5,11,17,23-Tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxy Calix[4]arene: Crystal Structure and pH Sensing Properties

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Treatment of 5,11,17,23-tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxy calix[4]arene (**2**) with HCl in DMF or NaOH in MeOH produced 5,11,17,23-tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]-arene•4DMF (2•4DMF) and 5,11,17,23-tetrakis[(*p*-carboxyphenylsodium)azo]-25,26,27,28-tetrahydroxycalix[4]-arene (**3**), respectively, which were characterized by elemental analysis, IR, UV-vis, ¹H NMR and ¹³C NMR. An X-ray analysis of 2•4DMF revealed that its calix[4]arene core adopts a flattened cone conformation in which opposed phenyl groups take parallel or sharply inclined positions. The intra- and intermolecular hydrogen-bonding interactions and the π ··· π interactions form a 2D hydrogen-bonded wavelike network. Compound **2** had a unique reversible color change in a wide pH range from 1 to 13.5 and showed interesting pH sensing properties.

Keywords p-carboxyphenylazocalix[4]arene, synthesis, crystal structure, NMR shift, pH sensing properties

Introduction

The design and construction of chemical sensors¹⁻³ for the visual discrimination of varied pH values has aroused much attention due to their increasing applications in the common chemical reactions, environmental technology and biological technology.⁴⁻⁷ As a good chemosensor, it should exhibit an appropriate, rapid and reversible response towards H^+ in a wide pH range and should not affect the ongoing measurement. So far, a number of pH sensing compounds have been synthesized,⁸⁻¹⁸ some of which showed potential application as the pH probes. These pH sensing compounds were usually functioned via one or two pairs of proton donor-acceptor groups such as $R_1R_2R_3NH^+ \cdots CO_2^-$.^{13,14} Those with two pairs of proton donor-acceptor groups like $CO_2^- \cdots R_1 R_2 R_3 NH^+ \cdots N \cdots OH^{15-18}$ seemed more sensitive than those with one pair of proton donor-acceptor groups. However, most of the aforementioned pH sensing compounds showed a relatively narrow pH region from 5 to 9. In fact, few examples were involved in the lower pH region (pH \leq 5) or the higher pH region (pH>9). Moreover, compounds with three or four pairs of proton donor-acceptor groups were less explored for their pH sensing properties.

On the other hand, a number of azocalix[4] arene derivatives have recently been prepared, ¹⁹⁻²⁵ and employed for the recognition of metal ions¹⁹⁻²⁴ and the discrimination of different types of amines,²⁵ but scarcely explored for their pH sensing properties. Compound 25,26,27,28tetrahydroxycalix [4] arene $(1)^{26}$ was employed to prepare an azocalix[4]arene derivative with four carboxyl groups, 5,11,17,23-tetrakis[(p-carboxyphenyl)azo]-25, 26,27,28-tetrahydroxycalix[4]arene (2).²⁷ However, its crystal structure has not been determined yet and its pH sensing properties are virtually unknown. We are interested in the physical and chemical properties of azocalix[4]arene derivatives with proton donor-acceptor groups. We found that 2 could respond to different pH values ranged from 1 to 13.5. This conversion between 2 and its sodium salt 3 (Scheme 1) was reversible accompanying an intriguing reversible color change. In this paper, we report the crystal structure of 2.4DMF and its pH sensing properties.

