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

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Kazuaki Harata[a]; Le Xin Song[a]; Hisayuki Morii[a]
[a] Biomolecules Department, National Institute of Bioscience and Human-Technology, Tsukuba, Ibaraki, Japan

To cite this Article Harata, Kazuaki , Song, Le Xin and Morii, Hisayuki(2000) 'X-ray Structure of a 1:2 Complex of Hexakis (3-*O*-acetyl-2,6-di-*O*-methyl)-α-cyclodextrin with Butylacetate', Supramolecular Chemistry, 11: 3, 217 — 224
To link to this Article: DOI: 10.1080/10610270008049131
URL: http://dx.doi.org/10.1080/10610270008049131

SUPRAMOLECULAR CHEMISTRY, Vol. 11, pp. 217–224
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X-ray Structure of a 1:2 Complex of Hexakis (3-*O*-acetyl-2,6-di-*O*-methyl)-α-cyclodextrin with Butylacetate

KAZUAKI HARATA*, LE XIN SONG and HISAYUKI MORII

Biomolecules Department, National Institute of Bioscience and Human-Technology, 1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

(Received 14 July 1999)

Crystal structure of a 1:2 complex of hexakis(3-*O*-acetyl-2,6-di-*O*-methyl)-α-cyclodextrin (ADMACD) with butylacetate was determined by the X-ray method. The space group of the crystal is $P2_12_12_1$ with $Z=4$ and $D_x=1.293\,g\,cm^{-3}$, and the cell dimensions are $a=11.087(2)$, $b=23.543(3)$, and $c=31.739(6)$ Å. The structure was solved by the direct method and refined to the *R*-value of 0.123 for all the 4993 observed reflections with $I>0$. The ADMACD molecule is in a round shape with the pseudo hexagonal symmetry. Methyl and acetyl groups point towards the outside of the molecule. Because of the acetyl groups attached to O3 and methyl groups attached to O6, the intramolecular cavity is ca. 3 Å deeper than the cavity of native α-CD. One butylacetate molecule is coaxially accommodated with its acetyl group at the O6 side in the host cavity while the other guest molecule is located in an intermolecular space between host molecules which are stacked to form a head-to-tail channel-type packing structure along the *a* axis.

Keywords: Hexakis(3-*O*-acetyl-2,6-di-*O*-methyl)-α-cyclodextrin, crystal structure, inclusion complex, X-ray analysis, macrocyclic structure

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more D-glucose units. One of most prominent properties of these compounds is the formation of inclusion complexes with a variety of guest molecules [1]. Many attempts in chemical modification of CDs have been made to improve or to alter their inclusion property [2]. We have been investigating the structure of inclusion complexes of methylated CDs and have demonstrated that the methylation changes not only the macrocyclic structure of CDs but also the geometry of their guest inclusion. On the other hand, only a few investigations have been reported for acylated CDs [3, 4]. In the previous paper, we revealed that peracetylated α-CD is in the shape of a rectangular box and includes one water molecule in the crystalline state [5].

*Corresponding author.

Recently, 3-*O* acylated 2,6-di-*O*-methyl CDs have been investigated in the use as stationary phases of gas chromatography for the enantiomeric separation [6]. To evaluate the effect of 3-*O* acylation on the macrocyclic structure and guest inclusion, we determined the structure of hexakis(3-*O*-acetyl-2,6-di-*O*-methyl)-α-CD (ADMACD).

