Synthesis and photoreactions of polymethyl substituted [2.2]metacyclophanes

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Photo-oxygenation of 4,5,6,8,12,13,14,16-octamethyl[2.2]metacyclophane using a high-pressure mercury lamp produced a mixture of mono- and bis-endoperoxides in quantitative yield, while irradiation with sunlight in chloroform afforded 1,2,3,6,7,8-hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene in 20% yield.

Keywords: cyclophanes, photo-oxygenation, endoperoxide, dihydropyrene, deoxygenation

Photochemically-generated singlet oxygen ($^1O_2$) cycloadds to conjugated dienes and arenes to give endoperoxides.[1-3] The endoperoxides are important intermediates in photo-oxidation reactions but, in most cases, are too unstable to be isolated in order to study their structures. On the other hand, cyclophanes belong to a remarkable class of compounds, which has attracted extensive studies.[4,5] Strained aromatic rings in cyclophanes, such as in [2.2.2.2](1,2,4,5)cyclophane[6] and [2.2]paracyclophane diene,[7,8] readily undergo photocycloaddition with $^1O_2$ in the presence of photosensitising dyes. Recently, it was reported that the photoirradiation of a mono-{Dewar benzene (bicyclo[2.2.0]hexadiene)} isomer of the [1.1]MCP (MCP = metacyclophane) gave the corresponding endoperoxide.[9,10] In this case, no additional sensitiser was used. This result suggests that strained MCPs are reactive in photocycloaddition reactions with $^1O_2$.

Furthermore, introduction of methyl groups to the benzene ring of [2.2]MCP also increases the strain in the molecule. Therefore, there is substantial interest in preparing the polymethyl substituted [2.2]MCPs to investigate the relationship between strain and reactivity.

We now report the synthesis of polymethyl substituted [2.2]MCPs and conversion into the corresponding *trans*-10b,10c-dimethyl-10b,10c-dihydropyrenes by spontaneous oxidation in $CHCl_3$ solution on sunlight irradiation. The first successful preparation and characterisation of a stable mono- and bis-endoperoxide of polymethyl substituted [2.2]MCPs using a high pressure mercury lamp is also reported.

Results and discussion

The preparative route to 4,5,6,8,12,13,14-heptamethyl [2.2]MCP (**6a**) and 4,5,6,8,12,13,14,16-octamethyl[2.2]MCP (**6b**) is shown in Scheme 1 following our previously reported procedure.[11–16] The starting compounds, bis(chloromethyl) benzenes **2a** and **2b** were prepared in good yields by the chloromethylation of the corresponding methylbenzenes **1a** and **1b** with chloromethyl methyl ether in the presence of zinc chloride. Bis(chloromethyl)benzene **2b** was converted into the mercaptomethyl derivative **3b** in 72% yield according to the reported procedure.[17] The desired **6a** and **6b** were prepared from the corresponding **2** and **3b** *via* the disulfides **4** and bissulfones **5** according to the reported methods.[11–16] Thus, the cyclisation of bis(chloromethyl)benzenes **2a** and **2b** and the mercaptomethyl derivative **3b** was carried out under highly diluted conditions in 10% ethanolic KOH in the presence of a small amount of $NaBH_4$, giving *anti*-2,11-dithia[3.3]MCPs **4a** and **4b** in 80 and 72% yields, respectively. Oxidation of **4** with *m*-chloroperbenzoic acid in $CHCl_3$ afforded the corresponding bissulfones *anti*-**5** in almost quantitative yields. Pyrolysis of both bissulfones, **5a** and **5b** under reduced pressure (1 torr) at 500 °C was carried out by a reported method[17,18] to afford exclusively *anti*-**6a** and **6b** in 75 and 71% yields, respectively.

