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## Structure Reports

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# 3,4-Dicyanophenyl 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-glucopyranoside

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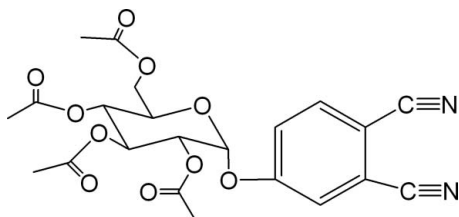
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 Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.009$  Å;  $R$  factor = 0.059;  $wR$  factor = 0.112; data-to-parameter ratio = 8.6.

The title compound,  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_{10}$ , was prepared by the glycosidation method through nitrite displacement on substituted nitrophthalonitrile. The molecule contains a benzene ring, two nitrile groups and an acetyl-protected D-glucose fragment which adopts a chair conformation. The absolute configuration was determined by the use of D-glucose as starting material. All substituents of the protected sugar are in equatorial positions, with the exclusive presence of the  $\alpha$ -anomer. The crystal packing is stabilized by  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{N}$  hydrogen-bonding interactions.

## Related literature

For related literature, see: Alvarez-Mico *et al.* (2006, 2007); Burkhardt *et al.* (2007); Ribeiro *et al.* (2006); Huang *et al.* (2005); Dinçer *et al.* (2004); Berven *et al.* (1990); Ocak *et al.* (2004).



## Experimental

## Crystal data

 $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_{10}$ 
 $M_r = 474.42$ 

 Orthorhombic,  $P2_12_12_1$ 
 $a = 8.175$  (2) Å

 $b = 10.2076$  (10) Å

 $c = 29.562$  (6) Å

 $V = 2466.9$  (8) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 0.10$  mm<sup>-1</sup>
 $T = 295$  (2) K

 $0.6 \times 0.5 \times 0.1$  mm

## Data collection

Bruker P4 diffractometer  
Absorption correction: none  
5277 measured reflections  
2639 independent reflections  
1348 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$   
3 standard reflections  
every 97 reflections  
intensity decay: none

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.059$ 
 $wR(F^2) = 0.112$ 
 $S = 1.06$ 

2639 reflections

307 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.16$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.18$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C5}-\text{H5A}\cdots\text{O2}$	0.93	2.57	3.016 (7)	110
$\text{C11}-\text{H11A}\cdots\text{O6}$	0.98	2.27	2.675 (6)	103
$\text{C12}-\text{H12A}\cdots\text{O8}$	0.98	2.30	2.713 (8)	104
$\text{C13}-\text{H13A}\cdots\text{O1}$	0.98	2.40	2.800 (6)	104
$\text{C20}-\text{H20A}\cdots\text{O10}$	0.97	2.23	2.617 (7)	102
$\text{C5}-\text{H5A}\cdots\text{O6}^i$	0.93	2.41	3.224 (8)	146
$\text{C9}-\text{H9A}\cdots\text{O6}^i$	0.98	2.46	3.346 (7)	151
$\text{C10}-\text{H10A}\cdots\text{O10}^{ii}$	0.98	2.40	3.283 (7)	149
$\text{C15}-\text{H15C}\cdots\text{N1}^{iii}$	0.96	2.58	3.465 (9)	153

 Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .

Data collection: XSCANS (Bruker, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2165).

