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Synthesis of Chiral Calix[4]arene Derivative and Evaluation of its Recognition Properties

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The article describes the synthesis and extraction properties of a new chiral calix[4]arene Schiff base ligand **5**, which has been synthesized from 5,17-diformyl-25,27-bis-(4-nitrobenzyloxy)-26,28-dihidroxycalix[4]arene (**4**) by treatment with (S)-(-)-1-phenylethylamine. In this synthesis, it was thought to explore the role of chiral, as well as Schiff base sites in the recognition of targeted species ions (such as dichromate anions) as well as neutral/chiral molecules. At low pH, the ligand **5** is more effective for transferring the dichromate anions from an aqueous into a dichloromethane layer; may be due to the protonation of nitrogen atoms.

The extraction properties of ligand **5** towards the some selected α-amino acid methylesters are also reported. However, the ligand **5** did not display any selectivity towards the selected α-amino acid methylesters.

Keywords: Calixarene, solvent extraction, ion recognition, chromium(VI), oxoanions

1 Introduction

Calixarenes are metacyclophanes comprising phenolic and methylene units. They are very known as very attractive and excellent ionophores because of providing a platform for the attachment of convergent binding groups either at the lower rim with the phenolic hydroxyl functions, or the upper rim positions to create host molecules mainly for the attraction of simple cations, anions and small molecules. Moreover, these compounds are cylinder-shaped with various cavity sizes and can form a variety of host-guest type inclusion complexes, similar to cyclodextrins (1–5).

There are many advantages to using calixarenes as host molecules because of their unique properties. The weak forces which play a major role in complex formation include hydrogen bonding, π-π interactions, electrostatic interactions, and dipole-dipole moments. Calixarenes provide all of those characteristics (6–10). The chiral recognition is one of the most important and fascinating area in host-guest chemistry or supramolecular chemistry (11–12). The preparation of chiral macrocyclic sensor molecules, having ability for visual discrimination between the enantiomers of chiral guest species have attracted considerable attention from a wide range of chemists especially in the fields of organic, biological and medicinal chemistry. The design of such molecules constitutes a timely and challenging research topic, and has lead to the synthesis of several chromogenic host molecules (13–15).

In the present paper we wish to report the synthesis and extraction studies of a novel calix[4]arene derivative bearing a chiral moiety at the upper rim and chromogenic nitro groups at the lower rim. This approach could provide an efficient methodology to develop improved optical sensors for biological and/or chemically important ions and amines.

2 Experimental

2.1 Instrumentation

Melting points were determined on a Electrothermal 9100 apparatus in a sealed capillary. ^{1}H-NMR spectra were recorded using a Varian 400 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-Visible spectra were obtained on a Shimadzu 160 A UV-Visible recording spectrophotometer. Elemental analysis data were performed on a Leco CHNS-932 analyzer. A Crison MicropH 2002 digital pH meter was used for the pH measurements.

2.2 Reagents

All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich, and used

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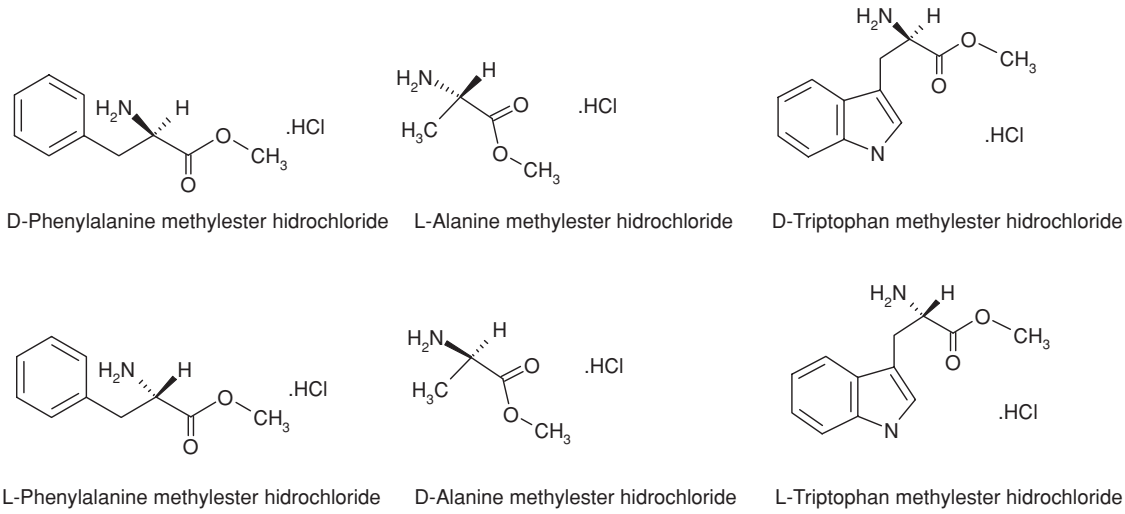


