Synthesis of Substituted Dibenzoequinenes

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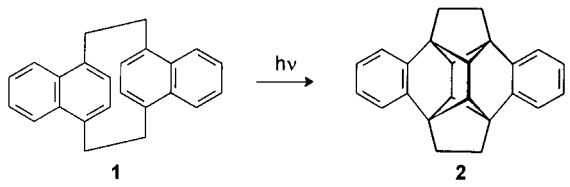
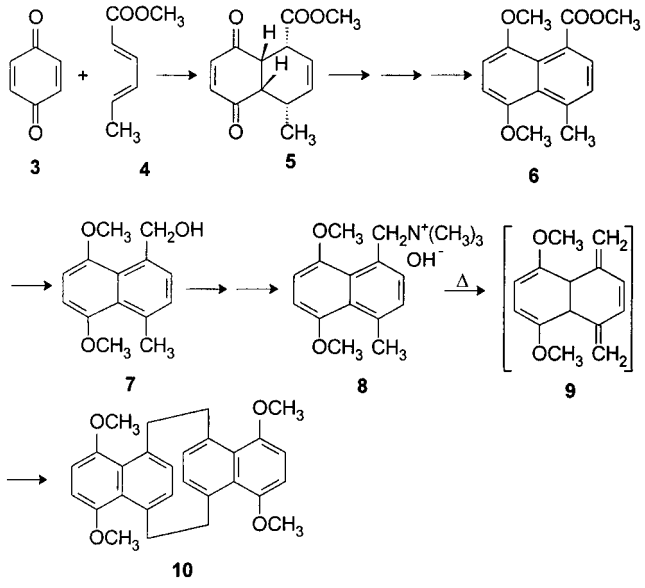
The naphthalenophanes with four donor groups such as 4,7,14,17-tetramethoxy-*anti*-[2.2](1,4)naphthalenophane (**10**), the corresponding *syn*-isomer **10a**, and 4,7,14,17-tetramethyl-*anti*-[2.2](1,4)naphthalenophane (**17**) together with the naphthalenophanes with four acceptor groups, 4,7,14,17-tetracyano-*anti*-[2.2](1,4)naphthalenophane (**21**), and 5,6,15,16-tetracarbethoxy-*anti*-[2.2](1,4)naphthalenophane (**23**), belonging to point group C_{2h} for the *anti*- and C_{2v} for the *syn*-isomer, have been synthesized following mostly known procedures. Furthermore, the preparation of 5,6-dicarbethoxynaphthaleno-[2.2](1,4)naphthalenophane (**27**) and 2,5-dimethoxynaphthaleno-*anti*-[2.2](1,4)-5,8-naphthochinonophane (**28**) with one donor and one acceptor substituted ring supplements the series. The irradiation of **10**, **21**, **23**, and **27** yields 2,2′,5,5′-tetramethoxydibenzoequinene (**30**), 2,2′,5,5′-tetracyanodibenzoequinene (**31**), 3,3′,4,4′-tetracarbethoxydibenzoequinene (**32**) and 3,4-dicarbethoxydibenzoequinene (**33**). Structural investigations on **30** by means of the X-ray method show a strong folding of the cyclobutane rings. The average bond length of the four-membered rings in **30** was found to be 1.579(2) Å. The values obtained for the bond lengths and bond angles resemble those of the parent system **2**. Long ethano bonds (1.556−1.591 Å) in the bridges were found in the *syn*- and *anti*-naphthalenophanes **10a**, **14**, and **17** by means of X-ray structure analysis.

Thirty years ago Wasserman and Keehn[1] discovered a simple path to a highly strained hydrocarbon which was named[2] dibenzoequinene (**2**). By irradiation of *anti*-[2.2](1,4)naphthalenophane (**1**) in benzene this hydrocarbon was formed in 50% yield (Scheme 1). In connection with our interest to investigate the interaction in nonconjugated π-systems,[3] this system was attractive to us due to the presence of a highly strained central σ-system with a bridged diasterane moiety[4] separating two benzene rings. To explore whether substitution products of **2** can be prepared, we embarked in the synthesis of donor- and acceptor-substituted dibenzoequinenes. The simple pathway used for **2** was also adopted for our efforts. Therefore we first needed procedures to build up substituted derivatives of **1**. In this respect we relied on work published by the groups of H. A. Staab,[5] D. J. Cram,[6] and H. Hopf.[7]

Scheme 1



Scheme 2



A. Synthesis of Substituted [2.2](1,4)-Naphthalenophanes of C_{2h}-Symmetry

The synthesis of 4,7,14,17-tetramethoxy-*anti*-[2.2]-(1,4)naphthalenophane (**10**) was published by Staab and Herz.[5] The key steps of the synthesis are summarized in Scheme 2. The thermolysis of the ammonium salt **8** in refluxing xylene yields the *anti*- and *syn*-isomers **10** and **10a** in about 10% yield.

