

Serial synthesis of oxa[3._n]cyclophanes and homooxalix[*n*]arenes *via* reductive coupling of arenedialdehydes, and their X-ray structures †

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A wide range of oxa[3._n]cyclophanes and homooxalix[*n*]arenes is prepared from the corresponding arenedialdehyde *via* reductive homocoupling reaction in a one-pot fashion. Heterocoupling reaction of arenedialdehyde with bis(trimethylsilyloxymethyl)benzene provides a series of macrocyclic ethers including a new type of oxalixarene, which consists of the moieties of oxa[3._n]cyclophane and homooxalix[*n*]arene; *m*- or *p*-phenylene, and 5-substituted 2-methoxy-*m*-phenylene are tethered by CH₂OCH₂ linkages. A series of macrocycles are separated with gel permeation chromatography (GPC) and identified with NMR (¹H, ¹³C) and mass (MALDI-TOF) spectra. Their solid-state conformations are elucidated by X-ray crystallographic analyses.

Introduction

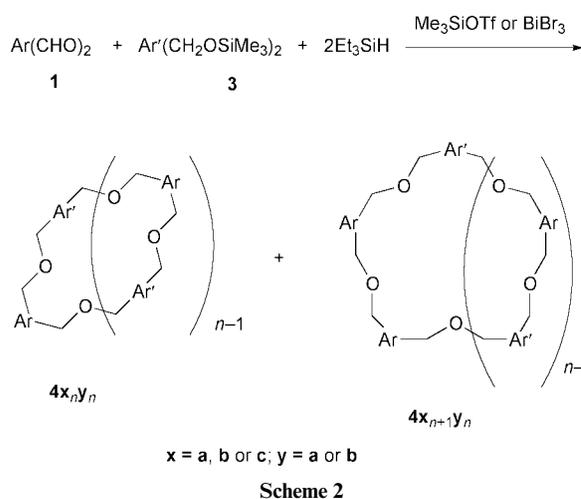
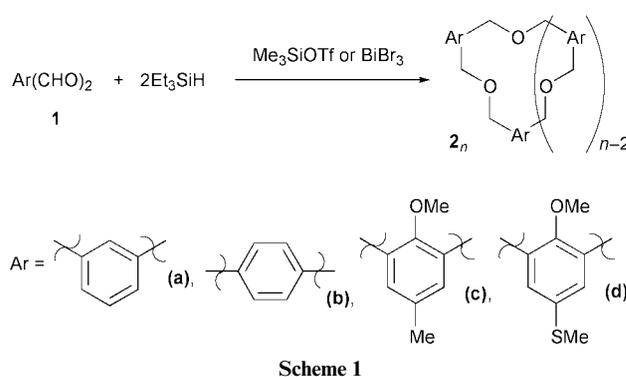
Oxacyclophanes represent an important class of host molecules due to the dual characteristics of cyclophanes and crown ethers. Among them, homooxalix[*n*]arenes are the most promising receptors following calixarenes. Actually, hexahomotrioxalix[3]arenes¹ and octahomotetraoxalix[4]arenes^{1d,2} with or without *O*-protection exhibit characteristic affinities for alkali and alkaline-earth metal cations,³ ammonium ions,^{2a,3c,4} lanthanide ions,⁵ and buckminsterfullerene, C₆₀.⁶ Although such macrocycles with relatively small ring size (*n* = 3, 4) have been studied extensively, larger ones still remain unexplored despite the potential of the inclusion properties of neutral molecules⁷ and cationic organic guests.^{2a,4b,8} This is because no methods to supply these molecules have been reported so far in contrast to calix[*n*]arenes.⁹ As an extension of our study utilizing reductive coupling reactions¹⁰ for the preparation of oxacyclophanes,^{1a,10a} we have found that a series of oxa[3._n]cyclophanes and *O*-protected homooxalix[*n*]arenes can be prepared from the corresponding arenedialdehydes *via* reductive homo- and heterocoupling reactions. In this report, we describe serial syntheses and X-ray structures of these macrocyclic ethers.

