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Note

Crystal structures of cyclomaltohexaose (α-cyclodextrin) complexes with *p*-bromophenol and *m*-bromophenol

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Abstract

Crystal structures of cyclomaltohexose (α-cyclodextrin) complexes with *p*-bromophenol and *m*-bromophenol have been determined by single-crystal X-ray diffraction. The space group of the α-cyclodextrin–*p*-bromophenol complex is $P2_12_12_1$ with unit cell dimensions of $a = 15.318(3)$, $b = 24.733(3)$, $c = 13.457(2)$ Å, and that of the α-cyclodextrin–*m*-bromophenol complex is $P2_12_12$ with unit cell dimensions of $a = 25.858(7)$, $b = 27.263(8)$, $c = 8.145(3)$ Å. In crystals, the α-cyclodextrin–*p*-bromophenol complex and the α-cyclodextrin–*m*-bromophenol complex form a layer-type and a channel-type molecular packing structure, respectively. The intermolecular hydrogen-bond interactions of the hydroxyl groups of bromophenols are closely related to the molecular packing structure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclodextrin; Bromophenol; X-ray structure; Crystal structure

Cyclomaltooligosaccharides (cyclodextrins, CDs) are cyclic oligosaccharides with α-$(1 \rightarrow 4)_n$-linked cyclic structure of six (α-), seven (β-), or eight (γ-) glucose units, all having a truncated conical structure with the primary hydroxyl groups at the narrow side (head) and the secondary hydroxyl groups at the wide side (tail). CDs (hosts) can include a variety of molecules (guests) to form stable inclusion complexes,[1,2] and many crystal structures of CD complexes with various guests have been reported.[3] These X-ray structures show that the molecular packing structures of CD complexes in crystals are dependent on the structures of guest molecules. For example, molecular packing structures of α-CD complexes with benzene derivatives as guests have been divided into two types as shown in Fig. 1. One type is a layer-type structure in which α-CDs are arranged in a two-dimensional layer, and the layers are stacked in the crystals (Fig. 1(a)). Another type is a channel-type structure in which α-CDs form a one-dimensional column with head-to-head (Fig. 1(b)) and/or head-to-tail (Fig. 1(c)) orientations, and guests are located on the inside of the α-CD column. The molecular packing structures should be closely related to the structures of guest molecules. In order to elucidate the relationship between them, structural analyses of the CD complexes with systematically selected guest molecules are very useful.

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Here we report the crystal structures of α-CD complexes with *p*-bromophenol and *m*-bromophenol, which are isomers with slightly different structures. These X-ray structures clearly show how the hydroxyl groups with different positions relative to the para- and meta-bromo groups affect the molecular packing structure.

Crystals of the α-CD–*p*-bromophenol complex and α-CD–*m*-bromophenol complex were prepared by dissolving α-CD (0.1 mmol) and *p*-bromphenol and/or *m*-bromophenol (0.1 mmol) in water (5 mL) at 50 °C. By slow evaporation of these solutions at 25 °C, suitable crystals for X-ray data collection were obtained.

Diffraction data of both crystals were collected by a Rigaku AFC7R diffractometer on a Rigaku rotating anode X-ray generator with graphite monochromated CuK$_\alpha$ radiation using the $2\theta/\omega$ scan mode. For the α-CD–*p*-bromophenol complex, diffraction data up to $2\theta = 140°$ were processed. Crystal data are, $C_{36}H_{60}O_{30}{\cdot}C_6H_5BrO{\cdot}5H_2O$, space group $P2_12_12_1$, $a = 15.318(3)$, $b = 24.733(3)$, $c = 13.457(2)$ Å, $V = 5098$ Å^3, $Z = 4$. The initial phase angles were determined by a direct method using the TEXSAN crystallographic software package of Molecular Structure Corporation.[4] Water molecules were located on a difference Fourier map. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms, except hydroxyl hydrogen atoms, were introduced by geometrical calculations and

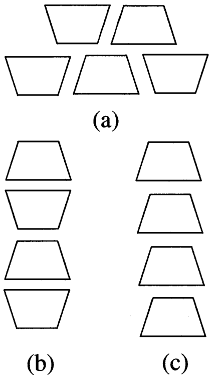
(a)
(b) (c)

Fig. 1. Schematic diagrams of molecular packing structures of α-CD complexes in crystals: (a) a layer-type structure; (b) a channel-type structure with a head-to-head orientation and (c) a channel-type structure with a head-to-tail orientation are shown.

