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Conformational Studies of Selectively Methylated [2.2](1,3)(1,4)Cyclophanes. Steric Effects in the Relative Conformational Ground States

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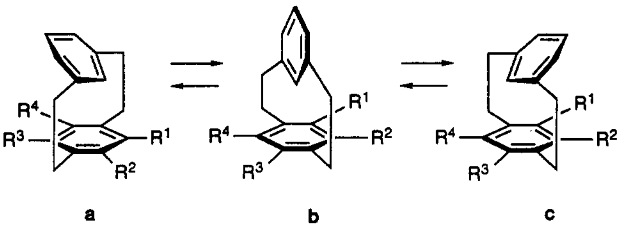
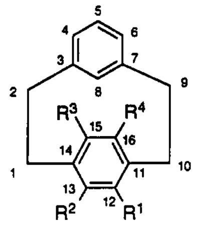
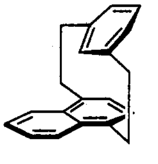
Three selectively methylated [2.2](1,3)(1,4)cyclophanes, namely, 12,15-dimethyl-, 12,16-dimethyl-, and 12,13,14,15-tetramethyl[2.2](1,3)(1,4)cyclophanes, were synthesized from their corresponding dithia[3.3](1,3)(1,4)cyclophanes by the photochemical desulfurization method. Dynamic ^{1}H NMR spectroscopy was employed to estimate the relative conformational barrier in each [2.2]cyclophane. The results show that there is an increase of about 13 kJ mol^{-1} going from the parent [2.2](1,3)(1,4)cyclophane to its 12,15- and 12,16-dimethyl derivatives. This is consistent with the fact that the presence of the methyl substituents increases the relative conformational ground-state energy more than it would affect the transition-state energy. The conformational barrier of the 12,13,15,16-tetramethyl derivative was unexpectedly found to be similar to those of the two dimethylated derivatives. This however could be explained by a decrease in the transition-state energy due to inward bending of the (1,4)-bridged ring accompanied by a decrease in conformational ground-state energy due to outward bending of the methyl groups.

[2.2](1,3)(1,4)cyclophane (1)[1a] was perhaps the first [2.2]-cyclophane found to exhibit conformational mobility.[1] From dynamic ^{1}H NMR spectroscopic measurements and stereochemical data, it was shown[1] that 1 exhibits a flipping process of the (1,3)-bridged with respect to the (1,4)-bridged ring as shown in **1a** ⇄ **1c** possibly via the transition state **1b**. It was later reported that substitution on the (1,3)-[1h] or (1,4)-bridged ring,[1h] and annelation of the bridge-(s)[2] or the (1,4)-bridged ring,[1h] would affect the conformational barrier of the flipping processes in such [2.2](1,3)(1,4)cyclophanes due to changes in the transition-state and/or ground-state energies. The derivative **8** was however found to be conformationally rigid up to 150 °C.[3]





1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^2 = Me$; $R^3 = R^4 = H$
3, $R^1 = R^3 = Me$; $R^2 = R^4 = H$
4, $R^1 = R^4 = Me$; $R^2 = R^3 = H$
5, $R^1 = R^2 = R^3 = R^4 = Me$
6, $R^1 = Me$; $R^2 = R^4 = H$; $R^3 = F$
7, $R^1 = F$; $R^2 = R^4 = H$; $R^3 = Br$



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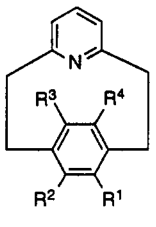

9, $R^1 = R^2 = R^3 = R^4 = H$
10, $R^1 = R^3 = Me$; $R^2 = R^4 = H$
11, $R^1 = R^2 = R^3 = R^4 = Me$

Among the derivatives of 1 having substituted (1,4)-bridged rings, the conformational analysis[1h] of **6** and **7** indicated qualitatively the dependence of conformational barrier on the steric bulk of substituents. Contribution from the polar effect of substituent(s) however could not be evaluated readily and separately. The series of related [2.2]pyridinoparacyclophanes **9–11** was found[4] to have very similar conformational barriers, suggesting that steric effect of the methyl groups on the (1,4)-bridged ring has very little effect on the conformational flipping process in these systems. It was however recently reported that the [2.2](1,3)(1,4)cyclophane **2** exists only as **2a**, which was conformationally rigid up to 150 °C.[5] The steric effect of the methyl groups in **2** is thus expected to affect the conformational ground-state energies of **2a** and **2c** significantly. To gain a better understanding of steric effects similar to that in **2**, we have completed a comparative study of the conformational behavior of selectively methylated derivatives of **1**, namely, [2.2](1,3)(1,4)cyclophanes **3–5**.

