

Curved Aromatic Compounds, Part 2^[‡]

1,7-Dioxa[7](2,7)pyrenophane: The Pyrene Moiety Is More Bent than That of C₇₀

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Dedicated to Professor V. Boekelheide on the occasion of his 80th birthday

Abstract: The synthesis of the highly strained title compound **8a** was achieved by the valence isomerization and in situ dehydrogenation of the cyclophanediene **7a** at only 80 °C. A single-crystal X-ray structure determination of **8a** revealed that the pyrene moiety is remarkably bent, the two ends forming an angle of 109.2°. This degree of lengthwise bend slightly exceeds that present in the pyrene unit found in the equator of *D*_{5h} C₇₀, rendering it the most bent pyrene group yet prepared. The expectation of unusual reactivity is borne out by the apparent Diels–Alder reaction between **8a** and tetracyanoethylene (TCNE) to give adduct **9**.

Keywords: arenes · cyclophanes · fullerene fragments · polycycles · strained molecules

Introduction

Since the initial discovery of the fullerenes^[1] and the subsequent isolation of C₆₀,^[2] considerable attention has been directed towards the synthesis and study of polynuclear aromatic hydrocarbons (PAHs) having curved aromatic surfaces that correspond to segments of the surfaces of the fullerenes.^[3] Several such buckybowls have been prepared so far, the majority of them by routes that employ pyrolytic techniques (900–1300 °C) to impart curvature to the aromatic skeleton.

Our involvement in this area derives from our interest in cyclophane chemistry.^[4] It has long been known that *para*- and *meta*-substituted rings of many small cyclophanes adopt boat-like geometries as a consequence of molecular strain.^[5] The benzene ring (the second smallest fullerene fragment) is clearly very flexible^[6] and can tolerate a substantial degree of distortion from planarity while maintaining all, or many, of the characteristics commonly associated with aromaticity. As many medium- and large-sized PAHs can be found in the

curved surfaces of the fullerenes, it was somewhat surprising that, at the outset of our work in this area, there had been no systematic experimental study of any polynuclear aromatic hydrocarbon to its tolerance to distortion from planarity over the full dimensions of its aromatic surface. This is not to say, however, that isolated examples were not known.^[7] Nevertheless, we became interested in the preparation and study of [*n*]cyclophanes in which the benzene ring has been replaced by a polynuclear aromatic hydrocarbon (PAH).

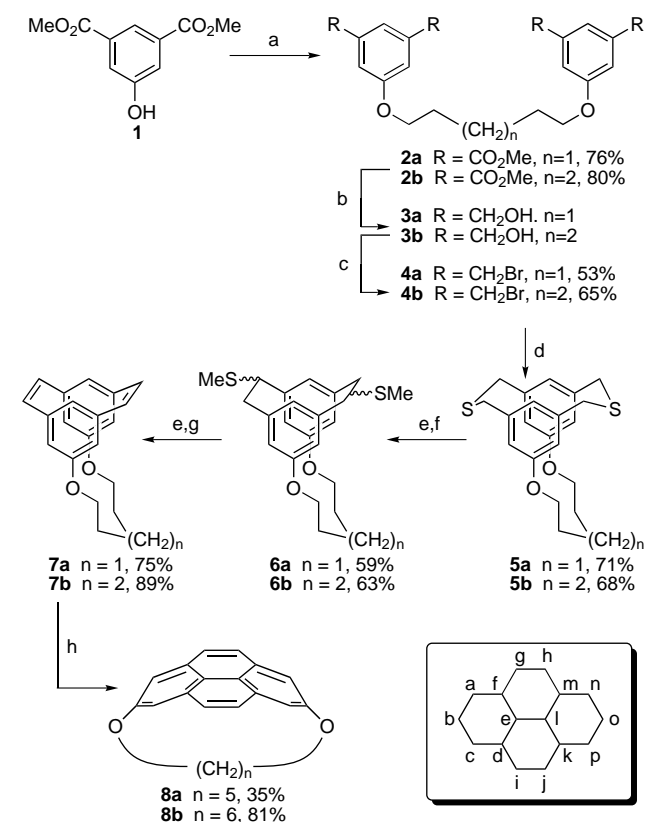
Our initial work in this area was directed toward the pyrene nucleus (a repeating subunit around the equators^[8] of *D*_{5h} C₇₀ and *D*_{6h} C₈₄), which we envisaged preparing by the valence isomerization of a metacyclophane-1,9-diene to a 10b,10c-dihydropyrene^[9] followed by dehydrogenation.^[10] This led to the synthesis of 1,8-dioxa[8](2,7)pyrenophane **8b** (see Scheme 1) from the tethered metacyclophanediene **7b**.^[4b] At the time, we reported that attempts to prepare the next smaller member of the series **8a** (from **7a**) had met with failure. We now report the successful synthesis and X-ray crystal structure of the considerably more distorted **8a**.

