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Synthesis and photochromism of 1,2-dicyano[2.n]metacyclophan-1-enes

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ABSTRACT: Syntheses and photochromic properties of 1,2-dicyano[2.n]metacyclophan-1-enes are described. Dicyanometacyclophan-1-enes have been prepared by novel intramolecular coupling reaction of 1,n-bis[(cyanomethyl)phenyl]alkanes in the presence of phase transfer catalyst. The photocyclization reaction of the prepared metacyclophan-1-enes took place upon irradiation with UV light and the pale yellow solution turned to violet due to the formation of the closed forms. The spectra and the color of the solutions returned to the initial states by the visible irradiation. The lifetimes of the closed forms were dependent on the chain length (*n*). As the chain length is shorter, the lifetime becomes longer. This is due to the steric energy of metacyclophan-1-ene. Hence, it becomes possible to control the thermal stability of the photoisomer by the change of chain length (*n*). The quantum yield for photocyclization reaction is the highest among 1,2-dicyanodiarylethene family, since the conformation of the metacyclophan-1-ene is fixed to the photoactive form. Synthesis and photochromic properties of 1,2-dicyano[2.n]metacyclophan-1-enes bearing various kinds of substituents are also described. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; cyclophane; quantum yield; photocyclization; absorption spectrum; molecular switch

INTRODUCTION

Photochromism is defined as 'the light-induced reversible change of color'.[1] When we irradiate the light to isomer A, the structure of A changes isomer B which has different color from that of isomer A. Isomer B returns to isomer A upon irradiation with the light having different wavelength or by heat. These reactions are reversible. The photochromic compounds can be classified into two types, P type and T type. In the P type, the isomerization takes place only by photoirradiation. Then, this type of photochromic compound is thermally irreversible and both isomers are thermally stable. In the T type, the isomerization occurs not only by photoirradiation but also thermally.

Among various photochromic compounds, dithienylethenes are especially of interest in their thermally irreversible and high fatigue resistant properties.[1b,2] The aromatic stabilization energy of thiophene is smaller than benzene, therefore both photoisomers have similar energy of formation and the energy barrier between them are too high to overcome thermally in this system.[2a] Although the dithienylethenes are most promising candidate for the organic photomemory, the open form of a dithienylethene has two conformations, anti-parallel and parallel conformation. These conformations exchange slowly at even room temperature.[2a] From the anti-parallel conformation, photocyclization reaction takes place; however the parallel conformation is photo-inactive and the existence of the parallel conformation decreases the quantum yield for photocyclization reaction.[2a]

On the other hand, it is known that small [m.n]metacyclophanes have large steric energy arising from both the steric repulsion between aromatic rings and inner substituents and/or electrostatic repulsion of the benzene rings.[3] The aromatic stabilization energy of the metacyclophane is getting smaller as the ring size of the metacyclophane becomes smaller. When this system would be applied to the photochromic [2.n]metacyclophan-1-enes which are composed of two aromatic rings, one ethene bridge and one alkyl bridge,[4] it becomes possible to control the thermal stability of the photoisomers by the change of the bridge length (*n*). That is to say, the steric energy is dependent on the *n* number, and the energy difference between two isomers could be controlled. On the other hand, when *n* number is small, the ring flipping of the aromatic ring would be prohibited because of the steric hindrance between the aromatic rings and the inner substituents.[3] Therefore, when a small metacyclophan-1-ene is once fixed to the

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anti-conformation, the photoinactive syn conformation no longer forms and the quantum yield for photocyclization reaction would become higher.

These facts encouraged us to develop the novel photochromic [2.n]metacyclophan-1-enes with various substituents.

EXPERIMENTAL

The light source used was 500 W super high-pressure mercury lamp and monochromic light was obtained by passing through color filters and/or a monochromator (Jobin Yvon).

Preparation of 4-*tert*-butyl-2-chloromethyl-1-propylbenzene(2c)

To a stirred solution of 4-*tert*-butylpropylbenzene (**1c**)[5] 20.2 g (0.114 mol) and 15.8 ml of chloromethyl methyl ether (0.196 mol) in 25 ml CH_2Cl_2 in ice bath, 4.8 ml of $TiCl_4$ (0.070 mol) was added dropwise and the mixture was stirred for 2 h at same temperature. The reaction mixture was poured into ice water and extracted with CH_2Cl_2. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and distillation of the residue afforded 5.7 g of **2c** (0.025 mol) in 22% yield. **2c**: colorless oil, bp 122 °C/10 mmHg, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.02 (t, 3H, $J = 7$ Hz), 1.28 (s, 9H), 1.60–1.75 (m, 2H), 2.64 (t, 2H, $J = 7$ Hz), 4.65 (s, 2H), 7.16–7.32 (m, 3H); MS $m/z = 224$ (M^+). Anal. Calcd for $C_{14}H_{21}Cl$: C, 74.81; H, 9.42. Found: C, 74.67; H, 9.56.

