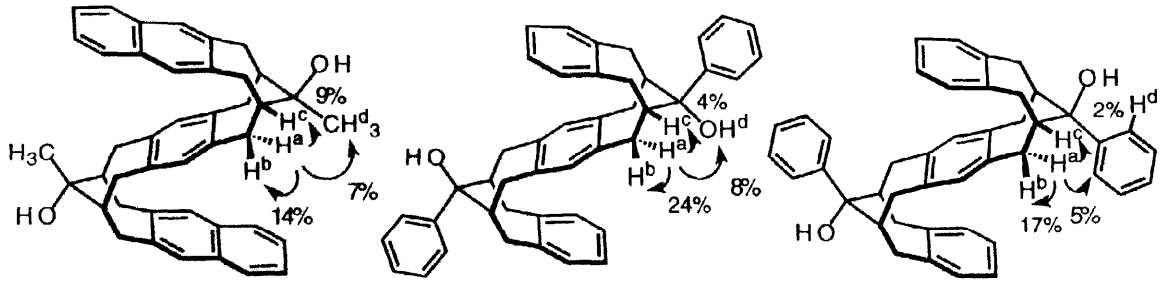
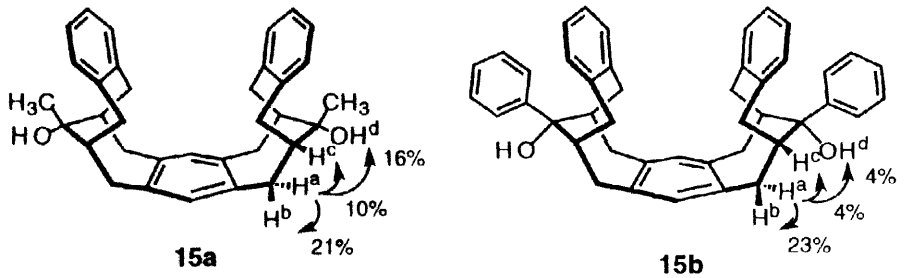


Fig.3 NOE Data of **10a**



12c **10b** **12b**

Fig. 4 NOE Data of **10b** and **12b,c**



15a **15b**

Fig. 5 NOE Data of **15a,b**

the central benzo ring. Diol **15a** is thought to exist as an equilibrium mixture of (boat-chair)-(twin-chair), (chair-boat)-(twin-chair), (twin-chair)-(boat-chair), and (twin-chair)-(chair-boat) conformers in solution (**Fig. 6**).[7] The structure of *endo,endo*-**15b** was similarly determined. The presence of only one peak for the hydroxyl protons supports a symmetric structure for **15b** and by NOE experiment the arrangement of the two phenyl groups introduced by the Grignard addition could be determined. X-ray crystallographic analysis shows a symmetric *exo,exo*-structure for **17a**. On the other hand, **16a** has an unsymmetric *exo,endo*-structure. The ^{1}H NMR spectrum at -60 °C shows a complex signal pattern and overlapping peaks for the methylene protons. Therefore, the conformation of **16a** remains unknown. The *exo,endo*-structure of **16b** is shown by the presence of two singlets due to the two hydroxyl protons (δ= 1.54 and 1.68 ppm, respectively) in the ^{1}H NMR, but again the conformation could not be determined because of complex overlapping of the methylene signals. By X-ray crystallographic analysis, compound **17a** was found to take the (twin-chair)/(chair-boat)-

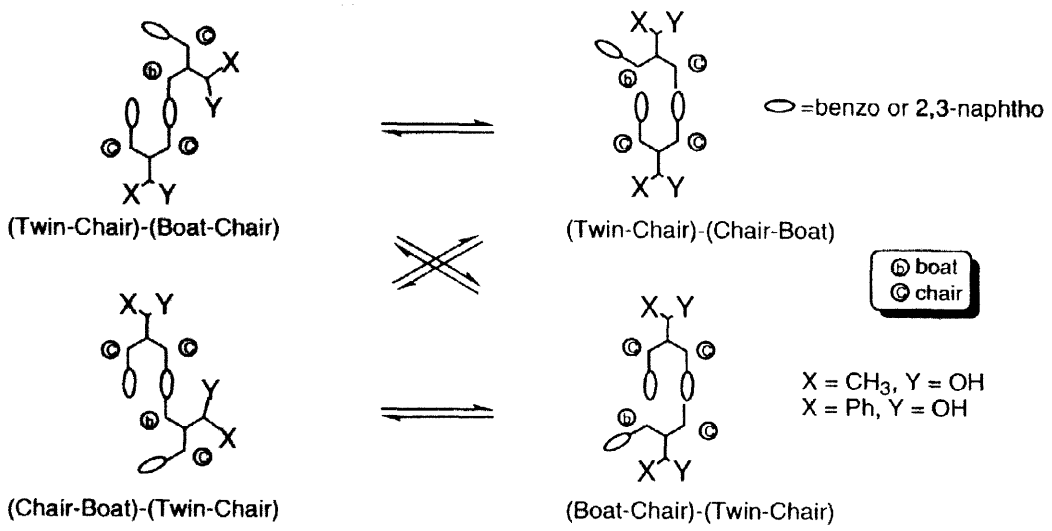


Fig. 6 Conformation Change of *syn*-layered [3.3][3.3]Orthocyclophanes

conformation in the solid state (**Fig. 7**). The two hydroxyl groups of *exo,exo*-**17a** are oriented in different directions. In solution, **17a** exists as an equilibrium mixture of two equivalent conformers, in which one bicyclo[4.4.1]undecane-unit takes a (twin-chair) conformation and the other has either a chair-boat or a boat-chair conformation. At room temperature the ^1H NMR spectrum of **17a** shows three broad peaks for the aromatic protons, eight sharp peaks for the methylene protons and a broad peak for the methine protons. At -60 °C, four aromatic peaks could be observed, and the methylene and methine protons appeared as complicated multiplets of sharp peaks. These facts suggest the presence of an equilibrium between two equivalent (twin-chair)/(chair-boat)-conformers. In this conformation, the benzo rings at both ends come close to each other, as evidenced by the separation of C18 and C7 by 369 nm. This may lead to a steric repulsion between the two outer benzo rings, and all benzo rings in **17a** are deformed from planarity to a certain degree (**Fig. 8**). The central benzo ring is bent to a lesser extent than the outer rings. Such a repulsion does not exist in a bis(chair-boat) conformation of **17a**, however, this conformation is less favorable in the arrangement of the outer benzo rings with hydroxyl