## References

- Alvarez-Mico, X., Calvete, M. J. F., Hanack, M. & Ziegler, T. (2006). *Tetrahedron Lett.* **47**, 3283–3286.  
Alvarez-Mico, X., Calvete, M. J. F., Hanack, M. & Ziegler, T. (2007). *Carbohydr. Res.* **342**, 440–447.  
Berven, L. A., Dolphin, D. & Withers, S. G. (1990). *Can. J. Chem.* **68**, 1859–1866.  
Bruker (1996). XSCANS. Version 2.2. Bruker AXS Inc., Madison, Wisconsin, USA.  
Bruker (1997). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
Burkhardt, A., Buchholz, A., Görls, H. & Plass, W. (2007). *Acta Cryst.* **E63**, o387–o388.  
Dinçer, M., Ađar, A., Akdemir, N., Ađar, E. & Özdemir, N. (2004). *Acta Cryst.* **E60**, o79–o80.  
Huang, X., Zhao, F., Wang, R.-J., Zhang, F. & Tung, C.-H. (2005). *Acta Cryst.* **E61**, o4384–o4386.  
Ocak, N., Işik, Ş., Akdemir, N., Kantar, C. & Ađar, E. (2004). *Acta Cryst.* **E60**, o361–o362.  
Ribeiro, A. O., Tomé, J. P. C., Neves, M. G. P. M. S., Tomé, A. C., Cavaleiro, J. A. S., Iamamoto, Y. & Torres, T. (2006). *Tetrahedron Lett.* **47**, 9177–9180.

## supporting information

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## 3,4-Dicyanophenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranoside

Yuejing Bin, Fuqun Zhao, Fushi Zhang and Ru-Ji Wang

### S1. Comment

Phthalocyanine has been used in applications based upon their close structural relationship of the phthalocyanines with porphyrin complexes. However, a serious limitation of phthalocyanine is their insolubility. Phthalocyanine compounds are made soluble in a variety of solvents by appropriate peripheral substitution. The synthesis routes of amphiprotic glucose-appended phthalocyanines include the preparation of dicyanophenyl glucopyranoside as precursor and further macrocyclization forming phthalocyanine-glucoconjugates. These glucose-appended phthalocyanines are highly soluble and self-assemble in water (Ribeiro *et al.*, 2006). Aggregation of these phthalocyanine compounds in solution and in the solid state significantly affects the optical properties of such solutions and films. The crystal structure of phthalocyanine is difficult to attain. The structure of the precursors could provide some clues to elucidate the self-assembly of phthalocyanine-glucoconjugates. The precursor of the phthalocyanine-glucoconjugates is the title compound, 3,4-dicyanophenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranoside, which was prepared by the glycosidation method through nitrite displacement on substituted nitrophthalonitrile. The main products were exclusively the thermodynamically favored  $\alpha$ -anomers obtained by reversible S<sub>N</sub>Ar reactions in polar aprotic solvents like Me<sub>2</sub>SO or DMF in the presence of a base (Berven *et al.*, 1990). We report here the crystal structure of the title compound.

In the title compound (Fig. 1) the 2,3,4,6-tetra-*O*-acetyl-*D*-glucopyranoside ring mean plane is oriented exactly perpendicular to that of the phthalocyanine ring. The four acetyl groups with atoms are in equatorial positions (Burkhardt *et al.*, 2007). The crystal structure reveals a <sup>4</sup>C<sub>1</sub> chair conformation for the sugar ring, with the 3,4-dicyanophenyl substituent at C9 in the vertical position, corresponding to the exclusive presence of the  $\alpha$ -anomer of the saccharide, in agreement with the <sup>1</sup>H NMR results (Alvarez-Mico *et al.*, 2006, 2007). The C1≡N1 (1.132 (8) Å) and C2≡N2 (1.130 (8) Å) bond distances are consistent with a triple bond character, and are in good agreement with the literature values (Dinçer *et al.*, 2004; Ocak *et al.*, 2004; Huang *et al.*, 2005).

The crystal structure (Fig. 2) is stabilized by intra- and intermolecular C—H⋯O and C—H⋯N hydrogen bonding interactions (Table 1).

