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*Short Communication*

# Separation of Xylenes by Extractive Crystallization with Calixarenes

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**Abstract.** Several calixarenes **1**–**5** and benzopinacolone **6** were recrystallized from 1 : 1 : 1 mixtures of the three xylene isomers. *p-Iso*-propylcalix[4]arene **1** was shown to extract *p*-xylene with 86% selectivity. *p-Iso*-propylbishomooxacalix[4]arene **5** extracts *o*-xylene with 84% selectivity.

**Key words.** Calixarenes, xylene isomers, crystallization, host–guest.

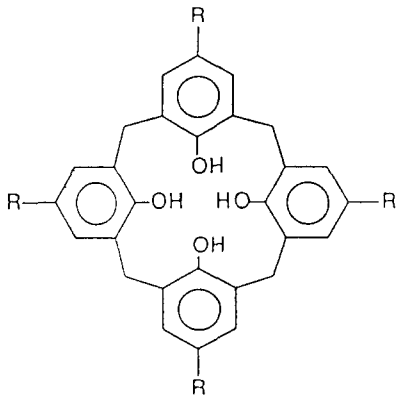
## 1. Introduction

During the past decade, extensive work has been devoted to the design of macrocyclic host molecules able to recognize small neutral molecules by inclusion in their architecture. In this respect, calixarenes are made of 2-hydroxy-1,3-phenylene methylene units having (similar) properties such as unique cavity structures, the ability to form molecular complexes in solution and in the solid state with aromatic molecules [1]. For example *p-tert*-butylcalix[4]arene crystallizes with one molecule of anisole to form a well-defined 2 : 1 complex with precise geometries between the host and guest partners [2]. In solution, the formation of host–guest complexes between calixarenes and a series of aromatic hydrocarbons with different size showed a correlation between the dimensions of the hydrocarbons and the size of the calixarenes [3].

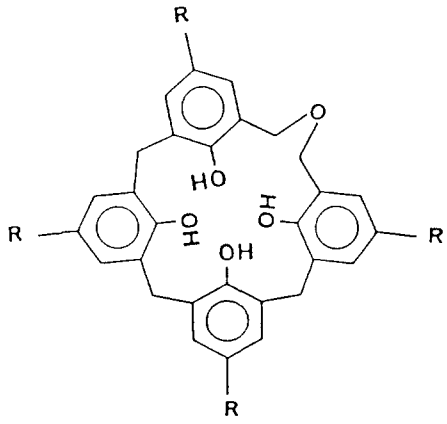
In this communication we report our recent results on the isomer separation of the xylenes by extractive crystallization with calixarenes (Figure 1).

## 2. Experimental

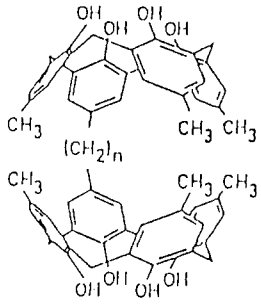
The experiments were conducted as follows: crystalline complex compounds were prepared by refluxing to dissolution calixarenes (100–150 mg) in a 1 : 1 : 1 mixture of the three xylene isomers (1–2 mL). The solutions were allowed to crystallize or precipitate during 24 h. The solid part was separated by filtration with suction. 50–60% weight of solid complexes were recovered. An aliquot part of this solid was dissolved in chloroform and injected into a gas chromatograph to determine



**1** R = *iso*-propyl
**2** R = *tert*-butyl
**3** R = *tert*-octyl



**5** R = *iso*-propyl



**4** n = 8

Fig. 1. General formula of calixarenes.

the ratio of the xylenes present in the solid. Conditions used: Supelco column; phase: supelcowax 10; column length: 30 m; film thickness: 1.00 $\mu$m; carrier gas: nitrogen; linear gas rate: 0.2 bar; column temperature: 50°C; injector temperature: 220°C; detector temperature: 200°C. Each experiment was run twice and three injections were made for each of them (error 0.5%). Figure 2 shows the gas chromatography elution pattern for (b) *p-iso*-propylcalix[4]arene **1** crystals compared to (a) the initial 1 : 1 : 1 xylenes solution.