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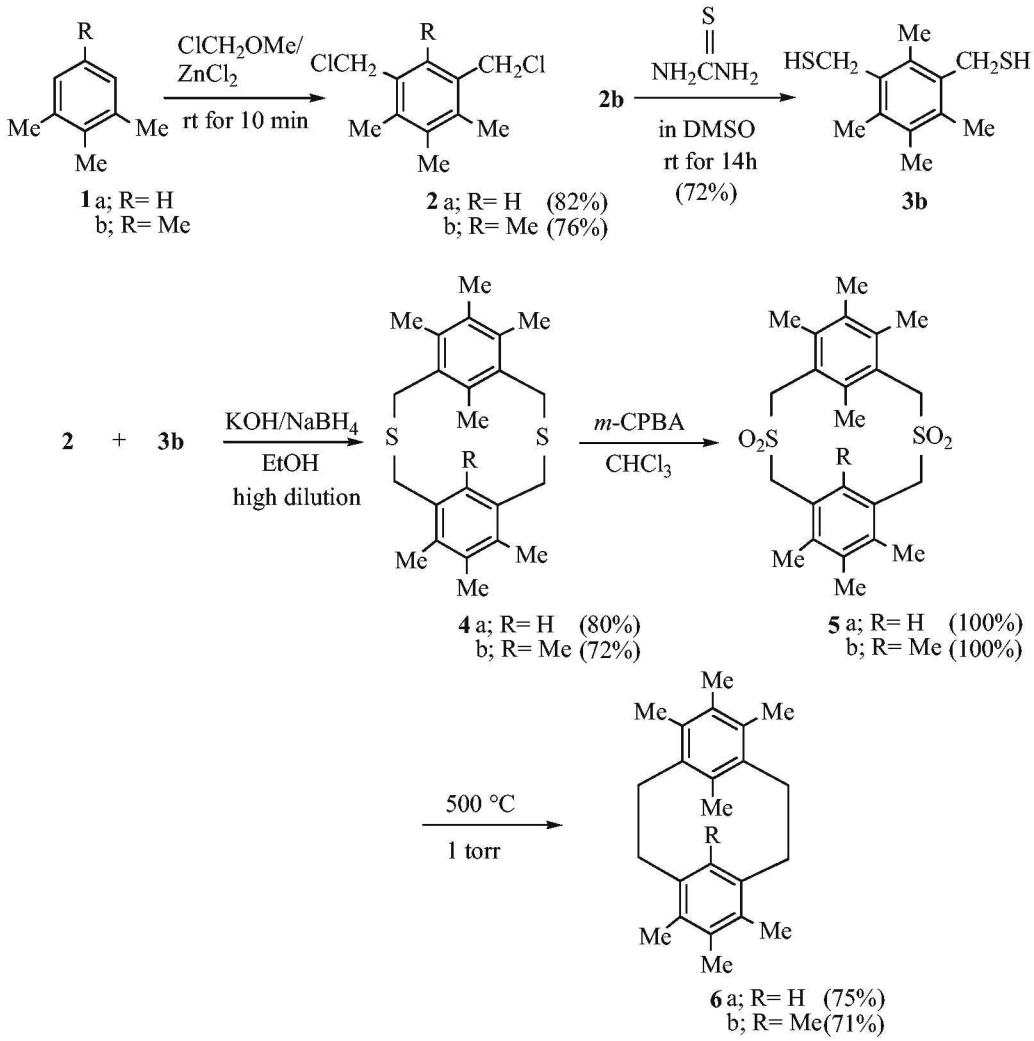
The assignments of structure for **6a** and **6b** were readily apparent from their ^1H NMR spectra. The ^1H NMR spectra of conformers **6a** and **6b** show methyl protons at δ 0.45 and 0.44 ppm, respectively. The internal aromatic proton at the 16-position of **6a** is also observed up field (δ 3.75 ppm). Thus, the internal methyl protons of the *anti* conformers show an upfield shift due to the ring current of the opposite aromatic ring.[4,5,17,18] These observations strongly suggest that compounds **6a** and **6b** adopt an *anti*-conformation.

When an initially colourless solution of 4,5,6,8,12,13,14,16-octamethyl[2.2]MCP solution of **6b** in $CHCl_3$ was exposed to sunlight, it gradually became dark green. This colour change strongly suggests the formation of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene.[19] The progress of the photo-reaction was monitored by ^1H NMR. After 4 h its ^1H NMR spectrum showed a new methyl signal at δ –3.92 ppm together with the original internal methyl signal at δ 0.45 ppm. 1,2,3,6,7,8-Hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **7b** was isolated as deep green prisms by silica gel chromatography in 20% yield along with recovery of the starting compound **6b**. However, when the solution of **6a** was exposed to daylight for 4 h, a similar colour change was not observed. Only an intractable mixture of products was obtained. The cyclophane structure did not survive this treatment a fact proven by the disappearance of the internal methyl protons at δ 0.44 ppm and the internal aromatic proton at δ 3.75 ppm.

