This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

X-Ray Structure of *i*-Cyclodextrin

Kazuaki Harata[a]; Tomohiro Endo[b]; Haruhisa Ueda[b]; Tsuneji Nagai[c]
[a] Biomolecules Department, National Institute of Bioscience and Human-Technology, Ibaraki, Japan [b] Department of Physical Chemistry, Hoshi University, Tokyo, Japan [c] Faculty of Pharmaceutical Sciences, Hoshi University, Tokyo, Japan

To cite this Article Harata, Kazuaki , Endo, Tomohiro , Ueda, Haruhisa and Nagai, Tsuneji(1998) 'X-Ray Structure of *i*-Cyclodextrin', Supramolecular Chemistry, 9: 2, 143 — 150
To link to this Article: DOI: 10.1080/10610279808034979
URL: http://dx.doi.org/10.1080/10610279808034979

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 9, pp. 143–150
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Harwood Academic Publishers imprint,
part of The Gordon and Breach Publishing Group.
Printed in India.

X-Ray Structure of *i*-Cyclodextrin

KAZUAKI HARATA [a,*], TOMOHIRO ENDO [b], HARUHISA UEDA [b] and TSUNEJI NAGAI [c]

[a] *Biomolecules Department, National Institute of Bioscience and Human-Technology, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan;*
[b] *Department of Physical Chemistry, Hoshi University, 4-41, Ebara 2-chome, Shinagawa-ku, Tokyo 142, Japan;*
[c] *Faculty of Pharmaceutical Sciences, Hoshi University, 4-41, Ebara 2-chome, Shinagawa-ku, Tokyo 142, Japan*

(Received 13 July 1997; In final form 13 September 1997)

Crystal structure of *i*-cyclodextrin consisting of 14 glucose units were determined by the X-ray method. The crystal of 9 hydrate belongs to a monoclinic space group $C2$ with $Z = 2$ and cell dimensions are $a = 36.536(9)$, $b = 10.085(4)$, $c = 20.944(2)$ Å, and $\beta = 114.97(2)°$. The molecule with crystallographic twofold symmetry is in a saddle-like shape where the elliptical macrocyclic ring is bent by 75.2°. The seven glucose units in the asymmetric unit are arranged in a left-handed helical fashion to form a U-shape. Distances from the center of the molecule to each O4 atom are in the range from 7.6 to 9.7 Å indicating the presence of a large cavity in the molecule. Adjacent two glucose units in the asymmetric portion is in *cis* arrangement where the O2H hydroxyl group forms a hydrogen bond with O3H of next glucose unit. In contrast, symmetry-related glucose units are connected with *trans* arrangement and the O3H hydroxyl group is hydrogen-bonded to O6H of the adjacent glucose unit. The latter conformation of the glycosidic linkage is the first observation in cyclodextrins and α-1,4-linked glucose oligomers. The asymmetric portion of the molecule is arranged in a zigzag mode along the twofold screw axis and symmetry-related molecules are partly interdigitated. The vacant space in the molecule forms a continuous channel along the twofold axis, suggesting the possibility of the formation of crystalline inclusion complexes.

Keywords: *i*-cyclodextrin, crystal structure, X-ray analysis, macrocyclic structure

INTRODUCTION

Cyclodextrins are a family of macrocyclic oligosaccharides consisting of six or more glucose units and have potential ability to form inclusion compounds with a variety of guest materials [1]. Crystal structures have been determined for α-, β-, γ- and δ-cyclodextrin [2–5] and their inclusion complexes [6]. French and co-workers [7] have reported cyclodextrins with the number of glucose units from 9 to 13. We have isolated and purified those cyclodextrins and characterized their physicochemical properties [8–10]. Recently, it has been reported that potato D-enzyme produces cyclodextrins consisting of 17 or more glucose units [11]. The molecular dynamics simulation of those cyclodextrins has proposed the helical folding of the macrocyclic ring [12].

i-Cyclodextrin (*i*-CDx, cyclomaltotetradecaose) consists of 14 glucose units. The structure of *i*-CDx is of particular interest in comparison with the structure of previously reported smaller cyclodextrins. The macrocyclic ring of α-, β- and γ-CDx are in a round shape but δ-CDx has a considerably warped macrocyclic ring. The

---

*Corresponding author.

i-CDx ring is twice as large as that of *β*-CDx and its three-dimensional structure and physicochemical properties are unknown. Here, we report the crystal structure of *i*-CDx and will discuss the macrocyclic conformation in comparison with smaller cyclodextrins.

