Carbohydrate Research, 192 (1989) 147–157
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPLEXATION OF AROMATIC CARBOXYLIC ACIDS WITH HEPTAKIS(2,6-DI-*O*-METHYL)CYCLOMALTOHEPTAOSE IN CHLOROFORM AND WATER

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(Received December 22nd, 1988; accepted for publication, March 14th, 1989)

ABSTRACT

Complexation of various aromatic carboxylic acids with heptakis(2,6-di-*O*-methyl)cyclomaltoheptaose (DM-βCD) in chloroform and water has been studied by u.v. absorption, induced c.d., and n.m.r. spectroscopy. The inclusion complex of dimethylaminobenzoic acid is axial in water but equatorial or lid-type in chloroform, that of anthracene-9-carboxylic acid is axial in water and equatorial in chloroform, that of pyrene-1-carboxlic acid is lid-type in water at pH 9.0, and that of ferrocenecarboxylic acid depends on the dissociation of the carboxyl group.

INTRODUCTION

The inclusion complexes of cyclomalto-oligosaccharides (cyclodextrins, CDs) with aromatic molecules have been studied by u.v. absorption, induced c.d.[1], fluorescence[2], and n.m.r. spectroscopy[3]. The accuracy of induced c.d. for determining the orientation of aromatic guest molecules in 1:1 complexes has been confirmed severally[1], and so-called axial[1], equatorial[1b], and lid-type[4] inclusion complexes are known. The type and stoichiometry of inclusion depend on the type of aromatic molecules and the CD. For example, cyclomaltoheptaose (βCD) forms only 1:1 axial inclusion complexes with *p*-disubstituted benzenes[1a], most naphthalenes[1b,d,e], anthracenes[1d,f,g], or pyrene[1d,2c] in water. Although *N,N*-dimethylformamide[1d], methyl sulfoxide[5], ethylene glycol[1d], *etc.* have been employed as solvents in addition to water, this behaviour has been thought to hold for many solvents. On the other hand, mainly non-modified CDs have been used especially in studies of induced c.d. The availability[6] of di- and tri-*O*-methyl derivatives of CDs has enabled such hydrophobic solvents as benzene and chloroform[7] to be used. However, to our knowledge, no studies of induced c.d. have been reported hitherto on host–guest complexes using di- or tri-*O*-methyl CDs. 2,6-Di-*O*-methyl CDs are not only soluble in many common organic solvents, but are also more soluble than non-modified CDs in water[8].

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0008-6215/89/$ 03.50

We now report on the induced c.d. spectra of water- and chloroform-soluble aromatic molecules in the presence of heptakis(2,6-di-*O*-methyl)-βCD (DM-βCD).

EXPERIMENTAL

General. — *p*-Dimethylaminobenzoic acid (DMBA), anthracene-9-carboxylic acid (A9C), ferrocenecarboxylic acid (FCA), and *p*-phenylazobenzoic acid (PAC) were recrystallized from benzene, ethanol, hexane, and acetic acid, respectively. Pyrene-1-carboxylic acid (PYC), obtained from pyrene-1-carboxaldehyde by oxidation with Ag_2O in ethanol–2M NaOH (10:1) followed by acidification with dilute HCl and subsequent recrystallization from ethanol, had m.p. 267.5° (Found: C, 82.63; H, 4.05. $C_{17}H_{10}O_2$ calc.: C, 82.91; H, 4.09%). The sodium salt (PYNa) of PYC used for studies of induced c.d. in chlolesteric mesophase was prepared from PYC and an equimolar amount of NaOH in methanol. Anthracene-1-carboxylic acid (A1C), prepared from 1-chloroanthraquinone by reaction with CuCN in *N,N*-dimethylformamide, hydrolysis of the CN group with dilute H_2SO_4, and reduction of the quinone moiety with zinc and ammonia, had m.p. 244° (from ethanol) (Found: C, 80.16; H, 4.58. $C_{15}H_{10}O_2$ calc.: C, 81.07; H, 4.54%). βCD and DM-βCD were donated by Japan Maize Co. Ltd. In order to make a left-handed chlolesteric mesophase, a 7:3 mixture of chlolesteryl nonanoate and cholesteryl chloride was stirred and heated to ~130° and cooled to ~50°[9].