The structure of product **7b** was determined on the basis of elemental analyses and spectroscopic data. The ^1H NMR spectrum of **7b** shows internal methyl protons as a singlet at δ –3.92 and other methyl protons as singlets at δ 2.91 and 3.12 ppm (relative intensity 1:2). Four aromatic protons are observed as a singlet at δ 8.59, which are clearly associated with the protons at C-4, C-5, C-9 and C-10.

Although Renfore and coworkers[20] reported preparation of 1,2,3,6,8-pentamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene in which the internal methyl substituent is surrounded by annulene π-electrons, its synthetic route from easily available compound, 2,4,6-trimethylphenol involving Stevens rearrangement and Hofmann elimination seem to be too long for practical purposes. Therefore, the presently developed preparative route to 1,2,3,6,7,8-hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **7b** from [2.2]MCP **6b** should be useful for the preparation of polymethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrenes.

Interestingly, irradiation of 4,5,6,8,12,13,14-heptamethyl [2.2]MCP **6a** in acetone using a high pressure mercury lamp produced endoperoxide **8a** in 70% yield (Scheme 3). Although no additional photosensitiser was added, the reaction leading to **8a** is thought to proceed via $^1O_2$. Thus, the reaction was slowed remarkably by addition of 1,4-diazabicyclo[2.2.2] octane, a known $^1O_2$ quencher. It may well be possible that the [2.2]MCP **6a** itself acts as sensitiser in the reaction. Furthermore, of the strain in **6a** might be released at the

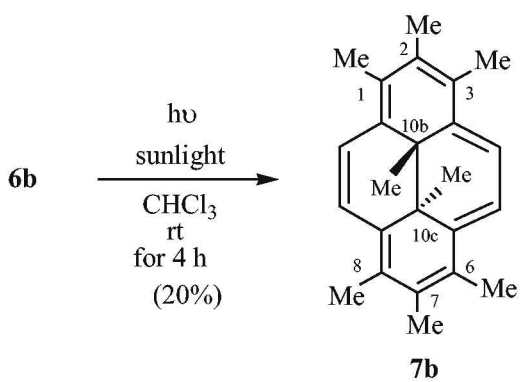


Scheme 1

carbon atoms located on the internal 8-position by a change in its hybridisation mode from sp^2 to sp^3.

When irradiation of 4,5,6,8,12,13,14,16-octamethyl [2.2]MCP **6b** using a high-pressure mercury lamp in acetone under the same reaction conditions produced an inseparable mixture of mono-endoperoxide **8b** and bis-endoperoxide **9b** in quantitative yield in the ratio of 44 and 66% (Scheme 3).

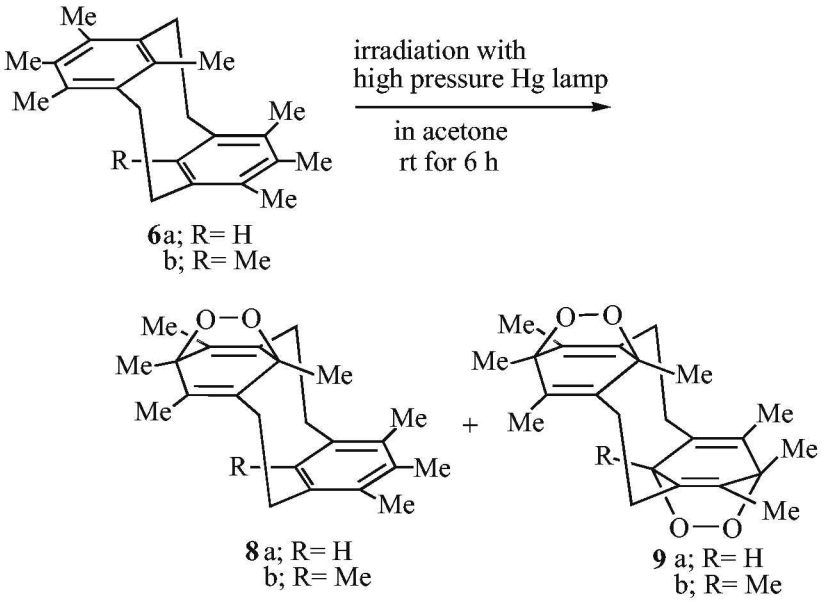
The similarly substituted hexamethylbenzene **10** itself is inert under the irradiation conditions mentioned above, although it has been reported that the formation of the unstable endoperoxide **11** can be detected by ^{1}H NMR spectroscopy in the reaction mixture, when methylene blue was used as a photosensitiser. Epidioxy hydroperoxide **12** is the final product by an ene reaction of **11** (Scheme 4).[21,22]



