HETEROCYCLES, Vol. 54, No. 1, 2001, pp. 249 - 257, Received, 8th May, 2000

[2_2]METACYCLOPHANEDIENES WITH FURAN BRIDGES

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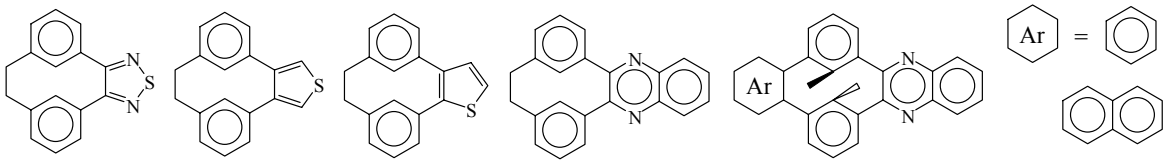
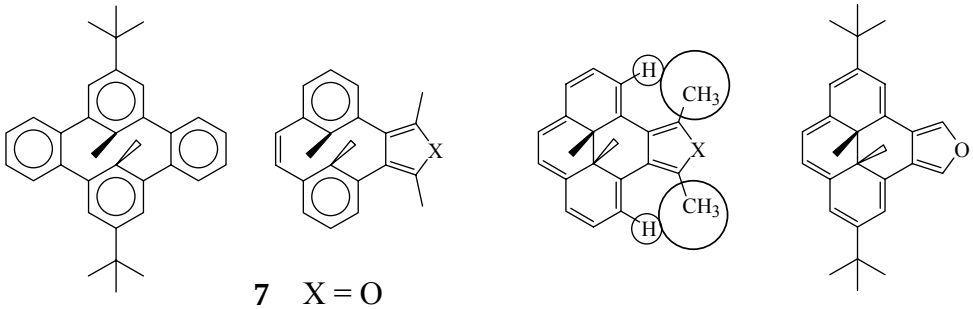
Abstract - [2_2]Metacyclophanedienes with either one furan and one benzene or two furans on the bridges are thermally stable and do not convert to their isomeric dihydropyrenes, unlike the compounds with one furan or one benzene on the bridge.

Huge numbers of cyclophanes have been prepared.[1] However, surprisingly few have heterocycles on the bridges. In the case of [2_2]metacyclophanes, four are known, **1-4**. Oxidation of **1** gave the pyrene,[2] while **2-4** were prepared for chirality studies.[3] Five cyclophanediene derivatives are also known: we prepared the benzo- and naphthoquinoxalino derivatives **(5)** in 1986,[4] and were somewhat surprised when they did not easily close



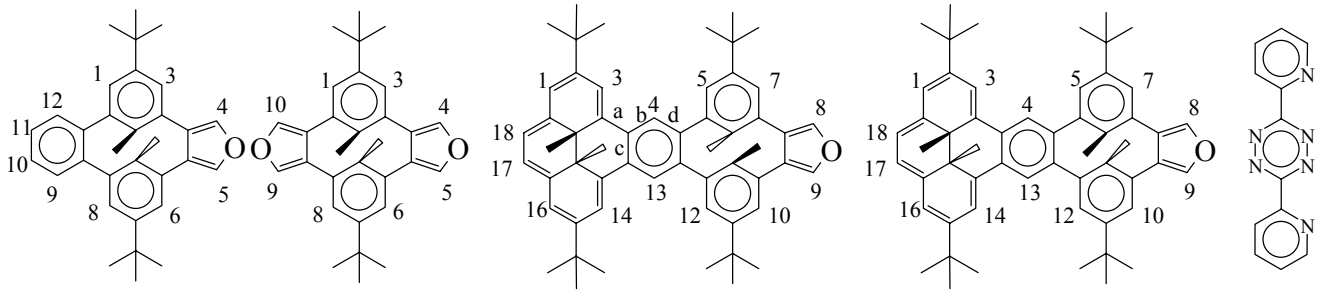
1 **2** **3** **4** **5**

to the analogous dihydropyrenes. Only later, when we prepared[5] the dibenzo derivative (**6**) did we understand that the heterocycle was not stopping the cyclophanediene-dihydropyrene interconversion.[6] Lai was the first to prepare a [2_2]metacyclophanediene with a furan (**7**)[7] or pyrrole (**8**)[8] on the bridge. Interestingly, the steric



