Synthesis and Diels-Alder Reactions of 1,2-Dimethylene- and 1,2,9,10-Tetramethylene[2.2]paracyclophane: New Routes to Bridge-Anellated [2.2]Paracyclophanedienes☆

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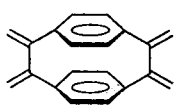
The title compounds **8** and **1** have been synthesized in three steps each from 1,2-dibromo[2.2]paracyclophan-1-ene (**2**) and 1,2,9,10-tetrabromo[2.2]paracyclophane-1,9-diene (**4**), respectively. Copper-mediated coupling of vinyl bromides **2** and **4** with methyl- and phenylmagnesium bromide gives substituted [2.2]paracyclophanes **3-CH$_3$**, **3-Ph**, **5-CH$_3$**, and **5-Ph** in good yields. The high reactivity of the [2.2]paracyclophane-1,2-dimethylene moieties in **8** and **1** in Diels-Alder reactions has been verified in cycloadditions with *p*-benzoquinone to give **10** and **13** and with naphthalene 1,4-endoxide to yield **12**.

Although extremely well-established, the Diels-Alder reaction has been used for a new type of application in recent years: Suitable bis-dienes and bis-dienophiles react in repetitive Diels-Alder fashion to give linear polymers of medium to high molecular weights[1]. Because of secondary stereochemical effects, however, only a few precise geometries of the connecting six-membered rings have been realized so far. The physical properties of linear ladder-type polymers are expected to be unusual[2], and they should greatly depend on the properties of the monomers. Inflexibility and strain are attributes of the [2.2]paracyclophane skeleton[3]. These could be incorporated into a polymer structure by the repetitive Diels-Alder reaction, if a suitable bifunctionally substituted derivative like 1,2,9,10-tetramethylene[2.2]paracyclophane (**1**) were available. This communication deals with the cuprous iodide-catalyzed coupling of 1,2-dibromo[2.2]paracyclophan-1-ene (**2**) and 1,2,9,10-tetrabromo[2.2]paracyclophane-1,9-diene (**4**) with Grignard reagents of give precursors to phenanthrene-anellated compounds **6**, **7** as well as 1,2-dimethylene[2.2]paracyclophane (**8**) and the tetramethylene derivative **1**. Model reactions of **8** and **1** are included, repetitive Diels-Alder reactions of **1** toward polymers will be reported in a forth coming paper[4].

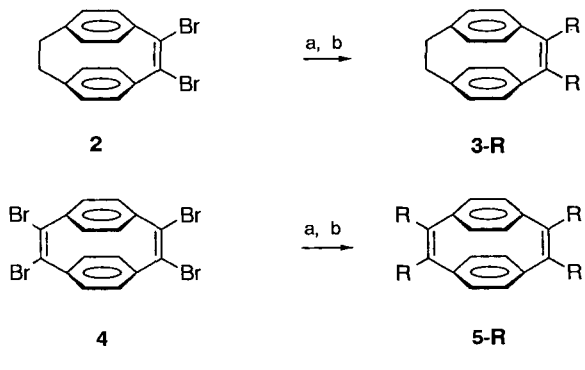


1

Dibromide **2**[5,6] and tetrabromide **4**[6] are accessible in reasonably large quantities from [2.2]paracyclophane by a sequence of photochemical bromination, elimination of hydrogen bromide, addition of bromine, and repeated dehydrobromination[6,7]. The carbon skeleton of **1** ought to be assembled by replacing all four bromine atoms in **4** by methyl groups. Although there are literature reports on the conversion of vinyl halides to allylic systems via organometallics, for cases of 1,2-dihaloalkenes elimination has been observed exclusively[8].

Reaction of **2** and **4** with methylmagnesium bromide in the presence of 30 mol-% of cuprous iodide yielded 1,2-dimethyl[2.2]paracyclophan-1-ene (**3-CH$_3$**) and 1,2,9,10-tetramethyl[2.2]paracyclophane-1,9-diene (**5-CH$_3$**) as the major products (80 and 65%, respectively). Mechanistically these reactions might proceed by halogen-metal exchange, elimination of magnesium bromide, addition of a second equivalent of methylmagnesium bromide to the liberated strained alkyne[9], and copper-induced coupling of the resulting vinyl Grignard reagent with methylmagnesium bromide[10].

