Medium-sized cyclophanes. Part 53.[1] Synthesis and conformational studies, and photoinduced cyclization of *syn*-[n.2]metacyclophanenes

Takehiko Yamato, Koji Fujita, Keigo Futatsuki, and Hirohisa Tsuzuki

Abstract: A series of [n.2]metacyclophanenes (**3**) and (**6**) were prepared in good yields by a McMurry cyclization of 1,n-bis(3-acetyl-4-methoxyphenyl)alkanes (**2**) and 1,3-bis(3-formyl-4-methoxyphenyl)propane (**5**), respectively. Compounds **3b**, **3c** exist in the *syn*-conformation due to the steric repulsion between the methyl groups at the ethano bridge and the methoxy groups at the aromatic rings while compound **6** prefers the *anti*-conformation typical of [3.2]metacyclophanes. The assignment of *syn*-conformations has been confirmed by ^{1}H NMR analyses and X-ray diffraction studies. Photoinduced transannular cyclization of [n.2]metacyclophanenes (**3**) and (**6**) in the presence of iodine as an oxidant afforded phenanthrene-anellated polycyclic aromatic hydrocarbons. Apparently, the rate of the photocyclization of *anti*-**6** was found to be much faster than that of *syn*-**3b** and almost completed within 1 h. Thus, the different reactivities for the irradiation of *syn*- and *anti*-conformer were observed. The reason for the present preference for the formation of *trans*-dihydrophenanthrene rather than *cis*-dihydrophenanthrene as the intermediate might be attributable to the more stable chair form transition state than boat one and the conformational fixation to the chair form in the ground and transition state is possible in the *anti*-conformer.

Key words: cyclophanes, strained molecule, McMurry reaction, C—C coupling, conformation analysis, cyclizations, photolysis, transannular reactions, transition states.

Résumé : Faisant appel à une réaction de cyclisation de McMurry des 1,n-bis(3-acétyl-4-méthoxyphényl)alcanes (**2**) et 1,3-bis(3-formyl-4-méthoxyphényl)propane (**5**) respectivement, on a préparé une série de [n,2]métacyclophanènes (**3**) et (**6**). Les composés **3b** et **3c** existent dans la conformation syn en raison de la répulsion stérique entre les groupes méthyles du pont éthano et les groupes méthoxy des noyaux aromatiques alors que le composé **6** adopte la conformation anti des [3,2]métacyclophanes. L'attribution des conformations *syn* a été confirmée par des analyses de RMN du ^{1}H et des études de diffraction des rayons X. La cyclisation transannulaire photoinduite des [n,2]métacyclophanènes (**3**) et (**6**) en présence d'iode, utilisé comme antioxydant, conduit à des hydrocarbures aromatiques polycycliques du type phénanthrène avec annellation. Apparemment, la vitesse de photocyclisation du produit *anti*-**6** est beaucoup plus rapide que celle du *syn*-**3b** et elle est pratiquement complète en une heure. Ainsi, on a pu observer des réactivités différentes pour l'irradiation des conformères *syn* et *anti*. La raison de la formation observée d'une préférence pour la formation comme intermédiaire du *trans*-dihydrophénanthrène plutôt que du *cis*-dihydrophénanthrène pourrait être attribuée à l'état de transition en forme chaise qui est plus stable que celui en forme bateau ainsi que le fait que la conformation des états tant fondamental que de transition du conformère *anti* peut être fixée à la forme chaise.

Mots clés : cyclophanes, molécule tendue, réaction de McMurry, couplage C—C, analyse conformationnelle, photolyse, réactions transannulaires, états de transition.

[Traduit par la Rédaction]

Introduction

Although the parent [2.2]metacyclophane (MCP = metacyclophane) was first reported as early as 1899 by Pelligrin (2), the synthesis of *syn*-[2.2]MCP was not realized until 85 years later. Mitchell et al. (3) have successfully prepared *syn*-[2.2]MCP at low temperature by using (arene)chromiumcarbonyl complexation to control the stereochemistry. Later, Itô and co-workers (4) also isolated and characterized *syn*-[2.2]MCP without complexation. However, *syn*-[2.2]MCP isomerizes readily to the *anti*-isomer above 0°C. On the other hand, Mitchell and Boekelheide (5) and Staab

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et al. (6) succeeded in synthesizing intraannularly substituted *syn*-[2.2]MCPs, respectively. However, reports on synthesis and reactions of *syn*-[n.2]MCP-ene have not been published so far.

In cyclophane chemistry, the reductive coupling of carbonyl compounds by low-valent titanium, the McMurry reaction (7), has been used before by Mitchell and Weerawana (8) to synthesize cyclophanes with glycol units as bridges, by Tanner and Wennerström (9), and recently by Hopf and Mlynek (10) and Grützmacher et al. (11) for a cyclization of suitable dialdehydes to yield unsaturated cyclophanes.

In this paper, we report on the syntheses of *syn*- and *anti*-[n.2]MCP-enes using the low-valent titanium induced McMurry reaction and photoinduced transannular cyclization reaction to afford phenanthrene-anellated polycyclic aromatic hydrocarbons.

Results and discussion

1,2-Bis(4-methoxyphenyl)ethane (**1a**) has been prepared according our previous paper (12). The cross coupling reactions (13) of 4-methoxyphenylmagnesium bromide with 1,3-dibromopropane and 1,4-dibromobutane have been carried out in the presence of cuprous bromide as a catalyst in a mixture of hexamethylphosphoric triamide (HMPA) and tetrahydrofuran at reflux temperature to give the desired 1,3-bis(4-methoxyphenyl)propane (**1b**) and 1,4-bis(4-methoxyphenyl)butane (**1c)** in satisfactory yields. Although the $AlCl_3$–$MeNO_2$-catalyzed acetylation of compound **1a** with acetyl chloride at 20°C led to complete diacylation, a mixture of the desired 1,2-bis(3-acetyl-4-methoxyphenyl)ethane (**2a)** and other isomers was obtained. The desired product **2a** was isolated in pure by the fractional recrystallization from hexane–benzene (1:1) in 29% yield. In contrast, the $AlCl_3$–$MeNO_2$-catalyzed acetylation of compounds **1b** and **1c** with acetic anhydride or acetyl chloride at 20°C led to regioselective acylation at the meta positions of the 1,n-diphenylalkanes affording the desired 1,n-bis(3-acetyl-4-methoxyphenyl)alkanes (**2b**) and (**2c**) in good yields.

1,2-Bis(3-acetyl-4-methoxyphenyl)ethane **(2a**) was subjected to reductive coupling by the McMurry reaction (7) following the Grützmacher's procedure (11) (Scheme 1). Although none of the desired [2.2]MCP-1-ene (**3a**) was observed, the dimer **4a** was obtained in 19% yield. This finding seems to be due to the much more strained structure of **3a** than dimer **4a** during the formation of the unsaturated C=C linkage. Although several cyclizations of **2a** were attempted under the various reaction conditions, no formation of the desired **3a** was observed, with only dimer **4a** being obtained. Thus, during the McMurry reaction the intramolecular cyclization to afford **3a** might be quite difficult.

The structure of product dimer **4a** was determined on the basis of its elemental analysis and spectral data. The mass spectral data for dimer **4a** (M^+ m/z = 588) strongly supports cyclic dimeric structure. In the ^1H NMR spectrum of tetramethoxyMCP **4a**, methyl protons, methoxy protons, ArCH_2CH_2Ar methylene protons, and the ArC*H*=C*H*Ar olefinic protons each appear as a singlet at 27°C. This behavior indicates that the rate of conformational ring flipping of macrocycle **4a** is faster than the NMR time scale above this temperature. However, in dimer **4a** even at –60°C in

Scheme 1.

