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Bisacetals of Aromatic Ring-annelated Benzo[*a*,*d*]bis{bicyclo[4.4.1]undeca-3,8-diene-11-one}. [3.3][3.3]Orthocyclophanes with Triple-layered Benzo/benzo/benzo- and Naphtho/benzo/naphtho-system

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Abstract: Tetraesters *anti*-**9a,b** and *syn*-**9a,b**, which have three aromatic rings, were prepared by the reaction of benzocycloheptenediester **7** with 1,2,4,5-tetrakis(bromomethyl)benzene. Subsequent hydrolysis and pyrolysis gave diketones *anti*-**11a,b** and *syn*-**11a,b**, which were acetalized to yield bisacetals *anti*-**5a,b** and *syn*-**5a,b**. X-Ray crystallographic analyses indicate a symmetric (twin-chair)/(twin-chair)-conformation of *anti*-**5a,b**, in which two naphtho or benzo rings sandwich one benzene ring. *Anti*-**5a** and *anti*-**5b**[9b] are rigid structures. The protons of their central aromatic rings show an up-field shift, due to an anisotropic effect of the facing outer aromatic units. In contrast, *syn*-**5a,b** are flexible structures. The UV-spectra of *anti*-**5a,b** show a long wavelength shift, as compared to *syn*-**5a,b**, suggesting a through-space interaction among the aromatic rings.

Introduction

There exists a great interest in phenomena associated with closely stacked π-systems. Apart from the investigation of their altered chemical and physical properties due to π-π-interactions, multi-decked π-systems have also been viewed as a starting point for conducting organic crystals.

At the outset, much research on fixed, stacked π-systems focused on para- and meta-cyclophane chemistry, as is evidenced by a number of monographs on the cyclophane family.[1] Extensive work has been done on multi-layered para- and meta-cyclophanes in the last three decades.[2] In this context, a "molecular ribbon" containing six *syn*-[3.3]metacyclophane units was synthesized just recently. With its seven fourfold bridged benzene rings it is one of the most extended cyclophane systems to date.[3]

In many para- and meta-cyclophanes some of the inherent molecular strain is released by a bending of the aromatic units, usually into a boat conformation. In some multi-layered cyclophanes the aromatic units exist in twisted conformations.[4] It is not always easy to differentiate the effect on the electronic spectra of cyclophanes due to deviations from planarity of the aromatic subunits from those due to π–π transannular interactions.[5] To

this effect, the preparation of compounds with closely stacked, but non-distorted aromatic ring systems are still of interest. Compounds **1**-3[6, 7] and **4**[8,9] are [3.3]orthophanes with layered aromatic rings (**Fig. 1**).

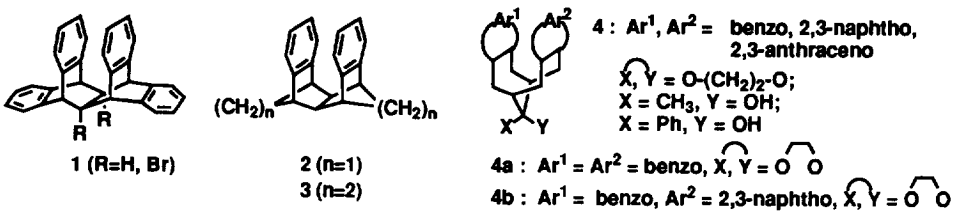


Fig. 1 Layered [3.3]orthocyclophanes

In contrast to [3.3]para- and [3.3]meta-cyclophanes, the aromatic rings of **1-4** are planar and non-distorted. Orthocyclophanes **1-4** show a π-π through-space interaction between the two non-distorted aromatic rings, held rigidly face to face, as evidenced by a long wavelength shift observed in the UV/VIS spectra of **1-4**, as well as an up-field shift of aromatic protons. It seemed of interest to extend our [3.3]orthocyclophane systems **4**[6-11] to triple-decker [3.3][3.3]orthocyclophanes *anti*-**5**[9b]. Here, the aromatic rings at the top and at the bottom of triple-decker structure in *anti*-**5** are stacked in an *anti*-orientation (**Fig. 2**). In the schematic side-view, the [3.3][3.3]orthocyclophane-substructure of *anti*-**5** looks like the alphabetical character *S*.

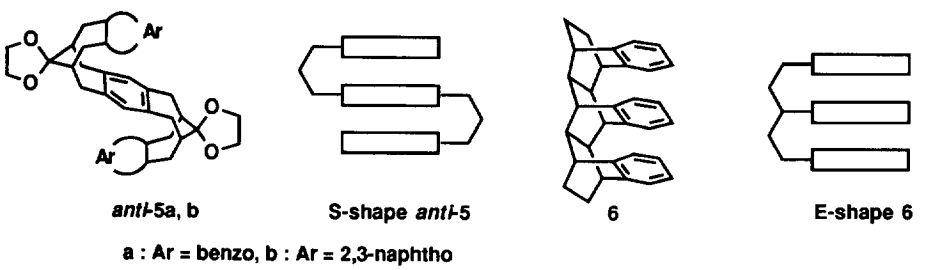


Fig. 2 Structures of 5 and 6 and their schematic side views

Recently, the preparation of all-*syn*-sesterbenzobicyclo[2.2.0]octane **6** was reported, in which the three planar benzo-rings of **6** are stacked in the *syn*-orientation.[10] In contrast to *anti*-**5**, the schematic side-view of **6** looks like the alphabetical character *E* (**Fig. 2**).

