Molecular Complexation of Arenediazonium Ions by a Calix[4]arene Possessing Two Ester Groups: Molecular Tweezers

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Abstract: The spectroscopic behaviors of arenediazonium ions in the absence and the presence of a novel calix[4]arene *1,3-alternate* conformer possessing two (ethoxycarbonyl) methoxy groups **4** were studied by UV-visible, ¹H NMR, and IR spectra for the first time. *1,3-alternate* conformer **4** exhibits the large hypsochromic shifts of 85 nm and the binding constants (K_a) values are greater than 10^4 M^{-1} , indicating the fact that **4** strongly associates with the diazo group, the interaction being comparable with that with 18-crown-6. However, **4** can not inhibit the dediazonation of the diazo group indicating the mechanism (A), the macrocyclic effect which sterically inhibits dediazonation proceeding from the linear $\text{Ar-N}^+ \equiv \text{N}$ inserted in the crown ring to the bulky π -intermediate **II**, is responsible for the stabilization of the diazo group.

Key words: supramolecule, arenediazonium ion, hypsochromic shift, binding constant, calix[4]arene, *1,3-alternate* conformer, ionophore, molecular tweezers, 18-crown-6

1 Introduction

The supramolecular chemistry of calixarenes has been studied (1-3), because they are useful building-blocks in the design of long-range biological electron-transfer models (4) and ultimately of synthetic enzyme mimics as functionalized supramolecules (5-7). The calix[4]arene bearing four (ethoxycarbonyl)methoxy groups **1** exhibits the ionophoric nature and capable of binding alkali metal, alkaline earth metal, diazonium ions are crown ethers do (8-12). For example, it is proposed that an arenediazonium ion is "encapsulated" in the cavity constructed with the ionophoric $-\text{OCH}_2\text{COO}-$ groups (Fig.1). Here, one question occurs to us which is related to the essential behaviors of calix[4]arene as

ionophores: that is, if calix[4]arene really forms the encapsulated complex as illustrated in Fig. 1, then are all four ester groups of the calix[4]arene necessary to being capable of binding arenediazonium ion? As expected from the complex structure, the association constants (K_a) for calixarene-arendiazonium complexes are affected by both electronic effects and steric effects. We thus studied the spectroscopic behaviors of arenediazonium ions in dichloroethane in the absence and the presence of a novel calix[4]arene *1,3-alternate* conformer possessing two (ethoxycarbonyl)methoxy groups **4** and estimated the stoichiometry and the nature of the ion pairs for the first time (Fig. 2).

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2 Experimental

The synthesis of 1,3-alternate-shaped 25,27-dipropoxy-26,28-bis(ethoxycarbonyl-methoxy)-calix[4]arene **4** was described previously (4). UV-visible spectra were obtained with a Shimadzu UV-3101PC spectrometer. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz at room temperature (25°C) in the Fourier transform mode. Chloroform- d_1 was used as a solvent and tetramethylsilane (TMS) was used as an internal reference for ^1H NMR measurement. IR spectra were recorded on AVATAR 370 FT-IR from Thermo Nicolet. 1,2-Dichloroethane was freshly distilled over calcium hydride.

The kinetic measurement for the dediazonation of **3**

is as follows. The plots of OD_{289} of **3** vs. reaction time were first-order for up to three half-lives.

3 Results and Discussion

To investigate whether arenediazonium salts are complexed and stabilized by two ester groups of **4**, we employed 4'-dimethylaminoazobenzene-4-diazonium tetrafluoroborate **2** which serves as a spectroscopic probe. **2** possesses push-pull type substituents which cause an intramolecular charge-transfer band, so that the absorption maximum (λ_{max}) should reflect sensitively the reduction of the positive charge at the diazo group (12). The λ_{max} of **2** shifted to shorter wavelengths with several isobestic points with increasing **4** concentrations. The spectral change is similar to that in the

Fig. 1 Encapsulation of Arenediazonium Ion by Calix[4]arene **1**.

Fig. 2 Encapsulation of Arenediazonium Ion by Two Ester Groups of **4**.

presence of **1** or 18-crown-6. This hypsochromic shift indicates that intramolecular charge-transfer is suppressed because of the reduction of the positive charge at the diazo group. From a plot of the absorbance for the generating $\lambda_{\max}$ vs. host concentration we evaluated the stoichiometry and the binding constants (K_a) by the molar ratio method (13). If the spectral change was relatively small, we employed the continuous variation method to determine the stoichiometry. The results are summarized in **Table 1**.

1,3-alternate conformer **4** and 18-crown-6 exhibit the large hypsochromic shifts of 85–120 nm and the K_a values are greater than 10^4 M^{-1} , indicating the fact that **4** strongly associates with the diazo group, the interaction being comparable with that with 18-crown-6. In contrast, **1** exhibits a small hypsochromic shift (20 nm) and causes a small K_a of only 100 M^{-1} . It is known as to the ion selectivity, **1** binds Na^+ selectively (14), whereas **4** is more selective for K^+ (15), of course, 18-crown-6 forms the considerably stable K^+ complex. In other words, the K^+ -selective ionophores are able to complex strongly the diazo group, however, the Na^+ -selective ionophore is not.