## 3. Results and Discussion

Xylene ratio distributions, corresponding to the percentage extraction of *o*-, *m*- and *p*-xylenes upon crystallization with different calixarenes **1**–**5** [4–6] are presented in Scheme I. In order to compare with Toda's compound we also carried out a crystallization with benzopinacole **6** [7]. It is evident from Scheme I that compound **1** extracts the *para*-isomer with a good selectivity (86%). *meta*-Xylene is 14% extracted while the *ortho*-isomer is not extracted at all. In contrast one observes that *p-iso*-propylbishomooxacalix[4]arene **5** crystallizes selectively with the *ortho*-

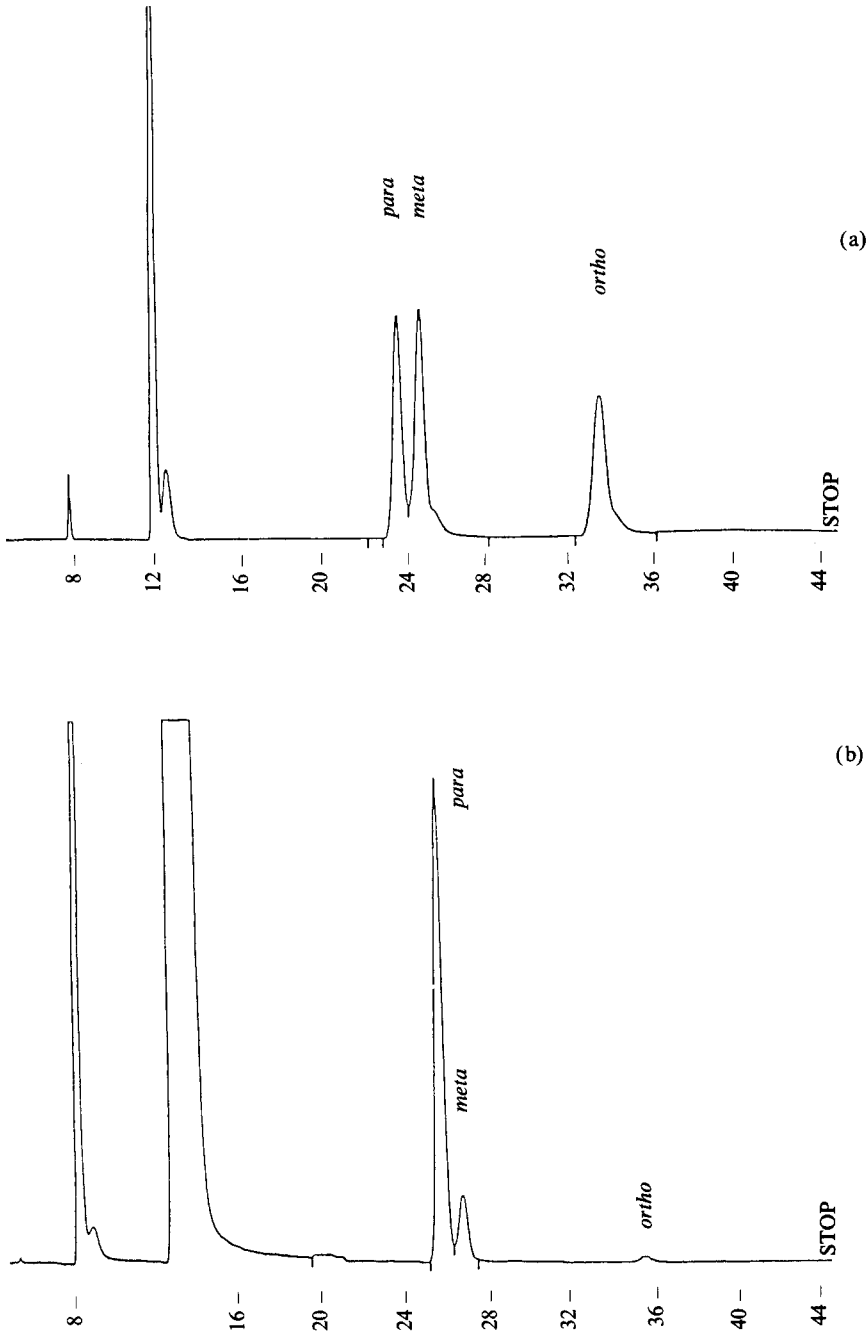
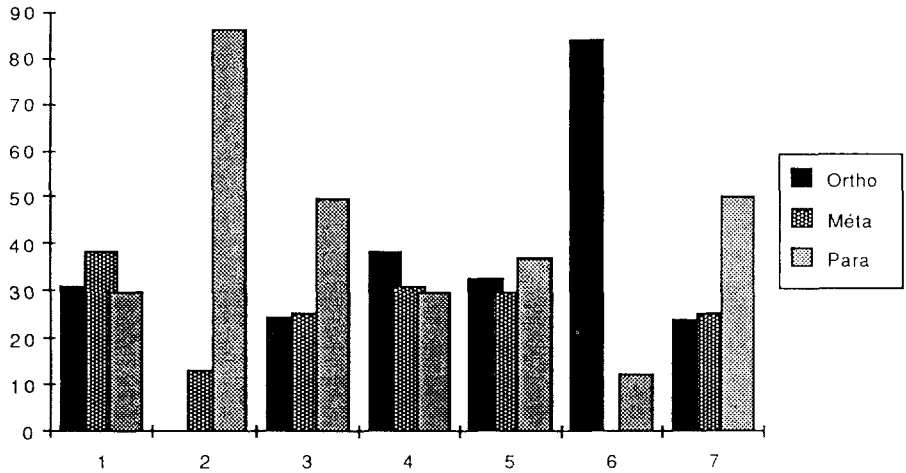



Fig. 2. Elution patterns of xylene isomers: (a) 1 : 1 : 1 initial mixture; (b) crystals of *p-iso*-propyl-calix[4]arene **1** dissolved in chloroform.




