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# Preparation and Photo-thermal Isomerization of Azo[2.2.1]- and Azo[2.2.3]metacyclophane Tweezers

Tsuyoshi SAWADA, Thies THIEMANN, and Shuntaro MATAKA

Azo[2.2.1]metacyclophane (MCP) tweezer **11** and azo[2.2.3]MCP tweezer **12** were prepared from [2.2.1]MCP **1a** and [2.2.3]MCP **8**, respectively, by *ipso*-nitration followed by reductive coupling using $LiAlH_4$. The photochemical and thermal isomerization of azo[2.2.n]MCP tweezers were studied by UV spectroscopy. The activation parameter ($E_a$) of the thermal *cis-trans* isomerization of **11** and **12** was determined as 81.7 kJmol$^{-1}$ and 90.9 kJmol$^{-1}$, respectively.

## Introduction

Molecular tweezers have been investigated as a new type of host molecule.[1)] Thus, Vögtle et al. have reported the preparation of molecular tweezers having [2.2]metacyclophane moieties connected by an acetylene unit.[1c)]

We have been studying the conformational behavior of MCPs having three aromatic rings.[2-10)] Recently, we found that trimethoxy[2.2.n]MCPs (n=1[7)], 2[8,9)],3[10)]) show an alternate conformations.

We were intrigued whether [2.2.n]MCPs connected at the alternated aromatic moiety may be suitable for a new type of molecular tweezer, where the alternation controls the cavity size. Especially, molecular tweezers which have two [2.2.n]MCPs connected by an azo unit, may be of interest as the azo unit can be isomerized both photochemically as well as thermally. In this paper, the preparation and photo-thermal isomerization of azo[2.2.n]MCP tweezers (n=1, 3) are reported.

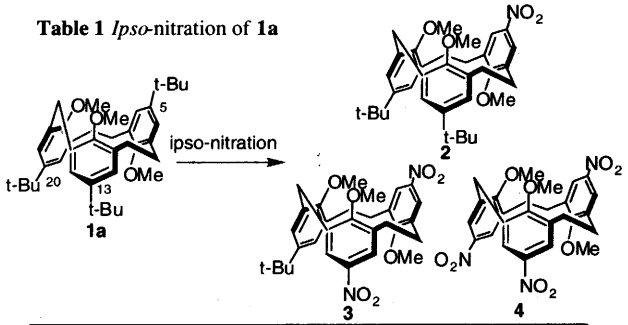
## Results and Discussion

*Ipso- nitration of [2.2.n]MCPs*

Previously, we have shown that both the 2,2-alternate conformer **1a** and the 1,2-alternate conformer **1b** could be isolated in the case of trimethoxy[2.2.1]MCPs.[7)] The results of the *ipso*-nitration of [2.2.1]MCPs **1a** and **1b**, using $Cu(NO_3)_2$ or $HNO_3$, are shown in Table 1 and Table 2, respectively.

The *ipso*-nitration of the 2,2-alternate conformer of [2.2.1]MCP **1a** with $HNO_3$ gave the mono-, di-, and trinitro[2.2.1]MCPs, **2**, **3**, and **4**, but, in the case of the nitration using $Cu(NO_3)_2$, the trinitro[2.2.1]MCP **4** was not formed, and the mononitro[2.2.1]MCP **2** could be obtained selectively by controlling the amount of $Cu(NO_3)_2$.

**Table 1** *Ipso*-nitration of **1a**




| Reagebt | eq. | Time | Yield[a)] 2 | 3 | 4 |
|---|---|---|---|---|---|
| fum. $HNO_3$[b)] | Excess | 70 min | 66% | 23% | |
| // | // | 24 h | | | 56% |
| $Cu(NO_3)_2$[c)] | 1.1 | 5h | 77% | | |
| // | 2.2 | // | 41% | 33% | |
| // | 3.3 | // | 16% | 55% | |
| // | 6.6 | // | 5% | 76% | |

a) Isolated Yield. b) in AcOH / $CH_2Cl_2$ at rt. c) in $Ac_2O$ / $CH_2Cl_2$ at rt