U.v. absorption, induced c.d., and fluorescence spectra were recorded with a Shimadzu UV-250 spectrophotometer, a JASCO J-400X spectrodichrometer, and a Shimadzu RF-500 spectrofluorophotometer, respectively. Cells of pathlengths of 1, 2, 5, 10, and 20 mm were used. 500-MHz ^{1}H-N.m.r. spectra were obtained with a Jeol GX-500 spectrometer.

RESULTS AND DISCUSSION

In deducing the orientation of guest molecules in DM-βCD, the following information was used. (*a*) The electronic transitions parallel to the molecular axis of CDs produce positive induced c.d., whereas those normal to the axis show negative induced c.d.[1]. (*b*) The sign of the calculated rotational strength does not change by movement of guest molecules along the x-, y-, and z-axes, although their magnitude is affected[1a] (the origin of the axes is the centre of the CD and the z-axis is parallel to the molecular axis). (*c*) The rotation of the guest molecule in the x–y plane has no influence on the calculated rotational strength, whereas that in the x–z (or y–z) plane has a marked influence[1f]. Fig. 1 represents the dependence of calculated rotational strength on the rotation of the electric transition moment in the x–z plane[10], obtained by using the Kirkwood–Tinoco coupled oscillator model[11]. Fig. 1 shows (for example, by curve *a*) that the transitions that are polarized normal to the molecular axis of CD (negative induced c.d.) can produce positive induced c.d. when the guest molecules are rotated >36°, and that the intensity is approxi-

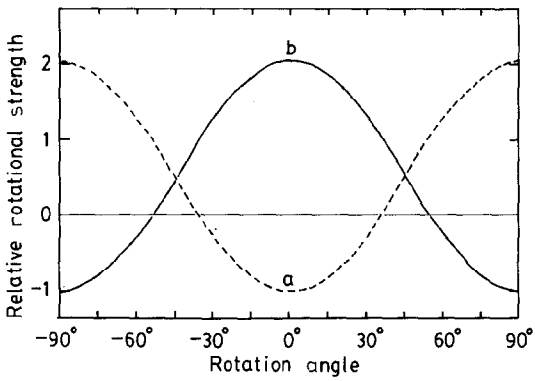

Fig. 1. The dependence of the calculated rotational strength of a CD–chromophore complex on the angle of rotation in the x–z plane. Curves a and b are the transitions that are normal and parallel to the molecular axis of the CD, respectively.

mately double when the guests are rotated by ~90°. Inversely, as curve *b* shows, the transitions that are parallel to the molecular axis of the CD (positive induced c.d.) can yield a negative induced c.d. when the guest molecules are rotated ~54°; when the guest molecules are rotated by ~90°, the intensity is approximately halved. Also, positive induced c.d. is more likely than negative induced c.d. for a wide range of rotation of guest molecules.

U.v. absorption and induced c.d. spectroscopy. — Fig. 2 shows the u.v. absorption and induced c.d. spectra of DMBA under various conditions. The induced c.d. spectrum was recorded in the thermotropic cholesteric mesophase in order to reconfirm the direction of polarization of the bands, although that of the band of longest wavelength for benzene derivatives with *para* electron-withdrawing and electron-donating groups is generally along the long axis[1a]. A negative induced c.d. trough and a shoulder appeared that corresponded exactly to an absorption peak at 320 nm and a shoulder at 247 nm. Since, in the mesophase employed, transitions polarized along the long axis produce negative induced c.d. whereas those polarized along the short axis yield positive induced c.d. signals[9], the above bands of DMBA are polarized along the long axis. The induced c.d. of DMBA in the presence of DM-βCD in chloroform is negative, corresponding to the absorption envelope of longest wavelength, although the region of the second band could not be recorded because of the solvent cut-off. Interpretation using argument (*a*) above indicates that the long axis of DM-βCD is almost normal to the molecular axis of DM-βCD (either equatorial or lid-type inclusion). In order to prove that DMBA and DM-βCD form a 1:1 inclusion complex in chloroform, continuous variation experiments were carried out where ([DMBA] + [DM-βCD])/ M = 2.4×10^{-3} (const.) (not shown). The largest $|[\theta]|$ value was obtained when [DMBA] and [DM-βCD] were equal. Using a 1-mm cell, $|[\theta]|$ was ~200 at 294 nm, when [DMBA] = [DM-βCD].