Table 1
Atomic coordinates and temperature factors with estimated standard deviations of non-hydrogen atoms

Atom (residue)	*x*	*y*	*z*	U_{eq}
α-CD–p-bromophenol (p-BrPh) complex				
C1(G1)	0.9506(4)	−0.1957(2)	0.8538(4)	0.042(1)
C2(G1)	0.8777(4)	−0.1558(2)	0.8780(4)	0.045(1)
C3(G1)	0.8868(3)	−0.1052(2)	0.8156(4)	0.039(1)
C4(G1)	0.9776(3)	−0.0816(2)	0.8283(4)	0.039(1)
C5(G1)	1.0470(4)	−0.1239(2)	0.8091(4)	0.046(1)
C6(G1)	1.1386(5)	−0.1045(3)	0.8317(7)	0.074(2)
O2(G1)	0.7958(3)	−0.1827(2)	0.8593(4)	0.061(1)
O3(G1)	0.8244(3)	−0.0662(2)	0.8466(3)	0.0521(9)
O4(G1)	0.9867(3)	−0.0387(1)	0.7586(2)	0.0432(8)
O5(G1)	1.0316(3)	−0.1709(2)	0.8708(3)	0.0524(9)
O6(G1)	1.1482(4)	−0.0819(3)	0.9281(5)	0.098(2)
C1(G2)	1.0128(4)	0.0129(2)	0.7921(4)	0.043(1)
C2(G2)	0.9398(4)	0.0524(2)	0.7720(4)	0.043(1)
C3(G2)	0.9221(4)	0.0543(2)	0.6612(4)	0.040(1)
C4(G2)	1.0055(3)	0.0694(2)	0.6082(3)	0.0351(9)
C5(G2)	1.0806(4)	0.0322(2)	0.6366(3)	0.042(1)
C6(G2)	1.1673(4)	0.0510(3)	0.5967(5)	0.062(2)
O2(G2)	0.8632(3)	0.0386(2)	0.8270(3)	0.055(1)
O3(G2)	0.8576(3)	0.0943(2)	0.6368(3)	0.0533(9)
O4(G2)	0.9882(2)	0.0638(1)	0.5039(2)	0.0380(7)
O5(G2)	1.0896(3)	0.0298(2)	0.7436(3)	0.0458(8)
O6(G2)	1.1823(4)	0.1069(2)	0.6209(4)	0.080(1)
C1(G3)	1.0087(3)	0.1069(2)	0.4384(4)	0.038(1)
C2(G3)	0.9272(3)	0.1179(2)	0.3775(3)	0.038(1)
C3(G3)	0.9022(3)	0.0669(2)	0.3214(3)	0.0344(9)
C4(G3)	0.9777(3)	0.0427(2)	0.2643(3)	0.0350(9)
C5(G3)	1.0642(3)	0.0422(2)	0.3224(4)	0.040(1)
C6(G3)	1.1442(4)	0.0340(2)	0.2586(5)	0.050(1)
O2(G3)	0.8570(3)	0.1363(1)	0.4389(3)	0.0426(8)
O3(G3)	0.8299(2)	0.0760(1)	0.2553(3)	0.0422(7)
O4(G3)	0.9512(2)	−0.0114(1)	0.2426(2)	0.0385(7)
O5(G3)	0.0775(2)	0.0922(1)	0.3742(3)	0.0413(7)
O6(G3)	1.1491(3)	0.0711(2)	0.1784(3)	0.062(1)
C1(G4)	0.9645(4)	−0.0326(2)	0.1465(3)	0.039(1)
C2(G4)	0.8819(4)	−0.0629(2)	0.1174(4)	0.041(1)
C3(G4)	0.8721(3)	−0.1156(2)	0.1730(4)	0.039(1)
C4(G4)	0.9559(3)	−0.1484(2)	0.1705(3)	0.038(1)
C5(G4)	1.0313(3)	−0.1136(2)	0.2056(4)	0.039(1)
C6(G4)	1.1201(4)	−0.1418(2)	0.2010(5)	0.050(1)
O2(G4)	0.8063(3)	−0.0296(2)	0.1295(3)	0.054(1)
O3(G4)	0.8024(3)	−0.1446(2)	0.1287(4)	0.0538(9)
O4(G4)	0.9422(2)	−0.1931(1)	0.2354(2)	0.0387(7)
O5(G4)	1.0373(3)	−0.0669(1)	0.1425(3)	0.0423(7)
O6A(G4)	1.1462(6)	−0.1516(4)	0.0965(7)	0.060(2)
O6B(G4)	1.1847(5)	−0.1103(3)	0.2545(6)	0.054(2)
C1(G5)	0.9575(3)	−0.2465(2)	0.2007(3)	0.037(1)
C2(G5)	0.8768(4)	−0.2803(2)	0.2222(4)	0.041(1)
C3(G5)	0.8621(4)	−0.2845(2)	0.3334(4)	0.041(1)
C4(G5)	0.9458(3)	−0.3016(2)	0.3856(4)	0.037(1)
C5(G5)	1.0255(4)	−0.2692(2)	0.3539(3)	0.037(1)
C6(G5)	1.1108(4)	−0.2913(2)	0.3928(4)	0.043(1)
O2(G5)	0.8026(3)	−0.2576(2)	0.1753(3)	0.0503(9)
O3(G5)	0.7930(3)	−0.3217(2)	0.3559(3)	0.0529(9)

