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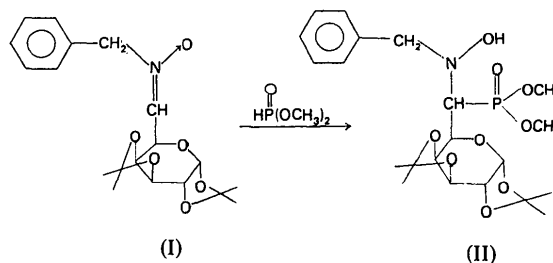# Structural Chirality of an α-Aminophosphonic Acid Derivative

BY MICHAEL DYRBUSCH AND ERNST EGERT

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Abstract. (6R)-6-(N-Benzyl-N-hydroxyamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-ylphosphonic acid dimethyl ester, $C_{21}H_{32}NO_9P$, $M_r = 473.5$, orthorhombic, $P2_12_12_1$, $a = 9.552$ (1), $b = 14.395$ (1), $c = 17.992$ (1) Å, $V = 2473.9$ (3) Å^3, $Z = 4$, $D_x = 1.271$ Mg m^{-3}, Mo Kα, $\lambda = 0.7107$ Å, $\mu = 0.15$ mm^{-1}, $F(000) = 1008$, room temperature (295 K), $R = 0.049$ for 3584 observed reflections. η refinement was employed to determine the absolute configuration of the molecule. All bond lengths and angles are as expected. The N atom is *trans* to the galactopyranose ring O atom. The molecules pack together with a hydrogen bond between the hydroxyl and phosphate P=O groups.

Introduction. α-Aminophosphonic acids are of great interest because of their potential biological activity (Horiguchi & Kandatsu, 1959; Kittredge & Roberts, 1969). An important reaction step in the course of their enantioselective synthesis (Hoppe & Schöllkopf, 1985) is the stereospecific addition of dimethyl phosphonate to the α-D-galactose derivative (I). The absolute configuration of the reaction product (II) was confirmed by X-ray structural analysis using the anomalous scattering of the phosphorus atom.

(I)   (II)

Experimental. Crystals from ethyl acetate/hexane, colourless rectangular prisms, dimensions $0.8 \times 0.2 \times 0.2$ mm; Stoe four-circle diffractometer; lattice parameters measured by centring 60 reflections with $20 < 2\theta < 25°$; data collection with profile-fitting method (Clegg, 1981); $2\theta_{max} = 50°$ ($-11 \leq h \leq 11$, $k \leq 17$, $l \leq 21$); 4286 unique reflexions including Friedel opposites (measured at -2θ, $\omega-2\theta$, χ, φ in order to reduce systematic errors); 3584 with $|F| > 3\sigma(F)$ treated as observed; empirical absorption correction [$R_{int} = 0.036$ for 400 azimuthal scans, transmission factors: 0.85 (max.), 0.75 (min.)]; structure solved by Patterson and Fourier techniques; $R = 0.113$ after isotropic refinement with unit weights; all hydrogen

$C_{21}H_{32}NO_9P$

Table 1. *Atomic fractional coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *with e.s.d.'s in parentheses*

