concentrated in vacuo. The residue was chromatographed (SiO_2, $CHCl_3$) and then passed through a short Florisil column (Et_2O) to remove colored impurities. This gave 11 mg of juncusol (**1**) (81%): mp 174.5–175.5 °C (benzene); IR (KBr) 3350, 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (3 H, s), 2.26 (3 H, s), 2.64 (4 H, s), 5.17 (1 H, dd, $J_{AX} = 17$, $J_{AB} = 2$ Hz), 5.40 (1 H, dd, $J_{BX} = 11$, $J_{AB} = 2$ Hz), 6.68 (3 H, m), 7.50 (1 H, d, $J = 9$ Hz); MS *m/e* 266 (M^+), 251, 237.

Juncusol Diacetate. Synthetic juncusol (6 mg) was dissolved in dry pyridine (0.5 mL) and placed under nitrogen. Acetic anhydride (9 μL, 4 equiv) was added dropwise and the mixture was stirred for 12 h at room temperature and then poured into 1 N HCl. The acid was extracted with methylene chloride and the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed (SiO_2, $CHCl_3$) and filtered through Florisil (Et_2O) to yield 7 mg (88%) of juncusol diacetate, mp 189–191 °C (benzene). This was identical with a sample prepared by acetylation of natural juncusol: NMR ($CDCl_3$) δ 2.16 (3 H, s), 2.20 (3 H, s), 2.36 (6 H, s), 2.75 (4 H, s), 5.26 (1 H, dd, $J_{AX} = 17$, $J_{AB} = 2$ Hz), 5.55 (1 H, dd, $J_{BX} = 11$, $J_{AB} = 2$ Hz), 6.84 (3 H, m), 7.66 (1 H, d, $J = 9$ Hz); MS *m/e* 350, 308, 266.[28]

Acknowledgment. Partial support of this work by Grant CA-18846 from the National Cancer Institute, U.S. Public Health Service, and by Hoffmann-La Roche Inc. is gratefully acknowledged. D.P.C. acknowledges with thanks a Sherman Clarke Fellowship. The authors are grateful to Dr. Jean-Pierre Gesson (University of Poitiers, France) for calling to their attention the modified Sommelet–Hauser procedure and wish to thank Drs. P. M. Hendrick and J. M. Hewitt (Eastman Kodak Research Laboratories) for a ^{13}C NMR of juncusol dimethyl ether and Mr. J. Rizzi for performing the simple Hückel calculations. We would also like to thank Dr. D. H. Miles for a reference sample of juncusol and Drs. S. W. Pelletier and N. V. Mody for providing spectral data of juncusol and juncusol diacetate.

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The Complexation Chemistry of Cyclohexaamyloses. 3. Per-*O*-methylcyclohexaamylose Adducts with 4-Biphenylcarboxylate and *p*-Methylcinnamate Anions[1,2]

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Abstract: Conductometric and ^{13}C NMR spectrometric analyses of aqueous solutions containing 4-biphenylcarboxylate (BPC) or *p*-methylcinnamate (PMC) anions and per-*O*-methylcyclohexaamylose (MCy) indicate formation of MCy_2, MCy·BPC, MCy_2·BPC, MCy·PMC, and MCy_2·PMC complexes. Values of equilibrium constants for each complex formation reaction were estimated at 30 °C. Intrinsic ^{13}C chemical shifts of the various adducts were calculated as well. These are discussed in terms of (1) preferential binding of phenyl and *p*-tolyl terminals of BPC and PMC, respectively, in the binary complexes, (2) face to face orientations of the wide MCy apertures in the MCy_2 and ternary adducts, and (3) noncentered occlusion of the PMC anion within the cavity of its ternary complex.

