Synthesis of 4,16-dimethoxy-1,2-dimethyl[2.4]metacyclophan-1-ene and 8,17-dimethoxy-1.2-dimethyl-10-thia[2.3.4](1,3,5)cyclophan-1-ene

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McMurry cyclisation of 1,4-bis(3-acetyl-4-methoxyphenyl)butane afforded flexible 4,16-dimethoxy-1,2-dimethyl[2.4] metacyclophan-1-ene, which was converted to the corresponding triple bridged 8,17-dimethoxy-1,2-dimethyl-10-thia[2.3.4](1,3,5)cyclophan-1-ene. The conformational studies of these cyclophan-1-enes in solution are also described.

Keywords: cyclophanes, [2.4]metacyclophan-1-ene, McMurry reaction, conformation, strained molecules, triple bridged cyclophane

Although the parent [2.2]metacyclophane (MCP = metacyclophane) was first reported as early as in 1899 by Pellegrin,[1] the synthesis of *syn*-[2.2]MCP was not realised until 85 year later. Mitchell *et al.*[2] have successfully prepared *syn*-[2.2]MCP at low temperature by using (arene)chromiumcarbonyl complexation to control the stereochemistry. Later, Itô and coworkers[3] have also isolated and characterised *syn*-[2.2]MCP without complexation. However, *syn*-[2.2]MCP isomerises readily to the *anti*-isomer above 0°C. On the other hand, Boekelheide[4] and Staab[5] succeeded in synthesising intra-annularly substituted *syn*-[2.2]MCPs, respectively. However, reports on synthesis and reactions of *syn*-[2.*n*]MCP have not been published so far. On the other hand, Boekelheide *et al.* reported the synthesis of triple bridged [2_3](1,3,5)cyclophanes as a key compound to synthesise the superphane.[6,7] Bodwell *et al.* also reported the synthesis of [2.2.*n*](1,3,5)cyclophane-1,9-dienes to afford 1,*n*-dioxa[*n*](2,7)pyrenophanes.[8] These cyclophanes adopt rigid *syn*-conformation with overlaying aromatic rings. Thus there is substantial interest to synthesise the flexible [2.*n*] MCP-1-enes and conversion to triple bridged [2.3.*n*](1,3,5)-thiacyclophane-1-enes or [2.2.*n*](1,3,5)cyclophane-1,9-dienes, which can adopt the *syn*-conformation and the flexibility arising from the ring inversion can be completely restricted.

Recently, we have reported the preparation of 1,2-dimethyl [2.3]MCP-1-enes[9–11] by using the reductive coupling of carbonyl compounds by low-valent titanium, the McMurry reaction[12–15] as a key step. While in [2.3]MCP-1-enes the aromatic rings preferentially appear to adopt the *syn*-arrangement, its hgher homologue, *i.e.* [2.*n*]MCP-1-enes, can be expected to adopt the mobile *anti*- or *syn*-conformation. We now report on the synthesis of [2.4]MCP-1-ene using the low-valent titanium induced McMurry reaction and conversion to *syn*-10-thia [2.3.4](1,3,5)cyclophan-1-ene. The conformational studies of these cyclophane-1-enes in solution are also described.

Results and discussion

1,4-Bis(4-methoxyphenyl)butane **1** has been prepared according our previous papers.[9,10] Thus the cross coupling reaction[16,17] of 4-methoxyphenylmagnesium bromide with 1,4-dibromobutane has been carried out in the presence of cuprous bromide as a catalyst in a mixture of hexamethylphosphoric triamide (HMPA) and tetrahydrofuran at reflux temperature to give the desired 1,4-bis(4-methoxyphenyl)butane **1** in 80% yield. $AlCl_3$–$MeNO_2$-catalysed acetylation of compound **1** with acetic anhydride or acetyl chloride at 20°C led to regioselective acylation at the meta positions of the 1,4-diphenylbutane affording the desired 1,4-bis(3-acetyl-4-methoxyphenyl)butane **2** in 71% yield. 1,4-Bis(3-acetyl-4-methoxyphenyl)butane **2** was subjected to reductive coupling by the McMurry reaction following the improved Grützmacher's procedure[13] (Scheme 1). Thus, the reductive coupling reaction of **2** carried out using $TiCl_4$-Zn in refluxing THF under the high dilution conditions afforded the desired compound 4,16-dimethoxy-1,2-dimethyl of [2.4]MCP-1-ene **3** in 23% yield along with an intractable mixture of products. This result was different result from that of the similar McMurry cyclisation of 1,4-bis(5-acetyl-2-methoxyphenyl)butane in the absence of pyridine, which afforded the corresponding [4.1]MCP by the $TiCl_4$ or acids induced pinacol rearrangements.[11] Surprisingly, when the present cyclisation reaction was carried out in the presence of pyridine, the yield of **3** increased to 69%.

