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A HIGH-RESOLUTION C.P.–M.A.S. ^{13}C-N.M.R. STUDY OF SOLID-STATE CYCLOMALTOHEXAOSE INCLUSION-COMPLEXES: CHEMICAL SHIFTS AND STRUCTURE OF THE HOST CYCLOMALTOHEXAOSE

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ABSTRACT

High-resolution, solid-state ^{13}C-n.m.r. spectra were obtained for several crystalline cyclomaltohexaose inclusion-complexes. The resonances of C-1, C-4, and C-6 of the host were dispersed. The averaged ^{13}C shifts of these resonances were in good agreement with the ^{13}C shifts observed in solution, where the dispersion due to conformational diversity is expected to be averaged by rapid interconversion of the conformers. This result indicates that the most plausible source of the solid-state ^{13}C-shift dispersions of the resonances of C-1 and C-4 is the diversity of conformations about the glycosidic linkage. The molecular origins of conformation-dependent ^{13}C shifts are discussed.

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 wider rims, respectively. Each CD can accept various guest molecules into its cavity and form inclusion complexes in the solid state as well as in solution[1].

High-resolution ^{13}C-n.m.r. spectroscopy is one of the most useful methods in the analysis of the structure and molecular dynamics of CD inclusion-complexes both in aqueous solution[2–8] and in the solid state[9–11]. In recent years, the techniques of high-power dipolar decoupling, cross-polarisation (c.p.), and magic-angle spinning (m.a.s.) have been developed to observe high-resolution, high signal-to-noise ratio n.m.r. spectra of dilute nuclei, such as ^{13}C, in the solid state[12]. The ^{13}C shifts observed in the solid by c.p.–m.a.s. methods are usually quite similar to those observed in solution, but fixation of the molecular geometry and packing in the solid state bring about different chemical shifts even for nuclei that are

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chemically equivalent in solution. Thus, ^{13}C shifts in the solid state may be used in the elucidation of both molecular and crystal structures.

Earlier, ^{13}C-n.m.r. studies of aqueous solutions of cyclomaltohexaose (α-CD) inclusion-complexes with various guest compounds revealed a linear correlation between the complexation-induced ^{13}C shifts of the resonance of C-1 and the enthalpy change (ΔH) on complexation[6]. This correlation has been considered to reflect the nature of the bonding between α-CD and the guests, by relating the observed ^{13}C shifts of the C-1 resonance to conformational changes of the glycosyl residues without any verification[6]. Although the chemical shifts of the C-1 resonance of amylose in solution have been reported to be sensitive to the conformation of the glycosidic linkage[13], in general the ^{13}C shifts of the C-1 resonance observed in solution do not reflect any particular conformer of the α-CD macrocycle or glycosidic linkage but the average of rapidly interconverting conformers[2,7]. Therefore, observations of solid-state c.p.–m.a.s. ^{13}C-n.m.r. spectra of crystalline α-CD inclusion-complexes, the crystallographic structures of which have been analysed by X-ray methods, are of particular interest for the elucidation of the origins of ^{13}C shifts of α-CD resonances on complexation.

We now report on the c.p.–m.a.s. ^{13}C-n.m.r. spectral features of α-CD in the inclusion complexes with water, *p*-nitrophenol (PNP), *p*-hydroxybenzoic acid (PHBA), *m*-nitrophenol (MNP) and benzoic acid (BA). The last four of these complexes in aqueous solution have been characterised by ^{1}H- and ^{13}C-n.m.r. spectroscopy[3,5,6,14–18], and the molecular structures of the first four complexes have been characterised[19–21] by X-ray diffraction. The c.p.–m.a.s. ^{13}C-n.m.r. chemical shifts and line shapes have been analysed[11] for PNP, PHBA, MNP, and BA in the solid-state CD inclusion-complexes.

EXPERIMENTAL

Materials. — All compounds were recrystallised from aqueous solution before use. The α-CD inclusion-complexes of PNP, PHBA, MNP, and BA were obtained by slowly cooling a hot, saturated, equimolar aqueous solution of α-CD and the respective guest. The hydrated α-CD crystal was also grown from aqueous solution. Three crystal forms have been reported for α-CD · water complexes[19]; two of these are hexahydrates (forms I and II), and the other is a 7.57 hydrate (form III). Since form I grows preferentially under normal conditions[19b], the crystal obtained by us must be this form; α-CD molecules in form I and II have almost identical conformations[19b].

