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ORIGINAL PAPER

Molecular Recognition of 1,5 Diamino Anthraquinone by *p*-tert-butyl-Calix(8)arene

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Abstract The molecular recognition properties of *p*-tert-butyl-calix(8)arene with 1,5 -diamino anthraquinone (1,5 DAAQ) were studied by using UV–Visible and Fluorescence spectroscopic techniques. The binding constant was determined by using the Benesi-Hilde brand expression. It was found that the host–guest complex was formed between 1,5 DAAQ and *p*-tert-butyl- calix(8)arene in the 1:2 Stoichiometry ratio.

Keywords 1, 5 -Diaminoanthraquinone · *p*-tert-butyl-calix (8)arene · Molecular recognition · Host–Guest interaction · Absorption and fluorescence spectroscopy

Introduction

Anthraquinone is an aromatic organic compound and it is the most important quinone derivative of anthracene. The anthraquinone is chemically stable under normal conditions. Anthraquinones naturally occur in some plants like aloe, cascara, senna, buckthorn etc. Natural anthraquinone derivatives tend to have laxative effects [1]. Anthraquinone derivatives are important class of a system that absorb in the visible region. They are used principally in photographic dye chemicals, in paper industries as a catalyst, in textile industry for colouring textile materials and in medicine as an antioxidant. The biological effects of these drugs are due to the interaction of the chromophore group with DNA [2]. Diamino anthraquinones find applications in the field of biochemistry and electrochemistry. They are used in the synthesis of electroactive dendrimers and preparation of solid state redox super capacitors [3]. In general the optical properties of the anthraquinone derivatives depend on the position of the substituents, the ability to form hydrogen bonds and the occurrence of intermolecular interactions [4].

Calixarenes are a class of versatile molecular hosts with growing applications in the field of supramolecular chemistry [5]. The calixarenes which are macrocyclic compounds containing cavities of molecular sized dimensions, are interesting because of their potential as enzymic mimics [6]. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions. The molecular recognition refers to the specific interaction between two or more molecules through non covalent bonding such as hydrogen bonding, hydrophobic forces and Vander waals forces. Because of its special cavity structure, high melting point and thermal stability, it was found to be useful in gas chromatography as stationary phase [7]. Calixarene is an ideal candidate for the construction of new types of dendrimers and plays very important role in the recognition for cations, anions and neutral molecules [8, 9]. Calixarenes are basket-like macrocyclic receptor molecules consisting of cyclic arrays of phenol moieties linked by methylene groups. Calixarenes possess functionalization sites on both upper and lower rims [10].

Calixarenes have internal cavities of different size formed by a belt of phenyl rings; these cavities are capable to accommodate a guest molecule of a definite size, which allows their use in molecular recognition. Expenses for the preparation of calixarenes from P-substituted phenols and

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formaldehyde are relatively low, which is important factor for practical applications [11]. They have been widely investigated and used because of their complex forming properties and their derivatives are used as sensing components in ionic sensors [12]. The recognition of neutral organic molecules by synthetic receptors is a topic of current interest in supramolecular and also in analytical chemistry. The selectivity character of calixarene for complexation with different species can be modified by changing the cavity size by the different functionalization at the lower and upper rims of the molecule. The interactions of calixarene with neutral species involve competition between complexation and solvation process. Non electrostatic forces resulting from the interaction of the electronic systems of neutral host and those of neutral guest are of primary importance in "host–guest interaction". Calixarenes form complexes with electron deficient neutral aromatics predominantly through π–π type interaction [13]. Many articles are published in recent years on theoretical and experimental works on Calixarene [12–14]

There are number of analytical techniques available for the investigations of host–guest complexation studies. Among the analytical methods we have used UV–visible absorption and Fluorescence spectroscopic techniques to study the molecular recognition of 1, 5 DAAQ with *p*-tert-butyl Calix (8) arene. Our group has recently been reported guest–host interaction of *p*-tert-butyl Calix(8)arene with 2 methyl-1,4 napthoquinone [15] and *p*-tert-butyl Calix(8)arene with 2,3 bis Chloromethyl-1,4 Anthraquinone [16]. In the present study we have choosen *p*-tert-butyl-Calix(8)arene as a host and 1,5 Diamino anthraquinone as a guest to investigate the molecular recognition of 1,5 DAAQ with *p*-tert-butyl Calix (8)arene. In the present study we have determined stoichiometry ratio and the binding constant between 1,5 - DAAQ - *p*-tert-butyl Calix(8)arene.