Results and discussion

2-Methoxy-5-methylisophthalaldehyde **1c**¹¹ and 2-methoxy-5-(methylthio)isophthalaldehyde **1d** were prepared from the corresponding 4-substituted phenols *via* diformylation¹² followed by methylation. *m*- and *p*-Bis(trimethylsilyloxymethyl)benzenes were prepared from the corresponding alcohols with Me₃SiCl and Et₃N in diethyl ether.¹³ The reductive coupling reactions were carried out in the presence of Et₃SiH and a catalytic amount of a Lewis acid, Me₃SiOTf^{10b,c} or BiBr₃,^{10a} to give a series of macrocyclic ethers (Schemes 1 and 2). After separation using GPC, the mass of the macrocycles was determined by MALDI-TOF-MS spectra.

Homocoupling reaction (Scheme 1, Table 1)

A wide range of macrocyclic ethers, oxa[3._n]metacyclophanes



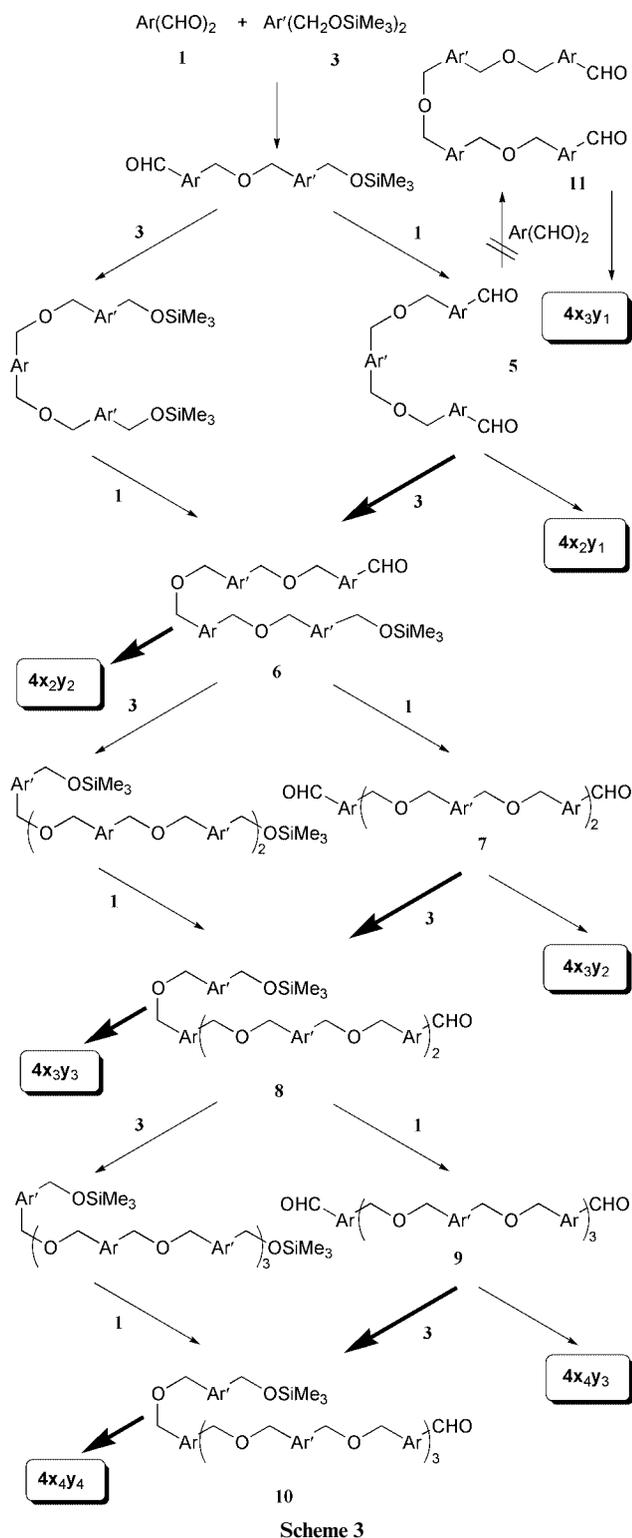
(**2a_n**, *n* = 3–8), oxa[3._n]paracyclophanes (**2b_n**, *n* = 4–11), *p*-methylhomooxalix[*n*]arenes (**2c_n**, *n* = 3–9),² and *p*-(methylthio)homooxalix[*n*]arenes (**2d_n**, *n* = 4–7), were prepared in the yields summarized in Table 1. Total yields of the homologues of oxa[3._n]metacyclophanes were 60–68% (runs 1–3), and the trimer (**2a₃**) was obtained in 35–39% yield as a major product. On the other hand, total yields of other macrocycles (**2b_n**, **2c_n** and **2d_n**) were decreased to 13–46% (runs 4–13), and pentamer (**2b₅**), tetramer (**2c₄**) and tetramer (**2d₄**) were major homologues in series of the products, **2b_n**, **2c_n** and **2d_n**, respectively. The