Sch. 1. The chemical structures of some selected α-amino acid methylesters.

without further purification. Commercial grade solvents such as chloroform, methanol, acetone, ethyl acetate, and hexane were distilled, and then stored over 4Å molecular sieves. Acetonitrile and DMF were dried from calcium hydride and stored under N_2 over 4 Å molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous $MgSO_4$. Thin layer chromatography (TLC) was performed using Merck prepared plates (silica gel 60 F_{254} on aluminum). Column chromatography seperations were performed on Merck Silica Gel 60 (230-400 Mesh). All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

The following a-amino acid methylester hydrochlorides obtained from Aldrich at the highest purity commercially available were used in this study: L-phenylalanine methylester hydrochloride (L-PheOMe), D-phenylalanine methylester hydrochloride (D-PheOMe), L-alanine methylester hydrochloride (L-AlaOMe), D-alanine methylester hydrochloride (D-AlaOMe), L-tryptophan methylester hydrochloride (L-TrpOMe) and D-tryptophan methylester hydrochloride (D-TrpOMe), (Scheme 1).

2.3 Synthesis

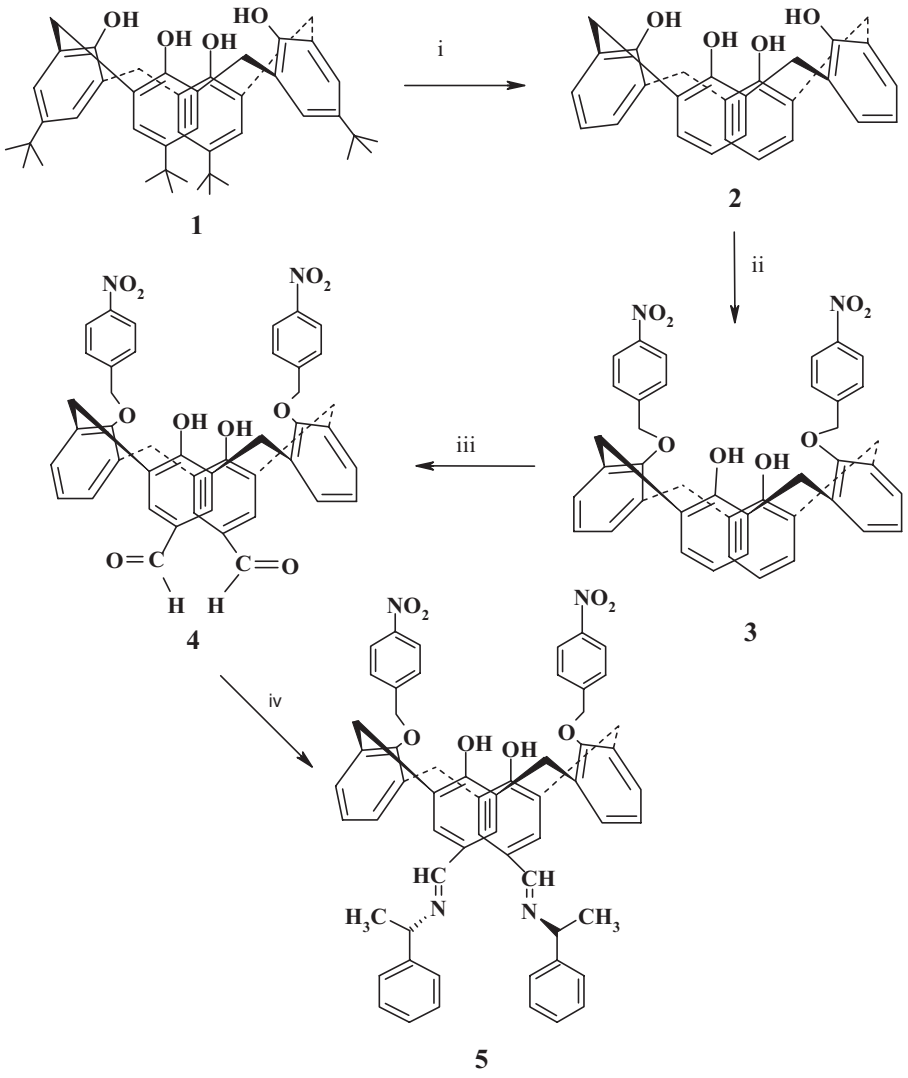
Compounds **1** and **2** were synthesized according to previously published methods (16, 17). Compounds **3**–**5** as illustrated in Scheme 2 were synthesized as follows:

