

Note

Synthesis and crystal and molecular structure of 4-(D-arabino-tetritol-1-yl)-4-imidazolin-2-ylideneammonium chloride

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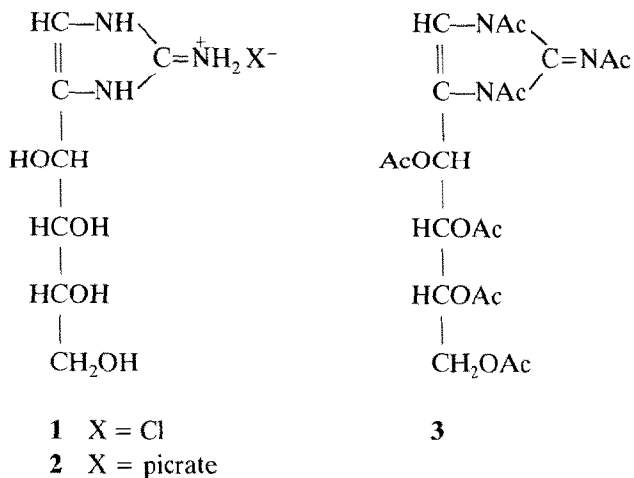
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4-(D-arabino-Tetritol-1-yl)-4-imidazolin-2-ylideneammonium chloride (**1**) was synthesised by the reaction of 1-amino-1-deoxy-D-arabino-hexulose with cyanamide and isolated *via* the picrate **2**. Compound **1** has been obtained¹ by the reaction of 2-amino-2-deoxy-D-glucose with cyanamide.



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Treatment of **1** with acetic anhydride-pyridine gave 1,3-diacetyl-2-acetylimino-4-(1,2,3,4-tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-4-imidazoline (**3**).

The structures of **1-3** were supported by elemental analyses and spectral data. The $^3J_{\text{H,H}}$ values for **3** established that, in solution in chloroform, the molecules exist essentially in ${}_3G^+$ and **P** conformations².

The crystal structures^{3,4} of analogous 4-imidazoline derivatives indicated their

TABLE I

NON-HYDROGEN ATOMIC CO-ORDINATES ($\times 10^4$) FOR **1** (E.S.D. VALUES IN PARENTHESES) AND THERMAL PARAMETERS ($\times 10^3$)

Atom	x/a	y/b	z/c	U_{eq}^a
Cl	2079(3)	324(0)	-536(4)	39(1)
N-1	2122(9)	-1732(30)	3223(11)	26(4)
N-2	941(10)	-4817(35)	1411(12)	40(4)
N-3	153(9)	-1851(30)	2861(11)	29(4)
O-6	2079(8)	3455(24)	5944(10)	32(3)
O-7	3164(7)	-1795(22)	7021(9)	25(3)
O-8	5297(7)	3540(25)	6692(9)	30(3)
O-9	6176(8)	-1631(26)	8027(11)	39(4)
C-2	1079(12)	-2891(35)	2432(14)	31(5)
C-4	622(11)	95(44)	3968(13)	29(4)
C-5	1832(10)	156(36)	4186(12)	23(4)
C-6	2778(11)	1866(30)	5236(13)	20(4)
C-7	3738(11)	106(40)	6313(13)	28(5)
C-8	4642(11)	1923(33)	7443(13)	26(5)
C-9	5481(12)	257(45)	8653(12)	38(5)

$$^a U_{eq} = \frac{1}{3} \sum U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j).$$

TABLE II

BOND LENGTHS (\AA) AND ANGLES (DEGREES) FOR **1**^a

N-1-C-5	1.410	O-9-C-9	1.443
N-2-C-2	1.331	C-4-C-5	1.331
N-1-C-5	1.410	O-9-C-9	1.443
N-3-C-4	1.402	C-6-C-7	1.538
O-6-C-6	1.408	C-7-C-8	1.557
O-7-C-7	1.408	C-8-C-9	1.516
C-2-N-1-C-5	108.7	C-5-C-6-C-7	110.9
C-2-N-3-C-4	109.7	O-6-C-6-C-7	111.7
N-2-C-2-N-3	124.3	O-7-C-7-C-6	112.0
N-1-C-2-N-3	107.4	C-6-C-7-C-8	110.0
N-1-C-2-N-2	128.1	O-7-C-7-C-8	110.2
N-3-C-4-C-5	106.9	O-8-C-8-C-7	107.9
N-1-C-5-C-4	107.1	C-7-C-8-C-9	111.7
C-4-C-5-C-6	129.0	O-8-C-8-C-9	112.8
N-1-C-5-C-6	123.7	O-9-C-9-C-8	109.1
O-6-C-6-C-5	104.1		

^aMean e.s.d.'s, 0.014 \AA and 0.8°.

conformations, the existence of extensive electronic delocalisation on the imidazole group, and the presence of a protonated imino-imidazole group.