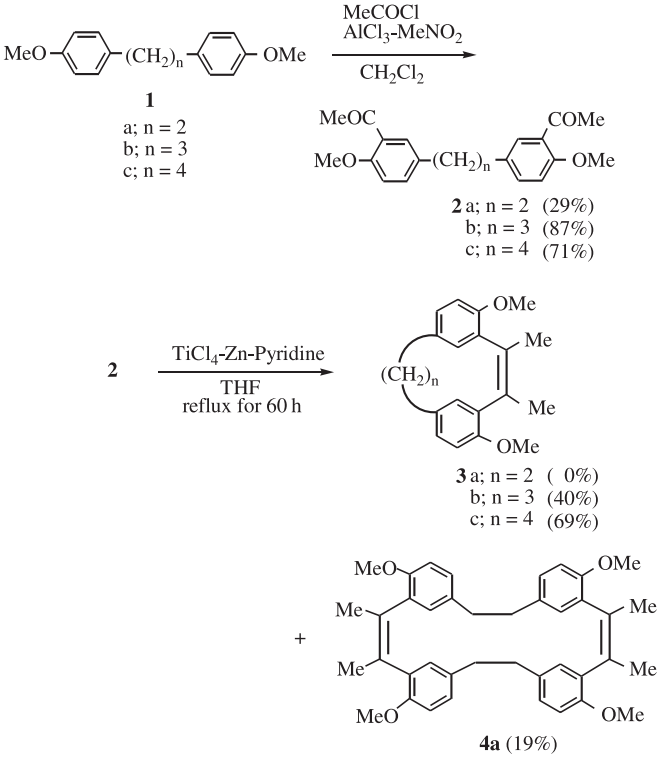
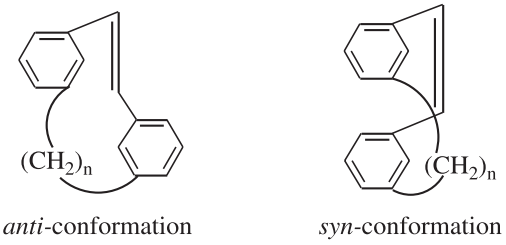


Fig. 1. Possible conformations of [n.2]metacyclophan-1-enes.

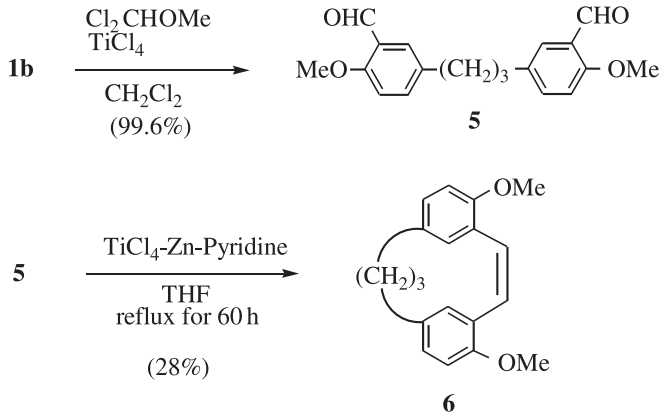


$CDCl_3$–CS_2 (1:3) the singlet signal of the ArCH_2CH_2Ar ethylene protons and the ArC*H*=C*H*Ar olefinic protons both remain unsplit. These observations indicate the flexible structure of **4a** similar to that of the saturated [2_4]MCP (14) in spite of the introduction of two additional double bonds of the ethylene bridge.

Similarly, 1,n-bis(3-acetyl-4-methoxyphenyl)alkanes (**2b**) and **2c** were subjected to reductive coupling by the McMurry reaction (Scheme 1). Novel [n.2]MCP-enes (**3b**) and (**3c**) have been prepared in 40% and 69% yields.

[n.2]MCP-enes adopt either a "staircase" *anti*-conformation or a *syn*-conformation with overlaying aromatic rings (15) (Fig. 1). Depending on the size of the bridges (16) and on the presence of intraannular substituents (17), the interconversion between the *syn*- and *anti*-conformers occur by ring flipping. ^1H NMR spectrum of **3b** showed the doublet of the intraannular proton H_i at δ = 6.95 (J = 2.0 Hz) apart from at δ = 6.33 and 6.60 of the other two protons at the aromatic rings. The methyl protons at the bridged double bond and methoxy protons were observed as a singlet at δ = 2.18 and 3.59, and the protons of the trimethylene bridge generate a complicated signal pattern as expected for a rigid

Scheme 2.



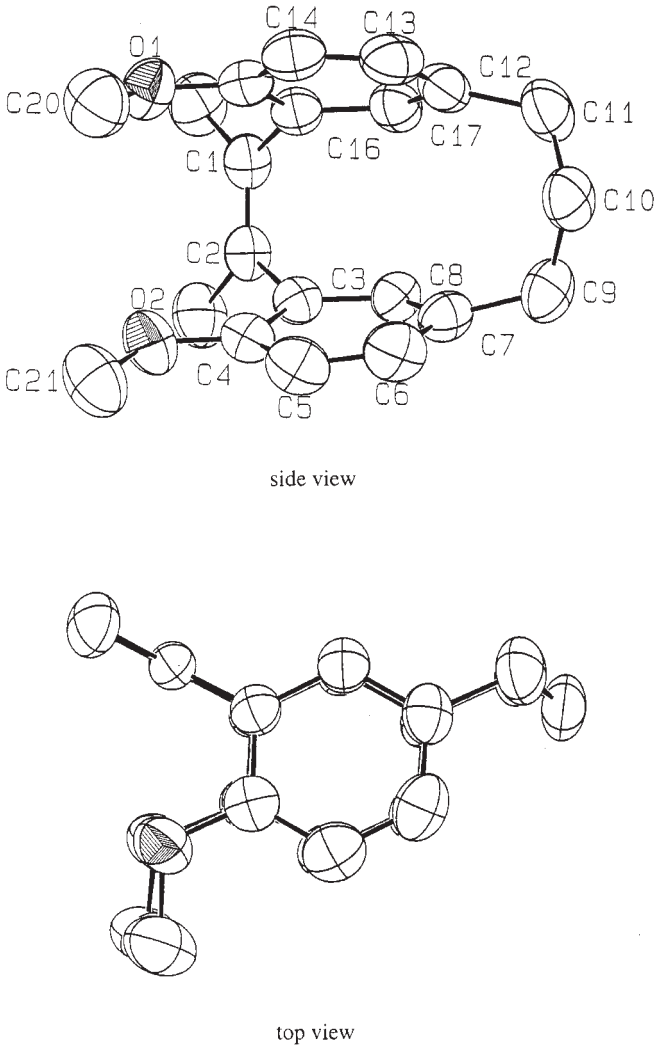
syn-[3.2]MCP-10-ene. The protons of the benzylic CH_2 group were observed as two multiplets centered at $\delta = 2.58$ and 2.91 which are further split by coupling with the protons of the central CH_2 group. This central CH_2 group was also observed as two multiplets centered at $\delta = 1.28$ and 2.18. This peak pattern ascribed to six chemically distinct protons of the propano bridge proves the absence of a *syn–syn* interconversion which would exchange H_A and H_B of each CH_2 group. Interestingly, similar findings were also observed in *syn*-[4.2]MCP-11-ene (*syn*-**3c**) in spite of being expected to be more flexible structure attributable to the larger cyclophane ring size. These observations suggest that the introduction of a double dond of the ethylene bridge as well as the substituents such as methyl groups and methoxy groups might control the *syn*- and *anti*-conformation of [n.2]MCP-enes (**3**).

To study the conformation of [n.2]MCP-enes **3** in more detail, we have investigated the conformation of the corresponding [3.2]MCP-10-ene **6**, which was prepared in 28% yield by the McMurry cyclization of 1,3-bis(3-formyl-4-methoxyphenyl)propane (**5**) under the same reaction conditions like *syn*-**3b** (Scheme 2).

Interestingly, in contrast to **3**, the doublet of H_i at $\delta = 6.05$ ($J = 2.4$ Hz) in the ^{1}H NMR spectrum of **6** shows clearly that **6** adopts a staircase *anti*-conformation as known for other [3.2]MCP-10-enes (11*a*, 11*b*) and [3.2]MCPs (13*c*, 15, 16). In addition, the protons of the trimethylene bridge give rise to two multiplets centered at $\delta = 2.35$ and 1.84, respectively, providing a fast interconversion of the two anti conformations of **6** by ring flipping. However, as the temperature of the solution in $CDCl_3$–CS_2 (1:3) is decreased, a single peak of the benzyl protons splits into a pair of doublets below 0°C. The energy barrier to the conformational ring flipping estimated from the coalescence temperature (T_c) is 12.4 kcal mol^{-1}. This finding indicates more flexible structure of **6** than that of *syn*-**3b** in spite of the same ring size.

