

# Studies on Properties of Tetra-*p*-nitro-tetra-*O*-alkyl-calix[4]arenes

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This paper reports the properties of the novel tetra-*p*-nitro-tetra-*O*-alkyl-calix[4]arenes (alkyl = *n*-C<sub>4</sub>H<sub>9</sub>, 1; *n*-C<sub>8</sub>H<sub>17</sub>, 2; *n*-C<sub>12</sub>H<sub>25</sub>, 3; *n*-C<sub>16</sub>H<sub>33</sub>, 4). X-ray crystallographic analysis and <sup>1</sup>H NMR revealed that they exist as pinched-cone conformation in crystal or cone conformation in solution. EFISH experiments at 1064 nm in CHCl<sub>3</sub> indicated that tetra-*p*-nitro-tetra-*O*-butyl-calix[4]arene (1) has higher hyperpolarizability β<sub>z</sub> values than the corresponding reference compound *p*-nitrophenyl butyl ether, without red shift of the charge transfer band. Compounds 2, 3 and 4 with longer alkyl chains can form monolayer at the air/water.

**Keywords** Calix[4]arene, conformation, monolayer, NLO property, crystal structure

## Introduction

Calixarenes are a versatile class of macrocyclic compounds which have attracted extensive interest due to their ability in forming host-guest complexes and acting as enzyme mimic.<sup>1-3</sup> Moreover, a number of calixarenes with D-π-A units or amphiphilic architecture, their second-order nonlinear optical (NLO) properties or LB film characters have been investigated, respectively.<sup>4-8</sup> Recently, our interest lies on the synthesis of calixarenes which have abilities of forming ultra thin ordered films or with NLO properties and their possible applications. For this purpose, tetra-*p*-nitro-tetra-*O*-alkyl-calix[4]arenes 1-4 (Fig. 1) have been prepared in our laboratory

through thorough *O*-alkylation with bromides in the presence of NaH followed by *iso*-nitration. Compounds 1-4 gave MS, NMR and EA data in accord with the assigned structures.<sup>9</sup> <sup>1</sup>H NMR and X-ray crystallographic structural analysis have indicated that these calix[4]arenes exist in a pinched-cone conformation, *i. e.* four D-π-A units are oriented at nearly the same direction. In addition, compounds 2-4 have both hydrophobic fragments and hydrophilic groups (NO<sub>2</sub>) so that stable monolayer can be formed at the air/water.

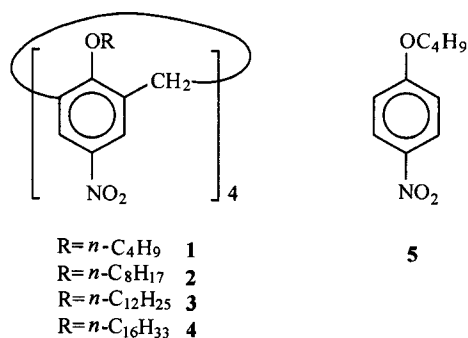


Fig. 1 Compounds used in the work.

## Experimental

### X-ray crystallographic structural analysis

Single crystals of compound 1 were obtained from

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acetone solution by slow evaporation. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm). The data were collected at a temperature of  $15 \pm 1^\circ\text{C}$  to a maximum  $2\theta$  value of  $55.1^\circ$ . The structure was solved by direct methods and expanded using Fourier technique.<sup>10</sup> All calculations were performed with the TEXSAN<sup>11</sup> crystallographic software package of molecular structure corporation. Crystal data of compound **1**:  $\text{C}_{44}\text{H}_{52}\text{N}_4\text{O}_{12}$ , monoclinic, space group:  $C2/c$ ,  $a = 1.3130(2)$  nm,  $b = 2.1484(3)$  nm,  $c = 1.9644(4)$  nm,  $\beta = 105.65(3)^\circ$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.177$  g/cm<sup>3</sup>, final  $R$  indices [ $I > 2\sigma(I)$ ],  $R = 0.0790$ .

#### EFISH measurement

Electric field induced second harmonic generation (EFISH) experiments were performed with a fundamental wavelength of 1064 nm in  $\text{CHCl}_3$ . Five different solutions in the 0.1–1.0 mmol/L concentration range were measured. The hyperpolarizability  $\beta_z$  of the molecules were calculated according to the literature.<sup>12</sup> The charge-transfer band  $\lambda_{\text{CT}}$  was determined by UV-240 ultraviolet-visible spectrophotometer.

#### The molecular monolayer of compounds 2–4

The monolayer was formed by spreading a chloroform solution ( $1.0 \times 10^{-3}$  mol/L) on water surface or subphases containing 0.1 mol/L KCl. A Brewster angle microscopy (BAM) was mounted on a Langmuir trough with a temperature control system ( $20.0 \pm 0.1^\circ\text{C}$ ). He-Ne laser was used as a light source. Reflect light was detected by an analyzer. The surface pressure was recorded in computer.

