Conformational Change Forced by Cesium Ion Complexation in Crystal Violet Derivative Possessing Tris(monoaza-15-crown-5) Structure

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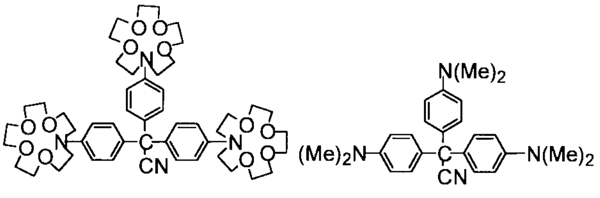
A Crystal Violet derivative incorporating a tris(monoaza-15-crown-5) structure exhibits an anomalous absorbance change in the absorption spectrum of its acetonitrile solution, which was induced only by cesium ion but not by other alkali metal ions. A consideration about its complex conformation explains the cesium ion specificity and a molecular orbital calculation suggests the correlation between the conformation and absorbance.

We have designed a Crystal Violet derivative incorporating a tris(monoazacrown ether) structure, modeling after previously reported biscrowned Malachite Green derivative.[1,2] The crowned Malachite Green derivative captures a potassium ion by its two crown ether rings, which sandwich a cation cooperatively. The present triscrowned Crystal Violet has three crown rings and is supposed to catch a bigger cation than potassium ion, as well as to perform such photochemical control of metal ion complexation as biscrowned Malachite Green shows.[1] In this work, we report the cation complexation of triscrowned Crystal Violet and its unique absorbance dependence on cesium ion concentration in the absorption spectrum and also discuss its conformational change caused by cesium ion complexation.

Scheme1.



1 **2**

The synthesis of triscrowned Crystal Violet **1** was described elsewhere.[2] A control compound, Crystal Violet leuconitrile **2** was synthesized by cyanization of Crystal Violet chloride purchased from Wako Chemicals. Samples for metal ion extraction were equal volumes (3 cm^3) of a 1,2-dichloroethane solution of 2.1×10^{-3} mol dm^{-3} triscrowned Crystal Violet and an aqueous solution containing a mixture of 0.1 mol dm^{-3} alkali metal hydroxide and 7.5×10^{-5} mol dm^{-3} picric acid. After shaking the mixture, the absorption spectra of picrate ion in the aqueous phase (λ_{max} = 350 nm) was measured to obtain extraction percentage. Absorption spectra of acetonitrile solutions containing a Crystal Violet derivative (1×10^{-5} mol dm^{-3}) and an appropriate concentration of an alkali metal perchlorate were taken under dark conditions. Molecular orbital (MO) calculation by a semi-empirical method was performed to consider the Crystal Violet structure. The excited states were calculated by ZINDO method, fixing dihedral angles of the dimethylaniline moiety. All calculations were performed with Gaussian 98 program using a Windows computer.

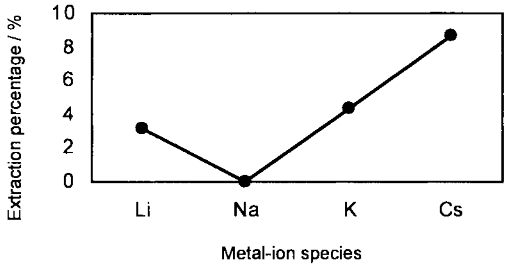


Figure 1. Alkali metal ion extraction by triscrowned Crystal Violet **1**.

Triscrowned Crystal Violet **1** extracts cesium ion more than other alkali metal ion (Figure 1). Considering that the highest extraction percentage of biscrowned Malachite Green was observed for potassium ion[2] and that the sandwich type complexation is an important factor to raise the percentage of potassium ion, the cesium ion complexation with triscrowned Crystal Violet is probably performed by the intramolecular cooperation by the three crown rings of **1**. It is well known that sodium ion fits into the ring of monoaza-15-crown-5 ether.[3] Sodium ion, therefore, tends to form a multinuclear metal complexes with triscrowned Crystal Violet, which in turn suppressed the metal ion extraction due to the significantly increased hydrophilicity of the highly charged complexes.