Results and Discussion

The synthesis of **8a** is outlined in Scheme 1. Diester **1** was treated with NaH, 1,5-dibromopentane and tetrabutylammonium iodide (TBAI) to afford the tetraester **2a** (76%). Reduction with LiAlH₄ afforded tetraol **3a**, which was

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[‡] Part 1, see ref. [4b].



Scheme 1. Synthesis of **8a, b** from **1**. Reagents and conditions: a) NaH, TBAI, $\text{Br}(\text{CH}_2)_n\text{Br}$ for **2a**/ $\text{Br}(\text{CH}_2)_n\text{Br}$ for **2b**, THF, reflux; b) LiAlH_4 , THF, 0°C to room temperature; c) 2:1 48% HBr:concentrated H_2SO_4 ; d) $\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$, 10:1 CH_2Cl_2 :EtOH, room temperature; e) $(\text{MeO})_2\text{CHBF}_4$, CH_2Cl_2 , room temperature; f) *t*BuOK, THF, room temperature; g) *t*BuOK, *t*BuOH/THF, room temperature; h) DDQ, benzene, reflux.

converted without purification or isolation to give tetrabromide **4a**. In fact purification of **2a** and **2b** is not necessary. Virtually identical overall yields could be obtained by taking diester **1** straight through three steps to **4a** (53%) and **4b** (65%). The $\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$ -mediated self-coupling^[4a] of **4a** then gave the dithiacyclophane **5a** (71%). Methylation of the sulfur atoms with the Borch reagent^[11] and Stevens rearrangement of the resulting bis-sulfonium salt afforded a mixture of thioethers **6a** (59% for two steps). Remethylation of the sulfur atoms and subsequent treatment with *t*BuOK/*t*BuOH then gave the cyclophanediene **7a** (73% for two steps).

Subjection of **7a** to the conditions employed for the conversion of **7b** into **8b** (2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzene, reflux) resulted in complete consumption of the starting material according to thin-layer chromatography (TLC) analysis, but no traces of **8a** could be isolated from the reaction mixture after workup and careful chromatography. Recalling that **8b** slowly decomposed in CDCl_3 solution,^[4b] it seemed possible that the more strained **8a** might actually have formed, but decomposed under the reaction conditions or during chromatography. Indeed performing the chromatography very rapidly proved to be somewhat successful and **8a** was isolated in 35% yield. Slower chromatography resulted in substantially reduced

yields and less pure product. Another modification was the inclusion of a base wash during workup. This removed much of the deep color from the reaction mixture, but it is not clear whether this contributed to an enhancement of the yield. Applying these modifications to the synthesis of **8b** led to an increase in the yield from the initially reported yield of 67%^[4b] to 81%. Noteworthy are the comparatively very mild conditions (refluxing benzene) under which the severe bend in the polycyclic aromatic skeleton is generated. Like **8b**, pyrenophane **8a** appears to be stable for many months in the solid state.

The ^1H NMR spectrum of **8a** exhibits signals in the aromatic region at $\delta = 7.72$ (10-H, 11-H, 15-H, 16-H) and 7.22 (9-H, 12-H, 14-H, 17-H) (see Scheme 2 for numbering). The analogous protons of **10** are observed at $\delta = 7.84$ and 7.44, and those of 2,7-dimethoxypyrene^[12] appear at $\delta = 7.97$ and 7.69. The highest field signals of the bridge protons, at $\delta = -2.10$, are of those attached to C4. This compares to $\delta = -1.46$ for **8b** and $\delta = 1.67$ for **4a**.

