



Spectroscopic and thermal properties of newly mixed azocalix[4]arene ester derivatives



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ABSTRACT

The mono-, di-, tri-, and tetra-acryloyl esters of *p*-chloroazocalix[4]arene which include the first examples of mixed azo ester dyes were synthesized by reacting acryloyl chloride with sodium salts of *p*-chloroazocalix[4]arene in tetrahydrofuran with inert atmosphere. Diazonium salt of *p*-chloroaniline was synthesized by using *n*-amlynitrite and coupled with calix[4]arene in anhydrous condition. This is the diazo coupling reactions used for the first time for synthesized azocalix[4]arene. The characterization of synthesized compounds by spectroscopic methods revealed that azocalix[4]arenes adopt a cone conformation if they contain at least one free phenolic group. The structures of these compounds have been characterized by infrared (IR), ultraviolet–visible (UV–VIS), proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR). Differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to determine the thermal behaviors of the compounds.

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1. Introduction

Calixarene are well known macrocyclic molecules of defined size promising for versatile supramolecular and biological applications due to their multiple availability for chemical modification within a concentrated space [1–3]. Calixarene are ideal host compounds with their unique cavity shaped structure and modifiable lower and upper rims. Compared with other host compounds, the conformations of calixarenes which result from the free rotation about the σ bonds of the Ar–CH₂–Ar groups are flexible [4]. By changing the chemical groups of the upper and/or lower rim, it is possible to prepare different derivatives with differing selectivities for various guest ions and molecules [5,6]. Furthermore, they are appropriately designed, and they exhibit a large variety of functions; e.g. as inclusion compounds, selective complexing agents for metal ions, and catalysts [7–10]. The purpose of studying calixarenes properties can be explained by not only pure scientific interest in the unusual complex structure and rich conformational possibilities of their molecules but also by wide practical applications of this class of compounds [8–11].

The cavity-shaped macrocycles have attracted much attention mainly in supramolecular and analytical chemistry because they can form typical host–guest complexes with many neutral

molecules and ions like cyclodextrins and crown ethers [12]. Owing to their non-planar structure, calix[4]arenes can exist in one of the four conformations, and have been designated as cone, partial cone, 1,2-alternate and 1,3-alternate [13–16]. Conformation can be locked by placing the substituents at OH groups larger than methyl. The cone and partial cone conformers were usually synthesized by the alkylation and acylation reaction at the lower rim of calix[4]arene. However, 1,2-alternate and 1,3-alternate conformers were observed only under certain reaction conditions [17–20].

Thermal analysis play an important role in the study of the structure and the stability of the calixarenes. Heat resistance is one of the main properties of dyes used in high temperature processes such as the dyeing of textile fibers, ink-jet printing and photocopying. It is also a crucial property in the high technology devices such as lasers and electro optical devices [21]. The thermal behavior of azocalix[4]arene esters with acryloyl groups have not been reported previously.

Synthesis of calixarenes which include an azo group can be created by a useful method for the development of molecular diagnostics. These chromogenic calixarenes can be used as sensor materials for metal ions and organic molecules. For example, various researchers have recently studied the typically substituted azocalix[*n*]arenes for their use in ionic and molecular recognition [7]. Although the monomeric [22] and tetrameric azocalix[4]arene [23] derivatives were present in the literature, monomeric and dimeric *p*-chloroazocalix[4]arene and mono-, di-, tri- and tetra-

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esters of azocalix[4]arene were synthesized for the first time in this study. The calix[4]arene compounds containing azo groups have been prepared by the reaction of diazotized *p*-chloroaniline with calix[4]arene in dry condition in the order of molar ratios 1:1 and 1:2. First *p*-chloroazocalix[4]arene reacts with metallic sodium and then with acryloyl chloride in N₂ atmosphere in the order of 1:1; 1:2; 1:3 and 1:4, and therefore it becomes an acryloyl derivatives of azocalix[4]arene.