#### Result and discussion

##### Pinched-cone conformation

As shown in Fig. 2, compound **1** exists in pinched-cone conformation having  $C_2$  symmetry. Two *p*-nitrophenyl planes ( $P_1$  and  $P_2$ ) make an angle of  $13.2^\circ$  with the  $C_2$  axis respectively, so they are nearly parallel to each other, whereas the other two *p*-nitrophenyl planes ( $P_3$  and  $P_4$ ) make an angle of  $55.9^\circ$  with the  $C_2$  axis respectively (Fig. 3). In  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ); the peaks of  $\text{ArCH}_2\text{Ar}$  protons of compounds **1–4** appear as doublet at 3.32–3.48 ( $\text{H}_{\text{exo}}$ ) and 4.35–4.52

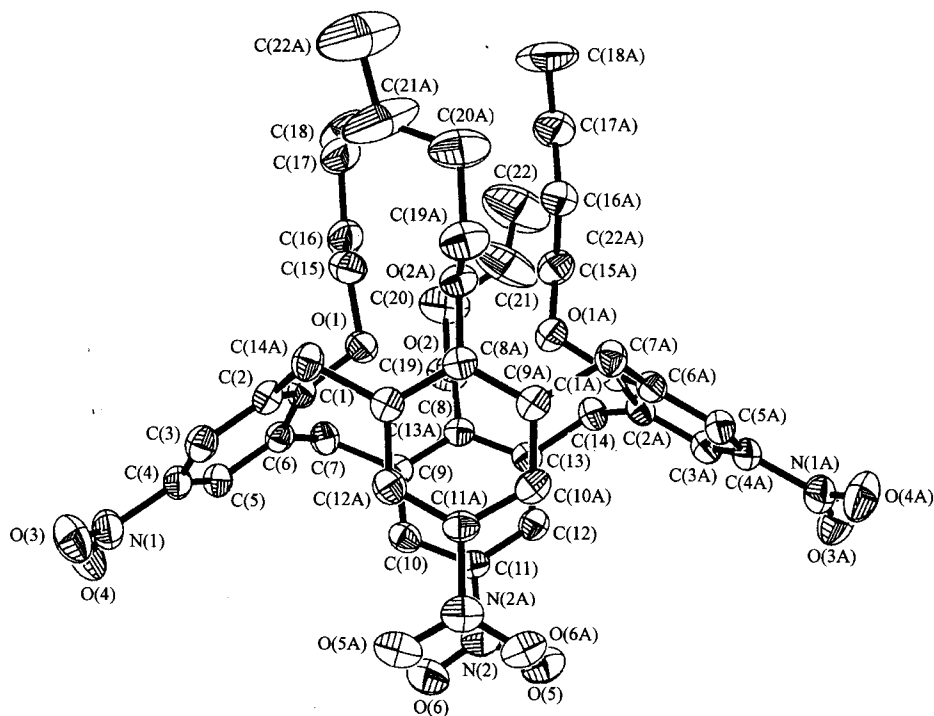
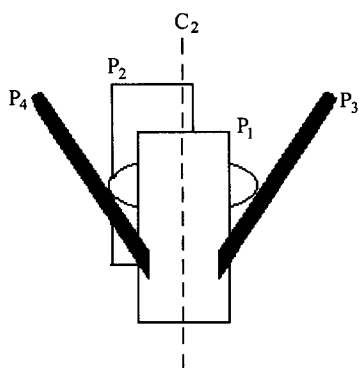


Fig. 2 ORTEP drawing of the compound **1**.



**Fig. 3** Relative orientation of the aromatic moieties in pinched-cone conformation.

( $H_{endo}$ ) and the chemical shift difference of  $H_{exo}$  and  $H_{endo}$  is about 1.0. These data indicate that the conformation of compounds **1**–**4** is consistent with the cone form in solution.<sup>13,14</sup> Therefore, four D- $\pi$ -A units are oriented at nearly the same direction, which is necessary for the formation of the monolayer at air/water and very important for NLO properties.

#### NLO properties

The hyperpolarizabilities ( $\beta_z$ ) and the absorption maximum of the charge-transfer band ( $\lambda_{CT}$ ) for **1** and **5** are summarized in Table 1.

**Table 1** Hyperpolarizabilities ( $\beta_z$ ) and charge-transfer band ( $\lambda_{CT}$ ) for **1** and **5** (in  $\text{CHCl}_3$ )

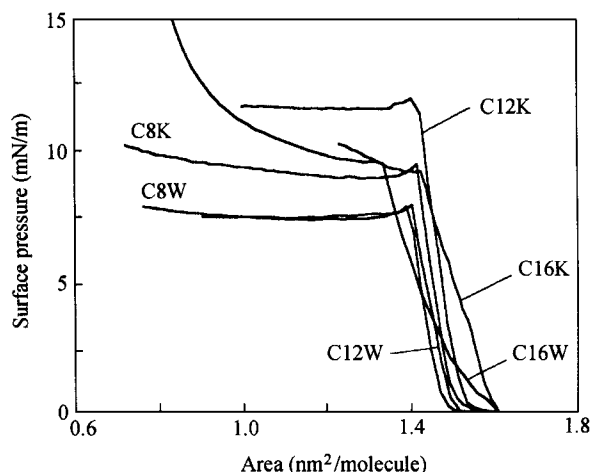
Compd.	$\beta_z$ ( $10^{-30}$ esu) <sup>a</sup>	$\lambda_{CT}$ (nm)
<b>1</b>	31	291
<b>5</b>	12	312

<sup>a</sup>EFISH experiments were performed at 1064 nm.

