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Morphology and induced circular dichroism spectra on the aggregation of a cyclodextrin complex with an azo dye

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Orange II (*I*) is easily soluble in H_2O. It requires several months for the formation of needle-like crystals from a 0.16 M (saturated) aqueous solution. But when 0.03 M γ-cyclodextrin (γ-CD) is added to an equivalent of (*I*) at RT, the solution exhibits enhancement of the viscosity in an hour, and the microscopic viewing indicates the formation of a *pine needle-like aggregate.* Enough old millet jelly-like one shows well arranged stripe pattern upon rubbing. In the induced c.d. spectrum, the $\pi \rightarrow \pi^*$ band of this complex appears at ~500 nm in the solution state, but in the aggregate state, it changes to the *J-band due to the head-to-tail stacking of (I) and the H-band due to* parallel stacking. When MeOH is poured onto the aggregate, the latter changes colour from orange to silver-gray, but keeps the same shape. The driving force for the aggregate formation may be

(1) van der Walls contact between γ-CD and two molecules of (*I*),
(2) π-π interaction between the two molecules of (*I*) in γ-CD,
(3) H-bonding and stacking effects between γ-CD.

In this chiral aggregate, γ-CD works as an adhesive for the azo dye.

INTRODUCTION

Cyclodextrins (CD) work sometimes as a deaggregating agents[1-3] and sometimes as aggregating agents.[4] As the former example, 2-OH-propyl-β-CD suppresses the self-assembling of an insulin solution by metal ion.[1] As the latter example, self-assembling metal rotaxane complexes of α-CD are reported.[4]

Phenylthio- and phenylsulphilthio β-CD are rare examples which demonstrate the ability to form helical polymers by repetition of this intermolecular inclusion; they work simultaneously as both guest and host molecules and the hydrophilic benzenesulfonate group is intermolecularly included in the CD cavity of another molecule. The packing state of the above CD complexes is proved from X-ray crystallographic data.[5]

Previously, in the course of a spectroscopic investigation of CD complexes with azo dyes, it was found that γ-CD and orange II [*p*-(2-hydroxy-1-naphthylazo)-benzenesulfonic acid sodium salt (*I*)] form an aggregate.[6]

In this paper, characterization of this aggregate and the driving force for aggregation were investigated by microscopic viewing and c.d. spectra.

RESULTS AND DISCUSSION

Polarized microscopic observation

Photos 1 and 2 are needle- and pine needle-like crystals of (*I*) obtained from a 0.16 M (saturated) aqueous solution. It takes several months to get such crystals. But if 0.03 M γ-CD is added to an equivalent of (*I*), the solution causes enhancement of the viscosity in an hour. A shape becomes vague and a pine needle-like aggregate appears (Photos 3, 4). With this time it becomes long and wide in texture, but keeps this phase for several years (Photo 5). When one old enough is rubbed by a cover glass, a well arranged stripe texture appears (Photo 6). The width of the stripe is 15 ~ 18 μm. The texture dried by the incident light of a microscope often shows a partially well arranged rod-like pattern (Photo 7).

When the aggregate is dropped into a MeOH solution by pipette, it changes colour from orange to silver-gray (Photo 8). EtOH works similarly, but slower. *n*-PrOH does not work to the aggregate. In all cases, the aggregate keeps its original shape, but the silver-grayish one becomes more fragile and slimer. On raising the temperature above 60 °C, a phase transition was observed and the whole view becomes dark. DSC measurements also show a small endothermic peak at 60 °C (0.03 mcal/s).