Scheme 1



a: RMgBr, CuI, THF, -78°C to room temp. – b: Br_2, CH_2Cl_2, -15°C.

The reaction was extended to phenylmagnesium bromide to afford 1,2-diphenyl[2.2]paracyclophan-1-ene (**3-Ph**)

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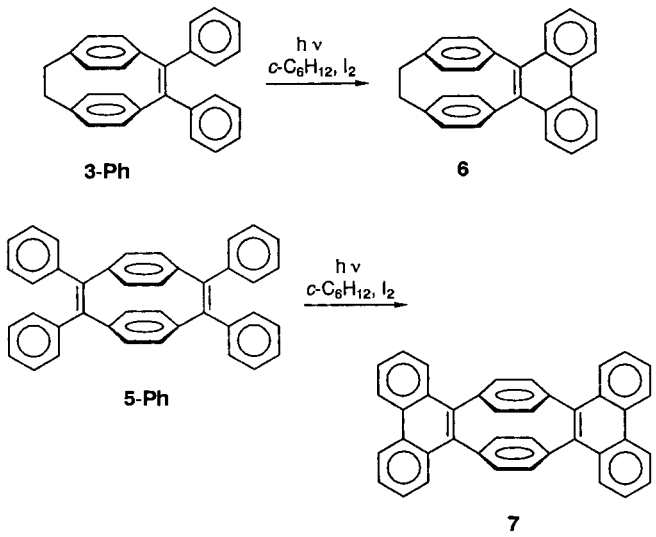
(66%) and 1,2,9,10-tetraphenyl[2.2]paracyclophane-1,9-diene (**5-Ph**) (25%); the latter, in close analogy to literature procedures, gave bisphenanthreno[2.2]paracyclophane (**7**) by oxidative photocyclization[11]. Similarly, **3-PH** could be photocyclized and oxidized to 1,2-phenanthreno[2.2]paracyclophan-1-ene (**6**). This approach to phenanthreno-bridged [2.2]paracyclophanes complements that reported by Hopf et al.[12].

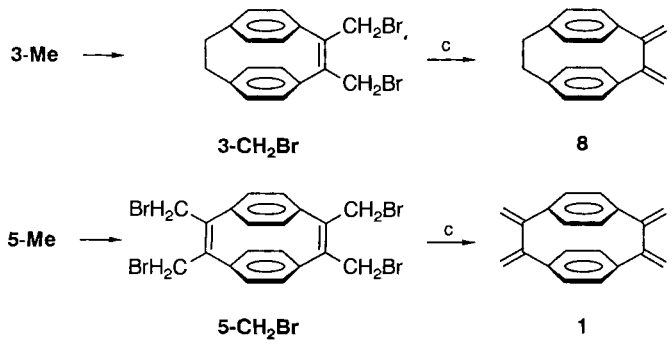
Scheme 2



By treating a solution of **3-CH$_3$** at −15°C with 2 equiv. of bromine, dibromide **3-CH$_2$Br** was obtained in good yield (68%). This transformation probably occurred by addition of bromine to the double bond, twofold dehydrobromination to diene **8**, followed by 1,4-addition of bromine. It was not possible to terminate the reaction at the intermediate target diene **8**. In an analogous manner, **5-CH$_2$Br** was obtained by starting with **5-CH$_3$**.

The conversion of **5-CH$_2$Br** and **3-CH$_2$Br** to the target dienes **1** and **8** is easily performed by elimination with activated zinc[13] promoted by ultrasound[14].

Scheme 3

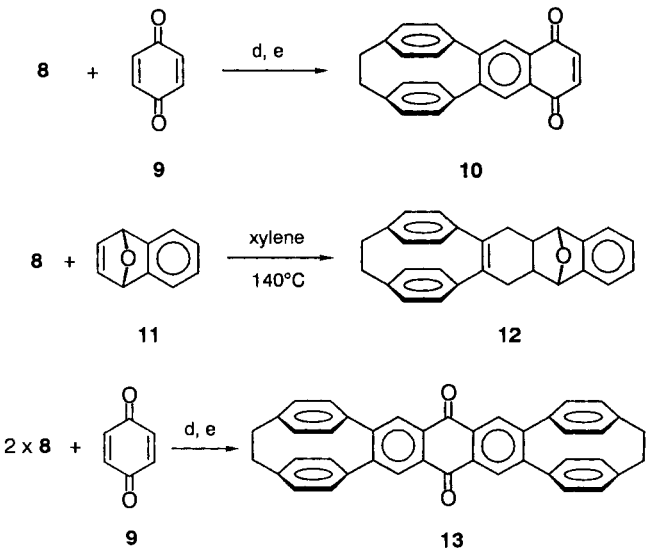


c: Zn^* (activated), dioxane, ultrasound, room temp.

