Synthesis and Solid-State Structural Analysis of Exotetradentate Ligands Based on Mesitylene-Derived [1.1.1.1]Metacyclophane Fixed in a 1,3-Alternate Conformation

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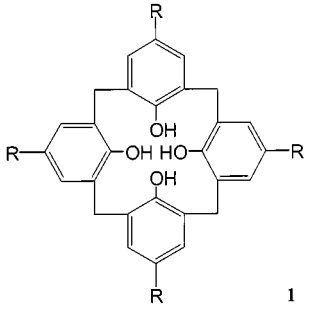
A series of new tetradentate ligands based on the [1.1.1.1]metacyclophane backbone fixed in a 1,3-alternate conformation was achieved. For the strategy developed, the common synthon for the preparation of twelve ligands bearing four interaction sites occupying the apices of a pseudo-tetrahedron [H, SH, CN, SCH_3, CO_2H, CHO, PPh_2, $P(O)Ph_2$, NO_2, NH_2, pyridine, and *para*-methoxyphenyl] was the tetrabromo derivative **7**. In addition to the classical characterisation methods applied to all reported ligands, compounds **7**, **9**, **12**, and **13** were structurally studied in the solid state by single-crystal X-ray diffraction, which indeed confirmed their 1,3-alternate conformation.

Introduction

Molecular networks are molecular assemblies possessing translational symmetry. In principle, these architectures are finite or infinite hypermolecules obtained by translation of one or several assembling cores, which are defined as structural nodes of the network. The assembling core may be regarded as a recognition pattern based on any type of intermolecular interactions. The number of translations in different directions of space defines the dimensionality of the network. Single translations result in 1-D networks, whereas two and three translations generate 2- and 3-D networks respectively. Although molecular networks of restricted size may be obtained by stepwise synthesis, large-size architectures may only be obtained by self-assembly processes between tectons that act as informed and active molecular construction modules. In terms of energy, the design of the tecton is governed by the nature of the assembling core. For the design of the latter, in principle, any type of reversible intermolecular interactions may be used. A variety of molecular networks based on weak van der Waals interactions (mainly of the inclusion type)[1] or on hydrogen[2−4] or coordination bonds[5−7] have been reported over the last decade. Concerning geometrical features, a tecton is by definition a construction unit possessing at least two interaction sites oriented in divergent fashion. In other terms, a tecton is either an exoreceptor or an exoligand.

Although the design of 1-D molecular networks may be straightforward, by use of tectons bearing only two interaction sites oriented in a divergent fashion, the formation of 2- and 3-D networks requires rather elaborate tectons. In particular, the design of specific tectons giving rise to the formation of 3-D networks appears to be rather challenging.[6,8−10] In this context, tectons possessing four interaction sites occupying the apices of a tetrahedron are of special interest. This type of arrangement may be obtained through the use of calix[4]arene derivatives in 1,3-alternate conformations (Scheme 1).[11] However, because of the flexibility of the calix backbone, this conformation must be imposed by appropriate functionalisation of the hydroxy groups. In order to introduce four coordination sites at the *para* position of the aromatic rings, further functionalisation of the upper rim is required, thus necessitating further synthetic steps.[12−14]



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Scheme 1

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Another possibility may be based on the metacyclophane skeleton **2** (Figure 1), formed through bridging of four mesitylene units by methylene units.[15] Indeed, owing to the steric hindrance between the methyl groups, this type of backbone is rather rigid and adopts the blocked 1,3-alternate conformation over a wide range of temperature (−60 °C to 150 °C).[16] A two-step synthesis of compounds **2** bearing one to four OH groups has been reported previously.[17] We have shown that the tetracyano compound **8**[12] and the tetrapyridine compound **20**,[10] in the presence of silver cation and under self-assembly conditions, give rise to a tubular and an interpenetrated 3-D coordination network, respectively. The synthesis of the cyclophane backbone **2** bearing two bipyridine or quinoline units has also been reported.[18]

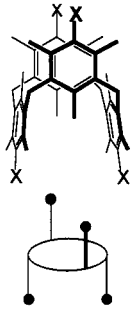
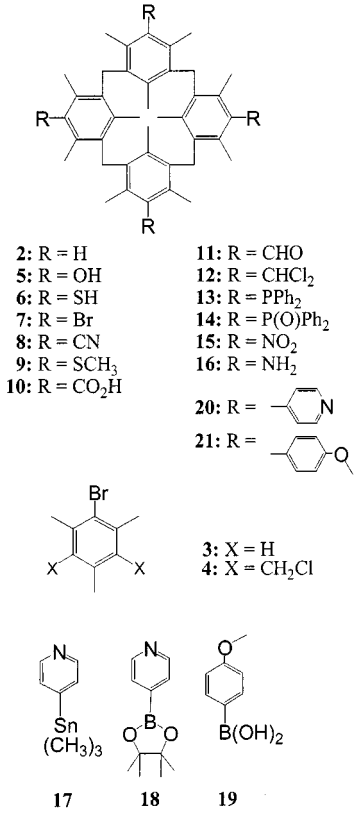


Figure 1. The metacyclophane **2** in 1,3-alternate conformation with four interaction sites (top) and its schematic representation (bottom); the dark circles represent interaction sites

In this contribution we report the synthesis and solid-state structural analysis of a series of new ligands based on the metacyclophane backbone **2** (Scheme 2) and bearing a wide variety of interaction sites such as SH (**6**), CN (**8**), SCH_3 (**9**), CO_2H (**10**), PPh_2 (**13**), $P(O)Ph_2$ (**14**), NO_2 (**15**), NH_2 (**16**), and PhOMe (**21**).