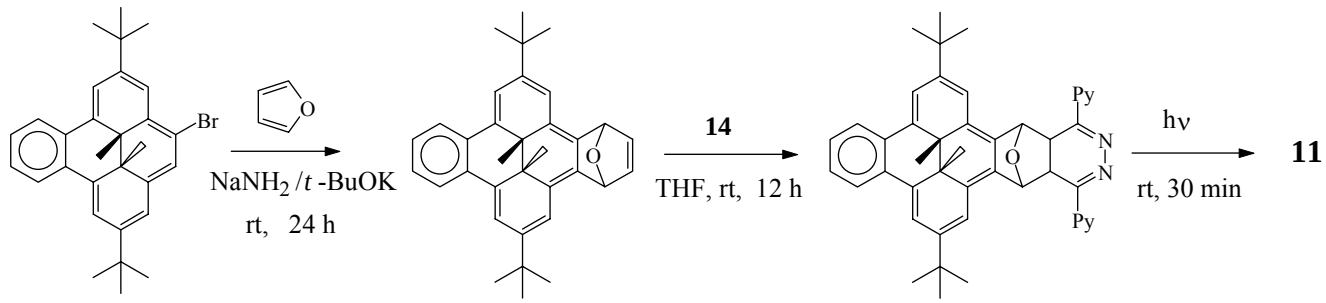
6 **7** X = O **8** X = N-c-Hexyl **9** **10**

interaction between the heterocycle-methyl hydrogens and the dihydropyrene hydrogens, shown in the closed form (**9**), destabilise the dihydropyrene relative to the cyclophanediene, making the latter the major product of the thermal equilibrium, and thus make **7** or **8** isolable. In contrast, in the absence of these methyl groups, we have shown[9] that the closed form, dihydropyrene (**10**) is thermally stable. This paper reports the syntheses of the furano-benzocyclophanediene (**11**), the bis-furanocyclophanediene (**12**), and the furano-annuleno-cyclophanedienes (**13a,b**), all of which exist as the thermally stable cyclophanediene valence isomers.



11 **12** **13a** **13b** **14**

Syntheses: Warrener=s[10] exceptionally useful and mild conversion of a Diels-Alder aryne-furan adduct with the dipyridyltetrazene (**14**) was the key synthetic step used to generate the furans (**11-13**). Thus reaction of