1 and **8**[15] are stable crystalline compounds, which can be stored as solids in a refrigerator (+6°C) for months. In solution and exposed to air these compounds slowly decompose.

The Diels-Alder reactivities of **1** and **8**[15] were tested in reactions with *p*-benzoquinone (**9**) and naphthalene 1,4-endoxide (**11**). Upon heating a mixture of **8** and excess **9** in 1,2-dichlorobenzene to 140°C a Diels-Alder adduct was formed. Treatment of the reaction mixture with dichlorodicycano-*p*-benzoquinone (DDQ) led to 1,2(6,7)-naphthoquinono[2.2]paracyclophan-1-ene (**10**). Under similar conditions the addition of **8** to **11** afforded the cycloadduct **12** in high yield. The reaction of two equivalents **8** with *p*-benzoquinone (**9**) followed by dehydrogenation yielded the "twin-phane" **13**.

Scheme 4



d: Dichlorobenzene, 140°C. – e: $CHCl_3$, DDQ, 50°C.

More extended systems generated by Diels-Alder reactions of bifunctional bisdiene **1** with **9** were completely insoluble in organic solvents and could not be fully characterized by spectroscopic techniques. Only field desorption mass spectrometry and IR spectroscopy can give a hint to their structure. In order to be able to characterize oligomeric and polymeric products with repeating [2.2]paracyclophane units, one definitely needs intermediate chain substituents (C_5 to C_8) in the reacting monomers to increase solubility[1b,4].

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Experimental

^{1}H NMR: Bruker WM 250 (250 MHz); δ = 0 for tetramethylsilane as internal standard, δ = 7.26 for chloroform. – ^{13}C NMR: Bruker WM 250 (63 MHz); δ = 77 for $CDCl_3$; assignments were aided by the measurement of DEPT spectra, + designates primary and tertiary, – secondary and C_{quat} quaternary carbon atoms. – IR: Perkin-Elmer 297 and 399. – MS: Varian MAT CH7 (70 eV). – Melting points: Electrothermal melting point apparatus, uncor-

rected. – Column chromatography (CC): Merck silica gel 60, 70–230 mesh. – TLC: Silica gel on aluminum sheets (Merck F_{254}).

1,2-Dimethyl[2.2]paracyclophan-1-ene (**3-CH$_3$**): To a mixture of 750 mg (2.1 mmol) of **2** and 706 mg (3.7 mmol) of copper(I) iodide in 50 ml of THF was added dropwise at −78 °C under N_2 and with stirring 4.75 ml (12.4 mmol) of methylmagnesium bromide (2.6 M solution in ether). The reaction mixture was allowed to warm up to room temp., stirred for an additional 6 h, mixed with 2 ml of methanol, diluted with 200 ml of dichloromethane, and washed with three 100-ml portions of water. The organic layer was dried with $MgSO_4$, filtered, and the solvent evaporated in vacuo. The solid residue was chromatographed over 20 g silica gel [petroleum ether (60–80 °C), R_f = 0.24] and recrystallized from hexane to yield 385 mg (80%) of **3-CH$_3$** as a white solid, m.p. 186 °C. – IR (KBr): $\tilde{\nu}$ = 3009 cm^{-1}, 2948, 1584, 1091. – ^{1}H NMR ($CDCl_3$): δ = 2.22 (s, 6H, CH_3), 3.01 [s, 4H, 9(10)-H], 6.39 (AB system, δ_A = 6.36, δ_B = 6.43, ^3J = 8 Hz, 8H). – ^{13}C NMR ($CDCl_3$): δ = 18.73 (+, CH_3), 34.70 [−, C-9(10)], 131.02 and 132.00 (+), 138.02 and 144.09 (C_{quat}). – MS (70 eV): *m/z* (%) = 234 (85) [M^+], 219 (100) [$M^+ - CH_3$].