To obtain the 4,7,14,17-tetramethyl-*anti*-[2.2](1,4)naphthalenophane (**17**) we followed a route first used by Reich and Cram[6] and later modified by de Meijere et al.[8] The reaction commences with 4,5,12,13-tetrabromo-[2.2]-(1,4)paracyclophane (**11**).[9] The reaction of **11** with *n*-butyllithium (*n*-BuLi) in the presence of 2,5-dimethylfuran yielded two diastereomeric mono-adducts (**12**, **13**) and three diastereomeric bis-adducts (**14**−**16**) (Scheme 3). All

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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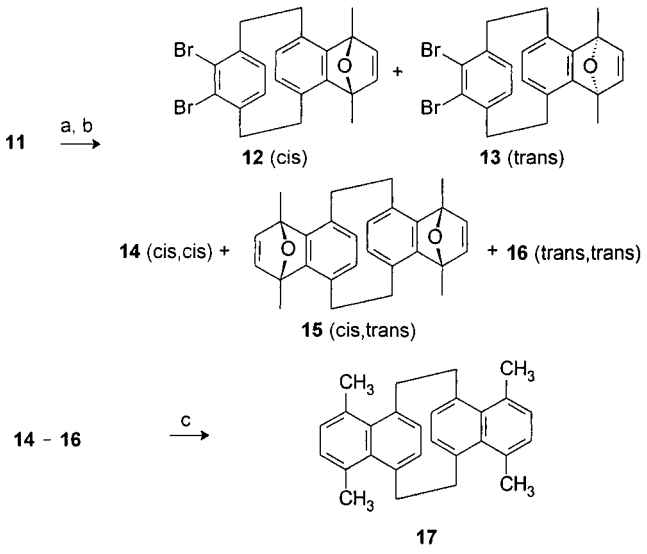
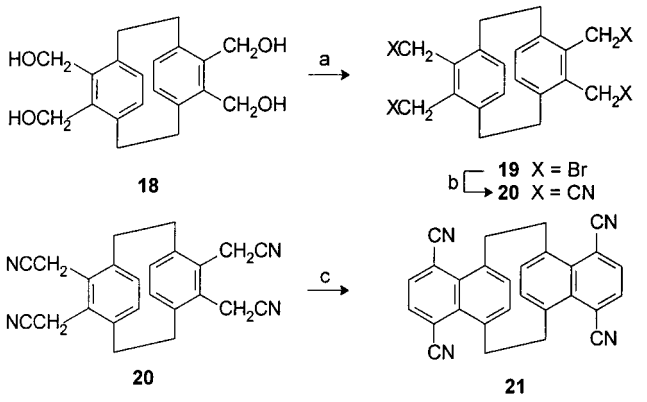
Scheme 3[a]



[a] (a) *n*-BuLi, THF, -40°C; (b) 30 eq. dimethylfurane, -40°C; (c) $LiAlH_4$, $TiCl_4$, NEt_3, THF, 68%.

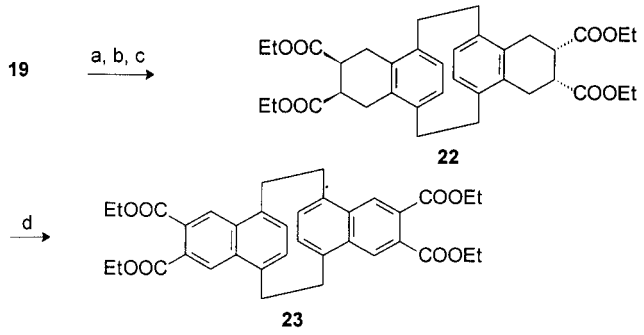
Scheme 4[a]



[a] (a) PBr_3, 0°C, CH_2Cl_2, 61%; (b) KCN, 18-crown-6, DMSO, 79%; (c) N,N′-bis(2,4- dimethylphenyl)glyoxaldiimine, cat. KOH, DMA, 21%.

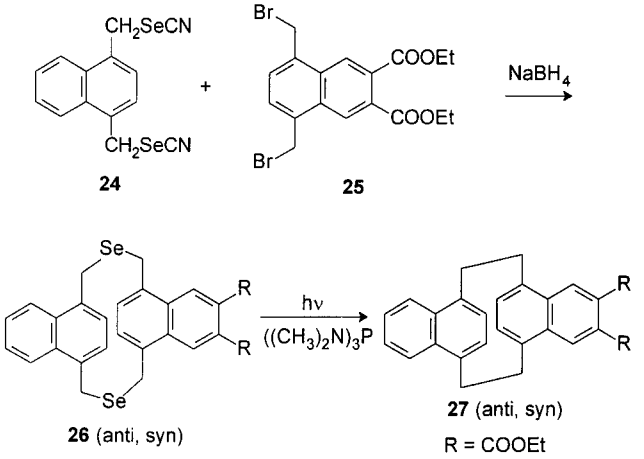
five isomers could be separated by column chromatography. The *cis,cis*-(**14**) and *trans,trans*-(**16**) isomers could be discriminated from the *cis,trans*-(**15**) isomer by means of ^{13}C NMR spectroscopy. The discrimination of **14** and **16** was possible with the help of X-ray crystallography. We were able to grow single crystals of **14** and investigate the molecular structure (Figure 1) thus establishing the configuration of **14** unequivocally. All three bis-adducts (**14**−**16**) could be converted to 4,7,14,17-tetramethyl-*anti*-[2.2](1,4)naphthalenophane (**17**) (Scheme 3) in 68% yield by means of $TiCl_4/LiAlH_4$ in the presence of triethylamine.[10] The structure of **17** was confirmed by investigating single crystals by X-ray analysis (Figure 1). The compound 4,7,14,16-tetracyano-*anti*-[2.2](1,4)naphthalenophane (**21**) was synthesized by the sequence shown in Scheme 4. Starting from 4,5,12,13-tetrakis(hydroxymethyl)-[2.2](1,4)paracyclophane (**18**),[11] the tetrabromide **19** could be prepared in good yields. Reaction of **19** with KCN in DMSO in presence of 18-crown-6 yields 79% of the tetracyanide **20**.[12] Condensation with *N,N′*-bis(2,4-dimethylphenyl)glyoxaldiimine[13] affords the desired cyclophane **21** in 21% yield.

