Synthesis and optical resolution of naphthalene-containing inherently chiral calix[4]arenes derived by intramolecular ring closure or stapling of proximal phenyl units

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New methods for the preparation of inherently chiral calix[4]arenes have been developed. The molecular asymmetry in these calix[4]arenes is created by an asymmetrical disposition of naphthalene rings on the upper rim. In compound 1, monoformylcalix[4]arene 5 was transformed into naphthalene-containing calix[4]arene by ring closure. In compound 2, *p*-chloromethyl groups are intramolecularly cross-linked with 3-hydroxymethyl-2-naphthol. This 'stapling reaction' results in a *syn* isomer 2a and an *anti* isomer 2b, the latter being classified into an inherently chiral calix[4]arene. Racemic *anti* 2 could be 'perfectly' optically resolved by an HPLC method with a chiral-packed column. The chiral products were thoroughly characterized by various spectroscopic methods. These results indicate that the naphthalene skeleton is very useful for creating molecular asymmetry in calix[4]arenes.

Calixarenes are cyclic oligomers and easily accessible by base-catalysed condensation of *p*-substituted phenols and formaldehyde.[1,2] Calix[4]arenes, due to their unique cavity-shaped architecture, are frequently used for the construction of receptors for complexation of ions and/or neutral molecules.[3,4] In particular, the design and synthesis of chiral calix[4]arene derivatives are of great interest because of their possible application to the enantioselective recognition of suitable guest molecules.[3] Until now, several approaches to chiral calix[4]arenes have appeared in the literature (schematically depicted in Fig. 1). The oldest synthesis of chiral derivatives consists of the simple introduction of chiral substituents into calix[4]arenes (type **I**) either at the lower (by alkylation)[4–6] or at the upper rim (by Friedel–Crafts acylation).[7] Another possibility involves chiral arrangement of several achiral substituents at the lower rim of conformationally rigid calix[4]arenes.[8,9] This is an example of so-called inherent chirality (type **II**). More recently, several inherently chiral calix[4]arenes have been prepared by *meta*-substitution of the aromatic ring in calix[4]arenes (type **III**).[10,11]

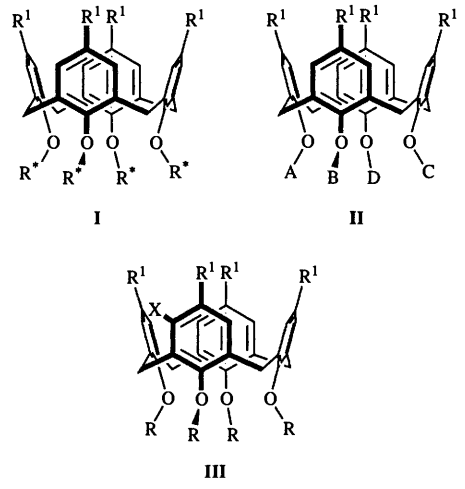


Fig. 1 Classification of 'chiral' calix[4]arenes

Two approaches are here addressed representing novel strategies for the preparation of inherently chiral calix[4]arenes. The first approach is based on the transformation of the upper rim into a naphthalene system (as in **1**), which makes the whole molecule asymmetric due to its rigidity.[12] Such a reaction is known from naphthalene chemistry where the formyl group is useful as a starting functional group.[13] The second approach is to staple two pairs of proximal phenyl units[14] by an asymmetric naphthalene unit (as in **2**). In this case the cross-link reaction results in a *syn* isomer **2a** and an *anti* isomer **2b**, the latter isomer being classified as an inherently chiral calix[4]arene. We report here on the synthesis and spectroscopic characterization of **1** and **2** together with the optical resolution of **2b** by HPLC with a chiral-packed column.

Results and discussion

Synthesis and spectroscopic characterizations of 1

The reaction pathway used for the synthesis of **1** is depicted in Scheme 1. Starting cone-25,26,27,28-tetrapropoxycalix[4]arene **3** was monobrominated to **4** by *N*-bromosuccinimide (NBS) in butan-2-one and then converted into monoformyl calix[4]arene **5** by lithiation followed by a reaction with DMF. Derivative **6** was obtained in 86% yield by Knoevenagel condensation with pentane-2,4-dione in boiling toluene with piperidine as catalyst. For the acetalization step we stirred a $HC(OCH_3)_3$–MeOH (1:1, v/v) solution containing **6** in the presence of Amberlyst-15 (strong acid catalyst). This method has been shown[13] to yield only acetal in the *trans* position to the aromatic ring which can be transformed into the desired product by pyrolytic reactions. Following the original procedure[13] the sequential acetalization–pyrolysis procedure has been accomplished by refluxing **7** in 1-methylnaphthalene solution to give **1** in overall 19% yield (based on **6**).

