The crystal structure of DECAR is stabilized by two hydrogen bonds, N3—H3···O2 and N6—H6···O5, which connect the molecules along a and b, respectively (Table 2 and Fig. 2). No other short intermolecular distances were found.

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Structure of Galactitol Hexa(p-chlorobenzoate)

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Abstract. Galactitol hexa(p-chlorobenzoate) (I), $C_{48}H_{32}Cl_6O_{12}$, $M_r = 1013\cdot492$, monoclinic, $P2_1/n$, $a = 7\cdot863$ (2), $b = 23\cdot880$ (7), $c = 12\cdot345$ (5) Å, $\beta = 96\cdot97$ (3)°, $V = 2300$ (1) Å^3, $D_x = 1\cdot46$ g cm^{-3} for $Z = 2$, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu = 4\cdot4$ cm^{-1}, $F(000) = 1036$, $T = 295$ K, $R = 0\cdot047$ for 1267 unique observed reflections with $|F_o| > 3\sigma(|F_o|)$ and 298 refined parameters. The molecule, which is a *meso* form, has crystallographically induced $\bar{1}$ symmetry. It consists of a planar zigzag carbon chain with terminal p-chlorobenzoate groups in *gauche* conformation. The orientation of terminal groups is different from that observed in the parent molecule, galactitol.

Introduction. There has been considerable interest in the stereochemistry of acyclic polyol molecules and their derivatives. Solid state conformations have been extensively studied for many years by X-ray crystallography. Application of CD spectroscopy for studying conformations of p-chlorobenzoylated polyols in solution has stimulated our X-ray investigations of this group of polyol derivatives (Gawroński & Gawrońska, 1990). We hope to be able to establish some rules which govern the stereo- structure of p-chlorobenzoylated polyols. The first in a series is the hexa(p-chlorobenzoate) derivative of galactitol. Although this particular compound, being a *meso* form, cannot be used in chiroptical studies, it still serves as a model for deriving contributions to the Cotton effects from the p-chlorobenzoate chromophores in various positions and orientations.

(I)

Experimental. Single crystals suitable for X-ray study were grown by slow evaporation from dioxane solutions; crystal *ca* $0\cdot3 \times 0\cdot4 \times 0\cdot5$ mm was selected for data collection. Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Accurate cell constants were from setting angles of 15 reflections; ω–2θ scans, variable scan speed. Two standard reflections remeasured every 100 reflections showed no change in intensity greater than $3\cdot6\sigma(I)$. 3128 reflections measured, $\theta \le 22\cdot5°$, only 1267 observed $[|F_o| > 3\sigma(|F_o|)]$ due to poor scattering

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$), *with e.s.d.'s in parentheses*