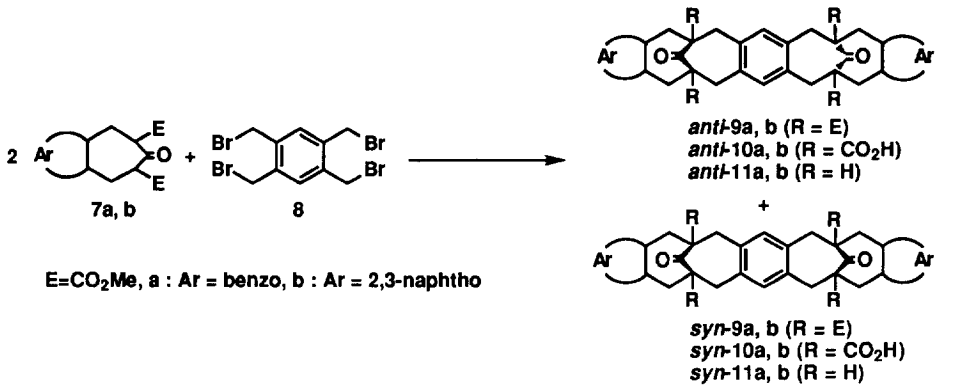
The present article describes the synthesis of triple-layered [3.3][3.3]orthophane *anti*-**5** having benzene and naphthalene rings as ring components and two acetal units in an *anti*-configuration.

Results and Discussion

Preparation of [3.3][3.3]Orthocyclophane Acetals.

Preparation of the precursor diketone *anti*-**11a** with three benzene rings was attempted by the reaction of 2 moles of benzocycloheptenediester **7**[8a] with one mole of 1,2,4,5-tetrakis(bromomethyl)benzene **8** (**Scheme 1**).The reaction was carried out at room temperature under phase transfer conditions using dichloromethane as a solvent, tetrabutylammonium bromide as a catalyst, and 23% aqueous sodium hydroxide as a base. The expected tetraester *anti*-**9a** with two keto-groups in *anti*-configuration was obtained as a 1:1-mixture with the

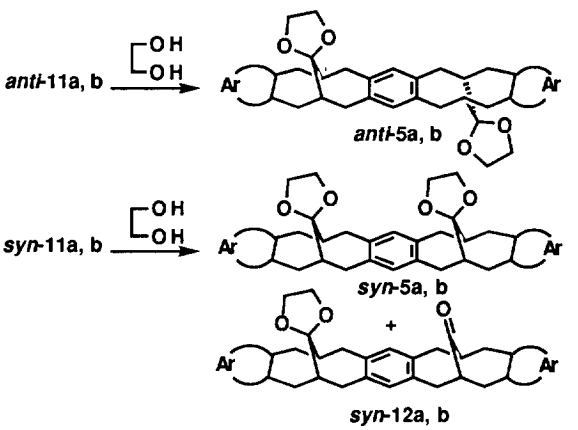
syn-isomer **9a**. Compounds *anti*-**9a** and *syn*-**9a** could be purified by column chromatography. Hydrolysis of *anti*-**9a** and *syn*-**9a** under alkaline conditions gave the corresponding tetracarboxylic acids *anti*-**10a** and *syn*-**10a** in good yields. Thermal decarboxylation of *anti*-**10a** and *syn*-**10a** at 310 °C gave the desired diketones *anti*-**11a** and *syn*-**11a** in 68 % and 60 % yields, respectively. Diketones *anti*-**11b** and *syn*-**11b**, both of which have two naphthalene rings and one benzene ring, were prepared similarly, starting from naphthocycloheptenonediester **7b**.



Scheme 1

Anti-**9**, *syn*-**9**, *anti*-**11** and *syn*-**11** have two sets of flexible bicyclo[4.4.1]undeca-11-one substructures and may exist as an equilibrium mixture of conformers. ^{1}H-NMR spectra of *syn*-**11b**, *anti*-**9** and *syn*-**9** show broad signals at room temperature and sharp multiple peaks at -60 °C in $CDCl_3$, thus indicating a fast conformational change observable in the NMR time scale. *Syn*-**11b**, *anti*-**9** and *syn*-**9** do not take a (twin-chair)-conformation because their aromatic protons do not show to a up-field shift compared to 1,2,4,5-tetramethyl-benzene (**13**), 1,2-dimethylbenzene (**14**) and 2,3-dimethylnaphthalene (**15**). However, their conformations could not be clarified because of their complicated spectra.

Acetalization of *anti*-**11** and *syn*-**11** was carried out in the presence of a catalytic amount of *p*-toluenesulfonic acid in either benzene or a mixed solvent of benzene/ nitrobenzene (v/v=1/1) under reflux (**Scheme 2** and **Table 1**). Upon cooling, bisacetal *anti*-**5a,b** precipitated from the reaction mixture when *anti*-**11a,b** was reacted with a large excess of ethylene glycol (EG) in a mixed solvent of benzene/ nitrobenzene under reflux for 48 h.



Scheme 2

syn-Diketone **11b** gave monoacetal *syn*-**12b** or bisacetal *syn*-**5b** selectively, depending upon the reaction time and the amounts of glycol used; the treatment of *syn*-**11b** with 7.1 equivalent amounts of EG for 48 h gave

syn-**12b**, while *syn*-**5b** was obtained in the treatment using an 72-folds excess of EG for 18 h. A smaller amount of EG were needed in the acetalization of benzo derivative *syn*-**11a**. A mixture of *syn*-monoacetal **12a** and *syn*-bisacetal **5a** was formed in the reaction of *syn*-**11a** with 4.7 equivalent amounts of EG for 1 h. The reaction afforded only *syn*-**5a** after 12 h. Bisacetal *syn*-**5a** is moisture-sensitive in solution and easily gives *syn*-**12a**, which is less readily hydrolyzed than *syn*-**5a**.

