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Acta Cryst. (1990). **C46**, 1718–1720

Structure of 4-(D-galacto-Pentaacetoxypropyl)-1-phenylpyrazole

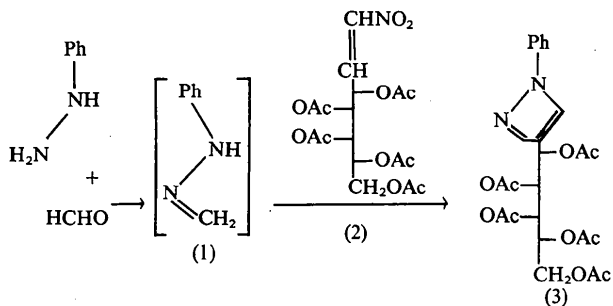
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(Received 21 July 1989; accepted 4 December 1989)

Abstract. 1,2,3,4,5-Penta-*O*-acetyl-5-(1-phenyl-4-pyrazolyl)-D-arabinitol, C₂₄H₂₈N₂O₁₀, *M*_r = 504.49, monoclinic, *P*2₁, *a* = 21.663 (7), *b* = 5.644 (8), *c* = 10.884 (3) Å, β = 102.06 (5)°, *V* = 1301 (2) Å³, *Z* = 2, *D*_m = 1.29, *D*_x = 1.28 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 0.095 mm⁻¹, *F*(000) = 532, *T* = 300 K, final *R* = 0.072 for 1639 observed reflections. The dihedral angle between the pyrazole and phenyl rings is 25.9 (4)° and between the pyrazole ring and galacto chain 57.5 (7)°. The molecules are linked by van der Waals forces.

Introduction. Gomez-Guillen, Hans, Lassaletta & Martin Zamora (1989) reported the synthesis of 4-(D-galacto-pentaacetoxypropyl)-1-phenylpyrazole (3) by the reaction of formaldehyde phenylhydrazone (1), generated *in situ*, with 3,4,5,6,7-penta-*O*-acetyl-1-nitro-1,2-dideoxy-D-galacto-hept-1-enitol (2).



The compound (3) is a substance of considerable interest as a precursor of *C*-nucleosides of pyrazole and has a structure very similar to the natural ones, such as pyrazomycin. To elucidate the geometric and conformational details of this compound we undertook its structure analysis.

Experimental. Colourless needle-shaped crystal. *D*_m measured by flotation, crystal size: 0.18 × 0.32 × 0.52 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα; accurate cell parameters from 25 strong reflections with 4 < θ < 13°; 2283 independent reflections with θ < 22° in the range (0 ≤ *h* ≤ 22, 0 ≤ *k* ≤ 5, -11 ≤ *l* ≤ 11) of which 1639 were considered observed [*I* < 2σ(*I*)]. Intensities corrected for Lp effects, but absorption and extinction corrections ignored. Two standard reflections (413 and 213) monitored after every 100 reflections showed no significant variation in intensity. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares refinement based on *F* of the positional and isotropic thermal parameters for non-H atoms; then positional and anisotropic thermal parameters; all H atoms located from difference syntheses; further refinement with anisotropic thermal parameters for non-H atoms and fixed H atoms with isotropic temperature factors corresponding to those of carrier atoms. Final *R* =

Table 1. Atomic parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for 4-D-galacto-pentacetoxypentyl-1-phenylpyrazole

