Carbohydrate Research, 129 (1984) 9–20
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A CROSS-POLARISATION–MAGIC-ANGLE SPINNING ^{13}C-N.M.R. STUDY OF SOLID-STATE CYCLOAMYLOSE INCLUSION-COMPLEXES WITH SUBSTITUTED BENZENES: ^{13}C-CHEMICAL SHIFTS AND MOLECULAR DYNAMICS OF THE INCLUDED GUESTS

YOSHIO INOUE*, TAKEHIRO OKUDA, FU-HUA KUAN, AND RIICHIRÔ CHÛJÔ
Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama 2-chome, Meguro-ku, Tokyo 152 (Japan)

(Received October 11th, 1983; accepted for publication, November 15th, 1983)

ABSTRACT

The chemical shifts and line-shapes of cross-polarisation–magic-angle sample spinning ^{13}C-n.m.r. resonances have been analysed for *p*-nitrophenol, *p*-hydroxybenzoic acid, benzoic acid, and *m*-nitrophenol in the solid state and likewise for inclusion complexes with host cyclomalto-hexaose and -heptaose. The trends of the chemical-shift displacements induced by complexation with the cycloamyloses in the solid state did not fully correspond with those for solutions. The line-shapes showed evidence of the rotational motion of the benzene compounds in the cavity of cyclomaltohexaose, but not in that of cyclomaltoheptaose.

INTRODUCTION

The cycloamyloses (cyclodextrins, CD) are cyclic oligosaccharides composed of at least six (1→4)-linked α-D-glucosyl residues, which have the shape of a hollow, truncated cone with primary and secondary hydroxyl-groups crowning the narrower and the wider rims, respectively. The interior of the cavity of CD is relatively hydrophobic, whereas the exterior is relatively hydrophilic. Each CD can accept various guest molecules into the cavity, without any covalent bonds being formed, and form host–guest inclusion complexes in the solid state as well as in solution[1–3].

High-resolution n.m.r. spectroscopy is of value in the analysis of the geometry and dynamics of CD inclusion-complexes in solution [4–8]. High-resolution, ^{13}C-n.m.r. spectra of solids have become easily measurable by combining high-power dipolar decoupling, cross-polarisation (CP), and magic-angle spinning (MAS) techniques[9]. The observed, isotropic chemical shifts are usually very close to the corresponding chemical shifts in solution, but fixation of the molecular geometry and packing in the solid state bring about different chemical shifts even

* To whom inquiries should be addressed.

0008-6215/84/$ 03.00 © 1984 Elsevier Science Publishers B.V.

for carbon atoms that are chemically equivalent in solution. Recently, CP–MAS ^{13}C-n.m.r. spectroscopy has proved to be useful[10–20] for the characterisation of oligo- and poly-saccharides, including CD.

We have reported[21] on the CP–MAS ^{13}C-n.m.r. spectra of the crystalline inclusion-complexes of cyclomaltohexaose (cyclohexa-amylose, α-CD) with *p*-nitrophenol (PNP) and *p*-hydroxybenzoic acid (PHBA). We now report on the CP–MAS ^{13}C-spectral features of *m*-nitrophenol (MNP) and benzoic acid (BA), as well as PNP and PHBA, in α-CD inclusion-complexes, and of PNP in the cyclomaltoheptaose (cyclohepta-amylose, β-CD) inclusion-complex in the solid state. The α-CD inclusion-complexes of these guests in aqueous solution have been well characterised by ^{1}H- and ^{13}C-n.m.r. spectroscopy[4,6,7,22–24]. In solution, these guests form 1:1 complexes with α-CD. The molecular structure of the crystalline complexes between α-CD and PNP[25], PHBA[25], and MNP[26] have been characterised by X-ray diffraction; both PNP and PHBA form 1:1 inclusion complexes with α-CD, whereas MNP forms a 2:1 complex with one MNP located in the α-CD cavity and the other sandwiched between α-CD molecules. We now report on an analysis of the chemical shifts and line-shapes of CP–MAS ^{13}C-n.m.r. spectra, based on the X-ray crystallographic data and by comparison with the corresponding ^{13}C-data for solutions.

EXPERIMENTAL

Materials. — All compounds were commercial materials and were recrystallised from saturated aqueous solution. Each solid-state inclusion-complex was obtained by slowly cooling a hot aqueous solution containing CD and guest compound in a 1:1 molar ratio[21,25,26].

