Synthesis and Rigid Conformers of 14,15-Dimethyl-2,11-dithia[3.3]-(1,3)(1,4)cyclophane and 12,13-Dimethyl[2.2](1,3)(1,4)cyclophane

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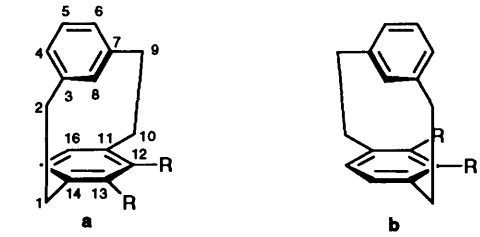
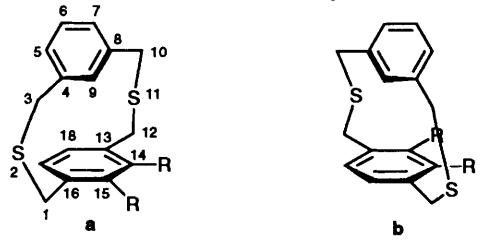
The dithiacyclophane **4** was synthesized from 2,3-dimethylaniline in seven steps. Only the conformer **4b** was isolated. Photodesulfurization of **4b** however resulted only in the isolation of the cyclophane **2a** indicating an abrupt change in conformational preference going from the [3.3]phane to the [2.2]phane. Their stereochemistry could be assigned readily from the chemical shifts of the aryl protons or methyl protons on the (1,4)-bridged ring. Dynamic ^{1}H NMR studies indicated that both **2a** and **4b** remained conformationally fixed up to 150 °C. The conformational preference depends on the non-bonding interaction between H8 (of **2a**) or H9 (of **4a**) and the methyl groups and that between the (1,3)-bridged ring and the methyl groups in **2b** and **4b**.

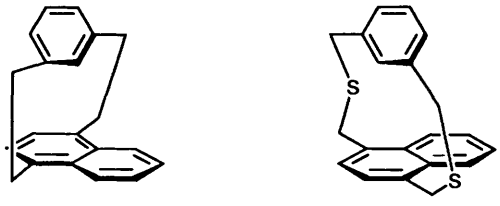
The conformational behaviour of (1,3)(1,4)cyclophane **1**, represented by a flipping process (**1a** ⇌ **1b**)[1-3] of the (1,3)-bridged ring, could be readily studied by dynamic ^{1}H NMR spectroscopy. Whereas replacement of H8 in **1** by a larger substituent was reported to result in rigid conformers of several derivatives of **1**,[4] substituents at C5 of the (1,3)-bridged ring or C12/C15 of the (1,4)-bridged ring did not seem to restrict the interconversion process although an effect on the conformational barrier was evident.[5] Such conformational mobility of the (1,3)-bridged ring was also observed in some triple-layered (1,3)(1,4)cyclophane systems.[6] The conformational barrier in dithia(1,3)(1,4)cyclophane **3** was not estimated presumably due to a much higher conformational mobility.[4b,7] It was however recently reported that (1,3)(1,4)cyclophane **5**[8] and dithia(1,3)-(1,4)cyclophane **6**[9] both exist as the respective rigid conformers up to 150 °C. The conformational rigidity in these systems is dependent on two kinds of non-bonding interaction, namely the π–π repulsion between the (1,3)-bridged ring and the non-bridged naphthalene ring, and the steric interaction due to H_i projecting into the non-bridged naphthalene ring. There was however no good model of 12,13-disubstituted (1,3)(1,4)cyclophane to illustrate whether purely non-bonding steric interactions, namely that between the (1,3)-bridged ring and the C12/C13 substituents and that between H9 and the C12/C13 substituents, would also result in certain conformational preference. We describe in this paper the synthesis and conformational behaviour of 12,13-dimethyl[2.2](1,3)(1,4)cyclophane **2** and 14,15-dimethyl-2,11-dithia[3.3](1,3)(1,4)cyclophane **4**.