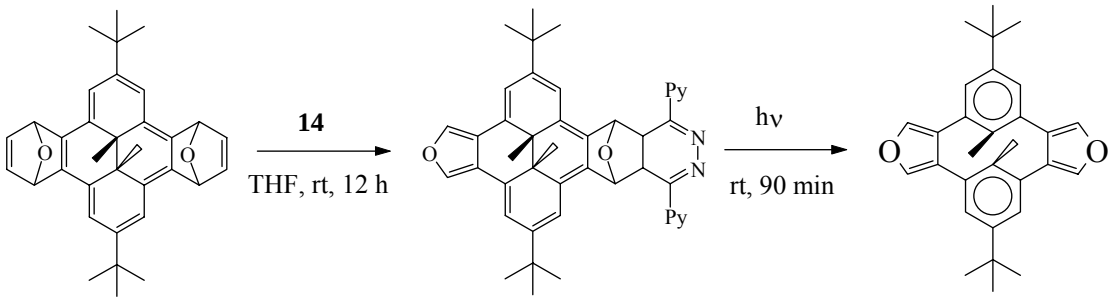


15 **16** **17**

the bromobenzodihydropyrene (**15**)[9] with $NaNH_2$ and a catalytic amount of potassium *tert*-butoxide in excess furan at room temperature for 24 h gave 41% of the orange-brown adduct (**16**), mp 212-213° C. Reaction of this with the tetrazene (**14**) in THF at room temperature for 12 h then gave the adduct (**17**), which did not spontaneously form[10] furan, but required 30 min irradiation with a tungsten bulb, and then gave 67% of furan (**11**) as colorless crystals, mp 237-238°C. The spectral and chemical properties of **11** are discussed below. Similarly, reaction of the bis-furan adduct (**18**)[5] with excess tetrazene (**14**) for 12 h gave the purple dihydropyrene (**19**), in which one furan had formed, which on irradiation with light from a tungsten bulb gave 45% of the bis-furan (**12**). Note that with only one furan fused to the dihydropyrene, the closed form (**19**) is found, but addition of the second furan causes the dihydropyrene immediately to open to the cyclophanediene

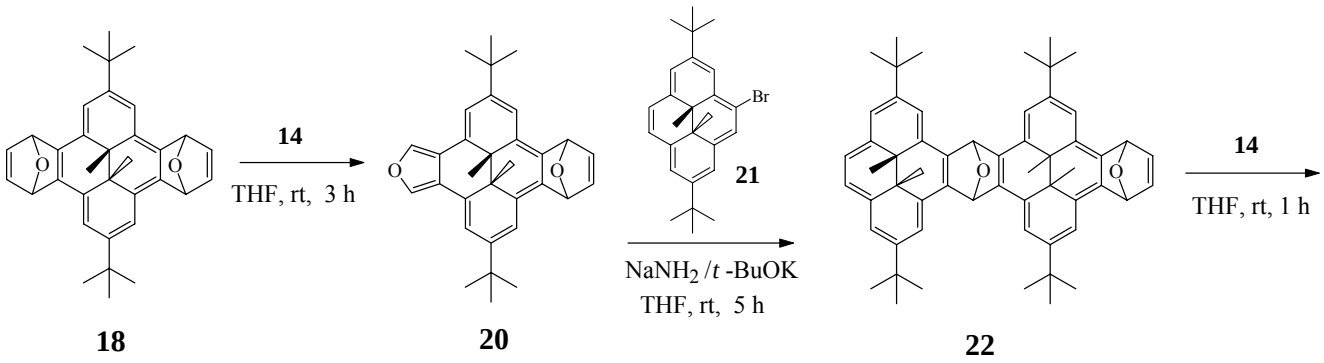
form (**12**). The bis-furan (**12**) forms colorless crystals which sublime at about 234°C.

If the bis-adduct (**18**) is reacted with one equivalent of tetrazene (**14**) for 3h, then the monofuran-monoadduct (**20**) is formed, which can be reacted with the aryne derived from bromide (**21**) to give 72% of approximately

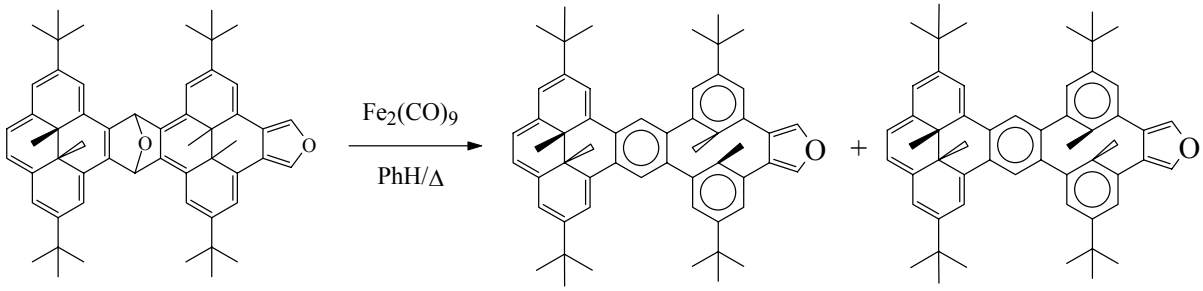


18 **19** **12**

equal amounts of four isomers of **22** (the internal methyl groups are *trans* within each dihydropyrene).



