

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 ($\mathbf{H}_2\mathbf{L}^1$ and \mathbf{HL}^2) is described. The synthesis of $\mathbf{H}_2\mathbf{L}^1$ and \mathbf{HL}^2 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 $\mathbf{H}_2\mathbf{L}^1$ and \mathbf{HL}^2 . Solvatochromicity of these ligands indicates their potential for NLO applications.

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

Introduction

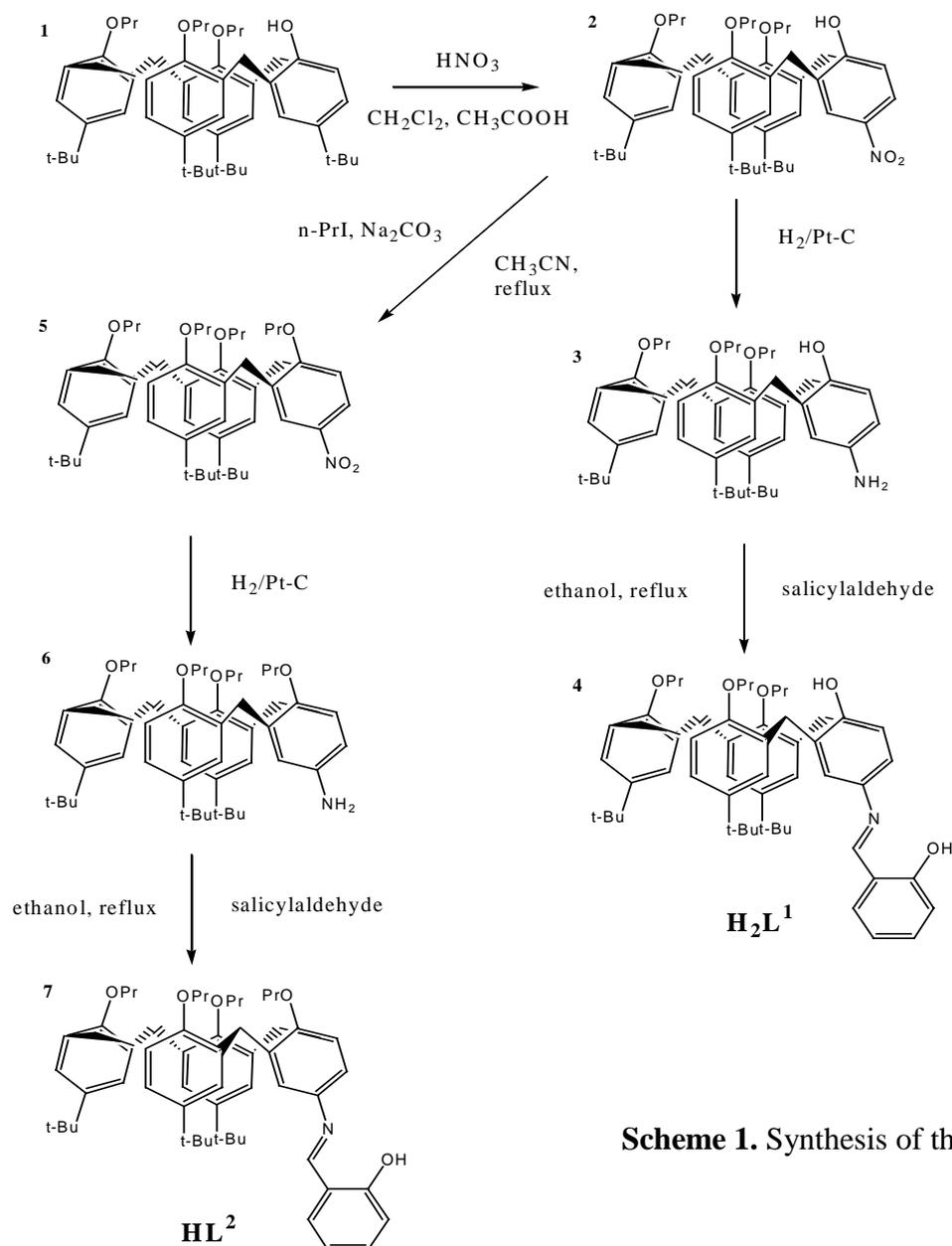
Calix[4]arenes can be easily functionalized both at the phenolic OH groups (lower rim) and, after partial removal of *tert*-butyl groups, at the para positions of the phenol rings (upper rim) [1-3]. The vast majority of these modified calixarenes exist in the cone conformation in which there is a cavity 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*-butylcalix[4]arenes for the preparation of nitrocalix[4]arenes. In this work we used the selectively *ipsonitrated p-tert*-butylcalix[4]arenes as starting materials for the preparation of two monoamine *p-tert*-butylcalix[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_2L^1 and HL^2