1 R = H; **2** R = CH_3



3 R = H; **4** R = CH_3



5 **6**

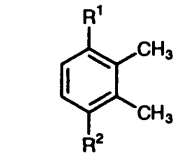
Dithia(1,3)(1,4)*cyclophane* **4**.—1,2-Dimethylbenzene could not be directly functionalized at C3/C6 selectively. Thus the aniline **7** was first brominated using *N*-bromosuccinimide in dimethyl formamide,[10] a mild reagent known to result in selective nuclear monobromination of reactive aromatic compounds. In all our attempts however a mixture of products was obtained and the desired monobrominated aniline **8** could only be isolated by repeated column chromatography on silica gel in an optimized yield of about 35%. On treatment of the diazonium salt prepared from **8** with cuprous bromide, the dibromide **9** was isolated as a colourless oil only in 27% yield after chromatography. The dibromide **9** underwent the von-Braun reaction[11] in the presence of a slight excess of cuprous cyanide in dimethylformamide to afford a 57% yield of the dicyanide **10**. Conversion of **10** to the dialdehyde **11** in good yield (87%) was readily achieved by diisobutylaluminium hydride. When **11** was treated with sodium borohydride the diol **12** was obtained. Reaction of the diol **12** with phosphorus tribromide in benzene afforded the dibromide **13** in 81% yield. Although nucleophilic attack at the bromomethyl groups in **13** was expected to be sterically hindered by the adjacent methyl groups, a coupling reaction between **13** and 1,3-bis(mercaptomethyl)benzene **15**[12] under high dilution conditions[13] led to the isolation of dithiacyclophane **4** in about 80% yield. The mass spectrum of the product shows a strong molecular ion at *m/z* 300 consistent with the general structure of **4**. The isolated product was shown to be **4b** by ^{1}H NMR spectroscopic analysis (see later discussion).

(1,3)(1,4)*Cyclophane* **2**.—Photochemical desulfurization[14] is perhaps the most direct method to convert a dithia[3.3]cyclophane to the corresponding [2.2]cyclophane. Irradiation of a solution of the dithiacyclophane **4b** (100–500 mg) in trimethyl phosphite or trimethyl phosphite–benzene (1:1) (10–50 cm^3)

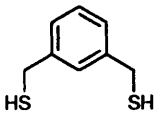
Table 1 Proton chemical shifts of selected methylated benzene, dithia[3.3](1,3)(1,4)cyclophanes and [2.2](1,3)(1,4)cyclophanes

	δ						
	14[19]	**1**[3b]	**17**[6,15]	**2a**	**3**[4b]	**19**[15]	**4b**
CH_3	2.20, 2.26	absent	1.65, 2.43	2.34	absent	2.16	1.86
H[a]	absent	5.37	5.51	5.03	5.52	5.63	5.81
H[b]	6.84	5.81, 7.13	5.69, 6.78	5.68	6.80	6.69	6.92

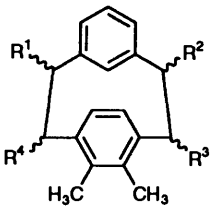
[a] 9-H in a 2,11-dithia[3.3](1,3)(1,4)cyclophane or 8-H in a [2.2](1,3)(1,4)cyclophane. [b] Aryl protons in the reference compound or the (1,4)-bridged ring of the cyclophanes.



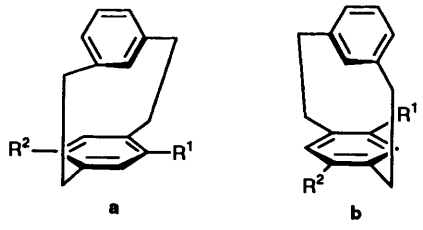
7 $R^1 = NH_2$; $R^2 = H$
8 $R^1 = NH_2$; $R^2 = Br$
9 $R^1 = R^2 = Br$
10 $R^1 = R^2 = CN$
11 $R^1 = R^2 = CHO$
12 $R^1 = R^2 = CH_2OH$
13 $R^1 = R^2 = CH_2Br$
14 $R^1 = R^2 = CH_3$



15

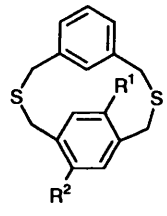


16a; $R^1 = R^2 = SMe$; $R^3 = R^4 = H$
b; $R^1 = R^2 = H$; $R^3 = R^4 = SMe$
c; $R^1 = R^3 = SMe$; $R^2 = R^4 = H$

