Synthesis and demethylation of 4,22-dimethoxy [2.10]metacyclophan-1-yne with BBr_3 to afford a novel [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane

Yuki Uchikawa, Kazuya Tazoe, Syogo Tanaka, Xing Feng, Taisuke Matsumoto, Junji Tanaka, and Takehiko Yamato

Abstract: 4,22-Dimethoxy[2.10]metacyclophan-1-yne was prepared by bromination of [2.10]metacyclophan-1-ene followed by the dehydrobromination of the bromine adduct with KOBu-*t*. Treatment of 4,22-dimethoxy[2.10]metacyclophan-1-yne with BBr_3 in CH_2Cl_2 at room temperature led to the demethylation and a successive intramolecular cyclization reaction to afford a novel [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane in good yield. Similar treatment of a mixture of the corresponding *meso*- and *dl*-1,2-dibromo-4,22-dimethoxy[2.10]metacyclophane with BBr_3 in CH_2Cl_2 under the same conditions described above afforded *cis*-4b,9b-dihydro[10]benzofuro[3,2-*b*]benzofuranophane in 83% yield.

Key words: metacyclophan-1-ene, dehydrobromination, metacyclophan-1-yne, double intramolecular cyclization, benzofuranophane.

Résumé : On a préparé le 4,22-diméthoxy[2,10]métacyclophan-1-yne par une bromuration du 4,22-diméthoxy[2,10]métacyclophan-1-ène suivie d'une déshydrobromuration de l'adduit bromé à l'aide de *tert*-butylate de potassium. La réaction du 4,22-diméthoxy[2,10]métacyclophan-1-yne avec du BBr_3, en solution dans le CH_2Cl_2, à la température ambiante, conduit successivement à une déméthylation et une réaction de cyclisation intramoléculaire qui fournit un nouveau [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochrométhénophane, avec un bon rendement. Un traitement semblable d'un mélange de *méso*- et de *dl*- 1,2-dibromo-4,22-diméthoxy[2,10]métacyclophane avec du BBr_3, en solution dans le CH_2Cl_2, dans les conditions décrites plus haut, conduit au 4b,9b-dihydro[10]benzofuro[3,2-*b*]benzofuranophane, avec un rendement de 83 %.

Mots-clés : métacyclophan-1-ène, déshydrobromuration, métacyclophan-1-yne, double cyclisation intramoléculaire, benzofuranophane.

[Traduit par la Rédaction]

Introduction

Cyclophanes belong to one of the remarkable compound classes that has attracted extensive studies.[1–3] In 1982, Psiorz and Hopf reported the identification of some elusive strained paracyclophyne intermediates, which were indirectly confirmed by the fact that giving Diels–Alder adducts were produced with dienophiles or that trimerization to the hexaphenyl benzene derivatives occurred.[4–8] Later, Meijere and Wong[5] reported the existence of the strained cyclophynes as an intermediate, which was established by a trapping method. Ramming and Gleiter[9] reported the syntheses of [*n*]MCP-diynes (MCP = metacyclophane) and their transformation of propargylic moieties into allenic moieties, as well as reactions with strong bases. Recently, Kawase and co-workers[10–12] reported the synthesis of [2_n]MCP-*n*-ynes by bromination–dehydrobromination of the corresponding MCP-*n*-enes, which were considerably strained with bent triple bonds. Although we attempted to prepare [2.3]- and [2.4]-MCP-1-ynes by the dehydrobromination of the corresponding 1,2-dibromo[2.3]- and [2.4]-MCPs,[13] no formations of the desired [2.3]- and [2.4]-MCP-ynes were observed because of the considerably strained bent triple bonds. Instead, only 1-bromo[2.3]- and [2.4]-MCP-1-enes, along with [2.3]- and [2.4]-MCP-1-ones, were obtained. On the other hand, we succeeded in preparing the larger ring sized 8,22-dimethoxy[2.8]- and 8,24-dimethoxy[2.10]-MCP-1-ynes with bent triple bonds by the bromination–dehydrobromination of the corresponding [2.*n*]MCP-1-enes.[13]

On the other hand, recently, Yamaguchi and co-workers[14–18] reported the double intramolecular cyclizations of diarylacetylenes to construct a series of fully ring-fused ladder π-conjugated skeletones with various main group elements, such

Received 4 November 2011. Accepted 16 January 2012. Published at www.nrcresearchpress.com/cjc on 4 April 2012.

Y. Uchikawa, K. Tazoe, S. Tanaka, X. Feng, and T. Yamato. Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga 840-8502, Japan.
T. Matsumoto and J. Tanaka. Institute for Material Chemistry and Engineering, Kyushu University, 6-1, Kasugakoen, Kasuga 816-8580, Japan.

Corresponding author: Takehiko Yamato (e-mail: yamatot@cc.saga-u.ac.jp).

as Si, B, P, and S, as the bridging moieties. Thus, there is substantial interest in the synthesis of the larger sized [2.*n*]MCP-1-ynes having nucleophilic substituents such as OH and OMe groups at the ortho position to the acetylenic linkage, which can afford convenient starting materials for the attempted preparation of a series of fully ring-fused [2.*n*]cyclophanes by the double intramolecular cyclizations of the diarylacetylene moiety (Scheme 1). In this paper, we describe the first preparation of 4,22-dimethoxy[2.10]MCP-1-ene using the low-valent titanium-induced McMurry reaction and their conversion to 4,22-dimethoxy[2.10]MCP-1-yne, which was treated with BBr_3 to afford a novel [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane by the intramolecular cyclizations of the diarylacetylene moiety.

Results and discussion

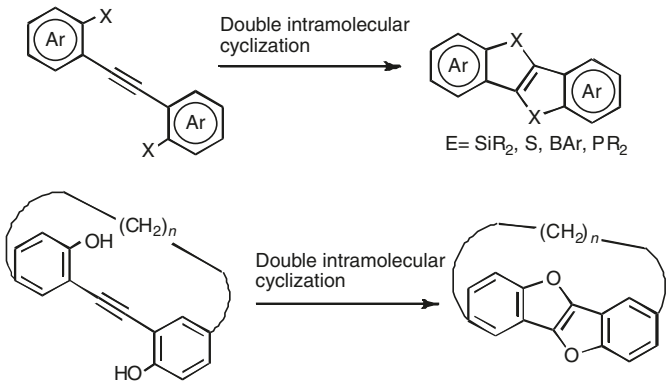
1,10-Bis(4-methoxyphenyl)decane (**2**) was prepared according to our previous reports.[19–24] The cross-coupling reaction of 4-methoxyphenylmagnesium bromide with 1,10-dibromodecane was carried out in the presence of cuprous bromide as a catalyst in a mixture of hexamethylphosphoric triamide (HMPA) and tetrahydrofuran (THF) at reflux temperature to give the desired 1,10-bis(4-methoxyphenyl)decane (**2**) in 82% yield. The $TiCl_4$-catalysed formylation of compound **2** with Cl_2CHOMe at 20 °C led to regioselective formylation at the meta positions of the 1,10-diphenylalkane, affording the desired 1,10-bis(3-formyl-4-methoxyphenyl) decane (**3**) in 83% yield. Compound **3** was subjected to reductive coupling by the McMurry reaction.[25–43] The novel desired [2.10]MCP-1-ene (**4**) was obtained in 94% yield along with the corresponding 1,2-diol (**5**). The ^{1}H NMR spectrum of **4** shows two kinds of methoxy protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two isomers, (*E*)-**4** and (*Z*)-**4** (Scheme 2), were separated in 52% and 42% yield, respectively.

