

INDUCED CIRCULAR DICHRISM SPECTRA OF CYCLOBUTA[1,2-*b*:3,4-*b'*]-
DIQUINOXALINE

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ABSTRACT. The induced circular dichroism (i.c.d.) and absorption spectra of the β -cyclodextrin (β -c.d.) complex with cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline (I) have been measured. The linear dichroism (l.d.) spectra of I in stretched polyethylene sheet have been also measured. The absorption bands of I have been assigned by using the observed spectra and the results of CNDO/S CI calculations. The i.c.d. spectra of the first absorption band have shown the Cotton-effect at high concentrations. This fact indicates that the β -c.d. complex with I forms dimers at high concentrations.

1. INTRODUCTION

Several authors have shown that from the signs of the induced circular dichroism (i.c.d.) spectra of β -cyclodextrin (β -c.d.) 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 -c.d. (refs. 1-4). These investigations show 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 -c.d. inclusion complex is known. Conversely information concerning this molecular orientation can be obtained from knowledge of the directions of the transition moments of the guest molecule. The main aim of this paper is to assign the electronic absorption bands of cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline (I) and to predict the molecular orientation of I in the β -c.d. inclusion complex from the l.d. spectra. The concentration

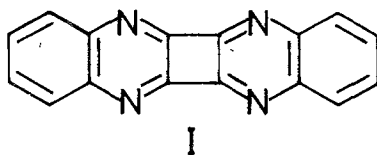


Figure 1. The structure of cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline.

dependence of the i.c.d. spectra of the β -c.d. inclusion complex has been also investigated. The structure of I is shown in Figure 1.

2. EXPERIMENTAL

The compound I was received from Professor S. Hünig of Würzburg Universität. The compound I was recrystallized from cyclohexane five times. Commercially available β -c.d. was recrystallized four times from aqueous solution. The solvents used were of spectroscopic grade.

The i.c.d. and absorption spectra were measured at room temperature using a Jasco J-500C circular dichrograph with a J-DP 501N data-processor and a Hitachi 200-20 recording spectrophotometer. Stoppered silica cells of 5.0 and 10.0 cm path lengths were used. The concentration of β -c.d. was adjusted to 0.01 M throughout the i.c.d. measurement. The l.d. in stretched polyethylene sheet was measured at *ca.* -140 °C with a Hitachi 200-20 recording spectrophotometer equipped with a rotatable polarized sheet. Polyethylene sheets were prepared in the usual way with chloroform solution of the solute for swelling (refs. 5-7). A single sheet *ca.* 0.1 cm thick was suitable for all spectral regions. The reduction factors for the short and long axes were 0.28 and 1.0, respectively. A molecular model indicated that the cross-section of I parallel to the long axis was larger than that perpendicular to the long axis, so that the long axis should be the axis of molecular orientation.

3. MOLECULAR ORBITAL CALCULATIONS

The transition energies, oscillator strengths (*f*) and polarisation directions were predicted by the CNDO/S CI method (ref. 8). 82 singly excited configurations with an energy < 98.0 kK (kilo Kaiser) and 45 doubly excited configurations having an energy < 118.0 kK were included in the configuration interaction treatment. The known bond lengths and bond angles for quinoxaline and the four-membered ring of biphenylene were used in the calculations on I.

4. RESULTS AND DISCUSSION

The absorption and l.d. spectra are shown in Figure 2, where the i.c.d. spectra of the β -c.d. complex with I are also shown. As the polaroid sheet exhibits an absorption band at wavenumbers > 45.0 kK, we cannot observe the l.d. spectra at wavenumbers > 45.0 kK. The CNDO/S CI calculations show that the first absorption band [(20.0-27.5) kK] of I consists of two $\pi \rightarrow \pi^*$ electronic transitions computed at 25.3 and 31.6 kK (one is a very strong transition (*f* = 0.53) polarized along the long axis and the other is forbidden) and two $n \rightarrow \pi^*$ electronic transitions predicted at 26.1 and 29.5 kK (one is forbidden and the other is a very weak transition polarized out-of-plane). These $n \rightarrow \pi^*$ transitions are probably too weak to be observed. As it seems that the β -c.d.

