Demethylation of 5,\textit{n}-di-\textit{tert}-butyl-8,\textit{n}-dimethoxy[2.\textit{n}]metacyclophane-1-yynes with BBr$_3$ to afford novel [\textit{n}]benzofuranophanes

Thamina Akther$^a$, Md. Monarul Islam$^{a,b}$, Taisuke Matsumoto$^c$, Junji Tanaka$^c$, Xing Feng$^d$, Carl Redshaw$^e$ and Takehiko Yamato$^{a,*}$

$^a$Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjomachi 1, Saga-shi, Saga 840-8502, Japan. Fax: (internat.) + 81(0)952/28-8548.
$^b$Chemical Research Division, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhanmondi, Dhaka-1205, Bangladesh
$^c$Institute of Material Chemistry and Engineering, Kyushu University, 6-1, Kasugakoen, Kasuga 816-8580, Japan
$^d$Beijing Institute of Graphic Communication, Beijing 102600, PR China
$^e$Department of Chemistry, The University of Hull, Cottingham Road, Hull, Yorkshire, HU6 7RX, UK

**Abstract:** Novel [\textit{n}]benzofuranophanes (\textit{n} = 8 & 10) 2a–b have been prepared by successive intramolecular cyclization from 5,19-di-\textit{tert}-butyl-8,22-dimethoxy[\textit{n}]metacyclophane-1-yne (syn-1a–b) by treatment with BBr$_3$ in CH$_2$Cl$_2$ at room temperature for 8 h. [2.\textit{n}]Benzofuranophanes 2a–b were also obtained by treatment of 1,2-di-\textit{endo}-bromo-5,19-di-\textit{tert}-butyl-8,22-dimethoxy[\textit{n}]metacyclophane (meso-3a–b) with BBr$_3$ in CH$_2$Cl$_2$ by using same reaction condition. $^1$H NMR spectra of 2a–b reveals the formation of intramolecular hydrogen bonding between hydroxyl proton with the oxygen of furan moiety and X-ray analysis shows that the length between H (OH) and O (furan) are 1.981 and 1.823 Å, respectively. The conformation of [8]benzofuranophane 2a in solution is rigid and restricted rotation around the diaryl linkage rather than [10]benzofuranophane 2b because of weak intramolecular hydrogen bonding and short length of cross-linking chain.

**Keywords:** [2.\textit{n}]metacyclophanes, demethylation, [\textit{n}]benzofuranophanes, intramolecular hydrogen bond.
**HIGHLIGHT**

- Novel hydroxy[n]benzofuranophanes have been synthesized by intramolecular cyclization.
- Intramolecular hydrogen bonding between hydroxyl proton and the oxygen of furan ring was observed.
- Weak intramolecular hydrogen bonding causes the rigid structures of [n]benzofuranophanes.
1. Introduction

Cyclophanes have been gathering much attention on physical and chemical properties due to their rigid structure with intriguing geometry [1–5]. To study the molecular functions based on the novel structures, several macrocyclic cyclophanes with strained acetylenic bonds have been synthesized by using the McMurry coupling as a key step [6–8]. The strained cyclophynes was synthesized as an intermediate by a trapping method [9–12]. \([n]\)MCP-diynes (MCP = metacyclophe) easily reacts with strong bases to achieve allenic and olefinic isomers which change the basic characteristics of cyclic diynes [13]. Fallis with his co-workers have reported the synthetic route of novel acetylenic cyclophanes by Pd- and Cu-mediated coupling reactions [14,15]. On the other hand, we have succeeded to prepare dimethoxy[2.\(n\)]MCP-1-ynes with bent triple bonds [16] by the bromination-dehydrobromination of the corresponding [2.\(n\)]MCP-1-enes [17–19]. These latter intermediates 1,2-dibromo-4,22-dimethoxy[2.10]MCPs can afford convenient starting materials for the preparation of 4b,9b-dihydro[10]benzofuro[3,2-\(b\)] benzofuranophane by double intramolecular cyclization in presence of \(\text{BBr}_3\) in \(\text{CH}_2\text{Cl}_2\) at room temperature [18].

Yamaguchi and co-workers released a series of fully ring-fused ladder \(\pi\)-conjugated skeletons by the double intramolecular cyclization of diaryl acetylenes [20–24]. A highly efficient and atom-economic construction of 2 substituted 5-hydroxybenzofurans featuring the dienone-phenol rearrangement reaction of quinols containing an alkyne moiety [25–27]. Recently, our group has illustrated an efficient synthetic route to achieve arene-based macrocyclic [3.3.1]MCPs containing a benzofuran ring. Treatment of [3.3.1]MCP-2,11-dione with TMSCl (trimethyl silyl chloride) can afford dihydrobenzofuran and benzofuran rings by simple intramolecular nucleophilic cyclization [28]. Due to the innate structural aspects, we anticipated that 5,\(n\)-di-tert-butyl-8,\(n\)-dimethoxy[2.\(n\)]MCP-1-ynes would provide a unique platform for the framework of unsymmetrical benzofuranophane and inspired us to attempt the synthesis of cyclophane containing benzofuran analogues. The mainly purpose of this research is present an efficient approach to synthesize unsymmetrical benzofuranophanes, furthermore, the relationship between structure with their properties have been investigated details.
2. Experimental

2.1. General procedures

All reagents used were procured from commercial sources and were used without further purification. All the solvents used were dried and distilled by the usual procedures before use. $^1$H and $^{13}$C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and Varian-400MR-vnmrs400 and referenced to 7.26 and 77.0 ppm, respectively for chloroform-D solvent with SiMe$_4$ as an internal reference: J-values are given in Hz. Infrared (IR) spectra were obtained on a Nippon Denshi JIR-AQ2OM spectrophotometer as KBr disks. 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. All melting points (Yanagimoto MP-S1) are uncorrected. Silica gel columns were prepared by use of Merk silica gel 60 (63-200 μm).

2.2. Materials

The starting materials 5,19-di-tert-butyl-8,22-dimethoxy[2.8]MCP-1-yne (syn-1a) and 5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP-1-yne (syn-1b) were synthesized by dehydrobromination reaction in presence of HOBu$_t$ as published report [17,30]. anti-15,16-di-endo-bromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP (dl-5a) and syn-15,16-di-endo-bromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP (meso-3a) were prepared according to the literatures [17,30]. 1,2-di-endo-bromo- (meso-3b) and 1-endo,2-exo-dibromo-5,21-di-tert-butyl-8,24-dimethoxy[2.10] MCP (dl-5b) were processed according to the reported procedure [17,30,31].