Table 1 (*Continued*)

Atom (residue)	x	y	z	U_{eq}
O4(G5)	0.9309(2)	−0.2929(1)	0.4897(2)	0.0408(7)
O5(G5)	1.0315(2)	−0.2688(1)	0.2471(2)	0.0387(7)
O6(G5)	1.1169(3)	−0.3483(2)	0.3767(3)	0.0513(9)
C1(G6)	0.9433(4)	−0.3353(2)	0.5591(4)	0.041(1)
C2(G6)	0.8634(4)	−0.3350(2)	0.6260(4)	0.046(1)
C3(G6)	0.8579(4)	−0.2804(2)	0.6770(4)	0.044(1)
C4(G6)	0.9439(3)	−0.2669(2)	0.7276(4)	0.038(1)
C5(G6)	1.0235(4)	−0.2760(2)	0.6637(4)	0.039(1)
C6(G6)	1.1086(4)	−0.2738(2)	0.7207(4)	0.049(1)
O2(G6)	0.7869(3)	−0.3481(2)	0.5715(3)	0.065(1)
O3(G6)	0.7874(3)	−0.2808(2)	0.7475(3)	0.057(1)
O4(G6)	0.9404(3)	−0.2109(1)	0.7537(2)	0.0409(8)
O5(G6)	1.0202(3)	−0.3277(1)	0.6143(3)	0.0421(7)
O6(G6)	1.1031(3)	−0.2994(2)	0.8156(3)	0.061(1)
Br1(*p*-BrPh)	1.07904(5)	−0.11877(3)	0.50688(6)	0.0710(2)
C1(*p*-BrPh)	0.9561(4)	−0.1134(2)	0.4957(4)	0.050(1)
C2(*p*-BrPh)	0.9170(4)	−0.0642(2)	0.4768(5)	0.057(1)
C3(*p*-BrPh)	0.8283(4)	−0.0614(2)	0.4656(5)	0.057(2)
C4(*p*-BrPh)	0.7774(4)	−0.1074(2)	0.4730(4)	0.047(1)
C5(*p*-BrPh)	0.8168(4)	−0.1564(2)	0.4938(5)	0.057(1)
C6(*p*-BrPh)	0.9066(4)	−0.1589(2)	0.5059(6)	0.062(2)
O1(*p*-BrPh)	0.6890(3)	−0.1065(2)	0.4613(4)	0.065(1)
Water1	1.1129(5)	−0.2509(2)	0.0128(4)	0.089(2)
Water2	1.1494(6)	0.0260(3)	0.0058(5)	0.122(3)
Water3	0.8305(9)	−0.2926(6)	−0.0210(9)	0.182(5)
Water4	0.749(1)	−0.4438(6)	0.628(2)	0.32(1)
Water5	1.247(1)	−0.1766(6)	−0.015(1)	0.217(6)
α-CD–m-bromophenol (m-BrPh) complex				
C1(G1)	0.161(1)	0.001(2)	0.871(4)	0.06(1)
C2(G1)	0.184(1)	−0.022(2)	1.012(4)	0.06(1)
C3(G1)	0.241(1)	−0.013(1)	1.028(4)	0.05(1)
C4(G1)	0.270(1)	−0.019(1)	0.873(3)	0.033(8)
C5(G1)	0.241(1)	0.004(1)	0.724(3)	0.04(1)
C6(G1)	0.265(2)	−0.003(2)	0.554(4)	0.08(2)
O2(G1)	0.1530(8)	−0.007(1)	1.156(3)	0.067(9)
