

This is the first example of a less twisted (30°), biologically active colchinoid having a conformation similar to the one proposed for the colchicine-tubulin complex (Detrich *et al.*, 1981).

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Structure of Ethyl 2-Chloro-4-methyl-6-(1-pyrrolidiny)benzoate

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Abstract. $C_{14}H_{18}ClNO_2$, $M_r = 267.7$, orthorhombic, $Pbca$, $a = 10.571$ (3), $b = 12.081$ (5), $c = 21.384$ (6) Å, $V = 2731$ Å³, $Z = 8$, $D_x = 1.30$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.59$ cm⁻¹, $F(000) = 1136$, $T = 293$ K, $R = 0.0357$ for 716 observed reflections. In molecules of the title compound the ester substituent is forced from conjugation with the aromatic ring and nitrogen lone pair by steric interaction with the adjacent chlorine.

Introduction. The selective preparation of highly functionalized vinylogous urethanes (Schlessinger, Doss & Richardson, 1986) has attracted widespread interest over the years, and such substances have a variety of applications in agriculture and medicine.

Our interest in the stereoelectronic effects of related enamines (Natale, 1982) and vinylogous imidates (Natale, McKenna, Niou, Borth & Hope,

1985) has led us to examine the solid-state structure of the title compound. The title compound is readily available by the phosphorus-oxochloride-promoted dimerization of enamines (Harris, Huppertz & Phillips, 1975). We have also observed that the title compound is produced as a by-product in the preparation of ethyl 3,5-dimethylisoxazolecarboxylate (McMurry, 1973) when $POCl_3$ is used to dehydrate nitroethane to the nitrile oxide in the presence of an enamine (Quincy & Natale, 1985).

Experimental. The title compound was isolated as a by-product of the nitrile oxide cycloaddition of the pyrrolidine enamine of ethyl acetoacetate (McMurry, 1973; Quincy & Natale, 1985). Suitable crystals, $0.45 \times 0.25 \times 0.3$ mm, were obtained by slow evaporation from a 1:1 mixture of ethanol and ethyl acetate. The data were collected on a Nicolet R3/m diffractometer by the ω -scan technique (Campana, Shepard & Litchman, 1980) using graphite-

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monochromatized Mo K α radiation. The measured intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. Cell constants were determined by a least-squares fitting of setting angles of the diffractometer from 16 reflections between 12 and 24° in 2θ . 1048 reflections up to $(\sin\theta)/\lambda = 0.42 \text{ \AA}^{-1}$ were measured. The range of hkl values was $0 < h < 9$, $0 < k < 10$, $0 < l < 18$; three standard reflections (515, 206 and 125) were monitored throughout the experiment and showed less than 2% variation in intensity. 869 unique reflections, with 716 with $F > 3\sigma(F)$, were observed.

The structure was solved with *SHELXTL* (Sheldrick, 1984) using direct methods. It was refined by full-matrix least squares on F^2 with anisotropic parameters for all non-H atoms. All H atoms were restricted to N—H, O—H and C—H distances of 0.96 Å and their thermal parameters set at $1.2U_{\text{eq}}$ of the associated C atom. 166 parameters were refined, and the final R values were $R = 0.0357$ and $wR = 0.0398$ with $w = 1/[\sigma^2(F) + g(F^2)]$ and $g = 0.00062$. The largest peaks in the final Fourier difference synthesis were 0.17 and -0.18 e \AA^{-3} , $\Delta/\sigma = 0.013$ (average). The goodness of fit was 1.602. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the thermal ellipsoids along with the atom-numbering scheme. The atomic coordinates and the isotropic temperature factors for all non-H atoms are shown in Table 1, and the bond lengths and bond angles are listed in Table 2.*

* 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 51953 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

