The Preparation of Helical Cyclophanes Containing Five-membered Rings

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Keywords: Cycloadditions / Cyclophanes / Helical structures / Novel dienes / Polycyclic aromatic hydrocarbons (PAHs)

Cycloadditions between the indenone derivatives prepared in situ from the bromides **12a** and **12b** and 4-vinyl[2.2]paracyclophane (**11**) yielded the Diels–Alder adducts **13a** and **13b** in acceptable yields. When these were heated in the presence of DDQ in toluene, the fluorenophanes **14a** and **14b** were produced in good yields. The diol **17** obtained from the tetralonophane **15** on treatment with $POCl_3$/pyridine was dehydrated to the diene **18**, which could be trapped by *p*-benzoquinone (**19**) to provide the cycloadducts **20** and **21**; the former was oxidized to the latter by DDQ treatment. Although the even more highly annelated helical phane system **22** could be prepared from **17** and **12a**, its aromatization to the ketone **24** or the hydrocarbon **25** failed. All new compounds were characterized by their spectroscopic data, in particular by extensive NMR investigations. A single-crystal X-ray structure analysis for the parent hydrocarbon phenanthreno[2.2]paracyclophane (**5**) is reported.

Introduction

For some time[1] we have been interested in building more complex molecular structures from the two archetypal layered compounds in organic and organometallic chemistry: [2.2]paracyclophane (**1**) and ferrocene (**2**). We have combined these two building elements to furnish, inter alia, extended rigid structures such as **3**[2] and, more recently, flexible metallocenophanes such as **4** (Scheme 1).[3]

Whereas the metallocenophanes **3** are achiral, the derivatives **4** are chiral (whether R = H or not), making them interesting candidates as catalysts in stereoselective polymerization reactions.[3] In this paper we would like to present still another approach to chiral metallocenophanes, which exploits the helicity of angularly annelated paracyclophanes. Although we have still not attained our synthetic goals, we have proceeded far enough along the route to novel helical cyclophane ligands to discuss our first results in this area.

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Results and Discussion

Design of Helical Cyclophane Ligands

The starting point of our considerations is [2.2](1,4)phenanthrenoparacyclophane (**5**),[4,5] the parent hydrocarbon of all angularly annelated [2.2]cyclophanes. A five-membered ring may be annelated to its phenanthrene deck in several ways; two such possibilities are shown as **6** and **7** in Scheme 2. In the former case a "closed" structure results, resembling that of many other helicenes incorporating a five-membered ring element.[6] In alternative **7**, the resulting structure is more open. Finally, when the two non-bridged six-membered rings of **5** are "separated" by a five-membered ring, the result is hydrocarbon **8**, which formally contains a fluorene unit. Needless to say, the annelation process can in principle be extended and numerous variations are conceivable, allowing the deliberate design of a metallocenophane ligand with a predetermined geometry. If the benzo layer of **5** is also replaced by an angularly annelated structural element, hydrocarbons such as **9** can result. In fact, we have recently described the first synthesis of the parent molecule of **9** − i.e., the hydrocarbon without the condensed five-membered rings − and various of its geometrical isomers.[4]

Ligands such as **9** are related to the helicenes **10** investigated thoroughly by Katz and co-workers, who also have been successful in converting these into chiral metallocenes.[7,8] The main difference between the structures discussed here and those described by the American authors is that our helicenes contain an additional "step" provided by the [2.2]paracyclophane nucleus, through which the helical annelation is continued at a "higher level". Whereas helicenophanes such as **5**−**7** are always chiral, regardless of the number of annelated rings, the situation can be different

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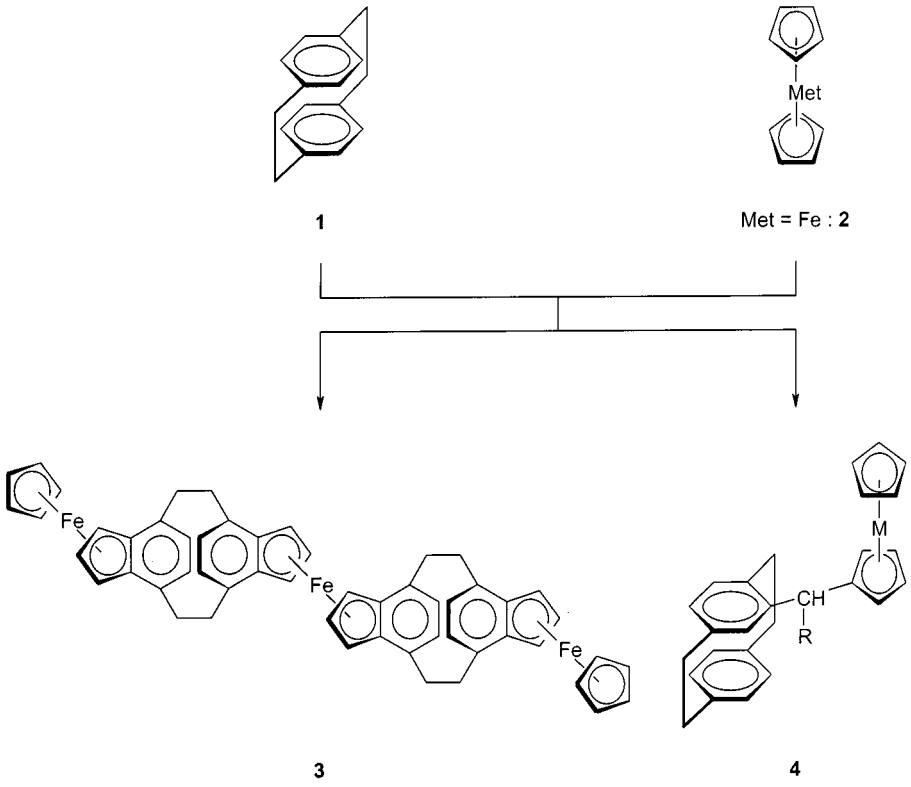
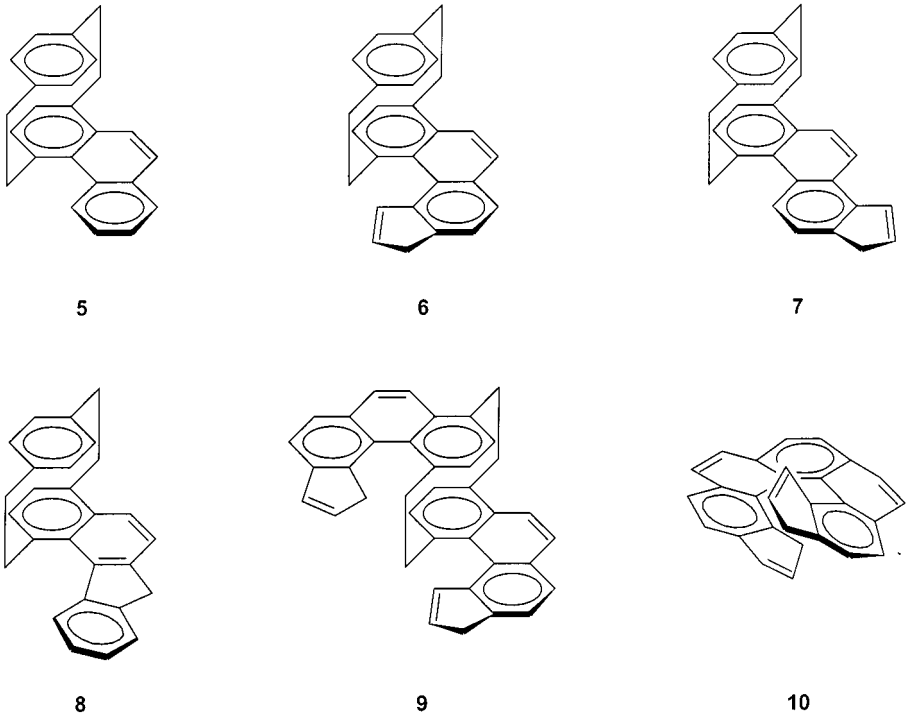


Scheme 1. Construction of structurally complex metallocenophanes from **1** and **2**



Scheme 2. From phenanthrenophane **5** to helicenophanes containing five-membered rings

for isomers of **9**, which can possess a center of symmetry. To investigate the spectroscopic, stereochemical, and chemical consequences of this introduction of a step in an otherwise continuous helix has been and remains one of the purposes of our investigations.

