JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 1
1983

Molecular Orientation of Naphthalene-1,4-diol in a β-Cyclodextrin Inclusion Complex

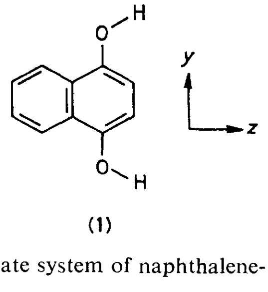
Masafumi Ata and Hiroyuki Yamaguchi*

Department of Chemistry, Faculty of Science, Kumamoto University, 2–39–1 Kurokami, Kumamoto 860, Japan

The assignment of the absorption band determined from the signs of the induced circular dichroism spectra of the β-cyclodextrin (β-CD) complex with naphthalene-1,4-diol (**1**) is compared with the assignment given by measuring the dichroic spectra of (**1**) in a stretched sheet of poly(vinyl alcohol), to conclude that (**1**) is oriented in the β-CD inclusion complex such that it is an axial inclusion.

It has been reported that the β-cyclodextrin (β-CD) complex with 2-methylnaphthalene-1,4-diol plays an important role in the synthetic pathways of vitamin K$_1$ or K$_2$.[1,2] Several authors have shown that from the signs of the induced circular dichroism (i.c.d.) spectra of β-CD complexes with guest molecules it is possible to determine the polarisation directions of the electronic transitions of the guest molecule included in the cavity of β-CD.[3–9] These investigations demonstrate that the i.c.d. spectra can provide very simply the directions of the transition moments of the guest molecule when its molecular orientation in the β-CD inclusion complex is known. Conversely information concerning this molecular orientation can be gathered from knowledge of the directions of the transition moments of the guest molecule.

We have investigated the assignment of the electronic absorption bands of (**1**) and are able to predict the molecular orientation of (**1**) in the β-CD inclusion complex from the i.c.d. spectra. The results are shown in Figure 2. There is both a positive and a negative i.c.d. curve in the region of the first absorption band (*ca.* 26.7—36.0 × 10^3 cm^{-1}). The signs of the i.c.d. spectra are positive in the 36.0—43.7 × 10^3 cm^{-1} region of the second absorption band and in the 43.7—50.0 × 10^3 cm^{-1} region of the third absorption band. A study on the basis of the Kirkwood–Tinoco coupled oscillator expression has indicated that the positive and negative signs in the i.c.d. spectra of the guest molecules axially included in β-CD are produced respectively by electronic transitions parallel to and perpendicular to the molecular axis of the β-CD.



(**1**)

Figure 1. Co-ordinate system of naphthalene-1,4-diol.

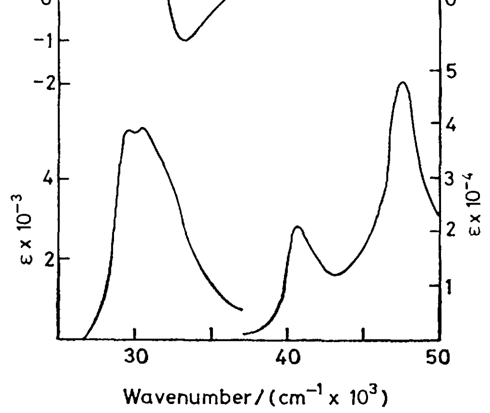


Figure 2. Induced circular dichroism (top) and absorption (bottom) spectra of the β-cyclodextrin complex with naphthalene-1,4-diol in aqueous solution. The concentration of β-cyclodextrin in distilled water was 1.20 × 10^{-2} M. The i.c.d. measurements were made on deaerated solutions in which the concentration of naphthalene-1,4-diol ranged from 2.97 × 10^{-4} to 2.30 × 10^{-5} M. All measurements were made at room temperature.

From theoretical considerations it can be seen that the first absorption band is composed of two (first and second) electronic transitions with the first transition moment parallel to the z axis and the second parallel to the y axis of (**1**). The second and third absorption bands contain transitions having polarisations parallel to the z axis of (**1**). Our assignment for the first band is in complete accord with the assignment given by measuring the dichroic spectra in a stretched sheet of poly(vinyl alcohol).[10] The dichroic spectra indicate that two (the third and fourth) electronic transitions with different polarisations lie close together in the second band. It would be expected that the fourth electronic transition would inherently have a negative i.c.d. value. An apparent reduction of the negative i.c.d. value of the fourth transition may occur owing to overlap-cancellation by the third and fifth transitions (both transitions show positive i.c.d. values as shown in Figure 2), so that the negative i.c.d. curve does not appear in the i.c.d. spectra of the second band. A semi-empirical SCF–MO–CI calculation has predicted that fifth and sixth electronic transitions with different polarisations exist in the third absorption band.[10] As the computed intensity of the sixth electronic transition is very weak,[10] we are unable to observe the negative i.c.d. curve of the sixth transition on the high-energy side of the third absorption band.

As described above, it can be concluded from the general agreement between the assignment determined from the signs of the i.c.d. spectra of the β-CD complex with (**1**) and the assignment determined by means of the dichroic spectra of (**1**) in a stretched sheet of poly(vinyl alcohol)[10] that the molecular orientation of (**1**) in the β-CD inclusion complex is axial.

Received, 1st October 1982; Com. 1159

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