Results and Discussion

The starting material for the synthesis of compounds **8**−**21** was the tetrabromo derivative **7**. The first attempt to prepare this was based on bromination of the tetrahydroxy derivative **5**. However, the use of known reagents for bromination of phenol derivatives, such as PBr_3, PPh_3/Br_2,[19] failed. The direct synthesis of tetrabromo compound **7**, based on the procedure used for the preparation of **5**,[17] was therefore investigated, starting with the commercially available compound **3**. Compound **4** was obtained in 84% yield by treatment of **3** with 2 equiv. of $ClCH_2OCH_3$ in CH_2Cl_2 in the presence of a stoichiometric amount of $SnCl_4$ at room temperature. Upon heating an equimolar mixture of **3** and **4** overnight at 70 °C in $EtNO_2$ in the presence of catalytic amounts of $SnCl_4$, the cyclic metacyclophane **7** was obtained in 74% yield. Interestingly, owing to its low solubility in $EtNO_2$, the pure compound **7** could be isolated as a fine powder by simple filtration and washing several times with methanol.



Scheme 2

The conformation of compound **7** in the solid state was studied by X-ray diffraction methods on single crystals obtained by slow diffusion of CH_3OH into a $CHCl_3$ solution containing **7** (see Table 1, Exp. Sect.). The crystal is composed only of **7**, without any solvent molecule present in the lattice. Compound **7** indeed adopts the 1,3-alternate conformation in which the four Br atoms (d_{C-Br} = 1.92 Å) are located in alternate fashion below and above the main plane of the cyclophane, composed of four methylene units (Figure 2). The distance between two Br atoms located on the same face of the molecule is 7.87 Å. No specific intermolecular interactions between the cyclophane units is observed in the lattice. In $CDCl_3$ solution, the ^1H NMR spectrum showed only three sharp singlets at δ = 1.11, 2.59 and 4.09 for compound **7**, indicating, as expected, that the 1,3-alternate conformation was retained in solution.

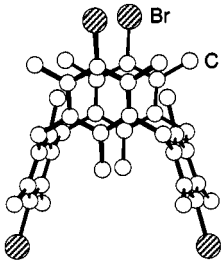


Figure 2. Crystal structure of the tetrabromo compound **7**, showing the 1,3-alternate conformation adopted by the cyclophane backbone; H atoms are omitted for sake of clarity; for selected bond lengths and angles, see text

The ability of the tetrabromo compound **7** to undergo the bromine/lithium exchange reaction was demonstrated by treatment of **7** with 8 equiv. of *t*BuLi in THF at −78 °C. The tetralithiated derivative was the starting synthon for the preparation of compounds **2**, **6**, **9**−**11**, and **13**. Indeed, quenching of the tetralithiated derivative with a 10% aqueous H_2SO_4 solution afforded the cyclophane **2** in quantitative yield. This compound has been prepared previously by another route.[17] Interestingly we found in the course of this study that compound **2** may be obtained directly in rather high yield (> 75%) by treatment of mesitylene with $ClCH_2OCH_3$ in CH_2Cl_2 at room temperature in the presence of $SnCl_4$.

Compound **2** was used as the starting material for the synthesis of the tetranitro compound **15**. Indeed, treatment of a CH_2Cl_2 solution containing compound **2** with a HNO_3/H_2SO_4 mixture at room temperature afforded the tetranitro compound **15** in 81% yield.

In order to obtain the tetraamino compound **16**, compound **15** was reduced. In a first attempt, stannous chloride[20] was employed both under acidic and under non-acidic conditions, unfortunately with no success. Finally, satisfactory results (78% yield) were obtained by treatment of compound **15** with $NaBH_4$ in dry THF at room temperature in the presence of Pd on C.[21] It is worth noting that a large excess of $NaBH_4$ (17 equiv. by nitro functions) was necessary to observe the complete conversion of all four nitro groups. However, when $LiAlH_4$ under reflux was used instead of $NaBH_4$, only 4 equiv. of the reducing agent was necessary and the reaction proceeded overnight in 70% yield.

Treatment of the lithiated derivative with S_8 in dry THF afforded the tetramercapto derivative **6** in 51% yield. It is worth noting that the synthesis of this compound has previously been achieved by a multi-step strategy,[22] starting with the tetrahydroxy derivative **5** and transforming it first into its tetra *O*-thiocarbamoyl derivative, then, by a rather delicate thermal transposition,[23] into the tetra-*S*-thiocarbamoyl compound and subsequent reduction to the desired compound **6** with $LiAlH_4$.