2.3. Synthesis of 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[8](7,3′)benzofuranophane (2a)

To a solution of 5,19-di-tert-butyl-8,22-dimethoxy[2.8]MCP-1-yne (syn-1a) (60 mg, 0.13 mmol) in CH$_2$Cl$_2$ (6 mL) at 0 °C was gradually added a solution of BBr$_3$ (0.14 mL, 1.32 mmol) in CH$_2$Cl$_2$ (0.1 mL). After the reaction mixture has been stirred at room temperature for 8 h, it was poured into ice-water (10 mL), extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined extracts were washed with water (3 × 10 mL), dried over MgSO$_4$ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-
chloroform (3:1) as eluent to give the crude compound 2a as a colorless solid. Recrystallization from hexane gave 5-\textit{tert}-butyl-1-\{(5-\textit{tert}-butyl-2′-hydroxyphenyl)\} [8](7,3′)benzofuranophane 2a (35 mg, 73 %) as colorless prisms, M.p. 173–174 °C. IR (KBr): ν  = 3427 (OH), 2959, 2856, 1476, 1362, 1203 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ: 1.17–1.77 (12 H, m, CH₂), 1.31 (9 H, s, tBu), 1.37 (9 H, s, tBu), 2.80–2.86 (2H, m, CH₂), 2.89–2.96 (2H, m, CH₂), 6.91 (1H, s, furan–H), 7.11 (1H, d, J = 2.4 Hz, Ar–H), 7.12 (1H, d, J = 2.4 Hz, Ar–H), 7.18 (1H, s, J = 2.4 Hz, OH, exchanged by D₂O), 7.22 (1H, d, J = 2.4 Hz, Ar–H), 7.44 (1H, d, J = 2.4 Hz, Ar–H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 28.15 (CH₂), 29.17 (CH₂), 29.70 (CH₂), 29.80 (CH₂), 29.93 (CH₂), 30.06 (CH₂), 30.28 (CH₂), 31.51 (C(CH₃)_3), 31.91 (C(CH₃)_3), 34.04 (CH₂), 34.77 (CH₂), 102.01 (ArC), 115.02 (ArC), 116.00 (ArC), 122.68 (ArC), 123.29 (ArC), 125.70 (ArC), 127.98 (ArC), 128.67 (ArC), 131.77 (ArC), 142.93 (ArC), 146.89 (ArC), 150.78 (ArC), 151.33 (ArC), 155.32 (ArC) ppm. EI-MS: m/z 432 [M⁺]. C₃₀H₄₀O₂ (432.65): calcd. C 83.28, H 9.32. Found: C 83.72, H 8.32.

2.4. Synthesis of 5-\textit{tert}-butyl-1-\{(5-\textit{tert}-butyl-2′-hydroxyphenyl)\}[10](7,3′)benzofuranophane (2b)

To a solution of 5,21-di-\textit{tert}-butyl-8,24-dimethoxy[2.10]MCP-1-yne (syn-1b) (60 mg, 0.12 mmoL) in CH₂Cl₂ (6 mL) at 0 °C was gradually added a solution of BBr₃ (0.12 mL, 1.23 mmoL) in CH₂Cl₂ (0.10 mL). After the reaction mixture has been stirred at room temperature for 0.5 h, it was poured into ice-water (10 mL), extracted with CH₂Cl₂ (3 × 10 mL). The combined extracts were washed with water (2 × 10 mL), dried over MgSO₄ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-chloroform (2:1) as eluent to give the crude compound 2b as a colorless solid. Recrystallization from ethanol gave 5-\textit{tert}-butyl-1-\{(5-\textit{tert}-butyl-2′-hydroxyphenyl)\}[10](7,3′)benzofuranophane 2b (44 mg, 79 %) as colorless prisms, M.p. 127–128 °C. IR (KBr): ν  = 3529, 3514 (OH), 2955, 2933, 2857, 1481, 1459, 1365, 1261, 1232 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ: 1.21–1.48 (12 H, m, CH₂), 1.33 (9 H, s, tBu), 1.38 (9 H, s, tBu), 1.68–1.74 (2H, m, CH₂), 1.78–1.88 (2H, m, CH₂), 2.74–2.77 (2H, m, CH₂), 2.84–2.89 (2H, m, CH₂), 6.91 (1H, s, furan–H), 7.14 (1H, d, J = 2.4 Hz, Ar–H), 7.16 (1H, d, J = 2.4 Hz, Ar–H), 7.34 (1H, d, J = 2.4 Hz, Ar–H), 7.44 (1H, d, J = 2.4 Hz, Ar–H), 7.67 (1H, s, OH, exchanged by D₂O) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 26.61 (CH₂), 27.57 (CH₂), 27.95 (CH₂), 28.52 (CH₂), 28.77 (CH₂), 28.96 (CH₂), 29.16 (CH₂), 29.32 (CH₂),
29.90 (CH$_2$), 31.26 (CH$_2$), 31.51(C(CH$_3$)$_3$), 31.89(C(CH$_3$)$_3$), 34.06 (CH$_2$), 34.74 (CH$_2$), 102.54 (ArC), 114.87 (ArC), 115.04 (ArC), 121.75 (ArC), 122.91 (ArC), 125.57 (ArC), 127.95 (ArC), 129.09 (ArC), 130.99 (ArC), 142.78 (ArC), 146.89 (ArC), 150.10 (ArC), 151.15 (ArC), 155.72 (ArC) ppm. EI-MS: $m/z$ 460 [M$^+$]. C$_{32}$H$_{44}$O$_2$ (460.70): calcd. C 83.43, H 9.63. Found: C 83.36, H 9.63.

2.5. Synthesis of 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[8](7,3′)benzofuranophane (2a)

To a solution of syn-15,16-di-endobromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP (meso-3a) (80 mg, 0.13 mmol) in CH$_2$Cl$_2$ (8 mL) at 0 °C was gradually added a solution of BBr$_3$ (0.12 mL, 1.29 mmol) in CH$_2$Cl$_2$ (0.2 mL). After the reaction mixture has been stirred at room temperature for 8 h, it was poured into ice-water (10 mL), extracted with CH$_2$Cl$_2$ (3 $\times$ 10 mL). The combined extracts were washed with water (3 $\times$ 10 mL), dried over MgSO$_4$ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-chloroform (3:1) as eluent to give crude compound 2a as a colorless solid. Recrystallization from hexane gave 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[10] (7,3′)benzofuranophane 2a (35 mg, 73 %) as colorless prisms.

Similary, compound dl-5a was treated with BBr$_3$ in CH$_2$Cl$_2$ at room temperature for 8 h to afford 2a in 73 % yield as colorless prisms.

2.6. Synthesis of 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[10](7,3′)benzofuranophane (2b)

To a solution of 1,2-di-endobromo-5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP (meso-3b) (60 mg, 0.09 mmol) in CH$_2$Cl$_2$ (6 mL) at 0 °C was gradually added a solution of BBr$_3$ (0.09 mL, 0.92 mmol) in CH$_2$Cl$_2$ (0.1 mL). After the reaction mixture has been stirred at room temperature for 0.5 h, it was poured into ice-water (10 mL), extracted with CH$_2$Cl$_2$ (3 $\times$ 10 mL). The combined extracts were washed with water (2 $\times$ 10 mL), dried over MgSO$_4$ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-chloroform (4:1) as eluent to give crude compound 2b as a colorless solid. Recrystallization from ethanol gave 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[10] (7,3′)benzofuranophane 2b (35 mg, 83 %) as colorless prisms.
Similarly, compound 1-endo,2-exo-dibromo-5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP (dl-5b) was treated with BBr₃ in CH₂Cl₂ at room temperature for 0.5 h to afford 2b in 87% yield as colorless prisms.