Results and Discussion

(a) Synthesis. Desulfurization of [3.3]dithiacyclophanes, which could be obtained readily by intermolecular coupling reactions under high dilution conditions,[6] could

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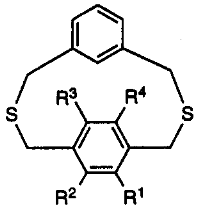
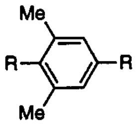
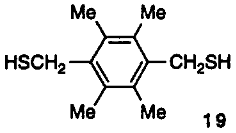
be achieved by several methods[7] to afford the corresponding [2.2]cyclophanes. The dithiacyclophane **13** was thus prepared as reported.[8] The dithiacyclophane **14** is known[9] but its precursor, the dibromide **16**,[9] was prepared in this work by an alternative route with a higher overall product yield. Thus treatment of the dicarboxylic acid **17**[10] with thionyl choride followed by immediate reduction of the acid chloride with lithium aluminum hydride afforded the diol **18** in 89% yield. Reaction of **18** with phosphorus tribromide readily gave the desired dibromide **16** (86%). In the synthesis of dithiacyclophane **15**, the coupling of dimercaptan **19**[11] and 1,3-bis(bromomethyl)benzene under high dilution conditions gave **15**, mp 132–134 °C, in only 27% yield.



12, $R^1 = R^2 = R^3 = R^4 = H$
13, $R^1 = R^3 = Me$; $R^2 = R^4 = H$
14, $R^1 = R^4 = Me$; $R^2 = R^3 = H$
15, $R^1 = R^2 = R^3 = R^4 = Me$



16, $R = CH_2Br$
17, $R = COOH$
18, $R = CH_2OH$



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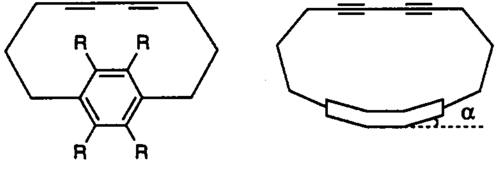

20, R = H; α = 1.8°
21, $R = CH_3$; α = 4.2°

Table 1. Proton Chemical Shifts in Selected Dithia[3.3](1,3)(1,4)cyclophanes

phane	δH9	δH[a]	δCH_3	δCH_2[b]	δCH_2[c]
12	5.60	6.89		3.44	3.84
13	5.68	6.73	2.15	3.49	(3.70, 3.98)[d]
14	5.69	6.61	2.19	3.35, 3.50	3.74, 3.90
15	5.61		2.14	3.42	4.01

[a] Aryl protons on the (1,4)-bridged ring. [b] Methylene protons adjacent to (1,3)-bridged ring. [c] Methylene protons adjacent to (1,4)-bridged ring. [d] δ_A and δ_B of an AB quartet.

Table 2. Conformational Barriers in Selected [2.2](1,3)(1,4)Cyclophanes

	1[a]	3[b]	4[c]	5[c]
δH[d]	7.25, 5.75	6.85, 5.64	6.77, 5.63	
Δν (Hz)	150	363	103	
T_c (K)	460	400	399	
$\Delta G_c^{\ddagger}$ (kJ mol^{-1})	91.4	76.1	80.1	
δCH_3		2.40, 1.63	2.41, 1.65	2.27, 1.58
Δν (Hz)		231	68.4	62.1
T_c (K)		393	399	400
$\Delta G_c^{\ddagger}$ (kJ mol^{-1})		76.2	81.4	81.9
ΔH_f[e] (kJ mol^{-1})	225	174	174	142

[a] Spectra determined in hexachlorobutadiene on a 100-MHz spectrometer; see ref 1b. [b] Spectra determined in $C_6D_5NO_2$ on a 300-MHz spectrometer. [c] Spectra determined in $C_6D_5NO_2$ on a 90-MHz spectrometer. [d] Aryl protons on the (1,4)-bridged ring. [e] ΔH_f calculated by AM1 method; value for **2** is 181 kJ mol^{-1}.