The positional and isotropic thermal parameters for the non-hydrogen atoms of **1** are given in Table I, and the bond lengths and angles together with their estimated deviations in Table II. The C–H distances range from 0.953 to 1.036 Å with an average value of 1.005 Å, and the N–H distances range from 1.001 to 1.054 Å with an average of 1.015 Å.

The bond distances and angles in the sugar chain have the expected values and will not be discussed. The imidazole part of the molecule is protonated and, consequently, the three nitrogens are chemically equivalent. The C-2–N bond lengths (mean value 1.335 Å) are shorter than those of the other C–N bonds (1.403 and 1.410 Å) and their values are intermediate between those of double (1.265 Å) and single bonds (1.470 Å). This finding indicates delocalisation of the double bonds of the imidazole group, and delocalisation of the positive charge on C-2, and

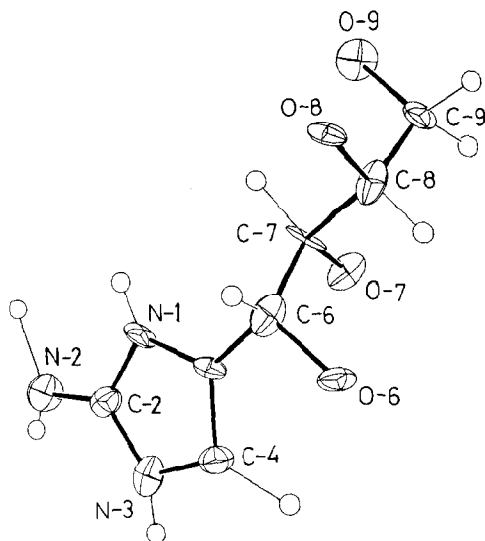


Fig. 1. Ortep view of **1** along the *b* axis, showing the atomic numbering. Thermal ellipsoids enclose 50% probability (Cl is not included).

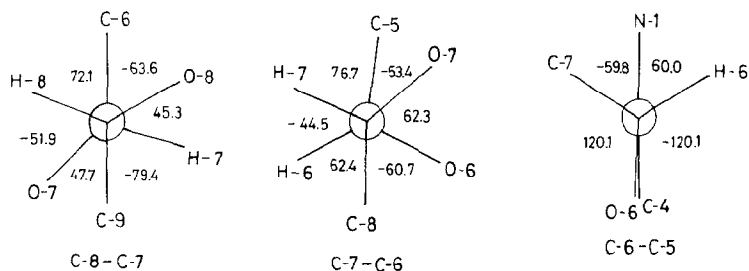


Fig. 2. Some Newman projections. The torsion angle C-4–C-6–C-5–O-6 is -0.2° .

probably on the hydrogens bonded to the three nitrogens. This feature is also exhibited by the analogues. The imidazole ring is planar [maximum deviation from the least-squares plane, 0.005(9) Å]: the substituents at N-2 and C-6 also lie in this plane [at $-0.011(8)$ and $0.013(10)$ Å, respectively, from the mean square plane]. The sugar chain is also planar [maximum deviation from the least-squares plane, $-0.061(13)$ Å]. The dihedral angle between the sugar and the imino-group planes is $62.0(8)^\circ$.

Fig. 1 shows the Ortep⁵ view of **1** along the *b* axis together with the atomic numbering. Thermal ellipsoids enclose 50% probability, and the Newman projections corresponding to the C–C bonds of the sugar chain are shown in Fig. 2. According to the Klyne–Prelog⁶ rules, the configurations of the chiral centres C-6,7,8 are *S*, *R*, and *R* in accordance with the *D*-arabino structure.

