Synthesis and Characterization of Two New p-tert-Butylcalix[4]-arene Schiff Bases.

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Abstract: Synthesis and characterization of two new Schiff bases of p-tert-butylcalix[4]arene (H₂L₁ and HL₂) is described. The synthesis of H₂L₁ and HL₂ has been achieved by the condensation of salicylaldehyde with the amine group of upper rim monoamine p-tert-butylcalix[4]arene in ethanol. These compounds have been characterized on the basis of elemental analysis and spectral data. Solvatochromicity and fluorescence properties were observed and measured for H₂L₁ and HL₂. Solvatochromicity of these ligands indicates their potential for NLO applications.

Keywords: Calix[4] arene, monosubstitution, Schiff base.

Introduction

Calix[4]arenes can be easily functionalized both at the phenolic OH groups (lower rim) and, after partial removal of tert-butyl groups, at the para positions of the phenol rings (upper rim) [1-3]. The vast majority of these modified calixarenes exist in the cone conformation in which there is a cavity suitable for reception of different ionic and neutral species [4]. Furthermore, the most significant feature of the chemistry of these molecules is their ability to bind selectively alkali and alkaline earth cations [5,6]. Compared to the number of reports on the binding of alkali metal ions with calixarenes, reports on the binding of transition metal ions are still limited [7-9]. From this point of view
calixarene Schiff base ligands are in the center of interest [10-12]. Monofunctionalized calixarenes are potentially excellent starting materials for the selective design of new materials. Reinhoudt et al. [13] reported the ipsonitration of p-tert-buthylcalix[4]arenes for the preparation of nitrocalix[4]arenes. In this work we used the selectively ipsonitated p-tert-buthylcalix[4]arenes as starting materials for the preparation of two monoamine p-tert-buthylcalix[4]arenes functionalized at the upper rim and studied their conversion to the salicylaldehyde Schiff bases, 4 and 7.

Results and Discussion

Synthesis of the Schiff Bases

Schiff bases are potentially capable of forming stable complexes with metal ions [9,14-16]. In the present work the synthesis of (4) and (7) according to the Scheme 1 is described.

Scheme 1. Synthesis of the H$_2$L$^1$ and HL$^2$
The cone mononitro-\textit{p-tert}-butylcalix[4]arene 2 was obtained from the mono \textit{ipsonitration} of monohydroxycalixarene using a modified method [17]. The mononitro derivatives 2 and 5 were reduced to the corresponding monoamines by hydrogenation over a palladium-charcoal catalyst. The condensation of compounds 3 and 6 with salicylaldehyde gave the Schiff base ligands H$_2$L$_1$ and HL$_2$ as NO donors with a \textit{p-tert}-butylcalix[4]arene moiety (Scheme 1). The $^1$H-NMR spectrum of the ligands indicated the calixarene to be in a cone conformation. The conclusion that H$_2$L$_1$ and HL$_2$ exist in cone conformations was deduced from the presence of two sets of characteristic AB systems (figures 1 and 2) as described in the Experimental Section [18]. The analytical results of the isolated solid ligands with their melting points and colors are compiled in Table 1.

### Table 1. Colors, yields, melting points and analytical results of H$_2$L$_1$ and HL$_2$

| Compound       | Formula Weight | Color  | m.p, (°C) | Yield, % | Calcd. (Found) | %  |
|----------------|----------------|--------|-----------|----------|----------------|----|
| H$_2$L$_1$.H$_2$O | (C$_{56}$H$_{73}$NO$_6$) | 838.17 | Yellow    | 192      | 86             | 80.25 (79.42) 8.54 (8.69) 1.67 (1.44) |
| HL$_2$         | (C$_{59}$H$_{77}$NO$_5$) | 880.25 | Yellow    | 172      | 84             | 80.50 (80.74) 8.82 (8.79) 1.59 (1.88) |

**IR Spectra**

The characteristic IR absorptions are given in Table 2. The observed microanalytical data for C, H, and N atoms shows that H$_2$L$_1$ contains a water molecule that is identified by broad O-H absorptions around 3547-3400 cm$^{-1}$.

### Table 2. Characteristic IR bands of the H$_2$L$_1$ and HL$_2$ as KBr Pellets ( cm$^{-1}$ )

| Compound     | $\nu$ (H$_2$O ) | $\nu$ ( O-H ) | $\nu$ ( C-H ) | $\nu$ ( C=N ) |
|--------------|-----------------|---------------|---------------|--------------|
| H$_2$L$_1$.H$_2$O | 3420 mbr        | 3547          | 2960, 2874 s  | 1620         |
| HL$_2$       | -               | 3540          | 2960, 2875 s  | 1620         |

**Electronic Spectra**

The electronic spectra were recorded in chloroform and acetonitrile (Table 3). An important property for distinguishing potential NLO materials is the existence of solvatochromicity [19], i.e., the solvent dependent shift of the absorption bands in the UV/vis spectra. Both H$_2$L$_1$ and HL$_2$ display strong negative solvatochromicity as shown in Table 3. Negative solvatochromicity can be attributed to the stabilization of polar ground states in polar solvents.