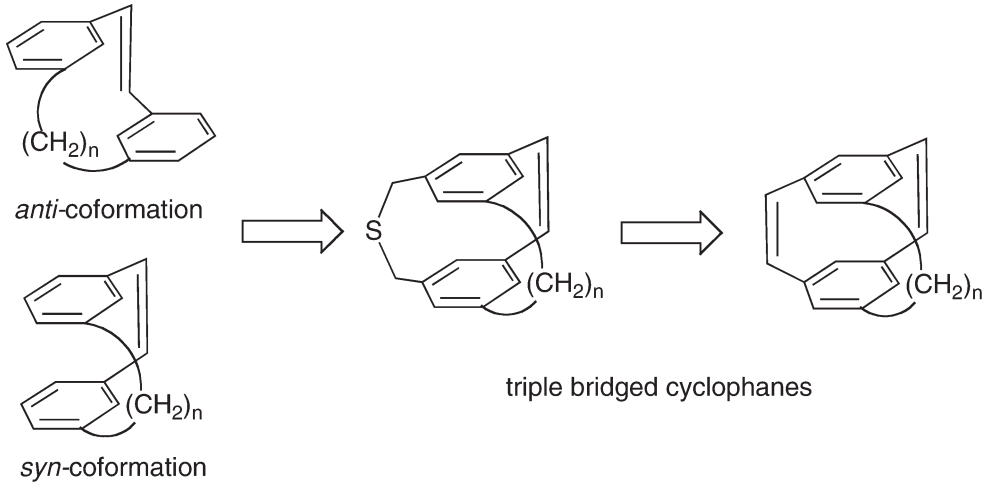

Fig. 1 Possible conformations of [2.*n*]MCP-enes and conversion to the triple bridged cyclophanes.

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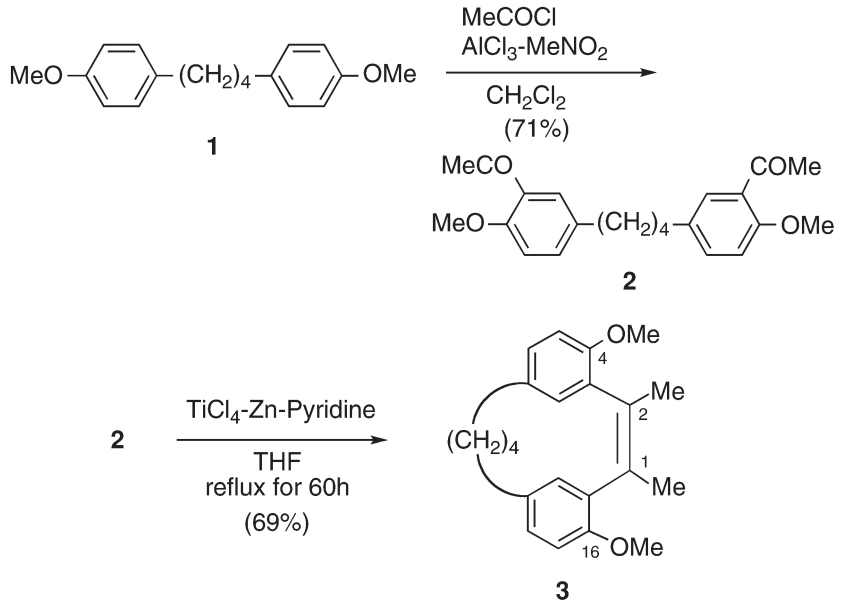


