Refinement

Refinement on F
$R = 0.032$
$wR = 0.051$
$S = 2.81$
508 reflections
62 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.25×10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.5187 (1)	0	0.2475 (1)	0.0336 (3)
O7	0.1876 (1)	0	0.1265 (1)	0.0316 (3)
C1	0.3253 (2)	0	0.0858 (2)	0.0296 (4)
C2	0.4136 (1)	−0.1557 (2)	0.1945 (1)	0.0306 (3)
C3	0.3213 (1)	−0.1901 (2)	0.3229 (1)	0.0331 (3)
C4	0.2292 (1)	0	0.2976 (2)	0.0293 (4)
H1	0.325 (2)	0	−0.029 (2)	0.032 (4)
H2	0.453 (1)	−0.276 (2)	0.147 (1)	0.043 (3)
H3	0.264 (2)	−0.312 (2)	0.302 (1)	0.060 (4)
H4	0.376 (1)	−0.201 (2)	0.430 (1)	0.035 (3)
H5	0.147 (2)	0	0.351 (2)	0.044 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.458 (1)	C2—H2	0.98 (1)
O7—C1	1.420 (2)	C3—C4	1.524 (1)
O7—C4	1.443 (2)	C3—H3	0.97 (2)
C1—C2	1.539 (1)	C3—H4	0.98 (1)
C1—H1	0.98 (2)	C4—H5	0.97 (2)
C2—C3	1.524 (2)		
C2—O1—C2^{i}	88.69 (8)	C3—C2—H2	118.4 (8)
C1—O7—C4	96.8 (1)	C2—C3—C4	99.8 (1)
O7—C1—C2	107.78 (9)	C2—C3—H3	111.7 (8)
O7—C1—H1	112. (1)	C2—C3—H4	112.3 (7)
C2—C1—C2^{i}	82.92 (9)	C4—C3—H3	110.1 (9)
C2—C1—H1	121.1 (6)	C4—C3—H4	114.2 (7)
O1—C2—C1	90.88 (8)	H3—C3—H4	109 (1)
O1—C2—C3	109.71 (9)	O7—C4—C3	101.94 (8)
O1—C2—H2	113.0 (7)	O7—C4—H5	110. (1)
C1—C2—C3	101.28 (9)	C3—C4—C3^{i}	109.5 (1)
C1—C2—H2	119.8 (7)	C3—C4—H5	115.6 (4)

Symmetry code: (i) $x, -y, z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974)

Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*; Main *et al.*, 1980). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX MolEN*.

We thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BK1244). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bedford, A. F., Beezer, A. E., Mortimer, C. T. & Springall, H. D. (1963). *J. Chem. Soc.* pp. 3823–3828.
Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
Bürgi, H.-B., Baldridge, K. K., Hardcastle, K., Frank, N. L., Gantzel, P., Siegel, J. S. & Ziller, J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1454–1456.
Drian, C. le & Vogel, P. (1988). *Helv. Chim. Acta*, **71**, 1399–1405.
Drian, C. le & Vogel, P. (1993). *J. Org. Chem.* **58**, 2328–2330.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Hall, H. K., DeBlauwe, F. & Pyriadi, I. (1975). *J. Am. Chem. Soc.* **97**, 3854–3855.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Luger, P. & Buschmann, J. (1984). *J. Am. Chem. Soc.* **106**, 7118–7121.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Vogel, P., Fatton, D., Gasparini, F. & le Drian, C. (1990). *Synth. Lett.* pp. 173–185.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). C**52**, 2929–2932

2,4-Dinitrophenyl Phenyl Sulfone

JAVIER ELLENA,[a] GRACIELA PUNTE[a] AND NORMA S. NUDELMAN[b]

[a]*Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC67 - (1900) - La Plata, Argentina, and* [b]*Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Ciudad Universitaria, Pabellón 2, Buenos Aires, Argentina. E-mail: ellena@ayelen.fisica.unlp.edu.ar*

(Received 13 March 1996; accepted 1 July 1996)

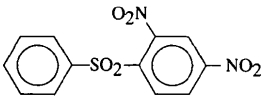
Abstract

The crystal structure of the title compound, $C_{12}H_8N_2O_6S$, has been determined by single-crystal X-ray diffraction. The compound crystallizes in the noncentro-

symmetric $P2_1$ space group. The substituted aromatic ring has a slightly deformed boat conformation. The *o*-NO_2 and *p*-NO_2 groups are twisted out of the plane of the phenyl ring. The unsubstituted aromatic ring is planar and the dihedral angle between the mean plane of the rings is 71.1 (2)°. Short C—H···O intermolecular contacts stabilize the three-dimensional structure.

