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4,5,12,13-Tetrabromo[2.2]paracyclophane — A New Bis(aryne) Equivalent

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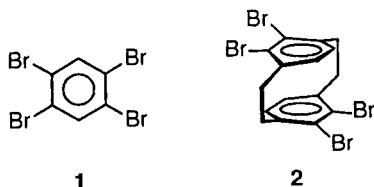
Key Words: [2.2]Paracyclophanes / 1,2-Dibromoarenes / *anti*-[2.2]Paracyclophanes / Aryne generation / Diels-Alder reactions

The reaction of **2** with *n*BuLi at -78°C generates aryne intermediates within the aromatic rings of [2.2]paracyclophane which are trapped in Diels-Alder reactions with dienes like furan, 1,9-diphenylisobenzofuran, or cyclopentadiene. Reductive deoxygenation with low-valent titanium reagents or TMSI converts the adducts of furan and isobenzofuran into

anti-[2.2]paracyclophanes **4** and **5**, respectively. The reaction of two aryne intermediates with [2.2](2,5)furanophane (**7**) yields **8** with three [2.2]paracyclophane units arranged in a stair-like fashion; yet, in this compound the highly shielded oxygen atoms cannot be removed anymore by reduction.

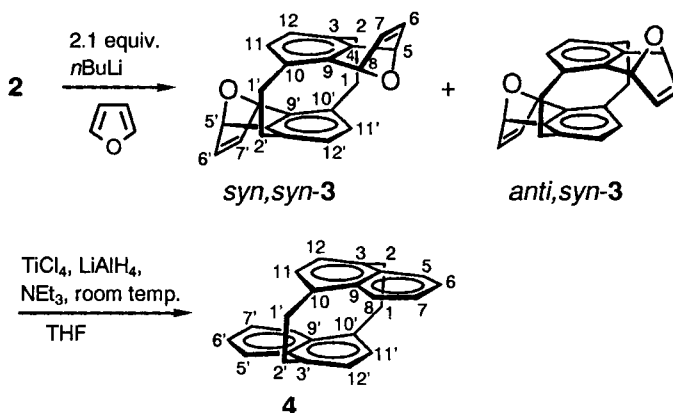
One of the most useful synthetic methods of generating aryne intermediates is the treatment of 1,2-dibromoarenes with *n*BuLi at low temperature^[1]. By trapping the strained intermediate with suitable dienes, a variety of benzo-anelated bi-, tri-, or oligocyclic skeletons are available in moderate to excellent yields.

We have recently reported on the facile synthesis of 4,5,12,13-tetrabromo[2.2]paracyclophane (**2**)^[2]. As shown by X-ray structure analysis, the two dibromobenzene units in **2** are rigidly held in a parallel orientation like the benzene rings in the parent skeleton of [2.2]paracyclophane^[3], but slightly displaced with respect to each other, as the torsion angle of 14° in the ethano bridges indicates^[2]. Like 1,2,4,5-tetrabromobenzene (**1**), which can be used as a bis(dehydrobenzene) precursor^[4], **2** ought to be considered a bis(aryne) precursor^[5], in which the two 1,2-dibromobenzene units are held apart by the ethano bridges, but strongly interact electronically through the σ bonds^[6]. Tetrabromide **2** can therefore be considered a 1,2,4,5-tetrabromobenzene extended into the third dimension.



Indeed, by treatment of a solution of **2** in THF with 2.1 equiv. of *n*BuLi in the presence of furan at -30°C , the two isomeric *syn,syn* and *anti,syn* cycloadducts **3** are obtained in 12 and 15% yield, respectively^[*]. Formation of the *anti,anti* isomer has not been observed. The geometry of the *syn,syn*

product has been proved by X-ray crystal structure analysis (Figure 1)^[7]. Bond distances and angles in both the [2.2]paracyclophane and 7-oxanorbornadiene moieties of *syn,syn*-**3** are quite normal, and so is the out-of-plane bending of the *para*-bridged benzene rings (see Figure 1). The bonds C(4)–C(5) and C(9)–C(8) (and the corresponding ones on the other side of the molecule) are bent by 2.7° inward towards the second benzene ring, corresponding to the known altered hybridization of the benzene carbon atoms towards sp^3 in out-of-plane-bent aromatic rings like those in [2.2]paracyclophane^[8]. The two benzene decks in *syn,syn*-**3** are slightly shifted apart causing a twist in the two-carbon bridges between them [dihedral angle C(3)–C(2)–C(1)–C(10a) 9.2°].



