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[14][14]Metaparacyclophane: First Example of an [m][n]Metaparacyclophane[†]

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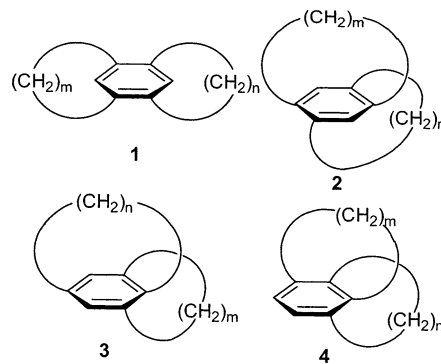*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, P. R. China*

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Abstract: The synthesis of [14][14]metaparacyclophane, the first [m][n]metaparacyclophane ever known, is described. The reaction sequence began with the bis-chloromethylation of [14]paracyclophane in refluxing CS_2, which yielded a nonseparable mixture of 16,19- and 16,20-bis(chloromethyl)-[14]paracyclophane in an 8:1 ratio. Acetolysis of these dichlorides gave the corresponding diacetate mixture from which the minor component 16,20-bis(acetoxymethyl)[14]-paracyclophane was isolated and elaborated into the desired cyclophane via the disulfone of 2,15-dithia[16][14]meta-paracyclophane and subsequent sulfur dioxide extrusion by a one-flask Ramberg–Bäcklund reaction procedure followed by hydrogenation.

Cyclophanes are noted for their structural diversity,[1] and even simple members can be synthetically challenging. Defined by a rather spartan makeup of an aromatic ring to which two aliphatic bridges are attached, each in meta or para fashion, [m][n]cyclophanes are generally counted among the simple members of the family. The manners in which the two bridges are disposed in relation to each other give rise to four different types of [m][n]-cyclophanes as illustrated by the all-carbon benzenophanes shown in Figure 1. Of these four structural subsets, [m]-[n]metameta(1,3−4,6)cyclophanes (**1**) are most easily accessible, and a number of these compounds with n, m ≥ 8 were synthesized in our laboratory some years ago in a rather uneventful manner.[2] The synthesis of [m][n]-paraparacyclophanes (**2**), particularly in their enantiomerically pure or enriched forms, is somewhat more demanding but that too has been achieved first by Nakazaki's group[3] and later by us.[4] However, the remaining [m][n]metaparacyclophanes (**3**) and [m][n]-metameta(1,3−2,4)cyclophanes (**4**), modest as their structural motifs may be, presented considerable synthetic challenges on account of the difficulties anticipated in

[†] Dedicated to Professor Thomas C. W. Mak on the occasion of his 65th birthday.

(1) (a) Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964. (b) Keehn, P. M.; Rosenfield, S. M. *Cyclophanes*; Academic Press: New York, 1983. (c) Diederich, F. *Cyclophanes*; The Royal Society of Chemistry: Cambridge, U.K., 1991. (d) Vögtle, F. *Cyclophane Chemistry*; Wiley: Chichester, U.K., 1993.

(2) Man, T.-O. M. Phil. Thesis, The Chinese University of Hong Kong, 1983.

(3) (a) Nakazaki, M.; Yamamoto, K.; Tanaka, S. *Tetrahedron Lett.* **1971**, 341. (b) Nakazaki, M.; Yamamoto, K.; Tanaka, S. *J. Org. Chem.* **1976**, *41*, 4081. (c) Nakazaki, M.; Yamamoto, K.; Ito, M.; Tanaka, S. *J. Org. Chem.* **1977**, *42*, 3468.

(4) Chan, T.-L.; Hung, C.-W.; Man, T.-O.; Leung, M.-k. *Chem. Commun.* **1994**, 1971.
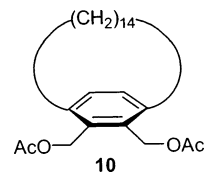
FIGURE 1.

the assembly of the respective contiguous three- and four-point bridgehead attachments in them. Indeed, none of these cyclophanes until now has succumbed to synthesis. Reported herein is our synthetic route to [14][14]meta-paracyclophane (**16**), the first example of the [m][n]-metaparacyclophane series.