Preparation of 1,2-bis(4-*tert*-butyl-1-propylphen-2-yl)ethane(3c)

To a suspension of 2.74 g of magnesium turnings (0.11 mol) in 10 ml of dry diethyl ether under Ar was added dropwise to a solution of 7 ml of CH_3I (0.11 mol) in 32 ml of dry diethyl ether slowly. To the stirring mixture, a solution of 8.6 g of **2c** (38 mmol) in 22 ml of dry diethyl ether was added dropwise for 30 min and the mixture was refluxed in oil bath for 1 h. The reaction mixture was poured into ice water and acidified with 10% HCl and extracted with diethyl ether. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue afforded **3c** as colorless oil in 79% yield. **3c**: colorless oil, bp > 170 °C/30 mmHg, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.02 (t, 6H, $J = 7$ Hz), 1.25 (s, 18H), 1.55–1.63 (m, 4H), 2.63 (t, 4H, $J = 7$ Hz), 2.91 (s, 4H), 7.05–7.14 (m, 6H); MS $m/z = 378$ (M^+). Anal. Calcd for $C_{28}H_{42}$: C, 88.82; H, 11.18. Found: C, 88.59; H, 11.24.

Preparation of 1,2-bis(5-*tert*-butyl-1-chloromethyl-2-propylphen-3-yl)ethane (4c)

To a mixture of 2.0 g of **3c** (5.3 mmol) and 2.0 ml of chloromethyl methyl ether (25 mmol) in 5 ml of CH_2Cl_2 in ice bath, 4.8 ml of $TiCl_4$ (0.070 mol) was added dropwise and the mixture was stirred for 2 h at same temperature. The reaction mixture was poured into ice water and extracted with CH_2Cl_2. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was subjected to a column chromatography (silica-gel). Recrystallization of a hexane-chloroform eluate from hexane afforded 1.0 g of **4c** in 40% yield. **4c**: colorless prisms (hexane), mp 145.0–147.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.09 (t, 6H, $J = 7$ Hz), 1.28 (s, 18H), 1.50–1.60 (m, 4H), 2.65 (m, 4H), 2.92 (s, 4H), 4.62 (s, 4H), 7.14 (d, 2H, $J = 2$ Hz), 7.22 (d, 2H, $J = 2$ Hz); MS $m/z = 474$ (M^+). Anal. Calcd for $C_{30}H_{44}Cl_2$: C, 75.77; H, 9.32. Found: C, 75.68; H, 9.56.

Preparation of 1,2-bis(5-*tert*-butyl-1-cyanomethyl-2-methylphen-3-yl)ethane (5a)

A two-phase solution of 35.0 g of 1,2-bis(5-*tert*-butyl-1-chloromethyl-2-methylphen-3-yl)ethane (**4a**)[6] (84 mmol), 8.7 g of NaCN (176 mmol), 450 mg of NaI (3.0 mmol), and 2.2 g of tetra-*n*-butylammonium bromide (6.8 mmol) in 100 ml of benzene and 50 ml of water was vigorously stirred at 70°C for 5 h. The organic phase was separated and the aqueous phase was extracted with toluene and the extract was mixed with the separated organic phase. The mixed solution was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and recrystallization of the residue from hexane afforded 27.0 g of **5a** (67.5 mmol) in 80% yield. **5a**: colorless prisms (hexane), mp 133.0–138.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.27 (s, 18H), 2.11 (s, 6H), 2.90 (s, 4H), 3.65 (s, 4H), 7.04 (d, 2H, $J = 2$ Hz), 7.19 (d, 2H, $J = 2$ Hz); MS $m/z = 400$ (M^+). Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.95; H, 9.06; N, 6.99. Found: C, 83.86; H, 9.41; N, 6.72.

Preparation of 1,2-bis(5-*tert*-butyl-1-cyanomethyl-2-ethylphen-3-yl)ethane (5b)

Compound **5b** was obtained from 1,2-bis(5-*tert*-butyl-1-chloromethyl-2-ethylphen-3-yl)ethane (**4b**)[4c] in a similar manner described above. The yield was 65%. **5b**: colorless prisms (hexane), mp 148.0–149.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.14 (t, 6H, $J = 7$ Hz), 1.28 (s, 18H), 2.60 (q, 4H, $J = 7$ Hz), 2.91 (s, 4H), 3.71 (s, 4H), 7.08 (d, 2H, $J = 2$ Hz), 7.20 (d, 2H, $J = 2$ Hz); MS $m/z = 428$ (M^+). Anal. Calcd for $C_{30}H_{40}N_2$: C, 84.06; H, 9.41; N, 6.54. Found: C, 84.24; H, 9.43; N, 6.33

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Preparation of 1,2-bis(5-*tert*-butyl-1-cyanomethyl-2-propylphen-3-yl)ethane (5c)

Compound **5c** was obtained from **4c** in a similar manner described above. The yield was 61%. **5c**: colorless prisms, mp 157.0–158.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.03 (t, 6H, $J = 7$ Hz), 1.30 (s, 18H), 1.52 (m, 4H, $J = 7$ Hz), 2.51 (m, 4H), 2.88 (s, 4H), 3.70 (s, 4H), 7.11 (d, 2H, $J = 2$ Hz), 7.26 (d, 2H, $J = 2$ Hz); MS $m/z = 456$ (M^+). Anal. Calcd for $C_{32}H_{44}N_2$: C, 84.16; H, 9.71; N, 6.13. Found: C, 84.35; H, 9.63; N, 6.02.