Scheme 5[a]



[a] (a) Zn-Cu, DMF; (b) maleic acid anhydride; (c) EtOH/H + (d) DDQ, chlorobenzene

Scheme 6



To prepare 5,6,15,16-tetracarbethoxy-*anti*-[2.2](1,4)naphthalenophane (**23**), we followed a route designed by Hopf et al.[7] which is shown in Scheme 5.

B. Syntheses of Substituted [2.2](1,4)Naphthalenophanes of C_s-Symmetry

The donor- (**10**, **17**) and acceptor-substituted (**21**, **23**) cyclophanes were completed by two examples in which one (**27**) contains only one acceptor-substituted naphthalene ring and one (**28**) in which one naphthalene fragment has acceptor and the other donor substituents. To prepare these species we followed the procedures described by Misumi et al.[14] and Staab et al.,[5] respectively. The synthesis of **27** could be completed (Scheme 6) by reacting 5,8-bis(bromomethyl)-2,3-dicarboethoxynaphthalene (**25**) with 1,4-bis[(cyanoseleno)methyl]naphthalene (**24**) to yield a 4:10 mixture of the *syn*- and *anti*-isomers of **26**. The mixture could be transformed into a mixture of *syn*- and *anti*-isomers (1.4:10) of **27** by irradiation of a THF solution of **26** in the presence of tris(dimethylamino)phosphine.

The oxidation of **10** with Ce^{IV} yields a mixture of the donor−acceptor product 2,7-dimethoxynaphthaleno-*anti*-

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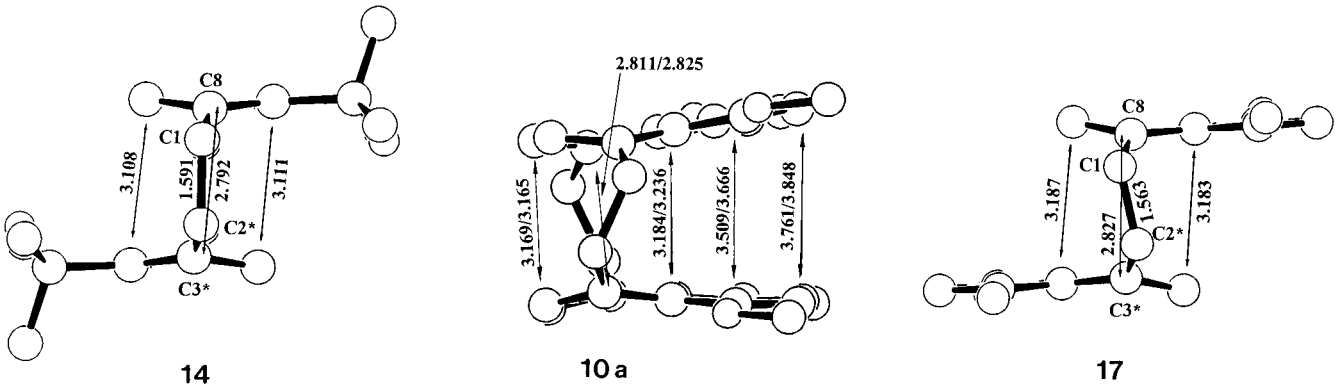
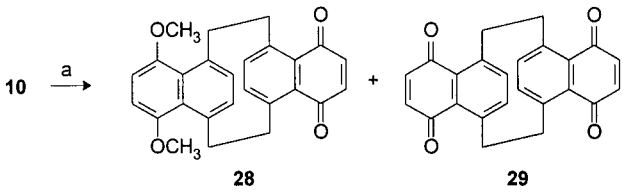


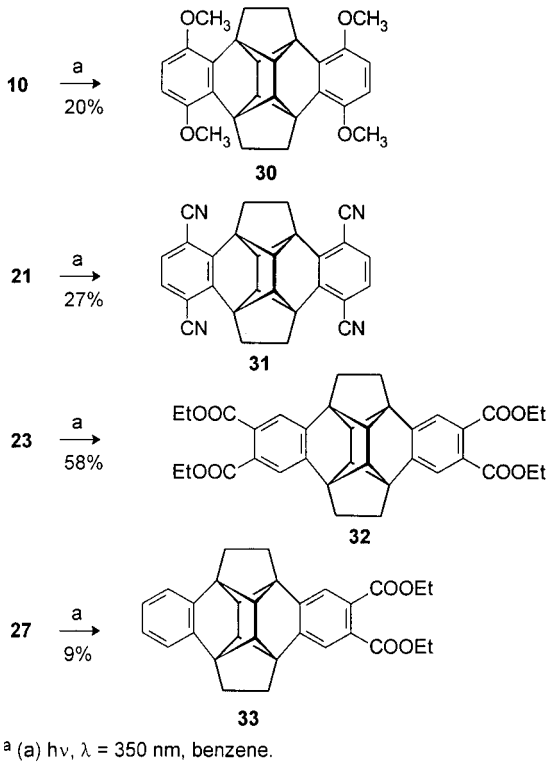
Figure 1. Side view of compound **10a** (only one of both independent molecules), **14**, and **17**.[15]

Scheme 7[a]



[a] (a) $(NH_4)_2Ce^{IV}(NO_3)_6$, CH_3CN, $CHCl_3$.

Scheme 8[a]



[a] (a) hν, λ = 350 nm, benzene.

[2.2](1,4)-5,8-naphthochinonophane (**28**) (33%) and *anti*-[2.2](1,4)-5,8-naphthochinonophane (**29**) (20%) (Scheme 7).