It is clear from Table 1 that the compound **1** has higher hyperpolarizability  $\beta_z$  values than the corresponding reference compound *p*-nitrophenyl butyl ether (**5**), and no red shift of the charge transfer band has been observed, which makes such systems possible as frequency doubling materials. Based on the pinched-cone conformation, four D- $\pi$ -A moieties of **1** do not behave as totally independent NLO unit, so  $\beta_z$  is 2.58 times the value of the reference compound **5** which has only one D- $\pi$ -A units.

#### Formation of monolayer at the air/water

Fig. 4 shows the surface pressure-area isotherms of compounds **2**, **3** and **4** at the air/water surface or the subphase containing 0.1 mol/L KCl solution. The chain length of the compound **1** is too short to form monolayer at air/water. The monolayer of **2** shows an onset of surface pressure at  $1.5 \text{ nm}^2/\text{molecule}$ . Upon compression, the surface pressure goes up steeply to  $8 \text{ mN/m}$ . No obvious change of the surface pressure is observed upon further compression. Therefore, this surface pressure can be regarded as collapse pressure. The limiting area extrapolated from the linear part of the isotherm is found to be  $1.46 \text{ nm}^2/\text{molecule}$ . Because compounds **2** and **1** have similar hydrophilic head groups, this value is in accord with the nitro-substituted rim based on X-ray crystallographic structural analysis of **1**. Obviously, it is standing on the water surface. Addition of KCl into the subphase caused the increase of the collapse surface pressure and a slight expansion of the limiting molecular area. For the derivative with longer alkyl chains, slight increase of the limiting area is observed. Again enlargement of the molecular area and increment of the surface pressure occur when adding KCl into the subphase. For compound **4**, the limiting area is found to be  $1.35 \text{ nm}^2/\text{molecule}$ , and the surface pressure be  $10 \text{ mN/m}$ . Addition of KCl also increases limiting area of the monolayer.



**Fig. 4** Surface pressure-area isotherms of **2**, **3** and **4**. C8W (C8K), C12W (C12K), C16W (C16K) mean compounds **2**, **3**, **4** monolayer on water surface (on 0.1 mol/L KCl solution), respectively.

## Conclusion

Tetra-*p*-nitro-tetra-*O*-alkyl-calix[4]arenes with a cone conformation have higher hyperpolarizability  $\beta_z$  values than the corresponding reference compound *p*-nitrophenyl butyl ether, and no red shift of the charge transfer band has been observed. On the other hand, compounds **2**, **3** and **4** with longer alkyl chains can form the monolayer at air/water. Therefore, they may be possible as novel ordered film or materials with NLO properties.

## References

- 1 Vicens, J.; Bhoer, V. *Calixarenes--A Versatile Class of Macrocyclic Compounds*, Dordrecht, Kluwer, **1991**.
- 2 Pochini, A.; Ungaro, R. In *Comprehensive Supramolecular Chemistry*, Eds.: Lehn, J. M.; Votle, F., Pergamon, New York, **1996**, pp.103—142.
- 3 Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713.
- 4 Dedek, P.; Janout, V.; Regen, S. L. *J. Org. Chem.* **1993**, *58*, 6553.
- 5 Velzen, E. U. T.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 3597.
- 6 Moreira, W. C.; Dutton, P. J.; Aroca, R. *Langmuir*, **1995**, *11*, 3137.
- 7 Biigler, J.; Sommerdijk, N. A. J. M.; Visser, A. J. W. G.; Hoek, A. V.; Nolte, R. J. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1999**, *121*, 28.
- 8 Kenis, P. J. A.; Noordman, O. F. J.; Houbrechts, S.; Hummel, G. J. V.; Harkema, S.; Veggel, F. C. J. M. V.; Clays, K.; Engbersen, J. F. J.; Persoons, A.; Hulst, N. F. V.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 7875.
- 9 Li, Q.; Lu, G. Y.; Liu, F.; Huang, X. H.; Hu, H. W. *Chin. J. Org. Chem.* **1998**, *18*, 542 (in Chinese).
- 10 Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
- 11 TEXSAN, *Crystal Structure Analysis Package*, Molecular Structure Corporation, **1985 & 1992**.
- 12 Lerhaeg, L.; Sainyn, C.; Persoons, A. *Organic Molecules for Nonlinear Optics and Photonics*, Kluwer, Netherland, **1991**, p.177.
- 13 Jaime, C.; Mendoza, J. D.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.
- 14 Lu, G. Y.; Chen, Z. J.; Zhao, R. Z.; Huang, X. H.; Hu, H. W. *Chem. J. Chin. Univ.* **1996**, *17*, 1244 (in Chinese).

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