### S2. Experimental

A suspension of anhydrous D-glucose (25 g, 0.15 mol) and anhydrous sodium acetate (12.5 g, 0.15 mol) in 100 mL (1.1 mol) of acetic anhydride was slowly heated to reflux temperature in a round-bottomed flask. Then the heater was removed and the reaction left to reflux. Once the colour of the solution changed from colourless to yellow, the solution was poured onto 1 liter of crushed ice and stirred for 2 h. The solid product was filtered off, washed with water and recrystallized from ethanol to yield colourless crystals of 1,2,3,4,6-penta-*O*-acetyl-*D*-glucopyran (27 g; yield 50%; m. p. 135° C). To a solution of ethylenediamine (1.2 g, 20 mmol) in DMF (10 ml), glacial acetic acid (1.2 g, 20 mmol) was added dropwise, then 1,2,3,4,6-penta-*O*-acetyl-*D*-glucopyran (7.8 g, 20 mmol) was added and the mixture stirred at RT for 5 h. Water (100 ml) was added and the mixture extracted with acetic ester. The organic phase was subsequently

washed with 2 N HCl, saturated NaHCO<sub>3</sub> solution and concentrated *in vacuo*. The compound obtained (5.0 g, 14.4 mmol) and 4-nitrophthalodinitrile (1.8 g, 10.4 mmol) were dissolved in DMF (15 ml), the new roasted anhydrous potassium carbonate (4 g) was added to the solution as three batches in 1 h, and stirred at *R. T.* for 48 h. The mixture was poured into ice water, and the precipitated product was filtered off, washed with water and recrystallized from toluene to give the title compound (2.4 g; yield 50%; m. p. 159–160° C; m/z 497.23 [*M*+Na]<sup>+</sup>).

### S3. Refinement

All hydrogen atoms were generated geometrically with C—H = 0.93–0.97 Å and included in the refinement with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic and methylene C})$  or  $1.5U_{\text{eq}}(\text{C})$  (methyl C). In the absence of significant anomalous dispersion effects Friedel pairs were merged prior to the final refinement. The absolute configuration was determined by the use of D-glucose as starting material.