Our synthesis of **16** was made possible by an investigation of the bis-chloromethylation of [14]paracyclophane (**5**) using a mixture of chloromethyl methyl ether and stannic chloride in carbon disulfide. Whereas at −5 °C this reaction gave a single product within the limit of detection by 300 MHz ^{1}H NMR spectroscopy, raising the temperature to the boiling point of carbon disulfide led to a chromatographically nonseparable mixture, in an 8:1 ratio, of the same product and a minor isomer. Isolations of the individual bis-chloromethylated [14]paracyclophane isomers were achieved by first converting the above mixture into a mixture of diacetates which became separable and subsequently re-converting each diacetate into the corresponding dichloride (Scheme 1). The structures of the major/minor dichloride/diacetate pairs in Scheme 1 were settled in the manner described below.

That the major diacetate isomer was resolvable into two enantiomers by HPLC over a chiral column established its structure as 16,19-bis(acetoxymethyl)[14]-paracyclophane (**8**) and, therefore, that of the major dichloride isomer as 16,19-bis(chloromethyl)[14]para-cyclophane (**6**). As for the minor diacetate isomer, the 14-peak pattern for the signals of the polymethylene bridge carbons together with a four-peak pattern for those of the aromatic carbons in the ^{13}C NMR spectrum of this compound pinned down its structure as 16,20-bis-(acetoxymethyl)[14]paracyclophane (**9**) and ruled out the possibility of its being the 16,17-isomer, **10**, which would have exhibited a seven-peak and a three-peak signal patterns for the bridge and aromatic carbons, respectively. It follows from the structure of **9** that the minor dichloride product from the bis-chloromethylation of **5** was 16,20-bis(chloromethyl)[14]paracyclophane (**7**).
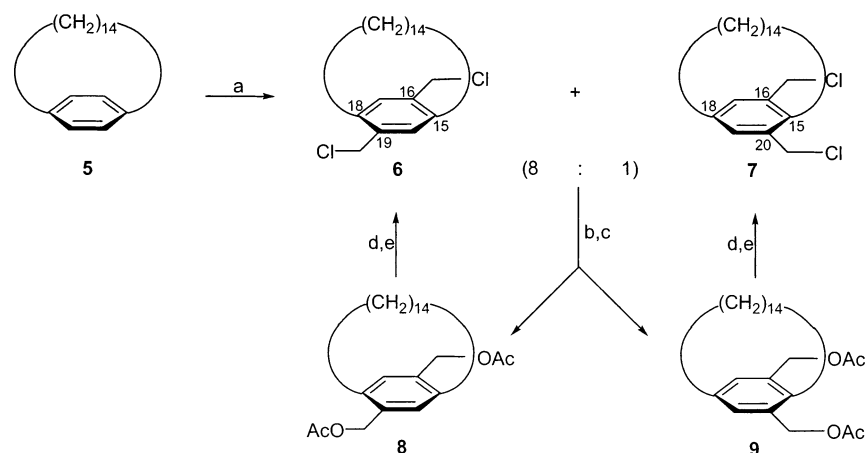
SCHEME 1*a*

a Reagents and conditions: (a) CH₃OCH₂Cl, SnCl₄, CS₂, reflux, 50% of **6** and **7** (8:1) as an inseparable mixture; (b) NaOAc, HOAc, reflux; (c) separation by silica gel column chromatography, 41% of **8** and 5% of **9** from **5**; (d) KOH, MeOH, reflux; (e) SOCl₂, CH₂Cl₂, rt, 81% of **6** from **8**; 85% of **7** from **9**.

The propitiously positioned acetoxymethyl groups in **9** rendered it an ideal building block for constructing an [*m*][*n*]metaparacyclophane, despite the disadvantage of **9** being a minor product in Scheme 1. However, this disadvantage was assuaged somewhat by the recyclability of the major diacetate isomer **8** to furnish additional amounts of **9** through an operation consisting of (1) conversion of **8** into **6**, (2) equilibration of **6** into a mixture of **6** and **7** under the bis-chloromethylation condition of **5**, and (3) conversion of mixture **6** and **7** into mixture **8** and **9**, from which **9** could be gleaned.