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	3974 (3)	3249 (2)	7619 (2)	54 (1)
C(2)	2462 (4)	3130 (2)	7350 (1)	53 (1)
C(3)	2067 (3)	3671 (2)	6656 (2)	47 (1)
C(4)	3256 (3)	3751 (2)	6079 (1)	42 (1)
C(5)	4628 (3)	3357 (2)	6349 (1)	39 (1)
O(5)	4869 (2)	3648 (1)	7096 (1)	45 (1)
C(6)	5877 (3)	3677 (2)	5888 (1)	39 (1)
O(11)	4395 (3)	2348 (1)	7806 (1)	72 (1)
O(21)	2363 (2)	2171 (1)	7171 (1)	58 (1)
C(22)	3314 (4)	1687 (2)	7645 (2)	64 (1)
C(23)	3919 (5)	883 (3)	7227 (2)	80 (2)
C(24)	2575 (4)	1404 (3)	8363 (2)	99 (2)
O(31)	1802 (2)	4602 (1)	6873 (1)	59 (1)
O(41)	3402 (2)	4731 (1)	5975 (1)	60 (1)
C(42)	2200 (3)	5172 (2)	6267 (2)	54 (1)
C(43)	1056 (3)	5211 (2)	5687 (2)	70 (1)
C(44)	2609 (5)	6115 (2)	6551 (2)	87 (1)
N(61)	5620 (2)	3458 (1)	5110 (1)	42 (1)
O(61)	5863 (2)	2464 (1)	5042 (1)	52 (1)
C(62)	6542 (3)	3904 (2)	4566 (2)	56 (1)
C(63)	6399 (4)	4949 (2)	4572 (2)	57 (1)
C(64)	5099 (4)	5370 (2)	4547 (2)	74 (1)
C(65)	4962 (6)	6327 (3)	4530 (2)	104 (2)
C(66)	6144 (7)	6861 (3)	4560 (2)	121 (2)
C(67)	7451 (6)	6452 (3)	4579 (2)	116 (2)
C(68)	7566 (4)	5500 (2)	4594 (2)	83 (1)
P(61')	7549 (1)	3234 (1)	6257 (1)	49 (1)
O(61')	8676 (3)	3228 (1)	5707 (1)	64 (1)
O(62')	7279 (2)	2268 (1)	6630 (1)	59 (1)
O(63')	7696 (5)	1406 (2)	6303 (2)	90 (1)
O(64')	7842 (2)	3899 (1)	6924 (1)	67 (1)
C(65')	8433 (5)	3666 (3)	7603 (2)	104 (2)

atoms located by difference synthesis and refined with fixed individual temperature factors [$U(\mathrm{H}) = 1\cdot2 \times U_{eq}(\mathrm{C,O})$, riding model with C–H 0·96 Å employed for H atoms on C(63') and C(65')]; refinement (based on F) of 367 parameters with *SHELXTL* (Sheldrick, 1983) converged at $R = 0\cdot049$, $wR = 0\cdot048$, $w = [\sigma^2(F) + 0\cdot0005F^2]^{-1}$, $(\Delta/\sigma)_{max} = 0\cdot05$ in last cycle, $-0\cdot3 < \Delta\rho < 0\cdot3$ e Å^{-3} in final difference map. The absolute configuration was determined by η refinement (Rogers, 1981) starting from both configurations [$\eta = 1\cdot1$ (2) for the correct structure]; scattering factors from *International Tables for X-ray Crystallography* (1974); atomic parameters are listed in Table 1.*

Discussion. The structure determination shows that the configuration of C(6) is R (Fig. 1). All bond lengths and angles are as expected (Table 2). The chain from O(61) to C(63) shows a *trans* arrangement with the pyramidal N(61) *trans* to the ring atom O(5). The intermolecular

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·533 (5)	C(1)–O(5)	1·396 (3)
C(1)–O(11)	1·400 (4)	C(2)–C(3)	1·519 (4)
C(2)–O(21)	1·421 (3)	C(3)–C(4)	1·544 (4)
C(3)–O(31)	1·417 (3)	C(4)–C(5)	1·508 (4)
C(4)–O(41)	1·429 (3)	C(5)–O(5)	1·426 (3)
C(5)–C(6)	1·525 (4)	C(6)–N(61)	1·456 (3)
C(6)–P(61')	1·843 (3)	O(11)–C(22)	1·434 (4)
O(21)–C(22)	1·428 (4)	C(22)–C(23)	1·498 (5)
C(22)–C(24)	1·526 (5)	O(31)–C(42)	1·416 (3)
O(41)–C(42)	1·414 (3)	C(42)–C(43)	1·512 (4)
C(42)–C(44)	1·502 (4)	N(61)–O(61)	1·454 (2)
N(61)–C(62)	1·465 (4)	C(62)–C(63)	1·512 (4)
C(63)–C(64)	1·382 (5)	C(63)–C(68)	1·368 (5)
C(64)–C(65)	1·385 (5)	C(65)–C(66)	1·367 (8)
C(66)–C(67)	1·381 (8)	C(67)–C(68)	1·376 (5)
P(61')–O(61')	1·463 (2)	P(61')–O(62')	1·565 (2)
P(61')–O(64')	1·561 (2)	O(62')–C(63')	1·430 (4)
O(64')–C(65')	1·386 (4)		