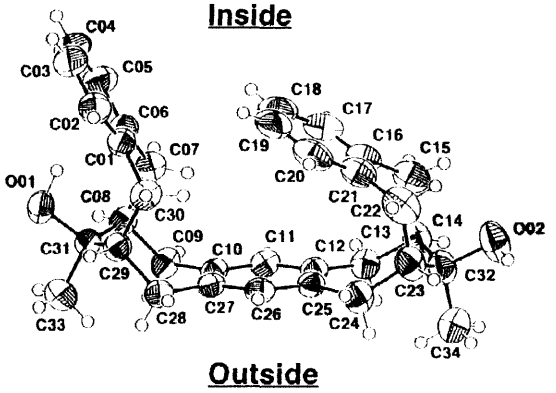


Fig. 7 ORTEP view of **17a**

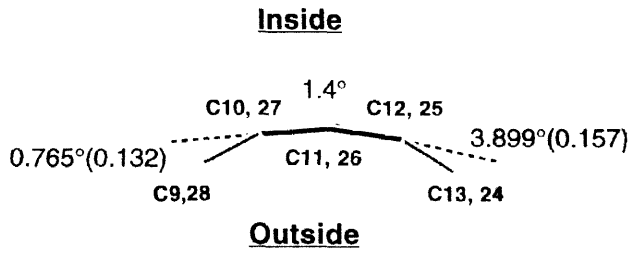


Fig. 8 Side view of **17a**

substituents. The corresponding symmetric conformer **17b** was not found in the reaction of **9a** and PhMgBr.

Monoalcohols **13, 14, 18, and 19** have a rigid twin-chair unit and either a flexible chair-boat or boat-chair substructure in the molecule. The assignment of the configurations of **13, 14, 18, and 19** by means of ^{1}H NMR spectra is difficult, since each of the alcohols shows broad peaks even at -60 °C. The *endo*-configuration of **13** was determined by X-ray crystallographic analysis and, consequently, the stereostructure of isomeric monoalcohol **14** can be assigned as *exo*. The (twin-chair)-(chair-boat) conformation of **13** in the solid state was clarified by X-ray crystallographic analysis (**Fig. 1**). In the twin-chair part of **13**, the naphtho ring and the central benzo ring are held at distances of 299-374 pm. Thus, the dihedral angle (16.7°) between the rings is smaller than the one (18.1°) in the triple-layered orthocyclophane bisacetal **5b**.[5)]

UV Spectra of [3.3][3.3]Orthocyclophane alcohols.

UV spectral data for benzenophane(alcohol) derivatives **10-19** and diketones are given in **Table 4**. *Anti*-diketone **7a** is insoluble in all solvents useful for the UV-measurements.

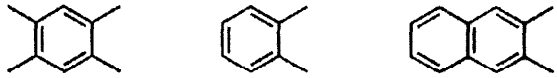
When aromatic rings are stacked face-to-face, a long wavelength shift in the UV/VIS spectra is seen, as has also been reported in the case of multi-layered meta- and paracyclophanes.[1b,8)] The UV spectrum of ketone **9a** shows no shift to longer wavelengths, when compared to that of the reference compounds **20** and **21** (280 and 274 nm). A broad absorption band could be found at longer wavelengths in the spectra of bis(alcohols) **10a-12a**, where the conformation is fixed in the bis(twin-chair) conformation. The values for λ_{max} (301-303 nm) of isomers **10a, 11a, and 12a** are very close to those reported for triple-layered orthocyclophane bis(acetal) **5a** (299 nm).[5)] These results are in sharp contrast to the finding that the λ_{max} (272 nm) of triple-layered phane **6** is almost identical to that (273 nm) of the corresponding double-layered phane **2**.[4b)] On the other hand, no difference is seen in the λ_{max}-values of *syn*-bis(alcohol)s **15a-17a** and *syn*-mono(alcohol)s **18** and **19**. These facts show that the major conformation of **15a-17a** is a composite of one bicyclo[4.4.1]undecane-subunit of the (twin-chair)-conformation and one of the (chair-boat)-conformation, as shown by X-ray crystallographic analysis. From comparison of the λ_{max}-values of bis(alcohol)s **10a-12a**, monoalcohols **18-19**, and ketone **9a**, it can be said that the stacking of one dimethylbenzo-unit causes a long wavelength shift of about 10 nm.

Table 4 UV Spectra of *anti*- and *syn*-[3.3][3.3]Orthocyclophanes.