As summarized in Table 1, the aryl protons on the (1,4)-bridged ring and the methyl protons of all three dithiacyclophanes concerned appear as sharp singlets. This is consistent with either a perpendicularly-oriented (1,3)-bridged ring with respect to the (1,4)-bridged ring or a rapidly flipping (1,3)-bridged ring. Some interesting features were however observed in a comparison of the methylene proton chemical shifts in the above dithiacyclophanes. The methylene protons attached to the (1,4)-bridged ring in **12**[12] are more deshielded compared to those adjacent to the (1,3)-bridged ring. In **15**, the methylene protons adjacent to the (1,4)-bridged ring are further deshielded due to steric interactions with the methyl groups while those attached to (1,3)-bridged ring appear at an almost identical shift as observed for **12**. The above argument is further supported by the resolution of methylene protons in **13** and **14**. The four methylene groups in **14** are nonequivalent and appear as four sharp singlets due to the fast interconversion processes. An NOE experiment carried out with irradiation at the methyl signal led to a strong enchancement of the singlet at δ 3.90 and a weaker enchancement at the singlet at δ 3.35. Another NOE experiment carried out with irradiation at the signal of the aryl protons on the (1,4)-bridged ring led mainly to an enhancement of the singlet at δ 3.74. Thus the most deshielded singlet at δ 3.90 could be assigned to the methylene protons in close proximity to the methyl groups. The singlet at δ 3.74 would correspond to the other methylene protons attached to the (1,4)-bridged ring.

Photochemical desulfurization[7c,d] is perhaps the most direct method for converting a dithia[3.3]cyclophane to the corresponding [2.2]cyclophane. Irradiation of solutions of **13**–**15** in trimethyl phosphite with light at 254 nm gave, after columun chromatography, the respective cyclophanes **3**–**5** in 20–30% yields. In all our attempts, no product derived from monodesulfurization was observed as reported in a similar reaction with the parent dithiacyclophane **12**.[12]

(b) Conformational Barriers in [2.2](1,3)(1,4)cyclophanes. From the ^1H NMR spectra (Table 2) of the cyclophanes **3**, **4**, and **5**, the aryl and/or methyl protons on the (1,4)-bridged ring in each cyclophane appear as two pairs of singlets. This is clearly consistent with a rigid conformation in which the aryl proton and/or methyl group(s) on one side of the (1,4)-bridged ring are shielded by the tilted (1,3)-bridged ring, similar to the results

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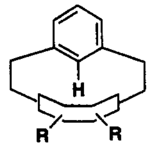
reported for the parent system 1.[1] The pair of rigid conformers of 1 or 5 are identical; those of 3 or 4 are however enantiomeric. Interconversion between any identical or enantiomeric pair of the above cyclophanes is expected to involve the unrestricted flipping of the (1,3)-bridged ring via a transition state in which the (1,3)-bridged ring is somewhat perpendicular to the (1,4)-bridged ring.

In order to give an estimate of the ground-state energies of the cyclophanes concerned, quantum mechanical calculations were used. The AM1 (Austin Model 1)[13] was used to calculate the heat of formation, ΔH_f, of the various [2.2](1,3)(1,4)cyclophanes on the basis of the X-ray crystallographic data obtained for the parent 1.[14] The ΔH_f values are taken as measures of the absolute ground-state energies of the cyclophanes. As given in Table 2, results from the AM1 calculations indicated that the heat of formation increases (more negative) as expected with increasing substitution on the (1,4)-bridged ring. Going from benzene, to toluene, to 1,2-dimethylbenzene, to 1,2,3-trimethylbenzene, and to hexamethylbenzene, a higher methylated compound is always more stable (ΔH_f is more negative) as formation of the methyl group(s) from carbon and hydrogen is always exothermic.[15] The respective stabilization energies per methyl group for the series with respect to benzene is 32.2, 32.7, 30.7, and 28.2 kJ, indicating that the steric interaction particularly in hexamethylbenzene is destabilizing the molecule appreciably. Considering the cyclophanes 1, 3/4, and 5, the approximate stabilization energies per methyl group with respect to 1 are 25.5 and 20.8, respectively. It is perfectly reasonable that the stabilization is less than that going from benzene to methylated benzenes, as some additional steric and geometrical strains are certainly induced in the cyclophanes by methyl substitution. However, in every case the methylated derivatives are more stable than the parent system as far as the absolute ground-state energies are concerned.