Treatment of the lithiated derivative with CH_3SSCH_3 in dry THF followed by reduction with $NaBH_4$ afforded the tetrakis(thiomethyl ether) **9** in 67% overall yield. The solid-state structure of compound **9** was again studied by X-ray diffraction on a single crystal obtained by slow diffusion of CH_3CN into a $CHCl_3$ solution containing **9** (Table 1). As in the case of compound **7**, mentioned above, the crystal is composed only of **9**, without any solvent molecule present in the lattice. Compound **9**, as expected, again adopts the 1,3-alternate conformation, with the four SMe groups (average d_{C-S} = 1.79 Å with an average C−S−C angle of 101.6°) located in an alternate fashion below and above the main plane of the cyclophane, composed of four methylene units (Figure 3). The distance between two S atoms located on the same face of the molecule is 8.72 Å. Again, no specific intermolecular interactions between the cyclophane units are observed in the lattice. In the ^1H NMR spectrum of **9** in $CDCl_3$ solution, in addition to the three sharp singlets corresponding to the methylene and methyl groups of the cyclophane backbone at δ = 1.13, 2.15 and 4.05, another sharp singlet at δ = 2.75, corresponding to the thiomethyl groups, was observed, again demonstrating the 1,3-alternate conformation of the compound **9** in solution.

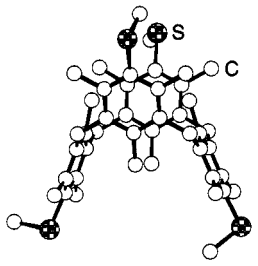


Figure 3. Crystal structure of the tetrakis(thiomethyl) compound **9**; the cyclophane adopts the 1,3-alternate conformation; H atoms are omitted for sake of clarity; for selected bond lengths and angles, see text.

The tetralithiated derivative was also used to prepare the tetracarboxy derivative **10** by treatment with CO_2 (gas). The 1,3-alternate conformation of compound **10** in the solid state was demonstrated by an X-ray diffraction study on its Cs^+ salt (not reported here).

Compound **11** was prepared in 83% yield by treatment of the tetralithiated salt of **7** with DMF. The same compound has previously been obtained by treatment of the cyclophane **2** with Cl_2CHOCH_3 in CH_2Cl_2.[17] Chlorination of the tetraformyl compound **11**, affording compound **12**, was achieved in 68% yield with PCl_5 in CH_2Cl_2. The structure of **12** was again studied in the solid state by X-ray diffraction on a single crystal obtained by slow concentration of a $CHCl_3$ solution of **12**. The crystal is composed of **12** and $CHCl_3$ solvent molecules. One of the two chloroform molecules and one of the four CCl_2 groups were found to be disordered. Compound **12**, as expected, again adopts the 1,3-alternate conformation in which the four CCl_2 groups (average d_{C-Cl} distance ca. 1.77 Å) are located in an alternate fashion below and above the main plane of the cyclophane, composed of four methylene units (Figure 4).

On treatment of the tetralithiated derivative of **7** with PPh_2Cl in dry THF, the tetrakis(diphenylphosphanyl) derivative **13** was obtained in only 7% yield. Thin layer chromatography revealed the presence of the mono-, di-, tri-, and tetrasubstituted metacyclophanes; however, the di- and

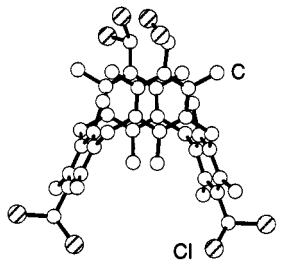


Figure 4. Crystal structure of compound **12**; one of the $CHCl_2$ groups was found to be disordered; H atoms and solvent molecules are omitted for sake of clarity; for selected bond lengths and angles, see text

trisubstituted species were found to be the most abundant. Despite the low polarity differences between these four compounds, the tetrasubstituted compound **13** could nevertheless be isolated by a rather laborious column chromatography method. The low yield of compound **13** may be attributed to steric hindrance induced by the rather bulky PPh_2 groups.

The structure of compound **13** in the crystalline phase was also investigated by X-ray diffraction on a single crystal obtained by slow diffusion of degassed CH_3CN into a degassed $CHCl_3$ solution of **13** (Table 1). The crystal is composed of **13** and $CHCl_3$ solvent molecules. One of the four PPh_2 groups was found to be disordered, resulting in a rather poor *R* value. Compound **13** also adopts the 1,3-alternate conformation, with the four PPh_2 groups (average d_{C-P} distance ca. 1.85 Å) located in an alternate fashion below and above the main plane of the cyclophane, composed of four methylene units (Figure 5). The distance between two P atoms located on the same face of the molecule is 7.68 Å. In $CDCl_3$ solution, the ^1H NMR spectrum of **13** consisted of three sharp singlets for the methylene and methyl groups, in agreement with the 1,3-alternate conformation. The observation of a unique signal at $\delta = -9.29$ by ^{31}P NMR spectroscopy was also in agreement with the proposed conformation.