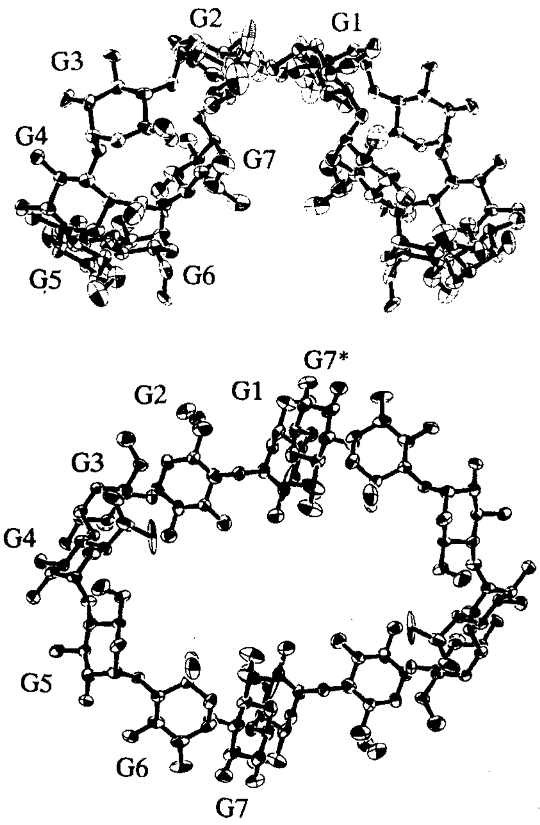

FIGURE 1 Structure of *i*-cyclodextrin. The molecule has a crystallographic twofold symmetry. The O6H hydroxyl groups of G2, G4, and G7 units are disordered and exhibit (+)-*gauche* and (−)-*gauche* conformations.

RESULTS

i-CDx was crystallized with the space group C2 from 70% aqueous 1-propanol solution. The structure was solved by the direct method combined with density modification and refined by the full-matrix least-squares method to the *R*-value of 0.114. The structure is shown in Figure 1. The molecule has a twofold crystallographic symmetry and the asymmetric unit contains seven glucose units designated from G1 to G7. The elliptical macrocyclic ring is folded in a saddle-like shape. The average bond distances, angles, and torsion angles for seven glucose units are given in Table I. The endo-cyclic torsion angles of the pyranose ring are in good agreement with those of smaller cyclodextrins. The primary hydroxyl group exhibits two types of conformation, which have been commonly observed in cyclodextrin crystals. The (−)-*gauche* conformation of the C6—O6 bond to the C5—O5 bond is found in the four glucose units, G1, G3, G5 and G6. On the other hand, the C6—O6 bond in the other glucose units are disordered and exhibits (+)-*gauche* and (−)-*gauche* conformations.

The conformation of the glycosidic linkage has been characterized by the four torsion angles, C3—C4—O4—C1′, C5—C4—O4—C1′, C4—O4—C1′—C2′ and C4—O4—C1′—O5′. The average values of those angles in glucose units from G2 to G7 are −135(9)°, 103(9)°, 108(16)°, and −133(14)°, respectively. On the other hand, a marked difference is observed in the O4G1 linkage connecting G1 and G7* units. The corresponding torsion angles are −156°, 79°, −62° and 66°. As shown in Figure 2, compared with the conformation of other O4 linkages, the G7* unit is ca. 180° rotated around the C4—O4 bond of the G1 unit. As the result, the G1 and G7* units are in *trans* arrangement in relation with the glycosidic linkage while the other adjacent two glucose units are in *cis* arrangement where the primary hydroxyl groups are located in the same side. Such unusual conformation of the O4G1 linkage affects the formation of intramolecular hydrogen bonds. Between the adjacent glucose units, except a pair of G1 and G7*, the secondary hydroxyl groups form hydrogen bonds with the O2—O3 distances in the range from 2.63 to 3.28 Å (Tab. II). However, between G1 and G7*, a hydrogen bond is formed between O3G1 and O6′G7*. The C6—O6 bond of the G7* unit is

TABLE I Average bond distances, angles and torsion angles

	1. Bond distances		
	Distance (Å)		Distance (Å)
C1—C2	1.52(4)	C3—O3	1.43(3)
C1—O5	1.40(4)	C4—C5	1.53(4)
C1—O4′	1.41(4)	C4—O4	1.42(3)
C2—C3	1.50(3)	C5—C6	1.51(4)
C2—O2	1.43(4)	C5—O5	1.45(3)
C3—C4	1.51(5)	C6—O6	1.40(7)
	2. Bond angles		
	Angle (°)		Angle (°)
C2—C1—O5	111(2)	C3—C4—C5	110(1)
C2—C1—O4′	109(2)	C3—C4—O4	111(3)
O5—C1—O4′	112(2)	C5—C4—O4	110(2)
C1—C2—C3	111(2)	C4—C5—C6	113(3)
C1—C2—O2	110(3)	C4—C5—O5	109(2)
C3—C2—O2	112(2)	C6—C5—O5	107(2)
C2—C3—C4	110(3)	C5—C6—O6	113(4)
C2—C3—O3	110(1)	C4—O4—C1′	118(2)
C4—C3—O3	111(2)	C5—O5—C1	114(1)
	3. Torsion angles		
	Angle (°)		Angle (°)
C1—C2—C3—C4	−53(4)	O2—C2—C3—O3	61(3)
C2—C3—C4—C5	55(3)	O3—C3—C4—O4	−62(4)
C3—C4—C5—O5	−57(4)	O4—C4—C5—C6	63(6)
C4—C5—O5—C1	61(3)	C3—C4—O4—C1′	108(16)
C5—O5—C1—C2	−59(3)	C5—C4—O4—C1′	−133(14)
O5—C1—C2—C3	54(3)	C4—O4—C1′—C2′	−135(9)
O2—C2—C1—O4′	55(3)	C4—O4—C1′—O5′	103(9)

