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Enantiomeric recognition of amino acid derivatives by chiral schiff bases of calix[4]arene

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Abstract—Novel calix[4]arene Schiff bases bearing chiral substituents both on the upper and the lower rims have been developed. These chiral receptors exhibit good chiral recognition ability towards α-amino acid ester hydrochlorides (up to $K_D/K_L = 4.36$, $\Delta\Delta G_0 = -3.65$ kJ mol^{-1}) in $CHCl_3$. The molecular recognition abilities and enantioselectivities for guests are also discussed from a thermodynamic point of view.

1. Introduction

Molecular recognition, and in particular chiral recognition, is one of the most fundamental and significant processes in living systems, ranging from primitive single cell organisms to the most complex of animals.[1] The specificity and efficacy of many biologically important reactions are based on chiral interactions. In most countries, producers of pharmaceuticals are required to evaluate the effects of individual enantiomers and to verify the enantiomeric purity of chiral drugs that are produced. Since most drug effects are due to interactions with chiral biological materials, each enantiomer may have different pharmacological properties in terms of activity, potency, toxicity, transport mechanism and metabolic route.[2]

Amino acids and their derivatives are among the most important molecules in natural living systems, and the study of the enantiomeric recognition of these compounds is of particular significance for understanding the interactions between biological molecules and their applications in separation science. The rational design of receptors with a chiral recognition ability for chiral amino acids is still receiving considerable attention, although numerous chiral macrocyclic receptors have been developed for amines, amino acids and related compounds.[3]

Calix[4]arenes[4] are highly specific ligands[5] and their potential applications as hosts and sensing agents for various analytes have received increasing interest.[6] With appropriate appended groups, Schiff bases combining calix[4]arene framework are good candidates as probe molecules for various species as they selectively entrap specific cations, anions or neutral molecules.

2. Results and discussion

2.1. Design and synthesis of the new chiral hosts

We have previously reported the synthesis and complexation studies of novel chiral calix[4]arenes[7] towards chiral amines[8] and amino acid derivatives.[9] In a previous study,[10] we reported the synthesis of the dialdehyde derivative of calix[4]arene tartaric ester derivative **1**. Chiral Schiff base derivatives **2**–**4** were prepared by the condensation of **1** and the corresponding (*S*)-(−)-1-phenylethylamine, (*R*)-(−)-1-cyclohexylethylamine and (*R*)-(−)-2-heptylamine with yields of 72%, 75% and 84%, respectively. The structures proposed for these novel chiral calix[4]arenes were confirmed by ^{1}H and ^{13}C NMR, IR, MS spectroscopy and elemental analysis (Scheme 1).

2.2. Complexation studies

It is well known that calix[*n*]arene derivatives act as receptors for ammonium cations through their aromatic cone cavity.[11] Calix[*n*]arenes exhibit a special ability for