The structure of **1** was established by ^1H NMR spectroscopy (400 MHz, $CDCl_3$, 25 °C) where the characteristic splitting pattern of the naphthalene part could be observed, H-2,3,4,5, (d:d:s:s = 1:1:1:1) together with a signal of the acetyl group at δ 2.73. Because of the asymmetrical structure, four pairs of doublets for the $ArCH_2Ar$ methylene protons (AX systems) are found in the spectrum, one of the equatorial signals (H-6) being shifted down to δ 4.03. Such an unusual downfield shift of the equatorial proton is obviously caused by the shielding effect of the naphthalene moiety which is very close to the H-6 proton. Further indirect proof of asymmetry is provided

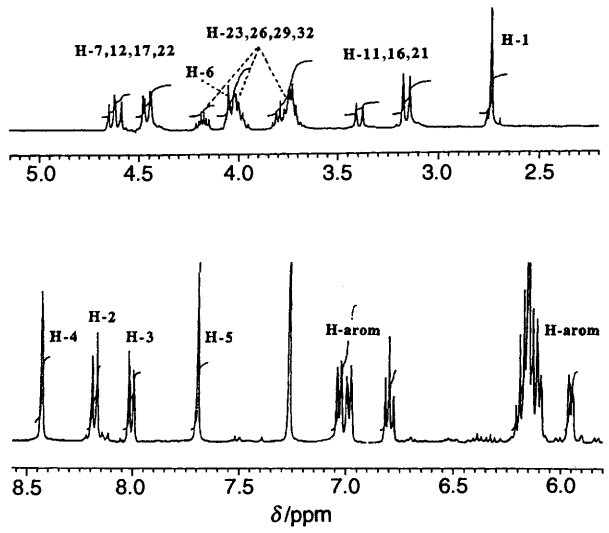
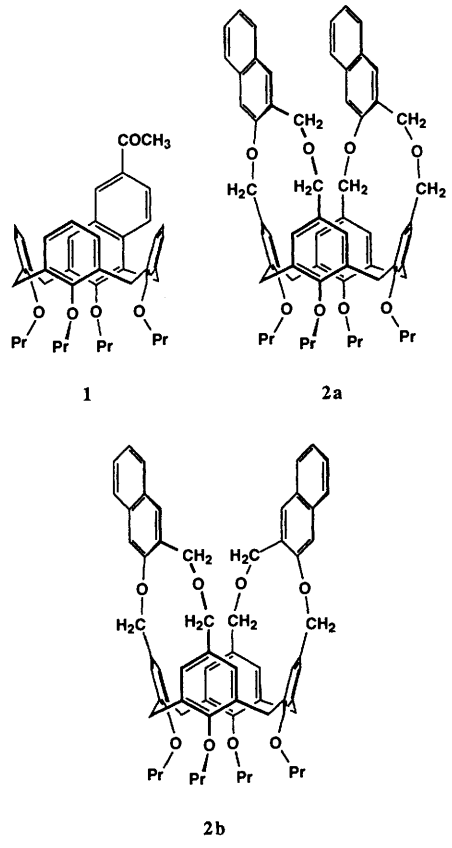


Fig. 2 Partial ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 25 °C)



by the presence of inequivalent protons in OCH_2 groups (see multiplet at δ 4.17: Fig. 2).

The ^{1}H NMR spectrum of racemic product **1** was also measured in the presence of (*S*)-(+)-2,2,2,-trifluoro-1-(9-anthryl)ethanol (Pirkle's reagent) to confirm the presence of both enantiomers. While the aromatic part of the spectrum is hidden by the signals of Pirkle's reagent and the aliphatic part remains unaffected, there is a visible splitting of an $ArCH_2Ar$ doublet at δ 3.38 (arrow in Fig. 3). The results clearly indicate that a naphthalene unit, which was introduced by transformation of an upper-rim-appended formyl group, can create asymmetry which makes a cone-immobilized calix[4]arene inherently chiral.

Synthesis and spectroscopic characterization of 2

Compounds **2a** and **2b** can be synthesized from **3** by only two steps (Scheme 2). The chloromethyl groups were introduced