Thus, with workable quantities of **9** in hand, we proceeded to complete the synthesis of [14][14]metaparacyclophane (**16**) by installing the second bridge in a manner shown in Scheme 2. Diacetate **9** was deacetylated smoothly to 16,20-bis(hydroxymethyl)[14]paracyclophane (**11**), which was converted into the corresponding dibromide **12**. Cyclocoupling of **12** with 1,12-dodecanedithiol in the presence of cesium carbonate led to 2,15-dithia-[16][14]metaparacyclophane (**13**) and thence to the disulfone **14**. The stage was now set for sulfur dioxide extrusion by the Ramberg–Bäcklund reaction procedure developed by us earlier[5] to furnish in modest yield [14]-[14]metaparacyclophane-1,13-diene (**15**) whose ¹H NMR spectrum indicated it to be a mixture of geometric isomers. Hydrogenation of **15** finally delivered [14][14]-metaparacyclophane (**16**) as a colorless oil.

Since Cram's landmark work almost half a century ago on the mounting of a bridge on the benzene ring by means of acyloin condensation,[6] several other approaches have been developed to handle the installation of medium- and large-sized polymethylene bridges onto aromatic platforms. These methods, each with its merits, include (1) Kumada's nickel-mediated cyclocoupling of the bis-Grignard reagent of an α,ω-dihaloalkane with a dihaloarene,[7] (2) sulfur dioxide extrusion from the disulfones of dithia-

SCHEME 2*a*
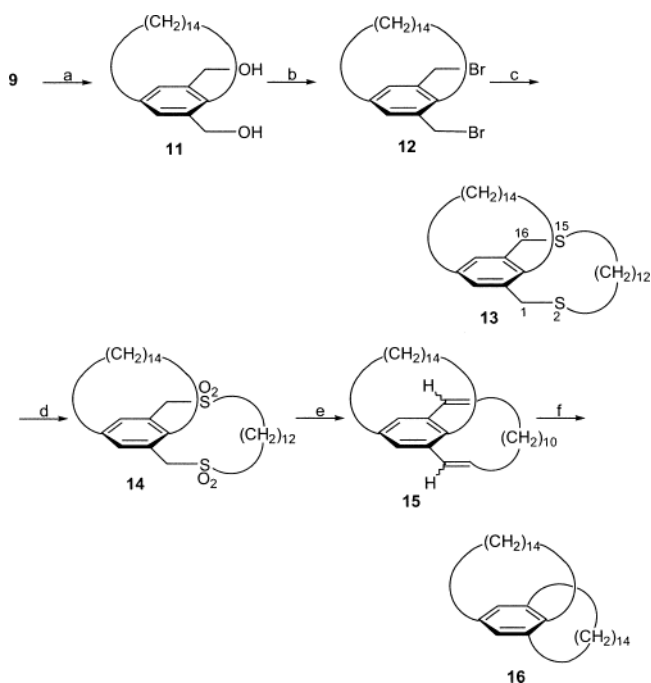
a Reagents and conditions: (a) KOH, MeOH, reflux, 96%; (b) PBr₃, C₆H₆–CH₃CN, pyridine, 0 °C → rt, 87%; (c) HS(CH₂)₁₂SH, Cs₂CO₃, EtOH–C₆H₆, 82%; (d) H₂O₂, HOAc, 0 °C, 97%; (e) CBr₂F₂, KOH/Al₂O₃, *t*-BuOH–CH₂Cl₂; (f) H₂, Pd/C, EtOAc, 28% in two steps.

cyclophanes by flash vacuum pyrolysis,[8] a method made popular by Vögtle,[9] and (3) cyclocoupling of a dibromoarene with the bis-9-BBN adduct of a diterminal diene under the Suzuki–Miyaura coupling conditions, a strategy successfully employed by Kwochka's group most recently.[10] Of particular relevance to our present work

(5) Chan, T.-L.; Fong. S.; Li, Y.; Man, T.-O.; Poon, C.-D. *Chem. Commun.* **1994**, 1771.
(6) Cram, D. J.; Daeniker, H. U. *J. Am. Chem. Soc.* **1954**, *76*, 2743.
(7) Tamao, K.; Kodama, S.; Nakasuka, T.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 4405.