Methods. — C.p.–m.a.s. ^{13}C-n.m.r. spectra (50 MHz) were recorded with a JEOL JNM FX-200 spectrometer and a c.p.–m.a.s. accessory. C.p. was carried out with r.f. field-strengths of $\sim 1.5 \times 10^{-3}$T (^{1}H) and $\sim 6.0 \times 10^{-3}$T (^{13}C), and a contact time of 2 or 5 ms. The m.a.s. rate was ~3.5 kHz. The spinning side-bands were not removed artificially, since they did not overlap with any other resonances and their intensities were insignificant. Samples of ~300 mg were measured in Kel-F bullet-

type rotors[22] (5.8-mm i.d.). The ^{13}C chemical shifts were referenced to the high-field resonance of external adamantane and were converted to the Me_4Si scale by adding 29.7 p.p.m. to the measured chemical shifts.

RESULTS

Figs. 1–5 show c.p.–m.a.s. ^{13}C-n.m.r. spectra of the α-CD inclusion-complexes investigated. Peak assignments for α-CD are based on the literature data[9–11]. The resonances of C-1, C-4, and C-6 were well differentiated, but those of C-2, C-3, and C-5 overlapped severely. Some of the C-1, C-4, and C-6 resonances of α-CD in complexes with water, PNP, PHBA, and BA were split into two or more peaks, and others were broadened; the C-1 and C-4 resonances of α-CD in the complex with MNP were sharp singlets.

The ^{13}C chemical shifts of α-CD in the solid state are summarised in Table I. The number of atoms which contributed to each peak of a given resonance was estimated roughly and normalised to 6, and the results are shown in parentheses for some carbon atoms. The weight-averaged chemical shifts are also shown for these carbon atoms. For comparison, the ^{13}C chemical shifts observed in aqueous solution[6] are also shown in Table I. In almost all instances, the ^{13}C shifts for single-peak resonances and the weight-averaged ^{13}C shifts for the multiplets of C-1, C-4, and C-6, observed in the solid state, are in good agreement with the ^{13}C shifts of the

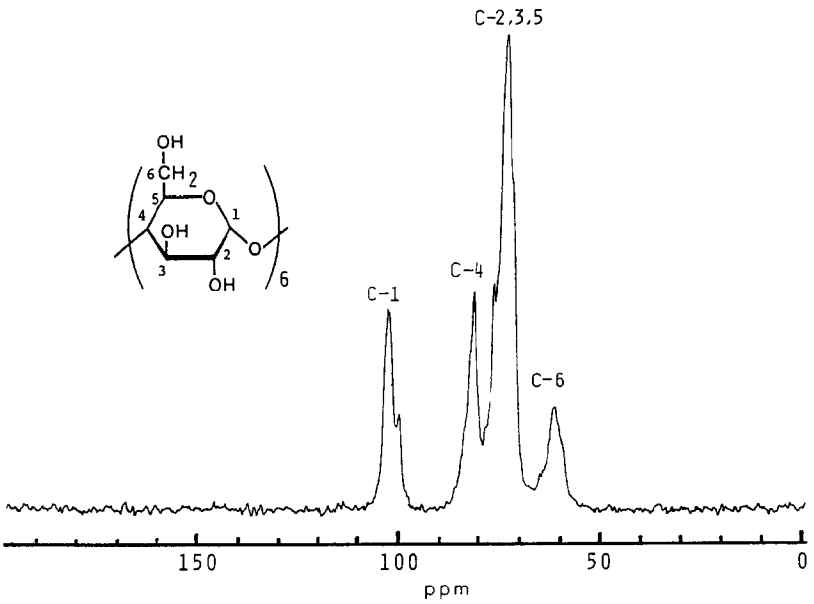

Fig. 1. C.p.–m.a.s. ^{13}C-n.m.r. spectrum of the α-CD · H_2O inclusion-complex (contact time, 2 ms; 400 scans with a repetition time of 5.0 s).