18 **20** **22**



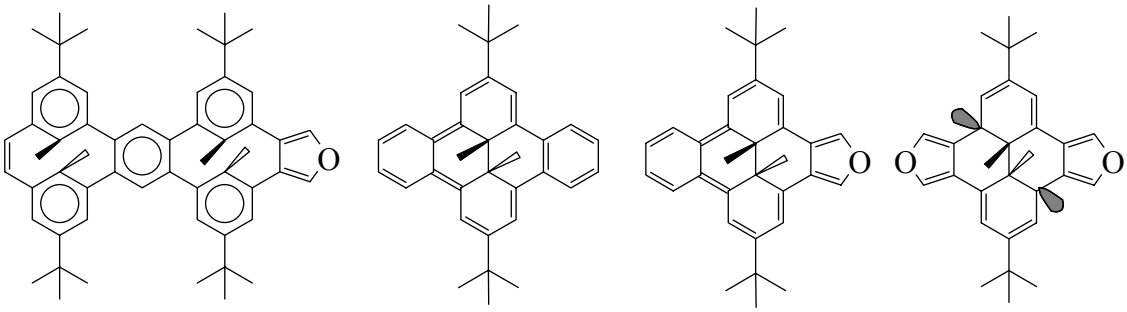
23 **13a** **13b**

These on reaction with tetrazene (**14**) gave 93% of mixed isomers (in unequal amounts) of furan (**23**), which on deoxygenation with $Fe_2(CO)_9$ gave 80% of the red furan (**13**), now as approximately a 70:30 mixture of the two isomers (**13a**) and (**13b**), which decomposed on attempted melting at about 172°C.

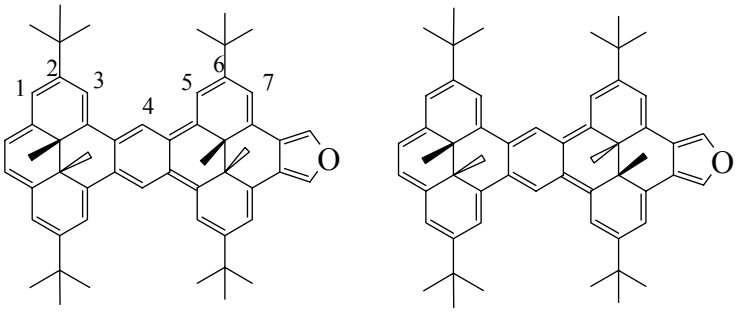
Properties of the furans

Furans (**11**) and (**12**) were colorless, stable crystals, consistent with only benzenoid absorptions; **13** however was red because of the benzodihydropyrenoid chromophore, with absorptions at λ_{max} 392 and 404 nm and a broad low intensity absorption at 450-600 nm, consistent with other benzo[e]dihydropyrenes.[12] On irradiation with visible light, these absorptions bleached with formation of the colorless cyclophanediene (**24**), and returned on irradiation of the latter with UV light. All benzenoid [e]-annelated dihydropyrenes preparedby

us, have shown this behaviour to date.[6,9,12,13] Dihydropyrenes annelated in both the [e] and the [l] positions have only been obtained recently,[5] and in the case of bis-benzene annelation, the open colorless cyclophanediene form, (**6**), is considerably (about 18 kcal/mole) more stable than the closed dihydropyrene isomer (**25**). Substitution of the benzene rings in **25** by furans is investigated in this paper.



24 **25** **26** **27**



28a **28b**

AM1 calculation[14] of the heats of formation (H_f) for each of the isomeric cyclophanediene (CPD) - dihydropyrene (DHP) pairs **11/26**, **13a/28a** and **13b/28b** was straight forward, and gave values for ΔH_f(DHP-CPD) = 19.07, 19.83 and 18.81 kcal/mole respectively, very similar to the value found for **6/25** (18.16 kcal/mole). In each case the open cyclophanediene form is the more thermally stable. Clearly substitution of a benzene by a furan in **6/25** has little effect on the isomerization. This is not the case for the bis-furan **12/27**. No normal Kekule structure for **27** can be written, and indeed the calculations all minimise the energy by lengthening the central bond to 2.71Δ, and equalising the other bonds, such that essentially the structure of the cyclophane (**12**) is obtained. Only by constraining the central bond to 1.53Δ (the value in dihydropyrenes) did we obtain a dihydropyrene like structure, and this was found to be some 54 kcal/mole less stable than the cyclophane (**12**). Clearly the CPD-DHP isomerization is completely shut down by flanking the cyclophane by two furans.

