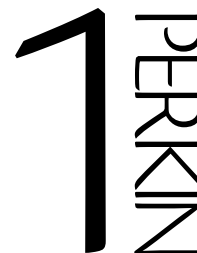


Preparation and structures of novel [2.2.2]metacyclophane tweezers



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[2.2.2]Metacyclophane (MCP) tweezers **7** and azo[2.2.2]MCP tweezers **8** were prepared from 21-nitro[2.2.2]MCP **2**, which was obtained by the *ipso*-nitration of [2.2.2]MCP **1**. X-Ray crystal structural analysis shows the MCP tweezers **7** to have the *anti*-conformation. The photothermal isomerization of azo[2.2.2]MCP tweezers **8** was studied by UV spectroscopy, and the activation energy of the thermal *cis*–*trans* isomerization was determined by UV measurements at variable temperatures to be $E^\ddagger = 71 \pm 7 \text{ kJ mol}^{-1}$. The complexation constant of **8** with silver ions was determined by the Benesi–Hildebrand method to be $73 \pm 3 \text{ L mol}^{-1}$.

Introduction

Molecular tweezers have been investigated as a new type of host molecule.¹ Recently, the preparation of molecular tweezers as guanidinium receptors has been reported, where directed hydrogen bond arrays are used in the binding of the guest.^{1a,b} There have also been some studies on molecular tweezers incorporating a metacyclophane (MCP) skeleton.² Vögtle and co-workers have reported the preparation of molecular tweezers possessing calixarene subunits^{2a,b} and have applied these calixarene moieties as stoppers in rotaxane structures. They have also reported on the preparation of molecular tweezers having [2.2]MCP moieties, and they have found that these molecules recognize carboxylic acids, where hydrogen bonding from the internal carboxylic groups has been deemed to be important.^{2c}

The authors have been studying the conformational behavior of MCPs with three aromatic rings,³ and, we have found that trimethoxy[2.2.*n*]MCPs (*n* = 1, 2, 3) show an alternate conformation.^{3a} We were intrigued as to whether [2.2.*n*]MCPs connected at the alternated aromatic moiety would be suitable for a new type of molecular tweezers, which would then have a total of four functional groups remaining within the [2.2.*n*]MCP units, and where the alternation controls the cavity size. Previously, we have communicated the preparation of [2.2.1]- and [2.2.3]MCP tweezers which have an azo linkage.⁴ In this paper the preparation and the chemical properties of two types of [2.2.2]MCP tweezers, **7** and **8**, are presented, in which the MCP subunits are connected either directly (**7**) or *via* an azo bridge (**8**).

Results and discussion

5,13,21-Tri-*tert*-butyl-8,16,24-trimethoxy[2.2.2]MCP **1** was prepared by the sulfur method.^{3a,d} *ipso*-Nitration⁴ of [2.2.2]MCP **1**, using Cu(NO₃)₂ or HNO₃, is shown in Scheme 1 and Table 1.

The *ipso*-nitration of MCP **1** with Cu(NO₃)₂ gave the mono-, di-, and trinitro[2.2.2]MCPs, **2**, **3**, and **4**, just as was the case with HNO₃. Moreover, the nitro[2.2.2]MCP **2** could be obtained selectively by controlling the amount of Cu(NO₃)₂.

It is interesting that only one conformational isomer, namely

Table 1 *ipso*-Nitration of **1**

Reagent	Equiv.	Time	Yield ^a (%)		
			2	3	4
Fuming HNO ₃ ^b	Excess	12 min	57	11	
		20 min		44	10
		3 h			69
Cu(NO ₃) ₂ ^c	1.1	5 h	94		
	2.2		46	30	
	3.3		26	46	7
	6.6			26	62