2.3.1. *25,27-Bis-(4-nitrobenzyloxy)-26,28-dihidroxycalix[4]arene (3)*

Calix[4]arene **2** (10 g, 23.5 mmol) was dissolved in 500 mL acetonitrile. K_2CO_3 (4.225 g, 30.6 mmol) was added to this solution and stirred for half an hour at room temperature. Then, *p*-nitrobenzylbromide was added to this mixture (11.2 g, 51.8 mmol) and refluxed for 4 h. The contents of the flask were cooled and most of the solvent was removed at reduced pressure. After that, 1N HCl aqueous solution 200 mL was added to the remaining contents of the flask, ppts were filtered, first washed with distilled water, then with hot methanol. Finally, yellowish crystals were obtained in 79% yield. M.p.: 264°C. ^{1}H NMR ($CDCl_3$): δ 3.34 (d, $J = 13$ Hz, 4H, Ar$\underline{CH_2}$Ar), 4.20 (d, $J = 13$ Hz, 4H, Ar$\underline{CH_2}$Ar), 5.10 (s, 4H, O$\underline{CH_2}$Ar), 6.62 (t, $J = 7$ Hz, 2H, Ar$\underline{H_4}$), 6.72 (t, $J = 7$ Hz, 2H, Ar$\underline{H_4}$), 6.85 (d, $J = 7.5$ Hz, 4H, Ar$\underline{H_{2,6}}$), 7.01 (d, $J =$ Hz, 4H, Ar$\underline{H_{2,6}}$), 7.56 (s, 2H, Ar$\underline{OH}$), 7.86 (d, $J = 8.5$ Hz, 4H, 4-nitrophenyl-$\underline{H_{3,5}}$), 8.06 (d, $J = 8.5$ Hz, 4H, 4-nitrophenyl-$\underline{H_{2,6}}$). Anal. Calcd: $C_{42}H_{34}N_2O_8$: C, 72.6; H, 4.9; N, 4.03%. Found: C, 72.9; H, 5.0; N, 4.1%.

2.3.2. *5,17-diformyl-25,27-bis-(4-nitrobenzyloxy)-26,28-dihidroxycalix[4]arene (4)*

To the solution of compound **3** (5.0 g, 7.2 mmol) in $CHCl_3$ (150 mL) was added a solution of 1,1-dichloromethyl methyl ether (27.26 g, 237.1 mmol) in $CHCl_3$ (100 mL)., After the addition of $TiCl_4$ (37.61 g, 198.3 mmol) solution in $CHCl_3$ (150 mL), the contents of the flask were stirred at room temperature for 2 h. Then, distilled water (200 mL) was added. Organic phase was separated, washed with water and dried with Na_2SO_4. After the removal of solvent, crude product was purified by column chromatography (ethylacetate:n-hexane 7:3). Yield 56%. M.p.: 200°C (decom.); IR (KBr): 1683 (C=O) cm^{-1} ^{1}H-NMR ($CDCl_3$): δ 3.68 (d, $J = 13$ Hz, 4H, Ar$\underline{CH_2}$Ar), 4.30 (d, $J = 13$ Hz, 4H, Ar$\underline{CH_2}$Ar), 5.29 (s, 4H, O$\underline{CH_2}$Ar), 7.02 (t, $J = 8$ Hz, 2H, Ar$\underline{H_4}$), 7.19 (d, $J = 8$ Hz, 4H, Ar$\underline{H_{2,6}}$), 7.20 (s, 4H, Ar$\underline{H_{2,6}}$), 7.62 (s, 2H, Ar$\underline{OH}$), 8.22 (d, $J = 9$ Hz, 4H, 4-nitrophenyl-$\underline{H_{3,5}}$), 8,45 (d, $J = 9$ Hz, 4H, 4-nitrophenyl-$\underline{H_{2,6}}$), 9.80 (s, 2H,$\underline{CHO}$). Anal. Calcd:$C_{44}H_{34}N_2O_{10}$: C, 71.0; H, 4.5; N, 3.77%. Found: C, 71.3; H, 4.1; N, 3.65 %.