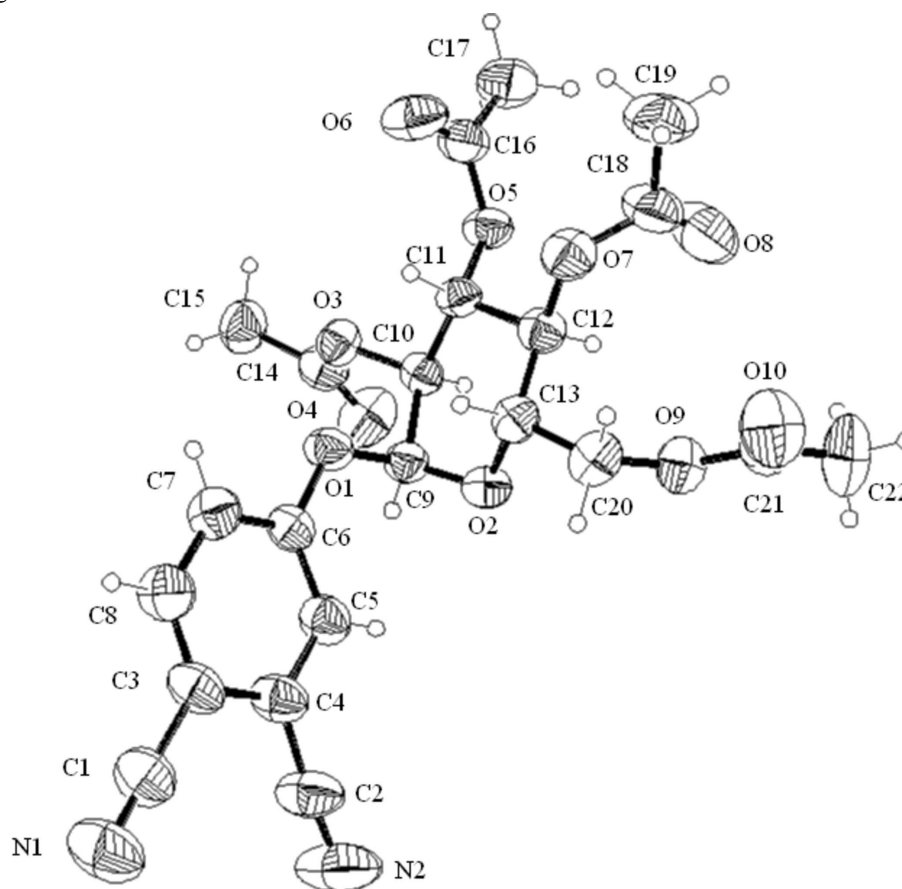
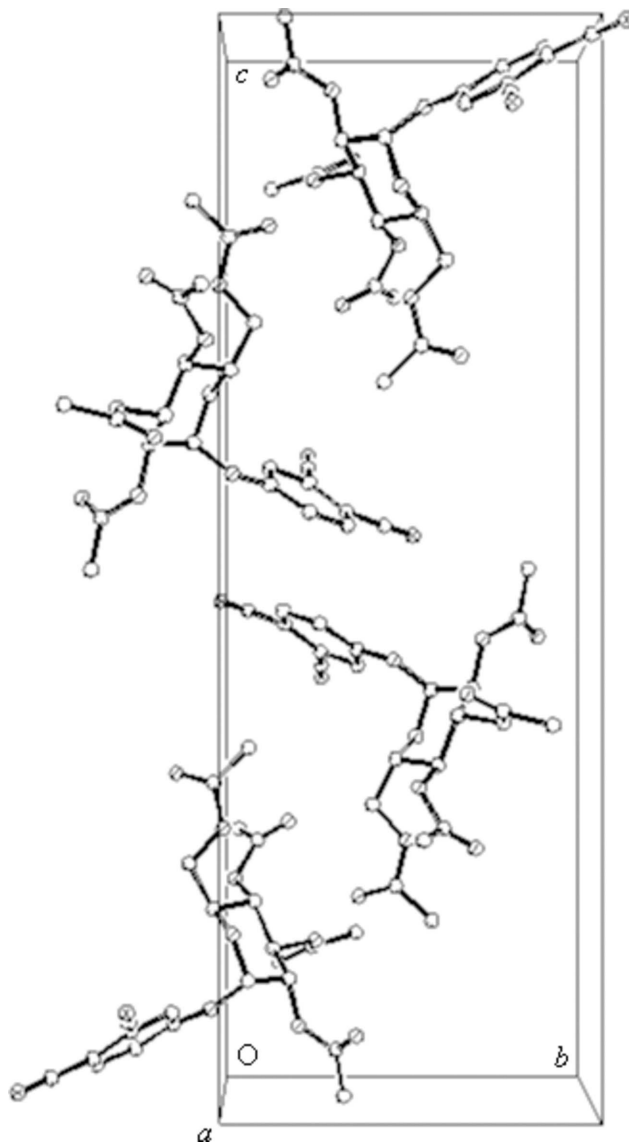


Figure 1

The molecular structure of the title compound with 35% probability ellipsoids and the atom numbering scheme.



**Figure 2**

Packing diagram of the title compound viewed along the  $a$  axis. H atoms are omitted for clarity.

### 3,4-Dicyanophenyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -*D*-glucopyranoside

#### Crystal data

$C_{22}H_{22}N_2O_{10}$

$M_r = 474.42$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.175$  (2) Å

$b = 10.2076$  (10) Å

$c = 29.562$  (6) Å

$V = 2466.9$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 992$

$D_x = 1.277$  Mg m<sup>-3</sup>

Melting point = 159–160 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 46 reflections

$\theta = 2.8$ – $12.4^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 295$  K