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

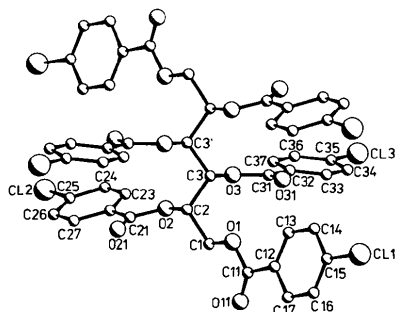|	x	y	z	U_{eq}
Cl(1)	−0·5643 (3)	−0·1437 (1)	−0·6815 (2)	0·116 (1)
Cl(2)	0·0249 (4)	0·1988 (1)	0·4906 (2)	0·132 (2)
Cl(3)	0·1047 (4)	−0·2702 (1)	0·2276 (2)	0·149 (2)
O(1)	−0·2898 (6)	0·0028 (2)	−0·2372 (4)	0·074 (3)
O(2)	−0·2472 (6)	0·0661 (2)	0·0313 (3)	0·064 (2)
O(3)	−0·3216 (5)	−0·0483 (2)	0·0149 (3)	0·056 (2)
O(11)	−0·0751 (7)	0·0228 (3)	−0·3330 (4)	0·095 (3)
O(21)	−0·3101 (8)	0·1536 (2)	−0·0277 (4)	0·095 (3)
O(31)	−0·3840 (7)	−0·1087 (2)	−0·1242 (4)	0·085 (2)
C(1)	−0·1990 (9)	0·0305 (3)	−0·1430 (5)	0·069 (3)
C(2)	−0·3342 (9)	0·0437 (3)	−0·0696 (5)	0·060 (3)
C(3)	−0·4362 (8)	−0·0074 (3)	−0·0400 (4)	0·051 (3)
C(11)	−0·209 (1)	−0·0000 (3)	−0·3257 (6)	0·069 (4)
C(12)	−0·306 (1)	−0·0352 (3)	−0·4131 (6)	0·062 (4)
C(13)	−0·436 (1)	−0·0708 (3)	−0·3929 (6)	0·069 (4)
C(14)	−0·515 (1)	−0·1040 (3)	−0·4742 (6)	0·083 (4)
C(15)	−0·464 (1)	−0·1017 (3)	−0·5768 (6)	0·077 (4)
C(16)	−0·336 (1)	−0·0667 (4)	−0·5995 (6)	0·088 (4)
C(17)	−0·253 (1)	−0·0331 (3)	−0·5179 (6)	0·083 (4)
C(21)	−0·253 (1)	0·1229 (3)	0·0437 (6)	0·068 (4)
C(22)	−0·1806 (9)	0·1401 (3)	0·1550 (5)	0·058 (3)
C(23)	−0·1329 (9)	0·1016 (3)	0·2360 (6)	0·069 (4)
C(24)	−0·069 (1)	0·1204 (4)	0·3411 (6)	0·082 (4)
C(25)	−0·052 (1)	0·1763 (4)	0·3623 (6)	0·082 (4)
C(26)	−0·100 (1)	0·2153 (3)	0·2829 (7)	0·087 (4)
C(27)	−0·167 (1)	0·1968 (3)	0·1778 (6)	0·082 (4)
C(31)	−0·3138 (9)	−0·0988 (3)	−0·0351 (6)	0·060 (4)
C(32)	−0·2040 (8)	−0·1391 (3)	0·0334 (5)	0·055 (3)
C(33)	−0·168 (1)	−0·1899 (3)	−0·0126 (6)	0·080 (4)
C(34)	−0·071 (1)	−0·2299 (3)	0·0463 (7)	0·086 (4)
C(35)	−0·014 (1)	−0·2192 (3)	0·1530 (7)	0·081 (4)
C(36)	−0·045 (1)	−0·1690 (3)	0·2016 (6)	0·076 (4)
C(37)	−0·1410 (9)	−0·1288 (3)	0·1412 (5)	0·060 (4)

Fig. 1. Perspective view of the molecule of galactitol hexa(*p*-chlorobenzoate) with atom-numbering scheme.

Table 2. *Bond lengths* ($\mathring{A}$), *angles* (°) *and selected torsion angles* (°), *with e.s.d.'s in parentheses*