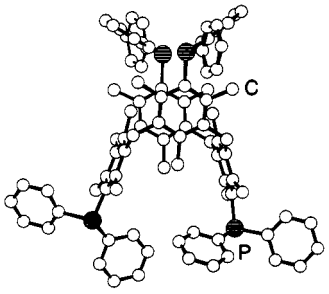


Figure 5. Crystal structure of tetrakis(diphenylphosphane) compound **13**; one of the phosphane groups was found to be disordered; H atoms and $CHCl_3$ solvent molecules are omitted for sake of clarity; for selected bond lengths and angles, see text

Compound **13** appeared to be rather unstable towards oxidation and it should be stored in the absence of oxygen. Indeed, it was oxidised into its phosphane oxide derivative **14** in the presence of air. The oxidative conversion process was monitored by both ^1H and ^{31}P NMR, which revealed that complete oxidation occurred at room temperature in the presence of air after 2 d. When the oxidation reaction was monitored by ^{31}P NMR spectroscopy, a unique signal at $\delta = -9.29$, corresponding to the precursor **13**, could be observed initially ($t = 0$). As the oxidation process proceeded, other signals corresponding to partially oxidised compounds appeared. After the oxidation was complete (48 h), a unique signal was again observed, now at $\delta = 30.68$ and corresponding to the phosphane oxide derivative **14**.

The ability of the tetrabromo compound **7** to undergo aromatic nucleophilic substitution was also investigated. Compound **8**, bearing four nitrile groups, was obtained in 83% yield by means of a classical Rosenmund−von Braun-type reaction[24] on treatment of **7** with CuCN in refluxing DMF. The structure of **8** in the solid state has been reported previously.[12]

The synthesis of diaryl derivatives of **2** by palladium-catalysed cross-coupling was investigated on the tetrabromo compound **7**. The first targeted ligand was compound **20**, bearing four pyridine units connected at position 4 with respect to the nitrogen atom.[10] The synthesis of **20** was first attempted, unfortunately without any success, by means of a Still-type coupling reaction between compound **7** and the known 4-(trimethylstannyl)pyridine (**17**).[25] The preparation of compound **20** was then attempted by means of the Suzuki palladium-catalysed cross-coupling reaction. Usually, these types of reactions are carried out at ca. 80 °C in the presence of Pd^0 as catalyst and in the presence of a base such as Na_2CO_3, NaOH, or $Ba(OH)_2$ in mixtures of solvents such as benzene/H_2O or DME/H_2O. In the case of sterically hindered compounds or with arylboronic acid derivatives bearing electron-withdrawing or -donating substituents, such aqueous conditions only rarely provide satisfactory results, in particular because of competitive hydrolytic deboronation.[26] In order to avoid this, an alternative procedure based on the condensation of compound **7** with the arylboronic acid ester **18**[27] was carried out at 130 °C in the presence of anhydrous Cs_2CO_3 and catalytic amounts of tetrakis(triphenylphosphane)palladium(0) in a mixture of dry toluene/DMF, affording compound **20** in an excellent 80% yield (this procedure, as well as the structural analysis of compound **20**, confirming its 1,3-alternate conformation, were previously reported in a communication and are not duplicated here[10]).

In marked contrast, when compound **7** was treated with the arylboronic acid **19**, bearing a methoxy group at the *para* position, under the same non-aqueous conditions, the cross-coupling reaction producing compound **21** proceeded in only 7% yield. Attempts to increase the yield failed.

In solution, as expected because of the steric hindrance induced by the two *ortho*-methyl groups in the cyclophane skeleton, the rotation around the C−C bond between the aromatic moiety of the cyclophane and the pyridine units in the case of the compound **20** and the methoxyphenyl units in that of compound **21** was considerably slowed down on the NMR timescale. Even at room temperature, this blocked rotation was observed for both compounds **20** and **21** by both ^1H and ^{13}C NMR spectroscopy, which revealed non-equivalence of protons and carbon atoms.

Conclusion

In conclusion, a series of new tetradentate ligands based on the [1.1.1.1]metacyclophane backbone fixed in 1,3-alternate conformation has been prepared and in some cases structurally characterised in the solid state by single-crystal X-ray diffraction. These ligands, bearing a variety of interaction sites occupying the apices of a pseudo-tetrahedron,

were designed to behave as exoligands in the formation of 3-D molecular networks. The ability of compounds **8**[12]and **20**[10] to generate coordination networks in the presence of silver cations has been demonstrated previously. Work along these lines with the reported new ligands and metal cations is currently in progress.

Experimental Section

General: All commercially available reagents were purchased and used without further purification. Reaction solvents were distilled by standard methods prior to use. Compounds were purified by column chromatography on Kieselgel 60 (Merck; 43−60 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker spectrometers at 400 and 300 MHz and at 50 MHz, respectively. Microanalyses were performed by the "Service de Microanalyses de la Fédération de Recherche Chimie", Université Louis Pasteur.

Crystal Structure Characterisation: X-ray diffraction data collection was carried out with a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation. For all structures, diffraction data were corrected for absorption and analysed using the OpenMolen package.[28] All non-H atoms were refined anisotropically. Crystal data and details of measurements are reported in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170004 (**7**), -170005 (**9**), -170006 (**12**), -170007 (**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

3,5-Bis(chloromethyl)-2,4,6-trimethylbromobenzene (4): Anhydrous $SnCl_4$ (14 mL, 120 mmol) was added dropwise at room temperature and under argon to a dry, stirred CH_2Cl_2 (100 mL) solution containing compound **3** (9.20 mL, 60 mmol) and $ClCH_2OCH_3$ (9.20 mL, 120 mmol). The mixture was further stirred overnight at room temperature, after which 2 N HCl (50 mL) was added and stirring was continued for another 10 min. The organic layer was separated and washed with 5% aqueous $NaHCO_3$ solution (75 mL) and H_2O (75 mL) and dried with $MgSO_4$. Evaporation of the solvent left a white residue, which was crystallised from a CH_2Cl_2/MeOH (75:150) mixture to afford the pure compound **4** (14.95 g, 84%) as colourless needles, m.p. 128−130 °C. $C_{11}H_{13}BrCl_2$ (296.03): calcd. C 44.63, H 4.43; found C 44.80, H 4.57. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 2.47 (s, 6 H, *ortho*-CH_3), 2.58 (s, 3 H, *para*-CH_3), 4.70 (s, 4 H, CH_2Cl). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 15.2, 20.9, 42.2, 127.8, 133.9, 136.1, 138.5.