Scheme 1

The structure of **3** was elucidated based on their elemental analysis and spectral data. Especially, the mass spectral data for **3** (M^+ = 322) strongly supports the cyclic structure. [2.*n*] MCP-1-enes adopt either a "stair-case" *anti* conformation or a *syn* conformation with overlaying aromatic rings[18,19] (Fig. 1). Depending on the size of the bridges[20] and on the presence of intraannular substituents,[18,19] the interconversion between the *syn* and *anti* conformers occur by ring flipping. ^{1}H NMR spectrum of **3** showed the doublet of the intra-annular proton H_i at δ = 6.90 (J = 2.4 Hz) apart from at δ = 6.41 and 6.59 ppm of the other two protons at the aromatic rings. The conformation of **3** was readily apparent from its ^{1}H NMR spectrum. Thus, the internal aromatic proton of *anti*-conformation should show an upfield shift due to the ring current of the opposite benzene ring.[19,21,22] The ^{1}H NMR spectrum of the [2.4]MCP-1-ene **3** prepared here shows that its structure corresponds exclusively to the *syn*-conformer. In addition, the protons of the butane bridge give rise to two multiplets centred at δ = 1.55 and 2.36 ppm, respectively, providing a fast *syn*–*syn* interconversion of the two *syn* conformations of **3** by ring flipping which would exchange H_A and H_B of each CH_2 group. However, as the temperature of the solution in $CDCl_3/CS_2$ (1:3) is decreased, a single peak of the benzyl protons splits into two multiplets at δ 2.2 and 2.5 ppm below 0°C (Fig. 2). The energy barrier to the conformational ring flipping estimated from the coalescence temperature (T_C = 0°C) is 13.0 kcal mol^{-1}. Interestingly, similar findings were also observed in the corresponding *anti*-6,14-dimethoxy-1,2-dimethyl[2.4]MCP-1-ene **4** (T_C = -30°C, $\Delta G^{\neq}$ = 10.7 kcal mol^{-1})[11,23] in spite of being expected to be similar flexible structure attributable to the same cyclophane ring size. These observations suggest that the introduction of a double bond of the ethylene bridge as well as the substituents such as methyl groups and methoxy groups might control the *syn*- and *anti*-conformation of the present [2.4]MCP-1-ene **3**.

The formylation of **3** with dichloromethyl methyl ether in the presence of $TiCl_4$ afforded the desired 5,15-diformyl [2.4]MCP-1-ene **5** as a colourless prisms in 66% yield. Several attempted reductive coupling reaction of **5** carried out using $TiCl_4$–Zn in the presence of pyridine in refluxing THF under the high dilution conditions failed. No formation of the desired 8,16-dimethoxy-1,2-dimethyl[2.2.4](1,3,5)cyclophan-1,9-diene **6** was observed under the conditions used. Only an intractable mixture of products was obtained.

Therefore, we have attempted to prepare 10-thia[2.3.4](1,3,5) cyclophan-1-ene **9** as shown in Scheme 3. Thus, 5,15-bis