Table 1. Acetalization of Diketone *anti*-**11** and *syn*-**11**.

Entry	Glycol/Diketone (mol/mol)	Solvent	Time (hr)	Products (Yield, %)
1	EG/*anti*-**11a** (59/1.0)	benzene/nitrobenzene (1/1)	48	*anti*-**5a** (60)
2	EG/*anti*-**11b** (91/1.0)	benzene/nitrobenzene (1/1)	48	*anti*-**5b** (89)
3	EG/*syn*-**11a** (4.7/1.0)	benzene	1	*syn*-**12a** (58)[a], *syn*-**5a** (40)[a]
4	EG/*syn*-**11a** (3.1/1.0)	benzene	12	*syn*-**5a** (70)
5	EG/*syn*-**11b** (7.1/1.0)	benzene	48	*syn*-**12b** (54)
6	EG/*syn*-**11b** (72/1.0)	benzene	18	*syn*-**5b** (60)

a) Relative yield.

Spectra

The ^{1}H NMR spectra indicates that triple-layered bis(*anti*-acetal) *anti*-**5a** and *anti*-**5b**[9b] both take a (twin-chair)/(twin-chair)-conformation, respectively. The methylene protons on the bridges appear as four sets of double doublets and the methine protons of the bridgehead positions as a multiplet peak. The stacked aromatic protons are shifted up-fields as compared to the aromatic protons of methyl-substituted aromatics **13**, **14** and **15**, due to the facing benzene and naphthalene rings (**Table 2** and **Fig.3**). Especially, the protons of the central benzo ring of *anti*-**5**, which appear as a singlet peak, show a large up-field shift, as compared to the aromatic protons of **13**.

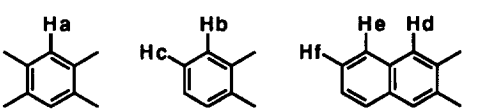


Fig.3 Protons Ha-Hf in 1,2,4,5-tetramethylbenzo, 1,2-dimethylbenzo, 2,3-dimethylnaphtho unit.

Table 2. Chemical shift of the aromatic protons of acetals **4**, *anti*-**5** and reference compounds **13-15** in $CDCl_3$.

Acetals	Chemical shift of aromatic protons, δ ppm
anti-**5a**	5.91 (Ha), 6.49-6.60 (Hb), 6.63-6.87 (Hc)
anti-**5b**	5.86 (Ha), 6.94 (Hd), 7.20-7.23 (He or Hg), 7.43-7.45 (He or Hf)
4a	6.66-6.73 (Hb and Hc)
4b	6.33-6.36, 6.61-6.64 (Hb and Hc), 7.12 (Hd), 7.24-7.27, 7.47-7.50 (He and Hf)
13	6.90 (Ha)
14	7.06-7.12(Hb and Hc)
15	7.36 (He or Hf), 7.58 (Hd), 7.71 (He or Hf)

For bisacetal *syn*-**5**, the (twin-chair)/(twin-chair)-conformation seems highly improbable. Acetal *syn*-**5** gave broad signals in ^{1}H NMR spectra at room temperature. Due to a slowed conformational process at -40 °C, the spectrum of *syn*-bisacetal **5b** (in pyridine-d5) shows three broad singlet peaks (each centered at δ = 6.10, 6.39 and 6.71 ppm) with an intensity ratio of 1:2:1. These up-field shifted aromatic proton signals indicate the presence of a (twin-chair)-conformation. The UV spectrum of *syn*-**5b** supports this, as will be described later. However, signals of the other aromatic protons and of the aliphatic bridges are still broad and complicated, thus, conformations of *syn*-**5** are not clear. *syn*-Monoacetal **12** is conceivable to be present as an equilibrium mixture of the (twin-chair)/(chair-boat)- and the (twin-chair)/(boat-chair) conformations as seen from ^{1}H-NMR spectrum of *syn*-**12b** at -60 °C in $CDCl_3$. The protons of the naphtho moieties appear as four sets of double doublet peaks and four singlet peaks. The protons of one naphtho moiety are influenced by the anisotropic effect of the other naphthalene ring and show an up-field shift. The conformers are not assigned, but their ratio is 1:4. The λ_{max} values of benzo-diketone *syn*-**11a** and naphtho-diketone *anti*-**11b** and *syn*-**11b** are very similar to those of tetramethylbenzene **13** (279 nm) and dimethylnaphthalene **21** (320 nm), respectively. Diketone *anti*-**11a** is barely soluble for UV measurement. Acetals *anti*-**5**, *syn*-**5** and *syn*-**12** show broad absorption bands at longer wavelengths, compared to those of *anti*-**11**, *syn*-**11**, **13** and **15** (**Table 3**).

Table 3. UV spectra in $CHCl_3$.