Comment

This report is part of a general study on 2,4-dinitrobenzenes with variation of the substituents at different positions (Ellena *et al.*, 1995). The aim of this investigation is to determine the parameters which govern the molecular geometry and organization both in the crystalline state and in solution. To add to the understanding of the effect of different substituents, a single-crystal X-ray study of the title compound, (I), was undertaken.



(I)

A view of the title molecule with the atom-labelling scheme is shown in Fig. 1. Analysis of the molecular geometry shows that the substituted phenyl ring has a slightly deformed boat conformation, with the C4 and C6 atoms out of the mean ring plane by 0.025 (4) and 0.030 (5) Å, respectively. The total puckering amplitude (Cremer & Pople, 1975) is Q_T = 0.028 (4). The nitro group in the *ortho* position is rotated 56.5 (2)° out of the ring plane, thus decreasing the steric interaction with the bridging group. The nitro group in the *para* position is twisted out of the mean ring plane by 18.5 (3)°. The unsubstituted aromatic ring displays an essentially planar geometry.

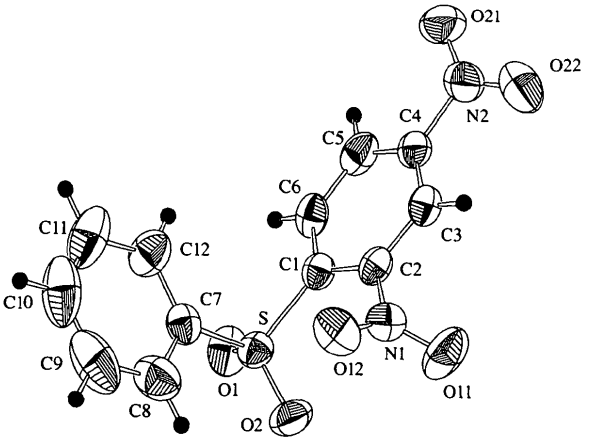


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title molecule showing the atom labelling and 50% probability ellipsoids.

The sulfone O1—S—O2 bond angle is 118.9 (2)°. Its departure from the ideal sp^3 bond-angle value indicates repulsion between the O atoms. This effect is explained by the induction of negative charge on the O atoms *via* resonance effects of the π electrons in the S—O bond. The observed value is also in agreement with the mean value [118.9 (2)°] retrieved from the 1995 version of the Cambridge Structural Database (Allen & Kennard, 1993) for sulfone groups in bridged diphenyl sulfones. The C1—S—C7 bond angle of 106.2 (2)° is larger than the mean value found for this angle in the same search [105.3 (3)°].

The bonds between the sulfone group and the rings are unsymmetrical. The C7—S bond length of 1.748 (4) Å is identical, within experimental error, to the mean value found for C(aromatic)—SO_2C bonds [1.763 (9) Å; Allen *et al.*, 1987], but the C1—S bond length of 1.788 (4) Å is 0.025 Å larger than the corresponding value. The C4—N2 bond length of 1.481 (6) Å is similar to the mean value of 1.471 (2) Å obtained by Domenicano *et al.* (1989) for the C—N bond length in nitrobenzene derivatives for which the substituents were chosen to avoid conjugation. For the nitro group in the *ortho* position, however, the C2—N1 bond length of 1.459 (5) Å is 0.012 Å smaller than the above mentioned mean value.

The three-dimensional structure is stabilized by a weak attractive interaction between one of the sulfone O atoms and the more acidic H atom of the substituted aromatic ring (see Table 2). This interaction explains the displacement of the C6 atom out of the ring plane.