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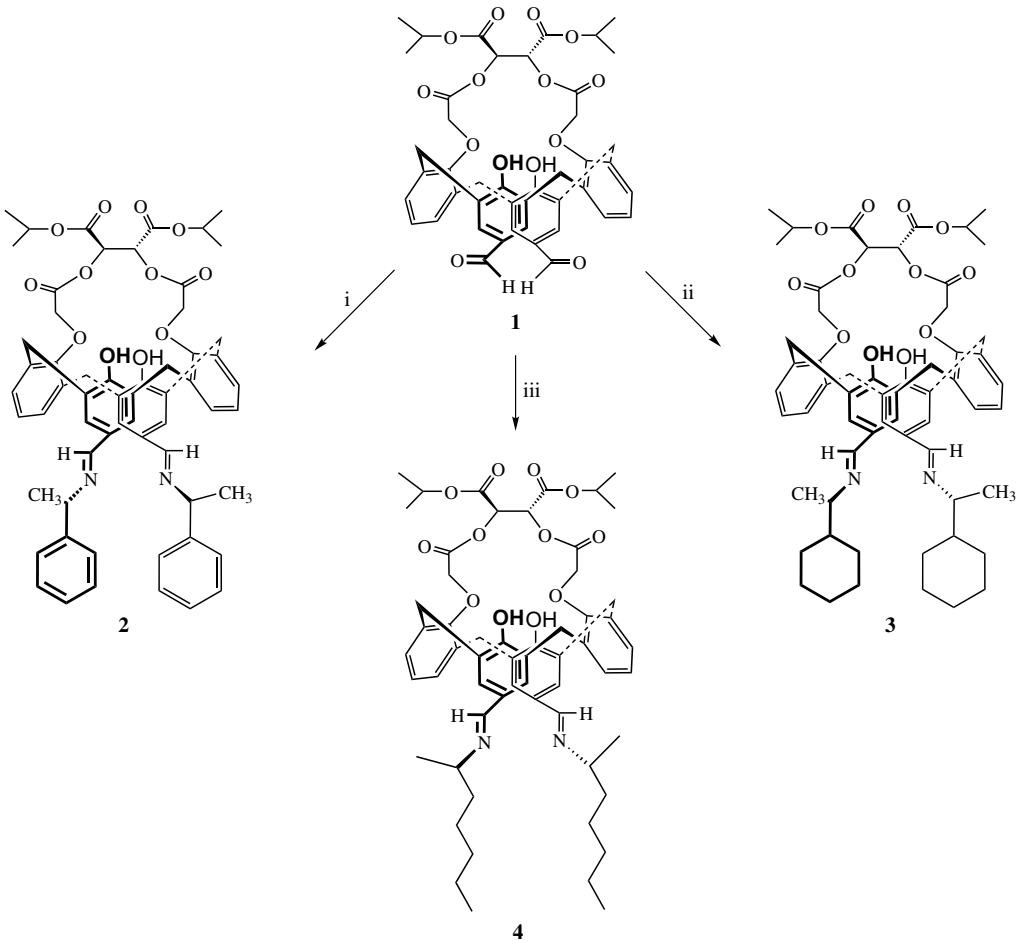


Scheme 1. (i) – (iii) (*S*)-(−)-1-Phenylethylamine, (*R*)-(−)-1-cyclohexylethylamine or (*R*)-(−)-2-heptylamine, $CHCl_3$/MeOH, reflux.

cation–π[12] interaction due to their preorganized aromatic rings. We have now extended these studies to the molecular selective recognition of α-amino acid ester hydrochlorides by the chiral dialdehyde derivative of calix[4]arene tartaric acid **1** compared with chiral Schiff base derivatives **2**–**4**. The binding constants (K) of inclusion complexes of the above-mentioned calix[4]arene receptors with amino acid esters were determined on the basis of the differential UV spectrometry in chloroform.[13] Titration experiments showed that the absorption maximum of all hosts gradually decreased with the addition of various concentrations of amino acid derivatives (Fig. 1).

With the assumption of a 1:1 stoichiometry, the complexation of amino acid derivatives (G) with chiral Schiff base derivative of calix[4]arene (H) is expressed by Eq. 1:

$$H + G \overset{K}{\rightleftharpoons} H \cdot G \tag{1}$$

Under the conditions employed, the concentration of calix[4]arene derivatives (8.33×10^{-5} mol dm^{-3}) is much smaller than that of amino acid derivatives, that is, $[H]_0 << [G]_0$. Therefore, the stability constant of the supramolecular system formed can be calculated according to the modified Hildebrand–Benesi equation,[14] Eq. 2, where $[G]_0$ denotes the total concentration of amino acid; $[H]_0$ refers to the total concentration of calix[4]arene derivative, $\Delta\varepsilon$ is the difference between the molar extinction coefficient for the free and complexed calix[4]arene derivative, and ΔA denotes the changes in the absorption of the modified calix[4]arene on adding amino acid derivatives.

$$1/\Delta A = 1/K\Delta\varepsilon[H]_0[G]_0 + 1/\Delta\varepsilon[H]_0 \tag{2}$$

For all guest molecules examined, plots of calculated $1/\Delta A$ values as a function of $1/[G]_0$ values give good straight lines, supporting 1:1 complex formation. Typical plots are shown for the complexation of compound **4** with D-phenylalanine methyl ester in Figure 2.