The ΔH_f values obtained above are the absolute ground-state energies which result from both stabilization due to methyl substitution and destabilization due to overall steric and geometric strains experienced by the respective cyclophanes. The trend observed in the ΔH_f values however does not necessarily represent that of the relative conformational ground states. The energy diagram of the conformational interconversion process can be envisioned as illustrated in Figure 1. The relative conformational ground states of the cyclophanes, if to be discussed independently, are expected to depend significantly on the steric interactions between H8 and the aryl and/or methyl protons on the (1,4)-bridged ring. This is supported by the fact that cyclophane 2 exists only in the rigid conformation **2a**. Assuming that the respective transition states involves basically one benzene ring held approximately perpendicular to another, the transition energies in the interconversion processes of cyclophanes 1 and 3–5 are not expected to change significantly. The relative conformational barrier is then expected to decrease going from the parent 1, to the dimethylated derivatives 3 and 4, and to the tetramethylated system 5.



R = H or CH_3

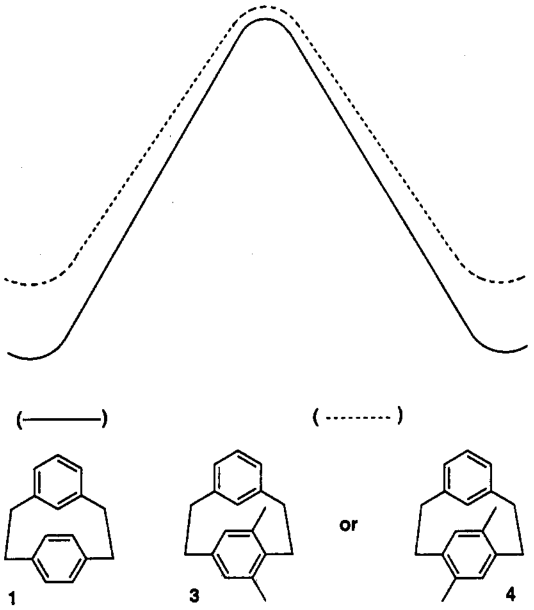


Figure 1. Potential energy diagram of conformational interconversion processes in 1, 3, and 4 based only on relative conformational ground/transition-state energies.

The temperature coalescence method[16] has been used extensively in the estimation of energy barriers to conformational interconversion in cyclophanes.[17] One limitation of this method is that the line width of the signals has to be small in comparison to the difference in frequency separation of the signals. In our studies (Table 2) the frequency separations are in the range of 60–360 Hz with line widths of methyl proton and aryl proton signals of <1.5 and <3 Hz, respectively. Thus either the aryl or methyl signals could be used conveniently as a probe to study the conformational interconversion processes.

In the conformational study (deuterated nitrobenzene; 90 MHz) of 4 (Table 2), respective signals of the pair of aryl protons and the pair of methyl groups on the (1,4)-bridged broadened as the temperature was raised. The two pairs of signals collapsed almost simulataneously at 126 °C and reappeared as separate broad singlets observed clearly at δ 6.20 and 2.03, respectively, in a spectrum taken at 150 °C. These chemical shifts occurred at the respective average positions of the corresponding pairs in the low temperature spectrum, indicating a true fluxional process consistent with **4a** $\rightleftarrows$ **4b**, rather than one conformer transforming to a different conformer. On the basis of the two sets of data obtained (Table 2), the energy barrier ($\Delta G_c^{\ddagger}$) was estimated at 80.1 and 81.4 kJ mol^{-1}, respectively. Some difficulty was encountered in the observation

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of the exact coalescence of the methyl signals due to an overlap with the methylene proton signals. This could account for the small difference in the two calculated values for $\Delta G_c^{\ddagger}$. A similar conformational study of **3** (deuterated nitrobenzene; 300 MHz) indicated coalescence of signals of aryl protons and methyl groups on the (1,4)-bridged ring at 127 and 120 °C, respectively. Almost identical $\Delta G_c^{\ddagger}$ values were obtained from the two sets of data (Table 2).