The structures of products (*E*)-**4** and (*Z*)-**4** were determined on the basis of their elemental analyses and spectral data. ^{1}H NMR signals of the olefinic protons for *E*- and *Z*-olefins should be observed at $\delta > 7.4$ ppm (*E*) and $\delta < 6.9$ ppm (*Z*).[44] The ^{1}H NMR spectrum of (*E*)-**4** in $CDCl_3$ shows a singlet at δ 7.36 ppm for olefinic protons and a doublet ($J = 2.4$ Hz) at δ 7.30 ppm for one aromatic proton ($H_{8,24}$), which is in a strongly deshielding region of the bridged double bond. In contrast, the ^{1}H NMR spectrum of (*Z*)-**4** in $CDCl_3$ shows a singlet at δ 6.70 ppm for olefinic protons and a set of doublets ($J = 2.4$ Hz) at δ 6.76, 6.98, and 7.03 ppm for the aromatic protons, which were observed at higher field owing to the strong shielding effect of the opposing benzene ring. These data strongly support that the structure of (*E*)-**4** is the E configuration and the structure of (*Z*)-**4** is the Z configuration, both having syn conformation. The structure of the syn-confomer is also readily assigned from the chemical shift of the internal proton Hi at δ 7.30 ppm for (*E*)-**4** and δ 7.03 ppm for (*Z*)-**4**.

Single-crystal X-ray diffraction structures of (*E*)-**4** recrystallized from hexane are illustrated in Fig. 1 with the atom-numbering system.

Compound (*E*)-**4** crystallized in the monoclinic space group *P*121/*a*. Compound (*E*)-**4** was located at general positions in the asymmetric unit of the crystal structure. The X-ray crystallographic analyses of (*E*)-**4** clearly show that the compound also adopts the anti conformation in the solid state. In addition, the double bond adopts the E configuration. These results seem to indicate that the double bond in (*E*)-**4** plays an important role in the fixation of the conformation in the solid state.

Scheme 1. Double intramolecular cyclization of diarylacetylenes and hydroxy[2.*n*]metacyclophan-1-ynes



In (*E*)-**4** the bond distance of C_1–C_2 is 1.341 Å, which is almost the same value as the distance between carbon atoms in ethylene. The bond distances of C_2–C_3 and C_1–C_{23} are 1.472 and 1.474Å, respectively, which are slightly shorter than those of C_7–C_9 (1.545 Å) and C_{18}–C_{19} (1.524 Å). The dihedral angles of C_9–C_{10}–C_{11}–C_{12}–C_{13}–C_{14}–C_{15}–C_{16}–C_{17}–C_{18}–C_1–C_2 between C_3–C_4–C_5–C_6–C_7–C_8 and C_{19}–C_{20}–C_{21}–C_{22}–C_{23}–C_{24} are different values, 3.15° and 0.15°, respectively, showing that the aromatic rings adopt the asymmetrical conformation in the molecule. This reflects the bond angles in the ethylenic bridge chain; the bond angles of C_1–C_2–C_3 and C_{23}–C_1–C_2 are different values (131.74° and 122.49°) that are larger than those of ethylene.

The structure of diol **5** was also determined on the basis of its elemental analyses and spectral data. Thus, we reported[44] the structure of *anti*-1,2-dihydroxy-6,13-dimethoxy[2.3]MCP and assigned it as a *trans*-diol with a exo–exo arrangement. We assigned the structure of **5** in a similar fashion. However, in the case of **5**, the similar upfield shift of the internal aromatic proton (δ 4.95 ppm for *anti*-1,2-dihydroxy-6,13-dimethoxy[2.3]MCP)[1–3,45,46] was not observed, but appeared in the normal aromatic region at δ 6.72 ppm ($J = 2.4$ Hz). This observation strongly suggests **5** adopts a syn conformation, different from that in *anti*-1,2-dihydroxy-6,13-dimethoxy[2.3]MCP. The other two aromatic protons was observed at δ 6.72 ($H_{5,21}$, $J = 8.4$ Hz) and 6.95 ($H_{6,20}$, $J = 2.4$, 8.4 Hz) ppm, respectively. Furthermore, the bridged methine protons show a downfield shift at δ 4.81 ppm as a doublet ($J = 2.1$ Hz), whereas those of 1,2-dihydroxy-6,13-dimethoxy[2.3]MCP are at δ 4.34 ppm. Thus, the bridged methine protons of **5** are in a strongly deshielding region of the oxygen atom of the methoxy groups on the benzene ring. These observations are strongly supported because the two OH groups are in an exo, exo arrangement and, therefore, **5** was found to be a *cis*-diol.

Attempted bromination of (*Z*)-4,22-dimethoxy[2.10]MCP-1-ene (*Z*)-**4** with an equimolar amount of benzyltrimethylammonium tribromide (BTMA Br_3), which was found to be a convenient solid brominating agent,[47] carried out in a

Scheme 2. Synthesis of (*Z*)- and (*E*)-4,22-dimethoxy[2.10]MCP-1-ene, (*Z*)-**4** and (*E*)-**4.**

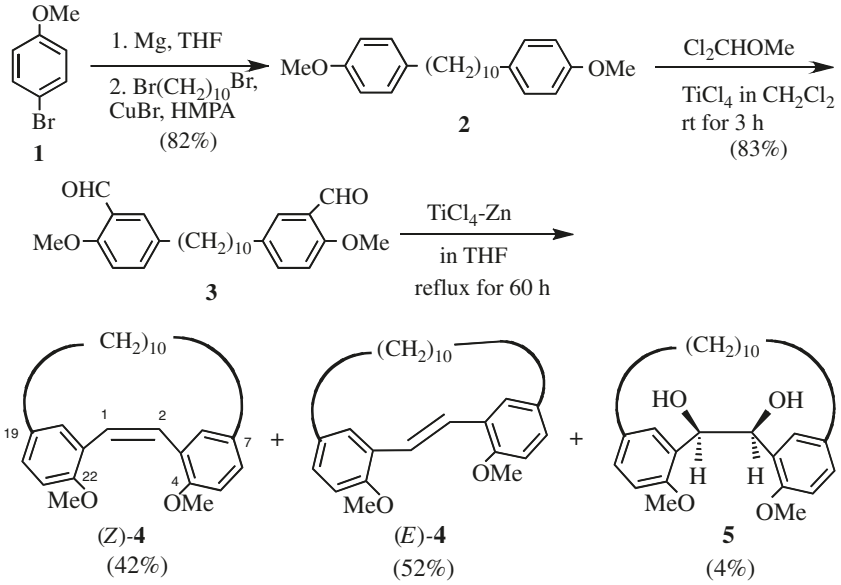
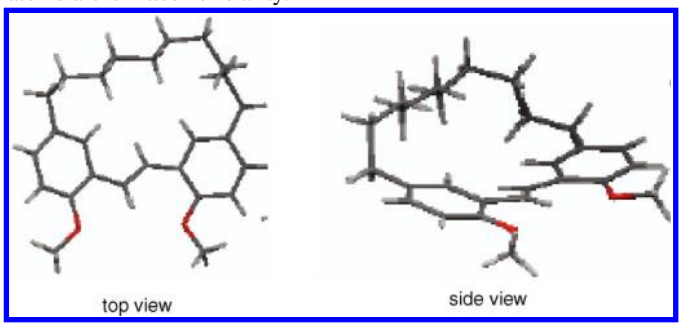


Fig. 1. Single-crystal X-ray diffraction structures of (*E*)-**4**. Hydrogen atoms are omitted for clarity.

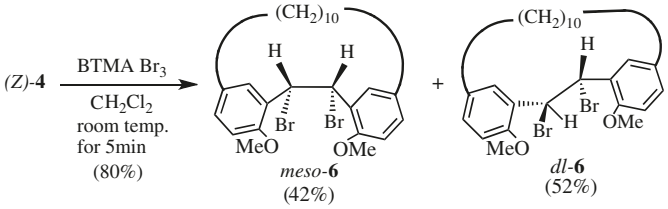


dichloromethane solution at room temperature for 5 min led to the expected cis- and trans-adducts **6** (*endo–endo*–Br and *endo–exo*–Br) to the bridged double bond in a ratio of 45:55 in 80% yield. Similar treatment of (*E*)-**4** with BTMA Br_3 under the same reaction conditions afforded a mixture of *meso*-**6** and *rac*-**6** (Scheme 3) in 91% yield in a ratio of 45:55.