Plate, colorless

$0.6 \times 0.5 \times 0.1$  mm

Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.056$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.5^\circ$ , $\theta_{\text{min}} = 2.1^\circ$
Graphite monochromator	$h = -9 \rightarrow 9$
$\omega$ scans	$k = -12 \rightarrow 12$
5277 measured reflections	$l = -35 \rightarrow 35$
2639 independent reflections	3 standard reflections every 97 reflections
1348 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.112$	$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 0.8P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2639 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
307 parameters	$\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.4684 (4)	0.4661 (4)	0.41414 (12)	0.0701 (11)
O2	0.3965 (4)	0.5287 (4)	0.34103 (13)	0.0670 (10)
O3	0.5901 (5)	0.7056 (4)	0.43421 (13)	0.0681 (10)
O4	0.4002 (7)	0.8623 (5)	0.43616 (17)	0.1139 (18)
O5	0.8048 (4)	0.7509 (4)	0.35957 (13)	0.0712 (11)
O6	1.0210 (5)	0.6471 (5)	0.38745 (18)	0.1015 (16)
O7	0.8182 (5)	0.5260 (4)	0.30029 (14)	0.0796 (12)
O8	0.8314 (7)	0.6754 (6)	0.2448 (2)	0.144 (2)
O9	0.4682 (5)	0.5005 (4)	0.24344 (15)	0.0786 (12)
O10	0.5851 (7)	0.3686 (5)	0.19353 (16)	0.1202 (19)
N1	-0.0545 (8)	-0.0194 (6)	0.4681 (2)	0.126 (2)
N2	-0.2037 (8)	0.2687 (7)	0.3913 (3)	0.152 (3)
C1	0.0363 (10)	0.0603 (7)	0.4593 (2)	0.093 (2)
C2	-0.0744 (9)	0.2681 (7)	0.4048 (3)	0.102 (3)
C3	0.1489 (8)	0.1642 (6)	0.4468 (2)	0.0793 (19)
C4	0.0938 (7)	0.2671 (6)	0.4191 (2)	0.0792 (18)

C5	0.1966 (7)	0.3700 (6)	0.4070 (2)	0.0753 (17)
H5A	0.1593	0.4382	0.3889	0.090*
C6	0.3586 (7)	0.3678 (6)	0.4229 (2)	0.0657 (16)
C7	0.4143 (8)	0.2645 (6)	0.4483 (2)	0.0771 (18)
H7A	0.5227	0.2631	0.4578	0.093*
C8	0.3113 (8)	0.1623 (6)	0.4598 (2)	0.086 (2)
H8A	0.3515	0.0919	0.4763	0.103*
C9	0.4184 (7)	0.5689 (5)	0.38547 (19)	0.0619 (15)
H9A	0.3145	0.6038	0.3968	0.074*
C10	0.5487 (6)	0.6784 (5)	0.38800 (19)	0.0591 (15)
H10A	0.5069	0.7580	0.3735	0.071*
C11	0.7051 (6)	0.6337 (5)	0.36433 (18)	0.0585 (14)
H11A	0.7621	0.5676	0.3825	0.070*
C12	0.6682 (7)	0.5818 (5)	0.31787 (19)	0.0654 (16)
H12A	0.6283	0.6519	0.2981	0.078*
C13	0.5412 (7)	0.4711 (5)	0.32161 (18)	0.0634 (15)
H13A	0.5831	0.4044	0.3425	0.076*
C14	0.5095 (9)	0.8067 (6)	0.4539 (2)	0.0795 (19)
C15	0.5743 (8)	0.8297 (6)	0.50044 (19)	0.096 (2)
H15A	0.5151	0.9003	0.5143	0.145*
H15B	0.6882	0.8519	0.4988	0.145*
H15C	0.5611	0.7516	0.5182	0.145*
C16	0.9631 (8)	0.7418 (7)	0.3712 (2)	0.0781 (18)
C17	1.0494 (8)	0.8681 (6)	0.3598 (2)	0.112 (3)
H17A	1.1629	0.8612	0.3678	0.168*
H17B	1.0004	0.9389	0.3763	0.168*
H17C	1.0398	0.8848	0.3279	0.168*
C18	0.8902 (9)	0.5880 (9)	0.2644 (3)	0.102 (3)
C19	1.0554 (7)	0.5319 (8)	0.2574 (3)	0.130 (3)
H19A	1.1076	0.5755	0.2325	0.194*
H19B	1.0462	0.4401	0.2509	0.194*
H19C	1.1196	0.5438	0.2843	0.194*
C20	0.5023 (8)	0.4075 (6)	0.27799 (19)	0.0785 (18)
H20A	0.5939	0.3534	0.2688	0.094*
H20B	0.4081	0.3508	0.2819	0.094*
C21	0.5168 (8)	0.4719 (7)	0.2017 (2)	0.0803 (18)
C22	0.4807 (12)	0.5694 (7)	0.1681 (2)	0.126 (3)
H22A	0.5217	0.5411	0.1393	0.189*
H22B	0.5318	0.6507	0.1763	0.189*
H22C	0.3645	0.5817	0.1662	0.189*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.061 (2)	0.062 (2)	0.088 (3)	-0.007 (2)	-0.002 (2)	0.012 (2)
O2	0.058 (2)	0.065 (2)	0.078 (3)	-0.006 (2)	-0.002 (2)	-0.002 (2)
O3	0.072 (3)	0.069 (2)	0.064 (2)	0.007 (2)	-0.003 (2)	-0.005 (2)
O4	0.117 (4)	0.113 (4)	0.111 (4)	0.050 (4)	-0.010 (3)	-0.029 (3)

