Synthesis and Conformational Behavior of Benzo[2.2]metaparacyclophan-9-ene, Dibenzo[2.2]metaparacyclophane and 1,4-Dimethyldibenzo[2.2]metaparacyclophane. X-ray Crystal Structure of Dibenzo[2.2]metaparacyclophane[1a-c]

Timothy Wong, Mabel S. M. Yuen, Thomas C. W. Mak,[1d] and Henry N. C. Wong*,[1e]

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Dibenzo[2.2]metaparacyclophane (**5**) and its 1,4-dimethyl derivative **6** have been synthesized utilizing low-valent-titanium deoxygenation as the key step. The conformational mobility of **5** and **6**, as well as that of benzo[2.2]metaparacyclophane (**3**) and benzo[2.2]metaparacyclophan-9-ene (**4**) have been studied by variable temperature NMR spectrometry. The results of this study, together with those reported for [2.2]metaparacyclophane (**1**) and [2.2]metaparacyclophane-1,9-diene (**2**), show that the free energy of activation for the flipping process ($\Delta G_c^{\ddagger}$) at the coalescence temperature (T_c) is closely related to the bond types of the bridges connecting the meta-bridged benzenes and the para-linked ones. In addition to these structural effects, the nonbonded interactions of H_1 and H_{15}, and that of H_{12} with H_{13} in **5** also influence such conformational behavior, as can be unequivocally substantiated by the synthesis and study of **6**. An X-ray crystallographic study has shown that **5** conforms closely to idealized C_s molecular symmetry with a dihedral angle of 147.2° between the pair of ortho-benzenes and a pronounced boat conformation for the para-bridged one.

The chemistry of cyclophanes has attracted considerable attention in the past 3 decades.[2] Of these intriguing compounds, [2.2]metaparacyclophane (**1**), first synthesized by Vögtle,[3] stands out because of its capability of showing a molecular flipping process (Figure 1). As a result of such dynamic character, the coalescence of H_a and H_x can be conveniently monitored by variable temperature ^{1}H NMR spectrometry.[4]

In three independent variable temperature ^{1}H NMR studies on **1**, the free energy of activation for the flipping process ($\Delta G_c^{\ddagger}$) were found to be 84,[3a] 87,[3c] and 92 kJ/mol,[3b] respectively, and the corresponding coalescence temperatures (T_c) were accordingly 140,[3a] 146,[3c] and 187 °C.[3b] Interestingly, [2.2]metaparacyclophane-1,9-diene (**2**), prepared by Boekelheide, showed a coalescence temperature at −96 °C, thus resulting in a $\Delta G_c^{\ddagger}$ of 35 kJ/mol.[5] It is likely that the bond distances of the bridges and the bridge angles are influential factors on the conformational mobility. In order to verify our arguments,

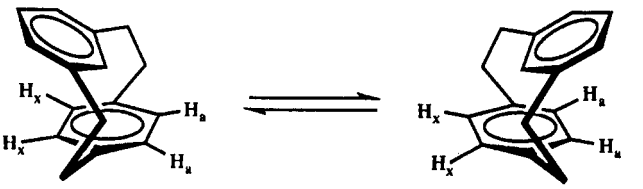
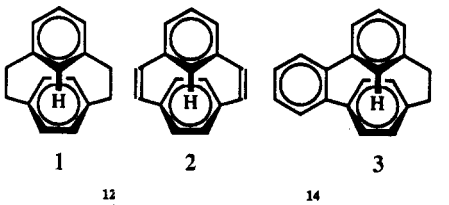
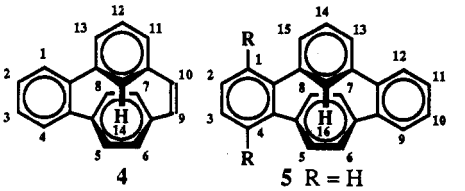


Figure 1. Conformational flipping of [2.2]metaparacyclophane (**1**).