Cyclohexaamylose, which we denote as Cy, forms complexes with a variety of molecules and ions in aqueous solutions. Among these we have studied the Cy complexes of 4-biphenylcarboxylate[1] (I) and *p*-methylcinnamate[2] (II) anions (Figure 1) (to be abbreviated BPC and PMC, respectively) and detected both Cy·PMC and Cy_2·PMC in solutions of Cy and PMC, but only the Cy_2·BPC complex in that system. ^{13}C NMR data indicate that the carboxylate terminal of PMC is preferentially bound in the wide rim of the Cy cavity. Other recent studies of Cy complexes with *p*-nitrophenolate[3] and

0002-7863/79/1501-1864$01.00/0

Table I. Intrinsic Chemical Shifts of Uncomplexed MCy and Its MCy_2 Dimer[a,b]

MCy carbon	$\delta_0^{(MCy)}$	$\Delta\delta_D^{(MCy)}$
1	98.81	0.68
2[c]	81.07	0.46
3	80.30	1.15
4	81.86	0.37
5	71.73	0.15
6	72.09	−0.08
2′[d]	58.81	−0.07
3′	61.00	0.67
6′	59.45	−0.04
standard error[e]	±0.02	±0.08
log K_D = 0.7 ± 0.2; 30 °C; D_2O		

[a] δ values are given in parts per million relative to external Me_4Si. [b] $\Delta\delta_D = \delta_D - \delta_0$; negative signs indicate upfield displacement. [c] Assignments may be reversed within the set C2, C3, C4. [d] Assignments may be reversed within the set C2′, C3′. [e] Based on instrumental resolution of ±0.02 ppm.

benzoic acid[4] suggest preferential substrate binding where the nitro group and carboxylic acid group, in the second case, are bound to Cy.

We wish to further explore the factors determining the nature and stereoselectivity of Cy binding and we now report an investigation of the complexes of BPC and PMC anions with per-*O*-methylcyclohexaamylose (III). This host molecule, which we denote as MCy, has geometric properties similar to those of unsubstituted Cy but differs primarily in hydrogen-bonding capability and polarity from the parent molecules. We employed ^{13}C NMR spectrometry to study the structures of the various complexes and to estimate their formation constants at 30 °C. A conductometric method verified the ^{13}C NMR equilibrium constants.

MCy Dimerization. ^{13}C NMR spectra of D_2O solutions of MCy consist of nine resonance lines corresponding to six sets of nine nonequivalent carbons. We observed that the chemical shifts of several of these resonances relative to external Me_4Si were markedly dependent on MCy concentration. Hypothesizing that these observed displacements are caused by reversible dimerization of MCy molecules, $2MCy \rightleftharpoons MCy_2$, we sought to characterize this dimerization reaction by measuring the ^{13}C NMR spectra of 11 D_2O solutions containing 0.005–0.06 *F* MCy. In the equations and discussion which follow, we adopt a chemical shift notation used in previous studies.[1,2] A given carbon resonance is denoted by both a superscripted symbol, i.e., (MCy 6) referring to the C6 carbon of MCy, and a subscripted symbol 0 or D referring to uncomplexed MCy and MCy_2 dimer, respectively. We assumed that the following set of model equations accounts for the dependence of observed chemical shifts ($\delta_{obsd}^{(MCy)}$) on MCy formality (F_{MCy}). Weighted-average composition of observed chemical shifts at the fast exchange limit (one such equation for each carbon resonance)

$$\delta_{obsd}^{(MCy)} = (\delta_0^{(MCy)}[MCy] + 2\delta_D^{(MCy)}[MCy_2])/F_{MCy} \qquad (1)$$