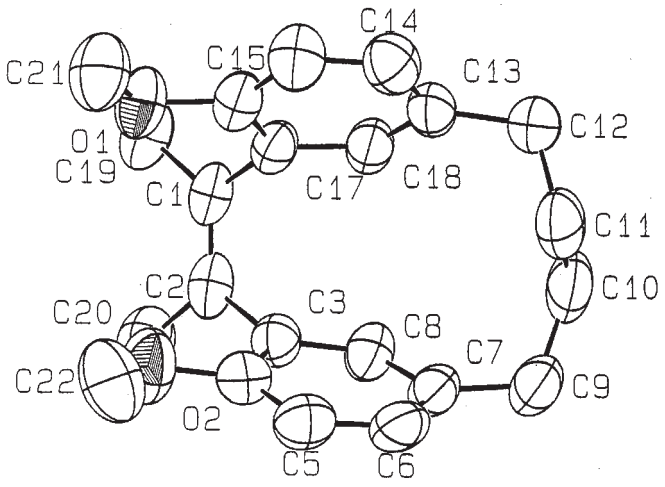
Usually, the parent [3.2]MCPs in which intraannular substituents are absent, preferably adopt an *anti*-conformation (15, 16). However, in the case of the MCP **3b** the *syn*-conformation is induced by substituents at the ethano bridge. The substituent effect on the preferred conformation (18) and the different molecule flexibility of **3b** and **6** can be attributed to the van der Waals repulsion between the four methyl groups in **3b**. In the *anti*-conformation of [3.2]MCP-10-ene (**6**) the twisted ethano bridge tends to flatten the staircase structure to release the local strain. However, this flattening is especially opposed by the two methoxy groups in the extraannular position 7 and 13 and the two methyl groups in the bridge position 10 and 11 of **3b**. This effect is absent in the *syn*-conformation and, as a consequence, **3b** favors this *syn*-conformation. The conformation of *syn*-**3b** and *syn*-**3c** has also been confirmed by X-ray crystallographic analysis.

Fig. 2. ORTEP drawing of *syn*-7,13-dimethoxy-10,11-dimethyl-[3.2]MCP-10-ene (*syn*-**3b**). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

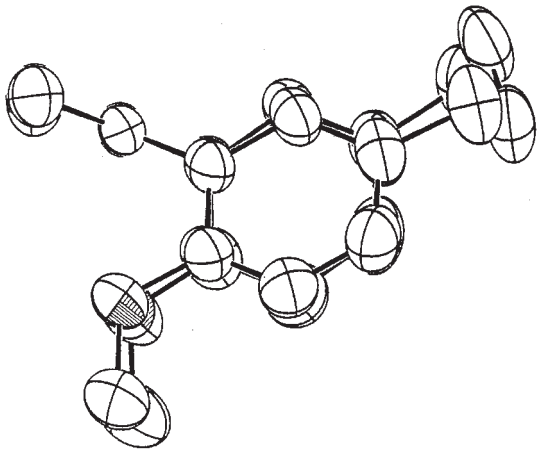


Single colorless crystals of the *syn*-**3b** and *syn*-**3c** suitable for X-ray crystallography were both obtained by recrystallization from methanol–chloroform (1:1). The perspective ORTEP drawings of the *syn*-**3b** and *syn*-**3c** are illustrated in Figs. 2 and 3, with the atom numbering system. Both compounds crystallized in the same monoclinic space group $P2_1/a$. The X-ray crystallography clearly reveals that both conformations of the *syn*-**3b** and *syn*-**3c** adopt the *syn*-form in which two aromatic rings face each other. Two aromatic rings of the *syn*-**3b** and *syn*-**3c**, which deviate from planarity to some extent, locate like an half-open bivalve

Fig. 3. ORTEP drawing of *syn*-8,14-dimethoxy-11,12-dimethyl-[4.2]MCP-11-ene (*syn*-**3c**). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.



side view



top view

using the C(3), C(7), C(12), and C(16) and C(3), C(7), C(13), and C(17) carbons as roots, respectively, to avoid π-electronic repulsion as shown in the side view of the ORTEP drawing. Although the double bond lengths between C(1)-C(2) in the *syn*-**3b** and *syn*-**3c** are reasonable, 1.332 and 1.354 Å, respectively, these compounds have quite different conformations of the two aromatic rings due to the different methylene chain length.

In the *syn*-**3b**, two aromatic rings distort like a boat shape and deviate from planarity to some extent. The C(4), C(7), C(12), and C(15) carbons are out of the C(3)-C(5)-C(6)-C(8) and C(13)-C(14)-C(16)-C(17) planes. The dihedral angles of the C(3)-C(5)-C(6)-C(8) plane between the C(3)-C(4)-C(5) and C(6)-C(7)-C(8) planes, and those of the C(13)-C(14)-C(16)-C(17) plane between the C(14)-C(15)-C(16) and C(12)-C(13)-C(17) planes are 1.77°, 4.52°, 1.53°, and 5.54°, respectively, showing that the aromatic rings in the *syn*-**3b** adopts unsymmetrically strained structure and the rigid ethylene chain against the flexible methylene chains might loose the strain. Furthermore, the intramolecular distances of C(3)-C(16), C(4)-C(15), C(5)-C(14), C(6)-C(13), C(7)-C(12), C(8)-C(17) are 2.745, 3.688, 4.493, 4.229, 3.318, and 2.764 Å, and the dihedral angle between the C(3)-C(5)-C(6)-C(8) and C(13)-C(14)-C(16)-C(17) planes is 39.88°. These clearly show that two aromatic rings in the *syn*-**3b** do not adopt parallel conformation to avoid an electrostatic interaction.

Two aromatic rings in the *syn*-**3c** also strain like a boat shape as well as those in the *syn*-**3b** and the carbons, C(4), C(7), C(13), and C(16) are remote from the C(3)-C(5)-C(6)-C(8) and C(14)-C(15)-C(17)-C(18) planes. The dihedral angles of the C(3)-C(5)-C(6)-C(8) plane between the C(3)-C(4)-C(5) and C(6)-C(7)-C(8) planes, and those of the C(14)-C(15)-C(17)-C(18) plane between the C(15)-C(16)-C(17) and C(13)-C(14)-C(18) planes are 1.76°, 3.85°, 1.65°, and 3.99°, respectively. The fact that the dihedral angles on the side of the methylene chains are somewhat smaller than the corresponding ones in the *syn*-**3b** might be attributed to the cancel of strain to some extent because of lengthening the methylene chains.

Interestingly, the intramolecular distances of C(3)-C(17), C(4)-C(16), C(5)-C(15), C(6)-C(14), C(7)-C(13), and C(8)-C(18) in the *syn*-**3c** are 2.842, 4.060, 5.336, 5.323, 4.135, and 3.038 Å, which are much longer than those of the corresponding carbons in the *syn*-**3b**. The dihedral angle between the C(3)-C(5)-C(6)-C(8) and C(14)-C(15)-C(17)-C(18) planes is 59.53°, which is ca. 20° larger than the appropriate dihedral angle in the *syn*-**3b**. These indicate that two aromatic rings in the *syn*-**3c** might tilt to a greater extent than those in the *syn*-**3b**, since the methylene chain length of the *syn*-**3c** is longer than that of the *syn*-**3b** and the rings are easy to avoid an electronic repulsion.

The substituents effect on the conformation was observed, for example, in 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene and its congeners which adopt their stable crown conformation, evidenced, in ^{1}H NMR spectra, by the characteristic AX quartet of the methylene bridges (19). Destabilization of the crown may arise from steric hindrance created either by geminal substitution of one methylene group (20) or by the presence of bulky substituents (21) such as a bromine atom or an allyl group at the aromatic positions *ortho* to the nine-membered ring except a methoxy group (21*d*, 21*e*).