1 2 3



4 5 R = H 6 R = Me

it was therefore of special interest to investigate and to compare the parameters of the flipping process for the known benzo[2.2]metaparacyclophane (**3**),[6,7] as well as those of the hitherto unknown benzo[2.2]metaparacyclophan-9-ene (**4**),[7] and dibenzo[2.2]metaparacyclophane (**5**).[7] We report herein the synthesis and variable temperature ^{1}H NMR study of **4** and **5**. Although less obvious, it is also possible that the nonbonded interactions of H_1 and H_{15}, and that of H_{12} with H_{13} in **5**, also constitute one

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(7) IUPAC name of **3**: 10,11-dihydro-12,15-etheno-5,9-methenobenzocyclotridecene, **4**: 12,15-etheno-5,9-methenobenzocyclotridecene, **5**: 14,17-etheno-5,9-methenodibenzocyclotridecane, **6**: 1,4-dimethyl-14,17-etheno-5,9-methenodibenzocyclotridecene.

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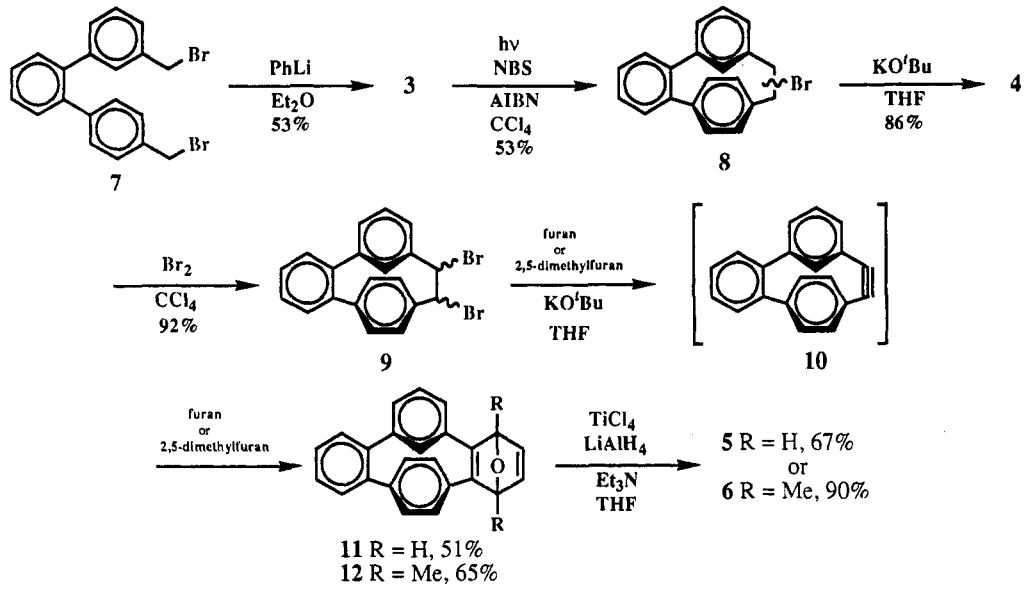
Scheme I



of the decisive factors affecting the magnitude of ΔG_c^* and T_c. To establish this structural significance, 1,4-dimethyldibenzo[2.2]metaparacyclophane (**6**)[7] has also been prepared and studied.

Results and Discussion

(a) Synthesis. As depicted in Scheme I, the synthesis of title compounds **4–6** was achieved by utilizing **3** as the pivotal starting material. Compound **3**, first synthesized in 6% yield by Vögtle via three steps starting from 3,4″-bis(bromomethyl)-1,1′:2′,1″-terphenyl (**7**),[6,8] was also prepared by us in 53% yield in one step using phenyllithium-induced coupling of **7**. Bromination of **3** with *N*-bromosuccinimide (NBS) in CCl_4 in the presence of a catalytic amount of azobis(isobutyronitrile) (AIBN) furnished the monobromide **8** as a mixture of several isomers, which were not purified further and subsequently dehydrobrominated with KO-*t*-Bu in THF, affording **4** as colorless crystals (from hexanes), mp 90–91 °C. The structure of **4** was established by ^{1}H-NMR spectrometry, which showed absorptions at δ 4.78 (s, H_{14}), 6.62–6.72, 7.23–7.27 (two d, J = 10 Hz, H_9, H_{10}), 6.93 (s, H_5, H_6, H_7, H_8), 6.88–6.89, 7.03–7.05 (two d, J = 7.5 Hz, H_{11}, H_{13}), 7.07–7.17 (t, J = 7.5, 7.5 Hz, H_{12}), 7.35–7.50 (m, H_2, H_3), and 7.55–7.61, 7.70–7.78 (two dd, J = 7.4, 1.7 Hz, H_1, H_4).