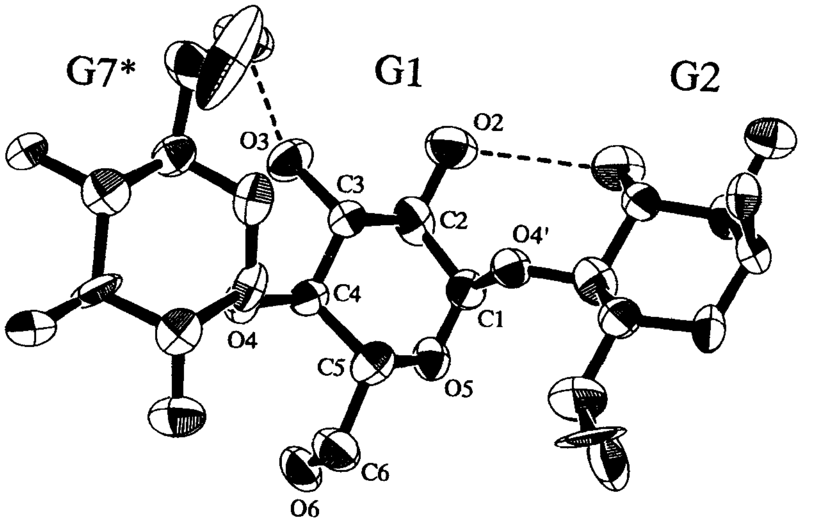

FIGURE 2 The structure showing two types of conformations of α-1,4-linkage. The G1 and G2 glucose units are in the *cis* form where the O2H hydroxyl group of G1 is hydrogen-bonded to the O3H hydroxyl group of G2 as shown with a dashed line. The G1 and G7* glucose units are in the *trans* form and the O3H hydroxyl group of G1 forms a hydrogen bond with the O6H hydroxyl group of G7*.

TABLE II Hydrogen bond distances

	Distance (Å)	Symmetry operator
O2G1—O3G2	2.87	x, y, z
O3G1—O6G6	2.70	$1-x, -1+y, 1-z$
—O6′G7	2.93	$1-x, y, 1-z$
O4G1—O2G4	2.94	$1/2+x, -1/2+y, z$
O5G1—OW5	2.94	x, y, z
O6G1—O2G4	2.91	$1/2+x, -1/2+y, z$
O2G2—O3G3	3.28	x, y, z
—O6′G4	2.77	$x, -1+y, z$
—OW4	2.91	x, y, z
O6G2—O3G4	2.82	$1/2-x, -1/2+y, -z$
O6′G2—O3G4	3.01	$1/2-x, -1/2+y, -z$
—OW2	2.78	$x, -1+y, -1+z$
—OW5	2.76	x, y, z
O2G3—O3G4	2.97	x, y, z
—O6G5	3.23	$x, -1+y, z$
—O2G6	3.17	$-1/2-x, 1/2+y, 1-z$
—OW1	2.81	x, y, z
O3G3—O5G4	2.83	$x, -1+y, z$
—O6G5	3.14	$x, -1+y, z$
—O6G3	2.82	$1/2-x, -1/2+y, -z$
O5G3—O6G4	3.11	$1/2-x, -1/2+y, -z$
O6G3—OW1	2.95	$1/2-x, -1/2+y, -z$
—O5G4	2.93	$1/2-x, -1/2+y, -z$
—O6G4	2.99	$1/2-x, -1/2+y, -z$
O2G4—O3G5	2.83	x, y, z
O3G4—O2G6	3.16	$1/2-x, -1/2+y, 1-z$
O4G4—OW3	2.93	$1/2-x, -1/2+y, 1-z$
O2G5—O3G6	2.74	x, y, z
O2G5—O6G6	2.82	$1/2-x, -1/2+y, 1-z$
O3G5—O6G6	3.01	$1/2-x, -1/2+y, 1-z$
O6G5—O2G6	3.03	$1/2-x, -1/2+y, 1-z$
—OW3	3.04	$1/2-x, -1/2+y, 1-z$
O2G6—O3G7	2.63	x, y, z
O3G6—OW3	2.79	x, y, z
O2G7—OW1	3.06	$1/2-x, -1/2+y, 1-z$
O3G7—OW1	2.98	$1/2-x, -1/2+y, 1-z$
—OW2	2.64	x, y, z
OW2—OW5	3.12	$x, 1+y, 1+z$
OW3—OW4	2.79	$1/2-x, 1/2+y, 1-z$

disordered and the O6′ atom with the (+)-*gauche* conformation is involved in the hydrogen bond.