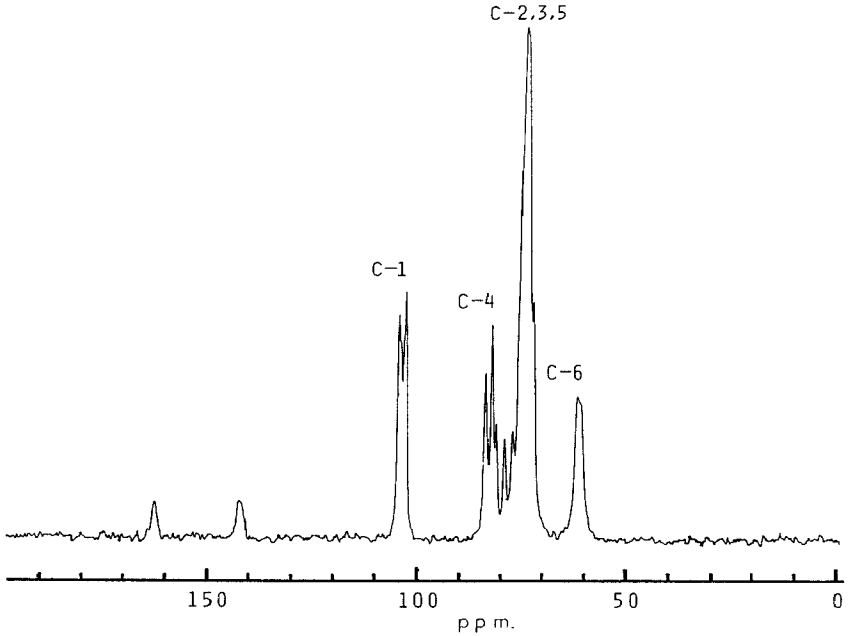

Fig. 2. C.p.–m.a.s. ^{13}C-n.m.r. spectrum of the α-CD · PNP inclusion-complex (contact time, 2 ms; 700 scans with a repetition time of 5.0 s). The signals at lower field are the resonances of PNP[11].

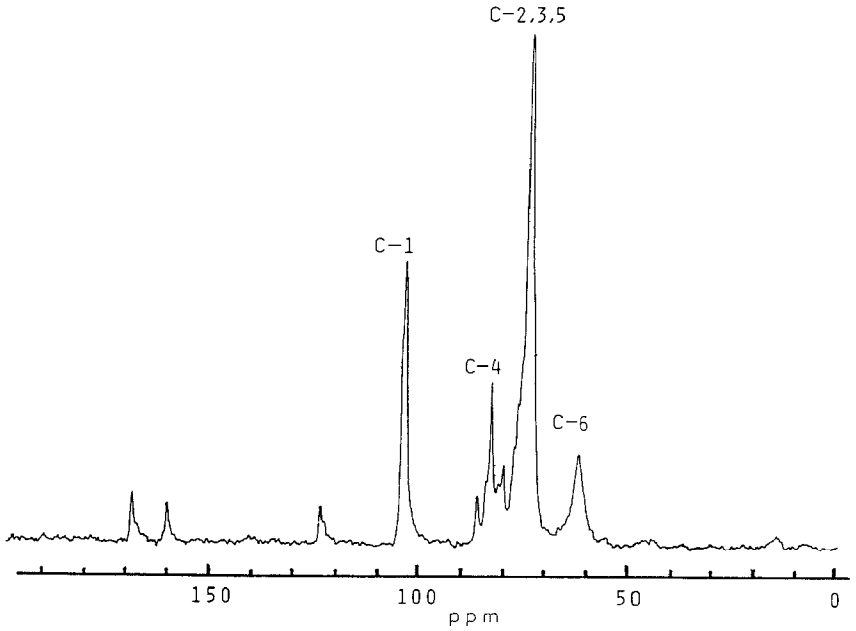

Fig. 3. C.p.–m.a.s. ^{13}C-n.m.r. spectrum of the α-CD · PHBA inclusion-complex (contact time, 2 ms; 700 scans with a repetition time of 5.0 s). The signals at lower field are the resonances of PHBA[11].