(8) (a) Vögtle, F.; Mew, P. K. T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 60. (b) Otsubo, T.; Misumi, S. *Synth. Commun.* **1978**, *8*, 285.
(9) Vögtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 514.
(10) Smith, B. B.; Hill, D. E.; Cropp, T. A.; Walsh, R. D.; Cartrette, D.; Hipps, S.; Shachter, A. M.; Pennington, W. T.; Kwochka, W. R. *J. Org. Chem.* **2002**, *67*, 5333.

is Vögtle's pyrolytic approach in using the disulfones of dithiacyclophanes as precursors for cyclophanes. For the synthesis of small and medium-sized cyclophanes, this one-step pyrolytic sulfur dioxide extrusion methodology continues to be a powerful synthetic tool. However, for the assembly of a long cyclophane bridge, our simple two-step sequence in executing the removal of the sulfone functionalities by the combination of a one-flask Ramberg−Bäcklund reaction and hydrogenation[4] offers a convenient alternative in that the need of a pyrolysis apparatus can be avoided. It should be pointed out that the idea of cyclophane synthesis by the Ramberg−Bäcklund reaction can be traced back to the early works of Sutherland[11] and of others,[12] but the effectiveness of this route can be greatly enhanced by application of the one-flask Ramberg−Bäcklund reaction described by us[5] as demonstrated by our previous synthesis of optically active [12][12]paraparacyclophane[4] and the present work.

In conclusion, an [*m*][*n*]metaparacyclophane, in the form of [14][14]metaparacyclophane (**16**), has now been inducted into the "Hall of Phane".[13] Construction of a long polymethylene bridge in cyclophanes by using, as precursor, the disulfone of the corresponding dithiapolymethylene bridge remains a powerful strategy, and in this context the synthetic usefulness of our variant[5] of the Ramberg−Bäcklund reaction for sulfur dioxide extrusion is once again demonstrated.

Experimental Section

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded in CDCl$_3$ unless otherwise stated on a Bruker DPX 300 spectrometer operating at 300 and 75 MHz, respectively. Low resolution mass spectra were obtained on an HP5989 spectrometer or a VG ZAB-HS spectrometer, and high-resolution mass spectra (HRMS) were obtained on a Bruker APEX 47e FRMS spectrometer. Preparative HPLC for resolution of 16,19-bis-(acetoxymethyl)[14]paracyclophane (**8**) was carried out by using a Chiralcel OD column (2 cm I.D × 25 cm length). When necessary, solvents were dried by redistillation over appropriate drying agents in the usual manners. Elemental analyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, UK.

Mixture of 16,19-Bis(chloromethyl)[14]paracyclophane (6) and 16,20-Bis(chloromethyl)[14]paracyclophane (7). To a solution of [14]paracyclophane (**5**)^{4,8b} (5.00 g, 18.4 mmol) and chloromethyl methyl ether (60 mL, excess) in carbon disulfide (75 mL) was added SnCl$_4$ (30 mL, excess) dropwise over 30 min under nitrogen. After being stirred for 4 h at 53−55 °C (oil bath temperature), the reaction mixture was poured into ice−water (200 mL). The aqueous mixture was further stirred for 1 h to allow complete hydrolysis of excess SnCl$_4$ and was thereafter extracted with CH$_2$Cl$_2$ (3 × 100 mL). The combined extract was washed with water (2 × 50 mL) and brine (50 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a yellow oil that was purified by flash chromatography over silica gel (150 g) using hexane as eluent to give an nonseparable mixture of compounds **6** and **7** (3.39 g, 50%) as a white solid: mp 55−59 °C; R_f = 0.39 (hexane). The separation and identification of **6** and **7** were made possible via their corresponding diacetate derivatives **8** and **9** as described below.