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

	x	y	z	U_{eq}
N(1)	9120 (4)	5290 (22)	1705 (7)	34 (3)
N(2)	8898 (4)	3012 (22)	1698 (10)	59 (4)
O(10)	7301 (3)	8548 (20)	1011 (6)	40 (2)
O(11)	7912 (3)	8966 (21)	3638 (6)	40 (3)
O(12)	6327 (3)	6618 (21)	2739 (6)	40 (2)
O(13)	6900 (3)	7374 (20)	5361 (6)	38 (3)
O(14)	6084 (3)	11436 (21)	5640 (6)	46 (3)
O(110)	6707 (5)	6280 (24)	-408 (8)	87 (5)
O(111)	8440 (4)	6294 (25)	4966 (8)	72 (4)
O(112)	5750 (4)	9166 (24)	1366 (8)	72 (4)
O(113)	7607 (4)	9585 (24)	6675 (8)	74 (4)
O(114)	5363 (3)	13943 (22)	4556 (6)	56 (3)
C(1)	8296 (5)	3261 (26)	1737 (11)	51 (5)
C(2)	8113 (4)	5663	1723 (8)	33 (3)
C(3)	8659 (5)	6884 (24)	1728 (9)	39 (4)
C(4)	9772 (4)	5712 (24)	1710 (9)	37 (4)
C(5)	10051 (5)	7819 (25)	2187 (10)	45 (4)
C(6)	10686 (5)	8195 (30)	2171 (10)	59 (5)
C(7)	11037 (5)	6536 (28)	1657 (10)	53 (4)
C(8)	10743 (5)	4518 (27)	1193 (10)	50 (4)
C(9)	118 (5)	4044 (26)	1185 (9)	44 (4)
C(10)	7467 (4)	6551 (24)	1820 (9)	35 (3)
C(11)	7423 (4)	7246 (24)	3146 (8)	31 (3)
C(12)	6801 (4)	8431 (23)	3196 (9)	38 (4)
C(13)	6740 (4)	9317 (25)	4486 (8)	35 (3)
C(14)	6075 (4)	10154 (25)	4475 (9)	49 (4)
C(110)	6908 (6)	8161 (27)	-100 (11)	56 (5)
C(111)	8404 (6)	8230 (31)	4534 (11)	57 (5)
C(112)	5823 (5)	7222 (30)	1804 (10)	51 (5)
C(113)	7351 (5)	7723 (28)	6399 (9)	46 (4)
C(114)	5685 (4)	13318 (27)	5534 (10)	43 (4)
C(210)	6766 (8)	10381 (31)	-863 (12)	89 (7)
C(211)	8885 (6)	10161 (32)	4889 (12)	74 (6)
C(212)	5403 (6)	5072 (30)	1399 (12)	74 (6)
C(213)	7519 (6)	5482 (29)	7150 (10)	63 (5)
C(214)	5705 (5)	14411 (28)	6796 (9)	53 (4)

0.072, $wR = 0.072$ [$w = 1/\sigma^2(F)$]. $S = 0.95$. $(\Delta/\sigma)_{max} = 0.09$. Residual electron density in final difference map, $\Delta\rho = \pm 0.3 \text{ e \AA}^{-3}$. The origin was defined by keeping fixed the y coordinate of atom C(2). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The absolute configuration was assumed on the basis of the compound used in the synthesis. The XRAY system (Stewart, Kundell & Baldwin, 1970) was used.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Bond distances and bond angles are listed in Table 2. The identification of the atoms and the configuration of the molecule are shown in the ORTEP (Johnson, 1976) drawing of Fig. 1.

The pyrazole ring is planar [maximum deviation from the mean plane 0.017 (12) \AA]. The C(4) atom attached to the pyrazole N(1) atom lies nearly in this plane [deviation -0.021 (9) \AA] but the C(10) atom

* 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 52824 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