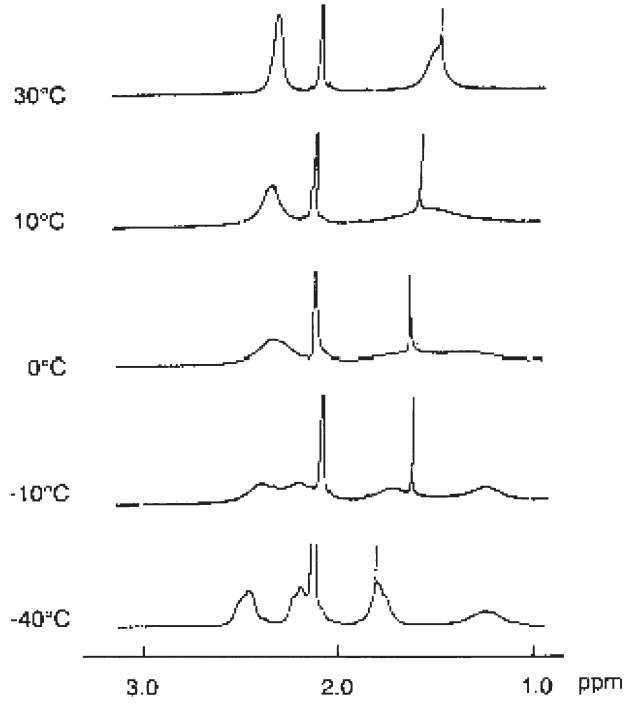
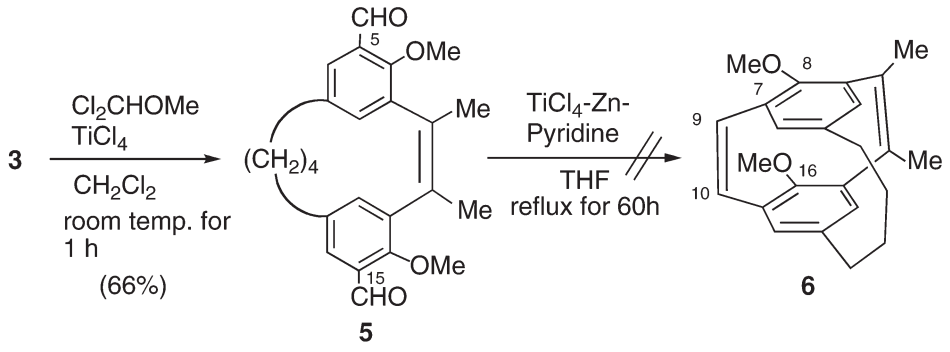


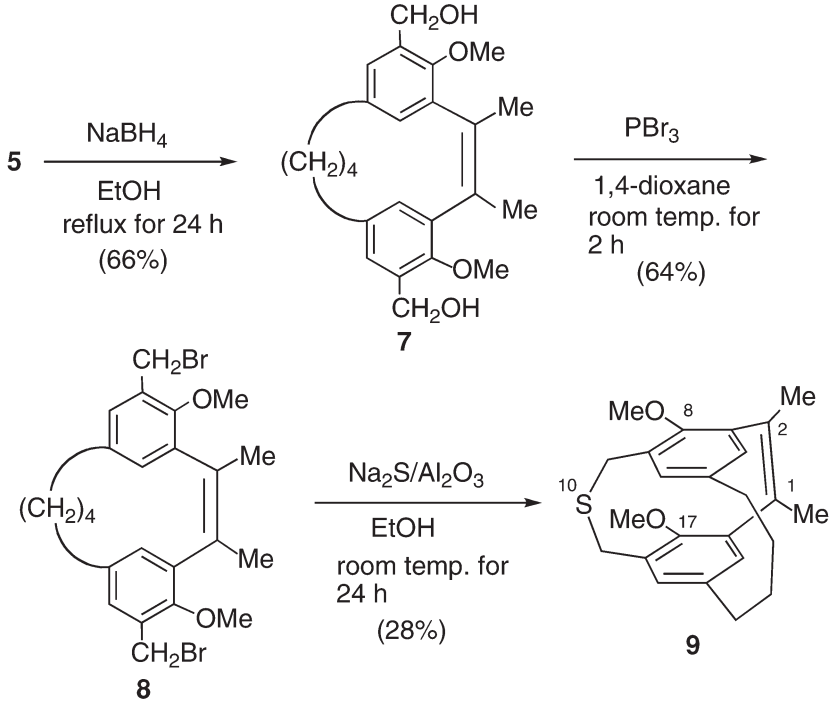
Fig. 2 Dynamic ^{1}H NMR spectrum of **3** at 300 MHz ($CDCl_3/CS_2$; 1:3).

(bromomethyl)-4,16-dimethoxy-1,2-dimethyl[2.4] MCP-1-ene **8** has been prepared in 64% yield by reduction of **5** with sodium borohydride in ethanol reflux followed by bromination of bis(hydroxymethyl) derivative **7** with PBr_3 in dioxane at room temperature for 2 h. The cyclisation of **8** has been carried out under the conditions of high dilution and in ethanolic Na_2S/Al_2O_3[24] to afford the corresponding 8,17-dimethoxy-1,2-dimethyl-10-thia[2.3.4](1,3,5)cyclophan-1-ene **9** in 28% yield.