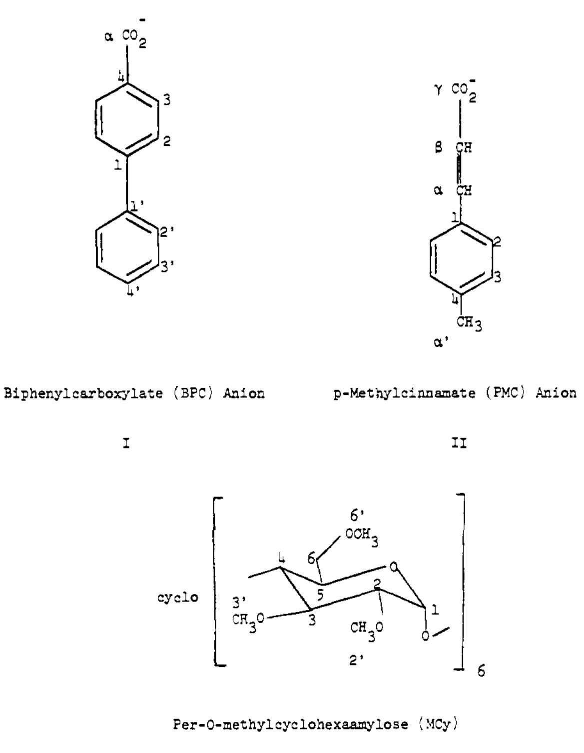
conservation of MCy

$$M_{MCy} = [MCy] + 2[MCy_2] \qquad (2)$$

dimer formation equilibrium

$$K_D = \frac{[MCy_2]}{[MCy]^2} \qquad (3)$$

Equations 1–3 were solved numerically for K_D and for each of the nine $\delta_0^{(MCy)}$ and nine $\delta_D^{(MCy)}$ parameters by means of a nonlinear regression technique.[1,2] The results and their statistical uncertainties are shown in Table I. The quality of fit of the model equations to the experimental data was excellent as was reflected in a completely random pattern of ($\delta_{calcd} - \delta_{obsd}$) residuals with a root mean square value of 0.005 ppm compared to an expected 0.02-ppm statistical uncertainty in the experimental measurements.



Biphenylcarboxylate (BPC) Anion

I

p-Methylcinnamate (PMC) Anion

II

Per-O-methylcyclohexaamylose (MCy)

III

Figure 1. Structural formulas and carbon number indexes of BPC, PMC, and MCy reactants.

Four of the nine MCy resonances which appear in the second column of Table I were assigned to specific carbons of uncomplexed MCy according to the following reasoning: (1) The extreme downfield peak at 98.81 ppm is assigned to the anomeric C1 carbon, the only member of the set which is attached to two oxygen atoms. (2) Only the peak at 72.09 ppm is observed to split into a triplet under gated ^1H-decoupling conditions. Since MCy contains only one methylene group, this resonance must be ascribed to C6. (3) The neighboring peak at 71.73 ppm is assigned to C5 because per-O-methylation of cyclohexaamylose is not expected to displace the resonance by more than ~2 ppm.[5] (4) Methoxy resonances corresponding to the peak at 59.45 ppm have been observed at 59.4 ppm for each of the following cycloamylose derivatives in D_2O solution: hexakis(2,6-di-*O*-methyl)cyclohexaamylose, heptakis(2,6-di-*O*-methyl)cycloheptaamylose,[6] and per-*O*-methylcycloheptaamylose. A similar constancy in the position of one methoxy resonance may be noted for the same compounds in $DCCl_3$ solutions.[7] The C6′ methoxy carbon is three bonds removed from the glucopyranosyl framework and thus should be least sensitive to environmental and perhaps conformational changes associated with transitions between the compounds compared above. On that basis we assign the peak at 59.45 ppm to the C6′ carbon. We cannot assign the remaining methine (81.07, 80.30, and 81.86 ppm) and methoxy (58.81 and 61.00 ppm) resonances to specific carbons in D_2O solution at this time. However, three of the four assigned carbons (C5, C6, and C6′) completely define the narrow rim of MCy and thus provide a useful means of determining the structure of MCy complexes. A second criterion is provided by noting that the group of methine carbons with ^{13}C resonances near 80 ppm

Table II. Intrinsic Chemical Shifts[a,b] of Species Involved in MCy-BPC and MCy-PMC Equilibria at 30 °C in D_2O

MCy-BPC System

MCy carbon	$\Delta\delta_1^{(MCy)}$	$\Delta\delta_2^{(MCy)}$	BPC carbon	$\delta_0^{(BPC)}$	$\Delta\delta_1^{(BPC)}$	$\Delta\delta_2^{(BPC)}$
1	1.12	1.88	α	176.31	−1.06	−5.35
2[c]	0.52	1.20	4	136.34	0.32	2.90
3	1.86	2.88	3[f]	130.19	−0.28	0.14
4	0.37	1.11	2[g]	128.11	0.49	−1.11
5	0.20	0.04	1	144.12	−0.13	−1.58
6	0.17	0.00	1′	140.93	0.85	2.14
2′[d]	0.39	−0.47	2′[g]	127.72	0.05	−1.87
3′	1.04	1.66	3′[f]	130.54	0.33	2.12
6′	−0.13	−0.15	4′	129.12	−0.37	−1.41
standard error[e]	±0.02	±0.02		±0.01	±0.05	±0.04
log K_1 = 3.0 ± 0.2	log K_2 = 2.2 ± 0.3		log K_1 = 2.8 ± 0.1	log K_2 = 2.4 ± 0.1		