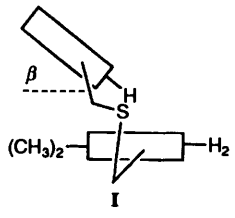


a **b**

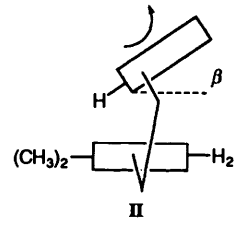
17 $R^1 = R^2 = CH_3$
18 $R^1 = CH_3$; $R^2 = F$



19 $R^1 = R^2 = CH_3$
20 $R^1 = F$; $R^2 = Br$



I



II

placed in a quartz tube was carried out with light at 254 nm using medium-pressure mercury lamps. The [2.2]cyclophane **2** was isolated in about 30% yield after column chromatography. In all our attempts, no product derived from monodesulfurization was observed as reported in a similar reaction with the parent dithiacyclophane **3**.[15] The isolated conformer was shown to be **2a** by ^1H NMR spectroscopic analysis (see later discussion).

In order to investigate whether the conformer **2b** could be prepared, the conversion of **4b** to **2** was attempted *via* an alternate route—a Wittig rearrangement[16]–Raney nickel reduction[17] sequence. Treatment of **4b** with lithium diisopropylamide followed by quenching with iodomethane afforded a mixture of **16**. Reduction of **16** with W-7 Raney nickel[18] however afforded only the conformer **2a**.

Conformational Studies.—The parent cyclophane **1**[1-3] and its derivatives, for examples **17**[6,15] and **18**,[5] are known to be conformationally rigid with the fixation of the (1,3)-bridged ring at room temperature. Two methyl signals at δ 1.65 and 2.43 (Table 1) were observed in the ^1H NMR spectrum of **17**. A mixture of **18a** and **18b** was prepared and their methyl signals appeared at δ 2.41 and 1.65 respectively. The methyl protons *syn* to the tilting (1,3)-bridged ring in **17** or **18b** are clearly shielded significantly. The cyclophane **2** is also expected to be conformationally rigid at room temperature. Its ^1H NMR spectrum however shows a 'normal' toluene methyl signal at δ 2.34 similar to those of **14** (Table 1) and the low field methyl signals of **17** and **18a**. This is clearly consistent with a rigid conformation **2a** having the (1,3)-bridged ring tilted above the aryl protons in the (1,4)-bridged ring thus shielding them to δ 5.68. Unexpectedly the cyclophane **2** does not allow flipping of the (1,3)-bridged ring up to a temperature of 150 °C. Dynamic ^1H NMR studies of a solution of **2a** in [$^2H_6$]-DMSO in the temperature range of 25–150 °C indicated no significant changes in the chemical shifts of 8-H, 15,16-H and methyl protons. The multiplets observed for the bridging methylene protons also remained practically unchanged supporting the high rigidity of the system.

The dithiacyclophane **4** with longer and more flexible bridges was initially expected to be conformationally mobile at room temperature similar to the behaviour observed for the parent system **3** and its derivatives such as **19**[15] and **20**.[5] The methylene protons in **19** and **20** are in principle diastereotopic. In their respective ^1H NMR spectra however only the methylene protons adjacent to the (1,4)-bridged rings were resolved. The methylene protons adjacent to the (1,3)-bridged rings have identical chemical shifts, perhaps due to rapid interconversion processes **19a** ⟷ **19b** and **20a** ⟷ **20b**, and appeared as singlets at δ 3.48 and 3.55 respectively. In the ^1H NMR spectrum of the isolated sample of **4**, the methylene protons appear as two sets of well resolved AB quartets. This observation suggests a fixed conformation for **4**. In addition the methyl signal is observed as a singlet at δ 1.86 which, although not shielded as much as those (δ 1.65) of **17** and **18b**, is significantly shifted upfield from those observed for its isomer **19** and 1,2,3,4-tetramethylbenzene **14**[19] (Table 1). This is obviously consistent with a rigid conformation **4b** having the (1,3)-bridged ring tilted above the methyl groups thus shielding them—an abrupt change in conformational preference going from **2a** to **4b**.