Stacked aromatic rings	[3.3][3.3]Orthocyclophanes (λ_{max} a), log ε)		
	Triple-layered phanes	Double-layered phanes	Ketones
Benzo/benzo/benzo	**10a** (303, 2.73), **10b** (301, 2.81) **11a** (301, 2.68), **11b** (298, 2.79) **12a** (301, 2.56), **12b** (304, 2.80) **5a** (299, 2.56)	**15a** (293, 2.74), **15b** (290, 2.76) **16a** (291, 2.63), **16b** (293, 2.63) **17a** (291, 2.64) **18** (291, 2.71), **19** (291, 2.65) **8a** (291, 2.66)	**9a** (280, 2.95)
Naphtho/naphto /naphtho	**10c** (341, 2.66), **11c** (340, 2.59) **12c** (340, 2.73), **5b** (340, 2.66)	**13** (338, 2.69), **14** (338, 2.63) **8b** (338, 2.39)	**7b** (322, 2.90) **9b** (322, 2.62)

a) nm.

Diketones **7b** and 2,3-dimethylnaphthalene **22** have their absorption maximum at λ_{max} = 322 nm. Stacking of benzo-rings and naphtho-rings in mono(alcohol)s induces a red-shift of 16 nm in the UV spectra of **13** and **14**, but a further stacking of another naphtho-ring causes only a small red-shift (2-3 nm) in the spectra of bis(alcohol)s **10c**, **11c**, and **12c** (λ_{max} =340-341 nm), as was also reported[5] in the case of **5a-b** and **8a-b**.



20 **21** **22**

Conclusions

The degree of π–π through-space interaction present in *anti*- and *syn*-[3.3][3.3]orthocyclophane alcohols **10-19** was estimated by ^{1}H NMR and electronic spectra and X-ray crystallographic analysis. In ^{1}H NMR spectra, the central benzene ring of *anti*-alcohols shows a large up-field shift as compared to 1, 2, 4, 5-tetramethylbenzene (**20**). This can be attributed to the anisotropic effect of a second, proximate and stacked aromatic ring. Just as in *anti*-bis(acetal) **5**[5], the conformations of *anti*-bis(alcohols) **10-12** are rigid and the overall structures symmetric. Also, X-ray crystallographic analysis clearly shows the symmetric structure of *anti*-bis(alcohol) **12a**. The conformation of *syn*-bis(alcohol)s **15-17** is too flexible to be determined by ^{1}H NMR spectroscopy. However, the X-ray crystal analysis of **17a** could be obtained. One of the two bicyclo[4.4.1]undeca sub-units in **17a** adopts a boat-chair conformation, while the other subunit takes the twin-chair conformation.

Additionally, the values for λ_{max} of the *anti*-benzo derivatives **10a-b**, **11a-b**, and **12a,b** show a shift to longer wavelengths with an increasing number of aromatic ring layers. In contrast, λ_{max} values of the *anti*-naphtho derivatives **10c**, **11c** and **12c** remain constant as the layers increase from two to three, with a doubling of the value for ε. This fact means that the absorption band at 340 nm of **12c** represents the sum of two 2,3-dimethylnaphthalene (**22**)/1,2,4,5-tetramethylbenzene (**20**) interactions. On the other hand, the value for λ_{max} of *syn*-bis(alcohol)s **15-17** in their electronic spectra is located at the same wavelength as compared to that of *syn*-monoalcohols **18** and **19**, respectively. This indicates that there are many conformers contributing to the electronic spectrum of the compound, in which the central benzo ring is stacked with one of the outer aromatic rings. Therefore, it can be concluded that the position of λ_{max} in the described orthophanes is mainly governed by the same type of aromatic stacking, in spite of differences in the stereochemistry of the bridges in multi-bridged orthophanes and in spite of differences in substituents on the bridges.

Experimental

General. Melting points are uncorrected. Infrared spectra were obtained in KBr pellets. UV/VIS spectra were measured in $CHCl_3$. ^{1}H NMR and Difference NOE spectra were recorded at 270 MHz. $CDCl_3$ served as the solvent. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS 700 instrument. Mass spectral analyses were performed under 70 eV electron-impact (EI) conditions. HPLC was carried out on a JASCO 880 HPLC (Develosil Packed Column: F 25 mm/250 mm).

Reaction of 2 with Grignard reagents. Typical Procedure. A solution of **7a** (0.423 g, 0.95 mmol) in THF (20 ml) was added dropwise at room temperature to a solution of MeMgI (4.80 mmol) in THF (50 ml) and the

mixture was heated under reflux for 48 hours under argon. 5 % aq. Hydrochloric acid (30 ml) was added to the reaction mixture, and the organic layer was separated, dried, and evaporated *in vacuo* to afford a solid, which was recrystallized from methanol to give a mixture (0.395 g, 87%) of benzo[1,2-*h*;4,5-*h*']bis(11-hydroxy-11-methylbenzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene)s **10a**, **11a**, and **12a**. HPLC (ethyl acetate/chloroform=1:4) of the mixture gave 96 mg (22%) of **10a**, 198 mg (43%) of **11a**, and 92 mg (22%) of **12a**.

endo,endo-Diol **10a:** mp 297-299 °C; colorless needles (methanol/chloroform); IR 3578 (sh), 3450 (br), 3054, 2996, 2910, 1494, 1438, 1378, 1293, 1228, 1117, 1072, 1046, 1023, 929, 909, 736 cm^{-1}; ^1H NMR 1.46 (s, 6H), 1.55 (s, 2H), 2.01-2.11 (br s, 4H), 2.26 (dd, J=5.6, 15.2 Hz, 4H), 2.65 (dd, J=5.4, 15.5 Hz, 4H), 3.11 (dd, J=3.0, 15.5 Hz, 4H), 3.19 (dd, J=0.3, 15.2 Hz, 4H), 5.92 (s, 2H), 6.50-6.55 (m, 4H), 6.63-6.78 (m, 4H); ^{13}C NMR 30.73, 35.06, 37.94, 44.69, 77.13, 124.80, 130.51, 132.83, 136.32, 139.21; EI-MS m/z 478 (M^+, 31), 337 (56), 233 (10), 155 (18), 129 (50), 104 (100); HRMS (M^+) Calcd for $C_{34}H_{38}O_2$: 478.2872, Found 478.2882.