Experimental

Materials and physical measurements

Compounds 1 and 2 were prepared according to the

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literature methods.^{26,27} Other chemicals and reagents were obtained from commercial sources and used as received. DMF was freshly distilled under reduced pressure, while the water that was used for potentiometric titration was deionized water. IR spectra were recorded with a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm⁻¹). The elemental analyses for C, H and N were performed on an EA1110 CHNS elemental analyzer. UV-Vis spectra were measured with a Varian 50 UV/Vis spectrophotometer. ¹H and ¹³C NMR spectra were recorded at ambient temperature with a Varian UNITYplus-400 spectrometer. The ¹H NMR chemical shifts were reported relative to TMS in (CD₃)₂SO. The ¹³C NMR chemical shifts were referenced to the (CD₃)₂SO signal. The thermal analysis was carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 5 $^{\circ}C \cdot min^{-1}$ and a flow rate of 100 cm³•min⁻¹ (N₂). All potentiometric titrations were run at 20 °C with stirring, and the concentrations of NaOH (0.0103 and 0.1008 mol•L⁻¹) were calibrated respectively by $(COOH)_2$ •2H₂O.²⁸ To calibrate the pH meter [Mettler-Toledo LAB pH (FE20)] at the elevated temperature, a three-point calibration was made prior to each experiment using METTLER TOLEDO standard buffer solutions (pH 4.01 at 25 °C; pH 7.00 at 25 °C; pH 10.01 at 25 °C), which had a known pH at each temperature studied.

Preparation of 5,11,17,23-tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene•4DMF (2•4DMF)

To a yellow solution of **2** (51 mg, 0.05 mmol) in DMF (5 mL) was added five drops HCl (1 mol•L⁻¹). The solution turned to red immediately. After being stirred at room temperature for 2 h, the resulting solu-

tion was filtered. Diethyl ether (30 mL) was carefully layered onto the filtrate to form red blocks of **2**•4DMF for one week, which were collected by filtration and dried in air. Yield 45 mg (68.7%); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 8.04 (d, *J*=8 Hz, 8H, ArH-a), 7.95 (s, 4H, CHO), 7.84 (s, 8H, ArH-c), 7.81 (d, *J*=8 Hz, 8H, ArH-b), 3.66—4.71 (8H, CH₂), 2.88 (s, 12H, NCH₃), 2.73 (s, 12H, NCH₃); ¹³C NMR (DMSO-*d*₆, 400 MHz) δ : 166.75, 162.27, 154.68, 144.71, 131.28, 130.51, 130.41, 124.20, 121.88, 35.76, 30.75; IR (KBr) *v*: 3419 (m), 2930 (w), 1715 (s), 1680 (s), 1668 (s), 1602 (s), 1525 (m), 1469 (m), 1415 (m), 1386 (m), 1331 (m), 1265 (vs), 1165 (w), 1116 (m), 864 (w), 777 (w), 697 (w), 667 (w), 535 (w) cm⁻¹. Anal. calcd for C₆₈H₆₈O₁₆N₁₂: C 62.38, H 5.23, N 12.84; found C 62.57, H 5.17, N 12.53.

Preparation of 5,11,17,23-tetrakis[(*p*-carboxyphenylsodium)azo]-25,26,27,28-tetrahydroxycalix[4]arene (3)

To a yellow solution of 2 (51 mg, 0.05 mmol) in MeOH (3 mL) was added solution of NaOH (0.2 mL, 1 $mol \bullet L^{-1}$, 0.2 mmol). The solution turned to deep red immediately, and was briefly stirred and filtered. EtOH (20 mL) was carefully layered onto the filtrate to form deep red crystals of 3 for 3 d, which were collected by filtration, washed with EtOH and Et₂O and dried in air. Yield 40 mg (72.4%); ¹H NMR (DMSO- d_6 , 400 MHz) δ : 7.93 (d, J=8 Hz, 8H, ArH-a), 7.72 (s, 8H, ArH-c), 7.64 (d, J=8 Hz, 8H, ArH-b), 3.63–4.42 (m, 8H, CH₂); ¹³C NMR [D₂O (0.1 mL) and DMSO- d_6 (0.5 mL), 400 MHz] $\delta: \ 164.61, \ 159.73, \ 154.14, \ 145.59, \ 140.49, \ 132.00,$ 131.11, 124.71, 122.41, 32.93; IR (KBr) v: 3417 (m), 2932 (w), 1653 (m), 1595 (vs), 1549 (s), 1473 (w), 1386 (vs), 1295 (m), 1272 (m), 1136 (w), 1117 (m), 870 (w), 842 (w), 794 (m), 703 (w), 635 (w) cm⁻¹. Anal. calcd for C₅₆H₃₆O₁₂N₈Na₄: C 60.87, H 3.28, N 10.14; found C 60.57, H 3.18, N 10.63.

