

while *p*-OCH₃ group showed electron-donating effect. Most of the substituents favored the singlet excited state in the photohydration of diynes but nitro group favored triplet excited state due to the efficient intersystem crossing.¹³

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Synthesis and Ionophoric Properties of Mono-Penta Type Mixed-Functionalized Ligands Based-upon *p*-tert- Butylcalix[6]arene

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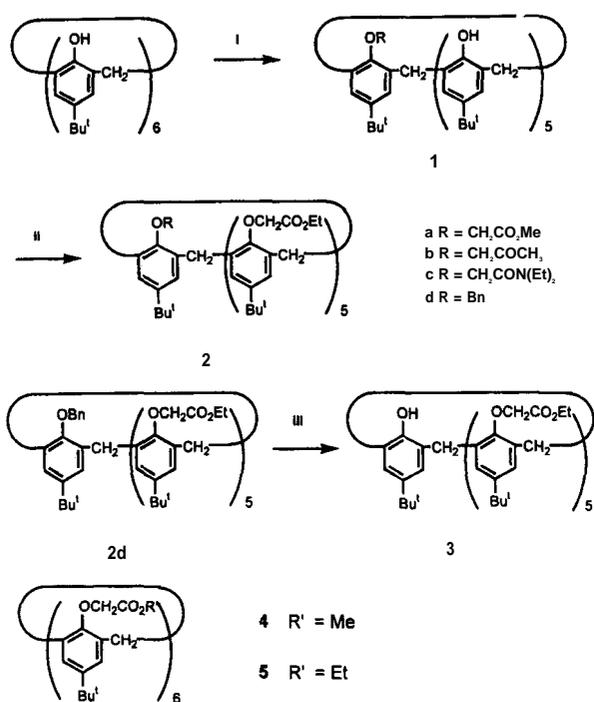
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Ester, amide, and ether functional groups have been ingeniously utilized by nature for the construction of many bioactive molecules having ionophoric properties. Representative of such ingenuity are valinomycin and related antibiotics.¹ There have been many attempts to mimic the ionophoric properties of these natural antibiotics for the development of new host systems.² Calixarenes are one of the most attractive and widely studied compounds for this purpose and many effective ligating groups have been incorporated into their molecular frameworks.³ However, in order to design more versatile calixarene-based host molecules useful for practical purposes, such as preparation of separation media and sensory materials, more elaborate structural transformations are necessary.⁴ In view of this, we prepared a series of mono-penta type mixed ligating ionophores based upon pentaethyl ester of *p*-tert- butylcalix[6] arene and investigated their ionophoric behaviors toward alkali metal cations.

Mono-penta type mixed ligands were prepared by selective monoalkylation for the introduction of mono-part substituent followed by exhaustive alkylation with ethyl bromoacetate (Scheme). Monoalkylation was performed by reacting with one or two equivalents of required methyl bromoacetate, chloroacetone, or *N,N*- diethyl bromoacetamide in

the presence of K₂CO₃ in THF according to the reported procedure to obtain monomethyl or monobenzyl ether of *p*-tert- butylcalix[6]arene (yield: 42-58%).⁵ The desired mixed-functionalized derivatives **2a-2c** were prepared by exhaustive alkylation of the appropriate mono-functionalized derivatives with a large excess of ethyl bromoacetate in refluxing acetone (yield: 69-82%).

To have a more versatile procedure for the synthesis of mono-penta type mixed ligands, the monophenol pentaester **3** was chosen as a key intermediate with the intent of utilizing benzyl ether moiety as a protecting group. Monobenzyl ether pentaethyl ester **2d** was prepared from monobenzyl ether of *p*-tert- butylcalix[6]arene⁶ by exhaustive alkylation with ethyl bromoacetate (K₂CO₃/acetone). Subsequent removal of benzyl group by treatment with trimethylsilyl bromide⁵ yield monophenol-pentaester **3** (65%). We attempted to introduce the desired functional group into the remaining phenol group of the *p*-tert- butylcalix[6]arene by alkylation with a suitable reagent but to no avail partly due to the steric congestion in monophenol **3**. For all the prepared ligands, ethoxycarbomethyl substituent was chosen as penta-part because of their widely investigated and relatively well-defined ionophoric properties toward many interesting guests.⁷