Cl(1)—C(15)	1·747 (8)	C(13)—C(14)	1·368 (11)
Cl(2)—C(25)	1·712 (8)	C(14)—C(15)	1·375 (11)
Cl(3)—C(35)	1·730 (8)	C(15)—C(16)	1·363 (12)
O(1)—C(1)	1·448 (8)	C(16)—C(17)	1·387 (12)
O(1)—C(11)	1·330 (9)	C(21)—C(22)	1·480 (10)
O(2)—C(2)	1·449 (8)	C(22)—C(23)	1·377 (10)
O(2)—C(21)	1·366 (9)	C(22)—C(27)	1·384 (11)
O(3)—C(3)	1·441 (7)	C(23)—C(24)	1·407 (10)
O(3)—C(31)	1·359 (8)	C(24)—C(25)	1·364 (12)
O(11)—C(11)	1·198 (10)	C(25)—C(26)	1·371 (12)
O(21)—C(21)	1·192 (9)	C(26)—C(27)	1·411 (12)
O(31)—C(31)	1·193 (9)	C(31)—C(32)	1·486 (10)
C(1)—C(2)	1·511 (10)	C(32)—C(33)	1·383 (10)
C(2)—C(3)	1·529 (9)	C(32)—C(37)	1·385 (9)
C(3)—C(3')	1·532 (8)	C(33)—C(34)	1·374 (11)
C(11)—C(12)	1·501 (11)	C(34)—C(35)	1·363 (12)
C(12)—C(13)	1·375 (11)	C(35)—C(36)	1·375 (11)
C(12)—C(17)	1·407 (11)	C(36)—C(37)	1·382 (10)
C(1)—O(1)—C(11)	116·4 (5)	C(21)—C(22)—C(27)	118·1 (6)
C(2)—O(2)—C(21)	116·4 (5)	C(21)—C(22)—C(23)	122·0 (6)
C(3)—O(3)—C(31)	116·6 (5)	C(23)—C(22)—C(27)	119·9 (6)
O(1)—C(1)—C(2)	105·2 (5)	C(22)—C(23)—C(24)	119·5 (6)
O(2)—C(2)—C(1)	107·4 (5)	C(23)—C(24)—C(25)	120·3 (7)
C(1)—C(2)—C(3)	113·8 (5)	Cl(2)—C(25)—C(24)	120·0 (6)
O(2)—C(2)—C(3)	107·2 (5)	C(24)—C(25)—C(26)	121·0 (7)
O(3)—C(3)—C(2)	109·7 (5)	Cl(2)—C(25)—C(26)	118·9 (6)
O(1)—C(11)—O(11)	123·4 (6)	C(25)—C(26)—C(27)	119·0 (7)
O(11)—C(11)—C(12)	125·1 (6)	C(22)—C(27)—C(26)	120·3 (6)
O(1)—C(11)—C(12)	111·5 (6)	O(3)—C(31)—O(31)	123·6 (5)
C(11)—C(12)—C(17)	117·4 (6)	O(31)—C(31)—C(32)	124·6 (5)
C(11)—C(12)—C(13)	122·7 (6)	O(3)—C(31)—C(32)	111·8 (5)
C(13)—C(12)—C(17)	119·9 (6)	C(31)—C(32)—C(37)	123·2 (5)
C(12)—C(13)—C(14)	120·4 (6)	C(31)—C(32)—C(33)	117·9 (6)
C(13)—C(14)—C(15)	119·7 (7)	C(33)—C(32)—C(37)	118·9 (6)
Cl(1)—C(15)—C(14)	120·2 (5)	C(32)—C(33)—C(34)	121·4 (6)
C(14)—C(15)—C(16)	121·3 (7)	C(33)—C(34)—C(35)	118·5 (7)
Cl(1)—C(15)—C(16)	118·6 (6)	Cl(3)—C(35)—C(34)	118·4 (6)
C(15)—C(16)—C(17)	120·0 (7)	C(34)—C(35)—C(36)	122·0 (7)
C(12)—C(17)—C(16)	118·8 (6)	Cl(3)—C(35)—C(36)	119·6 (5)
O(2)—C(21)—O(21)	122·9 (6)	C(35)—C(36)—C(37)	119·0 (6)
O(21)—C(21)—C(22)	125·7 (6)	C(32)—C(37)—C(36)	120·2 (6)
O(2)—C(21)—C(22)	111·4 (6)		
O(1)—C(1)—C(2)—O(2)	174·0 (5)	C(1)—C(2)—C(3)—C(3')	176·5 (6)
O(1)—C(1)—C(2)—C(3)	55·5 (7)	O(2)—C(2)—C(3)—C(3')	57·8 (6)
O(2)—C(2)—C(3)—O(3)	−59·4 (7)	O(3)—C(3)—C(3')—C(2')	−60·5 (6)
C(1)—C(2)—C(3)—O(3)	59·3 (7)		

for 1267 reflections and 298 parameters [$w^{-1} = \sigma^2(F)$ $+ 0·001F^2$]. Maximum $\Delta/\sigma = 0·04$; $-0·2 \le \Delta\rho \le$ $+ 0·2 \, e \, \mathring{A}^{-3}$. Atomic scattering factors for C, H, O and Cl were those stored in *SHELX*76. *PLUTO* (Motherwell & Clegg, 1978) was used for diagrams.