The above results obtained for **3** and **4** clearly indicated that reasonable estimates of the conformational energy barrier could be made by either probing the coalescence of the signals of aryl protons or that of the methyl groups on the (1,4)-bridged ring. This would provide a more accurate comparative study on the conformational energy barriers of cyclophanes **1**, **3**, **4**, and **5**, as the data reported[1] for **1** were based on the coalescence of the aryl proton signals while those determined for **5** have to depend on the coalescence of the methyl signals. The conformational energy barriers in the dimethylated derivatives **3** and **4** are 10–15 kJ mol^{-1} lower than that of the parent **1**. A plausible explanation (Figure 1) is that transition states in the conformational processes of these cyclophanes possess similar geometries of the (1,3)- and (1,4)-bridged rings, with the former being perpendicular to the latter. The relative stabilities of these transition states are thus not significantly affected by the substituents on the (1,4)-bridged ring. However, with methyl substituents in the (1,4)-bridged ring, more severe interactions are expected between the methyl groups and H8. These would increase the conformational ground-state energies in **3** and **4** relative to that in **1**. The overall result is that, going from **1** to **3** or **4**, the change in conformational ground-state energy would be much larger compared to the difference in the conformational transition-state energy (Figure 1). This in turn corresponds to a decrease in the conformational energy barrier in **3** and **4** as reflected in the $\Delta G_c^{\ddagger}$ values estimated experimentally.

The coalescence of the methyl signals of **5** was observed at 127 °C, corresponding to a $\Delta G_c^{\ddagger}$ value of 81.9 kJ mol^{-1}. It was initially expected that, going from the dimethylated **3** or **4** to tetramethylated **5**, there would be a further increase in conformational ground-state energy and thus a further decrease in conformational barrier for **5**. The results obtained (Table 2) however show that **3**, **4**, and **5** in fact have comparable $\Delta G_c^{\ddagger}$ values.

In the X-ray crystallographic studies of **20**[18] and **21**,[19] the benzene ring in each case was found to bend slightly, with the latter having a marginally larger angle α. A similar geometric change going from **3**/**4** to **5** would tend to lower the conformational transition-state energy in **5**. Using the structure[14] of cyclophane **1** as a reference, results from force field calculations (MM2PI)[20] indicate that the bendings of (1,4)-bridged benzene rings in **1**, **3**, and **4** are very similar but angle α is relatively larger for **5** by about 6°. Unlike most other related cyclophanes which exhibit the protons of the (1,4)-bridged ring bent toward the inner part of the cyclophane moiety, the methyl groups in **21** are found to bend away from the cyclophane cavity.[19] This phenomenon has also been observed in other highly substituted cyclophanes[21] and a plausible explanation is believed to be the steric repulsion among the methyl/methylene groups in **21**. Although we could not obtain structural data on **5**, a similar outward bending of the methyl groups in **5** is likely. This is supported by force field calculations (MM2PI)[20] which indicate that the methyl groups in **5** are tilted as expected by about 12°. This would undoubtedly reduce the interactions between H8 and the methyl groups. Thus going from **3**/**4** to **5**, the angle α factor seems to decrease the conformational transition-state energy while the bending of the methyl groups decrease the conformational ground state energy (Figure 2). This accounts for the unexpectedly "high" conformational barrier experimentally observed for **5**.