† Electronic supplementary information (ESI) available: full details of physical data for all new compounds. See <http://www.rsc.org/suppdata/p1/b1/b102031p/>

5-substituted 2-methoxy-*m*-phenylene were tethered by CH₂-OCH₂ linkages. By changing the concentrations of substrates and catalyst, the conditions in runs 6 and 10 proved to be the best of all conditions examined in the preparation of calixmeta- and paracyclophanes, respectively.

Reaction pathways (Scheme 3)

Plausible reaction pathways for the reductive heterocoupling reaction are illustrated in Scheme 3, where the reactions



between linear oligomers are omitted because of their low concentration. The product distribution in heterocoupling reactions suggests the following three points; 1) intermolecular homocoupling reaction of linear dialdehydes 5, 7 and 9 with

arendialdehyde 1 did not take place, which is supported by the facts that 4x_{n+2}y_n was not obtained at all and that the coupling reaction of an aldehyde in the presence of an equimolar amount of a silyl ether generally gives heterocoupling products exclusively;¹⁰ 2) linear dialdehydes 5, 7 and 9 preferred intermolecular heterocoupling with a bis(trimethylsilyloxymethyl)-arene 3 to intramolecular homocoupling because cyclized products, 4x_{n+1}y_n, were obtained in quite low yields; 3) intramolecular heterocoupling reactions of trimethylsilyloxyaldehydes 6, 8 and 10, that is, cyclization to 4x_ny_n, were easier than were intramolecular homocoupling reactions of 5, 7 and 9 because more 4x_ny_n was produced than 4x_{n+1}y_n.

X-Ray structures (Fig. 1)

In order to confirm the structures and elucidate their solid-state conformations, at least one compound of each series of the macrocyclic ethers was subjected to X-ray crystallographic analysis. The ORTEP drawings of 2a₆, 2b₆, 2c₄, 2c₆, 2d₄, 4c₂a₂ and 4c₂b₂ are shown in Fig. 1. The X-ray structures reveal that the repeat (asymmetric) units are one half in all the molecules except 2a₆, in which six-fold symmetry exists. The letters A–D in Fig. 1 refer to the corresponding aromatic rings in each structure, and A'–D' mean the planes of the repeat units. Two individual conformations were observed in the solid-state structure of 2d₄ (Fig. 1e-1 and -2). For homooxalixarenes (2c₄, 2c₆, 2d₄, 4c₂a₂ and 4c₂b₂), the dihedral angles between each aromatic ring (A–D) and the mean plane formed by the dibenzyl etheral oxygen atoms, and distances between faced aromatic rings (A–A' ~ D–D') are summarized in Table 3.

In Fig. 1a, 2a₆ includes a water molecule inside the circular cavity. The distance between the centers of O2 and C8 is 4.8 Å. Several other oxo[3_n]cyclophanes and homooxalix[n]arenes of larger size also had one-half to two equivalents of water or one equivalent of dichloromethane in the solid state, judging from the results of elemental analysis. These results show that the larger macrocyclic ethers are also considered to hold the small molecules within the cavity and are expected to work as receptors for some neutral organic molecules. Indeed, macrocyclic ethers analogous to 2a₆ and 2b₆ were reported to form equimolar complexes with benzene and dichloromethane in the solid state.⁷

Rectangular molecular structures, 16.4 × 8.1 Å and 16.5 × 9.5 Å, are observed in 2b₆ and 2c₆, respectively (Fig. 1b and 1d). The homooxalix[6]arene (2c₆) adopts a 1,2,3-alternate conformation, in which the methoxy groups on rings A, A', C and C', and the methyl substituents on rings B and B' point toward the interior of the macrocycle so as to fill the cavity as shown in Fig. 1d. Ring C is orientated in a perpendicular fashion (85.0°), while rings A and B are more flattened with angles of 39.2 and 39.4°, respectively.