The azo-ester compounds that contain unsaturated group like acryloyloxy moiety is scarce in the literature [20]. During this study, the first attempt was to understand the diazocoupling reaction of calix[4]arenes in order to rationally obtain chromogenic molecular filters that may be selective for metal ions and organic substrates. Afterwards, it's reported the synthesis of the newly synthesized mixed azocalix[4]arene-ester compounds which have polymerizable acryloyloxy group [24–27]. The spectroscopic properties of the compounds were determined by IR, UV–VIS, ¹H and ¹³C NMR techniques. Thermal studies decomposition points and amounts of volatile pyrolysis products were determined in nitrogen using TG, DTA and DTG curves.

2. Experimental

The uncorrected melting points were taken with a digital melting apparatus. The spectrum was recorded on a MATTSON 1000 FTIR spectrophotometer with the use of a KBr disc. Absorption spectra in ethanol, chloroform and DMF were determined on a UNICAM UV2 UV–VIS spectrophotometer. The ¹H NMR and ¹³C NMR spectra were taken on a Bruker AC 200 Fourier Transform Spectrometer that operates at 200 MHz in CDCl₃. The crystal data were collected on Bruker AXS SMART CCD diffractometer. Thermal analysis was carried out with a Shimadzu DTG-GOH simultaneous thermal analyzer combined with a TAS 100 thermogravimetric analyzer using CA. 3.5 mg samples which were heated at a rate of 10 deg/min from ambient temperature to 1400 °C. The measurement was obtained using a flowing nitrogen atmosphere. α-Al₂O₃ was used as a reference material. Elemental analyses were performed by the Instrumental Analysis Laboratory of METU Research Center.

2.1. General procedure for the synthesis of azo and acryloyl derivatives of calix[4]arene

In the first step, *p*-tert-butylcalix[4]arene was prepared by reacting *p*-tert-butylphenol with formaldehyde as described in the literature [18,28]. In the second step, calix[4]arene has been prepared by removing the *tert*-butyl group by the reaction of *p*-tert-butylcalix[4]arene with AlCl₃ according to reverse Friedel–Crafts reaction. In the third step, the azo derivatives of calix[4]arene have been synthesized by the reaction of 4-chlorophenyl diazenyl salt with calix[4]arene in dry DMF in the order of 1:1 and 1:2 molar ratio. In the fourth step, azocalix[4]arene reacts with metallic sodium in N₂ atmosphere in the order of 1:1, 1:2, 1:3 and 1:4 molar ratio. In the fifth step, the acryloyl derivatives of azocalix[4]arene have been synthesized by the reaction of sodium salts of azocalix[4]arene with acryloyl chloride in N₂ atmosphere in the order of 1:1, 1:2, 1:3 and 1:4 molar ratio. The structure of the compounds which were synthesized by the esterification reactions is shown in Fig. 1.

2.1.1. Synthesis of *p*-tert-butylcalix[4]arene [5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene] and calix[4]arene [25,26,27,28-tetrahydroxycalix[4]arene], 1

The *p*-tert-Butylcalix[4]arene was prepared by reacting *p*-tert-butylphenol with formaldehyde as described in the literature [28]. Afterwards, calix[4]arene was prepared by removing the *tert*-butyl

group by the reaction of *p*-tert-butylcalix[4]arene with AlCl₃ according to reverse Friedel–Crafts reaction [18].

2.1.2. Synthesis of *n*-amyl nitrite

(24 g; 0.347 mol) NaNO₂ was dissolved in 94 mL water. When the temperature falls to 0 °C (or slightly below), a mixture of 6 mL of water, 8 mL of concentrated sulfuric acid and 27.5 mL (0.25 mol) of pentan-1-ol, which had previously been cooled to 0 °C, are slowly introduced from the separatory funnel to the mixture. The rate of the addition must be controlled so that the temperature can be maintained at ± 1 °C. This addition takes 45–60 min. Afterwards, let the mixture stand for 1.5 h and then filter from the precipitated sodium sulphate. Separate the upper yellow pentyl nitrite layer (22.52 g; 76%), wash it with a solution containing 0.25 g of sodium hydrogen carbonate and 3.0 g of sodium chloride in 12.5 mL of water, and lastly dry it with 3.0 g of magnesium sulfate.