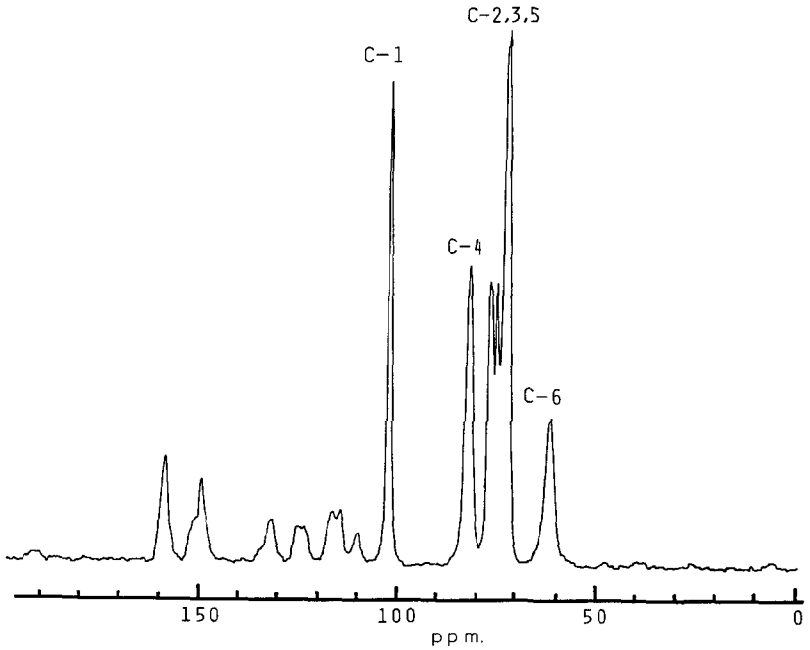

Fig. 4. C.p.–m.a.s. ^{13}C-n.m.r. spectrum of the α-CD · MNP inclusion-complex (contact time, 5 ms; 8000 scans with a repetition time of 8.0 s). The signals at lower field are the resonances of MNP[11].

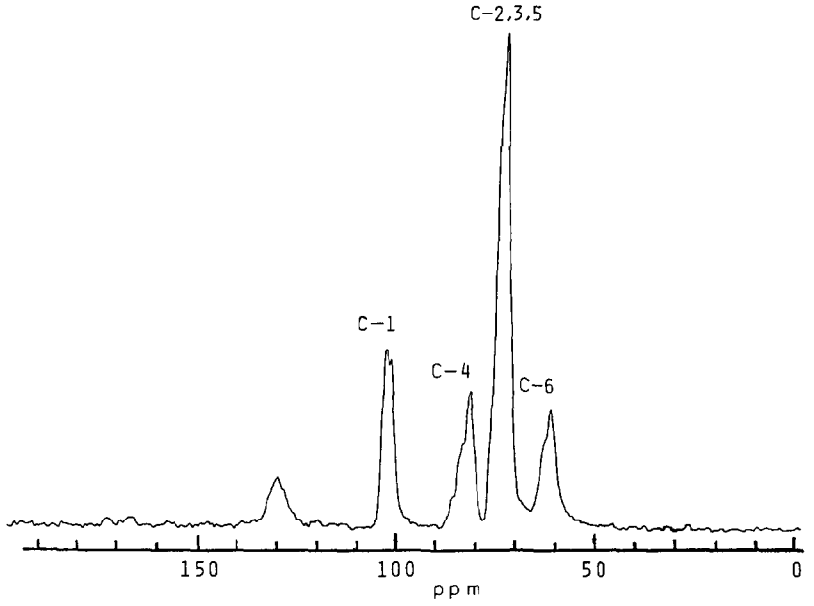

Fig. 5. C.p.–m.a.s. ^{13}C-n.m.r. spectrum of the α-CD · BA inclusion-complex (contact time, 2 ms; 650 scans with a repetition time of 5.0 s). The signals at lower field are the resonances of BA[11].