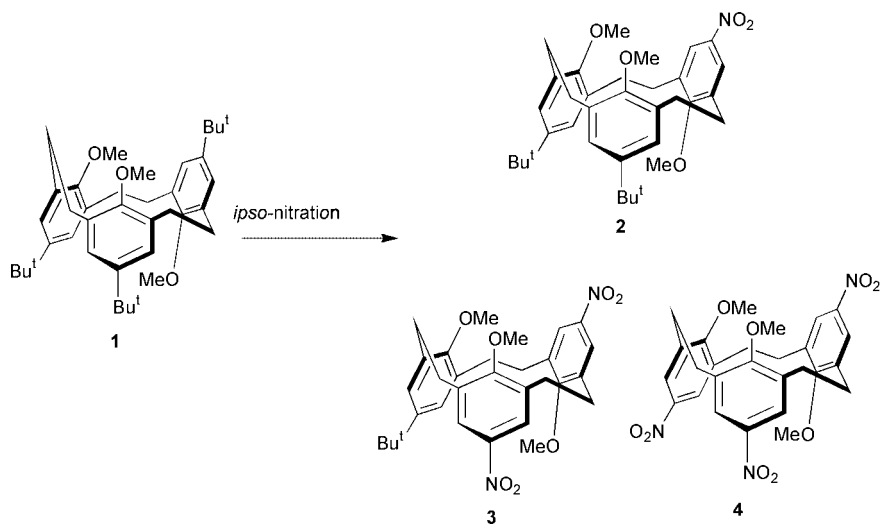
^a Isolated yield. ^b In AcOH–CH₂Cl₂. ^c In Ac₂O–CH₂Cl₂ at rt.

2, was obtained, although two conformational isomers of the mononitro[2.2.2]MCP could be expected to form. This result suggests that positions 5, 13, and 21 possess different reactivity towards *ipso*-nitration. It can be expected that the other two methoxy substituted arene units help to stabilize the intermediate cation. The nitration proceeds *syn* to the methoxy groups of the other, vicinally placed arenes, which are tilted towards each other due to the steric repulsion of the two *tert*-butyl groups on the other side (the side *anti* to the site of nitration).

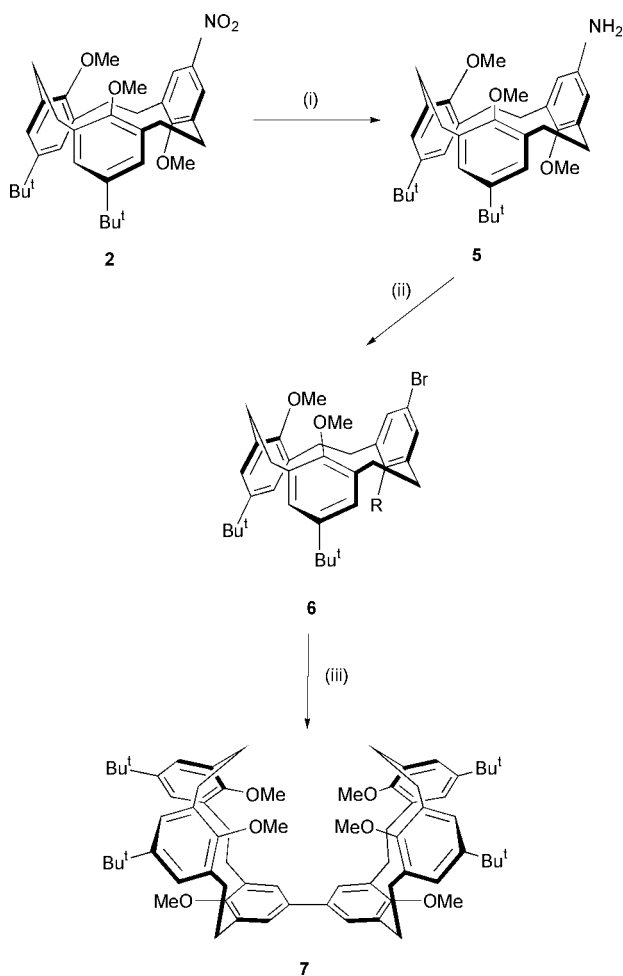
The preparation of [2.2.2]MCP tweezers **7** is shown in Scheme 2. Amino[2.2.2]MCP **5** was obtained from nitro[2.2.2]MCP **2** by reduction using Sn in aq. HCl solution. [2.2.2]MCP tweezers **7** were synthesized from **5** by the Sandmeyer reaction,⁵ followed by a Ni(0) coupling reaction.⁶ X-Ray crystal structural analysis shows the MCP tweezers **7** to have the *anti*-conformation in the solid state (Fig. 1).

