

drug seems to bind through two hydrogen bonds, one involving O18 of the drug and O2 of Thy3 of the base pair below (2.89 Å), and one involving N22 and O4 of Thy3 of the base pair below (2.99 Å). In the case of the C1295 complex ( $E = -2480$  kJ), which has no hydroxyl group at the 8 position, it is N19 of the drug that is involved in hydrogen bonding with O4 of Thy3 with a distance of 3.03 Å. The extra hydrogen bonding in the case of C1303 could be a possible reason for the better activity of C1303 and thus the lower energy of its complex with DNA.

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## Structure of Precursors of Higher-Carbon Sugars

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#### Abstract

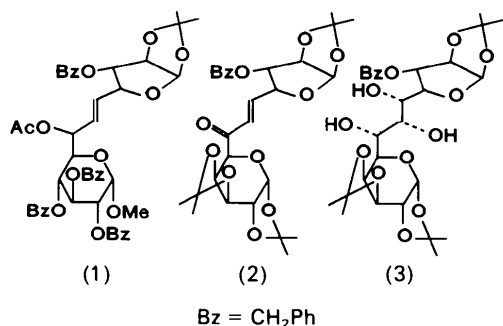
3-*O*-Benzyl-5-*C*-(1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galacto-heptopyranos-6-ulos-7-ylidene)-5-deoxy-1,2-*O*-isopropylidene- $\alpha$ -D-xylofuranose (2),  $C_{28}H_{36}O_{10}$ ,  $M_r = 532.59$ , monoclinic,  $P2_1$ ,  $a = 14.233$  (2),  $b = 9.271$  (1),  $c = 11.804$  (2) Å,  $\beta = 114.53$  (1)°,  $V = 1417.0$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.248$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.797$  mm<sup>-1</sup>,  $F(000) = 568$ , room temperature,  $R = 0.0472$  for 1960 reflections with  $F > 6\sigma(F)$ . 3-*O*-Benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-D-glycero- $\alpha$ -D-galacto-hexopyranos-6-yl)-1,2-*O*-isopropylidene-D-glycero- $\beta$ -L-ido-hexofuranose (3),  $C_{28}H_{40}O_{12}$ ,  $M_r = 568.62$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.912$  (1),  $b = 10.154$  (2),  $c = 32.704$  (5) Å,  $V = 2959.5$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.276$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.747$  mm<sup>-1</sup>,  $F(000) = 1216$ , room temperature,  $R = 0.0375$  for 2226 reflections with  $F > 6\sigma(F)$ . In (2) the results of crystal structure investigations and molecu-

lar mechanics calculations suggest some rotational flexibility of bonds linking the two sugar moieties with the three-carbon chain. In (3) a network of intra- and intermolecular O—H...O hydrogen bonds exists.

#### Introduction

This work is a continuation of our studies concerning the X-ray crystal structures of precursors of higher-carbon sugars.  $\alpha,\beta$ -Unsaturated ketones substituted at both ends of the allylic system with two different monosaccharide subunits are suitable starting materials for the preparation of higher sugars *via*, for example, osmylation of the double bond (Jarosz, 1988). The X-ray crystal structure analysis of unsaturated and saturated precursors of higher sugars provides valuable information about the conformations of these systems and makes correlation possible

between the conformations and the stereochemical outcome of the reaction of unsaturated derivatives with  $\text{OsO}_4$  (DeNinno, Danishefsky & Schulte, 1988). Previously we have solved the crystal structure of (1) (Ciunik, Paulsen, Luger & Jarosz, 1990). Here, we wish to report the results of the X-ray structure analysis of two compounds: with a three-carbon (2) and oxygenated (3) chain between two monosaccharide subunits, and to compare the orientation of these subunits with regard to the bridge between them in (1), (2) and (3) (see scheme below).



Both title compounds are precursors of dodecose. Compound (2) represents the higher-sugar enone system (Jarosz, 1987) and (3) the triol obtained by *cis*-hydroxylation of 3-*O*-benzyl-5-*C*-(1,2:3,4-di-*O*-isopropylidene-*D*-glycero- $\alpha$ -*D*-galacto-heptopyranos-7-ylidene)-5-deoxy-1,2-*O*-isopropylidene- $\alpha$ -*D*-xylofuranose (Jarosz, 1992).

### Experimental

Colourless crystals of both compounds were prepared and recrystallized from ethyl acetate/hexane by Jarosz (1992). The space groups were determined from oscillation and Weissenberg photographs ( $D_m$  not measured). All measurements were made on a Kuma KM-4 computer-controlled  $\kappa$ -axis diffractometer with graphite-monochromated  $\text{Cu K}\alpha$  radiation. The stability of each crystal was monitored by measurement of three standards every 50 reflections. The data were corrected for decay by appropriate scaling as well as for Lorentz and polarization effects. No absorption correction was applied. Experimental details are given in Table 1.