In the present system, the similar substituents effect like 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene might be also observed. To elucidate this, we have converted the methoxy group in *syn*-**3b** to hydroxy group by demethylation of *syn*-**3b** with boron tribromide (22). The desired diol **7b** was obtained in 44% yield. Similarly, dihydroxy[4.2]MCP-11-ene (**7c**) was obtained in 53% yield. Interestingly, the bridged double bond was stable in the acidic media quite differnt from the results obtained from the *anti*-[2.2]MCP-enes, in which the transannular cyclization reactions occur to afford the corresponding 4,5-dihydropyrenes under the acidic conditions (23). Furthermore, no *syn*- to *anti*-ring inversion occurred during the demethylation. The ^{1}H NMR spectra for *syn*-**7b** and *syn*-**7c** (in $CDCl_3$) show signals for the hydroxy groups at δ 5.29 and 5.15, respectively. It is well known that the stretching vibration of the OH groups at low frequency

Table 1. Conformational analysis of [n.2]MCP-enes **3**, **6**, and [n.2]MCPs **8**.

Compd	Number of methylene units (n)	Temp (°C)	^{1}H NMR (δ)[a] aromatic protons		Assignment
			H_i[b]	H_o[c]	
3b	3	27	6.95	6.33, 6.60	*syn*
3c	4	–40	6.93	6.41, 6.64	*syn*
6	3	–40	6.05	6.77, 6.97	*anti*
8b	3	27	4.87, 5.24	6.78, 6.97	*anti*
8c	4	–30	5.61, 5.92	6.77, 6.90	*anti*

[a]Determined in $CDCl_3$ at room temp by using $SiMe_4$ as a reference and expressed in ppm.

[b]H_i refers to internal protons.

[c]H_o refers to outer protons.

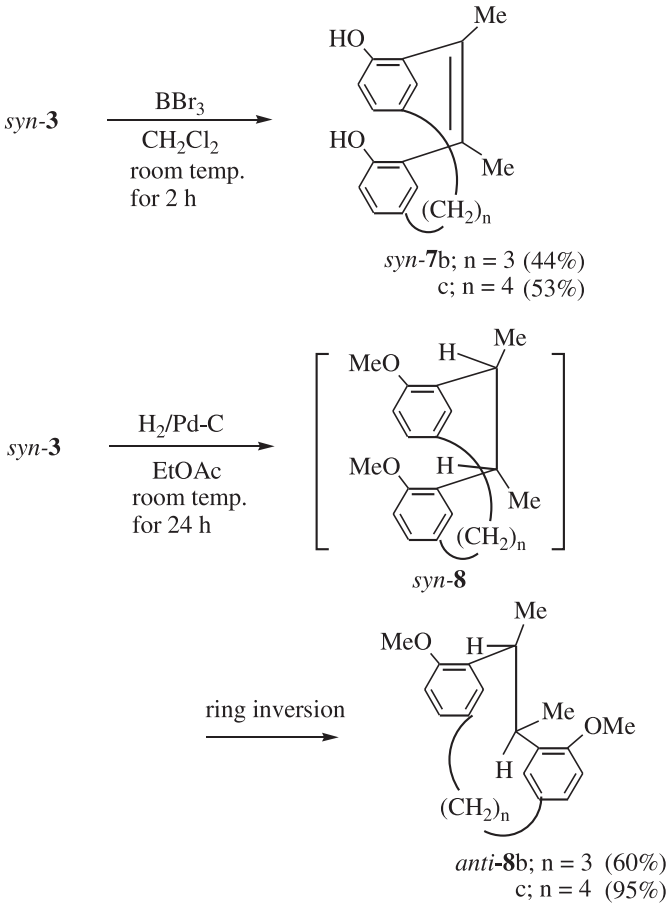
and the resonance for the protons of the OH groups at low field can be attributed to the intramolecular hydrogen bonding (13*c*, 22*d*, 24; for the circular intramolecular hydrogen bonding, see ref. (24*b*–*e*)). The υ_{OH} (3272 cm^{-1} for *syn*-**7b** and 3344 cm^{-1} for *syn*-**7c**) and δ_{OH} values in *syn*-**7b** and *syn*-**7c** in which two hydroxy groups are located in neighbouring positions, show slightly lower frequency IR vibrations and down-field NMR shifts, which imply that a weak hydrogen bond might exist. Therefore, it seems to assume that the *syn*-conformation of **7** might be due to the intramolecular hydrogen bonding. However, in DMSO-d_6 or pyridine-d_5 solution, which can disrupt the intramolecular hydrogen bonding, the ^{1}H NMR spectrum of *syn*-**7b** at room temperature is almost identical with that in $CDCl_3$ and no *anti*-conformer is observed. These findings might be attributable to the similar destabilization of the *anti*-conformation in *syn*-**7b** arising from steric hindrance between the hydroxy groups at the 7,13-positions and the methyl groups on the bridged double bond at 10,11-positions like *syn*-**3b**, but not the intramolecular hydrogen bonding among the two hydroxy groups.

An attempted hydrogenation of *syn*-**3b** in the presence of Pd-C in ethyl acetate at room temperature led to afford *anti*-**8b** in 60% yield. The desired product *syn*-**8b** has not been obtained. Thus, *syn*- to *anti*-ring inversion occurred during the hydrogenation (22). The same result was obtained in the case of the hydrogenation of *syn*-**3c** to afford *anti*-**8c**.

The structures of *anti*-**8b**, **8c** were assigned on the basis of elemental analyses and spectral data. The ^{1}H NMR spectral data of [n.2]MCP-enes **3**, **6** and [n.2]MCPs **8** are summarized in Table 1.

Griffin et al. (25) reported the structure of 1,2-dimethyl[2.2]MCP and assigned the *exo*-*endo*-arrangement (26). We have assigned the ^{1}H NMR signals of **8** in a similar fashion. In the ^{1}H NMR spectrum of *anti*-**8b** in $CDCl_3$ upfield shifts and the different chemical shifts for internal aromatic protons at δ 4.87 and 5.24 due to the ring current of the opposite aromatic ring were observed (27). These data strongly suggest that the structure of **8b** is the *anti*-conformer. Furthermore, the two methyl groups show different chemical shifts at δ 0.95 and 1.68 as a doublet with coupling constant J = 7.3 Hz. The higher field absorption is attributed to the *exo* methyl group and the lower field absorption is attributed to the *endo* methyl group which is in a strongly deshielding region of the oxygen atom of the methoxy group on the aromatic ring. These data strongly support that the two methyl groups are *exo*- and *endo*-arrangement and therefore, *anti*-**8b** is found to be *cis*-hydrogen adduct to the bridged double bond. This assignment is also applied to the hydrogenation product *anti*-**8c**.

Scheme 3.



The conformations of *syn*- and *anti*-[n.2]MCP-enes **3**, **6**, and *anti*-[n.2]MCP **8**, which have been prepared in the present work, in solution are studied by using variable temperature ^{1}H NMR spectroscopy and the results are compiled in Table 2.

The ^{1}H NMR spectrum of *syn*-**3b** and *anti*-**8b** in $CDCl_3$ at room temperature exhibits the split pattern of the protons at the methylene bridge. In spite of an increase of the temperature to 130°C in $CDBr_3$, no change of the spectrum is observed for saturated [3.2]-system *anti*-**8b**. However, in the case of the unsaturated [3.2]-system *syn*-**3b**, as the temperature

Table 2. The coalescence temperatures and energy barriers of *syn*- and *anti*-[n.2]MCP-enes **3**, **6**, and *anti*-[n.2]MCP **8**.[a]

Compd	Number of methylene units (n)	Solvent	T_c (°C)	$\Delta G^{\neq}$ (kcal mol^{-1})
syn-**3b**	3	$CDBr_3$	120	19.0
syn-**3c**	4	$CDCl_3$–CS_2	0	13.0
anti-**6**	3	$CDCl_3$–CS_2	0	12.4
anti-**8b**	3	$CDBr_3$	>130	—
anti-**8c**	4	$CDCl_3$–CS_2	35	14.4

[a]T_c and $\Delta G_c^{\neq}$ were determined in $CDCl_3$–CS_2 (1:3) or $CDBr_3$ using $SiMe_4$ as reference.

of the solution of the respective compound in $CDBr_3$, is increased, the individual peaks of the benzyl protons merge and eventually a single peak is observed above 120°C. This observation indicates that the rate of conformational ring flipping of *syn*-**3b** is faster than the NMR time scale at this temperature. The energy barrier to the conformational ring flipping estimated from the coalescence temperature (T_c) is 19.0 kcal mol^{-1}. The energy barriers for [4.2]-systems *syn*-**3c** and *anti*-**8c** were also estimated to be 13.0 (T_c = 0°C) and 14.4 (T_c = 35°C) kcal mol^{-1}, respectively. The unsaturated [3.2]-system *syn*-**3b** found to be about 6.0 kcal mol^{-1} larger than that for the corresponding [4.2]-system *syn*-**3c**. Thus, the solution conformation of [n.2]MCP-enes is sensitive to the chain length of the bridges. The ring inversion barriers determined by variable temperature ^{1}H NMR dramatically decrease with increasing length of the bridge by one unit.