The free-energy change (ΔG) for inclusion complexes formed by chiral calix[4]arene Schiff base derivatives and guest amino acid derivatives is calculated from the equilibrium constant K by Eq. 3 and is related to

$$\Delta G = -RT \ln K \tag{3}$$

the enthalpic and entropic changes (ΔH and ΔS) through the Gibbs–Helmholtz Eq. 4. Combining Eqs. 3 and 4, we obtain Eq. 5 which describes the temperature dependence of K. Thus, plots of the ln K values, as a function of the inverse of temperature, gave good linear relationships for the working temperature range (Fig. 2).

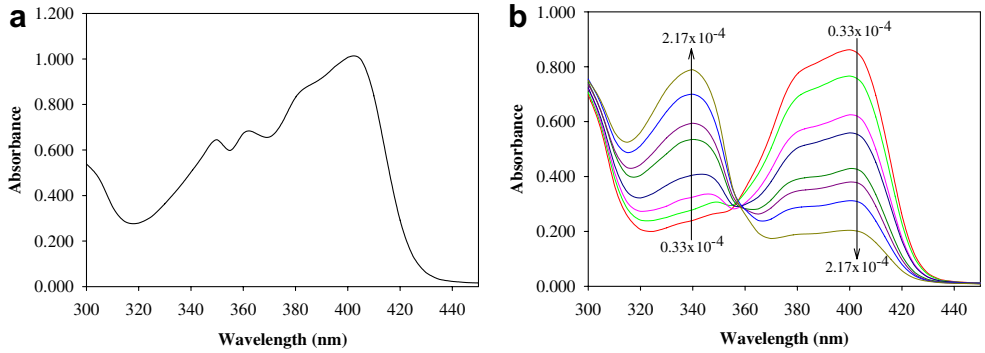


Figure 1. (a) UV–vis spectra of **4** in chloroform solution (8.33×10^{-5} mol dm^{-3}). (b) Spectral changes upon the addition of 0.33–2.17 $\times 10^{-4}$ mol dm^{-3} of D-Phe-OMe·HCl to a chloroform solution of **4** (8.33×10^{-5} mol dm^{-3}) at 25 °C.

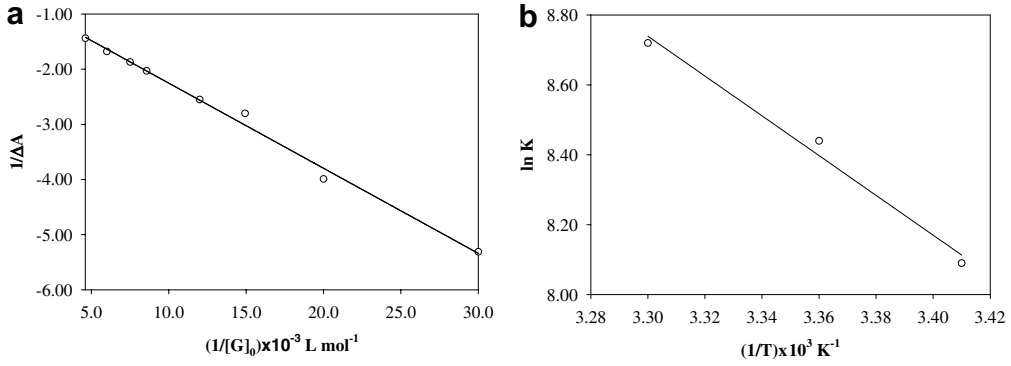


Figure 2. (a) Typical Benesi–Hildebrand plot of $1/\Delta A$ versus $1/[G]_0$ and (b) the plot of $\ln K$ versus $1/T$ for the host–guest complexation of **4** and D-Phe-OMe·HCl in $CHCl_3$ at 25 °C.