endo,exo-Diol **11a:** mp 244-246 °C; colorless prisms (methanol/chloroform); IR 3550 (sh), 3424 (br), 3054, 2994, 2910, 1508, 1493, 1436, 1373, 1298, 1232, 1103, 1064, 1050,1021, 927, 737 cm^{-1}; ^1H NMR 1.48 (s, 3H), 1.51 (s, 3H), 1.58 (br s, 2H), 2.08-2.19 (m, 4H), 2.33 (dd, J=15.2, 5.6 Hz, 2H), 2.44 (dd, J=15.8, 5.0 Hz, 2H), 2.56 (dd, J=14.5, 6.6 Hz, 2H), 2.67 (dd, J=15.8, 5.3 Hz, 2H), 2.84 (d, J=15.8 Hz, 2H), 3.15 (dd, J=15.8, 0.1 Hz, 2H), 3.28 (dd, J=14.5, 4.5 Hz, 2H), 3.45 (d, J=15.2 Hz, 2H), 6.06 (s, 2H), 6.55-6.58 (m, 2H), 6.67-6.69 (m, 2H), 6.71 (br s, 4H); ^{13}C NMR 30.0, 30.7, 35.0, 35.8, 37.7, 38.1, 44.7, 44.9, 77.2, 77.7, 124.3, 125.6, 129.4, 130.8, 133.9, 135.4, 136.7, 139.3, 140.0; EI-MS m/z 478 (M^+, 27), 355 (9), 286 (7), 181 (10), 155 (49), 129 (80), 104 (100); Anal. Calcd for $C_{34}H_{38}O_2$: C, 85.31; H, 8.00 %. Found: C, 85.59; H, 8.01 %.

exo,exo-Diol **12a:** mp 275-277 °C; colorless prisms (methanol/chloroform); IR 3664 (sh), 3392 (br), 3054, 2992, 2910, 1494, 1435, 1371, 1308, 1107, 1054, 928, 740 cm^{-1}; ^1H NMR 1.53 (s, 6H), 1.57 (br s, 2H), 2.12-2.20 (m, 4H), 2.47-2.58 (m, 8H), 2.96 (d, J=16.5 Hz, 4H), 3.37 (dd, J=14.9, 4.3 Hz, 4H), 6.12 (s, 2H), 6.65-6.73 (m, 8H); ^{13}C NMR 30.19, 35.88, 37.56, 44.89, 76.14, 124.99, 129.72, 134.73, 135.74, 140.16; EI-MS m/z ; EI-MS m/z 478 (M^+, 100), 304 (31), 287 (78), 156 (18), 129 (85); Anal. Calcd for $C_{34}H_{38}O_2$:C, 85.31; H, 8.00 %. Found:C, 85.24; H, 8.01 %.

Benzo[1,2-*h*;4,5-*h*']bis(11-hydroxy-11-phenylbenzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (**10b**, **11b**, and **12b**). A solution of **7a** (420 mg, 0.094 mmol) in THF(60 ml) was added dropwise at room temperature to a solution of PhMgBr (14.0 mmol) in THF (6 ml) and the mixture was heated under reflux for 48 hours under argon. 5 % aq. Hydrochloric acid (10 ml) was added to the reaction mixture, and the organic layer was separated, dried, and evaporated *in vacuo* to afford a solid, which was recrystallized from methanol to give a mixture (215 mg, 37%) of benzo[1,2-*h*;4,5-*h*']bis(11-hydroxy-11-phenylbenzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene)s **10b**, **11b**, and **12b**. HPLC (hexane/chloroform=1:4) of the mixture gave 31 mg (6%) of **10b**, 71 mg (12%) of **11b**, and 108 mg (19%) of **12b**. Recrystallization from a mixture of methanol/chloroform afforded **11b** and **12b** as a complex with chloroform in a non-stoichiometric ratio, respectively.

endo,endo-Diol **10b:** mp >280 °C (decomp.); white powder (methanol); IR 3544, 3058, 3014, 2914, 1494, 1443, 1040, 998, 948, 907, 766, 739, 698 cm^{-1}; ^1H NMR 1.52 (s, 2H), 2.55 (dd, J=5, 6 Hz, 4H), 2.71 (dd, J=7, 8 Hz, 4H), 2.90 (dd, J=4, 15 Hz, 4H), 3.09-3.21 (br s, 4H), 3.70 (dd, J=4, 14 Hz, 4H), 6.31 (s, 2H), 6.52-6.56 (m, 4H), 6.58-6.62 (m, 4H), 7.12-7.16 (m, 2H), 7.30 (d, J=5 Hz, 4H), 7.52 (d, J=8 Hz, 4H); ^{13}C NMR 35.02, 36.66, 39.64, 78.67, 125.08, 126.00, 126.81, 128.31, 128.35, 129.61, 133.64, 136.55, 139.19; EI-MS m/z 602 (M^+, 2), 584 (7), 566 (100), 475 (14), 461 (43), 348 (34), 229 (20), 217 (42); HRMS (M^+) Calcd for $C_{44}H_{42}O_2$: 602.3185, Found 602.3209.