2.7. Synthesis of 5-tert-butyl-1-(5′-tert-butyl-2′-methoxyphenyl)[10](7,3′)benzofuranophane (6b)

A mixture of 5-tert-butyl-1-(5′-tert-butyl-2′-hydroxyphenyl)[10](7,3′)benzofuranophane 2b (40 mg, 0.09 mmol) and NaH (29 mg, 1.22 mmol, 60%) in dry tetrahydrofuran (4 mL) was heated at reflux for 1 h under N₂. Then methyl iodide (0.05 mL, 0.87 mmol) was added and the mixture heated at reflux for an additional 3 h. After cooling the reaction mixture to room temperature, it was poured into ice-water (10 mL), extracted with CH₂Cl₂ (3 × 10 mL). The combined extracts were washed with water (2 × 10 mL), dried over MgSO₄ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane as eluent to give 5-tert-butyl-1-(5′-tert-butyl-2′-methoxyphenyl)[10](7,3′)benzofuranophane 6b (26 mg, 64%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 1.18–1.39 (12 H, m, CH₂), 1.33 (9 H, s, tBu), 1.39 (9 H, s, tBu), 1.44–1.60 (2H, m, CH₂), 1.68–1.85 (2H, m, CH₂), 2.01–2.17 (1H, m, CH₂), 2.37–2.49 (1H, m, CH₂), 2.67–2.83 (1H, m, CH₂), 2.86–3.07 (1H, m, CH₂), 3.42 (3H, s, OCH₃), 6.82 (1H, s, furan‒H), 7.12 (1H, d, J = 2.4 Hz, Ar‒H), 7.20 (1H, d, J = 2.4 Hz, Ar‒H), 7.31 (1H, d, J = 2.4 Hz, Ar‒H), 7.44 (1H, d, J = 2.4 Hz, Ar‒H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 26.68 (CH₂), 27.25 (CH₂), 27.88 (CH₂), 28.05 (CH₂), 28.10 (CH₂), 28.71 (CH₂), 28.84 (CH₂), 29.20 (CH₂), 30.74 (CH₂), 31.47 (CH₂), 31.79 (C(CH₃)₃), 31.95 (C(CH₃)₃), 34.24 (CH₂), 34.67 (CH₂), 59.67 (CH₂), 103.02 (ArC), 114.39 (ArC), 122.19 (ArC), 122.81 (ArC), 125.23(ArC), 126.25 (ArC), 128.15 (ArC), 128.45 (ArC), 135.86 (ArC), 145.62 (ArC), 145.80 (ArC), 152.35 (ArC), 154.97 (ArC), 155.71 (ArC) ppm. EI-MS: m/z 474 [M⁺]. C₃₃H₄₆O₂ (474.72): calcd. C 83.49, H 9.77. Found: C 83.37, H 9.61.

2.8. Synthesis of 3,8-Di-tert-butyl-1,6-dimethyl-cis-4b,9b-dihydrobenzofuro[3,2-b]benzofuran (8)

To a solution of (E)-1,2-bis(5-tert-butyl-2-methoxy-3-methylphenyl)ethane 7 (60 mg, 0.09 mmol) in CH₂Cl₂ (6 mL) at 0 °C was gradually added a solution of BBr₃ (0.09 mL, 0.92 mmol) in CH₂Cl₂ (0.1 mL). After the reaction mixture has been stirred at room temperature for 5 h, it
was poured into ice-water (10 mL), extracted with CH$_2$Cl$_2$ (3 $\times$ 10 mL). The combined extracts were washed with water (3 $\times$ 10 mL), dried over MgSO$_4$ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-CHCl$_3$ (4:1) as eluent to give crude 8 (80 %) as a colorless solid. 3,8-di-tert-butyl-1,6-dimethylcis-4b,9b-dihydrobenzofuro[3,2-b]benzofuran 8 was obtained as colorless prisms (hexane), M.p. 184–185 °C. IR (KBr): $\nu$ = 2944, 1616, 1487, 1362, 1181 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.31 (18 H, s, tBu $\times$ 2), 2.21 (6 H, s, CH$_3$), 6.23 (2 H, s, furan$-H$), 7.12 (1 H, d, $J$ = 2.4 Hz, Ar$-H$), 7.40 (1 H, d, $J$ = 2.4 Hz, Ar$-H$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 15.67 (C(CH$_3$)$_3$), 31.73 (C(CH$_3$)$_3$), 34.32 (CH$_2$), 87.13 (ArCO), 119.96 (ArC), 120.44 (ArC), 123.64 (ArC), 129.54 (ArC), 144.10 (ArC), 156.55 (ArC) ppm. EI-MS: $m/z$ 350 [M$^+$]. C$_{24}$H$_{30}$O$_2$ (350.51): calcd. C 82.24, H 8.63. Found: C 82.03, H 8.63.

2.9. Synthesis of 2-(5-tert-butyl-7-methylbenzofuran-2-yl)-4-tert-butyl-6-methylphenol (9)

To a solution of (E)-1,2-bis(5-tert-butyl-2-methoxy-3-methylphenyl)ethane 7 (60 mg, 0.09 mmol) in CH$_2$Cl$_2$ (6 mL) at 0 °C was gradually added a solution of BBr$_3$ (0.09 mL, 0.92 mmol) in CH$_2$Cl$_2$ (0.1 mL). After the reaction mixture has been stirred at room temperature for 5 h, it was poured into ice-water (10 mL), extracted with CH$_2$Cl$_2$ (3 $\times$ 10 mL). The combined extracts were washed with water (2 $\times$ 10 mL), dried over MgSO$_4$ and then concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane-CHCl$_3$ (1:4) as eluent to give crude 9 (10 %) as a colorless solid. 2-(5-tert-butyl-7-methylbenzofuran-2-yl)-4-tert-butyl-6-methylphenol 9 was obtained as colorless prisms (hexane), M.p. 143–145 °C. IR (KBr): $\nu$ = 3425 (OH), 2956, 2853, 1452, 1280 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.34 (9 H, s, tBu), 1.38 (9 H, s, tBu), 2.21 (3 H, s, CH$_3$), 2.55 (3 H, s, CH$_3$), 6.98 (1 H, s, furan$-H$), 7.12 (1 H, d, $J$ = 2.4 Hz, Ar$-H$), 7.16 (1 H, d, $J$ = 2.4 Hz, Ar$-H$), 7.43 (1 H, d, $J$ = 2.4 Hz, Ar$-H$), 7.46 (1 H, d, $J$ = 2.4 Hz, Ar$-H$), 7.79 (1 H, s, OH, exchanged by D$_2$O) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.37 (CH$_3$), 14.89 (CH$_3$), 15.41 (CH$_2$), 28.68 (CH$_2$), 30.79 (C(CH$_3$)$_3$), 33.50 (C(CH$_3$)$_3$), 101.98 (ArC), 113.64 (ArC), 118.93 (ArC), 119.21 (ArC), 120.03 (ArC), 122.36 (ArC), 124.50 (ArC), 126.91 (ArC), 128.51 (ArC), 141.80 (ArC), 142.82 (ArC), 145.75 (ArC), 148.69 (ArC), 155.58 (ArC). EI-MS: $m/z$ 352 [M$^+$]. C$_{29}$H$_{32}$O$_2$ (352.52): calcd. C 82.24, H 8.63. Found: C 82.03, H 8.63.
3. Results and Discussion

According to our previous reported, the starting compound 5,19-di-tert-butyl-8,22-dimethoxy[2.8]MCP-1-yne (syn-1a) was synthesized by dehydrobromination reaction of syn-15,16-di-endo-bromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP in presence of HOBu’ at 80 °C for 12 h, 48 % yield [17,30]. Subsequently, demethylation reaction of syn-1a with BBr₃, a commercially available, excellent demethylating or dealkylating agent for the cleavage of ethers also with subsequent cyclization, in CH₂Cl₂ solution at room temperature for 8 h (Scheme 1) afford the expected [8]benzofuranophane 2a in 67 % yield. So this example inspired us to further investigate the effect of the increase of carbon chain in MCP skeleton structure for BBr₃-induced cyclization reaction. The length of the cross-linking chain can be increased up to a certain level to form benzofuranophane. Therefore, [2.10]MCP is treated with BBr₃ for synthesis of benzofuranophane.