Methods. — CP–MAS ^{13}C-n.m.r. spectra were recorded with a JEOL JNM FX-200 spectrometer and a CP–MAS accessory, operated at 50 MHz and ambient temperature. Cross polarisation was carried out with r.f. field-strengths of ~15 gauss (^{1}H) and ~60 gauss (^{13}C), and a contact time of 2 or 5 ms. The MAS rate of the sample was 3.5 kHz. The spinning side-bands were not removed artificially[27], because they did not overlap with any other resonances and their intensities were very small in the spectra of the inclusion complexes[21]. The Opella–Frey pulse sequence was used to observe selectively the resonances of non-protonated carbons[28]. Samples of ~300 mg were measured in bullet-type rotors[29] (5.8-mm i.d.) made of Kel-F [poly(chlorotrifluoroethylene)]. The ^{13}C-chemical shifts were measured with respect to the high-field resonance of adamantane, which was taken as 29.7 p.p.m. downfield from the resonance of Me_4Si.

RESULTS

We have found[21] that the CP–MAS ^{13}C-resonances of the protonated carbons of PNP and PHBA broaden and disappear from the spectra following com-

plexation with α-CD (Figs. 1B and 2B*). To investigate these interesting phenomena further, CP–MAS ^{13}C-n.m.r. spectra of three new inclusion-complexes were measured, namely, PNP–β-CD (Fig. 1C), MNP–α-CD (Fig. 3B), and BA–α-CD (Figs. 4C and 4D). All resonances of the free guest compounds, except for BA, appeared in the region expected from the corresponding spectra of aqueous solutions[23], and are assigned as shown (Figs. 1A, 2A, and 3A). It is noteworthy that the signal-to-noise ratios for the spectra of free PNP and MNP were not improved even after a large number of accumulations. The resonances of PNP C-2 and PHBA C-3, which are *ortho* to the hydroxyl groups, are broad with small splitting, indicating

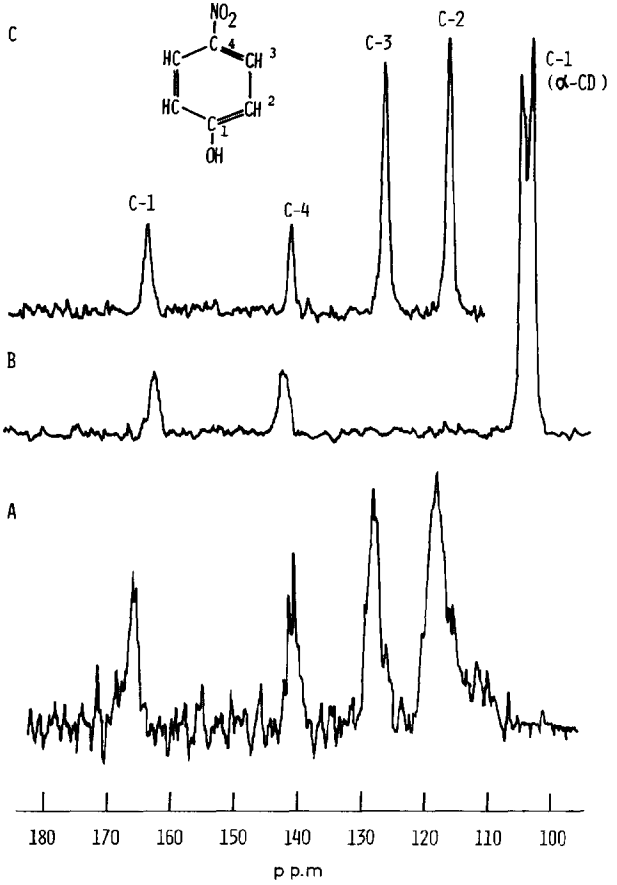

Fig. 1. CP–MAS ^{13}C-n.m.r. spectra (50 MHz) of (A) PNP (6000 scans; contact time, 2 ms; repetition time, 10 s), (B) PNP in the α-CD–PNP inclusion-complex (700 scans; contact time, 2 ms; repetition time, 5.0 s), and (C) PNP in the β-CD–PNP inclusion-complex (620 scans; contact time, 2 ms; repetition time, 5.0 s).

*The numbering of carbon atoms for PHBA shown in Fig. 2 obeys the usual convention, but is not the same as shown in the previous paper[21].