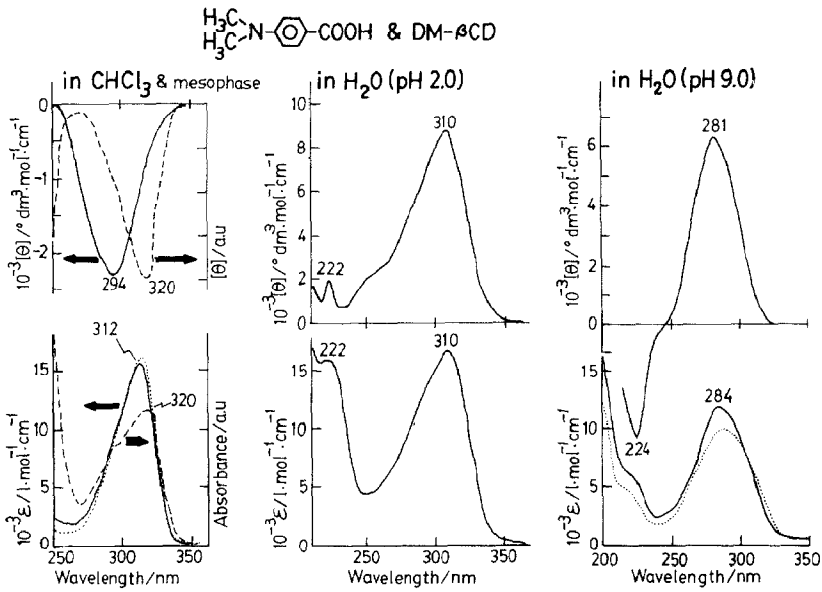

Fig. 2. Induced c.d. (top) and u.v. (bottom) spectra of DMBA in the absence (· · · ·) and presence (——) of DM-βCD or in the thermotropic cholesteric mesophase made of cholesteryl nonanoate and cholesteryl chloride (----). [DMBA]/M = 1.098×10^{-4} except in the mesophase: [DM-βCD]/M = 4.3×10^{-2} in chloroform and 3.9×10^{-2} in water.

The absorption spectrum of DMBA in water at pH 2.0 (5mM H_2SO_4) is similar to that in chloroform, suggesting similar ground-state structures. However, the induced c.d. spectrum in the presence of DM-βCD differs in that it displays positive peaks associated with the peaks in the absorption spectrum. Since these bands are polarized along the long axis and the coincidence of the wavelengths of the absorption and induced c.d. peaks is so marked, inclusion in this system is typical axial. When the carboxyl group of DMBA is dissociated at pH 9.0, the sign of the induced c.d. corresponding to the transition of second longest wavelength becomes negative. However, the inclusion in this system is also axial since the bands of longest wavelength for *para*-disubstituted benzene derivatives containing one electron-withdrawing and one electron-donating group correspond to the transition polarized along the long axis[1a]. Comparison of the induced c.d. spectra between pH 2.0 and 9.0 indicates that the direction of polarization of the band at shorter wavelength changes by dissociation of the carboxyl group from long-axis to short-axis polarization. Thus, the long axis of DMBA is nearly parallel to the molecular axis of DM-βCD in water, whereas, in chloroform, the axes are approximately mutually normal.