At higher temperature and prolonged reaction time 17,18-di-endo-bromo-13,21-di-tert-butyl-16,24-dimethoxy[2.10]MCP was treated with potassium tert-butoxide in refluxing HOBu’ at 80 °C for 3 h and synthesized 5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP-1-yne (syn-1b) in 93 % yield, along with 7 % monodehydrobrominated product as reported procedure [17,30]. Bromination of syn-1b with BBr₃ carried out in a CH₂Cl₂ solution at room temperature for 0.5 h generates [10]benzofuranophane 2b in 79 % yield. In this case, the reaction occurred within a very short time (3 h) than that of syn-1a.

Insert Scheme 1 in here

The structure of 2a was characterized by ¹H and ¹³C-NMR, mass spectra and elemental analysis, as well as single crystal X-ray diffraction. The ¹H-NMR spectrum of 2a (300 MHz, CDCl₃) shows five aromatic protons are observed as a singlet at δ 6.91 ppm and doublets at δ 7.11, 7.13, 7.23, 7.45 ppm, respectively, which are clearly associated with the unsymmetrical structure of 2a. The ¹H-NMR (300 MHz, CDCl₃) spectrum also exhibits the signal for one hydroxyl group in the lower magnetic field δ 7.18 ppm, which is exchanged by D₂O. This data is consistent with the existence of intramolecular hydrogen bonding between the hydroxyl group.
and the oxygen of the benzofuran ring. A peak for O–H band was observed at 3527 cm\(^{-1}\) in the IR spectrum. On the basis of the spectral data and the chemical conversion, compound 2a is assigned to the structure, 5-tert-butyl-1-(5’-tert-butyl-2’-hydroxyphenyl)[8](7,3’) benzofuranophane.

The \(^1\)H-NMR (300 MHz, CDCl\(_3\)) spectrum exhibits the signal for one hydroxyl group in the lower magnetic field \(\delta \) 7.67 ppm, which is exchanged by D\(_2\)O strongly suggested the highly formation of an intramolecular hydrogen bond. The IR spectrum of 2b also shows the absorption of the hydroxyl stretching vibration around 3511 cm\(^{-1}\). On the basis of the spectral data and the chemical analysis, compound 2b is assigned to the structure, 5-tert-butyl-1-(5’-tert-butyl-2’-hydroxyphenyl)[10](7,3’) benzofuranophane.

Despite the fact that the detailed reaction mechanism of generation of [n]benzofuranophane from 5,n-di-tert-butyl-8,n-dimethoxy[2,n]MCP-1-ynes is not clear at this time, it can be considered to have progressed as follows in Scheme 2. The mechanism of BBr\(_3\) reaction of starting material syn apparently proceeds via the formation of a complex A followed by elimination of an alkyl bromide. A can undergo hydrolysis to give a hydroxyl group based product B from which the electrophilic attack to the triple bond to initiate the cation intermediate C provided final compound [n]benzofuranophane by dehydrobromination. In this reaction, BBr\(_3\) as excellent demethylating or dealkylating agent, play a significant role to activate the cyclization reaction. The detailed mechanism of the BBr\(_3\)-induced cyclization reaction will discuss in below.

Insert Scheme 2 in here

Bromination of anti- and syn-5,10-di-tert-butyl-8,22-dimethoxy[2.8]MCP-1-ene with 1.1 equiv. of benzyltrimethylammonium tribromide (BTMABr\(_3\)), which was found to be a convenient solid brominating agent [29], in CH\(_2\)Cl\(_2\) solution at room temperature for 1 h and 2 h led to the trans and cis adduct anti-15,16-di-endo-bromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP (dl-5a) and syn-15,16-di-endo-bromo-11,19-di-tert-butyl-14,22-dimethoxy[2.8]MCP (meso-3a), respectively following previous report [17,30]. Both meso-3a and dl- 5a react with
BBR₃ in CH₂Cl₂ as former reaction conditions (Scheme 3) to afford compound 2a. Extension of reaction time to 8 h will give more percentage of the product.

Similarly, 1,2-di-endo-bromo- (meso-3b) and 1-endo,2-exo-dibromo-5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP (dl-5b) were prepared by bromination of (Z)- and (E)-5,2-di-tert-butyl-8,24-dimethoxy-[2.10]MCP-1-ene with 1.1 equiv. of BTMABr₃ in CH₂Cl₂ at room temperature for 5 min in 54 and 88 % yields, respectively, according to the reported procedure [17,30,31]. Under different conditions for demethylation of meso-3b to afford meso-4b with trimethylsilyl iodide in acetonitrile solution [32–34] was not succeeded. Only an awkward mixture of products was obtained. Interestingly, treatment of meso-3b with BBr₃ in CH₂Cl₂ at room temperature for 0.5 h divergent outcomes were procured.

However, the formation of the corresponding demethylation product, 1,2-di-endo-bromo-8,24-dihydroxy[2.10]MCP (meso-4b) was not observed during the reaction. Similar reaction to afford [10]benzofuranophane 2b was resulted in the treatment of dl-5b with BBr₃ in CH₂Cl₂ under the same conditions described above in 87 % yield (Scheme 3).

Insert Scheme 3 in here

The mechanism of formation of [n]benzofuranophane from meso compounds in presence of BBr₃ is based on speculation as shown in Scheme 4. The present BBr₃ induced conversion from 1,2-di-endo-bromo-5,n-di-tert-butyl-8,n-dimethoxy[2.n]MCP to desired [n]benzofuranophane possibly raised by demethylation of methoxy groups to provide the corresponding phenol derivatives meso-4a, b followed by the nucleophilic substitution at the C₂ carbon to afford five membered dihydrofuran skeleton (D) from which the final product [n]benzofuranophane was formed by dehydrobromination reaction.

Insert Scheme 4 in here

Intramolecular hydrogen bonding in compound 2 has been investigated in solution by NMR as a major tool. The evidence of hydrogen bonding can be provided by ¹H and heteronuclear chemical shifts, coupling constants, solvent and deuterium isotope effects on chemical shifts. The use of hydroxyl protons in hydrogen bonding and conformational NMR studies in solution,
displays experimental challenges because of rapid chemical exchange between hydroxyl groups and protic solvents. Proton exchange rates in alcohol –OH groups can be weakened by dissolving in DMSO-\textit{d}_6 or acetone-\textit{d}_6 or by using organic co-solvents and thus, have already been promoted in structural analysis of benzofuranophane. For compound 2a, in DMSO-\textit{d}_6 a very sharp peak for hydroxyl group observed at $\delta$ 8.71 ppm. In acetone-\textit{d}_6 the hydroxyl peak shifted to lower frequency at $\delta$ 7.97 ppm. In CDCl$_3$, the signal, this is further shifted to lowest frequency at $\delta$ 7.18 ppm. For compound 2b, in DMSO-\textit{d}_6 a very sharp peak for hydroxyl group observed at $\delta$ 8.35 ppm. In acetone-\textit{d}_6 the hydroxyl peak shifted to lower frequency at $\delta$ 7.91 ppm. In CDCl$_3$ the peak shifted to lowest frequency at $\delta$ 7.67 ppm. The phenolic hydroxyl proton form intramolecular hydrogen bond with the oxygen in benzofuran unit. The $^1$H NMR of 2a–b (400 MHz) in DMSO-\textit{d}_6 and acetone-\textit{d}_6 lead to shift the hydroxyl peak at low field region indicating that the intramolecular hydrogen bonding is disrupted in polar solvent and the formation of intermolecular hydrogen bonding with solvent (SI Fig. S4-1 & S4-2). For compound 2a OH peak shifted to lower field than that of compound 2b. This is because of the shorter number of carbon chain length, which causes more steric hindrance into the cyclophane system.