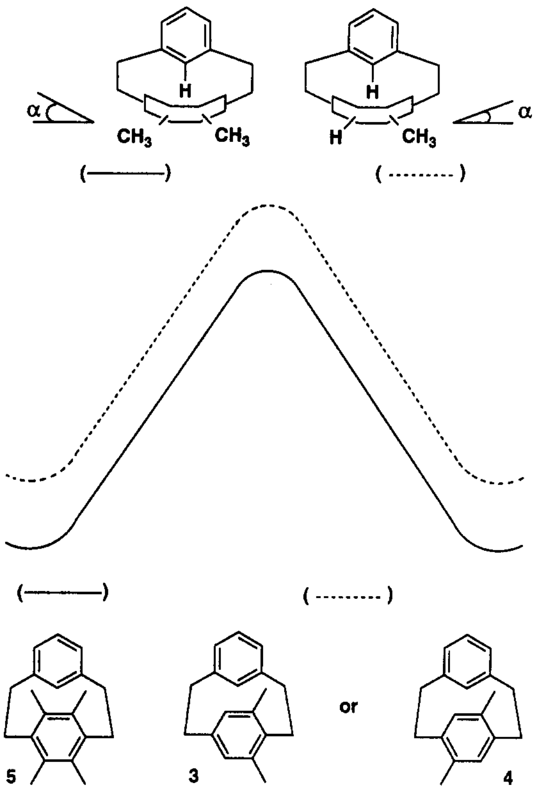

Figure 2. Potential energy diagram of conformational interconversion processes in **3**, **4**, and **5** based only on relative conformational ground/transition-state energies.

Experimental Section

All melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined in CDCl$_3$ (unless otherwise stated) on a JEOL FX90Q (90MHz) or a Bruker AC-F 300 (300 MHz) Fourier transform spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane, which was used as an internal standard. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer with 70-eV electron impact ionization being used. Relative intensities are given in parentheses. Only the molecular ion containing ^{79}Br is given for compound **16**. A correct isotope pattern was observed. UV photolysis was carried out in a Rayonet photochemical reactor Model RPR-100 (254 nm, 400 W). Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

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1,4-Bis(hydroxymethyl)-2,6-dimethylbenzene (18). The diacid 17[10] (1.00 g, 5 mmol) was suspended in thionyl chloride (125 mL) and heated at reflux for 8 h under nitrogen. Excess thionyl chloride was removed by distillation. The diacyl chloride was immediately dissolved in dry THF (20 mL) and the solution was then added dropwise to a well-stirred suspension of lithium aluminum hydride (0.85 g, 21 mmol) in dry THF (150 mL) under nitrogen. After the addition, the mixture was heated at reflux for another 4 h after which it was cooled in an ice bath. Ethyl acetate was added until no effervescence was observed, followed by addition of 50% sulfuric acid until all solids dissolved. The mixture was extracted with dichloromethane, washed successively with aqueous sodium bicarbonate solution and water, dried, and evaporated under reduced pressure to yield the diol **18**, 0.50 g (89%). A sample was recrystallized from cyclohexane to give colorless crystals of **18**, mp 143–145 °C: ^{1}H NMR δ 7.05 (s, 2 H, ArH), 4.74 (s, 2 H, CH_2O), 4.61 (s, 2 H, CH_2O), 2.44 (s, 6 H, CH_3), 1.59 (s, 2 H, OH; exchanged with D_2O); IR (KBr) 3340 (br, O–H), 2900, 1600, 1430, 1370, 1340, 1200, 1040, 1020, 980, 860, 770, 720 cm^{-1}; MS ($M^{\bullet +}$) *m/z* 166 (52), 148 (100), 119 (50), 105 (60), 91 (60); M_r calcd for $C_{10}H_{14}O_2$ 166.0994, found (MS) 166.1000. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.88; H, 8.66.

1,4-Bis(bromomethyl)-2,6-dimethylbenzene (16). Phosphorus tribromide (5.00 mL, 52.8 mmol) was added to a suspension of the diol **18** (1.13 g, 7 mmol) in dry benzene, and the mixture was stirred at room temperature under nitrogen for 18 h. The mixture was then cooled in an ice bath and water was added slowly. The organic layer was washed, dried, and evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane as the eluant to give the dibromide **16**, 2.07 g (86%). A sample was recrystallized from cyclohexane to afford colorless crystals of **16**, mp 140–142 °C (lit.[9] mp 140–142 °C).

