

# Synthesis, characterization, conformational equilibrium and intramolecular hydrogen bond analysis of Novel Azocalix[4]arenes including acryloyl moiety using DFT studies

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## ABSTRACT

Azocalix[4]arenes were synthesized via diazo-coupling reaction with aniline in 1:1, 1:2, 1:3 and 1:4 molar ratio. Novel Azocalix[4]arenes having Acryloyl moiety were prepared esterification reaction with metallic sodium and Acryloyl chloride with the same molar ratio of Azocalix[4]arene derivatives. The spectroscopic characterizations of the compounds were made by using IR, UV–Vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies. In our study, the validation of the exact conformation of Azocalix[4]arene existing in a Cone, Partial Cone, 1,2-Alternate and 1,3-Alternate was realized by spectroscopic and DFT analyses. These results reveal that the compounds exist in the Cone conformation because of the existence of Intramolecular Hydrogen Bonds (IHBs) in the calixarene core. According to the conformational analysis, Cone conformation corresponds to the minimum energy for compounds 6, 7 and 8, as well. Both DFT and NMR results confirmed that a conformational rearrangement of compound 9 is 1,3-Alternate conformer. The experimental results were correlated with the theoretical calculations. In addition, Natural Bond Orbital (NBO) calculations were used to examine the electronic characteristics of the intramolecular hydrogen bonds. NBO energies show that the main contributions to energy stabilization correspond to LP → σ\* interactions for IHBs, O···O–H and the delocalisation LP → π\* for O–C=O.

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## 1. Introduction

Calixarenes are the family of supramolecular macrocycles which are not only easily available with different ring size and selectively functionalized, but also capable of forming inclusion complexes with suitable guest molecules [1–4]. Moreover, Calixarenes can adjust their cavities to better fit the guest molecules, an important property which makes them an important class of building blocks for supramolecular assemblies and molecular recognition [5,6]. Because of the electron-rich cavity and their flexible structures, Calixarenes can hold a wide range of organic molecules and molecular ions. Moreover, they are as well as useful as synthetic receptors, catalysts, analytical sensors, and model structures for biomimetic studies [7–11]. They are functionalized both at the phenolic hydroxyl groups (lower rim) and at the para positions of the phenol rings (upper rim) [2,12]. Their phenolic hydroxyl groups

are capable of forming intramolecular and intermolecular hydrogen bonds which have the main role in the conformational rearrangements of the Calixarenes [7,13]. They can exist in four discrete conformations: cones, partial cone, 1,2-alternate, 1,3-alternate [2,6,14,15]. On the other hand, some instances may only base on experimental values since the conformational equilibrium of such rather big molecules as Calixarenes and their derivatives become unclear for that reason [14,15]. Hence, Quantum chemical calculations have successfully been used in the characterization of the conformational flexible molecules such as Calixarenes [15,16].

In this study, we synthesized novel Azocalixarenes which consist of acryloyl moiety, and their characterization was made by using UV–Vis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic methods. One of the aims of this study is to analyse experimental results obtained by the reaction of Azocalixarenes with Acryloyl chloride by comparing with Density Functional Theory (DFT) results. We analyzed a conformational structure of the compounds by using both experimental data and theoretical calculations since similar studies are scarce in the literature. The determination of the exact conformation of the azocalixarene is important for evaluation of

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the fine-tuning of the complex formation ability and selectivity of the host-guest interactions for sensor applications, as well as physical properties of Calixarenes [8,12,14,17]. In our theoretical approach, we evaluate stability and conformational equilibrium of Azocalix[4]arenes using a DFT study, which includes calculation of structural and electronic properties of the Azocalix[4]arenes. The intramolecular hydrogen bonds (IHBs) were predicted by the theoretical calculations and spectroscopic assessment. We utilized Natural Bond Orbital (NBO) analysis in order to determine the main contributions to energy stabilization correspond to donor-acceptor interactions for intramolecular hydrogen bonds and the delocalisation of electron density between occupied Lewis type (bond or lone pair) NBOs and unoccupied non-Lewis NBOs.

## 2. Experimental method

### 2.1. Materials

All the solvents and chemicals were obtained from Aldrich (USA) and Merck Chemical Company (Germany) without further purification. Solvents were of spectroscopic grade. Melting points were measured, with filling a compound with an open capillary tube about 4 mm high, using a digital melting point apparatus (Stuart Melting Point 30) that the increase in temperature is no more than 2 °C per minute. Absorption spectra were determined on a UNICAM UV2 (UK) UV-Vis spectrophotometer over the range of  $\lambda$  between 200 and 800 nm using a glass cell with a path length of 10 mm at room temperature. The UV-Vis measurements were taken using ethanol (polar protic), chloroform (apolar aprotic) and DMF (polar aprotic) solvents as a reference between  $1 \times 10^{-5}$  M and  $5 \times 10^{-5}$  M concentrations. The FT-IR spectra were recorded on a MATTSON 1000 FTIR (USA) spectrophotometer by using the ATR (Attenuated Total Reflection) apparatus ( $4000\text{--}400\text{ cm}^{-1}$ ) in the solid phase. Nuclear magnetic resonance spectra were recorded on a Bruker (Germany) AC 400 Fourier Transform Spectrometer (FTS) that operates at 400 MHz in deuterated Dimethylsulphoxide ( $\text{DMSO-}d_6$ ) using Tetramethylsilane (TMS). Elemental analysis (C, H and N) was performed using a LECO CHNS-932 instrument (USA) by the Instrumental Analysis Laboratory of METU Central Laboratory.