The structures were solved by direct methods with *SHELXS90* (Sheldrick, 1990) and refined by full-matrix least-squares methods using *SHELX76* (Sheldrick, 1976; expanded to 372 parameters) with anisotropic thermal parameters for non-H atoms. At intermediate stages in the refinement, difference maps showed all H atoms; in the subsequent rounds of calculations the H atoms were positioned on geometrical grounds ( $\text{C-H } 1.08 \text{ \AA}$ ) and included (as

Table 1. *Experimental data*

	(2)	(3)
Crystal size (mm)	$0.2 \times 0.2 \times 0.3$	$0.15 \times 0.2 \times 0.3$
No. of reflections	25	25
$\theta$ range ( $^\circ$ )	15–20	15–25
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan width, $\Delta\omega$ ( $^\circ$ )	$1.2 + 0.35\tan\theta$	$1.1 + 0.35\tan\theta$
Scan range, $2\theta$ ( $^\circ$ )	4–160	4–160
Scan speed (min $^{-1}$ )	0.4–6	0.9–9
Check reflections	320, 421, 414	230, 227, 208
Crystal decay (%)	3	4
Ranges of $hkl$	$-8 \rightarrow 16, 0 \rightarrow 11, 0 \rightarrow 15$	$0 \rightarrow 10, 0 \rightarrow 12, 0 \rightarrow 41$
No. of reflections		
Total	3103	3474
Unique	2947	3474
Observed, $F > 6\sigma(F)$	1960	2226
$R_m$ for equiv. reflections	0.011	-
Structure refinement (on $F^2$ 's)	Full matrix	Full matrix
No. of parameters	343	362
Weighting scheme ( $w$ )	$0.4735(\sigma^2 + 0.0006F^2)^{-1}$	$1.6208(\sigma^2 + 0.0007F^2)^{-1}$
Extinction parameter	0.015	0.004
$R$	0.0472	0.0375
$wR$	0.0533	0.0426
Max. shift to e.s.d. ( $\Delta/\sigma$ )	0.05	0.002
Min./max. final $\Delta\rho$ ( $\text{e \AA}^{-3}$ )	$-0.16/0.44$	$-0.16/0.21$

riding atoms) in the structure-factor calculations with individual isotropic thermal parameters; in the final cycles of refinement all H-atom parameters were fixed. Scattering factors were those incorporated in *SHELX76*. Final atom parameters are presented in Table 2.\*

### Discussion

The numbering scheme and overall conformation of the molecules in both crystals are shown in Fig. 1. Puckering parameters and the conformations of the rings are presented in Table 3. Bond distances, valence and selected dihedral angles are listed in Table 4.

The fused-ring system in the pyranoid part of the title compounds has almost the same geometry because of the presence of the two *O*-isopropylidene groups. The pyranoid rings have the  ${}^0S_2$  twist-boat conformation with a small deviation towards the  ${}^0H_5$  half-chair.

The fused-ring system in the furanoid part, using previously described nomenclature symbols (Krajewski, Gluziński, Urbańczyk-Lipkowska, Banaszek & Dobler, 1984) has the 'pure'  ${}^3T_4, {}^3E$  conformation in (2) and the  $E_4, E_4$  conformation in (3).

The absolute configuration of the chiral centres at C(6), C(7) and C(5') in (3) was determined to be  $6R, 7S, 5'S$  with reference to the known configurations of  $\alpha$ -*D*-galacto-pyranose and  $\alpha$ -*D*-xylofuranose.

\* Lists of structure factors, anisotropic temperature factors, H-atom parameters, interatomic distances and valence angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55275 (65 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE1000]

Table 2. Positional ( $\times 10^4$ ) and thermal parameters ( $\times 10^3$ ) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Compound (2)	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
O(1)	4756 (2)	5659 (5)	2687 (3)	70 (1)
O(2)	5398 (2)	4244 (5)	4381 (3)	63 (1)
O(3)	7718 (2)	3468 (5)	3983 (4)	78 (1)
O(4)	8530 (3)	5453 (5)	5042 (4)	78 (1)
O(5)	6443 (2)	6267 (-)	3059 (3)	59 (1)
O(6)	7755 (3)	8688 (5)	5479 (4)	81 (1)
O(1')	9294 (5)	9965 (6)	510 (7)	90 (2)
O(2')	8654 (3)	12181 (5)	520 (4)	85 (1)
O(3')	6514 (2)	10760 (5)	1091 (4)	73 (1)
O(4')	8413 (2)	9205 (5)	1658 (3)	63 (1)
C(1)	5705 (3)	5158 (6)	2733 (4)	58 (1)
C(2)	6002 (3)	3940 (6)	3721 (4)	57 (1)
C(3)	7121 (4)	3935 (6)	4622 (5)	68 (1)
C(4)	7567 (4)	5440 (6)	5124 (4)	62 (1)
C(5)	6876 (3)	6631 (6)	4352 (4)	55 (1)
C(6)	7502 (4)	8026 (6)	4506 (4)	58 (1)
C(7)	7780 (3)	8477 (6)	3496 (4)	57 (1)
C(12)	4457 (4)	4862 (6)	3497 (5)	65 (1)
C(13)	3689 (4)	3702 (7)	2803 (5)	70 (1)
C(14)	4052 (5)	5871 (8)	4201 (7)	97 (2)
C(34)	8730 (4)	4075 (7)	4646 (7)	86 (2)
C(35)	9335 (5)	3158 (10)	5784 (10)	146 (3)
C(36)	9211 (6)	4261 (11)	3757 (11)	134 (3)
C(1')	8304 (5)	9737 (7)	501 (6)	78 (1)
C(2')	7807 (4)	11220 (7)	316 (5)	71 (1)
C(3')	7505 (4)	11349 (6)	1395 (5)	64 (1)
C(4')	8289 (3)	10379 (6)	2374 (4)	58 (1)
C(5')	7980 (3)	9847 (6)	3358 (4)	60 (1)
C(12')	9427 (5)	11460 (8)	340 (7)	92 (2)
C(13')	10482 (5)	11981 (15)	1317 (9)	125 (3)
C(14')	9336 (8)	11701 (11)	-960 (9)	127 (3)
C(31')	5675 (4)	11728 (7)	570 (5)	70 (1)
C(32')	4751 (4)	11094 (6)	690 (4)	65 (1)
C(33')	4841 (4)	10101 (8)	1602 (7)	89 (2)
C(34')	3965 (6)	9573 (10)	1694 (9)	117 (3)
C(35')	2982 (5)	9999 (9)	830 (10)	112 (3)
C(36')	2913 (5)	11027 (11)	-49 (7)	104 (2)
C(37')	3756 (5)	11566 (9)	-118 (5)	85 (2)