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$\ln K = -\Delta H/RT + \Delta S/R \quad (5)$$

The association constants (K), the free-energy change ($-\Delta G_0$) calculated from the slope and the intercept, and the thermodynamic parameters are shown in Table 1, along with the enantioselectivity K_D/K_L for the complexation of D/L-amino acid esters by these hosts. Inspection of Table 1 shows that these chiral receptors can recognize not only differences between the molecular size and shape of amino acid derivatives, but also the chirality of the L- or D-isomer.

UV–vis spectroscopic studies indicate that chiral selectors **2**–**4** show good recognition ability for the enantiomers of phenylalanine (Phe-OMe·HCl) and alanine methyl ester hydrochlorides (Ala-OMe·HCl), while parent compound **1** forms much weaker complexes with both amino acid esters and can hardly recognize the chirality of the L- or D-isomers (entries 1–4).

Table 1 also shows the enantiomeric discrimination of a pair of α-amino acid ester hydrochlorides, characterized by the value of K_D/K_L, which are 1.52–4.36 or $-\Delta\Delta G$ 1.03–3.65 kJ mol^{-1} for chiral calix[4]arene receptors **2**–**4**. It was found that chiral hosts **2** and **3** gave stronger binding and better recognition ability for Ala-OMe·HCl than Phe-OMe·HCl, whereas receptor **4** exhibits good enantioselectivity for Phe-OMe·HCl, affording K_D/K_L 4.36 or $-\Delta\Delta G$ 3.65, although it forms relatively weaker complexes with both α-amino acid ester hydrochlorides.

The D/L-enantioselectivities are highly sensitive to the Schiff base moiety attached to the upper rim of calix[4]-arene and shape of the substituted group in amino acid derivatives. The steric hindrance between the ammonium cation and Schiff base moiety around the stereogenic centre of the host may play an important role in chiral recognition and is expected to be minimized for the D-isomer in all cases. Therefore, the D-isomers of amino acid ester hydrochlorides form more favourable complexes with the chiral selectors than the L-isomers (Fig. 3).

The complexation of the α-amino acids occurs by inserting the aromatic or aliphatic apolar group (R) into the calixarene cavity. This seems to be determined by the need for the charged groups of the amino acids to stick out of the apolar calixarene cavity in order to be exposed to the polar medium. In view of the molecular structure, interestingly phenylalanine methyl ester hydrochloride shows weak binding properties towards chiral calix[4]arene derivatives **2**–**4**. One possible explanation is that, owing to the large size of the R phenyl group, the inclusion of the phenylalanine methyl ester would involve less encapsulation of the amino acid charged groups inside the calixarene cavity.

Table 1. Binding constants (K), enantioselectivities (K_D/K_L) and thermodynamic parameters for the complexation of D/L-amino acid esters with the chiral receptors **1**–**4** in $CHCl_3$ at 25 °C