RESULTS AND DISCUSSION

Structure of 3-*O*-acetyl-2,6-di-*O*-methylglucose

Structure and numbering scheme of ADMACD are shown in Figures 1 and 2. The structure analysis revealed that the crystal consists of 54% ADMACD and 46% 3-*O*-monomethyl ADMACD in which one acetyl group is replaced by a methyl group as denoted by an asterisk in Figure 1. The commercial hexakis(2,6-di-*O*-methyl)-α-CD (DMACD, Toshin Chemicals Co.) is a mixture of DMACD and 3-*O*-monomethyl DMACD [7] and the acetylation produced the corresponding two compounds which were co-crystallized. All 3-*O*-acetyl-2,6-di-*O*-methylglucose units are in the $^4C_1$ chair conformation. Two types of orientations of C6—O6 bonds, which have been observed in crystal structures of CDs [8], are observed. One is in a (+)-*gauche* conformation with respect to the C5—O5 bond in the G3 unit and the G1, G2, G4, and G5 units show the (−)-*gauche* conformation. The C6—O6 bond of the G6 unit is statistically disordered and shows the two alternate conformations. Acetyl groups in the G2, G4, G5, and G6 units are in the orientation with their $C9H_3$ methyl groups being *trans* to C3—O3 bonds while the acetyl groups in the G1 and G3 units are in the *cis* orientation. The $C7H_3$ and $C10H_3$ methyl groups, which are *trans* to C2—C3 and C5—C6 bonds, respectively, are in the same orientation as those found in the structures of DMACD [7] and permethylated α-CD [9]. The orientation of acetyl groups is so restricted as to avoid steric hindrance with adjacent methoxy groups.

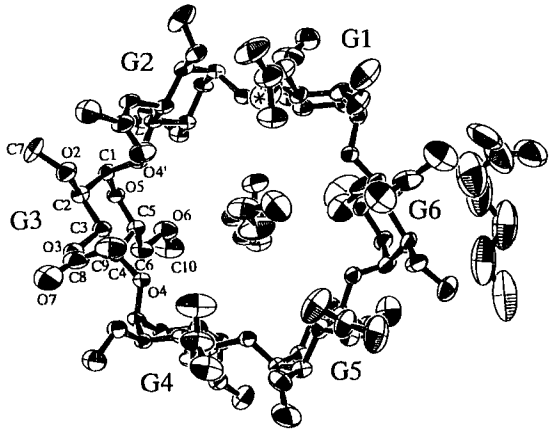

FIGURE 1 Structure and numbering of the 1:2 complex of ADMACD with butylacetate. An asterisk denotes the 3-*O* methyl group in the G1 unit. Thermal ellipsoids are drawn with 20% probability [15].

Macrocyclic Conformation

The parameters describing the macrocyclic conformation of ADMACD are given in Table I. The molecule has a pseudo six-fold symmetry and

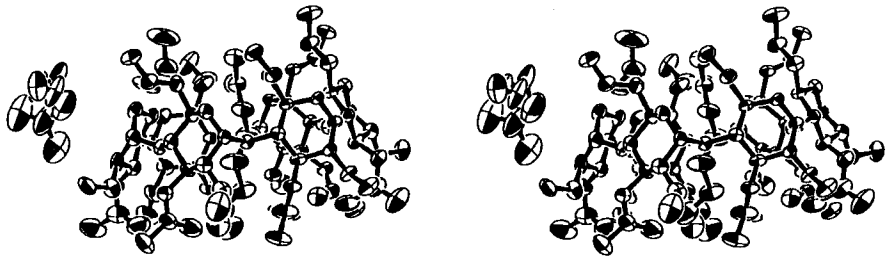

FIGURE 2 A stereo-drawing of the side view of the 1:2 complex of ADMACD with butylacetate.

TABLE I Geometrical parameters describing the macrocyclic conformation

	O4 angle (°)	Tilt angle (°)[a]	O4···Center(Å)[b]
G1	121	9.8	4.24
G2	119	15.7	4.31
G3	120	22.7	4.29
G4	120	10.4	4.24
G5	120	14.5	4.31
G6	118	27.0	4.29
Average	120	16.5	4.28
	O4···O4′ (Å)	O2···O3′ (Å)	
G1-G2	4.35	3.14	
G2-G3	4.19	3.34	
G3-G4	4.32	3.19	
G4-G5	4.32	3.20	
G5-G6	4.24	3.41	
G6-G1	4.29	3.26	
Average	4.28	3.26	