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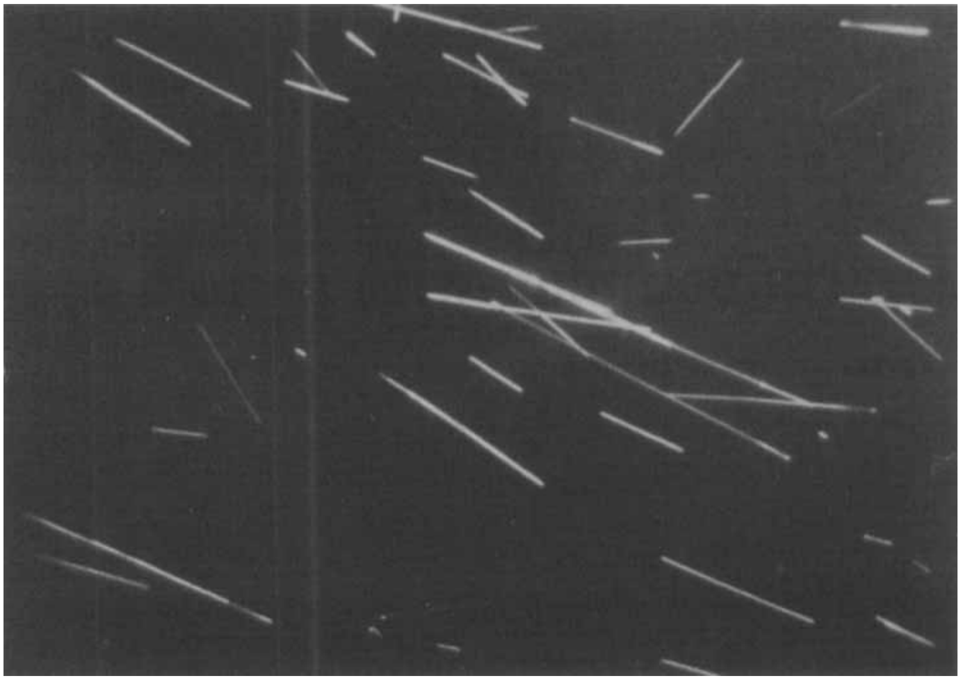

Photo 1 Needle-like crystal of orange II (the length of the longest needle is 0.7 mm). (See color plate at the back of this issue.)

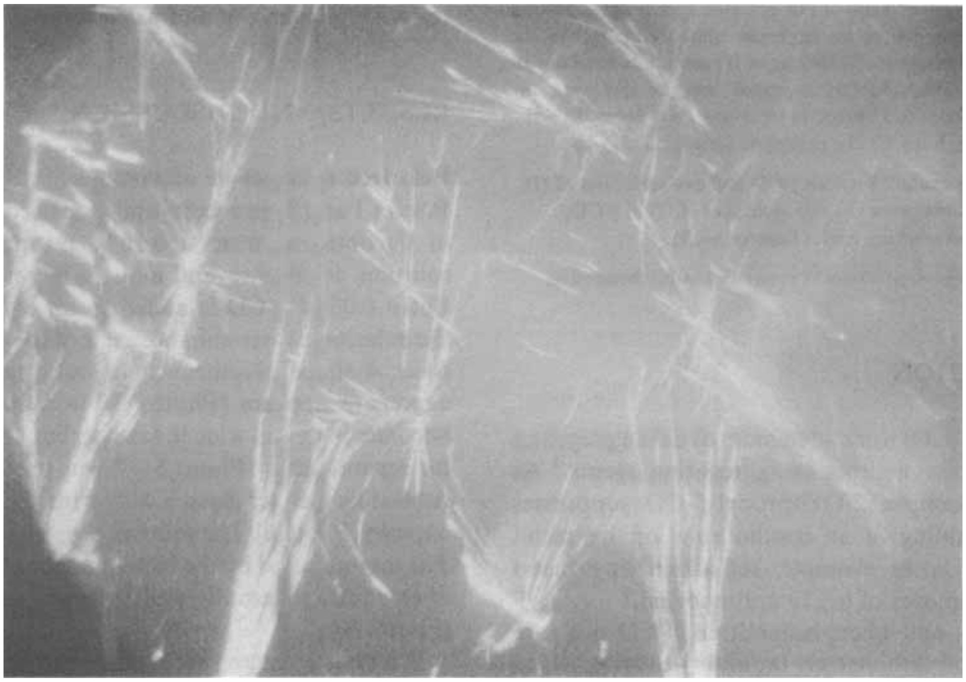

Photo 2 Pine needle-like crystals of orange II (rubbed a saturated solution by cover glass). (See color plate at the back of this issue.)