TABLE I

^{13}C CHEMICAL SHIFTS (p p.m. RELATIVE TO EXTERNAL Me_4Si) OF α-CD IN α-CD INCLUSION-COMPLEXES IN THE SOLID STATE AND IN SOLUTION[a,b]

Complex	*State*	*C-1*	*C-4*	*C-2,3,5*	*C-6*	*Ref.*
	Solid	102.9(5) 100 2(1)	81.6(b) (6)	76 5 73.2(b)	61.8(b) (6)	
α-CD · H_2O		av. 102.4				
	Solution	102.41	82 26	72.88; 74.47; 73.07	61.59	6
	Solid	104.3(3) 102.7(3)	83.4(2) 82.0(2)	76.9 74.1(b)	61 5(3) 60.5(3)	
α-CD · PNP		av 103 5	81.0(1) 78.8(1)	72.1	av 61 0	
			av. 81.7_5			
	Solution	102.83	82 36	72.83; 74.84; 72.87	61.13	6
	Solid	103.5(b)	85.8(1) 83.7(1) 82 4(2) 80 9(1) 79.6(1)	73.8(b)[c]	61.7(b) (6)	
α-CD · PHBA						
			av. 82.4_7			
	Solution	102.90	82 32	73.02; 74.78, 72.56	61.12	6
	Solid	101.8(6)	81 9(6)	76.5 74 7	60 9(6)	
α-CD · MNP				72.1		
	Solution	102.83	82 40	72.90; 74 72, 72 92	61.17	6
	Solid	103.1(4) 101.7(2)	83.6(3) 81.8(3)	73.1(b)[c]	61.2(b) (6)	
α-CD · BA		av 102 6	av. 82 7			
	Solution	102.87	82 30	72.99; 74.71; 72.68	61.15	6

[a]Numbers shown in parentheses are roughly estimated numbers of atoms (total 6) which contribute to a given peak. [b]Av. means weight-averaged chemical shift, b denotes broad [c]Not discriminated in the solid-state spectra

corresponding carbon atoms observed for aqueous solutions, within a probable experimental error of ±0.5 p.p.m.

DISCUSSION

The possible origins of the splittings and/or dispersions in the solid-state ^{13}C resonances of C-1, C-4, and C-6 of α-CD were examined first. Solid-state c.p.–m.a.s. ^{13}C line-widths are typically 10–100 times broader than those in the liquid

state and a large fraction of the solid-state line-width is due to chemical shift dispersion[23–25]. This dispersion has been attributed to magnetic susceptibility effects, solid-state magnetic inequivalences, and variations in bond angles, conformations, and molecular packing[23–25]. α-CD is not expected to have significant local or bulk magnetic anisotropies since there are no relevant chemical structures. Possible anisotropic magnetic effects of the included aromatic compounds on the C-1, C-4, and C-6 resonances should also be insignificant, since significant dispersions of these resonances were observed in α-CD complexes of water, PNP, PHBA, and BA, but not in the α-CD · MNP complex.

The relevance of the conformational variations to the chemical shift dispersions of the C-1, C-4, and C-6 resonances is suggested by the fact that the ^{13}C shifts for singlets and the weight-averaged ^{13}C shifts for multiplets in the solid state are in good agreement with the ^{13}C shifts of the corresponding carbon atoms observed for aqueous solutions. In solution, ^{13}C shift dispersion due to conformational variations is averaged by rapid interconversion of possible conformers.