Single-crystal X-ray analysis of **8a**^[13] (Figure 1) revealed a pyrene moiety considerably more distorted than that of **8b**, which itself is substantially more distorted than all other known pyrenophanes.^[4b, 7c-h] In attempting to evaluate the

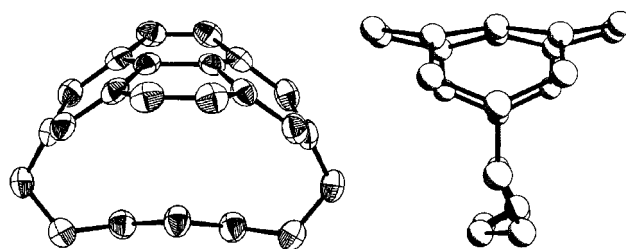


Figure 1. Side (ORTEP) and front (PLUTO) views of **8a** in the crystal.

extent of these distortions, our analysis of **8a** relied on the angles formed between adjacent planes of carbon atoms, much as the angle α has been used to assess the bend of the benzene ring in $[n]$ paracyclophanes.^[5] In so doing, it can be seen that the bend is quite evenly distributed over the surface of the pyrene unit (Table 1) and the overall bend, as measured by the angle between C8-C9-C17 and C12-C13-C14, is 109.1° . In direct comparison to an experimental^[14a] value (94.0°) for C_{70} , it would appear that the pyrene component of **8a** is considerably more bent. However, it can be seen that bend in

Table 1. Bend angles [$^\circ$] in pyrenophanes and fullerenes.

	8a	D_{5h} C_{70} ^[a]	D_{5h} C_{70} ^[b]	8b ^[c]	D_{6h} C_{84} ^[b]
abc-acdf	18.2	11.0	18.0	16.2	15.0
acdf-def	16.6	11.0	18.0	13.3	15.0
def-ghij	19.9	25.0	18.0	15.6	15.0
ghij-klm	20.3	25.0	18.0	15.4	15.0
klm-kmnp	16.3	11.0	18.0	13.1	15.0
kmnp-nop	17.9	11.0	18.0	14.3	15.0
total	109.1	94.0	108.0	87.8	90.0
abc-klm	74.9	72.0	72.0	60.3	60.0
acdf-kmnp	73.1	72.0	72.0	57.3	60.0
def-mop	74.4	72.0	72.0	58.4	60.0

[a] Ref. [14a]. [b] Average bend angle between adjacent planes in the equator of the fullerene. [c] Ref. [4b].

the pyrene unit of C_{70} is not as evenly distributed. Since the large bend angles in the equator of C_{70} are underrepresented in a single pyrene moiety, it seemed more reasonable to compare our angle of 109.1° with the sum of the average bend angle in the equator of C_{70} (18.0°) over the length of a pyrene unit. This affords a value of 108.0° , which suggests that the pyrene moiety of **8a** is just slightly more bent than that of C_{70} . Perhaps a better approach is to look at the angles between those planes of carbons in **8a** that correspond to those in C_{70} which are related by the D_{5h} symmetry and consequently at 72.0° to one another. With bend angles of 74.9 , 73.1 and 74.4 (Table 1), the pyrene unit of **8a** again comes out as significantly more bent than that of C_{70} . The $C_{\text{aryl}}-\text{O}$ bonds form angles of 8.2° and 8.7° to the planes abc and nop, respectively.^[15]

In appraising the degree of curvature of fullerenes and fullerene fragments, Haddon has employed the POAV (pi orbital axis vector) analysis.^[16] Applying this method to the

Table 2. Pyramidalization angles [$^\circ$] for **9** and $D_{5h} C_{70}$.^[a,b]

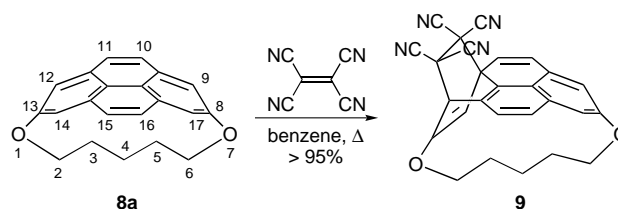
atom	9	$D_{5h} C_{70}$ ^[a]	$D_{5h} C_{70}$ ^[b]
b	2.9	8.8	8.7
d	5.3	10.1	10.3
e	6.9	8.8	8.7
f	6.0	10.1	10.3
k	5.3	10.1	10.3
l	6.8	8.8	8.7
m	5.7	10.1	10.3
o	2.7	8.8	8.7

[a] Calculated, ref. [18a]. [b] Experimental, ref. [14a].

quaternary carbon atoms of **8a** (Table 2), it can be seen that the values obtained are considerably lower than those for the corresponding carbon atoms of C_{70} .^[16d] This is a consequence of the boat-like geometry adopted by the central rings of **8a**, best seen in the side view in Figure 1. Thus, while the end-to-end bend of the pyrene unit in pyrenophane **8a** is greater than that of the pyrene subunit of C_{70} , the local curvature is less. However, as in the case of corannulene,^[3d] it is anticipated that POAV angles will increase as five-membered rings are successively annulated to **8a** and other $[n](2,7)$ pyrenophanes. Work aimed at achieving this goal is now underway.