Compound (3)	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
O(1)	9262 (4)	5041 (3)	1261 (1)	60 (1)
O(2)	11624 (4)	4433 (3)	1100 (1)	56 (1)
O(3)	12088 (4)	7099 (3)	395 (1)	64 (1)
O(4)	12779 (4)	8573 (3)	879 (1)	63 (1)
O(5)	9894 (3)	7219 (3)	1126 (1)	42 (1)
O(6)	12396 (3)	8819 (3)	1832 (1)	46 (1)
O(7)	9801 (3)	7706 (2)	2187 (1)	36 (0)
O(1')	5979 (3)	10974 (3)	2983 (1)	46 (1)
O(2')	4642 (3)	9639 (2)	2572 (1)	45 (1)
O(3')	6638 (3)	10571 (3)	1655 (1)	40 (1)
O(4')	7732 (3)	11331 (2)	2475 (1)	39 (1)
O(5')	10607 (3)	10337 (3)	2316 (1)	46 (1)
C(1)	9749 (5)	5946 (4)	961 (1)	48 (1)
C(2)	11204 (5)	5359 (4)	797 (1)	47 (1)
C(3)	12444 (5)	6336 (4)	743 (1)	48 (1)
C(4)	12608 (5)	7357 (4)	1091 (1)	43 (1)
C(5)	11234 (4)	7378 (3)	1367 (1)	35 (1)
C(6)	11053 (4)	8673 (3)	1600 (1)	32 (1)
C(7)	9668 (4)	8668 (3)	1874 (1)	30 (1)
C(12)	10267 (6)	3957 (4)	1280 (1)	56 (1)
C(13)	10573 (9)	3628 (6)	1722 (1)	85 (2)
C(14)	9638 (8)	2804 (5)	1040 (2)	80 (2)
C(34)	12680 (8)	8392 (5)	451 (1)	73 (2)
C(35)	11559 (14)	9357 (8)	276 (3)	163 (4)
C(36)	14200 (10)	8472 (9)	264 (2)	130 (3)
C(1')	6215 (4)	11488 (3)	2590 (1)	33 (1)
C(2')	5297 (4)	10585 (3)	2305 (1)	33 (1)
C(3')	6467 (4)	9913 (3)	2034 (1)	34 (1)
C(4')	7900 (4)	10057 (3)	2287 (1)	31 (1)
C(5')	9371 (4)	10036 (3)	2056 (1)	33 (1)
C(12')	4656 (5)	10182 (4)	2978 (1)	42 (1)
C(13')	3285 (5)	11016 (5)	3049 (1)	55 (1)
C(14')	4815 (7)	9072 (5)	3280 (1)	72 (1)
C(31')	5572 (6)	10144 (7)	1358 (1)	82 (2)
C(32')	5911 (6)	10821 (5)	961 (1)	59 (1)
C(33')	7066 (7)	10367 (6)	722 (1)	76 (1)
C(34')	7400 (9)	10925 (8)	348 (2)	96 (2)
C(35')	6575 (11)	11942 (9)	217 (2)	110 (3)
C(36')	5418 (11)	12467 (7)	449 (3)	112 (2)
C(37')	5078 (8)	11872 (6)	829 (2)	89 (2)

The geometry of the acetal centre of the pyranoid and furanoid rings in (2) and (3) is characteristic of carbohydrates showing the anomeric effect (Kirby, 1983).

The three-carbon chain and both sugar subunits in (2) have the planar *sp,ap,ap,sp* conformation going from O(5) to O(4') while in (1) this conformation is quite different (*sc,ac,ap,ac*). The propylene chain and carbohydrate rings in (3) have the *sc,ap,ap,ap* conformation.

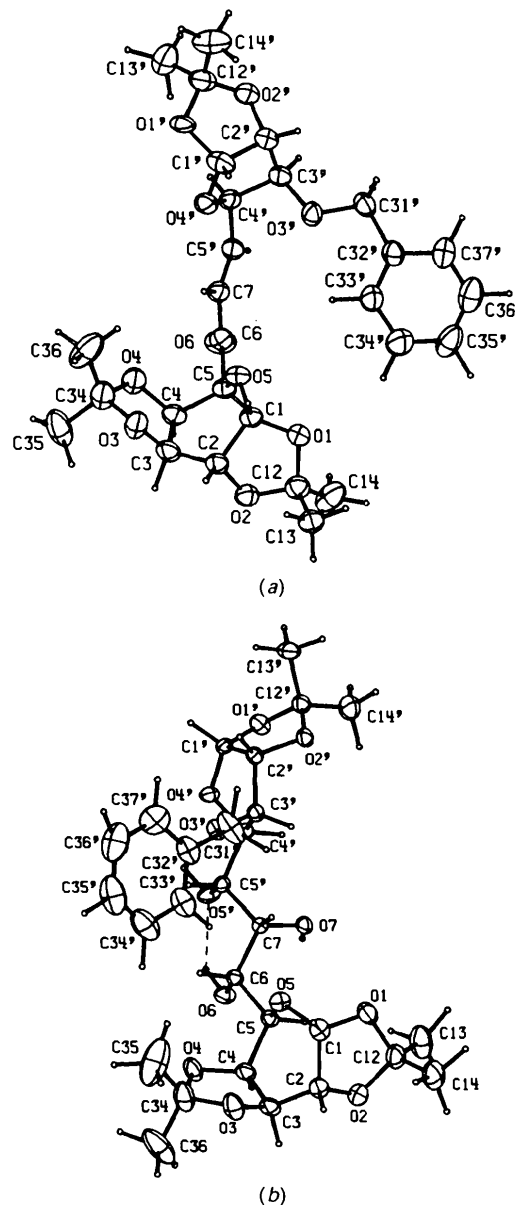


Fig. 1. ORTEP (Johnson, 1971) drawings of the molecular structures of (a) (2) and (b) (3) with crystallographic numbering scheme. The ellipsoids correspond to 30% probability contours of atomic displacement.