The induced c.d. and u.v. absorption spectra of A1C and A9C are shown in Figs. 3 and 4, respectively. An intense band of anthracene derivatives at 220–280 nm has been ascribed to the longitudinally polarized[9] ^1B_b transition[12] and the weaker band at 300–400 nm to the transversely polarized ^1L_a transition. However,

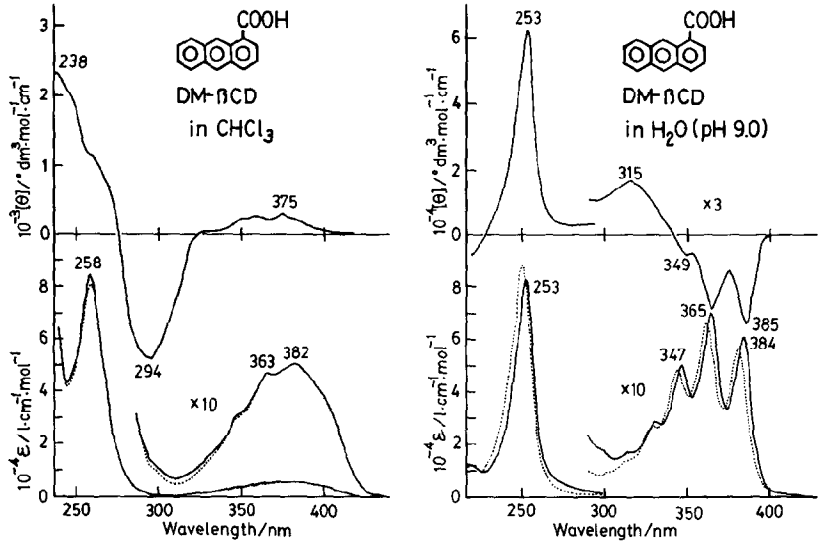

Fig. 3. Induced c.d. (top) and u.v. (bottom) spectra of A1C in the absence (· · · ·) and presence (——) of DM-βCD. [A1C]/M = 1.034×10^{-4}. [DM-βCD]/M = 3.8×10^{-2}.

the ^1L_a transition contains a longitudinally polarized component at 290–340 nm that has not often been observed[1d,12c] but has been detected in a few systems[1f,g,9]. The induced c.d. pattern of A1C and A9C in water is similar to that of a 1:1 axial inclusion complex of anthracene-2-sulfonic acid[1f] or anthracene-2,3-dicarboxylic acid[1g] and βCD in water. In chloroform, however, the induced c.d. spectra of these anthracene derivatives differ markedly from those in water. The induced c.d. pattern of A9C in chloroform and water is roughly symmetrical along the $[\theta] = 0$ axis, if the peak at 320 nm in water is regarded as shifted to 293 nm in chloroform. Thus, the sign of the induced c.d. signal is negative for the long-axis polarized ^1B_b transition in regions <330 nm and positive in the short-axis polarized ^1L_a transition. On the basis of arguments (*a*) and (*b*) and Fig. 1, this means that A9C forms an equatorial inclusion complex with DM-βCD in chloroform. The height of the torus of DM-βCD has been estimated[13] to be 10–11 Å compared to ~9.5 Å for the parent βCD[14]. Accordingly, the diameter of the cavity at the secondary face may also be larger than that (7 Å) of βCD[15]. However, since the length of the longitudinal axis of anthracene is ~11 Å (CPK model), the diameter of the cavity is too small for equatorial inclusion to occur. Thus, it is concluded that the DM-βCD molecule is flexible in chloroform. If the entrance of the secondary face becomes elliptical, equatorial inclusion may be possible. This is the second example of an equatorial complex (*cf.* the complex of 1,8-diaminonaphthalene with βCD[1b]).

It is not easy to describe the supramolecular structure of the A1C–DM-βCD complex in chloroform. It is inferred from Fig. 1 that both the short and the long axes of A1C are inclined significantly from the molecular axis of DM-βCD.