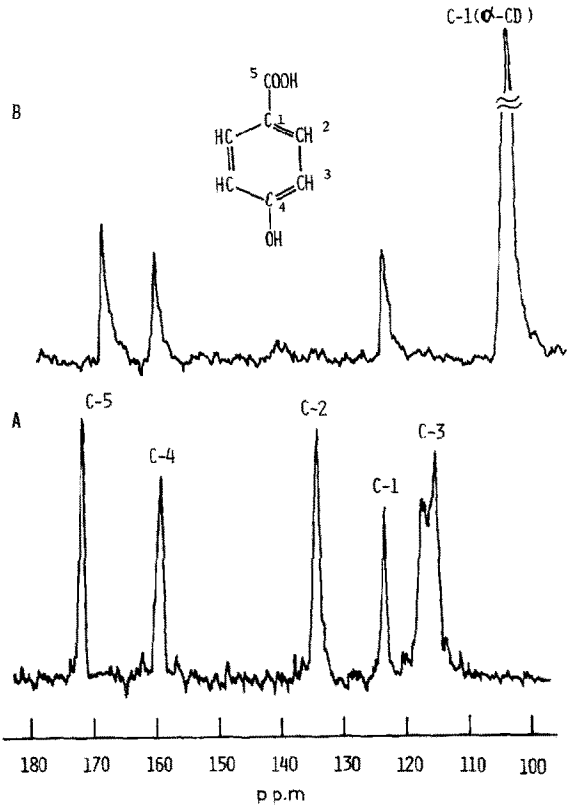

Fig. 2. CP–MAS ^{13}C-n.m.r. spectra (50 MHz) of (A) PHBA (200 scans; contact time, 2 ms; repetition time, 20 s), and (B) PHBA in the α-CD–PHBA inclusion-complex (700 scans; contact time, 2 ms; repetition time, 5.0 s).

non-equivalence of the two *ortho* carbons of each compound. The resonances from the carbons bonded to nitrogen, *i.e.*, C-4 for PNP and C-3 for MNP, were split into asymmetric doublets because of the ^{14}N–^{13}C dipolar coupling, which cannot be suppressed by magic-angle sample spinning[30,31].

The appearance of the aromatic carbon resonances of BA in the solid state (Fig. 4A) is different from that for solutions[23,32,33]. The resonances with relatively small shifts and relatively large line-widths cause severe overlapping and hide the peak separation. To ascertain the position of the C-1 resonance, non-protonated resonances were selectively observed (Fig. 4B).

Peak assignments for the complexed guests are based on those for the corresponding free guests. The resonances for complexed MNP, especially those for C-3, C-4, and C-6, appeared as doublets, corresponding to the presence of two kinds of MNP molecules in the complex with α-CD. The broad component of the C-3 doublet at 150.5 p.p.m. may be assigned to MNP included into the α-CD cavity for the reason described below. For comparison of signal intensities, the C-1 resonance of α-CD is included in the spectra of the complexed guests.

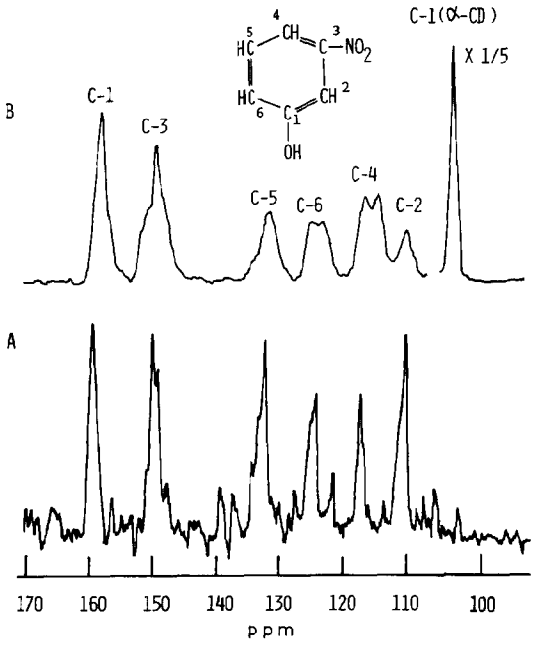

Fig. 3. CP–MAS ^{13}C-n.m.r. spectra (50 MHz) of (A) MNP (1600 scans; contact time, 5 ms; repetition time, 8.0 s), and (B) MNP in the α-CD–MNP (1:2) complex (8000 scans; contact time, 5 ms; repetition time, 8.0 s).

There are several striking differences between the spectra of free and complexed guest-compounds. The most outstanding is the broadening and virtual disappearance of the resonances of protonated carbons of PNP (Fig. 1B) and PHBA (Fig. 2B), as pointed out previously[21]. In these cases, the intensities of the remaining resonances are nearly full, as judged by comparison with those of the C-1 resonances of α-CD. The resonances of the protonated carbons of MNP, especially that of C-2, have decreased intensities for the complexes with α-CD (Fig. 3B). There are two remarkable changes in the spectra of the BA–α-CD complex (Fig. 4C). The first is the reduction in intensity with severe line-broadening of the C-1–C-4 overlapping resonances. The intensity ratio for the total C-1–C-4 resonance of BA to the C-1 resonance of α-CD, estimated by the cutting-and-weighing method, was 1:2.8, which is markedly smaller than that (1:1) expected stoichiometrically. The position of the C-1 resonance was again confirmed by selective observation (Fig. 4D). The second is the splitting of the carbonyl resonance into two peaks of equal amplitude, indicating the presence of at least two non-equivalent BA carbonyl groups per unit complex.