Experimental

1,5-DAAQ was kindly given by chemical physics group, TIFR, Mumbai. This dye was used without further purification. Chloroform was used as a solvent for this study. Chloroform from Merck chemical laboratory with 99% purity was used without further purification.

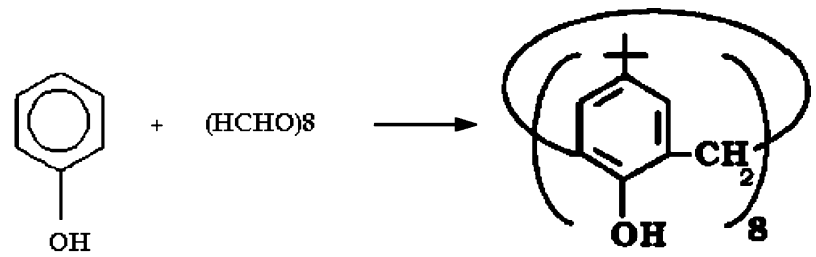
Calix (8) arene was prepared from *p*-tert butyl phenol and formaldehyde [17]. Thirty grams of *p*-tert-butyl phenol and 9.5 g of formaldehyde were dissolved in 150 ml of xylene. The mixture was refluxed at 120 °C for about four hours in an inert atmosphere to get a pale brown coloured precipitate. It was washed with suitable solvents and recrystallized to get a pure white powder of *p*-tert-butyl -calix (8) arene (Scheme 1).

The guest (1,5 DAAQ) and host (*p*-tert-butyl-calix(8) arene) solutions were prepared by using chloroform as a solvent. To determine the stoichiometry ratio by Job's continuous variation method, the two stock solutions of host and guest were mixed to a nine different ratio 1:9, 2:8, 3:7, 4:0, 5:5, 0:4, 7:3, 8:2, 9:1, keeping the total concentrations equal to 0.02 mM (i.e.[H]+[G]=0.02 mM). To determine the binding constant, 1,5DAAQ(0.01 mM) was added to the dilute solution of *p*-tert-butyl calix(8) arene at different concentrations [0.01 mM, 0.015 mM, 0.02 mM, 0.025 mM, 0.03 mM, 0.035 mM, 0.04 mM, 0.045 mM, 0.05 mM]. The solutions were kept in Ultrasonicator for 5 min in order to make the mixture homogeneous. The optical absorption spectra were recorded using Shimadzu UV-2450 spectrophotometer. Fluorescence measurements were made by Cary Varian Spectro fluorimeter. All the experiments were performed at room temperature.

Results and discussion

UV–visible spectral study

The molecular structure of 1,5-DAAQ was shown in Fig. 1. 1,5- DAAQ shows the absorption band in the visible region 400–500 nm. The absorption spectrum of anthraquinone derivatives give five Characteristic Л–Л* bands, four bands in the region of the wavelength between 220 nm and 350 nm and an n-Л* band at the longer