C.d. spectra

(*I*) has a length of 13 Å and a width of 6 Å. In neutral solution, it exists in a tautomeric equilibrium between the azo and hydrazone forms, and the latter form predominates. Each transition state in the absorption spectrum was assigned according to Popove;[7] the ^1B_b and ^1L_a transitions are 229 and 260 nm, respectively, which are aligned at angles of 11° and 93° with the long axis of the naphthalene nucleus. The band at 486 nm should be assigned to a charge transfer which forms an angle of 60° with the above axis. The longest conjugated chain in the molecule passes approximately through the sulfonate group and the more distant ring of the naphthalene residue.

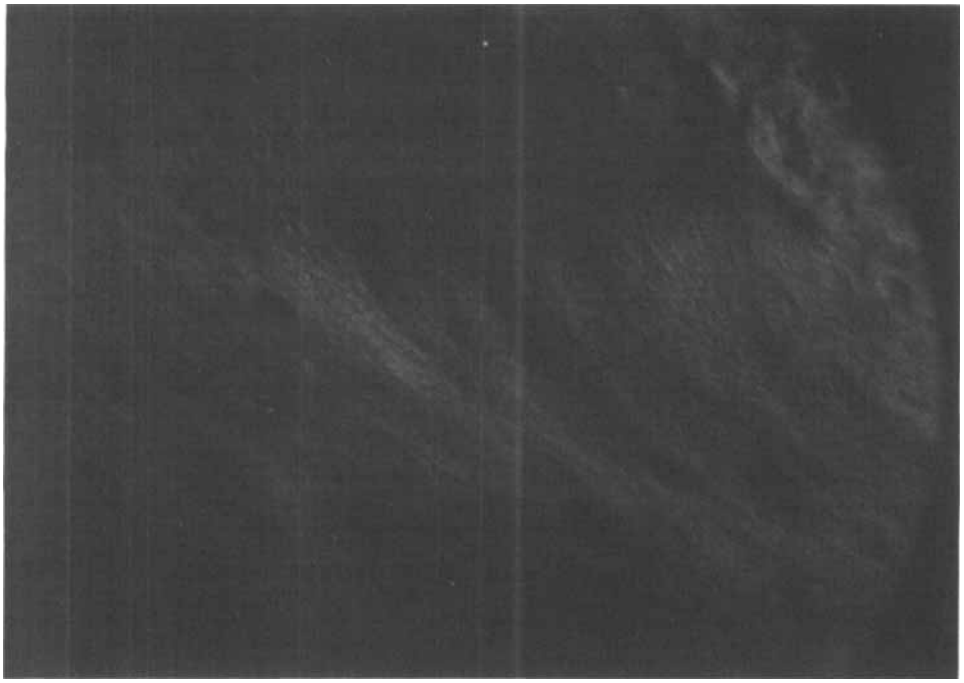

Photo 3 Several hours elapsed after adding γ-CD. (See color plate at the back of this issue.)

Photo 4 Several days elapsed after adding γ-CD. (See color plate at the back of this issue.)

Generally, the c.d. spectral pattern of the ^1B_b transition changes in sign according to the inclusion mode of the guest molecules.[8] For example, the above positive spectral pattern of (*I*)-β-CD and (*I*)-DM-β-CD complexes indicates that the naphthalene nucleus is included axially, but in the present (*I*)-γ-CD complex, this spectral peak cannot be detected due to the limitation induced by the photomultiplier voltage[9] (Fig 1).