Lower ring inversion barriers were observed for the unsaturated systems than those for saturated systems in spite of the smaller ring size due to the introduction of an additional double bond of the ethylene bridge. For example the barrier for ring inversion in the [4.2]-system decreases the rigidity of the system by about 1.4 kcal mol^{-1} in $CDCl_3$. The decreased rigidity of *syn*-[n.2]MCP-enes (**3**) may be attributed to the expanded bond angles of the bridged double bond.

Tetracyanoethylene (TCNE) complexes have often been used in studies on the relative π-base strength of various methyl-substituted benzenes (28). The π-basicity of the donor molecules increases with an increase in the number of substituted methyl groups and (or) stacking benzene rings and an increase in the face-to-face overlapping between aromatic nuclei (29). A solution of *anti*-[3.2]MCP-10-ene (*anti*-**6**) and TCNE in CH_2Cl_2 present a reddish brown colour and the charge-transfer band at 508 nm (log ε = 2.329) was observed in its UV spectrum. This absorption is due to the formation of 1:1 charge-transfer complex among the electron donor, [3.2]MCP, and the electron acceptor, TCNE. The position of absorption maximum and the shape of absorption curve remain unchanged when a 4–12-fold excess of TCNE was added. However, the charge transfer absorption band of the reference compound, 2,4-dimethylanisole (**9**) with TCNE was observed at 414 nm (log ε = 2.073). Such a red shift could be due to the through space electronic interaction of the opposite uncomplexed benzene ring, which tends to work as a π-electron donor.

In contrast to *anti*-[3.2]MCP-10-ene (*anti*-**6**), which exhibits the charge-transfer absorption band with TCNE at 508 nm (log ε = 2.329), a mixture of TCNE and *syn*-[3.2[MCP-10-ene (*syn*-**3b**) exhibits an absorption peak at 525 nm (log ε = 2.334), that of *syn*-[4.2[MCP-11-ene (*syn*-**3c**) is shifted to 466 nm (log ε = 2.001). Introduction of the one methylene to propane bridge of *syn*-**3b** causes a larger blue shift as indicated by the 60 nm shift for the CT-band of *syn*-**3c** due to the decreased transannular π-electron donation from the noncomplexed benzene ring to the complexed benzene ring. This finding is fairly consistent with the fact that the distance between two aromatic rings increased by one methylene bridge increased as previously described in the X-ray structures of *syn*-**3b** and *syn*-**3c**.

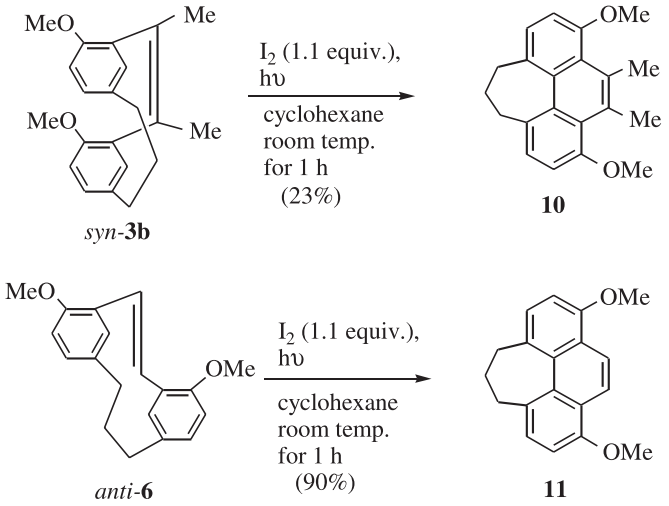
In the present [3.2]MCPs there are two possible conformers, *anti*- and *syn*-conformer. The through-space electronic interaction could be performed through the intraannular positions in the former conformer, but through face-to-face overlapping among the two benzene rings in the latter conformer (30). Thus, the charge-transfer complex would be stabilized by two types of the through-space electronic interaction, i.e., face-to-face overlapping and intraannular interaction with the opposing benzene ring, thus shifting the charge-transfer absorption band to the red region. The higher red shift of [3.2]MCP-10-ene (17 nm) are obtained in *syn*-conformer rather than in *anti*-conformer. Therefore, face-to-face overlapping might be much more favorable to stabilize the charge-transfer than the intraannular interaction.

In spite of two routes for the photocyclization of stilbenes such as staircase *anti*-conformation and "face-to-face overlapping" *syn*-conformation are possible (31), the latter reaction pathway has not been established due to the lack of the model compounds. Most investigations of the photoconversion of stilbene derivatives to 9,10-dihydrophenanthrenes have used *anti*-[2.2]MCP-1-enes (32) and *anti*-[2.2]MCP-1,9-dienes (5*a*). Boekelheide et al. (32) reported the photocyclization of *anti*-[2.2]MCP-1-enes in the presence of oxidants to afford the corresponding phenanthrenes, but limited to *anti*-conformation. Later, Mitchell et al. (33) also reported the synthesis of *syn*-[2.2]MCP-1,9-diene, which valence isomerized to *cis*-dihydropyrene, but readily isomerized to *anti*-cyclophane systems. Thus, there is substantial interest in investigating the photocyclization of present *syn*-[n.2]MCP-enes to explore the above reaction pathways.

Actually, when *syn*-**3b** was irradiated in the presence of iodine as an oxidant at room temperature for 1 h, the desired phenanthrene **10** was obtained only in 23% yield along with recovery of the starting compound. In contrast, similar reaction of *anti*-**6** carried out under the same reaction conditions afforded the cyclization product **11** in 90% yield.

The rate of the photocyclization of *anti*-**6** was found to be much faster than that of *syn*-**3b** and almost completed within 1 h. The different reactivities for the irradiation of *syn*-**3b** and *anti*-**6** were observed. In the present photocyclization reaction of *syn*-**3b**, the photoinduced *syn*–*anti*-isomerization might be possible to afford the corresponding *anti*-conformer *anti*-**3b**, which is cyclized to the cyclization product

Scheme 4.



10. In fact, the irradiation of *syn*-**3b** in the absence of iodine as an oxidant at room temperature was attempted, but none of the formation of *anti*-conformer *anti*-**3b** was observed under the present reaction conditions. This result indicates that the cyclization product **10** might be directly formed via the *syn*-**3b**, but not the corresponding *anti*-**3b** as an intermediate.

Examination of molecular models led us to believe that the transformation of *anti*-**6** into phenanthrene **11** should be straightforward, since in the conformationally rigid stilbene moiety of *anti*-**6**, the π orbitals involved in the required photochemically produced disrotatory cyclization leading eventually to the phenanthrene **11** are apparently very close in space. The reason for the present preference for the formation of *trans*-dihydrophenanthrene rather than *cis*-dihydrophenanthrene as the intermediate might be attributable to the more stable chair form transition state than boat one and the conformational fixation to the chair form in the ground and transition state is possible in the *anti*-conformer.

In conclusion, a new synthesis of *syn*- and *anti*-[n.2]MCPenes by a McMurry cyclization has been developed and applied to the synthesis of phenanthrene-anellated polycyclic aromatic hydrocarbons substituted at positions 4 and 5 by the successive photoinduced transannular cyclization reaction. Further studies on the present novel photoinduced transannular cyclization reaction of **3** and **6** are now in progress.

Experimental

All melting points (Yanagimoto MP-S1) were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Nippon Denshi JEOL FT-270 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV (*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 by Yanaco MT-5. GLC analyses were performed by Shimadzu gas chromatograph GC-14A (Silicone OV-1, 2 m, programmed temperature rise, 12°C/min, carrier gas nitrogen, 25 mL/min).

Materials

1,n-Bis(4-methoxyphenyl)alkanes **1** were prepared following previous reports (12, 13).