Preparation of 1,2-bis(5-*tert*-butyl-1-cyanomethyl-2-methoxyphen-3-yl)ethane (5d)

Compound **5d** was obtained from **4d**[6] in a similar manner described above. The yield was 83%. **5c**: colorless prisms, mp 146.0–149.0°C (hexane), ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.27 (s, 18H), 2.94 (s, 4H), 3.73 (s, 4H), 3.77 (s, 6H), 7.12 (d, 2H, $J = 2$ Hz), 7.23 (d, 2H, $J = 2$ Hz); MS $m/z = 432$ (M^+). Anal. Calcd for $C_{28}H_{36}N_2O_2$: C, 77.74; H, 8.39; N, 6.48. Found: C, 77.56; H, 8.39; N, 6.46.

Preparation of 1,3-bis(5-*tert*-butyl-1-cyanomethyl-2-methylphen-3-yl)propane (5e)

Compound **5e** was obtained from **4e**[7] in a similar manner described above. The yield was 85%. **5e**: colorless prisms (hexane), mp 135.0–139.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.31 (s, 18H), 1.75–1.90 (m, 2H), 2.29 (s, 6H), 2.68–2.76 (m, 4H), 3.68 (s, 4H), 7.17 (d, 2H, $J = 2$ Hz), 7.20 (d, 2H, $J = 2$ Hz); MS $m/z = 414$ (M^+). Anal. Calcd for $C_{29}H_{38}N_2$: C, 84.01; H, 9.24; N, 6.76. Found: C, 84.49; H, 8.49; N, 6.21.

Preparation of 1,4-bis(5-*tert*-butyl-1-cyanomethyl-2-methylphen-3-yl)butane (5f)

Compound **5f** was obtained from **4f**[7] in a similar manner described above. The yield was 80%. **5f**: colorless prisms (hexane), mp 130.0–135.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.30 (s, 18H), 1.60–1.72 (m, 4H), 2.25 (s, 6H), 2.65–2.72 (m, 4H), 3.68 (s, 4H), 7.16 (d, 2H, $J = 2$ Hz), 7.20 (d, 2H, $J = 2$ Hz); MS $m/z = 428$ (M^+). Anal. Calcd for $C_{30}H_{40}N_2$: C, 84.06; H, 9.41; N, 6.54. Found: C, 83.68; H, 9.60; N, 6.28.

Preparation of 5,13-di-*tert*-butyl-1,2-dicyano-8,16-dimethyl[2.2]metacyclophan-1-ene (6a)

To a vigorously stirred two-phase solution of 40.0 g of NaOH (1.0 mol), 2.5 g of tetra-*n*-butylammonium bromide (7.7 mmol), and 50 ml of CCl_4 in 100 ml of benzene and 40 ml of water at 70°C, a solution of 25.0 g of **5a** (63 mmol) in 100 ml of benzene and 100 ml of CCl_4 was added dropwise for 2 h and the mixture was stirred vigorously at the same temperature for 4 h. The product was extracted with toluene and the extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was subjected to silica-gel column chromatography. Recrystallization of the hexane-CH_2Cl_2 (1:1) eluate from hexane-acetone (4:1) afforded 8.0 g of **6a** (20 mmol) in 32% yield. **6a**: yellow prisms (hexane-acetone), mp 222.0–224.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 0.73 (s, 6H), 1.30 (s, 18H), 2.50 (m, 2H), 2.98 (m, 2H), 7.19 (s, 4H); MS $m/z = 396$ (M^+). Anal. Calcd for $C_{28}H_{32}N_2$: C, 84.80; H, 8.13; N, 7.06. Found: C, 84.79; H, 8.33; N, 7.07.

Preparation of 5,13-di-*tert*-butyl-1,2-dicyano-8,16-diethyl[2.2]metacyclophan-1-ene (6b)

Compound **6b** was obtained from **5b** in a similar manner described above. The yield was 16.7%. **6b**: orange prisms (hexane), mp 175.0–180.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 0.24 (t, 6H, $J = 7$Hz), 0.32–0.42 (m, 4H), 1.26 (s, 18H), 2.21–2.30 (m, 2H), 2.72–2.81 (m, 2H), 6.89 (d, 2H, $J = 2$Hz), 6.93 (d, 2H, $J = 2$Hz); MS $m/z = 424$ (M^+). Anal. Calcd for $C_{30}H_{36}N_2$: C, 84.86; H, 8.55; N, 6.60. Found: C, 84.63; H, 8.58; N, 6.70.