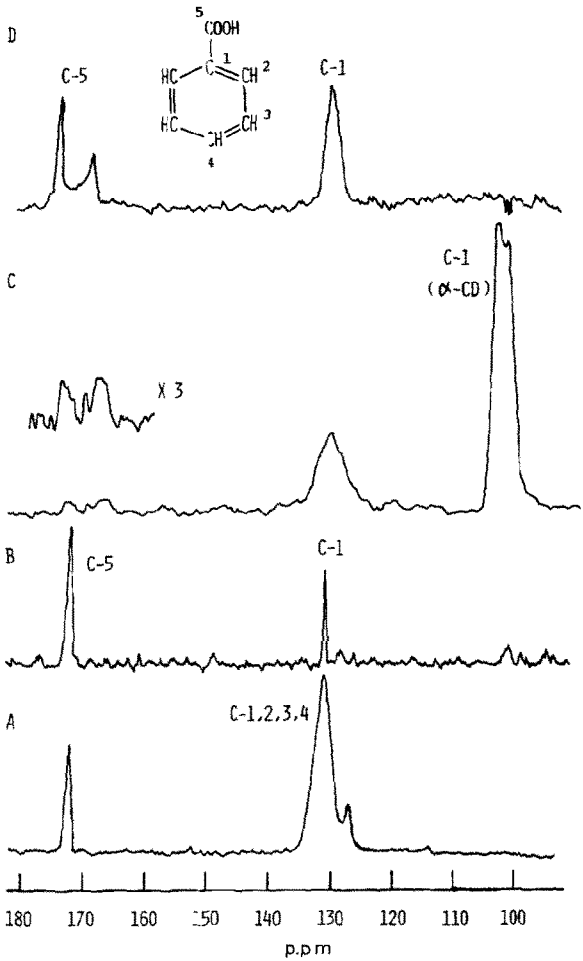

Fig. 4. CP–MAS ^{13}C-n.m.r. spectra (50 MHz) of (A) BA (7500 scans; contacttime, 5 ms; repetition time, 8.0 s), (B) BA non-protonated carbons (6000 scans; contact time, 2 ms; delay period without proton decoupling prior to data acquisition, 75 μs; repetition time, 5.0 s), (C) BA in the α-CD–BA inclusion-complex (650 scans; contact time, 2 ms; repetition time, 5.0 s), and (D) BA non-protonated carbons in the α-CD–BA inclusion-complex (11,000 scans; contact time, 2 ms; delay period without proton decoupling prior to data acquisition, 100 μs; repetition time, 5.0 s).

In the spectra of the PNP–β-CD complex (Fig. 1C), all of the PNP resonances appeared clearly with sharp line-shape and without severe reduction in intensity. The ^{14}N–^{13}C splitting of the C-4 resonance of PNP could not be observed in the spectra of α- and β-CD complexes.

Table I contains the ^{13}C-chemical shifts of guests in the solid states, and, for comparison, those for aqueous solutions.

TABLE I

^{13}C-CHEMICAL SHIFTS[a] OF GUEST COMPOUNDS IN THE FREE STATE, AND ^{13}C-DISPLACEMENTS[b] INDUCED BY COMPLEXATION WITH CYCLOAMYLOSES

Compound			*Carbon atom*						*Ref.*
			1	*2*	*3*	*4*	*5*	*6*	
PNP	Solid	Free	165.6	117.5	127.9	140.7[e]	—	—	
		Complex with α-CD	(−3.2)	—[c]	—[c]	(+1.8)	—	—	
		Complex with β-CD	(−1.4)	(−1.6)	(−1.7)	(+0.6)	—	—	
	Solution[d]	Free	163.75	116.77	127.50	141.47	—	—	23
		Complex with α-CD	(+1.88)	(+0.23)	(+0.87)	(−1.21)	—	—	23
MNP	Solid	Free	158.8	109.5	149.1[e]	116.5	132.3	123.2	
		Complex with α-CD	(−0.6)	(−0.1)	(+1.4) (+0.8)	(−0.2) (−2.4)	(−1.0)	(+1.9) (−0.2)	
	Solution[d]	Free	157.57	111.29	149.72	116.37	131.49	123.59	23
		Complex with α-CD	(+1.14)	(+0.80)	(−0.71)	(+0.18)	(−0.05)	(+1.26)	23
PHBA	Solid	Free	123.6	134.5	116.6	159.9	172.0	—	
		Complex with α-CD	(−0.4)	—[c]	—[c]	(−0.1)	(−3.7)	—	
	Solution[d]	Free	122.54	133.2	116.48	161.81	171.55	—	23
		Complex with α-CD	(−0.78)	(+1.70)	(−0.85)	(+0.72)	(−1.65)	—	23
BA	Solid	Free	130.8	130.9	130.9	130.9	172.2	—	
		Complex with α-CD	(−1.2)	—[c]	—[c]	—[c]	(+1.4) (−4.0)	—	
	Solution[d]	Free	130.91	130.64	129.74	134.72	171.97	—	23
		Complex with α-CD	(−1.18)	(+1.59)	(−0.76)	(+0.93)	(−1.70)	—	23

[a]In p.p.m. downfield from Me_4Si. [b]Shown in parentheses as the difference between chemical shifts in the free and complexed states. Negative signs indicate upfield displacements. [c]Not determined. [d]In ^2H_2O. [e]Averaged shifts for ^{13}C–^{14}N split doublets (141.3 and 140.1 p.p.m. for PNP, and 149.47 and 148.69 p.p.m. for MNP).