The cone mononitro-*p-tert*-butylcalix[4]arene **2** was obtained from the mono *ipson*itration 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 **H₂L¹** and **HL²** as NO donors with a *p-tert*-butylcalix[4]arene moiety (Scheme 1). The ¹H-NMR spectrum of the ligands indicated the calixarene to be in a cone conformation. The conclusion that **H₂L¹** and **HL²** 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 H₂L¹ and HL²

Compound	Formula Weight	Color	m.p, (°C)	Yield, %	Calcd. (Found) %		
					C	H	N
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 H₂L¹ contains a water molecule that is identified by broad O-H absorptions around 3547-3400 cm⁻¹.

Table 2. Characteristic IR bands of the H₂L¹ and HL² as KBr Pellets (cm⁻¹)

Compound	v (H ₂ O)	v (O-H)	v (C-H)	v (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 **H₂L¹** and **HL²** display strong negative solvatochromicity as shown in Table 3. Negative solvatochromicity can be attributed to the stabilization of polar ground states in polar solvents.

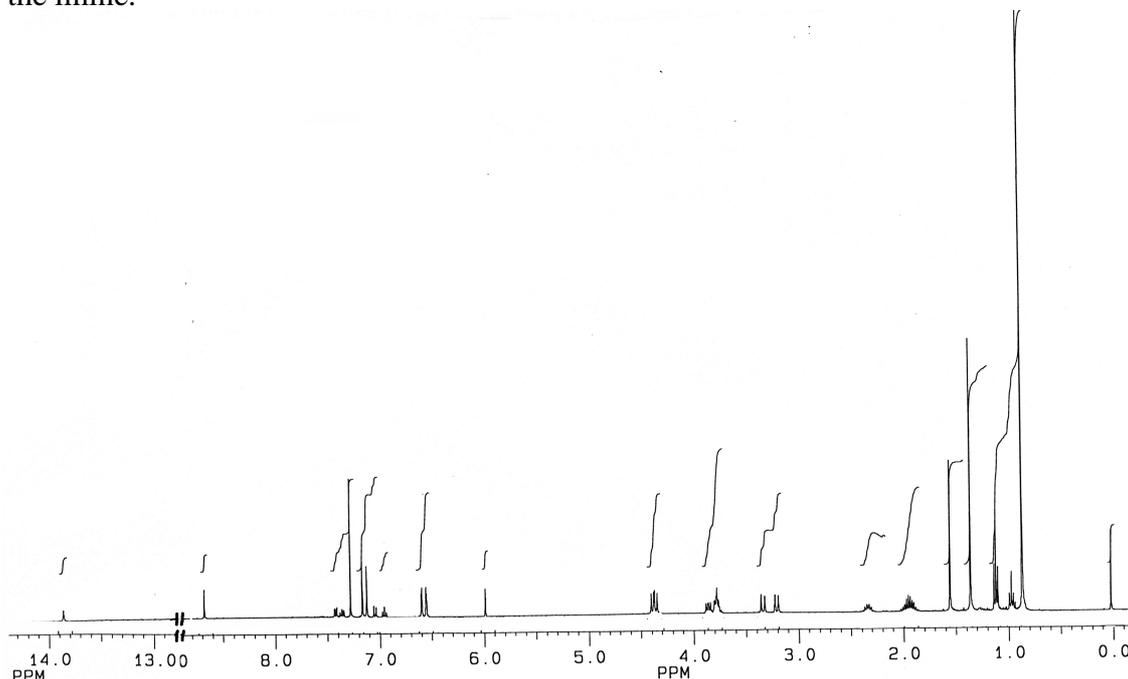
Table 3. electronic spectra of H_2L^1 and HL^2

