

Communication

Studies on Properties of *p*-Nitrophenylazo Calix[4]arene DerivativesJIN, Chuan-Ming^{a,b}(金传明) GUI, Min-Zhi^c(归敏芝) LU, Guo-Yuan^{* ,a}(陆国元) GUO, Xun^a(郭勋)
ZHANG, Hong^{* ,c}(张宏) YOU, Xiao-Zeng^a(游效曾)^a Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu 210093, China^b Department of Chemistry and Environment Engineering, Hubei Normal University, Huangshi, Hubei 435002, China^c National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, Jiangsu 210096, China

The *p*-nitrophenylazo calix[4]arene derivatives **1a**—**1d** with nonlinear optical (NLO) properties were prepared by the diazo-coupling reaction of calix[4]arene with *p*-nitrophenyl diazonium. The diazotization reaction of *p*-nitroaniline was carried out with isoamyl nitrite as a source of nitrous acid in EtONa/EtOH under refluxing condition. X-Ray crystallographic analysis and ¹H NMR spectra reveal that they exist as cone conformation in crystal state or in solution. HRS measurements at 1064 nm in THF indicate that *p*-nitrophenylazo calix[4]arenes have higher hyperpolarizability β_2 values than the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethyl-phenol, without red shift of the charge transfer band. The tetrakis *p*-nitrophenylazo calix[4]arene (**2**) with longer alkyl chains can form monolayer at the air/water interface.

Keywords calix[4]arene, NLO property, crystal structure, conformation, LB film

Organic compounds with second-order nonlinear optical (NLO) properties have various potential in the development of materials for applications such as frequency doubling and optical switching.^{1,2} Traditional organic NLO materials are organic molecules that contain electron-donating and electron-accepting groups connected via a conjugated π system, *i. e.*, so called D- π -A structure. Generally, the second-order nonlinear hyperpolarizability β of a molecule increases with increasing length of the conjugated π system and increasing strength of the donor and acceptor.³ Unfortunately, an increase in the β value is accompanied by a red shift in the absorption spectra due to a larger π -conjugated length and/or stronger donor and acceptor substituents, *i. e.*, there is a tradeoff between nonlinearity and transparency.⁴ To resolve this problem, much effects have been made in designing organic molecules with both high β value and good transparency.⁴ For example, lambda-shaped molecules,^{5,6} charged ionic compounds,^{7,8} rigid multi-chromophore molecules⁹ and chromophore molecules with different types of conjugation bridge combinations¹⁰ perform rather well in the nonlinearity-transparency tradeoff.

Recently, Reinhoudt *et al.*¹¹ introduced strong electron-withdrawing moieties, such as (nitro) ethenyl, (tricyano)ethenyl, (4-nitrophenyl) ethenyl, at the upper rim of calix[4]arene to form preorganized multi-chromophore molecules with NLO activity. EFISHG (electric field induced second harmonic generation) experiments showed that the preorganized multi-chromophore molecules have higher β value than the corresponding mono-chromophore molecules, and the red shift of the absorption band does not exceed 20 nm. We have also demonstrated that calix[4]arene system with NLO active moieties is a promising organic molecule with high β value and good transparency.¹² Encouraged by these results, we designed and synthesized *p*-nitrophenylazo calix[4]arene derivatives **1a**—**1d** with NLO properties. **1a**—**1d** were obtained by a novel method in which the diazotization reaction of aromatic amines was carried out with isoamyl nitrite as a source of nitrous acid in EtONa/EtOH under refluxing condition, followed by diazo-coupling with calix[4]arene (Scheme 1). When the ratios of *p*-nitroanilines to calix[4]arene were 4:1, 3:1, 2:1 and 1:1, the yields of **1a**, **1b**, **1c** (proximal isomer) and **1d** were 61.9%, 17.2%, 33.5% and 52.0%, respectively. The purification of products was performed on G60 silica gel column chromatography (CH₃COOC₂H₅:CH₃COCH₃ = 10:1, V:V). In the ¹H NMR spectra of **1c**, the methylene hydrogens of ArCH₂Ar display three pairs of doublets (δ 4.41, 4.39; 4.37, 3.84; 3.71, 3.59) with a ratio of 1:2:1, and three peaks of the methylene carbons appear at δ 31.9, 32.5 and 33.4. Therefore compound **1c** was proximal isomer.¹³ The main reason is that the statistical probability of diazo-coupling at the proximal positions is higher than that at the distal positions, which is similar to our previous work.¹⁴ In order to explore the possibility of self-assembly ordered thin films by means of Langmuir-Blodgett technique, **2** was prepared through *O*-alkylation of **1a** with dodecyl bromide as alkylating agent in the presence of K₂CO₃.¹⁵ ¹H NMR, ¹³C NMR, MS, IR and elemental analy-