p- tert-butyl phenol (formaldehyde)8 Calix(8)arene

Scheme 1

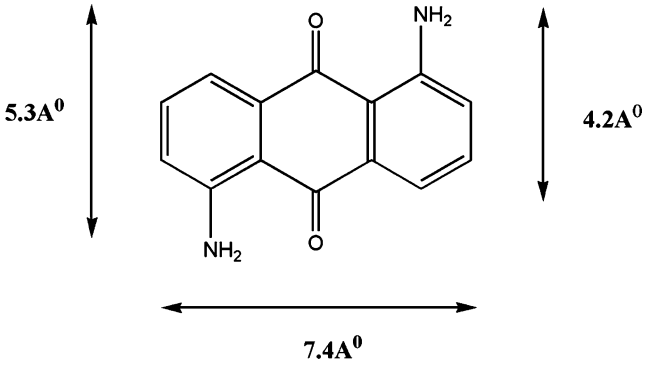


Fig. 1 Molecular structure of 1,5 diamino anthraquinone

wavelength near 400 nm. When an electron donating group such as hydroxyl or amino group is substituted a new Л–Л* absorption band appears in the visible region [18]. 1,5 DAAQ is a bifunctional molecule. It has both electron donor and acceptor groups [19]. The absorption spectrum of 1,5 DAAQ in chloroform shows a absorption maximum at 475 nm. The molecular structure of *p*-tert-butyl-calix (8) arene is shown in Fig. 2. *p*-tert-butyl-calix (8)arene consists of 8 phenol units connected via methylene bridges in the ortho position with respect to hydroxyl group. Figure 3 shows the absorption spectrum of *p*-tert-butyl-calix (8) arene and 1,5-DAAQ in different molar ratios keeping the total concentration 0.02 mM. In the UV–visible spectrum of 1,5 DAAQ with *p*-tert-butyl-calix (8)arene, there are three absorption bands at 241 nm, 291 nm and 475 nm. Among the three, we have taken 291 nm band for this investigation of host–guest interaction. For the molar ratio from 1:9 to 9:1 there is no change in the λ_{max} (291 nm), but there is a change in the optical density. The optical density of 291 nm band decreased with increasing the concentration of 1,5 DAAQ. The absorption spectra of 1,5 DAAQ with *p*-tert-butyl-calix(8) arene does not show isobestic point, which indicates the multiple site binding and dye aggregation may occur within the used range of concentration [20]. The absence of new absorption bands has ruled out the formation of the charge transfer complex between the 1,5-DAAQ and *p*-tert-butyl-calix(8)arene.