Compound	ν (cm^{-1})		$\Delta\nu$ (cm^{-1})	λ_{ex} (nm) (excitation)	λ_{em} (nm) (emission)
	CHCl_3	CH_3CN			
H_2L^1	277	281	400	390	526
HL^2	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 H_2L^1 and HL^2 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.

$^1\text{H-NMR}$ Spectra

$^1\text{H-NMR}$ spectra of H_2L^1 and HL^2 are shown in Figures 1 and 2, respectively. Assignments of $^1\text{H-NMR}$ 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 H_2L^1 and HL^2 , justifies the existence of intramolecular hydrogen bonding between the hydrogen atom of the hydroxy group and the nitrogen atom of the imine.

**Fig.1.** $^1\text{H-NMR}$ Spectra of H_2L^1

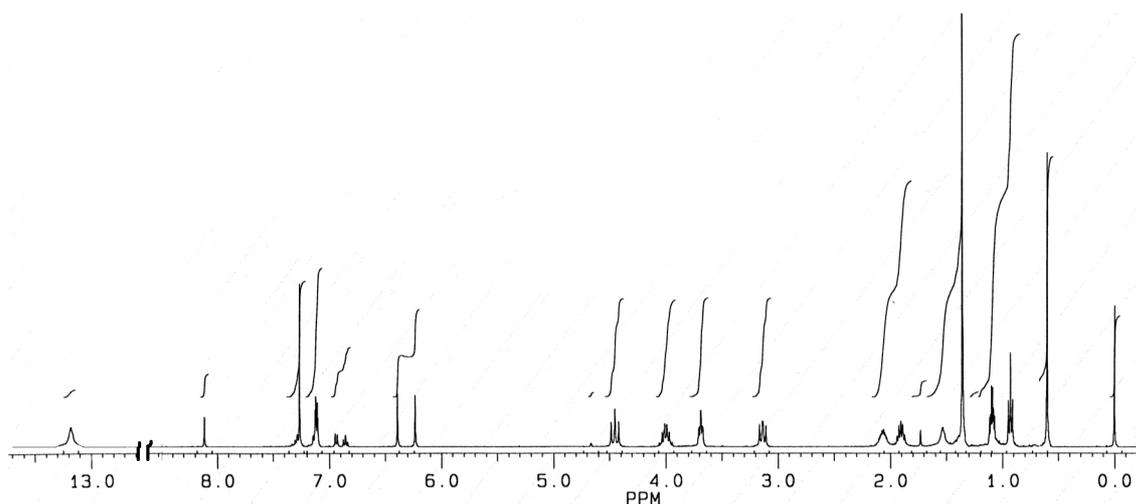


Fig. 2. $^1\text{H-NMR}$ Spectra of **HL²**

Conclusions

In this paper we present the preparation of two Schiff bases of *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. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM-400MHz in CDCl_3 with Me_4Si as an internal standard. Elemental analysis were recorded on Carlo-Erba-Analysor Model 1104. IR spectra were recorded on Bruker IFS 25. Compound **1**, *p-tert*-buthylcalix[4]tripropoxyarene, 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 .

1H -NMR spectra of H_2L^1 : δ 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).

1H -NMR spectra of HL^2 : δ 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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