Preparation of 5,13-di-*tert*-butyl-1,2-dicyano-8,16-dipropyl[2.2]metacyclophan-1-ene (6c)

Compound **6c** was obtained from **5c** in a similar manner described above. The yield was 10%. **6c**: yellow prisms (hexane), mp 182.5–183.4°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 0.52 (t, 6H, $J = 7$Hz), 0.75–0.93 (m, 4H), 1.20–1.34 (m, 4H), 1.30 (s, 18H), 2.46–2.49 (m, 2H), 2.97–3.02 (m, 2H), 7.12 (d, 2H, $J = 2$Hz), 7.18 (d, 2H, $J = 2$Hz); MS $m/z = 452$ (M^+).

Preparation of 5,13-di-*tert*-butyl-1,2-dicyano-8,16-dimethoxy[2.2]metacyclophan-1-ene (6d)

Compound **6d** was obtained from **5d** in a similar manner described above. The yield was 23%. **6d**: orange prisms (hexane), mp 239.0–240.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 1.31 (s, 18H), 3.18 (s, 6H), 2.52–2.62 (m, 2H), 2.68–2.77 (m, 2H), 7.12 (d, 2H, $J = 2$Hz), 7.19 (d, 2H, $J = 2$Hz); MS $m/z = 428$ (M^+). Anal. Calcd for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.47; H, 7.58; N, 6.57.

Preparation of 5,14-di-*tert*-butyl-1,2-dicyano-8,17-dimethyl[2.3]metacyclophan-1-ene (6e)

Compound **6e** was obtained from **5e** in a similar manner described above. The yield was 4.9%. **6e**: colorless prisms

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(hexane), mp 269.5–271.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 0.86 (s, 6H), 1.31 (s, 18H), 1.96–2.00 (m, 2H), 2.42–2.52 (m, 2H), 2.62–2.72 (m, 2H), 7.16 (d, 2H, $J = 2$Hz), 7.20 (d, 2H, $J = 2$Hz); MS $m/z = 410$ (M^+). Anal. Calcd for $C_{29}H_{34}N_2$: C, 84.83; H, 8.35; N, 6.82. Found: C, 84.58; H, 8.62; N, 6.42.

Preparation of 5,15-di-*tert*-butyl-1,2-dicyano-8,18-dimethyl[2.4]metacyclophan-1-ene (6f)

Compound **6f** was obtained from **5f** in a similar manner described above. The yield was 21%. **6f**: colorless prisms (hexane), mp 264.0–265.0°C, ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 0.90–1.11(m, 2H), 1.02 (s, 6H), 1.32 (s, 18H), 1.33–1.50(m, 2H), 2.21–2.31 (m, 2H), 2.72–2.77 (m, 2H), 7.03 (d, 2H, $J = 2$Hz), 7.32 (d, 2H, $J = 2$Hz); MS $m/z = 424$ (M^+). Anal. Calcd for $C_{30}H_{36}N_2$: C, 84.86; H, 8.55; N, 6.60. Found: C, 84.71; H, 8.74; N, 6.65.

RESULTS AND DISCUSSION

Molecular design

As mentioned above, [2.n]metacyclophan-1-enes are sorts of diarylethenes, and two aromatic rings are fixed by two intramolecular bridges (Fig. 1). One can expect following novel features in the photochromism of these [2.n]metacyclophan-1-enes: (1) control of thermal stability by the change of 'X' becomes possible; (2) high quantum yield for photocyclization reaction can be expected because the conformation can be fixed to the photoactive one; (3) various types of derivatives with various absorption of light can be synthesized by the change of the functional group R; (4) photochromic reaction in the limited space is possible since the geometry change before/after photochromic reaction is small.

Figure 2 shows the calculated energies of formation of the open forms (**6a**, **6e**, **6f**) and closed form (**7a**, **7e**, **7f**) of 1,2-dicyano[2.n]metacyclophan-1-enes having various chain lengths. The calculations were carried out with AM1 in MOPAC. When the chain length (n) is short in the open form like $n = 2$, the steric repulsion occurs between the inner methyl groups and the opposite benzene rings. Then, the energy of formation increases in small cyclophanes. On the other hand, when the chain length of the closed form is long, the alkyl chain should be folded in small space and this increases the energy of formation.