DISCUSSION

^{13}C-Chemical shifts of guests. — In general, the chemical shifts measured by the CP–MAS technique reflect conformations frozen out in the solid state, as well as the crystal packing effects and such fixed interactions as hydrogen bonding[34,35]. Usually, these effects are not so large as to make impossible the assignment of resonances by analogy with n.m.r. assignments for solutions. The ^{13}C-chemical shifts for almost all guests in the free solid-state agree, well within the probable experimental error, with the corresponding chemical shifts for aqueous solutions. The

substituents, *i.e.*, nitro, hydroxyl, and carboxyl, of these compounds participate in intermolecular hydrogen-bonding in the crystalline state[36–38]. In aqueous solution, they are considered to be hydrated through hydrogen bonds. At least a part of the chemical-shift difference between the solid state and solutions may be due to the difference in the strength or partner of the hydrogen bond.

Earlier ^{13}C-n.m.r. studies of α-CD inclusion-complexes with substituted benzenes in aqueous solution showed the included lead carbons to be largely shielded, in contrast to the deshielding of the corresponding *para*-carbons[23,24,39]. On this basis, PNP, PHBA, and MNP in aqueous solution are considered to be included into the α-CD cavity, with the nitro, carboxyl, and nitro groups, respectively, in the lead. These conformations are the same as those in the crystal[25,26]. As seen from the data in Table I, the same rules for chemical shifts cannot apply to the shift displacements of the ^{13}C-signals for the PNP– and MNP–α-CD complexes in the solid state. The resonances of the lead carbons of PNP(C-4) and MNP(C-3) show shifts to lower field, and the corresponding *p*-carbon resonance for PNP(C-1) shows a relatively large shift to higher field. These shifts are opposite to those observed for solutions. The shift of the signal for the *p*-carbon (C-6) of MNP cannot be discussed because the assignments of the doublet are not clear, but the C-1 resonance (singlet appearance) of MNP also shows the opposite shift. For the β-CD inclusion-complex with PNP, there are no crystallographic data or solution ^{13}C-n.m.r. data. The CP–MAS ^{13}C-data suggest that, in the solid state, PNP is included into the β-CD cavity in the same manner as for α-CD, namely, with the nitro group in the lead, since the displacements of C-1 and C-4 resonances of PNP induced by β-CD complexation have the same signs as those induced by α-CD.

The C-1 resonances for PHBA and BA were shifted to higher field by the complexation with α-CD, both in the solid state and in solution. These results suggest that the BA molecule is included into the α-CD cavity with the carboxyl group in the lead, although there are no crystallographic data on the BA–α-CD complex. The carboxyl resonance of PHBA also shows the same shifts to higher field in both states. The sign of the C-4 shift for PHBA in the solid state is opposite to that in solution, but its magnitude is very small as compared to the shifts for other carbons. As shown above, the sign and magnitude of the ^{13}C-shifts for guests induced by complexation with CD in the solid state are not entirely the same as those in solution. The absolute chemical shifts for the signals of the guests in the complexed state in the solid and in solution are also not the same, as is the case for the non-complexed molecules. These results may be due to differences in environmental and dynamic effects on the guests in the solid state and in solution. The CD-induced shift in the solid state is caused by transference of the guest molecule from the free state, surrounded by the same molecules, to the CD cavity, whereas that in solution is caused by transference from the free state surrounded by water molecules. In the solid complexes, the lead groups of included PNP (nitro) and PHBA (carboxyl) are hydrogen-bonded to the water molecules and the primary hydroxyl groups of CD, and the hydroxyl groups of these and MNP are hydrogen-

bonded strongly to the hydroxyl groups of neighbouring CD molecules[25,26], whereas, in solution, the included guest molecules have their hydroxyl groups exposed to the aqueous medium[23,24] and they can rotate nearly freely in the CD cavity[5,8,40,41]. In order to discuss the shifts quantitatively, further information, especially on the state of complex in solution, is required.