X-ray structure determination

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo Ka (λ =0.71073 Å). Single crystals of 2•4DMF suitable for X-ray analysis were obtained directly from the above preparation. A red blocks of **2**•4DMF with dimensions 0.44 mm \times 0.28 mm \times 0.20 mm was mounted at the top of a glass fiber with grease, and cooled at 223 K in a liquid-nitrogen stream. Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystal. Indexing was performed from 6 images, each of which was exposed for 5 s. Cell parameter was refined by using the program CrystalClear (Rigakuand MSC, version 1.3, 2001) on all observed reflections between θ of 3.056° and 25.0°. Its crystal data are described as follows: C₆₈H₆₈N₁₂O₁₆, FW = 1309.4, monoclinic, space group C2/c, a =24.034(5) Å, b=8.8591(18) Å, c=30.989(6) Å, $\beta=$ $103.22(3)^{\circ}$, V=6423(2) Å³, Z=4, F(000)=2752, $D_{c}=$ 1.354 g•cm⁻³, μ =0.098 mm⁻¹. A total of 20378 reflections were measured in the range of $3.31^{\circ} \le \theta \le 25.00^{\circ}$, of which 5643 were unique ($R_{int} = 0.0729$). The collected data were reduced by using the program *Crystal-Clear* (Rigaku and MSC, Ver.1.3, 2001), and an empirical absorption correction (multi-scan) was applied, resulting in the transmission factors ranging from 0.968 to 0.983. The reflection data was also corrected for Lorentz and polarization effects.

The crystal structure of 2•4DMF was solved by direct method applying SHELXTL-97 program²⁹ and refined by full matrix least-square on F^2 . For 2•4DMF, one azobenzene group and one DMF solvent molecule were found to be disordered over two positions with an occupancy factor of 0.523/0.477 for N3/N3A, N4/N4A, C22-C27/C22A-C27A, O8/O8A, N6/N6A, and C32-C34/C32A-C34A. All non-hydrogen atoms were refined anisotropically. The H atoms of the CO₂H groups and one of the hydroxyl groups were located from Fourier maps. All other H atoms were placed in the geometrically idealized positions [d(O - H) = 0.83 Å, with $U_{\rm iso}({\rm H}) = 1.5 U_{\rm eq}({\rm C})$ for hydroxyl groups; $d({\rm C-H}) =$ 0.97 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups; d(C)-H)=0.98 Å, with $U_{iso}(H)$ =1.2 $U_{eq}(C)$ for methylene groups; d(C-H)=0.94 Å, with $U_{iso}(H)=1.2U_{eq}(C)$ for methine groups; d(C-H)=0.94 Å, with $U_{iso}(H)=1.2$ $U_{eq}(C)$ for phenyl groups] and constrained to ride on their parent atoms. The final refinement based on 4098 observed reflections with $I > 2\sigma(I)$ and 518 variable parameters converged to R=0.1260, wR=0.2916 (w= $1/[\sigma^2(F_0^2) + (0.0878P)^2 + 15.5855P]$, where $P = (F_0^2)^2$ $+2F_{c}^{2})/3$), S=1.196, (Δ/σ)_{max}=0.005, ($\Delta\rho$)_{max}=0.517 and $(\Delta \rho)_{\min} = -0.241 \text{ e/Å}^3$.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC No. 736244. Cpoies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

Results and discussion

Treatment of 2 with HCl in DMF followed by diffusing diethyl ether into the solution produced 2•4DMF as red blocks, while its reactions with NaOH in MeOH afforded a tetrasodium salt 3 as deep red crystals. Compounds 2•4DMF and 3 were relatively stable toward oxygen and moisture, and soluble in DMF and DMSO. The elemental analysis of 2•4DMF and 3 were consistent with their chemical formula.