Bromination of **4** gave an isomeric mixture of dibromides **9**, which could be separated into isomers **9a** and **9b** by flash column chromatography on silica gel. The structures of **9a** and **9b** have not been elucidated, and a mixture of **9a** and **9b** was used in the subsequent step in light of the fact that they both should give cyclophyne **10** upon dehydrobromination. Thus, treatment of the isomeric mixture of **9** with KO-*t*-Bu in the presence of a large excess of freshly distilled furan led to the isolation of the isomeric endoxide **11**, presumably via the intermediate **10**.[9,10] The isomeric endoxide **11** was not separated and was directly deoxygenated with low-valent titanium[1b,11] to give the title compound **5** in 67% yield. Cyclophane **5** formed colorless crystals (from hexanes), which decomposed at ca. 250 °C. The structure of **5** was established by ^{1}H-NMR spectrometry. In d_6-acetone solution at 24 °C, the protons H_5, H_6, H_7 and H_8 gave rise to only a single extremely broad peak at δ 6.95, which was difficult to detect. This interesting result indicates that the absorptions of the four *p*-phenylene protons of **5** coalesce at 24 °C due to the flipping of the *m*-phenylene ring (vide infra). The other protons of **5** showed signals at δ 5.12–5.14 (br t, J = 1.8, 1.8 Hz, H_{16}), 7.08–7.12 (dd, J = 8.0, 1.8 Hz, H_{13}, H_{15}), 7.25–7.32 (t, J = 8.0, 8.0 Hz, H_{14}), 7.40–7.55 (m, H_2, H_3, H_{10}, H_{11}), and 7.57–7.61, 7.72–7.80 (two dd, J = 7.5, 1.7 Hz, H_1, H_4, H_9, H_{12}). The assignment of the proton absorptions was supported by a 2D ^{1}H–^{1}H COSY study.[12] An X-ray crystallographic study of **5** has also been carried out (vide infra).

Cyclophane **6** was prepared by utilizing a similar strategy. Thus, in situ trapping of **10** with freshly distilled 2,5-dimethylfuran afforded endoxide **12**. Surprisingly, it appeared that **12** was a single isomer, as can be substantiated by its ^{1}H NMR spectrum[12] (two 3 H methyl signals at δ 1.84 and 2.06) and ^{13}C-NMR spectrum (26 carbon signals),[12] as well as by its sharp melting range (162–162.5 °C). Finally, **12** was deoxygenated with low-valent titanium to provide **6** in 90% yield, mp 104 °C, whose structure was also established by ^{1}H-NMR spectrometry. Cyclophane **6** exhibited absorptions at δ 2.30 (s, 3 H), 2.61 (s, 3 H), 5.42 (t, J = 1.5, 1.5 Hz, H_{16}), 6.47 (s, H_7, H_8), 6.86–7.00 (two dt, J = 7.7, 1.4, 1.4 Hz, H_{13}, H_{15}), 7.14–7.23 (t, J = 7.7, 7.7 Hz, H_{14}), 7.16–7.27 (ABq, J = 7.9 Hz, H_2, H_3), 7.24–7.38 (ABq, J = 8.7 Hz, H_5, H_6), 7.35–7.49 (m, H_{10}, H_{11}), and 7.50–7.55, 7.67–7.72 (two dd, J = 7.4, 1.7 Hz, H_9, H_{12}). The assignment of proton absorptions was again assisted by a 2D ^{1}H–^{1}H COSY spectrum.[12]

(b) Determination of ΔG_c^* and T_c of the Flipping Process. In order to determine the free energy of activation (ΔG_c^*) and the coalescence temperature (T_c) for the conformational flipping process, a series of variable temperature ^{1}H NMR studies on compounds **3**,[6] **4**, **5**, and **6** were carried out.[12] The ΔG_c^* and T_c of **3** had been determined previously on a 90-MHz NMR spectrometer

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(12) See supplementary material.