Line-broadening mechanisms of resonances of included guests. — Some resonances of the guests were broadened and their intensities severely reduced by forming inclusion complexes with α-CD. In particular, those of protonated carbons of PNP and PHBA disappeared from the spectra. These phenomena are not observed in the spectra of the PNP–β-CD complex. Several explanations for the line-broadening and intensity reduction in the CP–MAS ^{13}C-spectra of organic solids are possible, which can be separated into two classes. The first concerns inappropriate setting of such experimental conditions as insufficient proton-decoupling fields, off-resonance proton irradiation, magic-angle mis-setting, and/or rotor instabilities. The size of line-broadening due to these causes in an ordinary experiment is an order of 1 p.p.m. at most[42], undoubtedly less than the observed linewidth. An excess or insufficient CP contact-time is also possible as a cause of this class. Depending on the nature of the CD and guest compounds, and on the strength of the interaction between them, the mobility of guests may differ more or less from the mobility of CD. Consequently, the relaxation rates of the protons may depend on the nature of the guests, so that the intensities of the ^{13}C-signals of guests and CD may vary considerably with the contact time. The disappearance of only the resonances of guests cannot be explained on the basis of inappropriate CP contact-time without assuming a fairly large extent of molecular motion, which will be discussed below. It is inconceivable that inappropriate setting of experimental conditions caused the intensity reduction and the disappearance of the peaks, since the resonances for the quaternary carbons of the guests, as well as for all carbons of α-CD, appear with high signal-to-noise ratio.

The second class involves the nature of the guests themselves, and is further divided into static and dynamic mechanisms that arise from chemical-shift dispersion and molecular motion[42], respectively. When the included guest molecule can occupy two or more magnetically non-equivalent positions in the α-CD cavity, the resonances of some carbons should show a splitting, resulting in severe line-broadening in an extreme case. This mechanism may contribute a certain degree to the line-broadening, but it cannot be a main mechanism, because it is difficult to interpret the selective disappearance of resonances. In fact, the observable resonances in the spectra of PNP– and PHBA–α-CD complexes have linewidths that are not so large as those of the corresponding free states.

Line-broadening due to molecular motion may have three possible mechanisms: (*a*) coalescence due to an exchange among magnetically non-equivalent sites[43,44], (*b*) motional modulation of the resonance frequency *via* chemical-shift anisotropy[42,45], and (*c*) motional modulation of the ^{1}H–^{13}C dipolar coupling[42,46]. For (*a*), two conditions must be satisfied, namely, (*i*) there should be at

least two magnetically non-equivalent sites for the included guest in the α-CD cavity; or two similar carbons of the guest (for example, C-2,2 and C-3,3 of PNP and PHBA, which are nearly equivalent within the resolution of ~2 p.p.m. in the free state) should become significantly non-equivalent in the α-CD cavity; and (*ii*) the guest molecule should exchange its position between the non-equivalent sites, or two non-equivalent carbons should interchange their non-equivalent environments at a rate close to their chemical-shift differences, which means that the exchange rate is intermediate on the n.m.r. time-scale. Under these conditions, the corresponding peaks coalesce and may disappear in an extreme case, where the exchange rate may be[43,47] of the order $\sim 10^2$ s^{-1}. For PNP and PHBA, the two C-2 and two C-3 nuclei are essentially non-equivalent in the solid state, because the geometry of the substituents is asymmetric with respect to the plane that includes C-1 and C-4 and is perpendicular to the aromatic plane[25,36]. To conform to mechanism (*a*), the aromatic ring must undergo 180° flips about its two-fold axis (through C-1,4), since the substituents form relatively strong hydrogen-bonds in the solid-state complexes as described above. If the rate of flip is sufficiently high compared to the chemical-shift difference, two signals (C-2 and C-3) would be observable at the average position, as in solution spectra[7,23]. For very slow flips or a rigid state, up to four lines might be discerned for these carbons. The resonances due to the quaternary carbons of PNP, PHBA, and BA can hardly be affected by the 180°-flip motion, because they are situated on the axes of rotation.

Mechanism (*b*) arises from a loss of phase coherence in the transverse ^{13}C-magnetisation, as a result of random motional modulation of the resonance frequency *via* the anisotropic ^{13}C-chemical shift[42,45]. The size of this line-broadening depends on the strength of the static field (B_0) and the MAS frequency (ν_{rot}); the maximum line-broadening was estimated to be 40 Hz for a typical aliphatic carbon, and 1 kHz for aromatic, carbonyl, vinyl, or carboxyl carbons, at $B_0 = 4.7$ T (corresponding to a ^{13}C frequency of 50 MHz) and $\nu_{rot} = 5$ kHz[42]. Although the MAS frequency in this experiment is insufficient to overcome fully the large chemical-shift anisotropy of the aromatic and carboxyl carbons, it is difficult to explain the selective disappearance of the protonated carbons by this mechanism.