It has been proposed[9] that the ^{13}C shifts of the C-1 and C-4 resonances of α-CD are related to the dihedral angles ϕ and ψ at the glycosidic linkage, respectively. Here, the angles ϕ and ψ are defined as the torsion angles O(n,4) · · · C(n,1)—O(n + 1,4)—C(n + 1,4) and C(n,1)—O(n + 1,4)—C(n + 1,4) · · · O(n + 2,4), respectively (n indicates[19a] the nth glucosyl residue of α-CD). According to this proposal[9], the C-1 peaks appearing in the ranges 99.0–100.7 and 101.9–102.7 p.p.m. are ascribed, respectively, to ϕ values of 169 ±7° and 160 ±2°; the C-4 peaks in the ranges 75.6–76.2, 80.1–80.9, and 81.1–82.3 p.p.m. are ascribed, respectively, to ψ values of −150 ±5°, −168 ±9°, and −183 ±7°. This proposal has shortcomings. It is easy to find exceptions to the stated dihedral angles, although the corresponding resonances appear within the specified ranges. For example, the reported set of dihedral angles (ϕ,ψ) of the form I α-CD · H_2O complex is (162.6, −169.9), (165.9, −172.9), (147.6, −181.4), (147.4, −131.2), (160.9, −175.8), and (171.1, −162.6), which contains several angles out of the specified range, while the observed ^{13}C shifts lie in the allowed range, *i.e.*, 100.0–102.9 p.p.m. for C-1 and 81.6 p.p.m. (broad) for C-4 resonances. Further, according to this proposal, the relative intensities of these split peaks cannot be explained. For example, the reported ϕ values of the α-CD · 1-propanol complex (169.6, 170.6, 168.4, 159.3, 171.1, 160.8)[26]. Thus, the intensity ratio of the higher- (100.4 p.p.m.) to the lower-field peaks (102.7 p.p.m.) of the C-1 resonance must be 4:2, but the experimental findings of the C-1 splittings (Fig. 1c of ref. 9) are clearly the reverse, *i.e.*, between 2:4 and 1:5. Although the c.p.–m.a.s. technique, by its nature, does not yield completely reliable, quantitative spectral intensities, the general comparisons between intensities of peaks among the same resonance in a given spectra are valid[27]. What is more important is that the conformation of the glycosidic linkage is defined not by ϕ or ψ alone but by both ϕ and ψ. The definitions of (ϕ,ψ) involve "virtual" O-4 · · · C-1 and C-4 · · · O-4 bonds, and thus they depend also on the conformation of the glucopyranose ring. The (ϕ,ψ) set is useful

for describing the overall α-CD macrocyclic conformation[19a] but is not the best parameter for describing the conformation of the glycosidic linkage.

Quantitatively, the rotational state about the glycosidic linkage is more pertinently specified[28] by four angles ϕ_1, ϕ_1', ϕ_2, and ϕ_2', which specify, respectively, the torsion angles O-5—C-1—O-4′—C-4′, C-2—C-1—O-4′—C-4′, C-1—O-4′—C-4′—C-3′, and C-1—O-4′—C-4′—C-5′. Although it is very difficult to find general correlations between these four angles and the extent of the ^{13}C shift dispersions, qualitatively it may be said that the smaller the distribution of these four angles, the narrower is the ^{13}C shift dispersion. For example, six sets of (ϕ_1, ϕ_1', ϕ_2, ϕ_2') for form I of the α-CD · H_2O crystal[19a] are widely distributed as follows, (112.8, −126.5, 135.3, −103.2), (104.8, −136.7, 131.0, −110.5), (107.5, −133.0, 128.4, −115.4), (88.2, −150.0, 116.6, −123.7), (90.4, −151.9, 170.4, −69.3), and (100.7, −138.8, 120.6, −118.5), and correspondingly the ^{13}C shift dispersions of the C-1 and C-4 resonances are larger than those of the α-CD · MNP complex[21]; two sets of (111.5, −130.3, 127.8, −114.7), two sets of (107.2, −132.4, 129.9, −112.7), and two sets of (113.1, −129.3, 129.1, −116.4), giving the corresponding C-1 and C-4 resonances as sharp singlets. These results also support the expectation that the variations in the ^{13}C shifts of the C-1 and C-4 resonances are associated with the conformation of the glycosidic linkage.

In seeking to clarify the molecular origin(s) of the conformation-dependence of the ^{13}C shifts of C-1 and C-4 resonances, the model of Grant and Cheney[29,30] can be employed as a good approximation to see how the ^{13}C chemical shift is affected by the through-space steric perturbations. According to the steric hindrance model of Grant and Cheney, the ^{13}C shift of a CH group is influenced by the mutual repulsion of the bonded hydrogen atom and a nearby non-bonded hydrogen atom. The expression of the model is $\Delta\delta = -1680\cos\theta\exp(-26.71r)$, where $\Delta\delta$ is the chemical shift difference (p.p.m.), r is the hydrogen–hydrogen distance in nm, and θ is the angle between the CH bond and the inter-hydrogen separation vector. The examination of a CPK space-filling model suggests that the main steric interaction, which is expected to influence significantly the ^{13}C shifts of the C-1 and C-4 resonances and the strength of which depends on the conformation of the glycosidic linkage, is the H-1—H-4 repulsion. Fig. 6 shows a part of the ^{13}C shift map of the C-4 resonance perturbed by the H-1—H-4 repulsion, calculated as a function of ϕ_1 and ϕ_2 using the above expression. The bond lengths and the bond angles are assumed to be constant, *i.e.*, C–O and C–H bond lengths are 0.143 and 0.109 nm, and C–O–C and O–C–H bond angles are 119.00° and 109.47°, respectively. Fig. 6 generally demonstrates the non-monotonous dependence of steric perturbation of the C-4 shifts on the conformation of the glycosidic linkage. The same is also true for the C-1 resonance. Actually, the bond length and the bond angle are not always constant for the six glucopyranosyl residues of α-CD. Thus, the chemical shift dispersions of the C-1 and C-4 resonances due to steric perturbation were calculated for α-CD complexes with water, PNP, and PHBA, for which the X-ray crystallographic data, including the coordinates of hydrogen atoms, have been re-