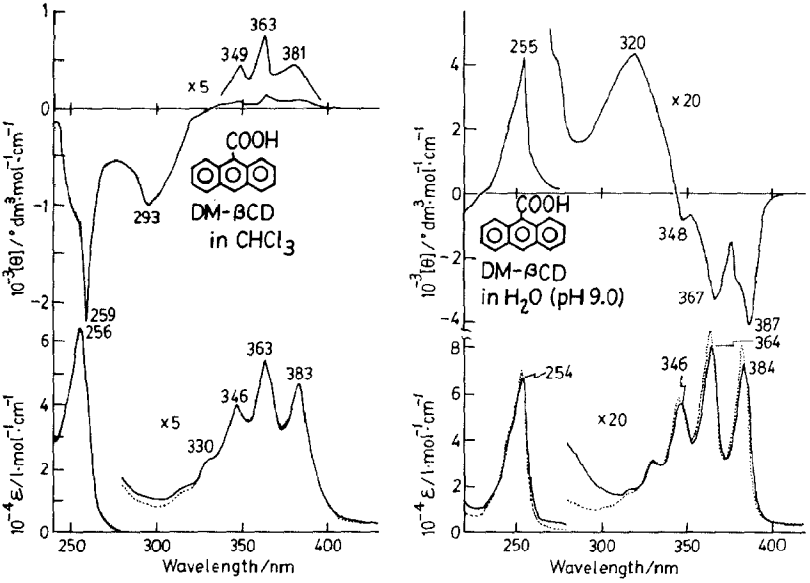

Fig. 4. Induced c.d. (top) and u.v. (bottom) spectra of A9C in the absence (· · · ·) and presence (——) of DM-βCD. [A9Cl]/M = 1.867×10^{-4}. [DM-βCD]/M = 3.8×10^{-2}.

Fig. 5 shows the spectra for PYC. In order to obtain information on the polarization of the bands, an induced c.d. spectrum was recorded in the mesophase (broken line). In the range 230–420 nm, positive induced c.d. appeared only at 270–300 nm, indicating that this region alone is polarized along the short axis. In chloroform in the presence of DM-βCD, there was a small induced c.d. trough at 330–380 nm. Since this region is assigned to a longitudinally polarized ^1L_a transition[1d,9], this phenomenon suggests, based on Fig. 1 and argument (*b*), that the long axis of PYC is inclined by slightly more than ~54°, plausibly ~60°. An intense negative induced c.d. at 270–320 nm confirms that the inclusion is not equatorial. In contrast, the supramolecular structure in water at pH 9.0 is much clearer. The sign of the induced c.d. spectrum of PYC in the presence of DM-βCD at pH 9.0 was negative throughout and there was extensive coincidence of wavelengths between the absorption peaks and induced c.d. troughs. In addition, PYC exists as a monomer in this system, as shown by the emission spectrum [for a dimer, there is a peak at 470–500 nm (excimer emission)][2c]. Based on these facts, knowledge on the direction of polarization of bands obtained above, and the arguments (*a*) and (*b*), it is concluded that PYC and DM-βCD form an exemplary lid-type[4] inclusion complex in water at pH 9.0. The size of the unsubstituted pyrene molecule is believed to be the best for axial inclusion with βCD[1d,2c]. Methylation of the hydroxyl groups in the host structure and replacement of one hydrogen by carboxyl in the guest induce a dramatic change in the structure of a host–guest complex.

The spectra for PAC are shown in Fig. 6. *trans*-Azobenzene derivatives generally show a broad weak band at 400–550 nm and an intense band at 320–330

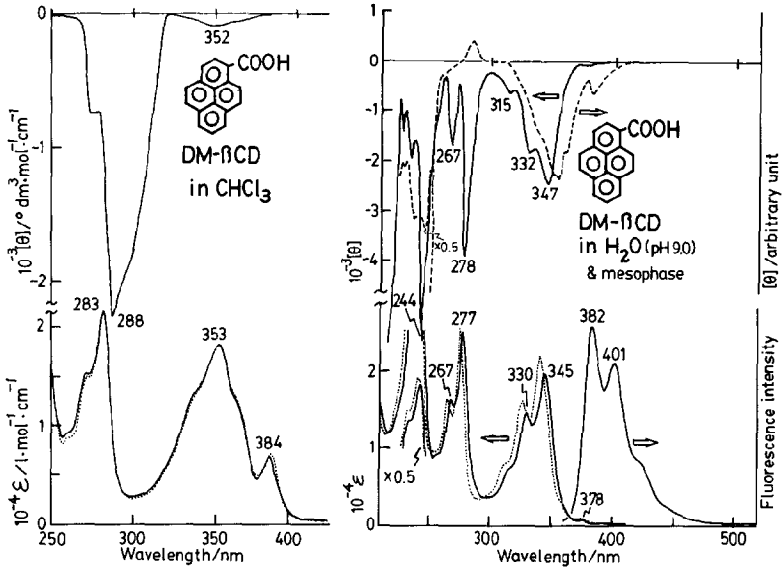

Fig. 5. Induced c.d. (top), u.v. (bottom), and fluorescence (bottom) spectra (excitation at 350 nm) of PYC in the absence (· · · ·) and presence (——) of DM-βCD or in the thermotropic cholesteric mesophase (----); [PYC]/M = 8.12×10^{-5} except in the mesophase: [DM-βCD]/M = 3.9×10^{-2}.