***rac*-, (+)-, and (−)-16,19-Bis(acetoxymethyl)[14]para-cyclophane (8).** Sodium acetate (4.10 g, 50.0 mmol) was added in one lot at room temperature to a solution of the above mixture of 16,19-bis(chloromethyl)[14]paracyclophane (**6**) and 16,20-bis-(chloromethyl)[14]paracyclophane (**7**) (1.85 g, 5.0 mmol) in HOAc (50 mL). Having been heated under reflux for 1 day, the reaction mixture was cooled to room temperature and water (40 mL) was added. The aqueous mixture was extracted with hexane (3 × 40 mL), and the combined extracted was washed with water (2 × 50 mL) and brine (50 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a yellow oil that was purified by flash chromatography over silica gel (60 g) using EtOAc−hexane (1/20, v/v) as eluent to give a fore-running fraction of pure *rac*-**8** (1.70 g, 82%) as a colorless oil: R_f = 0.35 [EtOAc−hexane (1/10, v/v)]; ^{1}H NMR δ 0.83−1.27 (3 overlapped broad peaks, 20H), 1.54−1.69 (m, 4H), 2.09 (s, 6H), 2.49−2.61 (m, 2H), 2.83−2.94 (m, 2H), 5.06 (d, J = 12.2 Hz, 2H), 5.19 (d, J = 12.2 Hz, 2H), 7.15 (s, 2H); ^{13}C NMR δ 21.06, 24.89, 26.29, 27.12, 27.22, 28.25, 29.20, 31.00, 64.14, 131.79, 133.66, 138.61, 170.92; MS m/z 416 (M$^+$, 0.5), 387 (18), 356 (80), 296 (100), 281 (35). Anal. Calcd for C$_{26}$H$_{40}$O$_4$: C, 74.96; H, 9.68. Found: C, 74.92; H, 9.66.

Resolution of the optically active (+)-16,19-bis(acetoxymethyl)-[14]paracyclophane (**8**) and (−)-16,19-bis-(acetoxymethyl)[14]-paracyclophane (**8**) was carried out by HPLC on a preparative Chiralcel OD column. Enantiomer (+)-**8**: HPLC 33.5min [FR 3.0 mL/min, ^{i}PrOH−hexane (1/40, v/v)]; [α]$^{21}_D$ +32.3 (c = 0.91, CHCl$_3$). Enantiomer (−)-**8**: HPLC 45.5min [FR 3.0 mL/min, ^{i}PrOH−hexane (1/40, v/v)]; [α]$^{21}_D$ −32.5 (c = 1.44, CHCl$_3$).

16,20-Bis(acetoxymethyl)[14]paracyclophane (9). In the flash chromatographic separation of the acetolysis product mixture above, a second fraction followed *rac*-**8**. This material was rechromatographed using EtOAc−hexane (1/25, v/v) as eluent to give pure **9** (212 mg, 10%) as a colorless oil: R_f = 0.40 [EtOAc−hexane (1/10, v/v)]; ^{1}H NMR δ 0.85−1.15 (2 overlapped broad peaks, 12H), 1.15−1.30 (br, 8H), 1.45−1.70 (m, 4H), 2.09 (s, 6H), 2.64 (t, J = 6.1 Hz, 2H), 2.82 (t, J = 6.2 Hz, 2H), 5.06 (d, J = 12.3 Hz, 2H), 5.25 (d, J = 12.3 Hz, 2H), 7.15 (s, 2H); ^{13}C NMR δ 21.25, 24.90, 25.22, 26.30, 26.52, 26.98, 27.30, 27.59, 27.69, 28.36, 28.40, 29.47, 29.63, 34.55, 64.80, 131.07, 134.54, 137.27, 140.15, 171.13; FABMS m/z 417 (M + H$^+$, 1), 373 (21), 297 (100), 145 (41), 119 (33), 55 (30). Anal. Calcd for C$_{26}$H$_{40}$O$_4$: C, 74.96; H, 9.68. Found: C, 74.85; H, 9.63.