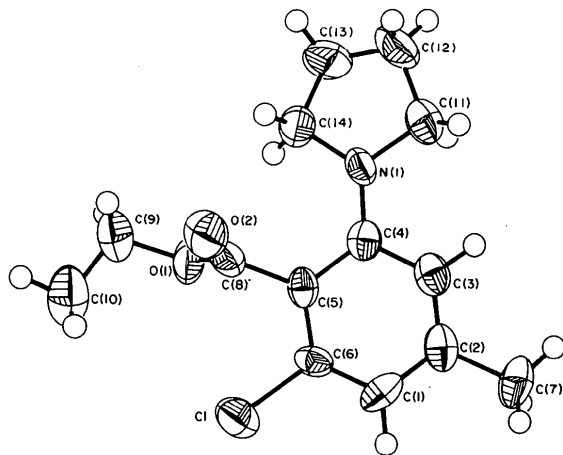


Fig. 1. Structure of ethyl 2-chloro-4-methyl-6-(1-pyrrolidinyl)benzoate.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

Estimated standard deviations in the least significant digits are given in parentheses.

	x	y	z	U_{iso}^*
Cl	2792 (1)	976 (1)	1767 (1)	74 (1)
C(1)	2035 (5)	-726 (5)	1054 (2)	57 (2)
C(2)	1171 (7)	-1306 (4)	701 (2)	53 (2)
C(3)	-44 (6)	-935 (4)	658 (2)	54 (2)
C(4)	-456 (5)	37 (4)	960 (2)	45 (2)
C(5)	438 (5)	662 (3)	1298 (2)	45 (2)
C(6)	1652 (5)	230 (4)	1342 (2)	48 (2)
C(7)	1547 (5)	-2340 (4)	352 (2)	79 (2)
C(8)	201 (4)	1820 (4)	1526 (3)	53 (2)
C(9)	-89 (5)	2963 (5)	2439 (3)	94 (3)
C(10)	1117 (6)	3442 (4)	2610 (3)	108 (3)
C(11)	-2633 (4)	-319 (4)	581 (2)	63 (2)
C(12)	-3868 (4)	283 (4)	676 (3)	85 (2)
C(13)	-3733 (4)	796 (4)	1304 (3)	87 (3)
C(14)	-2351 (4)	1115 (4)	1339 (2)	60 (2)
N(1)	-1695 (4)	353 (3)	915 (1)	50 (1)
O(1)	119 (3)	1866 (2)	2149 (2)	67 (1)
O(2)	96 (3)	2593 (3)	1188 (2)	73 (1)

* The equivalent isotropic U for anisotropic atoms is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (Å) and angles (°)

Estimated standard deviations in the least significant digits are given in parentheses.

Cl—C(6)	1.757 (5)	C(11)—C(12)	1.509 (7)
C(1)—C(2)	1.376 (8)	C(12)—C(13)	1.485 (8)
C(1)—C(6)	1.370 (7)	C(13)—C(14)	1.513 (6)
C(2)—C(3)	1.363 (9)	C(8)—O(1)	1.336 (8)
C(2)—C(7)	1.509 (6)	C(8)—O(2)	1.186 (7)
C(3)—C(4)	1.409 (7)	C(9)—C(10)	1.447 (8)
C(4)—C(5)	1.409 (7)	C(9)—O(1)	1.479 (7)
C(4)—N(1)	1.368 (6)	C(5)—C(6)	1.389 (7)
C(5)—C(8)	1.503 (7)	N(1)—C(11)	1.466 (6)
N(1)—C(14)	1.467 (5)		
C(1)—C(2)—C(3)	119.7 (5)	C(4)—C(5)—C(8)	123.6 (5)
C(1)—C(2)—C(7)	121.2 (5)	C(6)—C(5)—C(8)	118.7 (4)
C(2)—C(1)—C(6)	118.6 (5)	Cl—C(6)—C(1)	117.5 (4)
C(3)—C(2)—C(7)	119.1 (5)	Cl—C(6)—C(5)	118.5 (4)
C(2)—C(3)—C(4)	122.2 (5)	C(1)—C(6)—C(5)	124.0 (4)
C(3)—C(4)—C(5)	118.3 (5)	C(4)—N(1)—C(11)	121.8 (4)
C(3)—C(4)—N(1)	119.7 (5)	C(4)—N(1)—C(14)	125.7 (4)
C(5)—C(4)—N(1)	122.0 (4)	C(11)—N(1)—C(14)	109.2 (3)
C(4)—C(5)—C(6)	117.0 (4)	C(11)—C(12)—C(13)	103.9 (4)
N(1)—C(11)—C(12)	104.6 (4)	C(12)—C(13)—C(14)	104.1 (4)
C(13)—C(14)—N(1)	105.4 (4)	C(5)—C(8)—O(1)	112.0 (4)
C(5)—C(8)—O(2)	123.4 (6)	O(1)—C(8)—O(2)	124.6 (5)
O(1)—C(9)—C(10)	109.4 (4)	C(8)—O(1)—C(9)	117.7 (4)