MCy-PMC System

MCy carbon	$\Delta\delta_1^{(MCy)}$	$\Delta\delta_2^{(MCy)}$	MCy carbon	$\delta_0^{(PMC)}$	$\Delta\delta_1^{(PMC)}$	$\Delta\delta_2^{(PMC)}$
1	1.58	1.01	γ	176.90	−1.71	−2.09
2[c]	0.57	0.53	β	124.25	1.50	1.80
3	2.60	1.55	α	141.71	−1.11	−1.51
4	−0.04	0.32	1	133.41	1.55	1.27
5[e]	0.2[h]	−0.2[h]	2	130.59	−0.16	−0.50
6[e]	0.2[h]	−0.2[h]	3	128.72	0.50	0.02
2′[d]	−0.49	−0.23	4	141.32	−3.14	−2.04
3′	1.35	0.88	δα′	21.41	2.01	0.72
6′	−0.08	−0.10				
standard error[e]	±0.04	±0.04		±0.01	±0.06	±0.04
log K_1 = 2.2 ± 0.1	log K_2 = 2.1 ± 0.1					

[a] δ values are given in parts per million relative to external Me_4Si. [b] $\Delta\delta_n = \delta_n - \delta_0$; negative signs indicate upfield displacement. [c] Assignments may be reversed within the set C2, C3, C4. [d] Assignments may be reversed within the set C2′, C3′. [e] Based on instrumental resolution of ±0.02 ppm. [f,g] These assignments may be reversed. [h] Because of resonance peak overlap, C5 and C6 measurements suffer from poor precision. These estimates are uncertain to ±0.2 ppm.

corresponds to C2, C3, and C4, which are all located at the wide rim or central band of the molecule.

Inspection of $\Delta\delta_D^{(MCy)} \equiv \delta_D^{(MCy)} - \delta_0^{(MCy)}$ values listed in Table I reveals that none of the narrow rim carbons are significantly perturbed upon dimerization (0.15, −0.08, and −0.04 ppm for C5, C6, and C6′, respectively). On the other hand, the conformationally responsive[5] C1 carbon is substantially displaced (0.68 ppm). The sets of C2′ and C3′ methoxy carbons are situated in outer and inner bands of the wide rims, and are perturbed by −0.07 and 0.67 ppm. The C2, C3, and C4 carbon set, located at the wide rim or in the central band of the molecule, shows large perturbations ranging from 0.37 to 1.15 ppm. Thus, the significant perturbations of ^{13}C resonances noted here correspond to carbon atoms which are located either at the wide MCy rim or in the central band of the molecule (C1 and C4). Therefore, we conclude that the wide apertures of the MCy constituents are oriented "face to face" in the MCy_2 dimer.

^{13}C NMR Studies of Complexes of MCy with an Anionic Guest. Separate experiments were done to measure complex formation constants and intrinsic ^{13}C NMR chemical shifts in systems of MCy and both BPC and PMC anions. The data were fitted to a common set of model equations similar to those given in ref 2 but suitably modified to account for formation of MCy_2 dimer. These equations together with either $\delta_{obsd}^{(MCy)}$ or $\delta_{obsd}^{(A^-)}$ data were solved in separate calculations for K_1, K_2, and either $\delta^{(MCy)}$ or $\delta^{(A^-)}$ intrinsic shift parameters. A multiple regression technique described earlier[1,2] was employed.