Dynamic ^1H NMR studies (Fig. 1) of a solution of **4b** in [$^2H_5$]-nitrobenzene showed that the chemical shift of 17,18-H remained practically constant in the temperature range of 25–150 °C. The respective chemical shifts of 9-H and the methyl protons, and the chemical shift difference, $\Delta\delta(\delta_A - \delta_B)$, of each AB system however seem to change linearly with temperature (Fig. 1). The above results are perhaps due to small changes in ring current effects on the chemical shifts of those signals by a slight tilting process (varying average angle β; refer to **I**) of the (1,3)-bridged ring in **4b** similar to other reported examples.[9,20] The small changes observed, particularly those of

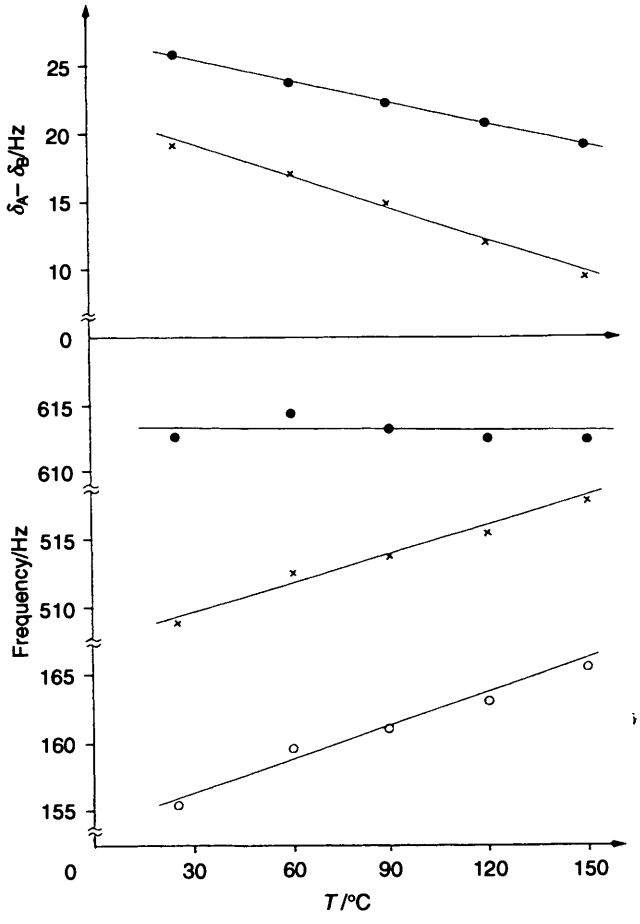


Fig. 1 Plot of (*a*) $\delta_A - \delta_B$ (●: higher-field AB; ×: lower-field AB) and (*b*) proton chemical shift (●: 17,18-H; ×: 9-H; ○: CH_3) *vs.* temperature for dithiacyclophane **4b**

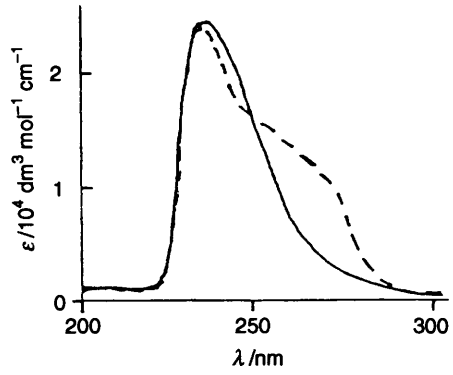


Fig. 2 UV Absorption spectra (dichloromethane) of cyclophane **2a** (- - - -) and dithiacyclophane **4b** (——)

chemical shifts of 9-H, 17,18-H and methyl protons, do not suggest a change from one conformer of **4b** to the other. It is in fact consistent with a rigid conformer **4b** with no flipping of the (1,3)-bridged ring, although the same observation could also be explained by a less likely assumption that the ratio of **4a** and **4b** stayed constant over the considerable temperature range studied. The methyl protons in **4a** and **4b** would be in very different magnetic environments and should be expected to result in a significant continuous shift going from a single conformer to a free flipping process involving the equilibrium **4a** ⇌ **4b**. The two sets of methylene protons of **4b** appear clearly as two AB systems. Rapid interconversion between **4a** ⇌ **4b** might cause the methylene protons adjacent to the (1,3)-bridged ring to have very similar averaged chemical shifts as mentioned for **19** and **20**. There was however no coalescence of the AB systems up to a temperature of 150 °C further supporting the absence of flipping of the (1,3)-bridged ring.