The stretched aliphatic bridge of **8a** exhibits O-C-C and C-C-C bond angles ranging from 114.3° to 117.6° and averaging 116.5° . Surprisingly, these values are smaller than those observed for the bridge of the presumably less strained **8b**. Here the range of angles is 115.0° to 119.4° and the average is 117.2° . However, the average bond length in the bridges of **8a** (1.537 \AA) is slightly longer than that in **8b** (1.517 \AA).

The expectation of unusual chemistry arising from the strained nature of **8a** was foreshadowed by its reaction with TCNE to give compound **9**^[17] (Scheme 2). This is the apparent product of a Diels–Alder reaction, although $[2+2]$ cycloaddition followed by rearrangement cannot be ruled out at this time. The further exploration of the chemistry of **8a** and **8b** is currently under investigation, as are attempts to prepare their hydrocarbon analogues.



Scheme 2. Reaction of **8a** with TCNE.

Experimental Section

General: Reactions were performed under air unless otherwise indicated. THF was distilled from sodium benzophenone ketyl under N_2 immediately prior to use. Spectroscopic grade benzene was degassed under reduced pressure prior to use. All other solvents were used as received. Chromatographic purification was accomplished with 230–400 mesh silica gel. TLC plates were visualized by using a short wave (254 nm) UV lamp. Melting points were obtained on a Thomas Hoover 7427-H10 Melting Point Apparatus and are uncorrected. IR spectra (cm^{-1}) were recorded on Perkin Elmer 1320 spectrophotometer in solution in 1 mm NaCl cells. ^1H NMR spectra were obtained on a General Electric GE-300 NB at 300.1 MHz in CDCl_3 at room temperature; shifts relative to internal TMS standard; coupling constants are reported in Hz. Reported multiplicities are apparent. ^{13}C NMR spectra were recorded at 75.47 MHz at room temperature; chemical shifts are relative to solvent (δ 77.0 for CDCl_3), number of attached protons were determined by an attached proton test experiment. Low and high resolution mass spectrometric data were obtained on a V.G. Micromass 7070HS instrument operating at 70 eV. Combustion analyses were performed by the Microanalytical Services Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta.

1,5-Bis(3,5-bis(methoxycarbonyl)phenoxy)pentane (2a): To a solution of **1** (8.13 g, 38.7 mmol), 1,5-dibromopentane (4.47 g, 19.4 mmol) and tetrabutylammonium iodide (0.74 g, 2.0 mmol) in dry THF (200 mL) under N_2 was added 60% NaH dispersion (1.64 g, 41.0 mmol) in small portions at a rate such that the evolution of hydrogen did not become too vigorous. The cloudy mixture was then refluxed for 3 h, after which the reaction was quenched with saturated aqueous NH_4Cl solution (2 mL) and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (150 mL), saturated NaCl solution (25 mL), dried (MgSO_4), filtered and concentrated to yield crude **2a** as a yellow solid. This was normally used in the following step without purification, but pure **2a**, a white solid, could be obtained by flash chromatography eluting with first CH_2Cl_2 and then 5% ethyl acetate/hexanes (7.16 g, 76%). **2a:** M.p. $111-113^\circ\text{C}$ (heptane); IR (CHCl_3): 2950 (m), 2860 (w), 1720 (s), 1590 (m), 1340 (s), 1310 (s); ^1H NMR: δ = 8.26 (t, $^4J(\text{H,H}) = 1.4$, 2H), 7.74 (d, $^4J(\text{H,H}) = 1.4$, 4H), 4.08 (t, $^3J(\text{H,H}) = 6.2$, 4H), 3.94 (s, 12H), 1.93–1.88 (m, 4H), 1.72–1.68 (m, 2H); ^{13}C NMR: δ = 166.1, 159.0, 131.7, 122.8, 119.7, 68.2, 52.4, 28.8, 22.6; MS (70 eV, EI): m/z (%): 488 (17) [M^+], 457 (27), 279 (84), 223 (20), 211 (43), 210 (26), 179 (50), 151 (18), 69 (100), 68 (24); HRMS: calcd $\text{C}_{25}\text{H}_{28}\text{O}_{10}$ 488.1681; found 488.1685.