Discussion. A perspective view of the molecule with atom-numbering scheme is shown in Fig. 1. Positional coordinates for non-H atoms are given in Table 1. The bond lengths and angles and selected torsion angles involving non-H atoms are provided in Table 2.*

The molecule is a *meso* form and the potential symmetry centre is utilized in the crystal structure. As in the crystal structures of some other hexitols (Berman & Rosenstein, 1968; Berman, Jeffrey &

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52345 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

power of the crystal, index range h 0/8, k 0/25, l −13/13. The background and integrated intensity for each reflection were evaluated from a profile analysis according to Lehmann & Larsen (1974) using the *PRARA* program (Jaskólski, 1982). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); non-H atoms refined anisotropically. Positions of H atoms calculated, assigned isotropic thermal parameter $U = 0·08 \, \mathring{A}^2$, allowed to ride on parent C atoms. Refinement on F_o by full-matrix least squares (*SHELX*76; Sheldrick, 1976); $R = 0·047$; $wR = 0·057$

Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1969) the C—C bonds have the staggered conformation leading to a planar zigzag chain of C atoms. The terminal O atoms of the p-chlorobenzoate groups do not form an extension to the planar carbon chain (*anti* conformation) but rather adopt the *gauche* conformation [defined by the O(1)—C(1)—C(2)—C(3) torsion angle]. The conformation of the O—C—C—O fragments of the main chain is *ap* [C(1)—C(2)], *Msc* [C(2)—C(3)] and *ap* [C(3)—C(3′)] as follows from the pertinent O—C—C—O torsion angles (Table 2) (for nomenclature, see Klyne & Prelog, 1960).

The investigated compound differs in structure from the parent compound, galactitol, which has only approximate $\bar{1}$ symmetry in the crystal and crystallizes in the centrosymmetric space group as a racemate of unsymmetrical conformers. In addition, in the crystal structure of galactitol the planar carbon chain is extended by two terminal O atoms and so the conformation of the terminal groups is *anti*, while the *gauche* conformation is favoured in the present case.

Angles between ring 1 (C12–C17) and rings 2 (C22–C27), and 3(C32–C37) are 55·9 (2) and 77·9 (2)°, respectively, whereas the angle between rings 2 and 3 is 23·5 (3)°. The three rings form angles of 46·7 (5), 69·9 (3) and 77·9 (3)° with the plane of the planar carbon chain and angles of 14·0 (2), 5·8 (3) and 8·1 (3)° with the respective carboxylic moieties.

The geometrical parameters of the aromatic rings, which are planar within experimental error, are normal, the mean C—C distances and the mean C—C—C angles being 1·381 (14) Å and 120·0 (10)°, respectively. As in other benzoic acid derivatives the

exocyclic angles have different values, the angle smaller than 120° being on the side of the carbonyl O atom. Significant narrowing of the angles opposite to the C=O bonds is also systematically observed.

The three C_{sp^3}—C_{sp^3} distances have a mean value of 1·524 (9) Å. Packing of the molecules in the crystal is determined primarily by normal van der Waals contacts.

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Structure of Pyridinium Dihydrogenphosphate Phosphoric Acid

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Abstract. $C_5H_6N^+.H_2PO_4^-.H_3PO_4$, $M_r = 275\cdot1$, triclinic, $P\bar{1}$, $a = 7\cdot708$ (5), $b = 8\cdot176$ (5), $c = 9\cdot566$ (5) Å, $\alpha = 115\cdot39$ (5), $\beta = 98\cdot47$ (5), $\gamma = 90\cdot80$ (5)°, $V = 536\cdot7$ (9) Å³, $Z = 2$, $D_x = 1\cdot702$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 4\cdot405$ cm⁻¹, $F(000) = 284$, $T = 295$ K, final $R = 0\cdot034$ for 3404 unique reflexions. The aggregates of $H_2PO_4^-$ anions and H_3PO_4 molecules bridged by hydrogen bonds form a three-dimensional anionic subnetwork inside which the pyridinium ions are anchored. The existence of an $(H_5P_2O_8)_n^{n-}$ polymeric anion is supported by structural considerations.