The suitable crystals 2a and 2b for single crystal X-ray analysis were cultivated from a hexane-chloroform ($V_{hexane} : V_{Chloroform} = 1:1$) by slow evaporation process at room temperature. Compound 2a crystallizes in the orthorhombic crystal system with space group Pbca, whereas compound 2b in the monoclinic crystal system with space group Cc. The key crystallographic data are summarized in Table 1 and each crystal structure 2a and 2b are shown in Figure 1.

**Insert Table 1 in here**

The X-ray structure of novel [8]benzofuranophane 2a and [10]benzofuranophane 2b were displayed in Figure 1. In 2a, the benzofuran ring is not co-planer with phenyl ring with a torsion angle of 34.2$^\circ$, the hydroxyl (OH) at the 2-position of benzene has formed an intramolecular hydrogen bonding with the adjacent oxygen atom (O2), and the distance of O2-H2…O1 is 1.98 Å. Similarly, in compound 2b with 10 carbon line alkyl, the torsion angle (23.5$^\circ$) is less than 2a between benzofuran ring and phenyl ring, which indicated the length of alkyl would affect the molecular conformation; for example, hydroxyl (OH) in 2a is strongly affected by steric effects of the neighbor carbon line alkyl, however, the compound 2b with longer line alkyl would
release the strain. Indeed, as our speculation, some methylene groups are involved in a strong intermolecular interaction and disorder with occupancy ratio 0.5:0.5 for C23, C24 and C25 in X-ray structure, respectively. However, no disordered structure was observed in compound 2b. Also the bond angle of O2–H2–O1 for 2b (148.42°) and 2a (134.98°) clearly demonstrated that the strong intramolecular hydrogen bonding occurs in 2b rather than 2a.

**Insert Figure 1 in here**

In case of compound 2b the present conformational rigidity might be attributed to the strong intramolecular hydrogen bond among the hydroxyl group and the oxygen atom on the benzofuran ring which strongly reduce the conformational ring flipping. The hydrogen bond O2-H2...O1 was 1.82 Å, which is a reasonable distance for intramolecular hydrogen bonding.

In addition, the intramolecular hydrogen bonds were further confirmed by the temperature-dependent NMR. The conformation of this compound in solution is rigid and the signals of the benzylic methylene protons do not coalesce below 150 °C in DMSO. This finding strongly suggest the restricted rotation around the diaryl linkage of [10]benzofuranophane 2b. Both 1H NMR and X-ray results strongly suggest that compound 2b have stronger intramolecular hydrogen bonding in comparison with compound 2a.

To gain a deep insight into the synergistic effect of the steric effects and intramolecular hydrogen bonding for molecular conformation in benzofuranophane derivatives, the hydroxyl group in 2b was replaced by a methyl group as follows Scheme 5. After that compound 2b was treated with methyl iodide in the presence of NaH in anhydrous THF solution at room temperature for 3 h, the corresponding methoxy derivative 6b was obtained in 64 % yield. The hydroxyl group of compound 2b is converted into the larger methoxy group. The 1H-NMR peak of OH disappears from the spectrum and conducts internal methoxy proton as a singlet at δ 3.41 ppm and H proton of benzofuran ring as a singlet at δ 6.91 ppm (relative intensity 3:1).

**Insert Scheme 5 in here**

In fact, 1,2-dibromo-1,2-bis(5-tert-butyl-2-methoxy-3-methylphenyl)ethane 7 as reference compound, was treated with BBr₃ in CH₂Cl₂ under the same conditions as those in meso-3b, but
only the recovery of the starting compound resulted (Scheme 6). When the reaction time was extended to 5 h instead of 0.5 h, resulted the corresponding 2-(2-hydroxyphenyl)benzofuran 9 in 10 % yield along with the further cyclisation product, cis-4b,9b-dihydrobenzofuro[3,2-b] benzofuran 8 in 80 % yield [35–37]. Prolonged the reaction time to 24 h resulted in the exclusive formation of the compound 8. These results strongly support the reaction mechanism for the formation of the benzofuran skeleton as described above.

**Insert Scheme 6 in here**

The much faster reaction was observed in meso-3b than that of 7 under the same reaction conditions for treatment of BBr₃ in CH₂Cl₂ at room temperature. The enhanced reactivity towards the nucleophilic attack of phenolic oxygen in the C₂ carbon may be attributable to the cyclophane structure of meso-5b in which the reaction site can be sterically much closer than that in compound 7.

**Insert Scheme 7 in here**

Second cyclization of 9 to 8 might be attributable to the conformational flexibility of 9 around the diaryl linkage of 2-arylbenzofuran. However, in the case of [n]benzofuranophane, formation of compound 10 was not observed by prolonging the reaction time (Scheme 7). The rotation around the diaryl linkage to form conformer E might be restricted due to its cyclophane structure containing sterically hindered tertiary butyl group.

**Conclusions**

We have denoted an expedient preparation procedure of novel [8]benzofuranophane 2a and [10]benzofuranophane 2b by treatment of 5,19-di-tert-butyl-8,22-dimethoxy[2.8]MCP-1-yne (syn-1a) and 5,21-di-tert-butyl-8,24-dimethoxy[2.10]MCP-1-yne (syn-1b) with BBr₃ in CH₂Cl₂ at room temperature, respectively by intramolecular cyclization reaction. Enthrallingly, meso-3a, dl-5a, meso-3a and dl-5b under the same reaction conditions with BBr₃ in CH₂Cl₂ rendered
compound 2a and 2b in good yield. Further studies on the synthesis, reactions and chemical properties of different [n]benzofuranophanes are now in progress will be reported in due time.

Acknowledgments

This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University)”. We would like to thank the OTEC at Saga University for financial support.

References


Highlights

♦ Novel hydroxy\([n]\)benzofuranophanes have been synthesized by intramolecular cyclization.
♦ Intramolecular hydrogen bonding between hydroxyl proton and the oxygen of furan ring was observed.
♦ Weak intramolecular hydrogen bonding causes the rigid structures of \([n]\)benzofuranophanes.
Fig. 1 X-ray structures for 2a and 2b.
Scheme 1

\[
\text{syn-1a; } n = 8 \\
\text{b; } n = 10 \\
\]

\[
\text{BBr}_3 \text{ in CH}_2\text{Cl}_2 \text{, room temp.} \\
\]

\[
2\text{a; } n = 8 \quad (67 \%) \\
2\text{b; } n = 10 \quad (79 \%) \\
\]

Scheme 2

\[
syn-1\text{a, b} \quad \text{BBR}_3 \quad -\text{MeBr} \\
\]

\[
\text{A} \quad \text{H}_2\text{O} \\
\]

\[
\text{B} \quad \text{C} \\
\]

\[
\text{2a, b} \quad -\text{H}^+ \\
\]

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Scheme 3

Scheme 3 shows the conversion of meso-3a; n = 8 to meso-4a; n = 8, 2a; n = 8 (73 %) and 2b; n = 10 (83 %) via BBr₃ in CH₂Cl₂ at room temperature.