IR and NMR spectra

In the IR spectra of **2**•4DMF and **3** (Figure S1 and S2), there exists a very strong and broad O—H stretching vibration at 3417—3419 cm⁻¹. Similar band was also found in calix[4]arene-*p*-tetrasulphnonic acid,³⁰ implying that the OH groups in **3** kept intact. The N=N and C=O stretching vibrations at 1680/1668 cm⁻¹ (**2**•

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4DMF) were shifted relative to those of 3 (1653/1595 cm⁻¹), which may be due to the deprotonation of **2**•4DMF. The ¹H NMR spectrum of **2**•4DMF in DMSO- d_6 measured at ambient temperature showed the correct aromatic/DMF proton ratios for 2 and four DMF solvent molecules. The ¹H NMR spectrum of **3** in DMSO- d_6 exhibited a singlet and two doublets for the phenyl group at δ 7.72 (ArH-c), δ 7.92–7.94 (ArH-a), δ 7.63–7.65 (ArH-b), and the methylene groups at δ 3.63–4.42. Interestingly, slow addition of 4 equiv. of NaOH to a solution of 2 (0.1 mol·L⁻¹) in DMSO- $d_6/$ D₂O made its solution color be turned from yellow to light red, red, and deep red (3), which were monitored by ¹H NMR spectra at ambient temperature (Figure 1). It showed that the signals of proton a (δ 8.04–8.06), b $(\delta 7.81 - 7.83)$, and c $(\delta 7.84)$ had a distinct upfield shift relative to those of proton a' (δ 7.92–7.94), b' (δ 7.63– 7.65), and c' (δ 7.72) of **3** upon addition of NaOH. Such shifts might be ascribed to the more conjugation between the more naked CO_2^- groups and the azobenzenecalix[4]arene core.³¹ In addition, the sharp signals of 2 gradually turned into the broad ones of 3, suggesting that there existed a proton exchange equilibrium between the two compounds.



Figure 1 The ¹H NMR signals of proton a, b, and c of **2** showing upfield shifts relative to those of proton a', b', and c' of **3** upon addition of NaOH. Line 1: **2** (0.1 mol•L⁻¹); Line 2: **2**+NaOH; Line 3: **2**+2NaOH; Line 4: **2**+3NaOH; Line 5: **2**+4NaOH=**3**.

Crystal structure

The identities of **2**•4DMF was further confirmed by X-ray crystallography, but attempts to grow better single crystals of **3** always failed. **2**•4DMF crystallizes in the monoclinic space group C2/c, and its asymmetric unit consists of half of 5,11,17,23-tetrakis[(*p*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene and two DMF solvent molecules. The calix[4]arene core of **2** adopts a flattened cone conformation in which opposed phenyl rings have parallel or sharply inclined positions (Figure 2), which were observed in some calix-[4]arene derivatives such as 5,17-bis(*p*-methoxyphenyl-azo)-26,28-dihydroxy-25,27-bis(propargyloxy) calix[4]-arene²² and 5,11,17,23-tetrakis(phenylazo)-25,26,27,28-

tetrahydroxy calix[4]arene.³² The mean C—O [1.307(7) Å] and C=O [1.209(6) Å] bond lengths of carboxyl groups of **2**•4DMF (Table S1) were normal relative to those found in calix[4]arenecarboxylic acids.^{33,34} Each azo group adopts a *trans*-configuration. The mean N= N [1.296(4) Å] bond length of **2**•4DMF is 0.03—0.08 Å elongated relative to those observed in 26,28-bis[((diethylamino)carbonyl)methoxy]-25,27-dioxy-5,11,17,23-tetrakis(phenylazo)calix[4]arene-(ethylacetate-O)-potassium (1.267(2) Å)²⁴ and 5,11,17,23-tetrakis(phenylazo)-25,26,27,28 -tetrahydroxycalix[4]arene (1.244(2) Å).³²



Figure 2 View of the molecular structure of **2** with labeling scheme and 30% thermal ellipsoids. Only one of the disordered azobenzene group is shown. Symmetry code: A, -x + 1, y, -z + 3/2.

