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Prototropic tautomerism and solid-state photochromism of *N*-phenyl-2-aminotropones

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1. Introduction

Photochromic materials have received considerable attention in recent years because of their various kinds of potential usefulness [1-5]. Although a large number of photochromic compounds have been synthesized and studied, photochromic organic solids, which are of high performance and easiness for handling superior to photochromic solutions, are few in number [6,7]. Therefore, development of new photochromic organic crystals is one of the first important steps for the fundamental studies concerning development of photoelectronic systems. N-Salicylideneamines (Schiff bases) are well known to exhibit photochromic phenomena in the crystal state [8-11]. The photocoloration of Schiff bases involves excited state proton transfer, which is based on the alteration of basicity (or acidity) of related functional groups (OH and NH) in the photoexcited state. As a new candidate for such photosensitive organic chromophores based on prototropic tautomerism, we focused our interest on 2-hydroxytropone (tropolone) derivatives. Since their discovery, tropolone natural products and synthetic tropolone derivatives have attracted considerable interest due to the unique

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ABSTRACT

N-(4-X-phenyl)-2-aminotropones (X = methoxy, chloro, or nitro substituent) and their clathrate crystals with deoxycholic acid (DCA) were prepared and their prototropic phenomena were determined. Each 2-aminotropone derivative existed as a keto-amine form in the crystal state irrespective of its substituent, which influenced the stability of keto-amine or enol-imine structure in solution. X-Ray crystal structure analysis of*N*-(4-methoxyphenyl)-2-aminotropone revealed the existence of bimolecular hydrogen bonds and close molecular packing, which would inhibit structural change necessary to photo-induced prototropic tautomerization. Thus,*N*-phenyl-2-aminotropones did not show photocoloration in the crystal state, while their clathrate crystals with DCA were found to exhibit photochromism.

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structure and properties of the tropolone ring [12,13]. Tropolone undergoes a proton tunneling from hydroxyl group to carbonyl oxygen atom [14,15]. Spectroscopic studies on some tropolone derivatives have revealed that tautomerism due to five-membered intramolecular prototropy is in very fast equilibrium in solution and in gas phase [16–18]. Such tautomerism in the crystal state has been less demonstrated in detail [19,20]; thus, photo-induced prototropic features of tropolone analogues have been hardly demonstrated. Some years ago aminotropone derivatives have been studied concerning new optical systems [21]. In view of the structural resemblance to the central part of N-salicylideneaniline, we considered that N-phenyl-2-aminotropone might be lead to new photochromic compounds whose coloration would occur due to ESIPT. Herein, we will report tautomeric behavior between NH form and OH form of *N*-phenylaminotropones and their photochromic property in deoxycholic acid (DCA) crystal lattice for the first time.

2. Experimental

2.1. Methods and instruments

All melting points (mp) were measured by a Yanaco model MP-500V micro melting point apparatus and were uncorrected. ¹H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) in CDCl₃ and CD₃COCD₃ as the solvent. Chemical shifts are given as δ -values



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in ppm relative to tetramethylsilane (TMS) as the internal standard. IR spectra were measured using JASCO FT/IR-420 spectrometer. UV/VIS spectra were measured by JASCO UVIDEC-650 spectrometer or JASCO V-560DS spectrometer. Elementary analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds affiliated to the Faculty of Science in Kyushu University.

2.2. General procedure of synthesis of N-phenyl-2-aminotropone derivatives (1–3)

A mixture of freshly prepared 2-chlorotropone (141 mg, 1.00 mmol) [22], 4-substituted aniline (1.00 mmol) and triethylamine (104 mg, 1.03 mmol) in benzene (10 ml) was refluxed for 166 h with stirring. After being cooled, the solution was washed with water and the organic layer was evaporated. The residue was recrystallized from aqueous ethanol to give the product as yellow to orange crystals.

2.2.1. N-(4-chlorophenyl)-2-aminotropone (1)

Yellow needles. Yield 97 mg (42%), mp 144.6–144.9 °C, ¹H NMR (270 MHz, CDCl₃); δ 6.78–7.42 (m, 9H, Ar–*H* and CP–*H*), 8.67 (s, 1H, N*H*). IR (KBr): 3208 (ν_{N-H}) cm⁻¹. Anal. Calc for C₁₃H₁₀ClNO: C, 67.40; H, 4.35; N, 6.05%. Found: C, 67.43; H, 4.30; N, 6.10%.

