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Guest differentiation in a $6^{I},6^{II}$-disubstituted *β*-cyclodextrin

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.014 Å
Disorder in main residue
R factor = 0.096
wR factor = 0.255
Data-to-parameter ratio = 10.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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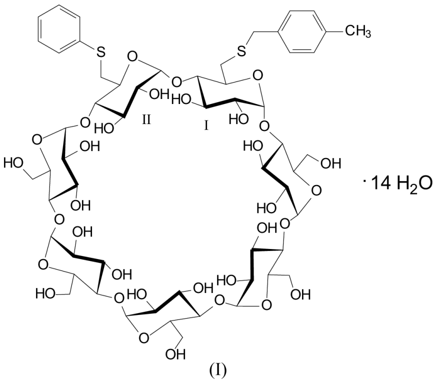
The structure of $6^{I},6^{II}$-dideoxy-6^{I}-(*p*-methylbenzylthio)-6^{II}-phenylthio-*β*-cyclodextrin tetradecahydrate, $C_{56}H_{82}O_{33}S_2\cdot 14H_2O$, has been determined. Of the two substituents, only the phenylthio moiety is included in the cavity of adjacent disubstituted *β*-cyclodextrin (*β*-CD) units, forming a helical polymer.

Comment

Compared to the abundance of cyclodextrin (CD) inclusion compounds which have been determined by X-ray crystallography (Saenger, 1984; Harata, 1996), relatively few structures of substituted CD's other than *O*-methylated derivatives have been elucidated (Harata, 1998). In the case of *β*-CD's monosubstituted at the primary carbon (C-6), the tethered substituent of one *β*-CD unit, such as *tert*-butylthio (Hirotsu *et al.*, 1982; Fujita *et al.*, 1985), phenylthio and phenylsulfinyl (Kamitori *et al.*, 1987), azido (Charpin *et al.*, 1990), 2-hydroxypropyloxy (Harata *et al.*, 1991) and (6-aminohexyl)-amino (Mentzafos *et al.*, 1996), is included in the cavity of another substituted *β*-CD. This simultaneous functioning of a molecule as host and guest provides unique three-dimensional self-assemblies, most notably helical polymers (Hirotsu *et al.*, 1982; Kamitori *et al.*, 1987). We report here the X-ray crystallographic study of $6^{I},6^{II}$-dideoxy-6^{I}-(*p*-methylbenzylthio)-6^{II}-phenylthio-*β*-*cyclo*dextrin, (I), a *β*-CD derivative carrying two different substituents at the primary C-6 of vicinal *gluco*pyranosyl residues, with the result that exclusively the phenylthio moiety is intermolecularly included into the cavity of another unit, making it a unique case of guest differentiation.



(I)

The molecular structure of (I) is shown in Fig. 1. The *β*-CD macrocycle has an approximate sevenfold axis and a round shape, with all glucose residues in the $^4C_1$ chair conformation.