[a] The angle made by the O4 plane and the plane through C1, C4, O4, and O4′ of each 3-O-acetyl-2,6-di-O-methylglucose unit.
[b] The distance from the center of O4 hexagon to each O4 atom.

the macrocyclic conformation is similar to that of permethylated α-CD rather than peracetylated α-CD. The hexagon composed of glycosidic oxygen atoms has diameter and side length of 4.28 Å, which are slightly larger than 4.24 Å of DMACD and 4.19 Å of peracetylated α-CD. The six glycosidic O4 atoms are coplanar with the average deviation of 0.076 Å from their least-squares plane. The pyranose rings are not perpendicular to the O4 plane but incline with their O6 side towards the inside of the macrocycle by angles 9.4° – 27.1° which were measured between the O4 plane and the plane through C1, C4, O4, and O4′ of each glucose unit. In DMACD, intramolecular O3–H···O2 hydrogen bonds are formed between adjacent glucose units. As the result, the O2···O3′ distance and tilt angle are restricted to around 3.0 Å and 14°, respectively. In contrast, the acetylation of O3H hydroxyl groups disables the molecule from forming intramolecular hydrogen bonds. The average O2···O3′ distance in ADMACD between adjacent glucose units, 3.26 Å, is larger than those of α-CD and DMACD [7], but smaller than 3.71 Å of peracetylated α-CD. The O2···O3′ distances and tilt angles of ADMACD are comparable to those of permetylated α-CD, indicating the similar macrocyclic structure of these α-CDs. However, because of the acetyl group attached to O3, which is bulkier than the methyl group, the intramolecular cavity of ADMACD is deeper than the cavity of permethylated α-CD.

Crystal Packing

The ADMACD molecules are stacked along the a axis to form a head-to-tail channel-type structure (Fig. 3). The molecular axis is not perpendicular to the bc plane but so inclines as that the O4 plane makes an angle of 23.0° with the channel axis. A similar head-to-tail packing structure has been observed in α-CD complexes and permethylated α-CD complexes. The repetition unit along the channel is 11.1 Å which is comparable to 11.3 Å in the permethylated α-CD complex with *p*-nitrophenol [10] but longer than 8.1 Å in the α-CD complex with *m*-nitroaniline [11]. Adjacent two columns are related by a twofold screw axis perpendicular to the column direction. As shown in Figure 4, one column is surrounded by six columns.

Host-guest Interaction

The ADMACD cavity accommodates one butylacetate molecule with its acetyl group located at