Bisacetal	λ_{max} (nm)	ε	Monoacetal	λ_{max} (nm)	ε	Ketone	λ_{max}[a)]	ε
anti-**5a**	299	525						
anti-**5b**	340	457				*anti*-**11b**	322	794
syn-**5a**	291	457	*syn*-**12a**	289	513	*syn*-**11a**	280	891
syn-**5b**	338	251[a)]	*syn*-**12b**	338	240[a)]	*syn*-**11b**	322	417

a) Shoulder.

syn-Monoacetal **12a** shows a long-wavelength shift of 9-10 nm, as compared to *syn*-**11a** and **13**. A similar long wavelength shift (10-12 nm) is disclosed on comparison of the spectrum of *syn*-bisacetal **5a** with those of *syn*-**11a** and **13**. In the spectrum of *anti*-bisacetal *anti*-**5a** an even longer bathochromic shift is observed; 19-20 nm as compared to *syn*-**11a** and **13**, and 8-10 nm as compared to *syn*-**5a** and *syn*-**12a**. Thus, in *anti*-**5a**, one stacked dimethylbenzo-unit causes a long wavelength shift of about 10 nm. These results are in sharp contrast to the observation that λ_{max} values[10)] of triple-layered phane **6** and the corresponding double-layered phane **3** are almost identical (272 and 273 nm, respectively). Such a shift with an increase of the number of the layers could not be observed in the spectrum of naphtho *anti*-**5b**. The λ_{max} value (340 nm) of *anti*-**5b** is very close to those of *syn*-bisacetal **5b** and *syn*-monoacetal **12b** (each 338 nm). The values of λ_{max} of *anti*-**5b**, *syn*-**5b** and *syn*-**12b** are shifted by 16-20 nm, as compared to *anti*-**11b**, *syn*-**11b** and **15**. No C-T complex formation with TCNE was observed for *anti*-**5a** and *anti*-**5b**, probably due to poor solubilities of the acetal *anti*-**5** in appropriate solvents.[9b)]

X-Ray crystal structure analysis.

ORTEP views of *anti*-bisacetal *anti*-**5a** and *anti*-**5b** clearly indicate a high symmetry of the molecule with stacking of planar and non-distorted aromatic rings (**Fig. 4** and 5[9b)]). ORTEP view of [3.3]benzonaphthophane **4b** is given in **Fig. 6**.

Table 4. The shortest and longest interplanar distances and the dihedral angles of **4a**, **4b**, ***anti*-5a** and ***anti*-5b**

Acetal	Interplanar Distance (pm)		Angle (°)	Bisacetal	Interplanar Distance (pm)		Angle (°)
	Shortest	Largest			Shortest	Largest	
4a	303	410	25.0	*anti*-**5a**	300	390	21.8
4b	305	402	23.2	*anti*-**5b**	300	380	18.1

The shortest distance between the facing rings in *anti*-**5** is 300 pm. The values are close to those of double-layered phanes **4** (303 pm for **4a**[8a]) and 305 pm for **4b**, respectively), triple-layered orthocyclophane **6** with *syn*-oriented benzenes (309 pm) and the corresponding double-layered phane **3** (304 pm).

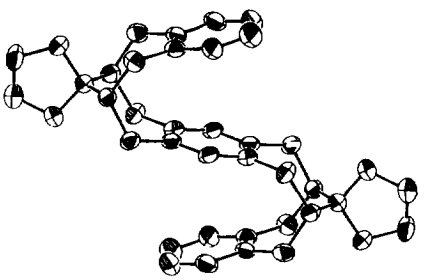


Fig. 4 ORTEP view of *anti*-5a

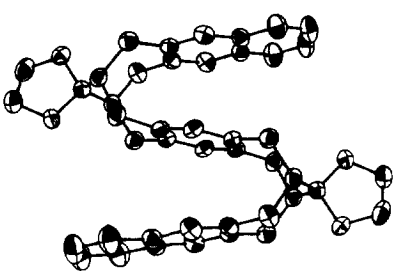


Fig. 5 ORTEP view of *anti*-5b

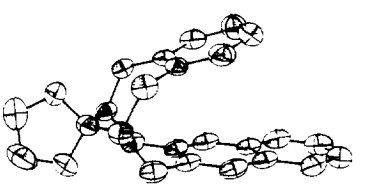


Fig. 6 ORTEP view of 4b

The aromatic rings come closer to each other in triple-layered *anti*-**5** than in the corresponding double layered phane **4** (Table **4**). The dihedral angles between the plane of two benzene rings are 21.8° in triple-layered phane *anti*-**5a** and the corresponding angle for the benzene/naphthalene-stacking is 18.1° in *anti*-**5b**; the angles of dibenzophane **4a**[8a] and benzo-naphthophane **4b** are 25.0° and 23.2°, respectively. Thus, the dihedral angles are smaller by about 5° when the number of layers increases from two to three. These facts are in sharp contrast to triple-layered orthocyclophane **6** with *syn*-oriented benzenes, which is structurally very similar to the corresponding double-layered phane **3**; the dihedral angles between each benzo unit and the inner plane are reported to be 21.7° for **6** and 21.2° for **3** and it is stated that in **6**, repulsion increases with the number of overlapping, fully conjugated orbitals (HOMOs from benzene).

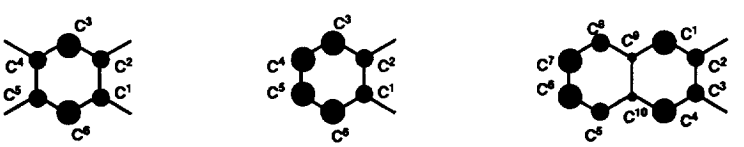


Fig. 7 Net atomic charge of dimethyl- and tetramethylbenzene and dimethylnaphthalene. The size of black circles indicates dimension of net atomic charge.