4,11,18,25-Tetrabromo-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (7): A dry, stirred $EtNO_2$ solution (200 mL) of **3** (5.18 mL, 33.8 mmol), **4** (10 g, 33.8 mmol) and anhydrous $SnCl_4$ (1 mL) was heated at 70 °C under argon overnight. Upon cooling to room temperature, the solution was filtered, affording a light pink powder that was washed several times with small portions of cold $EtNO_2$ (3 × 25 mL) and MeOH (3 × 25 mL) to provide pure compound **7** (10.6 g, 74%) as a fine, white powder, m.p. > 300 °C. $C_{40}H_{44}Br_4$ (844.4): calcd. C 56.90, H 5.25; found C 56.94, H 5.39. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.11 (s, 12 H, *para*-CH_3), 2.59 (s, 24 H, *ortho*-CH_3), 4.09 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.6, 22.5, 35.2, 128.3, 133.6, 134.6, 138.7.

4,11,18,25-Tetracyano-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (8): A stirred suspension of **7** (50 mg, 0.6 mmol) and CuCN (530 mg, 5.9 mmol) in dry DMF (30 mL) was refluxed for 15 h. After a few minutes the solution became dark brown while the suspension dissolved. The solution was cooled to 100 °C, after which a solution of $FeCl_3$ (1 g, 6.2 mmol) in 10% aqueous HCl (20 mL) was added dropwise. The resulting green solution was further stirred at 100 °C for 1 h. The mixture was allowed to come to room temperature and filtered. The light brown residue was washed with a 10% aqueous HCl solution (25 mL) and H_2O (25 mL). The pure compound **8** was obtained in 83% yield (311 mg) as a white solid after chromatography

Table 1. X-ray data for compounds **7**, **9**, **12**, and **13**

	7	**9**	**12**	**13**
Empirical formula	$C_{40}H_{44}Br_4$	$C_{44}H_{56}S_4$	$C_{44}H_{48}Cl_8{\cdot}2CHCl_3$	2 $(C_{88}H_{84}P_4){\cdot}5CHCl_3$
Formula mass	844.43	713.19	1099.25	3127.98
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	*Fddd*	*C*2/*c*	*Pbca*	$P2_1/a$
a [Å]	9.4970(4)	21.194(2)	18.6631(2)	21.7225(9)
b [Å]	24.222(2)	11.9565(5)	21.5190(2)	17.0798(5)
c [Å]	31.1140(9)	15.710(1)	24.6928(3)	23.3268(8)
α [°]	90	90	90	90
β [°]	90	103.378(5)	90	109.268(5)
γ [°]	90	90	90	90
U [Å^3]	7157(1)	3873.0(8)	9916.9(2)	8169.8(5)
$D_{calcd.}$ [g·cm^{-3}]	1.57	1.22	1.47	1.27
Z	8	4	8	2
Colour	colourless	colourless	colourless	colourless
Crystal dim. [mm]	0.20×0.08×0.06	0.18×0.14×0.12	0.18×0.12×0.08	0.20×0.14×0.14
μ(Mo-K_α) [mm^{-1}]	4.525	0.276	0.811	0.383
T [K]	173	294	173	173
Number of data measured	11552	4459	22664	19228
Number of data with $I > 3\sigma(I)$	1181	1994	5249	7049
R	0.043	0.069	0.065	0.111
Rw	0.080	0.081	0.073	0.125

(SiO_2, CH_2Cl_2), m.p. > 300 °C. $C_{44}H_{44}N_4 \cdot 2H_2O$ (664.89): calcd. C 79.48, H 7.28, N 8.43; found C 79.65, H 7.05, N 8.12. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.13 (s, 12 H, *para*-CH_3), 2.63 (s, 24 H, *ortho*-CH_3), 3.97 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.9, 19.9, 32.3, 113.7, 118.5, 137.7, 140.4.

3,5,7,10,12,14,17,19,21,24,26,28-Dodecamethyl[1.1.1.1]metacyclophane (2): *t*BuLi (1.7 M/pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min and quenched with a large excess of a 10% aqueous H_2SO_4. The solution was stirred for a further 30 min at −78 °C, after which it was allowed to come to room temperature. The solvent was removed in vacuo and the resulting residue was dissolved in $CHCl_3$. The organic layer was washed with a 10% aqueous H_2SO_4 solution (75 mL), saturated aqueous $NaHCO_3$ (75 mL) and saturated aqueous NaCl solution (75 mL) before being dried ($MgSO_4$). Evaporation of the solvent provided a yellow residue, which was triturated well several times with Et_2O. Filtration afforded **2** (187 mg, 100%) as a white solid, m.p. > 300 °C. $C_{40}H_{48} \cdot H_2O$ (546.8): calcd. C 87.86, H 9.22; found C 87.42, H 8.92. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.18 (s, 12 H, *para*-CH_3), 2.34 (s, 24 H, *ortho*-CH_3), 3.88 (s, 8 H, Ar-CH_2-Ar), 6.80 (s, 4 H, *H*-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.9, 21.4, 31.9, 130.3, 133.2, 135.9, 137.6.

