

Fig. 3. The crystal structure.

contact distance of 2.611 (6) Å. This results in an opening of the C(10)–C(1)–C(2) and C(1)–C(2)–C(7) angles to 126.0 (3) and 127.5 (3)° respectively, closing of the endocyclic angle at C(1) to 115.3 (4)° and lengthening of the C(1)–C(10) bond. It is also noteworthy that the longer bond to *tert*-butyl, C(10)–C(16), is to the *tert*-butyl group which lies closer to the plane of the aromatic ring (see Table 2) and that this group makes the larger angle with the C(1)–C(10) bond.

The crystal structure, shown in Fig. 3, consists of sheets of molecules approximately parallel to the (100) planes in the crystal. Molecules within these sheets are stacked obliquely with the aromatic rings at approximately 45° to the sheets. All intramolecular contacts are of the van der Waals type.

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The Structure of Ethyl 5,6,7,8,9-Pentaacetoxy-2-amino-4-nitromethyl-D-glycero-D-manno-2-nonene-3-carboxylate, C₂₃H₃₄N₂O₁₄

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Abstract. $M_r = 562.5$, orthorhombic, $P2_12_12_1$, $a = 17.367$ (1), $b = 18.176$ (1), $c = 9.446$ (1) Å, $V = 2981.7$ (3) Å³, $Z = 4$, $D_m = 1.26$, $D_x = 1.25$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.95$ mm⁻¹, $F(000) = 1192$, $T = 300$ K, final $R = 0.057$ for 2303 observed independent reflections. The configuration around the chiral centres C(8), C(7), C(6), C(5) and C(4) of the sugar chain is *R*, *R*, *R*, *S* and *S*, that is *D-glycero-D-manno*. The molecule has an intramolecular hydrogen bond

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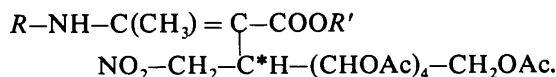
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between the N and O atoms of the amino and carbonyl groups, showing a chelate structure. Packing of the molecules is governed by normal van der Waals contacts.

Introduction. Crystals of the title compound were prepared by Gómez-Sánchez, Mancera, Rosado & Bellanato (1980). They reported an easy way to obtain 3-(pentaacetoxypropyl)pyrrole derivatives by a

Michael-type addition of 3-(alkylamino)crotonic esters to pentaacetoxy-1-nitro-1-heptenes and the further cyclization of the adducts



Open-chain sugar nitro-olefins [polyacetoxy-1-nitro-alk-1-enes, NO₂-HC=CH-(CHOAc)₄-CH₂OAc, and oxygen-protected 2-C-glycosyl-1-nitroethylenes, R-NH-C(CH₃)=CH-CO₂R'] are attractive as potential starting materials for the synthesis of functionalized branched-chain sugars and C-(polyhydroxy-alkyl)- and C-glycosylheterocyclic compounds derived from them.

The title compound is an intermediate in the synthesis of 3-(pentaacetoxypropyl)pyrrole, a substance which has aroused interest as a precursor of C-glycosylpyrroles. A new chiral centre is produced (marked with an asterisk) and two diastereoisomers could result, although only one product has been isolated and detected chromatographically. The configuration could not be established from chemical and spectroscopic considerations.

The crystal structure of the title compound (R = H, R' = C₂H₅) has been determined as part of a systematic structural investigation of conformational aspects of this type of compound; the structures of two of these [R = C₄H₉, R' = C₂H₅ (Vega, López-Castro & Márquez, 1981) and R = H, R' = CH₃ (Vega, López-Castro & Márquez, 1983)] have been solved.

Experimental. Crystals are colourless prisms; well-formed crystal 0.22 × 0.20 × 0.25 mm used; unit-cell parameters calculated by least-squares refinement of 25 independent reflections, automatic Philips PW 1100 four-circle diffractometer; systematic absences consistent with P₂,2₁,2₁; D_m by flotation in CCl₄/PhCl. Reflections in range θ < 60° (h < 21, k < 22, l < 12) measured by ω/2θ scans, scan width 2.8°, scan speed 20° min⁻¹ in 2θ; two reflections (240 and $\bar{2}40$) monitored during data collection, variation in intensities < 2% of mean value. 2303 independent reflections out of 2899 measured considered observed [I > 2σ(I)]; intensities corrected for Lorentz and polarization effects, not for absorption (μR ~ 0.2) or extinction. Structure solved by direct methods with MULTAN77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). E map computed with best phase set located 32 of the 39 non-hydrogen atom positions, remaining atoms located from a Fourier synthesis. Refinement on F by full-matrix least squares. Scattering factors from *International Tables for X-ray Crystallography* (1974). w = 1/σ²(F). Positions of H atoms calculated; non-hydrogen atoms anisotropic, H atoms isotropic (H positions not refined); final R and wR = 0.057; H atoms assigned isotropic temperature factors equal to