endo,exo-Diol **11b:** mp 228-230 °C; colorless plates (methanol/chloroform); IR 3542, 3056, 3014, 2914, 1495, 1444, 996, 945, 907, 766, 738, 698 cm^{-1}; ^1H NMR 1.33 (s, 1H), 1.45 (s, 1H), 2.29-2.44 (m, 4H), 2.56-2.84 (m, 8H), 3.08 (d, J=8 Hz, 2H), 3.22-3.31 (br s, 2H), 3.63 (d, J=15 Hz, 2H), 3.91 (dd, J=0.1, 12 Hz, 2H), 6.26 (s, 2H), 6.50-6.52 (br s, 4H), 6.89-6.91 (br s, 4H), 6.97-7.02 (m, 2H) 7.06-7.11 (m, 3H), 7.29 (m, 3H), 7.50 (d, J=8 Hz, 2H); ^{13}C NMR 35.02, 35.81, 39.37, 39.53, 39.88, 77.68, 78.51, 125.03, 125.36, 125.62, 125.82, 126.22, 126.77, 127.31, 127.80, 128.27, 128.99, 130.67, 132.82, 136.35, 136.73, 139.35, 139.93, 146.12, 146.61; EI-MS m/z 602 (M^+, 8), 568 (23), 566 (100), 461 (43), 348 (56), 217 (60); HRMS (M^+) Calcd for $C_{44}H_{42}O_2$: 602.3185, Found 602.3183. Anal. Calcd for ($C_{44}H_{42}O_2$ + 1.3 $CHCl_3$): C, 71.79; H, 5.76 %. Found: C, 71.75; H, 5.61 %.

exo,exo-Diol **12b:** Yield 108 mg; mp 284-286 °C; colorless prisms (methanol/chloroform); IR 3544, 3056, 3014, 2914, 1495, 1444, 1070, 1001, 947, 906, 762, 738, 699 cm^{-1}; ^1H NMR 1.56 (s, 2H), 2.45-2.58 (m, 8H), 2.74 (dd, J= 3, 12 Hz, 4H), 3.09-3.29 (br s, 4H), 3.53 (br d, J=14 Hz, 4H), 6.02 (s, 2H), 6.68 (dd, J= 5, 13 Hz, 8H), 6.90-6.98 (br s, 2H), 7.25-29 (m, 4H), 7.58 (d, J=8 Hz, 4H); ^{13}C NMR 35.01, 36.64, 39.62, 78.65, 125.07, 125.98, 127.31, 127.92, 128.34, 129.60, 133.62, 136.53, 139.16; EI-MS m/z 602 (M^+, 2), 564 (13), 568 (100), 461 (23), 328 (66), 204 (35); HRMS (M^+) Calcd for $C_{44}H_{42}O_2$: 602.3185, Found 602.3189. Anal. Calcd for ($C_{44}H_{42}O_2$ + 1.3 $CHCl_3$): C, 71.79; H, 5.76 %. Found: C, 71.24; H, 5.61 %.

Benzo[1,2-*h*;4,5-*h'*]bis(11-hydroxy-11-methylnaphtho[2,3-*c*]bicyclo[4.4.1]undeca-3,8-diene) (**10c**, **11c**, and **12c**). According to the typical procedures described above a mixture (296 mg, 78%) of **10c**, **11c**, and **12c** was obtained in the reaction of **7b** (356 mg, 0.651 mmol) and MeMgI (1.08 g, 6.51 mmol) and the isomers were separated by HPLC (hexane/chloroform=1/9 as eluant). Compounds **11c** and **12c** were obtained as hydrates in the recrystallization from methanol/chloroform, respectively.

endo,endo-Diol **10c:** Yield 15 mg (4%); mp > 305 °C (decomp.); colorless plates (methanol/chloroform); IR 3448, 2914, 1438, 1105, 1053, 929, 905, 873, 724; ^1H NMR 1.42 (s, 6H), 1.55 (br s, 2H), 1.85-1.97 (m, 4H), 2.11 (dd, J=16.2, 5.1 Hz, 4H), 2.64-2.79 (m, 8H), 3.13 (d, J=16.2 Hz, 4H), 5.71 (s, 2H), 6.90 (s, 4H), 7.20-7.24 (m, 4H), 7.44-7.47 (m, 4H); EI-MS m/z 578 (M^+, 11), 543 (25), 199 (28), 181 (39), 155 (100); HRMS (M^+) Calcd for $C_{42}H_{42}O_2$: 578.3185, Found 578.3196. Anal. Calcd for $C_{42}H_{42}O_2$: C, 86.85; H, 7.64 %. Found: C, 87.08; H, 7.91 %.

endo,exo-Diol **11c:** Yield 234 mg (62%); mp > 279 °C (decomp.); colorless needles (methanol/chloroform); IR

3428, 3048, 2992, 2916, 2850, 1460, 1436, 1107, 929, 903, 865, 742 cm^{-1}; ^1H NMR 1.19 (s, 3H), 1.21 (s, 3H), 1.44 (s, 1H), 1.51 (s, 1H), 1.87-2.08 (m, 4H), 2.19 (dd, J=14, 0.2 Hz, 2H), 2.21-2.31 (m, 2H), 2.53 (dd, J=14, 3 Hz, 2H), 2.80 (dd, J=14, 2 Hz, 2H), 2.92-2.95 (m, 4H), 3.19 (d, J=7 Hz, 2H), 3.42-3.44 (m, 2H), 5.75 (s, 2H), 6.86 (s, 2H), 6.93 (s, 2H), 7.09-7.20 (m, 4H), 7.37-7.46 (m, 4H); EI-MS m/z 578 (M^+, 24), 542 (68), 205 (100), 181 (82), 178 (76), 154 (86); HRMS (M^+) Calcd for $C_{42}H_{42}O_2$: 578.3185, Found 578.3186. Anal. Calcd for ($C_{42}H_{42}O_2 + H_2O$): C, 84.53; H, 7.43 %. Found: C, 84.13; H, 7.74 %.