The non-bonded steric repulsion encountered in **2b** and **4b** is that between the (1,3)-bridged ring and the methyl groups. On the other hand, in **2a** and **4a**, the steric interaction between H8 (of **2a**) or H9 (of **4a**) and the methyl groups is involved. From the conformational behaviour of **2**, it is evident that the former interaction is the commanding factor for preference to **2a**. A favourable factor for dithiacyclophane **4** to adopt the conformation **4b** could be the longer and more flexible C–S–C bridges. The (1,3)-bridged ring is held sufficiently far away from the methyl groups to avoid an unfavourable non-bonding interaction. These results complement those reported for rigid conformers of dithiacyclophane **5**[9] and cyclophane **6** respectively.[8] Going from longer and more flexible C–S–C bridges to shorter and more rigid ethylene bridges in both series results in an abrupt change in conformational preference although the respective non-bonding interactions involved vary.

The π–π interactions between face-to-face arrangement of two aromatic rings in cyclophanes are common.[21] A significant bathochromic shift and broadening of adsorption bands in their UV absorption spectra are sometimes observed.[22] In **2a** and **4b**, the extent of π–π interaction between the (1,3)- and (1,4)-bridged rings depends on the degree of tilting (angle β; refer to **I** and **II**) of the former ring with respect to the latter. The UV spectrum (Fig. 2) of **4b** shows only one major absorption at 236 nm similar to one typical of alkyl benzenes. The long and flexible C–S–C bridges allow tilting of the (1,3)-bridged ring at a large angle β resulting in insignificant π–π interaction between the two benzene rings. Going from **4b** to **2a**, bathochromically shifted and broader bands (Fig. 2) are clearly observed in the UV spectrum of **2a** indicating a much stronger π–π interaction resulting from two closely stacked benzene rings due to the shorter and more rigid ethylene bridges. The crystallographic data[23] reported for **1** indicate that the two benzene rings are orientated in a somewhat vertical stack and **2a** is expected to adopt a similar geometry (refer to **II**). A theoretical prediction based on π–π interactions[21] would suggest that the benzene rings in a [*n.n*](1,3)(1,4)cyclophane such as **2a** and **4b** would in principle prefer an offset stacking orientation. Space-filling molecular models of **4b** suggest that the longer bridges in **4b** would allow the two aromatic rings to get closer to the optimum offset stack predicted by theory.[21] This could also partly account for the switch in conformational preference between **2a** and **4b**.

Going from **1** to **2a** and **3** to **4b**, the chemical shifts of the aryl protons in the (1,4)-bridged ring would be affected slightly by the substituents. H9 in **4b** as expected appears at a lower field (Table 1) than the averaged signal of H9 in **3** which passes through the shielding zone of the (1,4)-bridged ring in the conformational process represented by **3a** ⇌ **3b**. On the other hand, both **1** and **2a** exist as rigid conformers at room temperature. In order to minimize the non-bonding interaction between H8 and the methyl groups in **2a**, an 'outward sliding' (refer to **II**) of the (1,3)-bridged ring is expected and consistent with a more shielded H8 in **2a** than that in **1** (Table 1).

Experimental

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 Perkin-Elmer R32 (90 MHz) spectrometer or a JEOL FX90Q (90 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. UV–VIS spectra were determined in cyclohexane and recorded on a Hewlett Packard 8052A Diode-array spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV electron impact ionization being used. Relative intensities are given in parentheses. Only the molecular ion containing ^{79}Br is given for compounds containing bromine. Correct isotope patterns were obtained in all cases. 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. All evaporations were carried out under reduced pressure on a rotary evaporator at about 40 °C, and all organic layers were washed with water (unless otherwise stated) and dried with anhydrous magnesium or sodium sulfate.