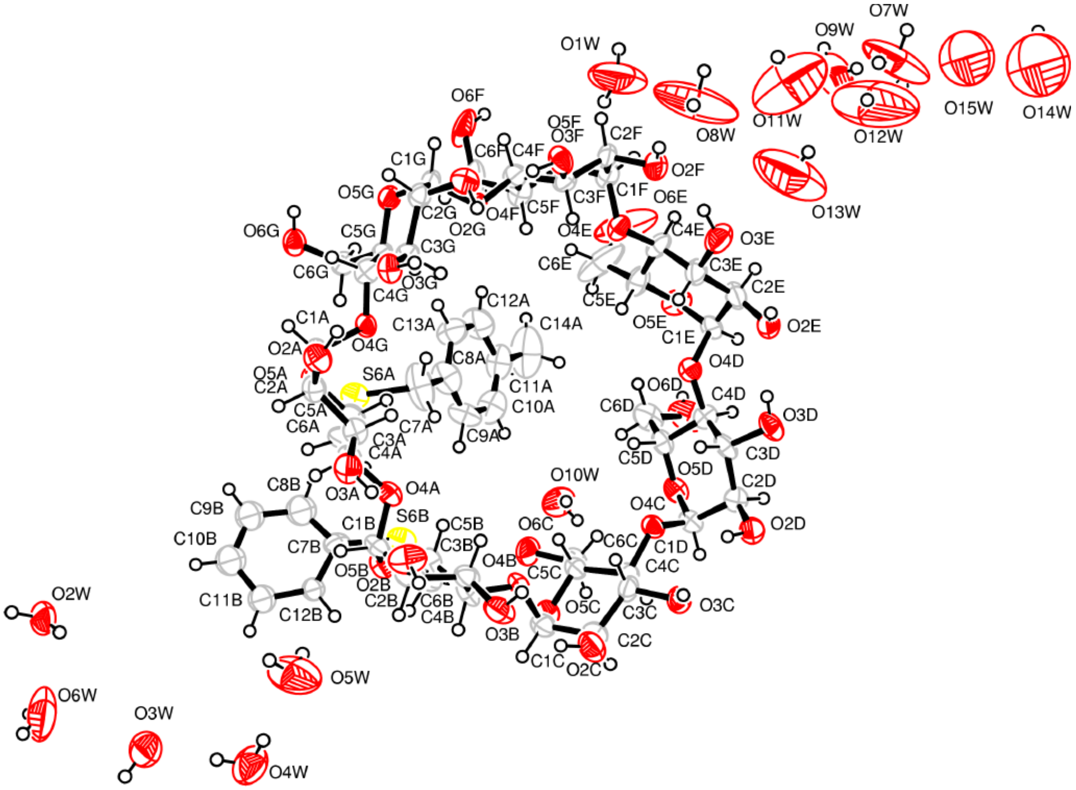


Figure 1

A view of (I) from the secondary OH group side, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

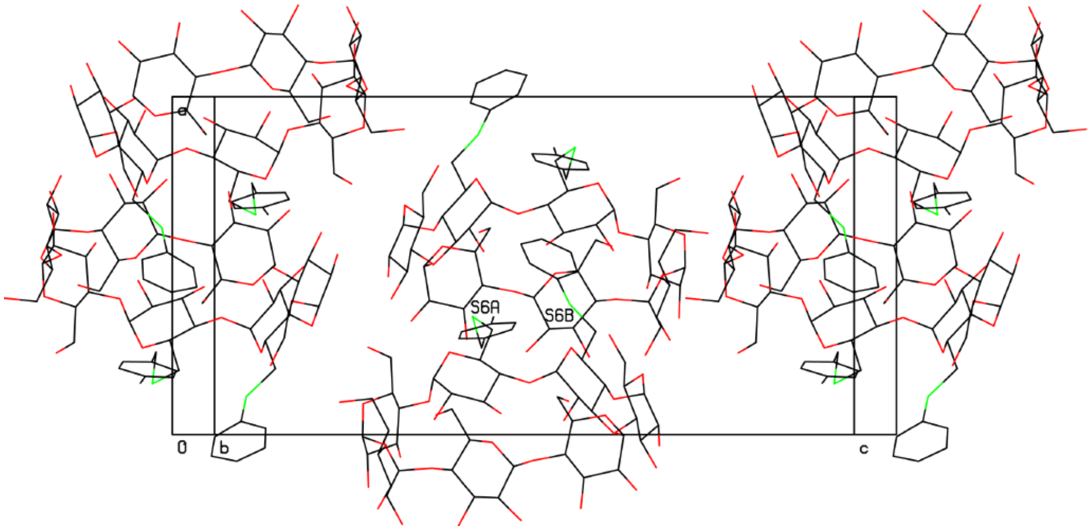


Figure 2

A packing diagram of (I), showing the guest–host stack. The H atoms and the solvent water molecules have been omitted and the view is along the *b* axis.

The secondary hydroxyl groups between neighbouring glucose residues form intramolecular hydrogen bonds, which may maintain the round shape of the cyclodextrin ring; the seven glycosidic O4 atoms are coplanar within 0.11 Å. The heptagon composed of seven O4 atoms is approximately regular, since the side lengths of the heptagon are in the range 4.33 (7)–4.46 (7) Å and the O—O—O angles vary from 124.8 (2) to 133.5 (2)°. The glucose residues are inclined to the perpendicular axis of the O4 atoms plane to make the hydrophobic cavity smaller at the primary hydroxyl site. The packing of the disubstituted β-CD macrocycles is unique in that, of the two residues that may be included intermolecularly into the cavity of another molecule, exclusively the phenylthio group is selected for penetrating the cavity from the wider secondary hydroxyl group side (Fig. 2), thereby providing a most interesting case of guest differentiation by a β-CD cavity. The methylbenzylthio moiety, on the other hand, is partially spread over the top of its own primary hydroxyl group side, thus partially capping the narrower opening of the β-CD macrocycle, making this supramolecular self-assembly a unique