2.2.2. N-(4-methoxyphenyl)-2-aminotropone (2)

Orange granular crystals. Yield 101 mg (44.4%), mp 104.0–106.4 °C, ¹H NMR (270 MHz, CDCl₃); δ 3.85 (s, 3H, OCH₃, 6.71–7.56) (m, 9H, Ar–*H* and CP–*H*), 8.64 (s, 1H, N*H*). IR (KBr): 3220 (ν _{N–H}) cm⁻¹. Anal. Calc for C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16%. Found: C, 73.86; H, 5.79; N, 6.02%.

2.2.3. N-(4-nitrophenyl)-2-aminotropone (3)

Orange granular crystals. Yield 39 mg (16%), mp 224.5–228.0 °C, ¹H NMR (270 MHz, CDCl₃); δ 6.94–7.49 (m, 9H, Ar–*H* and CP–*H*), 8.93 (s, 1H, OH). IR (KBr): 3190 (ν_{N-H}) cm⁻¹. Anal. Calc for C₁₃H₁₀NO₃: C, 64.46; H, 4.16; N, 11.56%. Found: C, 64.19; H, 4.36; N, 11.33%.

2.3. Formation of DCA clathrate crystals 1@DCA

A mixture of **1** (93 mg, 0.40 mmol) and DCA (628 mg, 1.60 mmol) was recrystallized from a mixed solvent of methanol and ethyl acetate (1:1). Resultant white-yellow fine crystals were washed by the mixed solvent several times and used for photocoloration measurement without further purification.

2.4. Photocoloration measurement

Crystalline powders of DCA clathrate compounds were placed between two glass plates and were stored in the dark at 30 °C before the experiments were carried out. Photocoloration was accomplished by irradiating the sample with 365 nm light using a handheld UV lamp (UVP MINERALLIGHT®LAMP UVGL-25). Reaction rate of thermal fading of resultant photochrome was monitored by measuring electronic reflectance spectra at 30 °C at appropriate intervals. The first-order rate constants *k* for thermal fading reactions of the photocolored species were calculated from the variation in absorbance data at the optimum wavelength λ (Table 1) with time using the expression $kt = \ln\{(A_0 - A_\infty)/(A_t - A_\infty)\}$, where A_0, A_∞ , and A_t are the observed absorbance data at zero time, at the end of the reaction (8–10 half-lives) and at time *t* (s), respectively.

2.5. X-Ray crystallography of 2

A single crystal suitable for X-ray diffraction was obtained by recrystallization of **2** from cyclohexane. The crystal was mounted at

Table 1

Lattice parameters of DCA clathrate crystals with *N*-salicylideneaniline (**SA@DCA**) and **1** (**1@DCA**)

Compound	SA@DCA	1@DCA
Crystal system	orthorhombic	orthorhombic
Lattice parameters		
а	13.212 Å	7.223 Å
b	13.884 Å	12.464 Å
С	25.709 Å	25.325 Å
Space group	P2 ₁ 2 ₁ 2 ₁	$P2_12_12_1$

the end of a glass fiber and coated with epoxy resin. X-Ray diffraction experiments were performed on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Data analyses were carried out with the WinGX software package [23]. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 with SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. The molecular figure was obtained by ORTEP3 [25] and Raster3D [26]. Mercury software was used for the crystal packing drawing [27].

Crystal data. C₁₄H₁₃NO₂, orthorhombic, space group *P*bca (#61), *a* = 7.825(3) Å, *b* = 15.379(7) Å, *c* = 18.124(6) Å, *V* = 2180.9(15) Å³, *Z* = 8, Final *R* (*I* > 2 σ (*I*)), *R*₁ = 0.044, *wR*₂ = 0.0851.

Full crystallographic data for the structure of **2** in this paper have been deposited with the Cambridge Crystallographic Data Centre under deposition number ********. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc. cam.ac.UK).

3. Results and discussion

3.1. Synthesis and tautomerization of N-(4-substituted-phenyl)-2aminotropones

Desired N-(4-substituted-phenyl)-2-aminotropones 1 - 3(Scheme 1) were synthesized according to the amination of 2-chrolotropone with the corresponding anilines. The yielded compounds were identified by elemental analyses and ¹H NMR spectroscopy. Each resonance signal at $\delta = 8.67$ ppm for **1** and at δ = 8.64 ppm for **2** in the NMR spectra in CDCl₃ was assigned to the N–H proton for a keto–amine chelation form, while a singlet peak at $\delta = 8.93$ ppm for **3** was reasonably assigned to the OH proton for an enol-imine chelation form. Such a stable form was confirmed by IR spectra of 1–3 in CCl₄ solution (Fig. 1). Compounds 1 and 2 showed characteristic bands at 3209 cm⁻¹ and 3220 cm⁻¹ due to the NH stretching vibration. In the IR spectrum of **3**, however, an absorption band due to the OH stretching vibration appeared at 3419 cm⁻¹. These results can be interpreted by the resonance effect of substituents at the 4-position of benzene ring. π -Electrondonating group can enhance the basicity of nitrogen atom of the