Table 3. Puckering parameters of rings

Cremer & Pople (1975) ring-puckering parameters were calculated using PUCK2 (Luger & Bülow, 1983).

Ring conformation	Ring
	Ring: $\overline{O(5)C(1)C(2)C(3)C(4)C(5)}$
	Compound (2) $Q = 0.645$ (5) Å, $\theta = 82.0$ (5)°, $\phi = 328.2$ (5)°
	Compound (3) $Q = 0.642$ (4) Å, $\theta = 80.2$ (4)°, $\phi = 328.9$ (4)°
	Ring: $\overline{O(4')C(1')C(2')C(3')C(4')}$
	Compound (2) $q_2 = 0.355$ (6) Å, $\varphi_2 = 310$ (1)°
	Compound (3) $q_2 = 0.365$ (3) Å, $\varphi_2 = 324.3$ (6)°
	Ring: $\overline{O(1)C(1)C(2)O(2)C(12)}$
	Compound (2) $q_2 = 0.316$ (5) Å, $\varphi_2 = 288.4$ (9)°
	Compound (3) $q_2 = 0.293$ (4) Å, $\varphi_2 = 289.7$ (8)°
	Ring: $\overline{O(3)C(3)C(4)O(4)C(34)}$
	Compound (2) $q_2 = 0.324$ (6) Å, $\varphi_2 = 174$ (1)°
	Compound (3) $q_2 = 0.240$ (5) Å, $\varphi_2 = 187$ (1)°
	Ring: $\overline{O(1')C(1')C(2')O(2')C(12')}$
	Compound (2) $q_2 = 0.203$ (7) Å, $\varphi_2 = 287$ (2)°
	Compound (3) $q_2 = 0.299$ (4) Å, $\varphi_2 = 323.0$ (7)°

The similar orientations of the C(6)—C(7) bonds with regard to the pyranoid rings in (1) and (3) are a result of the presence of the pyranoid ring in the *gluco* form in (1) and in the *galacto* form in (3) as well as the opposite chirality of the C(6) atom in these compounds (6*S* and 6*R*, respectively). Both of these cases suggest that in the *gluco*- and/or *galacto*-pyranosides and in the presence of the *sp*<sup>3</sup>-hybridized C(6) atom linked to an oxygen substituent the *sc* orientation of the O(5) and C(7) atoms is preferable.

Different orientations of the furanoid ring with respect to the allylic or propylene chain in (1), (2) and (3) [the O(4') and C(7) atoms have the *ac,sp* and *ap* conformations, respectively] suggest that this fragment of the title molecules is more flexible. To examine this more closely we carried out molecular mechanics calculations (*MM2* program; Allinger, 1987). In the first round of calculations we optimized the molecular geometry of (1), (2) and (3) obtained from crystal structure analysis. Next, using the *DRIVER* option, the potential-energy profiles for rotation, firstly, of the furanoid ring around the C(4')—C(5') bond and then of the pyranoid ring around the C(5)—C(6) bond were calculated. The results of these calculations, presented in Figs. 2(a)–2(f), only illustrate changes in potential energies for transitions between the 'vicinal' conformations, e.g. *sp* → ±*sc* or *ap* → ±*ac* etc. The calculated energy profiles suggest that in the case of (1) the furanoid end is indeed more flexible than the pyranoid one, and in the case of (2) and (3) the flexibility of both ends of the molecules is approximately similar but both ends of (2) are more flexible than in compound (3) (in the calculations the problem of hydrogen bonds was omitted). Flexibility of the furanoid ends in (1) and (2), and the pyranoid end in (2) arises from the presence of *sp*<sup>2</sup>-hybridized carbon atoms [C(5') and C(6)] vicinal respectively to these rings. As shown in Figs. 2(a), 2(c) and 2(d), the respective

Table 4. Bond lengths (Å), valence angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses