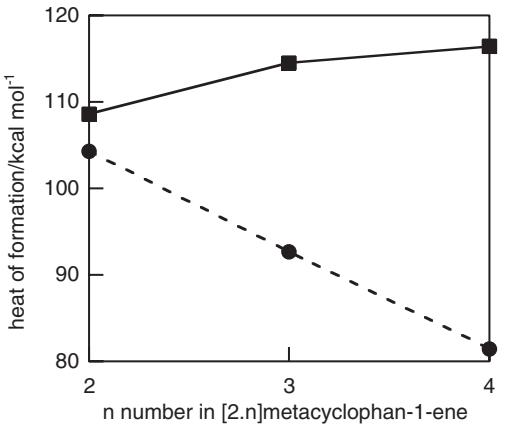

Figure 2. Energies of formation of the open (dot line) and closed form (solid line) of [2.n]metacyclophan-1-enes

Hence, in the closed form, the energy of formation becomes higher, as the chain length becomes longer as shown in Fig. 2. Then, as the chain length becomes shorter, the difference of the energy of formation of the each photoisomer becomes smaller. In general, when the energy difference between two photoisomers is small, the activation energy for thermal reaction would become large and in this system the higher energy one is thermally unstable.[8] In [2.n]metacyclophan-1-ene system, when the chain length n is short, the energy difference is small and the thermal stability becomes higher. On the other hand, when the chain length (n) is long, the energy difference becomes large and the closed form can easily return to the open form thermally. Therefore, it is predictable that the change of the length of the methylene chain (n) enables us to control the thermal stability of photochromic [2.n]metacyclophan-1-ene.

Figure 3 shows the concept for high quantum yield for photocyclization reaction of [2.n]metacyclophan-1-enes. In small [2.n]metacyclophan-1-ene system, the ring flipping hardly occurs since there is steric hindrance between the inner substituents and the opposite benzene rings. Therefore, once we isolate the photoactive anti-conformation of [2.n]metacyclophan-1-ene, it would never give the photoinactive syn conformation and the quantum yield would be expected to be higher.

Synthesis and characterizations

Scheme 1 shows the syntheses of [2.n]metacyclophan-1-enes having various substituents and chain length. Intramolecular coupling reactions of bis(cyanomethyl)ar-

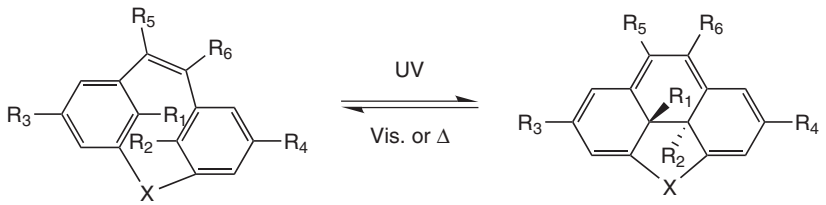

Figure 1. Photochromic reaction of [2.n]metacyclophan-1-ene

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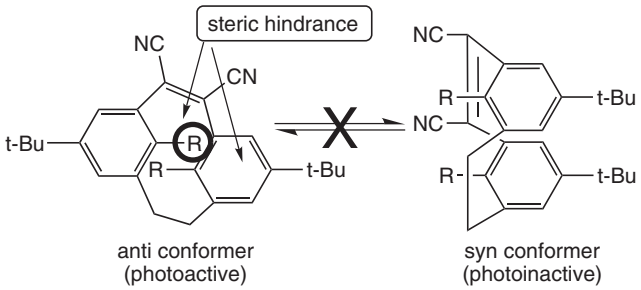


Figure 3. Concept for high quantum yield for photocyclization reaction in [2.n]metacyclophan-1-enes