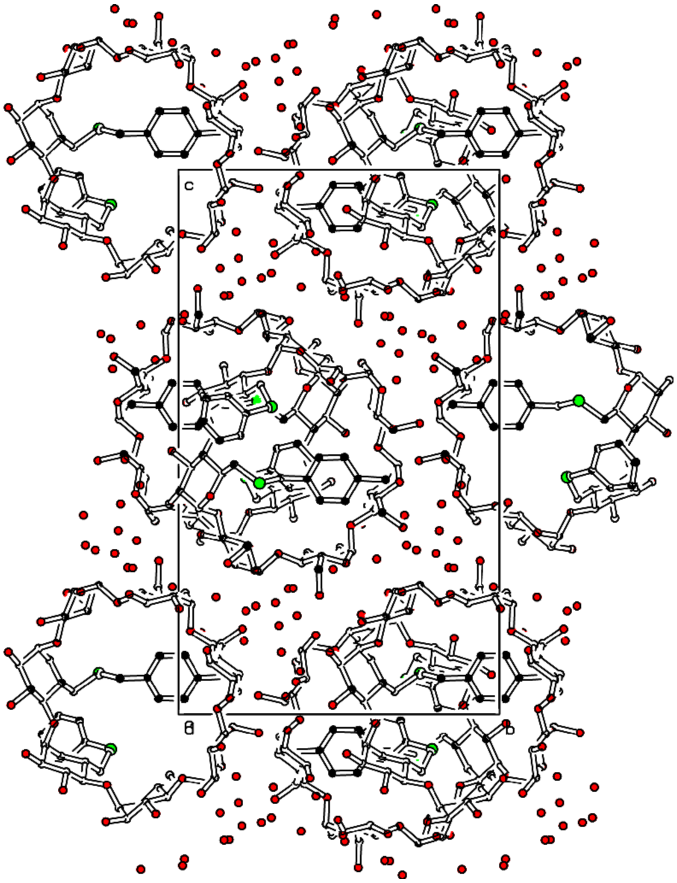


Figure 3
A packing diagram, viewed along the *a* axis, showing the hydrophobic guest–host stacks surrounded by OH groups and water molecules.

example in crystal engineering. The guest–host stacks surrounded by crystal water molecules run parallel to the *a* axis. As seen in Fig. 3 the hydrophobic cores are clearly separated from the hydrophilic surface and the crystal water molecules.

Experimental

The title compound was synthesized as described elsewhere (Fujita, 2003). Colourless crystals were obtained from a water–acetonitrile (4:1) solution.