The structure of **9** was elucidated based on its elemental analysis and spectral data. The mass spectral data for **9** (M^+ = 380) strongly supports the cyclic structure. The 300 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$ showed a doublet of the two protons of the aromatic rings at δ 6.66 and 7.18 ppm (J = 2.1 Hz). These observations strongly suggest that its structure corresponds exclusively to the *syn*-conformation. The



Scheme 2



Scheme 3

intra-annular proton H_i was observed at the slightly lower field (δ 7.18 ppm) than that of the corresponding *syn*-4,16-dimethoxy-1,2-dimethyl[2.4]MCP-1-ene **3** (δ 6.99 ppm) due to being in a deshielding region of the bridged double bond. The protons of the tetra-methylene bridge gave rise to a complicated signal pattern as expected for a rigid [2.4.3](1,3,5) cyclophan-1-ene **9**. The protons of the benzylic CH_2 group were observed as two multiplets centred at δ 3.46 and 4.13 ppm J = 13.2 Hz which were further split by coupling with the protons of the central CH_2 group. This central CH_2 group was also observed as two multiuplets centred at δ 1.56 and 2.50 ppm. The peak pattern ascribed to eight chemically distinct protons of the butano bridge proved the absence of a *syn–syn* interconversion which would exchange H_A and H_B of each CH_2 group. These findings suggest the rigid structure of [2.3.4](1,3,5)cyclophan-1-ene **9** at this temperature. In fact, the signals of the benzyl protons of **9** do not coalescence below 150°C in $CDBr_3$, and the energy barrier of flipping is above 25 kcal mol^{-1}. This result suggests that the introduction of one extra CH_2SCH_2 bridge into the flexible [2.4]MCP-1-ene **3** can completely inhibit the flexibility arising from the ring inversion.

Conclusions

We have demonstrated a convenient preparation of flexible *syn*-4,16-dimethoxy-1,2-dimethyl[2.4]MCP-1-ene **3** by McMurry reaction of 1,4-bis(3-acetyl-4-methoxy-phenyl)butane **2**. The conversion of **3** to the corresponding triple bridged 8,17-dimethoxy-1,2-dimethyl-10-thia[2.3.4](1,3,5)cyclophan-1-ene **9**, which adopts rigid *syn*-conformation. Further studies on the chemical properties of 8,17-dimethoxy-1,2-dimethyl-10-thia[2.3.4](1,3,5)cyclophan-1-ene **9** and conversion to the corresponding [2.2.4](1,3,5)cyclophan-1,9-diene **6** 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 Yanaco MT-5.

Preparation of 1,4-bis(4-methoxyphenyl)butane **1** *has been previously described.*[9]

1,4-Bis(3-acetyl-4-methoxyphenyl)butane (**2**): To a solution of 1,3-bis(4-methoxyphenyl)butane **1** (3.84 g, 15 mmol) and acetyl chloride (3.15 mL, 45 mmol) in methylene dichloride (60 mL) was added a solution of aluminum chloride (8.91 g, 67.5 mmol) in nitromethane (15 mL) at 0°C. After the reaction mixture had been stirred at room temperature for 3 h, it was poured into ice-water (100 mL). The organic layer was extracted with CH_2Cl_2 (50 mL × 2). The extract was

washed with water (50 mL × 2), dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with $CHCl_3$ as eluent to give crude **2b** as a colourless solid. Recrystallisation from hexane:benzene (1:1) gave 1,4-bis (3-acetyl-4-methoxyphenyl)butane (**2**) (4.42 g, 71%) as colourless prisms [from hexane:benzene (1:1)]; m.p. 74–76°C; ν_{max}(KBr)/cm^{-1} 1669 (C=O); δ_H ($CDCl_3$) 1.60 (4H, m, CH_2), 2.57 (4H, m, CH_2), 2.60 (6H, s, *Me*), 3.88 (6H, s, O*Me*), 6.87 (2H, d, *J* = 8.3, Ar*H*), 7.25 (2H, dd, *J* = 8.3, 2.4, ArH), and 7.52 (2H, d, *J* = 2.4, ArH); *m/z* 354 (M^+) (Found: C, 74.26; H, 7.18. $C_{22}H_{26}O_4$ (354.5) requires C, 74.55; H, 7.39%).