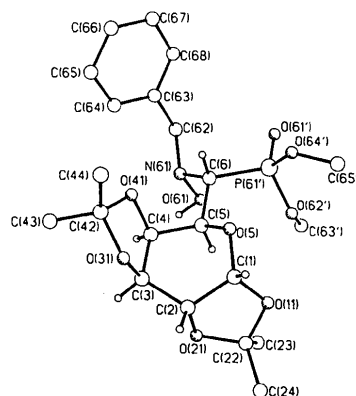|			
C(2)–C(1)–O(5)	114·2 (2)	C(2)–C(1)–O(11)	104·0 (2)
O(5)–C(1)–O(11)	111·6 (2)	C(1)–C(2)–C(3)	115·8 (2)
C(1)–C(2)–O(21)	104·1 (2)	C(3)–C(2)–O(21)	107·2 (2)
C(2)–C(3)–C(4)	114·1 (2)	C(2)–C(3)–O(31)	107·6 (2)
C(4)–C(3)–O(31)	104·2 (2)	C(3)–C(4)–C(5)	113·2 (2)
C(3)–C(4)–O(41)	103·5 (2)	C(5)–C(4)–O(41)	109·2 (2)
C(4)–C(5)–O(5)	109·5 (2)	C(4)–C(5)–C(6)	113·0 (2)
O(5)–C(5)–C(6)	107·3 (2)	C(1)–O(5)–C(5)	114·5 (2)
C(5)–C(6)–N(61)	109·0 (2)	C(5)–C(6)–P(61')	112·2 (2)
N(61)–C(6)–P(61')	114·7 (2)	C(1)–O(11)–C(22)	111·1 (2)
C(2)–O(21)–C(22)	107·2 (2)	O(11)–C(22)–O(21)	104·8 (2)
O(11)–C(22)–C(23)	109·6 (3)	O(21)–C(22)–C(23)	108·8 (3)
O(11)–C(22)–C(24)	109·9 (3)	O(21)–C(22)–C(24)	110·0 (3)
C(23)–C(22)–C(24)	113·5 (3)	C(3)–O(31)–C(42)	106·8 (2)
C(4)–O(41)–C(42)	108·5 (2)	O(31)–C(42)–O(41)	104·1 (2)
O(31)–C(42)–C(43)	111·0 (2)	O(41)–C(42)–C(43)	110·3 (2)
O(31)–C(42)–C(44)	109·4 (2)	O(41)–C(42)–C(44)	108·8 (3)
C(43)–C(42)–C(44)	112·9 (3)	C(6)–N(61)–O(61)	105·5 (2)
C(6)–N(61)–C(62)	116·5 (2)	O(61)–N(61)–C(62)	106·2 (2)
N(61)–C(62)–C(63)	112·2 (2)	C(62)–C(63)–C(64)	121·1 (3)
C(62)–C(63)–C(68)	120·2 (3)	C(64)–C(63)–C(68)	118·7 (3)
C(63)–C(64)–C(65)	121·4 (4)	C(64)–C(65)–C(66)	118·8 (5)
C(65)–C(66)–C(67)	120·5 (4)	C(66)–C(67)–C(68)	119·9 (5)
C(63)–C(68)–C(67)	120·7 (4)	C(6)–P(61')–O(61')	113·3 (1)
C(6)–P(61')–O(62')	108·6 (1)	O(61')–P(61')–O(62')	114·0 (1)
C(6)–P(61')–O(64')	102·7 (1)	O(61')–P(61')–O(64')	113·1 (1)
O(62')–P(61')–O(64')	104·2 (1)	P(61')–O(62')–C(63')	123·3 (2)
P(61')–O(64')–C(65')	127·1 (2)		

Fig. 1. Perspective view of (II) with the atom numbering (only the hydroxy and tertiary H atoms are shown).

packing is stabilized by a hydrogen bond from O(61) to O(61') [O(61)···O(61') 2·68 Å, O(61)–H···O(61') 169°] with the two molecules related by a 2_1 axis parallel to **a**.