Alternative Synthesis of 2: A solution of $ClCH_2OCH_3$ (4.7 mL, 62.1 mmol) in dry CH_2Cl_2 (30 mL) was slowly added dropwise, under argon and at room temperature, to a vigorously stirred solution of mesitylene (8.64 mL, 62.1 mmol) and anhydrous $SnCl_4$ (8.2 mL, 70 mmol) in dry CH_2Cl_2 (60 mL). The solution turned orange and then red, while a precipitate started to form after half of the addition. After complete addition, the mixture was stirred overnight at room temperature. A mixture of MeOH/HCl (29 mL/1 mL) was added. The solid was filtered and washed with small portions of MeOH and then Et_2O, to afford **2** (6.15 g, 75%) as a white solid.

4,11,18,25-Tetramercapto-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (6): *t*BuLi (1.7 M/pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min, after which solid S_8 (455 mg, 14.2 mmol) was added. The reaction mixture was allowed to come to room temperature and stirring was continued for another 8 h. $NaBH_4$ (760 mg, 20 mmol) was added to the mixture, and the resulting orange mixture was stirred overnight at room temperature. The excess of $NaBH_4$ was quenched by addition of a 10% aqueous H_2SO_4 solution (30 mL). The organic layer was separated, washed with a 10% aqueous H_2SO_4 solution (75 mL) and H_2O (75 mL), and dried with $MgSO_4$. Evaporation of the solvent afforded a yellowish oil, which was purified by chromatography (SiO_2, CH_2Cl_2/hexane, 20:80) to afford the pure compound **6** (120 mg, 51%) as a white solid after recrystallisation from a $CHCl_3$/MeOH (10:20) mixture, m.p. > 300 °C. $C_{40}H_{48}S_4 \cdot CHCl_3$ (776.47): calcd. C 63.55, H 6.38; found C 62.77, H 6.74. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.12 (s, 12 H, *para*-CH_3), 2.53 (s, 24 H, *ortho*-CH_3), 3.20 (s, 4 H, SH), 4.06 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.7, 20.3, 34.4, 128.8, 132.9, 133.7, 138.1.

4,11,18,25-Tetramethylthio-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (9): *t*BuLi (1.7 M/pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min, after which neat CH_3SSCH_3 (0.325 mL, 3.55 mmol) was added and the mixture was slowly (2 h.) allowed to come to room temperature. Excess CH_3SSCH_3 was destroyed by addition of $NaBH_4$ (342 mg, 9 mmol) and stirring at room temperature for 30 min. The mixture was then poured into an aqueous NaOH (1 M, 100 mL) solution. The organic layer was separated, and the aqueous phase was extracted with $CHCl_3$ (2 × 75 mL). The combined organic phases were washed with aqueous NaOH (1 M, 75 mL), dried with $MgSO_4$ and concentrated to dryness. The resulting light brown solid was crystallised from a toluene/acetonitrile (1:2) mixture to afford **9** (170 mg, 67%) as a white solid, m.p. > 300 °C. $C_{44}H_{56}S_4$ $0.75H_2O$ (726.72): calcd. C 72.72, H 7.97; found C 72.60, H 7.90. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.13 (s, 12 H, *para*-CH_3), 2.15 (s, 12 H, -SCH_3), 2.75 (s, 24 H, ortho-CH_3), 4.05 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.2, 19.6, 20.2, 34.9, 134.6, 136.3, 137.8, 138.4.

3,5,7,10,12,14,17,19,21,24,26,28-Dodecamethyl[1.1.1.1]-metacyclophane-4,11,18,25-tetracarboxylic Acid (10): *t*BuLi (1.7 M in pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min, after which CO_2 (gas) was bubbled through the solution for a period of 4 h while the temperature of the mixture was increased to 25 °C. The mixture was further stirred at room temperature overnight. Aqueous H_2SO_4 solution (10%, 25 mL) was added and the organic layer was separated, further washed with 10% aqueous H_2SO_4 solution (75 mL), dried with $MgSO_4$, and concentrated to dryness. The resulting residue was dissolved in boiling absolute EtOH (75 mL) and the warm solution was filtered to remove insoluble materials. H_2O (50 mL) was added to the filtrate. After reduction of the volume of the solution by concentration and then cooling in an ice bath, compound **10** (220 mg, 88%) was isolated as a white solid by filtration, m.p. > 300 °C. $C_{44}H_{48}O_8 \cdot 1.25$THF (777.08): calcd. C 74.02, H 7.35; found C 73.95, H 7.26. ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 1.09 (s, 12 H, *para*-CH_3), 2.26 (s, 24 H, *ortho*-CH_3), 3.87 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ([D$_6$]DMSO, 50 MHz, 25 °C): δ = 17.9, 18.0, 31.3, 127.7, 135.1, 135.7, 137.1, 172.3. IR (KBr): ν_{CO} = 1706.5 cm^{-1}.