$C_{18}H_{18}$ Calcd. 234.1409 Found 234.1396 (MS)

1,2,9,10-Tetramethyl[2.2]paracyclophane-1,9-diene (**5-CH$_3$**): To a mixture of 1.00 g (1.923 mmol) of **4** and 1.45 g of copper(I) iodide in 60 ml of THF, kept at −78 °C, was added with stirring 9 ml (23.4 mmol) of methylmagnesium bromide (2.6 M solution in ether). The mixture was allowed to warm up to room temp. and was sonicated[14] for 16 h. After the addition of 2 ml of methanol the reaction mixture was diluted with 300 ml of dichloromethane, washed with water (3 × 100 ml), dried with $MgSO_4$, filtered, and the filtrate was evaporated to dryness in vacuo. Chromatography over 30 g of silica gel [petroleum ether (60–80 °C), R_f = 0.35] yielded 323 mg (65%) of **5-CH$_3$**, white solid, m.p. 181 °C. – IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1}, 2980, 2902, 1436, 732. – ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 12H, CH_3), 6.45 (s, 8H). – ^{13}C NMR ($CDCl_3$): δ = 18.47 (+, CH_3), 129.88 (+), 137.05 (C_{quat}), 143.36 (C_{quat}). – MS (70 eV): *m/z* (%) = 260 (100) [M^+], 245 (29) [$M^+ - CH_3$], 230 (62) [$M^+ - 2\ CH_3$], 215 (42) [$M^+ - 3\ CH_3$].

$C_{20}H_{20}$ Calcd. 260.1565 Found 260.1565 (MS)

1,2-Diphenyl[2.2]paracyclophan-1-ene (**3-Ph**): To a mixture of 300 mg (0.82 mmol) of **2** and 201 mg (1.0 mmol) of copper(I) iodide in 50 ml of THF was added with stirring 7 ml (3.5 mmol) of phenylmagnesium bromide (0.5 M solution in ether) at −78 °C. After warming up to room temp., the mixture was stirred for an additional 12 h. Workup was performed as described for **3-CH$_3$**, and chromatography over 50 g of silica gel [petroleum ether (60–80 °C)/dichloromethane, 8:2] yielded three fractions: I (R_f = 0.9): biphenyl, not isolated. – II (R_f = 0.2): 40 mg (17%) of *1-phenyl[2.2]paracyclophan-1-ene*, m.p. 184 °C. – IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1}, 2946, 1495, 1096. – ^{1}H NMR ($CDCl_3$): δ = 3.08 [s, 4H, 9(10)-H], 6.53 (AB system, δ_A = 6.51, δ_B = 6.54, ^3J = 8.0 Hz, 8H, phanarene H), 7.37 (m, 3H), 7.75 (m, 3H). – ^{13}C NMR ($CDCl_3$): δ = 34.80 (−), 34.85 (−), 126.53 (+), 127.85 (+), 128.56 (+), 130.63 (+), 131.80 (+), 132.27 (+), 132.59 (+), 132.60 (+), 138.44 (C_{quat}), 138.90 (C_{quat}), 139.08 (C_{quat}), 139.17 (C_{quat}). – MS (70 eV): *m/z* (%) = 282 (100) [M^+].

$C_{22}H_{18}$ (282.4) Calcd. C 93.62 H 6.38 Found C 93.76 H 6.43

III (R_f = 0.1): 195 mg (66%) of **3-Ph**, white solid, m.p. 225 °C. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2850, 1494, 1093, 747. – ^{1}H NMR ($CDCl_3$): δ = 3.07 [s, 4H, 9(10)-H], 6.58 (AB system, δ_A = 6.56, δ_B = 6.60, ^3J = 9 Hz, 8H, phanarene H), 7.13 (m, 6H, phenyl H), 7.35 (m, 4H, phenyl H). – ^{13}C NMR ($CDCl_3$): δ = 34.65 [−, C-9(10)], 127.01 (+), 128.03 (+), 130.09 (+), 132.53 (+), 132.86 (+), 138.62 (C_{quat}), 139.83 (C_{quat}), 142.91 (C_{quat}), 144.66 (C_{quat}). – MS (70 eV): *m/z* (%) = 358 (100) [M^+].