1-*Amino*-4-*bromo*-2,3-*dimethylbenzene* **8**.—A solution of *N*-bromosuccinimide (44.06 g, 248 mmol) in dry DMF (100 cm^3) was added dropwise to a solution of 1-amino-2,3-dimethylbenzene **7** (30.00 g, 248 mmol) in dry DMF (50 cm^3) and the mixture was stirred at room temperature for 24 h. The mixture was then poured into water and extracted with dichloromethane. The organic layer was washed, dried and evaporated. The product mixture was chromatographed on silica gel with hexane–dichloromethane (1:1) as the eluent. The product **8** (33.48 g, 34%) was obtained as a thick oil (Found: M^+, 199.0001. $C_8H_{10}NBr$ requires *M*, 198.9997); ν_{max}/cm^{-1} 3480, 3380, 2920, 1620, 1460, 1300, 1140, 1050, 800, 740 and 700; δ_H 7.18 (1 H, d, *J* 8.7 Hz, 5-H), 6.42 (1 H, d, *J* 8.7 Hz, 6-H), 3.47 (2 H, br s, NH_2), 2.36 (3 H, s, CH_3) and 2.11 (3 H, s, CH_3); *m*/*z* 199 (M^+, 100%) and 120 (51).

1,4-*Dibromo*-2,3-*dimethylbenzene* **9**.—A mixture of 48% hydrogen bromide (7.5 cm^3, 62 mmol) and 1-amino-2,3-dimethylbenzene **8** (5.00 g, 25 mmol) was kept in an ice-bath and cooled to 0 °C by the addition of ice. Sodium nitrite (1.75 g, 25 mmol) in water (4 cm^3) was added to the rapidly stirring mixture while the temperature was kept below 10 °C by the addition of pieces of ice. In a separate flask, copper(I) bromide (1.97 g, 14 mmol) in 48% hydrogen bromide (2.0 cm^3, 15 mmol) was warmed to reflux temperature. The solution of the diazonium salt was then added from a dropping funnel in 4 parts to the copper(I) bromide at a rate which allowed continuous gentle reflux. After the addition the mixture was heated at reflux for an additional 30 min. On cooling, the residue was extracted with dichloromethane. The organic layer was washed, dried and evaporated under reduced pressure. Chromatography on silica gel with hexane as the eluent afforded the dibromide **9** (1.79 g, 27%) as a colourless oil (Found: C, 36.5; H, 3.2. M^+, 261.9010. $C_8H_8Br_2$ requires C, 36.40; H, 3.06%. *M*, 261.8993); ν_{max}/cm^{-1} 2920, 1440, 1380, 1140, 1000, 830, 800, 770; δ_H 7.23 (2 H, s, ArH), 2.43 (6 H, s, CH_3); *m*/*z* 262 (M^+, 59%), 183 (66) and 103 (35).

2,3-*Dimethylbenzene*-1,4-*dicarbonitrile* **10**.—The dibromide **9** (4.85 g, 18 mmol) and copper(I) cyanide (3.79 g, 42 mmol) were stirred in DMF (30 cm^3) and heated at reflux for 4 h. The hot solution was then poured into a mixture of ammonia–ice (1:1, 150 cm^3) and stirred for 30 min. The residue was extracted with dichloromethane, washed twice with 1 mol dm^{-3} hydrochloric acid and water, dried and evaporated. The white solid obtained was recrystallized from cyclohexane to yield colourless crystals of **10** (1.63 g, 57%), m.p. 139–141 °C (Found: C, 76.6; H, 5.0; N, 17.7. $C_{10}H_8N_2$ requires C, 76.90; H, 5.16; N, 17.94%); ν_{max}/cm^{-1} 2220, 1470, 1410, 1380, 1270 and 840; δ_H 7.55 (2 H, s, ArH) and 2.56 (6 H, s, CH_3); *m*/*z* 156 (M^+, 100%), 141 (91) and 128 (17).

2,3-*Dimethylbenzene*-1,4-*dicarbaldehyde* **11**.—Diisobutylaluminium hydride (6 mmol) in hexane (6 cm^3), was added to a solution of the dinitrile **10** (0.15 g, 1 mmol) in dry benzene (8 cm^3) under nitrogen. After the addition the mixture was stirred at room temperature for 20 h. The mixture was then cooled in an ice-bath and decomposed with methanol (5 cm^3), followed by methanol–water (1:1, 10 cm^3) and finally conc. hydrochloric acid–water (1:2) was added until the solution was slightly acidic. The mixture was extracted with dichloromethane, and the organic layers were combined, washed with sodium hydrogen carbonate, water, then dried and evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane–dichloromethane (1:1) as the eluent to give **11** as pale yellow crystals (0.13 g, 87%), m.p. 78 °C (Found: M^+, 162.0704. $C_{10}H_{10}O_2$ requires *M*, 162.0684); ν_{max}/cm^{-1} 1670, 1560, 1380, 1240, 850, 820 and 780; δ_H 10.42 (2 H, s, CHO), 7.78 (2 H, s, ArH) and 2.65 (6 H, s, CH_3); *m*/*z* 162 (M^+, 100%), 133 (30) and 105 (40).