O5	0.057 (2)	0.065 (3)	0.091 (3)	-0.009 (2)	-0.005 (2)	0.008 (2)
O6	0.062 (3)	0.089 (3)	0.153 (4)	0.006 (3)	-0.017 (3)	0.007 (3)
O7	0.069 (3)	0.080 (3)	0.089 (3)	0.021 (3)	0.002 (2)	-0.007 (3)
O8	0.106 (4)	0.159 (5)	0.167 (6)	0.018 (4)	0.039 (4)	0.058 (5)
O9	0.092 (3)	0.071 (3)	0.072 (3)	0.011 (3)	0.000 (3)	-0.008 (2)
O10	0.153 (5)	0.099 (4)	0.108 (4)	0.027 (4)	0.019 (4)	-0.021 (3)
N1	0.121 (6)	0.075 (4)	0.181 (7)	-0.021 (4)	0.017 (5)	0.017 (4)
N2	0.077 (4)	0.114 (5)	0.266 (9)	-0.018 (5)	-0.039 (6)	0.042 (6)
C1	0.104 (6)	0.066 (4)	0.109 (5)	-0.010 (5)	0.005 (5)	0.004 (4)
C2	0.071 (5)	0.074 (5)	0.162 (7)	-0.012 (4)	-0.010 (5)	0.016 (5)
C3	0.082 (5)	0.056 (4)	0.101 (5)	-0.009 (4)	0.015 (4)	0.005 (4)
C4	0.071 (4)	0.058 (4)	0.109 (5)	-0.004 (4)	0.004 (4)	0.006 (4)
C5	0.076 (4)	0.063 (4)	0.086 (4)	-0.002 (4)	0.003 (4)	0.010 (4)
C6	0.067 (4)	0.060 (4)	0.070 (4)	-0.005 (3)	0.006 (3)	0.003 (3)
C7	0.079 (4)	0.066 (4)	0.086 (4)	0.003 (4)	-0.005 (4)	0.003 (4)
C8	0.087 (5)	0.063 (4)	0.107 (5)	0.004 (4)	-0.006 (4)	0.013 (4)
C9	0.057 (4)	0.061 (3)	0.068 (4)	-0.005 (3)	-0.001 (3)	0.004 (3)
C10	0.058 (4)	0.052 (3)	0.067 (4)	0.003 (3)	0.006 (3)	0.005 (3)
C11	0.051 (3)	0.054 (4)	0.070 (4)	0.000 (3)	-0.005 (3)	0.005 (3)
C12	0.060 (4)	0.060 (4)	0.076 (4)	0.010 (3)	-0.001 (3)	0.004 (3)
C13	0.065 (4)	0.056 (3)	0.069 (4)	0.007 (3)	-0.005 (3)	0.001 (3)
C14	0.076 (5)	0.071 (4)	0.092 (5)	-0.004 (4)	0.007 (4)	-0.001 (4)
C15	0.114 (6)	0.100 (5)	0.075 (4)	-0.009 (5)	-0.009 (4)	-0.007 (4)
C16	0.062 (4)	0.089 (5)	0.084 (5)	-0.006 (4)	0.005 (4)	-0.003 (4)
C17	0.097 (5)	0.109 (6)	0.130 (6)	-0.048 (5)	-0.012 (5)	0.001 (5)
C18	0.066 (5)	0.126 (8)	0.114 (7)	0.000 (5)	0.022 (5)	-0.002 (6)
C19	0.065 (5)	0.180 (8)	0.144 (7)	0.011 (6)	0.018 (5)	-0.035 (7)
C20	0.090 (5)	0.063 (4)	0.083 (4)	0.002 (4)	-0.013 (4)	-0.002 (4)
C21	0.092 (5)	0.072 (4)	0.077 (5)	-0.016 (4)	0.005 (4)	-0.007 (4)
C22	0.204 (9)	0.103 (5)	0.072 (4)	0.014 (7)	-0.009 (5)	0.010 (5)