Upon reductive deoxygenation with low-valent titanium reagents^[9], both isomers *syn,syn*- and *anti,syn*-**3** yield the known *anti*-[2.2]naphthalenophane **4**^[10] in 69% yield. The same product is obtained by catalytic hydrogenation of **3** and acidic workup.

The aryne intermediate from **2** is trapped more efficiently by 2,5-diphenylisobenzofuran to lead to a mixture of *syn,syn* and *anti,syn* cycloadducts in 33 and 25% yield, respectively. The bridging oxygen atoms in these adducts are inert to-

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[*] The stereochemical descriptors *syn* and *anti* refer to the orientation of the oxygen bridge in the oxabicyclo[2.2.1]heptadiene subunit with respect to the [2.2]paracyclophane skeleton.

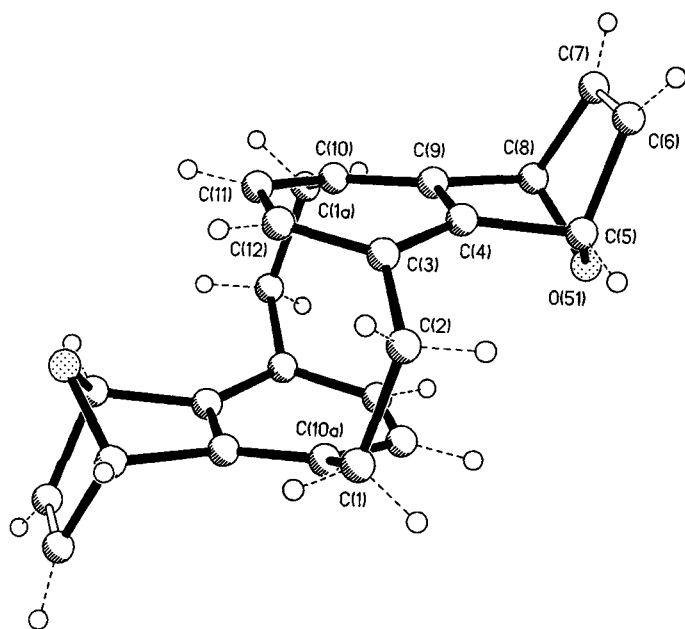
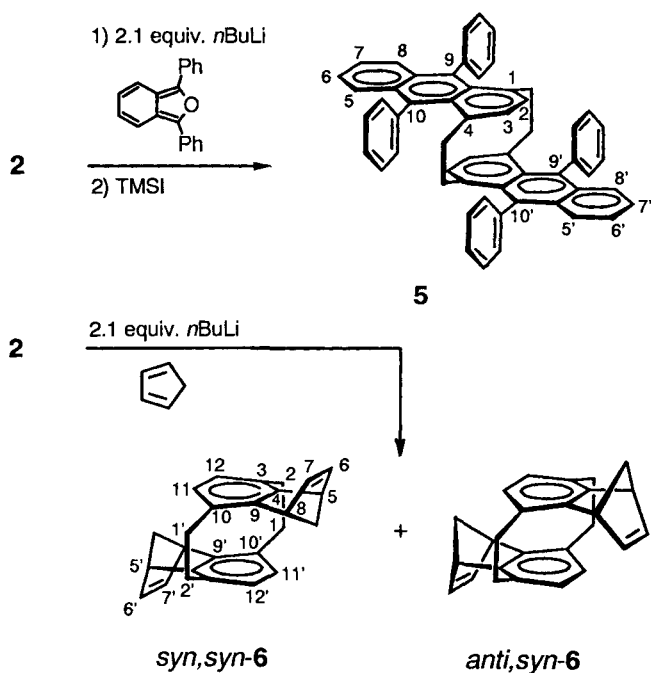