ported[19a,20]. The results in Table II clearly show that the observed magnitude of the ^{13}C shift dispersions of the C-1 and C-4 resonances could be brought about by conformation-dependent, hydrogen–hydrogen steric repulsion. Unfortunately, however, the calculated results could not reproduce quantitatively the observed resonances. To explain more quantitatively the ^{13}C shift dispersion, the contributions from other intra- and inter-molecular shielding effects must be taken into account, and/or a more pertinent expression must be used for steric perturbation.

Similar ^{13}C shift dispersions have been observed for the C-1 and C-4 resonances of several types of cellulose and their derivatives[31–36]. At present, there are different explanations to account for the multiplets of the C-1 and C-4 resonances of cellulose, *e.g.*, the existence of conformational diversity of glycosidic linkages, existence of polymorphs, existence of independent chains in the unit cell, or molecular packing effects. For α-CD, the molecular packing effects could not be fully excluded. The packing state of α-CD molecules in the crystal of an α-CD inclusion-complex depends on the type of guest molecule. The crystal of the form I α-CD · H_2O complex is a cage type[19a], those in the α-CD · PNP and α-CD · PHBA complexes are layer types[20], and that in the α-CD · MNP complex is a channel type[21]. In the crystal of the α-CD · MNP complex, the symmetry of α-CD molecular packing as well as that of the α-CD macrocycle are very high as compared with those in other complexes. Such differences in molecular packing can also contribute more or less to the ^{13}C shift dispersions of the C-1, C-4, and C-6 resonances.

For the α-CD C-6 resonances, it has also been proposed that the ^{13}C shifts

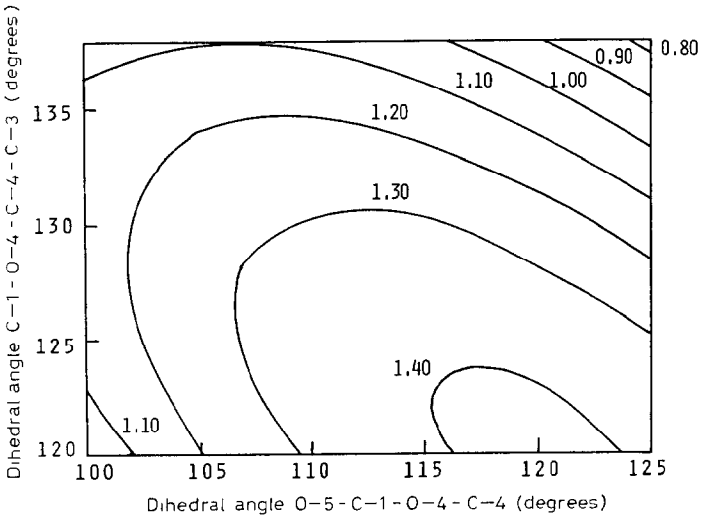

Fig. 6. Dependence of ^{13}C chemical shifts (in p.p.m.) of the C-4 resonance of α-CD on the dihedral angles of the glycosidic linkage, O-5—C-1—O-4—C-4 and C-1—O-4—C-4—C-3, calculated by using the expression of Grant and Cheney[29,30]. Bond lengths (C–O, C–H) and bond angles (C–O–C, O–C–H) are assumed to be constant (0.143, 0.109 nm, and 119.00 and 109.47°, respectively).