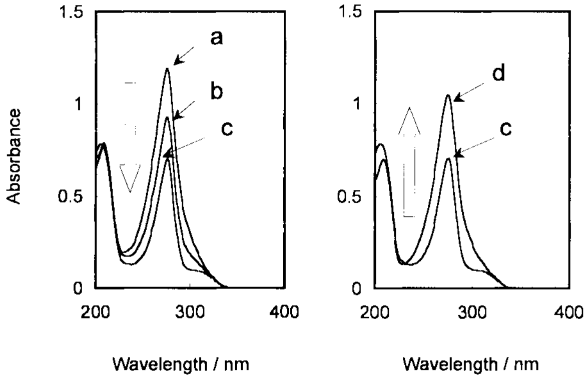


Figure 2. Absorption-spectral changes of triscrowned Crystal Violet 1(1 × 10^{-5} mol dm^{-3}) in acetonitrile without (a) and with CsClO$_4$ (1 × 10^{-7} mol dm^{-3} (b), 1 × 10^{-5} mol dm^{-3} (c), 1 × 10^{-3} mol dm^{-3} (d). Molar ratio of cesium ion to compound 1 is 0(a), 0.01(b), 1(c), 100(d) respectively.)

Absorbance at 270 nm in the absorption spectrum of compound **1** depends on cesium ion concentration. It is reduced with increasing cesium ion concentration at the low concentration (Figure 2, left). When the concentration reaches equal to that of triscrowned Crystal Violet (1×10^{-5} mol dm^{-3}), the absorbance is about half of that without cesium ion. Further addition of cesium ion recovers its absorbance (Figure 2, right). The absorption dependence is very interesting because cesium ion itself has no absorption at 270 nm and triscrowned Crystal Violet does not undergo any ionization without UV irradiation. If photo-ionization occurs, the absorption at 270 nm decreases and another absorption around 620 nm appears.[4] Any absorption in visible light region was, however, not observed in this case. Compound **2**, whose chemical structure is the same as compound **1** except the crown ether moiety, did not show such an absorbance dependence on cesium ion concentration. We also examined the absorption dependence of compounds **1** and **2** on other alkali metal ions. The results are summarized in Table 1. The absorbance dependence was observed only in the system of **1** and cesium ion. It is obvious from the extraction data that cesium ion is complexed with **1**. We, therefore, anticipated that this unique phenomenon of **1** comes from its conformational change on complexing cesium ion. Comparing among the cesium, sodium, and potassium ion complexes of **1**, the complex conformation should be different from one another. Since sodium ion forms 1:1 complexes with the monoaza-15-crown-5 ether ring, its complex formation hardly affects the conformation of the Crystal Violet skeleton. Potassium ion may be bound intramoleculary by the two crown rings of **1** and the resulting conformation change is not very tough for the Crystal Violet skeleton. Intramolecular cooperation of three crown rings is, however, necessary for complexing a cesium ion and its complexation must be accompanied by serious distortion of Crystal Violet skeleton.

Table 1. Absorption-spectral changes of Crystal Violet derivatives by addition of alkali metal ion

	Na^+	K^+	Cs^+
Compound **1**	×	×	○
Compound **2**	×	×	×

Sodium, potassium and cesium perchlorate (0, 1×10^{-7}, 1×10^{-5}, 1×10^{-3} mol dm^{-3}) were added individually to an acetonitrile solution of Crystal Violet derivatives. Symbol "○"means that the absorbance of Crystal Violet derivative depends on metal ion concentration as shown in Figure 2. Symbol "×" means that the absorption spectra are almost the same at any of the metal ion concentration.)