The last mechanism (*c*) arises from molecular motion with a rate close to, or just the same as, the nutation rate of the proton-decoupling field, so that the coupling process becomes inefficient and the ^{13}C-resonance broadens. This mechanism is particularly likely for carbons having directly bonded protons[42,46], where the rate of motion may be of the order $\sim 10^5$ s^{-1}. As discussed above, the selective line-broadening of the guest resonances due to complexation with α-CD is explainable more reasonably by assuming the appropriate molecular motion than by assuming an inappropriate experimental setting. Based on few experimental data, it is hard to specify the type of molecular motion responsible for the line-broadening. We suppose that it is librational flip motion of the aromatic ring around the axis along the symmetry axis of the CD cavity, that is, the two-fold axis through C-1,4 for PNP, PHBA, and BA. The absence of such an axis may be the reason why the intensity reduction or line-broadening is small for MNP.

The difference between the solid-state n.m.r. line-shapes, which indicate the presence of motion, and X-ray data, which indicate an apparent immobility, can be reconciled with a motional model where the aromatic ring undergoes librational flip motion with a very small amplitude. The rotation of the aromatic ring with a large angle may be restricted in the α-CD cavity, because of severe steric hindrance[25]. Thus, mechanism (*c*) of the second class is the more likely. The result is consistent with the fact that mononuclear aromatic compounds included in the α-CD cavity are able to rotate rapidly in solution[5,8,40]. The reason why all carbons of PNP included in the β-CD cavity, in contrast with those in α-CD, show sharp resonances is also deducible from the geometry and dynamics of the β-CD inclusion-complexes in solution. In solution, a mononuclear aromatic compound in the β-CD complex is more deeply inserted into the cavity and suffers more-severe steric hindrance than is the case for the α-CD complex[24]. As a result, its molecular motion is more extensively restricted in the β-CD cavity than in that of α-CD[8,40]. The same situation may also be true in the solid state, although not all of the results for solutions necessarily correspond with those for the solid.

In conclusion, high-resolution, CP–MAS, ^{13}C-n.m.r. spectroscopy of solids is a sensitive method for obtaining microscopic information about chemical and physical properties of the guests included in the CD complexes, although it is unlikely to replace X-ray crystallography for obtaining detailed information about atomic positions in the complexes.

ACKNOWLEDGMENTS

The authors thank Dr. T. Fujito and Mr. K. Deguchi of JEOL Ltd., Akishima, Tokyo, for recording the CP–MAS ^{13}C-n.m.r. spectra.

REFERENCES

1 M. L. BENDER AND M. KOMIYAMA, *Reactivity and Structure Concepts in Organic Chemistry*, Vol. 6, *Cyclodextrin Chemistry*, Springer–Verlag, New York, 1978.
2 W. SAENGER, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 344–362.
3 W. HINZE, *Sep. Purif. Methods*, 10 (1981) 159–237.
4 P. V. DEMARCO AND A. L. THAKKAR, *Chem. Commun.*, (1970) 2–4.
5 J. P. BEHR AND J. M. LEHN, *J. Am. Chem. Soc.*, 98 (1976) 1743–1747.
6 D. J. WOOD, F. E. HRUSKA, AND W. SAENGER, *J. Am. Chem. Soc.*, 99 (1977) 1735–1740.
7 R. BERGERON AND R. ROWAN, *Bioorg. Chem.*, 5 (1976) 425–436.
8 Y. INOUE, Y. KATÔNO, AND R. CHÛJÔ, *Bull. Chem. Soc. Jpn.*, 52 (1979) 1692–1697.
9 M. MEHRING, *High Resolution NMR Spectroscopy in Solids*, Springer–Verlag, New York, 1976; J. SCHAEFER AND E. O. STEJSKAL, in G. C. LEVY (Ed.), *Topics in Carbon-13 NMR Spectroscopy*, Vol. 3, Wiley, New York, 1979, pp. 283–324; C. S. YANNONI, *Acc. Chem. Res.*, 15 (1982) 201–208.
10 W. L. EARL AND D. L. VANDERHART, *J. Am. Chem. Soc.*, 102 (1980) 3251–3252.
11 W. L. EARL AND D. L. VANDERHART, *Macromolecules*, 14 (1981) 570–574.
12 R. H. ATALLA, J. C. GAST, D. W. SINDORF, V. J. BARTUSKA, AND G. E. MACIEL, *J. Am. Chem. Soc.*, 102 (1980) 3249–3251.
13 H. SAITÔ, R. TABETA, AND T. HARADA, *Chem. Lett.*, (1981) 571-574.
14 H. SAITÔ AND R. TABETA, *Chem. Lett.*, (1981) 713–716.
15 J. KUNZE, A. EBERT, B. SCHROTER, K. FRIGGE, AND B. PHILIPP, *Polym. Bull.*, 5 (1981) 399–406.