14,18-Dimethyl-2,11-dithia[3.3](1,3)(1,4)cyclophane (14). A solution of 1,4-bis(bromomethyl)-2,6-dimethylbenzene (**16**) (1.20 g, 4.5 mmol) and 1,3-bis(mercaptomethyl)benzene[7b,22] (0.77 g, 4.5 mmol) in benzene (180 mL) was added dropwise over a period of 8 h to a vigorously stirred solution of potassium hydroxide (0.75 g, 13.5 mmol) in 95% ethanol (750 mL) at room temperature under nitrogen. After an additional 18 h of stirring, the bulk of the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, washed, dried, and evaporated. The resulting yellow solid was preadsorbed on silica gel and chromatographed using hexane/dichloromethane (3:1) as the eluant to yield dithiacyclophane **14**, 0.46 g (34%). A sample was recrystallized from hexane to give colorless crystals of **14**, mp 119–121 °C (lit.[9] mp 120–122 °C).

14,15,17,18-Tetramethyl-2,11-dithia[3.3](1,3)(1,4)-cyclophane (15). This was prepared from 1,3-bis(bromomethyl)-benzene (2.94 g, 11 mmol) and the bis(mercapto) compound **19**[11] (2.54 g, 11 mmol) according to the procedure described for the preparation of dithiacyclophane **14**. Recrystallization from benzene/ethanol (8:1) gave colorless crystals of **15** (1.01 g, 28%), mp 132–134 °C: ^{1}H NMR δ 7.0–7.1 (m, 3H, H5, H6, H7), 5.61 (br s, 1H, H9), 4.01 (s, 4H, CH_2), 3.42 (s, 4H, CH_2), 2.14 (s, 12H, CH_3); IR (KBr) 1440, 1410, 1370, 1215, 1170, 1000, 890, 810, 790, 780, 750, 720, 700 cm^{-1}; MS ($M^{\bullet +}$) *m/z* 328 (90), 191 (100), 161 (57), 158 (52). Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52. Found: C, 73.33; H, 7.34; S, 19.28.

General Procedure for Photochemical Desulfurization. (a) 12,15-Dimethyl[2.2](1,3)(1,4)-cyclophane (3). Trimethyl phosphite (10 mL) was added to a solution of the dithiacyclophane **13**[8] (0.30 g, 1 mmol) in benzene (2 mL) in a quartz tube. The solution was irradiated with a medium pressure mercury lamp for 18 h with stirring. After irradiation, the mixture was cooled and hexane (100 mL) was added. The solution was then washed with 1 M hydrochloric acid (100 mL). The organic layer was separated, washed, dried, and evaporated under reduced pressure. The yellow oil obtained was chromatographed on silica gel with hexane as the eluant to give **3** as a colorless oil, 0.15 g (23%). The product solidified on standing. Recrystallization from pentane yielded colorless crystals of **3**, mp 64–65 °C (lit.[8] mp 65–66 °C).

(b) 12,16-Dimethyl[2.2](1,3)(1,4)cyclophane (4) was prepared from the dithiacyclophane **14** (0.30 g, 1 mmol). The desired cyclophane **4**, 0.19 g (29%), was obtained as a colorless oil which solidified on standing. A sample recrystallized from cyclohexane afforded colorless crystals of **4**, mp 55–56 °C (lit.[9] mp 56 °C).

(c) 12,13,15,16-Tetramethyl[2.2](1,3)(1,4)cyclophane (5) was prepared from the dithiacyclophane **15** (0.74 g, 2 mmol). The cyclophane **5** was isolated as a colorless oil, 0.18 g (30%). The sample solidified on standing. Recrystallization from cyclohexane gave colorless crystals of **5**, mp 134–136 °C: ^{1}H NMR δ 6.6–7.0 (m, 3H, H4, H5, H6), 5.36 (br s, 1H, H8), 2.9–3.2 (m, 8H, CH_2), 3.05 (s, 6H, CH_3), 2.74 (s, 6H, CH_3); IR (KBr) 1430 (br), 1360, 1220, 1170, 1160, 910, 800, 760, 730, 710, 700 cm^{-1}; MS ($M^{\bullet +}$) *m/z* 264 (85), 249 (18), 235 (9), 159 (100), 132(17), 104 (23). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.32.

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