Both homooxalix[4]arenes (2c₄ and 2d₄, Figs. 1c and 1e) adopt 1,2-alternate conformations, and all the methoxy groups orientate toward the cavity with dihedral angle of between 23.3 and 86.2°. In the packing structure of 2d₄, the planes A and B in one conformer (Fig. 1e-1) are parallel to the planes C and D in the other conformer (Fig. 1e-2), respectively, indicating that the positions of oxygen atoms comprising the reference mean planes are different in these two conformers of 2d₄. All the distances between the opposite-faced aromatic rings in 2c₄ and 2d₄ are around 8 Å, and the four aromatic rings in each conformer form nearly a square cavity. Although several crystal structures of hexahomotrioxalix[3]arenes with or without *O*-protection have been elucidated so far,^{1b,5a,18} those of larger homologues are the first to be disclosed here, for compounds 2c₄, 2c₆ and 2d₄.

The calixarenes, 4c₂a₂ and 4c₂b₂, also make square-shaped cavities, with across-cavity distances of 7.30 and 8.10, and 7.70 and 9.25 Å, respectively. Similarly, the cavities are filled with the methoxy groups on rings A and A' (Fig. 1f and 1g). As

Table 2 Serial synthesis of oxa[3,*n*]cyclophanes and homooxacalix[*n*]arenes *via* reductive heterocoupling reaction

Run	x (Ar) (mmol)	y (Ar') (mmol)	Catalyst (mol%)	Solvent (ml)	React. temp. ($^{\circ}$ C)	React. time (t/h)	Yield (%) ^a					Total		
							4x ₂ y ₁	4x ₂ y ₂	4x ₃ y ₂	4x ₃ y ₃	4x ₄ y ₃		4x ₄ y ₄	4x ₅ y ₅ ^b
1	a (1.0)	a (1.0)	Me ₃ SiOTf (5)	CH ₂ Cl ₂ (30)	0	2	4	30	1	9	0	5	2	51
2	a (2.0)	a (2.0)	BiBr ₃ (5)	MeCN (20)	rt	2.5	5	17	4	10	0	7	6	49
3	b (1.0)	b (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (30)	0	1		4	3	13	1	5	5	31
4	b (1.0)	b (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (20)	0	1.5		3	2	13	1	4	3	26
5	b (1.0)	b (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (20)	0	4		3	3	12	2	4	3	27
6	c (1.0)	a (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (30)	0	1		25	3	7	1	4		40
7	c (1.0)	a (1.0)	Me ₃ SiOTf (5)	CH ₂ Cl ₂ (30)	0	3		27	2	4	2	2		37
8	c (1.0)	a (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (60)	0	4		17	3	4	2	2		28
9	c (1.0)	a (1.0)	Me ₃ SiOTf (20)	CH ₂ Cl ₂ (60)	0	2		21	3	6	2	2		34
10	c (1.0)	b (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (40)	0	4		11	4	4	2	3		24
11	c (1.0)	b (1.0)	Me ₃ SiOTf (20)	CH ₂ Cl ₂ (40)	0	4		9	3	5	2	3		22
12	c (1.0)	b (1.0)	Me ₃ SiOTf (10)	CH ₂ Cl ₂ (20)	0	4		9	3	3	1	2		18

^a Isolated yields. ^b Although these compounds were not fully identified, they were highly expected to be 4x₅y₅ from ¹H NMR spectra and retention time in GPC.