An MO calculation suggests the correlation between the distortion and absorption change in the Crystal Violet derivative. We applied compound **2** for MO calculation as a simple model of compound **1**, because the difference between compounds **1** and **2** is in the crown ether ring that has no absorption in UV region. The molecular models of two typical conformers A and B thus obtained are displayed in Figure 3. The dihedral angle of C(4)–C(5)–N(35)–C(40) is 30° for conformer A and –60° for conformer B. Table 2 shows the oscillator strength[5] from 240 nm to 340 nm. The absorption wavelength of conformer A is slightly red-shifted as compared with conformer B. The reason is that conformer A is less distorted and has a stabilized structure. Conformer A gives the higher values in the oscillator strength than conformer B does. It means that integrated absorbance of conformer A exceeds that of conformer B. The rotation of a nitrogen atom in the dimethylaniline moiety around the axis of C(5)–N(35) bond affects absorption; the conformation in which the nitrogen lone pair electrons at the dimethylaniline moiety are not coplanar to benzene ring affords a strong absorption and the other one in which the lone pair electrons are coplanar to the benzene ring decreases the absorption. The interesting absorption-spectral change of triscrowned Crystal Violet **1** observed in Figure 2 results form the nitrogen atom rotation from conformer A to a more distorted one B. When a cesium ion is placed in the center of a cavity form by the three crown rings of triscrowned Crystal Violet, its three crown rings have to rotate to attain a position suitable to capture a cesium ion. In the higher cesium ion concentrations than that of **1**, more than one cesium ion participates in the complexation of a triscrowned Crystal Violet and then 1:2 complex of triscrowned Crystal Violet and cesium ion is thereby formed. Actually, the binuclear complex was observed in elecrtospray-ionization mass spectrometry. The conformation of the 1:2 complex should differ from that of the 1:1 complex because the crown rings rotate to offer binding sites for excess cesium ions. The rotation is directed toward conformer A, which is suitable for the 1:2 complex, and the reverse conformation changes results in the absorbance recovery in the higher cesium ion concentrations as shown in Figure 2.

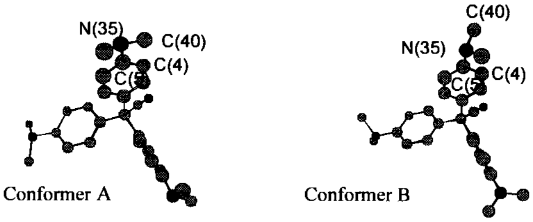


Figure 3. Calculated molecular models for Crystal Violet derivative

Table 2. Oscillator strength for conformers A and B

Conformer A

Oscillator strength	Wavelength/ nm
0.0237	281.42
0.0247	282.31
0.0447	283.87

Conformer B

Oscillator strength	Wavelength/ nm
0.0191	276.18
0.0184	277.59
0.0320	279.00

The differential NOE (nuclear Overhauser effect) NMR spectra supported the correlation between the complexation with a cesium ion and conformational change. The addition of equimolar cesium ion decreased the peak area of crown ring protons of compound **1**, on the irradiation at its benzene ring protons. This indicates that the distance between its benzene ring and crown ether is extended by the cesium ion complexation of **1** accompanying its remarkable conformational change.

We conclude that cesium ion complexation by triscrowned Crystal Violet **1** is accompanied by the interesting absorbance changes, which results from its conformational change on the complexation. This triscrowned Crystal Violet also undergoes photochemical control of metal ion complexation and a study about cesium ion effect on photochromism of triscrowned Crystal Violet is also under way.

References and Notes

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5 The relationship between oscillator strength and molecular absorption coefficient is defined by the equation; $f = \{4 \ln(10mc\varepsilon_0)\int\varepsilon(\nu)d\nu\} / Le^2$. (f: oscillator strength, m: electron mass, c: light speed, ε_0: permittivity in vacuum, ε: molecular absorption coefficient, L: Avogadro constant, ν: frequency, e: elementary electric charge).