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Structure of 2α-Bromo-1β,7β-epoxytrachelanthamidine: A New Heterocyclic Ring System

BY JAN. A. GLINSKI, DONALD VANDERVEER AND LEON H. ZALKOW*

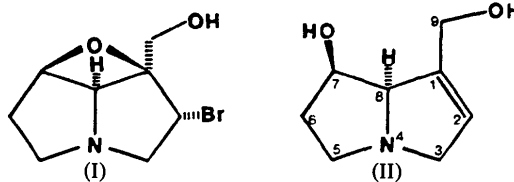*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*

Abstract. $C_8H_{12}BrNO_2$, $M_r = 234\cdot1$, orthorhombic, $P2_12_12_1$, $a = 6\cdot196$ (2), $b = 8\cdot971$ (2), $c = 15\cdot797$ (5) Å, $U = 878\cdot1$ (4) Å^3, $Z = 4$, $D_m = 1\cdot770$, $D_x = 1\cdot767$ g cm^{-3}, $\lambda(Mo\,K\bar{\alpha}) = 0\cdot71069$ Å, $\mu = 39\cdot71$ cm^{-1}, $F(000) = 472$, $T = 298$ K, $R = 0\cdot037$ for 1395 observed reflections. The pyrrolizidine rings of the title compound (I) are planar within 0·277 Å, and both assume envelope conformations. The oxetane ring of (I) has all angles close to 90°. The distances $O(2)\cdots N'$ (2·826 Å) and $H(O2)\cdots N'$ (1·82 Å) suggest intermolecular H bonding between N and the O atom of the CH_2OH group. The absolute configuration of (I), which can be related to its precursor retronecine [Warren & Von Klemperer (1958). *J. Chem. Soc.* pp. 4574–4575; Warren (1970). *The Alkaloids*, Vol. XII, edited by Manske, ch. 4, pp. 246–262. London: Academic Press; and references therein], was confirmed by comparison of the refinement values of (I) with its enantiomer for which $R = 0\cdot057$ was obtained.

Introduction. The pyrrolizidine alkaloids continue to be of great interest because of their broad range of biological activity (Roitman, 1983; Huxtable, 1979). Recently, there have been intensive studies of the antitumor activity of the N-oxides of the pyrrolizidine alkaloids and of their semisynthetic analogs (Zalkow, Glinski, Gelbaum, Fleischmann, McGowan & Gordon, 1985; Gelbaum, Gordon, Miles & Zalkow, 1982). Most of these alkaloids are esters of the necine base retronecine (II). Recently, we reported the X-ray structure of retronecine and its C7 epimer heliotridine (Gelbaum, Glinski, VanDerveer & Zalkow, 1985). As part of a program to modify the retronecine skeleton, in anticipation of altering biological activity, we attempted to prepare epoxides of retronecine and heliotridine, and have recently reported X-ray structures of such epoxides (Glinski, VanDerveer & Zalkow, 1985). Surprisingly, treatment of retronecine with N-bromoacetamide gave the expected epoxide only as a minor product, and as a major product the new heterocyclic compound, 2α-bromo-1β,7β-epoxytrachelanthamidine (I) whose structure is reported here for the first time.

Experimental. The compound (I) is a major constituent of a reaction mixture resulting from the treatment of (II) with N-bromoacetamide in 30% sulfuric acid followed by basification. The reaction mixture, after chromatography, afforded crystalline (I), m.p. 444·5–446 K (uncorrected), $[\alpha]_D^{25\cdot0°C} = +0\cdot6°$ [ethanol, 1·6 g dm^{-3}]. Crystal density by flotation in $CBrCl_3$–hexane. Axial photographs showed the crystal of (I), ca 0·60 × 0·10 × 0·15 mm (from methanol), to be orthorhombic and systematic extinctions indicated space group $P2_12_12_1$. Unit-cell parameters and orientation matrix for (I) determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite mono-