Table I. Coalescence Temperature (T_c), Free Energy of Activation for the Conformational Flipping Process ($\Delta G_c^{\ddagger}$), and NMR Operating Frequency of Compounds 1–6

compounds	T_c (°C)	$\Delta G_c^{\ddagger}$ (kJ/mol)	NMR operating frequency (MHz)	ref
6	>140	89.9 ± 0.4	250	13
1	140	84	60	3a
	146	87	60	3c
	187	92	100	3b
3	100	76	90	6
	116	75	250	1c
5	24	57	250	1c
4	−41	44	250	1c
2	−96	35	100	5

by Vögtle and Wittek to be 100 °C and 76 kJ/mol, respectively.[6] On our 250-MHz NMR spectrometer, we found that both the two two-proton absorptions at δ 6.07–6.25 and at 7.29–7.47 (obscured by the absorptions of the *o*-phenylene protons) broadened at 85 °C, coalesced at 116 °C (T_c), and reappeared again as a four-proton broad absorption at δ 6.69. The calculated $\Delta G_c^{\ddagger}$ of **3** is therefore 75 kJ/mol.[4] On the other hand, upon cooling of a d_6-acetone solution of **4**, its four-proton signal at δ 6.93 (H_5, H_6, H_7, H_8) broadened. This signal was difficult to detect at −41 °C, and eventually two broad signals at δ 6.51 and 7.52 reappeared again at below −51 °C, each being integrated for two protons. This situation duly corresponds to a $\Delta G_c^{\ddagger}$ of 44 kJ/mol at T_c = −41 °C for **4**.[4] Interestingly, both heating and cooling were necessary for measuring the $\Delta G_c^{\ddagger}$ for **5**. Experimentally, heating of **5** in $CDBr_3$ from 24 °C to 96 °C caused the extremely broad four-proton peak at δ 6.95 (H_5, H_6, H_7, H_8) to narrow gradually, eventually appearing at 96 °C as a singlet. Cooling of a d_6-acetone solution of **5** from 24 °C to −21 °C nonetheless gave rise to two two-proton singlets at δ 6.51 and 7.50. The signal at δ 7.50 was obscured by that of the *o*-phenylene protons. The $\Delta G_c^{\ddagger}$ and T_c of **5** are therefore 57 kJ/mol and 24 °C, respectively.[4] The determination of $\Delta G_c^{\ddagger}$ and T_c for **6** was unsuccessful because the absorptions corresponding to H_5, H_6, H_7 and H_8 at δ 6.39 and 7.19–7.33 (in d_6-DMSO) only broadened and were still rather distinct at 140 °C. We were unable to go beyond 140 °C on our NMR spectrometer. In conformity with this result, it is obvious that the $\Delta G_c^{\ddagger}$ of **6** should be larger than 85 kJ/mol and its T_c should be higher than 140 °C. Indeed, a computer simulation of the ABCD signals (H_5, H_6, H_7, H_8) of **6** gave a $\Delta G_c^{\ddagger}$ of 89.9 ± 0.4 kJ/mol.[12,13] Due to this moderate energy barrier, resolution of **6** by chromatography on a swollen microcrystalline triacetylcellulose column[14] has so far been unfruitful at room temperature.[13]