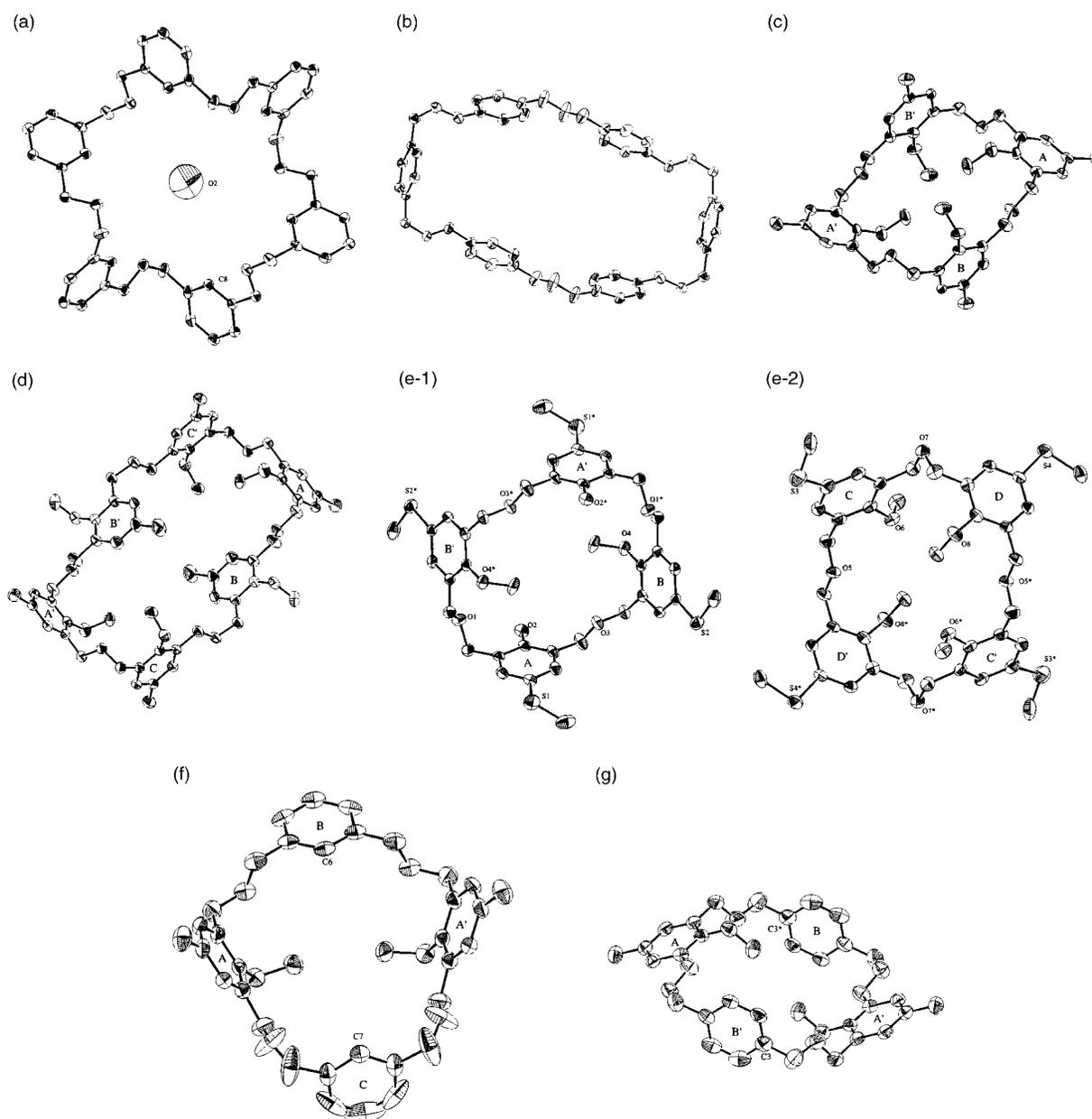


Fig. 1 ORTEP drawings for **2a₆** (a), **2b₆** (b), **2c₆** (c), **2c₆** (d), **2d₄** (e-1, -2), **4c₂a₂** (f) and **4c₂b₂** (g). Hydrogen atoms are omitted for clarity.

compared with the structures of octahomotetraoxacalix[4]arenes, **2c₄** and **2d₄**, the cavity of **4c₂a₂** is narrower, probably due to the lack of substituents on rings B and C. In **4c₂b₂**, the

lack of substituents on rings B and B' makes the distance of A–A' shorter than that in **2c₄**, resulting in the longer distance for B–B' in spite of their similar conformations.

Table 3 Dihedral angles and distances between aromatic rings (A–D, A'–D') in homooxalixarenes

Compound	Dihedral angle (°) ^a				Distance (Å) ^b				Conformation
	A	B	C	D	A–A'	B–B'	C–C'	D–D'	
2c₄	23.3	83.2			8.36	8.14			1,2-alternate
2c₆	39.2	39.4	85.0		14.6	9.27	13.5		1,2,3-alternate
2d₄	86.2	50.1	53.9	54.1	8.65	7.90	7.42	8.35	1,2-alternate
4c_{2a2}	58.7	74.4	14.3		7.30	8.10 ^c			1,3-alternate ^d
4c_{2b2}	33.7	80.5			7.70	9.25 ^e			alternate

^a Between each aromatic ring and mean plane defined by dibenzylic ethereal oxygen atoms. ^b Between methoxy-bearing carbons in oppositely faced aromatic rings unless otherwise noted. ^c Distance between C6 in ring B and C7 in ring C in Fig. 1f. ^d C6 and C7 in rings B and C orientate upward, while methoxy groups in ring A and A' orientate downward in Fig. 1f. ^e Distance between C3 and C3* in Fig. 1g.