Figure 1. Molecular structure of 5,5',8,8'-tetrahydro-syn,syn-5,8:5',8'-diepoxy-anti-[2.2](1,4)naphthalenophane (*syn,syn*-3); selected dihedral angle and interplanar angles [°]: C(3)–C(2)–C(1)–C(10a) 9.2; C(12)–C(3)–C(4)/C(4)–C(9)–C(11)–C(12) 11.8, C(9)–C(10)–C(11)/C(4)–C(9)–C(11)–C(12) 12.1, C(4)–C(5)–C(8)–C(9)/C(5)–C(6)–C(7)–C(8) 111.0, C(4)–C(9)–C(11)–C(12)/C(4)–C(5)–C(8)–C(9) 2.7

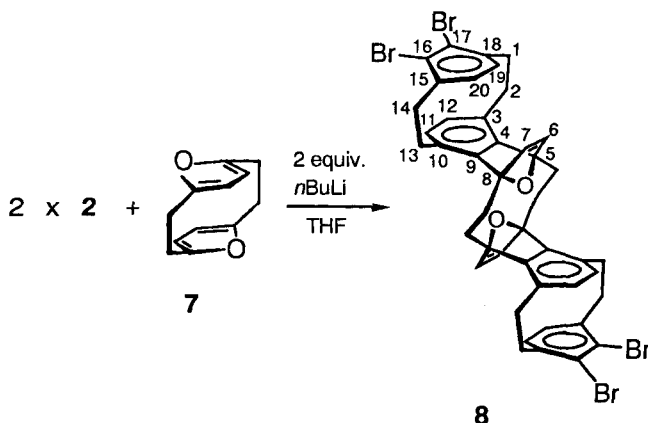
wards reductive removal with low-valent titanium reagents. A successful, stepwise deoxygenation to 9,9',10,10'-tetraphenyl-*anti*-[2.2](1,4)anthracenophane **5**, however, is achieved by treatment with in situ generated trimethylsilyl iodide^[11].

Even cyclopentadiene is a suitable diene to trap the bis-(aryne) intermediate from **2**. When generated in the presence of **2**, a mixture of nearly equal amounts of the *syn,syn* and



anti,syn cycloadducts **6** is obtained in 45% yield and characterized by its ¹H NMR spectrum.

By treatment of **2** with 1.0 equiv. of *n*BuLi, only one of the two 1,2-dibromobenzene moieties reacts, whereas the second one remains unchanged. Thus, when 2.0 equiv. of **2** are treated with 2.0 equiv. of *n*BuLi in the presence of [2.2]furanophane (**7**)^[12] as the trapping agent, only a single product is obtained. Its constitution has been derived from spectroscopic data to be **8**, in which three [2.2]paracyclophane units are connected in a stair-like fashion. Unfortunately, all attempts to remove the shielded oxygen atoms from **8** in order to aromatize the two central rings, have failed.



As demonstrated with the preparation of **4** and **5**, this new procedure offers a short and flexible access to *anti*-[2.2]arenophanes in only three steps from commercially available [2.2]paracyclophane.

Solutions of the anthracenophane **5** show intense fluorescence. Upon comparison of the UV/Vis and fluorescence spectra of **5** with those of 9,10-diphenylanthracene (DPA)^[13] a loss of the fine structure is noticeable (see Figure 2). Corresponding maxima of the long-wave absorption band of **5** reveal a bathochromic shift of 17–21 nm with respect to