Hydrocarbon **5** was previously prepared by us in racemic form by photochemical ring-closure of 4-styryl[2.2]paracyclophane.[5] At that time we were unable to determine its structure by X-ray crystallography, due to poor crystal quality. However, if this very simple helicenophane were to

be used as a building element for larger structures, it would be highly desirable to know its degree of helicity (pitch, deviation of planarity of the phenanthrene ring). Fortunately, we have now been successful in obtaining single crystals of (+)-**5** suitable for X-ray structural analysis, and its structure in the crystal is shown in Figure 1.

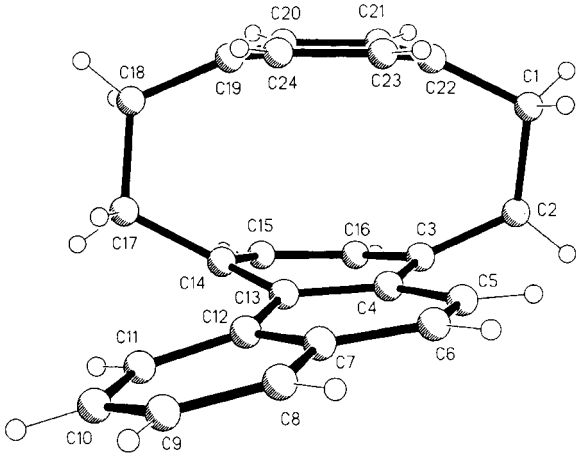


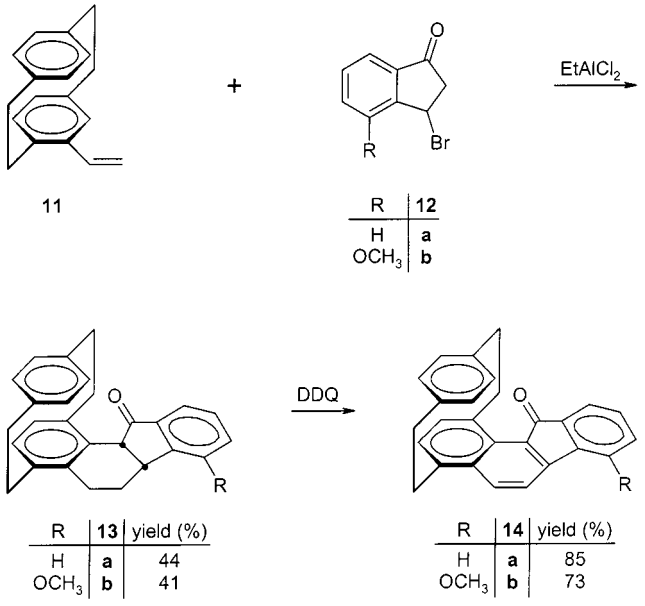
Figure 1. Structure of (+)-**5** in the crystal; radii of hydrogen atoms are arbitrary

Compound **5** crystallizes with one independent molecule, in the chiral space group $P2_1$. The relative configuration of the measured crystal of **5** was determined as (4*S*, 13*S*). The absolute configuration cannot be determined crystallographically. The [2.2]paracyclophane skeleton shows the characteristic features of the parent compound. The aromatic rings are puckered, resulting in a boat conformation. The planes for the four coplanar carbon atoms of each ring are markedly twisted with respect to each other. This distortion, represented by the torsion angle C(17)···C(2)−C(1)···C(18), amounts to 36.4(2)°, in contrast to 0° in the unsubstituted parent compound (crystallographic inversion symmetry). The phenanthrene moiety causes the bridgehead carbon atom C(14) to be more distinctly bent (by 18.9(2) pm) out of the plane of the four coplanar C atoms − C(4), C(13), C(15), and C(16) − than the other three bridgeheads [14.4(5) (C19) to 14.8(4) pm (C22)].

The C(11)−C(12)−C(13)−C(14) torsion angle of the phenanthrene bay area in **5** amounts to 19.0(4)°. Additionally, the C(11)−C(12)−C(13) and C(12)−C(13)−C(14) bond angles in this area are larger than those in phenanthrene itself: 123.5(2)° and 123.1(2)°, respectively. The rings of the phenanthrene moiety have different conformations. The C(3)−C(4)−C(13)−C(14)−C(15)−C(16) ring shows the boat conformation typical of [2.2]paracyclophanes. The slightly helical structure of (**5**) is reflected in a half-boat conformation for the next ring with five coplanar atoms C(4), C(5), C(6), C(7), and C(12) (mean deviation: 1.6 pm). The carbon atom C(13) lies 11.5(4) pm out of this plane. The final ring [C(7) to C(12)] is nearly planar (mean deviation: 2.3 pm). The bond lengths and angles in this part of the molecule correspond to the expected values for phenanthrenes.

Preparation of Helicenophanes Containing Five-Membered Rings

The first member of this novel type of [2.2]paracyclophane, the ketone **14**, was prepared by the route outlined in Scheme 3, by employment of a methodology developed in our laboratory that had already proved its worth during the syntheses of various polycyclic aromatic compounds and helicenes.[6a,6d,9]



Scheme 3. The preparation of the fluorenonophane **14a** and its methoxy derivative **14b**

To construct the carbon framework of the future helicenophane, Diels−Alder additions between the known[10] 4-vinyl[2.2]paracyclophane (**11**) and 2-inden-1-one and 4-methoxy-2-inden-1-one were carried out under various conditions. These dienophiles were obtained in situ from the bromoketones **12**, either by heating a toluene solution of them in the presence of ethylaluminium dichloride or in the presence of triethylamine under high pressure (9 kbar). As these experiments − listed in Table 1 − show, the conditions have a profound influence on the outcome of the process.