Inherent in our treatment of the ^{13}C data is the assumption that the intrinsic chemical shifts of MCy, MCy_2, A^-, and each of the complexes are independent of both concentration and ionic strength. We have verified these conditions for BPC and PMC in earlier work and our current results with pure MCy solutions seem to indicate that both MCy and MCy_2 have intrinsic chemical shifts that are at least concentration independent. We sought to determine any ionic strength dependence of MCy or MCy_2 resonances by comparison of spectra of (1) 0.05 F MCy, (2) 0.05 F MCy, 0.05 F LiCl, and (3) 0.05 F MCy, 0.05 F LiCl, 0.06 F NaCl. The three solutions gave spectra which were identical within the ±0.02 ppm precision of our measurements. The resonances observed with these solutions reflect the weighted average of MCy and MCy_2 resonances according to eq 1 and we concluded that the intrinsic chemical shifts of both MCy and MCy_2 are independent of the ionic strength up to 0.11 F. These results lead us to conclude further that the chemical shifts of the various MCy, A^- complexes are concentration and ionic strength independent as well.

^{13}C NMR Studies of MCy·BPC and MCy_2BPC Formation Constants and Structures. In this series of experiments we measured the ^{13}C resonances of MCy and BPC carbon atoms in 62 D_2O solutions of MCy (0.00–0.06 F) and BPC (0.00–0.10 F) at 30 °C over a wide range of host/guest molar ratios. All the observed peaks were accounted for by nonequivalent carbons of MCy and BPC, and the BPC resonance assignments have been previously described.[1] Results of calculations done as described in the previous section are shown in Table II.

Examination of the residuals ($\delta_{calcd} - \delta_{obsd}$) revealed no systematic trends and the root mean square scatter of ±0.02 ppm was consistent with the spectrometer resolution. The values of log K_1 and log K_2 represent best estimates obtained from MCy data and BPC data independently. These estimates refer to a D_2O solvent at 30 °C and are in agreement with one another and with the log K values determined by conductometric measurements with H_2O solvent as will be described in a following section.

Interpretation of the intrinsic resonances listed in Table II indicates some of the structural features of the various complexes. Our discussion consists of two parts, the first of which deals with resonance displacements of MCy carbons and the second with BPC carbons.

1. MCy Resonance Displacements. MCy_2 Dimer. The intrinsic resonances of dimer carbons $\delta_D^{(MCy)}$ and their displacements $\Delta\delta_D^{(MCy)}$ from uncomplexed MCy peaks were obtained with standard errors of ±0.04 and ±0.05 ppm, respectively. These $\delta_D^{(MCy)}$ and $\Delta\delta_D^{(MCy)}$ values matched corresponding entries in Table I to within their statistical uncertainties and so were not included in Table II.

Ternary MCy_2·BPC Complex. Inspection of $\Delta\delta_2^{(MCy)}$ displacements reveals little or no perturbation of narrow rim carbons C5, C6, and C6′ (0.04, 0.00, and −0.15 ppm, respectively). This is in contrast to the substantial displacement of C2′, C3′ (−0.47 and 1.66 ppm), C2, C3, C4 (1.20, 2.88, and 1.11 ppm), and C1 (1.88 ppm) resonances. The perturbed carbons are either located at the wide rims or are likely to reflect changes in rotamer populations about C1-O-C4 bridges[5] and so we conclude that the wide rims are oriented "face to face" in the MCy_2·BPC complex. In a space-filling model of this adduct BPC is completely occluded within a cavity zone defined by the duplicate bands of interglucosyl oxygens and this structure is confirmed by the very small values of $\Delta\delta_2^{(MCy5)}$ and $\Delta\delta_2^{(MCy6)}$. We note that the magnitudes of nearly all displacements are smaller in the MCy_2 dimer than in the ternary complex MCy_2·BPC. Perturbations of MCy carbons in MCy_2·BPC presumably involve both MCy-MCy and MCy-BPC interactions while perturbations in MCy_2 are due only to MCy-MCy interactions. Comparison of Tables I and II suggests that both kinds of interactions have similar effects on the MCy carbon atoms as reflected in the signs of the perturbations.