It is interesting that only one isomer, namely **2**, was obtained, although two isomers of the mono-nitro[2.2.1]MCP could be expected to form. This result suggests that the reactivity of positions 5, 13 and 20 are different towards *ipso*-nitration. It can be expected that the other two methoxy substituted arene units help stabilize the intermediately formed cation. The nitration proceeds *syn* to the methoxy groups of the other, vicinally placed arenes, which are tilted towards each other on that side due to the steric repulsion of the two *tert*-butyl groups on the other side (side *anti* to the site of nitration).

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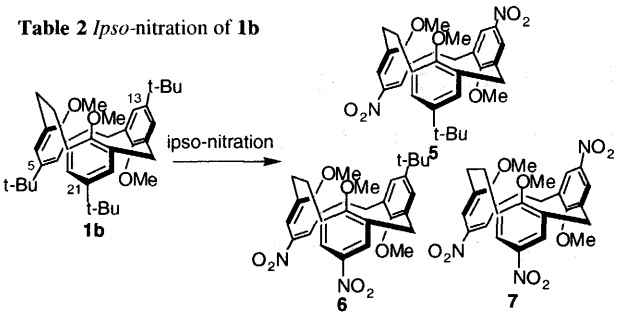
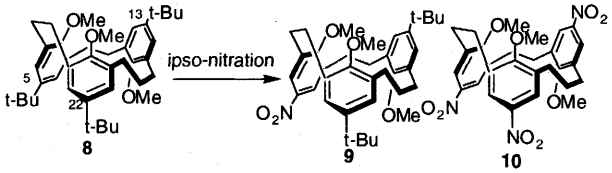
**Table 2** *Ipso*-nitration of **1b**



| Reagebt | eq. | Time | Yield[a] 5 | 6 | 7 |
|---|---|---|---|---|---|
| fum. $HNO_3$[b] | Excess | 1 h | 35% | 26% | 19% |
| // | // | 24 h | | | 57% |
| $Cu(NO_3)_2$[c] | 1.1 | 5h | complex mixture | | |
| // | 6.6 | // | 42% | 23% | |

a) Isolated Yield. b) in AcOH / $CH_2Cl_2$ at rt. c) in $Ac_2O$ / $CH_2Cl_2$ at rt

**Table 3** *Ipso*-nitration of **8**



| Reagebt | eq. | Time | Yield[a] 9 | 10 | recovery |
|---|---|---|---|---|---|
| fum. $HNO_3$[b] | Excess | 1h | | 69% | |
| $Cu(NO_3)_2$[c] | 1.1 | 5h | 67% | | 20% |
| // | 6.6 | // | 14% | 9% | |

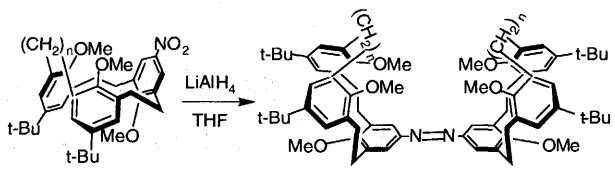
a) Isolated Yield. b) in AcOH / $CH_2Cl_2$ at rt. c) in $Ac_2O$ / $CH_2Cl_2$ at rt

On the other hand, the 1,2-alternate conformer **1b** afforded the di- and trinitro[2.2.1]MCPs **5** - **7**, but the mononitro derivative was not formed (Table 2). In the case of **1b**, the reactivity of the *ipso*-nitration at 5,13 and 20 position is almost the same, and dinitro[2.2.1]MCPs **5** and **6** were formed readily.

The *ipso*-nitration of [2.2.3]MCP **8** is shown in Table 3. In the case of [2.2.3]MCP **8**, mononitro[2.2.3]MCP **9** and trinitro derivative **10** were formed by using $Cu(NO_3)_2$, but the dinitro derivatives was not isolated. On the other hand, only trinitro derivative **10** was obtained by using $HNO_3$. The mononitro [2.2.3]MCP **9** was prepared selectively by controlling the amount of $Cu(NO_3)_2$.