Scheme

The ¹H NMR spectra of the mono-penta type mixed ligands are in general featureless and/or too complicated for extraction of detailed information at room temperature, which is characteristic of many conformationally flexible derivatives of calix[6]arenes. However, ¹H NMR spectra of some derivatives turn into a relatively well resolved one either upon raising the temperature or when complexed with suitable guest, such as ethylammonium picrate or cesium tetraphenylborate in CDCl₃.⁸ For example, upon complexation with ethylammonium picrate, monomethyl-pentaethyl ester **2a** displays a relatively simple spectral pattern, especially in the region of bridging methylene protons, comprised of a characteristic well-defined pair of doublets at δ 3.45 and 4.44 ppm implying the cone conformation.⁹ On the other hand, the ¹H NMR resonances of monophenol-pentaethyl ester **3** are found to transform into a sharp and well resolved spectrum at an elevated temperature in CDCl₂-CDCl₂ (130 °C) as shown in Figure 1. That is, the aromatic region consists of six sharp lines (δ 7.16, 7.15, 7.05, 7.00, 6.92 and 6.74) while the bridging methylene region displays three lines (δ 4.08, 4.06 and 3.96). The resonances of *tert*-butyl groups consist of four lines at 1.42, 1.21, 1.18 and 0.97 with an intensity ratio of 1 : 1 : 2 : 2. At higher temperatures the complicated conformational spectral pattern of **3** is averaged out to yield relatively well resolved ¹H NMR lines.

To assess the ion binding properties of mixed-functionalized derivatives of *p-tert*-butylcalix[6]arene, standard solvent extraction experiments of metal picrate salt into CH₂Cl₂ were carried out and the results are summarized in Table 1. For comparison, the results of closely related hexamethyl ester **4** and hexaethyl ester **5** are also listed.

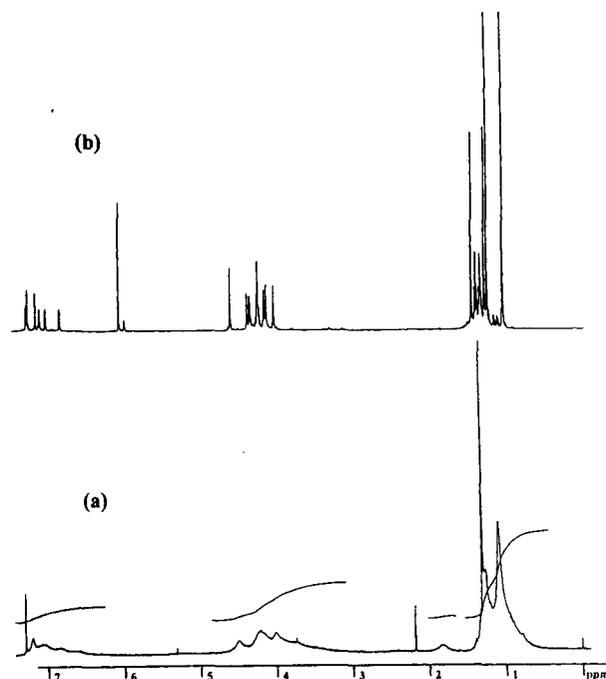


Figure 1. ¹H NMR spectra of **3** (a) at 300 K in CDCl₃ and (b) at 403 K in CDCl₂/CDCl₂.

Table 1. Extraction of Metal Picrates by Mixed-functionalized *p-tert*-Butylcalix[6]arene Derivatives

Ligands	% Extraction			
	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
2a	9.8	19.1	20.2	37.3
2b	24.7	41.2	35.4	47.6
2c	13.8	22.4	20.3	38.5
2d	25.4	30.0	32.4	52.2
3	5.1	17.7	24.6	25.1
4	2.1	6.5	6.1	15.3
5	14.1	42.3	39.8	64.3

Organic phase: [Ligand]=3.5 × 10⁻³ M, (CH₂Cl₂, 3.0 mL). Aqueous phase: [MPic⁻]=7.0 × 10⁻³ M, (3.0 mL). Measurements are made in triplicate at 25 °C.

The effects of replacing only one ethyl ester function with diverse substituents are remarkable. They exhibited widely differing ionophoric properties toward alkali metal cations. Mixed-functionalized *p-tert*-butylcalix[6]arenes **2a-2d** generally resembled the discrimination behavior of the hexaethyl ester **5** with somewhat reduced extraction efficiency and selectivity. That is, in general, Cs⁺ > Rb⁺ ≈ K⁺ > Na⁺. Introduction of an *N,N*-diethylamide functional group in pentaester results in slight reduction of binding affinity, quite contrary to the anticipation that the combination of an amide function having higher dipole moment¹⁰ with ester functions as selectivity generating site, as modeled in **2c**, might afford improved binding characteristics. One noteworthy thing is the behavior of monobenzyl-pentaethyl ester derivative **2d**, which exhibited the extraction behavior similar to that of the hexaethyl ester **5**. The fact that the replacement of an ethoxycarbomethyl substituent by benzyl ether¹¹ does not inflict any harmful effect is interesting

when compared with the results shown by the rest compounds containing the other ligating substituents. Significant effects on ionophoric properties may be brought forth even by minimal changes in structure, as evidenced by the results obtained for monomethyl-pentaethyl ester **2a** and hexaethyl ester **5**.

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