The structure of *syn*-phane **6** can be seen as a stacking of three 1,2-dimethylbenzo units, while in the structure of *anti*-**5a** and *anti*-**5b**, a 1,2,4,5-tetramethylbenzeno unit is sandwiched by either two 1,2-dimethylbenzo or two 2,3-dimethylnaphthaleno units. As the alkyl bridges of phanes **4** and **5** are hindered and some stress of the molecules should be located in these bridges, it is not correct to directly equate the bridges with methyl groups. However, from PM3 calculations[11] for net atomic charges of **13**, **14** and **15** (**Fig. 7**), there should be a polarization of π-electrons of the aromatic rings in double-layered [3.3]orthocyclophane-subunit of *anti*-**5** and **6**, from the bridge-side to outer side of the rings. When looked at from the side, **6** has a plane of symmetry, while *anti*-**5** has a point of inversion. The charge distribution should be different in *syn*-modus **6** and *anti*-modus **5**.

The dihedral angles of naphthophanes **4b** and *anti*-**5b** are smaller, as compared to those of benzophanes **4a** and *anti*-**5a**. This fact suggests that the interactions in **4b** and *anti*-**5b** between the different aromatic rings are less repulsive in nature than those in **4a** and *anti*-**5a**.

Experimental

General. Melting points are uncorrected. Infrared spectra were obtained in KBr pellets. UV/VIS spectra were measured in $CHCl_3$. ^1H NMR spectra were recorded at 270 MHz. $CDCl_3$ served as a solvent unless otherwise stated. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS 700 instrument. Mass spectral analyses were performed under 70eV electron-impact (EI) conditions. HPLC was carried out on a JASCO 880 HPLC (Develosil Packed Column: *F* 25 mm/250 mm). Column chromatography was done on Wako gel C-300 (200-300 mesh).

Preparation of anti-9 and syn-9 Typical procedure. To a vigorously stirred mixture of Bu_4NBr (2.0 g, 6.20 mmol), 23% aqueous NaOH (80 ml), and CH_2Cl_2 (80 ml) was added dropwise at room temperature a CH_2Cl_2 solution (110 ml) of **7b** (8.00 g, 24.5 mmol) and **8** (5.51 g, 12.3 mmol). After the mixture was stirred at room temperature for 3 h, the organic layer was separated, dried, and evaporated in vacuo, leaving a residue which was chromatographed on silica gel (chloroform/ethyl acetate=20:1) to give *anti*-**9b** and *syn*-**9b**. Further recrystallisation in methanol/chloroform gave pure *anti*-**9b** (2.97 g, 31%) and *syn*-**9b** (3.16 g, 33%).

Tetramethyl *anti*-benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-6,10,17,21-tetracarboxylate (*anti*-9a): Yield 35%; mp 328-330 °C; colorless prisms (methanol/chloroform); IR (KBr) 2950, 1740, 1698, 1434, 1235, 1093, 1073, 970, 837, 760; ^1H NMR ($CDCl_3$) 2.71-3.63 (16H, br m), 3.70-3.79 (12H, m), 7.12-7.38 (10H, m); EI-MS *m/z* 678 (M^+, 69), 660 (100), 569 (61), 541 (69), 483 (48), 404 (24); Anal. Calcd for $C_{40}H_{38}O_{10}$: C, 70.77; H, 5.65 %. Found: C, 70.66; H, 5.81 %.

Tetramethyl *syn*-benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-6,10,17,21-tetracarboxylate (*syn*-9a): Yield 38%; mp >330 °C (decomp.); colorless prisms (methanol/chloroform); IR (KBr) 2950, 1741, 1699, 1494, 1437, 1234, 1093, 1073, 970, 837, 761; ^1H NMR ($CDCl_3$) d 2.67-3.65 (16H, br m), 3.70-3.80 (12H, m), 7.10-7.34 (10H, m); EI-MS m/z 678 (M^+, 78), 660 (100), 646 (24), 569 (37), 541 (74), 483 (48), 434 (10), 316 (17), 241 (26), 183 (18), 104 (61); Anal. Calcd for $C_{40}H_{38}O_{10}$: C, 70.77; H, 5.65 %. Found: C, 70.58; H 5.68 %.

Tetramethyl *anti*-benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-7,11,20,24-tetracarboxylate (*anti*-9b): mp >300 °C (decomp.); white powder (chloroform); IR (KBr) 3075, 3025, 2960, 2850, 1739, 1699, 1501, 1436, 1323, 1278, 1238, 1210, 1179, 1111, 1073, 1037, 988, 890, 758; ^{1}H NMR (at room temperature in $CDCl_3$) 2.65-2.82 (2H, br d, J=15.5Hz), 2.82-3.00 (4H, br s), 3.00-3.14 (2H, br d, J=15.5Hz), 3.20-3.35 (2H, br d, J=15.5Hz), 3.47-3.64 (2H, br d, J=15.5Hz), 3.64-3.94 (14H, br m), 7.13-7.23 (2H, br s), 7.30-7.40 (2H, br m), 7.42-7.52 (2H, br m), 7.58-7.86 (4H, br m); HRMS (M^+) Calcd for $C_{48}H_{42}O_{10}$: 778.2776, Found 778.2778.

Tetramethyl *syn*-benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-7,11,20,24-tetracarboxylate (*syn*-9b): mp 237-240 °C; white powder (methanol); IR 3075, 3025, 2960, 2850, 1739, 1699, 1501, 1430, 1323, 1272, 1260, 1230, 1207, 1179, 1111, 1090, 1070, 1037, 969, 888, 756; ^{1}H NMR ($CDCl_3$) 2.72-3.58 (16H, br m), 3.58-3.77 (12H, br m), 7.05-7.16 (2H, br m), 7.38-7.58 (4H, br m), 7.69-7.92 (8H, br m); EI- MS *m/z* 778 (M^+, 2), 554 (4), 410 (6), 386 (5), 256 (10), 83 (100), 69 (24); Anal. Calcd for $C_{48}H_{42}O_{10}$: C, 74.02; H, 5.44 %. Found: C, 73.70; H, 5.57 %.

