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# Synthesis, crystal structure and Hirshfeld surface analysis of tert-butyl N -acetylcarbamate 

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This article reports a practical synthesis of tert-butyl acetylcarbamate, $\mathrm{C}_{7} \mathrm{H}_{13}{ }^{-}$ $\mathrm{NO}_{3}$, from $N$-Boc-thioacetamide and the study of its crystal structure. The reaction proceeds in the presence of natural phosphate as a catalyst, with excellent yield, simple workup and benign environment. The crystal structure was refined using a transferred multipolar atom model. In the crystal, symmetrical pairs of strong $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds connect the molecules into dimers with an $R_{2}^{2}(8)$ ring motif. The interactions between neighbouring dimers are mostly van der Waals, between hydrophobic methyl groups. Hirshfeld surface analysis shows the major contributions to the crystal packing are from $\mathrm{H} \cdots \mathrm{H}(42.6 \%)$ and $\mathrm{O} \cdots \mathrm{H}(26.7 \%)$ contacts.

## 1. Chemical context

Carbamates are widely used as agrochemicals, in the polymer industry, in peptide synthesis (Dibenedetto et al., 2002) and in medicinal chemistry, where many derivatives are specifically designed to make drug-target interactions through their carbamate moiety (Ghosh \& Brindisi, 2015). Here we report the crystal structure of tert-butyl-acetylcarbamate, $\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NO}_{3}$ (I), which we obtained while attempting to synthesize polyfunctional amidines (which are useful in synthetic fields, especially as templates for the development of various novel heterocycles) using heterogeneous catalysis on natural phosphates (NP) - readily available, stable, easy to handle and regenerate, non-toxic and inexpensive catalysts with both basic and acidic active sites (Sebti et al., 1994, 1996).


We followed the procedure described by Lee et al. (1998), but using natural phosphate (NP) as a catalyst instead of Lewis acids such as $\mathrm{ZnCl}_{2}, \mathrm{Et}_{3} \mathrm{O}^{+} \mathrm{BF}_{4}^{-}$and $\mathrm{FeCl}_{2}$. The synthesis was carried out by blending $N$-(t-Boc)thioacetamide with various aminoesters, in the presence of $\mathrm{NEt}_{3}$ and NP . The


Figure 1
View of molecule (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the $50 \%$ probability level.
reaction yielded (I) instead of the desired amidine, i.e. the sulfur atom was substituted by oxygen. In the absence of NP, no product was obtained and the starting materials were recovered.

## 2. Structural commentary

The title compound, $\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NO}_{3}$, (Fig. 1) crystallizes in the space group $P 2_{1} / n$ with one molecule per asymmetric unit. The


Figure 2
View of the molecular dimer linked by a double hydrogen bond.


Figure 3
Molecular packing of (I), viewed along the $a$ axis, showing different orientations of the dimers.

Table 1
Hydrogen-bond geometry ( $\AA^{\circ},{ }^{\circ}$ ).

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C} 4-\mathrm{H} 4 A \cdots \mathrm{O} 2$ | 1.10 | 2.48 | $3.0651(14)$ | 112 |
| $\mathrm{C} 3-\mathrm{H} 3 C \cdots \mathrm{O} 2$ | 1.10 | 2.49 | $2.9928(15)$ | 107 |
| $\mathrm{~N} 1-\mathrm{H} 1 \cdots \mathrm{O}^{\mathrm{i}}$ | $1.01(1)$ | $1.92(1)$ | $2.9285(11)$ | $173(1)$ |

Symmetry code: (i) $-x+1,-y,-z+1$.
skeleton of the molecule is nearly planar if the C3 and C4 atoms are excluded, the root-mean-square deviation from the mean plane being $0.070 \AA$. The $\mathrm{C}_{3} \mathrm{H}_{3}$ and $\mathrm{C} 4 \mathrm{H}_{3}$ methyl groups, located on either side of the mean plane, generate two weak intramolecular hydrogen bonds with the carbonyl O2 atom located in the plane $[\mathrm{C} 3-\mathrm{H} 3 \mathrm{C} \cdots \mathrm{O} 2$ and $\mathrm{C} 4-$ $\mathrm{H} 4 A \cdots \mathrm{O} 2, d(\mathrm{H} \cdots \mathrm{O})=2.49$ and $2.48 \AA$, respectively; Table 1].