Preparation of 1,n-bis(3-acetyl-4-methoxyphenyl)alkane (2) — typical procedure

To a solution of 1,3-bis(4-methoxyphenyl)propane (**1b**) (3.84 g, 15 mmol) and acetyl chloride (3.15 mL, 45 mmol) in methylene dichloride (60 mL) was added a solution of aluminum chloride (8.91 g, 67.5 mmol) in nitromethane (15 mL) at 0°C. After the reaction mixture had been stirred at room temperature for 3 h, it was poured into ice water (100 mL). The organic layer was extracted with CH_2Cl_2 (2 × 50 mL). The extract was washed with water (2 × 50 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with $CHCl_3$ as eluent to give crude **2b** as a colorless solid. Recrystallization from hexane–benzene (1:1) gave 1,3-bis(3-acetyl-4-methoxyphenyl)propane (**2b**) (4.42 g, 87%) as colorless prisms, mp 46–48°C. IR (KBr) υ_{max}: 1667 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.85–1.95 (2 H, m), 2.55–2.62 (4 H, m), 2.60 (6 H, s), 3.89 (6 H, s), 6.90 (2 H, d, *J* = 8.0), 7.27 (2 H, dd, *J* = 8.0, 2.0), 7.52 (2 H, d, *J* = 2.0). MS *m*/*z*: M^+ 340. Anal. calcd. for $C_{21}H_{24}O_4$ (340.42): C 74.09, H 7.11; found: C 74.20, H 7.15.

Compounds **2a** and **2c** were similarly prepared in 29 and 71% yields, respectively.

*1,2-Bis(3-acetyl-4-methoxyphenyl)ethane (**2a**)*

Colorless prisms (hexane–benzene (1:1)), mp 114–115°C. IR (KBr) υ_{max}: 1664 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.60 (6 H, s), 2.84 (4 H, s), 3.89 (6 H, s), 6.87 (2 H, d, *J* = 8.7), 7.23 (2 H, dd, *J* = 8.7, 2.4), 7.54 (2 H, d, *J* = 2.4). MS *m*/*z*: M^+ 326. Anal. calcd. for $C_{20}H_{22}O_4$ (326.4): C 73.6, H 6.79; found: C 73.45, H 6.89.

*1,4-Bis(3-acetyl-4-methoxyphenyl)butane (**2c**)*

Colorless prisms (hexane–benzene (1:1)), mp 74–76°C. IR (KBr) υ_{max}: 1669 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.60 (4 H, m), 2.57 (4 H, m), 2.60 (6 H, s), 3.88 (6 H, s), 6.87 (2 H, d, *J* = 8.3), 7.25 (2 H, dd, *J* = 8.7, 2.4), 7.52 (2 H, d, *J* = 2.4). MS *m*/*z*: M^+ 354. Anal. calcd. for $C_{22}H_{26}O_4$ (354.5): C 74.55, H 7.39; found: C 74.26, H 7.18.

McMurry coupling reaction of 2 — typical procedure

The McMurry reagent was prepared from $TiCl_4$ [23.8 g (13.8 mL), 125 mmol] and 18 g (275 mmol) of Zn powder in 500 mL of dry THF, under nitrogen. A solution of **2b** (3.06 g, 9 mmol) and pyridine (22.5 mL, 200 mmol) in dry THF (250 mL) was added within 60 h from two Hershberg funnels to the black mixture of the McMurry reagent by using a high-dilution technique (34) with continuous refluxing and stirring. The reaction mixture was refluxed for an additional 8 h, cooled to room temp., and hydrized with aqueous 10% K_2CO_3 (200 mL) at 0°C. The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated.

The residue was chromatographed over silica gel (Wako C-300, 300 g) with benzene as eluents to give crude **3b** as a colorless solid. Recrystallization from benzene gave *syn*-7,13-dimethoxy-10,11-dimethyl[3.2]metacyclophan-10-ene (*syn*-**3b**) (1.10 g, 40%) as colorless prisms, mp 162–163°C. ^{1}H NMR ($CDCl_3$) δ: 1.20–1.45 (1 H, m), 2.10–2.25 (1 H, m), 2.18 (6 H, s), 2.50–2.65 (2 H, m), 2.85–2.98 (2 H, m), 3.59 (6 H, s), 6.33 (2 H, d, *J* = 8.0), 6.60 (2 H, dd, *J* = 2.0, 8.0), 6.95 (2 H, d, *J* = 2.0). MS *m/z*: M^+ 308. Anal. calcd. for $C_{21}H_{24}O_2$ (308.42): C 81.78, H 7.84; found: C 81.71, H 7.78.

Similarly, the McMurry coupling reaction was carried out for compounds **2a** and **2c** in the same manner as described above.

For **2a** the residue was chromatographed over silica gel (Wako C-300, 300 g) with benzene–$CHCl_3$ (1:1) as eluents to give crude **4a** as a colorless solid. Recrystallization from $CHCl_3$ gave **4a** (500 mg, 19%) as colorless prisms.

For **2c** the residue was chromatographed over silica gel (Wako C-300, 300 g) with hexane–benzene (1:1) as eluents to give crude *syn*-**3c** as a colorless solid. Recrystallization from hexane gave *syn*-**3c** (2.01 g, 69%) as colorless prisms.

*4,14,20,30-Tetramethoxy-1,2,17,18-tetramethyl[2.2.2.2]-metacyclophane-1,17-diene (**4a**)*

Colorless prisms ($CHCl_3$), mp 280–282°C. IR (KBr) υ_{max}: 2930, 1497, 1456, 1262, 1253, 1229, 1133, 1050, 1031, 810 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.15 (12 H, s), 2.50 (8 H, broad s), 3.58 (12 H, s), 6.56 (4 H, d, *J* = 8.3), 6.71–6.80 (4 H, broad s), 6.83 (4 H, dd, *J* = 8.3, 2.0). MS *m/z*: M^+ 588. Anal. calcd. for $C_{40}H_{44}O_4$ (588.79): C 81.6, H 7.53; found: C 81.81, H 7.68.

syn-*8,14-Dimethoxy-11,12-dimethyl[4.2]metacyclophan-11-ene (*syn-***3c**)

Colorless prisms (hexane), mp 160–161°C. IR (KBr) υ_{max}: 2923, 1493, 1442, 1252, 1226, 1032, 805, 797 cm^{-1}. ^{1}H NMR ($CDCl_3$) (27°C) δ: 1.55 (4 H, broad s), 2.14 (6 H, s), 2.36 (4 H, broad s), 3.63 (6 H, s), 6.41 (2 H, d, *J* = 8.3), 6.59 (2 H, dd, *J* = 2.4, 8.3), 6.90 (2 H, d, *J* = 2.4). ^{1}H NMR ($CDCl_3$) (–40°C) δ: 1.1–1.4 (2 H, broad s), 1.72–1.92 (2 H, broad s), 2.17 (6 H, s), 2.1–2.3 (2 H, broad s), 2.4–2.6 (2 H, broad s), 3.67 (6 H, s), 6.41 (2 H, d, *J* = 8.3), 6.64 (2 H, dd, *J* = 2.4, 8.3), 6.93 (2 H, d, *J* = 2.4). MS *m/z*: M^+ 322. Anal. calcd. for $C_{22}H_{26}O_2$ (322.45): C 81.95, H 8.13; found: C 82.07, H 8.15.

Preparation of 1,3-bis(3-formyl-4-methoxyphenyl)-propane (5)

To a solution of 1,3-bis(4-methoxyphenyl)propane (**1b**) (2.24 g, 8.75 mmol) and Cl_2CHOCH_3 (2.28 mL, 25.2 mmol) in CH_2Cl_2 (20 mL) was added a solution of $TiCl_4$ (6.0 mL, 54.5 mmol) in CH_2Cl_2 (20 mL) at 0°C. After the reaction mixture was stirred at room temp for 3 h, it was poured into a large amount of ice water (400 mL) and extracted with CH_2Cl_2 (2 × 200 mL). 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 $CHCl_3$ as eluent to give crude **5**. Recrystallization from hexane gave 2.81 g (99.6%) of 1,3-bis(3-formyl-4-methoxyphenyl)propane (**5**) as colorless prisms, mp 93–94°C. IR (KBr) υ_{max}: 1682 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.88–2.00 (2 H, m), 2.60–2.67 (4 H, m), 3.95 (6 H, s), 6.95 (2 H, d, *J* = 8.8), 7.39 (2 H, dd, *J* = 8.8, 2.4), 7.66 (2 H, d, *J* = 2.4), 10.48 (2 H, s). MS *m/z*: M^+ 312. Anal. calcd. for $C_{19}H_{20}O_4$ (312.37): C 73.06, H 6.45; found: C 73.19, H 6.32.