O3(G1)	0.2640(8)	−0.0382(8)	1.160(3)	0.048(7)
O4(G1)	0.3188(7)	0.0011(9)	0.887(3)	0.049(7)
O5(G1)	0.1887(9)	−0.0106(9)	0.722(3)	0.056(8)
O6(G1)	0.264(2)	−0.051(2)	0.516(4)	0.15(2)
C1(G2)	0.077(1)	0.179(1)	0.861(4)	0.06(1)
C2(G2)	0.065(1)	0.147(1)	1.004(4)	0.06(1)
C3(G2)	0.109(1)	0.111(1)	1.026(4)	0.06(1)
C4(G2)	0.116(1)	0.078(1)	0.876(4)	0.05(1)
C5(G2)	0.123(1)	0.114(1)	0.723(3)	0.04(1)
C6(G2)	0.117(2)	0.086(1)	0.550(4)	0.06(1)
O2(G2)	0.0651(9)	0.1803(9)	1.140(3)	0.061(8)
O3(G2)	0.095(1)	0.0773(9)	1.160(3)	0.065(8)
O4(G2)	0.1628(8)	0.0525(9)	0.888(3)	0.041(7)
O5(G2)	0.0796(9)	0.1485(8)	0.719(3)	0.047(7)
O6(G2)	0.135(2)	0.115(1)	0.430(3)	0.13(2)
C1(G3)	0.202(1)	0.335(1)	0.840(4)	0.06(1)
C2(G3)	0.166(1)	0.329(1)	0.985(4)	0.04(1)
C3(G3)	0.149(1)	0.278(1)	1.007(4)	0.05(1)
C4(G3)	0.126(1)	0.254(1)	0.855(3)	0.036(9)
C5(G3)	0.165(1)	0.263(1)	0.707(3)	0.031(9)
C6(G3)	0.139(1)	0.258(2)	0.529(4)	0.07(1)
O2(G3)	0.1936(8)	0.348(1)	1.124(3)	0.071(9)
O3(G3)	0.1150(9)	0.2721(9)	1.142(3)	0.054(7)
O4(G3)	0.1237(8)	0.2035(7)	0.878(3)	0.033(6)
O5(G3)	0.1784(9)	0.3165(8)	0.703(3)	0.045(7)
O6A(G3)	0.091(2)	0.274(3)	0.519(7)	0.11(2)
O6B(G3)	0.177(2)	0.257(2)	0.414(5)	0.09(2)
C1(G4)	0.406(1)	0.305(2)	0.854(5)	0.08(1)
C2(G4)	0.383(1)	0.331(2)	0.996(4)	0.08(1)
C3(G4)	0.327(1)	0.319(1)	1.015(4)	0.04(1)
C4(G4)	0.296(1)	0.329(1)	0.854(4)	0.05(1)
C5(G4)	0.324(1)	0.301(2)	0.717(4)	0.08(1)
C6(G4)	0.304(2)	0.310(2)	0.533(6)	0.13(3)
O2(G4)	0.412(1)	0.318(1)	1.140(4)	0.15(2)
O3(G4)	0.3038(8)	0.347(1)	1.136(3)	0.053(8)
O4(G4)	0.2458(9)	0.3073(9)	0.874(3)	0.058(7)
O5(G4)	0.377(1)	0.318(1)	0.707(3)	0.073(9)
O6(G4)	0.305(2)	0.357(2)	0.497(5)	0.22(3)
C1(G5)	0.484(2)	0.125(1)	0.835(4)	0.08(1)