***rac*-16,19-Bis(chloromethyl)[14]paracyclophane (6).** Potassium hydroxide (0.78 g of the commercial 85% pellets, excess) was added in one lot at room temperature to a solution of *rac*-16,19-bis(acetoxymethyl)[14]paracyclophane (**8**) (498 mg, 1.2 mmol) in methanol (50 mL). The reaction mixture was refluxed for 2h and then cooled to room temperature. The solvent was removed in vacuo and the residue was diluted with water (50 mL). The aqueous mixture was extracted with CH$_2$Cl$_2$ (3 × 30 mL), and the combined extract was washed with water (2 × 20 mL) and brine (20 mL) and dried over MgSO$_4$. Removal of solvent in vacuo left a white solid which was dried overnight under reduced pressure in a desiccator, and without further purification this material was dissolved in CH$_2$Cl$_2$ (30 mL). To the resultant CH$_2$Cl$_2$ solution was added SOCl$_2$ (2 mL, excess). After the solution was stirred overnight at room temperature, the solvent and excess SOCl$_2$ were removed under reduced pressure. The residue was diluted with water (20 mL) and extracted with CH$_2$Cl$_2$ (2 × 30 mL). The combined extract was washed with water (2 × 15 mL) and brine (15 mL) and dried over MgSO$_4$. Removal of solvent in vacuo afforded a yellow oil which was flash chromatographed over silica gel (40 g) using hexane as eluent to furnish **6** (358 mg, 81%) as a white solid: mp 56−57 °C; R_f = 0.39 (hexane); ^{1}H NMR δ 0.85−1.30 (3 overlapped broad peaks, 20H), 1.59−1.71 (m, 4H), 2.52−2.62 (m, 2H), 2.95−3.05 (m, 2H), 4.55 (d, J = 11.3 Hz, 2H), 4.69 (d, J = 11.3 Hz, 2H), 7.16 (s, 2H); ^{13}C NMR δ 24.95, 26.32, 27.09, 27.22, 28.24, 29.00, 30.97, 43.85, 132.42, 135.71, 138.59. Anal. Calcd for C$_{22}$H$_{34}$Cl$_2$: C, 71.53; H, 9.28. Found: C, 71.71; H, 9.39.

16,20-Bis(chloromethyl)[14]paracyclophane (7). In a manner similar to the conversion of **8** to **6** described above, **9** (50.0 mg, 0.12 mmol) gave **7** (38.0 mg, 85%) as a white solid: mp 54−56 °C; R_f = 0.39 (hexane); ^{1}H NMR δ 0.85−1.30 (3 overlapped broad peaks, 20H), 1.58−1.70 (m, 4H), 2.64 (t, J = 6.2 Hz, 2H), 2.94 (t, J = 6.1 Hz, 2H), 4.56 (d, J = 11.4 Hz, 2H), 4.77 (d, J =

(11) Potter, S. E.; Sutherland, I. O. *Chem. Commun.* **1973**, 520.
(12) (a) Doomes, E.; Beard, R. M. *Tetrahedron Lett.* **1976**, 1243. (b) Cooke, M. P. *J. Org. Chem.* **1981**, *46*, 1747.
(13) Bodwell, G. T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2085.

11.4 Hz, 2H), 7.17 (s, 2H); ^{13}C NMR δ 25.02, 25.17, 25.39, 26.32, 26.58, 26.90, 26.99, 27.32, 27.62, 28.40, 29.37, 29.44, 29.67, 34.40, 44.90, 131.91, 136.74, 140.73; CIMS *m/z* 370 (M + 2$^+$, 5), 368 (M$^+$, 8), 199 (48), 128 (60), 55 (100). Anal. Calcd for C$_{22}$H$_{34}$Cl$_2$: C, 71.53; H, 9.28. Found: C, 71.73; H, 9.41.

16,20-Bis(hydroxymethyl)[14]paracyclophane (11). Potassium hydroxide (0.39 g of commercial 85% pellet, excess) was added in one lot at room temperature to a solution of 16,20-bis-(acetoxymethyl)[14]paracyclophane (**9**) (249 mg, 0.60 mmol) in methanol (25 mL). The reaction mixture was refluxed for 2 h and then cooled to room temperature. The solvent was removed in vacuo, and the residue was diluted with water (25 mL). The aqueous mixture was extracted with CH$_2$Cl$_2$ (2 × 20 mL), and the combined extract was washed with water (2 × 15 mL) and brine (15 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a white solid which was purified by flash chromatography over silica gel (30 g) using EtOAc−CH$_2$-Cl$_2$−hexane (1/2/10, v/v/v) as eluent to give **11** (192 mg, 96%) as a white solid: mp 114−115 °C; R_f = 0.38 [EtOAc−hexane (1/2, v/v)]; ^{1}H NMR δ 0.82−1.15 (2 overlapped broad peaks, 12H), 1.15−1.30 (br, 8H), 1.50−1.71 (br, 4H), 2.66 (t, J = 6.1 Hz, 2H), 2.85 (t, J = 6.2 Hz, 2H), 4.62 (d, J = 12.5 Hz, 2H), 4.85 (d, J = 12.5 Hz, 2H), 7.18 (s, 2H); ^{13}C NMR δ 25.04, 25.30, 26.33, 26.51, 26.57, 27.05, 27.33, 27.63, 27.70, 28.36, 28.42, 29.56, 29.83, 34.71, 63.60, 128.58, 135.19, 139.49, 140.29; CIMS *m/z* 332 (M$^+$, 6), 295 (55), 156 (100), 105 (84), 91 (90), 55 (95). Anal. Calcd for C$_{22}$H$_{36}$O$_2$: C, 79.47; H, 10.91. Found: C, 79.52; H, 11.03.