The spectral pattern of the above transition in the γ-CD complexes with the analogous azo dyes which have a higher conjugated structure shows splitting,[9] so in the γ-CD series the ^1B_b transition cannot give information about the direction of inclusion. The

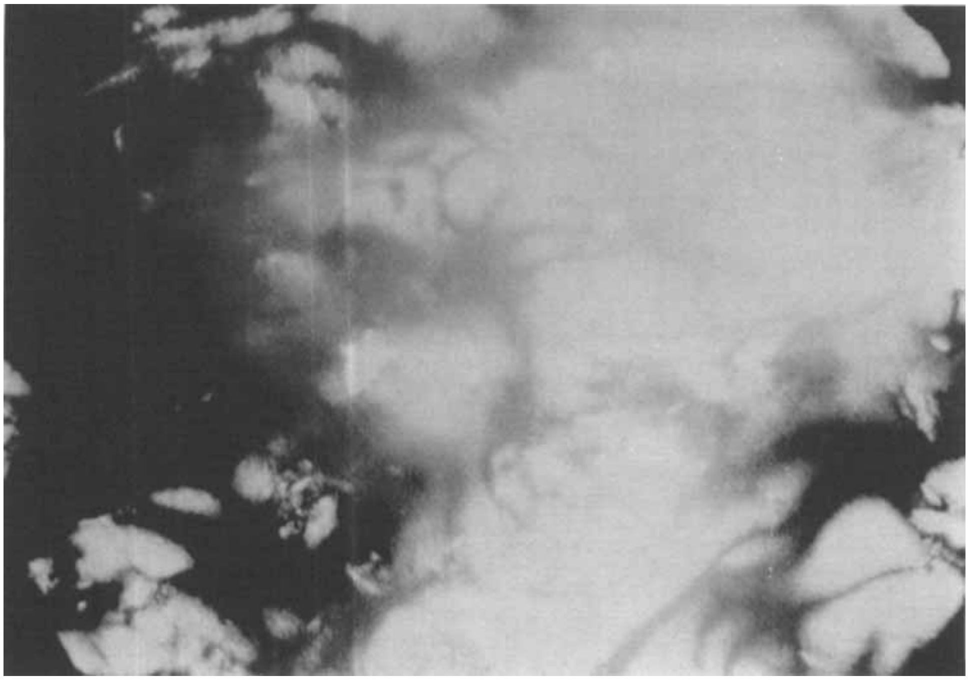

Photo 5 More than one year elapsed after adding γ-CD. (See color plate at the back of this issue.)