*Reductive coupling of mononitro[2.2.n]MCP*

The preparation of azo[2.2.n]MCP tweezers **11** and **12** is shown in Scheme 1. By using $LiAlH_4$ in THF, only one step was required to form the azo[2.2.n]MCP tweezers **11** and **12**. The low yield of **12**, compared with that of **11**, seems to be due to the conformation of [2.2.3]MCP **9**. From $^1$H-NMR spectra, it can be deduced that mononitro[2.2.3]MCP **9** interconverts between the major 2,3-alternate and minor cone form just as in



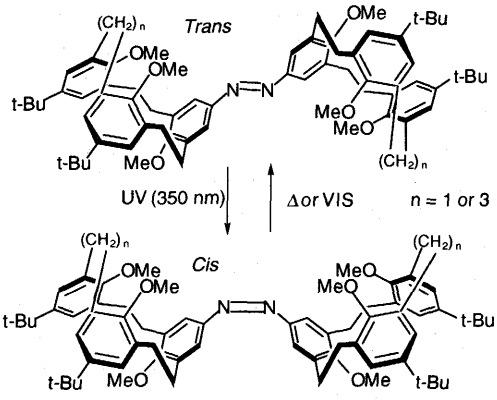
**Scheme 1**

[2.2.3]MCP **8**.[10] This may negatively influence the coupling reaction .

In the case of [2.2.3]MCP tweezer **12**, no conformational interconversion of the MCP skeleton was observed. It is thought that the conformational interconversion of **12** is suppressed by steric repulsion within the molecule.

*Photo-thermal isomerization of azo[2.2.n]MCP tweezers*

In the case of MCP tweezers **11** and **12**, a photochemical isomerization of the azo moiety could be observed and the isomerization from *cis* to *trans* could be reversed thermally (Scheme 2).



**Scheme 2**

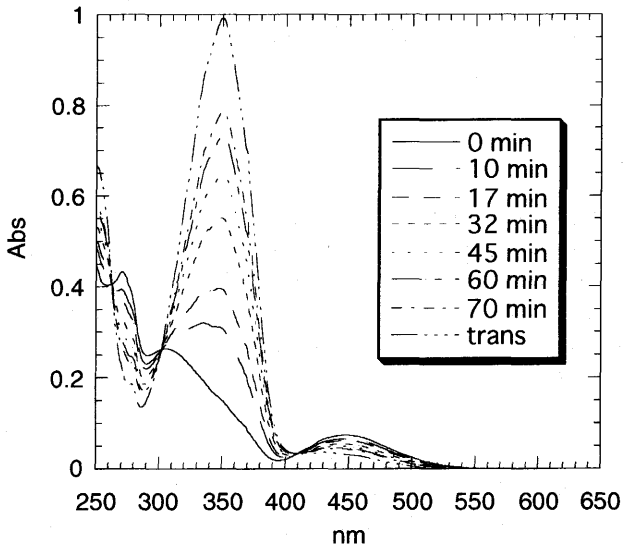



**Fig. 1** Thermal *cis* – *trans* isomerization of **12**.

Irradiation of MCP tweezers **11** and **12** using a high

pressure mercury lamp equipped with a color filter (355 nm) gave a mixture of *cis*- and *trans* isomers. These *cis*-isomers of the MCP tweezers isomerized to the *trans* isomers at rt. Thermal isomerization of **11** and **12** could be monitored by UV spectroscopy.

The UV spectra taken during the thermal isomerization of **12** are shown in Fig. 2. The activation parameters for the *cis-trans* isomerization were obtained in a THF solution of **12** at a concentration of 3.9 x $10^{-5}$ mol/L. The kinetic studies were carried out by using variable temperature UV spectroscopy[11], and the activation parameters of **11** and **12** was determined to be 81.7 kJmol$^{-1}$ and 90.9 kJmol$^{-1}$, respectively (Fig. 3, Fig. 4).