The macrocyclic conformation of cyclodextrins has been described in terms of the geometry of polygons composed of glycosidic O4 atoms because the O4 atoms are fairly coplanar in α-, β-, and γ-CDx. In contrast, O4 atoms in *i*-CDx are arranged in a saddle-like shape as shown in Figures 3 and 4. The O4—O4 distance between the adjacent glucose units is in the range from 4.38 to 4.61 Å and the average value of 4.51(7) Å is in good agreement with that of γ-CDx.

The molecule has a large cavity as indicated by the distance from the center of the molecule to each O4 atom, which is distributed in the range from 7.6 to 9.7 Å. The width and height of the saddle-shaped O4 polygon is 17.1 and 7.0 Å, respectively (Fig. 4). Seven O4 atoms of G2—G7 and G1* are roughly coplanar with the average deviation of 0.93 Å from their least-squares plane. The two planes in the molecule make an angle of 75.2°.

Crystal structure is shown in Figures 5 and 6. The *i*-CDx molecule is located on the twofold

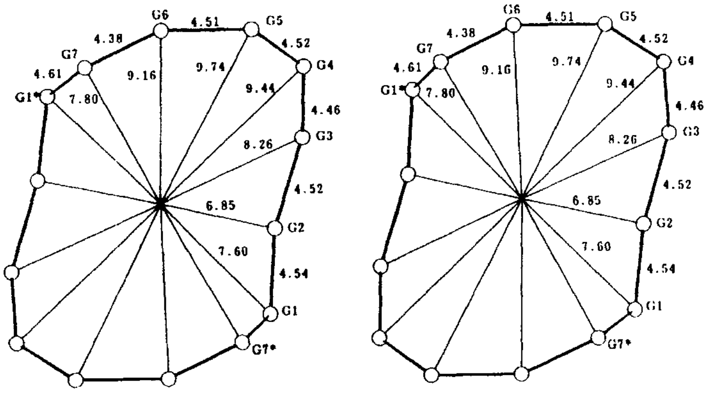

FIGURE 3 Stereo-drawing of the geometry of O4 arrangement. The O4—O4 distances between adjacent glucose units are shown by thick lines. Thin lines denote distances from the center of the molecule to each O4 atom.

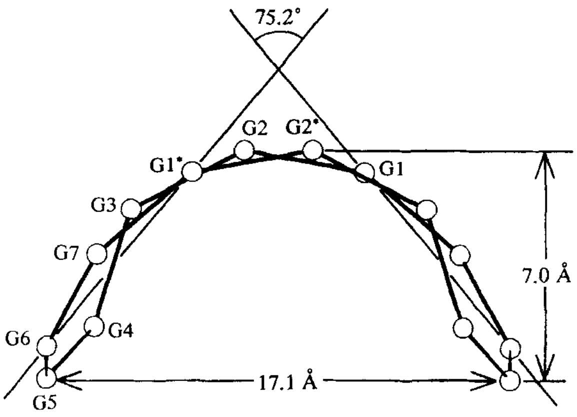

FIGURE 4 Side view of the arrangement of fourteen O4 atoms. The seven O4 atoms of G2 – G7 and G1* units are roughly coplanar and two planes in the molecule makes an angle of 75.2°.

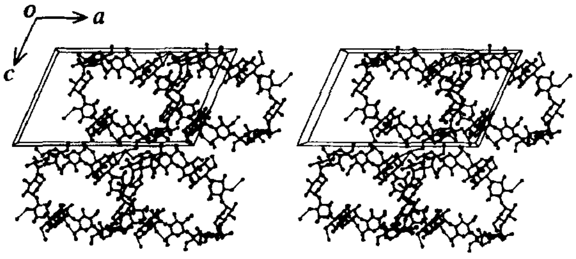

FIGURE 5 Crystal structure viewed along the *b* axis. Water molecules are shown by full circles. Hydrogen bonds involving water molecules are denoted by thin lines.

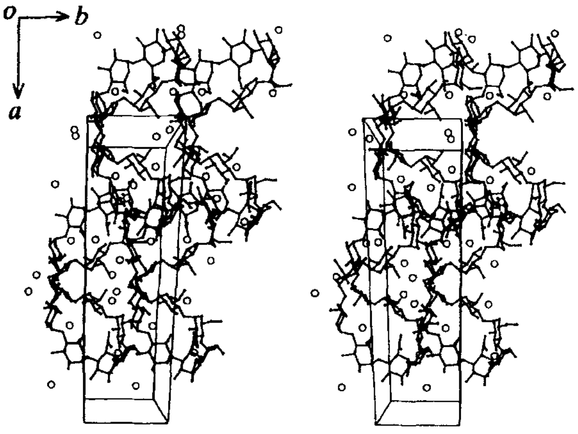

FIGURE 6 Crystal structure viewed along the *c* axis. Water molecules are shown by open circles.

