

## Two diastereomers of 9-(2,6-dichlorophenyl)-4a-hydroxy-3,3,6,6-tetramethyl-1,2,3,4,4a,5,6,7,8,9a-decahydroxanthene-1,8-dione in the same crystal

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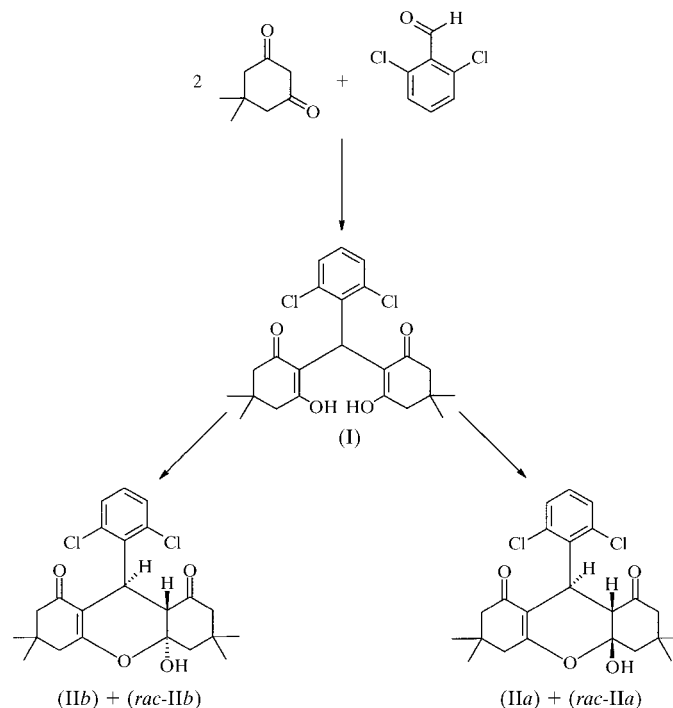
The reaction of dimedone with 2,6-dichlorobenzaldehyde leads to the title compound,  $C_{23}H_{26}Cl_2O_4$ . In principle, the reaction could yield eight different stereoisomers. We have found four of them in the same crystal as two enantiomeric pairs of diastereomers, which means that the asymmetric unit is built up of two different diastereomers. Two of the three chiral centres display the same configuration, while the third is different in the two molecules in the asymmetric unit. The packing of the molecules is stabilized by hydrogen bonds between the hydroxy group and the carbonyl group attached to the cyclohexene ring. The resulting chains are built up by both diastereomers occupying alternating positions.

### Comment

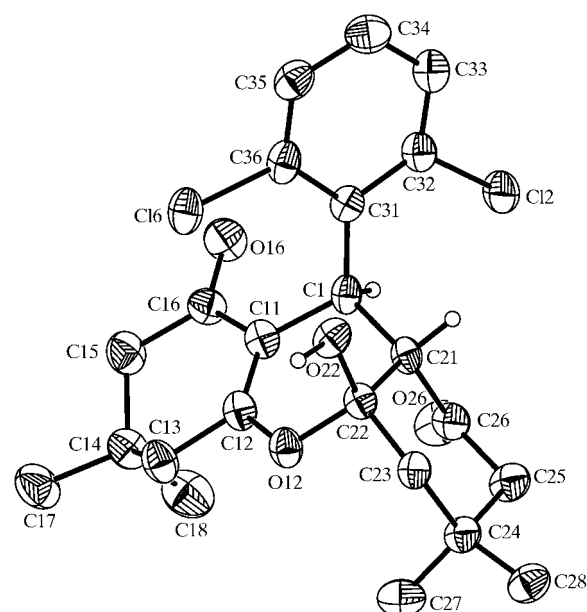
Some years ago, we accidentally encountered the twinned crystal structures of two similar compounds bearing the bis-dimedone moiety, *viz.* bis(2-hydroxy-4,4-dimethyl-6-oxo-1-cyclohexenyl)phenylmethane (Bolte *et al.*, 1997) and 2,2'-methylenebis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (Bolte & Scholtysik, 1997). Since these compounds can be prepared easily (Hünig *et al.*, 1979), we decided to synthesize various derivatives with the objective of finding out if these are also twinned (Bolte *et al.*, 2001). Unfortunately, the reaction described here did not lead to the desired compound, (I), but to the products (IIa) and (IIb) (see Scheme below). The interesting feature of this product, however, is that the reaction leads to four stereoisomers as two enantiomeric pairs of diastereomers.

The two diastereomers differ in the configuration of the chiral centre C22 and C22A (Figs. 1 and 2). This difference can also be described by the connection between the cyclohexane and central rings (Table 1). In (IIa), the two rings are *cis* and in (IIb) *trans* with respect to each other. The conformation of the

cyclohexane ring can be described as a chair. The other two rings display a sofa conformation with five atoms in a common plane and one atom [C14 0.632 (7), C21 0.603 (5), C14A 0.573 (6) and C21A 0.625 (5) Å] deviating from this plane.