C. Syntheses of Substituted Dibenzoequinenes

The prepared substituted *anti*-[2.2](1,4)naphthalenophanes **10**, **17**, **21**, **23**, **27**, and **28** were dissolved in degassed benzene and irradiated with a Rayonet Photochemical Reactor at a wavelength of 350 nm (Scheme 8). The desired dibenzoequinenes could be purified by column chromatography in yields ranging from 10 to 50%.

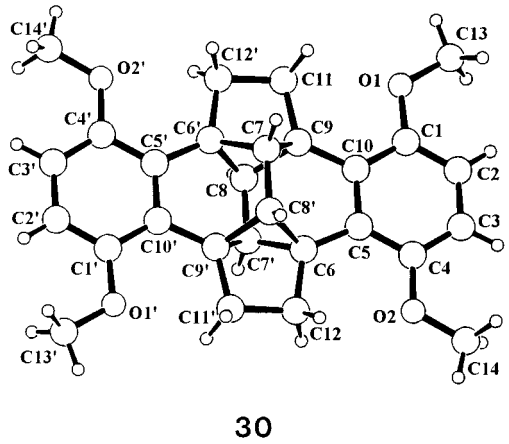


Figure 2. Molecular structure of **30**.[15]

In the cases of **17**, **28**, and **29** we could not detect the desired dibenzoequinenes. The structure of the product obtained in the case of **17** could not be identified. In the case of **28** and **29** no photoreaction could be observed.

The structural assignment of **30**−**33** is based on their spectroscopic data, especially the signals of the quaternary sp^3 carbons at $\delta = 56$. In the case of **30** the structure was confirmed by an X-ray structure analysis of single crystals.

D. Structural Investigations

The molecular structures of **10a**, **14**, and **17** are shown in Figure 1. In the naphthalenophane **10a** the naphthalene rings are in *syn*-orientation, and in **14** and **17** they have an *anti*-orientation. While compound **10a** has two crystallographically independent but chemically equal molecules in the asymmetric unit, the other two molecules **14** and **17** are positioned upon a crystallographic center of symmetry. The naphthalene rings of **10a** are disordered in one of the independent molecules and are twisted against each other by 14.4(3)° in the second one. Both naphthalene rings are tilted by 9.0(1)° and 8.0(1)° resulting in interplanar C···C distances of 2.82 Å at the bridgehead atoms and 3.73 Å on the average at the peripheral atoms (Figure 1).

The lengthening of the central bond of the ethano bridges in the naphthalenophanes **10a** (1.559(4)/1.556(4) Å), **17** (1.563(2) Å), and **14** (1.591(1) Å) increases with decreasing torsion angles (**10a**: 38.3(4)°/33.8(4)°; **17**: 29.1(2)°; **14**: 10.7(2)°). The comparable geometric parameters of parent compound **1**[16] are 1.572/1.569 Å and 16.6/11.8°.

Table 1. Comparison between Selected Bond Lengths (Å) and Bond Angles (deg) of 2[16] and 30. For the numbering of the atoms, see Figure 1

	2[16]	30
C5−C6	1.468	1.491(2)
C9−C10	1.502	1.491(2)
C6−C7′	1.579	1.579(2)
C6−C8′	1.596	1.580(2)
C7−C9	1.547	1.581(2)
C8−C9	1.585	1.577(2)
C7−C8′	1.521	1.521(2)
C6−C12	1.532	1.531(2)
C9−C11	1.542	1.524(2)
C11−C12′	1.573	1.557(2)
C7···C8		2.086(2)
C6′···C9		2.099(2)
C6′−C7−C9	83.8	83.3(1)
C6′−C8−C9	82.0	83.4(1)
C7−C9−C8	83.8	82.7(1)
C7−C6′−C8	82.4	82.7(1)

The bridged six-membered rings of the naphthalenophanes are distorted to boat conformation because of the intramolecular repulsive forces. The bow and stern planes are tilted by 14.4(2)° (**10a**), 12.3(1)° (**14**), and 14.3(2)° (**17**) on the average against the central plane of the boat. The bridging C-atoms of the CH_2-groups rise above the planes of their corresponding three neighboring six ring atoms by 0.32 Å (**10a**), 0.29 Å (**14**), and 0.30 Å (**17**) on the average.

The molecular structure of **30** is shown in Figure 2. In the crystal two molecules of **30** were contained in the unit cell with the space group $P2_1/c$ which required the molecule to possess a center of symmetry. In Table 1 the most relevant geometrical data of the equinene **30** are compared with those of **2**.[17] Of special interest are the distances and bond angles in the cyclobutane units of **30**. The cyclobutane rings are strongly folded by 124.2(1)° (C6′,C7,C9/C6′,C8,C9) and 124.5(1)° (C7, C6′,C8/C7,C9,C8) causing relatively short distances between C7···C8 (2.086(2) Å) and C6···C9 (2.099(2) Å). The angles in the four-membered rings in **30** (92.7 to 83.4, Table 1) deviate considerably from the expected 90°. The values obtained for **30** are close to those reported for **2** (Table 1).

The average bond length of the four-membered rings in **30** was found to be 1.579(2) Å) which is the same magnitude as that reported for **2** (1.576 Å). These values are considerably longer than the average bond length of cyclobutane compounds (1.554 Å[18]). This difference is accounted for by the strong folding of the cyclobutane rings in **2** and **30** caused by the ethano bridges and the repulsion between the C7···C8 and C6···C9 centers. The high strain in **2** and **30** causes also a strong folding of the five-membered ring fragments. The interplanar angles of the envelope form are 117.6(1)° and 118.2(1)°.