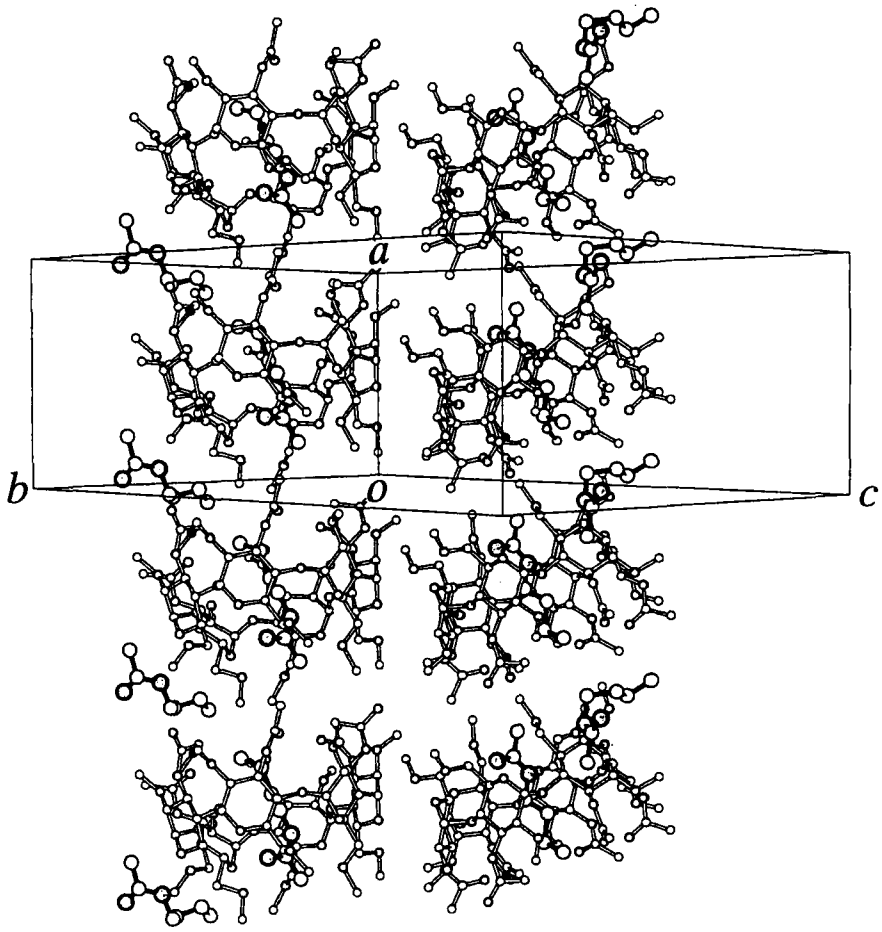

FIGURE 3 The head-to-tail channel-type packing structure of the complex. Oxygen atoms are shaded and guest molecules are shown with large circles. The 3-*O* methyl group in the G1 unit is shown with filled circle.

the O6 side while the other guest molecule is found in an intermolecular space between host molecules. Figure 5 shows the host-guest contacts less than 3.7 Å with thin lines. The butylacetate molecule is in van der Waals contacts in the host cavity. ADMACD is similar in its shape to permethylated α-CD while peracetylated α-CD has such a small cavity that includes a water molecule [5] and no evidence has been reported for the complex formation with other guests. In crystals of permethylated α-CD complexes, guest molecules are included at the O2, O3 side which is wider than the O6 side because of the inclination of methyl glucose units. The depth of the cavity in α-CD or DMACD is comparable to the dimension of 3-iodopropionic acid [12]. In contrast, the butylacetate molecule which is larger than 3-iodopropionic acid is accommodated in the ADMACD cavity and occupies the whole cavity. Therefore, the present crystal structure suggests the complexing ability of ADMACD with guest molecules bulkier than those found in α-CD, DMACD, or permethylated α-CD complexes.

MATERIALS AND METHODS

ADMACD was prepared by the acetylation of DMACD with acetic anhydride in pyridine and