O(11)—C(111)	1.351 (13)	O(14)—C(14)	1.456 (13)
O(11)—C(11)	1.454 (14)	C(2)—C(1)	1.411 (14)
O(13)—C(113)	1.344 (11)	C(2)—C(3)	1.367 (14)
O(13)—C(13)	1.446 (15)	C(111)—C(211)	1.501 (21)
O(10)—C(10)	1.429 (15)	C(110)—C(210)	1.499 (21)
O(10)—C(110)	1.344 (12)	C(12)—C(13)	1.522 (14)
O(12)—C(112)	1.370 (11)	C(12)—C(11)	1.514 (14)
O(12)—C(12)	1.462 (14)	C(13)—C(14)	1.512 (14)
C(10)—C(2)	1.511 (14)	C(1)—N(2)	1.320 (14)
C(10)—C(11)	1.517 (13)	C(5)—C(4)	1.384 (18)
O(112)—C(112)	1.193 (20)	C(5)—C(6)	1.395 (16)
O(111)—C(111)	1.185 (21)	C(4)—C(9)	1.396 (17)
C(113)—O(113)	1.197 (19)	C(4)—N(1)	1.431 (12)
C(113)—C(213)	1.508 (20)	N(2)—N(1)	1.372 (17)
C(114)—O(14)	1.359 (16)	C(8)—C(9)	1.379 (15)
C(114)—C(214)	1.497 (16)	C(8)—C(7)	1.350 (20)
C(114)—O(114)	1.198 (12)	C(3)—N(1)	1.349 (15)
O(110)—C(110)	1.168 (19)	C(6)—C(7)	1.394 (20)
C(112)—C(212)	1.524 (21)		
C(111)—O(11)—C(11)	117.6 (10)	O(10)—C(110)—C(210)	112.3 (11)
C(113)—O(13)—C(13)	118.2 (9)	O(12)—C(12)—C(11)	104.2 (9)
C(10)—O(10)—C(110)	117.1 (10)	O(12)—C(12)—C(13)	110.6 (8)
C(112)—O(12)—C(12)	118.2 (9)	C(13)—C(12)—C(11)	115.3 (7)
O(10)—C(10)—C(11)	108.9 (9)	O(13)—C(13)—C(12)	107.6 (9)
O(10)—C(10)—C(2)	109.6 (7)	C(12)—C(13)—C(14)	111.2 (7)
C(2)—C(10)—C(11)	113.2 (7)	O(13)—C(13)—C(14)	109.7 (7)
O(13)—C(113)—C(213)	112.5 (10)	C(2)—C(1)—N(2)	112.2 (11)
O(13)—C(113)—O(113)	123.8 (10)	C(4)—C(5)—C(6)	118.6 (11)
O(113)—C(113)—C(213)	123.5 (10)	C(5)—C(4)—N(1)	119.8 (10)
C(214)—C(114)—O(114)	126.4 (11)	C(5)—C(4)—C(9)	120.2 (10)
O(14)—C(114)—O(114)	123.1 (10)	C(9)—C(4)—N(1)	119.8 (10)
O(14)—C(114)—C(214)	110.3 (8)	C(10)—C(11)—C(12)	112.4 (7)
O(12)—C(112)—O(112)	122.9 (10)	O(11)—C(11)—C(12)	106.0 (9)
O(112)—C(112)—C(212)	126.4 (11)	O(11)—C(11)—C(10)	109.6 (8)
O(12)—C(112)—C(212)	110.5 (10)	C(1)—N(2)—N(1)	104.3 (10)
C(114)—O(14)—C(14)	115.0 (8)	C(9)—C(8)—C(7)	123.4 (11)
C(10)—C(2)—C(3)	130.1 (7)	C(2)—C(3)—N(1)	107.9 (9)
C(10)—C(2)—C(1)	125.4 (8)	C(4)—C(9)—C(8)	118.4 (11)
C(1)—C(2)—C(3)	104.1 (6)	C(5)—C(6)—C(7)	121.6 (12)
O(11)—C(111)—O(111)	123.0 (11)	C(8)—C(7)—C(6)	117.5 (11)
O(111)—C(111)—C(211)	125.6 (12)	N(2)—N(1)—C(3)	111.3 (9)
O(11)—C(111)—C(211)	111.2 (11)	C(4)—N(1)—C(3)	128.5 (10)
O(10)—C(110)—O(110)	122.2 (11)	C(4)—N(1)—N(2)	120.1 (9)
O(110)—C(110)—C(210)	125.4 (11)		

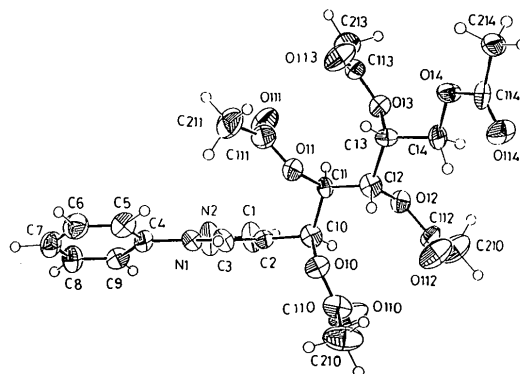


Fig. 1. A view of the molecule along b , showing atomic numbering.

attached to C(2) is displaced by -0.075 (9) \AA. The average C—C bond length is 1.389 (14) \AA, the average C—N bond length 1.335 (16) \AA, and the N—N bond length is 1.373 (17) \AA, similar to other substituted pyrazoles and indicates a high degree of electronic delocalization.