Sch. 2. The synthetic route of preparation of compounds **3**–**5**. (i) Fenol, $AlCl_3$; (ii) K_2CO_3, *p*-nitrobenzylbromide; (iii) 1,1-dichlormethyl methyl ether, $TiCl_4$; (iv) (S)-(-)-1-phenylethyl amine.

2.3.3. *Treatment of compound 4 with (S)-(-)-1-phenylethylamine (5)*

Compound **4** (1.25 g, 1.67 mmol) was dissolved in chloroform-ethanol (1:2). (S)-(-)-1-phenylethyl amine (0.50 g, 4.1 mmol) and $MgSO_4$ (1.0 g) were added. The reaction mixture was refluxed for 24 h. The contents were cooled and the solvent was removed at reduced pressure. The remaining crude product was washed first with dilute acid (1N HCl) and then with water. Recrystallized from ethanol gave compound **5** in 51% yield. M.p.: >350°C. IR (KBr): 1661 (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.55 (d, 6H, ArCHC$\underline{H_3}$), 3.47 (d, J = 13 Hz, 4H, Ar$\underline{CH_2}$Ar), 4.27 (d, J = 13 Hz, 4H, Ar$\underline{CH_2}$Ar), 4.95 (q, 2H, Ar$\underline{CH}$CH$_3$), 5.22 (s, 4H, O$\underline{CH_2}$Ar), 6.60 (t, J = 8Hz, 2H, Ar$\underline{H_4}$), 6.94 (brs, 10H, $\underline{ArH}$-CH-CH$_3$), 7,11 (d, J = 8 Hz, 4H, Ar$\underline{H_{2-6}}$) 7.26 (s, 4H, Ar$\underline{H_{2,6}}$), 7.50 (s, 2H, Ar$\underline{OH}$), 7.92 (d, J = 9 Hz, 4H, 4-nitrophenyl-$\underline{H_{3,5}}$), 8,38 (d, J = 9 Hz, 4H, 4-nitrophenyl-$\underline{H_{2,6}}$), 8.98 (s, 2H, $\underline{CH}$=N). Anal. calcd:$C_{60}H_{52}N_4O_8$: C, 75.3; H, 5.4; N, 5.8 %. Found: C, 75.8; H, 5.2; N, 5.5%.

2.4 Analytical Procedure

Dichromate extraction experiments were performed following Pedersen's procedure (18). A 10 mL of a 2.0×10^{-5} M aqueous picrate, or a 1.0×10^{-4} M dichromate solution and 10 mL of 1×10^{-3} M solution of calixarene (**2**–**5**) in dichloromethane were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. The solutions were then magnetically stirred in a thermostated water-bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate/dichromate ion remaining in the aqueous phase was then determined

spectrophotometrically. Blank experiments showed that no picrate/dichromate extraction occurred in the absence of calixarene. The percent extraction (E %) has been calculated as:

$$(E\,\%) = A_o\text{-}A/A_o \times 100 \qquad (1)$$

where A_o and A are the initial and final concentrations.

3 Results and Discussion

The main focus of this work is the design of new calixarene based ligand that is easily accessible, that has effective binding character for a particular set of ions/molecules, and can be potentially useful for multiple applications such as laboratory, clinical, environmental and industrial process analysis. To achieve the desired goal, *p-tert*-butylcalix[4]arene **1** has been chosen as the precursor. A synthetic strategy has been developed to enable its derivatization. Such a synthetic route is depicted in Scheme 2. The syntheses for compounds **1** and **2** are based on previously published procedures (16, 17). Alternatively, the substitution of calix[4]arene **2** at its lower rim has been carried out in the presence of K_2CO_3 in dry acetonitrile with *p*-nitro-benzylbromide to afford the cone conformer **3** in 79% yield. ^{1}H-NMR spectroscopy is a versatile tool for the identification of calix[4]arene conformations (19). The ^{1}H-NMR spectrum of **3** has a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.34 and 4.20 ppm ($J = 13$ Hz), which indicates that the compound **3** exists in the cone conformation. Selective formylation of compound **3** with 1,1-dichloromethyl methyl ether in the presence of titanium tetrachloride in chloroform afforded **4** in 56% yield. Examination of IR as well as ^{1}H-NMR spectra of **4** confirms its formation. The IR spectrum of **4** shows a carbonyl band at 1683 cm^{-1}, whereas ^{1}H-NMR spectrum shows a singlet at 9.8 ppm, which is an indication of the presence of aldehyde functionalities. The ^{1}H NMR spectrum of **4** has also a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.68 and 4.30 ppm ($J = 13$ Hz), which indicates that the compound **4** too, exists in the cone conformation.