2.1.3. Synthesis of 4-chlorophenyldiazonium salt [*p*-Chlorophenyldiazenyl salt]

4-Chloroaniline (1.5 g; 11.76 mmol) was dissolved in 14 mL absolute ethyl alcohol with 1.20 mL H₂SO₄ in an ice bath at 0 °C. Following this, 6.82 mL of *n*-amyl nitrite (1.47 g; 12.56 mmol) solution was added dropwise to produce a diazonium salt. After stirring 30 min, diazonium salt was precipitated by adding diethyl ether. The precipitated salt was filtered and washed with cold ether. And then, was dried in a vacuum. It must be remembered that solid diazonium salts are very sensitive to shock when they are perfectly dry.

2.1.4. Synthesis of the monodiazenyl derivative of calix[4]arene [5-(4-Chlorophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene] [E-5-((4-chlorophenyl) diazenyl)-25,26,27,28-tetra-hydroxycalix[4]arene], 2

Diazonium salt (98 mg; 0.707 mmol) was dissolved in 0–5 °C in dry DMF (5 mL) and within half an hour it was added dropwise to a stirred mixture of calix[4]arene (300 mg; 0.707 mmol) in dry DMF (20 mL) at 0–5 °C. Cold pyridine was added dropwise to the ultimate solution until that pH became 7–8 under ice cooling. After stirred for 4 h at 0–5 °C, the ultimate solution was acidified to pH ~ 1–2 with 0.1 N cold HCl. Afterwards, a large quantity of orange precipitated was formed and then it was filtered and washed with cold ether and water. The product was purified from acetonitrile/water to give a present compound of m.p. 305–306 °C. Yield: %62. TLC (Chloroform/Hexane (4:3)): R_f: 0.32, IR (KBr pellet, cm⁻¹): 3510–2981 (OH), 2948, 2895 (–CH₂–), 1601 (–C=C–), 1266, 1247, 1110 (C–O), 1095 (–C–Cl). ¹H NMR (200 MHz, CDCl₃, ppm): δ 10.20 (4H, s, ArOH (H7)), 7.44–7.40 (2H, m, Ar_{azo}H (H3', H5')), 7.78–7.72 (2H, m, Ar_{azo}H (H2', H6')), 7.68 (2H, s, Ar_{calix}H (H9, H11)), 7.20–7.06 (6H, m, Ar_{calix}H (H2, H4)), 6.82–6.68 (3H, m, Ar_{calix}H (H3)), 4.28 (4H, s, ArCH₂Ar (H6)), 3.58 (4H, s, ArCH₂Ar (H6)). ¹³C NMR (200 MHz, CDCl₃, ppm): δ 148.5 (C1'), 136.1 (C4'), 124.1 (C2', C6'), 127.5 (C3', C5') (Ar_{azo}C); 151.0 (C7), 152.0 (C10), 147.2 (C13), 128.9 (C8, C12), 129.2 (C1, C5), 128.3 (C2, C4), 122.4 (C3), 123.8 (C9, C11) (Ar_{calix}C); 31.7 (C6, Ar–CH₂–Ar).

2.1.5. Synthesis of bisdiazenyl derivative of calix[4]arene [5,17-Bis(4-Chlorophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene] [E-5,17-Bis((4-chlorophenyl) diazenyl)-25,26,27,28-tetrahydroxycalix[4]arene], 3

The procedure used in 2 was used in 3, too. Therefore, **3** was synthesized by using calix[4]arene (0.30 g; 0.707 mmol) and 4-chlorophenyldiazonium salt (0.212 g; 1.4 mmol) in dry DMF (20 mL) at 0–5 °C and purified by using acetonitrile–water. M.p. >300 °C. Yield: %25. TLC (Chloroform/Hexane (4:3)): R_f: 0.63, IR (KBr pellet, cm⁻¹): 3528–2981 (OH), 2948, 2895 (–CH₂–), 1594 (–

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