The results obtained in our study, as well as in those obtained by other research groups are outlined in Table I. As can be seen, the $\Delta G_c^{\ddagger}$ at T_c appears to bear an intrinsic correlation with the bond types of the bridges connecting the meta-bridged benzene and the para-linked one. Boekelheide[5] ascribed the decreased energy barrier for the exchange process in **2** as compared to that of **1** to two main factors: (1) the lowering of the energy of the transition state by conjugative stabilization as the meta-bridged ring becomes coplanar with the two vinyl bridges; (2) the widening of the bridge angles from 109.5° (sp^3) to 120° (sp^2) compensates for the effect of bond shortening. It is likely that the torsional strain (Pitzer strain) resulted from the eclipsed methylene protons of **1** in its transition state also plays a significant role.[15] Compound **5**, whose flipping transition state is lowered by conjugative stabilization and whose bridge angles are widened to 120°, was expected to display a similar value of $\Delta G_c^{\ddagger}$ as that of **2**. However, the $\Delta G_c^{\ddagger}$ of **5** was found to be intermediate between those of **1** and **2**. This observation may be attributed to the unfavorable nonbonded interaction between H_1 and H_{15} as well as that between H_{12} and H_{13} of **5** as it approaches the transition state of the conformational flipping process. Such argument is also applicable to cyclophanes **3** and **4** and is expectedly outstanding in **6**, whose C_1-methyl group should have an even larger nonbonded interaction with H_{15}, thus resulting in the largest $\Delta G_c^{\ddagger}$ value amongst all the known [2.2]metaparacyclophanes (Table I). All the flipping processes were not detrimental to the cyclophanes, as can be proven by the appearance of identical ^1H NMR spectra at ambient temperature after either heating or cooling of the cyclophanes.

(c) X-ray Crystallographic Study of Dibenzo[2.2]metaparacyclophane (5). Compound **5**, $C_{24}H_{16}$, crystallizes as colorless flat prisms in space group $P2_1$ (No. 4) with a = 10.773(4), b = 6.489(1), c = 12.178(4), β = 107.95(3)° and Z = 2. Diffraction measurements were made at 18 °C on a Nicolet R3/MV system (graphite-monochromatized Mo K_α radiation, λ = 0.71073 Å) using a single crystal dimensions 0.38 × 0.24 × 0.18 mm. The intensities ($2\theta_{max}$ = 50°, 1641 unique data) were corrected for absorption (transmission factors 0.931 to 1.000) using ψ-scan data and processed with the learned-profile procedure. Structure solution was accomplished by direct phase determination based on negative quartets. The carbon atoms were refined anisotropically, and the hydrogen atoms were introduced in their idealized positions with assigned isotropic thermal parameters. Convergence for 1017 observed reflections [$|F_o| > 3\sigma(|F_o|)$] and 216 variables was reached at R_F = 0.069 and R_{wF^2} = 0.093 with the weighting scheme $w = [\sigma^2(|F_o| + 0.0012|F_o|^2]^{-1}$. All calculations were performed on a DEC MicroVAX-II computer using the SHELXTL-PLUS program package.[16] Tables of atomic coordinates and thermal parameters are deposited as supplementary material.[12,17]

The molecular structure of **5**, as illustrated in Figure 2, approximates closely to expected C_s symmetry. The ortho-bridged benzene rings C(7)–C(12) and C(19)–C(24) make a dihedral angle of 147.2°. The para-bridged benzene ring adopts a boad conformation with C(13) and C(16) displaced by 0.23 and 0.20 Å, respectively, from the mean plane of the other four atoms. Distortion of the meta-bridged benzene ring occurs mainly at C(1), which is displaced by 0.12 Å from the mean plane of C(2)–C(6).

Experimental Section

Benzo[2.2]metaparacyclophane (3).[6] PhLi was prepared by adding bromobenzene (46.3 g, 0.3 mol) in anhyd Et_2O (100 mL) dropwise to a stirred suspension of finely divided lithium (4.5 g, 0.65 mol) in anhyd Et_2O (150 mL) under N_2 within 3.5 h.

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(17) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

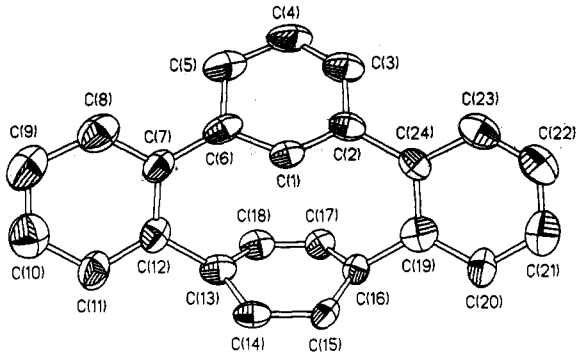

Figure 2. Molecular structure of dibenzo[2.2]metaparacyclophane (**5**). The atoms are shown as thermal ellipsoids at the 30% probability level.