Preparation of anti-10 and syn-10. Typical Procedure. After a mixture *syn*-**9b** (2.58 g, 3.31 mmol), KOH (3.12 g), ethanol (120 ml) had been refluxed for 4 h, it was poured into water, acidified with concentrated HCl to pH 1, and allowed to stand overnight. The precipitate was filtered and dried, giving tetracarboxylic acid *syn*-**10b** (2.20 g, Y. 92 %), which was subjected to pyrolysis without purification.

***anti*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-6,10,17,21-tetracarboxylic acid (*anti*-10a)**: Yield 94%; mp 289-291 °C (decomp.); white powder; IR (KBr) 3452, 2954, 1738, 1695, 1239; EI-MS *m/z* 534 (M^+, 68), 490 (92), 446 (21), 367 (100), 288 (14), 201 (16), 183 (27), 129 (42).

***syn*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-6,10,17,21-tetracarboxylic acid (*syn*-10a)**: Yield 95%; mp 288-291 °C (decomp.); white powder; IR (KBr) 3456, 2930, 1741, 1702, 1157; EI-MS *m/z* 446 (M^+-4CO_2, 28), 367 (9), 157 (9), 129 (9), 44 (100).

***anti*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-7,11,20,24-tetracarboxylic acid (*anti*-10b)**: Yield 91%; mp > 308 °C (decomp.); white powder; IR (KBr) 3450, 3060, 2949, 2600 (br), 1721, 1699, 1501, 1430, 1327, 1238, 1201, 1121, 892, 750, 690; EI-MS *m/z* 634 (M^+-2CO_2, 8), 590 (90), 546 (100), 412 (22), 391 (20), 233 (19), 155 (52).

***syn*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one)-7,11,20,24-tetracarboxylic acid (*syn*-10b)**: mp > 308 °C (decomp.); white powder; IR (KBr) 3450, 3051, 2951, 2600 (br.), 1721, 1699, 1501, 1430, 1328, 1238, 1201, 1122, 892, 750, 690; EI-MS *m/z* 634 (M^+-2CO_2, 9), 590 (72), 546 (100), 391 (25), 233 (19), 155 (51).

Preparation of anti-5, 11, 12 and syn-5, 11, 12. Typical procedure. syn-**10b** (1.40 g, 1.94 mmol) obtained above was heated at 310 °C until gas evolution ceased. It was triturated with CH_2Cl_2 and insoluble materials were filtered off.The filtrate was chromatographed with chloroform and cyclohexane as eluent, and was recrystallized from benzene and tetrachloromethane to give *syn*-**11b** (0.636 g, Y. 60 %).

***anti*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (*anti*-11a)**: Yield 65%; mp >361 °C (decomp.); white powder (N,N-dimethylformamide); IR (KBr) 2998, 2940, 1698, 1492, 1453, 1353, 1310, 1187, 890, 767, 742; HRMS (M^+) Calcd for $C_{32}H_{30}O_2$: 446.2229, Found 446.2246

***syn*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (*syn*-11a)**: Yield 79%; mp 133-135 °C; colorless needles (toluene); IR (KBr) 3008, 2984, 2930, 1696, 1487, 1443, 1353, 1321, 1187, 1124, 1087, 888, 769, 743; ^1H NMR ($CDCl_3$) 2.42-2.83 (16H, br m), 3.08-3.18 (4H, br s), 7.00-7.27 (10H, m); EI-MS m/z 446 (M^+, 100), 341 (7), 289 (4), 157 (80); Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.05; H 6.78 %. Found: C, 86.00; H, 6.95 %.

***anti*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (*anti*-11b)**: Yield 63%; mp >340 °C (decomp.); white powder (chloroform); IR (KBr) 3076, 3025, 2946, 2851, 1699, 1498, 1441, 1431, 1322, 1118, 890, 749; ^1H NMR (at room temperature in $CDCl_3$) 2.37-3.01 (16H, br m), 3.01-3.19 (4H, br m), 6.81-7.08 (2H, br m), 7.15-7.37 (4H, br m), 7.37-7.71 (8H, br m); EI-MS *m/z* 547 (M^++1, 84), 546 (M^+, 92), 391 (35), 178 (40), 155 (100); Anal. Calcd for $C_{40}H_{34}O_2$: C, 87.88; H, 6.27 %. Found: C 87.71; H 6.35 %.

***syn*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) (*syn*-11b)**: mp 204-206 °C; white powder (methanol); IR (KBr) 3098, 3001, 2923, 2846, 1698, 1497, 1422, 1322, 1116, 879, 742; ^1H NMR (at room temperature in $CDCl_3$) 2.35-3.11 (16H, br m), 3.11-3.28 (4H, br m), 6.91-7.13 (2H, br m), 7.27-7.44 (4H, br m), 7.44-7.80 (8H, br m); EI-MS *m/z* 547 (M^++1, 21), 546 (M^+, 13), 391 (10), 207 (33), 178 (41), 165 (84), 155 (100); Anal. Calcd for $C_{40}H_{34}O_2$: C 87.88; H 6.27 %. Found: C 87.55; H 6.21 %.

Acetalation. Typical procedure. A mixture of *syn*-**11b** (100 mg, 0.183 mmol), ethylene glycol (0.818 g, 13.5 mmol), and a catalytic amount of *p*-TosOH in benzene (20 ml) was refluxed with a Dean-Stark water separator for 18 h. After cooling, the precipitate was filtered to gave *syn*-**5b** (68.7 mg, 60 %). Yields of mono- and bis-acetals are given in **Table 1**.