The case of **13/28** is interesting, in that there are two isomers of each. AM1 calculates **13b** to be more stable than **13a** by about 0.41 kcal/mole. In fact two isomers (**13a** and **13b**) were obtained in a 70:30 ratio. However, this 70:30 ratio was not set up in the formation step, **20** to **22**, since about equal amounts of the four

isomers of **22** were obtained. The subsequent reaction, **22** to **23** appears to favour the isomer leading to **13a**. There are really not many assignable differences in the proton spectra. The main differences in the ^{1}H NMR signals are: H-4 (δ 9.10 and 8.95 for **13a, 13b** respectively), H-3 (δ 8.51 and 8.31), and the dihydropyrene internal methyl signals (δ -1.66 and -1.37). Models (from the AM1 structures) suggest that the cyclophane rings of **13b** twist more out of the plane of the dihydropyrene ring than those for **13a**. Thus the 2-6 distance in **13b** is 7.84Δ but 7.61Δ in **13a**. The most deshielded hydrogens, H-3,4, suffer more steric compressionin **13a**, 1.973Δ calculated separation, than in **13b**, where their separation is 2.023Δ. Indeed both H-3 and H-4 are in fact more deshielded in **13a** than **13b** and so support our structure assignment, but the effect is not large. In both cases the dihydropyrene carbons distort out of the plane of the benzene carbons: In **13b** the 3-a-b4 [see structure **13a** for these angle labels] dihedral angle is 18^o and the benzene c-b-4-d [see**13a**] dihedral angle is 3^o, while in **13a** they are 14^o and -1^o respectively. This is consistent with the difference in chemical shift for the internal methyl protons of 0.3 ppm, where the less distorted **13a** has the most shielded hydrogens (δ -1.67). The cyclophane portions of the structures in **6, 11, 12** and **13** are all rather similar, and are not changed from [2$_2$]metacyclophane-1,9-diene itself. Thus the internal methyl groups are bent approximately 16^o out of the plane of the benzene rings, and the dihedral angle between the bridge (formal) double bond and phane benzene ring plane is about 56^o, the distance between the internal methyl carbons is 4.0Δ and the distance between the internal ring carbons is 2.67Δ, none of which change significantly by changing the cyclophane-**ene** bond into either a furan or benzene. The furans **(11-13**) however appear less reactive in Diels-Alder reactions than furan itself. For example, reaction of **12** with dimethyl acetylenedicarboxylate does not appear to go, and reaction of **11** and **13** with the aryne derived from **21** is at best very sluggish.

Conclusions

Calculations indicate that conversion of the bridge **>ene=** bond of [2$_2$]metacyclophanedienes into a furan or a benzene does not perturb the structure much. However when both bridge bonds are annelated byeither [c]-fused furans or benzenes, the cyclophanediene form rather than the isomeric dihydropyrene form is the more thermally stable. Indeed, experimentally the dibenzo-**, (6**), benzo-furano-, (**11**), annulenobenzo-furano- (**13**), and difurano-, (**12**), annelated metacyclophanedienes are found to be the thermally stable isomers.
The isomeric dihydropyrenes are sufficiently less thermally stable than these metacyclophanedienes to make the photoconversion inefficient.

ACKNOWLEDGEMENT

We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for support of this work. We dedicate this paper to Professor Sho Ito on the occasion of his 77th birthday.