C2(G5)	0.505(1)	0.160(1)	0.963(4)	0.05(1)
C3(G5)	0.465(1)	0.198(1)	1.004(4)	0.06(1)
C4(G5)	0.452(1)	0.228(1)	0.854(4)	0.05(1)
C5(G5)	0.438(2)	0.190(1)	0.703(4)	0.08(1)
C6(G5)	0.438(2)	0.218(2)	0.536(5)	0.08(2)
O2(G5)	0.510(1)	0.129(1)	1.108(4)	0.10(1)
O3(G5)	0.480(1)	0.234(1)	1.129(3)	0.07(1)
O4(G5)	0.4059(7)	0.2541(8)	0.873(3)	0.032(6)
O5(G5)	0.481(1)	0.154(1)	0.686(3)	0.071(8)
O6(G5)	0.479(2)	0.240(1)	0.476(4)	0.17(2)
C1(G6)	0.366(1)	−0.026(1)	0.861(4)	0.06(1)
C2(G6)	0.399(1)	−0.020(1)	1.001(4)	0.05(1)
C3(G6)	0.418(1)	0.031(1)	1.013(4)	0.04(1)
C4(G6)	0.439(1)	0.052(1)	0.852(3)	0.04(1)
C5(G6)	0.400(1)	0.041(1)	0.711(4)	0.07(1)
C6(G6)	0.426(1)	0.053(2)	0.537(4)	0.07(1)
O2(G6)	0.373(1)	−0.037(1)	1.146(3)	0.08(1)
O3(G6)	0.459(1)	0.037(1)	1.131(3)	0.077(9)
O4(G6)	0.4402(9)	0.1030(9)	0.872(3)	0.061(8)
O5(G6)	0.387(1)	−0.0101(9)	0.706(2)	0.07(1)
O6(G6)	0.471(1)	0.030(2)	0.522(5)	0.20(2)
Br1(*m*-BrPh$_1$)	0.2668(3)	0.1552(3)	0.8537(7)	0.147(3)
O1(*m*-BrPh$_1$)	0.229(2)	0.146(2)	1.489(3)	0.32(3)
C1(*m*-BrPh$_1$)	0.265(1)	0.144(1)	1.365(2)	0.21(3)
C2(*m*-BrPh$_1$)	0.251(1)	0.1496(9)	1.201(2)	0.17(2)
C3(*m*-BrPh$_1$)	0.2871(9)	0.1469(6)	1.079(2)	0.08(1)
C4(*m*-BrPh$_1$)	0.338(1)	0.138(1)	1.115(3)	0.25(3)
C5(*m*-BrPh$_1$)	0.353(1)	0.132(2)	1.277(4)	0.34(4)
C6(*m*-BrPh$_1$)	0.317(1)	0.134(1)	1.401(3)	0.30(3)
Br1(*m*-BrPh$_2$)	−0.0317(4)	0.0567(5)	1.218(1)	0.111(4)
O1(*m*-BrPh$_2$)	−0.0502(7)	0.0896(6)	0.871(3)	0.11(2)
C1(*m*-BrPh$_2$)	−0.0250(5)	0.0447(7)	0.871(2)	0.03(1)
C2(*m*-BrPh$_2$)	−0.0124(3)	0.0221(4)	0.724(3)	0.03(1)
C3(*m*-BrPh$_2$)	−0.0124(4)	0.0223(4)	1.019(2)	0.03(1)
Water1	0.436(1)	−0.071(1)	1.407(5)	0.12(1)
Water2	0.014(1)	0.166(1)	1.441(3)	0.086(9)