The best yields, 44% and 41%, respectively, were obtained when indenones **12a** and **12b** were treated with ethylaluminium dichloride as a catalyst[11] in refluxing toluene. These conditions regioselectively produced cycloadducts **13a** and **13b**. Drops in yield and regioselectivity were observed when the cycloaddition reactions were carried out under thermal and high pressure conditions. Omission of the ethylaluminium dichloride catalyst, with the cycloaddition between **11** and **12a** being performed in the presence of triethylamine in carbon tetrachloride, provided a 1:1.5 mixture of two compounds: **13a** and another product. Although the latter could be isolated neither by column chromatography nor by HPLC, it was tentatively considered to be the regioisomer of **13a** on the basis of GC/MS analysis, of the

Table 1. Diels–Alder reactions of 4-ethenyl[2.2]paracyclophane (**11**) with ketones **12**

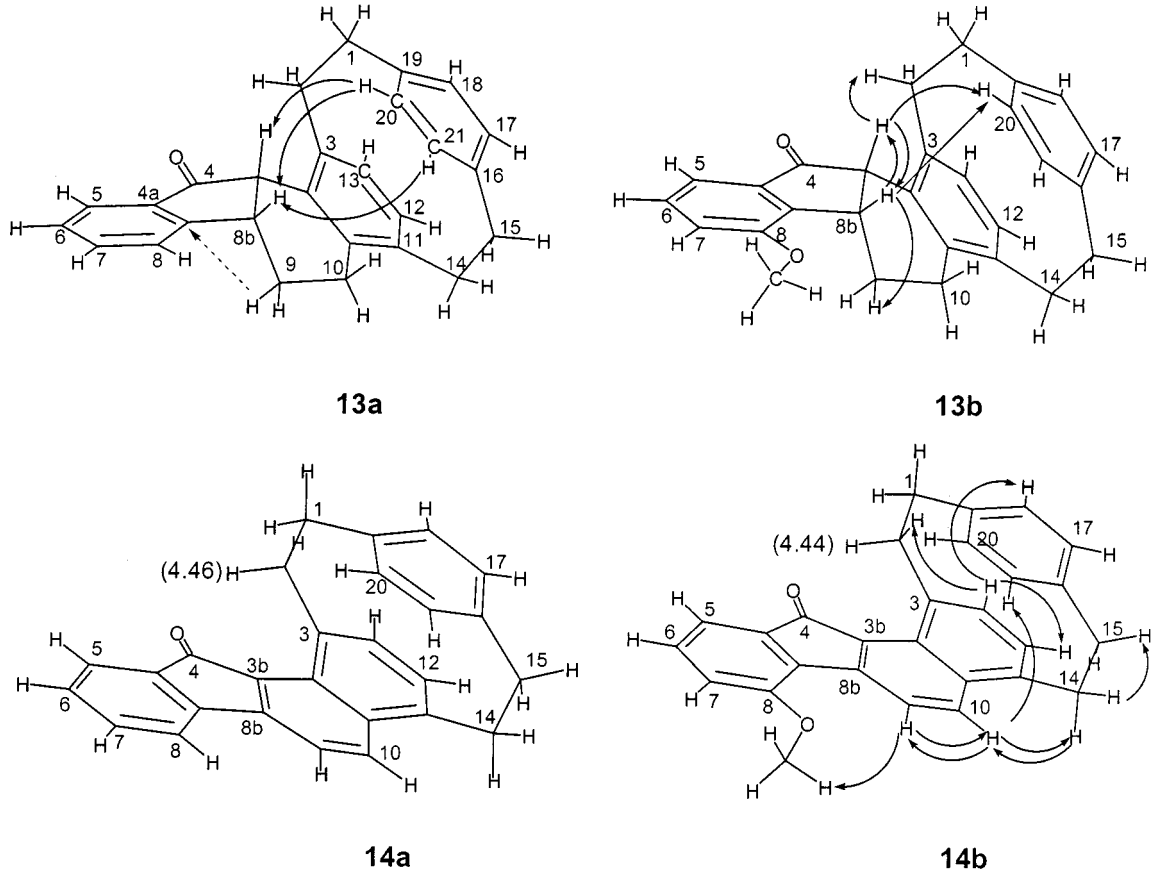
Ketone	Ketone/diene[a]	$EtAlCl_2$/ketone[a]	Reaction temp. (°C)	Reaction time (h)	Solvent	Pressure (kbar)	Product(s)	Yield (%)[b]
12a	1.1	0.25	reflux	24	toluene	–	**13a**	44
	1.1	0.25	50	16	CH_2Cl_2	9	**13a**	20[d]
	1.1[c]	–	reflux	48	CCl_4	–	**13a** 1:1.5[e]	7
	1.1[c]	–	50	16	CCl_4	9	**13a** 1:1.5[e]	20[f]
12b	1.1	0.25	reflux	24	toluene	–	**13a**	41
	1.1[c]	–	reflux	48	CCl_4	–	**14b** 1:1.2[e]	5
	1.5[c]	–	50	18	CCl_4	9	**14b** 1:1.2[e]	18

[a] Ratio of equivalents. – [b] The yields refer to isolated compounds. – [c] The reaction was accomplished using a bromoketone/triethylamine ratio of 1:1.3. – [d] A marked diene decomposition occurred when the reaction was performed under these conditions. – [e] Regioisomeric mixture. – [f] A longer reaction time caused partial aromatization of compound **13a** but no increase in the yield.

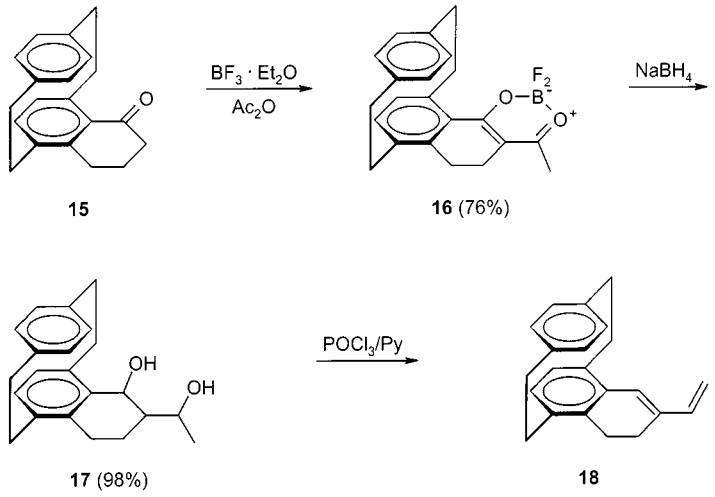
regiochemical outcome of the Diels–Alder reaction, and because DDQ oxidation of this mixture gave **14a** together with another product in 1:1.5 ratio. Unfortunately we could not separate these two products either. A similar situation was observed in the Diels–Alder cycloaddition of **11** and **12b**. These results indicate that whereas the catalyst[12] increases the yield and markedly effects the regiochemistry of the reaction, no effect is produced by high pressure.[13]

The exact structure determination of the cycloadducts **13**, in which the carbonyl group of the five-membered ring points toward one of the ethano-bridges, is based on extensive NMR investigations, especially the determination of various NOEs between easily identifiable protons. These results are summarized in Scheme 4.

The regiochemistry of the carbonyl function of **13a** follows from the observation that 9-H methylene protons do



Scheme 4. Minimized energy conformations of the derivatives **13** and **14**; the arrows indicate observed NOEs; dotted arrow indicates long-range hetero-correlation

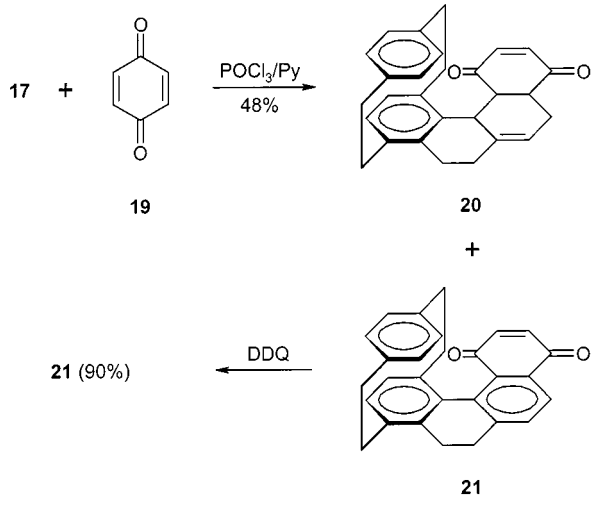


Scheme 5. Preparation of the diol **17**, a crucial intermediate for the preparation of more extended helicenophanes

not give long-range heterocorrelation with the carbonyl carbon, but rather with C(8a). The position of the carbonyl function of **13b** was deduced from the NOE effects on 2-H and 20-H observed upon selective irradiation of 3b-H, and also on the 9-H and 20-H protons upon selective irradiation of 8b-H.