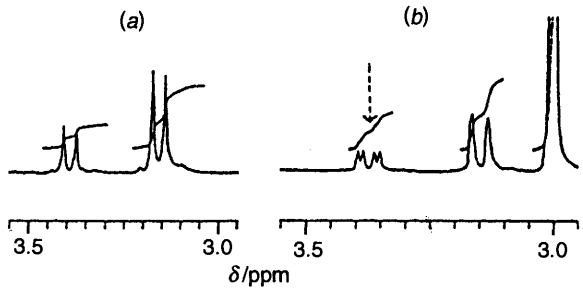
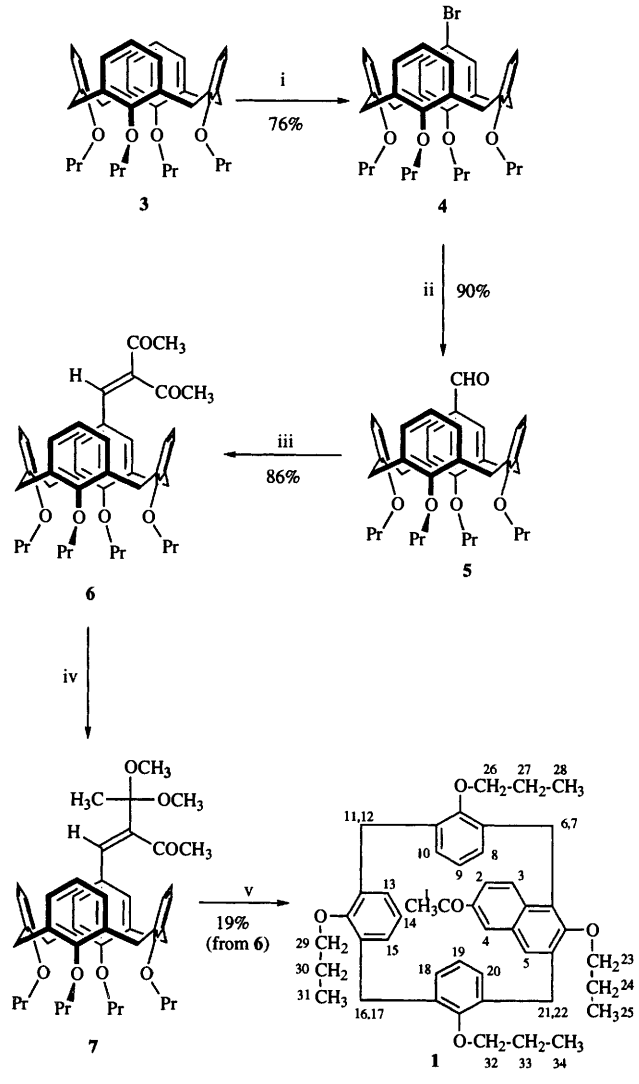
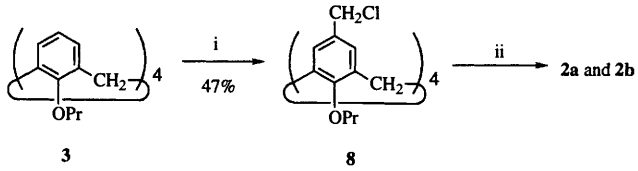


Fig. 3 Partial ^{1}H NMR spectra of **1** (400 MHz, $CDCl_3$, 25 °C) in the absence (*a*) and the presence (*b*) of Pirkle's reagent: [**1**] = 5 mmol dm^{-3}, [Pirkle's reagent] = 50 mmol dm^{-3}



Scheme 1 *Reagents:* i, NBS in butan-2-one; ii, BuLi in THF, −75 °C, then DMF; iii, pentane-2,4-dione, piperidine in toluene; iv, $CH(OCH_3)_3$, MeOH, Amberlyst 15; v, 1-methylnaphthalene, reflux



Scheme 2 *Reagents and conditions:* i, *p*-HCOH, HCl, CH_3COOH, H_3PO_4, 1,4-dioxane, reflux, 36 h; ii, A: 3-hydroxymethyl-2-naphthol, NaH, DMF, 24 h, B and C: 3-hydroxymethyl-2-naphthol, M_2CO_3, acetone, 48 h

Table 1 Stapling reactions of **4** with 3-hydroxymethyl-2-naphthol (HMN)

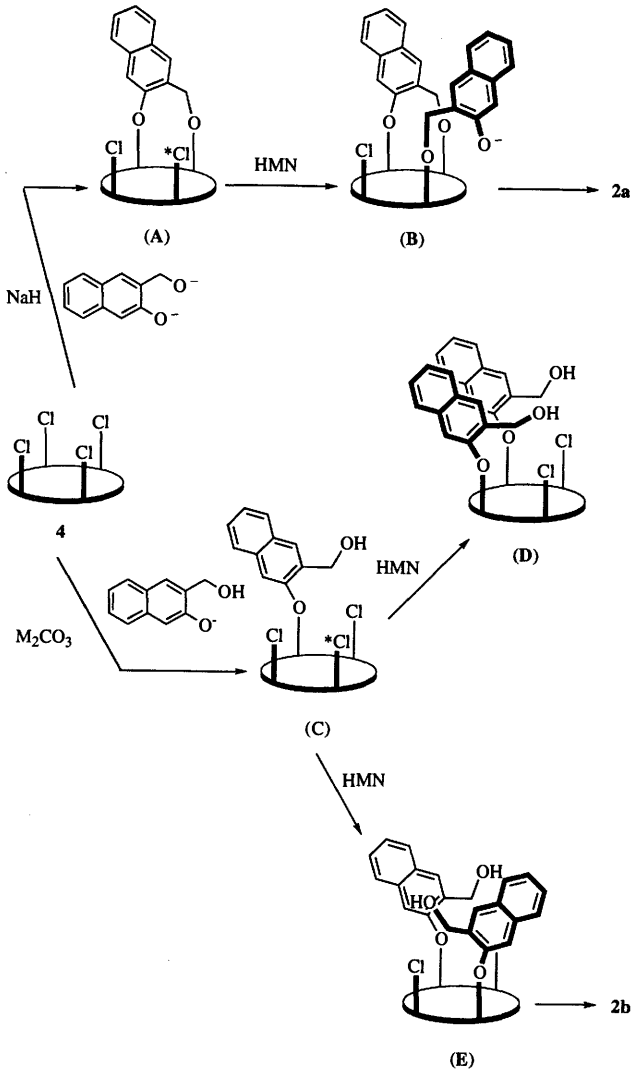
Base	Solvent	HMN/**8**	Procedure[a]	Yield (%)[b]	Distribution (%)[b]	
					2a	**2b**
NaH	DMF	6	i	46	99	1
Cs_2CO_3	Acetone	4	ii	63	79	21
Cs_2CO_3	Acetone	2	iii	54	76	24
Cs_2CO_3	Acetone	4	iii	16	69	31
K_2CO_3	Acetone	4	ii	17	66	34
K_2CO_3	Acetone	2	iii	11	31	69
K_2CO_3	Acetone	4	iii	4	41	59
Na_2CO_3	Acetone	4	ii	3	16	84
Na_2CO_3	Acetone	2	iii	7	29	71
Na_2CO_3	Acetone	4	iii	4	5	95