Experimental

The title compound was prepared according to standard procedures (Bunnett & Nudelman, 1969) and crystallized by slow evaporation from methanol (m.p. 430.0–430.7 K, literature corrected 434 K; Bost, Turner & Norton, 1932).

Crystal data

$C_{12}H_8N_2O_6S$
M_r = 308.26
Monoclinic
$P2_1$
a = 10.661 (2) Å
b = 5.478 (2) Å
c = 11.383 (3) Å
β = 104.57 (2)°
V = 643.4 (3) Å^3
Z = 2
D_x = 1.591 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 8–17°
μ = 0.283 mm^{-1}
T = 293 (2) K
Prism
0.40 × 0.08 × 0.04 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer

R_{int} = 0.0498
θ_{max} = 25.02°

$\theta/2\theta$ scans
Absorption correction: none
1341 measured reflections
1270 independent reflections
1127 observed reflections $[I > 2\sigma(I)]$

$h = 0 \rightarrow 12$
$k = 0 \rightarrow 6$
$l = -13 \rightarrow 13$
1 standard reflection frequency: 100 min intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0371$
$wR(F^2) = 0.0866$
$S = 1.137$
1270 reflections
194 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.264$ e Å^{-3}
$\Delta\rho_{min} = -0.201$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1992)
Extinction coefficient: 0.026 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.06 (15)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.13520 (9)	0.0710 (2)	0.71019 (9)	0.0442 (3)
O1	0.0757 (3)	−0.0129 (7)	0.5898 (3)	0.0598 (9)
O2	0.2075 (3)	−0.0980 (6)	0.7966 (3)	0.0617 (8)
O11	0.4890 (3)	0.1959 (9)	0.9379 (3)	0.0835 (12)
O12	0.3006 (3)	0.2963 (8)	0.9599 (2)	0.0658 (10)
O21	0.4378 (3)	1.0088 (7)	0.5376 (3)	0.0802 (12)
O22	0.5910 (4)	0.8977 (9)	0.6915 (4)	0.0863 (12)
N1	0.3811 (3)	0.2827 (7)	0.9023 (3)	0.0491 (9)
N2	0.4841 (4)	0.8756 (8)	0.6236 (4)	0.0594 (10)
C1	0.2411 (3)	0.3128 (8)	0.6914 (3)	0.0405 (9)
C2	0.3495 (3)	0.3859 (8)	0.7803 (3)	0.0398 (9)
C3	0.4321 (3)	0.5644 (9)	0.7584 (3)	0.0446 (9)
C4	0.4018 (4)	0.6718 (9)	0.6458 (4)	0.0449 (10)
C5	0.2970 (4)	0.6018 (11)	0.5550 (3)	0.0534 (12)
C6	0.2178 (4)	0.4194 (9)	0.5781 (3)	0.0468 (11)
C7	0.0141 (4)	0.2058 (9)	0.7672 (3)	0.0449 (10)
C8	−0.0218 (5)	0.0948 (12)	0.8607 (4)	0.0723 (14)
C9	−0.1275 (6)	0.1816 (17)	0.8974 (6)	0.098 (2)
C10	−0.1927 (5)	0.3815 (17)	0.8421 (6)	0.096 (2)
C11	−0.1561 (5)	0.4936 (15)	0.7500 (5)	0.088 (2)
C12	−0.0524 (4)	0.4073 (11)	0.7112 (4)	0.0642 (13)