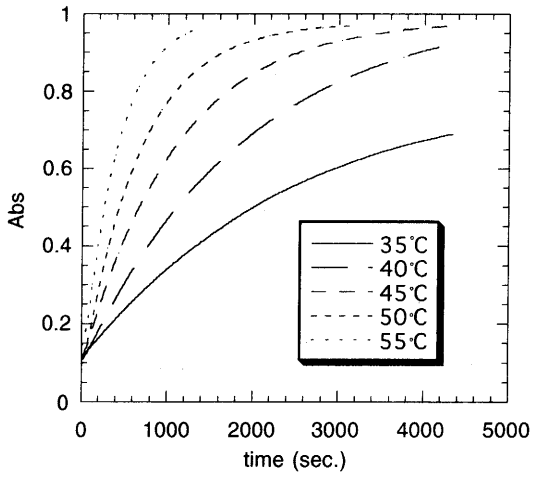



**Fig. 2** Variable temperature UV measurement at 350 nm in the thermal *cis-trans* isomerization of **12**.

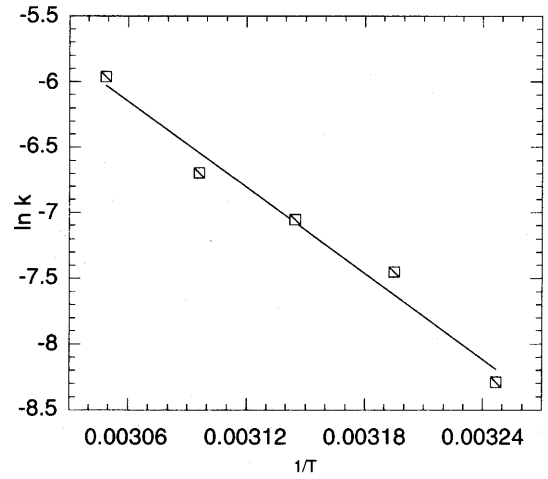



**Fig. 3** Arrhenius plot of thermal *cis-trans* isomerization of **12**.

Although it could well be expected that the difference of the [2.2.n]MCP skeletons will affect the thermal *cis-trans* isomerization, the difference of the activation parameter ($E_a$) between **11** and **12** is only 9.2 kJmol$^{-1}$. This result suggests that the MCP skeleton of MCP tweezers is not so important for the stability of the *cis* isomer. Therefore the azo[2.2.n]MCP tweezers **11** and **12** show almost the same photo-thermal isomerization behavior.

The molecular recognition characteristics of azo[2.2.n]MCP tweezers are currentry under investigation.

## Experiments

**General**- All m.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko IR-700 spectrometer as KBr pellets. $^1$H NMR spectra (internal $Me_4Si$) were measured on a JEOL EX270 NMR spectrometer unless stated otherwise. Mass spectra were recorded on a JEOL JMS-01SA-2 spectrometer at 75eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C300).

*13,20-Di-tert-butyl-8,16,23-trimethoxy-5-nitro[2.2.1]-MCP (2):* Copper nitrate 3-hydrate (41 mg, 0.2 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1a** (100 mg, 0.18 mmol) in acetic anhydride (30 mL) at rt. After the reaction mixture was stirred for 5h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and recrystallized from ethanol to give **2** (77 mg, 77%), colorless needles (ethanol), mp 247-249 °C ; MS (m/z) 545 ($M^+$); E.A. Found: C, 74.87; H, 7.94; N, 2.57%. Calcd. for $C_{35}H_{47}O_5N_1$: C, 74.49; H, 7.76; N, 2.52%; IR ν(cm$^{-1}$) 1518, 1352; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 1.22 (18 H, s, *tert*-Bu), 1.35 (3 H, s, methoxy H), 2.76–2.86 (4 H, m, bridge H), 3.13–3.39 (4 H, m, bridge H), 3.21 (1 H, d, $^2J$ = 12.2 Hz, bridge. H), 3.43 (6 H, s, methoxy H), 4.01 (1 H, d, $^2J$ = 12.2 Hz, bridge. H), 6.96 (2 H, d, $^4J$ = 2.6 Hz, arom. H), 7.07 (2 H, d, $^4J$ = 2.6 Hz, arom. H), 8.18 (2 H, s, arom. H).