Experimental Section

4,5-Dibromo-12,15-dimethyl-12,15-epoxy-[2.2](1,4)naphthaleno-paracyclophanes (12, 13) and 4,7,14,17-Tetramethyl-4,7:14,17-diepoxy-*anti*-[2.2](1,4)naphthalenophanes (14, 15, 16). A 1.6 M solution of *n*-butyllithium in hexane (5.3 mL, 8.1 mmol) was added dropwise within 4 h to a stirred solution of **11** (1.9 g, 3.6 mmol)[8] and of 2,5-dimethylfuran (10.5 g, 0.109 mol)[19] in 300 mL of dry THF at −40 °C. The orange-colored solution was stirred overnight at ambient temp. After adding 10 mL of methanol, the mixture was diluted with 500 mL of CH_2Cl_2 and washed three times with water. The organic layer was dried over Na_2SO_4, and the solvent was removed. The residue was chromatographed (silica gel, CH_2Cl_2) to give the two isomeric 4,5-dibromo-12,15-dimethyl-12,15-epoxy-[2.2](1,4)naphthaleno-paracyclophanes **12** (250 mg, 0.543 mmol, 15%) and **13** (110 mg, 0.239 mmol, 6.6%) both as orange oils, and the three isomeric 4,7,14,17-tetramethyl-4,7:14,17-diepoxy-*anti*-[2.2](1,4)naphthalenophanes **14** (140 mg, 0.353 mmol, 10%), and **15** and **16** (1:1 mixture, 360 mg, 0.908 mmol, 25%), all of them as colorless powders. Additionally 660 mg, 1.26 mmol, 35%, of **11** was reisolated. **12**: MS (EI; 70 eV): $M^+ = 460$, for $^{79}Br/^{81}Br$, correct isotopic peaks, analyzed only by mass spectroscopy. **13**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 6 H), 2.83−2.86 (m, 2 H), 3.03−3.14 (m, 4 H), 3.42−3.45 (m, 2 H), 6.12 (s, 2 H), 6.38 (s, 2 H), 6.95 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 18.1 (q), 30.5 (t), 37.0 (t), 127.7 (d), 131.1 (d), 144.7 (d), all the C (s) signals were obscured by noise. **14**: melting point 264 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.07 (s, 12 H), 2.81−2.92 (m, 4 H), 3.40−3.50 (m, 4 H), 6.10 (s, 4H), 6.69 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ =17.5 (q), 32.4 (t), 89.3 (s), 131.2 (s), 132.7 (d), 148.3 (d), 149.1 (s). Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found C, 84.86; H, 7.00. **15**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.89 (s, 6 H), 2.08 (s, 6 H), 2.72−2.83 (m, 2 H), 2.99−3.15 (m, 4 H), 3.38−3.49 (m, 2 H), 5.51, 6.06, 6.69 and 6.93 (all of them s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 17.8 (q), 18.2 (q), 31.4 (t), 31.5 (t), 88.7 (s), 89.4 (s), 130.4 (d), 130.6 (d), 131.4 (s), 131.7 (s), 144.5 (d), 148.2 (d), 149.6 (s), 149.9 (s). **16**: melting point 238 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.90 (s, 12 H), 2.99−3.15 (m, 8 H), 5.42 (s, 4 H), 6.97 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 18.4 (q), 30.8 (t), 88.5 (s), 128.3 (d), 130.8 (s), 144.3 (d), 151.0 (s). HRMS (EI, 70 eV) calcd for $C_{28}H_{28}O_2$ (M^+) 396.2089, found 396.2037.

4,7,14,17-Tetramethyl-*anti*-[2.2](1,4)naphthalenophane (17). About 5.2 g (~27 mmol) of freshly distilled $TiCl_4$ was added cautiously to a stirred suspension of 370 mg (9.75 mmol) of $LiAlH_4$ in 250 mL of dry THF under argon at 0 °C, until the reaction mixture turned to a green-yellow color. A 0.76 mL (0.55 g, 5.5 mmol) volume of triethylamine was added, and the mixture was heated to reflux within 30 min. After cooling to ambient temp, a solution of **14**, **15**, and **16** (mixture of all isomers; 240 mg, 0.605 mmol) in 100 mL of dry THF was added. The suspension was stirred overnight at ambient temp and poured on ice. The layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and the solvent was removed. The oily green residue was chromatographed (silica gel, hexane:CH_2Cl_2 1:1) to give 150 mg (0.41 mmol, 68%) of a light yellow powder. For analysis, this was sublimed at 225 °C (0.04 mbar), the resulting colorless **17** melts at 280 °C. UV/Vis (C_6D_6) λ_{max} = 316 (log ϵ = 3.88), 292 (3.91). ^1H NMR (CS_2/C_6D_6, 300 MHz): δ = 2.61 (s, 12 H), 2.63−2.66 (m, 4 H), 3.72−3.75 (m, 4 H) 5.71 (s, 4 H), 6.94 (s, 4 H). ^{13}C NMR (CS_2/C_6D_6, 75.5 MHz): δ = 24.7 (q), 39.1 (t), 129.2 (d), 131.3 (d), 131.5 (s), 135.5 (s), 136.4 (s). HRMS (EI, 70 eV) calcd for $C_{28}H_{28}$ (M^+): 364.2191, found 364.2222. Anal. Calcd for $C_{28}H_{28}$: C, 92.26; H, 7.74. Found C, 91.85; H, 7.84; (covered with V_2O_5).