1,4-*Bis*(*hydroxymethyl*)-2,3-*dimethylbenzene* **12**.—A mixture of the dialdehyde **11** (0.34 g, 2 mmol) and sodium borohydride (0.06 g, 2 mmol) in THF (30 cm^3) was stirred at room temperature for 24 h. The reaction mixture was decomposed with conc. hydrochloric acid–water (1:1) until the resultant solution was slightly acidic. The aqueous layer was saturated with sodium chloride and extracted with dichloromethane. The organic layers were combined, dried and evaporated under reduced pressure to give the alcohol **12**. Recrystallization from hexane–chloroform (1:1) gave colourless crystals of **12** (0.13 g, 39%), m.p. 125–126 °C (Found: C, 72.5; H, 8.3. M^+, 166.0990. $C_{10}H_{14}O_2$ requires C, 72.26; H, 8.49%. *M*, 166.0994); ν_{max}/cm^{-1} 3500–3100br, 2900, 1440, 1340, 1230, 1000, 840, 820 and 750; δ_H 7.16 (2 H, s, ArH), 4.67 (4 H, s, CH_2), 2.26 (6 H, s, CH_3) and 2.02 (2 H, s, OH; exchanged with D_2O); *m*/*z* 166 (M^+, 66%), 148 (100), 130 (31), 107 (61) and 91 (84).

1,4-*Bis*(*bromomethyl*)-2,3-*dimethylbenzene* **13**.—Phosphorus tribromide (0.30 cm^3, 3 mmol) was added to a suspension of the diol **12** (0.09 g, 0.5 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 eluent. The dibromide **13** was obtained as colourless crystals (0.12 g, 81%), m.p. 154–155 °C (Found: C, 41.3; H, 4.15; Br, 54.9. $C_{10}H_{12}Br_2$ requires C, 41.13; H, 4.14; Br, 54.73%); ν_{max}/cm^{-1} 2920, 1440, 1250, 1190, 830, 750 and 640; δ_H 7.14 (2 H, s, ArH), 4.51 (4 H, s, CH_2) and 2.32 (6 H, s, CH_3); *m*/*z* 292 (M^+, 5%), 211 (77), 132 (100) and 117 (19).

14,15-*Dimethyl*-2,11-*dithia*[3.3](1,3)(1,4)*cyclophane* **4b**.—A solution of dibromide **13** (60 mg, 0.2 mmol) and 1,3-bis(mercaptomethyl)benzene **14**[12] (40 mg, 0.2 mmol) in benzene (200 cm^3) was added dropwise over a period of 8 h to a vigorously stirred solution of potassium hydroxide (33 mg, 0.6 mmol) in 95% ethanol (750 cm^3) at room temperature under nitrogen. After stirring for an additional 18 h, the bulk of the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, washed, dried and evaporated. The residue was preadsorbed on silica gel and chromatographed using hexane–dichloromethane (3:1) as the eluent to yield dithiacyclophane **4b**. Recrystallization from cyclohexane gave colourless crystals of **4b** (50 mg, 79%), m.p. 162–163 °C (Found: C, 72.2; H, 6.8. $C_{18}H_{20}S_2$ requires C, 71.95; H, 6.71%); λ_{max}(dichloromethane)/nm 236 (ε 24 900 dm^3 mol^{-1} cm^{-1}); ν_{max}/cm^{-1} 2920, 1430, 1370, 1210, 1080, 890 and 760; δ_H 6.9–7.1 (3 H, br s, 5,6,7-H), 6.92 (2 H, s, 17,18-H), 5.81 (1 H, br s, 9-H), 3.79, 3.94 (4 H, AB, *J* 13.3 Hz, CH_2), 3.61, 3.28 (4 H, AB, *J* 15.0

Hz, CH_2) and 1.86 (6 H, s, CH_3); *m/z* 300 (M^+, 98%), 163 (100) and 133 (71).