16,20-Bis(bromomethyl)[14]paracyclophane (12). To a solution of 16,20-bis(hydroxymethyl)[14]paracyclophane (**11**) (150 mg, 0.33 mmol) in a dry mixed solvent of benzene (15 mL), acetonitrile (8 mL), and pyridine (0.3 mL) at 0 °C was added phosphorus tribromide (0.3 mL, excess). Upon stirring at 0 °C for 1 h and then room temperature for 3 h, the reaction mixture was quenched by water (30 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (2 × 30 mL) and the combined extract was washed with water (2 × 15 mL) and brine (10 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a yellow oil which was purified by flash chromatography over silica gel (30 g) using hexane as eluent to give **12** (180 mg, 87%) as a white solid: mp 65−66 °C; R_f = 0.47 (hexane) ^{1}H NMR δ 0.82−1.29 (3 overlapped broad peaks, 20H), 1.51−1.72 (m, 4H), 2.62 (t, J = 6.1 Hz, 2H), 2.94 (t, J = 6.2 Hz, 2H), 4.48 (d, J = 10.2 Hz, 2H), 4.67 (d, J = 10.2 Hz, 2H), 7.14 (s, 2H); ^{13}C NMR δ 25.15, 26.38, 26.64, 26.92, 27.26, 27.37, 27.63, 28.40, 28.47, 29.03, 29.37, 31.24, 32.59, 34.39, 132.32, 136.86, 137.06, 140.79; CIMS *m/z* 460 (M + 4$^+$, 0.3), 458 (M + 2$^+$, 0.6), 456 (M$^+$, 0.3), 377 (9), 375 (9), 296 (100), 145 (64). Anal. Calcd for C$_{22}$H$_{34}$Br$_2$: C, 57.65, H, 7.48. Found: C, 57.82; H, 7.56.

2,15-Dithia[16][14]metaparacyclophane (13). To a solution of cesium carbonate (306 mg, 0.94 mmol) in ethanol (20 mL) under nitrogen was added a solution of 16,20-bis(bromomethyl)-[14]paracyclophane (**12**) (172 mg, 0.38 mmol) and 1,12-dode-canedithiol (88.0 mg, 0.38 mmol) in dry benzene (20 mL) dropwise through a dropping funnel over 4 h. Upon completion of addition of reactants, the reaction mixture was further stirred for 2 h, and the solvent was removed in vacuo. The residue was diluted with water (20 mL) and extracted with CH$_2$Cl$_2$ (2 × 20 mL), and the combined extract was washed with water (15 mL) and brine (15 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a yellow oil which was purified by flash chromatography over silica gel (20 g) using hexane as eluent to give **13** (164.5 mg, 82%) as a colorless oil: R_f = 0.16 (hexane); ^{1}H NMR δ 0.80−1.65 (4 overlapped broad peaks, 44H), 2.30−2.42 (m, 4H), 2.59 (t, J = 6.0 Hz, 2H), 2.93 (t, J = 6.0 Hz,

2H), 3.55 (d, J = 13.1 Hz, 2H), 3.96 (d, J = 13.1 Hz, 2H), 7.00 (s, 2H); ^{13}C NMR δ 25.24, 25.33, 26.34, 26.54, 27.01, 27.11, 27.18, 27.36, 27.62, 27.72, 27.78, 27.93, 28.31, 28.44, 29.11, 31.23, 34.50, 34.57, 129.97, 136.40, 136.97, 139.34; CIMS *m/z* 530 (M$^+$, 3), 327 (100) 297 (22), 143 (58), 119 (41). Anal. Calcd for C$_{34}$H$_{58}$S$_2$: C, 76.91; H, 11.01. Found: C, 77.09; H, 11.11.