Cohesion in the crystal is ensured by hydrogen bonding. In the structure, the Cl anion is involved in four hydrogen bonds: N-2 \cdots Cl ($-x, y - \frac{1}{2}, -z$) = 3.279(11), N-3 \cdots Cl ($-x, y - \frac{1}{2}, -z$) = 3.176(9), O-7 \cdots Cl ($x, y, z + 1$) = 3.108(9), and O-9 \cdots Cl ($-x + 1, y - \frac{1}{2}, -z + 1$) = 3.039(8) Å. Other possible hydrogen bonds are N-1 \cdots O-8 ($-x + 1, y - \frac{1}{2}, -z + 1$) = 2.890(13), N-3 \cdots O-6 ($-x, y - \frac{1}{2}, -z + 1$) = 3.047(14), C-4 \cdots O-6 ($-x, y - \frac{1}{2}, -z + 1$) = 3.170(14), and O-7 \cdots O-6 ($x, y - 1, z$) = 2.706(10) Å.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi apparatus and are uncorrected. Microanalyses were performed by Instituto de Química Orgánica General, C.S.I.C., Madrid. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. I.r. spectra (KBr discs) were recorded with a Perkin–Elmer 299 spectrophotometer. ¹H-N.m.r. spectra were recorded with a Varian XL-200 (200 MHz, F.t.) spectrometer. T.l.c. was performed on Silica Gel HF₂₅₄ (Merck), using ether–hexane (6:1) and detection with iodine vapour. P.c. (descending) was performed on Whatman No. 1 paper with 1-butanol–pyridine–water (1:1:1) and detection with alkaline silver nitrate and Pauly's reagent.

4-(D-arabino-Tetritol-1-yl)-4-imidazolin-2-ylideneammonium picrate (2). — A solution of 1-amino-1-deoxy-D-arabino-hexulose acetate (3 g, 12.5 mmol) in water (12 mL) was adjusted to pH 7 with 5M sodium hydroxide, cyanamide (0.75 g, 17.8 mmol) was added, and the mixture was kept for 7 h at 70°. A solution of picric acid (6.1 g, 26.6 mmol) in methanol (90 mL) was added, and the mixture was concentrated and stored at 0° to give **2** (2.7 g, 50%), m.p. 178°, $[\alpha]_{589}^{25} -4^\circ$ (*c* 1, methyl sulphoxide); $\lambda_{\max}^{\text{MeOH}}$ 211, 267, 342, and 399 nm (ϵ_{nm} 13.2, 14.8, 6.2, and 4.9); ν_{\max} 3420, 3300 and 3240 (OH, NH), 1670 (C=N), 1630, 1610 and 1580 (C=C aromatic), 1560, and 1330 cm^{-1} (NO₂). ¹H-N.m.r. data [(CD₃)₂SO]: δ 11.60 (b, 2 H, NH-1,3), 8.60 (s, 2 H, H-3,5), 7.11 (s, 2 H, C=NH₂), 6.67 (s, 1 H, H-5), 5.22 (b, 1 H, HO-1), 4.73 (m, 4 H, H-1', HO-2,3,4), 3.51 (m, 4 H, H-2',3',4',4').

Anal. Calc. for C₁₃H₁₆N₆O₁₁: C, 36.13; H, 3.73; N, 19.44. Found: C, 35.83; H, 3.60; N, 19.80.

4-(D-arabino-Tetritol-1-yl)-4-imidazolin-2-ylideneammonium chloride (1). — To a solution of **2** (1 g, 2.3 mmol) in water (20 mL) was added M hydrochloric acid (7 mL) at 50°. The mixture was kept for 10 min at 50° and then cooled to room temperature, the picric acid was removed, and the filtrate was extracted with ether (3 × 15 mL). The pH of the aqueous solution was adjusted to 5 with Amberlite IR-45 (HO⁻) resin, the solution was filtered and lyophilised, and the residue was crystallised from ethanol to give **1** (0.42 g, 76%), m.p. 172–174°, R_F 0.20 (p.c.), $[\alpha]_{589}^{22} -14^\circ$ (c 1, water); $\lambda_{\max}^{\text{EtOH}}$ 214 (ϵ_{nm} 8.5); ν_{\max} 3420 and 3240 (OH, NH), 1670 (C=N), 1630 and 1570 (C=C). ¹H-N.m.r. data [(CD₃)₂SO]: δ 11.78 and 11.70 (s, 2 H, NH-1,3), 7.26 (s, 2 H, C=N₂), 6.68 (s, 1 H, H-5), 4.75 (s, 1 H, H-1'), 4.23 (w, 4 H, HO-1,2,3,4), 3.49 (m, 4 H, H-2',3',4',4').