Table 1. Final fractional coordinates (× 10⁴) and equivalent isotropic temperature factors (Å² × 10³) for non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U _{eq}
C(1)	6135 (4)	6141 (3)	7748 (7)	67 (2)
C(2)	6256 (3)	6430 (3)	6249 (6)	51 (2)
C(3)	6348 (3)	7157 (3)	5936 (6)	46 (2)
C(4)	6281 (3)	7752 (3)	7062 (6)	46 (2)
C(5)	5617 (3)	8289 (3)	6781 (6)	43 (2)
C(6)	4848 (3)	7910 (3)	6568 (6)	45 (2)
C(7)	4194 (3)	8475 (3)	6239 (6)	44 (2)
C(8)	3819 (3)	8357 (3)	4780 (6)	51 (2)
C(9)	3278 (4)	8969 (4)	4393 (8)	73 (3)
N(21)	6285 (3)	5882 (3)	5296 (6)	65 (2)
O(31)	6705 (3)	8099 (2)	4399 (4)	64 (2)
O(32)	6582 (3)	6960 (2)	3465 (5)	75 (2)
C(31)	6544 (3)	7366 (3)	4500 (7)	55 (2)
C(32)	6986 (4)	8372 (5)	3061 (8)	82 (3)
C(33)	7015 (7)	9166 (5)	3159 (11)	143 (5)
O(41)	7391 (4)	9011 (3)	9023 (7)	125 (3)
O(42)	7020 (4)	7956 (4)	9705 (6)	111 (3)
N(41)	7152 (4)	8400 (4)	8809 (7)	7 (2)
C(41)	7040 (3)	8175 (4)	7287 (7)	58 (2)
O(51)	5583 (2)	8760 (2)	8027 (4)	47 (1)
O(52)	5627 (4)	9785 (2)	6701 (6)	90 (2)
C(51)	5618 (4)	9507 (3)	7831 (8)	61 (2)
C(52)	5651 (5)	9898 (3)	9233 (8)	77 (3)
O(61)	7678 (2)	7503 (2)	7825 (4)	48 (1)
O(62)	3957 (3)	6749 (2)	6471 (5)	74 (2)
C(61)	4183 (3)	6933 (3)	7628 (8)	7 (2)
C(62)	3985 (4)	6575 (3)	9012 (8)	70 (2)
O(71)	3562 (2)	8378 (2)	7214 (4)	50 (1)
O(72)	3895 (3)	9395 (2)	8375 (6)	88 (2)
C(71)	3475 (3)	8871 (3)	8260 (6)	55 (2)
C(72)	2819 (4)	8674 (4)	9208 (7)	69 (2)
O(81)	4456 (2)	8332 (2)	3783 (4)	57 (1)
O(82)	3717 (3)	7709 (3)	2260 (5)	97 (2)
C(81)	4309 (4)	8001 (4)	2545 (7)	74 (3)
C(82)	4993 (4)	8031 (5)	1567 (7)	92 (3)
O(91)	3702 (3)	9657 (3)	4427 (2)	78 (2)
O(92)	3766 (6)	9710 (4)	2101 (6)	158 (4)
C(91)	3959 (6)	9942 (4)	3186 (9)	93 (3)
C(92)	4477 (6)	10578 (4)	3449 (10)	111 (4)

those of the carrier atoms. Final difference Fourier map showed strongest peak of ±0.28 e Å⁻³; max. Δ/σ = 0.3. The positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* Computations were performed with the XRAY system (Stewart, Kundell & Baldwin, 1970).

Discussion. Fig. 1 shows a schematic view of the molecule with the atom numbers, bond distances and angles for non-H atoms.

The main nonene chain has a planar zigzag part, as expected, comprising C(1), C(2), C(3) and C(4) with deviations less than 0.018 (6) Å from their best plane, but C(5), C(6), C(7), C(8) and C(9) are not coplanar, in contrast to analogous compounds. The five acetoxy groups are completely planar; the nitromethyl [maximum deviation 0.011 (7) Å] and ethoxycarbonyl groups [maximum deviation 0.13 (1) Å] are also essentially planar.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39477 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The torsion angles defining the orientations of the acetoxy groups with respect to the main nonene chain are: $C(9)-C(8)-O(81)-C(81) = -80.0(6)$, $C(8)-C(7)-O(71)-C(71) = -134.0(5)$, $C(7)-C(6)-O(61)-C(61) = 81.1(5)$, $C(6)-C(5)-O(51)-C(51) = -112.0(5)$ and $C(8)-C(9)-O(91)-C(91) = 99.5(7)^\circ$. The ethoxy-carbonyl and nitromethyl groups are slightly twisted from the chain; the pertinent torsion angles are: $C(4)-C(3)-C(31)-O(31) = 5.0(7)$, $C(4)-C(3)-C(31)-O(32) = -176.1(6)$ and $C(5)-C(4)-C(41)-N(41) = 87.1(6)^\circ$. The torsion angle $C(1)-C(2)-C(3)-C(4) = -4.2(9)^\circ$.

