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## Key indicators

Single-crystal X-ray study  
T = 190 K  
Mean  $\sigma(C-C)$  = 0.002 Å  
R factor = 0.032  
wR factor = 0.069  
Data-to-parameter ratio = 10.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## (2R,3S,4S,5R)-Methyl 5-cyano-2,3:4,5-di-O-isopropylidene-2,3,4,5-tetrahydropentanoate

The title nitrile, C<sub>13</sub>H<sub>19</sub>NO<sub>6</sub>, a formal oxidation product, was unexpectedly isolated during hydrogenation of an azide precursor in the presence of palladium black.

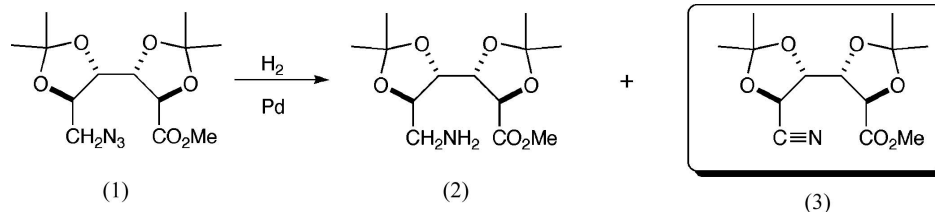
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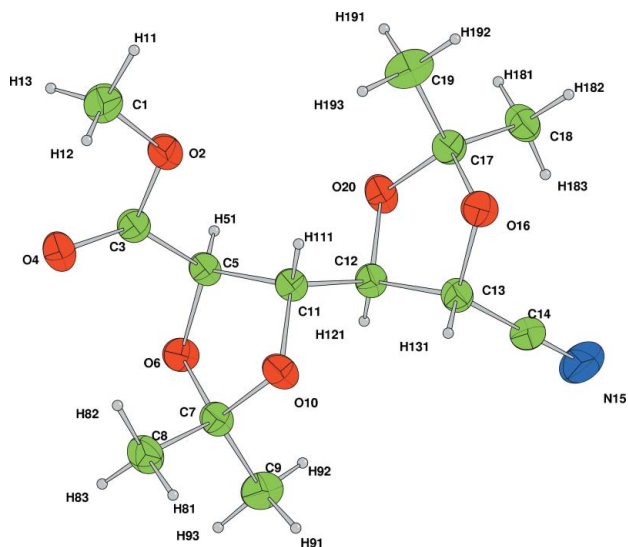
Online 27 July 2005

## Comment

The azide group is synthetically important due to its ability to be reduced under a variety of conditions, thus permitting the controlled introduction of an amine functionality (Scriven & Turnbull, 1988). Further reagents for the reduction of azides to form amines and amides continue to be discovered (Fazio & Wong, 2003); ruthenium(III) has been shown to be an efficient promoter for the formation of amides from azides and thioacids (Shangguan *et al.*, 2003). Although catalytic hydrogenation is a particularly useful method of azide reduction, often providing excellent yields whilst leaving other sensitive functionalities intact, surprising complications are still discovered; thus catalytic reduction of a series of bicyclic azides (RN<sub>3</sub>) resulted in the formation of a number of azoamines (RN=N–NH<sub>2</sub>) arising from simple addition of hydrogen to the terminal nitrogen of the azide (Beacham *et al.*, 1998). When the azido ester (1) was hydrogenated in the presence of palladium black in 1,4-dioxan, the majority of the products were derived from the amino ester (2) (Mayes, Simon *et al.*, 2004; Mayes, Stetz, Watterson *et al.*, 2004; Mayes, Stetz, Ansell & Fleet, 2004). However, significant amounts of the nitrile (3) were also formed during the reduction; this is unexpected, since the formation of the nitrile appears to be a formal oxidation occurring under reducing conditions. Although previous examples of the catalytic decomposition of primary azides to nitriles have been reported (Hayashi *et al.*, 1976; Kappe, 1990; Kotsuki *et al.*, 1997), this is the first example of the formation of a nitrile being formed under hydrogenation conditions. The structure of the unexpected product (3), including the relative configuration at C-5 (atom C13) bearing the nitrile, was firmly established by X-ray crystallographic analysis (Fig. 1); the absolute configuration arises from the use of D-galactose as the original starting material.



The crystal structure of (3) is unexceptional, consisting of layers of molecules lying parallel to the *ab* plane (Fig. 2). One face of the layer is relatively flat and consists of nitrile and



**Figure 1**

The title compound with displacement ellipsoids drawn at the 50% probability level. The H atoms are shown as spheres of arbitrary radius.

methyl groups facing an identical face of the next layer. The other face of the layer is pleated, with the methyl carboxylate groups of one layer interleaving with the corresponding groups on the adjacent face. There are no unexpectedly short *O*-methyl or *N*-methyl contacts.