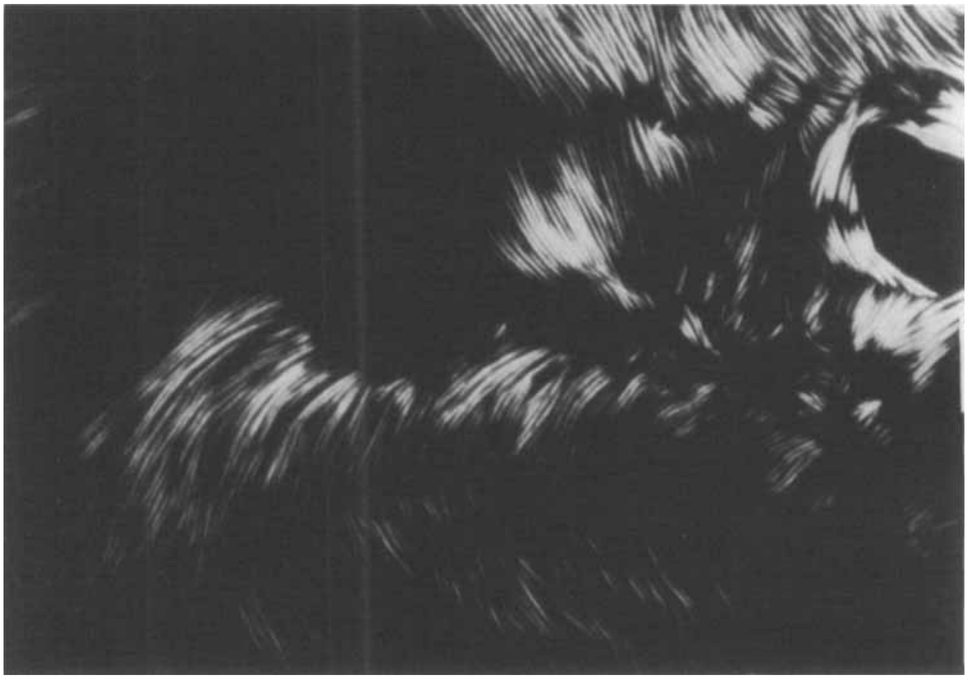

Photo 6 Texture when rubbed by cover glass. (See color plate at the back of this issue.)

existence of the naphthalene nuclei of the two molecules in one γ-CD may disturb the information about the orientation. The aggregate formation in the (*I*)-γ-CD complex may establish equatorial inclusion.

In the c.d. spectrum of a dilute solution, the π-π^* band shows negative splitting chirality and the $\Delta\varepsilon$ values of both extrema are unequal. This phenomenon is due to the exciton splitting and probes the mutual interaction between two molecules of (*I*) in γ-CD;[10] the two molecules of (*I*) must be incorporated from the long axis side with some crossing.[9]

The millet jelly-like aggregate grows in the concentrated solution (Photo 5). When it is put into a cell of 100 μm thickness, the $\pi \rightarrow \pi^*$ band at ~500 nm observed in

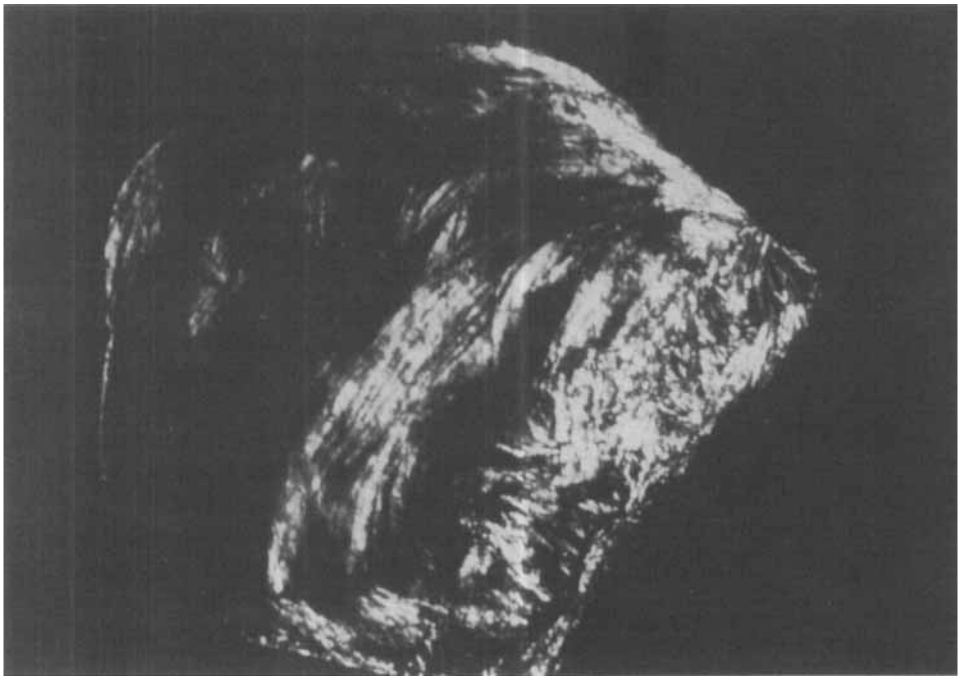

Photo 7 Aggregate dried by the incident light of the microscope. (See color plate at the back of this issue.)