*20-tert-Butyl-8,16,23-trimethoxy-5,13-dinitro[2.2.1]-MCP (3):* Copper nitrate 3-hydrate (247 mg, 1.2 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1a** (100 mg, 0.18 mmol) in acetic anhydride (30 mL) at rt. After the reaction mixture was stirred for 5h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant. The first fraction was evaporated and recrystallized from ethanol to give **2** (5.0 mg, 5%), and then, the second fraction was evaporated and recrystallized from ethanol to give 20-*tert*-butyl-8,16,23-trimethoxy-5,20-dinitro-[2.2.1]MCP **3** (75 mg, 76%); colorless needles (ethanol), mp 208-210 °C ; MS

(m/z) 534 ($M^+$); E.A. Found: C, 67.48; H, 6.45; N, 5.58%. Calcd. for $C_{30}H_{34}O_7N_2$: C, 67.40; H, 6.41; N, 5.28%; IR ν($cm^{-1}$) 1515, 1353; $^1$H-NMR ($CDCl_3$, 25°C) δ(ppm) 1.23 (9 H, s, *tert*-Bu), 1.90 (3 H, s, methoxy H), 2.51-2.97 (6 H, m, bridge H), 3.12-3.27 (2 H, m, bridge H), 3.34 (1 H, d, $^2J$ = 12.5 Hz, bridge. H), 3.38 (3 H, s, methoxy H), 3.52 (3 H, s, methoxy H), 4.08 (1 H, d, $^2J$ = 12.5 Hz, bridge. H), 7.00 (1 H, d, $^4J$ = 2.5 Hz, arom. H), 7.05 (1 H, d, $^4J$ = 2.5 Hz, arom. H), 7.92 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 7.95 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 8.14 (2 H, d, $^4J$ = 2.8 Hz, arom. H), 8.19 (2 H, d, $^4J$ = 2.8 Hz, arom. H).

*8,16,23-trimethoxy-5,13,20-trinitro[2.2.1]MCP* ***(4)***: Fuming nitric acid (0.5 g, 8.0 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1a** (95 mg, 0.17 mmol) in acetic acid and dichloromethane (1 : 1 ; v/v, 4 mL) at 0 °C. After the reaction mixture was stirred for 24 h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, sat. sodium hydrocarbonate water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and recrystallized from the 6:1 mixture of ethanol and chloroform to give **4** (50 mg, 56%), colorless plates (ethanol : chloroform 6:1; v/v), mp 288-290 °C ; MS (m/z) 523 ($M^+$); E.A. Found: C, 59.15; H, 4.79; N, 8.53%. Calcd. for $C_{26}H_{25}O_9N_3$: C, 59.65; H, 4.81; N, 8.03%; IR ν($cm^{-1}$) 1518, 1348; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 2.97 (3 H, s, methoxy H), 2.73–4.23 (12 H, m, bridge H), 3.44 (6 H, s, methoxy H), 7.91 (2 H, d, $^4J$ = 2.7 Hz, arom. H), 8.00 (2 H, d, $^4J$ = 2.7 Hz, arom. H), 8.13 (2 H, s, arom. H).

*20-tert-Butyl-8,16,23-trimethoxy-5,13-dinitro[2.2.1]-MCP* ***(5)*** *and 13-tert-butyl-8,16,23-trimethoxy-5,20-dinitro[2.2.1]MCP* ***(6)*** : Copper nitrate 3-hydrate (247 mg, 1.2 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1b** (100 mg, 0.18 mmol) in acetic anhydride (30 mL) at rt. After the reaction mixture was stirred for 5h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant. The first fraction was evaporated and recrystallized from ethanol to give 20-*tert*-butyl-8,16,23-trimethoxy-5,13-dinitro[2.2.1]-MCP **5** (41 mg, 42%). The second fraction was evaporated and recrystallized from ethanol to give 13-*tert*-butyl-8,16,23-trimethoxy-5,20-dinitro-[2.2.1]MCP **6** (22 mg, 23%).