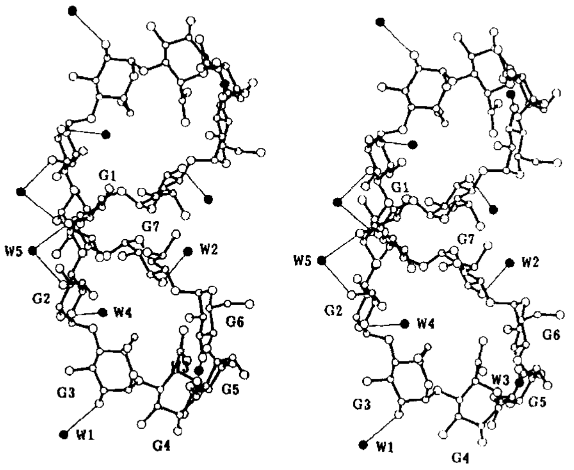

FIGURE 7 Stereo-view showing the hydrogen-bonding contacts of water molecules which are denoted by W1, W2, W3, W4 and W5. Hydrogen bonds are shown by thin lines.

axis and stacked along the *b* axis. The asymmetric part of the molecule is arranged in a zigzag mode and the G4 and G5 residues are partly inserted into the adjacent *i*-CDx ring (Fig. 6). The stacking of the molecule produces a continuous vacant channel formed by the intramolecular cavity along the twofold axis. The cloud of weak electron density, which is less than 0.4 eÅ^{-3}, was observed in the channel but could not be modeled as solvent molecules.

Intermolecular hydrogen bonds are listed in Table II. Five water molecules are located in the asymmetric unit and bound to *i*-CDx by hydrogen bonds (Fig. 7). As shown in Figure 8, water molecules are involved in the hydrogen bond network in the crystal. W1 forms hydrogen bonds with O2G3, O6G3, O2G7 and O3G7. O3G7 is linked to W2 which is also connected to O6G1 and W5. W5 forms a hydrogen bond bridge between O5G1 and O6′G2. W3 and W4 are linked by a hydrogen bonds and W3 also forms hydrogen bonds with O4G4 and O3G6. W4 is located inside the *i*-CDx ring and linked to O2G2 by a hydrogen bond.

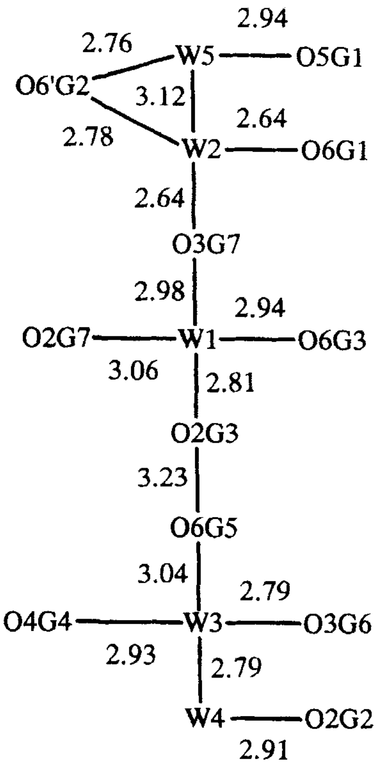

FIGURE 8 Hydrogen bond network involving water molecules.

DISCUSSION

Cyclodextrin producing enzyme, cyclodextrin glucanotransferase, produces several cyclodextrins called α-, β-, γ-, etc., in order of the increasing number of glucose units [13] X-ray structures have been reported for α-, β-, γ- and δ-CDx [2–5] which have 6, 7, 8 and 9 glucose units, respectively. α-, β- and γ-CDx have a round macrocyclic ring and form crystalline inclusion complexes by accommodating a variety of guest molecules in the cavity [6]. The macrocyclic conformation of δ-CDx is essentially the same as that of smaller cyclodextrins, but the macrocyclic ring is rather elliptical and warped like an arc to relieve the steric hindrance between adjacent glucose units and the distortion of O4 angles. The present structure of *i*-CDx revealed that the molecule is not in a round structure but folded into a saddle-like shape although no significant difference in the glucose conformation is observed in the comparison with other cyclodextrins. The average value of the O4 angle, 118(2), is in agreement with those found in maltosides [14–17], indicating no significant distortion on the glycosidic linkage. The average O4—O4 distance between adjacent glucose units is increased in order of α-, β- and γ-CDx while the O4 angle slightly decreases. The strain caused by the cyclization seems to be relieved in order of the increasing number of glucose units since the pyranose conformation of γ-CDx is similar to those of maltosides. On the other hand, as shown in δ-CDx and *i*-CDx, further increase of the number of glucose units results a less symmetrical macrocyclic structure to avoid the steric hindrance around the O4 linkage. As the result, the structure of *i*-CDx is no more round or planar. The molecule has the twofold symmetry and the structure of the asymmetric portion with the U-shape is in a left-handed helical loop.