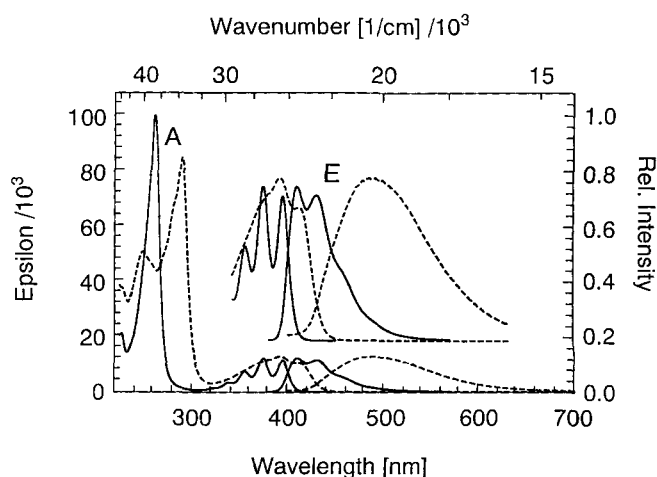


Figure 2. Electronic absorption (A) and emission (E) spectra of 9,10-diphenylanthracene (—, excitation at $\lambda = 356$ nm) and 9,9',10,10'-tetraphenyl-*anti*-[2.2](1,4)anthracenophane (**5**) (---, excitation at $\lambda = 392$ nm)

DPA which is due mainly to the 1,4-dialkyl substitution of the phanaromatic units, whereas the emission band of **5** shows a shift of 65 nm when compared with the center of the two maxima of DPA. This increase, even when calculated in wave numbers (1100 to 3200 cm^{-1} approx.), and the broadening of the band suggest that excimer fluorescence contributes to the emission spectrum of **5**.

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Experimental

IR: Perkin-Elmer 125, 297, and 399. — UV: Varian Cary 219. — Fluorescence: Perkin-Elmer MPF-44A. — ^1H , ^{13}C NMR: Bruker WM 250 and AW 400; the multiplicity of the ^{13}C -NMR signals was determined with the DEPT technique by using a last pulse angle of 135° . — EI/MS (70 eV): Varian MAT CH7, VG-70-250S (VG Analytical). — PE: Petroleum ether (boiling range 60 – 70°C).

General Procedure for the Generation of the Bis(aryne) from 4,5,12,13-Tetrabromo[2.2]paracyclophane (2**)**^[2] (GP 1): To a mixture of 1.0 mmol of **2** and the stated amount of diene in 80 ml of THF was added dropwise at -40°C 2.2 mmol of $n\text{BuLi}$, further diluted with 15 ml of hexane, over a period of 1 h . The mixture was allowed to warm up to room temp., then 2 ml of methanol and 50 ml of diethyl ether were added, and the mixture was washed with water ($3 \times 50\text{ ml}$). The organic layer was dried with K_2CO_3 , filtered, concentrated in vacuo, and the residue was chromatographed on silica gel.

5,5',8,8'-Tetrahydro-syn,syn(anti)-5,8:5',8'-diepoxy-anti-[2.2]-(1,4)naphthalenophane (3**)**: 524 mg (1.00 mmol) of **2** and 3.00 mmol of furan were allowed to react according to GP 1. The crude reaction product (162 mg ; 47%) was chromatographed on 50 g of silica gel [$\text{CH}_2\text{Cl}_2/\text{PE}$ (1:1)] to yield fraction I ($R_f = 0.35$, CH_2Cl_2): 41 mg (12%) of *syn,syn-3*. — ^1H NMR (250 MHz, CDCl_3): $\delta = 3.05$ (m, 8H), 5.58 [s, 4H, $5(5',8')\text{-H}$], 6.08 [s, 4H, $11(11',12,12')\text{-H}$], 6.90 [s, 4H, $6(6',7,7')\text{-H}$]. — ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 31.26$ (–), 80.81 (+), 130.95 (+), 131.65 (C_{quat}), 143.28 (+), 147.82 (C_{quat}). — II ($R_f = 0.2$, CH_2Cl_2): 51 mg (15%) of *anti,syn-3*. — ^1H NMR (250 MHz, CDCl_3): $\delta = 2.60$ – 3.20 (m, 8H), 5.41 (s, 2H), 5.52 and 5.59 (s, 4H), 6.00 (s, 2H), 6.83 and 7.10 (s, 4H). — ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 31.33$ and 31.60 (–), 80.71 and 80.93 (+), 128.57 and 130.43 (+), 131.23 and 132.10 (C_{quat}), 140.12 and 143.12 (+), 145.42 and 148.80 (C_{quat}). — MS, m/z (%): 340 (50) [M^+], 170 (100) [M^{2+}].