In the solid state, the dihedral angle between the phenyl groups directly linking the two MCP units is 66.7°. This means that in the solid state the MCP tweezers **7** adopt a twisted conformation along the axis of the biphenyl unit. However, dynamic NMR measurements on the MCP tweezers **7** show a flexible conformation, indicating that there is rotation of the two phenyl groups of the biphenyl unit in solution.

MCP tweezers **7** crystallized with inclusion of solvent molecules (chloroform). It was found that two chloroform molecules are located in the vicinity of the two methoxy



Scheme 1



Scheme 2 Reagents and conditions: (i) Sn, HCl, 1,4-dioxane, quant.; (ii) HBr, NaNO₂, CuBr, 47%; (iii) NiBr₂(PPh₃)₂, Zn, 18%.

oxygens of the biphenyl unit, while two other chloroform molecules are located above the center of the two benzene rings of the biphenyl unit. The distance between the methoxy oxygen and the chloroform carbon is only 3.17 Å, and the distances between the carbon atoms of one arene unit and the chloroform carbon are 3.62–4.00 Å. These results suggest the existence of C–H···O and C–H···π interactions between chloroform and MCP tweezers 7.

Azo[2.2.2]MCP tweezers 8 and its reference compound 10 were afforded by reductive coupling of MCP 2 and 2,6-dimethyl-4-nitroanisole 9 using LiAlH₄ (Scheme 3).

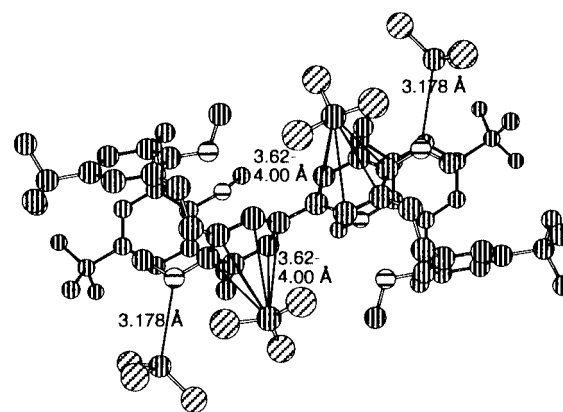


Fig. 1 Crystal structure of MCP tweezers 7·4 CHCl₃.

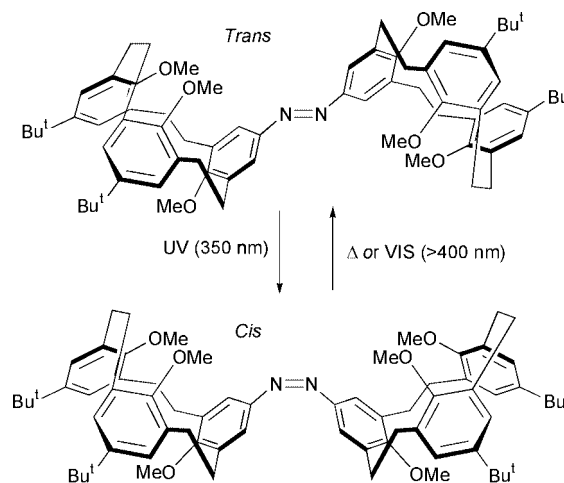


Fig. 2 Photochemical isomerization of azo[2.2.2]MCP tweezers 8.