The Newman projections corresponding to the C-C bonds of the main nonene chain and the C(4)-C(41) bond are shown in Fig. 2. According to the Klyne & Prelog (1960) rules the configurations around the chiral centres C(8), C(7), C(6), C(5) and C(4) are *R,R,R,S* and *S*, respectively, in accordance with the *D-glycero-D-manno* constitution.

The molecule has an intramolecular hydrogen bond between the N and O atoms of the amino and carbonyl groups: $N(21)\cdots O(32)$ 2.664(7) Å, $HN(21)\cdots O(32)$ 1.786 Å and $N(21)-HN(21)\cdots O(32)$ 134.7°. This confirms the chelate structure characteristic of these compounds (Vega, López-Castro & Márquez, 1981, 1983). The packing of the molecules is governed only by van der Waals contacts (Fig. 3).

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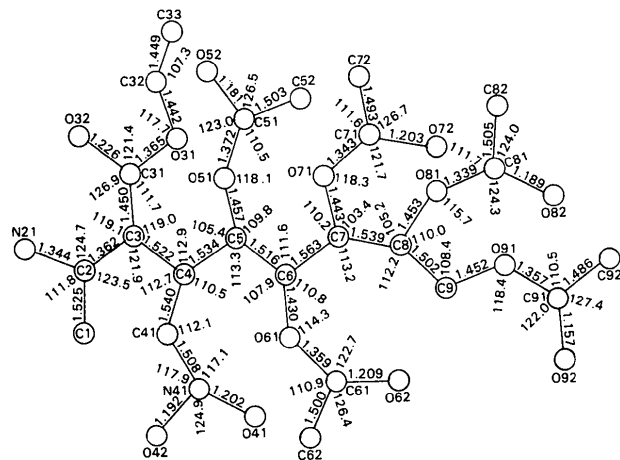


Fig. 1. View of the molecule with atom numbering, bond lengths (Å) and angles ($^\circ$); e.s.d.'s are 0.009–0.012 Å and 0.5–0.8 $^\circ$.

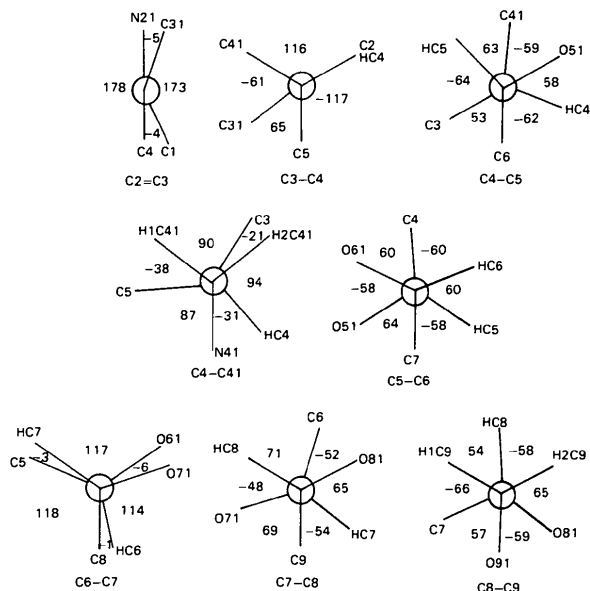


Fig. 2. Some Newman projections. Torsion angles in $^\circ$; e.s.d.'s are in the range 0.4–0.9 $^\circ$ (excluding those involving H atoms).