Binary MCy·BPC Complex. The pattern of $\Delta\delta_1^{(MCy)}$ displacements is similar to that in the ternary complex. The C5, C6, and C6′ carbons at the smaller MCy aperture are weakly perturbed (0.20, 0.17, and −0.13 ppm, respectively). Substantial displacements of the C1 resonance (1.12 ppm) and resonances of the set C2, C3, C4 (0.52, 1.86, and 0.37 ppm) and of the C2′, C3′ set (0.39 and 1.04 ppm) indicate a binary complex in which the BPC anion is partially occluded in the wider zone of the MCy cavity. The smaller displacements ascribable to carbon atoms at the wide rim or central band of MCy in the binary complex compared with the ternary complex are consistent with the absence of MCy-MCy and MCy-CO_2^- interactions in MCy·BPC.

2. BPC Resonance Displacements. The Cα displacements, ascribable to the carboxylate carbon in BPC, are strikingly different in the binary and ternary complexes (−1.06 and −5.35 ppm, respectively). The substantial shielding of Cα resulting from the addition of a second MCy molecule to the complex indicates that this process corresponds to complexation of the carboxylate terminal of BPC. As a consequence, the binary complex, MCy·BPC, must feature the phenyl rather than the carboxylate terminal bound in the MCy cavity.

^{13}C NMR Studies of MCy·PMC and MCy_2·PMC Formation Constants and Structures. ^{13}C NMR resonances of 44 D_2O solutions containing MCy (0.00-0.070 F) and *p*-methylcinnamate anion (PMC, 0.00-0.13 F) were recorded at 30 °C over a wide range of PMC/MCy molar ratios. All of the observed peaks could be ascribed to specific carbons of MCy and PMC.[2] The calculation of complex formation constants and intrinsic chemical shifts of MCy carbons is described in a previous section. Again the $(\delta_{calcd}^{(MCy)} - \delta_{obsd}^{(MCy)})$ residuals were randomly distributed and had a root mean square value of 0.02 ppm, which was comparable to the spectrometer resolution. The best fit values of log K_1 and log K_2 (D_2O, 30 °C) as found from MCy carbon resonances are in approximate agreement with the corresponding conductometric results (H_2O, 30 °C). In a second, separate calculation these estimates of log K_1 = 2.2 and log K_2 = 2.1 in addition to log K_D = 0.7 were treated as known parameters to obtain $\delta_0^{(PMC)}$, $\delta_1^{(PMC)}$, and $\delta_2^{(PMC)}$ using observed PMC carbon resonances. The root mean square fit was 0.02 ppm and the residuals were randomly scattered, indicating that no systematic errors were present. The results of both computations are included in Table II.

The dimer parameters $\delta_D^{(MCy)}$ and $\Delta\delta_D^{(MCy)}$ had standard errors of 0.05 and 0.07 ppm, respectively, and again are not listed because of their agreement with results shown in Table I.

Ternary and Binary Complexes. Comparison of ternary displacements at C5, C6, and C6′ (∼−0.2, ∼−0.2, and −0.10 ppm, respectively) with $\Delta\delta_2^{(MCy)}$ values at C1 (1.01 ppm), C2, C3, C4 (0.53, 1.55, and 0.32 ppm), and C2′, C3′ (−0.23, 0.88 ppm) indicates greater perturbation of sites at the wide aperture of MCy constituents in addition to conformationally sensitive bridgehead carbons. Following the reasoning previously applied to the MCy_2·BPC system, we conclude that the wide rims of MCy molecules are also oriented face to face in the MCy_2·PMC complex.

A similar pattern is evident in the binary complex parameters. Larger displacements of carbon resonances C1 (1.58 ppm), C2, C3, C4 (0.57, 2.60, −0.04 ppm), and C2′, C3′ (−0.49 and 1.35 ppm) compared to C5, C6, and C6′ (∼0.2, ∼0.2, and −0.08 ppm, respectively) suggest a binary complex model in which the PMC anion is constrained within the wider zone of the MCy cavity.