4,5,12,13-Tetrakis(cyanomethyl)-[2.2]paracyclophane (20). A suspension of **19** (2.4 g, 4.1 mmol)[7] in 50 mL of dry DMSO was added dropwise to a stirred suspension of KCN (2.7 g, 42 mmol; 2.5 equiv) and of 18-crown-6 (50 mg) in 75 mL of dry DMSO under argon. The mixture was stirred for 4 h and then poured on ice. The resulting precipitate was collected, washed with 50 mL of acetone, and dried under vacuo to yield **20** as a colorless powder (1.2 g, 3.3 mmol, 79%) which decomposes at 260 °C. Due to insolubility in common organic solvents, **20** could only be analyzed by mass spectroscopy. HRMS (EI, 70 eV): 364 (M^+, 37); 183 (15); 182 (100); 181 (14); 155 (10); 146 (12); calcd for $C_{24}H_{20}N_4$ (M^+): 364.1688, found 364.1711.

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4,7,14,17-Tetracyano-[2.2](1,4)naphthalenophane (21). A 25 mg amount of KOH powder was added to an argon-flushed suspension of **20** (1.04 g, 2.85 mmol) and *N*,*N*′-bis(2,4-dimethylphenyl)glyoxaldiimine[13] (1.81 g, 6.85 mmol; 2.4 equiv) in 50 mL of *N*,*N*-dimethylacetamide. The suspension was stirred for 6 h and was poured into 100 mL of a saturated solution of NH_4Cl at 0 °C. The mixture was extracted four times with CH_2Cl_2. The organic layer was washed with 10% H_2SO_4 and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed (silica gel, cyclohexane: ethylacetate 2:1) to give **21** as an orange powder (349 mg, 0.855 mmol, 30%). Recrystallization from nitromethane yields **21** as yellow needles (250 mg, 0.612 mmol, 21%), which do not melt until 310 °C. UV/Vis (CH_2Cl_2) $\lambda_{max} = 230$ ($\log \epsilon = 4.09$), 260 (4.27), 270 (4.27), 358 (3.66). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.16-3.21$ (m, 4 H), 4.69−4.74 (m, 4 H), 6.20 (s, 4 H), 8.00 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 35.1$ (t), 113.2 (s), 118.2 (s), 132.9 (d), 133.2 (d), 134.0 (s), 135.6 (s). HRMS (EI, 70 eV) calcd for $C_{28}H_{16}N_4$ (M^+): 408.1375, found 408.1383.

6,7-Dicarbethoxynaphthaleno-2,13-diselena-[3.3]-(1,4)naphthalenophane (26 *anti, syn*). Over a period of 18 h a solution of **24** (68 mg, 0.19 mmol, 1.2 equiv)[14] and of **25** (70 mg, 0.15 mmol, 1 equiv)[20] in 160 mL of peroxide-free THF and ethanol 1:1 was added to a stirred solution of $NaBH_4$ (58 mg, 1.5 mmol, 10 equiv) in 100 mL of peroxide-free THF and 5 mL of ethanol at 50 °C. The suspension was stirred for an additional 1 h and then cooled to rt. A 100 g amount of ice was added, and the mixture was concentrated in vacuo to 150 mL. After addition of 200 mL of brine, the mixture was extracted three times with CH_2Cl_2. The organic layer was washed with water, and dried over Na_2SO_4, and the solvent was removed. The residue was filtered over silica gel to give a yellow oil (*anti*:*syn* 10:3.5, according to ^{1}H NMR), which was used without further purification. **26** *anti*: ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 1.17$ (t, $J = 7.2$ Hz, 6 H), 3.43 (dd, $J = 14.0$ Hz, 2 H), 3.48 (dd, $J = 14.5$ Hz, 2 H), 4.01 (dd, $J = 14.0$ Hz, 2 H), 4.08 (dd, $J = 14.3$ Hz, 2 H), 4.34 (q, $J = 7.2$ Hz, 4 H), 5.91 (s, 2 H), 6.26 (s, 2 H), 7.35 (AA′BB′, 4 H), 7.75 (AA′BB′, 4 H), 8.61 (s, 2 H). ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 14.3$ (q), 26.3 (t), 27.1 (t), 61.6 (t), 124.5 (d), 125.4 (d), 126.5 (d), 126.6 (d), 129.0 (s), 129.1 (d), 131.8 (s), 132.3 (s), 132.6 (s), 133.4 (s), 168.0 (s). **26** *syn*: ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 1.18$ (t, $J = 7.2$ Hz, 6 H), 3.72−3.93 (m, 8 H), 4.29 (q, $J = 7.2$ Hz, 4 H), 6.60 (s, 2 H), 6.68 (s, 2 H), 7.07 (AA′BB′, 4 H), 7.66 (AA′BB′, 4 H), 8.39 (s, 2 H). ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 14.3$ (q), 26.0 (t), 26.5 (t), 61.2 (t), 124.5 (d), 125.2 (d), 126.8 (d), 127.6 (d), 130.1 (d), 131.3 (s), 131.3 (s), 131.6 (s), 131.9 (s), 167.7 (s), one carbon (q) not detected.