EXPERIMENTAL

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome-alumel thermocouple. IR spectra, major peaks only, calibrated with polystyrene, were recorded on a Bruker IFS25 FT-IR spectrometer as KBr disks. UV-VIS spectra were recorded on a Cary 5 or a Perkin-Elmer Lambda-4B spectrometer in cyclohexane. ^{1}H NMR spectra were recorded at 360 MHz on a Bruker AMX 360, using $CDCl_3$ as solvent (unless otherwise stated below). Protons were assigned by COSY/NOESY experiments. ^{13}C NMR spectra were recorded at 90.6 MHz in $CDCl_3$, using the solvent peak at 77.0 ppm for calibration, and assigned where relevant using HETCOR spectra. Exact MS measurements used a Kratos Concept-H instrument with perfluorokerosene as calibrant. Elemental analyses were carried out by Canadian Microanalytical Services Ltd, Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$. SiGel refers to Merck Silica Gel, 70-230 mesh, and PE to distilled petroleum ether or hexanes, bp 30-60^{o}.

Benzodihydropyryne-furan adduct (16)

Sodium amide (750 mg, 160 mmol) and potassium *t*-butoxide (15 mg, 0.13 mmol) were added toasolution of furan (5 mL) and the bromodihydropyrene (**15**)[9] (110 mg, 0.233 mmol) in dry THF (10 mL) under argon. The mixture was stirred in the dark at *ca*. 20^{o}C for 24 h, and then was filtered through a 3 cm layer of Celite on 1 cm SiGel, rinsing with additional THF-hexane (1:1) (3 x 25 mL). The filtrate was evaporated and the residue was chromatographed over alumina (neutral, 5% water deactivated) using benzene:hexane (1:1) as eluant and yielded 44 mg (41%) of **16** as orange-brown crystals, mp 212-213^{o}C from benzene-hexane; IR 1474, 1367, 1253, 1034, 875, 858, 825 and 752 cm^{-1}; ^{1}H NMR (THF-d_8) δ 8.66-8.60 (m, 2, H-11,14),8.08 and 8.06 (d, 1 each, J = 1.3 Hz, H-1,10), 7.52-7.31 (m, 2, H-12,13); 7.24 and 7.22(d, 1 each, J = 1.3 Hz, H-3,8), 6.83 and 6.72 (dd, 1 each, J = 5.6, 1.8 Hz, H-5,6); 6.03 and 5.99 (dd, 1 each, J = 1.8, 0.7 Hz, H-4,7), 1.468 and 1.464 (s, 9 each, $C(CH_3)_3$), -0.98 and -1.20 (s, 3 each, $-CH_3$); ^{13}C NMR (THF-d_8) δ 144.85, 144.58, 138.80 and 137.88 (C-5,6), 136.40, 136.35, 135.16, 134.77, 130.67, 130.59, 129.02, 128.83, 128.58, 126.91 (C-12,13), 125.34 and 125.28 (C-11,14), 117.64 and 117.57 (C-1,10), 115.62 and 115.54 (C3,8), 80.22 and 80.15(C-4,7), 39.18, 38.38, 35.97, 30.58 ($C(CH_3)_3$), 19.98 and 17.68 (internal Me); MS (CI) $C_{34}H_{36}O$ = M; found *m/z* 461(MH^+).

1,2-(3,4-Furano)-9,10-benzo[2$_2$]metacyclophane (11)

The adduct (**16**) (38.1 mg, 0.083 mmol) was stirred with tetrazene (**14**)[11] (48 mg, 0.20mmol) in dry THF (20 mL) under argon in the dark for 12 h. The mixture was then irradiated using a 250W tungsten household lamp while cooled in an ice-bath for 30 min. The solvent was then evaporated and the residue was taken up in hexane:benzene (7:3) and filtered through a short (4 cm) column of neutral alumina (deactivated by 5% water)

to give 24 mg (67%) of cyclophane (**11**) as a colorless solid, mp 237-238°C from benzene; IR 1465, 1362, 1236, 1046, 869, 794, 760 cm^{-1}; ^1H NMR δ 7.73 (s, 2, H-4,5), 7.75-7.70 (m, 2, H-9,12), 7.46-7.41 (m, 2,H-10,11), 6.979, 6.976, 6.967 (each d, J = 2.2 Hz, 1,2,1, H-1,3,6,8), 1.28 (s, 18, -$C(CH_3)_3$), 0.93 (s, 6, -CH_3); ^{13}C NMR δ 150.11, 142.93, 140.17, 137.89 (C-4,5), 137.46, 131.69, 130.18, 129.00 (C-9,12), 128.16 (C-10,11), 128.49 and 127.45 (C-1,3,6,8), 34.14, 31.38 ($C(CH_3)_3$), 17.97 (CH_3); MS (CI) *m/z* 435 (MH^+); Anal. Calcd for $C_{32}H_{34}O$: C, 88.43; H, 7.88. Found: C, 88.45; H, 7.99.