It is noteworthy that displacements of strongly perturbed MCy carbons are larger in MCy·PMC than in MCy_2·PMC. Also we see that PMC chemical shift displacements $\Delta\delta_2^{(PMC)}$ and $\Delta\delta_1^{(PMC)}$ in the ternary and binary complexes are similar in magnitude, a relationship which is in contrast to the corresponding situation in BPC. In particular, the carboxylate carbon resonance displacements in the PMC system are similar in the two complexes ($\Delta\delta_1^{(PMC\gamma)} = -1.71$ ppm and $\Delta\delta_2^{(PMC\gamma)} = -2.09$ ppm) whereas in the BPC system the corresponding values are quite different ($\Delta\delta_1^{(BPC\alpha)} = -1.06$ ppm and $\Delta\delta_2^{(PBC\alpha)} = -5.35$ ppm). We interpret these observations as suggesting a ternary MCy_2·PMC structure in which the bulk of the PMC anion is bound within one MCy constituent. Such a "noncentered" binding mode is equivalent to capping a binary MCy·PMC complex with another MCy molecule while constraining the PMC guest to the original binary cavity. Any given MCy resonance displacement in the ternary MCy_2·PMC complex thus is an average of the two corresponding carbons on the two MCy molecules and these carbons are now magnetically nonequivalent because of the asymmetric position of the PMC guest. One such carbon is in a magnetic environment similar to the corresponding carbon in the binary MCy·PMC and the other is in a magnetic environment similar to that carbon in the dimer MCy_2, having no guest in its cavity. Consequently, this model would predict that in the fast exchange limit any given displacement value $\Delta\delta_2^{(MCy)}$ is roughly an average of the corresponding $\Delta\delta_1^{(MCy)}$ and $\Delta\delta_D^{(MCy)}$. This prediction is, indeed, borne out by an examination of the corresponding entries in Tables I and II and so this model explains why most $\Delta\delta_1^{(MCy)} > \Delta\delta_2^{(MCy)}$. The noncentered model also explains why PMC resonances are so similar in the binary and ternary complexes. The capping of the binary complex with another MCy without appreciable reorientation of the guest (PMC) cannot cause any substantial changes in the magnetic environments of PMC carbons and so further shift displacements are minimal. In particular, the carboxylate carbon in PMC is shielded by only 0.38 ppm by this capping process, whereas in BPC the formation of the ternary complex shields the carboxylate carbon in that ion by about 4.3 ppm with respect to the binary complex. This striking difference suggests that PMC in the binary MCy·PMC is oriented with the carboxylate outside the MCy cavity with its solvation sphere in place and that the capping of this adduct by another MCy

Table III. Results of Calculations with Conductance Measurements of MCy-Lithium *p*-Methylcinnamate and MCy-Lithium 4-Biphenylcarboxylate Aqueous Solutions at 30 °C

parameter	LiPMC, initial concn 0.004 M	LiBPC, initial concn 0.003 M	LiBPC, initial concn 0.007 M
log K_1	3.0	2.7	2.8
log K_2	2.2	2.6	2.6
$\lambda_0{}^0$ [a]	29.9	30.1	29.7
$\lambda_1{}^0$ [a]	22.	16.	15.
$\lambda_2{}^0$ [a]	15.	11.	12.
fit, %	0.05	0.04	0.06

[a] mho cm^2 equiv^{-1}.

leaves that solvation sphere essentially intact. In contrast, the much larger shielding effect in BPC suggests that solvation molecules are lost from the BPC carboxylate when the ternary complex is formed.

Conductometric Estimates of Complex Formation Constants. We wished to confirm our ^{13}C NMR results for log K in these systems by an independent experimental method and have recently shown how the complex formation constants for the reaction of cyclohexaamylose (Cy) with an ionic species can be estimated from measurements of electrolytic conductance.[1] In our earlier measurements, the conductance of a solution of LiBPC was monitored after stepwise additions of a Cy solution. In the present work, the dimerization of MCy represents an additional complication which is accounted for by suitable modification of eq 5–11 of ref 1. These equations form the set of model equations which represent the behavior of the aqueous solutions with respect to the stepwise formation constants K_1 and K_2, the conductance parameters $\lambda_0{}^0$, $\lambda_1{}^0$, $\lambda_2{}^0$ and the species concentrations. The model equations and experimental data yield estimates of the various constants through a nonlinear regression technique described in ref 1 and 9.

The results of this analysis confirmed the existence of both binary and ternary complexes and the values of their formation constants as determined by ^{13}C NMR. These results are shown in Table III.