McMurry coupling reaction of 5

The McMurry reagent was prepared from $TiCl_4$ [23.8 g (13.8 mL), 125 mmol] and 18 g (275 mmol) of Zn powder in 500 mL of dry THF, under nitrogen. A solution of **5** (3.21 g, 9 mmol) and pyridine (22.5 mL, 200 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 additional 8 h, cooled to room temp, and hydrized with aqueous 10% K_2CO_3 (200 mL) at 0°C. The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 300 g) with hexane–benzene (1:1) as eluents to give crude **6** as a colorless solid. Recrystallization from methanol gave *anti*-7,13-dimethoxy[3.2]metacyclophan-10-ene (*anti*-**6**) (711 mg, 28%) as colorless prisms, mp 94–95°C. IR (KBr) υ_{max}: 1593, 1485, 1461, 1276, 1255, 1242, 1114, 1027, 797, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.78–1.89 (2 H, m), 2.20–2.50 (4 H, broad s), 3.85 (6 H, s), 6.05 (2 H, d, *J* = 2.4), 6.77 (2 H, d, *J* = 8.3 Hz), 6.88 (2 H, s), 6.97 (2 H, dd, *J* = 8.3, 2.44). MS *m/z*: M^+ 308. Anal. calcd. for $C_{19}H_{20}O_2$ (280.37): C 81.4, H 7.19; found: C 81.62, H 7.26.

Demethylation of syn-3b

To a solution of *syn*-**3b** (32.2 mg, 0.105 mmol) in CH_2Cl_2 (5 mL) at 0°C was gradually added a solution of BBr_3 (0.03 mL, 0.3 mmol) in CH_2Cl_2 (1 mL) over a period of 15 min. After the reaction mixture has been stirred at room temperature for 2 h, it was poured into ice water (50 mL), extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with water (2 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo to leave a residue. The residue was recrystallized from hexane–ethyl acetate (1:1) gave *syn*-7,13-dihydroxy-10,11-dimethyl[3.2]metacyclophan-10-ene (*syn*-**7b**) (14.1 mg, 44%) as colorless prisms, mp 189–189.5°C. IR (KBr) υ_{max}: 3272 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.23 (6 H, s), 2.05–2.28 (2 H, broad s), 2.45–2.62 (2 H, broad s), 2.78–2.98 (2 H, broad s), 5.29 (2 H, s, replaced by D_2O), 6.33 (2 H, d, *J* = 8.30), 6.56 (2 H, dd, *J* = 8.30, 2.44), 6.85 (2 H, d, *J* = 2.44). MS *m/z*: M^+ 306. Anal. calcd. for $C_{19}H_{20}O_2$ (280.37): C 81.4, H 7.19; found: C 81.62, H 7.28.

Compound *syn*-**7c** was similarly prepared in 53% yield.

syn-*8,14-Dihydroxy-11,12-dimethyl[4.2]metacyclophan-11-ene (*syn-***7c**)

Colorless prisms (hexane–ethyl acetate (1:1)), mp 194–194.5°C. IR (KBr) υ_{max}: 3344 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.40–1.75 (4 H, broad s), 2.19 (6 H, s), 2.20–2.42 (4 H, broad s), 5.15 (2 H, broad s, replaced by D_2O), 6.38 (2 H, d, *J* = 8.3), 6.52 (2 H, dd, *J* = 2.4, 8.3), 6.80 (2 H, d, *J* = 2.4). MS *m/z*: M^+ 294. Anal. calcd. for $C_{20}H_{22}O_2$ (294.38): C 81.6, H 7.53; found: C 81.91, H 7.50.

Table 3. Crystallographic data and data collection details for *syn*-10,11-dimethyl-7,13-dimethoxy[3.2]MCP-10-ene (*syn*-**3b**) and *syn*-11,12-dimethyl-8,14-dimethoxy[4.2]MCP-11-ene (*syn*-**3c**).

	syn-**3b**	*syn*-**3c**
Formula	$C_{21}H_{24}O_2$	$C_{22}H_{26}O_2$
Mol. mass	308.42	322.45
Crystal size (mm)	0.4 × 0.25 × 0.25	0.30 × 0.25 × 0.25
	monoclinic	monoclinic
Space group	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)
Z	4	4
a (pm)	1924.58 (26)	1983.78 (19)
b (pm)	759.26 (6)	819.66 (6)
c (pm)	1225. 00 (17)	1155.81 (13)
β (°)	102.80 (1)	98.9677 (85)
V (m^3)	1745.5 (4) × 10^{-30}	1856.4 (3) × 10^{-30}
D_c (gm^{-3})	1.154	1.174
Radiation	Cu-K_α	Cu-K_α
μ (Cu-K_α) (cm^{-1})	5.4	5.29
Total no. of unique reflections	3142	3365
R	0.117	0.067
R_w	0.091	0.107

Reduction of *syn*-3 with H_2 in the presence of Pd-C — typical procedure

To a solution of *syn*-**3b** (30 mg, 0.097 mmol) in ethyl acetate (40 mL) was added Pd-C (5%, 15 mg) and stirred for 24 h under the hydrogen atomosphere at room temp. The reaction mixture was concentrated. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane–benzene (1:1) as eluents to give *anti*-**8b** (18.1 mg, 60%) as a colorless solid. Recrystallization from methanol gave *anti*-10-*exo*,11-*endo*-dimethyl-7,13-dimethoxy[3.2]metacyclophane (*anti*-**8b**) as colorless prisms, mp 84–85°C. ^{1}H NMR ($CDCl_3$) δ: 0.95 (3 H, d, J = 7.3), 1.68 (3 H, d, J = 7.3), 1.80–2.00 (2 H, m), 2.00–2.15 (1 H, m), 2.17–2.34 (1 H, m), 2.33–2.46 (1 H, m), 2.68–2.80 (2 H, m), 3.61–3.76 (1 H, m), 3.78 (3 H, s), 3.85 (3 H, s), 4.87 (1 H, d, J = 2.4), 5.24 (1 H, d, J = 2.4), 6.78 (2 H, d, J = 8.3), 6.93–7.01 (2 H, m). MS m/z: M^+ 310. Anal. calcd. for $C_{21}H_{26}O_2$ (310.44): C 81.25, H 8.44; found: C 81.12, H 8.28.

Compound *anti*-**8c** was similarly prepared in 95% yield.

anti-*11*-exo,*12*-endo-*Dimethyl-8,14-dimethoxy[4.2]metacyclophane (*anti-***8c***)*

Colorless prisms (methanol), mp 93–94°C. ^{1}H NMR ($CDCl_3$) (27°C), δ: 0.70–2.89 (16 H, broad m), 3.81 (6 H, s), 5.52–6.00 (2 H, s), 6.75 (2 H, d, J = 8.3), 6.86 (2 H, dd, J = 8.3, 2.4). ^{1}H NMR ($CDCl_3$–CS_2 (1:3)) (–30°C) δ: 0.82–1.08 (2 H, broad s), 0.98 (3 H, d, J = 7.3), 1.45–1.62 (2 H, broad s), 1.68 (3 H, d, J = 7.3), 2.09–2.28 (2 H, m), 2.55 (1 H, d, J = 7.3), 2.60–2.78 (2 H, m), 3.66 (1 H, d, J = 7.3), 3.80 (3 H, s), 3.87 (3 H, s), 5.61 (1 H, d, J = 2.4), 5.92 (1 H, d, J = 2.4), 6.77 (2 H, d, J = 8.3), 6.86–6.96 (2 H, m). MS m/z: M^+ 306. Anal. calcd. for $C_{22}H_{28}O_2$ (324.47): C 81.44, H 8.7; found: C 81.45, H 8.63.