In the last step, compound **4** has been converted into chiral ligand **5** by treatment with (S)-(-)-1-phenylethyl amine in chloroform:ethanol. The ligand **5** has been obtained in 51% yield. In IR spectrum of **5** the absence of aldehydic band at 1683 cm^{-1} and appearance of a new band at 1661 cm^{-1} reveals the formation of **5**. UV-Vis. spectrum of new compound (**5**) shows two absorption bands at 393 and 510 nm (Fig. 1). Again the ^{1}H-NMR spectrum of **5** confirms its cone conformation due to the AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.47 and 4.27 ppm ($J = 13$ Hz).

Table 1. Extraction Percentage of Sodium Dichromate with **2**, **3** and **5**[a] Dichromate Anion Extracted (%)

	pH					
Ligand	*1.5*	*2.5*	*3.5*	*4.5*	*5.5*	*7*
2	3	12	11	<10	<10	<10
3	10	13	6	<10	<10	<10
5	96	89	63	<10	<10	<10

[a] Liquid-liquid extraction. Aqueous phase, [sodium dichromate] = 1×10^{-4} M; organic phase, dichloromethane, [ligand] = 1×10^{-3} M at 25°C, for 1 h.

3.1 Extraction Studies

3.1.1. *Dichromate anion extraction*

Recently, efforts have been made to synthesize modified calixarenes that can be used as hosts for simple anions (20–27). In this study, we have targeted a new ligand (**5**) based on a calixarene frame-work that can be employed as a host for cations, and may be suitable for anion extraction. Anion recognition and sensing is an increasingly

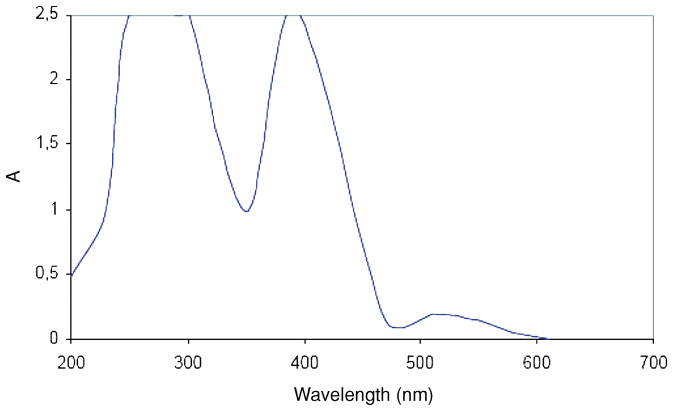


Fig. 1. UV-Vis. Spectrum of compound **5**.

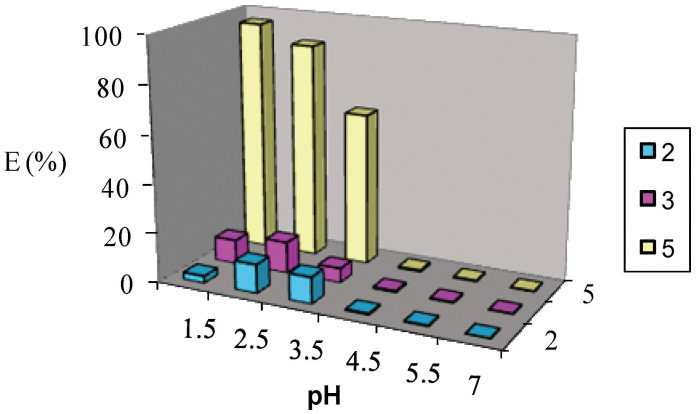


Fig. 2. A graphic representation of the dichromate extraction results with **2**, **3** and **5** at 25°C.