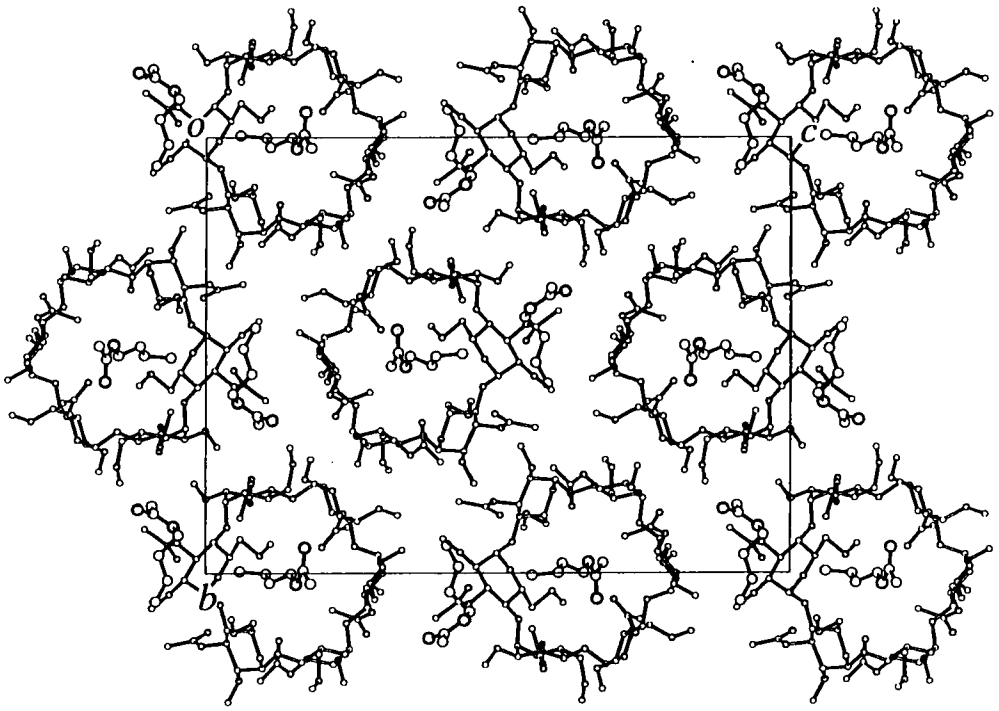

FIGURE 4 Crystal structure viewed along the *a* axis.

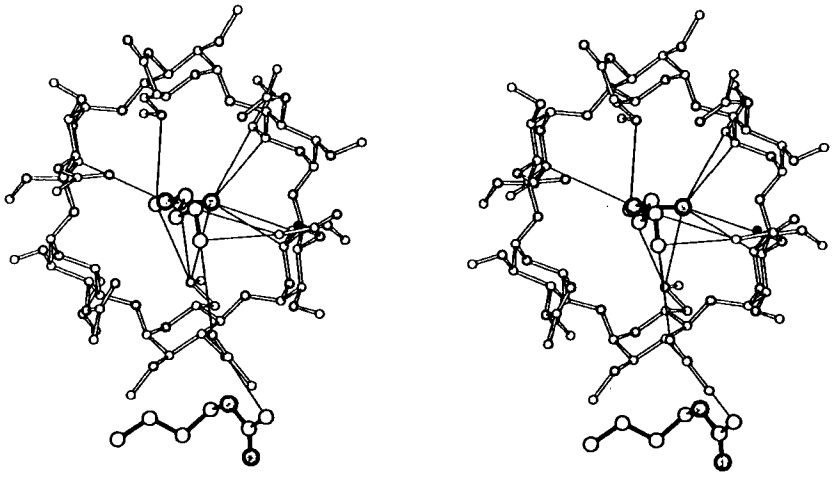

FIGURE 5 A stereo-view showing host-guest contacts less than 3.7 Å with thin lines. Guest molecules are drawn with large circles. Oxygen atoms are shaded.

crystallized by the slow evaporation of ethanol-butylacetate (1:4) solution. X-ray data were measured on a Nonius CAD4 diffractometer with graphite monochromated CuKα radiation. The structure was solved by direct method combined with density modification (program SnB [13]) and refined by the full-matrix least-squares method (program SHELX-97 [14]). In the course of refinement, it was found that the crystal contains ADMACD and 2,2′,2″,2‴,2⁗,

2''''',3,6, 6',6'',6''',6''''',6'''''-trideca-*O*-methyl-3',3'', 3''',3''''',3'''''-penta-*O*-acetyl-α-CD (3-*O*-methyl ADMACD) which consists of one 2,3,6-tri-*O*-methylglucose unit and five 3-*O*-acetyl-2,6-di-*O*-methylglucose units. The *R*-value was 0.123 for 4993 reflections with $I>0$ and 0.096 for the reflections with $F>4\sigma(F)$. The maximum and mean shift/esd values were 0.11 and 0.016, respectively. The maximum values of positive and negative residual electron densities were 0.55 and $-0.33\,e\text{Å}^{-3}$, respectively. Atomic parameters are given in Table II.