3,5,7,10,12,14,17,19,21,24,26,28-Dodecamethyl[1.1.1.1]-metacyclophane-4,11,18,25-tetracarbaldehyde (11): *t*BuLi (1.7 M/pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min, after which neat, dry DMF (2.2 mL, 28.4 mmol) was added and the milky solution was stirred for another 30 min at −78 °C before being allowed to warm slowly to room temperature (4 h). A 10% aqueous H_2SO_4 solution (30 mL) and $CHCl_3$ (50 mL) were added. The organic layer was separated, washed with a 10% aqueous H_2SO_4 solution (75 mL) and dried with $MgSO_4$, and the solvents were evaporated to dryness. The resulting slightly yellow solid was purified by chromatography (SiO_2, CH_2Cl_2) to afford **11** (188 mg, 83%) as slightly yellow crystals after crystallisation from a $CHCl_3$/THF (1:2) mixture, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.21 (s, 12 H, *para*-CH_3), 2.49 (s, 24 H, *ortho*-CH_3), 4.01 (s, 8 H, Ar-CH_2-Ar), 10.63 (s, 4 H, -C*H*O). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 16.7, 19.1, 31.0, 133.6, 135.1, 138.2, 139.7, 197.6.

4,11,18,25-Tetrakis(dichloromethyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (12): PCl_5 (5 g, 24 mmol) was added in one portion, at room temperature and under argon, to a stirred solution of **11** (1 g, 1.56 mmol) in dry CH_2Cl_2 (50 mL). The resulting clear yellow solution was refluxed

for 3 d. After this had cooled to room temperature, crushed ice (75 g) was added and stirring was maintained for 15 min. The organic layer was separated and dried with $MgSO_4$ and the solvents were evaporated to dryness. The resulting mixture was triturated with Et_2O and filtered to afford **12** (920 mg, 68%) as a white solid, decomposed 200−220 °C. $C_{44}H_{48}Cl_8$ (860.49): calcd. C 61.42, H 5.62; found C 61.42, H 5.79. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.12 (s, 12 H, *para*-CH_3), 2.59 (s, 24 H, *ortho*-CH_3), 4.00 (s, 8 H, Ar-CH_2-Ar), 7.33 (s, 4 H, -C*H*Cl_2). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.4, 32.6, 69.4, 134.8, 137.4.

4,11,18,25-Tetrakis(diphenylphosphanyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (13): *t*BuLi (1.7 M in pentane, 1.7 mL, 2.89 mmol) was added dropwise, at −78 °C and under argon, to a stirred suspension of **7** (300 mg, 0.355 mmol) in dry THF (40 mL). The yellow solution was stirred at −78 °C for 30 min, after which neat PPh_2Cl (0.64 mL, 3.55 mmol) was added. The solution was stirred for a further 2 h at −78 °C and allowed to warm to room temperature, and stirring under argon was continued overnight. After evaporation of the solvent, the obtained yellow residue was dissolved in $CHCl_3$ (100 mL), washed with saturated aqueous $NaHCO_3$ (75 mL) and NaCl (75 mL) solutions and dried with $MgSO_4$, and the solvent was removed to afford a white residue, which was purified by chromatography (SiO_2, hexane/CH_2Cl_2, 70:30) to give the compound **13** (31 mg, 7%) as a white solid, m.p. 238−240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.32 (s, 12 H, *para*-CH_3), 2.38 (s, 24 H, *ortho*-CH_3), 3.98 (s, 8 H, Ar-CH_2-Ar), 7.20−7.35 (m, 40 H, *H*-Ar PPh_2). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.7, 22.5, 22.9, 127.2, 128.3, 130.7, 131.0, 131.9, 137.3, 137.6, 138.2, 139.0, 139.1, 141.0, 141.3 ^{31}P NMR ($CDCl_3$, 75 MHz, 25 °C): δ = −9.3.

4,11,18,25-Tetrakis(diphenylphosphoryl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (14): A $CHCl_3$ solution (5 mL) of compound **12** (10 mg, 0.0079 mmol) was stirred in the presence of air for 2 d at room temperature. Upon removal of the solvent, compound **14** (10.5 mg, 100%) was obtained as a light brown solid; m.p. > 300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.40 (s, 12 H, *para*-CH_3), 2.22 (s, 24 H, *ortho*-CH_3), 3.87 (s, 8 H, Ar-CH_2-Ar), 7.37−7.42 (m, 20 H, *H*-Ar), 7.60−7.66 (m, 20 H, *H*-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 14.8, 19.1, 23.2, 23.3, 127.3, 128.6, 128.8, 130.7, 130.9, 131.2, 135.6, 138.8, 139.0, 139.5, 139.7. ^{31}P NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 30.7.