exo,exo-Diol **12c:** Yield 45 mg (12%); mp > 315 °C (decomp.); colorless needles (methanol/chloroform); IR 3428, 2993, 2914, 2850, 1449, 1460, 1433, 928, 902, 865, 741 cm^{-1}; ^1H NMR 1.24 (s, 2H), 1.30 (s, 6H), 1.96-2.02 (m, 4H), 2.22-2.44 (m, 8H), 2.53 (dd, J=17, 4 Hz, 4H), 3.58 (br d, J=16 Hz, 4H), 5.57 (s, 2H), 6.76 (s, 4H), 7.07 (dd, J=3, 3Hz, 4H), 7.33 (dd, J=3, 3 Hz, 4H); EI-MS m/z 578 (M^+, 37), 542 (31), 336 (60), 205 (100), 178 (80); HRMS (M^+) Calcd for $C_{42}H_{42}O_2$: 578.3185, Found 578.3195. Anal. Calcd for ($C_{42}H_{42}O_2 + H_2O$): C, 84.53; H, 7.43 %. Found: C, 84.60; H, 7.67 %.

26-Hydroxy-26-methyl-27-oxobenzo[1,2-*h*;4,5-*h*']bis(naphtho[2,3-*c*]bicyclo[4.4.1]undeca-3,8-diene). (**13** and **14**). According to the typical procedures described above, a mixture (0. 45 g, 85%) of **13** and **14** was obtained in the reaction of **7b** (0. 53 g, 0. 95 mmol) and MeMgI (0.79 g, 0.475 mmol) and the isomers were separated by HPLC (hexane/chloroform=1:9).

endo-Alcohol **13:** Yield 19 mg (64%); mp > 296 °C (decomp.); (methanol/chloroform); IR 3428, 3050, 2918, 1693, 1501, 1459, 1433, 1105, 1027, 926, 981, 745 cm^{-1}; ^1H NMR 1.19-3.93 (br, 26H), 6.50 (s, 2H), 7.13 (br, 12H); EI-MS m/z 525 ($M^+ + 1$, 33), 524 (M^+, 14), 507 (64), 229 (18), 217 (32), 157 (49), 141 (37), 129 (79), 115 (100); HRMS (M^+) Calcd for $C_{41}H_{38}O_2$: 562.2872, Found 562.2863.

exo-Alcohol **14 :** Yield 7 mg (21%); mp > 280 °C (decomp.); colorless needles (methanol/chloroform); IR 3446, 3050, 2994, 2914, 1693, 1502, 1437, 1260, 1105, 1052, 1032, 929, 802, 744 cm^{-1}; ^1H NMR 1.59-1.61 (brs, 1H), 1.73 (s, 3H), 1.98-2.63 (m, 12H), 2.77-2.90 (m, 2H), 3.02 (dd, J=14, 2 Hz, 2H), 3.40 (br d, 14 Hz, 2H), 3.81 (br d, J=13 Hz, 2H), 6.43 (s, 2H), 7.16 (s, 2H), 7.22 (m, 2H), 7.30 (m, 2H), 7.38 (s, 2H), 7.48 (m, 2H), 7.60 (m, 2H); EI-MS m/z 525 ($M^+ + 1$, 33.0), 524 (M^+, 14), 507 (64), 229 (18), 217 (32), 157 (49), 141 (37), 129 (79), 115 (100); HRMS (M^+) Calcd for $C_{41}H_{38}O_2$: 562.2872, Found 562.2853.

Benzo[1,2-*h*;4,5-*h*']bis(11-hydroxy-11-methylbenzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene) (**15a**, **16a**, and **17a**). According to the typical procedures described above, a mixture (400 mg, 87 %) of **15a**, **16a**, and **17a** was obtained in the reaction of **9a** (417 g, 0.934 mmol) and MeMgI (776 mg, 4.67 mmol) and the isomers were separated by HPLC (hexane/chloroform=1/4). Recrystallization from methanol afforded **15a** and **16a** as a complex with methanol, respectively, and **17a** as a hydrate.

endo,endo-Diol **15a:** Yield 119 mg (27%); mp 281-282 °C; colorless prisms (methanol); IR 3550, 3432, 3050, 2998, 2914, 1508, 1492, 1435, 1374, 1298, 1102, 1052, 923, 903, 748; ^1H NMR 1.48 (s, 6H), 1.63 (br s, 2H), 2.20-2.33 (m, 4H), 2.52 (dd, J=14.8, 7.6 Hz, 4H), 2.62 (dd, J=16.2, 5.0 Hz, 4H), 3.07-3.22 (m, 8H),

6.48 (s, 2H), 6.59 (br s, 4H), 6.90 (br s, 4H); ^{13}C NMR 35.87, 38.04, 45.32, 77.21, 126.21, 129.14, 135.11, 136.31, 140.34; EI-MS m/z 479 (M^+ + 1, 24), 304 (24), 287 (56), 155 (100), 129 (80); HRMS (M^+) Calcd for $C_{34}H_{38}O_2$: 478.2872, Found 478.2876. Anal. Calcd for ($C_{34}H_{38}O_2$ + 0.2 CH_3OH): C, 84.68; H, 8.06 %. Found: C, 84.57; H, 8.56 %.