Entry	Host	Guest[a]	$K \times 10^{-3}$ ($dm^3\ mol^{-1}$)	K_D/K_L	$-\Delta G$ (kJ mol^{-1})	$-\Delta\Delta G$[b]	ΔH (kJ mol^{-1})	$\Delta\Delta H$[c]	ΔS (J mol^{-1})	$\Delta\Delta S$[d]
1	**1**	D-Phe-OMe·HCl	0.021	1.10	7.54	0.24	82.41	2.29	301.5	8.6
2	**1**	L-Phe-OMe·HCl	0.019		7.30		80.12		292.9	
3	**1**	D-Ala-OMe·HCl	0.037	1.06	8.95	0.14	86.17	0.65	318.7	2.5
4	**1**	L-Ala-OMe·HCl	0.035		8.81		85.52		316.2	
5	**2**	D-Phe-OMe·HCl	17.91	1.52	24.26	1.03	40.70	1.98	218.1	10.3
6	**2**	L-Phe-OMe·HCl	11.78		23.23		38.72		207.8	
7	**2**	D-Ala-OMe·HCl	41.73	1.69	26.36	1.30	24.63	3.31	171.0	15.3
8	**2**	L-Ala-OMe·HCl	24.69		25.06		21.32		155.7	
9	**3**	D-Phe-OMe·HCl	8.01	1.66	22.27	1.26	18.81	5.95	137.8	24.2
10	**3**	L-Phe-OMe·HCl	4.82		21.01		12.86		113.6	
11	**3**	D-Ala-OMe·HCl	36.56	1.95	26.03	1.65	29.09	4.03	184.8	19.1
12	**3**	L-Ala-OMe·HCl	18.75		24.38		25.06		165.7	
13	**4**	D-Phe-OMe·HCl	4.62	4.36	20.91	3.65	47.16	8.66	228.4	41.3
14	**4**	L-Phe-OMe·HCl	1.06		17.26		38.50		187.1	
15	**4**	D-Ala-OMe·HCl	3.82	1.78	20.44	1.43	84.58	6.74	352.4	27.1
16	**4**	L-Ala-OMe·HCl	2.15		19.01		77.84		325.3	

[a] Phe-OMe: phenylalanine methyl ester hydrochloride; Ala-OMe: alanine methyl ester hydrochloride.
[b] $\Delta\Delta G = \Delta G_D - \Delta G_L$.
[c] $\Delta\Delta H = \Delta H_D - \Delta H_L$.
[d] $\Delta\Delta S = \Delta S_D - \Delta S_L$.

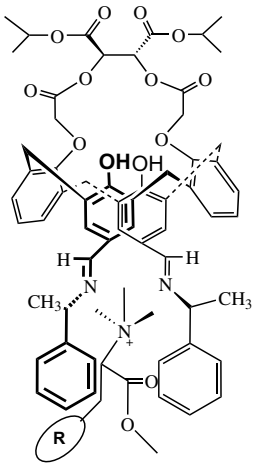


Figure 3. Inclusion of ammonium cation by host **2**.

3. Conclusion

In conclusion, these chiral receptors exhibit good chiral recognition ability toward the enantiomers of α-amino acid derivatives. The cooperative binding of Schiff base moieties, steric effects, structural rigidity or flexibility, hydrogen bond, cation–π and π–π stacking between the aromatic groups may be responsible for the enantiomeric recognition of amino acid derivatives.

4. Experimental

4.1. General information

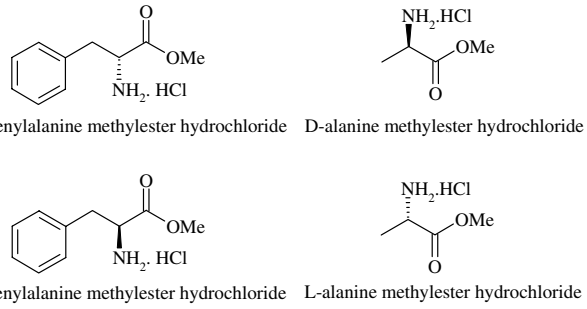
Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^1H and ^{13}C NMR spectra were recorded using a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were obtained on a Perkin–Elmer 1605 FTIR spectrometer using KBr pellets. Optical rotations were measured on Atago AP-100 digital polarimeter. The HPLC measurements were carried out on Agilent 1100 equipment connected with a Zorbax RX-C18 column. Elemental analyses were performed using a Leco CHNS-932 analyzer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer.

Analytical TLC was performed using Merck prepared plates (Silica Gel 60 F_{254} on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Toluene was distilled from CaH_2 and stored over sodium wire. Other commercial grade solvents were distilled, and then stored over molecular sieves. The drying agent employed was anhydrous $MgSO_4$.

Analytical grade α-amino acid methylester hydrochlorides were purchased from Aldrich and employed without further purification as guest molecules for the experiments: that is, L-alanine methylester hydrochloride (L-Ala-OMe), D-alanine methylester hydrochloride (D-Ala-OMe), L-phenylalanine methylester hydrochloride (L-PheO-Me) and D-phenylalanine methylester hydrochloride (D-Phe-OMe) (Scheme 2).