Photochemical isomerization of the azo moiety of 8 was observed. This isomerization could be reversed thermally (Fig. 2). Irradiation of MCP tweezers 8 using a high pressure mercury lamp equipped with a glass filter (Toshiba color glass filter UV-D35, transmission peak 350 nm) gave a mixture of *cis* and *trans* isomers. The *cis* isomer of the MCP tweezers isomerized to the *trans* isomer at rt. The isomerization of 8 was monitored by UV spectroscopy (Fig. 3).

The activation energy of the thermal isomerization of 8 and of its reference compound 10 was determined from an Arrhenius plot to be $E^{\ddagger} = 71 \pm 7$ kJ mol⁻¹ and 68 ± 17 kJ mol⁻¹, respectively.⁷ These results suggest that the thermal

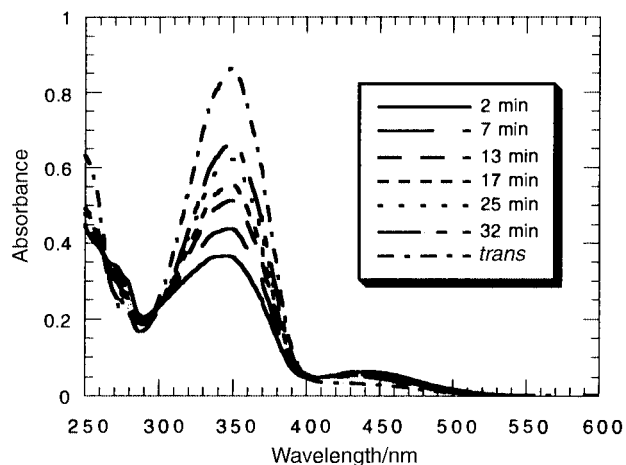
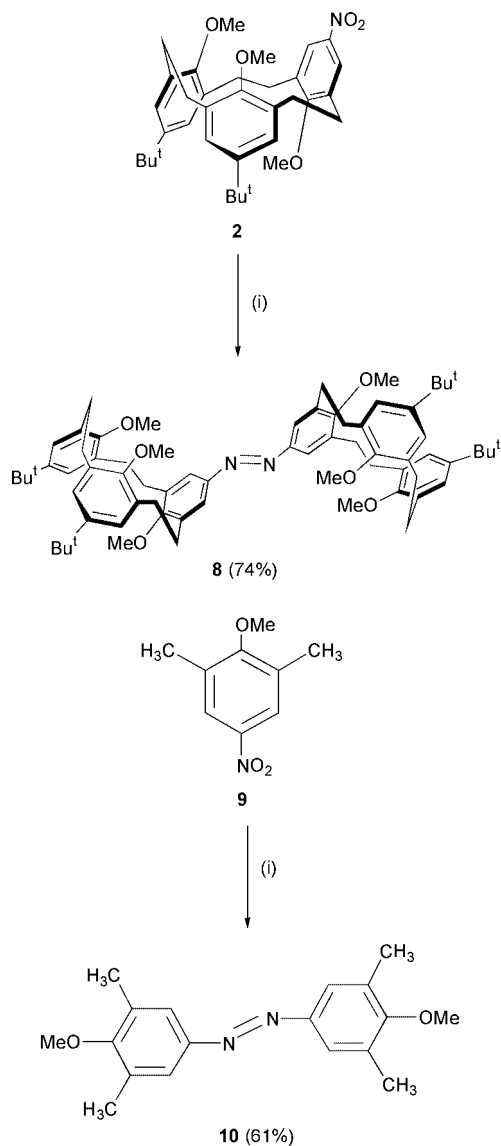


Fig. 3 Thermal isomerization of azo[2.2.2]MCP tweezers **8** in THF at 40 °C.



Scheme 3 Reagents and conditions: (i) LiAlH_4 , THF.

isomerization is not influenced remarkably by steric repulsion between the two MCP units.