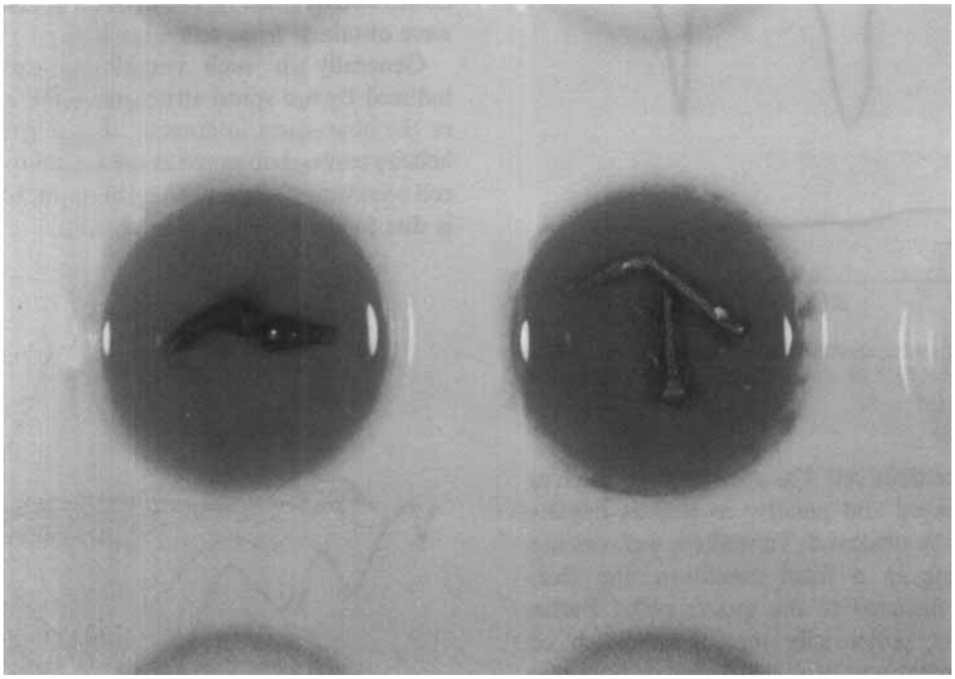

Photo 8 MeOH added (right); EtOH added (left); several days elapsed. (See color plate at the back of this issue.)

the solution state is replaced by ~547 nm and ~353 nm, respectively (Fig 2). The former is the J-band due to the head-to-tail[11,12] stacking of (*I*) and the latter is the H-band due to parallel stacking.[13-15] Those signals may not be due to the absorption of light by the individual molecule, but due to the molecular arrangement; in the chiral host aggregate the azo molecules appear to create intermolecular interactions and produce large ellipticities, because the aggregate can be oriented at a wall of the thin cell. The same pattern appears in liquid crystal polymers.[16] The visible spectrum shows only the clinic points at the corresponding regions.

The aggregate is apt to move due to perturbation

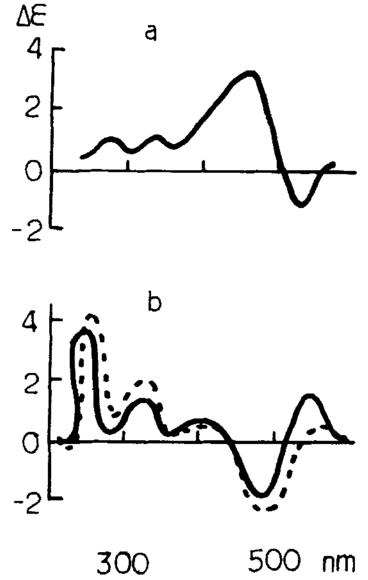

Figure 1 C.d. spectra in the solution state: (a) orange II-γ-CD; (b) orange II-β-CD ——; orange II-DM-β-CD ---. (Orange II 2×10^{-4} M and γ-CD 10^{-3} M in 0.1 M phosphate buffer at pH 6.0).