As observed in smaller cyclodextrins, intramolecular hydrogen bonds between O2H and O3H of the adjacent glucose unit play an important role in the stabilization of the macrocyclic conformation. The intramolecular O2—O3 hydrogen bonds observed in *i*-CDx seem to make a major contribution to stabilize the macrocyclic structure as also observed in the crystal of the iodine complex of maltohexaose [18]. The calculation of the conformational energy of the glycosidic linkage has indicated two types of low energy conformations [19]. The lowest energy conformation corresponds to the *cis* type arrangement of glucose units with the O2—O3 hydrogen bond. The *cis* type arrangement has been observed in the structures of smaller cyclodextrins and linear oligosaccharides [14–18]. The *trans* type arrangement with O3—O6 hydrogen bonds corresponds to the other low energy conformation. The structure of *i*-CDx presents the first evidence of the *trans* type arrangement. Because of the limited conformational flexibility of macrocyclic ring, the *trans* type arrangement is only possible in large cyclodextrins and not observed in the previously reported structure of smaller cyclodextrins. The *trans* type arrangement is energetically less favorable but the structure of *i*-CDx demonstrated that it could be stabilized in a large macrocycle.

α-, β- and γ-CDx form inclusion complexes with a variety of guest molecules. In the complexed state, cyclodextrins are round and guest molecules are accommodated in the cylindrical cavity. No evidence has been reported for the complex formation of δ-CDx or larger cyclodextrins. The crystal structure of *i*-CDx exhibits the presence of large vacant space which seems to be capable of forming inclusion complexes. The stack of the molecule along the twofold axis produces a continuous channel. The cloud of weak electron density observed in the channel along the twofold axis suggests the presence of solvent molecules which are so disordered that could not be resolved. Therefore, *i*-CDx can be expected to form inclusion complexes with a bulky guest not included in α-, β- and γ-CDx.

EXPERIMENTAL

i-CDx was isolated from commercial cyclodextrin powder (DEXY PEARL K-50, Ensuiko Sugar Refining Co.) according to the previously reported procedure for the isolation of cyclodextrins with 10–13 glucose units [9, 10]. The molecular weight was determined by FAB-MS and the cyclic structure was indicated by NMR spectroscopy. Details of the purification and characterization of *i*-CDx will be published elsewhere. Crystals for the X-ray analysis were prepared by slow evaporation of 70% aqueous 1-propanol solution.

X-ray measurements were carried out on a Nonius CAD4 diffractometer. The lattice parameters were determined by using 25 reflections in the 2θ range of 30–40°. Intensity data were collected with $\theta-2\theta$ scan mode in the 2θ range of $0°-120°$ at 293 K and 3859 ($F_0 > 3\sigma(F)$) independent reflections were observed. The structure was solved by the direct method combined with density modification and refined by the full-matrix least-squares method. Position of hydrogen atoms of methene and methylene groups was calculated and included in the structure factor calculation. The refinement with 771 parameters converged at the R-value of 0.114 for 3859 reflections. The maximum values of positive and negative residual electron density were 0.43 and -0.26 eÅ^{-3}, respectively. The maximum and mean values of shift/esd of refined parameters were 0.013 and 0.001, respectively. Computer programs, SnB [20] and SHELXL-93 [21], were used for the structure determination and refinement, respectively. ORTEP-III [22] was used for drawing the structures with thermal ellipsoids. Atomic coordinates are given in Table III.

TABLE III Atomic parameters

	$x/10^{-4}$	$y/10^{-4}$	$z/10^{-4}$	occupancy	B_{eq}/A^2
C1G1	4983 (4)	5911 (16)	2332 (8)	1.00	6.46
C2G1	5243 (4)	6509 (20)	3029 (8)	1.00	7.39
C3G1	5410 (4)	7788 (17)	2899 (6)	1.00	6.24
G4G1	5588 (4)	7642 (15)	2395 (6)	1.00	5.68
C5G1	5280 (4)	6959 (17)	1709 (7)	1.00	6.82
C6G1	5466 (7)	6679 (20)	1179 (12)	1.00	9.16
O2G1	5067 (4)	6641 (17)	3492 (6)	1.00	9.75
O3G1	5717 (3)	8241 (13)	3571 (5)	1.00	8.10
O4G1	5757 (2)	8807 (10)	2247 (4)	1.00	6.17
O5G1	5159 (2)	5741 (10)	1903 (5)	1.00	6.48
O6G1	5799 (3)	5890 (15)	1433 (6)	1.00	8.57
C1G2	3373 (4)	6191 (17)	1226 (8)	1.00	6.33
C2G2	3631 (4)	5513 (15)	1908 (8)	1.00	6.33
C3G2	4029 (4)	6116 (17)	2240 (6)	1.00	6.23
C4G2	4236 (5)	6061 (19)	1744 (9)	1.00	8.10
C5G2	3969 (4)	6758 (22)	1052 (6)	1.00	7.69
C6G2	4162 (7)	6629 (35)	557 (11)	1.00	14.94
O2G2	3426 (3)	5630 (12)	2376 (5)	1.00	8.06
O3G2	4278 (3)	5475 (15)	2895 (6)	1.00	9.32
O4G2	4614 (2)	6699 (10)	2039 (5)	1.00	6.31
O5G2	3575 (3)	6113 (13)	768 (13)	1.00	8.07
O6G2	3965 (10)	7283 (51)	– 55(12)	0.49	16.47
O6′G2	4130 (7)	5454 (42)	248 (16)	0.51	15.48
C1G3	2229 (4)	9751 (13)	665 (6)	1.00	5.57
C2G3	2185 (3)	8310 (15)	686 (6)	1.00	5.57
C3G3	2573 (4)	7626 (15)	1180 (6)	1.00	5.66
C4G3	2894 (4)	7926 (13)	884 (6)	1.00	5.66
C5G3	2913 (4)	9399 (13)	821 (6)	1.00	5.67