| Compound     | $\nu$ (C-H) | $\nu$ (C=N) |
|--------------|-------------|-------------|
| H$_2$L$_1$.H$_2$O |             |             |
| HL$_2$       |             |             |
Table 3. electronic spectra of H₂L¹ and HL²

| Compound | ν ( cm⁻¹) | Δν ( cm⁻¹) | λₑₓ (nm) (excitation) | λₑₘ (nm) (emission) |
|----------|----------|-----------|-----------------------|---------------------|
| CHCl₃    |          |           |                       |                     |
| CH₃CN    |          |           |                       |                     |
| H₂L¹     | 277      | 281       | 400                   | 390                 | 526                 |
| HL²      | 287      | 290       | 300                   | 390                 | 522                 |

As a result these Schiff bases are good candidates for NLO chromophores due to their strong solvatochromicity. UV/Vis fluorescence of H₂L¹ and HL² was observed when they were irradiated at a wavelength of 390 nm whereby they emitted a light with a wavelength of 526 and 522 nm, respectively.

¹H-NMR Spectra

¹H-NMR spectra of H₂L¹ and HL² are shown in Figures 1 and 2, respectively. Assignments of ¹H-NMR signals can be found in the Experimental Section. The downfield signal of the proton of hydroxy group of the salicylaldehyde moiety, the salicylidene part of H₂L¹ and HL², justifies the existence of intramolecular hydrogen bonding between the hydrogen atom of the hydroxy group and the nitrogen atom of the imine.

Fig.1. ¹H-NMR Spectra of H₂L¹
Conclusions

In this paper we present the preparation of two Schiff bases of \textit{p-tert}-buthylcalix[4]arene derivatives. Both these Schiff base ligands have fluorescence properties which suggest their potential for analytical applications. Also the solvent dependent UV/Vis spectra and solvatochromicity of these compounds show their potential for NLO applications.

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Experimental

General

Melting points are taken on a Büchi SMP-20 apparatus and are uncorrected. $^1$H-NMR spectra were recorded on a Bruker AM-400MHz in CDCl$_3$ with Me$_4$Si as an internal standard. Elemental analysis were recorded on Carlo-Erba-Analysor Model 1104. IR spectra were recorded on Bruker IFS 25. Compound 1, \textit{p-tert}-buthylcalix[4]trioxyarene, was prepared according to a literature procedure [20].
Preparation of $H_2L^1$ and $HL^2$

According to the Scheme 1, mononitro derivatives were reduced to the corresponding monoamines by hydrogenation over palladium-charcoal catalyst and then used for the preparation of the $H_2L^1$ and $HL^2$ as follows: salicylaldehyde (170 mg, 1.36mmol) was added to a solution of 1.36 mmol of corresponding monoamine, 3 or 6, in ethanol (30 mL) and the mixture was refluxed for 24h. After cooling the reaction mixture, the yellow colored $H_2L^1$ product was precipitated by addition of water but $HL^2$ was precipitated without addition of water. Both were recrystallized from ethanol, yields 86% for $H_2L^1$ and 84% for $HL^1$.

$^1$H-NMR spectra of $H_2L^1$: $\delta$ 13.85 (1H, s, H-O, sal.), 8.65 (1H, s, H-C=N), 7.44 (2H, dd, Ar-H) 7.35 (4H, m, Ar-H, sal), 7.13 (2H, dd, Ar-H), 6.55 (4H, dd, Ar-H), 5.95 (1H, s, O-H), 4.38 and 3.25 (4H, dd, Ar-CH2-Ar, $J = 12.9$ Hz), 3.85 (2H, t, OCH2), 3.75 (4H, t, OCH2), 4.33 and 3.19 (4H, dd, Ar-CH2-Ar, $J = 13.8$ Hz), 2.3 (2H, m, CH2), 1.95 (4H, m, CH2), 1.35 (9H, s, C(CH3)3), 1.1 (6H, t, 2CH3), 0.95 (3H, t, CH3), 0.85 (18H, s, C(CH3)3).

$^1$H-NMR spectra of $HL^2$: $\delta$ 13.20 (1H, s, H-O, sal.), 8.15 (1H, s, H-C=N), 7.29 (2H, dd, Ar-H) 7.25 (4H, m, Ar-H, sal), 7.11 (2H, dd, Ar-H), 6.40 (4H, dd, Ar-H), 4.47 and 3.15 (4H, dd, Ar-CH2-Ar, $J = 13.0$ Hz), 4.05 (2H, t, OCH2), 4.00 (2H, t, OCH2) 3.70 (4H, t, OCH2), 4.42 and 3.12 (4H, dd, Ar-CH2-Ar, $J = 13.5$ Hz), 2.07 (4H, m, CH2), 1.90 (4H, m, CH2), 1.31 (18H, s, C (CH3)3), 1.5 (6H, t, 2CH3), 0.92 (6H, t, CH3), 0.60 (9H, s, C(CH3)3).

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*Sample Availability:* Samples are available from the authors

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