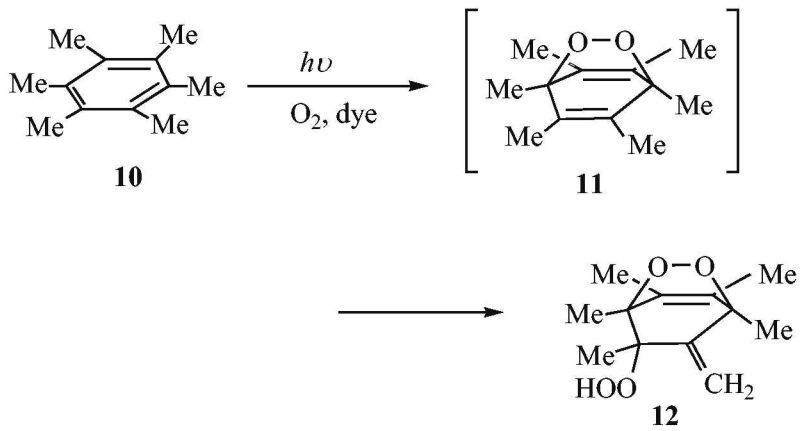
Scheme 2

Compared to **11**, endoperoxide **8a** is stable enough to be recrystallised from acetone. On the other hand, endoperoxide **11**, which was not isolated, was reported to decompose completely at 40 °C in 1 h as measured by ^{1}H NMR spectroscopy. Thermal deoxygenation of **8a** was also monitored by ^{1}H NMR spectroscopy. In fact, after heating a solution of **8a** in $CDCl_3$ for 6 h, the new signals derived from [2.2]MCP **6a** were observed in the ratio of 15:85 (**6a**:**8a**) at 40 °C and 45:55 (**6a**:**8a**) at 50 °C. As a result, the thermal deoxygenation of **8a** was found to have occurred in a similar manner to those of the endoperoxides of 1,4-dimethylnaphthalene and of 9,10-diphenylanthracene.[23]

The structure of product **8a** was determined on the basis of elemental analyses and spectroscopic data. Thus, the ^{1}H NMR spectrum of **8a** shows five kinds of methyl resonances as singlets at δ 0.02 (3H), 1.26 (3H), 1.90 (3H), 2.17 (6H) and 2.24 (6H) ppm, in which one methyl group shows a much larger upfield shift (δ 0.02 ppm) than in [2.2]MCP **6a** (δ 0.44 ppm) due to the ring current effect of the opposite benzene ring. By changing the carbon atom located on the internal 8-position from sp^2 to sp^3 an internal methyl group was located much closer to the opposite benzene ring. In contrast, the internal 16-proton appeared in the normal aromatic region (δ 6.53 ppm) in comparison with **6a** at δ 3.75 ppm due to the disappearance of the benzene ring by forming the endoperoxide.



Scheme 3



Scheme 4

We have assigned the ^{1}H NMR signals of **8b** in a similar fashion. In contrast, the methyl protons were observed as singlets at δ 1.22 (6H), 1.51 (6H) and 1.85 (12H) ppm, respectively. No upfield shifts of the internal 8,16-methyl groups were observed. This finding strongly suggests that the both benzene rings of **6b** were photo-oxygenated and the structure of **9b** is assigned the structure, 4,5,6,8,12,13,14,15-octamethyl[2.2]MCP-5,8, 13,16-bis-endoperoxide.