1,2;9,10-bis(3,4-Furano)[2_2]metacyclophane (12)

The adduct (**18**)[5] (40 mg, 0.084 mmol) was stirred with tetrazene (**14**)[11] (80 mg, 0.34 mmol) in dry THF (40 mL) under argon in the dark for 12 h. The mixture was then irradiated using a 250W tungsten household lamp while cooled in an ice-bath for 1.5 h. The solvent was then evaporated and the residue was taken up in hexane:CH_2Cl_2 (6:1) and filtered through a short (5 cm) column of neutral alumina (deactivated by 5% water) (warning: solutions of **12** oxidize on standing) to give 16 mg (45%) of cyclophane **12** as a colorless solid, which sublimes at 234°C without melting; IR 1363, 1239, 1131, 1047, 877, 796, 760 cm^{-1}; ^1H NMR δ 7.73 (s, 4, H-4,5,9,10), 6.99 (s, 4, H-1,3,6,8), 1.28 (s, 18, $C(CH_3)_3$), 0.81 (s, 6, -CH_3); ^{13}C NMR δ 149.94, 138.16 (C-4,5,9,10), 137.42, 132.08, 129.44, 127.24 (C-1,3,6,8), 34.09, 31.41 ($C(CH_3)_3$), 17.81 (CH_3); MS (CI) *m/z* 425 (MH^+); Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.80; H, 7.87.

Isofuran (20)

Tetrazene (**14**)[11] (51.3 mg, 0.22 mmol) was added to a cooled (0°C) solution of the adduct (**18**)[5] (103.4mg, 0.22 mmol) in dry THF (50 mL) under N_2 and was stirred for 3 h. The solvents were evaporated and the residue was chromatographed on neutral alumina (deactivated by 3% NH_4OH) using hexane:benzene (1:1) as eluant and gave 28.3 mg (29%) of the isofuran (**20**) as a red-orange solid. This was normally used directly in the next step as quickly as possible. ^1H NMR δ 8.017 and 8.012 (d each, J = 1.7 Hz, 2, H-11,12), 6.836 and 6.830 (d each, J = 1.4 Hz, 2, H-1,10), 6.675 and 6.570 (dd each, J = 5.6, 1.8 Hz, 2, H-5,6), 6.409 and 6.381 (d each, J = 1.4 Hz, 2, H-3,8), 5.737 and 5.701 (dd each, J = 1.8, 1.4 Hz, 2, H-4,7), 1.241 and 1.239 (s, 9 each, $C(CH_3)_3$), 0.373 and 0.137 (s, 3 each, -CH_3); ^{13}C NMR δ 144.56, 144.28, 137.01 and 136.99 (C-11,12), 136.69 and 135.45 (C-5,6), 132.12, 131.67, 131.10, 131.04, 128.75, 128.60, 120.72, 120.61, 116.79 and 116.74 (C-1,10), 113.76 and 113.71 (C-3,8), 78.83 and 78.81 (C-4,7), 42.37, 41.64, 34.67, 34.65, 29.56 ($C(CH_3)_3$), 22.04, 19.76; MS (CI) $C_{32}H_{34}O_2$ = M; found *m/z* 451 (MH^+).