	(2)	(3)
O(1)—C(1)	1.408 (6)	1.413 (5)
O(1)—C(12)	1.407 (8)	1.420 (6)
O(2)—C(2)	1.408 (7)	1.416 (5)
O(2)—C(12)	1.432 (6)	1.429 (6)
O(3)—C(3)	1.418 (8)	1.413 (5)
O(3)—C(34)	1.438 (6)	1.427 (6)
O(4)—C(4)	1.414 (8)	1.424 (5)
O(4)—C(34)	1.429 (9)	1.415 (5)
O(5)—C(1)	1.405 (5)	1.407 (5)
O(5)—C(5)	1.429 (6)	1.440 (5)
O(6)—C(6)	1.217 (7)	1.425 (5)
O(7)—C(7)	—	1.420 (4)
O(1')—C(1')	1.421 (11)	1.403 (5)
O(1')—C(12')	1.424 (10)	1.427 (5)
O(2')—C(2')	1.437 (8)	1.423 (4)
O(2')—C(12')	1.377 (10)	1.438 (5)
O(3')—C(3')	1.413 (7)	1.416 (5)
O(3')—C(31')	1.414 (7)	1.426 (6)
O(4')—C(1')	1.399 (8)	1.412 (5)
O(4')—C(4')	1.433 (7)	1.440 (4)
O(5')—C(5')	—	1.425 (5)
C(1)—C(2)	1.551 (7)	1.525 (6)
C(2)—C(3)	1.504 (6)	1.496 (6)
C(3)—C(4)	1.546 (8)	1.546 (5)
C(4)—C(5)	1.508 (7)	1.521 (5)
C(5)—C(6)	1.538 (8)	1.528 (5)
C(6)—C(7)	1.464 (8)	1.525 (5)
C(7)—C(5')	1.326 (8)	1.534 (5)
C(12)—C(13)	1.510 (8)	1.508 (5)
C(12)—C(14)	1.515 (11)	1.517 (7)
C(34)—C(35)	1.519 (11)	1.512 (12)
C(34)—C(36)	1.482 (16)	1.488 (11)
C(1')—C(2')	1.520 (9)	1.542 (5)
C(2')—C(3')	1.509 (10)	1.529 (5)
C(3')—C(4')	1.523 (7)	1.529 (5)
C(4')—C(5')	1.487 (8)	1.513 (5)
C(12')—C(13')	1.543 (10)	1.505 (6)
C(12')—C(14')	1.502 (14)	1.505 (6)
C(31')—C(32')	1.500 (9)	1.500 (6)
C(32')—C(33')	1.381 (10)	1.372 (7)
C(32')—C(37')	1.409 (7)	1.370 (8)
C(33')—C(34')	1.385 (12)	1.380 (8)
C(34')—C(35')	1.403 (10)	1.338 (12)
C(35')—C(36')	1.382 (14)	1.387 (13)
C(36')—C(37')	1.333 (11)	1.415 (11)
C(1)—O(1)—C(12)	110.9 (4)	109.9 (3)
C(2)—O(2)—C(12)	106.2 (4)	106.8 (3)
C(3)—O(3)—C(34)	106.1 (4)	108.6 (3)
C(4)—O(4)—C(34)	110.2 (5)	111.2 (3)
C(1)—O(5)—C(5)	114.0 (3)	112.9 (3)
C(1')—O(1')—C(12')	109.5 (6)	108.8 (3)
C(2')—O(2')—C(12')	110.0 (5)	107.7 (3)
C(3')—O(3')—C(31')	116.0 (4)	112.4 (3)
C(1')—O(4')—C(4')	108.5 (4)	108.3 (3)
O(1)—C(1)—O(5)	111.4 (3)	111.1 (3)
O(1)—C(1)—C(2)	103.1 (4)	104.6 (3)
O(5)—C(1)—C(2)	112.8 (4)	114.6 (3)
O(2)—C(2)—C(1)	103.4 (4)	103.8 (3)
O(2)—C(2)—C(3)	108.7 (4)	109.1 (3)
C(1)—C(2)—C(3)	114.3 (4)	114.3 (3)
O(3)—C(3)—C(2)	108.5 (4)	107.0 (3)
O(3)—C(3)—C(4)	103.8 (4)	104.3 (3)
C(2)—C(3)—C(4)	114.5 (5)	115.3 (3)
O(4)—C(4)—C(3)	103.7 (4)	103.5 (3)
O(4)—C(4)—C(5)	111.1 (4)	111.3 (3)
C(3)—C(4)—C(5)	111.6 (4)	111.7 (3)
O(5)—C(5)—C(4)	110.9 (4)	110.0 (3)
O(5)—C(5)—C(6)	107.3 (4)	106.4 (3)
C(4)—C(5)—C(6)	110.1 (4)	113.1 (3)
O(6)—C(6)—C(5)	117.7 (5)	105.5 (3)
O(6)—C(6)—C(7)	123.4 (5)	111.6 (3)
C(5)—C(6)—C(7)	118.9 (4)	112.1 (3)
O(7)—C(7)—C(6)	—	111.0 (3)
O(7)—C(7)—C(5')	—	111.0 (3)
C(6)—C(7)—C(5')	121.2 (5)	111.4 (3)
O(1)—C(12)—O(2)	104.5 (4)	104.7 (3)
O(1)—C(12)—C(13)	111.1 (5)	109.1 (4)
O(1)—C(12)—C(14)	109.9 (5)	110.0 (4)
O(2)—C(12)—C(13)	111.0 (5)	108.5 (4)
O(2)—C(12)—C(14)	107.5 (5)	111.1 (4)
C(13)—C(12)—C(14)	112.5 (5)	113.1 (4)
O(3)—C(34)—O(4)	103.7 (5)	105.6 (4)
O(3)—C(34)—C(35)	109.5 (6)	107.7 (5)

Table 4 (cont.)