1,6-Bis(3,5-bis(methoxycarbonyl)phenoxy)hexane (2b): Using the procedure described above for **2a**, **1** (2.05 g, 9.75 mmol), 1,6-dibromohexane (1.20 g, 4.92 mmol), tetrabutylammonium iodide (0.40 g, 1.1 mmol) and 60% NaH dispersion (0.43 g, 10.8 mmol) afforded, after flash chromatography, **2b** (1.97 g, 80%) as a white solid. Approximately tenfold scale-up of this reaction resulted in only slightly lower yields. **2b:** M.p. $135-136^\circ\text{C}$ (heptane); IR (CHCl_3): 2940 (w), 1720 (s), 1590 (m), 1340 (m), 1310 (m); ^1H NMR: δ = 8.26 (t, $^4J(\text{H,H}) = 1.4$, 2H), 7.74 (d, $^4J(\text{H,H}) = 1.4$, 4H), 4.06 (t, $^3J(\text{H,H}) = 6.4$, 4H), 3.94 (s, 12H), 1.88–1.84 (m, 4H), 1.59–1.54 (m, 4H); ^{13}C NMR: δ = 166.1, 159.1, 131.6, 122.6, 119.7, 68.5, 52.3, 29.2, 25.9; MS (70 eV, EI): m/z (%): 502 (18) [M^+], 471 (17), 293 (9), 211 (44), 210 (30), 179 (37), 83 (76), 55 (100); $\text{C}_{26}\text{H}_{30}\text{O}_{10}$ (502.52): calcd C 64.50, H 6.86; found C 64.35, H 6.98.

1,5-Bis(3,5-bis(bromomethyl)phenoxy)pentane (4a): A solution of crude tetraester **2a** (9.34 g, 19.1 mmol) in dry THF (200 mL) was added dropwise to a magnetically stirred suspension of LiAlH_4 (7.61 g, 201 mmol) in dry THF (150 mL) under N_2 at 0°C . When the addition was complete, the

mixture was allowed to warm to room temperature and stirred for 14 h. The reaction was quenched by the slow addition of ethyl acetate (40 mL) and then H₂O (1 mL), with cooling. The solvents were then removed under reduced pressure and the grey solid residue was redissolved in 2:1 HBr/H₂SO₄ (200 mL). The mixture was heated at 100–110 °C for 1 h, allowed to cool and diluted with H₂O (400 mL). The aqueous solution was extracted with CH₂Cl₂ (3 × 100 mL) and the combined organic layers were washed with H₂O (100 mL), saturated aqueous NaHCO₃ solution (100 mL), and H₂O (100 mL), dried (MgSO₄), filtered and concentrated to yield a brown oil. Flash chromatography (35% CH₂Cl₂/hexanes) afforded pure **4a** (6.56 g, 53% from diester **1**) as a white solid. **4a**: M.p. 95–97 °C (heptane); IR (CH₂Cl₂): 2940 (w), 2880 (w), 1590 (s), 1160 (m), 1050 (m); ¹H NMR: δ = 6.99 (t, ⁴J(H,H) = 1.2, 2H), 6.85 (d, ⁴J(H,H) = 1.4, 4H), 4.43 (s, 8H), 3.99 (t, ³J(H,H) = 6.3, 4H), 1.85 (quint, ³J(H,H) = 6.7, 4H), 1.69–1.65 (m, 2H); ¹³C NMR: δ = 159.4, 139.5, 121.7, 115.2, 67.8, 32.9, 28.9, 22.7; MS (70 EV, EI): *m/z* (%): 630 (5), 628 (8) [*M*⁺], 626 (6), 547 (7), 351 (20), 349 (39), 347 (22), 60 (100); C₂₁H₂₄Br₄O₂ (628.04): calcd C 40.16, H 3.85; found C 39.77, H 3.62.

1,6-Bis(3,5-bis(bromomethyl)phenoxy)hexane (4b): Using the procedure described above for **4a**, crude tetraester **2b** (9.25 g, 18.4 mmol), LiAlH₄ (7.65 g, 202 mmol) and 2:1 HBr/H₂SO₄ (200 mL) afforded, after flash chromatography, **4b** (8.32 g, 65% from diester **1**) as a white solid. **4b**: M.p. 99–101 °C (heptane); IR (CHCl₃): 2920 (m), 2860 (m), 1590 (s), 1050 (m); ¹H NMR: δ = 6.99 (s, 2H), 6.86 (s, 4H), 4.43 (s, 8H), 3.98 (t, ³J(H,H) = 6.4, 4H), 1.85–1.80 (m, 4H), 1.57–1.53 (m, 4H); ¹³C NMR: δ = 159.3, 139.5, 121.7, 115.2, 68.0, 32.9, 29.1, 25.8; MS (70 EV, EI): *m/z* (%): 644 (8), 642 (13) [*M*⁺], 640 (9), 563 (6), 561 (6), 481 (6), 363 (9), 241 (27), 83 (90), 55 (100); C₂₂H₂₆Br₄O₂ (642.06): calcd C 41.16, H 4.08; found C 41.16, H 4.02.