Another conversion is shown from dl-5a; n = 8 to 2a; n = 8 (76 %) and 2b; n = 10 (87 %) via BBr₃ in CH₂Cl₂ at room temperature.
Scheme 4

\[ \text{meso-3a, b} \xrightarrow{\text{BBr}_3, \text{MeBr}} \text{2a, b} \]

\[ \text{H}_2\text{O} \xrightarrow{\text{Sn2}} \text{D} \]

\[ \text{meso-4a, b} \]

Scheme 5

\[ \text{2b} \xrightarrow{\text{NaH, Mel in CH}_2\text{Cl}_2, \text{room temp., 3 h (80 %)}} \text{6b} \]
Scheme 6

\[
\begin{align*}
\begin{array}{c}
\text{Me} \\
\text{OMe} \\
\text{Br} \\
\text{Me} \\
\text{tBu}
\end{array}
\end{align*}
\xrightarrow{\text{BBr}_3 \text{ in CH}_2\text{Cl}_2} \\
\text{room temp.} \\
5 \text{ h}
\]

7

\[
\begin{align*}
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{tBu}
\end{array}
\end{align*}
\]

8 (80 %)

\[
\begin{align*}
\begin{array}{c}
\text{Me} \\
\text{tBu}
\end{array}
\end{align*}
\]

9 (10 %)

Scheme 7

\[
\begin{align*}
\begin{array}{c}
\text{tBu}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{tBu}
\end{array}
\end{align*}
\]

E

\[
\begin{align*}
\begin{array}{c}
\text{tBu}
\end{array}
\end{align*}
\]

10
Demethylation of \(5,n\)-di-\(\text{tert}\)-butyl-8,\(n\)-dimethoxy[2,\(n\)] metacyclophane-1-ynes with BBr\(_3\) to afford novel \([n]\)benzofuranophanes

Thamina Akther\(^a\), Md. Monarul Islam\(^b\), Taisuke Matsumoto\(^c\), Junji Tanaka\(^c\), Xing Feng\(^d\), Carl Redshaw\(^e\) and Takehiko Yamato\(^{a,}\*\)

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
<table>
<thead>
<tr>
<th>Complex</th>
<th>2a</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{30}$ H$</em>{40}$ O$_{2}$</td>
<td>C$<em>{32}$ H$</em>{44}$ O$_{2}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>432.64</td>
<td>460.67</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbc$\alpha$</td>
<td>Cc</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>28.1308(5)</td>
<td>14.6104(12)</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>18.0592(3)</td>
<td>21.5562(19)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>9.95585(18)</td>
<td>9.0564(4)</td>
</tr>
<tr>
<td>$\alpha$ [$^\circ$]</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\beta$ [$^\circ$]</td>
<td>--</td>
<td>100.897(4)</td>
</tr>
<tr>
<td>$\gamma$ [$^\circ$]</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Volume [Å$^3$]</td>
<td>5057.77(16)</td>
<td>2800.8(4)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Dcalcd [Mg/m$^3$]</td>
<td>1.136</td>
<td>1.092</td>
</tr>
<tr>
<td>temperature [K]</td>
<td>123</td>
<td>100</td>
</tr>
<tr>
<td>unique reflns</td>
<td>4616</td>
<td>2512</td>
</tr>
<tr>
<td>obsd reflns</td>
<td>3514</td>
<td>2235</td>
</tr>
<tr>
<td>parameters</td>
<td>326</td>
<td>314</td>
</tr>
<tr>
<td>$R$(int)</td>
<td>0.0408</td>
<td>0.0270</td>
</tr>
<tr>
<td>$R[I &gt; 2\sigma(I)]$ [$^a$]</td>
<td>0.0628</td>
<td>0.0822</td>
</tr>
<tr>
<td>$wR_{2}[all \ data]$ [$^b$]</td>
<td>0.1691</td>
<td>0.2292</td>
</tr>
<tr>
<td>GOF on $F^2$</td>
<td>1.039</td>
<td>0.963</td>
</tr>
</tbody>
</table>

[$^a$] Conventional $R$ on $F_{\text{all}}$: $\Sigma||F_o|| - |F_c||/\Sigma|F_o|$.  
[$^b$] Weighted $R$ on $|F_{\text{all}}|^2$: $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$
Supporting Information for

Demethylation of 5,\(n\)-di-\(\text{tert}\)-butyl-8,\(n\)-dimethoxy\([2.n]\) metacyclophane-1-ynes with \(\text{BBr}_3\) to afford novel \([n]\)benzofuranophanes

Thamina Akther\(^a\), Md. Monarul Islam\(^{a,b}\), Taisuke Matsumoto\(^c\), Junji Tanaka\(^c\), Xing Feng\(^d\), Carl Redshaw\(^e\) and Takehiko Yamato\(^a,\ast\)

\(^a\)Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840-8502, Japan. Fax: (internat.) + 81(0)952/28-8548.
\(^b\)Chemical Research Division, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhanmondi, Dhaka-1205, Bangladesh
\(^c\)Institute of Material Chemistry and Engineering, Kyushu University, 6-1, Kasugakoen, Kasuga 816-8580, Japan
\(^d\)Beijing Institute of Graphic Communication, Beijing 102600, PR China
\(^e\)Department of Chemistry, The University of Hull, Cottingham Road, Hull, Yorkshire, HU6 7RX, UK

Corresponding author:
Prof. Dr. Takehiko Yamato
Phone: +81 952 28 8679; fax: +81 952 28 8548.
E-mail address: yamatot@cc.saga-u.ac.jp
Table Contents

1) Figure S1-1 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 2a
2) Figure S1-2 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 2a
3) Figure S1-3 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 2b
4) Figure S1-4 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 2b
5) Figure S1-5 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 6b
6) Figure S1-6 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 6b
7) Figure S1-7 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 9
8) Figure S1-8 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 9
9) Figure S1-9 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 10
10) Figure S1-10 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 10
11) Figure S2-1 FT-IR for 2a
12) Figure S2-2 FT-IR for 2b
13) Figure S3-1 Mass spectrum for 2a
14) Figure S3-2 Mass spectrum for 6b
15) Figure S4-1 Solvent variation $^1$H NMR spectrum for 2a
16) Figure S4-2 Solvent variation $^1$H NMR spectrum of 2b
17) Figure S5-1 Crystal structure for 2a
18) Figure S5-2 Crystal structure for 2b
Figure S1-1 $^1$H–NMR spectrum (300 MHz, 298 K, *CDCl$_3$) for 2a.

Figure S1-2 $^{13}$C–NMR spectrum (100 MHz, 298 K, *CDCl$_3$) for 2a.
Figure S1-3 $^1$H–NMR spectrum (300 MHz, 298 K, CDCl$_3$) for 2b.