nm, which have been ascribed to the n–π^* and π–π^* transitions, respectively[16]. Of these, the π–π^* transition has a direction of polarization approximately parallel to the "lengthwise" axis of the molecule. In water at pH 9.0, PAC produced a positive induced c.d. peak corresponding to this π–π^* transition. Accordingly, inclusion in water is assigned as axial. No induced c.d. spectrum on the n–π^* transition in the presence of CDs has been reported hitherto. However, since the arguments (*a*)–(*c*) should apply, at least in principle, for n–π^* transitions also, the positive induced c.d. in the n–π^* band region suggests that the direction of the electric transition moment of this band does not depart much from the axis of DM-βCD. As shown in Fig. 1, the sign of the induced c.d. depends on the relative orientation of the electric dipole moment of the bands of the included chromophores and the axis of DM-βCD.

In chloroform, there is a negative induced c.d. trough corresponding to the π–π^* transition, but its position does not accord with that of the absorption peak. Since the direction of polarization of this π–π^* transition is approximately parallel to the lengthwise axis, then, based on the arguments (*a*) and (*b*) and Fig. 1, this indicates that the "lengthwise" axis of PAC inclines by $>\sim 60°$ from the molecular axis of DM-βCD. Also, since the shape of the absorption spectrum indicates that PAC is in the *trans* form[16] and the length of PAC (~16 Å, CPK model) is much larger than the diameter of the cavity of DM-βCD, the PAC molecule appears to be trapped obliquely at the entrance of the cavity of DM-βCD.

Fig. 7 shows the spectra for FCA. The absorption peak at ~440 nm has been

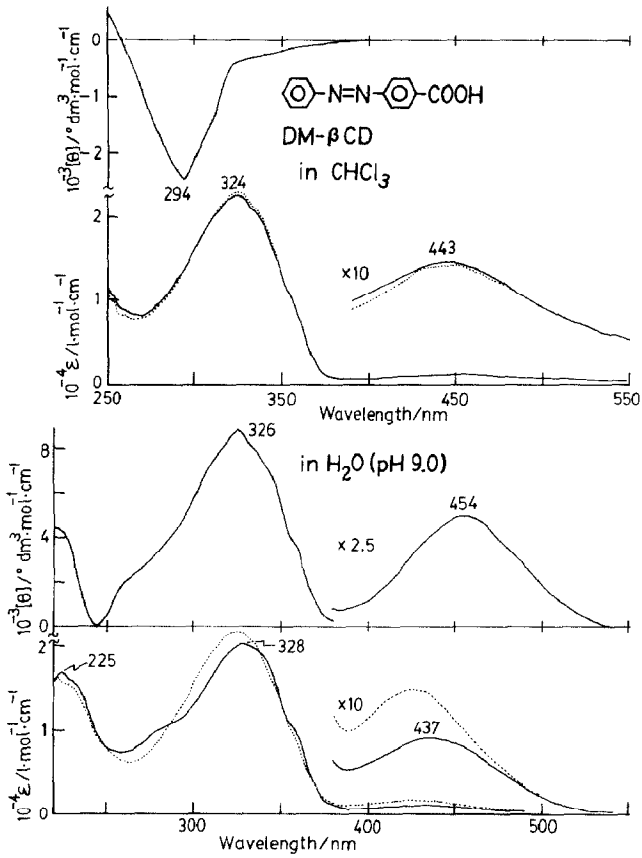

Fig. 6 Induced c.d. and u.v. spectra of PAC in the absence (· · · ·) and presence (——) of DM-βCD; [PAC]/M = 6.453×10^{-5}, [DM-βCD]/M = 3.8×10^{-2}.