[a] For procedures i, ii and iii see Experimental section. [b] Yield and distribution were determined by HPLC.

into *para* positions with the aid of acid catalysis. Compound **8** was treated with 3-hydroxymethyl-2-naphthol (HMN) in the presence of base (NaH, Na_2CO_3, K_2CO_3 or Cs_2CO_3).[15] NaH was first used as base. The product was afforded in a moderate yield (46%) but, surprisingly, the ^1H NMR and HPLC analyses showed that *it contains nearly* 100% *of achiral* **2a** (Table 1). To search for the alternative reaction conditions which may give chiral **2b** we used M_2CO_3 ($M^+ = Na^+$, K^+ or Cs^+) as base although we were afraid that each might be insufficiently basic to dissociate the hydroxymethyl group. Surprisingly again, these reactions gave **2b** in addition to **2a** although the total yields were generally lower (except 54% for Cs_2CO_3 in acetone) than that for NaH (46%: Table 1). The highest **2b** selectivity was observed for Na_2CO_3 in acetone (**2a**/**2b** = 5:95) although the total yield was only 4%

How can we rationally explain the influence of the reaction conditions on the **2a** *vs.* **2b** product ratio? It is seen from Table 1 that, in general, strong base (NaH > Cs_2CO_3 > K_2CO_3 > Na_2CO_3) tends to give the higher total yield and the higher **2a** selectivity. When NaH was used as base, both OH groups in HMN should be dissociated because of its strong basicity. As shown in Scheme 3, this situation would facilitate the stapling reaction to yield (**A**) in preference to the nucleophilic attack of a second HMN. Then, (**A**) reacts with a second HMN. The **2a** selectivity observed for NaH implies that the nucleophilic attack of a second HMN tends to occur in a *syn* orientation. Since the nucleophilicity of (naphthalene)CH_2O^- is stronger than that of (naphthalene)O^-, it is reasonable to consider that (naphthalene)CH_2O^- primarily attacks the sterically less crowded chloromethyl group [* in (**A**)]. This reaction yields (**B**), which finally cyclizes intramolecularly to **2a**.

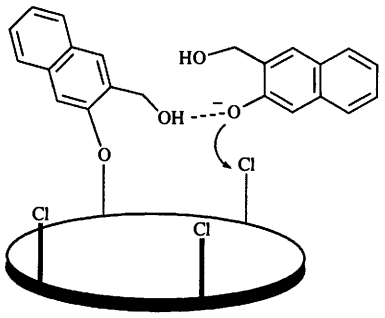
When M_2CO_3 ($M^+ = Na^+$, K^+ or Cs^+) was used as base, its moderate basicity can dissociate the naphtholic OH but not so the hydroxymethyl OH. Thus, the reaction of **4** and HMN in the presence of M_2CO_3 would primarily result in (**C**). If (naphthalene)O^- in second HMN attacks a proximal chloromethyl group, the product is (**D**) which eventually yields **2a**. On the other hand, if it attacks a distal chloromethyl group, the product is (**E**) which eventually yields **2b**. Of the three chloromethyl groups the distal one [* in (**C**)] should be sterically least crowded and most easily attacked by (naphthalene)O^-. Examination of Table 1 reveals that this is the case in Na_2CO_3 but not so in Cs_2CO_3. In general, Cs^+ salts are classified into a relatively loose ion pair whereas Na^+ salts are classified into a relatively tight ion pair.[16] Hence, one possible rationale can be found in the hydrogen-bonding interaction between (**C**) and (naphthalene)O^-. When (naphthalene)O^- approaches (**C**), the dissociated naphtholate anion can form a hydrogen bond with the undissociated hydroxymethyl OH in (**C**) [as in (**F**) in Scheme 4]. Examination of CPK molecular models reveals that this interaction guides (naphthalene)O^- to the proximal chloromethyl group (as in Scheme 4). If the stronger hydrogen-bonding interaction is



Scheme 3

expected for the looser naphtholate·Cs^+ ion pair, the reaction in the presence of Cs_2CO_3 should give **2a** as a major product.