Table 1 (*Continued*)

Atom (residue)	x	y	z	U_{eq}
Water3	0.155(1)	0.379(1)	1.417(4)	0.08(1)
Water4	0.073(1)	0.126(1)	0.582(4)	0.08(1)
Water5	0.141(1)	−0.055(1)	1.439(5)	0.13(1)
Water6	0.546(2)	0.161(2)	1.379(6)	0.18(2)

were not refined. The crystal structure was refined to $R = 0.063$ (5293 reflections, all unique reflections) and $R_1 = 0.053$ (4660 reflections with $F_o > 4\sigma(F_o)$) by a full-matrix least-squares method using the program SHELX97,[5] based on 723 parameters and 650 restraints. For the α-CD–*m*-bromophenol complex, diffraction data up to $2\theta = 120°$ were processed, because the crystal gave poor diffraction data at high resolution ($2\theta > 120°$). Crystal data are, $C_{36}H_{60}O_{30}\cdot1.5\ C_6H_5BrO\cdot6\ H_2O$, space group $P2_12_12$, $a = 25.858(7)$, $b = 27.263(8)$, $c = 8.145(3)$ Å, $V = 5742$ Å^3, $Z = 4$. The initial phase determination by a direct method had failed. The molecular replacement method using the structure of α-CD as a probe model was carried out using the program X-PLOR,[6] and a clear solution for the orientation and position of the model in an unit cell was obtained. After the refinement of the α-CD structure, *m*-bromophenol and water molecules were located on the difference Fourier map, and their atoms except Br atoms were refined isotropically due to a lack of high-resolution data. The crystal structure was refined to $R = 0.102$ (1268 reflections, $I_o > 3\sigma(I_o)$) by a full-matrix least-squares method using the program SHELX97,[5] based on 690 parameters and 870 restraints. Atomic coordinates and temperature factors of both complexes are listed in Table 1.

In the α-CD–*p*-bromophenol complex, α-CD forms a 1:1 complex with *p*-bromophenol as shown in Fig. 2.[7] The crystal structure is isomorphous to those of the α-CD complexes with *p*-chlorophenol[8] and *p*-iodophenol,[9] and there are one α-CD and one *p*-bromophenol molecules in the asymmetric unit. The *p*-bromophenol is deeply included into the α-CD, and its molecular plane is almost perpendicular to the O-4 plane made by the six O-4 atoms of the α-CD. The α-CD is distorted to an ellipsoid shape due to the deeply included phenyl ring of *p*-bromophenol as shown in Fig. 2(a). The Br atom is situated at the centre of the C-5 plane of the α-CD. Although the Br atom does not have any hydrogen-bond interactions with hydroxyl groups, it seems to form weak hydrogen-bond interactions with the hydrogen atoms attached to the C-5 atoms (H-5 atoms), which are involved in hydrogen-bond interactions in other oligosaccharides.[10,11] The distances between them are 3.17, 3.20, 3.59, 3.43, 3.29 and 3.74 Å as indicated in Fig. 2(a), and these distances are around the van der Waals contacts (3.15 Å (Br–H)). However, all H-5 atoms in the α-CD point to the Br atom, and the center of the C-5 plane is very favorable to an electronegative atom, as reported before.[7] The α-CD–*p*-bromophenol complex has a layer-type packing structure, and the secondary hydroxyl groups of α-CDs have intermolecular hydrogen-bond interactions to the primary hydroxyl groups and the secondary hydroxyl groups of other α-CDs as shown in Fig. 2(b). Since *p*-bromophenol is deeply included into host α-CD with the Br atom being at the head, the para-positioned hydroxyl group of *p*-bromophenol is located at the secondary hydroxyl group site of host α-CD, forming intermolecular hydrogen-bond interactions with the O-6 and O-2 atoms of other host α-CDs as shown in Fig. 2(b). This position of the hydroxyl group and its hydrogen-bond interactions become strong driving forces for the formation of a layer-type molecular packing structure.