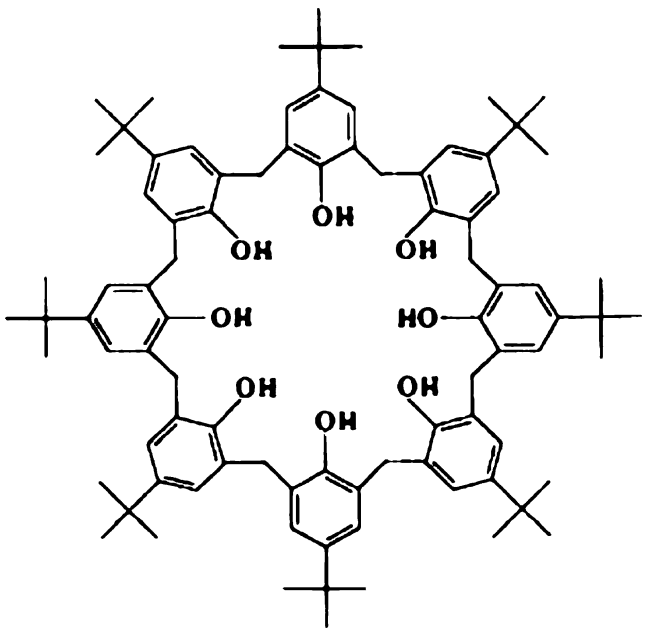


Fig. 2 Molecular structure of *p*-tert-butyl-Calix(8)arene

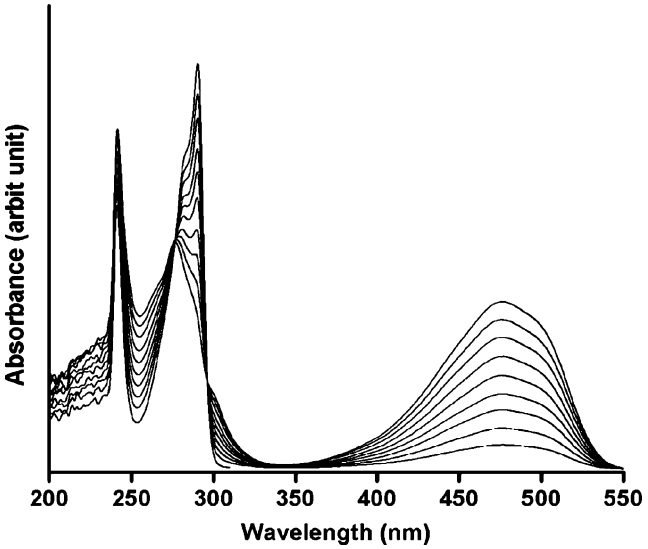


Fig. 3 Absorption spectra of calix(8)arene+1,5 DAAQ in different molar ratios

We have used Job's continuous variation method to determine the stoichiometric ratio of the Guest–Host complex formed. Figure 4 shows the job's plot for 1,5-DAAQ -*p*-tert-butyl-calix(8)arene complex in absorption spectroscopy. Generally continuous variation plot shows a maximum δA at a particular mole fraction of host which provides the stoichiometry of the complex formed. That is the absorbance value of the complex is higher than that of the free guest [21]. In our case we did not observe

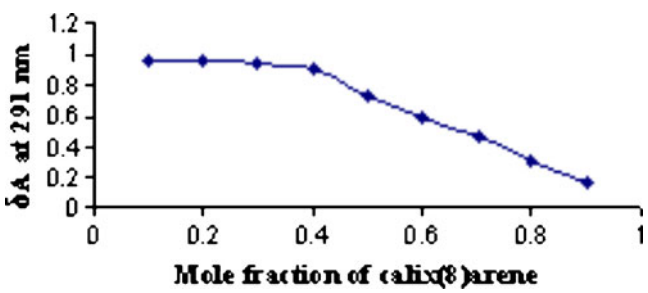


Fig. 4 Job's plot-Variation of δA at 291 nm with the mole fraction of calix(8)arene[Total concentration of Guest+Host=0.02 mM]

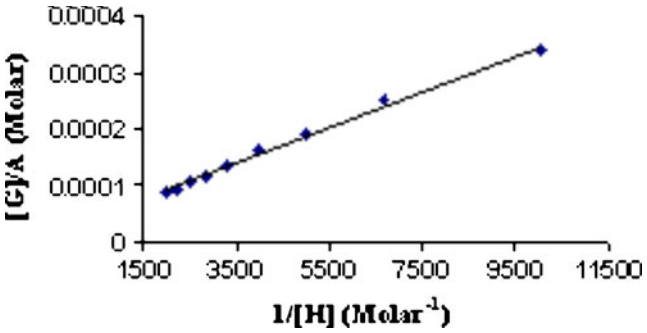


Fig. 5 Plot of [G]/A vs 1/[H] at 291 nm

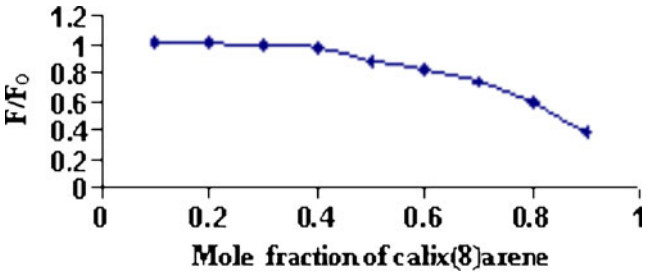


Fig. 7 Variation of F/F_0 with the mole fraction of Calix(8)arene [Total concentration of Guest+Host=0.02 mM]

maximum δA value than free guest .But we observed a lower absorbance value in the *p*-tert-butyl-calix(8)arene-1,5- DAAQ complex than the free guest. This may be due to the intermolecular hydrogen bond formation between guest and host molecules [16].