The purity of the substances and the courses of reactions were monitored by TLC using TLC aluminum sheets with Silica gel 60 F254 (Merck). The preparative TLC chromatography was carried out on  $20 \times 20$  cm glass plates covered by Silica gel 60 GF254 (Merck) or  $\text{Al}_2\text{O}_3$  type G (Fluka). The column chromatography was performed using Silica gel 60 (Merck).

### 2.2. Synthesis

#### 2.2.1. General procedure for the synthesis of acryloyl derivatives of azo dyes

*p*-tert-butylcalix[4]arene [18] and calix[4]arene [19] were synthesized as described by the previous method. Azocalix[4]arenes were synthesized via a diazo-coupling reaction with aniline in 1:1, 1:2, 1:3 and 1:4 molar ratio (Fig. 1). Acryloyl derivatives of Azocalix[4]arene were synthesized by the reaction of Azocalix[4]arene with metallic sodium and Acryloyl-Chloride in 1:1, 1:2, 1:3 and 1:4 molar ratio in an inert atmosphere at room temperature (Fig. 2).

#### 2.2.2. Synthesis of monodiazenyl derivative of calix[4]arene [5-phenylazo-25,26,27,28-tetrahydroxycalix[4]arene] {E-5-(phenyldiazenyl)-25,26,27,28-tetra-hydroxycalix[4]-arene}, 2

A solution of phenyldiazonium chloride, which is prepared from aniline (0,171 mL; 1.88 mmol), sodium nitrite (0.129 g; 1.88 mmol) and conc. HCl (0.85 mL) in water (20 mL) between 0 and 5 °C, after stirring for 30 min is added dropwise to a cold (0 °C) solution of calix[4]arene (0.8 g; 1.88 mmol) in DMF (20 mL). Sodium acetate trihydrate was added dropwise into obtained solution until pH became 6–7 under ice cooling. After stirring for 4 h between 0 and 5 °C the obtained solution was acidified to pH=1–2 with 0.1 N cold HCl and a large quantity of the orange precipitated formed was then filtered and washed with cold ether and water. The product was purified from acetonitrile/water to give a present compound of m.p. 288–289 °C. Yield %40. TLC (Chloroform/Hexane (4:3))  $R_f$ :0.35, IR (KBr pellet,  $\text{cm}^{-1}$ ): 3375 (OH), 3340–2973 (OH), 2953, 2876 ( $-\text{CH}_2-$ ), 1666, 1594 ( $-\text{C}=\text{C}-$ ), 1455, 1414 ( $-\text{N}=\text{N}-$ ), 1251, 1151 ( $\text{C}-\text{O}$ ).  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  10.19 (4H, s, ArOH (H7)), 7.47 (3H, m,  $\text{Ar}_{\text{azo}}\text{H}$  (H3',H4',H5')), 7.79 (2H, d,  $J = 7.5$  Hz,  $\text{Ar}_{\text{azo}}\text{H}$  (H2',H6')), 7.70 (2H, s,  $\text{Ar}_{\text{calix}}\text{H}$  (H9,H11)), 7.06 (6H, m,

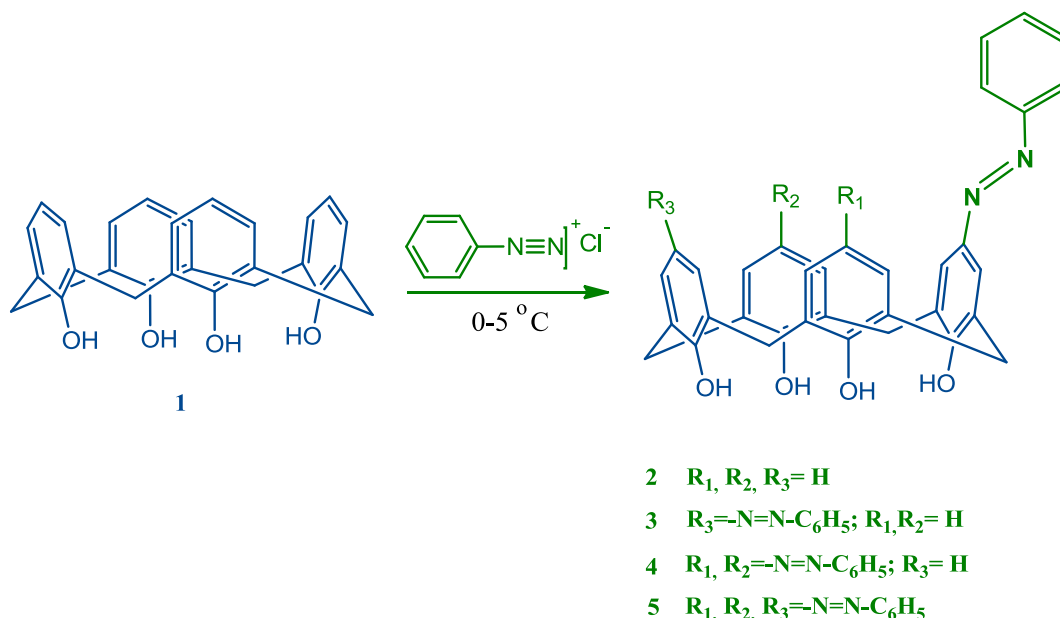


Fig. 1. Synthesis route of Azocalix[4]arene (2–5).

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