**5**: colorless plates (ethanol), mp 240-242 °C ; MS (m/z) 534 ($M^+$); E.A. Found: C, 67.12; H, 6.32; N, 5.13%. Calcd. for $C_{30}H_{34}O_7N_2$: C, 67.40; H, 6.41; N, 5.28%; IR ν($cm^{-1}$) 1517, 1336; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 1.21 (9 H, s, *tert*-Bu), 2.54–3.86 (12 H, m, bridge H), 3.24 (3 H, s, methoxy H), 3.34 (3 H, s, methoxy H), 3.53 (3 H, s, methoxy H), 6.92 (1 H, d, $^4J$ = 2.3 Hz, arom. H), 6.96 (1 H, d, $^4J$ = 2.3 Hz, arom. H), 7.60 (1 H, d, $^4J$ = 2.3 Hz, arom. H), 7.79 (1 H, d, $^4J$ = 2.3 Hz, arom. H), 8.05 (2 H, s, arom. H).

**6**: colorless needles (ethanol), mp 220-222 °C ; MS (m/z) 534 ($M^+$); E.A. Found: C, 67.48; H, 6.33; N, 4.80%. Calcd. for $C_{30}H_{34}O_7N_2$: C, 67.40; H, 6.41; N, 5.28%; IR ν($cm^{-1}$) 1510, 1345; $^1$H-NMR ($CDCl_3$, 25°C) δ(ppm) 1.36 (9 H, s, *tert*-Bu), 2.58–3.70 (10 H, m, bridge H), 3.18 (3 H, s, methoxy H), 3.28 (3 H, s, methoxy H), 3.57 (3 H, s, methoxy H), 3.73 (2 H, brs, bridge. H), 7.13 (2 H, s, arom. H), 7.54 (1 H, d, $^4J$ = 3.0 Hz, arom. H), 7.82 (1 H, d, $^4J$ = 3.0 Hz, arom. H), 7.87 (2 H, d, $^4J$ = 2.6 Hz, arom. H), 7.90 (2 H, d, $^4J$ = 2.6 Hz, arom. H).

*8,16,23-trimethoxy-5,13,20-trinitro[2.2.1]MCP* ***(7)***: Fuming nitric acid (0.5 g, 8.0 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1b** (95 mg, 0.17 mmol) in acetic acid and dichloromethane (1 : 1 ; v/v, 4 mL) at 0 °C. After the reaction mixture was stirred for 24 h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, sat. sodium hydrocarbonate water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and recrystallized from the 6:1 mixture of ethanol and chloroform to give **7** (51 mg, 0.097 mmol, 57%), colorless plates (ethanol: chloroform 6:1; v/v), mp 288-290 °C ; MS (m/z) 523 ($M^+$); E.A. Found: C, 59.94; H, 4.87; N, 7.63%. Calcd. for $C_{26}H_{25}O_9N_3$: C, 59.65; H, 4.81; N, 8.03%; IR ν($cm^{-1}$) 1466, 1346; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 2.60–3.57 (10 H, m, bridge H), 3.30 (3 H, s, methoxy H), 3.35 (3 H, s, methoxy H), 3.63 (3 H, s, methoxy H), 3.74 (1 H, d, $^2J$ = 15.5 Hz, bridge. H), 3.98 (1 H, d, $^2J$ = 15.5 Hz, bridge. H), 7.61 (1 H, d, $^4J$ = 2.5 Hz, arom. H), 7.82 (1 H, d, $^4J$ = 2.5 Hz, arom. H), 7.89 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 7.93 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 8.07 (2 H, d, $^4J$ = 2.6 Hz, arom. H), 8.12 (2 H, d, $^4J$ = 2.6 Hz, arom. H).