To corroborate that **2b** is an enantiomeric mixture we measured the ^1H NMR spectra in the absence and the presence of Pirkle's reagent. As shown by arrows in Fig. 4, the signals assignable to the $ArCH_2Ar$ and $ArCH_2O$ methylene protons split into pairs, indicating that **2b** is consistent with an inherently chiral calix[4]arene. Interestingly, the peak splitting upon addition of Pirkle's reagent was also observed for **2a** (Fig. 5). The *syn* isomer **2a** has a plane of symmetry and is, therefore, achiral. However, the structure can be regarded as a sort of



(F)

Scheme 4

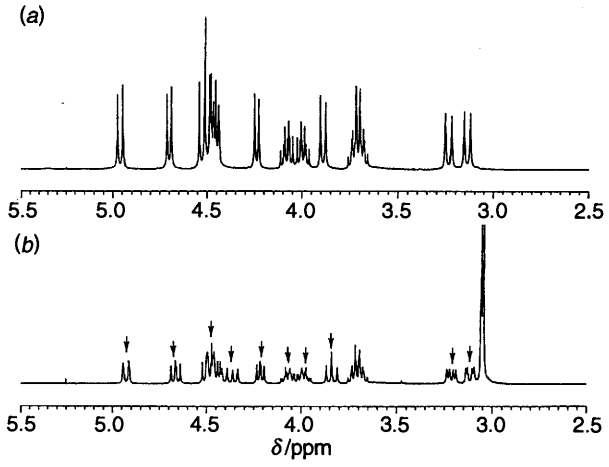


Fig. 4 Partial ^{1}H NMR spectra of **2b** (400 MHz, $CDCl_3$, 25 °C) in the absence (*a*) and the presence (*b*) of Pirkle's reagent: [**2b**] = 3.4 mmol dm^{-3}, [Pirkle's reagent] = 33.7 mmol dm^{-3}

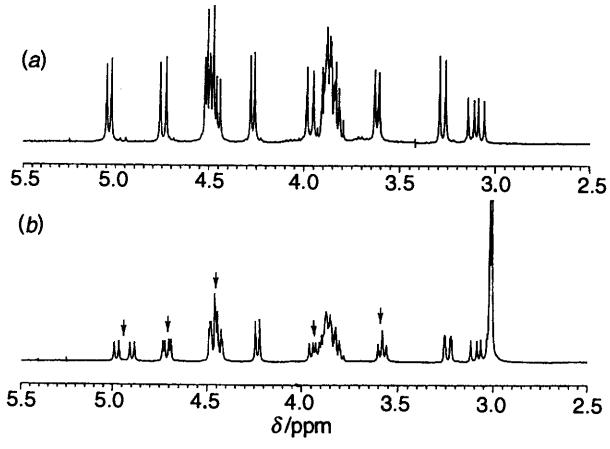


Fig. 5 Partial ^{1}H NMR spectra of **2a** (400 MHz, $CDCl_3$, 25 °C) in the absence (*a*) and the presence (*b*) of Pirkle's reagent: [**2a**] = 3.4 mmol dm^{-3}, [Pirkle's reagent] = 33.7 mmol dm^{-3}

meso isomer. When Pirkle's reagent interacts with one of these two chiral centers, the *meso* isomer can apparently behave as an optically active isomer.

Optical resolution of 2b

To the best of our knowledge, there are four precedents for optical resolution of calix[4]arene derivatives[8–10] and only one precedent for optical resolution of homooxacalix[3]arene derivatives.[3,17] The fifth successful example is here reported for the optical resolution of **2b** by HPLC with a chiral-packed column. As shown in Fig. 6, the enantiomers could be separated 'perfectly', the separation factor (3.17) probably being the

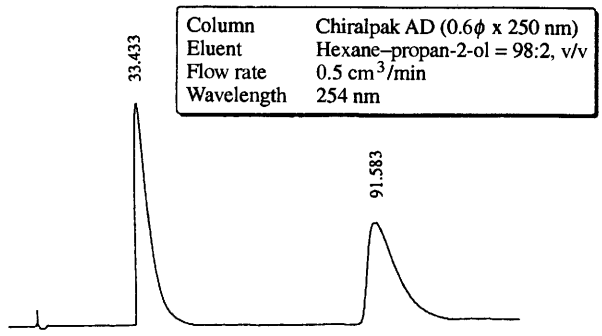


Fig. 6 Chromatogram for resolution of racemic **2b**. For separation conditions, see the data given in the Figure. Numbers recorded on the peaks are the retention time (*t*/min).