*Geometric parameters (Å, °)*

O1—C6	1.371 (6)	C9—C10	1.546 (6)
O1—C9	1.409 (6)	C9—H9A	0.9800
O2—C9	1.388 (6)	C10—C11	1.528 (7)
O2—C13	1.441 (6)	C10—H10A	0.9800
O3—C14	1.355 (7)	C11—C12	1.503 (7)
O3—C10	1.434 (6)	C11—H11A	0.9800
O4—C14	1.182 (7)	C12—C13	1.539 (7)
O5—C16	1.343 (7)	C12—H12A	0.9800
O5—C11	1.454 (6)	C13—C20	1.478 (7)
O6—C16	1.178 (7)	C13—H13A	0.9800
O7—C18	1.369 (8)	C14—C15	1.493 (8)
O7—C12	1.449 (6)	C15—H15A	0.9600
O8—C18	1.168 (9)	C15—H15B	0.9600
O9—C21	1.327 (7)	C15—H15C	0.9600
O9—C20	1.422 (6)	C16—C17	1.509 (8)

O10—C21	1.218 (7)	C17—H17A	0.9600
N1—C1	1.132 (8)	C17—H17B	0.9600
N2—C2	1.130 (8)	C17—H17C	0.9600
C1—C3	1.452 (9)	C18—C19	1.481 (9)
C2—C4	1.439 (9)	C19—H19A	0.9600
C3—C8	1.382 (8)	C19—H19B	0.9600
C3—C4	1.407 (8)	C19—H19C	0.9600
C4—C5	1.392 (7)	C20—H20A	0.9700
C5—C6	1.406 (8)	C20—H20B	0.9700
C5—H5A	0.9300	C21—C22	1.438 (8)
C6—C7	1.371 (7)	C22—H22A	0.9600
C7—C8	1.383 (8)	C22—H22B	0.9600
C7—H7A	0.9300	C22—H22C	0.9600
C8—H8A	0.9300		
C6—O1—C9	118.0 (4)	C13—C12—H12A	110.8
C9—O2—C13	113.1 (4)	O2—C13—C20	110.5 (5)
C14—O3—C10	116.2 (5)	O2—C13—C12	106.4 (4)
C16—O5—C11	117.3 (5)	C20—C13—C12	113.9 (5)
C18—O7—C12	117.4 (5)	O2—C13—H13A	108.6
C21—O9—C20	117.5 (5)	C20—C13—H13A	108.6
N1—C1—C3	178.0 (9)	C12—C13—H13A	108.6
N2—C2—C4	176.4 (10)	O4—C14—O3	122.9 (7)
C8—C3—C4	118.7 (6)	O4—C14—C15	127.0 (7)
C8—C3—C1	121.9 (7)	O3—C14—C15	110.1 (6)
C4—C3—C1	119.4 (6)	C14—C15—H15A	109.5
C5—C4—C3	121.3 (6)	C14—C15—H15B	109.5
C5—C4—C2	119.7 (6)	H15A—C15—H15B	109.5
C3—C4—C2	118.9 (6)	C14—C15—H15C	109.5
C4—C5—C6	118.1 (6)	H15A—C15—H15C	109.5
C4—C5—H5A	121.0	H15B—C15—H15C	109.5
C6—C5—H5A	121.0	O6—C16—O5	123.3 (7)
O1—C6—C7	116.7 (6)	O6—C16—C17	127.2 (6)
O1—C6—C5	122.8 (6)	O5—C16—C17	109.5 (6)