The phenyl group is planar [maximum deviation 0.009 (11) \AA].

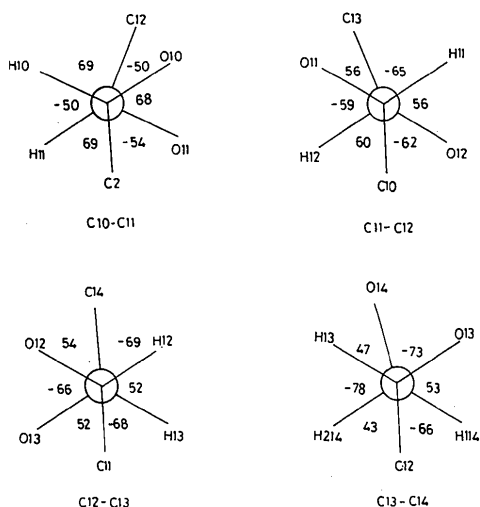


Fig. 2. Some Newman projections (angles in $^{\circ}$).

The sugar chain C(10)—C(11)—C(12)—C(13)—C(14) is planar [maximum deviation 0.014 (11) Å]. The orientation of the acetoxy groups with respect to the sugar chain is defined by the torsion angles: C(13)—C(14)—O(14)—C(114) = 144.5 (10), C(14)—C(13)—O(13)—C(113) = -113.0 (11), C(13)—C(12)—O(12)—C(112) = 106.0 (11), C(12)—C(11)—O(11)—C(111) = 130.7 (11) and C(11)—C(10)—O(10)—C(110) = 135.0 (10) $^{\circ}$. Bond lengths are in good agreement with those in analogous compounds.

Fig. 2 shows the Newman projections corresponding to the C—C bonds of the sugar chain. The configurations around the chiral centres C(13), C(12), C(11) and C(10) are *R*, *S*, *R* and *S*, respectively (Klyne & Prelog, 1960), in accordance with the *D*-galacto constitution.

The dihedral angle between the pyrazole and phenyl rings is 25.9 (4) $^{\circ}$, and that between the pyrazole ring and the *galacto* chains is 57.5 (7) $^{\circ}$.

The intermolecular linkages are due to van der Waals forces and there are no abnormal intermolecular distances.

The authors thank 'La Junta de Andalucia' for financial support.

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Acta Cryst. (1990). **C46**, 1720–1723

1-Ethynyl-2,7-dimethoxynaphthalene: an Example of Hydrogen Bonding Between an Ethynylic Hydrogen and a Methoxyl Oxygen

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(Received 25 August 1989; accepted 22 December 1989)

Abstract. C₁₄H₁₂O₂, *M_r* = 212.3, triclinic, *P* $\bar{1}$, *a* = 6.6160 (12), *b* = 11.359 (2), *c* = 16.217 (2) Å, α = 80.640 (11), β = 86.305 (13), γ = 78.858 (12) $^{\circ}$, *V* = 1179.2 (4) Å³, *Z* = 4, *D_x* = 1.196 g cm⁻³, λ (Cu *K* α) = 1.54184 Å, μ = 6.01 cm⁻¹, *F*(000) = 448, *T* = 295 K, *R* = 0.039 for 3488 observations (of 4844 unique data). The crystal consists of two independent molecules related by a C—H \cdots O contact. The donor is the ethynylic H on one molecule, and the acceptor

is the methoxyl O *ortho* to the ethynylic group on the other molecule. The \equiv C—H \cdots O bond length (C to O distance) is 3.260 (2) Å and the angle at H is 164 (1) $^{\circ}$. The naphthalene ring system of the two independent molecules shows an average deviation from planarity of 0.007 (2) and 0.008 (2) Å with respective maximum deviations of 0.015 (1) and 0.014 (2) Å.

Introduction. The title compound, (1), prepared by the reaction of 1-acetyl-2,7-dimethoxynaphthalene

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