TABLE III (Continued)

	$x/10^{-4}$	$y/10^{-4}$	$z/10^{-4}$	occupancy	$B_{\mathrm{eq}}/\mathrm{A}^2$
C6G3	3200 (4)	9871 (16)	516 (7)	1.00	6.38
O2G3	1926 (3)	8128 (11)	1118 (5)	1.00	7.57
O3G3	2510 (3)	6241 (9)	1192 (6)	1.00	7.16
O4G3	3280 (2)	7484 (10)	1324 (4)	1.00	5.92
O5G3	2521 (2)	9955 (9)	396 (4)	1.00	5.42
O6G3	3038 (4)	9148 (15)	− 250 (7)	1.00	9.88
C1G4	2053 (4)	13925 (13)	2017 (6)	1.00	5.41
C2G4	1727 (4)	12969 (13)	1601 (6)	1.00	5.23
C3G4	1886 (3)	11608 (13)	1584 (6)	1.00	5.27
C4G4	2211 (4)	11699 (14)	1348 (7)	1.00	6.00
C5G4	2536 (3)	12580 (15)	1830 (7)	1.00	6.00
C6G4	2889 (5)	12781 (20)	1625 (9)	1.00	9.05
O2G4	1410 (2)	12964 (11)	1868 (5)	1.00	6.70
O3G4	1562 (2)	10724 (11)	1186 (4)	1.00	6.45
O4G4	2364 (2)	10388 (8)	1348 (4)	1.00	5.06
O5G4	2351 (3)	13885 (9)	1767 (5)	1.00	6.82
O6G4	2773 (6)	13116 (21)	915 (9)	0.81	11.92
O6′G4	3244 (8)	12955 (73)	2259 (30)	0.19	16.06
C1G5	2459 (4)	15605 (16)	4589 (7)	1.00	6.23
C2G5	2063 (4)	14893 (17)	4276 (7)	1.00	6.41
C3G5	2053 (3)	13881 (14)	3711 (6)	1.00	5.32
C4G5	2186 (4)	14575 (14)	3215 (5)	1.00	5.57
C5G5	2606 (4)	15223 (17)	3612 (6)	1.00	6.22
C6G5	2726 (5)	16040 (23)	3115 (7)	1.00	8.88
O2G5	1973 (3)	14304 (16)	4792 (5)	1.00	9.01
O3G5	1648 (3)	13392 (12)	3324 (4)	1.00	7.27
O4G5	2204 (3)	13594 (9)	2719 (4)	1.00	6.04
O5G5	2568 (3)	16171 (10)	4083 (4)	1.00	6.85
O6G5	2447 (5)	16739 (21)	2623 (6)	1.00	12.82
C1G6	3658 (5)	14286 (15)	7032 (6)	1.00	6.45
C2G6	3222 (5)	14600 (16)	6956 (6)	1.00	7.27
C3G6	2923 (4)	14349 (14)	6217 (7)	1.00	6.22
C4G6	3009 (3)	15100 (14)	5697 (6)	1.00	5.24
C5G6	3456 (4)	14826 (17)	5790 (6)	1.00	6.52
C6G6	3573 (4)	15831 (22)	5370 (7)	1.00	7.93
O2G6	3172 (5)	13836 (14)	7489 (5)	1.00	10.46
O3G6	2531 (3)	14634 (14)	6156 (5)	1.00	8.23
O4G6	2760 (2)	14695 (8)	5020 (4)	1.00	5.24
O5G6	3742 (3)	15027 (11)	6533 (4)	1.00	6.80
O6G6	3570 (3)	17151 (13)	5573 (8)	1.00	9.65
C1G7	4478 (4)	9857 (14)	8046 (8)	1.00	6.20
C2G7	4287 (4)	10731 (16)	8451 (7)	1.00	6.82
C3G7	3917 (6)	11455 (20)	7952 (7)	1.00	8.52
C4G7	4040 (5)	12251 (16)	7419 (7)	1.00	6.98
C5G7	4210 (4)	11351 (15)	7055 (7)	1.00	6.42
C6G7	4340 (7)	11974 (19)	6560 (11)	1.00	11.82
O2G7	4187 (4)	9859 (13)	8892 (5)	1.00	8.81
O3G7	3757 (4)	12262 (13)	8301 (6)	1.00	8.57
O4G7	3682 (2)	12901 (9)	6922 (4)	1.00	5.59
O5G7	4569 (3)	10641 (11)	7565 (5)	1.00	7.49
O6G7	4424 (8)	10993 (23)	6150 (13)	0.75	13.55
O6′G7	4708 (13)	12728 (60)	7004 (27)	0.25	19.77
OW1	1371 (5)	6060 (17)	507 (10)	1.00	12.62
OW2	4269 (8)	13741 (25)	9332 (15)	1.00	17.93
OW3	2229 (5)	14561 (24)	7175 (8)	1.00	13.55
OW4	3475 (6)	8233 (33)	3004 (16)	1.00	19.60
OW5	4701 (23)	3566 (74)	969 (44)	0.51	29.79