## 3. Supramolecular features

In the crystal, a centrosymmetric dimer of molecules is held together by two $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}=\mathrm{C}$ hydrogen bonds, $\mathrm{N} 1-$ $\mathrm{H} 1 \cdots \mathrm{O} 3$ and its symmetry equivalent $[d(\mathrm{H} \cdots \mathrm{O})=1.92$ (1) $\AA$, Table 1], which represent the strongest interactions in the packing and create an inversion-symmetric supramolecular motif of graph-set $R_{2}^{2}(8)$ (Fig. 2). Fig. 3 shows the packing of these dimers. If we consider the Hirshfeld surface around the dimer as a whole, this surface is constituted mainly by hydrophobic ( C and $\mathrm{H}-\mathrm{c}$ ) atoms ( $81 \%$ ) and oxygen atoms ( $13 \%$ ). The interactions between neighbouring dimers are mostly hydrophobic: H-c $\cdots$ H-c between methyl groups ( $43 \%$ ) and $\mathrm{C} \cdots \mathrm{H}-\mathrm{c}$ between carbonyl and methyl groups ( $21 \%$ ). Weak $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds also occur between dimers ( $23 \%$ ). The steric hindrance of the methyl groups causes an offset of the molecules of consecutive dimers, so that no strong hydrogen bond is observed between the dimers. Consequently, the crystal appears to be stabilized by strong hydrogen bonding within the dimers and van der Waals forces without.

## 4. Hirshfeld analysis

MoProViewer (Jelsch et al., 2005) was used to further investigate and visualize the intermolecular interactions in the crystal. The Hirshfeld surface was computed from the model


Figure 4
Two-dimensional fingerprint plots of the major contacts on the Hirshfeld surface.

Table 2
Statistical analysis of intermolecular contacts on the Hirshfeld surface.
$\mathrm{H}-\mathrm{c}$ and $\mathrm{H}-\mathrm{n}$ signify hydrogen atoms bound to C (hydrophobic) and N (hydrophilic), respectively. Reciprocal contacts ( $X \cdots Y$ and $Y \cdots X$ ) are merged. The most prevalent and enriched contacts are highlighted in bold.

| Atom | $\mathrm{H}-\mathrm{n}$ | N | O | $\mathrm{H}-\mathrm{c}$ | C |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $S_{x}(\%)$ | 5.5 | 1.5 | 15.5 | 64.0 | 13.5 |
| $C_{x y}(\%)\left(E_{\mathrm{xy}}\right)$ |  |  |  |  |  |
| $\mathrm{H}-\mathrm{n}$ | $0.4(1.39)$ |  |  |  |  |
| N | $0(0)$ | $0(0)$ |  |  |  |
| O | $5.9(\mathbf{3 . 4 1})$ | $0(0)$ | $0.4(0.16)$ |  |  |
| $\mathrm{H}-\mathrm{c}$ | $4.2(0.59)$ | $2.8(\mathbf{1 . 4 6})$ | $\mathbf{2 0 . 8}(1.04)$ | $\mathbf{4 1 . 6}(0.99)$ |  |
| C | $0.2(0.13)$ | $0.1(0.41)$ | $3.4(0.86)$ | $\mathbf{1 8 . 5}(\mathbf{1 . 1 2})$ | $1.6(1.00)$ |