When treated with potassium *tert*-butoxide in refluxing HOBu-*t* at 80 °C for 2 h, bromine adduct **6** gave the didehydrobromination product [2.10]MCP-1-yne (**7**) in 72% yield.

The structure of **7** was determined on the basis of its elemental analysis and spectral data. The ^{1}H NMR spectrum of **7** shows two internal protons as a doublet at δ 7.39 ($H_{8,24}$, J = 2.1 Hz) ppm and two aromatic protons at δ 6.78 ($H_{5,21}$, J = 8.4 Hz) and 7.03 ($H_{6,20}$, J = 2.1, 8.4 Hz) ppm. The chemical shift for the internal protons at normal aromatic protons strongly supports that the structure of **7** is the syn-conformer. A deshielded internal proton was observed in the NMR spectrum of **7** at δ 7.39 ppm in comparison with other aromatic protons, which is in a strongly deshielding region owing to the π-electrons of the triple bond. The chemical shifts of the ^{1}H and ^{13}C NMR signals arising from the benzene rings of **7** are comparable to those of the acyclic reference compound **11**,[13] which was prepared from 2-formyl-5-methylanisole (**8**) in three. steps, the same procedure

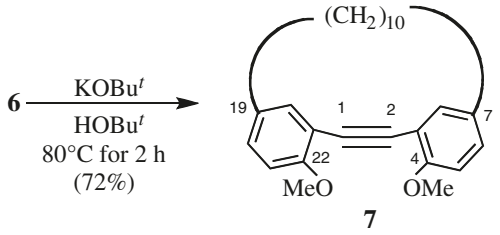
Scheme 3. Bromination of (*Z*)-**4** with BTMA Br_3.



as that for **7** (Scheme 4). Interestingly, the signals of the acetylenic carbons were observed at slightly lower field (δ 91.48 ppm for **7**) than that of **11** (δ 89.69 ppm, Scheme 5); this reflects the relatively small strain in the triple bond owing to bending and is almost the same value of that of [2_4]MCP-1,9,17,25-tetrayne (δ 92.20 ppm), but much lower than that of 1,5-cyclooctadiyne (δ 95.8 ppm)[48] or [2_3]MCP-1,9,17-triyne (δ 99.86 ppm).[11]

Single-crystal X-ray diffraction structures of **7** recrystallized from hexane are illustrated in Fig. 2 with the atom-numbering system. Compound **7** crystallized in the monoclinic space group $P21/a$ (Z = 8). All remaining hydrogen atoms are not shown for clarity. The structure was solved by direct-methods (Sir2002) and refined using the full-matrix least-squares method and Fourier synthesis. The X-ray structure determination of **7** clearly indicates that the structure of **7** is also the syn-conformer in the solid state, and the two methoxy groups are lying on the same side of the inner ring toward the outer direction to avoid steric repulsion with the bridge chain, the same as in (*E*)-**4**. The bond distance of C_1–C_2 is 1.20 Å, which is almost equal to the distance between carbon atoms in acetylene. The bond distances of C_2–C_3 and C_1–C_{23} are 1.43 and 1.43 Å, respectively, which are much shorter than those of C_7–C_9 (1.52 Å) and C_{18}–C_{19} (1.51 Å). Interestingly, the acetylenic moiety in the bridge chain does not adopt a different linear structurethan reference compound **11**; the bond angles of C_1–C_2–C_3 and C_2–C_1–C_{23} are unusual values, 169.6°and 170.2°. Thus, this clearly shows that **7** is a slightly bent molecule and supports the lower field shifts of

Scheme 4. Didehydrobromination of **6** with potassium *tert*-butoxide.



Scheme 5. Synthesis of acyclic reference compound **11**.

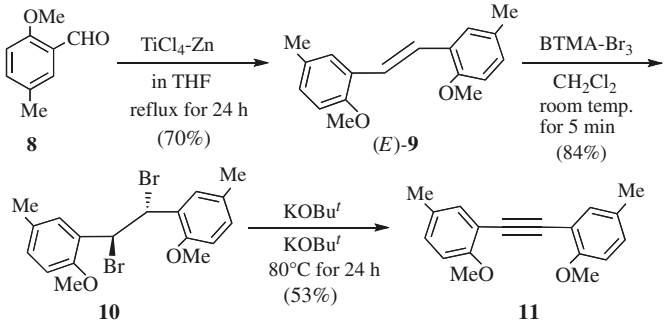
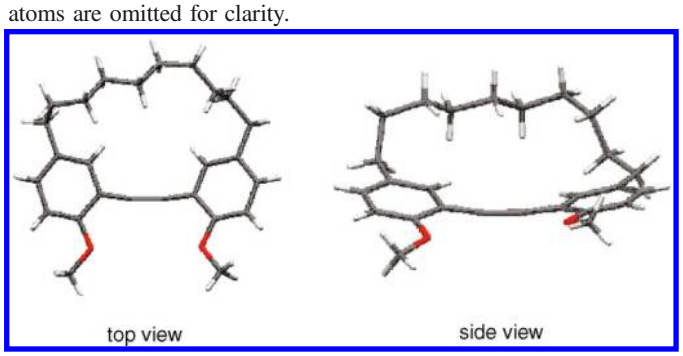


Fig. 2. Single-crystal X-ray diffraction structures of **7**. Hydrogen atoms are omitted for clarity.

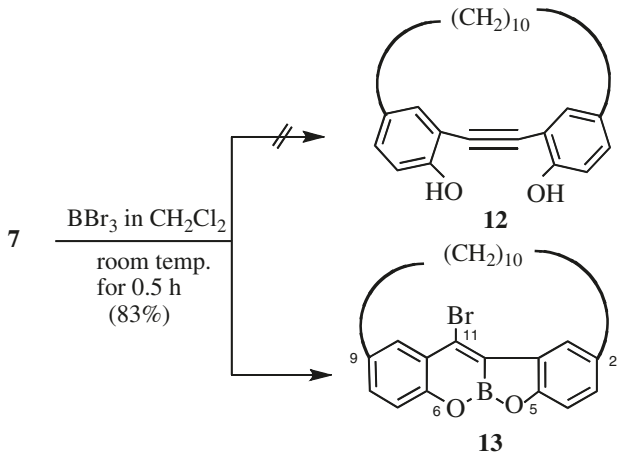


the signals of the acetylenic carbons in its ^{13}C NMR spectrum.

Attempted demethylation of **7** to afford **12** with trimethylsilyl iodide in acetonitrile solution[42–52] under various conditions failed. Only an intractable mixture of products was obtained. Interestingly, treatment of **7** with BBr_3 in CH_2Cl_2 at room temperature for 0.5 h afforded a novel [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane (**13**) in 83% yield (Scheme 6). No formations of the expected 4,22-dihydroxy[2.10]MCP-1-ene (**12**) or [10]benzofuro[3,2-*b*]benzofuranophane (Scheme 1) derived from the double intramolecular cyclizations of diarylacetylene and the OH groups of **12** were observed under the conditions used.

The structure of **13** was elucidated based on its elemental analysis and spectral data. Especially, the mass spectral data for **13** (M^+ = 435, 437) strongly supports one bromine atom containing product. The ^{1}H NMR spectrum in $CDCl_3$ exhibited six aromatic protons at δ 6.84 (d, J = 8.4), 6.86 (d, J = 2.4 Hz), 7.01 (dd, J = 2.4, 8.4 Hz), 7.18 (d, J = 8.4 Hz), 7.23 (dd, J = 1.2, 8.4 Hz), and 7.95 (d, J = 1.2 Hz) ppm, which were clearly associated with the unsymmetrical structure of **13**. On the basis of the spectral data, compound **13**

Scheme 6. Treatment of **7** with BBr_3 in CH_2Cl_2.