TABLE II Atomic parameters

Atom	x	y	z	Occupancy	U_{eqv}(Å^2)
C1_1	0.3941(15)	0.1660(6)	0.5344(4)	1.000	0.115(4)
C2_1	0.5177(15)	0.1901(6)	0.5357(5)	1.000	0.126(4)
C3_1	0.5799(11)	0.1781(5)	0.5765(3)	1.000	0.096(3)
C4_1	0.5065(10)	0.1940(4)	0.6142(3)	1.000	0.086(3)
C5_1	0.3767(11)	0.1727(5)	0.6088(4)	1.000	0.104(3)
C6_1	0.2938(13)	0.1937(6)	0.6425(6)	1.000	0.152(6)
C7_1	0.6641(25)	0.2079(11)	0.4806(6)	1.000	0.247(13)
C8_1	0.8024(17)	0.1878(11)	0.5732(10)	0.535	0.194(12)
C9_1	0.8123(40)	0.1275(12)	0.5597(19)	0.535	0.248(20)
C8'_1	0.7847(30)	0.1617(19)	0.5773(29)	0.465	0.250(22)
C10_1	0.2174(19)	0.2892(8)	0.6455(9)	1.000	0.216(10)
O2_1	0.5822(12)	0.1714(5)	0.5005(3)	1.000	0.162(4)
O3_1	0.6930(9)	0.2065(4)	0.5780(3)	1.000	0.130(3)
O4_1	0.5605(6)	0.1724(2)	0.6503(2)	1.000	0.082(1)
O5_1	0.3273(9)	0.1862(4)	0.5677(4)	1.000	0.125(3)
O6_1	0.3051(12)	0.2526(5)	0.6506(6)	1.000	0.218(6)
O7_1	0.8911(21)	0.2177(14)	0.5793(14)	0.535	0.281(18)
C1_2	0.5735(11)	0.2068(4)	0.6868(3)	1.000	0.088(3)
C2_2	0.6966(11)	0.2001(4)	0.7028(3)	1.000	0.092(3)
C3_2	0.7182(9)	0.1398(4)	0.7171(4)	1.000	0.089(3)
C4_2	0.6258(9)	0.1228(4)	0.7476(3)	1.000	0.082(2)
C5_2	0.5011(10)	0.1319(4)	0.7309(3)	1.000	0.084(3)
C6_2	0.3999(10)	0.1194(4)	0.7601(3)	1.000	0.092(3)
C7_2	0.8541(22)	0.2629(9)	0.6807(6)	1.000	0.218(11)
C8_2	0.9150(10)	0.0985(5)	0.7238(4)	1.000	0.124(4)
C9_2	1.0352(11)	0.1055(8)	0.7432(6)	1.000	0.173(7)
C10_2	0.3371(15)	0.1330(6)	0.8304(4)	1.000	0.136(5)
O2_2	0.7807(7)	0.2171(3)	0.6717(2)	1.000	0.110(2)
O3_2	0.8367(6)	0.1368(3)	0.7360(2)	1.000	0.099(2)
O4_2	0.6423(6)	0.0613(2)	0.7558(2)	1.000	0.082(1)
O5_2	0.4898(6)	0.1909(2)	0.7178(2)	1.000	0.088(2)
O6_2	0.4200(8)	0.1482(3)	0.7984(2)	1.000	0.112(2)
O7_2	0.8902(10)	0.0597(4)	0.6996(4)	1.000	0.163(4)
C1_3	0.6347(11)	0.0415(5)	0.7968(3)	1.000	0.089(3)
C2_3	0.7370(13)	0.0002(5)	0.8052(4)	1.000	0.107(3)
C3_3	0.7235(10)	−0.0486(4)	0.7739(4)	1.000	0.099(3)
C4_3	0.6031(10)	−0.0779(5)	0.7781(3)	1.000	0.092(3)
C5_3	0.5029(9)	−0.0335(4)	0.7772(3)	1.000	0.085(3)
C6_3	0.3850(11)	−0.0595(5)	0.7914(5)	1.000	0.118(4)
C7_3	0.8925(17)	0.0529(8)	0.8382(5)	1.000	0.173(7)
C8_3	0.9030(14)	−0.1054(6)	0.7621(6)	1.000	0.162(6)
C9_3	0.9130(17)	−0.0841(7)	0.7182(6)	1.000	0.183(7)
C10_3	0.1780(14)	−0.0426(9)	0.8013(8)	1.000	0.208(10)
O2_3	0.8524(9)	0.0258(4)	0.8014(3)	1.000	0.127(3)
O3_3	0.8122(8)	−0.0895(3)	0.7868(3)	1.000	0.121(2)
O4_3	0.5918(6)	−0.1142(2)	0.7424(2)	1.000	0.085(1)
O5_3	0.5259(7)	0.0138(3)	0.8047(2)	1.000	0.091(2)
O6_3	0.2904(8)	−0.0228(4)	0.7839(4)	1.000	0.138(3)
O7_3	0.9805(13)	−0.1384(6)	0.7771(6)	1.000	0.252(8)
C1_4	0.5638(9)	−0.1729(4)	0.7477(3)	1.000	0.081(2)