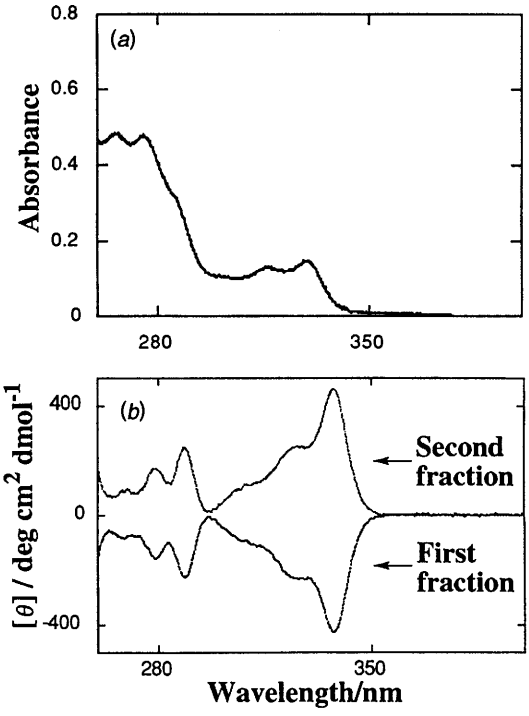


Fig. 7 Absorption (*a*) and CD (*b*) spectra of **2b** in dichloromethane at 25 °C: [**2b**] = 2.85 mmol dm^{-3}

largest in the optical resolution of inherently chiral calix[4]arenes.

The optical resolution of **2b** was carried out with Daicel Chiralpak AD (mobile phase; hexane–propan-2-ol = 98:2, v/v). Because of the very high separation factor it was possible to recover both the first fraction and the second fraction in 50% yield and 100% ee. The absorption and CD spectra are shown in Fig. 7. In the absorption spectrum the absorption bands for the naphthalene moieties appear at 300–350 nm whereas those for the calix[4]arene benzene moieties appear at a wavelength shorter than 300 nm. In the CD spectrum the first fraction [(−)-**2b**] gave the negative Cotton effect for both the naphthalene region and the benzene region whereas the second fraction [(+)-**2b**] gave a positive Cotton effect reciprocal to that for (−)-**2b**. Inherently chiral calix[4]arenes, the asymmetry for which is made up from introduction of different substituents into OH groups, feature sharp exciton-coupling bands in CD spectroscopy.[8,9] This is due to the dipole–dipole interaction among phenyl units in calix[4]arene which are enforced to be chirally orientated by the steric crowding in the lower rim. The absence of such exciton-coupling bands in **2b** implies that although **2b** possesses an inherently chiral structure, the calix[4]arene mother skeleton is not so distorted by steric hindrance or steric crowding.

Conclusions

The present study showed that the naphthalene skeleton, which is conveniently introduced into calix[4]arene by ring closure on a phenyl unit or stapling of two pairs of proximal phenyl units, can create asymmetry which makes calix[4]arene inherently chiral. Furthermore, optical resolution of **2b** has proved to be very easy. Until now, inherently chiral calix[4]arenes have been synthesized only with difficulty, the optical resolution then being particularly difficult. We consider that the use of the naphthalene skeleton provides a breakthrough of these difficulties.

Experimental

General details

^{1}H NMR, IR and circular dichroism spectroscopic measurements were carried out with a JEOL GSX-400 spectrometer, a JASCO A-100 infrared spectrometer and a JASCO spectropolarimeter J-720, respectively. HPLC experiments were performed on a JASCO PU-980 pump equipped with a JASCO UV-970 variable wavelength detector at a flow rate of 0.5 ml min^{-1} at room temperature and monitored at 254 nm.

Materials

The synthesis of cone-25,26,27,28-tetrapropoxycalix[4]arene **3**, which was used as a starting material for the syntheses of both **1** and **2**, was reported previously.[18]

5-Bromo-25,26,27,28-tetrapropoxycalix[4]arene (cone 4)

N-Bromosuccinimide (1.60 g, 8.99 mmol) was added to a butan-2-one solution (80 cm^3) containing calix[4]arene **3** (5.00 g, 8.43 mmol) and the reaction mixture was stirred at room temperature for 24 h. After evaporation of solvent, the residue was extracted with chloroform. The crude product obtained by evaporation was purified by column chromatography on silica gel with hexane–chloroform (4:1, v/v) as the eluent to give the *title compound* as a solid (4.14 g, 73%), mp 151–153 °C (Found: C, 71.36; H, 7.02. $C_{40}H_{47}O_4Br$ requires C, 71.55; H, 7.09%); δ_H($CDCl_3$; 25 °C) 0.90–1.03 (12 H, m, $OCH_2CH_2CH_3$), 1.86–1.91 (8 H, m, $OCH_2CH_2CH_3$), 3.09, 3.16, 4.40 and 4.45 (each 2 H, each d, Ar_2CH_2Ar), 3.75–3.87 (8 H, m, $OCH_2CH_2CH_3$), 6.40 and 6.49 [2 H, d, ArH(*meta*)], 6.60 and 6.68–6.80 [1 H and 5 H, resp., t and m, resp., ArH(*para*)].

