

SECOND HARMONIC GENERATION IN INCLUSION COMPLEXES

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ABSTRACT. Second harmonic generation(S.H.G.) in inclusion complexes between dimethyl β -cyclodextrin(dimethyl β -CD) and nitroaniline derivatives occurs. This is due to the destruction of the centrosymmetric crystal structure in nitroaniline derivatives caused by forming inclusion complexes. S.H.G. intensity of dimethyl β -CD complex with N-methyl-nitroaniline is 5.5 times as large as that of urea.

1. Introduction

Recently organic molecular crystals have been of particular interest due to their large optical nonlinearities and high optical damage threshold(1),(2). It was reported that aromatic molecules, possessing donor-acceptor pairs, exhibit very large optical nonlinearities (3). However, most aromatic molecular crystals, such as para nitroaniline (p-NA), possess a centrosymmetric crystal structure, which forbids second harmonic generation (S.H.G.) (4). Various methods have been proposed for overcoming this limitation including the addition of bulky substituents in an asymmetric manner (4), the introduction of chiral substituents (5) or ion pairs onto molecular crystals (6).

This paper describes a new method of removing crystalline centrosymmetric geometry in aromatic derivatives for S.H.G. by forming inclusion complexes between cyclodextrin and aromatic derivatives.

2. Preparation of inclusion complex

A method for destroying the centrosymmetric crystal structure is shown in Fig.1.

In this experiment, three nitroaniline derivatives, i.e. p-nitro-aniline(p-NA), 2-hydroxy-4-nitroaniline(HNA) and N-methyl-4-nitroaniline (NMNA), were chosen as guest molecules because of their large optical nonlinearity. As a host molecule, dimethyl β -cyclodextrin (dimethyl β -CD) was used. It is well known that dimethyl β -CD forms an inclusion complex with many kinds of aromatic derivatives.

Commercially available dimethyl β -CD and nitroaniline derivatives were employed as starting materials after purification by a recrystallization method.

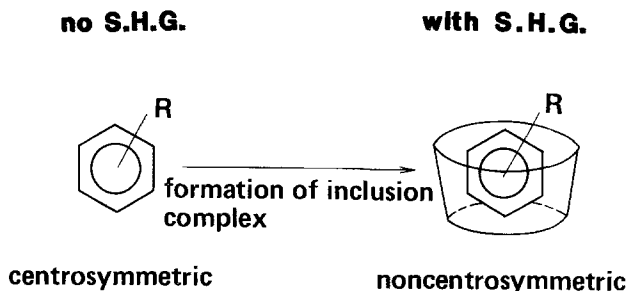


Figure 1. Destruction method of centrosymmetric crystal structure.

2.1. Formation of inclusion complex in H_2O

To investigate whether dimethyl β -CD can form inclusion complexes with nitroaniline derivatives, the dissociation constants (K) for p-NA, HNA and NMNA were measured by u.v. spectral titration (7). Figure 2 shows the u.v. spectra of p-NA in H_2O at $25^\circ C$ for various dimethyl β -CD concentrations.

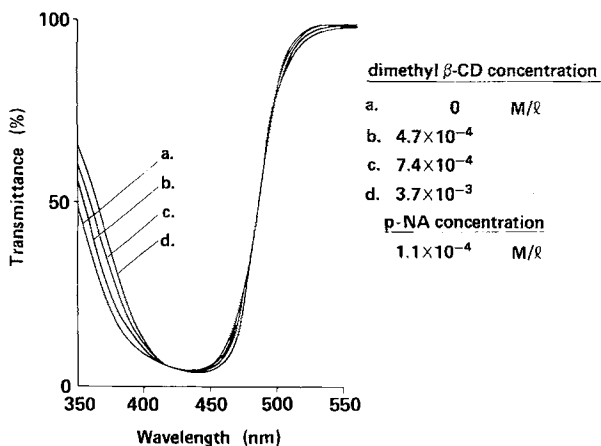


Figure 2. u.v. spectra of p-NA in H_2O at $25^\circ C$ for various dimethyl β -CD concentrations.

The absorption maxima of p-NA (λ_{max}) shifted to longer wavelength as dimethyl β -CD concentration increased. This means that dimethyl β -CD forms an inclusion complex with p-NA in H_2O . The dissociation constant (K) of the dimethyl β -CD complex with p-NA was estimated from the spectral shift of the absorption maxima on the basis of the Hildebrand and Bennesi relation (7). Inclusion complex with p-NA has a dissociation constant of $2.6 \times 10^{-4} \text{ mol}^{-1}$.

Estimated dissociation constants for three complexes used are listed in Table I. The dimethyl β -CD complexes with p-NA, HNA and NMNA are stable in H_2O solution because these constants are very small.

Table I Estimated dissociation constants (K) for the dimethyl β -CD complexes.

guest molecule	dissociation constant (K) /M ⁻¹
HNA	1.5×10^{-4}
p-NA	2.6×10^{-4}
NMNA	3.7×10^{-4}

2.2. Preparation of inclusion complex crystal

Fine crystals of dimethyl β -CD complex were precipitated from an aqueous solution containing dimethyl β -CD and nitroaniline derivatives with a 1:1 molar ratio. The solubility of the dimethyl β -CD complex became poor as the solution temperature increased. Using this property, crystals were precipitated by maintaining the temperature at 80°C (8).