Figure S1-4 $^{13}$C–NMR spectrum (100 MHz, 298 K, CDCl$_3$) for 2b.
Figure S1-5 $^1$H–NMR spectrum (300 MHz, 298 K, * CDCl$_3$) for 6b.

Figure S1-6 $^{13}$C–NMR spectrum (100 MHz, 298 K, * CDCl$_3$) for 6b.
Figure S1-7 $^1$H–NMR spectrum (300 MHz, 298 K, *CDCl$_3$) for 8.

Figure S1-8 $^{13}$C–NMR spectrum (100 MHz, 298 K, *CDCl$_3$) for 8.
Figure S1-9 $^1$H–NMR spectrum (300 MHz, 298 K, CDCl$_3$) for $\mathbf{9}$. 

Figure S1-10 $^{13}$C–NMR spectrum (100 MHz, 298 K, CDCl$_3$) for $\mathbf{9}$. 

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Figure S2-1 FT-IR spectrum for 2a.

Figure S2-2 FT-IR spectrum for 2b.
Figure S3-1 Mass spectrum for 2a.

Figure S3-2 Mass spectrum for 6b.
Figure S4-1 $^1$H–NMR spectra for 2a (400 MHz, 293 K); (A) CDCl$_3$, (B) (CD$_3$)$_2$CO, (C) (CD$_3$)$_2$SO.

Figure S4-2 $^1$H–NMR spectra for 2b (400 MHz, 293 K); (A) CDCl$_3$, (B) (CD$_3$)$_2$CO, (C) (CD$_3$)$_2$SO.
Figure S5-1 X-ray crystal structure for 2a.
Figure S5-2 X-ray crystal structure for 2b.
checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yt1511a

Bond precision: C-C = 0.0034 Å Wavelength=1.54187

Cell: 
a=28.1308(5)  b=18.0592(3)  c=9.95585(18)
alpha=90  beta=90  gamma=90
Temperature: 123 K

Volume 5057.77(15)  5057.77(16)
Space group P b c a  P b c a
Hall group -P 2ac 2ab  -P 2ac 2ab
Moiety formula C30 H40 O2  C30 H40 O2
Sum formula C30 H40 O2  C30 H40 O2
Mr 432.62  432.64
Dx,g cm\(^{-3}\) 1.136  1.136
Z 8  8
Mu (mm\(^{-1}\)) 0.527  0.528
F000 1888.0  1888.0
F000' 1892.92
h,k,lmax 33,21,11  33,21,11
Nref 4616  4616
Tmin,Tmax 0.904,0.929  0.771,0.929
Tmin' 0.854

Correction method= # Reported T Limits: Tmin=0.771 Tmax=0.929
AbsCorr = MULTI-SCAN

Data completeness= 1.000  Theta(max)= 68.242
R(reflections)= 0.0628( 3514)  wr2(reflections)= 0.1691( 4616)
S = 1.039  Npar= 326

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
**Alert level B**

DIFMX01_ALERT_2_B  The maximum difference density is > 0.1*ZMAX*1.00  
_refine_diff_density_max given = 0.830  
Test value = 0.800

PLAT097_ALERT_2_B  Large Reported Max. (Positive) Residual Density 0.83 eA⁻³

**Alert level C**

DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75  
The relevant atom site should be identified.

PLATO94_ALERT_2_C  Ratio of Maximum / Minimum Residual Density ... 2.68 Report  
PLAT203_ALERT_2_C  Atom C12  has ADP max/min Ratio ..... 3.5 prolart  
PLAT220_ALERT_2_C  Large Non-Solvent C  Ueq(max)/Ueq(min) Range 4.0 Ratio  
PLAT241_ALERT_2_C  High  Ueq as Compared to Neighbors for ..... C26 Check  
PLAT242_ALERT_2_C  Low  Ueq as Compared to Neighbors for ..... C9 Check

**Alert level G**

CHEMS02_ALERT_1_G  Please check that you have entered the correct _publ_requested_category classification of your compound;  
FI or CI or EI for inorganic; FM or CM or EM for metal-organic;  
FO or CO or EO for organic.  
From the CIF: _publ_requested_category  CHOOSE FI FM FO CI CM CO or  
From the CIF: _chemical_formula_sum:C30 H40 O2

PLATO95_ALERT_5_G  No _iucr_refine_instructions_details in the CIF Please Do !  
PLAT007_ALERT_5_G  Number of Unrefined Donor-H Atoms .............. 1 Report  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C23  is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C24  is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C25  is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C123 is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C124 is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *C125 is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12D is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12E is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12F is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12G is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12H is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12I is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12J is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H12K is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H23A is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H23B is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H24A is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H24B is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H25A is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H25B is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H26A is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Atom Site Occupancy of *H26B is Constrained at 0.500 Check  
PLAT300_ALERT_4_G  Main Residue Disorder .......... Percentage = 9 Note  
PLAT779_ALERT_4_G  Suspect or Irrelevant (Bond) Angle in CIF ..... # 119 Check  
PLAT779_ALERT_4_G  Suspect or Irrelevant (Bond) Angle in CIF ..... # 169 Check  

0 ALERT level A  = Most likely a serious problem - resolve or explain  
2 ALERT level B  = A potentially serious problem, consider carefully  
6 ALERT level C  = Check. Ensure it is not caused by an omission or oversight  
28 ALERT level G  = General information/check it is not something unexpected

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation); however, if you intend to submit to Acta Crystallographica Section C or E, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the Notes for Authors of the relevant journal for any special instructions relating to CIF submission.

---

PLATON version of 21/06/2015; check.def file version of 21/06/2015
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) y0602

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.  CIF dictionary  Interpreting this report

Datablock: y0602

Bond precision:  C-C = 0.0089 Å  Wavelength=0.71073 Å

Cell:  
\[ a=14.6104(12) \]  \[ b=21.5562(19) \]  \[ c=9.0564(4) \]  
\[ \alpha=90^\circ \]  \[ \beta=100.897(4) \]  \[ \gamma=90^\circ \]  

Temperature:  100 K

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>2800.8(4)</td>
</tr>
<tr>
<td>Space group</td>
<td>C _C _C</td>
</tr>
<tr>
<td>Hall group</td>
<td>C -2yc</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C32 H44 O2</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C32 H44 O2</td>
</tr>
<tr>
<td>Mr</td>
<td>460.67</td>
</tr>
<tr>
<td>Dx,g cm(^{-3})</td>
<td>1.092</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Mu (mm(^{-1}))</td>
<td>0.066</td>
</tr>
<tr>
<td>F000</td>
<td>1008.0</td>
</tr>
<tr>
<td>F000'</td>
<td>1008.39</td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>17,26,11</td>
</tr>
<tr>
<td>Nref</td>
<td>5313[ 2663]</td>
</tr>
<tr>
<td>Tmin,Tmax</td>
<td>0.991,0.995</td>
</tr>
<tr>
<td>Tmin'</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Correction method= Not given

Data completeness= 0.94/0.47  Theta(max)= 25.680

R(reflections)= 0.0822( 2235)  wR2(reflections)= 0.2290( 2512)

\[ S = 0.963 \]  \[ Npar= 314 \]

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.  
Click on the hyperlinks for more details of the test.