Conclusions

We have demonstrated that photo-oxygenation of 4,5,6,8, 12,13,14,16-octamethyl-[2.2]MCP **6b** using a high pressure mercury lamp produced a mixture of mono- and bis-endoperoxides in good yield, while irradiation with sunlight in chloroform afforded 1,2,3,6,7,8-hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **7b** in 20% yield. Further studies on the chemical properties of the photo-oxygenation products and 1,2,3,6,7,8-hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene are now in progress.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by a Yanaco MT-5 instrument.

CAUTION: Appropriate precautions were taken in handling chloromethyl methyl ether due to the established carcinogenicity. (Precautions were also taken with **2a** and **2b** (irritants) and **8a**, **8b** and **9b** (possible explosive behaviour).

Preparation of 2,6-*bis(chloromethyl)*-1,3,4,5-*tetramethylbenzene* (**2b**): To a solution of 1,2,3,5-tetramethylbenzene **1b** (67.1 g, 0.5 mol) and chloromethyl methyl ether (150 ml) was added zinc chloride (40 g, 0.29 mol) at room temperature. After the reaction mixture was stirred for 10 min, it was poured into ice-water (300 ml) and extracted with CH_2Cl_2 (200 ml × 3). The CH_2Cl_2 extract was washed with water (200 ml) and saturated aqueous NaCl (100 ml × 2), and then dried (Na_2SO_4). Evaporation of solvent under reduced pressure gave a colourless solid. Recrystallisation from hexane gave the title compound **2b** as colourless prisms (88.0 g, 76%), m.p. 110–111 °C (lit.,[24] 114 °C).

Similarly, 1,5-bis(chloromethyl)-2,3,4-trimethylbenzene (**2a**) was prepared in 82% yield as colourless prisms (hexane), m.p. 112–115 °C (lit.,[24] 121–122 °C) by chloromethylation of 1,2,3-trimethylbenzene (**1a**) under the same reaction conditions as described above.

Preparation of 2,6-*bis(mercaptomethyl)*-1,3,4,5-*tetramethylbenzene* (**3b**): A solution of **2b** (9.25 g, 0.40 mmol) and thiourea (6.7 g, 88 mmol) in DMSO (50 ml) was stirred at room temperature under an atmosphere of nitrogen for 14 h. After the reaction mixture was

poured into a solution of NaOH (20 g) in water (200 ml), the solution was stirred for 1 h, acidified with aqueous 10% HCl and extracted with CH_2Cl_2 (100 ml × 2). The CH_2Cl_2 extract was washed with water (100 ml) followed by saturated aqueous NaCl (100 ml) and dried (Na_2SO_4). Evaporation of solvent under reduced pressure gave a colourless solid. Recrystallisation from hexane gave the title compound **3b** as colourless prisms (6.5 g, 72%), m.p. 81–82 °C; ν_{max}/cm^{-1} (KBr) 3040, 2960, 2900, 2550, 1430, 1370, 1225, 1010, 790 and 675; δ_H ($CDCl_3$) 1.54 (2H, t, J = 7.0 Hz, *SH*), 2.18 (3H, s, *CH*$_3$), 2.29 (6H, s, *CH*$_3$), 2.40 (3H, s, *CH*$_3$) and 3.76 (4H, s, *CH*$_2$); *m/z* 226 (M^+). (Found: C, 63.61; H, 8.13. $C_{12}H_{18}S_2$ (226.4) requires C, 63.66; H, 8.01%).