## Experimental

The azide ester (1) was hydrogenated in the presence of palladium black in 1,4-dioxan (Mayes, Simon *et al.*, 2004) and the title material crystallized from ethyl acetate/hexane.

### Crystal data

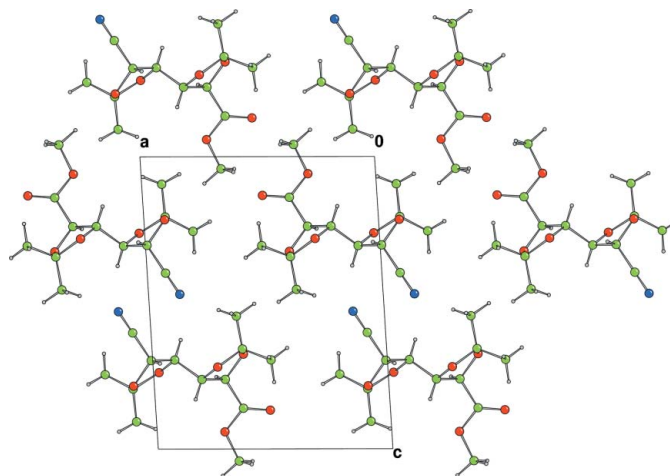
$C_{13}H_{19}NO_6$	$D_x = 1.280 \text{ Mg m}^{-3}$
$M_r = 285.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1417 reflections
$a = 10.4312 (3) \text{ \AA}$	$\theta = 3\text{--}27^\circ$
$b = 5.4469 (1) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 13.0536 (5) \text{ \AA}$	$T = 190 \text{ K}$
$\beta = 93.4825 (10)^\circ$	Block, colourless
$V = 740.31 (4) \text{ \AA}^3$	$0.80 \times 0.50 \times 0.30 \text{ mm}$
$Z = 2$	

### Data collection

Nonius KappaCCD diffractometer	1848 independent reflections
$\omega$ scans	1848 reflections with $I > -3\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.020$
( <i>DENZO/SCALEPACK</i> ;	$\theta_{\text{max}} = 27.5^\circ$
Otwinowski & Minor, 1997)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.87$ , $T_{\text{max}} = 0.97$	$k = -6 \rightarrow 7$
4978 measured reflections	$l = -16 \rightarrow 16$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.15P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
$wR(F^2) = 0.069$	$(\Delta\rho)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
1848 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
182 parameters	Extinction correction: Larson
H-atom parameters constrained	(1970), equation 22
	Extinction coefficient: $1.6 (3) \times 10^2$



**Figure 2**

Packing diagram of (3), viewed along the *b* axis.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—O2	1.456 (2)	C11—C12	1.530 (2)
O2—C3	1.3378 (18)	C12—C13	1.522 (2)
C3—O4	1.1996 (19)	C12—O20	1.4235 (19)
C3—C5	1.521 (2)	C13—C14	1.490 (2)
C5—O6	1.4178 (18)	C13—O16	1.420 (2)
C5—C11	1.523 (2)	C14—N15	1.136 (2)
O6—C7	1.438 (2)	O16—C17	1.443 (2)
C7—C8	1.516 (2)	C17—C18	1.513 (2)
C7—C9	1.510 (2)	C17—C19	1.510 (2)
C7—O10	1.4461 (19)	C17—O20	1.439 (2)
O10—C11	1.4222 (18)		
C1—O2—C3	115.80 (12)	O10—C11—C12	110.98 (12)
O2—C3—O4	123.87 (15)	C11—C12—C13	111.06 (12)
O2—C3—C5	110.05 (12)	C11—C12—O20	110.43 (12)
O4—C3—C5	126.05 (14)	C13—C12—O20	102.95 (11)
C3—C5—O6	112.57 (12)	C12—C13—C14	112.31 (15)
C3—C5—C11	113.63 (13)	C12—C13—O16	103.07 (13)
O6—C5—C11	103.27 (12)	C14—C13—O16	111.41 (13)
C5—O6—C7	109.03 (12)	C13—C14—N15	179.74 (19)
O6—C7—C8	110.98 (15)	C13—O16—C17	107.76 (13)
O6—C7—C9	108.91 (15)	O16—C17—C18	111.13 (16)
C8—C7—C9	112.88 (15)	O16—C17—C19	108.22 (16)
O6—C7—O10	105.41 (13)	C18—C17—C19	113.72 (16)
C8—C7—O10	108.12 (13)	O16—C17—O20	104.95 (13)
C9—C7—O10	110.29 (13)	C18—C17—O20	108.84 (14)
C7—O10—C11	109.36 (12)	C19—C17—O20	109.61 (14)
C5—C11—O10	103.10 (11)	C17—O20—C12	110.26 (12)
C5—C11—C12	111.47 (12)		

In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration is arbitrarily assigned. The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.11) reflect changes in the illuminated volume of the crystal. The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry ( $C-H = 0.93\text{--}0.98 \text{ \AA}$ ) and displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$ ], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure:

*CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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