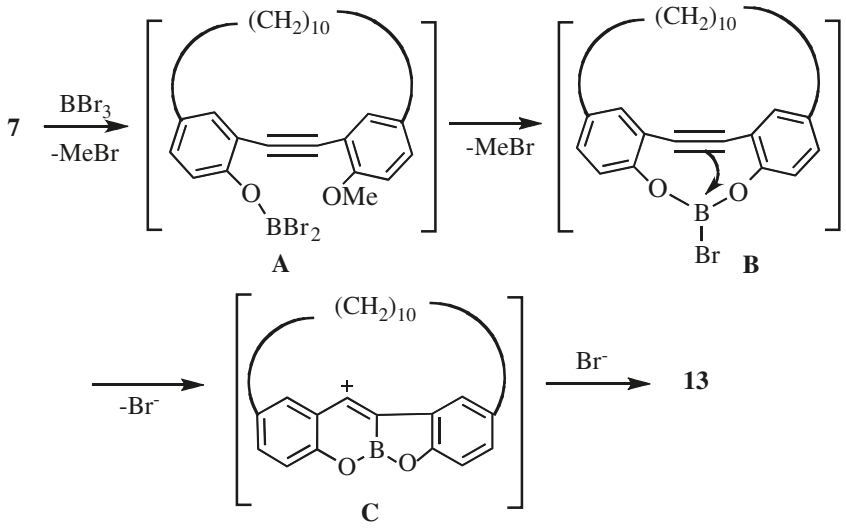
was assigned the structure, [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane.

Although the detailed mechanism of formation of [10]benzofurochromenophane (**13**) is not clear at the present stage, one might assume the reaction pathway as shown in Scheme 7. The present BBr_3-induced transformation from **7** to **13** probably occurred by demethylation of one methoxy group to afford the corresponding intermediate **A** followed by the second demethylation reaction along with the intramolecular cyclization reaction to afford the intermediate **B**, from which the electrophilic attack to the triple bond to generate the vinyl cation intermediate **C** occurred. Succesively, the nucleophilic attack to the vinyl cation intermediate **C** afforded compound **13** (Scheme 7). The present cyclization of the intermediate **B** to **C** might be attributable to conformational flexibility of the intermediate **B** and a short distance among the ethynyl group and boron atom as an electrophile owing to the *syn*-MCP skeletone. In fact, similar treatment of reference compound **11** with BBr_3 under the same conditions afforded only the intractable mixture of products. No formation of the corresponding benzofurochromene was observed under the conditions used.

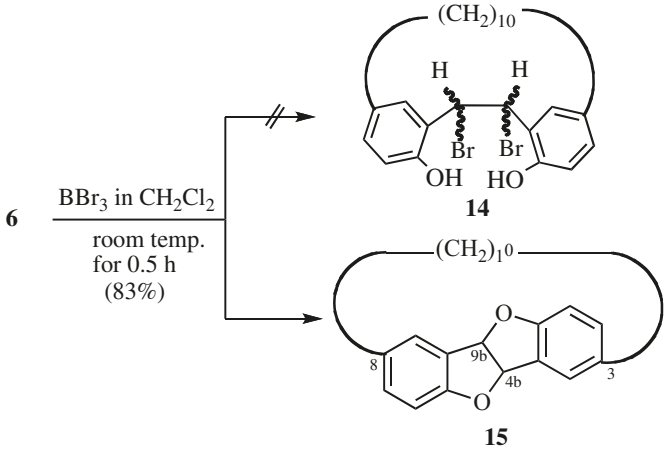
To study the present [10]benzofurochromenophane formation reaction in more detail, we attempted to carry out the treatment of dibromide **6** with BBr_3. In fact, the treatment of a mixture of *meso*- and *dl*-**6** with BBr_3 in CH_2Cl_2 under the same conditions described above afforded *cis*-4b,9b-dihydro [10]benzofuro[3,2-*b*]benzofuranophane (**15**) in 83% yield, but not [10]benzofurochromenophane (Scheme 8).

The present BBr_3-induced transformation from **6** to **15** probably occurred by the demethylation of methoxy groups to afford the corresponding phenol derivative **D**, followed by a nucleophilic attack by phenolic oxygen to the bromide carbon at the C_2 carbon to afford the benzofuran intermediate **E**, from which the second nucleophilic attack to the bromide carbon at the C_3 position of benzofuran occurred to afford benzofuro[3,2-*b*]benzofuranophane skeletone intermediate **G**. The second cyclization of the intermediate **E** to **F** might be attributable to conformational flexibility of the intermediate **E** around the diaryl linkage of 2-arylbenzofuran. Deprotonation from the intermediate **G** afforded compound **15** (Scheme 9). From this proposed reaction mechanism for the BBr_3-induced transformation of **6** to **15**, one might assume the importance

Scheme 7. Proposed reaction mechanism for the formation of **13**.



Scheme 8. Reaction of a mixture of *meso*- and *dl*-**6** with BBr_3 in CH_2Cl_2.



of the intramolecularly cyclized nine-membered intermediate **B** to afford **13** during the demethylation of **7** with BBr_3.

Conclusions

We have demonstrated a convenient preparation of 4,22-dimethoxy[2.10]MCP-1-yne (**7**) and conversion to a novel [10]benzofurochromenophane (**13**) by treatment with BBr_3 in CH_2Cl_2 at room temperature via demethylation and a successive intramolecular cyclization reaction. Interestingly, similar treatment of a mixture of the corresponding *meso*- and *dl*-1,2-dibromo-4,22-dimethoxy[2.10]MCP (**6**) with BBr_3 in CH_2Cl_2 under these same conditions afforded *cis*-4b,9b-dihydro[10]benzofuro[3,2-*b*]benzofuranophane (**15**) in 83% yield by double intramolecular cyclization. Further studies on the chemical properties of [10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane **13** and *cis*-4b,9b-dihydro[10]benzofuro[3,2-*b*]benzofuranophane **15** are now in progress.

Experimental

All melting points were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Nippon Denshi JEOL FT-300 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. Mass spectra were obtained on a Nippon Denshi JIR-AQ2OM mass spectrometer at an ionization energy of 70 eV using a direct-inlet system through GLC; *m*/*z* values reported include the parent ion peak. Infrared (IR) spectra were obtained on a Nippon Denshi JIR-AQ2OM spectrophotometer as KBr disks. Elemental analyses were performed with a Yanaco MT-5. Gas–liquid chromatograph (GLC) analyses were performed with a Shimadzu GC, GC-14A (silicone OV-1, 2 m; programmed temperature rise, 12 °C min^{-1}; carrier gas, nitrogen, 25 mL min^{-1}).