Scheme I: % Extraction of *o*-, *m*-, and *p*-xylenes.

| | |
|---|---|
| 1. Starting mixture | |
| 2. *p-iso*-propylcalix[4]arene **1** | ref. 4 |
| 3. *p-tert*-butylcalix[4]arene **2** | ref. 1 |
| 4. *p-tert*-octylcalix[4]arene **3** | ref. 1 |
| 5. double-*p*-methylcalix[4]arene (-$CH_2$-)8 **4** | ref. 5 |
| 6. *p-iso*-propylbishomooxacalix[4]arene **5** | ref. 6 |
| 7. benzopinacole **6** | ref. 7 |

Scheme I. Percentage of *o*-, *m*- and *p*-xylenes.

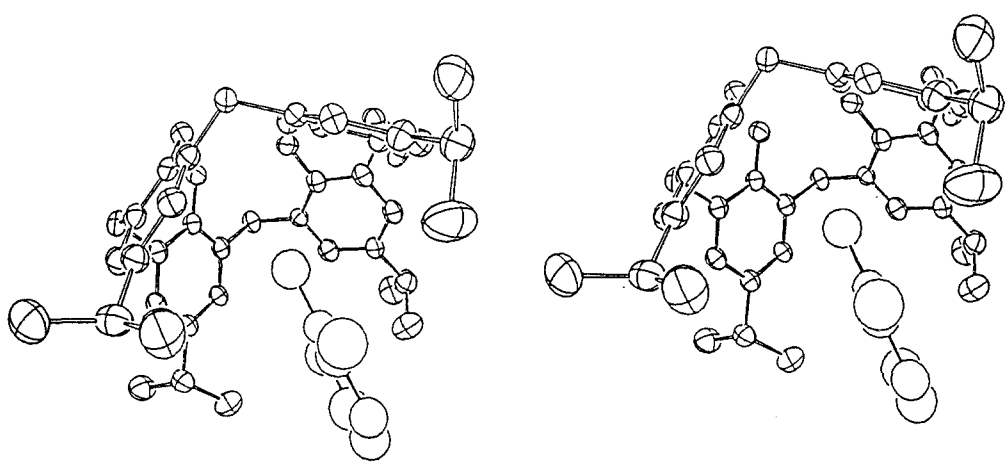


Fig. 3. 1:1 complex of molecule **5** with *ortho*-xylene.

isomer with a comparable selectivity (84%) while *para*-xylene is extracted with 16% selectivity. The other calixarenes were shown to be less selective.

The complexes **1** – *para*-xylene (mp 245–247°C) and **5** – *ortho*-xylene (mp 290–294°C) have 1 : 1 stoichiometry as evidenced by proton nmr on dissolved samples in $CDCl_3$ (based on the ratio of the signal of methyl groups of the xylene and the signal of the methyl groups of the *iso*-propyl of the calixarenes) and elemental analysis.

The crystalline structure of the 1 : 1 complex **5**-*ortho*-xylene was determined by X-ray diffraction techniques: space group $P2_1/n$; crystal system: monoclinic; cell constant: $a = 18.803(3)$ Å, $b = 24.714(4)$ Å; $c = 9.203(1)$ Å; $Z = 4$; $V$ (unit cell volume) $= 4208.6$ Å$^3$; $D_c$ (calc. density) $= 1.151$ g/cm$^3$. The details of the crystal data and structure will be published elsewhere. As shown in Figure 3, molecule **5** is in a cone conformation. The *ortho*-xylene molecule lies in the cavity. Several $CH_3$-$\Pi$ interactions between the methyl groups of the xylene and the phenol units of molecule **5** maintain the supramolecular structure and probably are responsible of the observed selectivity.

We also notice that none of the xylene isomers are extracted by calix[6]arenes and calix[8]arenes.

## 4. Conclusion

To conclude we have shown that *o*- and *p*-xylene are selectively extracted by crystallization, probably due to the recognition of the substrate molecules by the calixarene cavity. These selectivities may be of good use in small scale separations, in chromatographic applications and in large scale commercial separation plants [8]. The X-ray crystalline structure of **1**-*para*-xylene complex is being determined.

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