complex with I makes an axial inclusion complex, the positive i.c.d. spectra of this band mean that it consists of electronic transitions polarized along the long axis. This assignment is confirmed from the l.d. spectra of the band. The negative peak in the i.c.d. spectra at 30.0 kK supports that there is an electronic transition with polarisa-

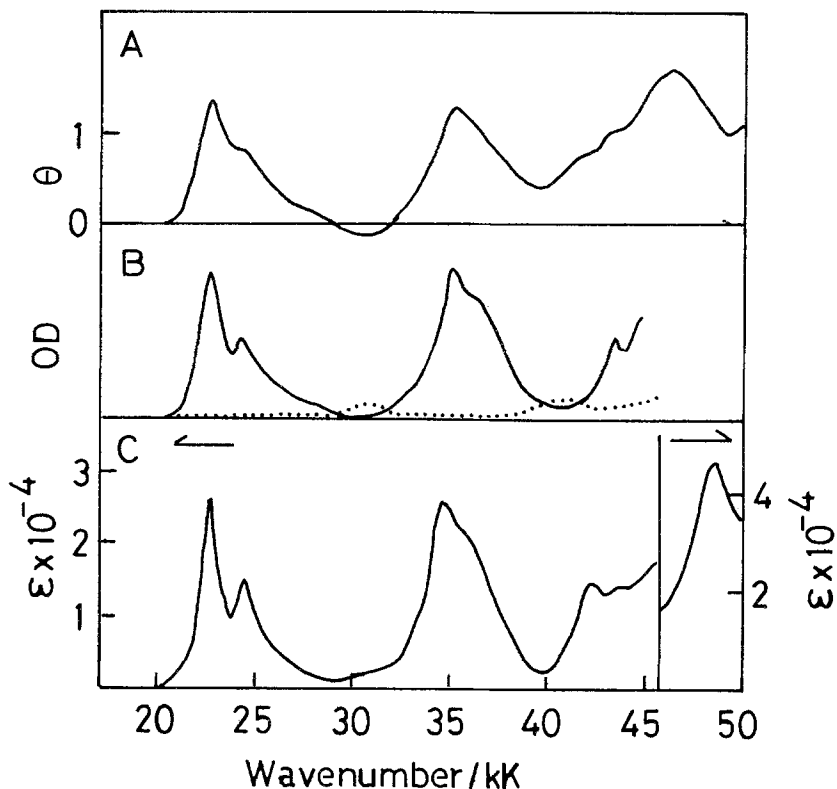


Figure 2. The i.c.d. spectrum (A) of the β -c.d. inclusion complex. The linear dichroism spectrum (B) (full line, polarized along the long axis; dotted line, polarized along the short axis) at -140°C . The electronic spectrum (C) at room temperature in cyclohexane.

tion direction parallel to the short axis at 30.0 kK. The l.d. spectra, like the i.c.d. spectra, also show that a weak electronic transition polarized along the short axis exists at 30.0 kK. The electronic transition corresponds to the $\pi \rightarrow \pi^*$ electronic transition ($f = 0.04$) predicted at 32.5 kK. Table I shows that there are three $\pi \rightarrow \pi^*$ forbidden transitions at 33.8, 34.2 and 37.0 kK. These transitions are probably too weak to appear in the electronic absorption spectra. The l.d. and i.c.d. spectra reveal that the strong transition parallel to the long axis exists at 34.6 kK. This transition corresponds to the ninth electronic transition predicted at 38.3 kK ($f = 0.71$). The l.d. spectra

indicate that there is a weak transition with polarisation direction parallel to the short axis at 40.0 kK. It seems that this transition corresponds to the tenth electronic transition computed at 41.9 kK ($f = 0.01$). The l.d. and i.c.d. spectra indicate that there is at least an electronic transition polarized along the long axis in the wavenumber region (40.0-47.0) kK. The CNDO/S CI calculations show that the twelfth transition computed at 44.6 kK ($f = 0.32$) exists in this region. It may be thought that there are two (eleventh and thirteenth) $\pi \rightarrow \pi^*$ forbidden transitions predicted at 42.6 and 44.7 kK in this spectral region. As mentioned 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 -c.d. complex with I and the assignment determined by means of the l.d. spectra that the molecular orientation of I in the β -c.d. inclusion complex is axial. The CNDO/S CI calculations are in good agreement with the experimental results.