Table 2. *Selected geometric parameters (Å, °)*

S—O2	1.427 (3)	C3—C4	1.373 (5)
S—O1	1.433 (3)	C4—C5	1.372 (6)
S—C7	1.748 (4)	C5—C6	1.375 (7)
S—C1	1.788 (4)	C6—H6	0.93
O21—N2	1.221 (5)	C7—C8	1.361 (6)
O22—N2	1.211 (5)	C7—C12	1.378 (7)
O11—N1	1.216 (4)	C8—C9	1.381 (8)
O12—N1	1.206 (4)	C9—C10	1.364 (10)
N2—C4	1.481 (6)	C10—C11	1.355 (9)
N1—C2	1.459 (5)	C11—C12	1.373 (6)
C1—C6	1.380 (5)	C6—O1^{i}	3.252 (4)
C1—C2	1.390 (5)	H6—O1^{i}	2.477 (4)
C2—C3	1.380 (6)		
O2—S—O1	118.9 (2)	C3—C2—N1	116.2 (3)
O2—S—C7	109.8 (2)	C1—C2—N1	122.1 (4)
O1—S—C7	107.4 (2)	C4—C3—C2	117.4 (4)
O2—S—C1	108.4 (2)	C3—C4—C5	122.7 (4)
O1—S—C1	105.3 (2)	C3—C4—N2	118.2 (4)
C7—S—C1	106.2 (2)	C5—C4—N2	119.1 (4)
O22—N2—O21	125.2 (5)	C4—C5—C6	118.8 (4)
O22—N2—C4	118.0 (4)	C5—C6—C1	120.7 (4)
O21—N2—C4	116.8 (4)	C8—C7—C12	120.5 (4)
O12—N1—O11	125.9 (4)	C8—C7—S	118.7 (4)
O12—N1—C2	117.9 (3)	C12—C7—S	120.5 (3)
O11—N1—C2	116.2 (3)	C7—C8—C9	119.6 (6)
C6—C1—C2	118.7 (4)	C10—C9—C8	119.8 (6)
C6—C1—S	117.0 (3)	C11—C10—C9	120.5 (6)
C2—C1—S	124.1 (3)	C10—C11—C12	120.4 (7)
C3—C2—C1	121.6 (4)	C11—C12—C7	119.2 (5)

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O1^{i}	0.93	2.477 (4)	3.252 (4)	140.9

Symmetry code: (i) $-x, \frac{1}{2} + y, 1 - z$.

The title structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1985). The Fourier map obtained showed all non-H atoms. The model was refined by a full-matrix least-squares procedure on F^2 by means of *SHELXL*93 (Sheldrick, 1992). All the H atoms were placed in calculated positions and refined riding over the bonded C atoms. Isotropic displacement parameters were used in the first steps and anisotropic ones afterwards, except for H atoms, which were refined isotropically. Calculations were carried out on a PC 486.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4/*PC*. Data reduction: *MolEN* (Fair, 1990). Molecular graphics: *PLUTON* (Spek, 1990) and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93. Geometrical calculations: *PARST* (Nardelli, 1983).

The authors thank E. E. Castellano for helpful discussions, the Instituto de Quimica e Fisica de Sao Carlos, Brazil, for experimental facilities, and CONICET for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1230). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 131–137.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, S1–S19.
Bost, R. W., Turner, J. O. & Norton, N. S. (1932). *J. Am. Chem. Soc.* **54**, 1985–1987.
Bunnett, J. F. & Nudelman, N. S. (1969). *J. Org. Chem.* **34**, 2038–2042.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1989). *Struct. Chem.* **1**, 107–122.
Ellena, J., Punte, G., Rivero, B. E., Remedi, M. V., de Vargas, E. B. & de Rossi, R. (1995). *J. Chem. Crystallogr.* **12**, 801–805.
Enraf–Nonius (1993). *CAD*-4/*PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1992). *SHELXL93. Program for the Refinement of Crystal Structures*. Beta test version. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Acta Cryst. (1996). C**52**, 2932–2936

Inclusion of the Main Pheromone Component of *Dacus oleae*, 1,7-Dioxaspiro[5,5]undecane, in β-Cyclodextrin

NICOLE RYSANEK, GENEVIÈVE LE BAS, FRANÇOISE VILLAIN AND GEORGES TSOUCARIS

ERS 128 CNRS, Centre pharmaceutique, Université Paris XI, Avenue JB Clément, 92290 Châtenay Malabry, France

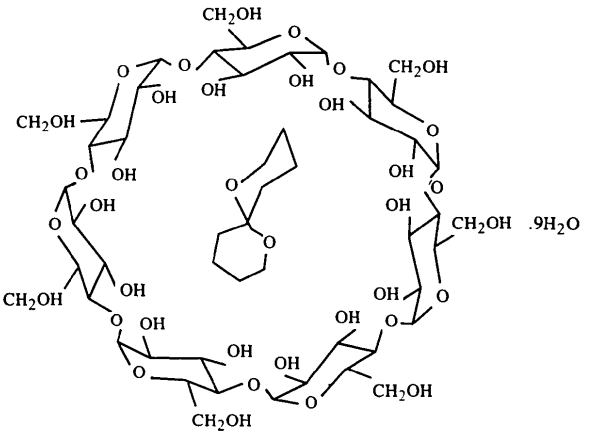
(*Received 9 October 1995; accepted 1 May 1996*)