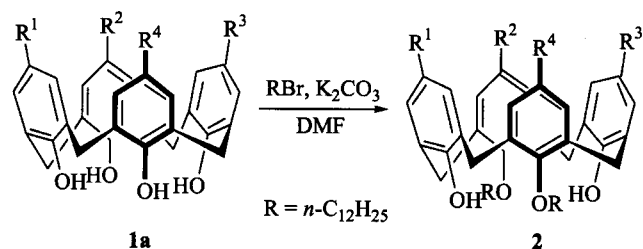
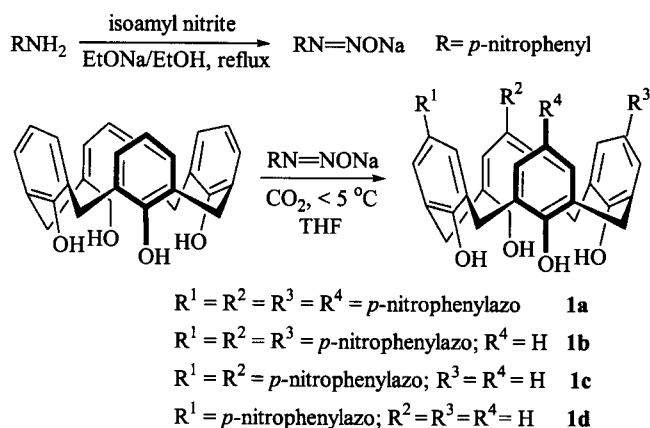
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sis data of **1a**–**1d** and **2** were given in accord with the assigned structures.

Scheme 1 Synthesis of *p*-nitrophenylazo-substituted calix[4]arenes



Red-brown single crystals were obtained by slow evaporation of the chloroform solution of **1d** and an X-ray crystallographic structural analysis was carried out.¹⁶ ORTEP view of **1d** is given in Fig. 1. The azo group of compound **1d** exists in an *anti*-form. N = N bond length is 0.1162 (6) nm, N(2)–N(3)–C(4) and N(3)–N(2)–C(29) bond angles are 108.3(5)° and 105.0(5)°, respectively. The dihedral angle between the two phenyl rings attached to N = N bond is 6.7°, so they are nearly in the same plane. The dihedral angle between the aromatic rings are 73.8° [C(1)–C(6) and C(8)–C(13)], 72.7° [C(8)–C(13) and C(15)–C(20)], 108.0° [C(15)–C(20) and C(22)–C(27)] and 109.2° [C(22)–C(27) and C(1)–C(6)], respectively, so the calix[4]arene moiety in **1d** exists in a distorted cone conformation. In ¹H NMR spectra in CDCl₃ solution, the methylene hydrogens of ArCH₂Ar of **1a** and **2** appeared as one pair of doublets at δ 3.80, 4.78 and 3.72, 4.46, those of **1b** and **1d** appeared as two pairs of doublets (1:1) at δ 4.55, 4.49; 3.64, 3.49 and at δ 4.34, 4.29; 3.71, 3.59, respectively, and those of **1c** appeared as three pairs of doublets (1:2:1) at δ 4.41, 4.39, 4.37, 3.84, 3.71, 3.59. The ¹H NMR chemical shift values and splitting pattern of the methylene hydrogens indicate that all azocalix[4]arenes mainly exist in the cone conformation in solution.^{13,17,18} Moreover, in the ¹³C NMR spectra in CDCl₃ solution, all signals of the methylene carbons appeared within the range of δ 31.3–33.6. This is also consistent with the cone conformation.¹⁸ Therefore, D-π-A units are oriented at nearly the same direction, which is very important for NLO properties and necessary for the formation of the monolayer of **2** at air/water interface.

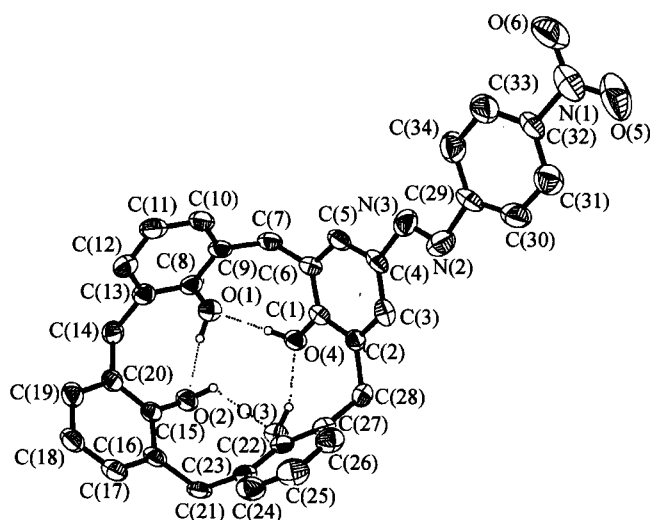


Fig. 1 ORTEP drawing of compound **1d**.