Preparation of 5,6,7,9,14,15,16,18-octamethyl-2,11-dithia[3.3]metacyclophane (**4b**): A solution of **2b** (4.78 g, 20 mmol) and **3b** (4.52 g, 20 mmol) in benzene (100 ml) was added dropwise over a period of 12 h from a Herschberg funnel with stirring under nitrogen to a solution of potassium hydroxide (4.0 g, 71 mmol) and sodium borohydride (1 g) in ethanol (4 l). After the addition, the reaction mixture was concentrated and the residue was extracted with CH_2Cl_2 (200 ml × 2). The CH_2Cl_2 extract was concentrated and the residue was chromatographed on silica gel (Wako C-300, 400 g) (hexane-benzene, 1 : 1 v/v, as eluent) to give a colourless solid. Recrystallisation from hexane-benzene 1 : 1 (v/v) gave 5,6,7,9,14,15,16,18-octamethyl-2,11-dithia[3.3]metacyclophane (**4b**) as colourless prisms (5.57 g, 72%), m.p. >300 °C; ν_{max}/cm^{-1} (KBr) 3020, 2930, 1445, 1410, 1300, 1260, 1220, 1105, 1020, 805 and 730; δ_H ($CDCl_3$) 1.16 (6H, s, *CH*$_3$), 2.22 (6H, s, *CH*$_3$), 2.41 (12H, s, *CH*$_3$), 3.67 (4H, d, J = 13.7 Hz, *CH*$_2$) and 3.76 (4H, d, J = 13.7 Hz, *CH*$_2$); *m/z* 384 (M^+) (Found: C, 75.05; H, 8.45. $C_{24}H_{32}S_2$ (384.64) requires C, 74.94; H, 8.39%).

The cyclisation reaction of **2a** and **3b** was carried out using the same procedure as described above to afford **4a** in 80% yield.
5,6,7,9,14,15,16-heptamethyl-2,11-dithia[3.3]metacyclophane (**4a**) was formed as colourless prisms (5.92 g, 80%), m.p. 195–196 °C; ν_{max}/cm^{-1} (KBr) 3050, 2950, 2900, 1430, 1370, 1280, 1215, 1060, 1000, 905, 785, 765, 740 and 720; δ_H ($CDCl_3$) 1.68 (3H, s, *CH*$_3$), 2.10 (3H, s, *CH*$_3$), 2.18 (6H, s, *CH*$_3$), 2.30 (3H, s, *CH*$_3$), 2.41 (6H, s, *CH*$_3$), 3.01 (2H, d, J = 16.0 Hz, *CH*$_2$), 3.58 (2H, d, J = 16.0 Hz, *CH*$_2$), 3.80 (2H, d, J = 12.0 Hz, *CH*$_2$), 4.04 (2H, d, J = 12.0 Hz, *CH*$_2$) and 4.48 (1H, broad s, Ar-H); *m/z* 370 (M^+) (Found: C, 74.64; H, 8.24. $C_{23}H_{30}S_2$ (370.6) requires C, 74.54; H, 8.16%).

Preparation of 5,6,7,9,14,15,16,18-octamethyl-2,11-dithia[3.3]metacyclophane-2,2,11,11-tetraoxide (**5b**): To a solution of **4b** (2.72 g, 7.1 mmol) in $CHCl_3$ (150 ml) was added *m*-chloroperbenzoic acid (3.40 g, 16.7 mmol, 85% purity) at 0 °C while stirring with a magnetic stirrer. After the solution was stirred for 24 h at room temperature, the solvent was evaporated *in vacuo* to leave the residue which was washed with 10% $NaHCO_3$ (100 ml), water (50 ml) and ethanol to afford 5,6,7,9,14,15,16,18-octamethyl-2,11-dithia[3.3]metacyclophane-2,2,11,11-tetraoxide (**5b**) as colourless prisms (3.20 g, 100%), m.p. >300 °C; ν_{max}/cm^{-1} (KBr) 3020, 2930, 1445, 1410, 1360, 1260, 1220, 1105, 1020, 805 and 730; δ_H ($CDCl_3$) 1.17 (6H, s, *CH*$_3$), 2.26 (6H, s, *CH*$_3$), 2.50 (12H, s, *CH*$_3$), 4.53 (4H, d, J = 14.8 Hz, *CH*$_2$) and 4.62 (4H, d, J = 14.8 Hz, *CH*$_2$); *m/z* 320 (M^+-2SO_2) (Found: C, 64.35; H, 7.08. $C_{24}H_{32}S_2O_4$ (448.64) requires C, 64.25; H, 7.19%).