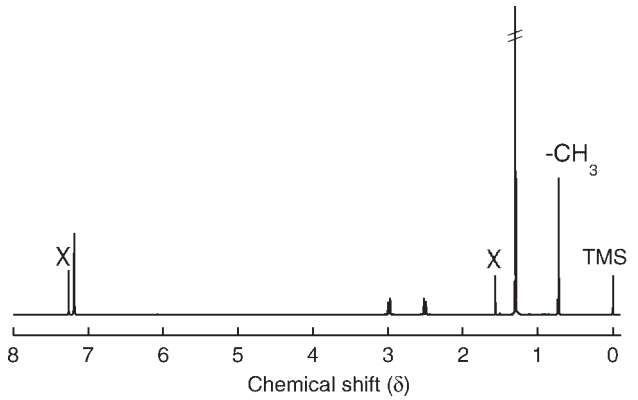
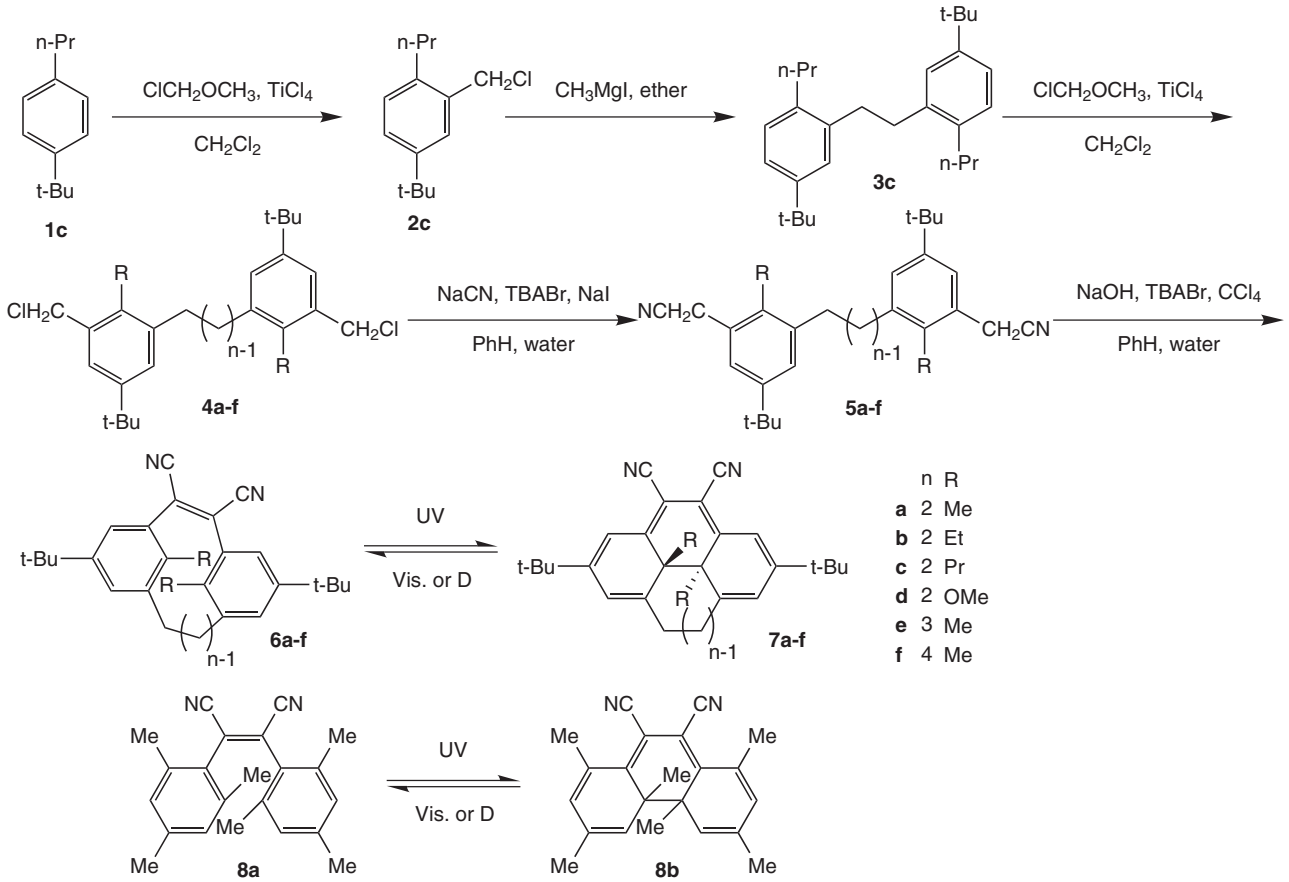


Figure 4. ^{1}H NMR spectrum of **6a** in $CDCl_3$ (300 MHz, 25°C)

enes have been accomplished by a modified manner to that described in the literature, which indicated the intermolecular coupling reaction of the cyanomethylarenes.[9] When we compared the yields for the intramolecular cyclization reaction, the yield for the formation of the smallest [2.2] system **6a**, which is supposed to be the most distorted, was the best in dimethyl[2.n]metacyclophan-1-ene syntheses (**6e**, **6f**). With an even number of the incorporated methylene groups in the cyclophane bridge, the yields of the ring closure reaction were fairly good ($n = 2$, 32%; $n = 4$, 21%), and not good yield was found in odd number of methylene groups in the cyclophane bridge ($n = 3$, 4.9%). This is probably due to the conformation of the intermediates. The intermediates for [2.2] and [2.4]metacyclophane-1-enes are more stable than that for [2.3]cyclophan-1-ene, then we could observe odd-even rule in this intramolecular coupling reaction.

Figure 4 shows the ^{1}H NMR spectrum (in $CDCl_3$, 300 MHz, 25°C) of **6a** as example. The signals for inner methyl group appeared at $\delta = 0.73$ which is about 1.4 ppm higher magnetic field shifted compared with that of 4-*tert*-butyltoluene. This is due to the shielding effect of the ring current of the opposite benzene rings,[10] therefore