The complexation properties of azo MCP tweezers **8** and **10** with silver cations were also investigated.⁸ Although the complexation of the irradiated mixture of *cis* and *trans* isomers of **8** with silver cations could not be observed as the mixture isomerized to the *trans* isomer too quickly, the UV spectrum of

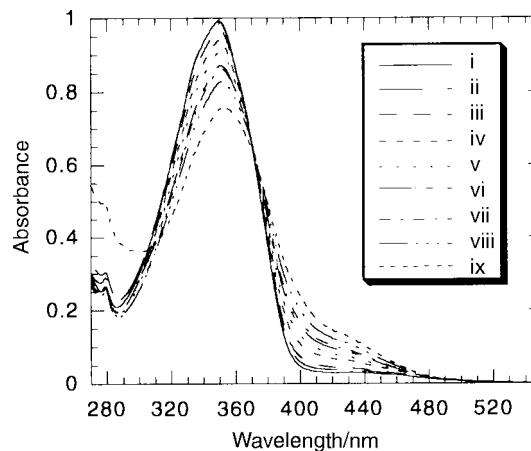


Fig. 4 UV spectra of MCP tweezers **8** in THF solution ($0.456 \text{ mmol L}^{-1}$) in the presence of AgOTf; i: 0 mmol L^{-1} , ii: $0.424 \text{ mmol L}^{-1}$, iii: 1.21 mmol L^{-1} , iv: 3.41 mmol L^{-1} , v: 5.33 mmol L^{-1} , vi: 7.61 mmol L^{-1} , vii: 9.19 mmol L^{-1} , viii: 13.4 mmol L^{-1} , ix: 24.2 mmol L^{-1} .

the *trans* isomer of **8** in the presence of AgOTf shows a red shift of the absorption peak, which is dependent on the ground-state complexation between the silver cation and the azobenzene group⁸ (Fig. 4).

The $^1\text{H-NMR}$ spectrum of **8** in the presence of AgOTf also supports the formation of a complex, since the chemical shifts of the methoxy and aromatic protons at the position *ortho* to the azo group show a low-field shift ($\delta_{\text{H}} +0.05$, $+0.07$). The complexation constant of the *trans* isomer of **8** with silver cations was determined from a Benesi–Hildebrand plot⁹ to be $73 \pm 3 \text{ L mol}^{-1}$. In the case of the reference compound **10**, the complexation constant was measured to be only $9.3 \pm 0.6 \text{ L mol}^{-1}$. These results suggest that there is an electrostatic contribution of the methoxy groups of **8** to the stabilization of the complex with silver cations.

Experimental

All melting points are uncorrected. IR spectra were measured for samples as KBr pellets on either a JASCO IR-700 or a Nippon Denshi JIR-AQ20M spectrometer. $^1\text{H-NMR}$ spectra were determined in CDCl_3 at 270 MHz with a JEOL EX-270 instrument. UV spectra were measured on a HITACHI 220A spectrophotometer using cyclohexane as solvent. Mass spectra were measured on a JEOL JMS-72 MStation machine at 75 eV using a direct inlet system or FAB system. Elemental analysis was performed on a YANAKO MT-5 instrument.

5,13-Di-*tert*-butyl-8,16,24-trimethoxy-21-nitro[2.2.2]MCP **2** and 5-*tert*-butyl-8,16,24-trimethoxy-13,21-dinitro[2.2.2]MCP **3**

Fuming nitric acid (0.5 g, 8.0 mmol) was added to a stirred solution of trimethoxy[2.2.1]MCP **1a** (97 mg, 0.17 mmol) in acetic acid and dichloromethane (1:1, v/v, 4 mL) at 0 °C. After the reaction mixture had been stirred for 12 min, it was poured into ice water (50 mL), and extracted with dichloromethane (100 mL). The extract was washed with water, sat. aq. sodium hydrogen carbonate, dried over anhydrous MgSO_4 , and concentrated. The residue was chromatographed on silica gel using dichloromethane as eluant. The first fraction was evaporated and recrystallized from a mixture of ethanol and chloroform (4:1, v/v) to give 5,13-di-*tert*-butyl-8,16,24-trimethoxy-21-nitro[2.2.2]MCP **2** (54 mg, 57%). The second fraction was evaporated and recrystallized from a mixture of ethanol and chloroform (6:1, v/v) to give 5-*tert*-butyl-8,16,24-trimethoxy-13,21-dinitro[2.2.2]MCP **3** (10 mg, 11%).