Fig. 1. IR spectra of 1-3 (i) in CCl₄ solution and (ii) in KBr disk.

amino group to stabilize NH form. On the other hand, OH form is predominant in the case of **3** with electron-withdrawing substituent. Thus, distribution of the tautomeric isomers is dependent on the electronic effect of substituents in solution. It should be noted, however, that all the compounds in KBr disks showed characteristic single bands at around 3200 cm⁻¹ due to NH stretching vibration, which exhibited that the molecules existed as keto–amine forms in the crystal state.

3.2. X-Ray crystal structure of 2

In order to obtain accurate structural information of *N*-phenyl-2aminotropone in the crystal state, X-ray crystal structure of **2** was determined. The particular hydrogen atom considered is located at the nitrogen atom in the five-membered chelating structure (Fig. 2): the bond distance of N–H is 0.92 Å. Thus, it is confirmed that the molecule exists as NH form. The bond angle of N–H…O is 110.4° and the interatomic N(1)…O(1) distance is 2.54 Å, which is close enough for the proton to transfer between the nitrogen and oxygen atoms.

Crystal structure of **2** is shown in Fig. 3, in which a pair of molecules form a firm dimer connected by intermolecular double hydrogen bonds between the N–H and carbonyl oxygen atoms (intermolecular N···O distance: 3.04 Å and N–H···O angle: 148.6°). Each dimer is in contact with proximate dimers. According to partial packing diagrams around troponyl and benzene rings, in which symmetry codes are (i) X, Y, Z, (ii) -1 + 1/2 + X, +Y, 1/2 - Z, and (iii) 1/2 + X, +Y, 1/2 - Z, the distance between the least-squares plane defined by the troponyl ring(i) and adjoining H(8) of (ii) is 2.92 Å, and the distance between the least-squares plane of the troponyl ring(i) and adjoining C(4) of (iii) is 3.42 Å, respectively. Similarly, the shortest distances from the benzene ring (i) to neighboring H(9) of (ii) and (iii) are 3.09 Å and 2.82 Å, respectively. It is worthwhile to note that intermolecular hydrogen bonds stabilize keto–amine structure in the crystal state, while intramolecular hydrogen bond is



Fig. 2. Molecular structure of 2 with numbering scheme.

predominant in CCl_4 solution. Neither crystals nor solutions of *N*-phenyl-2-aminotropone exhibited photocoloration; thus, aminotropone **1**–**3** are not photochromic.

3.3. Photochromism of N-phenyl-2-aminotropone in DCA clathrate crystal lattice

The mechanism of photocoloration of Schiff bases involves excited state intramolecular proton transfer (ESIPT) from the phenolic hydroxyl group to the imine nitrogen atom through sixmembered chelating structure, followed by molecular structural alteration to stabilize a resultant keto-amine structure [8-11]. N-Salicylideneamines as well as 2-aminotropones do not exhibit photochromic phenomenon in solution due to the fast thermal relaxation of the photochrome in solution. In every crystal of such a compound, ESIPT occurs. A decisive condition for organic dyes to exhibit crystalline photochromism is to secure reaction room for photo-induced reactions in the crystal lattice [10]. From the inspection of crystal packing diagram of 2, intermolecular interaction via hydrogen bonding and molecular aggregation by aromatic rings led to close structure, which inhibits molecular structure alteration induced by prototropic tautomerization. Accordingly, these crystals do not show any color change after photo-irradiation.



Fig. 3. Crystal packing diagram of 2 along the *a* axis.