	(2)	(3)
O(3)—C(34)—C(36)	108.2 (6)	109.5 (5)
O(4)—C(34)—C(35)	109.1 (6)	109.4 (5)
O(4)—C(34)—C(36)	109.9 (6)	110.0 (5)
C(35)—C(34)—C(36)	115.6 (7)	114.2 (6)
O(1)—C(1)—O(4)	109.7 (6)	110.2 (3)
O(1)—C(1)—C(2)	105.5 (6)	104.7 (3)
O(4)—C(1)—C(2)	108.4 (5)	106.2 (3)
O(2)—C(2)—C(1)	103.2 (5)	104.4 (3)
O(2)—C(2)—C(3)	108.8 (5)	109.5 (3)
C(1)—C(2)—C(3)	103.3 (5)	104.7 (3)
O(3)—C(3)—C(2)	111.1 (5)	111.7 (3)
O(3)—C(3)—C(4)	107.7 (4)	109.8 (3)
C(2)—C(3)—C(4)	102.6 (4)	102.3 (3)
O(4)—C(4)—C(3)	103.4 (4)	103.3 (3)
O(4)—C(4)—C(5)	111.0 (4)	108.4 (3)
C(3)—C(4)—C(5)	115.3 (4)	116.9 (3)
O(5)—C(5)—C(7)	-	107.0 (3)
O(5)—C(5)—C(4)	-	111.6 (3)
C(7)—C(5)—C(4)	124.2 (5)	110.9 (3)
O(1)—C(12)—O(2)	106.8 (6)	103.5 (3)
O(1)—C(12)—C(13)	110.2 (7)	110.6 (3)
O(1)—C(12)—C(14)	109.2 (7)	109.7 (3)
O(2)—C(12)—C(13)	108.9 (7)	110.6 (3)
O(2)—C(12)—C(14)	110.5 (7)	108.6 (3)
C(13)—C(12)—C(14)	111.2 (7)	113.4 (4)
O(3)—C(31)—C(32)	109.0 (5)	108.4 (4)
C(31)—C(32)—C(33)	122.2 (5)	119.4 (4)
C(31)—C(32)—C(37)	119.3 (5)	121.4 (5)
C(33)—C(32)—C(37)	118.5 (6)	119.3 (5)
C(32)—C(33)—C(34)	120.1 (7)	121.9 (5)
C(33)—C(34)—C(35)	120.1 (8)	118.8 (7)
C(34)—C(35)—C(36)	118.6 (8)	122.0 (8)
C(35)—C(36)—C(37)	121.3 (8)	118.4 (8)
C(32)—C(37)—C(36)	121.3 (7)	119.6 (6)
O(1)—C(1)—O(5)—C(5)	76.1 (5)	77.1 (4)
O(2)—C(2)—C(1)—O(5)	101.0 (4)	104.3 (4)
O(3)—C(3)—C(2)—C(1)	-71.6 (5)	-73.9 (4)
O(4)—C(4)—C(5)—O(5)	76.8 (5)	76.5 (4)
O(5)—C(1)—C(2)—C(3)	-17.0 (6)	-14.4 (5)
O(5)—C(5)—C(4)—C(3)	-38.4 (6)	-38.6 (4)
O(5)—C(5)—C(6)—O(6)	164.9 (5)	-179.3 (3)
O(5)—C(5)—C(6)—C(7)	-16.2 (6)	59.2 (3)
O(6)—C(6)—C(7)—O(7)	-	-53.7 (4)
O(6)—C(6)—C(7)—C(5)	-25.3 (8)	70.5 (3)
O(7)—C(7)—C(5)—O(5)	-	59.6 (3)
O(1)—C(1)—C(2)—C(3)	-125.9 (6)	-115.5 (3)
O(2)—C(2)—C(1)—O(4)	104.9 (5)	116.2 (3)
O(3)—C(3)—C(4)—O(4)	80.1 (5)	82.7 (3)
O(3)—C(31)—C(32)—C(33)	25.2 (8)	78.5 (6)
O(4)—C(1)—C(2)—C(3)	-8.4 (6)	1.1 (3)
O(4)—C(4)—C(3)—C(2)	-37.2 (5)	-36.1 (3)
O(4)—C(4)—C(5)—O(5)	-	56.7 (3)
O(4)—C(4)—C(5)—C(7)	-4.2 (7)	175.9 (3)
O(5)—C(5)—C(7)—C(6)	-	64.6 (3)
C(1)—O(5)—C(5)—C(4)	70.2 (5)	69.8 (4)
C(1)—O(5)—C(5)—C(6)	-169.6 (4)	-167.4 (3)
C(1)—C(2)—C(3)—C(4)	43.7 (6)	41.6 (5)
C(2)—C(1)—O(5)—C(5)	39.3 (5)	41.1 (4)
C(2)—C(3)—C(4)—C(5)	-15.3 (6)	-14.3 (5)
C(5)—C(6)—C(7)—C(5)	155.9 (5)	-171.6 (3)
C(6)—C(7)—C(5)—C(4)	178.6 (5)	173.5 (3)
C(1)—O(4)—C(4)—C(3)	33.2 (5)	39.1 (3)
C(1)—O(4)—C(4)—C(5)	157.4 (4)	163.7 (3)
C(1)—C(2)—C(3)—C(4)	27.3 (6)	21.2 (3)
C(2)—C(1)—O(4)—C(4)	-15.7 (6)	-25.2 (3)
C(2)—C(3)—O(3)—C(31)	-90.7 (6)	-85.7 (4)
C(3)—O(3)—C(31)—C(32)	-161.7 (5)	-176.0 (3)

torsion angles observed in the crystal structures differ from the angles corresponding to the minimum on the energy profiles, whereas in the other cases (Figs. 2*b*, 2*e*, 2*f*) both values are similar and the rotation barriers are higher. The potential-energy profile was also calculated for the C(6)—C(7) bond in (1). Fig. 2(*g*) shows that the energy difference between the *ac* conformation observed in the crystal structure [the C(5)—C(6)—C(7)—C(5')] torsion angle

is 102.5 (5)<sup>o</sup>] and the *sc* conformation predicted from the molecular mechanics calculations is relatively small.