1,7-Dioxa-15,24-dithia[7.3.3](1,3,5)cyclophane (5a): To a solution of tetrabromide **4a** (7.21 g, 11.5 mmol) in 18% EtOH/CH₂Cl₂ (1000 mL) was added freshly prepared Na₂S/Al₂O₃^[4a] (10.42 g, 28.5 mmol) in small portions over 1 h. The reaction was stirred vigorously for 12 h, filtered and concentrated. Flash chromatography of the residue (CH₂Cl₂) afforded **5a** (3.02 g, 71%) as a white solid. **5a**: M.p. 126–128 °C (heptane); ¹H NMR: δ = 6.75 (s, 2H), 6.40 (s, 4H), 4.09 (t, ³J(H,H) = 4.9, 4H), 3.78 (AB half spectrum, ²J(H,H)_{AB} = 14.8, 4H), 3.74 (AB half spectrum, ²J(H,H)_{AB} = 14.8, 4H), 1.73–1.76 (m, 4H), 1.64–1.55 (m, 2H); ¹³C NMR: δ = 158.0, 138.5, 124.1, 113.5, 65.7, 38.9, 27.3, 21.8; MS (70 EV, EI): *m/z* (%): 373 (25), 372 (100) [*M*⁺], 308 (12), 122 (34), 121 (17), 69 (30); HRMS: calcd C₂₁H₂₄O₂S₂ 372.1216; found 372.1219.

1,8-Dioxa-16,25-dithia[8.3.3](1,3,5)cyclophane (5b): Using the procedure described above for **5a**, tetrabromide **4b** (2.10 g, 3.27 mmol) and freshly prepared Na₂S/Al₂O₃^[4a] (2.67 g, 7.05 mmol) afforded, after flash chromatography, **5b** (860 mg, 68%) as a white solid. **5b**: M.p. 165–167 °C (heptane); ¹H NMR: δ = 6.70 (s, 2H), 6.38 (s, 4H), 3.86 (t, ³J(H,H) = 5.3, 4H), 3.79 (AB half spectrum, ²J(H,H)_{AB} = 14.7, 4H), 3.75 (AB half spectrum, ²J(H,H)_{AB} = 14.7, 4H), 1.76–1.68 (m, 4H), 1.64–1.55 (m, 4H); ¹³C NMR: δ = 159.0, 138.5, 124.4, 113.3, 64.6, 38.8, 28.0, 20.7; MS (70 EV, EI): *m/z* (%): 387 (25), 386 (100) [*M*⁺], 353 (10), 322 (12), 122 (40), 120 (19), 91 (31); HRMS: calcd C₂₂H₂₆O₂S₂ 386.1372; found 386.1373.

1,7-Dioxa[7.2.2](1,3,5)cyclophane-14,22-diene (7a): To a magnetically stirred solution of dithiacyclophane **5a** (3.02 g, 8.11 mmol) in CH₂Cl₂ (50 mL) was added Borch reagent (2.0 mL, 3.2 g, 19.8 mmol) by syringe under N₂. The reaction was stirred for 3 h and the solvent was removed under reduced pressure. The residue was quenched with 80% aqueous methanol (50 mL) and the resulting suspension was filtered to yield the crude bis(methylsulfonium) salt of **5a** (3.10 g, 66%). This was used immediately without further purification in the next step.

To a magnetically stirred slurry of the bis(methylsulfonium) salt of **5a** (2.66 g, 4.61 mmol) in dry THF (50 mL) was added *t*BuOK (2.46 g, 21.9 mmol) in one portion and the reaction was stirred at room temperature under N₂ for 3 h. The reaction was quenched with saturated aqueous NH₄Cl solution (1 mL) and the solvents were removed under reduced pressure. The residue was redissolved in CH₂Cl₂ (50 mL) and washed with saturated aqueous NH₄Cl solution (50 mL), H₂O (50 mL), saturated NaCl solution (50 mL), dried (MgSO₄), filtered through a plug of silica gel and concentrated to yield a mixture of isomers **6a** (1.92 g, 59% from dithiacyclophane **5a**) as a foamy, pale yellow solid. This was used without further purification in the next step.