Furthermore, for **13a**, the $^3J_{3b,8b}$ value of 6.9 Hz, together with the NOE effects observed on 3b-H and 8b-H on selective irradiation of 20-H and 21-H, indicates a *cis* stereochemical relationship between 3b-H and 8b-H and shows that these protons point toward the unsubstituted benzene ring of the paracyclophane unit, as depicted in Scheme 4.

In the case of compound **13b**, the assignment of the *cis* stereochemical relationship between 3b-H and 8b-H is based on the NOE effects observed between them. Furthermore, the NOEs on the 2-H and 20-H protons observed on irradiation of 3b-H, and on 9-H and 20-H on irradiation of 8b-H, confirm the *cis* stereochemical relationship between 3b-H and 8b-H, and show that these protons face the unsubstituted benzene ring of the paracyclophane unit, as also shown in Scheme 4. This thus indicates total *anti-endo* diastereoselectivity in the cycloaddition between **11** and **12**.



Scheme 6. Preparation of the helicenophane quinones **20** and **21**

When **13a/b** was refluxed in toluene in the presence of DDQ, aromatization was readily accomplished to provide the fluorenones **14a** and **14b** in good yields (85 and 73%, respectively). Again, structure assignment is based on thorough NMR correlation (see Scheme 4).

The regiochemistry of the carbonyl functions in fluorenones **14** is in agreement with the unusual downfield shift of the 2-H protons ($\delta = 4.46$ for **14a** and 4.44 for **14b**), due to the anisotropic effect of the carbonyl groups (Scheme 4). Furthermore, selective pre-irradiation of the 9-H resonance of **14b** resulted in signal enhancements of the resonance signals attributed to 10-H and the methoxy group protons, thus confirming the regiochemistry of the carbonyl function. Further support for the structure of **14b** was provided by the NOE enhancements observed on 9-H, 14-H, and 21-H on irradiation of 10-H, together with the other NOEs reported in Scheme 4.

One way to prepare more extended helicenophanes possessing five-membered ring units makes use of the diene **18**. The starting material was the ketone **15**, which was converted into diol **17** according to a procedure previously developed by us.[6b,6d] Treatment of **15** with boron trifluoride−diethyl ether in acetic anhydride yielded the BF_2−diketone complex **16** in 76% yield. When this was reduced with sodium borohydride in water, the diol **17** was isolated in almost quantitative yield (Scheme 5).

As shown by GLC analysis, **17** was produced as a mixture of isomers. This mixture, however, could be employed in subsequent steps without further purification or separation (see below). Although hydrocarbon **18** could indeed be prepared by treatment of **17** with phosphorus oxychloride/pyridine in refluxing toluene, it turned out to be so unstable that it could not be isolated in pure form. It was therefore generated in situ from the crude mixture of diols **17** during the cycloaddition step.

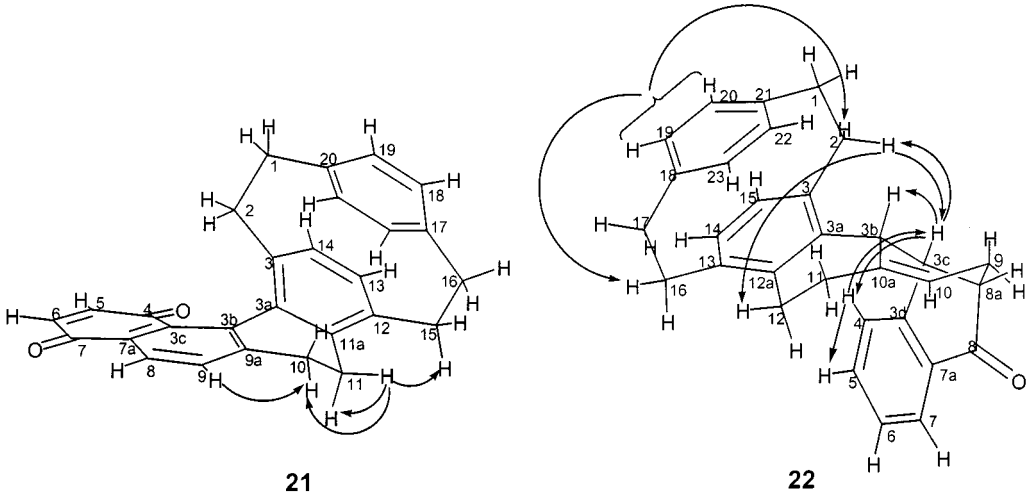
In an exploratory cycloaddition experiment, a mixture of the diols **17** was first refluxed in toluene for five hours in the presence of phosphorus oxychloride/pyridine, and then *p*-benzoquinone (**19**) was added as the dienophile. After heating of the reaction mixture under reflux for an additional 24 hours and workup, the products **20** and **21** were obtained in 48% overall yield in a ratio of 1:2.4, the latter clearly being an oxidation product of the former since *p*-benzoquinone also acts as an oxidant (Scheme 6). Since a complete separation of **20** and **21** by column chromatography could not be accomplished, the crude product mixture was dehydrogenated with DDQ. Although the quinone **21**, formed in 90% yield, and for which NOEs were again of invaluable help in providing unambiguous structural proof (see below), full aromatization to the corresponding [4]helicenophane quinone could not be achieved.

One reason for this failure might be excessively severe steric interactions between one methylene group of an ethano bridge of the phane and a quinone oxygen atom, in the event of complete aromatization being attained. In the dihydro derivative **21**, the presumably more flexible nonaromatic six-membered ring would allow these two groups to avoid each other more effectively.

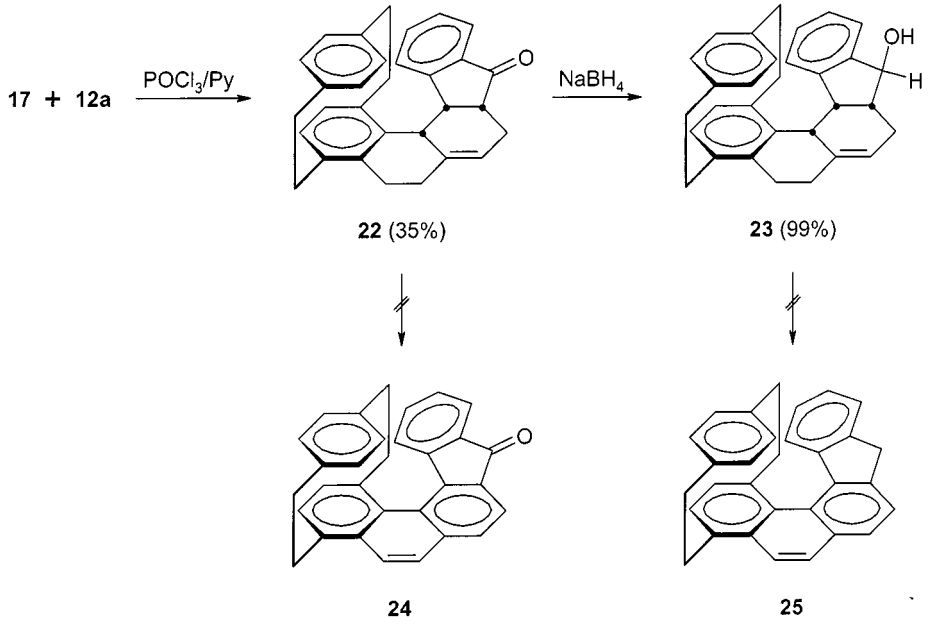
The structure proof for **21** is based on the ^{13}C multiplicities and on ^{1}H-{^{1}H} NOE experiments summarized in Scheme 7.