In the α-CD–*m*-bromophenol complex, α-CDs are arranged in a one-dimensional column structure along the crystallographic *c*-axis with a head-to-tail orientation, and the secondary hydroxyl groups of the α-CD have intermolecular hydrogen-bond interactions with the primary hydroxyl groups of other α-CDs as shown in Fig. 3(a). The *m*-bromophenol in the α-CD column is located between two α-CDs, making its molecular plane almost perpendicular to the O-4 plane of the α-CD. Another *m*-bromophenol exits in the outside of the α-CD column in a crystal, and it has the crystallographic twofold axis as shown in Fig. 3(b). Consequently, there are one α-CD and one and a half of *m*-bromophenol molecules in an asymmetric unit. Due to the meta-positioned hydroxyl group, the *m*-bromophenol cannot enter the cavity of the host α-CD as deeply *p*-bromophenol does, giving fewer van der Waals contacts between *m*-bromophenol and the host α-CD than those found in the α-CD–*p*-bromophenol complex. The Br atom is situated the center of the O-4 plane of the α-CD and forms a weak hydrogen-bond interaction (3.09 Å) with the H-5 atom as shown in Fig. 3(a). Interestingly, there is a hydrogen-bond interaction between the two adjacent *m*-bromophenols. The distance between the hydroxyl group and the Br atom is 3.09 Å as indicated in Fig. 3(a), which is the definitely short length of van der Waals contacts of 3.35 Å (Br–O). This guest–guest hydrogen-bond interaction is essential to arrange α-CDs in a one-dimensional column, leading to a channel-type molecular packing structure.