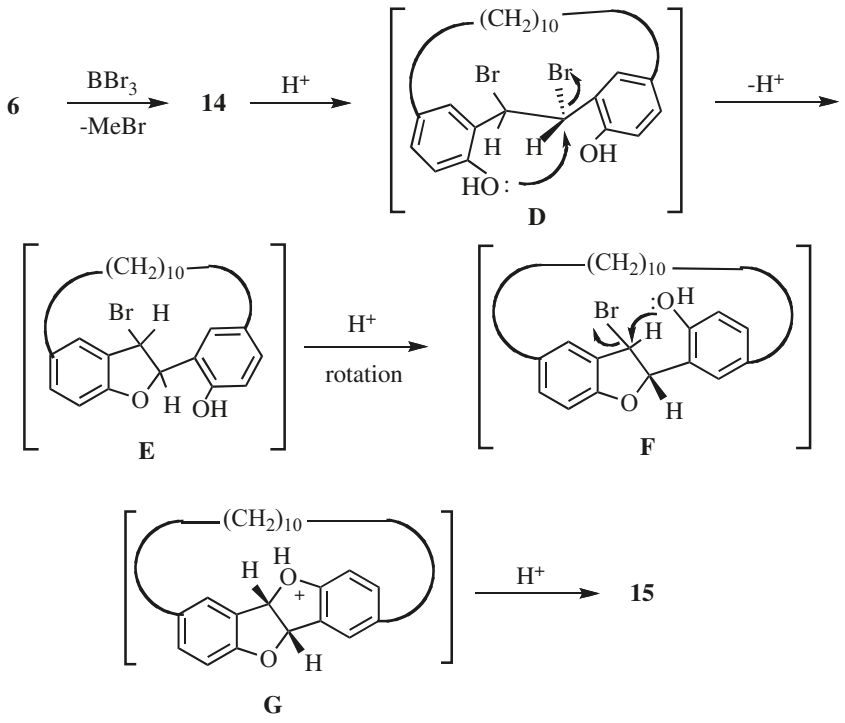
Preparation of 1,10-bis(4-methoxyphenyl)decane (2)

To a solution of 9.52 g (0.39 mol) of magnesium and a small amount of iodine in THF (10 mL) was added a solution of 4-bromoanisole (**1**) (33.7 g, 0.18 mol) in THF (40 mL) and the mixture was refluxed for 12 h. To a solution of 1,10-dibromodecane (18 g, 60 mmol) and CuBr (2.0 g, 14 mmol) in HMPA (10 mL) was added dropwise a solution of 4-methoxyphenylmagnesium bromide with gentle refluxing. After the reaction mixture was refluxed for an additional 24 h, it was quenched with a 10% aqueous ammonium chloride solution and extracted with CH_2Cl_2 (100 mL × 3). After the combined CH_2Cl_2 extracts were dried over Na_2SO_4, the solvent was evaporated in vacuo, and the residue was washed with methanol (100 mL) to afford 19 g of crude **2** as a colorless solid. Recrystallization from hexane gave **2** (17.5 g, 82%) as colorless prisms, mp 64–65 °C. ^{1}H NMR ($CDCl_3$) δ: 1.27 (broad s, 12H, *CH*$_2$), 1.54 (s, 4H, *CH*$_2$), 2.54–2.59 (m, 4H, *CH*$_2$), 3.78 (s, 6H, O*Me*), 6.82 (d, J = 8.8 Hz, 4H, Ar–*H*), 7.08 (d, J = 8.8 Hz, 4H, Ar–*H*). MS *m*/*z* (%): 354 (M^+). Anal. calcd for $C_{24}H_{34}O_2$ (354.53): C 81.31, H 9.67; found: C 81.42, H 9.54.

Preparation of 1,10-bis(3-formyl-4-methoxyphenyl)decane (3)

To a solution of 1,10-bis(4-methoxyphenyl)decane (**2**, 7.08 g, 20 mmol) and Cl_2CHOCH_3 (4.86 mL, 56 mmol) in CH_2Cl_2 (40 mL) was added a solution of $TiCl_4$ (6.7 mL,

Scheme 9. Proposed reaction mechanism for BBr_3-induced transformation from **6** to **15**.



61 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After the reaction mixture was stirred at room temperature (rt) for 3 h, it was poured into a large amount of ice water (200 mL) and extracted with CH_2Cl_2 (100 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, 500 g) with hexane – ethylacetate (4:1) as eluent to give crude **3**. Recrystallization from hexane gave 6.82 g (83%) of 1,10-bis(3-formyl-4-methoxyphenyl)decane (**3**) as colorless prisms, mp 63–64 °C. IR (KBr, cm^{-1}) ν_{max}: 1683 (C=O). ^1H NMR ($CDCl_3$) δ: 1.26 (broad s, 12H, *CH*$_2$), 1.55 (s, 4H, *CH*$_2$), 2.54–2.59 (m, 4H, *CH*$_2$), 3.91 (s, 6H, *OMe*), 6.10 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.36 (dd, *J* = 2.1, 8.4 Hz, 2H, Ar*H*), 7.63 (d, *J* = 2.1 Hz, 2H, Ar–*H*), 10.4 (s, 2H, C*H*O). MS *m*/*z* (%): 410 (M^+). Anal. calcd for $C_{26}H_{34}O_4$ (410.56): C 76.06, H 8.35; found: C 76.14, H 8.27.

McMurry coupling reaction of 3

The McMurry reagent was prepared from $TiCl_4$ (13.75 mL, 125 mmol) and Zn powder (18 g, 275 mmol) in dry THF (500 mL), under nitrogen. A solution of 1,10-bis(3-formyl-4-methoxyphenyl)decane (**3**, 4.72 g, 11.5 mmol) in dry THF (250 mL) was added within 60 h to the black mixture of the McMurry reagent by using a high-dilution technique with continuous refluxing and stirring. The reaction mixture was refluxed for an additional 8 h, cooled to rt, and hydrolysed with aqueous 10% K_2CO_3 (500 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (300 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, 500 g) with hexane – ethyl acetate (4:1) and ethyl acetate as eluents to give a mixture of (*E*)-**4** and (*Z*)-**4** as a colorless oil and **5** as a colorless solid. Recrystallization of hexane – ethyl acetate (4:1) eluents from hexane afforded (*E*)-**4** (2.28 g, 52%). The filtrate was condensed in vacuo to afford (*Z*)-**4** (1.83 g, 42%) as a colorless oil. The material obtained from the ethyl acetate eluent was recrystallized from hexane and afforded **5** (190 mg, 4%) as colorless prisms.

(*E*)-4,22-Dimethoxy[2.10]metacyclophan-1-ene ((*E*)-4)

(*E*)-**4** was obtained as colorless prisms (hexane), mp 102–103 °C. ^1H NMR ($CDCl_3$) δ: 1.46 (broad s, 12H, *CH*$_2$), 1.69 (broad s, 4H, *CH*$_2$), 2.55–2.67 (m, 4H, *CH*$_2$), 3.89 (s, 6H, O*Me*), 6.79 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.98 (dd, *J* = 2.4, 8.4 Hz, 2H, Ar–*H*), 7.30 (d, *J* = 2.4 Hz, 2H, Ar–*H*), 7.36 (s, 2H, =C*H*). ^{13}C NMR ($CDCl_3$) δ: 26.87, 28.35, 29.27, 29.99, 31.75, 55.47, 110.74, 126.62, 128.33, 128.53, 129.62, 133.41, 155.30. MS *m*/*z* (%): 378 (M^+). Anal. calcd for $C_{26}H_{34}O_2$ (378.55): C 82.49, H 9.05; found: C 82.41, H 8.99.

(*Z*)-4,22-Dimethoxy[2.10]metacyclophan-1-ene ((*Z*)-4)

(*Z*)-**4** was obtained as a colorless oil. ^1H NMR ($CDCl_3$) δ: 1.26 (m, 12H, *CH*$_2$), 1.43 (m, 4H, *CH*$_2$), 2.33–2.42 (m, 4H, *CH*$_2$), 3.69 (s, 6H, O*Me*), 6.70 (s, 2H, =C*H*), 6.76 (d, *J* = 8.4 Hz, 2H, Ar–*H*), 6.98 (dd, *J* = 2.4, 8.4 Hz, 2H, Ar–*H*), 7.03 (d, *J* = 2.4 Hz, 2H, Ar–*H*). MS *m*/*z* (%): 378 (M^+). Anal. calcd for $C_{26}H_{34}O_2$ (378.55): C 82.49, H 9.05; found: C 82.64, H 9.07.