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Alert level B

**PLAT029_ALERT_3_B** _differn_measured_fraction_theta_full_ Low ...... 0.943 Note

Alert level C

**DIFMX01_ALERT_2_C** The maximum difference density is > 0.1*ZMAX*0.75

_differn_density_max_ given = 0.734

Test value = 0.600

**DIFMX02_ALERT_1_C** The maximum difference density is > 0.1*ZMAX*0.75

The relevant atom site should be identified.

**STRVA01_ALERT_4_C** Flack test results are meaningless.

From the CIF: _refine_ls_abs_structure_Flack_ 0.000

From the CIF: _refine_ls_abs_structure_Flack_su_ 3.000

**PLAT094_ALERT_2_C** Ratio of Maximum / Minimum Residual Density .... 3.50 Report

**PLAT097_ALERT_2_C** Large Reported Max. (Positive) Residual Density 0.73 eA-3

**PLAT230_ALERT_2_C** Hirshfeld Test Diff for C30 -- C31 .. 5.4 su

**PLAT230_ALERT_2_C** Hirshfeld Test Diff for C31 -- C32 .. 5.2 su

**PLAT234_ALERT_4_C** Large Hirshfeld Difference C19 -- C22 .. 0.16 Ang.

**PLAT241_ALERT_2_C** High Ueq as Compared to Neighbors for ...... C31 Check

**PLAT242_ALERT_2_C** Low Ueq as Compared to Neighbors for ...... C19 Check

**PLAT242_ALERT_2_C** Low Ueq as Compared to Neighbors for ...... C30 Check

**PLAT340_ALERT_3_C** Low Bond Precision on C-C Bonds ............... 0.0089 Ang.

Alert level G

**PLAT002_ALERT_2_G** Number of Distance or Angle Restraints on AtSite 7 Note

**PLAT003_ALERT_2_G** Number of Uiso or Uij Restrained non-H Atoms ... 5 Report

**PLAT005_ALERT_5_G** No _iucr_refine_instructions_details_ in the CIF Please Do !

**PLAT007_ALERT_5_G** Number of Unrefined Donor-H Atoms .............. 1 Report

**PLAT032_ALERT_4_G** Std. Uncertainty on Flack Parameter Value High . 3.000 Report

**PLAT072_ALERT_2_G** SHELXL First Parameter in WGHT Unusually Large. 0.18 Report

**PLAT850_ALERT_4_G** SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

0 ALERT level A = Most likely a serious problem – resolve or explain

1 ALERT level B = A potentially serious problem, consider carefully

12 ALERT level C = Check. Ensure it is not caused by an omission or oversight

9 ALERT level G = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

11 ALERT type 2 Indicator that the structure model may be wrong or deficient

3 ALERT type 3 Indicator that the structure quality may be low

5 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation); however, if you intend to submit to Acta Crystallographica Section C or E, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the Notes for Authors of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 21/06/2015; check.def file version of 21/06/2015
Supporting Information for

Demethylation of 5,\textit{n}-di-\textit{tert}-butyl-8,\textit{n}-dimethoxy[2,\textit{n}] 
metacyclophane- 1-yynes with BBr\textsubscript{3} to afford novel 
[\textit{n}]benzofuranophanes

Thamina Akther\textsuperscript{a}, Md. Monarul Islam\textsuperscript{a,b}, Taisuke Matsumoto\textsuperscript{c}, Junji Tanaka\textsuperscript{c}, Xing Feng \textsuperscript{d},
Carl Redshaw\textsuperscript{e} and Takehiko Yamato\textsuperscript{a,*}

\textsuperscript{a}Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 
1, Saga-shi, Saga 840-8502, Japan. Fax: (internat.) + 81(0)952/28-8548.
\textsuperscript{b}Chemical Research Division, Bangladesh Council of Scientific and Industrial Research(BCSIR), 
Dhanmondi, Dhaka-1205, Bangladesh
\textsuperscript{c}Institute of Material Chemistry and Engineering, Kyushu University, 6-1, Kasugakoen, Kasuga 
816-8580, Japan
\textsuperscript{d}Beijing Institute of Graphic Communication, Beijing 102600, PR China
\textsuperscript{e}Department of Chemistry, The University of Hull, Cottingham Road, Hull, Yorkshire, HU6 7RX, UK

Corresponding author:
Prof. Dr. Takehiko Yamato
Phone: +81 952 28 8679; fax: +81 952 28 8548.
E-mail address: yamatot@cc.saga-u.ac.jp

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Table Contents

1) Figure S1-1 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 2a
2) Figure S1-2 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 2a
3) Figure S1-3 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 2b
4) Figure S1-4 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 2b
5) Figure S1-5 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 6b
6) Figure S1-6 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 6b
7) Figure S1-7 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 9
8) Figure S1-8 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 9
9) Figure S1-9 $^1$H-NMR spectrum (300 MHz, 293 K, *CDCl$_3$) for 10
10) Figure S1-10 $^{13}$C-NMR spectrum (100 MHz, 293 K, *CDCl$_3$) for 10
11) Figure S2-1 FT-IR for 2a
12) Figure S2-2 FT-IR for 2b
13) Figure S3-1 Mass spectrum for 2a
14) Figure S3-2 Mass spectrum for 6b
15) Figure S4-1 Solvent variation $^1$H NMR spectrum for 2a
16) Figure S4-2 Solvent variation $^1$H NMR spectrum of 2b
17) Figure S5-1 Crystal structure for 2a
18) Figure S5-2 Crystal structure for 2b
Figure S1-1 $^1$H–NMR spectrum (300 MHz, 298 K, $^*$ CDCl$_3$) for 2a.

Figure S1-2 $^{13}$C–NMR spectrum (100 MHz, 298 K, $^*$ CDCl$_3$) for 2a.
Figure S1-3 $^1$H–NMR spectrum (300 MHz, 298 K, * CDCl$_3$) for 2b.

Figure S1-4 $^{13}$C–NMR spectrum (100 MHz, 298 K, * CDCl$_3$) for 2b.
Figure S1-5 $^1$H–NMR spectrum (300 MHz, 298 K, * CDCl$_3$) for 6b.

Figure S1-6 $^{13}$C–NMR spectrum (100 MHz, 298 K, * CDCl$_3$) for 6b.
Figure S1-7 $^1$H–NMR spectrum (300 MHz, 298 K, * CDCl$_3$) for 8.

Figure S1-8 $^{13}$C–NMR spectrum (100 MHz, 298 K, * CDCl$_3$) for 8.
Figure S1-9 $^1$H–NMR spectrum (300 MHz, 298 K, * CDCl$_3$) for 9.

Figure S1-10 $^{13}$C–NMR spectrum (100 MHz, 298 K, * CDCl$_3$) for 9.
Figure S2-1 FT-IR spectrum for 2a.

Figure S2-2 FT-IR spectrum for 2b.
Figure S3-1 Mass spectrum for 2a.

Figure S3-2 Mass spectrum for 6b.
Figure S4-1 $^1$H–NMR spectra for 2a (400 MHz, 293 K); (A) CDCl$_3$, (B) (CD$_3$)$_2$CO, (C) (CD$_3$)$_2$SO.

Figure S4-2 $^1$H–NMR spectra for 2b (400 MHz, 293 K); (A) CDCl$_3$, (B) (CD$_3$)$_2$CO, (C) (CD$_3$)$_2$SO.
Figure S5-1 X-ray crystal structure for 2a.
Figure S5-2 X-ray crystal structure for 2b.