The calixarene–quinone interaction was further investigated by determining the association constant (K). The association constant can be measured by various spectroscopic methods. Among those methods here we used Bensi–Hildebrand method [22] to determine the association constant K. The following equation has been employed to determine the association constant between calixarene–quinone complexes [2]

$$\text{Calix(n)arene} + \text{Quinone} \leftrightarrow \text{Calixarene–Quinone complex}$$

In the present case

$$p\text{–tert–butyl–Calix(8)arene} + \text{1,5 DAAQ} \leftrightarrow \text{Calix(8)arene–1,5 DAAQ complex}$$
$$H + G \leftrightarrow HG$$

$$K = \frac{[HG]}{[H][G]} \quad (1)$$

Where [H] is the concentration of *p*-tert-butyl-calix(8) arene, [G] is the concentration of 1,5 DAAQ and [HG] is the concentration of calixarene–quinone complex.

To determine the association constant the absorptivities were measured at various ratios of *p*-tert-butyl-calix(8)arene to 1,5 DAAQ and the data were analysed by the Bensi–Hildebrand expression

$$\frac{[G]}{A} = \frac{1}{K\alpha[H]^n} + \frac{1}{\alpha} \quad (2)$$

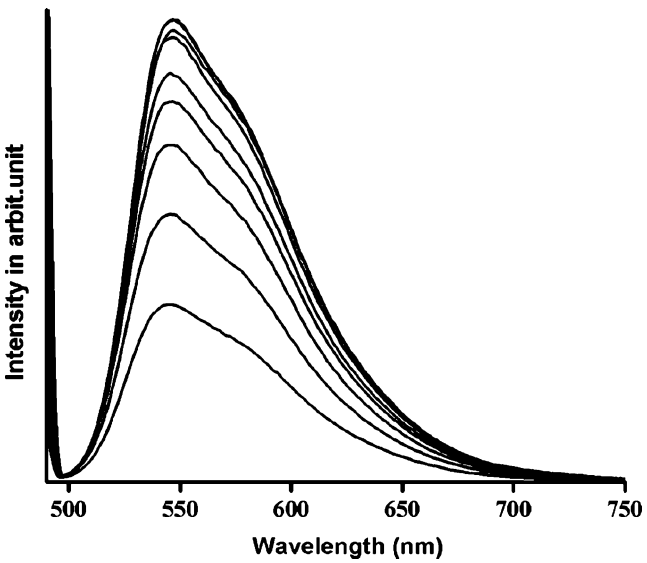
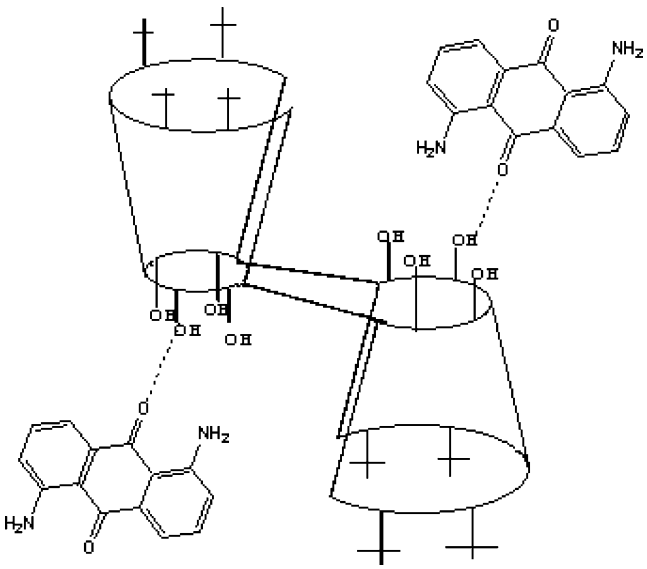


Fig. 6 Fluorescence spectra of calix(8)arene+1,5 DAAQ in different molar ratios



Scheme 2

Where A is absorptivity at 291 nm, α is the constant and K is the association constant for *p*-tert-butyl-calix(8)arene-1,5 DAAQ complex.