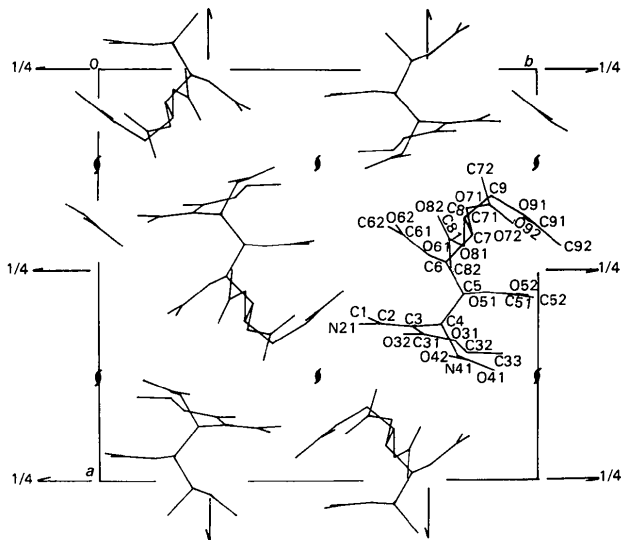


Fig. 3. Packing of the molecules viewed down *c*.

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4-Oxatetracyclo[9.2.1.0^{2,10}.0^{3,8}]tetradec-3(8)-ene-5-spiro-4'-tricyclo[5.2.1.0^{2',6'}]decan-3'-one, C₂₂H₂₈O₂

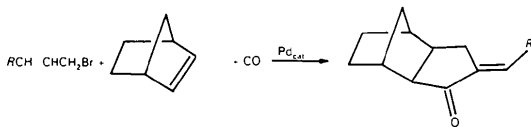
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Abstract. $M_r = 324.46$, monoclinic, $P2_1/c$, $a = 13.410$ (2), $b = 10.840$ (2), $c = 12.444$ (3) Å, $\beta = 98.42$ (4)°, $Z = 4$, $V = 1789.4$ (6) Å³, $D_x = 1.20$ g cm⁻³, Ni-filtered Cu K α radiation, $\lambda = 1.5418$ Å, $\mu = 5.49$ cm⁻¹, $F(000) = 704$, room temperature, $R = 0.060$, 1822 observed reflections. The six-membered ring shows a conformation near to a half chair, while the five-membered rings have envelope conformations. Ring distances C(1)–O(1) [1.381 (4) Å] and C(13)–O(1) [1.459 (4) Å] indicate some conjugation with the double bond, even though this bond [C(1)–C(10) 1.329 (5) Å] is not longer than normal.

Introduction. Sequential olefin and carbon monoxide insertion into a Pd–C bond, obtained from oxidative addition of allylic bromides $RCH=CHCH_2Br$ to Pd⁰ complexes, leads to five-carbon-atom ring closure followed by hydrogen elimination. In this way a catalytic reaction can be achieved according to the following scheme (Amari, Catellani & Chiusoli, 1984):



When $R = H$, however, the product is found in the form of a spirocyclic dimer, which easily crystallizes from 95% ethanol, m.p. 362–363 K.

Its structure was deemed worth studying because of the high degree of regio- and stereoselectivity of the reaction.

Experimental. D_m not determined. Colourless prism $0.11 \times 0.15 \times 0.62$ mm. Siemens AED single-crystal

diffractometer; General Automation Jumbo 220 computer. Cell parameters by least-squares fit of 23 automatically centred reflections ($15.4 \leq \theta \leq 48.9^\circ$). Intensity data with a modified version (Belletti, Uguzzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One check reflection every 50 counts, no significant decay. $2\theta_{\max} = 140^\circ$. $-16 \leq h \leq 16$, $0 \leq k \leq 13$, $0 \leq l \leq 15$. 3616 reflections collected, 3464 unique, $R_{\text{int}} = 0.0114$, 1822 observed at $2\sigma(I)$ level. Direct methods with *SHELX76* (Sheldrick, 1976) which was employed throughout the refinement procedure. H atoms (from ΔF map) isotropic, rest anisotropic, block-matrix least squares, $\sum w(\Delta F)^2$ minimized, $R = 0.060$, $R_w = 0.064$,* $w = 1.0/(\sigma^2 F + 0.001745 F^2)$, 130 and 200 parameters refined in the last cycles. $\Delta\rho_{\max} 0.29$ e Å⁻³. $(\Delta/\sigma)_{\max} 0.76$. Scattering factors of *SHELX76*. All calculations performed on a Gould SEL 32/77 computer.

Discussion. Atomic parameters are given in Table 1, bond distances and angles in Table 2. A drawing of the molecule is given in Fig. 1.

The structure of the compound, suggested by its elemental analysis and spectral data, is confirmed by X-ray analysis.

The six-membered ring adopts a conformation which is near to a half chair, leaving the C(12) out-of-plane of the remaining atoms of the ring by 0.66 (5) Å [0.16 (1) Å is the maximum out-of-plane distance for the five atoms of the ring plane]. This ring is rotated by 72.2 (2)° with respect to the spiro ring plane.

* Lists of structure factors, anisotropic thermal parameters, dihedral angles between planar parts and H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39566 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.