In the previous papers, we have reported that utilization of crystal lattice cavities in deoxycholic acid (DCA) clathrate crystals was one of the most effective methods for producing photochromic crystals [28–31]. Therefore, DCA clathrate compound with 1 (1@DCA) were prepared by mixing 1 with DCA in a mixed solvent of methanol and ethyl acetate. According to NMR peak analysis, yielded white-yellow fine crystals were found to contain **1** as well as solvent methanol as guest molecules. Such a phenomenon is observed in the case that desired guest molecules are not so desirable as N-salicylideneaniline [29]. The walls of guest rooms in deoxycholic acid crystal lattice to accommodate organic molecules are made of hydrocarbon moieties, and neighbouring molecules coexisting in the reaction room affect the rate of thermal bleaching reaction of the guest photochrome. X-Ray diffraction experiments on the best single crystal of 1@DCA revealed that the clathrate compound crystallized in the orthorhombic system of the space group of *P*2₁2₁2₁ (#19). Although we could not see the exact structure of 1@DCA because of difficulties in refinement due to severe disorder of guest molecules, guest 1 was suggested to be enclathrated within the cavities formed by host DCA molecules according to the comparison with the crystal data of already known DCA clathrate crystals with N-salicylideneaniline (SA@DCA) (Table 1) [31].

Upon exposure of **1@DCA** crystals to UV light, the white-yellow color of the crystals turned to pale orange, which returned slowly to the original yellow in the dark. Reflectance spectra of 1@DCA crystals before and after UV irradiation are shown in Fig. 4. It should be noted that this photocoloration is the first observation for the tropolone family and N-phenyl-2-aminotropones exhibit photochromism only within the DCA inclusion environment. The thermal fading reaction of the photoproduct was then monitored by the decreasing rate of absorption band at 490 nm due to the photocolored species at 30 °C. Kinetic analysis exhibited a good fit to a first-order equation and two consecutive first-order decays $(k_1 \text{ and } k_2)$ of the photochrome, corresponding to two-step isomerization to the stable form (Fig. 5). Rate constants of thermal fading of the photochrome were measured to be $k_1 = 5.9 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 3.3 \times 10^{-4} \text{ s}^{-1}$ for **1@DCA**. DCA inclusion crystal of 2 (2@DCA) was similarly prepared to exhibit similar spectral change before and after UV irradiation. By monitoring the decay of absorption band at 484 nm at 30 °C, rate constants (k_1 and k_2) of thermal fading of the photochrome were measured to be



Fig. 4. Solid state reflectance spectra of 1@DCA before (full line) and after (dotted line) UV irradiation.



Fig. 5. Kinetic plot of optical density decrease for the photocolored species derived from 1@DCA.

 $k_1 = 4.8 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 5.1 \times 10^{-5} \text{ s}^{-1}$ for **2@DCA**. These results indicate that the thermal isomerization proceeds through an unimolecular reaction pathway without any side reaction. Such a photochromic behavior is similar to that of *N*-salicylideneaniline, suggesting that the photocoloration of **1@DCA** and **2@DCA** would be based on photo-induced intramolecular prototropic tautomerism of **1** and **2**. Since *N*-phenyl-2-aminotropone exists as an NH form in the ground state and prototropic tautomerism is influenced by electronic state of the molecule, the photocolored species is reasonably assigned to an OH form with some distortion.

At this stage, two-step fading process for the photochrome of 1@DCA and 2@DCA is not understood unambiguously. In the case of Schiff base, such a phenomenon has been explained by assuming the framework relaxation from two types of photochromes, cisketo-amine form and trans-keto-amine form, coexisting in a photocolored crystal [32,33]. As for the system in this study, however, isomerization from two types of photochromes like syn-imino OH form and anti-imino OH form is not probable to occur in a limited size of reaction room constructed by DCA molecules. In contrast with these aspects, we also have reported that photochromicity of Schiff base was very sensitive to the size of reaction room in the crystal [34–36]. Consequently, stability of photochrome depended on the circumstances of molecules under consideration in the crystal lattice containing solvent molecules [37-39]. Both 1@DCA and 2@DCA crystals include methanol molecules along with 1 and 2; thus, some coexisting pseudopolymorphic structure due to enclathrated methanol molecules in the crystal might be responsible in part for the two consecutive decays of photochrome. Since the reflectance spectra had a poor quality in the UV region, mainly due to the light scattering in the solid-state, the detail of molecular structure could not be determined from the spectra due to $\pi - \pi^*$ electronic excitation.

4. Conclusion

N-Phenyl-2-aminotropone exhibited photochromism only within the DCA inclusion environment. The photocoloration in this study was small; however, the change of color was repeatable without any side alteration and the degree of spectral change and the fading rate constants measured were intact for the repeated experiments. Thus, effectiveness of DCA clathrate method for preparation of new series of photochromic crystals was confirmed in this study and photochromic properties of tropolone families could be revealed for the first time. Further works on the mechanism of the photocoloration reaction and other chromotropic behavior of aminotropone derivatives are under investigation.

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