Wittig Rearrangement of Dithiacyclophane **4b** *to form* **16**.—Lithium diisopropylamide was prepared by addition of butyllithium in hexane (2.7 cm^3, 2.3 mmol; 1.5 mol dm^{-3}) to diisopropylamine (0.65 cm^3, 5.3 mmol) in dry THF (10 cm^3). The base was then added dropwise to a solution of the dithiacyclophane **4b** (342 mg, 1.14 mmol) in dry THF (20 cm^3) under nitrogen at 0 °C. After 15 min, the green solution was quenched with methyl iodide. Water was added and the resulting mixture extracted with dichloromethane. The organic phase was washed, dried and evaporated. The yellow oil obtained was chromatographed on silica gel using hexane–dichloromethane (1 : 1) as the eluent to give a mixture of isomers of **16** (206 mg, 55%) (Found: M^+, 328.1322. $C_{20}H_{24}S_2$ requires *M*, 328.1319); ν_{max}/cm^{-1} 2920, 2840, 1580, 1460, 1380, 1210, 1160, 1080, 1040, 950, 890, 830, 780, 720 and 700; δ_H 6.8–7.3 (m, ArH), 5.70, 5.75 (s, 15, 16-H), 5.02, 5.30 (s, 8-H), 3.1–3.8 (m, CH), 1.6–2.9 (m, CH_2), 2.35 (s, $ArCH_3$), 2.17 (s, SCH_3), 2.01 (s, SCH_3) and 1.86 (s, SCH_3); *m/z* 328 (M^+, 24%), 314 (28), 299 (4), 266 (7), 196 (100), 182 (49), 167 (20), 151 (14) and 135 (14).

12,13-*Dimethyl*[2.2](1,3)(1,4)*cyclophane* **2a**.—(A) *Photochemical method.* Trimethylphosphite (10 cm^3) was added to a solution of dithiacyclophane **4b** (80 mg, 0.3 mmol) in benzene (2 cm^3) in a quartz tube. The solution was irradiated with a medium pressure mercury lamp for 18 h with stirring. The mixture was cooled and hexane (100 cm^3) was added. The organic layer was separated, washed, dried and evaporated under reduced pressure. Column chromatography of the crude product on silica gel using hexane as the eluent gave the desired cyclophane **2a** (18 mg, 30%) as a low melting solid, m.p. < 40 °C (Found: C, 91.2; H, 8.7. M^+, 236.1566. $C_{18}H_{20}$ requires C, 91.47; H, 8.53%. *M*, 236.1564); λ_{max}/nm 236 (ε 24 600 $dm^3\ mol^{-1}\ cm^{-1}$) 252 (16 600) and 272 (9700); ν_{max}/cm^{-1} 3020, 2940, 2880, 1610, 1480, 1450, 1380, 1180, 920, 880, 820, 800, 780, 750, 720 and 710; δ_H 6.7–7.1 (3 H, m, 4,5,6-H), 5.68 (2 H, s, 15,16-H), 5.03 (1 H, s, 8-H), 1.0–3.3 (8 H, m, CH_2) and 2.34 (6 H, s, CH_3); *m/z* 236 (M^+, 100%), 221 (78), 131 (86) and 104 (53).

(B) *Raney nickel reduction.* A mixture of isomers of **16** (0.20 g, 0.61 mmol) was added to absolute alcohol (10 cm^3) containing an excess (> 10 equiv.) of W-7 Raney nickel[18] and the mixture was heated at reflux for 24 h. The mixture was cooled and diluted with benzene. The crude product was chromatographed on silica gel with hexane as the eluent to give **2a**, 80 mg (56%), as a colourless oil which was identical (^1H NMR, IR, MS) to the previously obtained sample.

Acknowledgements

This work was supported (RP860606) by the National University of Singapore (NUS). A. H.-T. Yap thanks the NUS for the Research Studentship (1988–90). Assistance from the technical staff of the Department of Chemistry, NUS, is gratefully acknowledged.

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Paper 2/06819B
Received 23*rd December* 1992
Accepted 12*th March* 1993