assigned to a *d–d* transition of iron with some ring character gaining its intensity mainly through vibronic stealing[17]. Further, this peak contains roughly two components with absorption maxima at 420–430 and 460–470 nm. The induced c.d. spectra in this *d–d* transition region are similar in both chloroform and water (pH 9.0), revealing a negative-to-positive pattern when viewed from the side of longer wavelength. The above two components may be included in the corresponding induced c.d. However, the spectroscopic features in the <400 nm region are different. In chloroform, the sign of induced c.d. is positive, whereas in water at pH 9.0 it is negative. The induced c.d. spectra (<400 nm) of FCA–DM-βCD in chloroform and water at pH 9.0 are similar to those of FCA–βCD in water at pH 1 (carboxyl group not dissociated) and pH 9 (carboxyl group dissociated), respectively. Since the orientation of FCA and its anionic form in βCD differ by ~90°, the orientation of FCA in DM-βCD in chloroform may also differ significantly from that in water at pH 9.0. As shown by the Job's continuous variation plots in Fig. 7, FCA forms 1:1 complexes with DM-βCD in chloroform and water.

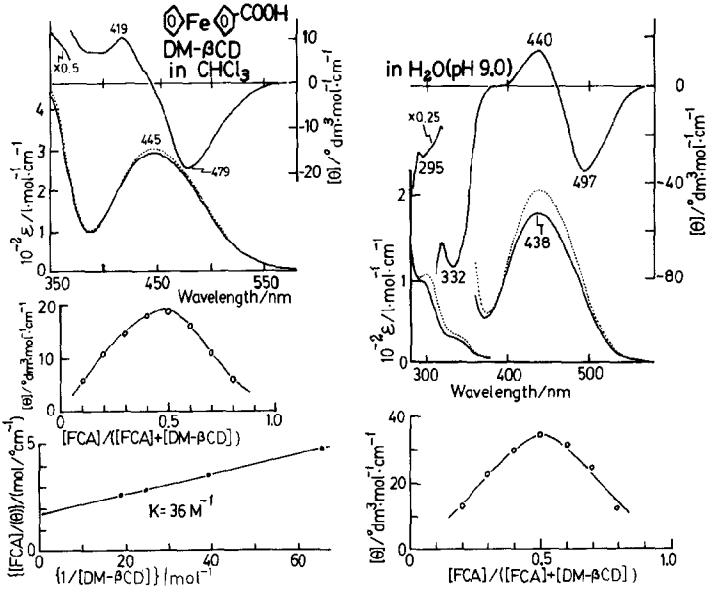

Fig. 7. Induced c.d. and u.v. spectra (top) of FCA in the absence (· · · ·) and presence (——) of DM-βCD, Job's continuous variation plots for the determination of the complex stoichiometry, and Benesi–Hildebrand plots for the determination of the complex formation constant. In the induced c.d. and u.v. spectra, [FCA]/M = 7.236×10^{-3} and [DM-βCD]/M = 3.3×10^{-2}. In the continuous variation experiments, ([FCA] + [DM-βCD])/M = 1.44×10^{-2} (const). In the Benesi–Hildebrand plots, [FCA]/M = 7.236×10^{-3} and [DM-βCD]/M = 2.65×10^{-3} and 4.03×10^{-2}.

N.m.r. spectroscopy. — The 500-MHz ^{1}H n.m.r. spectrum (Fig. 8) of 1mM DMBA in chloroform contained signals at 3.077 (s, 6 H), 7.983 and 6.704 p.p.m. (2 d, each 2 H, *J* 9.05 Hz). In the presence of ~35mM DM-βCD, these signals were shifted to 3.069, 7.961, and 6.714 p.p.m., respectively (Fig. 8A). On the other hand, the signal for HO-3 in 3mM DM-βCD was shifted from 5.067 to 5.074 p.p.m. on the addition of 10mM DMBA, although the shifts of the other proton resonances of DM-βCD were negligibly small (Fig. 8B). Thus, although the association of DMBA with DM-βCD was confirmed, a "rigid" equatorial inclusion complex is not formed. If such inclusion occurred at the entrance of the cavity of the DM-βCD, then the signals due to aromatic protons would become much more complex [deep equatorial inclusion is ruled out, since the long axis of DMBA (~11 Å, CPK model) is larger than the diameter of the cavity]. Also, deep axial inclusion obviously does not occur. The HO-3 groups of DM-βCD are on the secondary (wider) rim and since only the HO-3 protons were affected by the complexation, lid-type inclusion seems more probable than equatorial inclusion. Thus, complexation is considered to occur at the secondary face.