Compound 2. Colorless plates (ethanol–chloroform 4:1, v/v), mp 252–253 °C (Found: C, 74.66; H, 8.07; N, 2.48. $\text{C}_{35}\text{H}_{45}\text{O}_5\text{N}_1$ requires C, 75.10; H, 8.10; N, 2.50%); δ_{H} (270 MHz, CDCl_3)

1.20 (18 H, s, *tert*-Bu), 1.57 (3 H, s, methoxy H), 2.63–2.86 (8 H, m, bridge H), 3.19–3.45 (4 H, m, bridge H), 3.46 (6 H, s, methoxy H), 6.86 (2 H, d, $^4J = 2.3$ Hz, arom. H), 6.95 (2 H, d, $^4J = 2.3$ Hz, arom. H), 8.16 (2 H, s, arom. H); m/z 559 (M^+).

Compound 3. Colorless prisms (ethanol–chloroform 6:1, v/v), mp 224–226 °C (Found: C, 67.99; H, 6.56; N, 4.50. $C_{31}H_{38}O_7N_2$ requires C, 67.62; H, 6.98; N, 5.09%); δ_H (270 MHz, $CDCl_3$) 1.15 (9 H, s, *tert*-Bu), 2.63–2.86 (8 H, m, bridge H), 2.13 (3 H, s, methoxy H), 3.19–3.44 (4 H, m, bridge H), 3.49 (3 H, s, methoxy H), 3.54 (3 H, s, methoxy H), 6.89 (1 H, d, $^4J = 2.7$ Hz, arom. H), 6.95 (1 H, d, $^4J = 2.3$ Hz, arom. H), 7.81 (1 H, d, $^4J = 2.5$ Hz, arom. H), 7.87 (1 H, d, $^4J = 2.5$ Hz, arom. H), 8.13 (1 H, d, $^4J = 3.0$ Hz, arom. H), 8.16 (1 H, d, $^4J = 3.0$ Hz, arom. H); m/z 548 (M^+).

8,16,24-Trimethoxy-5,13,21-trinitro[2.2.2]MCP 4

Copper nitrate trihydrate (217 mg, 1.2 mmol) was added to a stirred solution of trimethoxy[2.2.2]MCP 1 (100 mg, 0.18 mol) in acetic anhydride (30 mL) at rt. After the reaction mixture was stirred for 5 h, it was poured into ice water (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 on silica gel using dichloromethane as eluant. The first fraction was evaporated and recrystallized from a mixture of ethanol and chloroform (6:1, v/v) to give 5-*tert*-butyl-8,16,24-trimethoxy-13,21-dinitro[2.2.2]MCP 3 (26 mg, 26%). The second fraction was evaporated and recrystallized from a mixture of ethanol and chloroform (6:1, v/v) to give 8,16,24-trimethoxy-5,13,21-dinitro[2.2.2]MCP 4 (60 mg, 62%) as colorless plates (ethanol–chloroform 6:1, v/v), mp 302–304 °C (Found: C, 60.14; H, 5.02; N, 7.53. $C_{27}H_{27}O_9N_3$ requires C, 60.32; H, 5.07; N, 7.82%); δ_H (270 MHz, $CDCl_3$) 2.95 (3 H, s, methoxy H), 2.76–3.78 (12 H, m, bridge H), 3.52 (6 H, s, methoxy H), 7.78 (2 H, d, $^4J = 2.8$ Hz, arom. H), 7.93 (2 H, d, $^4J = 2.8$ Hz, arom. H), 8.13 (2 H, s, arom. H); m/z 537 (M^+).