To a magnetically stirred solution of the mixture of isomers **6a** (1.92 g, 4.13 mmol) in CH₂Cl₂ (50 mL) was added Borch reagent (2.0 mL, 3.2 g, 19.8 mmol) by syringe under N₂ and the reaction was stirred at room temperature for 3 h. The solvents were then removed under reduced pressure and the resulting oily brown residue was suspended in a rapidly stirred mixture of 1:1 THF/*t*BuOH (80 mL). *t*BuOK (5.61 g, 50.0 mmol) was then added and stirring under N₂ was continued for 6 h. The solution was extracted with saturated aqueous NH₄Cl solution (50 mL), H₂O (50 mL), saturated NaCl solution (50 mL), dried (MgSO₄), filtered through a plug of silica and concentrated to yield a yellow solid. Flash chromatography (CH₂Cl₂) yielded diene **7a** (1.07 g, 73% from **6a**) as a white crystalline solid. **7a**: M.p. 138–140 °C (heptane); IR (CCl₄): 3000 (m), 2950 (m), 2890 (m), 1400 (s), 1300 (s), 1270 (s), 1160 (s), 1050 (m); ¹H NMR: δ = 7.14 (s, 4H), 6.87 (s, 2H), 6.12 (s, 4H), 4.06 (t, ³J(H,H) = 5.5, 4H), 1.54–1.45 (m, 4H), 1.19–1.09 (m, 2H); ¹³C NMR: δ = 155.9, 136.2, 135.9, 134.6, 114.0, 66.7, 29.1, 22.7; MS (70 EV, EI): *m/z* (%): 304 (100) [*M*⁺], 207 (33), 206 (96), 205 (32), 189 (63), 178 (51); HRMS: calcd C₂₁H₂₀O₂ 304.1462; found 304.1440.

1,8-Dioxa[8.2.2](1,3,5)cyclophane-15,23-diene (7b): Using the procedure described above for **7a**, dithiacyclophane **5b** (2.50 g, 6.47 mmol) and Borch reagent (1.6 mL, 2.6 g, 15.8 mmol) afforded the crude bis(methylsulfonium) salt of **5b** (3.25 g, 85%). Treatment of this with *t*BuOK (2.52 g, 22.4 mmol) as described above gave thioether mixture **6b** (1.71 g, 63% from **5b**) as a foamy yellow solid. This was used without further purification in the next step.

As described for **7a**, the mixture of isomers **6b** (1.71 g, 4.14 mmol), Borch reagent (1.4 mL, 2.2 g, 13.8 mmol) and then *t*BuOK (3.55 g, 31.9 mmol) afforded, after flash chromatography, diene **7b** (1.15 g, 89% from **6b**) as a white solid. **7b**: M.p. 117–118 °C (heptane); IR (CCl₄): 3005 (m), 2940 (s), 2880 (m), 1400 (s), 1300 (s), 1270 (s), 1160 (s), 1115 (m), 1040 (m); ¹H NMR: δ = 7.15 (s, 4H), 6.95 (t, ⁴J(H,H) = 1.1, 2H), 6.11 (d, ⁴J(H,H) = 1.0, 4H), 3.91 (t, ³J(H,H) = 6.0, 4H), 1.53–1.49 (m, 4H), 1.29–1.25 (m, 4H); ¹³C NMR: δ = 155.8, 136.2, 135.5, 134.7, 113.9, 67.4, 27.8, 22.8; MS (70 EV, EI): *m/z* (%): 319 (11), 318 (46) [*M*⁺], 207 (28), 206 (100), 205 (20), 189 (27), 178 (48); HRMS: calcd C₂₂H₂₂O₂ 318.1619, found 318.1623.