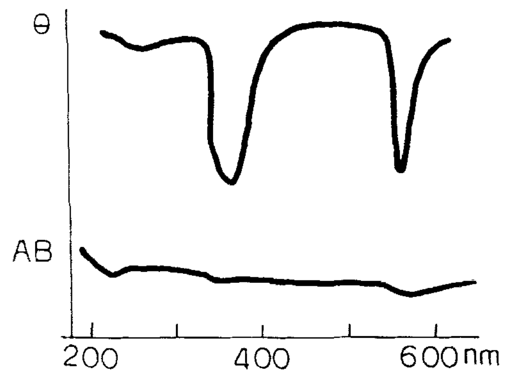

Figure 2 C.d. and visible spectra of an old aggregate in a 100 μm cell. (Orange II 4.6×10^{-2} M and γ-CD 10^{-1} M; 11 hours after sampling).

when filled in the thick cell. The apparent c.d. spectrum is seriously affected and positive as well as negative deflections can be observed. To make a well-oriented longer aggregate in a fixed condition, the chiral aggregate was fastened to the quartz plate. Putting the enough old millet jelly into a sandwich cell (< 50 nm thickness), and rubbing the upper glass plate in the transverse direction, the change of the c.d. spectrum with the time elapsed was measured (Fig 3 and Photo 6).

θ of the jelly measured 11 hours after sampling is nearly the same as that in the solution and the J-band cannot be perceived (Fig 3 (1) and (2)). No appreciable change could be detected when the cell was rotated around the light beam (Fig 3 (2)). With the elapse of time, the band in the $\pi \rightarrow \pi^*$ region moves to shorter wavelength, promotes the θ values, which at 430 nm finally reaches forty times larger than that of the c.d. spectrum in the solution (Fig 3 (4)). A spectral change could be produced by turning the cell carefully in the plane perpendicular to an incident light beam (Fig 3 (6)), although reproducibility is not so good. The aggregate contains an anisotropic part; this c.d. spectrum contains the linear dichroism related to an increase in θ as (*I*) in the aggregate is arranged by rubbing.[16,17]

Chart I suggests the scheme of the formation of the aggregate. (*I*) is included quickly, but loosely-fitted into the cavity of γ-CD as the 1:1 complex ($K_1 = 4.18 \times 10^2$ dm^3 mol^{-1}). The second (*I*) is included slowly but fastened into the same cavity and forms the 2:1 complex ($K_2 = 1.68 \times 10^6$ dm^3 mol^{-1}). The exposed part of the second (*I*) is included quickly into the cavity of the second γ-CD and forms the 2:2 complex ($K_3 = 1.77 \times 10^2$ dm^3 mol^{-1}). The benzenesulfonate part which is the exposed portion of the first (*I*) is included into the cavity of the third γ-CD which already forms the 1:1 complex, and forms the 3:3 complex.... The aggregation expands not only in the direction of the symmetry axis of the CD, but also in the other two dimensions (Photo 7). The above association constants were obtained from reference 18.

Generally in such complexes, c.d. spectra are induced by the spiral structure of the guest molecule or the host–guest interaction. In the present case, the helicity reversal observed at the mutually perpendicular cell orientation suggests that this induced c.d. spectrum is due to the host–guest interaction.