TABLE II (Continued)

Atom	x	y	z	Occupancy	U_{eqv}(Å^2)
C2_4	0.6387(9)	−0.2063(4)	0.7200(3)	1.000	0.079(2)
C3_4	0.6135(9)	−0.1939(4)	0.6758(4)	1.000	0.089(3)
C4_4	0.4797(9)	−0.2017(4)	0.6671(3)	1.000	0.077(2)
C5_4	0.4059(8)	−0.1713(4)	0.6993(3)	1.000	0.079(2)
C6_4	0.2710(10)	−0.1839(4)	0.6954(3)	1.000	0.089(3)
C7_4	0.8253(13)	−0.2471(6)	0.7385(6)	1.000	0.157(6)
C8_4	0.7659(14)	−0.2044(7)	0.6250(5)	1.000	0.189(8)
C9_4	0.8293(20)	−0.2430(8)	0.5961(6)	1.000	0.201(9)
C10_4	0.1350(12)	−0.2612(7)	0.6848(5)	1.000	0.153(6)
O2_4	0.7632(6)	−0.1968(3)	0.7283(3)	1.000	0.111(2)
O3_4	0.6820(7)	−0.2274(3)	0.6476(2)	1.000	0.102(2)
O4_4	0.4555(6)	−0.1829(2)	0.6256(2)	1.000	0.086(2)
O5_4	0.4423(6)	−0.1838(2)	0.7407(2)	1.000	0.078(1)
O6_4	0.2546(6)	−0.2437(3)	0.6956(2)	1.000	0.105(2)
O7_4	0.7894(16)	−0.1534(6)	0.6276(5)	1.000	0.259(9)
C1_5	0.3832(11)	−0.2153(4)	0.5989(3)	1.000	0.083(2)
C2_5	0.4372(14)	−0.2192(5)	0.5560(4)	1.000	0.114(4)
C3_5	0.4462(12)	−0.1580(5)	0.5370(3)	1.000	0.099(3)
C4_5	0.3251(12)	−0.1296(5)	0.5376(4)	1.000	0.098(3)
C5_5	0.2703(10)	−0.1324(4)	0.5802(3)	1.000	0.088(3)
C6_5	0.1395(12)	−0.1130(6)	0.5832(4)	1.000	0.111(4)
C7_5	0.5821(26)	−0.2926(8)	0.5399(8)	1.000	0.271(15)
C8_5	0.5898(15)	−0.1526(7)	0.4805(4)	1.000	0.166(6)
C9_5	0.6148(23)	−0.1649(14)	0.4363(4)	1.000	0.254(13)
C10_5	−0.0404(14)	−0.1050(11)	0.5451(7)	1.000	0.207(10)
O2_5	0.5519(11)	−0.2429(4)	0.5588(3)	1.000	0.146(3)
O3_5	0.4810(8)	−0.1651(4)	0.4937(2)	1.000	0.116(2)
O4_5	0.3424(7)	−0.0712(3)	0.5252(2)	1.000	0.099(2)
O5_5	0.2671(8)	−0.1915(3)	0.5951(2)	1.000	0.101(2)
O6_5	0.0711(15)	−0.1362(5)	0.5492(3)	1.000	0.140(3)
O7_5	0.6647(15)	−0.1335(10)	0.5045(5)	1.000	0.260(10)
C1_6	0.2633(15)	−0.0464(6)	0.4991(4)	1.000	0.114(4)
C2_6	0.3290(18)	−0.0146(6)	0.4641(4)	1.000	0.136(6)
C3_6	0.3984(13)	0.0340(5)	0.4845(4)	1.000	0.108(4)