3,5,7,10,12,14,17,19,21,24,26,28-Dodecamethyl-4,11,18,25-tetranitro[1.1.1.1]metacyclophane (15): Aqueous HNO_3 solution (68%, 10 mL) and aqueous H_2SO_4 (95%, 1 mL) were added at 0 °C to a stirred solution of **2** (1 g, 1.9 mmol) in CH_2Cl_2 (100 mL). The resulting mixture was stirred at room temperature for 48 h. The organic layer was separated and washed with water (3 × 100 mL). The resulting residue was triturated well with toluene and filtered. The obtained yellow solid was washed with MeOH (3 × 20 mL) to afford **15** (1 g, 81%) as a light yellow, crystalline solid, m.p. > 300 °C. $C_{40}H_{44}N_4O_8$ (708.8): calcd. C 67.78, H 6.26, N 7.90; found C 67.95, H 6.33, N 7.73. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.18 (s, 12 H, *para*-CH_3), 2.29 (s, 24 H, *ortho*-CH_3), 3.98 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 15.7, 18.8, 32.3, 124.5, 137.1, 137.9, 152.9.

4,11,18,25-Tetraamino-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (16): A solution of **15** (500 mg, 0.7 mmol) in dry THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (500 mg, 11.3 mmol) and 10% Pd/C (200 mg) in dry THF (40 mL), cooled to −10 °C. The addition of $LiAlH_4$ to the suspension of Pd/C in dry THF must be carried out with great caution. After complete addition, the mixture was refluxed overnight. After the mixture had cooled to room temperature, it was filtered and the solid residue was washed several times with THF (3 × 50 mL). The organic layer and the washes were combined and the solvents were evaporated to dryness to afford an orange solid residue, which after chromatography (SiO_2, CH_2Cl_2/MeOH, 95:5) gave the desired compound **16** (290 mg, 70%) as a light yellow solid; m.p. > 300 °C. $C_{40}H_{52}N_4\cdot 0.5CH_3OH$ (597.9): calcd. C 80.41, H 9.00, N 9.26; found C 80.55, H 8.96, N 8.83. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.13 (s, 12 H, *para*-CH_3), 2.24 (s, 24 H, *ortho*-CH_3), 3.48 (s, broad, 8 H, -NH_2), 4.01 (s, 8 H, Ar-CH_2-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 14.4, 18.2, 32.8, 118.2, 126.5, 137.5, 140.1.

3,5,7,10,12,14,17,19,21,24,26,28-Dodecamethyl-4,11,18,25-tetrakis(4-pyridyl)[1.1.1.1]metacyclophane (20): The arylboronic ester **18** (437 mg, 2.13 mmol) was added in one portion to a stirred solution of **7** (300 mg, 0.355 mmol), $Pd(PPh_3)_4$ (73 mg, 0.063 mmol) and Cs_2CO_3 (700 mg, 2.14 mmol) in a dry mixture of toluene/DMF (1:1, v/v; 60 mL), degassed with argon and heated at 100 °C. The mixture was then heated at 130 °C under argon for 48 h. The resulting solution was cooled to room temperature and filtered to remove insoluble materials, and the filtrate was concentrated to dryness to afford a solid residue. The pure compound **20** (236 mg, 80%) was obtained by chromatography (SiO_2, CH_2Cl_2/MeOH, 92:2) as a colourless solid, which was crystallised from a CH_2Cl_2/Et_2O (1:2) mixture, m.p. > 300 °C. $C_{60}H_{60}N_4\cdot 2H_2O$ (873.16): calcd. C 82.53, H 7.39, N 6.42; found C 82.40, H 7.33, N 6.69. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.35 (s, 12 H, *para*-CH_3), 2.07 (s, 24 H, *ortho*-CH_3), 4.07 (s, 8 H, Ar-CH_2-Ar), 7.09 (d, *J* = 8.8 Hz, 8 H, *H*-Py), 8.69 (d, *J* = 8.8 Hz, 4 H, *H*-Py), 8.72 (d, *J* = 8.8 Hz, 4 H, *H*-Py). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.1, 19.3, 32.8, 125.0, 125.3, 130.7, 135.5, 137.9, 138.4, 150.1, 150.2, 152.1.

4,11,18,25-Tetrakis(4-methoxyphenyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane (21): The arylboronic acid **19** (648 mg, 2.13 mmol) was added in one portion to a stirred solution of **7** (300 mg, 0.355 mmol), $Pd(PPh_3)_4$ (73 mg, 0.063 mmol) and Cs_2CO_3 (700 mg, 2.14 mmol) in a dry mixture of toluene/DMF (1:1, v/v; 60 mL), degassed with argon and heated at 100 °C. The mixture was then heated under argon at 130 °C for 48 h. The resulting solution was cooled to room temperature and filtered to remove insoluble materials, and the filtrate was concentrated to dryness to afford a solid residue that was purified by chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) to give **21** (24 mg, 7%) as a white solid, m.p. > 300 °C. $C_{68}H_{72}O_4\cdot H_2O$ (973.3): calcd. C 84.09, H 7.68; found C 83.96, H 7.54. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.37 (s, 12 H, *para*-CH_3), 2.10 (s, 24 H, *ortho*-CH_3), 3.89 (s, 12 H, methoxy) 4.08 (s, 8 H, Ar-CH_2-Ar), 7.00 (m, 16 H, *H*-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.9, 19.3, 33.1, 55.3, 113.5, 113.8, 130.4, 130.7, 131.9, 134.7, 136.3, 137.7, 140.4, 158.0.

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