***anti*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) bis(ethyleneacetal) (*anti*-5a)**: mp 396-397 °C; colorless needles; IR (KBr) 3050, 3010, 3000, 2920, 2840, 1494, 1436, 1291, 1231, 1135, 1104, 1059, 1034, 994, 947, 909, 843, 734; ^1H NMR ($CDCl_3$) 2.12-2.22 (4H, br s), 2.37 (4H, dd, J=15, 6 Hz), 3.12 (4H, br d, J=15 Hz), 3.22 (4H, dd, J=15, 3 Hz), 3.96-4.06 (8H, m), 5.91 (2H, s), 6.49-6.60 (4H, m), 6.63-6.87 (4H, m); EI-MS *m/z* 534 (M^+, 100), 429 (25), 201 (57), 157 (23), 129 (44), 115 (46); Anal. Calcd for $C_{44}H_{42}O_4$: C 83.25; H 6.67 %. Found: C 83.42; H 6.61 %.

***syn*-Benzo[*1,2-h;4,5-h'*]bis(benzo[*1,2-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) bis(ethyleneacetal) bisacetal (*syn*-5a)**: mp 133-135 °C; colorless needles (benzene); IR (KBr) 2898, 1479, 1436, 1103, 1069, 1042, 983, 951, 910, 872, 747; ^{1}H NMR ($CDCl_3$) 2.19 (4H, br s), 2.28-3.26 (16H, m), 3.82 (8H, br s), 6.38 (2H, s), 6.42-6.56 (4H, br s), 6.75-6.80 (4H, br s,); EI-MS *m/z* 535 (M^++1, 100), 534 (M^+, 79), 490 (3), 430 (44), 386 (5), 201 (35), 129 (28); Anal. Calcd for $C_{36}H_{38}O_4$: C, 80.85; H, 7.18 %. Found: C, 81.13;, H, 7.00 %.

***anti*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) bis(ethyleneacetal) (*anti*-5b)**: mp (decomp.) > 340 °C; colorless prisms; IR (KBr) 3051, 3000, 2930, 2870, 1500, 1428, 1320, 1132, 1101, 1064, 1035, 995, 980, 946, 898, 864, 742; ^{1}H NMR ($CDCl_3$) 2.06-2.17 (4H, br s), 2.19-2.22 (4H, m), 2.59-2.65 (4H, m), 3.16-3.22 (4H, m), 3.39 (4H, d, J=15.2 Hz), 3.89-3.96 (8H, m), 5.86 (2H, s), 6.94 (4H, s), 7.20-7.23 (4H, m), 7.43-7.45 (4H, m); ^{1}H NMR (pyridine-d_5) 2.25-2.28 (4H, br s), 2.42 (4H, dd, J=14.2, 5.3 Hz), 2.74 (4H, dd, J=15.2, 6.6 Hz), 2.96 (4H, d, J=14.2 Hz), 3.39 (4H, d, J=15.2 Hz), 3.77-3.92 (8H, m), 6.13 (2H, s), 7.18 (4H, s), 7.32-7.39 (4H, m), 7.65-7.72 (4H, m); EI-MS *m/z* 634 (M^+, 80), 572 (13), 479 (30), 251 (47), 207 (50), 179 (85), 167 (100), 155 (96); Anal. Calcd for $C_{44}H_{42}O_4$: C 83.25; H 6.67 %. Found: C 83.42; H 6.61 %.

***syn*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) bis(ethyleneacetal)bisacetal (*syn*-5b)**: mp > 333 °C (decomp.); white powder; IR (KBr) 3051, 3000, 2940, 2840, 1499, 1426, 1320, 1134, 1100, 1063, 1042, 1033, 982, 944, 898, 870, 840; ^{1}H NMR ($CDCl_3$) 2.22-3.88 (br, 28H), 6.40-7.15 (br, 6H), 7.32-7.51 (br, 4H) and 7.60-7.82 (br, 4H) at room temperature, (pyridine-d_5) 1.60-4.12 (br, 28H), 6.01-6.21 (br s, 0.5H), 6.39 (s, 1H), 6.63-6.79 (br s, 0.5H), 7.07 (s, 1H), 7.24-7.93 (m, 9H), 8.05-8.18 (br s, 1H) and 8.18-8.33 (br s, 1H) at -40 °C.; EI-MS m/z 634 (M^+, 87), 479 (29), 251 (58), 207 (36), 179 (87), 167 (100), 155 (85); Anal. Calcd for $C_{44}H_{42}O_4$: C, 83.25, H, 6.67 %. Found: C 83.38, H 6.52 % .

***syn*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) ethyleneacetal (*syn*-12a)**: mp 317-318 °C; colorless prisms (benzene); IR (KBr) 2894, 1701, 1494, 1436, 1102, 1032, 994, 754; ^{1}H NMR ($CDCl_3$) 2.25-2.32 (4H, br s), 2.44-3.16 (12H, m), 3.40-3.44 (4H, m), 4.09-!! (4H, br s), 6.15-6.19 (2H, m), 6.58 (2H, s), 6.65-6.68 (2H, m), 7.14 (4H, s); EI-MS m/z 490 (M^+, 55), 385 (96), 201 (100); Anal. Calcd for $C_{34}H_{34}O_3$: C, 83.22; H, 7.00 %. Found: C, 83.26, H, 7.14 % .