The NOE effects observed on protons 10-H and 15-H on irradiation of 11-H are diagnostic for confirmation of the C(10) and C(11) carbon atoms as secondary.

The possibility that high steric demand in our cycloadducts could indeed be a serious problem, which might even completely thwart this approach to these heliceno-



Scheme 7. Minimized energy conformations of the derivatives **21** and **22**; the arrows indicate observed NOEs



Scheme 8. Preparation of the partially hydrogenated helicenophane ketone **22**

phanes, is underlined by a cycloaddition experiment between **12a** and **17** under the above conditions (Scheme 8). Although the cycloaddition took place as expected, yielding the ketone **22** in 35% yield, all attempts to oxidize it to **24** with either benzoquinone or DDQ failed or resulted in destruction of the phane nucleus.

To assign the structure of **22**, extensive use was again made of NOE effects, which are also summarized in Scheme 7.

Selective pre-irradiation of the resonance due to 3c-H in ketone **22** resulted in enhancement of the resonance signals attributed to 2-H, 3b-H, and 4-H, indicating the regiochemistry of the carbonyl group at C(8) and a *cis* relationship between 3b-H and 3c-H; the values of relevant proton−proton coupling constants ($J_{3c,8c}$ = 6.5 Hz, $J_{3c,3b}$ = 6.8 Hz) confirmed the *cis* stereochemical relationship between 3c-H, 3b-H, and 8a-H.

Furthermore, the NOE enhancement on 2-H and 16-H observed on irradiation of both 19-H and 20-H, together with the NOE effects observed between 2-H and 3c-H, and 4-H and 3c-H are in agreement with the structure depicted in Scheme 7, indicating an *endo-anti* (with respect to the unsubstituted benzene ring of the paracyclophane unit) diastereoselectivity of the cycloaddition between **12a** and **17**.

When **22** was reduced to the alcohol **23** with sodium borohydride and this derivative was heated in triglyme or toluene over palladium on charcoal, again only negative results were achieved (destruction of the [2.2]paracyclophane system, possibly dehydration but not dehydrogenation as indicated by GC/MS-analysis).

Experimental Section

General: Melting points (uncorrected): Büchi melting point apparatus. − IR: Perkin−Elmer 983 in $CHCl_3$. − NMR: Varian Associates VXR-400 in $CDCl_3$, TMS as int. reference. ^1H and ^{13}C shift assignments are based on COSY, ^1H-{^1H}-NOE, and HETCOR experiments; quaternary carbon atoms were assigned by 2D long-range heterocorrelated experiments. − MS: Hewlett−Packard 5970 at 70 eV. − GC: Carlo Erba HRGC-5160 and Dani 8610. − For the X-ray crystallography of [2.2](1,4)phenanthrenoparacyclophane (**5**) (see below) a crystal of the (+)-enantiomer was used; the hydrocarbon was prepared from (+)-4-formyl[2.2]paracyclophane[14] by the procedure reported previously for the racemic compound.[5,15] − 4-Vinyl[2.2]paracyclophane (**11**) was prepared according to ref.[10] the bromo-ketones **12a** and **12b** according to ref.,[6a] and 6,7-dihydro-5*H*-[2.2](1,4)naphthalen-4-one-paracyclophane (**15**) according to ref.[16]

General Procedure for the Diels−Alder Reaction between the Ketones 12 and 4-Vinyl[2.2]paracyclophane (11): A hexane solution of $EtAlCl_2$ (1 M, 0.19 mL, 0.19 mmol) was added to a toluene (5 mL) solution of the ketone **12** (0.76 mmol) and the resulting mixture was stirred at room temp. for 30 min.[17] Subsequently, a toluene (1 mL) solution of diene **11** (0.68 mmol, 0.16 g) was added and the mixture was heated at reflux temperature for 24 h. After cooling to room temp., the reaction mixture was poured into ice-water, the layers were separated, and the aqueous layer was extracted thoroughly with dichloromethane. The combined organic extracts were washed with aqueous bicarbonate solution and dried (sodium sulfate). After removal of the solvents in vacuo, the crude cycloadduct **13** was purified by column chromatography on silica gel with hexane/ethyl acetate, 95:5 (v/v).

3b,8b,9,10-Tetrahydro-4*H*-indeno[1,2-*c*][2.2](1,4)naphthalen-4-one-paracyclophane (13a): 0.11 g (0.3 mmol, 44%), colorless plates (from hexane/ethyl acetate, 3:1) m.p. 170−171 °C. − IR: $\tilde{\nu}$ = 1716 cm^{-1} (C=O). − ^1H NMR: δ = 1.06 (ddd, J_1 = 12.5, J_2 = 12.1, J_3 = 4.1 Hz, 9-H), 2.32 (m, 1 H, 9-H), 2.75 (m, 1 H, 10-H), 2.81 (m, 1 H, 2-H), 2.91−3.16 (m, 4 H, 14-H, 15-H), 3.21 (m, 1 H, 2-H), 3.46 (m, 2 H, 1-H), 3.58 (ddd, J_1 = 12.1, J_2 = 6.9, J_3 = 4.3 Hz, 1 H, 8b-H), 3.63 (m, 1 H, 3b-H), 6.44 (d, J = 7.6 Hz, 1 H, 13-H), 6.49 (dd, J_1 = 7.9, J_2 = 1.8 Hz, 1 H, 20-H), 6.56 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 18-H), 6.60 (d, J = 7.6 Hz, 1 H, 12-H), 6.61 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 17-H), 6.81 (dd, J_1 = 7.9, J_2 = 1.8 Hz, 1 H, 21-H), 7.40 (dd, J_1 = 7.7, J_2 = 6.8 Hz, 1 H, 6-H), 7.59 (dd, J_1 = 7.0, J_2 = 1.3 Hz, 1 H, 8-H), 7.64 (dd, J_1 = 7.0, J_2 = 6.8 Hz, 1 H, 7-H), 7.78 (dd, J_1 = 7.7, J_2 = 1.1 Hz, 1 H, 5-H). − ^{13}C NMR: δ = 27.7 (C-10), 31.5 (C-9), 32.6, 33.49, 33.51, 33.52 (C-1, C-2, C-14, C-15), 39.1 (C-8b), 51.9 (C-3b), 124.7 (C-5), 125.2 (C-8), 126.8 (C-20 or C-21), 127.8 (C-20 or C-21), 127.9 (C-6), 130.6 (C-3), 132.0, 132.1 (C-12, C-13), 133.3, 133.7 (C-17, C-18), 134.4 (C-7), 134.8, 134.8 (C-3a, C-4a), 138.2 (C-11), 139.1, 139.5 (C-16, C-19), 140.3 (C-10a), 157.4 (C-8a), 202.1 (C-4). − MS: *m*/*z* (%) = 364 [M^+] (100), 260 (53), 245 (37), 231 (12), 215 (29), 202 (25), 104 (19), 78 (8). − $C_{27}H_{24}O$ (364.5): calcd. C 88.97, H 6.64; found C 88.21, H 6.60.