Abstract

The complex β-cyclodextrin–1,7-dioxaspiro[5,5]undecane nonahydrate, $C_{42}H_{70}O_{35}.C_9H_{16}O_2.9H_2O$, belongs to the class of β-cyclodextrin dimeric-type complexes. The racemic guest molecule is present in a disordered position. Both enantiomers are located in two different regions inside the channel formed by the host dimers.

Comment

The cyclodextrin (CD) cyclic oligosaccharides are well known for their ability to form inclusion complexes with a variety of guest molecules (Szejtli, 1989). The present guest is the synthetic racemate of (*R*)- and (*S*)-1,7-dioxaspiro[5,5]undecane (spiroacetal) which constitutes the major component of the olive fruit fly (*Dacus oleae*) pheromone (Baker *et al.*, 1980; Mazomenos & Haniotakis, 1981,1985). It is a liquid too volatile at ambient temperature to be used by itself in agriculture. Previous experiments have shown that there is stabilization upon complexation but the release rate for the β-CD–spiroacetal crystalline complex is almost negligible in dry conditions; the commercial methylated-CD–spiroacetal complexes lead to higher rates, although still too low for practical applications (Mazomenos, Kondilis, Moustakali, Hadjoudis & Tsoucaris, 1989). The crystal-structure determination of the title complex, (I), was undertaken to obtain information on the slow-release process for this pheromone component. Of further interest is the enantiomeric discrimination of the guest molecule by cyclodextrins.



(I)

The title complex crystallizes in the non-centrosymmetric space group *C*2; isomorphous structures have been already studied (Hamilton, Sabesan & Steinrauf, 1981; Hamilton & Sabesan, 1982; Le Bas, 1985). Normal values are observed for the bond lengths and angles of β-CD host molecule. The torsion angles controlling the orientation of the C6—O6 bonds indicate a *gauche–gauche* conformation for all residues. However, two primary hydroxyl groups, O62 and O65, are disordered over two sites; a *trans–gauche* conformation is observed for the minor site O65B while O62 exhibits positional disorder (Table 2).

The macrocyclic ring has the usual truncated-cone shape with a pseudo-sevenfold axis; the glycosidic O4*n* atoms (n = 1–7) form a planar heptagon whose sides have an average length of 4.37 (1) Å. The O4*n* atoms deviate by 0.014 Å from their optimum plane. The O4*n* atoms furthest from the centre *I* are almost opposite positions to each other [O43···*I* 5.21 (1), O47···*I* 5.31 (1) Å]; the shortest distances are O45···*I* 4.88 (1) and O42···*I* 4.97 (1) Å. This gives the cavity a slightly elliptical shape and could be related to the shape of the guest molecule. The average intramolecular distances between secondary O atoms are O3*n*···O2(n+1) 2.82 Å and average angles are C3*n*—O3*n*···O2(n+1) 116° and C2(n+1)—O2(n+1)···O3*n* 118 Å; these values correspond to intramolecular hydrogen bonds (hydrogen bonds are defined on the basis of O···O distances shorter than 3.0 Å and C—O···O angles greater than 100°). This structure belongs to the class of β-CD dimers already described in detail (Le Bas, 1985; Le Bas & Rysanek, 1987). This class of structures is characterized by the packing of the β-CD dimers in quasi-invariant layers (Le Bas, 1985; Le Bas & Tsoucaris, 1994). Two β-CD molecules related by the twofold crystallographic *b* axis form a head-to-head dimer. Face-to-face secondary hydroxyl groups are bound by seven hydrogen bonds [average distance O3*n*···O3*n*^{i} 2.80 Å, average angle C3*n*—O3*n*···O3*n*^{i} 118°; symmetry code: (i) $-x, y, -z+1$]. The axis of the dimers, defined as