5-Amino-13,21-di-*tert*-butyl-8,16,24-trimethoxy[2.2.2]MCP 5

Tin powder (380 mg, 3.2 mmol) was added to a stirred solution of 5,13-di-*tert*-butyl-21-nitro-8,16,24-trimethoxy[2.2.2]MCP 2 (100 mg, 0.18 mol) in 1,4-dioxane (35 mL) at rt. Then, conc. HCl solution (10 mL) was added dropwise to the reaction mixture over 30 min. After the reaction mixture had been stirred for 1 h, it was neutralized with aq. 20% NaOH solution and extracted with dichloromethane (100 mL). The combined extracts were washed with water, dried over anhydrous $MgSO_4$, and concentrated. The white powder obtained was collected and dried to give 5 (94 mg, 0.17 mmol) as a colorless powder, mp 119–123 °C; δ_H (270 MHz, $CDCl_3$) 1.20 (18 H, s, *tert*-Bu), 1.51 (3 H, s, methoxy H), 2.62–2.70 (8 H, m, bridge H, NH_2), 3.06–3.16 (2 H, m, bridge H), 3.44–3.51 (2 H, m, bridge H), 3.48 (6 H, s, methoxy H), 6.55 (2 H, s, arom. H), 6.85 (2 H, d, $^4J = 2.6$ Hz, arom. H), 6.95 (2 H, d, $^4J = 2.6$ Hz, arom. H); m/z 529 (M^+). This material was used without further purification to prepare 6.

5-Bromo-13,21-di-*tert*-butyl-8,16,24-trimethoxy[2.2.2]MCP 6

A suspension of 5-amino-13,21-di-*tert*-butyl-8,16,24-trimethoxy[2.2.2]MCP 5 (220 mg, 0.41 mmol) in aq. 24% HBr solution (40 mL) was stirred for 12 h at rt. A solution of sodium nitrite (120 mg, 1.7 mmol) in water (10 mL) was added dropwise to the reaction mixture over 10 min at 0 °C. After the reaction mixture had been stirred at 0 °C for 30 min, a suspension of copper(I) bromide (94 mg, 0.65 mmol) in aq. 24% HBr solution (10 mL) was added dropwise to the mixture over 10 min. After the reaction mixture had been stirred for 1 h at 60–70 °C, the mixture was poured into ice water (50 mL), stirred for 30 min, and extracted with dichloromethane (100 mL). The extract was

washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on silica gel using dichloromethane as eluant to give 6 (87 mg, 0.15 mmol, 36%) as colorless prisms (hexane), mp 225–228 °C (Found: C, 70.63; H, 7.58. $C_{35}H_{45}O_3$ requires C, 70.81; H, 8.07; N, 7.64%); δ_H (270 MHz, $CDCl_3$) 1.19 (18 H, s, *tert*-Bu), 1.52 (3 H, s, methoxy H), 2.57–2.71 (8 H, m, bridge H), 3.08–3.20 (2 H, m, bridge H), 3.41–3.47 (2 H, m, bridge H), 3.50 (6 H, s, methoxy H), 6.86 (2 H, d, $^4J = 2.6$ Hz, arom. H), 6.93 (2 H, d, $^4J = 2.6$ Hz, arom. H), 7.31 (2 H, s, arom. H); m/z 593 (M^+).