3b,8b,9,10-Tetrahydro-8-methoxy-4*H*-indeno[1,2-*c*][2.2](1,4)-naphthalen-4-one-paracyclophane (13b): 0.11 g (2.8 mmol, 41%), pale yellow plates (from hexane/ethyl acetate, 4:1) m.p. 235−236 °C. − IR: $\tilde{\nu}$ = 1717 cm^{-1} (C=O). − ^1H NMR: δ = 0.87 (dd, J_1 = 12.5, J_2 = 4.1 Hz, 9-H), 2.42 (ddd, J_1 = 16.5, J_2 = 12.5, J_3 = 3.9 Hz, 10-H), 2.51 (m, 1 H, 9-H), 2.77 (m, 1 H, 10-H), 2.82 (m, 1 H, 2-H), 2.88−3.16 (m, 4 H, 14-H, 15-H), 3.21 (m, 1 H, 2-H), 3.40 (m, 4 H, 1-H, 15-H), 3.53 (d, J = 6.9 Hz, 1 H, 3b-H), 3.68 (ddd, J_1 = 12.0, J_2 = 6.9, J_3 = 4.4 Hz, 1 H, 8b-H), 3.98 (s, 3 H, OMe), 6.44 (d, J = 7.7 Hz, 1 H, 13-H), 6.49 (dd, J_1 = 8.0, J_2 = 1.7 Hz, 1 H, 20-H), 6.56 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 18-H), 6.60 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 17-H), 6.61 (d, J = 7.7 Hz, 1 H, 12-H), 6.86 (dd, J_1 = 8.0, J_2 = 1.7 Hz, 1 H, 21-H), 7.09 (dd, J_1 = 6.8, J_2 = 2.0 Hz, 1 H, 7-H), 7.36 (dd, J_1 = 7.7, J_2 = 6.8 Hz, 1 H, 6-H), 7.39 (dd, J_1 = 7.7, J_2 = 2.0 Hz, 1 H, 5-H). − ^{13}C NMR: δ = 28.0 (C-10), 29.2 (C-9), 32.9, 33.5, 33.5, 33.5 (C-1, C-2, C-14, C-15), 36.2 (C-8b), 52.1 (C-3b), 55.6 (OMe), 115.1 (C-7), 116.3 (C-5), 126.8 (C-21), 127.8 (C-20), 129.1 (C-6), 130.7 (C-3), 131.9 (C-13), 131.9 (C-12), 133.2 (C-18), 133.7 (C-17), 136.3 (C-4a), 136.3 (C-3a), 138.3 (C-11), 139.1 (C-19), 139.4 (C-16), 140.3 (C-10a), 145.7 (C-8a), 202.1 (C-4). − MS: *m*/*z* (%) = 394 [M^+] (100), 290 (43), 275 (24), 247 (12), 231 (9), 215 (12), 202 (12), 189 (7), 104 (17), 78 (5). − $C_{28}H_{26}O_2$ (394.5): calcd. C 85.25, H 6.64; found C 84.82, H 6.65.

When the cycloadditions were performed under high pressure (9 kbar) without catalyst and in the presence of triethylamine to generate the dienophile in situ, a mixture of two compounds was obtained (see Table 1, main section). The minor component was identified as **13a** or **13b** by comparison with a pure sample, while the major component was probably the respective regioisomer, as shown by GC/MS analysis. The latter adduct could not be isolated in pure form because of the low yields of the cycloadditions (generally in the 18−20% range).

General Procedure for the DDQ Oxidation of Derivatives 13: A toluene solution (10 mL) of compound **13** (0.26 mmol) was treated with

DDQ (0.38 g, 1.67 mmol) at reflux temperature for 21 h. The reaction mixture was cooled to room temp. and diluted with diethyl ether, and the organic layer was washed with saturated aqueous sodium thiosulfate solution, 10% aqueous sodium hydroxide solution, and brine. After drying (magnesium sulfate), the solvent was removed in vacuo and the crude product **14** was chromatographed on silica gel with hexane/ethyl acetate (95:5).

4*H*-Indeno[1,2-*c*][2.2](1,4)naphthalen-4-one-paracyclophane (14a): 0.079 g (0.22 mmol, 85%), yellow needles (from hexane/ethyl acetate, 3:1) m.p. 212−213 °C. − IR: $\tilde{\nu}$ = 1702 cm^{-1} (C=O). − ^1H NMR: δ = 2.72 (m, 1 H, 1-H), 2.92 (m, 1 H, 15-H), 2.94 (m, 1 H, 1-H), 3.02 (m, 1 H, 14-H), 3.13 (m, 1 H, 2-H), 3.19 (m, 1 H, 15-H), 3.74 (m, 1 H, 14-H), 4.46 (m, 1 H, 2-H), 5.75 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 21-H), 5.78 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 20-H), 6.54 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 1 H, 18-H), 6.57 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 1 H, 17-H), 6.67 (d, J = 7.2 Hz, 1 H, 12-H), 6.83 (d, J = 7.2 Hz, 1 H, 13-H), 7.27 (dd, J_1 = 7.2, J_2 = 7.1 Hz, 1 H, 6-H), 7.45 (dd, J_1 = 7.3, J_2 = 7.1 Hz, 1 H, 7-H), 7.52 (dd, J_1 = 7.3, J_2 = 1.1 Hz, 1 H, 5-H), 7.60 (dd, J_1 = 7.2, J_2 = 1.1 Hz, 1 H, 8-H), 7.61 (d, J = 8.3 Hz, 1 H, 9-H), 7.87 (d, J = 8.3 Hz, 1 H, 10-H). − ^{13}C NMR: δ = 33.4 (C-14), 34.4 (C-15), 34.8 (C-1), 37.0 (C-2), 117.0 (C-9), 119.6 (C-5), 123.9 (C-8), 128.1 (C-20 or C-21), 129.2 (C-6), 129.8 (C-20 or C-21), 129.3 (C-3 or C-3a), 131.3 (C-3 or C-3a), 131.9 (C-12), 131.8 (C-17 or C-18), 132.0 (C-17 or C-18), 133.0 (C-10), 134.1 (C-7), 134.5 (C-4a), 136.3 (C-13), 137.0 (C-10a or C-11), 137.1 (C-16 or C-19), 137.6 (C-16 or C-19), 137.8 (C-3b), 139.5 (C-10a or C-11), 143.6 (C-8b), 145.7 (C-8a), 193.6 (C-4). − MS: *m*/*z* (%) = 360 [M^+] (29), 326 (1), 256 (100), 238 (1), 202 (2), 200 (3), 104 (6), 78 (3). − $C_{27}H_{20}O$ (360.4): calcd. C 89.97, H 5.59; found C 90.25, H 5.62.