By plotting [G]/A vs 1/ $[H]^n$ (Fig. 5) with different n values, the n that results a straight line was taken as the number of host molecules. From the intercept and the slope of the straight line the association constant has been determined. The association constant (K) is found to be 1×10^3 M^{-1}.

Fluorescence studies

Figure 6 shows the emission spectrum of *p*-tert-butyl-calix (8)arene and 1,5-DAAQ in different molar ratios keeping the total concentration 0.02 mM. 1,5-DAAQ has a fluorescence maximum at 546 nm. When the *p*-tert-butyl-calix(8) arene is added to 1,5 DAAQ in different molar ratio, there are changes in the fluorescence signatures. During the increased addition of *p*-tert-butyl-calix (8) arene the fluorescence maximum is red shifted up to the molar ratio 7:3 with respect to neat. Further addition of *p*-tert-butyl-calix(8)arene shows blue shift. Fluorescence quenching is also observed during the increased addition of *p*-tert-butyl-calix (8)arene. The observed fluorescence quenching may be due to the binding of 1,5 DAAQ with of *p*-tert-butyl-calix(8)arene. Generally an isoemissive point indicates two species are in equilibrium (i.e. formation of 1:1 complex) [23]. In the present case we did not observe the iso-emissive point. The absence of iso-emissive point in our case may be due to the interaction between more than one molecule of 1,5 DAAQ with one molecule of *p*-tert-butyl-calix(8)arene.

Generally larger red shifts are observed in polar solvents than in aploar solvents, which indicate that the excited states of the anthraquinone are more stabilized by polar solvents [16]. In the present case chloroform is a polar aprotic solvent. As already mentioned it shows a red shift in 1,5 DAAQ rich region and shows a blue shift in *p*-tert-butyl-calix(8)arene rich region. The observed red shift is due to intermolecular hydrogen bonding between the hydroxyl group of host molecule and carbonyl group of guest molecule. As the concentration of 1,5 DAAQ decreases the intermolecular hydrogen bonding of in *p*-tert-butyl-calix (8)arene with guest is not predominant. Figure 7 shows the variation of F/F_0 with the mole fraction of *p*-tert-butyl-calix(8)arene. F and F_0 are the fluorescence intensities in the presence and absence of *p*-tert-butyl-calix(8)arene. The variation of F/F_0 with the mole fraction shows the stoichiometry ratio of complexation is 1:2 as found in the case of absorption spectrum. The molecular dimension of the guest molecule is determined by Chem 3D. 1,5 DAAQ has a dimension of 5.3 A°×7.4A°. The inner cavity size of *p*-tert-butyl- calix(8)arene is 8.6 A° [24]. Since inner cavity of the *p*-tert-butyl-calix(8)arene is small compared to that of guest molecule, inclusion of two guest molecules inside the *p*-tert-butyl-calix(8)arene is not possible. *p*-tert-butyl-calix(8)arene exists in pinched cone conformation [9, 25, 26]. The observed stoichiometry ratio 1:2 is due to the intermolecular hydrogen bonding between carbonyl oxygen of the guest molecule and the hydroxyl group of host molecule [Scheme 2].

Conclusions

Optical absorption and fluorescence spectroscopic studies on 1,5 DAAQ were carried out to study the host–guest interaction of 1,5 DAAQ with *p*-tert-butyl-calix(8)arene. The stoichiometric ratio for 1,5 DAAQ with *p*-tert-butyl-calix(8)arene is 1:2 and the binding constant is found to be 1×10^3 M^{-1}. Our results suggest that intermolecular hydrogen bonding is mainly responsible for the strong binding between 1,5 DAAQ and *p*-tert-butyl-calix(8)arene.

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