5-Formyl-25,26,27,28-tetrapropoxycalix[4]arene (cone 5)

A hexane solution of BuLi (c = 1.45 mol dm^{-3}; 3.23 cm^3, 1.05 equiv.) was added at −74 °C to a solution of **4** (3.00 g, 4.47 mmol) in THF (50 cm^3) and the reaction mixture was stirred for 45 min at this temperature; then, DMF (4 cm^3) was added. After further stirring at room temperature for 2.5 h the reaction mixture was carefully quenched with methanol and then diluted with aqueous 1 mol dm^{-3} aq. HCl. The aqueous solution was extracted with chloroform, and the extract dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel with hexane–AcOEt (4:1, v/v) as the eluent to give the *title compound* as a solid (2.50 g, 90%), mp 190.5–193.0 °C (Found: C, 79.32; H, 7.79. $C_{41}H_{48}O_5$ requires: C, 79.33; H, 7.84%); ν_{max}/cm^{-1} 1680 (C=O), 1590 (C=C) and 1570 crude product was purified by column chromatography on silica gel with hexane–AcOEt (5:1, v/v) as the eluent to give the *title compound* as a solid (0.97 g, 86%), mp 161.0–163.0 °C (Found: C, 78.43; H, 7.66. $C_{46}H_{54}O_6$ requires C, 78.59; H, 7.76%); ν_{max}/cm^{-1} 1701 (C=O *trans* to aryl), 1640 (C=O *cis* to aryl) and 1602 and 1593 (C=C); δ_H($CDCl_3$; 25 °C) 0.93 and 1.04 (each 6 H, each t, $OCH_2CH_2CH_3$), 1.93 and 2.29 (each 3 H, each s, $COCH_3$), 1.90–1.96 (8 H, m, $OCH_2CH_2CH_3$), 3.14, 3.17 and 4.43 (2 H, 2 H and 4 H, resp., each d, $ArCH_2Ar$), 3.72–3.80 and 3.93 (each 4 H, each t, $OCH_2CH_2CH_3$), 6.31–6.35, 6.46 and 6.79–6.90 (3 H, 2 H and 6 H, resp., m, s and m, resp., ArH) and 7.00 (1 H, s, CH).

Preparation of 1

To a mixture of $CH(OCH_3)_3$ and MeOH (1:1, v/v; 20 cm^3) containing **6** (0.40 g, 5.69 mmol) was added Amberlyst-15 resin (0.2 g) and the reaction mixture was stirred under a nitrogen stream for 8 h at room temperature. Resin was then filtered off and the solution was stirred for 90 s with Amberlyst-21 to remove any traces of residual acidity. After removal of resin by filtration the crude acetal **7**, obtained by solvent removal, was carefully dried *in vacuo*. To the residual solid 1-methylnaphthalene (20 cm^3) was added, and the reaction mixture was refluxed under a nitrogen stream for 7 h (bp 240–243 °C) and then cooled. Solvent was removed by elution with hexane on column chromatography (silica gel) and the product was then purified using a hexane–AcOEt (8:1, v/v) as the eluent to give the *title compound* as a solid (74 mg, 19% over two steps), mp 199.0–202.0 °C (Found: C, 80.64; H, 7.57. $C_{46}H_{52}O_5$ requires: C, 80.65; H, 7.67%); ν_{max}/cm^{-1} 1685 (C=O) and 1605 and 1585 (C=C); δ_H($CDCl_3$; 25 °C) 0.91, 0.92 and 1.11 (3 H, 3 H and 6 H, resp., each t, $OCH_2CH_2CH_3$), 1.90–2.05 (8 H, m, $OCH_2CH_2CH_3$), 2.73 [3 H, s, $C(=O)CH_3$], 3.15, 3.38, 4.45, 4.46, 4.60 and 4.63 (2 H, 1 H, 1 H, 1 H, 1 H and 1 H, resp., each d, $ArCH_2Ar$), 3.70–3.82 and 4.14–4.22 (4 H and 1 H, resp., each m, $OCH_2CH_2CH_3$), 3.97–4.07 (4 H, m, $ArCH_2Ar$ and $OCH_2CH_2CH_3$), 5.95, 6.08–6.21, 6.79, 6.98, 7.03, 7.69, 8.01, 8.17 and 8.42 (1 H, 5 H, 1 H, 1 H, 1 H, 1 H, 1 H, 1 H and 1 H, resp., d, m, t, d, d, s, d, d and s, resp., ArH); m/z 684 (M^+).