16 G. E. MACIEL, D. J. O'DONNELL, J. J. H. ACKERMAN, B. H. HAWKINS, AND V. J. BARTSUKA, *Makromol. Chem.*, 182 (1981) 2297–2304.
17 F. HORII, A. HIRAI, AND R. KITAMARU, *Polym. Bull.*, 8 (1982) 163–170.
18 P. E. PFEFFER AND K. B. HICKS, *Carbohydr. Res.*, 111 (1983) 181–194.
19 H. SAITÔ, G. IZUMI, T. MAMIZUKA, S. SUZUKI, AND R. TABETA, *J. Chem. Soc., Chem. Commun.*, (1982) 1386–1388.
20 W. L. EARL AND F. W. PARRISH, *Carbohydr. Res.*, 115 (1983) 23–32.
21 Y. INOUE, T. OKUDA, AND R. CHÛJÔ, *Carbohydr. Res.*, 116 (1983) c5–c8.
22 M. KOMIYAMA AND H. HIRAI, *Bull. Chem. Soc. Jpn.*, 54 (1981) 828–831.
23 R. I. GELB, L. M. SCHWARTZ, B. CALDELINO, H. S. FUHRMAN, R. F. JOHNSON, AND D. A. LAUFER, *J. Am. Chem. Soc.*, 103 (1981) 1750–1757.
24 Y. INOUE, T. OKUDA, Y. MIYATA, AND R. CHÛJÔ, *Carbohydr. Res.*, 125 (1984) 65–76.
25 K. HARATA, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1416–1424.
26 K. HARATA, H. UEDAIRA, AND J. TANAKA, *Bull. Chem. Soc. Jpn.*, 51 (1978) 1627–1634.
27 W. T. DIXON, *J. Magn. Reson.*, 44 (1981) 220–223; *J. Chem. Phys.*, 77 (1982) 1800–1809.
28 S. J. OPELLA AND M. H. FREY, *J. Am. Chem. Soc.*, 101 (1979) 5854–5856.
29 V. J. BARTUSKA AND G. E. MACIEL, *J. Magn. Reson.*, 42 (1981) 312–321.
30 J. G. HEXEM, M. H FREY, AND S. J. OPELLA, *J. Chem. Soc.*, 77 (1982) 3847–3856.
31 A. NAITO, S. GANAPATHY, AND C. A. MCDOWELL, *J. Magn. Reson.*, 48 (1982) 367–381.
32 E. BREITMAIER AND W. VOELTER, *^{13}C-NMR Spectroscopy*, 2nd edn., Verlag Chemie, New York, 1978.
33 A. M. IHRIG AND J. L. MARSHALL, *J. Am. Chem. Soc.*, 94 (1972) 1756–1757.
34 E. T. LIPPMAA, M. A. ALLA, T. J. PEHK, AND G. ENGELHARDT, *J. Am. Chem. Soc.*, 100 (1978) 1929–1931.
35 F. IMASHIRO, S. MAEDA, K. TAKEGOSHI, T. TERAO, AND A. SAIKA, *Chem. Phys. Lett.*, 92 (1982) 642–645.
36 P. COPPENS AND G. M. J. SCHMIDT, *Acta Crystallogr.*, 18 (1965) 62–67, 654–663.
37 G. A. SIM, J. M. ROBERTSON, AND T. H. GOODWIN, *Acta Crystallogr.*, 8 (1955) 157–164.
38 F. PANDARESE, L. UNGARETTI, AND A. CODA, *Acta Crystallogr., Sect. B*, 31 (1975) 2671–2675.
39 R. J. BERGERON, M. A. CHANNING, G. J. GIBEILY, AND D. M. PILLOR, *J. Am. Chem. Soc.*, 99 (1977) 5146–5151.
40 Y. INOUE AND Y. MIYATA, *Bull. Chem. Soc. Jpn.*, 54 (1981) 809–816.
41 Y. INOUE, T. OKUDA, AND Y. MIYATA, *Carbohydr. Res.*, 101 (1982) 187–195.
42 D. L. VANDERHART, W. L. EARL, AND A. N. GARROWAY, *J. Magn. Reson.*, 44 (1981) 361–401.
43 L. LUNAZZI, *Tetrahedron Lett.*, (1975) 1205–1206.
44 L. M. GIERASCH, M. H. FREY, J. G. HEXEM, AND S. J. OPELLA, *ACS Symp. Ser.*, 191 (1982) 233–247.
45 D. SUWELACK, W. P. ROTHWELL, AND J. S. WAUGH, *J. Chem. Phys.*, 73 (1980) 2559–2569.
46 W. P. ROTHWELL AND J. S. WAUGH, *J. Chem. Phys.*, 74 (1981) 2721–2732.
47 M. H. FREY AND S. J. OPELLA, *J. Chem. Soc., Chem. Commun.*, (1980) 474–475.