X-Ray Structure Analysis of syn,syn-3^[14]: Diffractometer Stoe AED2, Mo-K_α radiation ($\lambda = 0.71073\text{ \AA}$), graphite monochromator, direct methods, refinement by full-matrix least squares of F^2 (SHELXL-92)^[15]. $\text{C}_{24}\text{H}_{20}\text{O}_2$, 340.4 g mol^{-1} . Triclinic crystals, crystal dimensions $0.50 \times 0.50 \times 0.20\text{ mm}$, space group $P\bar{1}$, $Z = 2$; unit cell dimensions: $a = 913.5(1)$, $b = 983.9(1)$, $c = 988.4(1)\text{ pm}$, $\alpha = 84.91(1)$, $\beta = 85.97(1)$, $\gamma = 72.76(1)^\circ$, $V = 0.8442(2)\text{ nm}^3$, $\rho_{\text{calcd.}} = 1.339\text{ g cm}^{-3}$, 2197 observed reflections (all independent) with $2\theta < 45^\circ$, $I > 2\sigma(I)$, $R = 0.055$, $wR2 = 0.1207$ ^[17]. Selected bond lengths [pm] and angles $^\circ$: C(1)–C(10) $150.5(5)$, C(1)–C(2) $156.3(6)$, C(2)–C(3) $150.8(5)$, C(3)–C(4) $138.2(5)$, C(3)–C(12) $139.7(5)$, C(4)–C(9) $140.8(5)$, C(4)–C(5) $151.9(5)$, C(5)–O(51) $144.5(5)$, C(5)–C(6) $152.7(6)$, O(51)–C(8) $144.1(4)$, C(6)–C(7) $131.9(6)$, C(11)–C(12) $137.0(5)$; C(10)–C(1)–C(2) $113.8(3)$, C(3)–C(2)–C(1) $112.8(3)$, C(4)–C(3)–

C(12) $114.7(3)$, C(4)–C(3)–C(2) $123.6(3)$, C(12)–C(3)–C(2) $120.0(3)$, C(3)–C(4)–C(9) $121.7(3)$, C(3)–C(4)–C(5) $133.6(3)$, C(9)–C(4)–C(5) $103.5(3)$, O(51)–C(5)–C(4) $101.1(3)$, O(51)–C(5)–C(6) $100.1(3)$, C(4)–C(5)–C(6) $106.2(3)$, C(8)–O(51)–C(5) $95.0(3)$, C(7)–C(6)–C(5) $105.5(4)$.

anti-[2.2]-(1,4)Naphthalenophane (4**)**: 2.40 ml (22.0 mmol) of titanium tetrachloride and 0.53 g (0.70 ml , 5.20 mmol) of triethylamine were added under N_2 to a cold suspension of 370 mg (9.70 mmol) of LiAlH_4 in 80 ml of THF, and the mixture was refluxed for 30 min . After cooling to room temp., 200 mg (0.59 mmol) of *syn,syn(anti)-3* was added in 30 ml of THF, and the mixture was stirred for 4 h . Then, excess LiAlH_4 was hydrolyzed by the addition of ice/water (100 ml), the mixture was diluted with 200 ml of CH_2Cl_2 , and the organic phase washed with water ($2 \times 100\text{ ml}$), dried with MgSO_4 , filtered and concentrated in vacuo. Chromatography of the residue on silica gel [$\text{CH}_2\text{Cl}_2/\text{PE}$ (1:1)] yielded 125 mg (69%) of **4** ($R_f = 0.6$). All spectroscopic data agree with the reported ones^[10].