1,7-Dioxa[7](2,7)pyrenophane (8a): Diene **7a** (0.552 g, 1.90 mmol) was dissolved in degassed benzene (50 mL) and DDO (0.441 g, 1.94 mmol) was added. This mixture was stirred at reflux for 12 h under N₂. After cooling, the mixture was extracted with 1M NaOH (50 mL) solution, dried (MgSO₄) and the solvent was removed under reduced pressure. The residue was immediately dissolved in CH₂Cl₂ (10 mL) and this solution was rapidly flushed through a short column of silica to yield pyrenophane **8a** (0.189 g, 35%). **8a**: M.p. 155 °C (decomp) (xylenes); IR (CDCl₃): 3040 (w), 2920 (s), 2840 (s), 1570 (m), 1540 (s), 1420 (m), 1290 (m), 1270 (m); ¹H NMR: δ = 7.72 (s, 4H), 7.22 (s, 4H), 3.33–3.29 (m, 4H), –0.01 to –0.07 (m, 4H), –2.06 to –2.14 (m, 2H); ¹³C NMR: δ = 152.0, 133.4, 126.7, 126.3, 123.1, 76.3, 27.9, 26.9; MS (70 EV, EI): *m/z* (%): 303 (22), 302 (93) [*M*⁺], 274 (14), 234 (36), 218 (21), 216 (20), 206 (15), 204 (64), 189 (39), 188 (100), 187 (33), 177 (20), 176 (74), 94 (39), 69 (51); C₂₁H₁₈O₂ (302.45): calcd C 83.42, H 6.00; found C 83.40, H 6.00.

1,8-Dioxa[8](2,7)pyrenophane (8b): As described above for **8a**, diene **7b** (1.15 g, 3.63 mmol) and DDO (1.66 g, 7.30 mmol) afforded, after flash chromatography, **8b** (0.92 g, 81%) as a white, crystalline solid. **8b**: M.p. 190 °C (decomp) (xylenes); IR (CCl₄): 3040 (w), 2970 (m), 2940 (m), 2880 (m), 1460 (m), 1430 (m), 1290 (m), 1270 (m); ¹H NMR: δ = 7.84 (s, 4H), 7.44 (s, 4H), 3.59 (t, ³J(H,H) = 4.6, 4H), 0.13–0.07 (m, 4H), –1.43 to –1.48 (m, 4H); ¹³C NMR: δ = 153.6, 132.7, 127.4, 126.9, 123.2, 77.7, 27.9, 26.7; MS (70 EV, EI): *m/z* (%): 317 (24), 316 (100) [*M*⁺], 288 (11), 234 (58), 206 (49), 205 (64), 188 (56), 176 (70); HRMS: calcd C₂₂H₂₀O₂ 316.1462; found 316.1451.

Reaction of 8a with TCNE to give adduct 9: A solution of pyrenophane **8a** (15.0 mg, 0.050 mmol) in benzene (8 mL) was added a solution of TCNE (22.5 mg, 0.176 mmol) in benzene (2 mL) and the mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed (CH₂Cl₂) to afford **9** (21.8 mg, 102%) as a white solid. **9**: M.p. 160 °C (decomp); ¹H NMR: δ = 7.66 (d, ³J(H,H) = 8.8 Hz, 1H), 7.53 (d, ³J(H,H) = 8.6 Hz, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.22 (d, ³J(H,H) = 9.9 Hz, 1H), 7.07 (d, ⁴J(H,H) = 1.9 Hz, 1H), 6.67 (d, ³J(H,H) = 9.9 Hz, 1H), 5.04 (d, ⁴J(H,H) = 1.9 Hz, 1H), 4.26 (dd, ³J(H,H) = 12.2, 6.8 Hz, 1H), 4.17 (d, ⁴J(H,H) = 1.9 Hz, 1H), 3.85 (ddd, ³J(H,H) = 12.8, 7.1, 1.8 Hz, 1H), 3.60–3.53 (m, 2H), 1.14–1.02 (m, 1H),

0.96–0.72 (m, 2H), 0.20–0.00 (m, 2H), –1.69 to –1.78 (m, 1H); ^{13}C NMR: δ (some quaternary carbons not observed) 171.5 (0), 156.6 (0), 147.5 (0), 136.6 (0), 132.9 (1), 132.7 (0), 129.9 (0), 127.3 (1), 127.2 (1), 126.3 (0), 124.8 (1), 123.5 (1), 121.6 (1), 111.4 (0), 111.3 (0), 111.2 (0), 111.0 (0), 106.6 (1), 76.3 (2), 71.9 (2), 54.0 (1), 32.6 (2), 30.6 (2), 28.2 (2); MS (70 EV, EI): m/z (%): 430 (7) [M^+], 303 (15), 302 (71), 234 (26), 218 (15), 216 (13), 206 (35), 205 (45), 189 (28), 188 (69), 187 (23), 176 (53), 128 (100), 94 (31), 76 (74), 69 (41); good HRMS or analytical data for this unstable compound could not be obtained.

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