after multipolar refinement but using electron density from the spherical-neutral atom model. The 2D fingerprint plots (Fig. 4) were generated with Crystal Explorer (Spackman et al., 2021). The most significant contributions for the contacts in the crystal packing (Table 2) are from $\mathrm{H} \cdots \mathrm{H}(46.2 \%), \mathrm{O} \cdots \mathrm{H} /$ $\mathrm{H} \cdots \mathrm{O}(26.7 \%)$ and $\mathrm{C} \cdots \mathrm{H} / \mathrm{H} \cdots \mathrm{C}$ contacts ( $18.7 \%$ ), whereas only $2.8 \%$ are from $\mathrm{N} \cdots \mathrm{H} / \mathrm{H} \cdots \mathrm{N}$ contacts. In the fingerprint plots (Fig. 4), the two reciprocal spikes at a short distance correspond to the $\mathrm{O} \cdots \mathrm{H}-\mathrm{N} / \mathrm{N}-\mathrm{H} \cdots \mathrm{O}$ contacts, i.e. strong hydrogen bonds. The $\mathrm{H} \cdots \mathrm{H}$ contacts show also a small spike on the diagonal line, the shortest distances being $2.447 \AA$ between $\mathrm{H} 2 B$ and $\mathrm{H} 7 A(x+1, y-1, z)$ (Fig. 5a). The intermolecular interactions were further evaluated by computing


Figure 5
(a) Hirshfeld and (b) van der Waals surfaces around molecule (I). The $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}$ and $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds as well as a short $\mathrm{H} \cdots \mathrm{H}$ contacts are shown. The surfaces are coloured according to the electrostatic potential.
the enrichment ratios ( $E$, see Table 2 ) in order to highlight which contacts are over-represented and are likely to represent energetically strong interactions and be the driving force in crystal formation (Jelsch et al., 2014). The enrichment values are obtained as the ratio between the shares of actual contacts $C_{\mathrm{xy}}$ and the random (equiprobable) contacts $R_{\mathrm{xy}}$, the latter calculated as if all types of contacts had the same propensity to occur and are obtained by probability products $\left(R_{\mathrm{xy}}=S_{\mathrm{x}} \cdot S_{\mathrm{y}}\right)$. The H-c. . H-c hydrophobic contacts are the most abundant on the Hirshfeld surface but have a unitary enrichment ratio. The $\mathrm{O} \cdots \mathrm{H}-\mathrm{c}$ and $\mathrm{C} \cdots \mathrm{H}-\mathrm{c}$ weak hydrogen bonds are the next most abundant interactions and are slightly enriched ( $E=1.04$ and 1.12 , respectively). While the strong $\mathrm{O} \cdots \mathrm{H}-\mathrm{n}$ hydrogen bonds in the fourth position represent only $5.9 \%$ of the contact surface, they are the most enriched at $E=3.41$. The Hc $\cdots \mathrm{N}$ contacts are over-represented with $E=1.46$ as the nitrogen atom interacts mostly with methyl groups on both sides of the $s p^{2}$ plane.

The Hirshfeld surface was partitioned into (H-c, C) and (H$\mathrm{n}, \mathrm{O}, \mathrm{N}$ ) atoms' shares in order to analyse the contacts in terms of hydrophobic and hydrophilic interactions. Overall, hydrophobic atoms ( C and $\mathrm{H}-\mathrm{c}$ ) comprise $77.5 \%$ of the surface, but the hydrophobic contacts between these atoms (61.8\%) are not significantly enriched at $E=1.03$. Contacts between hydrophilic atoms ( $22.5 \%$ of the surface), mostly in the form of strong hydrogen bonds, are enriched to $6.7 \%(E=1.32)$ while cross-interactions (between hydrophobic and hydrophilic atoms) are under-represented ( $31.6 \%, E=0.90$ ).

The electrostatic potential was computed on the Hirshfeld and van der Waals surfaces of the molecule (Fig. 5). The two surfaces show similar potential values which are both in the -0.12 to +0.12 e $\AA^{-1}$ range. The regions around the three oxygen atoms are electronegative while the NH group displays positive potential on the surface, followed by the methyl groups which are moderately electropositive.