Scheme 1

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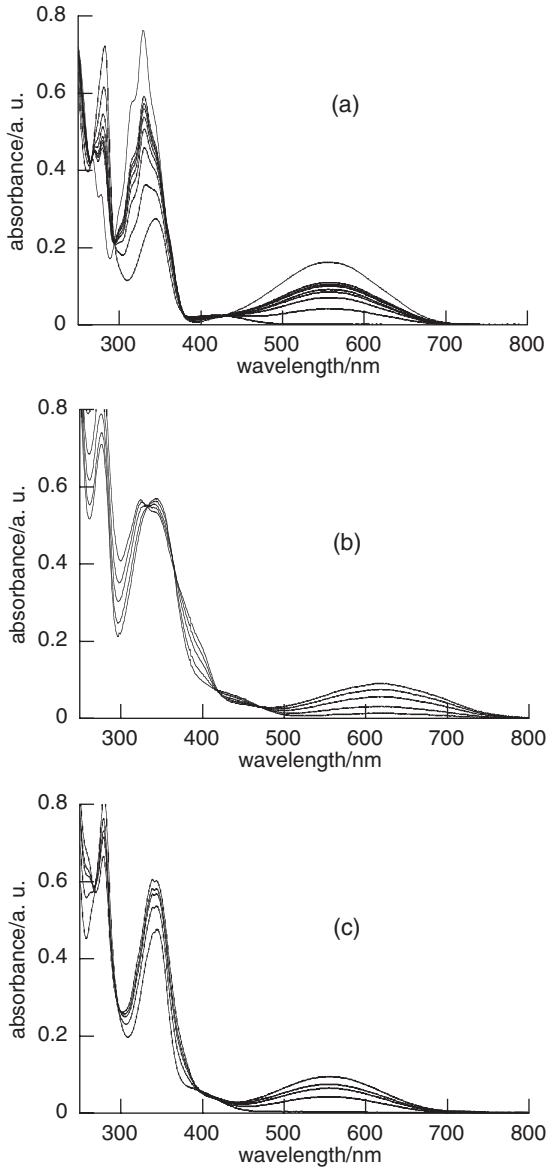

Figure 5. Absorption spectral changes upon irradiation with 313 nm light. (a) **6a** in hexane-CH_2Cl_2, (b) **6d** in CH_2Cl_2, and (c) **6e** in CH_2Cl_2.

the [2.2]metacyclophan-1-ene is anti-conformation which could carry out the photocyclization reaction. The dynamic ^{1}H NMR spectra were also measured at 150°C, however no change was observed. Therefore, the ring flipping never occurs below this temperature. We have already reported that the optically resoluted enantiomers of dimethyl[2.2]metacyclophan-1-ene derivative never racemized even at 200°C.[11] This fact also supported that no ring flipping occurs in this system in ambient temperature, since the racemization should take place via ring flipping of the benzene ring. On the other hand, the chemical shifts of the inner methyl groups of [2.3]metacyclophan-1-ene **6e** and [2.4]metacyclophan-1-ene **6f** appeared at 0.86 and 1.02 ppm, respectively. These signals are also shifted to the higher magnetic field compared with that of usual methyl group on benzene ring, then these [2.3] and [2.4]metacyclophan-1-enes were also photoactive anti-conformations.

Absorption spectral changes

As examples, Fig. 5a–c shows the absorption spectral changes of a hexane-CH_2Cl_2 (9:1) solution of **6a** and that of CH_2Cl_2 solutions of **6d** and **6e** upon irradiation with 366 nm light, respectively. The pale yellow solutions of the open forms turned to blue-violet by UV irradiation and the spectrum and color returned to the initial one by visible irradiation longer than 520 nm, showing photochromic properties. Although all synthesized [2.n]metacyclophan-1-enes showed photochromism, the thermal discoloration of the closed form of [2.4]metacyclophan-1-ene **7f** is too fast to measure the absorption spectrum of the closed form with our present instruments. The lifetime of **7f** was estimated to be shorter than 1 s at ambient temperature. Table 1 summarizes the absorption maxima of the open and closed forms of the synthesized [2.n]metacyclophan-1-enes. Although the absorption maxima are dependent on the inner substituents (R), no remarkable difference was observed in the chain length (*n*).

Thermal stability

The closed forms **7** thermally isomerized to return to the open form **6**. The lifetimes of the closed form were dependent on both the chain length (*n*) and the substituents (R). The activation energies for thermal ring opening reaction and the half-lifetimes of the closed forms are summarized in Table 2. When the chain length of the [2.n]metacyclophan-1-ene became longer, the activation energy decreased and the lifetime of the closed form became shorter as predicted. In case of tetrahydropyrene form, the half-lifetime of **7a** was 53 days at 273 K. While those of [2.4]metacyclophane could not be estimated, the thermal ring opening reaction was too fast.

Table 1. Absorption maxima (nm) of [2.n]metacyclophan-1-enes

Derivatives	**a**	**b**	**c**	**d**	**e**	**f**
Open form **6**	280, 345	286, 350	285, 351	276, 343	280, 345	280, 345
Closed form **7**	330, 555	339, 593	339, 592	325, 619	336, 555	—[a]

[a] Not available.

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Table 2. Activation energies[a] for thermal ring opening reaction and half-lifetimes of the closed form at 273 K

Derivatives **7**	**a**	**b**	**c**	**d**	**e**	**f**	**8**[9]
Activation energy (kcal mol^{-1})	17.0	16.2	18.8	NA	10.5	NA	NA
Pre-exponential factor (s^{-1})	6.6×10^6	2.2×10^6	1.6×10^8	NA	1.2×10^4	NA	NA
Half-lifetime	53 days	38 days	58 days	200 s[b]	25 min	<1 s	3 min[c]

[a] kcal mol^{-1}.
[b] At 303 K.
[c] Disappeared completely.