1,2-Dihydroxy-4,22-dimethoxy[2.10]metacyclophane (5)

Compound **5** was obtained as colorless prisms (hexane), mp 116–117 °C. ^1H NMR ($CDCl_3$) δ: 1.24 (broad s, 12H, *CH*$_2$), 1.42–1.46 (m, 4H, *CH*$_2$), 2.37–2.44 (m, 4H, *CH*$_2$), 3.53 (s, 6H, O*Me*), 3.86 (d, *J* = 2.1 Hz, 2H, O*H*), 4.81 (d, *J* = 2.1 Hz, 2H, C*H*), 6.61 (d, *J* = 8.1 Hz, 2H, Ar–*H*), 6.72 (d, *J* = 2.4 Hz, 2H, Ar–*H*), 6.95 (dd, *J* = 2.4, 8.1 Hz, 2H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ: 26.3, 26.5, 29.7, 34.5, 55.2,

109.8 100.1, 127.3, 127.8, 128.1, 130.3, 155.2. MS *m/z* (%): 394 ($M^+ - H_2O$). Anal. calcd for $C_{26}H_{36}O_4$ (412.57): C 75.69, H 8.8; found: C 75.73, H 8.78.

Bromination of (*Z*)-4 with BTMA Br_3

To a solution of (*Z*)-**4** (200 mg, 0.53 mmol) in CH_2Cl_2 (20 mL) was added BTMA Br_3 (220 mg, 0.58 mmol) at rt. After the reaction mixture was stirred at rt for 5 min, it was poured into a large amount of ice water (50 mL) and extracted with CH_2Cl_2 (50 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was recrystallized from hexane and gave 228 mg (80%) of a mixture of 1-*endo*-bromo-2-*exo*-bromo-4,22-dimethoxy[2.10]metacyclophane (*rac*-**6**) and 1,2-di-*endo*-bromo-4,22-dimethoxy[2.10]-metacyclophane (*meso*-**6**) in a ratio of 55:45 as colorless prisms, mp 148–149 °C. ^{1}H NMR ($CDCl_3$) (*rac*-**6**) δ: 1.36 (broad s, 12H, *CH*$_2$), 1.45 (m, 4H, *CH*$_2$), 2.41–2.46 (m, 4H, *CH*$_2$), 3.73 (s, 3H, O*Me*), 3.78 (s, 3H, O*Me*), 5.64 (d, *J* = 10.2 Hz, 1H, *CH*), 6.60 (d, *J* = 7.8 Hz, 1H, *Ar–H*), 6.70 (d, *J* = 10.2 Hz, 1H, *CH*), 6.87–6.92 (m, 5H, Ar–*H*); *meso*-**6** δ: 1.36 (broad s, 12H, *CH*$_2$), 1.45 (m, 4H, *CH*$_2$), 2.41–2.46 (m, 4H, *CH*$_2$), 3.91 (s, 6H, O*Me*), 6.36 (s, 2H, *CH*), 6.65 (d, *J* = 7.8 Hz, 2H, *ArH*), 6.89 (dd, *J* = 1.2, 7.8 Hz, 2H, *Ar–H*), 7.08 (d, *J* = 1.2 Hz, 2H, Ar–*H*). MS *m/z* (%): 536, 538, 540 (M^+). Anal. calcd for $C_{26}H_{34}Br_2O_2$ (538.35): C 58.01, H 6.37; found: C 58.27, H 6.42.

Similar treatment of (*E*)-**4** with BTMA Br_3 under the same conditions as noted in the previous paragraph afforded a mixture of *rac*-**6** and *meso*-**6** in 91% yield in a ratio of 55:45 as colorless prisms.

Dehydrobromination of 6 with KOBu-*t*

To a solution of a mixture of *meso*- and *dl*-**6** (180 mg, 0.33 mmol) in HOBu-*t* (24 mL) was added KOBu-*t* (1.18 g, 10.5 mmol) at rt. After the reaction mixture was stirred at 80 °C for 2 h, it was poured into a large amount of ice water (50 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was recrystallized from methanol and gave 89 mg (72%) of 4,22-dimethoxy[2.10]metacyclophan-1-yne (**7**) as colorless prisms, mp 113–114 °C. IR (KBr, cm^{-1}) ν_{max}: 2899, 2866, 2830, 2050 (C≡C), 1495, 1463, 1258, 1100, 1025, 802. ^{1}H NMR ($CDCl_3$) δ: 1.41 (m, 12H, *CH*$_2$), 1.60–1.72 (m, 4H, *CH*$_2$), 2.61–2.69 (m, 4H, *CH*$_2$), 3.89 (s, 6H, O*Me*), 6.78 (d, *J* = 8.4, 2H, Ar-*H*), 7.03 (dd, *J* = 8.4, 2.1 Hz, 2H, Ar*H*), 7.39 (d, *J* = 2.1 Hz, 2H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ: 26.65, 28.31, 29.17, 29.63, 31.76, 55.76, 91.48 (*sp*-C), 110.68, 112.11, 130.15, 133.52, 134.80, 156.56. MS *m/z* (%): 376 (M^+). Anal. calcd for $C_{26}H_{32}O_2$ (376.53): C 76.06, H 8.57; found: C 82.87, H 8.50.

McMurry coupling reaction of 8

The McMurry reagent was prepared from $TiCl_4$ (11.0 mL, 100 mmol) and Zn powder (14.4 g, 220 mmol) in dry THF (300 mL), under nitrogen. A solution of 2-formyl-5-methylanisole (**8**, 5.0 g, 33.3 mmol) in dry THF (70 mL) was added within 24 h to the black mixture of the McMurry reagent by using a high-dilution technique with continuous refluxing and stirring. The reaction mixture was refluxed for additional 8 h, cooled to rt, and hydrolysed with aqueous 10% K_2CO_3 (500 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (300 mL × 3). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was treated with hexane (100 mL) to afford a colorless solid. Recrystallization from hexane afforded (*E*)-1,2-bis(2-methoxy-5-methylphenyl)ethene ((*E*)-**9**, 3.15 g, 70%) as colorless prisms, mp 123–125 °C. ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 6H, *CH*$_3$), 3.85 (s, 6H, O*Me*), 6.78 (d, *J* = 8.3 Hz, 2H, Ar–*H*), 7.02 (dd, *J* = 2.2, 8.3 Hz, 2H, Ar–*H*), 7.42 (s, 2H, =C*H*), 7.45 (d, *J* = 2.2 Hz, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$) δ: 20.6, 55.6, 110.8, 123.1, 123.3, 126.9, 128.8, 129.8, 154.7. MS *m/z* (%): 268 (M^+). Anal. calcd for $C_{18}H_{20}O_2$ (268.36): C 80.56, H 7.51; found: C 80.41, H 7.69.

Bromination of (*E*)-9 with BTMA Br_3

To a solution of (*E*)-**9** (1.0 g, 3.73 mmol) in CH_2Cl_2 (100 mL) was added BTMA Br_3 (1.74 g, 4.46 mmol) at rt. After the reaction mixture was stirred at rt for 5 min, it was poured into a large amount of ice water (300 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was treated with hexane (100 mL) to afford a colorless solid. Recrystallization from hexane afforded 1,2-bromo-1,2-bis(2-methoxy-5-methylphenyl)-ethane (**10**, 1.35 g, 84%) as colorless prisms, mp 146–148 °C. ^{1}H NMR ($CDCl_3$) δ: 2.18 (s, 6H, *CH*$_3$), 3.74 (s, 6H, O*Me*), 6.11 (s, 2H, *CH*), 6.52 (d, *J* = 8.1 Hz, 2H, Ar–*H*), 7.12 (dd, *J* = 2.0, 8.1 Hz, 2H, Ar–*H*), 7.38 (d, *J* = 2.0 Hz, 2H, Ar–*H*). MS *m/z* (%): 426, 428, 430 (M^+). Anal. calcd for $C_{18}H_{20}Br_2O_2$ (428.17): C 50.61, H 4.76; found: C 50.49, H 4.71.