Crystal data

$C_{56}H_{82}O_{33}S_2\cdot14H_2O$
$M_r = 1599.56$
Orthorhombic, $P2_12_12_1$
$a = 14.4635\ (7)$ Å
$b = 17.3370\ (10)$ Å
$c = 29.388\ (2)$ Å
$V = 7369.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34217 reflections
$\theta = 1.6–24.7°$
$\mu = 0.18$ mm^{-1}
$T = 173\ (2)$ K
Prism, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
34217 measured reflections
9891 independent reflections
4958 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.118$
$\theta_{\max} = 28.3°$
$h = -18 \rightarrow 19$
$k = -23 \rightarrow 20$
$l = -39 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.096$
$wR(F^2) = 0.255$
$S = 1.10$
9891 reflections
941 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1146P)^2 + 1.2217P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0116 (9)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2O*A*···O3*G*	0.84	2.06	2.89 (1)	166
O3*A*—H3O*A*···O2*B*	0.84	1.95	2.76 (1)	162
O2*B*—H2O*B*···O13*W*$^{\rm i}$	0.84	2.16	2.87 (2)	143
O3*B*—H3O*B*···S6*A*$^{\rm ii}$	0.84	2.69	3.431 (7)	149
O2*C*—H2O*C*···O3*B*	0.84	2.16	2.92 (1)	150
O3*C*—H3O*C*···O6*G*$^{\rm ii}$	0.84	2.17	2.798 (9)	132
O6*C*—H6O*C*···O10*W*	0.84	2.15	2.82 (1)	137
O2*D*—H2O*D*···O3*C*	0.84	2.18	2.87 (1)	139
O3*D*—H3O*D*···O2*E*	0.84	1.91	2.72 (1)	159
O6*D*—H6O*D*···O2*W*$^{\rm ii}$	0.84	2.31	2.67 (1)	106
O2*E*—H2O*E*···O3*E*	0.84	2.42	2.85 (1)	113
O3*E*—H3O*E*···O2*F*	0.84	2.02	2.72 (1)	141
O6*E*—H6O*E*···O6*W*$^{\rm ii}$	0.84	1.83	2.65 (2)	166
O2*F*—H2O*F*···O8*W*	0.84	1.80	2.57 (2)	152
O3*F*—H3O*F*···O2*G*	0.84	1.96	2.79 (1)	169
O6*F*—H6O*F*···O3*G*$^{\rm iii}$	0.84	1.93	2.73 (1)	159
O2*G*—H2O*G*···O5*C*$^{\rm ii}$	0.84	2.57	3.24 (1)	137
O3*G*—H3O*G*···O6*C*$^{\rm ii}$	0.84	2.20	2.75 (1)	123
O6*G*—H6O*G*···O4*W*$^{\rm iv}$	0.84	1.98	2.77 (1)	158
O1*W*—H1*W*···O3*F*	0.85	2.26	3.10 (3)	173
O1*W*—H2*W*···O2*D*$^{\rm v}$	0.84	2.30	3.10 (3)	160
O2*W*—H3*W*···O3*A*$^{\rm vi}$	0.84	1.86	2.64 (1)	154
O2*W*—H4*W*···O10*W*$^{\rm vii}$	0.84	2.11	2.94 (1)	171
O3*W*—H5*W*···O6*F*$^{\rm viii}$	0.84	1.99	2.76 (1)	153
O3*W*—H6*W*···O6*E*$^{\rm i}$	0.84	2.43	3.24 (2)	161
O4*W*—H7*W*···O3*W*	0.84	1.97	2.78 (1)	161
O4*W*—H8*W*···O5*W*	0.84	1.91	2.73 (2)	167
O5*W*—H9*W*···O5*D*$^{\rm vii}$	0.84	2.32	3.09 (1)	151
O5*W*—H9*W*···O6*D*$^{\rm vii}$	0.84	2.40	3.05 (2)	135
O5*W*—H10*W*···O3*E*$^{\rm i}$	0.84	2.10	2.81 (2)	143
O6*W*—H11*W*···O3*D*$^{\rm ix}$	0.84	2.31	2.84 (2)	121
O6*W*—H12*W*···O2*A*$^{\rm vi}$	0.84	2.20	2.89 (2)	139
O7*W*—H13*W*···O2*G*$^{\rm x}$	0.84	1.88	2.69 (1)	161
O7*W*—H14*W*···O11*W*	0.84	2.25	2.79 (3)	123
O8*W*—H15*W*···O3*C*$^{\rm v}$	0.85	2.14	2.90 (2)	149
O8*W*—H16*W*···O1*W*	0.84	2.18	2.64 (3)	114
O9*W*—H17*W*···O1*W*$^{\rm x}$	0.85	2.18	3.03 (4)	178
O9*W*—H18*W*···O11*W*$^{\rm x}$	0.85	2.17	2.64 (4)	115
O10*W*—H19*W*···O6*C*	0.84	2.30	2.82 (1)	121
O10*W*—H20*W*···O3*W*$^{\rm xi}$	0.84	1.95	2.76 (1)	159
O11*W*—H21*W*···O7*W*	0.86	2.05	2.79 (3)	145
O11*W*—H22*W*···O9*W*$^{\rm xii}$	0.85	1.97	2.64 (4)	134
O12*W*—H23*W*···O7*W*	0.84	2.15	2.85 (4)	141
O12*W*—H24*W*···O1*W*$^{\rm x}$	0.84	1.99	2.58 (3)	126
O13*W*—H25*W*···O12*W*	0.84	2.54	3.02 (4)	117
O13*W*—H25*W*···O11*W*	0.84	2.62	3.26 (4)	134
O13*W*—H26*W*···O5*W*$^{\rm ii}$	0.83	1.86	2.67 (4)	163
O14*W*—H27*W*···O3*F*$^{\rm x}$	0.86	2.25	2.98 (4)	142
O14*W*—H28*W*···O2*D*$^{\rm xiii}$	0.85	1.84	2.61 (4)	151

Symmetry codes: (i) $x-\frac{1}{2}, -\frac{1}{2}-y, -z$; (ii) $\frac{1}{2}+x, -\frac{1}{2}-y, -z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}-x, -1-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (vi) $x-\frac{1}{2}, -\frac{3}{2}-y, -z$; (vii) $x, y-1, z$; (viii) $-\frac{1}{2}-x, -1-y, z-\frac{1}{2}$; (ix) $x-1, y-1, z$; (x) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xi) $x, 1+y, z$; (xii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xiii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

H atoms were treated as riding atoms. The positions of the H atoms of the water molecules were calculated with the program *HYDROGEN* (Nardelli, 1999) and included in the refinement with constrained geometry. A disorder of the phenyl ring was resolved by two sets of atomic coordinates and isotropic refinement.

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Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *HYDROGEN* (Nardelli, 1999); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and IUCr *SHELXL*97 template.

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