*13,22-Di-tert-butyl-8,16,25-trimethoxy-5-nitro[2.2.3]-MCP* ***(9)***: Copper nitrate 3 hydrate (156 mg, 0.65 mmol) was added to a stirred solution of trimethoxy[2.2.3]MCP **8** (300 mg, 0.54 mmol) in acetic anhydride (30 mL) at rt. After the reaction mixture was stirred for 24 h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and recrystallized from the 8:1 mixture of ethanol and chloroform to give **9** (207 mg, 67%), colorless prisms (ethanol:chloroform 8:1, v/v), mp 237-239 °C ; MS (m/z) 573 ($M^+$); E.A. Found: C, 75.26; H, 8.21; N, 2.83%. Calcd. for $C_{36}H_{47}O_5N_1$: C, 75.36; H, 8.26; N, 2.44%; IR ν($cm^{-1}$) 1515, 1341; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) (a; alternate : b;cone =5:3) a: 1.25 (9 H, s, *tert*-Bu), 1.27 (9 H, s, *tert*-Bu), 1.95–3.56

(14 H, m, bridge H), 3.09 (3 H, s, methoxy H), 3.16 (3 H, s, methoxy H), 3.37 (3 H, s, methoxy H), 6.86 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 6.94 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 7.03 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 7.08 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 7.60 (1 H, d, $^4J$ = 2.7 Hz, arom. H), 8.20 (1 H, d, $^4J$ = 2.6 Hz, arom. H); b: 1.36 (18 H, s, *tert*-Bu), 1.95–3.56 (14 H, m, bridge H), 3.56 (6 H, s, methoxy H), 4.21 (3 H, s, methoxy H), 6.25 (2 H, s, arom. H), 6.90 (2 H, d, $^4J$ = 2.7 Hz, arom. H), 7.19 (2 H, d, $^4J$ = 2.7 Hz, arom. H).

*8,16,23-Trimethoxy-5,13,25-trinitro[2.2.3]MCP* ***(10)***: Fuming nitric acid (0.5 g, 8.0 mmol) was added to a stirred solution of trimethoxy[2.2.3]MCP **8** (100 mg, 0.17 mmol) in acetic acid and dichloromethane (1 : 1 ; v/v, 4 mL) at 0 °C. After the reaction mixture was stirred for 1 h, it was poured into ice water, and extracted with dichloromethane (100 mL). The extract was washed with water, sat. aq. $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant and recrystallized from the 8:1 mixture of ethanol and chloroform to give **10** (86 mg, 87%), colorless prisms (ethanol : chloroform 6: 1; v/v), mp 260-261 °C ; MS (m/z) 551 ($M^+$); E.A. Found: C, 60.74; H, 5.02; N, 7.12%. Calcd. for $C_{28}H_{29}O_9N_3$: C, 60.97; H, 5.30; N, 7.62%; IR ν($cm^{-1}$) 1515, 1346; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 2.97 (3 H, s, methoxy H), 1.64–3.68 (14 H, m, bridge H), 3.71 (3 H, s, methoxy H), 3.72 (3 H, s, methoxy H), 7.10 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 7.75 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 7.89 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 7.94 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 8.11 (1 H, d, $^4J$ = 2.6 Hz, arom. H), 8.39 (1 H, d, $^4J$ = 2.6 Hz, arom. H).