The pyrrolidine ring shows the usual envelope conformation typical of saturated five-membered rings. Four of the five ring atoms are almost coplanar [as defined by the C(11)—N(1)—C(14)—C(13) dihedral angle of $6(1)^\circ$], while the fifth atom [C(12)] lies 0.524 \AA above this plane. The two rings are virtually coplanar; the planar part of the pyrrolidine ring is tilted *versus* the benzene ring by only $5(1)^\circ$.

The deviation from planarity in the benzene ring is very small. The highest deviation of 0.033 \AA is shown

by the C atom [C(5)] that is bound to the ester group. The orientation of the ester group with respect to the benzene ring would be expected to be anti- or synperiplanar because only these two conformations would allow resonance of the carbonyl group with the benzene π system. It is found that the ester group is out of plane by $103 (1)^\circ$ and thus is not stabilized by resonance. This is confirmed by the bond lengths of the carbonyl C to O [C(8)—O(2)] and to the ring C [C(8)—C(5)], which are $1.19 (1)$ and $1.50 (1)$ Å, respectively. Both bond lengths are typical for a C—O double bond and a C—C single bond. The out-of-plane orientation of the ester group with respect to the benzene ring must be due to steric hindrance by the two bulky groups, the pyrrolidine ring and the Cl atom, which are *ortho* to the ester group.

A relatively short bond length of a 1.34 Å is shown by the C(8)—O(1) single bond. In 3-hydroxy-5-phenylisoxazole the C—O single bond showed the same distance (Marongiu, Biagini & Carmas, 1969). C(9) and C(10) have unusually large thermal parameters, and slight positional disorder may explain the unusually short C(9)—C(10) distance of $1.447 (8)$ Å.

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X-ray Structure of a (D-galacto-Pentaacetoxypentyl)pyrazoline

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Abstract. 1-(3,5-Dimethyl-3-nitro-1-pyrazolin-4-yl)-penta-*O*-acetyl-D-galacto-pentitol, $C_{20}H_{29}N_3O_{12}$, $M_r = 503.5$, orthorhombic, $P2_12_12_1$, $a = 14.471 (9)$, $b = 14.518 (3)$, $c = 12.028 (2)$ Å, $V = 2527.0 (1.7)$ Å³, $Z = 4$, $D_x = 1.323$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 0.10$ mm⁻¹, $F(000) = 1064$, room temperature, final $wR = 0.035$ for 1836 observed reflexions. Bond distances and angles are all within the expected ranges. The pyrazoline ring exhibits approximate mirror symmetry and a puckering amplitude of $0.244 (6)$ Å. Torsion angles of the acetoxy groups with the sugar chain range from 33 to 72° . Crystal cohesion is mainly due to van der Waals interactions but there are two intermolecular hydrogen bonds

linking molecules related by screw axes along [100] and [001].

Introduction. The structure determination of 1-(3,5-dimethyl-3-nitro-1-pyrazolin-4-yl)-penta-*O*-acetyl-D-galacto-pentitol was undertaken as part of a continuing research project on C-nucleosides and precursors. The title compound was prepared as an intermediate product in the synthesis of (penta-acetoxypentyl)pyrazoles (III) with the sugar nitroolefins (I) as dipolarophiles. Initially, the cyclo-additions gave the pyrazolines (II), which were aromatized to the pyrazoles (Mancera, Rodriguez, Roffe & Galbis, 1988). The stereochemistry was