4.2. UV spectral measurement

The recognition abilities of chiral calix[4]arenes with amino acid derivatives were determined on the basis of the differential UV spectrometry in chloroform. The UV–vis spectra were measured at 20, 25 and 30 °C with a thermostated cell



Scheme 2. Chemical structures of the guests employed.

compartment by Shimadzu 160 UV spectrometer. The same concentrations of guest solution were added to the sample cell and reference cell (light path = 1 cm). The association constants were determined at 405 nm. The concentration of the hosts was 8.33×10^{-5} mol dm^{-3} with the increasing concentration between 0.33 and 2.17×10^{-4} mol dm^{-3} of the added guest.

4.3. General procedure for the synthesis of compounds 2–4

To a solution of **1** (320 mg, 0.4 mmol) in $CHCl_3$ (25 mL) was added a solution of the appropriate chiral amine (1.6 mmol) in MeOH (5 mL) and refluxed for 24 h in the presence of $MgSO_4$. The reaction mixture was allowed to cool to room temperature, and filtered. Evaporation of solvent and subsequent purification of the mixture by recrystallization from $CHCl_3$/MeOH afforded pure **2**–**4**.

4.3.1. (40*R*,50*R*)-(5*S*,17*S*)-Di(phenylethylimido)-25,27-dihydroxy-26,28-(40,50-di-1-methylethoxy-carbonyl-30,60-dioxa-20,70-dioxooctylene)-dioxycalix[4]arene 2. Yield 72% (290 mg); mp: 107–110 °C; $[\alpha]_D^{20} = +14.1$ (*c* 0.4, $CHCl_3$). IR (KBr): 3365 (OH), 1743 (OCO), 1638 (C=N) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.05 (d, $J = 6.2$, 6H, CH(CH_3)$_2$), 1.10 (d, $J = 6.2$, 6H, CH(CH_3)$_2$), 1.38 and 1.45 (d, 3H each, –CHCH_3), 3.40 (d, $J = 12.7$, 2H, ArCH_2Ar), 3.51 (d, $J = 13.0$, 2H, ArCH_2Ar), 4.10 (t, $J = 12.9$, 4H, ArCH_2Ar), 4.45 (q, 2H, –CHCH$_3$), 4.63 and 4.74 (d, 1H each, OCH), 5.05 (hep, $J = 6.22$, 2H, OCH(CH$_3$)$_2$), 6.20 (s, 4H, OCH_2CO), 6.81 (t, 2H, Ar*H para*), 7.01 (t, 2H, Ar*H para*), 7.20 (t, 4H, Ar*H meta*), 7.30 (d, 4H, Ar*H meta*), 7.37 (d, 4H, Ar*H ortho*), 7.48 (s, 2H, Ar*H*), 7.50 (s, 2H, Ar*H*), 8.21 (s, 2H, –CH), 8.51 (s, 2H, –OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 14.18, 21.8, 22.0, 23.4, 30.8, 31.5, 71.8, 72.4, 72.6, 127.5, 128.3, 129.2, 130.6, 130.9, 133.6, 134.5, 135.0, 149.8, 154.7, 158.7, 166.4. FAB-MS *m*/*z*: 1024.0 [M+Na]$^+$. Anal. Calcd for $C_{60}H_{60}O_{12}N_2$ (1001.1): C, 71.98; H, 6.04; N, 2.80. Found: C, 70.84; H, 6.45; N, 2.54.