Table 4 Crystal data of **2a₆**, **2b₆**, **2c₄**, **2c₆**, **2d₄**, **4c_{2a2}** and **4c_{2b2}**

	2a₆	2b₆	2c₄	2c₆	2d₄	4c_{2a2}	4c_{2b2}
Formula	C ₄₈ H ₅₀ O ₇	C ₄₈ H ₄₈ O ₆	C ₄₀ H ₄₈ O ₈	C ₆₀ H ₇₂ O ₁₂	C ₄₀ H ₄₈ O ₈ S ₄	C ₃₆ H ₄₀ O ₆	C ₃₆ H ₄₀ O ₆
Formula weight	738.92	720.90	656.81	985.22	785.05	568.71	568.71
Crystal system	trigonal	monoclinic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic
<i>a</i> (Å)	26.833(1)	15.226(2)	10.770(5)	8.982(1)	13.210(3)	23.388(2)	14.301(9)
<i>b</i> (Å)		6.357(2)	11.260(4)	17.865(2)	14.508(3)	17.227(2)	7.608(1)
<i>c</i> (Å)	4.955(2)	21.079(2)	15.146(7)	8.8358(7)	13.117(2)	7.655(1)	15.421(1)
<i>α</i> (°)				101.254(7)	100.26(2)		
<i>β</i> (°)		110.961(7)	105.77(4)	92.355(9)	107.11(2)		113.25(5)
<i>γ</i> (°)				93.19(1)	116.99(1)		
<i>V</i> (Å ³)	3089.9(10)	1905.1(5)	1767(1)	1386.5(2)	1992.3(8)	3084(1)	1541.7(2)
Temperature/°C	20	20	20	25	22.5	25	20
Space group	R-3 (No. 148)	P21/a (No. 14)	P21/a (No. 14)	P-1 (No. 2)	P-1 (No. 2)	Cmc21 (No. 36)	P21/a (No. 14)
Z-value	3	2	2	1	2	4	2
μ /cm ⁻¹	0.79 (Mo-K α)	0.81 (Mo-K α)	0.85 (Mo-K α)	6.57 (Cu-K α)	2.89 (Mo-K α)	6.61 (Cu-K α)	6.61 (Cu-K α)
No. of observations	952	1511	721	2438	3603	881	1532
	[<i>I</i> > 3.00 σ (<i>I</i>)]	[<i>I</i> > 3.00 σ (<i>I</i>)]	[<i>I</i> > 3.00 σ (<i>I</i>)]	[<i>I</i> > 3.00 σ (<i>I</i>)]	[<i>I</i> > 2.00 σ (<i>I</i>)]	[<i>I</i> > 3.00 σ (<i>I</i>)]	[<i>I</i> > 3.00 σ (<i>I</i>)]
No. of variables	86	245	217	326	469	196	191
<i>R</i>	0.055	0.058	0.047	0.048	0.059	0.057	0.061
<i>R_w</i>	0.086	0.093	0.060	0.078	0.088	0.085	0.110
GOF	1.19	1.38	1.22	1.39	1.34	1.40	1.76

Experimental

¹H (200 MHz) and ¹³C (50 MHz) NMR spectra were obtained with a Varian Gemini-200 for solutions in CDCl₃ with Me₄Si as an internal standard. Chemical shifts are reported in δ and the coupling constants (*J*) are in Hz. MALDI-TOF-MS analyses were performed by a Shimadzu/Kratos KOMPACT MALDI II. EI mass spectra were recorded on a Shimadzu GCMS QP5000 spectrometer. GPC separation was carried out by LC908 liquid chromatography (Japan Analytical Industry) equipped with Jaigel 1H and 2H columns (polystyrene gels). Mps were determined with a Yanaco MP-J3 apparatus and are uncorrected. Flash chromatography was performed with Wakogel C-300. CH₂Cl₂ was freshly distilled from CaH₂ under argon. Reagents were used as commercially received. 2-Hydroxy-5-methylisophthalaldehyde was purchased from TCI. *m*- and *p*-Bis(trimethylsilyloxymethyl)benzene were prepared by the reaction of the corresponding xylene-*o*,*o'*-diol with trimethylsilyl chloride in the presence of triethylamine in diethyl ether.¹³