1,2,9,10-Tetraphenyl[2.2]paracyclophane-1,9-diene (**5-Ph**): To 312 mg (0.59 mmol) of **4** and 272 mg (1.4 mmol) of copper(I) iodide in 40 ml of THF was added at −78 °C 4.7 ml (4.7 mmol) of phenylmagnesium bromide (1 M in ether), and the solution was allowed to warm up to room temp. The reaction was completed by sonication for 12 h[14] at 20 °C. Workup was carried out as described for **5-CH$_3$**, and chromatography over 50 g of silica gel [petroleum ether (60–80 °C)] yielded I (R_f = 0.7): biphenyl, not isolated. – II (R_f = 0.05): 76 mg (25%) of **5-Ph**, m.p. 318 °C. – IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2963, 1493, 1096, 695. – ^{1}H NMR ($CDCl_3$): δ = 6.83 (s, 8H), 7.22 (m, 12H, phenyl H), 7.45 (m, 8H, phenyl H). – ^{13}C NMR ($CDCl_3$): δ = 127.13 (+), 128.03 (+), 130.22 (+), 131.88 (+), 139.43 (C_{quat}), 143.49 (C_{quat}), 144.16 (C_{quat}). – MS (70 eV): *m/z* (%) = 508 (100) [M^+].

$C_{40}H_{28}$ Calcd. 508.2191 Found 508.2203 (MS)

1,2:9,10-Bis(9,10)phenanthreno[2.2]paracyclophane-1,9-diene (**7**): A solution of 76 mg (0.15 mmol) of **5-Ph** and 80 mg (0.31 mmol) of iodine in 550 ml of cyclohexane was irradiated with a 250-W Hg medium-pressure lamp for 12 h. The solution was concentrated in vacuo, the precipitated product collected by filtration, washed with 10 ml of chloroform and 10 ml of *n*-pentane and dried in vacuo to yield 38 mg (50%) of **7**, m.p. >350 °C. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 1608, 1448, 1055, 759. – ^{1}H NMR ($CDCl_3$): δ = 6.93 (s, 8H), 7.40 and 7.79 (m, 10H, phenanthrene H), 8.30 (d, ^3J = 7.5 Hz, 2H), 8.91 (d, ^3J = 7.5 Hz, 2H), 9.80 (m, 2H). – MS (70 eV): *m/z* (%) = 504 (100) [M^+], 252 (10) [M^{2+}].

$C_{40}H_{24}$ Calcd. 504.1878 Found 504.1850 (MS)

1,2(9,10)-Phenanthreno[2.2]paracyclophan-1-ene (**6**): A solution of 80 mg (0.22 mmol) of **3-Ph** and 56 mg (0.22 mmol) of iodine in 100 ml of cyclohexane was irradiated in a quartz tube with a 250-W Hg medium-pressure lamp for 4 h. The solvent was removed in vacuo and the residue chromatographed over 50 g of silica gel [petroleum ether (60–70 °C)/dichloromethane, 1:1, R_f = 0.48] to yield 61 mg (78%) of **6**, m.p. >280 °C. – IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1}, 1489, 1179. – ^{1}H NMR ($CDCl_3$): δ = 3.17 (s, 4H), 6.66 (s, 8H), 7.61 (m, 4H), 8.12 (d, ^3J = 9.0 Hz, 2H), 8.79 (d, ^3J = 9.0 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 34.86 (−), 122.67 (+), 126.48 (+), 126.75 (+), 128.66 (+), 129.77 (C_{quat}), 131.01 (C_{quat}), 132.60 (+), 132.95 (+), 138.93 (C_{quat}), 139.42 (C_{quat}), 141.55 (C_{quat}). – MS (70 eV): *m/z* (%) = 356 (100) [M^+], 178 (7) [M^{2+}].

$C_{28}H_{20}$ Calcd. 356.1565 Found 356.1581 (MS)

1,2-Bis(bromomethyl)[2.2]paracyclophan-1-ene (**3-CH$_2$Br**): 7 ml (2.76 mmol) of a 2% solution of bromine in dichloromethane was added dropwise to 308 mg (1.32 mmol) of **3-CH$_3$** in 40 ml of dichloromethane at −15 °C, and the mixture was stirred for 0.5 h. The organic phase was washed with 20 ml of satd. aqueous sodium thiosulfate and 20 ml of water, dried with $MgSO_4$, filtered, and the solvent was evaporated from the filtrate in vacuo. Chromatography over 50 g of silica gel (petroleum ether/dichloromethane, 1:1) yielded 350 mg (68%) of **3-CH$_2$Br**, white solid, m.p. 151 °C. – IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1494, 725. – ^{1}H NMR ($CDCl_3$): δ = 3.03 [s, 4H, 9(10)-H], 4.54 (s, 4H), 6.49 (s, 8H). – ^{13}C NMR ($CDCl_3$): δ = 29.38 (−), 34.73 (−), 132.49 (+), 138.28 (C_{quat}), 139.36 (C_{quat}), 143.51 (C_{quat}).