9,9',10,10'-Tetraphenyl-anti-[2.2]-(1,4)anthracenophane (5**)**: 524 mg (1.00 mmol) of **2** and 810 mg (3.00 mmol) of 2,4-diphenylisobenzofuran were allowed to react according to GP 1. The crude product was chromatographed on 80 g of silica gel [$1. \text{CH}_2\text{Cl}_2/\text{PE}$ (1:1), $2. \text{CH}_2\text{Cl}_2$]. — Fraction I ($R_f = 0.9$, CH_2Cl_2): 2,4-diphenylisobenzofuran, not isolated. — II ($R_f = 0.64$, CH_2Cl_2): 190 mg (25%) of 9,9',10,10'-tetrahydro-9,9',10,10'-tetraphenyl-anti,syn-9,10:9',10'-diepoxy-anti-[2.2]-(1,4)anthracenophane, white solid, m.p. $>280^\circ\text{C}$. — ^1H NMR (250 MHz, CDCl_3): $\delta = 2.05$ – 2.40 and 2.83 (m, 8H), 4.58 (s, 2H), 6.25 (s, 2H), 6.91 and 7.22 (m, 4H), 7.30 – 7.70 (m, 16H), 7.82 and 8.12 (m, 8H). — MS, m/z (%): 744 (41) [M^+], 105 (100). — III ($R_f = 0.46$, CH_2Cl_2): 242 mg (33%) of 9,9',10,10'-tetrahydro-9,9',10,10'-tetraphenyl-syn,syn-9,10:9',10'-diepoxy-anti-[2.2]-(1,4)anthracenophane, m.p. $>280^\circ\text{C}$. — ^1H NMR (250 MHz, CDCl_3): $\delta = 2.45$ and 2.80 (m, 8H), 4.70 and 6.20 (s, 4H), 6.90 (m, 2H), 7.30 – 7.65 (m, 18H), 7.85 and 8.08 (m, 8H). — MS, m/z (%): 744 (65) [M^+], 105 (100). — To a mixture of 30 mg (0.04 mmol) of the Diels-Alder products and 166 mg (1.00 mmol) of potassium iodide in 12 ml of acetonitrile was added 0.10 ml (0.80 mmol) of trimethylsilyl chloride, and the reaction mixture was stirred at room temp. for 16 h . The reaction was quenched by the addition of 20 ml of a satd. aqueous sodium thiosulfate solution. After dilution with 200 ml of CH_2Cl_2 , the organic phase was extracted with water ($2 \times 100\text{ ml}$), dried with MgSO_4 , filtered and concentrated in vacuo. Chromatography of the residue on 50 g of silica gel [$\text{CH}_2\text{Cl}_2/\text{PE}$ (1:1)] yielded 16 mg (55%) of **5** as a yellow solid, m.p. $>280^\circ\text{C}$. Elemental analyses revealed a considerable amount of solvents (CH_2Cl_2 and PE, approx. $6\text{ mol}\%$ each) enclosed in the crystals, which could not be removed by drying for $6\text{ d}/0.1\text{ Torr}$ and may account for the relatively low extinction coefficients observed for the two independent chromophores in **5** as compared to the one in 9,10-diphenylanthracene (cf. Figure 2). — IR (KBr): $\tilde{\nu} = 2919\text{ cm}^{-1}$, 1016 , 764 , 701 . — UV (CH_2Cl_2): λ_{max} ($\lg \epsilon$) = 412 nm (4.03), 392 (4.11), 377 (4.06 sh), 290 (4.93), 249 (4.71). — Fluorescence (CH_2Cl_2 , excitation at 392 nm): $\lambda_{\text{max}} = 486\text{ nm}$. — ^1H NMR (250 MHz, CDCl_3): $\delta = 1.65$ and 2.30 (m, 8H), 5.79 (s, 4H), 7.01 (m, 4H), 7.25 – 7.60 (m, 16H), 7.72 (m, 4H), 7.91 (m, 4H). — ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 37.20$ (–), 124.63 , 126.47 , 127.05 , 127.24 , 128.65 and 129.65 (+), 131.02 (C_{quat}), 131.09 and 131.44 (+), 133.25 , 136.08 , 137.45 , and 142.08 (C_{quat}). — MS, m/z (%): 712 (18) [M^+], 356 (100) [M^{2+}]. — $\text{C}_{26}\text{H}_{20}$: calcd. for [M^+] 712.3130 , found 712.3086 (MS); calcd. for [M^{2+}] 356.1565 , found 356.1569 (MS). — If the reaction was stopped and worked up after a reaction time of 30 min , 9,9',10,10'-tetrahydro-9,9',10,10'-tetraphenyl-9,10-epoxy-anti-[2]-(1,4)anthracenophane was obtained in 69% yield. — ^1H NMR (250 MHz, CDCl_3): $\delta = 1.35$, 1.55 , 2.20 , and 3.00