5,6-Dicarbethoxynaphthaleno-[2.2](1,4)naphthalenophane (27 *anti, syn*). An oxygen-free solution of **26** (*anti*:*syn* 10:3.5) (51 mg, 0.084 mmol) and of tris(dimethylamino)-phosphane (2 mL, 1.79 g, 11 mmol) in 50 mL of dry THF was irradiated for 1 h in a Rayonet photochemical reactor at $\lambda = 300$ nm. The yellow residue was filtered (silica gel, CH_2Cl_2) and then chromatographed (Alox(III), pentane:CH_2Cl_2 2:1) to give **27** (34 mg, 0.075 mmol, 90%; *anti*:*syn* = 10:1.4 according to ^{1}H NMR). **27** *anti*: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.45$ (t, $J = 7.1$ Hz, 6 H), 2.98−3.10 (m, 4 H), 3.72−3.83 (m, 4 H), 4.47 (q, $J = 7.1$ Hz, 4 H), 5.82 (s, 2 H), 5.89 (s, 2 H), 7.40−7.47 (AA′BB′, 2 H), 7.69−7.75 (AA′BB′, 2 H), 8.11 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 14.3$ (q), 31.9 (t), 32.1 (t), 61.6 (t), 124.9 (d), 124.1 (d), 126.7 (d), 127.6 (s), 128.1 (d), 129.3 (d), 134.4 (s), 134.8 (s), 135.2 (s), 135.8 (s), 168.3 (s). **27** *syn*: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.42$ (t, $J = 7.1$ Hz, 6 H), 3.27−3.32 (m, 4 H), 3.87−3.95 (m, 4 H), 4.39 (q, $J = 7.1$ Hz, 4 H), 6.74 (s, 2 H), 6.80 (s, 2 H), 6.92−6.95 (AA′BB′, 2 H), 7.69−7.75 (AA′BB′, 2 H), 7.87 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 14.3$ (q), 31.7 (t), 32.4 (t), 61.2 (t), 124.3 (d), 125.2 (d), 126.1 (d), 126.6 (s), 129.9 (d), 132.6 (d), 133.8 (s), 133.9 (s), 135.8 (s), 136.7 (s), 168.0 (s). **27** (*anti*, *syn*): UV/Vis (mixture, CH_2Cl_2) $\lambda_{max} = 240$ ($\log \epsilon = 4.62$), 272 (4.22), 320 (3.59), 362 (3.73). HRMS (EI, 70 eV) calcd for $C_{30}H_{28}O_4$ (M^+) 452.1988, found 452.1993.

4,7-Dimethoxynaphthaleno-*anti*-[2.2](1,4)-5,8-naphthochinonophane (28) and *anti*-[2.2](1,4)-5,8-Naphthochinonophane (29). A suspension of **10** (254 mg, 0.593 mmol)[5] in 40 mL of acetone and 15 mL $CHCl_3$ was cooled to −7 °C. During 1 h a solution of cerium(IV) ammonium nitrate (975 mg, 1.78 mmol) in 6 mL of water were added, and the resulting solution was stirred at 0 °C for 2 h. A 50 mL volume of water was added, and the mixture was extracted with $CHCl_3$. The solvent was removed, and the resulting brown solid was chromatographed (SiO_2, $CHCl_3$:hexane 1:1) to give unreacted **10** (24 mg, 0.056 mmol, 9%) and a mixture of the products **28** and **29** (150 mg) which was further chromatographed (SiO_2, CH_2Cl_2) to give **28** (78 mg, 0.19 mmol, 33%) as a red powder and **29** (43 mg, 0.12 mmol, 20%) as a yellow solid. **28**: mp: 192−194 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.63-2.73$ (m, 2 H), 2.86−2.96 (m, 2 H), 3.93 (s, 6 H), 4.03−4.28 (m, 4 H), 6.05 (s, 2 H), 6.45 (s, 2 H), 6.78 (s, 2 H), 6.80 (s, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): $\delta = 36.2$ (t), 36.5 (t), 56.2 (q), 106.7 (d), 128.4 (s), 130.9 (d), 132.5 (s), 134.6 (d), 136.3 (s), 138.2 (d), 143.3 (s), 152.4 (s), 186.8 (s). UV/Vis (CH_2Cl_2) $\lambda_{max} = 254$ ($\log \epsilon = 3.61$), 332 (2.52), 3.94 (2.69), 412 (270), 512 (230). HRMS (EI 70 eV) calcd for $C_{26}H_{22}O_4$ (M^+): 398.1518, found 398.1498. **29**: mp 260−262 °C dec; lit.[5]: >250 °C dec. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.96-3.06$ (m, 4 H), 3.93−4.44 (m, 4 H), 6.60 (s, 2 H), 6.81 (s, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): $\delta = 34.8$ (t), 133.3 (s), 137.9 (d), 138.4 (d), 144.2 (s), 186.4 (s). UV/Vis ($CHCl_3$) $\lambda_{max} = 250$ ($\log \epsilon = 4.30$), 394 (3.60). HRMS (EI 70 eV) calcd for $C_{24}H_{16}O_4$ (M^+): 368.1049, found 368.1051.

General Procedure for the Photochemical Conversion of the Naphthalenophanes (10, 21, 23, 27) to the Corresponding Dibenzoequinenes (30, 31, 32, 33). An oxygen-free solution of 0.3 mmol of the naphthalenophane in 250 mL of benzene (photochemical grade) was irradiated in a Rayonet photochemical reactor at 350 nm. After completion of the photochemical reaction, the benzene solution was concentrated in vacuo, and the residue was chromatographed on silica gel to give the corresponding dibenzoequinenes.