TABLE I. Transition energies (ΔE) and intensities (f)

Theoretical			Experimental	
$\Delta E/\text{kK}$	Polarisation ^a	f	$\Delta E/\text{kK}$	$\log \epsilon$
25.3	l	0.53	22.6	4.46
26.1	$n \rightarrow \pi^*$	forbidden		
29.5	out-of-plane			
31.6		forbidden		
32.5	s	0.04	30.0	
33.8		forbidden		
34.2		forbidden		
37.0		forbidden		
38.3	l	0.71	34.6 ^b	
41.9	s	0.01	40.0 ^b	
42.6		forbidden		
44.6	l	0.32	42.0	4.18
44.7		forbidden		

^a The l and s denote the long and short axes, respectively.

^b Obtained from the linear dichroism spectrum.

Figure 3 shows that the i.c.d. and absorption spectra depend upon the concentration of the β -c.d. complex with I. The i.c.d. spectra exhibit the positive peak around 22.0 kK in the case of low concentrations, while they generate the Cotton effect around 22.0 kK in the case of high concentrations. It is very interesting that the Cotton effect closely resembles that of dye-polypeptide system (refs. 9,10). Since the Cotton effect observed for dye-polypeptide system arises from dimeric dye bound to polypeptide, the i.c.d. band observed at high concentrations is attributed to a dimeric form of inclusion complexes. Examina-

tion of molecular model suggests that the β -c.d. cavity is too small to accommodate two molecules of I. A continuous variation diagram of the ellipticity change at 22.5 kK has indicated 1:1 complex formation. The results are shown in Figure 4. Furthermore, in the case of low concentrations, the continuous variation curve of the ellipticity change at 22.0 kK has shown a distinct maximum for equal concentrations of β -c.d. and I, characteristic of a 1:1 complex. The i.c.d. spectrum in Figure 3 (dotted line, 20-25 kK) clearly indicates that two β -c.d.-I complexes make a dimer at high concentrations with *S*-helicity (ref. 11). From

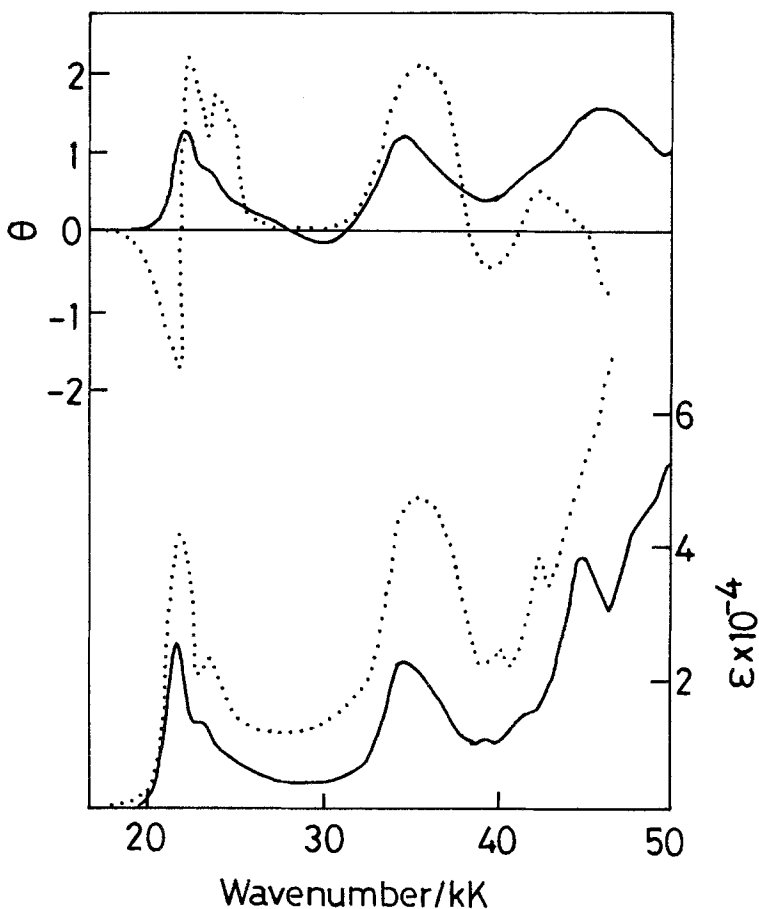


Figure 3. The induced circular dichroism (top) and electronic (bottom) spectra of the β -cyclodextrin complex with I (full line, 0.00000267 M; dotted line, 0.0000302 M).

these facts, it can be concluded that the compound I capped with β -c.d. is dimerized into dimers in a head-to-head mode through the uncapped part of I at high concentrations (see Figure 5).