TABLE II

PREDICTED SOLID-STATE ^{13}C CHEMICAL SHIFTS (p.p.m.) OF THE C-1 AND C-4 RESONANCES OF α-CD[a]

Glucosyl residue[b]	*α-CD · H_2O*		*α-CD · PNP*		*α-CD · PHBA*	
	C-1	*C-4*	*C-1*	*C-4*	*C-1*	*C-4*
1	−1.10	−0.93	−4.05	−1.29	−0.62	−1.12
2	−0.82	−0.94	−2.00	−0.35	−0.79	−0.79
3	−0.80	−0.82	−0.56	−0.63	−1.47	−1.04
4	−0.17	−0.68	−0.61	−2.58	−0.38	−2.14
5	−0.45	−0.39	−2.71	−0.83	−0.25	−0.47
6	−0.77	0.66	−0.54	−2.09	−2.17	−1.07

[a]Calculated using the expression of Grant and Cheney[29,30]; a negative sign indicates a low-field shift.
[b]The numbers of glucosyl residues correspond to those indicated in the X-ray crystallographic studies, *i.e.*, in ref. 19 for α-CD · H_2O, and in ref. 20 for α-CD · PNP and α-CD · PHBA complexes.

can be attributed to the conformation about the C-5–C-6 bond[9], *i.e.*, the C-6 signals that appear in the ranges 61.1–62.1 and 60.1–60.7 p.p.m. are assigned to *gauche–trans* and *gauche–gauche* conformations, respectively, as viewed from the C-6–O-6 orientation with respect to the C-4—C-5 and O-5—C-5 bonds. With these assignments, the appearance of the C-6 resonances of all α-CD complexes could not be explained quantitatively. For example, of the six CH_2OH groups in the α-CD · PNP complex[20], 0.5 adopt a *gauche–trans* conformation and 5.5 adopt a *gauche–gauche* conformation. Thus, the expected intensity ratio of *gauche–trans* to *gauche–gauche* peaks is 0.5:11.5, whereas the observed ratio of peaks at 61.5 and 60.5 p.p.m. is 1:1. Further, for the α-CD · MNP complex[21], the α-CD molecule contains three *gauche–trans* and three *gauche–gauche* conformers, whereas the C-6 resonance is a sharp peak at 60.9 p.p.m. For the ^{13}C shifts of the C-6 resonance, effects other than conformation, such as molecular packing and hydrogen bonding, must also be considered. Also, the C-6—O-6 bond-lengths in the α-CD · MNP complex are abnormally short (0.1171–0.1249 nm), compared with those in other complexes (*e.g.*, 0.1416–0.1445 nm in form I of the α-CD · H_2O complex). These short bond-lengths must also influence the ^{13}C shift of the C-6 resonance.

Finally, mention should be made of the linear relationship between the ^{13}C shifts induced in the α-CD C-1 resonance by complexation and the thermodynamic parameters for forming α-CD inclusion-complexes[6]. We have shown that the most plausible source of the solid-state ^{13}C shift dispersions of the α-CD C-1 and C-4 resonances is the diversity of the conformations about the glycosidic linkages. The fact that the (averaged) ^{13}C shifts of α-CD observed in the solid state are in good agreement with those observed in solution suggests that the ^{13}C shift of the C-1 singlets observed in solution is the average of the shifts of C-1 in the six units, each of which is involved in a glycosidic linkage having a specific conformation corresponding to that in the solid state. Averaging of the ^{13}C shifts in solution is made by conformational interconversion, which is sufficiently rapid on the n.m.r. time-

scale. The same situation is also valid for the C-4 resonance. The rapid interconversion is revealed by observing ^{13}C spin–lattice relaxation times[2,7], which indicate the rapid internal motion of the α-CD macrocycle as well as the included guest molecule. That the ^{13}C shift displacement of the C-1 resonance upon complexation in solution mainly arises from the change in average conformation of glycosidic linkages is consistent with the proposal of Gelb *et al.*[6]. No correlation was found between the reported ^{13}C shift displacements of the C-4 resonance and the thermodynamic parameters[6], although C-1 and C-4 are both involved in the glycosidic linkage and the ^{13}C shifts of both are sensitive to the conformation of the glycosidic linkage. It is not clear why the ^{13}C shifts of the C-1 resonance correlate well with the thermodynamic parameters whereas those of the C-4 resonance do not.

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