5,11,17,23-Tetrakis(chloromethyl)-25,26,27,28-tetrapropoxycalix[4]arene (cone 8)

This compound was synthesized in a manner similar to that described previously:[19] yield 47%, mp 174.0–175.3 °C.

General procedure i: syntheses of compounds 2a and 2b

Cone **8** (0.20 g, 0.25 mmol) dissolved in DMF (50 cm^3) was treated with oil-dispersed NaH (net 60%; 0.37 g, 9.1 mmol) at room temperature under a nitrogen stream. The reaction mixture was stirred at room temperature for 1 h and then treated with a solution of 3-hydroxymethyl-2-naphthol (0.40 g, 2.3 mmol) in DMF (30 cm^3), added from a dropping funnel over 4 h. The mixture was stirred at room temperature for 24 h. Unreacted NaH was decomposed by the addition of methanol. The mixture was diluted with 1 mol dm^{-3} aqueous HCl and then extracted with chloroform. The organic layer was washed twice with water, dried ($MgSO_4$), filtered and concentrated to

General procedure iii: syntheses of compounds 2a and 2b

A mixture of cone **8** (0.20 g, 0.25 mmol) and M_2CO_3 (M^+ = Na^+, K^+ or Cs^+) (20.0 mmol), suspended in acetone (40 cm^3) under a nitrogen stream, was treated with 3-hydroxymethyl-2-naphthol (0.09 g, 0.5 mmol or 0.17 g, 1.0 mmol), and then stirred at reflux for 48 h under a nitrogen stream. The purification method was similar to that described for general procedure i. The differences in the product distribution among i, ii and iii are discussed in Table 1.

2a: Mp 232.5–235.8 °C (Found: C, 79.81; H, 6.98. $C_{66}H_{68}O_8$·0.04$CHCl_3$ requires: C, 79.80; H, 6.90%); δ_H($CDCl_3$; 25 °C) 1.08 (12 H, t, $CH_3CH_2CH_2$), 1.95–2.14 (8 H, m, $CH_3CH_2CH_2$), 3.07, 3.12 and 3.27 (1 H, 1 H and 2 H, resp., each d, $ArCH_2Ar$), 3.63, 4.28, 4.74 and 5.03 (each 2 H, each d, $ArCH_2O$), 4.44–4.53 (8 H, m, $ArCH_2Ar$ and $ArCH_2O$), 3.81–3.91 (8 H, m, $CH_3CH_2CH_2$), 6.62, 6.72, 7.09 and 7.21 [each 2 H, each s, ArH (benzene ring)], 7.13, 7.36, 7.48, 7.61 and 7.69–7.74 [2 H, 2 H, 2 H, 2 H and 4 H, resp., s, t, t, s and m, resp., ArH (naphthalene ring)]; *m/z* 1011 ($M + Na^+$).

2b: Mp 282.8–285.0 °C (decomp.) (Found: C, 77.61; H, 6.86. $C_{66}H_{68}O_8$·0.3$CHCl_3$ requires C, 77.68; H, 6.72%); δ_H($CDCl_3$; 25 °C) 1.02 and 1.14 (each 3 H, each t, $CH_3CH_2CH_2$), 1.87–1.96 and 2.07–2.16 (each 4 H, each m, $CH_3CH_2CH_2$), 3.14 and 3.23 (each 2 H, each d, $ArCH_2Ar$), 3.89, 4.24, 4.69 and 4.86 (each 2 H, each d, $ArCH_2O$), 4.43–4.55 (8 H, m, $ArCH_2Ar$ and $ArCH_2O$), 3.67–3.74 and 3.98–4.10 (each 4 H, each m, $CH_3CH_2CH_2$), 6.21, 6.70 and 7.36 [each 2 H, s, ArH (benzene ring)], 6.01, 6.53, 6.98, 7.72, 7.93 [each 2 H, s, d, t, d and s, resp., ArH (naphthalene ring)], 7.20–7.25 [4 H, m, ArH (benzene ring) and ArH (naphthalene ring)]; *m/z* 1011 ($M + Na^+$). The inclusion of $CHCl_3$ peak could be detected by ^1H NMR spectroscopy in CD_2Cl_2.

Optical resolution

In order to resolve the racemates optically we tested three chiral-packed HPLC columns: Daicel Chiralpak OP, Daicel Chiralpak AD and Sumitomo Sumichiral. We found that Daicel Chiralpak AD shows excellent optical resolution ability for **2b** (mobile phase, hexane–propan-2-ol = 98:2, v/v). The eluent was divided into two fractions and one optical isomer was recovered from the first fraction and another optical isomer from the second fraction. Optically resolved **2b**:(−)-**2b** from the first fraction, mp > 260 °C (decomp.), recovery 50%, 100% ee (from HPLC analysis); (+)-**2b** from the second fraction, mp > 260 °C (decomp.), recovery 50%, 100% ee (from HPLC).

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