***syn*-Benzo[*1,2-h;4,5-h'*]bis(naphtho[*2,3-c*]bicyclo[4.4.1]undeca-3,8-diene-11-one) ethyleneacetal (*syn*-12b)**: mp 333-335 °C; colorless needles (benzene); IR (KBr) 3050, 3002, 2910, 2850, 1698, 1501, 1430, 1322, 1141, 1122, 1102, 1082, 1036, 998, 946, 899, 881, 742; ^{1}H NMR (at room temperature in $CDCl_3$) 2.22-2.84 (8H, m), 2.84-3.20 (4H, br s), 3.29-3.58 (4H, m), 4.09 (4H, br s), 5.80-6.03 (2H, br m), 6.17-6.42 (2H, br m), 6.85-7.07 (2H, br m), 7.09-7.18 (2H, br m), 7.60-7.68 (4H, br m), 7.85-7.99 (2H, br m); ^{1}H NMR (at -70 °C in $CDCl_3$) , 1.78-2.78 (20 H, m), 4.19-4.22 (4H, m), 5.57 (2H*4/5, dd, J=3, 6 Hz,), 5.69 (2H*4/5, dd, J=3, 6 Hz), 5.82 (2H*1/5, dd, J=3, 6 Hz), 5.98 (2H*1/5, dd, J=3, 6 Hz), 6.14 (1H*4/5, s), 6.24 (1H*4/5, s), 6.53 (1H*1/5, s), 6.68 (1H*1/5, s), 7.02-7.88 (6H+14H, m, stacked:non-stacked=6:7), 7.98 (2H*4/5, dd, J=6, 3 Hz), 8.06 (2H*4/5, dd, J=6, 3 Hz); EI-MS *m/z* 591

(M^++1, 100), 590 (66), 436 (11), 251 (51), 207 (14), 178 (38); Anal. Calcd for $C_{42}H_{38}O_3$: C, 85.39; H, 6.48 %. Found: C 85.48; H 6.27 %.

Single crystal X-ray diffraction analysis of 4b, *anti*-5a and *anti*-5b. 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 *anti*-**5b** and **4b** were solved by direct methods using SIR 88 and refined by full-matrix least-squares using MolEN. Refinement was essentially the same for the two 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 = $4Fo^2/(\sigma^2Fo^2+0.0016Fo^4)$ was used. While Structure of *anti*-**5a** was solved by direct methods using SIR 92 and refined by full-matrix least-squares using SHELXL. Refinement was essentially the same for the one compound in that all-non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to calculated positions. The weighting scheme w = $1/[\sigma^2(Fo^2)+ (0.0585P)^2+0.6964P]$, $P=(Fo^2+2Fc^2)/3$ was used. Crystallographic data collections and method of refinements are given in **Table 5**. The supplementary materials have been deposited at the Cambridge Crystallographic Data Center.

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Table 5. Crystallographic Data Collections and Refinements.

Compound	*anti*-**5a**	*anti*-**5b**	**4b**
Formula	$C_{36}H_{38}O_4$	$C_{44}H_{42}O_4$	$C_{25}H_{24}O_2$
Formula Weight	534.70	634.82	356.47
Temperature	23 °C	21 °C	21 °C
Crystal System	orthorhombic	monoclinic	monoclinic
Space Group	Pbca	$P2_1/a$	$P2_1/a$
Unit Cell Dimensions			
a	8.0860 (10)	17.924 (1)	18.426 (0)
b	21.467 (2)	8.004 (1)	8.013 (0)
c	15.782 (2)	11.947 (1)	12.829 (0)
α	90.00	90.00	90.00
β	90.00	108.85 (1)	102.34 (0)
γ	90.00	90.00	90.00
Volume	2739.5	1622.01	1850.5
Z	4	2	4
Density (Calculated)	1.296	1.30	1.28
Crystal Size (mm)	0.30 * 0.10 * 0.10	0.25 * 0.25 * 0.10	0.60 * 0.30 * 0.02
θ range	4.12-64.99	3.91-64.97	3.53-64.85
Index ranges			
h	0-9	-14-0	-15-14
k	-25-0	0-9	-9-0
l	0-18	-19-21	0-21
Radiation	CuKα	CuKα	CuKα
Monochromater	Graphite Crystal, Incident Beam	Graphite Crystal, Incident Beam	Graphite Crystal, Incident Beam
Data Collection Mode	ω-2θ scan	ω-2θ scan	ω-2θ scan
No, Refl. Measd.	2329	3130	3517
No. Unique Refl.	2329	2756	3151
No. Refl.	1632, $F > 2\sigma(F)$	1898, $F > 3\sigma(F)$	1356, $F > 3\sigma(F)$
Lin. Abs. Coeff. (cm^{-1})	6.17	6.0	5.8
Data/Parameter Ratio	2329/182	1898/280	1356/317
R, *Rw*	0.043, 0.109	0.042, 0.052	0.049, 0.054
Weighting Scheme	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+0.6964P]$, $P=(F_o^2+2F_c^2)/3$	$w=4Fo^2/(\sigma^2(Fo^2)+0.0016Fo^4$	$w=4Fo^2/(\sigma^2(Fo^2)+0.0016Fo^4$
Largest Diff. Peak/Hole (e. A^{-3})	0.23/-0.17	0.13/-0.22	0.21/-0.16
Solution by	Direct Method SIR 92	Direct Method SIR 88	Direct Method SIR 88
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, Hydrogen positions of riding model with fixed isotropic, B=5	Full Matrix LSQ, Hydrogen positions of riding model with fixed isotropic, B=5
Diffractometer	Enraf-Nonius FR-590	Enraf-Nonius FR-590	Enraf-Nonius FR-590
Program Used	MolEN	MolEN	MolEN

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