HRS (Hyper-rayleigh scattering) experiments¹⁹ for *p*-nitrophenylazo calix[4]arenes **1a**–**1d** and the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethyl-phenol (**1e**) were performed with a fundamental wavelength of 1064 nm in THF. The charge-transfer band λ_{CT} was determined by UV-240 ultraviolet-visible spectrophotometer. The hyperpolarizabilities β_z and the absorption maximum of the charge-transfer band (λ_{CT}) for **1a**–**1e** are summarized in Table 1.

Table 1 Hyperpolarizabilities β_z (in THF, at 1064 nm), charge-transfer band λ_{CT} and melting points for *p*-nitrophenylazo calix[4]arenes

Compd	$\beta_z (\times 10^{-30} \text{ esu})$	$\lambda_{\text{CT}} (\text{nm})$	m. p. ($^\circ\text{C}$)
1a	296.6	374	> 320
1b	275.2	378	> 320
1c	302.6	382	> 320
1d	233.1	378	302–304
1e	186.7	387	

It can be seen from Table 1 that the compounds **1a**–**1d** have higher hyperpolarizability β_z values than the corresponding reference compound **1e**, and a favorable blue-shift of the charge transfer band can be observed. Based on the cone conformation, two D-π-A moieties of **1c** do not behave as totally independent NLO unit, so β_z is 1.6 times the value of the reference compound **1e** which has only one D-π-A unit. It is surprising that **1c** with two D-π-A moieties has higher β_z value than **1a** and **1b** with four or three D-π-A moieties. The steric congestion at the upper rim area of calix[4]arene due to the bulk *p*-nitrophenyl-(*E*)-azo units may make the cone conformation flat, *i. e.*, the average angles of the D-π-A moieties with the dipole axis of **1a** or **1b** are much larger than those of **1c** and **1d**. It is also notable that the melting points of *p*-nitrophenylazo calix[4]arenes exceed 300 °C, so they have good thermal stability. Therefore, the calix[4]arene system with NLO active moieties is useful in resolving the nonlinearity-transparency-thermal stability tradeoff.

The monolayer of **2** can be formed by spreading 36 μL of 5×10^{-4} mol/L **2** chloroform solution onto the surface of deionized water.²⁰ The limiting molecular area and collapse pressure are 0.71 nm² and 60 mN/m, respectively. The shape of the isotherms is similar to that of amphiphile calix[4]arene derivatives in our previous work.²¹ Fig. 2 shows UV-vis spectra of 3-, 6-, 9-, 12-, 15- and 18-layer LB films of **2** deposited on quartz substrates from the surface of pure water.²² It can be seen that the absorption intensities of the bands increase directly with the layer number. These results demonstrate that **2** can form stable monolayer at the air-water interface and LB film can be prepared.

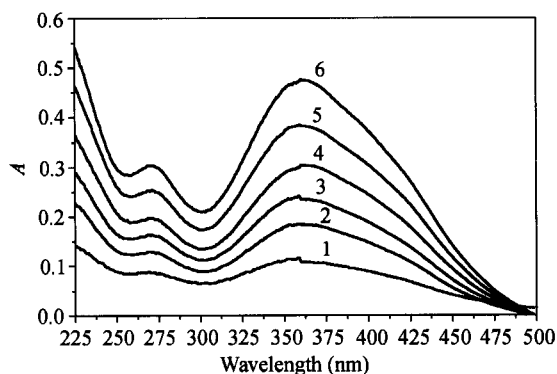


Fig. 2 UV-vis spectra of LB films of **2** deposited on quartz substrates from the surfaces of pure water. (1) 3-layer, (2) 6-layer, (3) 9-layer, (4) 12-layer, (5) 15-layer and (6) 18-layer.

In conclusion, the *p*-nitrophenylazo calix[4]arenes **1a**–**1d** have higher hyperpolarizability β_2 values than the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethyl-phenol, and no red shift of the charge transfer band has been observed. Therefore, calix[4]arenes with NLO-active moieties are promising and interesting building blocks for designing stable organic NLO materials with both high β value and good transparency. In addition, *p*-nitrophenylazo calix[4]arene (**2**) with longer alkyl chains can form the monolayer at air/water, so it may be possible to assemble novel ordered film with NLO properties.

References and notes

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