(m, 8H), 5.38 and 6.75 (s, 4H), 6.85 and 7.00 (m, 4H), 7.20–7.90 (m, 20H), 8.15 (m, 4H). — ^{13}C NMR (62.5 MHz, CDCl_3): δ = 34.01 and 36.92 (—), 90.28 (C_{quat}), 119.63, 124.74, 125.29, 126.58, 127.09, 127.18, 127.29, 127.97, 128.03, 128.72, 129.80, 131.64, 131.73, 131.85, and 132.99 (+), 133.79, 135.34, 136.88, 137.18, 141.96, 146.87, and 150.80 (C_{quat}). — MS, m/z (%): 728 (49) [M^+], 355 (100).

5,5',8,8'-Tetrahydro-syn,syn(anti)-5,8:5'8'-bis(methano)-anti-[2.2](1,4)naphthalenophane (6): 524 mg (1.00 mmol) of **2** and 0.40 ml (6.00 mmol) of cyclopentadiene were allowed to react according to GP 1. Chromatography of the crude product on 50 g of silica gel (PE) yielded 151 mg (45%) of *syn,syn(anti)*-**6**. — ^1H NMR (250 MHz, CDCl_3): δ = 0.91, 1.65, 2.15, and 2.31 (m, 8H), 3.00 (m, 16H), 3.86 (m, 8H), 5.37 and 5.82 (m, 8H), 6.72 and 6.92 (m, 8H). — ^{13}C NMR (62.5 MHz, CDCl_3): δ = 31.11, 31.39, and 31.50 (—), 47.59, 47.75, 47.92, and 48.11 (+), 67.52, 67.62, 68.28, and 68.46 (—), 127.96, 128.13, and 128.16 (+), 131.03, 132.02, 132.20, and 133.12 (C_{quat}), 139.28 and 139.51 (+), 144.28 and 144.41 (+), 147.87, 148.12, and 149.66 (C_{quat}).

Cyclophane 8: To a mixture of 100 mg (0.53 mmol) of **7** and 613 mg (1.30 mmol) of **2** in 80 ml of THF at -90°C was added dropwise 0.90 ml (1.30 mmol) of *n*BuLi (1.4 M in hexane) in 10 ml of hexane. The reaction mixture was allowed to warm up to room temp. during 12 h, then 2 ml of methanol and 200 ml of CH_2Cl_2 were added, the organic phase was washed with water (3×50 ml), dried with Na_2SO_4 , filtered and concentrated in vacuo. Chromatography of the residue on 100 g of silica gel [$\text{CH}_2\text{Cl}_2/\text{PE}$ (1:1)] yielded 145 mg (30%) of **8** (R_f = 0.23). — ^1H NMR (250 MHz, CDCl_3): δ = 2.25–3.10 (m, 24H), 5.60 (s, 4H), 6.10 (s, 4H), 6.60 (s, 4H). — ^{13}C NMR (62.5 MHz, CDCl_3): δ = 25.89, 32.19, and 34.34 (—), 90.53 (C_{quat}), 111.34 (+), 111.55 and 129.68 (C_{quat}), 130.76 and 143.45 (+), 153.14 and 160.14 (C_{quat}).

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