Similarly, oxidation of **4a** with *m*-CPBA was carried out using the same procedure as described above to afford **5a** in 100% yield.
5,6,7,9,14,15,16-heptamethyl-2,11-dithia[3.3]metacyclophane-2,2,11,11-tetraoxide (**5a**): Colourless prisms (3.1 g, 100%), m.p. >300 °C; ν_{max}/cm^{-1} (KBr) 3050, 2930, 1410, 1300, 1250, 1150, 1100, 915, 850, 780, 725 and 700; δ_H ($CDCl_3$) 1.91 (3H, s, *CH*$_3$), 2.19 (3H, s, *CH*$_3$), 2.29 (6H, s, *CH*$_3$), 2.44 (3H, s, *CH*$_3$), 2.59 (6H, s, *CH*$_3$), 3.98 (2H, d, J = 15.2 Hz, *CH*$_2$), 4.24 (2H, d, J = 15.2 Hz, *CH*$_2$), 4.46 (1H, broad s, ArH), 4.66 (2H, d, J = 13.8 Hz, *CH*$_2$) and 4.80 (2H, d, J = 13.8 Hz, *CH*$_2$); *m/z* 306 (M^+–2SO_2) (Found: C, 63.32; H, 6.96. $C_{23}H_{30}S_2O_4$ (434.60) requires C, 63.56; H, 6.96%).

Pyrolysis of disulfone **5b** *to give 4,5,6,8,12,13,14,16-octamethyl*[2.2]*metacyclophane* (**6b**): Carried out in an apparatus consisting of a horizontal tube (15 mm in diameter) passing through two adjacent tube furnaces, each of which was 20 cm long. The first furnace provided a temperature that would induce sublimation of the sulfone; the second was used at a higher temperature (500 °C) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace. Disulfone **5b** (1.14 g, 2.55 mmol) was pyrolysed at 500 °C under reduced pressure (1 torr) in the above apparatus as follows. The sample of disulfone was placed in the first furnace and small glass beads were packed into the second furnace. The product which sublimed was collected and chromatographed on silica gel (Wako C-300, 100 g) (hexane as eluent) to give a colourless solid. Recrystallisation from hexane gave 4,5,6,8,12,13,14,16-octamethyl [2.2]metacyclophane (**6b**) as colourless prisms (580 mg, 71%), m.p. >300 °C; ν_{max}/cm^{-1} (KBr) 3050, 2960, 1440, 1410, 1365, 1320, 1180, 1060, 1040, 1000, 880, 800 and 740; δ_H ($CDCl_3$) 0.45 (6H, s, *CH*$_3$), 2.17 (6H, s, *CH*$_3$), 2.32 (12H, s, *CH*$_3$), 2.43 (4H, d, J = 9.6 Hz, *CH*$_2$) and 3.17 (4H, d, J = 9.6 Hz, *CH*$_2$); *m/z* 320 (M^+) (Found: C, 90.13; H, 10.19. $C_{24}H_{32}$ (320.52) requires C, 89.94; H, 10.06%).

Pyrolysis of **5a** was carried out using the same procedure as described above to afford **6a** in 75% yield.
4,5,6,8,12,13,14-*Heptamethyl*[2.2]*metacyclophane* (**6a**): Colourless prisms, m.p. 210–211 °C; ν_{max}/cm^{-1} (KBr) 3017, 2970, 1460, 1440, 1410, 1370, 1325, 1180, 1060, 1020, 930, 880 and 745; δ_H ($CDCl_3$) 0.44 (3H, s, internal *CH*$_3$), 1.60–2.47 (4H, m, *CH*$_2$), 2.18 (3H, s, *CH*$_3$), 2.27 (3H, s, *CH*$_3$), 2.28 (6H, s, *CH*$_3$), 2.31 (6H, s, *CH*$_3$), 3.08–3.36 (4H, m, *CH*$_2$) and 3.75 (1H, broad s, Ar-*H*); *m/z* 306 (M^+) (Found: C, 90.37; H, 9.87. $C_{24}H_{30}$ (306.47) requires C, 90.13; H, 9.87%).