Although the blue color of the closed form **7f** ($n = 4$, R = Me) could be recognized during UV irradiation, the color suddenly disappeared by stopping the irradiation. Therefore, the closed form **7f** was too thermally unstable to measure the spectra in our present facilities.

When we compare the lifetimes of **7a–c** and **7e** with that of non-bridged type **8b**, of which lifetime was reported as 3 min,[9] the closed forms of [2.2] and [2.3]metacyclophan-1-enes are more thermally stable photochromic compounds. The closed form of [2.2]metacyclophan-1-ene having methoxy group **7d** easily isomerized to the open form. Similar phenomenon has been reported in the dithienylethene system.[12] The thermal ring opening reactions of the closed forms of the dithienylethenes having alkoxy group at their inner position were faster than those of the dithienylethenes with alkyl group.

The activation energies of the thermal isomerizations of **7a–c** and **7e** were studied by their Arrhenius plots (Fig. 6). The activation energies and pre-exponential factors for thermal reactions from the closed forms to the open forms are summarized in Table 2. The difference of the activation energies of **7a** and **7e** are due to the difference of the formation of energies of the open ring forms and those of the closed ring form as we have predicted. On the other hand, the thermal stabilities of the closed form of [2.2]metacyclophan-1-enes **7a–c** are scarcely different, while that of **7d** with methoxy group was quite unstable. Then, these results suggested that the electronic effect of the inner substituents is more efficient than their steric effects in the thermal ring opening reaction of the closed form of [2.2]metacyclophan-1-enes.

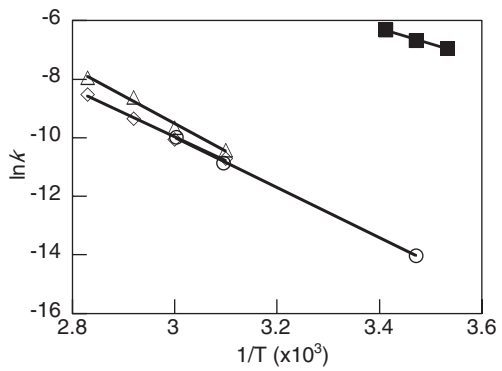

Figure 6. Arrhenius plots for thermal ring opening reactions of **7**; blank circle: **7a**, blank triangle: **7b**, blank rhombus **7c**, filled square **7e**.

Quantum yields for photochromic reactions

The quantum yields for photocyclization of [2.2]metacyclophan-1-ene **6a–c** and photo-ring opening reaction of **7a** were estimated and summarized in Table 3.[13] The quantum yields for the photocyclization reaction of **6a–c** upon irradiation with 313 nm light were estimated as 0.39, 0.33 and 0.35, respectively. The photocyclization quantum yield is dependent not only on the electronic structure of the compound but also on the structure, especially distance between the reactive atoms. These phenomena have been found in the photochromic reaction of the dithienylethenes in the single crystal.[15] Therefore, the photocyclization quantum yields of the dithienylethenes depend on the inner substituents since the distance is concerned with the steric hindrance between the inner substituents. In the [2.2]metacyclophan-1-ene system, the structure of the cyclophane is very rigid and the distance between the reactive carbon atoms is hardly influenced by the inner substituents. Therefore, the quantum yields of photocyclization reactions of **6a–c** become almost similar. The photocyclization quantum yields of dicyano[2.2]metacyclophan-1-enes are the highest in 1,2-dicyanodiarylethene family.[14] This is due to the fixation of metacyclophan-1-enes to the photoactive anti-conformation by double bridging. Then, one can say that the cyclophane structure could enhance the efficiency for photocyclization reaction. The quantum yield for photo-ring opening reaction of **7a** was estimated as 0.27.

CONCLUSIONS

We have demonstrated the syntheses and photochromic reactions of 1,2-dicyano[2.n]metacyclophan-1-ene

Table 3. Quantum yields for photocyclization and photo-ring opening reactions of **6a–c**

Derivatives	**6a**	**6b**	**6c**
Photocyclization	0.39	0.33	0.35
Photo-ring opening	0.27	—[a]	—[a]

[a] Not estimated.

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derivatives. Metacyclophan-1-ene system enables us to carry out to control the thermal stability of the photoisomer and highly efficient photochromic reaction. We have already extended the researches on these compounds to the enantiospecific photochromic reaction,[11] the photoreversible optical rotation change, [16] and the photoreversible refractive index change.[17] Also, we have already developed the heteroaromatic analogues of metacyclophan-1-enes and have reported a thermally irreversible heterophan-1-ene.[18] One of our next projects is to develop thermally irreversible photochromic system by use of [2.n]metacyclophan-1-enes bearing benzene rings.

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