Dihydropyrenobenzocyclophanes (13a,b) - sequence 20-22-23-13a,b

$NaNH_2$ (400 mg, 10 mmol) and *t*-BuOK (2 mg, 0.02 mmol)) were added to a solution of the isofuran (**20**)

(45.9 mg, 0.10 mmol) and bromide (**21**)[9] (56.1 mg, 0.13 mmol) in dry THF (40mL) under N_2, and the mixture was stirred for 5 h. The solvents were evaporated and the residue was filtered through neutral alumina (deactivated by 3% NH_4OH) using hexane:benzene (1:1) as eluant and gave 58 mg (72%) of the adduct (**22**) as a green solid which is a mixture of four isomers. The internal methyl protons appeared between δ-3. 1 and -4.4. MS (FAB) 793.6 ($C_{58}H_{64}O_2$ = 792). This sample (56 mg, 0.071 mmol) was stirred in THF (20mL) with tetrazene (**14**)[11] (18.3 mg, 0.078 mmol) under N_2 for 1 h. The solvent was evaporated and the residue was filtered through neutral alumina (deactivated by 3% NH_4OH) using hexane:benzene (1:1)as eluant and gave 51 mg (93%) of the furan (**23**) as a reddish-brown solid (mixed isomers). The internal methyl protons now appeared at about δ +0.5 and -0.5 (CPD) and -3.7 and -4.0 (DHP). MS (FAB) 767.5 ($C_{56}H_{62}O_2$ = 766). This sample (31 mg, 0.040 mmol) and $Fe_2(CO)_9$ (17.6 mg, 0.048 mmol) were refluxed in benzene (20 mL) for 1 h. The solvent was evaporated and the residue was chromatographed on neutral alumina (deactivated by 3% NH_4OH) using hexane:benzene (1:6) as eluant and gave 24.3 mg (80%) of cyclophane (**13**) as a red solid, mp 172°C (decomp, first colorless then black). By NMR, this sample consists of two isomers (**13a**) and (**13b**) in a 70:30 ratio. Because of this ratio, using COSY/NOESY, the following assignments could be made: **13a**: ^{1}H NMR δ 9.10 (s, H-4,13), 8.51 (d, J = 1.2 Hz, H-3,14), 7.79 (s, H-8,9), 7.50 (d, J = 1.1 Hz, H-1,16), 7.30 (s, H-17,18), 7.12 (d, J = 2.2 Hz, H-5,12), 7.06 (d, J = 2.2 Hz, H-7,10), 1.53 (s, *t*-Bu-2,15), 1.32 (s, *t*-Bu-6,11), 1.03 (s, Me-7b,12b), -1.66 (s, Me-18b,18c); ^{13}C NMR δ 137.97 (C-8,9), 129.20 (C-5,12),127.67(C-7,10), 123.62 (C-4,13), 121.23(C-17,18), 119.86 (C-1,16), 116.74 (C-3,14), 35.52, 34.88, 34.20, 31.44 (*t*-Bu-2,15), 30.84 (*t*-Bu-6,11), 18.21 (Me-7b,12b), 17.36 (Me-18b,18c), + see below. **13b**: ^{1}H NMR δ 8.95 (s, H-4,13), 8.31 (d, J = 1.2 Hz, H-3,14), 7.78 (s, H-8,9), 7.37 (d, J = 1.1 Hz, H-1,16), 7.15 (s,H-17,18), 7.12 (d, J = 2.2 Hz, H-5,12), 7.05 (d, J = 2.2 Hz, H-7,10), 1.49 (s, *t*-Bu-2,15), 1.31 (s, *t*-Bu-6,11), 1.03 (s, Me-7b,12b), -1.37 (s, Me-18b,18c); ^{13}C NMR δ 137.97 (C-8,9), 128.99 (C-5,12), 127.67 (C-7,10), 124.68 (C-4,13), 120.96(C-17,18), 119.86 (C-1,16), 117.40 (C-3,14), 35.59, 35.44, 34.30, 30.67 (*t*-Bu-2,15), 30.29(*t*-Bu-6,11), 18.21 (Me-7b,12b), 17.96 (Me-18b,18c), + see below. The following 18 quaternary ^{13}C NMR peaks could not be assigned to a particular isomer of **13a** or **13b**: 150.09, 144.72, 144.43, 141.12, 140.65, 140.48, 140.36, 138.56, 138.42. 137.63, 137.49, 135.73, 134.83, 134.33, 131.73, 130.07, 129.38, 128.97. MS (FAB) 750.5 ($C_{56}H_{62}O$ = 750).

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