Discussion

The reactions of MCy with BPC and PMC noted here differ in several respects from those of cyclohexaamylose (Cy) with the same anions. Firstly, Cy does not aggregate in the absence of substrates whereas MCy forms detectable concentrations of MCy$_2$ dimer under similar conditions. The large displacements noted in Table I, particularly those of C1 and C4 bridgehead carbons, suggest that these interactions alter the conformations at C1–O–C4 bonds of MCy upon dimerization.

The preferential binding of the nonionic terminals observed with both MCy·PMC and MCy·BPC also contrasts with Cy·PMC in which the charged acrylate side chain of PMC is preferentially bound. This reversal of binding specificity may be explained by the greater hydrophobic nature of the O-methylated MCy cavity. Apparently, anions may be stabilized within the Cy cavity by hydrogen bonding or other ion–dipole attractions to hydroxyl groups of Cy or by solvent-mediated interactions. Such ion–dipole or hydrogen bonding interactions do not seem to play an important role in MCy complexes. Presumably, interactions of the dipole–dipole or dipole-induced dipole type between MCy and the polarizable phenyl or *p*-tolyl groups are responsible for bonding in these complexes. The off-centered complexation in MCy$_2$·PMC seems to confirm that the bonding forces involve MCy and the hydrocarbon terminal of the substrate; MCy bonding with the ionic terminal is substantially weaker.

In conclusion, our results indicate that functional group modification of cyclohexaamylose may change the stereospecificity of complexation reactions. Studies of functionalized cyclohexaamyloses as enzyme models should take into consideration these binding mode changes as well as dimerization of the host and possible formation of ternary complexes.

Experimental Section

Materials. Lithium and sodium salts of BPC and PMC were prepared by neutralizing samples of the parent acid compounds by Li_2CO_3 or NaOH in hot aqueous solution. The crude salts were recrystallized twice from water. Solutions of LiPMC were analyzed by potentiometric titration with HCl and by a direct measurement of the conductance which gave results identical with the former method to within about ±0.5%. LiBPC solutions were analyzed by conductance measurements based on our earlier determination of $\lambda^0{}_{BPC}$.[1]

Samples of MCy were prepared by a method suggested by Hakamori.[10] A portion of NaH (8.0 g, 0.33 mol) was added to dimethyl sulfoxide (200 mL) under nitrogen purge and the reaction mixture was maintained at 70 °C for about 5 h to ensure complete formation of the dimethylsulfinyl carbanion. Into this solution was added dropwise a solution of cyclohexaamylose (10 g, 0.0096 mol) in dimethyl sulfoxide (35 mL) while the nitrogen purge continued. Finally, CH_3I (40 mL, 0.64 mol) was added dropwise at ~0 °C and the reaction mixture was left overnight. Following dilution with water (150 mL) MCy was isolated by extraction with four 50-mL aliquots of $CHCl_3$ which were subsequently combined, washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and 7 g of crude MCy was obtained. The product was dissolved in a minimum volume of water at about 4 °C and filtered, and the resulting solution was heated to 90 °C whereupon white, crystalline MCy (6.7 g, 57% yield, mp 205–206 °C, lit.[11] 205 °C) was isolated after vacuum drying at 50 °C.

TLC analysis employed acetone and 10% methanol–chloroform (v:v) solvents and gave single well-defined spots with R_f 0.58 ± 0.03 and 0.67 ± 0.03, respectively. Iodine staining and fluorescence quenching were employed for detection.

Infrared spectra of MCy in KBr pellets had no detectable bands in the hydroxyl stretch region near 3400 cm^{-1} and C, H analysis (C, 53.0; H, 7.77; theory C, 52.93; H, 7.90) confirmed that the MCy sample was anhydrous and contained no hydroxyl groups.

^{13}C NMR spectra recorded under high signal/noise conditions gave only nine resonances ascribable to MCy and no additional peaks above the noise level could be detected. ^{13}C NMR measurements with a Varian CFT-20 spectrometer and conductance measurements have both been described previously.[1,2]

Acknowledgments. We thank Professor Elkan R. Blout for providing access to the CFT-20 spectrometer at the Department of Biological Chemistry, Harvard Medical School. This work was supported in part by research grants from the National Institute of General Medical Sciences of the National Institutes of Health, U.S. Public Health Service (GM19645, GM26004).

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