The precipitated crystals were confirmed to be dimethyl β -CD complex by measuring X-ray diffraction and i.r. spectra. Figure 3 shows the X-ray diffraction patterns of the precipitated crystal made from dimethyl β -CD and p-NA(1:1) (pattern A) and physical mixture of dimethyl β -CD and p-NA(1:1) (pattern B). Neither of the X-ray diffraction peaks of dimethyl β -CD and p-NA shown in (B) is seen in the X-ray patterns of the precipitated crystal shown in (A). Therefore, the precipitated crystal is different from the physical mixture of crystals.

Figure 4 shows the i.r. spectrum of the precipitated crystal of (A). The precipitated crystal gives absorption peaks originating from dimethyl β -CD and p-NA. So the crystal is composed of them.

It can be concluded from these facts that the crystal is the inclusion complex between dimethyl β -CD and p-NA.

For the complexes of HNA and NMNA, the same conclusion was derived from X-ray diffraction and i.r. spectra.

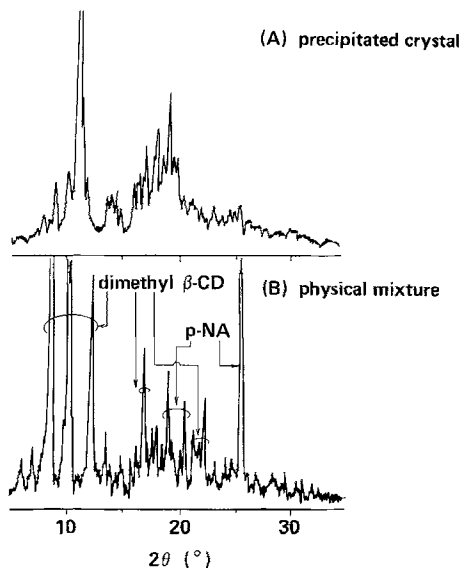


Figure 3. X-ray diffraction patterns of precipitated crystal and physical mixture.

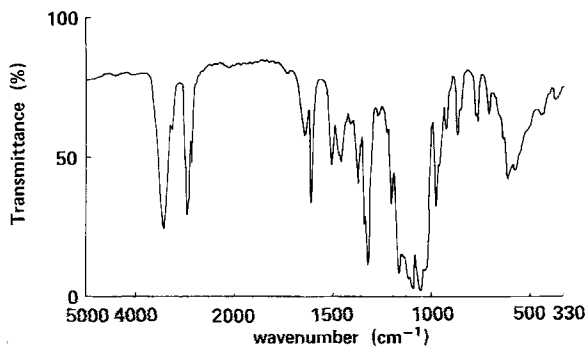


Figure 4. i.r. spectrum of dimethyl β -CD complex with p-NA.

3. S.H.G. intensity measurement of inclusion complexes

S.H.G. intensities in these dimethyl β -CD complex crystals were measured using the powder technique (9). Figure 5 shows experimental set up for S.H.G. measurement.

A Nd:YAG laser with a $1.064 \mu\text{m}$ wavelength was used as a pumping light source. Powder grain sizes of inclusion complexes were in the range of $105\text{--}125 \mu\text{m}$. Light emitted from the powder samples include both the pumping light and S.H.G. light with $0.532 \mu\text{m}$ wavelength. After eliminating the pumping light through i.r. filter, only S.H.G. light was detected.

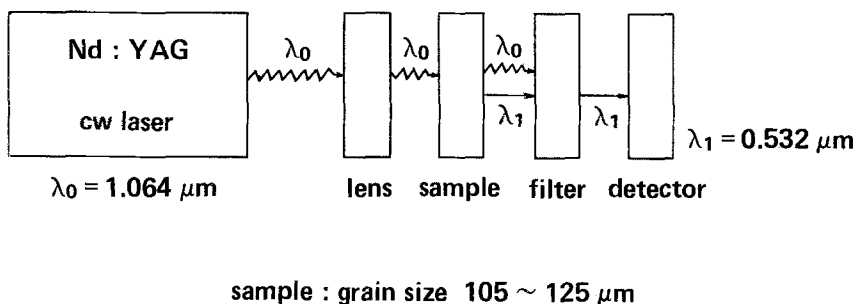


Figure 5. Scheme of S.H.G. measurement.

Table II lists the S.H.G. intensity ratio compared to urea for three nitroaniline derivatives and dimethyl β -CD.

Urea is usually used as a standard material. Although the S.H.G. intensity ratio of dimethyl β -CD and p-NA is below 0.1 and 0 respectively, the dimethyl β -CD complex with p-NA has a ratio of 4:1 compared to urea. This indicates that the formation of dimethyl β -CD complex destroys the centrosymmetric crystal structure.

Table II S.H.G. intensity ratio
(compared to urea)

compound	guest	complex
HNA	0	2
p-NA	0	4
MNMA	0	5.5
dimethyl β -CD	< 0.1	

The dimethyl β -CD complex with NMNA had the largest S.H.G. intensity, while the complex with HNA had the lowest among the three complexes. The optical nonlinearity of NMNA is larger than that of p-NA because of electron donation by the N-methylamino group. Conversely, the optical nonlinearity of HNA is less than that of p-NA owing to the presence of the hydroxy group, which is located at the neighbor position of the amino group and disturbs the intramolecular charge transfer between the NO_2 and NH_2 radicals (1).

Therefore, the intensity of the optical nonlinearity of the guest corresponds to S.H.G. intensity ratio of the complex. If organic molecules having larger optical nonlinearity can serve as a guest, inclusion complexes with larger S.H.G. intensity can be obtained.

4. Conclusion

A new method of destroying the centrosymmetric crystal structure which forbids second harmonic generation was demonstrated based on formation of inclusion complexes.

Since there is a wide variety of host and guest molecule combinations for inclusion complexes, the method demonstrated in this paper is effective in developing organic materials with large S.H.G..

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