The n.m.r. spectrum (Fig. 9) of PYC is complex, but is simplified on the addition of DM-βCD. Further studies were not attempted because of the complexity of the spectra and the low solubility of PYC in water.

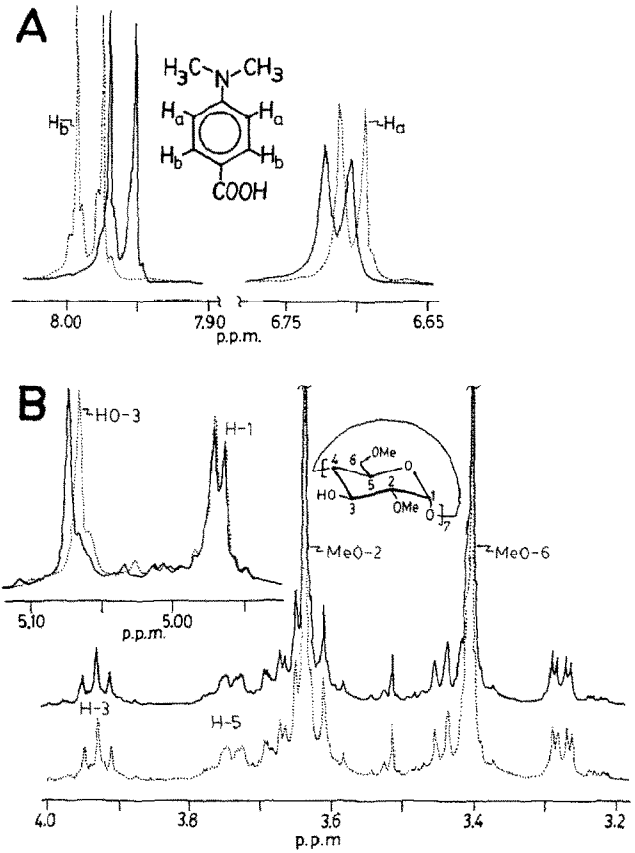

Fig. 8. Partial 500-MHz ^{1}H-n.m.r. spectra: A, DMBA in the absence (· · · ·) and presence (——) of DM-βCD; and B, DM-βCD in the absence (· · · ·) and presence (——) of DMBA in $CDCl_3$ (internal Me_4Si). For the concentration of DMBA and DM-βCD, see the text. In B, the assignment is based on ref. 6 and 18.

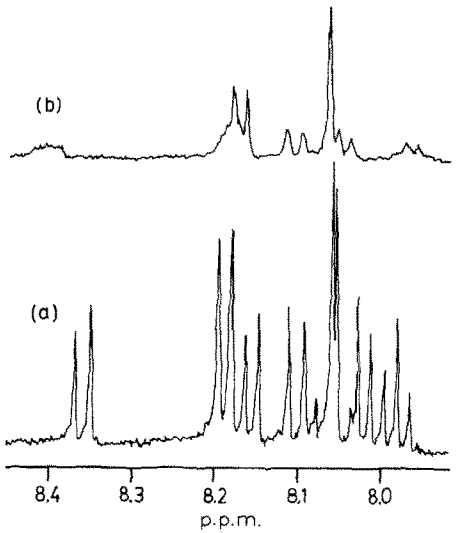

Fig. 9. Partial 500-MHz ^{1}H-n.m.r. spectra of 5×10^{-4}M PYC in D_2O at pD 9.0 in (a) the absence and (b) the presence of 5×10^{-4}M DM-βCD.

ACKNOWLEDGMENTS

We thank Messrs. F. Moriwaki and I. Suzuki for the donation of A1C and PYC, respectively.

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