Subsequently, the ethereal PhLi was transferred through a syringe and the solid residue was discarded.

3,4″-Bis(bromomethyl)-1,1′:2′,1″-terphenyl (**7**)[6] (8.1 g, 19.6 mmol) in anhyd Et_2O (1 L) was added dropwise with stirring to PhLi in anhyd Et_2O (350 mL) within 66 h under N_2 atmosphere. The resulting mixture was quenched with 1 N HCl (680 mL). The two layers were separated, and the aqueous layer was extracted with Et_2O (3 × 450 mL). The combined organic layer was dried over anhyd $MgSO_4$ and was evaporated. Cyclophane **3** (2.7 g, 53%) was obtained after flash column chromatography on silica gel (hexanes, R_f = 0.39): mp 118.5–119.5 °C (from hexanes) (lit.[6] mp 118–119 °C); ^{1}H NMR ($CDCl_3$) δ 2.24–3.27 (ABCD, J_{AB} = 0 Hz, J_{AC} = 11.8 Hz, J_{AD} = 6.5 Hz, J_{BC} = 5.7 Hz, J_{BD} = 11.8 Hz, J_{CD} = 11.8 Hz, 4 H), 5.43 (t, J = 1.6 Hz, 1 H), 6.07–6.25 centered at 6.16 (ABq of d, J = 8.0, 1.6 Hz, 2 H), 6.80–6.88, 6.91–6.99 (two d, J = 7.5 Hz, 2 H), 7.10–7.18 (t, J = 7.5 Hz, 1 H), 7.29–7.65 (m, 6 H); MS m/e = 256 (M^+); accurate mass, calcd for $C_{20}H_{16}$ 256.1253, found 256.1256. Anal. Calcd: C, 93.91; H, 6.29. Found: C, 93.95; H, 6.20.

9-Bromo- and 10-Bromobenzo[2.2]metaparacyclophane (8). To a stirred solution of cyclophane **3** (570 mg, 2.2 mmol) in absolute CCl_4 (50 mL) were added *N*-bromosuccinimide (NBS) (510 mg, 2.9 mmol, 1.3 equiv) and α,α′-azobis(isobutyronitrile) (AIBN) (catalytic amount). The mixture was irradiated with a sunlamp (500 W) for 13 h. The resulting precipitate was filtered after cooling and the filtrate was evaporated. Column chromatography of the residue on silica gel (hexanes/C_6H_6 = 9/1) afforded the starting material **3** (R_f = 0.57) (280 mg, 48%) and the monobromide **8** (R_f = 0.48) (0.4 g, 53%) as a mixture of isomers: mp 148–149 °C; ^{1}H NMR ($CDCl_3$) complex spectrum;[12] MS m/e = 336 (M^+ + 2), 334 (M^+), 225 (M^+ – Br); accurate mass, calcd for $C_{20}H_{15}Br$ 334.0358, found 334.0354. Anal. Calcd: C, 71.65; H, 4.51. Found: C, 71.18; H, 4.58.

Benzo[2.2]metaparacyclophan-9-ene (4). To a stirred solution of the isomeric mixture of monobromides **8** (170 mg, 0.5 mmol) in THF (17 mL) was added dropwise a solution of KO-*t*-Bu (1.7 g, 15 mmol) in THF (17 mL) under N_2 within 15 min. 2 N HCl (20 mL) was added to the mixture after stirring for 20 h. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 40 mL). The combined organic layer was dried over anhyd $MgSO_4$ and was evaporated. Cyclophane **4** was obtained after flash column chromatography on silica gel (hexanes) (R_f = 0.45) (110 mg, 86%): mp 91–92 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 4.78 (s, 1 H), 6.62–6.72 centered at 6.67 and 7.23–7.27 centered at 7.25 (two d, J = 10 Hz, 2 H) 6.93 (s, 4 H), 6.88–6.89 and 7.03–7.05 (two d, J = 7.5 Hz, 2 H), 7.07–7.17 centered at 7.12 (t, J = 7.5, 7.5 Hz, 1 H), 7.35–7.50 (m, 2 H), 7.50–7.61, 7.70–7.78 (two dd, J = 7.4, 1.7 Hz, 2 H); MS m/e = 254 (M^+); accurate mass, calcd for $C_{20}H_{14}$ 254.1096, found 254.1100. Anal. Calcd: C, 94.45; H, 5.55. Found: C, 94.67; H, 5.51.

