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Key indicators

Single-crystal X-ray study
 $T = 178\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.037
 wR factor = 0.095
Data-to-parameter ratio = 9.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(S)-4,16-Dihydroxymethyl-[2.2]para-
cyclophane bis-(1S)-camphanoate**The absolute configuration of the title compound, $\text{C}_{38}\text{H}_{44}\text{O}_8$, and in particular of its chiral cyclophane moiety, was determined by reference to the internal standard, (1S)-camphanoate. Molecules are associated into columns parallel to the b axis by a series of $\text{C}-\text{H}\cdots\text{O}$ interactions.

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Comment

[2.2]Paracyclophanes bearing two identical substituents in pseudo-*ortho* positions possess C_2 symmetry and are thus chiral. They are of interest as auxiliaries in asymmetric synthesis and have been the focus of increasing recent attention (Rossen *et al.*, 1997; literature summary in Rozenberg *et al.*, 2003). One such disubstituted cyclophane is 4,16-dihydroxymethyl-[2.2]paracyclophane, (1), which we prepared and resolved into its enantiomers some time ago (Hillmer, 1991). To determine the absolute configuration, we have now esterified the (+)-form with (–)-(1S)-camphanoyl chloride, (2), and determined the crystal structure of the diester, (3).

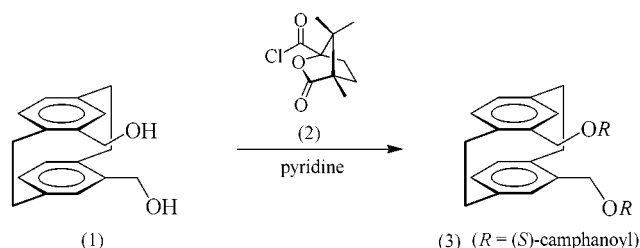


Fig. 1 shows the structure of (3); its absolute configuration in the cyclophane moiety is established as (*S*) by comparison with the known configuration of the camphanoyl residues. A stereochemical description of complex cyclophanes has been given by Pye & Rossen (1998).

Molecular dimensions are normal (*cf.* the structure of another paracyclophane camphanoyl derivative; Tochtermann *et al.*, 1987). The side chain conformations are defined by the torsion angles in Table 1; these are antiperiplanar in the regions C17–O17–C19 and C18–O18–C29. The molecules are connected by a series of $\text{C}-\text{H}\cdots\text{O}$ contacts that could be considered as weak hydrogen bonds. Table 2 shows all such contacts with $\text{H}\cdots\text{O} < 2.6\text{ \AA}$; all operate by translation parallel to the b axis, forming columns of molecules (Fig. 2).

Experimental

The dextrorotatory enantiomer of 4,16-dihydroxymethyl-[2.2]paracyclophane (1) was esterified with (–)-(1S)-camphanoyl chloride (2). The diastereomer (3) thus obtained was recrystallized from chloroform/pentane.

Crystal data

$C_{38}H_{44}O_8$
 $M_r = 628.73$
 Triclinic, $P1$
 $a = 6.740$ (2) Å
 $b = 11.295$ (3) Å
 $c = 11.647$ (3) Å
 $\alpha = 67.18$ (2)°
 $\beta = 81.59$ (2)°
 $\gamma = 85.49$ (2)°
 $V = 808.2$ (4) Å³

$Z = 1$
 $D_x = 1.292$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 49 reflections
 $\theta = 10$ –11.5°
 $\mu = 0.09$ mm⁻¹
 $T = 178$ (2) K
 Prism, colourless
 $0.70 \times 0.35 \times 0.20$ mm

Data collection

Nicolet R3 diffractometer
 ω scans
 Absorption correction: none
 4034 measured reflections
 4034 independent reflections
 3519 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 27.5^\circ$

$h = -8 \rightarrow 0$
 $k = -14 \rightarrow 14$
 $l = -15 \rightarrow 14$
 3 standard reflections
 every 147 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.04$
 4034 reflections
 421 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1873P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³

Table 1

Selected torsion angles (°).