The rotation of the furanoid ring around the C(4')—C(5') bond in the allylic chain may be dependent on substituents at the C(6) atom and on some electronic effects between the allylic chain and the furanoid ring because the *sp* orientation of the O(4') and C(7) atoms is observed in the presence of the O(6) carbonyl atom in (2). The difference between the C(4')—C(5') bond lengths in (1) and (3) is less than 2 $\sigma$  but between these bonds in (2) and (3) [1.487 (8) and 1.513 (5) Å, respectively] it is greater. The O(6) carbonyl atom in (2) also affects the mutual orientation of the pyranoid ring and the three-carbon chain compared to (1). The O(5) and C(7) atoms have the *sp* orientation in contrast to the *sc* conformation observed in the case of the *sp*<sup>3</sup>-hybridized C(6) atom [(1) and (3)]. The C(5)—C(6) bond lengths in all the structures discussed are similar. A small shortening of the C(6)—C(7) 1.468 (8) Å bond length in (2) compared with (1) [1.491 (6) Å] is observed.

The *O*-benzyl groups in both of the structures presented correspond to two out of the four possible conformations of benzyl alcohol and its ethers (Ito & Hirota, 1981). These conformations are described by the C—C(32')—C(31')—O(3') torsion angle ( $\omega$ ) which is 25.2 (8) in (2) and 78.5 (6)<sup>o</sup> in (3). In (2) this conformation corresponds to the case of an H atom of the methylene group perpendicular to the aromatic ring [ $\omega(\text{C—C—C—O}) = 30^\circ$ ], in (3) this orientation is intermediate between a variant with an H atom coplanar with the aromatic ring ( $\omega = 60^\circ$ ) and with the O atom perpendicular to the aromatic ring ( $\omega = 90^\circ$ ; see also Ciunik, Paulsen, Luger & Jarosz, 1990). The C(3')—O(3')—C(31')—C(32') torsion angle is -161.7 (5) and -176.0 (3)<sup>o</sup> in (2) and (3), respectively. The phenyl group in (2) is oriented approximately skew to the furanoid and pyranoid rings and coplanar with the three-carbon chain. In (3) this group is oriented almost perpendicular to the furanoid and pyranoid rings and parallel (but not coplanar) to the three-carbon chain. Because of this (2) seems to be flat and (3) 'bristling'.

In (3) there are one intra- and two intermolecular hydrogen bonds. In the first case, two O atoms, O(6) and O(5'), are linked *via* the H(O6) atom which closes the six-membered ring of atoms from the triol moiety [the O...O and H...O distances are 2.725 (4) and 1.97 Å, respectively, and the O—H...O angle is 134<sup>o</sup>], and in the case of the intermolecular hydrogen bonds, the molecules lying parallel to the [010] direction are connected *via* the O(7)—H(O7)...O(4')(2 -  $x$ , - $\frac{1}{2}$  +  $y$ ,  $\frac{1}{2}$  -  $z$ ) [O...O, H...O = 2.829 (4) and 2.03 Å, respectively, and  $\angle \text{O—H...O} = 139^\circ$ ] and O(5')—H(O5')...O(7)(2 -  $x$ , - $\frac{1}{2}$  +  $y$ ,  $\frac{1}{2}$  -  $z$ ) [O...O, H...O =