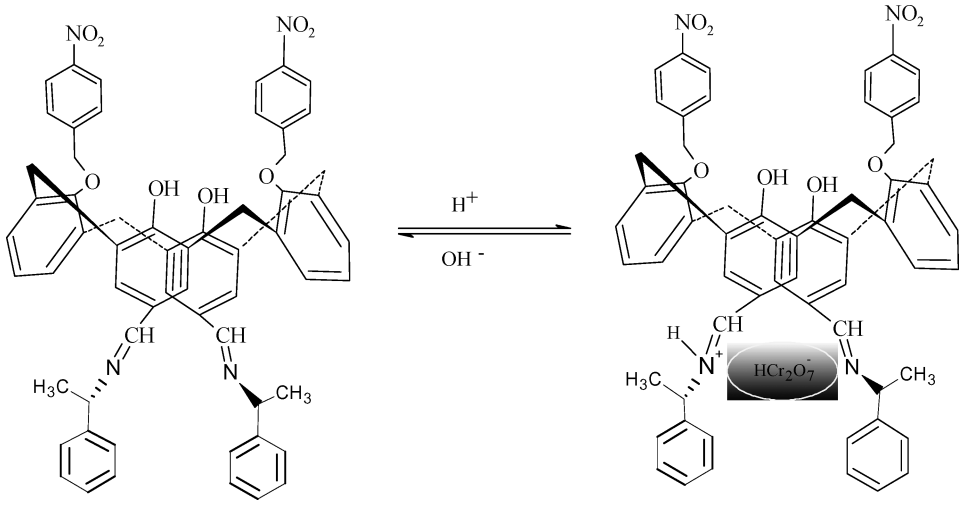


Fig. 3. Proposed structure of complexation of compound **5** with $HCr_2O_7^-$.

important research topic in supramolecular chemistry due to the importance of various anions in biological and environmental locations. Chromate and dichromate anions are important because of their high toxicity (4, 28–32) and their presence in soils and waters (33). For a compound to be effective as a host it is necessary that its structural features are compatible with those of the guest anions. The chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) ions are dianions where the periphery of the anions have oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. A recent development is the discovery that calix[4]arenes with nitrile substituents act as phase transfer extractants for chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) ions, and that their effectiveness is higher with aqueous solutions that are acidic (4, 34–36).

A preliminary evaluation of binding efficiencies of the ligands **2**, **3** and **5** was carried out by solvent extraction of $Na_2Cr_2O_7$ from aqueous into dichloromethane at different pH. The results are summarized in Table 1. From the extraction data given in Table 1 (Fig. 2), it is apparently clear that the starting materials **2** and **3** have not extracted $Cr_2O_7^{2-}/HCr_2O_7^-$ ions significantly. However, the conversion of **4** into a Schiff-base derivative (**5**) has increased the anion extraction ability of this compound in remarkable extent at low pH. This pronounced increase may be due to more rigid structural features and protonation of imide groups of **5**, which help in transferring anions as compared to **2** and **3** (Fig. 3).

3.1.2. *α-Amino acid methylesters extraction*

In this study, two-phase solvent extraction experiments were carried out to examine extraction behavior of α-amino acid methylesters from the aqueous phase into the organic phase (dichloromethane) by using an achiral (**3**) and a chiral calix[4]arene derivatives (**5**). The results of the picrate extraction studies are summarized in Table 2. These data were obtained by using a dichloromethane solution of the ligand (**3**, **5**) to extract ammonium picrates from the aqueous solution. The equilibrium concentration of picrate in aqueous phase was determined spectrophotometrically. From the extraction data given in Table 2, it has been observed that achiral calix[4]arene **3** transfer all amino acid species from aqueous phase into organic phase in trace amounts, and chiral calix[4]arene derivative **5** recognize all amino acid species. In this study, α-amino acid methylesters, having different molecular size, was used to investigate the effect of size on their extraction efficiency and it was observed that **5** did not display any selectivity towards α-amino acid methylester.

Table 2. Extraction percentage of selected α-amino acid methylesters with **3** and **5**[a]

Ligand	*L-AlaOMe*	*D-AlaOMe*	*L-PheOMe*	*D-PheOMe*	*D-TrpOMe*	*L-TrpOMe*
3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
5	28.7	28.8	32.5	30	30	32

[a]Aqueous phase, [ammonium picrate] = 2.0×10^{-5}M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3}; at 25°C, for 1 h.

4 Conclusions

The work reported here allows further conclusions to be made about the description of simple substituted calix[4]arene derivatives. This work confirms a convenient method for the synthesis of chiral calixarene-based ligands. Compound **4** is a versatile starting material for the synthesis of chiral calixarene-based ligands suitable for the extraction of both ions and neutral molecules. At low pH, the ligand is more effective for transferring the dichromate anions from an aqueous into a dichloromethane layer; may be due to the protonation of nitrogen atoms. In addition, it was observed that chiral compound **5** is better extractant than the achiral one (**4**) for α-amino acid methylesters, and there is no any selectivity in extraction phenomena by using this chiral calix[4]arene derivative (**5**).

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