9,10-Dibromobenzo[2.2]metaparacyclophane (9a) and (9b). To a stirred solution of cyclophane **4** (52 mg, 0.2 mmol) in anhyd CCl_4 (6 mL) was added Br_2 (129 mg, 0.8 mmol) in anhyd CCl_4 (6 mL) dropwise during 30 min. A solution of 0.6 N $Na_2S_2O_3$ (15 mL) was added after stirring for 5 h. The organic layer was separated and the aqueous layer was extracted with CCl_4 (3 × 15 mL). The combined organic layer was dried over anhyd $MgSO_4$ and was evaporated. Flash column chromatography on silica gel (hexanes/EtOAc = 25/1) afforded a mixture of dibromides **9a** (R_f = 0.53) (55 mg, 65%) and **9b** (R_f = 0.75) (23 mg, 27%). **9a**: mp 244.5–249.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.52 (d, J = 9.5 Hz, 1 H), 4.89 (d, J = 9.5 Hz, 1 H), 5.45 (br s, 1 H), 6.20–7.85 (m, 11 H); MS m/e = 416 (M^+ + 4), 414 (M^+ + 2), 412 (M^+), 333 (M^+ – Br); accurate mass, calcd for $C_{20}H_{14}Br_2$ 411.9462, found 411.9480. **9b**: mp 149–149.5 °C, ^{1}H NMR ($CDCl_3$) mixture of isomers, complex spectrum,[12] MS m/e = 416 (M^+ + 4), 414 (M^+ + 2), 412 (M^+), 333 (M^+ – Br). Anal. (**9a** + **9b**) Calcd: C, 58.00; H, 3.41. Found: C, 58.29; H, 3.52.

General Procedure for Endoxide Formation. (a) 1,4-Dihydro-1,4-endoxo-14,17-etheno-5,9-methenodibenzocyclotridecene (11). To a mixture of the dibromides **9** (290 mg, 0.7 mmol) and freshly distilled furan (21 mL, 0.29 mol) was added dropwise a suspension of KO-*t*-Bu (3.0 g, 27 mmol) in THF (20 mL) under N_2 within 1 h. After stirring for 25 h, the mixture was quenched with 1 N H_2SO_4 (45 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried over anhyd $MgSO_4$ and was evaporated. The isomeric mixture of endoxides **11** was obtained after column chromatography on silica gel (C_6H_6) (R_f = 0.40) (114 mg, 51%): mp >300 °C; ^{1}H NMR ($CDCl_3$) complex spectrum;[12] MS m/e = 320 (M^+); accurate mass, calcd for $C_{20}H_{16}O$ 320.1202, found 320.1201.

(b) 1,4-Dimethyl-1,4-endoxo-14,17-etheno-5,9-methenodibenzocyclotridecene (12) was prepared from dibromides **9** (92 mg, 0.2 mmol), freshly distilled 2,5-dimethylfuran (12 mL, 0.1 mmol), and KO-*t*-Bu (616 mg, 5.5 mmol) in THF (15 mL). Reaction time: 3 days. Column chromatography on silica gel (C_6H_6) (R_f = 0.39) gave endoxide **12** (51 mg, 65%): mp 162–162.5°C; ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 2.06 (s, 3 H), 4.56 (s, 1 H), 6.48–7.75 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 16.07, 16.48, 91.07, 92.13, 123.20, 126.00, 126.81, 127.55, 126.67, 127.88, 128.88, 129.35, 129.64, 131.86, 132.11, 133.17, 134.60, 137.99, 140.82, 141.80, 143.39, 144.59, 147.78, 148.46, 159.15, 162.17; MS m/e = 348 (M^+). Anal. Calcd: C, 89.62; H, 5.78. Found: C, 89.31; H, 5.45.