*trans-Azo[2.2.1]MCP tweezer* ***(11)*** : A solution of 5-nitro[2.2.1]MCP **2** (81 mg, 0.15 mmol) in dry THF (5 mL) was added to a stirred suspension of $LiAlH_4$ (0.5 g, 13 mmol) in dry THF (5 mL) at rt under an argon atmosphere. After the reaction mixture was stirred for 4h, it was poured into ethyl acetate (50 mL), and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using ether as eluant to give **11** (75 mg, 0.073 mmol, 49%), yellow plates (hexane:chloroform 4:1; v/v), mp 310 °C decomp. ; MS (m/z) 1027 ($M^+$+1, FAB); E.A. Found: C, 79.06; H, 8.42; N, 3.21%. Calcd. for $C_{68}H_{86}O_6N_2$: C, 79.49; H, 8.44; N, 2.73%; IR ν($cm^{-1}$) 2962, 1483, 1428, 1362, 1294, 1213; $^1$H-NMR ($CDCl_3$, 25℃) δ(ppm) 1.24 (36 H, s, *tert*-Bu), 1.40 (6 H, s, methoxy H), 2.63–2.86 (10 H, m, bridge H), 3.21 (2 H, d, $^2J$ = 11.9 Hz, bridge. H), 3.19–3.45 (6 H, m, bridge H), 3.43 (12 H, s, methoxy H), 4.04 (2 H, d, $^2J$ = 11.9 Hz, bridge. H), 6.99 (4 H, d, $^4J$ = 2.1 Hz, arom. H), 7.06 (4 H, d, $^4J$ = 2.1 Hz, arom. H), 7.94 (4 H, s, arom. H).

*trans-Azo[2.2.3]MCP tweezer* ***(12)*** : A solution of 5-nitro[2.2.3]MCP **9** (100 mg, 0.18 mmol) in dry THF (5 mL) was added to a stirred suspension of lithium aluminum hydride (0.5 g, 13 mmol) in dry THF (5 mL) at rt under an argon atmosphere. After the reaction mixture was stirred for 3 h, it was poured into ethyl acetate (50 mL), and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using ether as eluant to give **12** (15 mg, 16%), yellow needles (hexane:benzene 4:1, v/v), mp 315-317 °C; MS (m/z) 1083 ($M^+$+1, FAB); E.A. Found: C, 79.41; H, 8.83; N, 2.44%. Calcd. for $C_{72}H_{94}O_6N_2$: C, 79.81; H, 8.74; N, 2.59%; IR ν($cm^{-1}$) 2960, 1482, 1280, 1212; $^1$H-NMR ($CDCl_3$, 25°C) δ(ppm) 1.21 (36 H, s, *tert*-Bu), 1.25-1.18 (4 H, m, bridge H), 1.63 (6 H, s, methoxy H), 2.58-2.90 (12 H, m, bridge H), 3.45 (12 H, s, methoxy H), 3.20-3.54 (8 H, m, bridge H), 6.86 (4 H, d, $^4J$ = 2.3 Hz, arom. H), 7.00 (4 H, d, $^4J$ = 2.3 Hz, arom. H), 7.91 (4 H, s, arom. H).

*Kinetic procedure on variable temperature*[11]

A stock solution of the *trans* isomer of MCP tweezer **11** and **12** was prepared in THF (3.9 x $10^{-5}$ mol/L, 25 mL). Aliquotes (4 mL) were transferred to the UV cell made of quartz. The cell was sealed and irradiated with high-pressure mercury lamp (100W, Riko, UVL-100HA) equipped with a color glass filter (50 mm x 50 mm, peak: 350 nm, Toshiba, UV-D36c).

After irradiation for 10 min, the cell was set in for the UV spectrometer (Nihonbunko, UV570) equipped with a temperature control unit. The absorbance (350 nm) and times were recorded.

Activation energies were calculated from the raw kinetic observations of absorbance, temperature, and time by one-step procedure. The computational method consists of substituting the Arrhenius equation directly into the first-order rate expression by using eq. (1) – (4) (Abs, $Abs_0$, and $Abs_{inf}$ are absorbance at time t, time 0, and the infinity reading).

$$\int_0^t \frac{d(Abs - Abs_{inf})}{Abs - Abs_{inf}} = -\int_0^t k\,dt = -\int_0^t A\,e^{-Ea/RT}\,dt \quad (1)$$

$$Abs - Abs_{inf} = (Abs_0 - Abs_{inf})\exp(-A\,t\exp(-E_a/RT)) \quad (2)$$

$$\ln \frac{Abs - Abs_{inf}}{Abs_0 - Abs_{inf}} = -Ae^{-Ea/RT}t \quad (3)$$

$$\ln k = -E_a/RT + \ln A \quad (4)$$

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