Synthesis of 2-methoxyisophthalaldehydes (**1c** and **d**)

2-Methoxy-5-methylisophthalaldehyde 1c.¹¹ To a solution of 2-hydroxy-5-methylisophthalaldehyde (1.0 g, 6.1 mmol) in DMF (10 ml)–acetone (50 ml) were added MeI (6.2 ml, 0.10 mol) and K₂CO₃ (1.0 g, 7.2 mmol). After being stirred at rt for 21 h, the suspension was added to saturated aq. NaHCO₃ (100 ml) and extracted with diethyl ether (100 ml) twice. The combined organic layer was washed with saturated aq. NaCl (100 ml) once, dried over anhydrous MgSO₄, filtered and concentrated. The crude residue was recrystallized from hexane to afford **1c** (0.99 g, 86%).

2-Hydroxy-5-(methylthio)isophthalaldehyde.¹² Mp 105–106 °C; δ_{H} 2.52 (3H, s, SCH₃), 7.88 (2H, s, Ar-H), 10.21 (2H, s,

CHO), 11.45 (1H, s, OH); δ_{C} 17.2, 123.6, 130.0, 136.7, 161.6, 191.6 (Found: C, 55.00; H, 4.11. Calc. for C₉H₈O₃S: C, 55.09; H, 4.11%).

2-Methoxy-5-(methylthio)isophthalaldehyde 1d. The synthesis was identical to that of **1c**, but starting from 2-hydroxy-5-(methylthio)isophthalaldehyde, to give **1d** (88% yield), mp 130–131 °C; δ_{H} 2.54 (3H, s, SCH₃), 4.06 (3H, s, CH₃), 7.94 (2H, s, Ar-H), 10.39 (2H, s, CHO); MS (EI) *m/z* 211 ([M + H]⁺) (Found: C, 57.10; H, 4.85. Calc. for C₁₀H₁₀O₃S: C, 57.11; H, 4.80%).

General synthesis of oxacyclophanes via reductive homocoupling reaction

(The reaction conditions are also given in Table 1.)

To a stirred solution of arendialdehyde **1** and a Lewis acid catalyst, Me₃SiOTf or BiBr₃, in dichloromethane was added triethylsilane (2.2 equiv.) under argon. After being stirred for the time listed in Table 1, the mixture was poured into aq. NaHCO₃ and the water layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated. The crude residue was subjected to stepwise isolation with flash column chromatography on silica gel (1 : 3 or 1 : 2 ethyl acetate–hexane) followed by GPC. In the first step, the macrocycles **2_n** were separated from Et₃SiOSiEt₃ and linear polymers. Each macrocycle was isolated through the second step with GPC. The size of macrocycles (degree of oligomerization) was determined by MALDI-TOF-MS spectra using an ethanol–water (1 : 1) solution of 2,5-dihydroxybenzoic acid or α -cyano-4-hydroxycinnamic acid including 0.1% trifluoroacetic acid as matrix. Physical data of **2a_n**, **2b_n**, **2c_n** and **2d_n** are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p1/b1/b102031p/>.

General synthesis of oxacyclophanes *via* reductive heterocoupling reaction

(The reaction conditions are also given in Table 2.)

To a stirred solution of arenedialdehyde **1**, bis(trimethylsilyl) ether **3** and Lewis acid catalyst, Me₃SiOTf or BiBr₃, in dichloromethane was added triethylsilane (2.2 equiv.) under argon. After being stirred for the time listed in Table 2, the mixture was subjected to similar work-up, stepwise isolation, and characterization to those of the homocoupling reaction. Physical data of **4c_na_n**, **4c_{n+1}a_n**, **4c_nb_n** and **4c_{n+1}b_n** are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p1/b1/b102031p/>.

X-Ray crystallographic analyses of **2a₆**, **2b₆**, **2c₄**, **2c₆**, **2d₄**, **4c₂a₂** and **4c₂b₂** ‡

The crystal data and experimental parameters are listed in Table 4. The crystal data were collected on a Rigaku AFC7S four-circle diffractometer with a graphite monochromator. The structures were solved by direct methods using SIR92. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the TEXSAN crystallographic software package (Molecular Structure Corporation).

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‡ CCDC reference number(s) 163703–163706. See <http://www.rsc.org/suppdata/p1/b1/b102031p/> for crystallographic files in .cif or other electronic format.

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