C3—C4—C17—O17	90.7 (3)	C17—O17—C19—C20	-177.01 (19)
C4—C17—O17—C19	-169.00 (19)	O17—C19—C20—C25	106.1 (2)
C11—C16—C18—O18	-87.3 (3)	C18—O18—C29—C30	179.89 (19)
C16—C18—O18—C29	-166.57 (19)	O18—C29—C30—C35	112.0 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C22—H22A ⁱ ···O19 ⁱ	0.99	2.56	3.493 (4)	157
C32—H32A ⁱ ···O29 ⁱ	0.99	2.44	3.381 (3)	159
C17—H17A ⁱ ···O24 ⁱⁱ	0.99	2.58	3.442 (3)	146
C27—H27A ⁱ ···O24 ⁱⁱ	0.98	2.51	3.486 (3)	171
C9—H9A ⁱ ···O30 ⁱⁱ	0.99	2.59	3.556 (3)	167
C36—H36A ⁱ ···O34 ⁱⁱ	0.98	2.54	3.503 (4)	167

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$.

Methyl groups were included as idealized rigid groups (C—H 0.98 Å and H—C—H 109.5°), allowed to rotate but not tip. Other H atoms were included using a riding model with fixed C—H bond lengths (aromatic 0.95 Å and methylene 0.99 Å); $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}$ of the parent atom. The Flack parameter was indeterminate. The absolute configuration could be assigned on the basis of the known configuration of the camphanoate residues. Friedel pairs were present only for some reflections with $h = 0$ and were not merged.

Data collection: *P3* (Nicolet, 1987); cell refinement: *P3*; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

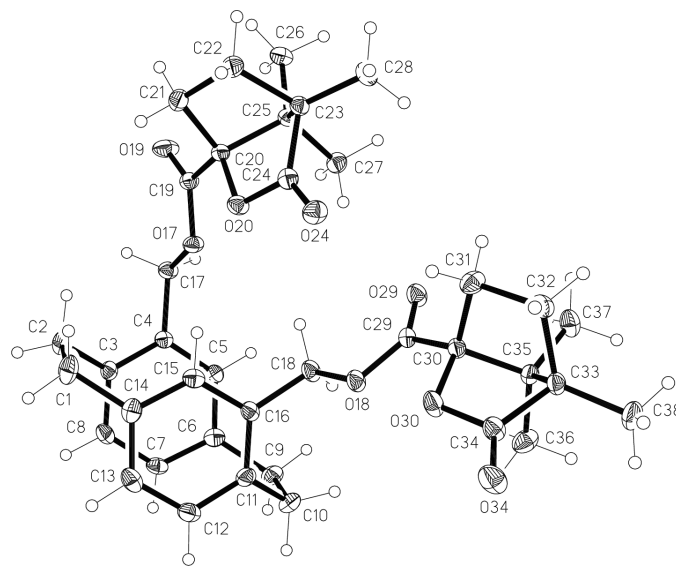


Figure 1

The molecule of compound (3) in the crystal. Ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

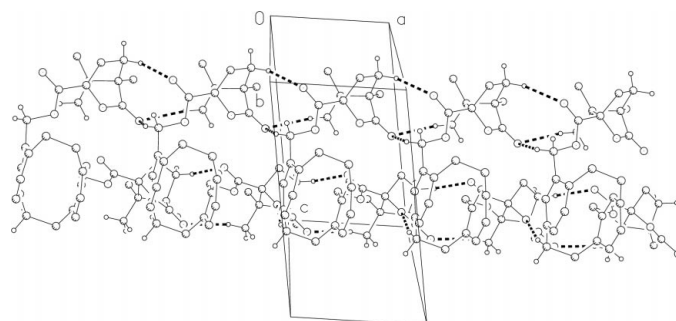


Figure 2

Packing of compound (3) in the crystal, viewed perpendicular to the *ac* plane. Only those H atoms involved in hydrogen bonding (dashed bonds), and their geminal neighbours are shown.

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