8-Methoxy-4*H*-indeno[1,2-*c*][2.2](1,4)naphthalen-4-one-paracyclophane (14b): 0.074 g (0.19 mmol, 73%), orange needles (from hexane/ethyl acetate, 4:1) m.p. 260−261 °C. − IR: $\tilde{\nu}$ = 1701 cm^{-1} (C=O). − ^1H NMR: δ = 2.72 (m, 1 H, 1-H), 2.92 (m, 1 H, 15-H), 2.95 (m, 1 H, 1-H), 3.04 (m, 1 H, 14-H), 3.18 (m, 1 H, 2-H), 3.20 (m, 1 H, 15-H), 3.74 (m, 1 H, 14-H), 4.04 (s, 3 H, OMe), 4.44 (m, 1 H, 2-H), 5.77 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 21-H), 5.82 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 20-H), 6.54 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 18-H), 6.58 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 17-H), 6.66 (d, J = 7.3 Hz, 1 H, 12-H), 6.82 (d, J = 7.3 Hz, 1 H, 13-H), 7.04 (m, 1 H, 7-H), 7.25 (m, 2 H, 5-H, 6-H), 7.85 (d, J = 8.4 Hz, 1 H, 10-H), 8.03 (d, J = 8.4 Hz, 1 H, 9-H). − ^{13}C NMR: δ = 33.4 (C-14), 34.4 (C-15), 34.8 (C-1), 37.0 (C-2), 55.7 (OMe), 116.3 (C-5), 117.6 (C-7), 121.2 (C-9), 128.1 (C-21), 128.5.9 (C-3 or C-3a), 129.9 (C-20), 130.6 (C-6), 131.2 (C-3 or C-3a), 131.6, 131.7, 131.9 (C-12, C-17, C-18), 133.0 (C-10), 133.0 (C-8a), 136.1 (C-13), 136.3 (C-4a), 136.8 (C-10a or C-11), 136.9 (C-3b), 137.1 (C-19), 137.6 (C-16), 139.5 (C-10a or C-11), 145.8 (C-8b), 155.0 (C-8), 193.7 (C-4). − MS: *m*/*z* (%) = 390 [M^+] (25), 286 (100), 242 (14), 213 (11), 189 (4), 104 (10), 78 (5), 44 (5). − $C_{28}H_{22}O_2$ (390.5): calcd. C 86.13, H 5.68; found C 86.61, H 5.70.

5-Ethenyl-6,7-dihydro[2.2](1,4)naphthalenoparacyclophane (18). − a) BF_2−Diketone Complex 16: BF_3-Et_2O (0.7 mL) was added to a stirred mixture of ketone **15**[16] (1 g, 3.62 mmol) and dry acetic anhydride (1.38 mL). Stirring was continued for 2 h at 65 °C and then at reflux temperature for 1.5 h. After standing at room temp. overnight, the precipitate was triturated with cold diethyl ether, filtered, and washed with cold diethyl ether to give the yellow crystalline BF_2-diketone complex **16** in 76% overall yield (1 g, 2.73 mmol), m.p. 215−219 °C (diethyl ether). − ^1H NMR: δ = 2.25 (s, 3 H, Me), 2.50−3.29 (m, 10 H), 4.20 (m, 2 H), 6.38−6.73 (m, 6 H). − MS: *m*/*z* (%) = 366 [M^+] (100), 286 (70), 261 (38), 104 (92), 43 (12).

b) Diol 17 (Mixture of Isomers): A solution of sodium borohydride (0.68 g, 17.95 mmol) in water (11 mL) was added to a refluxing solution of the complex **16** (1.00 g, 2.73 mmol) in 28 mL of ethanol. The mixture was allowed to reflux for 2.5 h, half of the solvent was evaporated at reduced pressure, and the remaining part was extracted with trichloromethane. The combined extracts were washed with saturated brine solution and dried (sodium sulfate). After removal of the solvents the mixture of diols **17** (0.87 g, 98%) was used in the next step without further purification.

c) 5-Ethenyl-6,7-dihydro[2.2](1,4)naphthalenoparacyclophane (18): Anhydrous pyridine (0.35 mL) and $POCl_3$ (0.29 mL, 0.51 g, 3.34 mmol) were added to a solution of the diols **17** (0.87 g, 2.67 mmol) in 35 mL of anhydrous toluene. The reaction mixture was heated under reflux for 5 h under nitrogen, allowed to cool to room temp., and poured into ice-water. After thorough extraction with diethyl ether, the combined extracts were dried ($MgSO_4$), and the solvent was evaporated to yield crude **18**. Because of its low stability, the diene could not be purified for characterization. It was hence generated in situ from **17** during the cycloaddition process. − MS: *m*/*z* (%) = 286 [M^+] (53), 227 (1), 182 (100), 167 (25), 152 (10), 104 (3), 78 (1).

Treatment of the Diols 17 with *p*-Benzoquinone (19): Anhydrous pyridine (0.17 mL), $POCl_3$ (0.14 mL, 1.61 mmol), and a few crystals of hydroquinone were added to a solution of the diols **17** (0.43 g, 1.34 mmol) in anhydrous toluene (15 mL). The reaction mixture was heated at reflux temperature for 5 h, followed by addition of *p*-benzoquinone (**19**, 1.39 g, 13.4 mmol). After the mixture had been heated under reflux for 24 h, excess **19** was removed by steam distillation, and the resulting residue was extracted with trichloromethane. Conventional workup yielded solid crude adduct, which was chromatographed on silica gel with hexane/ethyl acetate, 98:2 (v/v) to afford pure **21** (0.065 g, 0.16 mmol) and 0.19 g (0.49 mmol) of a 1:1.5 mixture of **20** and **21**, in 48% overall yield.

10,11-Dihydrobenzo[g][2.2](1,4)phenanthrene-4,7-quinone-paracyclophane (21): 0.065 g (0.16 mmol, 12%), red needles (from hexane/ethyl acetate, 3:1) m.p. 202−203 °C. − IR: $\tilde{\nu}$ = 1664 cm^{-1} (C=O). − ^1H NMR: δ = 2.50 (ddd, J_1 = 15.0, J_2 = 14.8, J_3 = 5.2 Hz, 11-H), 2.83−2.92 (m, 5 H, 1-H, 2-H, 10-H, 15-H, 16-H), 3.02 (ddd, J_1 = 15.0, J_2 = 5.4, J_3 = 2.0 Hz, 1 H, 11-H), 3.07−3.39 (m, 5 H, 1-H, 2-H, 10-H, 15-H, 16-H), 6.08 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 22-H), 6.34 (m, 1 H, 14-H), 6.38 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 21-H), 6.39 (m, 1 H, 13-H), 6.70 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 19-H), 6.75 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1 H, 18-H), 6.86 (d, J = 9.8 Hz, 1 H, 6-H), 6.91 (d, J = 9.8 Hz, 1 H, 5-H), 7.61 (m, 1 H, 9-H), 7.98 (d, J = 7.8 Hz, 1 H, 8-H). − ^{13}C NMR: δ = 24.0 (C-11), 28.5 (C-10), 32.5, 33.3, 34.9, 35.1 (C-1, C-2, C-15, C-16), 125.2 (C-8), 126.1 (C-4), 130.8 (C-22), 130.9 (C-3), 131.6 (C-18), 131.62 (C-3c), 132.0 (C-9), 131.98 (C-7a), 132.1 (C-13), 133.1 (C-19), 133.2 (C-14, C-21), 134.7 (C-3b), 135.0 (C-12 or C-3a), 136.1 (C-3a or C-12), 136.8 (C-6), 139.4 (C-7 or C-20), 139.7 (C-17 or C-20), 140.5 (C-5), 146.8 (C-9a), 185.0 (C-7). − $C_{28}H_{22}O_2$ (390.5): calcd. C 86.13, H 5.68; found C 86.59, H 5.65.