$C_{18}H_{16}Br_2$ Calcd. 389.9619 Found 389.9622 (MS)

1,2,9,10-Tetrakis(bromomethyl)[2.2]paracyclophane-1,9-diene (**5-CH$_2$Br**): To 509 mg (1.96 mmol) of **5-CH$_3$** in 30 ml of dichloromethane was added at −15 °C with stirring 20.3 ml (7.83 mmol) of

a solution of bromine in dichloromethane (1:50). The reaction mixture was stirred for an additional 2 h. The precipitated product was collected by filtration, washed with 50 ml of chloroform, and dried in vacuo to yield 600 mg (53%) of **5-CH_2Br** as a white solid, m.p. >290°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2360, 1489, 605. – ^1H NMR ($CDCl_3$): δ = 4.55 (s, 8H), 6.64 (s, 8H). – MS (70 eV): *m/z* (%) = 580/578/576/574/572 (6/8/100/29/9) [M^+], 499/497/495/493 (13/48/82/15) [M^+ – Br], 418/417/416/414 (8/30/63/5) [M^+ – 2 Br], 337/335 (47/50) [M^+ – 3 Br], 256 (44) [M^+ – 4 Br].

1,2-Dimethylene[2.2]paracyclophane (**8**): After sonication[14] of a mixture of 702 mg (1.8 mmol) of **3-CH_2Br** and 270 mg (4.1 mmol) of activated zinc[13] in 30 ml of dry 1,4-dioxane for 2 h, the reaction mixture was diluted with 30 ml of ether, filtered to remove unreacted zinc and zinc salts, the filtrate was washed with 50 ml of a satd. aqueous ammonium chloride solution and 50 ml of water, dried with $MgSO_4$, and the solvents were evaporated in vacuo. The solid residue was chromatographed over silica gel [petroleum ether (60–80°C), R_f = 0.25] to yield 227 mg (55%) of **8**, m.p. 160°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2926, 1394, 728. – ^1H NMR ($CDCl_3$): δ = 3.05 [s, 4H, 9(10)-H], 5.27 (d, ^2J = 1.7 Hz, 2H), 5.66 (d, ^2J = 1.7 Hz, 2H), 6.49 (AB system, δ_A = 6.46, δ_B = 6.53, ^3J = 8 Hz, 8H). – ^{13}C NMR ($CDCl_3$): δ = 34.58 (–), 108.91 (–), 132.47 (+), 133.39 (+), 138.30 (C_{quat}), 140.95 (C_{quat}), 153.39 (C_{quat}). – MS (70 eV): *m/z* (%) = 232 (100) [M^+].

$C_{18}H_{16}$ Calcd. 232.1252 Found 232.1252 (MS)

1,2,9,10-Tetramethylene[2.2]paracyclophane (**1**): A mixture of 200 mg (0.35 mmol) of **5-CH_2Br** and 105 mg (1.6 mmol) of activated zinc[13] in 30 ml of freshly distilled 1,4-dioxane was sonicated[14] at room temp. for 12 h. Workup was carried out as described for **8**, and flash chromatography over 50 g of silica gel [petroleum ether (60–80°C), R_f = 0.27] yielded 82 mg (92%) of **1** as a white crystalline solid, m.p. 160°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1}, 1597, 1485, 1073, 744. – ^1H NMR ($CDCl_3$): δ = 5.40 (d, ^2J = 1.7 Hz, 4H), 5.71 (d, ^2J = 1.7 Hz, 4H), 6.58 (s, 8H). – ^{13}C NMR ($CDCl_3$): δ = 109.77 (–), 132.45 (+), 139.41 (C_{quat}), 152.26 (C_{quat}). – MS (70 eV): *m/z* (%) = 256 (100) [M^+].