4.3.2. (40*R*,50*R*)-(5*R*,17*R*)-Di(cyclohexylethylimido)-25,27-dihydroxy-26,28-(40,50-di-1-methylethoxy-carbonyl-30,60-dioxa-20,70-dioxooctylene)-dioxycalix[4]arene 3. Yield 75% (300 mg); mp: 139–142 °C; $[\alpha]_D^{20} = -5.0$ (*c* 0.4, $CHCl_3$). IR (KBr): 3372 (OH), 1738 (OCO), 1636 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.07 (d, $J = 6.2$, 6H, CH(CH_3)$_2$), 1.14 (d, $J = 6.3$, 6H, CH(CH_3)$_2$), 1.20 (d, 6H, –CHCH_3), 1.55–1.68 (m, 20H, –CH_2), 1.76–1.82 (m, 2H, –CH), 2.86 (p, 2H, –CHCH$_3$), 3.38 (d, $J = 12.8$, 2H, ArCH_2Ar), 3.47 (d, $J = 13.1$, 2H, ArCH_2Ar), 4.13 (t, $J = 13.0$, 4H, ArCH_2Ar), 4.60 and 4.71 (d, 1H each, OCH), 5.10 (hep, $J = 6.24$, 2H, OCH(CH$_3$)$_2$), 6.23 (s, 4H, OCH_2CO), 6.83 (t, 2H, Ar*H para*), 7.14 (d, 4H, Ar*H meta*), 7.40 (s, 4H, Ar*H meta*), 8.05 (s, 2H, –CH), 8.36 (s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ (ppm): 21.5, 22.4, 23.2, 25.8, 26.4, 28.5, 29.0, 30.7, 31.2, 32.0, 66.8, 70.3, 72.4, 118.4, 123.5, 126.3, 127.2, 128.8, 129.3, 130.7, 131.3, 132.0, 132.9, 153.6, 155.8, 164.1, 166.7, 169.8, 171.2. FAB-MS *m*/*z*: 1036.1 [M+Na]$^+$. Anal. Calcd for $C_{60}H_{72}O_{12}N_2$ (1013.22): C, 71.12; H, 7.16; N, 2.76. Found: C, 70.65; H, 7.84; N, 2.27.

4.3.3. (40*R*,50*R*)-(5*R*,17*R*)-Di(2-heptylimido)-25,27-dihydroxy-26,28-(40,50-di-1-methylethoxy-carbonyl-30,60-dioxa-20,70-dioxooctylene)-dioxycalix[4]arene 4. Yield 84% (330 mg); mp: 204–206 °C; $[\alpha]_D^{20} = -30.6$ (*c* 0.4, $CHCl_3$). IR (KBr): 3361 (OH), 1745 (OCO), 1641 (C=N) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.95 (t, 6H, –CH$_2$CH_3), 1.10 (d, $J = 6.1$, 6H, CH(CH_3)$_2$), 1.17 (d, $J = 6.2$, 6H, CH(CH_3)$_2$), 1.28–1.64 (m, 22H, –CH_2 and –CHCH_3), 3.23 (h, 2H, –CHCH$_3$), 3.42 (d, $J = 13.5$, 2H, ArCH_2Ar), 3.52 (d, $J = 13.1$, 2H, ArCH_2Ar), 4.17 (t, $J = 13.2$, 4H, ArCH_2Ar), 4.75 and 4.86 (d, 1H each, OCH), 5.09 (hep, $J = 6.1$, 2H, OCH(CH$_3$)$_2$), 6.05 (s, 4H, OCH_2CO), 6.75 (t, 2H, Ar*H para*), 6.93 (d, 4H, Ar*H meta*), 7.48 (s, 4H, Ar*H meta*), 8.10 (s, 2H, –CH), 8.55 (s, 2H, –OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 12.9, 20.7, 21.2, 24.4, 27.6, 29.6, 31.6, 32.4, 38.7, 67.3, 69.2, 119.3, 123.5, 125.7, 128.4, 128.7, 129.5, 129.8, 133.5, 149.6, 154.3, 157.2, 159.2. FAB-MS *m*/*z*: 1012.2 [M+Na]$^+$. Anal. Calcd for $C_{58}H_{72}O_{12}N_2$ (989.20): C, 70.42; H, 7.34; N, 2.83. Found: C, 69.86; H, 7.94; N, 2.34.

Acknowledgements

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