DDQ Oxidation of the 20:21 Mixture: DDQ (0.76 g, 12.1 mmol) was added to a solution of the crude mixture of compounds **20** and **21** (0.19 g) in toluene (10 mL). The reaction mixture was heated at reflux temperature under nitrogen for 6 h and worked up as usual to afford derivative **21** in 90% yield.

Treatment of Diols 17 with 3-Bromoindan-1-one (12a): A solution of pyridine (0.18 mL) and $POCl_3$ (0.14 mL, 1.61 mmol) in 3 mL of carbon tetrachloride was added at reflux temperature under nitrogen to a stirred solution of **12a** (0.36 g, 1.70 mmol), the diols **17**

(0.4 g, 1.23 mmol), and a few crystals of hydroquinone in carbon tetrachloride (7 mL). After 24 h, the reaction mixture was allowed to cool to room temp. and worked up as described above to afford a solid residue, which was chromatographed on silica gel with hexane/ethyl acetate, 4:1 (v/v): 0.18 g (0.43 mmol, 35%) of **3b,3c,8a,9,11,12-hexahydro-8*H*-indeno[2,1-*c*](1,4)phenanthren-8-one-paracyclophane** (**22**), colorless plates, m.p. 253−254 °C (dichloromethane/ethyl acetate, 1:3, v/v). − IR: $\tilde{\nu}$ = 1705 cm^{-1} (C=O). − ^1H NMR: δ = 1.08 (ddd, J_1 = 15.2, J_2 = 14.7, J_3 = 4.1 Hz, 12-H), 2.10 (m, 1 H, 11-H), 2.38 (m, 1 H, 9-H), 2.50 (m, 2 H, 11-H, 12-H), 2.83 (ddd, J_1 = 13.4, J_2 = 9.6, J_3 = 4.8 Hz, 1 H, 16-H), 2.88 (ddd, J_1 = 14.4, J_2 = 7.5, J_3 = 1.8 Hz, 1 H, 9-H), 2.98 (ddd, J_1 = 7.1, J_2 = 6.5, J_3 = 1.8 Hz, 1 H, 8a-H), 3.00−3.25 (m, 5 H, 2 × 1-H, 2-H, 2 × 17-H), 3.26 (m, 1 H, 16-H), 3.61 (ddd, J_1 = 13.3, J_2 = 9.67, J_3 = 2.3 Hz, 2-H), 3.80 (dd, J_1 = 7.8, J_2 = 6.5 Hz, 1 H, 3c-H), 3.81 (dd, J_1 = 6.8, J_2 = 2.0 Hz, 1 H, 3b-H), 5.25 (d, J = 7.9 Hz, 1 H, 4-H), 5.62 (ddd, J_1 = 7.5, J_2 = 3.2, J_3 = 2.0 Hz, 1 H, 10-H), 6.43 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 23-H), 6.47 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 22-H), 6.50 (d, J = 7.6 Hz, 1 H, 15-H), 6.54 (d, J = 7.6 Hz, 1 H, 14-H), 6.61 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 20-H), 6.64 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1 H, 19-H), 6.94 (ddd, J_1 = 7.9, J_2 = 7.3, J_3 = 1.4 Hz, 1 H, 5-H), 7.10 (ddd, J_1 = 7.6, J_2 = 7.3, J_3 = 0.9 Hz, 1 H, 6-H), 7.53 (dd, J_1 = 7.6, J_2 = 1.4 Hz, 1 H, 7-H). − ^{13}C NMR: δ = 24.5 (C-12), 25.2 (C-9), 28.2 (C-11), 32.4 (C-16), 33.0 (C-2), 34.6 (C-1, C-17), 39.5 (C-3b), 46.0 (C-3c), 48.2 (C-8a), 119.7 (C-10), 122.2 (C-7), 127.07 (C-4), 127.08 (C-6), 130.4, 131.1, 133.0, 133.1, (C-19, C-20, C-22, C-23), 133.02, 133.32 (C-14, C-15), 133.7 (C-5), 135.1 (C-3a), 137.1, 137.4, 137.6, 138.7 (C-3, C-13, C-18, C-21), 139.0, 139.3, 139.4 (C-7a, C-10a, C-12a), 155.1 (C-3d), 209.7 (C-8). − MS: *m/z* (%) = 416 [M^+] (41), 388 (6), 311 (19), 286 (4), 268 (5), 252 (6), 239 (5), 182 (100), 167 (38), 152 (15), 128 (9), 104 (19), 91 (4), 78 (6). − $C_{31}H_{28}O$ (416.5): calcd. C 89.38, H 6.78; found C 89.08, H 6.80.

Reduction of 22 to the Isomeric Alcohols 23: $NaBH_4$ (0.12 g) was added to a stirred solution of cycloadduct **22** (0.13 g, 0.31 mmol) in MeOH/CH_2Cl_2 (1:1, 8 mL). After the mixture had been stirred for 2 h at room temp., water was added and the mixture was extracted twice with dichloromethane. The extract was washed with water and dried (sodium sulfate), and the solvents were evaporated to give 0.12 g (0.31 mmol, 99%) of a mixture of isomeric alcohols **23**.

Attempts to convert the cycloadduct **22** or the mixture of isomeric alcohols **23** into the [5]cyclopentahelicenophanes **24** and **25** met with failure.

X-ray Crystal Structural Analysis of (+)-5: A summary of the crystal data, data collection, and refinement parameters for the crystal structure of **5** is given in Table 2. A cut tablet was mounted on a glass fiber in inert oil and transferred to the cold gas stream of a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low-temperature attachment. Data were collected with ω/2θ-scans using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). Friedel-opposite reflections were merged. All unique data were used for calculations (program SHELXL-97, G. M. Sheldrick, University of Göttingen). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on F^2. The hydrogen atoms were refined with a riding model. Because **5** diffracted weakly, similarity restraints were applied to the *U* components.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168254. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data collection and refinement parameters for compound (+)-**5**.

Compound	**5**
Empirical formula	$C_{24}H_{20}$
Molecular mass	308.40
Crystal habit	colorless tablet
Crystal size (mm)	0.76 × 0.46 × 0.19
Crystal system	monoclinic
Space group	$P2_1$
Cell constants:	
a (pm)	782.7(2)
b (pm)	990.8(2)
c (pm)	1102.3(2)
α (°)	90
β (°)	105.14(2)
γ (°)	90
V (nm^3)	0.8252
Z	2
D_x (Mg m^{-3})	1.241
μ (mm^{-1})	0.070
F(000)	328
T (°C)	−130
$2\theta_{max}$	55
No. of reflections:	
measured	3487
unique	2013
R_{int}	0.036
Parameters	217
Restraints	237
$wR(F^2$, all refl.)	0.107
$R(F, >4\sigma(F))$	0.048
S	1.06
max. Δρ (e·Å^{-3})	0.19

Acknowledgments

This work was partially supported by the Fonds der Chemischen Industrie, Frankfurt am Main. A.T., A.M. and L.M. thank the MURST and CNR for financial support. E. G.-B. thanks the Hungarian Academy of Sciences.

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Received June 5, 2001
[O01269]