C4_6	0.3216(13)	0.0720(5)	0.5141(4)	1.000	0.105(3)
C5_6	0.2519(11)	0.0377(6)	0.5424(4)	1.000	0.111(4)
C6_6	0.1435(24)	0.0783(8)	0.5595(6)	1.000	0.224(11)
C7_6	0.3314(17)	−0.0789(8)	0.4087(4)	1.000	0.161(7)
C8_6	0.5452(17)	0.0649(7)	0.4352(5)	1.000	0.182(8)
C9_6	0.5602(26)	0.1025(11)	0.3967(7)	1.000	0.265(14)
C10_6	0.0038(27)	0.0672(18)	0.6126(11)	1.000	0.405(25)
O2_6	0.3991(11)	−0.0475(4)	0.4382(3)	1.000	0.137(3)
O3_6	0.4371(11)	0.0703(4)	0.4516(3)	1.000	0.140(3)
O4_6	0.4060(7)	0.1055(3)	0.5368(2)	1.000	0.101(2)
O5_6	0.1829(9)	−0.0078(4)	0.5221(3)	1.000	0.118(8)
O6_6	0.1097(14)	0.0405(8)	0.5938(5)	1.000	0.227(6)
O7_6	0.6172(15)	0.0334(9)	0.4517(6)	1.000	0.246(8)
CB1_7	0.5051(15)	−0.0012(10)	0.6483(7)	1.000	0.208(8)
CB2_7	0.5616(19)	−0.0224(10)	0.6112(8)	1.000	0.232(10)
CB3_7	0.6909(15)	−0.0012(9)	0.6046(7)	1.000	0.199(9)
CB4_7	0.7180(22)	0.0043(14)	0.5593(8)	1.000	0.274(15)
CB5_7	0.3012(12)	0.0064(5)	0.6688(4)	1.000	0.121(4)
CB6_7	0.1928(14)	−0.0240(7)	0.6809(6)	1.000	0.167(7)
OB1_7	0.3909(11)	−0.0254(4)	0.6562(4)	1.000	0.160(4)
OB2_7	0.3108(12)	0.0583(4)	0.6710(4)	1.000	0.177(4)
CB1_8	−0.0591(29)	0.0880(16)	0.4536(11)	1.000	0.468(21)
CB2_8	−0.0778(39)	0.0422(15)	0.4205(13)	1.000	0.464(23)
CB3_8	−0.0440(42)	−0.0156(16)	0.4351(17)	1.000	0.466(25)
CB4_8	−0.1103(49)	−0.0635(16)	0.4147(12)	1.000	0.467(33)
CB5_8	0.0828(23)	0.1383(10)	0.4108(8)	1.000	0.375(20)
CB6_8	0.2106(23)	0.1563(11)	0.4084(12)	1.000	0.354(24)
OB1_8	0.0605(26)	0.1075(17)	0.4448(9)	1.000	0.457(18)
OB2_8	0.0088(28)	0.1481(10)	0.3847(9)	1.000	0.411(20)

Crystal Data: $(C_{60}H_{96}O_{36})_{0.54}\cdot(C_{59}H_{96}O_{35})_{0.46}\cdot 2C_6H_{12}O_2$, *F.W.* = 1612.8, space group $P2_12_12_1$, $Z = 4$, $a = 11.087(2)$, $b = 23.543(3)$, $c = 31.739(6)$ Å, $V = 8284(3)$ Å^3, $D_x = 1.293$ g cm^{-3}.

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