Hexamethoxy[2.2.2]MCP tweezers 7

A suspension of $NiBr_2(PPh_3)_2$ (25 mg, 0.034 mmol), zinc powder (33 mg, 0.51 mmol), Et_4NI (43 mg, 0.17 mmol) in dry DMF (0.5 mL) was stirred for 1 h at rt. A solution of 5-bromo-13,21-di-*tert*-butyl-8,16,24-trimethoxy[2.2.2]MCP 6 (200 mg, 0.34 mmol) in dry DMF (5 mL) was added to the suspension. After the reaction mixture was stirred at 50 °C for 24 h, the precipitate was removed by filtration and the filtrate was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on silica gel using dichloromethane as eluant to give 7 (31.4 mg, 18%) as colorless prisms (hexane), mp 225–228 °C; δ_H (270 MHz, $CDCl_3$) 1.23 (36 H, s, *tert*-Bu), 1.58 (6 H, s, methoxy H), 2.59–2.91 (16 H, m, bridge H), 3.29–3.52 (8 H, m, bridge H), 3.60 (12 H, s, methoxy H), 6.89 (4 H, d, $^4J = 2.3$ Hz, arom. H), 7.03 (4 H, d, $^4J = 2.3$ Hz, arom. H), 7.48 (2 H, s, arom. H); m/z (FAB) 1026.6747 (M^+ , $C_{70}H_{90}O_3$ requires 1026.6737).

trans-Azo[2.2.2]MCP tweezers 8

A solution of 21-nitro[2.2.2]MCP 2 (100 mg, 0.18 mmol) in dry THF (5 mL) was added to a stirred suspension of lithium aluminium hydride (0.5 g, 13 mmol) in dry THF (5 mL) at rt under an argon atmosphere. After the reaction mixture had been stirred for 4 h, it was poured into ethyl acetate (50 mL), and then the mixture was poured into ice water (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 on silica gel using ether as eluant to give 8 (70 mg, 74%) as orange needles (hexane–benzene 4:1, v/v), mp 304–305 °C (Found: C, 79.43; H, 8.48; N, 2.44. $C_{70}H_{90}O_6N_2$ requires C, 79.66; H, 8.59; N, 2.67%); δ_H (270 MHz, $CDCl_3$) 1.21 (36 H, s, *tert*-Bu), 2.63–2.86 (12 H, m, bridge H), 1.66 (6 H, s, methoxy H), 3.19–3.45 (12 H, m, bridge H), 3.47 (12 H, s, methoxy 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); m/z 1055 ($M^+ + 1$, FAB).

4,4'-Dimethoxy-3,3',5,5'-tetramethylazobenzene 10

A solution of 3,5-dimethyl-4-methoxynitrobenzene 9¹⁰ (100 mg, 0.55 mmol) in dry THF (10 mL) was added to a stirred suspension of lithium aluminium 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 then the mixture was poured into ice water (50 mL) and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was recrystallized from hexane to give 10 (50 mg, 61%) as red prisms (hexane), mp 135–137 °C (Found: C, 72.49; H, 7.45; N, 9.32. $C_{18}H_{22}O_2N_2$ requires C, 72.46; H, 7.43; N, 9.39%); δ_H (270 MHz, $CDCl_3$) 2.37 (12 H, s, methyl H), 7.58 (4 H, s, arom. H); m/z 298 (M^+).

X-Ray crystal structure determination of 9a†

$C_{70}H_{90}O_6 \cdot 4 CHCl_3$. $M = 1504.90$, orthorhombic, $a = 37.110(8)$,

† CCDC reference number 207/449. See <http://www.rsc.org/suppdata/p1/b0/b003584j> for crystallographic files in .cif format.

$b = 10.064(2)$, $c = 20.820(9)$ Å, $V = 7775.7(41)$ Å³, $Z = 4$ (special position), $D_c = 1.286$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 4.291$ mm⁻¹, $Pbcn$ (no. 60), $0.33 \times 0.20 \times 0.10$ mm, $F(000)$ 3160, temperature of data collection 293 K, index ranges $-43 \leq h \leq 0$, $0 \leq k \leq 11$, $0 \leq l \leq 24$, reflections measured 6621, independent reflections 6621 [$R(\text{int}) = 0.000$, $R(\sigma) = 0.1548$]. Refinement method,¹¹ full-matrix least-squares refinement on F^2 . Data/restraints/parameters 6621/0/415. Final R and R_w values, 0.0862 and 0.2290. All calculations were performed on a MicroVAX3100 and IBM RISC System/6000 3100 using MolEN¹² and SHELXL-93.¹³

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