Photoreaction of **6b** *with sunlight*: A solution of **6b** (100 mg, 0.31 mmol) in chloroform (30 ml) was exposed to sunlight for 4 h at room temperature in a Pyrex round-bottom flask following the progress of the reaction using TLC. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel (Wako gel C-300) using hexane as eluent. The eluate was evaporated and the residue was recrystallised from hexane, giving 1,2,3,6,7,8-hexamethyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **7b** (20 mg, 20%) as deep green needles, m.p. 245–249 °C, ν_{max}/cm^{-1} (KBr) 2970, 2922, 1518, 1440, 1383, 1353, 1332, 804 and 687; δ_H ($CDCl_3$) –3.92 (6H, s, *CH*$_3$), 2.91 (6H, s, *CH*$_3$), 3.12 (12H, s, *CH*$_3$) and 8.59 (4H, s, ArH); *m/z* 316 (M^+) (Found: C, 90.97; H, 8.93. $C_{24}H_{28}$ (316.49) requires C, 91.08; H, 8.92%).

Photo-oxygenation of [2.2]metacyclophane **6a**: A solution of **6a** (100 mg, 0.33 mmol) in acetone (100 ml) was irradiated with a 100 W high pressure mercury lamp (Riko Kagaku Sangyo Co.) for 6 h at room temperature in air. A Pyrex filter was used. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel (Wako gel C-300) using dichloromethane as eluent. The eluate was evaporated and the residue was recrystallised from acetone, giving 4,5,6,8,12,13,14-heptamethyl[2.2]metacyclophane-5,8-endoperoxide (**8a**) (77 mg, 70%), as colourless prisms (acetone), m.p. 80 °C (decomp.); δ_H ($CDCl_3$) 0.02 (3H, s, *CH*$_3$), 1.26 (3H, s, *CH*$_3$), 1.90 (3H, s, *CH*$_3$), 1.88–1.95 (2H, m, *CH*$_2$), 2.17 (6H, s, *CH*$_3$), 2.24 (6H, s, *CH*$_3$), 2.36 (2H, ddd, J = 3.1. 4.0 and 12.5 Hz, *CH*$_2$), 2.66 (2H, ddd, J = 3.1, 3.6 and 12.7 Hz, *CH*$_2$), 3.03 (2H, ddd, J = 4.0, 12.5 and 12.7 Hz, *CH*$_2$) and 6.53 (1H, s, ArH); *m/z* 338 (M^+) (Found: C, 81.24; H, 8.80. $C_{23}H_{30}O_2$ (338.49) requires C, 81.61; H, 8.93%).

Photo-oxygenation of [2.2]metacyclophane **6b**: A solution of **6b** (100 mg, 0.32 mmol) in acetone (100 ml) was irradiated with a 100 W high pressure mercury lamp (Riko Kagaku Sangyo Co.) for 6 h at room temperature in air. A Pyrex filter was used. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel (Wako gel C-300) using dichloromethane as eluent. The eluate was evaporated to afford the residue (100 mg) as a colourless solid, which was found to be a mixture of endoperoxide **8b** and bis-endoperoxide **9b** in the ratio of 40:60 (determined by ^{1}H NMR spectrum). The residue was chromatographed on silica gel (Wako gel C-300) using dichloromethane as eluent to give a colourless solid (95 mg). However, several attempted isolations of pure **8b** and **9b** failed.

4,5,6,8,12,13,14,16-Octamethyl[2.2]metacyclophane-5,8-endoperoxide **8b**: δ_H ($CDCl_3$) 0.06 (3H, s, *CH*$_3$), 1.47 (3H, s, *CH*$_3$), 1.91 (6H, s, *CH*$_3$), 1.79–1.86 (2H, m, *CH*$_2$), 1.97 (3H, s, *CH*$_3$), 2.22 (3H, s, *CH*$_3$), 2.26 (6H, s, *CH*$_3$), 2.30–2.40 (2H, m, *CH*$_2$), 2.61 (2H, ddd, J = 3.1. 4.0 and 12.7 Hz, *CH*$_2$) and 2.96 (2H, ddd, J = 4,0, 12.5 and 12.7 Hz, *CH*$_2$).

4,5,6,8,12,13,14,16-Octamethyl[2.2]metacyclophane-5,8,13,16-bis(endoperoxide) **9b**: δ_H ($CDCl_3$) 1.22 (6H, s, *CH*$_3$), 1.51 (6H, s, *CH*$_3$), 1.85 (12H, s, *CH*$_3$), 2.12 (4H, d, J = 10.2 Hz, *CH*$_2$) and 2.57 (4H, d, J = 10.2 Hz, *CH*$_2$).

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