McMurry coupling reaction of **2:** The McMurry reagent was prepared from $TiCl_4$ [23.8 g (13.8 mL), 125 mmol] and 18 g (275 mmol) of Zn powder in 500 mL of dry THF, under nitrogen. A solution of **2** (3.06 g, 9 mmol) and pyridine (22.5 mL, 200 mmol) in dry THF (250 mL) was added within 60 h from two Hershberg funnels to the black mixture of the McMurry reagent by using a high-dilution technique[25–28] with continuous refluxing and stirring. The reaction mixture was refluxed for additional 8 h, cooled to room temperature, and hydrated with aqueous 10% K_2CO_3 (200 mL) at 0°C. The reaction mixture was extracted with CH_2Cl_2 (200 mL × 3). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with benzene as eluents to give crude **3** as a colourless solid. Recrystallisation from hexane gave syn-4,16-dimethoxy-1,2-dimethyl [2.4]metacyclophan-1-ene (syn-**3**) (2.0 g, 69%) as colourless prisms (from hexane); m.p. 160–161°C; ν_{max}(KBr)/cm^{-1} 2923, 1493, 1442, 1252, 1226, 1032, 805 and 797; δ_H ($CDCl_3$) (27°C) δ: 1.55 (4H, broad s, CH_2), 2.14 (6H, s, *Me*), 2.36 (4H, broad s, CH_2), 3.63 (6H, s, O*Me*), 6.41 (2 H, d, *J* = 8.3, Ar*H*), 6.59 (2H, dd, *J* = 2.4, 8.3, Ar*H*), and 6.90 (2 H, d, *J* = 2.4, Ar*H*). (–40°C, $CDCl_3/CS_2$ 1:3) δ: 1.1–1.4 (2H, broad s, CH_2), 1.72–1.92 (2H, broad s, CH_2), 2.17 (6H, s, *Me*), 2.1–2.3 (2H, broad s, CH_2), 2.4–2.6 (2H, broad s, CH_2), 3.67 (6H, s, O*Me*), 6.41 (2H, d, *J* = 8.3, Ar*H*), 6.64 (2 H, dd, *J* = 2.4, 8.3, Ar*H*), and 6.93 (2H, d, *J* = 2.4, Ar*H*); *m/z* 322 (M^+) (Found: C, 82.07; H, 8.15. $C_{22}H_{26}O_2$ (322.45) requires C, 81.95; H, 8.13%).

5,15-*Diformyl*-4,16-*dimethoxy*-1,2-*dimethyl*[2.4]*metacyclophan*-1-*ene* (**5**): $TiCl_4$ (0.21 mL, 27.3 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added to a solution of **3** (100 mg, 0.31 mmol) and Cl_2CHOCH_3 (0.366 mL, 4.1 mmol) in CH_2Cl_2 (8 mL). After the reaction mixture was stirred at room temperature for 1 h, it was poured into a large amount of ice-water (5 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako C–300, 200 g) with benzene as eluent to give **5** as a colourless solid. Recrystallisation from hexane gave 77 mg (66%) of **5** as colourless prisms, m.p. 130–131°C; ν_{max} (KBr)/ cm^{-1} 1683 (C=O); δ_H($CDCl_3$) 1.61 (4H, broad s, CH_2), 2.24 (6H, s, *Me*), 2.47 (4H, broad s, CH_2), 3.86 (6H, s, O*Me*), 7.20 (2H, d, *J* = 2.2 Hz, Ar*H*), 7.27 (2H, d, *J* = 2.2 Hz, Ar*H*) and 9.86 (2H, s, *CHO*); *m/z* 378 (M^+) (Found C, 75.92; H, 6.93. $C_{24}H_{26}O_4$ (378.47) requires C, 76.17; H, 6.92%).