endo,exo-Diol **16a:** Yield 168 mg (37%); mp 255-256 °C; white powder (methanol); IR 3560, 3428, 3050, 2996, 2914, 1491, 1436, 1375, 1102, 1048, 926, 748 cm^{-1}; ^1H NMR (at rt) 1.51-1.63 (br, 8H), 2.20-2.31 (m, 4H), 2.46-2.72 (br, 10H), 3.12-3.26 (br, 6H), 6.51-7.20 (br, 10H); ^1H NMR (at -60 °C) 1.31-1.41 (br s, 3H), 1.65-1.69 (br s, 5H), 2.20-2.39 (br, 4H), 2.39-2.64 (br, 8H), 2.86 (br d, J=12 Hz, 2H), 3.09 (br d, J=13 Hz, 2H), 3.35 (br d, J=12 Hz, 2H), 3.78 (br d, J=13 Hz, 2H), 5.98-6.02 (br s, 4H), 6.54-6.56 (br s, 2H), 6.67-6.71 (br s, 4H); EI-MS m/z 478 (M^+, 18.2), 355 (29.7), 287 (49), 181 (19), 155 (58), 129 (73), 104 (100); HRMS (M^+) Calcd for $C_{34}H_{38}O_2$: 478.2872, Found 478.2878. Anal. Calcd for ($C_{34}H_{38}O_2$ + 0.2 CH_3OH): C, 84.68; H, 8.06 %. Found: C, 84.48; H, 8.53 %.

exo,exo-Diol **17a:** Yield 102 mg (23%); mp 282-283 °C; colorless needles (methanol); IR 3444, 3050, 2996, 2914, 1494, 1436, 1374, 1107, 916, 746 cm^{-1}; ^1H NMR 1.57 (s, 6H), 1.62 (br s, 2H), 2.09-2.21 (m, 4H), 2.39 (dd, J=14.8, 6.0 Hz, 4H), 2.59 (dd, J=15.5, 6.3 Hz, 4H), 2.99 (dd, J=15.5, 4.6 Hz, 4H), 3.41 (dd, J=14.8, 0.1 Hz, 4H), 6.41 (s, 2H), 6.59-6.63 (m, 4H), 6.81-6.84 (m, 4H); ^{13}C NMR 31.48, 35.49, 37.32, 44.82, 77.21, 125.75, 130.06, 133.03, 137.39, 139.69; EI-MS m/z 478 (M^+, 90), 337 (100), 287 (4), 233 (12), 195 (18), 131 (39), 104 (46); HRMS (M^+), Calcd for $C_{34}H_{38}O_2$: 478.2872, Found 478.2867. Anal. Calcd for ($C_{34}H_{38}O_2$ + 1.5 H_2O): C, 80.75; H, 8.17 %. Found: C, 80.86; H, 8.50 %.

Benzo[1,2-*h*;4,5-*h*']bis(11-hydroxy-11-phenylbenzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene) (**15b** and **16b**). According to the typical procedures described above, a mixture (140 mg, 30 %) of **15b** and **16b** was obtained in the reaction of **9a** (420 mg, 0. 95 mmol) and PhMgBr (1.72 g, 9.50 mmol) and the isomers were separated by HPLC (ethyl acetate/chloroform=1:19). Recrystallization from a mixture of methanol/chloroform afforded **15b** and **16b** as a complex with chloroform in a non-stoichiometric ratio, respectively.

endo,endo-Diol **15b:** Yield 15 mg (5 %); mp 286-292 °C; colorless plates (methanol/chloroform); IR 3548, 3058, 2914, 1492, 1440, 1029, 998, 947, 901, 767, 754, 700 cm^{-1}; ^1H NMR 1.47 (br s, 2H), 2.61-2.88 (m, 12H), 3.07-3.30 (br s, 4H), 3.83 (d, J=15 Hz, 4H), 6.23-6.28 (br s, 4H), 6.62 (s, 2H), 6.62-6.64 (m, 4H), 7.05-7.29 (m, 4H+2H), 7.54-7.56 (m, 4H); EI-MS m/z 602 (M^+, 15), 584 (21), 566 (100), 461 (45), 348 (44), 243 (23), 217 (59); HRMS (M^+) Calcd for $C_{44}H_{42}O_2$: 602.3185, Found 602.3190. Anal. Calcd for ($C_{44}H_{42}O_2$ + 1.1 $CHCl_3$) : C, 73.79; H, 5.92 %. Found: C, 73.32; H, 5.55 %.

endo,exo-Diol **16b:** Yield 85 mg (20 %); mp 291-296 °C; colorless plates (methanol/chloroform); IR 3482, 3056, 3018, 2914, 1596, 1494, 1445, 1028, 1000, 948, 911, 769, 738, 699 cm^{-1}; ^1H NMR 1.54 (br s, 1 H), 1.68 (br s, 1 H), 2.45-3.71 (m, 20 H), 6.23-7.68 (m, 20 H); EI-MS m/z 602 (M^+, 33), 584 (39), 568 (26), 566 (94), 461 (43), 348 (65), 243 (32), 229 (33), 217 (100); HRMS (M^+) Calcd for $C_{44}H_{42}O_2$: 602.3185, Found 602.3186. Anal. Calcd for ($C_{44}H_{42}O_2$ + 1.2 $CHCl_3$) : C, 72.77; H, 5.84 %. Found: C, 73.17; H, 5.54 %.

Table 5. Crystallographic Data Collections and Refinements.