Dehydrobromination of 10 with KOBu-*t*

To a solution of a mixture of **10** (680 mg, 1.59 mmol) in HOBu-*t* (68 mL) was added KOBu-*t* (1.78 g, 15.9 mmol) at rt. After the reaction mixture was stirred at 80 °C for 24 h, it was poured into a large amount of ice water (50 mL) and extracted with CH_2Cl_2 (100 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, 500 g) with hexane as eluents to give a colorless solid. Recrystallization from hexane afforded 1,2-bis(2-methoxy-5-methylphenyl)ethyne (**11**, 223 mg, 53%) as colorless prisms, mp 114–115 °C. ^{1}H NMR ($CDCl_3$) δ: 2.28 (6H, s, *CH*$_3$), 3.89 (s, 6H, O*Me*), 6.78 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.07 (dd, *J* = 2.4, 8.4 Hz, 2H, Ar–*H*), 7.33 (d, *J* = 2.2 Hz, 2H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ: 20.27, 56.04, 89.69 (*sp*-C), 110.6, 112.46, 129.60, 130.04, 133.96, 157.86. MS *m/z* (%): 266 (M^+). Anal. calcd for $C_{18}H_{18}O_2$ (266.34): C 81.17, H 6.81; found: C 81.03, H 6.92.

Reaction of 7 with BBr_3

To a solution of **7** (60 mg, 0.16 mmol) in CH_2Cl_2 (6 mL) at 0 °C was gradually added a solution of BBr_3 (0.087 mL, 0.922 mmol) in (0.1 mL). After the reaction mixture was stirred at rt for 0.5 h, it was poured into ice water (10 mL) and then extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were washed with water (10 mL × 2), dried over Na_2SO_4, and concentrated in vacuo to leave a residue. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane–$CHCl_3$ (4:1) as eluent to give crude **13** as a colorless solid. Recrystallization from EtOH gave

[10](2,9)-5a,11a-benzofuro-5a-bora-11-bromochromenophane (**13**, 58 mg, 83%) as colorless prisms, mp 207–208 °C. IR (KBr, cm^{-1}) ν_{max}: 2900, 2354, 1539, 1502, 1454. ^1H NMR ($CDCl_3$) δ: 1.27–1.35 (m, 12H, CH_2), 1.60 (s, 4H, CH_2), 2.64–2.67 (m, 2H, CH_2), 2.76–2.79 (m, 2H, CH_2), 6.84 (d, J = 8.4, 1H, Ar–*H*), 6.86 (d, J = 2.4 Hz, 1H, Ar–*H*), 7.01 (dd, J = 2.4, 8.4 Hz, 1H, Ar–*H*), 7.18 (d, J = 8.4 Hz, 1H, Ar–*H*), 7.23 (dd, J = 1.2, 8.4 Hz, 1H, Ar–*H*), 7.95 (d, J = 1.2 Hz, 1H, Ar*H*). MS *m*/*z* (%): 435, 437 (M^+). Anal. calcd for $C_{24}H_{26}BBrO_2$ (437.19): C 65.94, H 5.99; found: C 65.63, H 6.06.

Reaction of 6 with BBr_3

To a solution of **6** (60 mg, 0.11 mmol) in CH_2Cl_2 (6 mL) at 0 °C was gradually added a solution of BBr_3 (0.087 mL, 0.922 mmol) in CH_2Cl_2 (0.1 mL). After the reaction mixture was stirred at rt for 0.5 h, it was poured into ice water (10 mL) and then extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were washed with water (10 mL × 2), dried over Na_2SO_4, and concentrated in vacuo to leave a residue. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane–$CHCl_3$ (4:1) as eluent to give crude **15** as a colorless solid. Recrystallization from EtOH gave *cis*-4b,9b-dihydro[10]benzofuro[3,2-*b*]benzofuranophane (**15**, 32 mg, 83%) as colorless prisms, mp 163–164 °C. ^1H NMR ($CDCl_3$) δ: 0.25–1.26 (m, 16H, CH_2), 2.58–2.64 (m, 4H, CH_2), 6.08 (s, 2H, C*H*), 6.99 (dd, J = 8.1, 2.4 Hz, 2H, Ar–*H*), 7.00 (d, J = 8.1 Hz, 2H, Ar–*H*), 7.42 (d, J = 2.4 Hz, 2H, Ar–*H*). MS *m*/*z* (%): 348 (M^+). Anal. calcd for $C_{24}H_{28}O_2$ (348.49): C 82.72, H 8.10; found: C 82.63, H 8.03.

Crystallographic data for (*E*)-4 and 7

Crystal data for (E)-4

$C_{26}H_{34}O_2$, M = 378.55, monoclinic, $P121/a$, a = 17.192(7), b = 6.489(3), c = 39.947(17) Å, V = 4357(3) $Å^3$, β = 102.1256(11), Z = 8, D_c = 1.154 g cm^{-3}, μ (Mo Kα) = 0.071 mm^{-1}, T = 123.1 K, colourless prisms; 9519 reflections measured on a Rigaku Saturn CCD diffractometer, of which 6779 were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.849 and 0.998) and Lp effects, R_{int} = 0.087, structure solved by direct methods (Sir2002), F^2 refinement, R_1 = 0.156 for 6779 data with $F^2 > 2s(F^2)$, wR_2 = 0.4034 for all data, 8360 parameters.

Crystal data for 7

$C_{26}H_{32}O_2$, M = 376.52, monoclinic, $P21/a$, a = 16.7234(14), b = 6.422(4), c = 41.504(9) Å, V = 4370(3) $Å^3$, β = 101.363(14), Z = 8, D_c = 1.145 g cm^{-3}, μ (Cu Kα) = 0.543 mm^{-1}, T = 113 K, colourless prisms; 53 123 reflections measured on a Rigaku Saturn CCD diffractometer, of which 7933 were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.750 and 0.947) and Lp effects, R_{int} = 0.044, structure solved by direct methods (Sir2002), F^2 refinement, R_1 = 0.0577 for 7933 data with $F^2 > 2s(F^2)$, wR_2 = 0.1814 for all data, 569 parameters (crystallographic data (excluding structure factors) for the structures in this paper can be found in the Supplementary data).

Supplementary data

Supplementary data are available with the article through the journal Web site http://nrcresearchpress.com/doi/suppl/10.1139/v2012-014. CCDC 779075 and 819676 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 144 1223 33603; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

This work was performed under the Cooperative Research Program of the Network Joint Research Center for Materials and Devices, Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Japan.