Preparation of 5,15-*bis(hydroxymethyl)*-4,16-*dimethoxy*-1,2-*dimethyl*[2.4]*metacyclo-phan*-1-*ene* (**7**): Sodium borohydride (250 mg, 6.61 mmol) was added gradually to a solution of **5** (250 mg, 0.66 mmol) in methanol (15 mL) under gently refluxing. After the reaction mixture was stirred under reflux for 24 h, it was poured into a large amount of ice-water (10 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated to afford **7** (240 mg) as a colourless solid. Recrystallisation from a mixture of hexane:CH_2Cl_2 (1:5) gave 166 mg (66%) of **7** as colourless prisms, m.p. 139–140°C; ν_{max} (KBr)/ cm^{-1} 3335 (OH); δ_H($CDCl_3$) 1.56 (4H, broad s, CH_2), 2.21 (6H, s, *Me*), 2.36 (4H, broad s, CH_2), 2.62 (2H, s, *OH*), 3.76 (6H, s, O*Me*), 4.45 (4H, s, CH_2), 6.65 (2H, d, *J* = 2.2 Hz, Ar*H*) and 6.77 (2H, d, *J* = 2.2 Hz, Ar*H*); *m/z* 382 (M^+) (Found C, 75.32; H, 7.87. $C_{24}H_{30}O_4$ (382.5) requires C, 75.36; H, 7.91%).

5,15-*Bis(bromomethyl)*-4,16-*dimethoxy*-1,2-*dimethyl*[2.4] *metacyclo-phan*-1-*ene* (**8**): A solution of PBr_3 (0.1 mL, 1.06 mmol) in dioxane (2 mL) was added to a solution of **7** (50 mg, 0.131 mmol) in 1,4-dioxane (2 mL) at 0°C. After the reaction mixture was stirred at room temperature for 12 h, it was poured into aqueous 10% $Na_2S_2O_8$. The mixture was stirred at room temperature for 15 min and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated to afford **8** as a yellow solid. Recrystallisation from a mixture of hexane:CH_2Cl_2 (5:1) gave 43 mg (64%) of **8** as colourless prisms, m.p. 144–145°C; δ_H($CDCl_3$) 1.47 (4H, broad s, CH_2), 2.21 (6H, s, *Me*), 2.38 (4H, broad s, CH_2), 3.36 (6H, s, O*Me*), 4.38 (4H, s, CH_2), 6.71 (2H, d, *J* = 2.1 Hz, Ar*H*) and 6.86 (2H, d, *J* = 2.1 Hz, Ar*H*); *m/z* 506, 508, 510 (M^+) (Found C, 56.57; H, 5.67. $C_{24}H_{28}O_2Br_2$ (508.3) requires C, 56.71; H, 5.55%).

8,17-*Dimethoxy*-1,2-*dimethyl*-10-*thia*[2.3.4](1,3,5)*cyclophan*-1-*ene* (**9**): Lumpy reagent (Na_2S/Al_2O_3) (58.2 mg, 0.394 mmol) was added to a solution of **8** (50 mg, 0.0985 mmol) in ethanol (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 24 h, it was treated with celite by filtration. The filtrate was concentrated to afford a yellow solid. The residue was chromatographed over silica gel (Wako C–300, 100 g) with benzene as eluent to give **9** (42mg) as a colourless solid. Recrystallisation from a mixture of hexane:AcOEt (5:1) gave 11 mg (28%) of **9** as colourless prisms, m.p. 162–163°C; δ_H($CDCl_3$) 1.56 (4H, m, CH_2), 2.23 (6H, s, *Me*), 2.50 (4H, m, CH_2), 3.46 (2H, d, *J* = 13.2 Hz, CH_2), 3.81 (6H, s, O*Me*), 4.13 (2H, d, *J* = 13.2 Hz, CH_2), 6.66 (2H, d, *J* = 2.1 Hz, Ar*H*) and 7.18 (2H, d, *J* = 2.1 Hz, Ar*H*); *m/z* 380 (M^+) (Found C, 75.32; H,7.57. $C_{24}H_{28}O_2S$ (380.55) requires C, 75.75; H, 7.42%).

The estimation of the activation energy of the ring flipping

The rate constant (k_c) of the observed conformational interconversion at the coalescence (T_c) can be calculated by using Eqn (1). The free energy of activation ($\Delta G_c^{\neq}$) at coalescence can then be estimated by using Eyring equation [Eqn (2)].[29,30]

$$k_c = \pi\Delta\upsilon / 2^{1/2} \quad (1)$$

$$\Delta G_c^{\neq} = 2.303RT_c\,(10.32 + \log T_c - \log k_c) \quad (2)$$

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