Anal. Calc. for C₇H₁₄ClN₃O₄: C, 35.08; H, 5.89; Cl, 14.80; N, 17.53. Found: C, 35.31; H, 6.10; Cl, 14.63; N, 17.58.

1,3-Diacetyl-2-acetylmino-4-(1,2,3,4-tetra-O-acetyl-D-arabino-tetritol-1-yl)-4-imidazoline (3). — Treatment of **1** (0.4 g, 1.6 mmol) with pyridine-acetic anhydride (1:1, 4 mL) in the usual way, with crystallisation of the product from ether-hexane, gave **3** (0.37 g, 45%), m.p. 114–115°, R_F 0.2 (t.l.c.; ether-hexane, 6:1), $[\alpha]_{589}^{22} -11^\circ$ (c 1, chloroform); ν_{\max} 3120 (=CH), 1745, 1735 (C=O ester), 1725 (NAc), 1710 C=N. ¹H-N.m.r. data (CDCl₃): δ 7.37 (d, 1 H, $J_{5,1'}$ 0.8 Hz, H-5), 6.08 (dd, 1 H, $J_{1',2'}$ 4.4 Hz, H-1'), 5.70 (dd, 1 H, $J_{2',3'}$ 7.2 Hz, H-2'), 5.20 (ddd, $J_{3',4'}$ 3.1, $J_{3',4'}$ 5.5 Hz, H-3'), 4.37 (dd, $J_{4',4'}$ 12.5 Hz, H-4'), 4.15 (dd, H-4'), 2.53 (s, 3 H, NAc), 2.27 (s, 6 H, 2 NAc), 2.13, 2.07, 2.03, and 2.04 (4 s, each 3 H, 4 OAc).

Anal. Calc. for C₂₁H₂₇N₃O₁₁: C, 50.70; H, 5.47; N, 8.45. Found: C, 50.59; H, 5.67; N, 8.49.

*Crystal analysis**. — The colourless prism of **1** (0.16 × 0.35 × 0.18 mm) belonged to the monoclinic system with systematic absences consistent with $P2_1$. The lattice parameters, refined using 25 reflections within the range $5^\circ < \theta < 11^\circ$, were $a = 11.292(2)$, $b = 4.916(2)$, $c = 9.559(2)$ Å, and $\beta = 106.3(1)^\circ$. The unit-cell volume V was 509.3 Å³, and the adsorption coefficient was 0.37 mm⁻¹.

An Enraf-Nonius CAD-4 diffractometer was used with monochromated MoK α radiation (0.7107 Å), $w/2\theta$ mode, $2\theta_{\max} = 50^\circ$ ($0 \leq h \leq 13$, $0 \leq k \leq 5$, $-11 \leq l \leq 11$). Two reference reflections (411 and $\bar{4}11$) were measured every hour to monitor crystal stability, and were re-centred after every hundred measured reflections to monitor crystal orientation. No significant changes in intensities were noted. From 1036 measured reflections, 626 were observed with $I \geq 2\sigma(I)$. $F(000) = 252$. Corrections were made for Lorentz-polarisation effects, but not for extinction and absorption. This last effect was not taken into account because the crystal absorption with Mo radiation was practically negligible.

The structure was solved by direct methods using the MULTAN-80

*Data from the analysis have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/406/Carbohydr. Res., 187 (1989) 139–144.

program⁷; 210 reflections with $E > 1.31$, 5 reflections in the starting set were used to determine the structure. The initial E map revealed most of the non-hydrogen atoms and the remainder were located from subsequent electron-density maps. After anisotropic refinement by full-matrix least squares of all the 15 non-hydrogen atoms in the asymmetric unit, the hydrogen atoms were located at geometrical positions and were assigned the same isotropic thermal parameters as the atoms to which they were bonded, and were included, but not refined, in the final stage of refinement. Refinement based on F (structure amplitudes) to minimise the function $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F_o)$; 142 parameters were refined (9 parameters per atom plus 1 for the scale); the over-determination ratio was 4.4 reflections/parameter. The refinement led to a final convergence with $R = 0.07$. All parameter shifts during the final cycle of refinement were less than 0.01σ . The y co-ordinate of Cl was held fixed. Atomic scattering factors were from the International Tables for X-Ray Crystallography⁸, and all calculations were carried out with the X-Ray System⁹.

The bond lengths (Å) and angles (°) in Table II were calculated by the program PARST, written by Nardelli¹⁰.

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