Evidence for the formation of ensemble **I** (**Fig. 2**) in dichloroethane came from ^1H NMR and IR spectroscopic studies. The large K_a (11500 M^{-1}) observed for **4** is rationalized as for the fitness between the ionophoric cavity formed by two ester groups and the ionic size of the diazo group of **2**. In addition, the structure pre-organized to the *1,3-alternate* conformation is also important. As for **4**, the δ -values in the presence of **2** generally shift to lower magnetic field, which effect is attributed to the electron-withdrawing nature of the diazo group of **2**. There is one exception, that is, the $\text{CH}_3\text{CH}_2\text{OCO}$ protons shift to higher magnetic field by

ca. 0.15 ppm. As illustrated in **Fig. 2**, the $\text{CH}_3\text{CH}_2\text{OCO}$ protons are forced to be located on the benzene ring when the two oxygens co-ordinate to the diazo group of **2**. Thus, these protons undergo a ring current effect which causes the upfield shift. On the other hand, the ^1H NMR spectrum for **1** was scarcely changed by the addition of excess **2**. According to the previous report as for the variation of the N,N-stretching frequency of the complexes (16), $\nu_{\text{N,N}}$ for benzenediazonium salt increases by 32 cm^{-1} upon complexation with dicyclohexano-18-crown-6. We thus prepared crystalline complexes of *para-tert*-butylbenzenediazonium tetrafluoroborate **3** with 18-crown-6 and **4**. The corresponding N,N-stretching frequencies are shown in **Table 2**. The data show that the frequency shifts upon complexation with 18-crown-6 (25 cm^{-1}) is larger than that upon complexation with **4** (15 cm^{-1}). Obviously in this case no conclusions regarding the kinetic or thermodynamic stability of the complexes can be made from their spectroscopic behavior.

It is known that the thermal decomposition of arenediazonium salts is slower when the salts are complexed by crown ethers (17), and two opposing theories are proposed: that is, the thermal decomposition is suppressed because of (A) the macrocyclic effect, which sterically forbids dediazonation proceeding from the linear $\text{Ar-N}^+ \equiv \text{N}$ inserted in the crown ring to the bulky π -intermediate **II** (**Scheme 1**), or (B) reduction of the positive charge at the diazo group. From the Eq. 1 depicted in **Scheme 2**, we estimated the first-order rate

Table 1 Absorption Maxima and Binding Constants for **2**^{a)}.

Host	$\lambda_{\max} / \text{nm}$	$\Delta\lambda / \text{nm}^{\text{b)}}$	K_a / M^{-1}
None	680 ($=\lambda_o$)		
18-Crown-6	560	120	180000
1	660	20	100
4	595	85	11500

a) All measurements were carried out with $3.0 \times 10^{-5} \text{ M}$ of **2** in dichloroethane at 35°C . $[\text{Host}] = 5.0 \times 10^{-4} \text{ M}$.

b) $\Delta\lambda = \lambda_o - \lambda_{\max}$

Table 2 N,N-Stretching Frequencies of **3**^{a)}.

Complex	$\nu_{\text{N,N}} / \text{cm}^{-1}$
<i>p</i> -t-Bu-C ₆ H ₄ N ₂ ⁺ BF ₄ [−] (3)	2300
3 •18-Crown-6	2325
3 • 4 (= ensemble I)	2315

a) Nujol, accuracy ca. $\pm 5 \text{ cm}^{-1}$.

Scheme 1 Transition Pathway of Arenediazonium Ion.

Scheme 2 Decomposition Pathway of Arenediazonium Ion **3** in the presence of Host.

Fig. 3 Dediazonation of **3** (2.0×10^{-4} M) in the Presence of Calixarenes and 18-Crown-6 in Dichloroethane at 35°C. Δ , **1**; $\bullet$, **4**; $\circ$, 18-crown-6.

constant (k_d) for the dediazonation of **3** in the presence of these hosts (**Fig. 3**) by monitoring the disappearance of the absorption band at 289 nm. 18-Crown-6 suppressed the dediazonation rate efficiently, in contrast the reaction was scarcely or only slightly inhibited by **1** and **2**. This would indicate that reduction of the positive charge at the diazo group of **3** is not responsible for stabilization. As reported previously (13-15), **4** shows a broad affinity not only for K^+ but also Cs^+ , whereas **1** shows a sharp Na^+ selectivity. This implies that **4** associates with alkali metal cations in an “induced fit” manner. **4** reduced the positive charge at the diazo group, however still possesses enough space for the transition from the linear $\text{Ar-N}^+\equiv\text{N}$ to the π -intermediate **II**. Eventually, the difference between **4** and 18-crown-6 proposes that mechanism (A) is responsible for the inhibition in dediazonation of **3**.

In conclusion, the present paper demonstrated that (i)

the calixarene **4** bearing two ester groups mostly forms the 1:1 complexes with arenediazonium ions and (ii) the resultant association constants (K_a) values are larger than 10^4 M^{-1} , although this compound can not inhibit the dediazonation of the diazo group showing the mechanism (A) is responsible for the stabilization of the diazo group. Further examination on the decisive role in the stabilization of arenediazonium salts by 1,3-*alternate*-shaped calix[4]arene possessing two ester groups as molecular tweezers is now under investigation.

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