$C_{20}H_{16}$ (256.3) Calcd. 93.75 H 6.25 Found C 93.69 H 6.28

1,2(6,7)Naphthoquinono[2.2]paracyclophan-1-ene (**10**): 22 mg (0.1 mmol) of **8** and 210 mg (0.19 mmol) of *p*-benzoquinone (**9**) were heated in 2 ml of dichlorobenzene at 140°C for 4 h. The solvent was removed in vacuo, the residue dissolved in 20 ml of chloroform and the reaction mixture stirred after the addition of 30 mg (0.13 mmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) for 12 h at 50°C. The solvent was evaporated and the residue subjected to flash chromatography over 50 g of silica gel (dichloromethane, R_f = 0.3) yielding 17 mg (53%) of **10**, yellow crystals, m.p. 220°C. – IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 1670 (C=O), 1603, 804. – ^1H NMR ($CDCl_3$): δ = 3.14 [s, 4H , 9(10)-H], 6.56 (AB system, δ_A = 6.52, δ = 6.59, $^3J_{AB}$ = 8 Hz, 8H), 7.06 (s, 2H), 8.29 (s, 2H). – ^{13}C NMR ($CDCl_3$): δ = 34.81 [–, C-9(10)], 123.63 (+), 130.73 (C_{quat}), 131.93 (+), 132.58 (+), 138.27 (C_{quat}), 140.16 (C_{quat}), 151.89 (C_{quat}), 158.77 (+), 185.22 (C_{quat}). – MS (70 eV): *m/z* (%) = 336 (100) [M^+].

$C_{24}H_{16}O_2$ Calcd. 336.1150 Found 336.1151 (MS)

2,3:6,7-Bis([2.2]paracyclophan-1-eno)anthraquinone (**13**): A mixture of 50 mg (0.22 mmol) of **8** and 12 mg (0.12 mmol) of **9** was heated in 1 ml of dichlorobenzene at 160°C for 8 h. The solvent was removed in vacuo, the residue dissolved in 20 ml of chloroform and the obtained solution stirred with 80 mg (0.35 mmol) of DDQ for 12 h at 50°C. The reaction mixture was diluted with 50 ml of chloroform, washed with 50 ml of dil. aqueous sodium hydroxide and 50 ml of water, dried with $MgSO_4$, and concentrated. The residue was subjected to flash chromatography over 30 g of silica gel with dichloromethane as eluent (R_f = 0.05) yielding 15 mg (25%) of **13**, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 2971 cm^{-1}, 1671 (C=O), 1588, 1093. – ^1H NMR ($CDCl_3$): δ = 3.16 (s, 8H), 6.617 and 6.621 (s, 16H, phanarene H), 8.57 (s, 4H). – MS (70 eV): *m/z* (%) = 564 (100) [M^+].

$C_{42}H_{28}O_2$ Calcd. 564.20892 Found 564.20893 (MS)

1',4',4a',9',10',10a'-Hexahydro-9',10'-epoxy-1,2(2,3)-anthraceno-[2.2]paracyclophan-1-ene (**12**): 30 mg (0.13 mmol) of **8** and 18.6 mg (0.13 mmol) of **11** were heated in 2 ml of xylene at 120°C for 6 h. The solvent was removed in vacuo and the solid residue washed with *n*-pentane. As verified by the ^1H- and ^{13}C-NMR spectra **12** was the only reaction product. – IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1}, 2930, 850, 724, 614. – ^1H NMR ($CDCl_3$): δ = 2.28 (m, 2H), 2.70 and 3.05 (m, 8H), 5.12 (s, 2H), 6.21 and 6.40 (m, 8H, phanarene), 7.10–7.30 (AA'BB' system, 4H). – ^{13}C NMR ($CDCl_3$): δ = 32.62 (–), 34.68 (–), 43.02 (+), 85.18 (+), 118.95 (+), 126.62 (+), 130.79 (+), 131.27 (+), 131.93 (+) and 131.96 (+), 138.44 (C_{quat}), 142.38 (C_{quat}), 142.79 (C_{quat}), 145.86 (C_{quat}). – MS (70 eV): *m/z* (%) = 376 (100) [M^+], 258/118 (29/28) [retro Diels-Alder products].

$C_{28}H_{24}O$ Calcd. 376.1827 Found 376.1817 (MS)

☆ Dedicated to Professor *Hans-Friedrich Grützmacher* on the occasion of his 60th birthday.

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