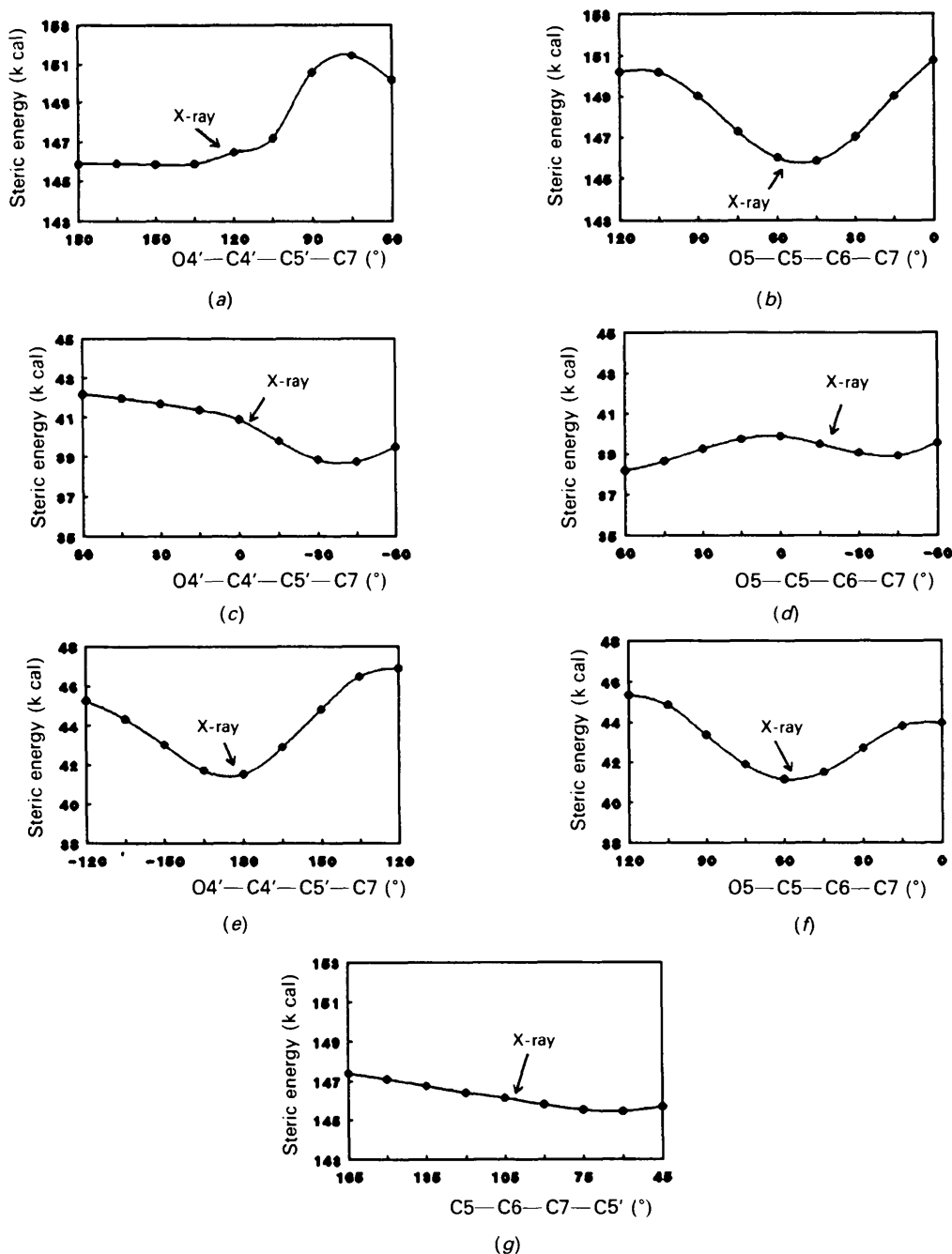


Fig. 2. Potential-energy profiles for the furanoid ring rotation around the C(4')—C(5') bond in (a) (1), (c) (2) and (e) (3), and for the pyranoid ring rotation around the C(5)—C(6) bond in (b) (1), (d) (2), (f) (3), and around the C(6)—C(7) bond in (g) (1). 1 kcal = 4.1868 kJ.

2.926 (4) and 1.99 Å, respectively, and  $\angle \text{O—H}\cdots\text{O} = 162^\circ$ ) network of weak bonds.

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## Crystal Structure Correlations in the Photochemistry of Dimethyl 9,10-Dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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### Abstract

The photochemistry of the title 9,10-dimethyldibenzobarrelene-11,12-diester (1) in solution and in the solid state exhibits unique differences as a function of reaction medium. In acetone the normal di- $\pi$ -methane reaction leads to a semibullvalene derivative, dimethyl 4b,8b-dimethyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate (2), while in acetonitrile an additional cyclooctatetraene (COT) photoproduct, dimethyl 5,11-dimethyldibenzo[*a,e*]cyclooctene-6,12-dicarboxylate (3), is obtained. In the solid state a new pentalene, dimethyl 5,10-dimethyl-5,10-dihydroindeno[2,1-*a*]indene-5,10-dicarboxylate (4), is formed as the major product. Crystal data for (1), (3) and (4):  $T = 294$  K,  $\text{Cu K}\alpha$ ,  $\lambda = 1.5418$  Å,  $\text{C}_{22}\text{H}_{20}\text{O}_4$ ,  $M_r = 348.40$ ; (1), triclinic,  $P\bar{1}$ ,  $a = 8.695$  (1),  $b = 13.633$  (1),  $c = 8.273$  (1) Å,  $\alpha = 98.51$  (1),  $\beta = 113.34$  (1),  $\gamma = 80.97$  (1)°,  $V = 885.2$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.307$  g cm<sup>-3</sup>,  $\mu = 6.9$  cm<sup>-1</sup>,  $F(000) = 368$ ,  $R = 0.057$  for 3046 reflections; (3), monoclinic,  $P2_1/n$ ,  $a = 9.124$  (2),  $b = 14.392$  (2),  $c = 14.328$  (1) Å,  $\beta = 94.30$  (1)°,  $V = 1876.1$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.233$  g cm<sup>-3</sup>,  $\mu = 6.5$  cm<sup>-1</sup>,  $F(000) = 736$ ,  $R = 0.048$  for 2289 reflections; (4), monoclinic,  $I2/a$ ,  $a = 19.020$  (6),  $b = 11.963$  (1),  $c = 17.083$  (4) Å,  $\beta = 105.15$  (1)°,  $V = 3752$  (2) Å<sup>3</sup>,  $Z = 8$  (two independent half-molecules per asymmetric unit),  $D_x = 1.233$  g cm<sup>-3</sup>,  $\mu = 6.5$  cm<sup>-1</sup>,  $F(000) = 1472$ ,  $R = 0.072$  for 1574 reflections. The structure of the solid-state photoproduct (4) provides an important clue in deriving a mechanism for its formation, involving a biradical intermediate with a pentalene-like skeleton.

This mechanism also accounts for the formation of COT (3), whose structure is not that expected on the basis of previous mechanistic studies.

### Introduction

Correlation of photochemical and crystal structural data for dibenzobarrelene-11,12-diester [with molecular skeletons similar to that of (1) in Fig. 1] has given detailed descriptions of the possible reaction pathways in the solid-state photolyses (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*). The reactions proceed *via* the di- $\pi$ -methane rearrangement (Zimmerman, 1980) to give dibenzosemibullvalene photoproducts [such as (2) in Fig. 1]. For unsymmetrically substituted dibenzobarrelenes, two regioisomeric semibullvalene photoproducts are obtained, and rationalization of the regio- and enantioselectivity has been derived from the photochemical-structural correlations; the most important factor has proved to be crystal packing (Garcia-Garibay *et al.*, 1990*a,b*).

The di- $\pi$ -methane rearrangement of the barrelenes is believed to proceed *via* the triplet excited state ( $T_1$ ) (the semibullvalene products are formed exclusively in the presence of a triplet sensitizer, such as acetone solvent) (Zimmerman, 1980). Direct irradiation also produces cyclooctatetraene (COT) derivatives, *via* a mechanism involving the singlet state ( $S_1$ ) (Fig. 1). These COTs have been well characterized for barrelene, benzobarrelene and naphthobarrelene derivatives, and support for the proposed intramolecular [2 + 2] cycloaddition mechanism (Fig. 1)