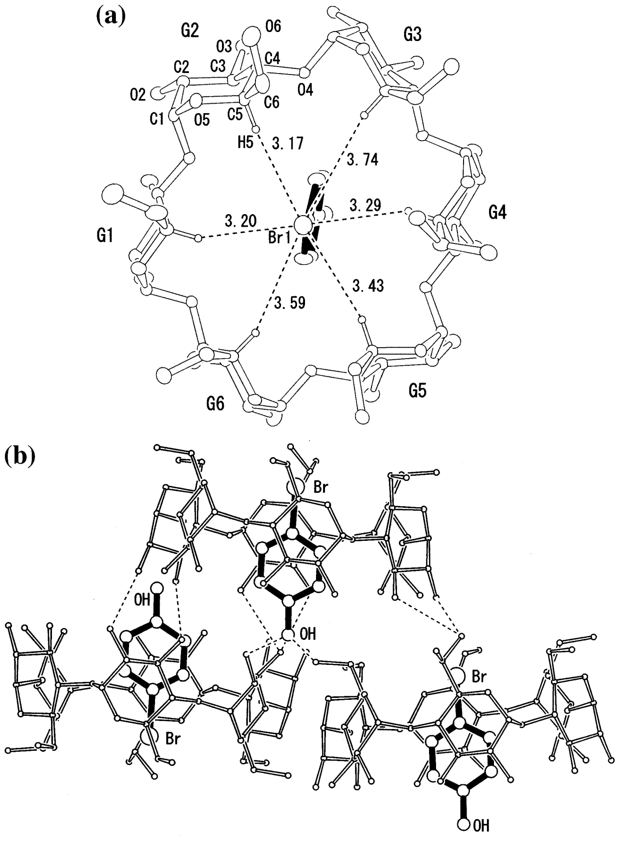

Fig. 2. (a) Molecular structure of the α-CD–*p*-bromophenol with the numberings of atoms and residues shown. The α-CD and the *p*-bromophenol are shown by open bonds and solid bonds, respectively, and all atoms except H-5 atoms are shown by thermal ellipsoids. The weak hydrogen-bond interactions between H-5 atoms and a bromine atom are drawn by dotted lines with the distances. (b) The layer-type molecular packing structure of α-CD–*p*-bromophenol complex is shown in the ball-and-stick representation. Intermolecular hydrogen-bond interactions are drawn by dotted lines.

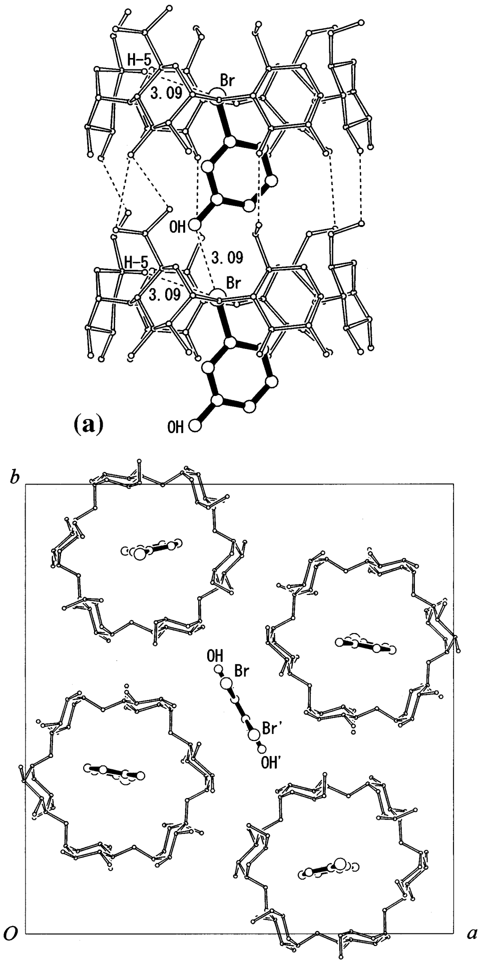

Fig. 3. (a) The molecular structure of the two adjacent α-CD–*m*-bromophenol complexes forming a one-dimensional column is shown in the ball-and-stick representation. Intermolecular hydrogen-bond interactions are drawn by dotted lines. Only one H-5 atom forming a weak hydrogen-bond interaction with the Br atom is plotted. (b) The crystal structure of α-CD–*m*-bromophenol complexes as viewed from the *c*-axis is shown. The center *m*-bromophenol has the crystallographic twofold axis, and the hydroxyl group and the Br atom are equally disordered into OH and OH′, and Br and Br′, respectively.

In the α-CD–*p*-bromophenol complex, the hydroxyl groups of *p*-bromophenol can form intermolecular hydrogen-bond interactions with other host α-CDs, and these intermolecular hydrogen-bond interactions are essential for the formation of a layer-type molecular packing structure. On the other hand, *m*-bromophenol is shallowly included into the α-CD relative to *p*-bromophenol, and the hydroxyl group of *m*-bromophenol is protruding out of the host α-CD. Therefore, with the hydroxyl group of *m*-bromophenol, it is impossible to form intermolecular hydrogen-bond interactions with other host α-CDs, and it forms a hydrogen-bond interaction with the Br atom of other *m*-bromophenol, giving a channel-type molecular packing structure. Thus different positions of the hydroxyl groups of the guest molecules and the different intermolecular hydrogen-bond interactions are closely related to the molecular packing structures.

1. Supplementary material

Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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