Compound	**12a**	**13**	**17a**
Formula	$C_{34}H_{38}O_2$ (+$CHCl_3$)	$C_{42}H_{42}O_2$	$C_{34}H_{38}O_2$
Formula Weight	598.01	578.80	478.64
Temperature (K)	293 (2)	296 (1)	293 (2)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit Cell Dimensions			
a	13.291 (2)	7.034 (1)	24.217 (8)
b	26.148 (9)	21.609 (6)	8.555 (2)
c	8.6050 (10)	20.082 (5)	13.0390 (10)
a	90.00	90.00	90.00
b	96.730 (10)	90.23 (1)	105.57 (2)
g	90.00	90.00	90.00
Volume	2969.9 (12)	3052.4	2602.2 (11)
Z	4	4	4
Density (Calculated)	1.337	1.26	1.222
Crystal Size (mm)	0.25 * 0.15 * 0.10	0.40 * 0.17 * 0.17	0.40 * 0.30 * 0.20
q range	3.38-64.97	3.00-64.98	3.52-64.98
Index ranges			
h	0-15	-8-0	-28-0
k	0-30	0-25	-10-0
l	-10-10	-23-23	-14-15
Radiation	CuKα	CuKα	CuKα
Monochromater	Graphite Crystal, Incident Beam	Graphite Crystal, Incident Beam	Graphite Crystal, Incident Beam
Data Collection Mode	w-2θ scan	w-2θ scan	w-2θ scan
No. Refl. Measd.	5275	5654	4524
No. Unique Refl.	5048	5196	4414
No. Refl.	3188, F > 2σ (F)	3832, F > 2σ (F)	3034, F > 2σ (F)
Lin. Abs. Coeff. (cm^{-1})	3.030	0.543	0.567
Data/Parameter Ratio	5048/367	5196/393	4414/332
R, *Rw*	0.0492, 0.1151	0.0418, 0.1085	0.0445, 0.1163
Weighting Scheme	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+0.6964P]$, $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+0.6964P]$, $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+0.6964P]$, $P=(F_o^2+2F_c^2)/3$
Largest Diff. Peak/Hole (e. A^{-3})	0.296/-0.427	0.171/-0.212	0.232/-0.170
Solution by	Direct Method SIR 92	Direct Method SIR 92	Direct Method SIR 92
Method of Refinement	Full Matrix LSQ, All H atoms were restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.3 times U~eq~ of the riding atoms.	Full Matrix LSQ, All H atoms were restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.3 times U~eq~ of the riding atoms.	Full Matrix LSQ, All H atoms were restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.3 times U~eq~ of the riding atoms.
Diffractometer	Enraf-Nonius FR-590	Enraf-Nonius FR-590	Enraf-Nonius FR-590
Program Used	MolEN, SHELXL93 (Enraf-Nonius)	MolEN, SHELXL93 (Enraf-Nonius)	MolEN, SHELXL93 (Enraf-Nonius)

22-Hydroxy-22-phenyl-23-oxobenzo[1,2-*h*;4,5-*h*']bis(benzo[1,2-*c*]bicyclo[4.4.1]undeca-3,8-diene) (**18** and **19**). According to the typical procedures described above, a mixture (155 mg, 42%) of **18** and **19** was obtained in the reaction of **9a** (314 mg, 0.703 mmol) and PhMgBr (638 mg, 3.52 mmol) and the isomers were separated by HPLC (ethyl acetate/chloroform=1:19). Compound **19** was obtained as a complex with chloroform in the recrystallization from methanol/chloroform.

Alcohol **18**: Yield 62 mg (16%); mp 275-277 °C; colorless powder (methanol/chloroform); IR 3482, 3056, 3018, 2914, 1695, 1596, 1492, 1445, 1028, 1000, 948, 911, 767, 738, 699 cm^{-1}; ^1H NMR 1.60-1.80 (br s, 1 H), 2.41-3.29 (m, 18 H), 3.91-4.15 (d, J=12 Hz, 2H), 6.12-6.19 (m, 4H), 6.62-6.69 (m, 4H), 6.71 (s, 2H), 7.28-7.29 (m, 1H), 7.40-7.41 (m, 2H), 7.73 (d, J= 8 Hz, 2H); EI-MS m/z 524 (M^+, 31), 506 (37), 288 (50), 217 (100), 217 (100); HRMS (M^+) Calcd for $C_{38}H_{36}O_2$: 524.2715, Found 524.2717. Anal. Calcd for $C_{38}H_{36}O_2$: C, 86.99; H, 6.92 %. Found: C, 86.84; H, 7.23 %.

Alcohol **19**: Yield 89 mg (26%); mp 249-251 °C; colorless needles (methanol/chloroform); IR 3438, 3014, 2914, 1697, 1494, 1088, 1041, 700 cm^{-1}; ^1H NMR 1.51-1.60 (br s, 1 H), 2.30-3.30 (m, 18 H), 4.03 (d, J= 14 Hz, 2H), 6.21-6.30 (m, 4H), 6.50 (s, 2H), 6.68-6.77 (m, 4H), 7.28-7.29 (m, 1H), 7.39-7.40 (m, 2H), 7.72 (d, J= 8 Hz, 2 H); EI-MS m/z 525 (M^++1, 33), 524 (M^+, 14), 507 (64), 229 (18), 217 (32); HRMS (M^+) Calcd for $C_{38}H_{36}O_2$: 524.2715, Found 524.2714. Anal. Calcd for ($C_{38}H_{36}O_2$ + $CHCl_3$): C, 72.73; H, 5.79 %. Found: C, 73.17; H, 5.54 %.

Single crystal X-ray diffraction analyses of 7a, 8, and the chloroform-complex of 12a. All crystallographic measurements were carried out at 296 K on a Enraf-Nonius FR-590 diffractometer operating in the ω-2θ scan mode using graphite monochromated CuKα-radiation (λ= 1.54184 Å). Structures of **7a**, **8** and **12a** were solved by direct methods, using SIR 92[9] and refined by full-matrix least-squares using SHELXL.[10] Refinement was essentially the same for the three compounds in that all-non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to calculated positions. The weighting scheme $w = 1/[\sigma^2(F_o^2)+ (0.0585P)^2+0.6964P]$, $P=(F_o^2+2F_c^2)/3$ was used. Crystallographic data collections and method of refinements are given in **Table 5**. The supplementary data has been deposited at the Cambridge Crystallographic Data Center.

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