General Procedure for Deoxygenation. (a) Dibenzo[2.2]metaparacyclophane (5). $TiCl_4$ (0.24 mL, 2.1 mmol) was added carefully to anhyd THF (10 mL) at 0 °C under N_2 atmosphere. $LiAlH_4$ (80 mg, 2 mmol) was added under the same condition and was followed by Et_3N (54 mg, 0.54 mmol) in anhyd THF (1 mL). The mixture was stirred and refluxed for 45 min. After that the mixture was allowed to cool to rt, and the endoxide **11** (6.1 mg, 0.02 mmol) in THF (2 mL) was added. The mixture was stirred for 1 h and a saturated K_2CO_3 solution (20 mL) was carefully added. The aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layer was dried over anhyd $MgSO_4$ and was evaporated. Thin-layer chromatography on silica gel (hexanes/C_6H_6 = 9/1) (R_f = 0.58) afforded **5** (4 mg, 67%): mp 250 °C dec; ^{1}H NMR (d_6-acetone, 24 °C) δ 5.12–5.14 centered at 5.13 (br t, J = 1.8, 1.8 Hz, 1 H), 6.95 (br s), 7.08–7.12 centered at 7.10 (dd, J = 8.0, 1.8 Hz, 2 H), 7.25–7.32 centered at 7.29 (t, J = 8.0, 8.0 Hz, 1 H), 7.40–7.55 (m, 4 H), 7.57–7.61, 7.72–7.80 (two d, J = 7.5 Hz, 4 H); MS m/e = 304 (M^+). Anal. Calcd: C, 94.70; H, 5.30. Found: C, 94.71; H, 5.29.

(b) 1,4-Dimethyldibenzo[2.2]metaparacyclophane (6) was prepared from $TiCl_4$ (1.2 mL, 11 mmoL) in THF (50 mL), $LiAlH_4$ (400 mg, 10.5 mmol), Et_3N (269 mg, 2.7 mmol) in anhyd THF (5 mL), and endoxide **12** (27 mg, 0.1 mmol) in THF (10 mL). Product **6** (R_f = 0.33) (24 mg, 90%): mp 104 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 1 H), 2.61 (s, 1 H), 5.42 (t, J = 1.7 Hz, 1 H), 6.47 (s, 2 H) 6.86–7.00 (two dt, J = 7.7, 1.4, 1.4 Hz, 2 H), 7.14–7.23 (t, J = 7.7, 7.7 Hz, 1 H), 7.16–7.27 (ABq, J = 7.9 Hz, 1 H), 7.24–7.38 (ABq, J = 8.7 Hz, 2 H), 7.35–7.49 (m, 2 H), 7.50–7.55, 7.67–7.72 (two dd, J = 7.4, 1.7 Hz, 2 H); ^{13}C NMR δ 20.56, 21.45, 125.13, 126.61, 127.25, 127.56, 127.60, 128.07, 128.46, 128.79, 129.59, 129.63, 130.77, 130.88, 131.40, 132.32, 132.46, 133.01, 140.87, 141.42, 141.55, 142.47, 142.84, 143.19, 143.46, 144.80; MS m/e = 332 (M^+), 302 (M^+ – 2 CH_3). Anal. Calcd: C, 93.94; H, 6.03. Found: C, 93.27; H, 6.29.

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Supplementary Material Available: ^1H NMR spectra of compounds **3–6, 8, 9a,b, 11,** and **12,** ^{13}C NMR spectra of compounds **6** and **12**, 2D ^1H–^1H COSY spectra of compounds **5** and **6**, computer simulation ^1H NMR methylene proton signals of **3**, variable temperature ^1H NMR spectra of **3–6**, computer simulation studies on the variable temperature ^1H NMR spectra of **5** and **6**, and the atomic coordinates, bond lengths, bond angles, anisotropic displacement, and H-atom coordinates for **5** (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.