References

(1) Keehn, P. M., Rosenfield, S. M. Eds. *Cyclophanes;* Academic Press: New York, 1983; Vol. 1, Chapter 6, pp 428.
(2) Vögtle, F. *Cyclophane Chemistry;* Wiley: Chichester, UK, 1993.
(3) Gleiter, R.; Hopf, H. *Modern Cyclophane Chemistry;* Wiley-VCH, Weinheim, Germany, 2004.
(4) (a) Psiorz, M.; Hopf, H. *Angew. Chem.* **1982**, *21* (8), 623. doi:10.1002/anie.198206231; (b) Psiorz, M.; Hopf, H. *Angew. Chem. Int. Ed. Engl.* **1982**, *21* (8), 623. doi:10.1002/anie.198206231.
(5) (a) Reiser, O.; Reichow, S.; de Meijere, A. *Angew. Chem.* **1987**, *99* (12), 1285. doi:10.1002/ange.19870991213; (b) Reiser, O.; Reichow, S.; de Meijere, A. *Angew. Chem. Int. Ed. Engl.* **1987**, *26* (12), 1277. doi:10.1002/anie.198712771.
(6) (a) Wong, T.; Cheung, S. S.; Wong, H. N. C. *Angew. Chem.* **1988**, *100* (5), 716. doi:10.1002/ange.19881000516; (b) Wong, T.; Cheung, S. S.; Wong, H. N. C. *Angew. Chem. Int. Ed. Engl.* **1988**, *27* (5), 705. doi:10.1002/anie.198807051.
(7) (a) König, B.; Heinze, J.; Meerholz, K.; de Meijere, A. *Angew. Chem.* **1991**, *103* (10), 1350. doi:10.1002/ange.19911031017; (b) König, B.; Heinze, J.; Meerholz, K.; de Meijere, A. *Angew. Chem. Int. Ed. Engl.* **1991**, *30* (10), 1361. doi:10.1002/anie.199113611.
(8) Chan, C. W.; Wong, H. C. *J. Am. Chem. Soc.* **1988**, *110* (2), 462. doi:10.1021/ja00210a025.
(9) Ramming, M.; Gleiter, R. *J. Org. Chem.* **1997**, *62* (17), 5821. doi:10.1021/jo970327r.
(10) Kawase, T.; Ueda, N.; Oda, M. *Tetrahedron Lett.* **1997**, *38* (38), 6681. doi:10.1016/S0040-4039(97)01564-5.
(11) Utsumi, K.; Kawase, T.; Oda, M. *Chem. Lett.* **2003**, *32* (4), 412. doi:10.1246/cl.2003.412.
(12) Kawase, T. *Synlett* **2007**, *2007* (17), 2609. doi:10.1055/s-2007-991078.
(13) Yamato, T.; Fujita, K.; Abe, T.; Tsuzuki, H. *New J. Chem.* **2001**, *25* (5), 728. doi:10.1039/b010205i.
(14) Fukazawa, A.; Yamaguchi, S. *Chem. Asian J.* **2009**, *4* (9), 1386. doi:10.1002/asia.200900179.
(15) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2008**, *47* (30), 5582. doi:10.1002/anie.200801834.
(16) Wakamiya, A.; Mori, K.; Araki, T.; Yamaguchi, S. *J. Am. Chem. Soc.* **2009**, *131* (31), 10850. doi:10.1021/ja905007s.
(17) Fukazawa, A.; Yamada, H.; Sasaki, Y.; Akiyama, S.;

Yamaguchi, S. *Chem. Asian J.* **2010**, *5* (3), 466. doi:10.1002/asia.200900517.
(18) Iida, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2011**, *133* (18), 6952. doi:10.1021/ja2019977.
(19) Yamato, T.; Matsumoto, J.-I.; Ide, S.; Suehiro, K.; Kobayashi, K.; Tashiro, M. *Chem. Ber.* **1993**, *126* (2), 447. doi:10.1002/cber.19931260223.
(20) (a) Yamato, T.; Sato, M.; Noda, K.; Matsumoto, J.; Tashiro, M. *J. Chem. Res. (S)* **1993**, *10*, 394; (b) Yamato, T.; Sato, M.; Noda, K.; Matsumoto, J.; Tashiro, M. *J. Chem. Res. (M)* **1993**, *10*, 2601.
(21) Yamato, T.; Matsumoto, J.; Ide, S.; Tokuhisa, K.; Suehiro, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57* (19), 5243. doi:10.1021/jo00045a044.
(22) Yamato, T.; Matsumoto, J.-I.; Tokuhisa, K.; Kajihara, M.; Suehiro, K.; Tashiro, M. *Chem. Ber.* **1992**, *125* (11), 2443. doi:10.1002/cber.19921251116.
(23) Yamato, T.; Matsumoto, J.; Sato, M.; Noda, K.; Tashiro, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, (10): 1299. doi:10.1039/p19950001299.
(24) Yamato, T.; Matsumoto, J.; Fujita, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, (1): 123. doi:10.1039/a704105e.
(25) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43* (17), 3255. doi:10.1021/jo00411a002.
(26) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16* (11), 405. doi:10.1021/ar00095a003.
(27) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schaefer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106* (17), 5018. doi:10.1021/ja00329a071.
(28) McMurry, J. E. *Chem. Rev.* **1989**, *89* (7), 1513. doi:10.1021/cr00097a007.
(29) Mitchell, R. H.; Weerawarna, S. A. *Tetrahedron Lett.* **1986**, *27* (4), 453. doi:10.1016/S0040-4039(00)85503-3.
(30) Tanner, D.; Wennerström, O.; Chattopadhyaya, J.; Carlberg, G. E.; Sterner, O.; Wickberg, B. *Acta Chem. Scand. Ser. B.* **1983**, *37b*, 693. doi:10.3891/acta.chem.scand.37b-0693.
(31) Hopf, H.; Mlynek, C. *J. Org. Chem.* **1990**, *55* (4), 1361. doi:10.1021/jo00291a052.
(32) Grützmacher, H.-F.; Neumann, E. *Chem. Ber.* **1993**, *126* (6), 1495. doi:10.1002/cber.19931260635.
(33) Shukla, R.; Brody, D. M.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2006**, *71* (16), 6124. doi:10.1021/jo060817w.
(34) Debroy, P.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2009**, *74* (5), 2080. doi:10.1021/jo802579f.
(35) Yamato, T.; Matsumoto, J.; Ide, S.; Suehiro, K.; Tashiro, M. *J. Chem. Res. (S)* **1993**, 394.
(36) Yamato, T.; Fujita, K.; Okuyama, K.; Tsuzuki, H. *New J. Chem.* **2000**, *24* (4), 221. doi:10.1039/b001145m.
(37) Yamato, T.; Fujita, K.; Futatsuki, K.; Tsuzuki, H. *Can. J. Chem.* **2000**, *78* (8), 1089. doi:10.1139/v00-110.
(38) Yamato, T.; Fujita, K.; Tsuzuki, H. *J. Chem. Soc., Perkin Trans. 1* **2001**, (17): 2089. doi:10.1039/b010075g.
(39) Yamato, T.; Miyamoto, S.; Hironaka, T.; Miura, Y. *Org. Lett.* **2005**, *7* (1), 3. doi:10.1021/ol0483403.
(40) Yamato, T.; Hironaka, T.; Shiino, M.; Saisyo, T.; Miyamoto, S. *J. Chem. Res.* **2006**, *2006* (2), 110. doi:10.3184/030823406776330990.
(41) Yamato, T.; Okabe, R.; Miyamoto, S.; Miyazaki, M. *J. Chem. Res.* **2006**, *2006* (9), 593. doi:10.3184/030823406778521509.
(42) Saisyo, T.; Hironaka, T.; Shiino, M.; Yamato, T. *J. Chem. Res.* **2006**, *2006* (10), 661. doi:10.3184/030823406779173659.
(43) Saisyo, T.; Shiino, M.; Shimizu, T.; Paudel, A.; Yamato, T. *J. Chem. Res.* **2008**, *2008* (8), 479. doi:10.3184/030823408X338701.
(44) Merz, A.; Karl, A.; Futterer, T.; Stacherdinger, N.; Schneider, O.; Lex, J.; Luboch, E.; Biernat, J. F. *Liebigs Ann. Chem.* **1994**, *1994* (12), 1199. doi:10.1002/jlac.199419941211.
(45) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46* (22), 4556. doi:10.1021/jo00335a047.
(46) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1983**, *48* (9), 1461. doi:10.1021/jo00157a015.
(47) Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Chem. Lett.* **1987**, *16* (4), 627. doi:10.1246/cl.1987.627.
(48) (a) Kloster-Jensen, E.; Wirz, J. *Angew. Chem.* **1973**, *85* (16), 723. doi:10.1002/ange.19730851608;; (b) Kloster-Jensen, E.; Wirz, J. *Angew. Chem. Int. Ed. Engl.* **1973**, *12* (8), 671. doi:10.1002/anie.197306711.
(49) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44* (8), 1247. doi:10.1021/jo01322a012.
(50) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, *1979* (01), 61. doi:10.1055/s-1979-28558.
(51) Yamato, T.; Matsumoto, J.; Tashiro, M. *J. Chem. Res.* **1994**, 178.
(52) Yamato, T.; Saruwatari, Y.; Yasumatsu, M.; Ide, S. *Eur. J. Org. Chem.* **1998**, *1998* (2), 309. doi:10.1002/(SICI)1099-0690(199802)1998:2<309::AID-EJOC309>3.0.CO;2-6.