C7—C6—C5	120.6 (6)	C16—C17—H17A	109.5
C6—C7—C8	120.8 (6)	C16—C17—H17B	109.5
C6—C7—H7A	119.6	H17A—C17—H17B	109.5
C8—C7—H7A	119.6	C16—C17—H17C	109.5
C3—C8—C7	120.4 (6)	H17A—C17—H17C	109.5
C3—C8—H8A	119.8	H17B—C17—H17C	109.5
C7—C8—H8A	119.8	O8—C18—O7	124.1 (7)
O2—C9—O1	112.7 (4)	O8—C18—C19	127.0 (9)
O2—C9—C10	110.4 (4)	O7—C18—C19	108.8 (8)
O1—C9—C10	108.1 (4)	C18—C19—H19A	109.5
O2—C9—H9A	108.5	C18—C19—H19B	109.5
O1—C9—H9A	108.5	H19A—C19—H19B	109.5
C10—C9—H9A	108.5	C18—C19—H19C	109.5
O3—C10—C11	107.2 (4)	H19A—C19—H19C	109.5



O3—C10—C9	110.4 (4)	H19B—C19—H19C	109.5
C11—C10—C9	109.8 (4)	O9—C20—C13	112.1 (5)
O3—C10—H10A	109.8	O9—C20—H20A	109.2
C11—C10—H10A	109.8	C13—C20—H20A	109.2
C9—C10—H10A	109.8	O9—C20—H20B	109.2
O5—C11—C12	108.3 (4)	C13—C20—H20B	109.2
O5—C11—C10	105.5 (4)	H20A—C20—H20B	107.9
C12—C11—C10	110.8 (4)	O10—C21—O9	120.9 (7)
O5—C11—H11A	110.7	O10—C21—C22	123.8 (7)
C12—C11—H11A	110.7	O9—C21—C22	115.4 (7)
C10—C11—H11A	110.7	C21—C22—H22A	109.5
O7—C12—C11	107.3 (4)	C21—C22—H22B	109.5
O7—C12—C13	107.9 (4)	H22A—C22—H22B	109.5
C11—C12—C13	109.2 (4)	C21—C22—H22C	109.5
O7—C12—H12A	110.8	H22A—C22—H22C	109.5
C11—C12—H12A	110.8	H22B—C22—H22C	109.5

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C5—H5A...O2	0.93	2.57	3.016 (7)	110
C11—H11A...O6	0.98	2.27	2.675 (6)	103
C12—H12A...O8	0.98	2.30	2.713 (8)	104
C13—H13A...O1	0.98	2.40	2.800 (6)	104
C20—H20A...O10	0.97	2.23	2.617 (7)	102
C5—H5A...O6 <sup>i</sup>	0.93	2.41	3.224 (8)	146
C9—H9A...O6 <sup>i</sup>	0.98	2.46	3.346 (7)	151
C10—H10A...O10 <sup>ii</sup>	0.98	2.40	3.283 (7)	149
C15—H15C...N1 <sup>iii</sup>	0.96	2.58	3.465 (9)	153

Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $-x+1, y+1/2, -z+1/2$ ; (iii)  $x+1/2, -y+1/2, -z+1$ .