2,2,15,15-Tetraoxo-2,15-dithia[16][14]metaparacyclophane (14). A solution of 2,15-dithia[16][14]metaparacyclophane (**13**) (184.0 mg, 0.34 mmol) and 30% hydrogen peroxide (1 mL, excess) in acetic acid (15 mL) was stirred at 0 °C for 2 h. Upon removal of solvent under reduced pressure, the white solid residue was dissolved in CH$_2$Cl$_2$ (30 mL), and the CH$_2$Cl$_2$ solution was washed with water (20 mL) and brine (20 mL) and dried over MgSO$_4$. Removal of solvent under reduced pressure afforded a white solid which was purified by flash chromatography over silica gel (20 g) using EtOAc−hexane (1/2, v/v) as eluent to afford pure **14** (200.5 mg, 97%) as a white solid: mp 272−273 °C; R_f = 0.38 [EtOAc−hexane (1/2, v/v)]; ^{1}H NMR (acetone-d_6) δ 0.80−1.45 (4 overlapped broad peaks, 40H), 1.45−1.80 (m, 8H), 2.68 (t, J = 6.1 Hz, 2H), 3.14 (t, J = 6.0 Hz, 2H), 4.28 (d, J = 14.2 Hz, 2H), 4.74 (d, J = 14.2 Hz, 2H), 7.35 (s, 2H); ^{13}C NMR δ 20.54, 25.04, 25.43, 26.33, 26.46, 27.01, 27.15, 27.27, 27.46, 28.10, 28.23, 28.33, 29.41, 29.80, 29.99, 34.48, 50.86, 58.34, 127.99, 133.32, 139.07, 141.05; FABMS *m/z* 595 (M + H$^+$, 39) 297 (100), 149 (53), 91 (35). Anal. Calcd for C$_{34}$H$_{58}$S$_2$O$_4$: C, 68.64; H, 9.83. Found: C, 68.69; H, 9.95.

[14][14]Metaparacyclophane (16). To a rapidly stirred slurry of 2,2,15,15-tetraoxo-2,15-dithia[16][14]metaparacyclophane (**14**) (100.0 mg, 0.16 mmol) and KOH/Al$_2$O$_3$[5] (2 g, excess) in CH$_2$-Cl$_2$−^{t}BuOH (10 mL, 1/1, v/v) was added CBr$_2$F$_2$ (10 mL) in one portion. Upon being stirred at room temperature for 2 h, the reaction mixture was filtered through a layer of silica gel under suction with liberal washing with CH$_2$Cl$_2$. Removal of solvent under reduced pressure afforded a colorless oil which was purified by flash chromatography over silica gel (10 g) using hexane as eluent to give the intermediate, presumably the configuration undefined [16][14]metaparacyclophane-1,13-diene (**15**) as a colorless oil. The diene was dissolved in EtOAc (20 mL) and hydrogenated in the presence of 5% Pd/C under a balloon of hydrogen at room temperature overnight. The resulting mixture was filtered through a layer of silica gel under suction to remove the Pd/C, and the filter cake was washed with EtOAc. Removal of solvent under reduced pressure afforded a colorless oil which was purified by flash chromatography over silica gel (10 g) using hexane as eluent to give pure **16** (20.0 mg, 28%) as a colorless oil: R_f = 0.93 (hexane); ^{1}H NMR δ 0.83−1.35 (4 overlapped broad peaks, 40H), 1.35−1.57 (2 overlapped broad peaks, 8H), 2.43−2.51 (m, 2H), 2.56 (t, J = 6.1 Hz, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.81−2.90 (m, 2H), 6.72 (s, 2H); ^{13}C NMR δ 14.28, 22.85, 26.38, 26.47, 26.57, 26.88, 27.36, 27.43, 27.71, 27.80, 28.01, 28.16, 28.25, 28.46, 28.57, 29.86, 30.29, 31.78, 32.80, 127.89, 135.64, 138.43, 140.65; SIMS *m/z* 466.6 (M$^+$); HRFABMS calcd for C$_{34}$H$_{58}$$^+$ (M$^+$) 466.4533, found 466.4569.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all relevant compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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