In the crystal of 2-4DMF, two intramolecular H-bonding interactions between the two hydroxyl 25,26,27,28-tetrahydroxycalix[4]arene groups in $[O(1)\cdots O(2)]$ and between one phenyl group and the O atom of the DMF solvent molecule $[C(5)\cdots O(8)]$ are observed. In addition, three intermolecular H-bonding interactions between the O atom of the carboxylate group and the O atom of the DMF molecule $[O(3)\cdots O(7)]$ (x, y, 1+z)] and between the methyl group and the O atom of the carboxylate group [C(30) \cdots O(6) (1-x, 2y, (1-z)] and between the O atoms of the carboxylate groups $[O(5)\cdots O(4) (1-x, 2-y, 1-z)]$ produce a 1D H-bonded double chain (Figure 3a). Furthermore, each chain is linked via evident $\pi \cdots \pi$ interactions (3.459) Å)^{33,34} between each phenyl group of azobenzene moieties, thereby forming a 2D H-bonded wave-like network (Figure 3b).

Thermogravimetric analysis (TGA)

The thermal analysis of **2**•4DMF was carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 5 $^{\circ}$ C•min⁻¹ and a flow rate of 100 cm³•min⁻¹ (N₂). Its TGA curve showed two stages of release of DMF solvent molecules (Figure S3). The first weight loss of 10.70% at 35.90 $^{\circ}$ C corresponds to the loss of two DMF solvent molecules (calculated 11.16%). The second weight loss (11.60%) in the range of 35.90 ---149.90 $^{\circ}$ C approximately amounts to the loss of the other two DMF solvents (calculated 11.16%). The results also confirmed that **2** was solvated by four DMF solvent molecules.



Figure 3 (a) View of one section of the 1D H-bonded double chain (looking along the *c*-axis) formed by intra- and inter-molecular H-bonding interactions in **2**•4DMF. (b) View of the 2D H-bonded wave-like network (extending along the *ac* plane) formed by intra- and inter-molecular H-bonding and $\pi \cdots \pi$ interactions.

UV-vis spectra

The UV-vis spectra of 2 $(1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1})$ titrated with diluted NaOH solution $(5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})$ was measured at room temperature (Figure 4a). Compound 2 was characterized by three absorptions. One peak at 265 nm and one broad peak at 360 nm may be assignable to the transition between the phenyl moiety and the π - π * transition of *trans*-azobenzene groups,³⁵ while the weak peak at 526 nm may be due to the n- π^* transition of the $-N=N^+-H$ moieties.³⁶ Upon addition of base, the two absorption maxima at 265 and 360 nm gradually increased in intensity and the absorption at 526 nm gradually disappeared accompanying appearance of one shoulder absorption at 442 nm. These changes may be ascribed to the deprotonation of the $-N = N^+ - H$ moieties, enhancing the internal-charge transfer character of the molecule.³⁷ Furthermore, the isosbestic point at 482 nm,³⁸ could be identified to be the change from H_4L to L^{4-39} During the titration of 2 with diluted NaOH solution, the corresponding color changes with different pH values from 1 to 13.5 were observed in Figure 4b. When the solution of **3** was titrated with HCl solution, the color of the solution was gradually turned back. Such a color change was reversible and may be ascribed to the protonation or deprotonation of the four p-carboxy- phenyl azo groups in the platform of calix[4]arene. The results showed that 2 possesses a good pH sensing properties.



pH 1.15 2.09 2.95 3.98 5.08 6.06 7.04 8.00 9.09 10.09 10.96 12.08 13.01 13.5 (b)

Figure 4 (a) UV-vis spectra of **2** $(4 \times 10^{-5} \text{ } \text{-mol} \cdot \text{L}^{-1})$ titrated with a dilute NaOH solution. (b) Color changes corresponding to different pH values [0.1 mL of **2** (1.7 g/L) in H₂O (10 mL)].

of 2•4DMF and 3 from treatment of 2 with HCl or NaOH. 2•4DMF contains a 2D H-bonded wavelike network formed by the intra- and intermolecular H-bonding interactions along with the $\pi \cdots \pi$ interactions. Compound 2 responded to H⁺ in a wide pH range from 1 to 13.5. The reversible conversion between 2 and 3 went along with a unique reversible color change. The results suggested that 2 may have a potential application as a good pH sensor. Studies on the respect of research are underway in our laboratory.

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Conclusion

In conclusion, we have demonstrated the preparation

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