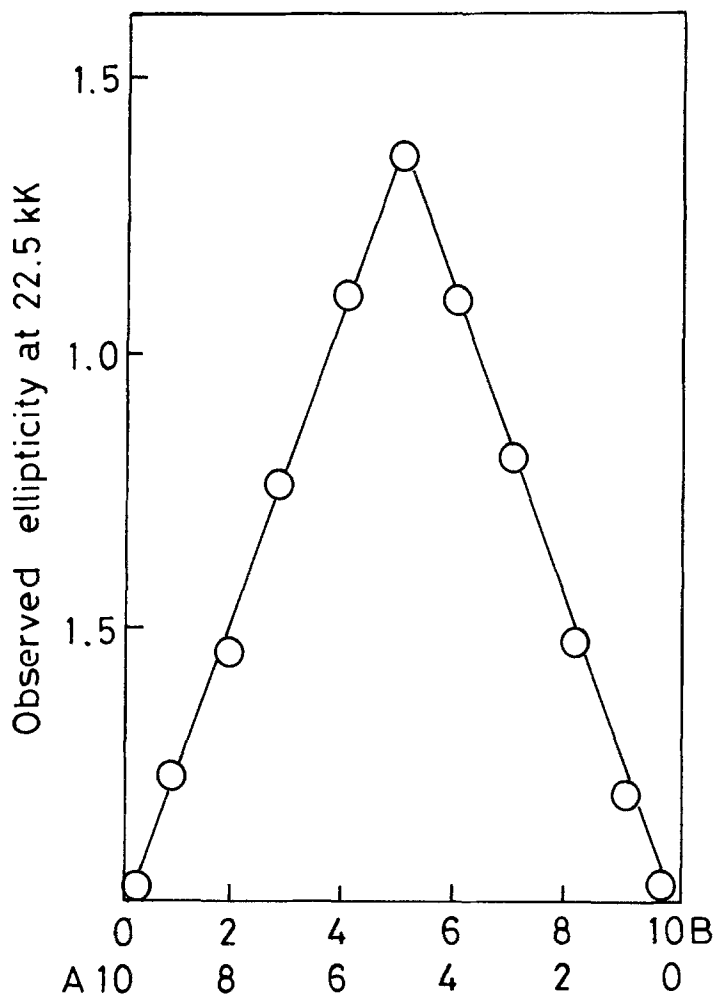


Figure 4. The continuous variation plots for β -cyclodextrin (A)-cyclobuta[1,2-*b*:3,4-*b'*]diquinoxaline (B).

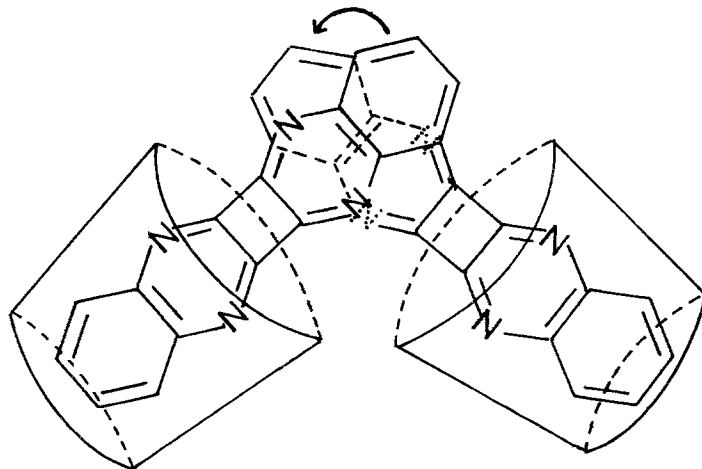


Figure 5. Model for dimer formation.

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