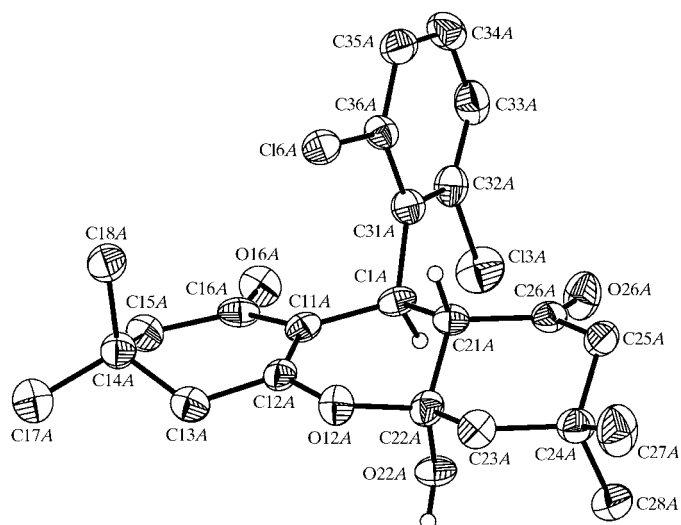


The crystal packing is stabilized by hydrogen bonds between the hydroxyl group and the carbonyl group attached to the cyclohexene ring. The resulting chains are built up by both diastereomers occupying alternating positions.



**Figure 1**

Perspective view of (IIa) with the atomic numbering; displacement ellipsoids are at the 50% probability level.



**Figure 2**  
Perspective view of (IIb) with the atomic numbering; displacement ellipsoids are at the 50% probability level.

## Experimental

Compound (II) was synthesized according to Cremlyn & Saunders (1993). However, the reaction did not terminate with the desired product, (I), but continued to a cyclization product.

### Crystal data

$C_{23}H_{26}Cl_2O_4$	$Z = 4$
$M_r = 437.34$	$D_x = 1.332 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.936 (3) \text{ \AA}$	Cell parameters from 6375 reflections
$b = 12.969 (4) \text{ \AA}$	$\theta = 0-25^\circ$
$c = 16.204 (5) \text{ \AA}$	$\mu = 0.324 \text{ mm}^{-1}$
$\alpha = 74.50 (1)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 90.16 (1)^\circ$	Block, colourless
$\gamma = 65.50 (1)^\circ$	$0.45 \times 0.40 \times 0.40 \text{ mm}$
$V = 2180.9 (11) \text{ \AA}^3$	

### Data collection

Siemens CCD three-circle diffractometer	$R_{\text{int}} = 0.079$
$\omega$ scans	$\theta_{\text{max}} = 27.48^\circ$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 15$
$T_{\text{min}} = 0.868$ , $T_{\text{max}} = 0.881$	$k = -16 \rightarrow 16$
27336 measured reflections	$l = -21 \rightarrow 21$
9912 independent reflections	307 standard reflections
5279 reflections with $I > 2\sigma(I)$	frequency: 1200 min
	intensity decay: none

### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.1543P)^2]$
$wR(F^2) = 0.241$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.916$	$(\Delta/\sigma)_{\text{max}} = 0.001$
9912 reflections	$\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$
525 parameters	$\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C12—O12	1.349 (5)	C12A—O12A	1.350 (5)
O12—C22	1.460 (5)	O12A—C22A	1.451 (5)
C16—O16	1.232 (5)	C16A—O16A	1.242 (5)
C22—O22	1.392 (4)	C22A—O22A	1.393 (5)
C26—O26	1.207 (5)	C26A—O26A	1.209 (5)
C32—Cl2	1.752 (4)	C32A—Cl3A	1.750 (4)
C36—Cl6	1.746 (4)	C36A—Cl6A	1.742 (4)
C12—O12—C22	118.3 (3)	C12A—O12A—C22A	115.7 (3)
C26—C21—C22—O22	170.7 (3)		
C26A—C21A—C22A—O22A	−73.3 (4)		

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O22A—H22A $\cdots$ O16 <sup>i</sup>	0.84	1.88	2.721 (4)	174
O22—H22 $\cdots$ O16A <sup>ii</sup>	0.84	1.96	2.799 (4)	176

Symmetry codes: (i)  $1 - x, 1 - y, 2 - z$ ; (ii)  $x, y - 1, z$ .

All H atoms were located by difference Fourier synthesis and were refined with fixed individual displacement parameters [ $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ ,  $1.2U_{\text{eq}}(\text{C})$  or  $1.2U_{\text{eq}}(\text{O})$ ] using a riding model with  $\text{O—H} = 0.84$ , aromatic  $\text{C—H} = 0.95$ , methyl  $\text{C—H} = 0.98$ , secondary  $\text{C—H} = 0.99$  or tertiary  $\text{C—H} = 1.00 \text{ \AA}$ . Additionally, the torsion angle about the  $\text{C—O}$  bonds of the hydroxyl groups was refined.

Cell refinement: SMART (Siemens, 1995); data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1447). Services for accessing these data are described at the back of the journal.

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