Crystal data: formula $C_{84}H_{140}O_{70}\cdot 9H_2O$; F.W. = 2432.1; colorless plates; crystal dimensions 0.2×0.4×0.5 mm; cell constants $a = 36.536(9)$, $b = 10.085(4)$, $c = 20.944(2)$ Å, $\beta = 114.97(2)°$; $V = 6992.2(3.3)$ Å^3; monoclinic; space group C2; $Z = 2$; $D_x = 1.155$ g · cm^{-3}; $\mu = 0.984$ cm^{-1}.

References

[1] Szejtli, J. (1982). *Cyclodextrins and their Inclusion Complexes*, Academiai Kiado, Budapest.

[2] Manor, P. C. and Saenger, W. (1974). *J. Am. Chem. Soc.*, **96**, 3630–3639.

[3] Linder, K. and Saenger, W. (1982). *Carbohydr. Res.*, **99**, 103–115.

[4] Harata, K. (1987). *Bull. Chem. Soc. Jpn.*, **60**, 2763–2767.

[5] Fujiwara, T., Tanaka, N. and Kobayashi, S. (1990). *Chem. Lett.*, 739–742.

[6] Harata, K. (1996). *Comprehensive Supramolecular Chemistry*, **3**, Cyclodextrins, Pergamon, Oxford, Chap. 9.

[7] French, D., Pulley, A. O., Effenberger, J. A., Rougvie, M. A. and Abdullah, M. (1965). *Arch. Biochem. Biophys.*, **111**, 153–160.

[8] Miyazawa, I., Ueda, H., Nagase, H., Endo, T., Kobayashi, S. and Nagai, T. (1995). *Eur. J. Pharm. Sci.*, **3**, 153–162.

[9] Endo, T., Ueda, H., Kobayashi, S. and Nagai, T. (1995). *Carbohydr. Res.*, **269**, 369–373.

[10] Endo, T., Nagase, H., Ueda, H., Kobayashi, S. and Nagai, T. (1997). *Chem. Pharm. Bull.*, **45**, 532–536.

[11] Takaha, T., Yanase, M., Takata, H., Okada, S. and Smith, S. M. (1996). *J. Biol. Chem.*, **271**, 2902–2908.

[12] Shimada, J., Handa, S., Kaneko, H. and Takada, T. (1996). *Macromolecules*, **29**, 6408–6421.

[13] Schmidt, G. (1996). *Comprehensive Supramolecular Chemistry*, **3**, Cyclodextrins, Pergamon, Oxford, Chap. 3.

[14] Chu, S. S. C. and Jeffrey, G. A. (1968). *Acta Crystallogr. Sect. B*, **23**, 1038–1049.

[15] Quigley, G. J., Sarko, A. and Marchessault, R. H. (1970). *J. Am. Chem. Soc.*, **92**, 5834–5839.

[16] Tanaka, I., Tanaka, N., Ashida, T. and Kakudo, M. (1976). *Acta Crystallogr. Sect. B*, **32**, 155–160.

[17] Takusagawa, F. and Jacobson, R. A. (1978). *Acta Crystallogr. Sect. B*, **34**, 213–218.

[18] Hinrichs, W. and Saenger, W. (1990). *J. Am. Chem. Soc.*, **112**, 2789–2796.

[19] Goebel, C. V., Dimpfl, W. L. and Brant, D. A. (1970). *Macromolecules*, **3**, 644–654.

[20] Miller, R., Gallo, S. M., Khalak, H. G. and Weeks, C. M. (1996). SnB: A Structure Determination Package User's Manual for Version 1.5.0, Hauptman-Woodward Medical Research Inst. Buffalo.

[21] Sheldrick, G. (1993). SHELXL-93, Institute fuer Anorg. Chemie, Goettingen.

[22] Burnett, M. N. and Johnson, C. K. (1996). ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-6895, Oak Ridge National Laboratory, Oak Ridge.