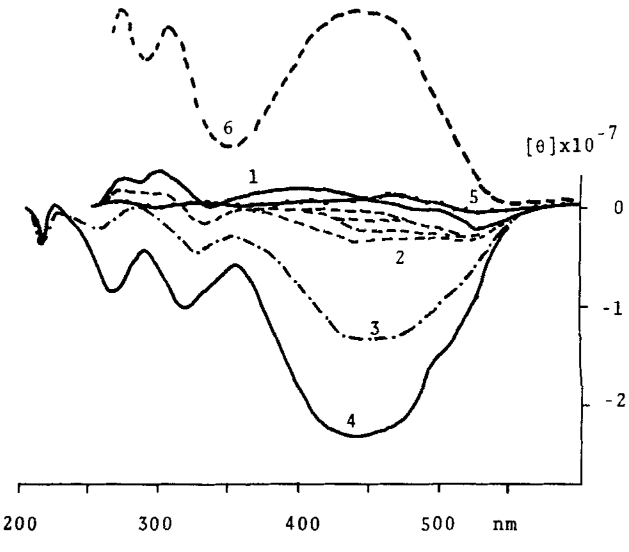

Figure 3 C.d. spectra of the aggregate in the sandwich cell (orange II 2×10^{-2} M and γ-CD 4.8×10^{-2} M); (1) 30 min. after sampling at the cell; (2) 1 day; (3) 2 days; (4) 5 days; (5) solution of orange II 2×10^{-4} M and γ-CD 2×10^{-3} M (0.5 cm thickness); (6) turning the cell in the plane perpendicular to the incident light beam.

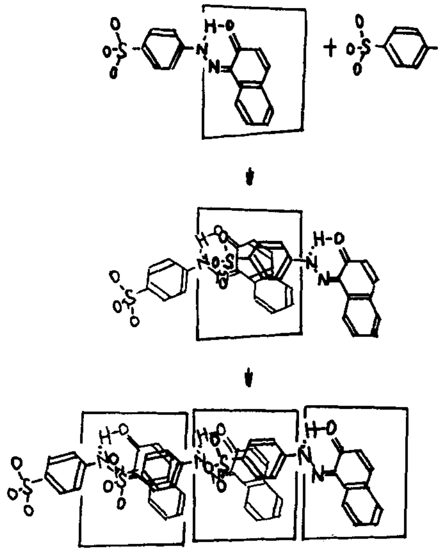

Chart I Assumed scheme of the aggregate formation.

Driving force for aggregation

1. (*I*) is apt to form dimers even in the dilute solution.[19] Complexation with γ-CD increases the ability to form the dimer by about 1000 times.[18] The complexation may help to increase the molecular length of the guest molecule and the cavity of γ-CD may fit best to include both the naphthalene nucleus of the first (*I*) and the benzene nucleus of the second (*I*). ^{1}H NMR proves the above suggestion; the γ-CD complex displays a larger ring current effect of the aromatic ring compared to the β-CD complex which cannot form an aggregate, especially at the benzenesulfonate side of (*I*).[20]

2. The aggregate extrudes the guest molecule (*I*) upon addition of MeOH, but keeps the original shape (Photo 8). This fact suggests that γ-CD also works to form aggregates by H-bonding and parallel stacking.

3. DSC measurements indicate that an endothermic peak at 60 °C is small (0.034 mcal/s). At this temperature, the driving forces to form the aggregate are supposed to disappear and give an isotropic homogeneous liquid. The aggregate holds together by fragile driving forces.

In conclusion, the aggregate is a molecular assemblage of γ-CD linked by inclusion of (*I*). In other words, γ-CD works as an adhesive and helps (*I*) to assemble.

MATERIALS AND METHODS

(*I*) was a standard sample distributed by the National Institute of Hygienic Sciences. γ-CD of guaranteed grade was purchased from Nakarai Ltd. and was dried over P_2O_5 in vacuo.

Polarized microscopic observations were carried out at room temperature on a Nikon microscope at 60 × magnification.

C.d. spectra in the solution state were measured with a Roussel-Jouan dichrographe No. III (Jobin-Yvon) using a 0.5 cm cell. 2×10^{-3} M host molecule and 2×10^{-4} M guest molecule were dissolved in 0.1 M phosphate buffer at pH 6.0.[9] C.d. spectra of the aggregate were measured with a Nihon Bunko ORD/UV-5 spectropolarimeter with a c.d. attachment using a 0.1 mm cell and a sandwich cell. (*I*) and γ-CD form 2:1 and 2:2 complexes in the solution state.[18,21]

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