Photoinduced cyclization of *anti*-6 in the presence of iodine

The mixture of *anti*-**6** (112 mg, 0.4 mmol) and iodine (112.0 mg, 0.44 mmol) was dissolved in cyclohexane (200 mL) in a Pyrex flask and then irradiated by a 400 W high-pressure mercury lamp while being monitored by GLC. Irradiation was continued until the disappearance of the reactant *anti*-**6** (1 h). The reaction mixture was washed with 10% sodium thiosulfate and water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 100 g) with hexane–benzene (1:1) as eluents to give **11** (100 mg, 90%) as a colorless solid. Recrystallization from hexane gave 1,8-dimethoxy-4,5-propanophenanthrene (**11**) as colorless prisms, mp 86–87°C. IR (KBr) υ_{max}: 2937, 1587, 1498, 1426, 1270, 1241, 1144, 1029, 810 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.44–2.55 (2 H, m), 2.76–2.81 (4 H, m), 4.02 (6 H, s), 6.92 (2 H, d, J = 7.8), 7.32 (2 H, d, J = 7.8), 8.11 (2 H, s). MS m/z: M^+ 278. Anal. calcd. for $C_{19}H_{18}O_2$ (278.35): C 81.99, H 6.52; found: C 81.73, H 6.33.

Compound **10** was similarly prepared in 23% yield.

*3,6-Dimethoxy-9,10-dimethyl-4,5-propanophenanthrene (**10**)*

Colorless prisms (methanol), mp 51–53°C. IR (KBr) υ_{max}: 2925, 1577, 1159, 1029, 803, 667 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.34–2.47 (2 H, m), 2.6–2.7 (4 H, m), 2.77 (6 H, s), 3.93 (6 H, s), 6.94 (2 H, d, J = 7.82), 7.18 (2 H, d, J = 7.82). MS m/z: M^+ 306. Anal. calcd. for $C_{21}H_{22}O_2$ (306.41): C 82.32, H 7.24; found: C 82.21, H 7.18.

Crystal data and refinement details for *syn*-3b and *syn*-3c

The unit cell constants were derived from least-squares analysis of the settings, on an Enraf–Nonius CAD4 FR 586 diffractometer, for 16 reflections for *syn*-**3b** and 25 reflections for *syn*-**3c** in the range 23.9° < θ < 24.6° for *syn*-**3b** and 22.0° < θ < 32.0° for *syn*-**3c**. The intensities of all independent reflections with 4° < 2θ < 140° for *syn*-**3b** and 4° < 2θ < 144° for *syn*-**3c** were measured with ω-2θ scan (ω scan width = 0.8 + 0.14 tan θ), Ni-filtered Cu–K_α radiation (λ = 1.54184 Å) was used. The structure was solved uneventfully by direct method (SIR88)[3] and difference Fourier syntheses, and refined in full-matrix least-squares method.

Table 4. Fractional atomic coordinates for the nonhydrogen atoms, with estimated standard deviations in parentheses, for *syn*-10,11-dimethyl-7,13-dimethoxy[3.2]metacyclophan-10-ene *(syn*-**3b**) and the isotropic equivalent displacement parameter defined as $B_{eq} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Atom	*x*	*y*	*z*	B_{eq}
O1	0.58744(8)	–0.3100(2)	0.1709(1)	5.70(4)
O2	0.58885(9)	0.1258(3)	0.0417(1)	5.76(4)
C1	0.5922(1)	–0.0376(3)	0.3212(2)	4.24(4)
C2	0.5935(1)	0.1181(3)	0.2716(2)	4.02(4)
C3	0.6570(1)	0.1609(3)	0.2246(2)	3.79(4)
C4	0.6552(1)	0.1503(3)	0.1103(2)	4.45(4)
C5	0.7184(1)	0.1598(4)	0.0735(2)	5.60(5)
C6	0.7827(1)	0.1715(4)	0.1508(2)	5.68(5)
C7	0.7865(1)	0.1857(3)	0.2636(2)	4.57(5)
C8	0.7221(1)	0.1915(3)	0.2973(2)	4.04(4)
C9	0.8556(1)	0.1796(4)	0.3506(2)	5.61(6)
C10	0.8882(1)	–0.0039(4)	0.3781(2)	5.90(6)
C11	0.8532(1)	–0.1260(4)	0.4492(2)	6.24(6)
C12	0.7824(1)	–0.2014(3)	0.3877(2)	4.86(5)
C13	0.7784(1)	–0.3265(3)	0.3038(2)	5.77(6)
C14	0.7144(1)	–0.3711(3)	0.2340(2)	5.53(6)
C15	0.6526(1)	–0.2848(3)	0.2433(2)	4.62(5)
C16	0.6539(1)	–0.1597(3)	0.3269(2)	4.17(4)
C17	0.7188(1)	–0.1296(3)	0.4022(2)	4.64(5)
C18	0.5314(1)	–0.1036(4)	0.3690(2)	6.07(6)
C19	0.5353(1)	0.2551(4)	0.2568(2)	5.62(6)
C20	0.5874(2)	–0.3650(5)	0.0623(3)	7.40(8)
C21	0.5836(2)	0.1146(5)	–0.0745(2)	7.27(8)

Table 5. Fractional atomic coordinates for the nonhydrogen atoms, with estimated standard deviations in parentheses, for *syn*-11,12-dimethyl-8,14-dimethoxy[4.2]metacyclophan-11-ene *(syn*-**3c**) and the isotropic equivalent displacement parameter defined as $B_{eq} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Atom	*x*	*y*	*z*	B_{eq}
O1	0.4222(1)	0.3732(4)	0.9651(2)	6.25(7)
O2	0.4134(2)	0.8045(4)	0.8287(3)	7.66(8)
C1	0.4001(2)	0.4031(5)	0.7251(3)	4.76(8)
C2	0.3997(2)	0.5510(6)	0.6729(3)	5.19(9)
C3	0.3421(2)	0.6681(5)	0.6799(3)	4.64(8)
C4	0.3497(2)	0.7917(5)	0.7625(3)	5.4(1)
C5	0.2953(2)	0.8913(5)	0.7764(4)	6.2(1)
C6	0.2324(2)	0.8633(5)	0.7075(4)	6.3(1)
C7	0.2231(2)	0.7419(5)	0.6239(3)	5.12(9)
C8	0.2799(2)	0.6516(5)	0.6083(3)	5.11(9)
C9	0.1534(2)	0.6992(7)	0.5598(4)	6.8(1)
C10	0.1347(2)	0.5164(7)	0.5720(4)	7.6(1)
C11	0.1267(2)	0.4716(7)	0.6951(4)	7.4(1)
C12	0.1514(2)	0.2948(6)	0.7300(4)	6.9(1)
C13	0.2236(2)	0.2972(5)	0.7929(4)	5.6(1)
C14	0.2387(2)	0.2821(6)	0.9144(4)	6.3(1)
C15	0.3039(2)	0.3013(7)	0.9732(4)	6.3(1)
C16	0.3563(2)	0.3432(5)	0.9129(3)	5.19(9)
C17	0.3441(2)	0.3575(5)	0.7896(3)	4.55(8)
C18	0.2786(2)	0.3266(5)	0.7343(3)	5.04(9)
C19	0.4561(2)	0.2791(6)	0.7226(4)	6.3(1)
C20	0.4550(2)	0.6146(7)	0.6101(4)	7.2(1)
C21	0.4353(2)	0.3887(7)	1.0876(4)	7.6(1)
C22	0.4220(3)	0.8954(8)	0.9299(5)	9.0(2)

All calculations were performed on a Micro VAX 3100 computer using a MolEN program package.[4]

Crystallographic data for *syn*-**3b** and *syn*-**3c** are given in Table 3.

The refined non-hydrogen atomic coordinates for *syn*-**3b** and *syn*-**3c** are listed in Tables 4 and 5, respectively, while the hydrogen coordinates, temperature factors (anisotropic for carbon atoms), scale factor, and secondary estimation coefficient for *syn*-**3b** and *syn*-**3c** are available on request.[5]

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[4] MolEN, an interactive structure solution procedure. Enraf–Nonius, Delft, The Netherlands. 1990.

[5] Hydrogen coordinates, temperature factors (anisotropic for carbon atoms), scale factors, and secondary estimation coefficients have been deposited as supplementary material and may be purchased from The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Ontario, Canada, K1A 0S2 (for information on ordering electronically). Crystallographic data for the structure(s) reported in this paper havebeen deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of the data can be obtained, free of charge, on application to The Director, (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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