2,2′5,5′-Tetramethoxydibenzoequinene (30): *hν* 7 h; chromatographed with hexane:CH_2Cl_2 1:1; yield: 20% of **30** (16% of **10** reisolated), mp 279−281 °C (recrystallized from CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.74$ (s, 4 H), 2.60 (s, 8 H), 3.78 (s, 12 H), 6.78 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 29.6$ (t), 50.1 (d), 54.3 (s), 56.5 (q), 110.3 (d), 127.9 (s), 151.2 (s). UV/Vis (CH_2Cl_2): $\lambda_{max} = 222$ ($\epsilon = 4.22$), 242 (3.86), 310 (3.88). Anal. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found C, 78.75; H, 6.37. **2,2′5,5′-Tetracyanodibenzoequinene (31)**: *hν* 2 h; chromatographed with CH_2Cl_2; yield 27% of **31**; no melting <270 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.01$ (s, 4 H), 2.96 (s, 8 H), 7.75 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 29.7$ (t), 49.3 (d), 55.9 (s), 113.1 (s), 117.7 (s), 132.7 (d), 141.1 (s). UV/Vis (C_6H_6): $\lambda_{max} = 272$ ($\log \epsilon = 3.85$); 302 (3.68); 314 (3.89). HRMS (EI 70 eV) calcd for $C_{28}H_{16}N_4$ (M^+): 408.1375, found 408.1378. **3,3′,4,4′-Tetracarbethoxydibenzoequinene (32)**: *hν* 15 h; chromatographed with cyclohexane:ethyl acetate 5:1; yield 58% of **32**; mp 179−184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.38$ (t, $J = 7.2$ Hz, 12 H), 1.67 (s, 4 H), 2.46 (s, 8 H), 4.39 (q, $J = 7.1$ Hz, 8 H), 7.26 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75.5): $\delta = 14.2$ (q), 25.9 (t), 48.6 (d), 56.3 (s), 61.6 (t), 123.9 (d), 130.3 (s), 140.7 (s), 168.1 (s). UV/Vis ($CHCl_3$): $\lambda_{max} = 234$ ($\log \epsilon = 4.60$); 292 (2.32). Anal. Calcd for $C_{36}H_{36}O_8$: C, 72.47; H, 6.08. Found C, 72.22; H, 6.11. **3,4-Dicarbethoxydibenzoequinene (33)**: *hν* 5.5 h; chromatographed with CH_2Cl_2; yield 9%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.39$ (t, $J = 7.2$ Hz, 6 H), 1.66 (s, 4 H), 2.43 (br s, 8 H,), 4.39 (q, $J = 7.2$ Hz, 4H), 7.37 (br s, 4 H), 7.69 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 14.2$ (q), 26.0 (t), 26.1 (t), 48.7 (d), 56.1 (s), 56.3 (s), 61.5 (t), 123.3 (d), 123.8 (d), 126.4 (d), 130.1 (s), 137.7 (s), 141.1 (s), 168.2 (s). UV/Vis (CH_2Cl_2): $\lambda_{max} = 228$ ($\log \epsilon = 4.55$); 256 (3.90); 290 (3.12). HRMS (EI, 70 eV) calcd for $C_{30}H_{28}O_4$: 452.1988, found 452.1973.

X-ray Diffraction Analyses of 10a, 14, 17, and 30. The X-ray data were collected with an Enraf-Nonius-CAD4-diffractometer (Mo K_α-radiation, graphite monochromator, $\omega-2\Theta$-

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Table 2. Crystallographic Data

compound	**10a**	**14**	**17**	**30**
empirical formula	$C_{28}H_{28}O_4$	$C_{28}H_{28}O_2$	$C_{28}H_{28}$	$C_{28}H_{28}O_4$
molecular mass [g/mol]	428.5	396.5	364.5	428.5
solvent	CH_2Cl_2	CH_2Cl_2/pentane	CH_2Cl_2/PE	CH_2Cl_2/PE
crystal size [mm]	0.5 × 0.5 × 0.25	0.5 × 0.5 × 0.28	0.4 × 0.2 × 0.15	0.5 × 0.4 × 0.4
crystal color	slight yellow	colorless	colorless	colorless
crystal shape	prism	prism	prism	prism
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	18.938(4)	10.131(2)	8.712(2)	9.536(1)
b [Å]	24.227(7)	11.156(2)	12.035(2)	7.142(1)
c [Å]	9.504(2)	10.338(1)	9.428(1)	15.799(2)
β [deg]	94.32(2)	118.16(1)	103.24(1)	101.79(1)
V [Å^3]	4348(2)	1030.1(5)	962.1(5)	1053.4(5)
D_{calc} [mg/m^3]	1.31	1.28	1.26	1.35
Z	8	2	2	2
F(000)	1824	424	392	456
temp [K]	293	293	293	293
h_{min}/h_{max}	0/24	0/13	0/11	0/12
k_{min}/k_{max}	0/31	0/14	0/15	0/9
l_{min}/l_{max}	−12/12	−13/13	−12/12	−20/20
$(\sin \Theta/\lambda)_{max}$ [Å^{-1}]	0.66	0.66	0.66	0.66
μ [mm^{-1}]	0.09	0.07	0.07	0.08
refl collected	10765	2594	2451	2667
refl unique	7525	2465	2311	2375
refl observed [$I > 2\sigma(I)$]	3871	2003	1396	1929
R_{int}	0.017	0.027	0.021	0.012
variables	584	192	183	201
$(\Delta/\sigma)_{max}$	<0.01	<0.01	<0.01	<0.01
R	0.055	0.041	0.040	0.046
R_w	0.152	0.106	0.091	0.061
S (Gof)	1.08	2.52	1.76	2.82
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.21	0.21	0.15	0.32
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.24	−0.23	−0.22	−0.26

scan). Intensities were corrected for Lorentz and polarization effects. We solved the structures by direct methods (**10a**, **30**: SHELXS-86;[22] **14**, **17**: MULTAN[23]) and refined the structural parameters of the non-hydrogen atoms anisotropically according to a full-matrix least-squares technique (F^2). All hydrogen atoms were refined isotropically (except in **10a**). The crystallographic data are listed in Table 2.

In **10a** the atoms O4, C1, C23, and C24 are disordered at two positions with a multiplicity of 50%. Calculations were done with the MolEN[24] program system, except refinement of **10a** which was carried out with SHELXL-93.[25] Further details of the crystal structure investigation are available upon request from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

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Supporting Information Available: NMR spectra of all new compounds (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, see any current masthead page for ordering information.

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