## 5. Database survey

The Cambridge Structural Database (Version 5.43, November 2021; Groom et al., 2016) was surveyed using ConQuest (version 2020.2.0; Bruno et al., 2002). The eight-membered supramolecular motif, with a double $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}=\mathrm{C}$ hydrogen bond between two amide groups, is quite common, being encountered in 10,336 crystal structures. The amide-ester fragment, encountered in 35 structures, exists in three different near-planar conformations (Fig. 6). Conformation (a) with the syn disposition of $\mathrm{C}=\mathrm{O}$ bonds appears in 23 structures, including the nearest reported analogue of (I),

(a)

(b)

(c)

Figure 6
Conformations of amide-ester derivatives.

Table 3
X-ray fluorescence (XRF) analysis (\%) of natural phosphate.

| $\mathrm{SiO}_{2}$ | $\mathrm{TiO}_{2}$ | $\mathrm{Al}_{2} \mathrm{O}_{3}$ | $\mathrm{Fe}_{2} \mathrm{O}_{3}$ | MgO | CaO | $\mathrm{Na}_{2} \mathrm{O}$ | $\mathrm{K}_{2} \mathrm{O}$ | $\mathrm{MnO}^{2}$ | $\mathrm{P}_{2} \mathrm{O}_{5}$ | $\mathrm{SO}_{3}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 14.17 | 0.058 | 17.51 | 0.530 | 0.245 | 31.66 | 0.319 | 0.113 | 0.016 | 26.18 | 0.060 |

1,1-dimethylethyl- N -propanoylcarbamate (II) (Brodesser et al., 2003). Two different anti conformations, (b) and (c), are adopted by nine and three compounds, respectively. Molecule (I) adopts the anti conformation (b). Compound (I) is the homologue of (II).

## 6. Synthesis and crystallization

Materials and physical methods. All reagents were purchased from Sigma-Aldrich. Reaction progress was monitored by thin-layer chromatography (TLC) on silica-gel plates (Fluka Kieselgel 60 F254). Flash chromatography purifications were performed on Interchim Puriflash (Puriflash columns $50 \mu$ ). X-ray fluorescence analysis was performed on a PANalytical AxiosmAX spectrometer.

Preparation of the catalyst. The NP used in this work comes from the Bofal phosphate deposit in Mauritania. Before being used in catalysis, it underwent quartering treatment, particlesize separation, aqueous dissolution, filtration and evaporation of water, calcination at 1173 K for 1 h and grinding. The fraction of $60-100 \mu \mathrm{~m}$ grain size was used. The nominal chemical compositions of this phosphate were given by X-ray fluorescence (XRF) analysis. The total amount of the natural inorganic components was $90.86 \%$ (Table 3). The rest was mainly organic matter, as indicated by the weight loss on combustion, which amounted to $10.43 \%$.

Preparation of tert-butyl acetylcarbamate (I). It should be noted that compound (I) was prepared in our attempt to synthesize polyfunctional amidines, which are useful in synthetic fields, especially as a template for the development of various new heterocycles. In the preparation, we used the same operating conditions as Lee et al. (1998), substituting NP as the catalyst for a Lewis acid. To a solution of $N$-(tBoc)thioacetamide ( $87.6 \mathrm{mg} ; 0.5 \mathrm{mmol}$ ), the hydrochloride salt of an amino ester ( 0.5 mmol ) and triethylamine $(1.65 \mathrm{mmol})$ in a dry solvent $(10 \mathrm{~mL}), \mathrm{NP}(87.6 \mathrm{mg})$ was added with stirring. The reaction was stirred for 30 min at room temperature. The mixture was filtered through a pad of celite. The residue was purified by Interchim Puriflash (Puriflash columns $50 \mu$ ) using a cyclohexane/ethyl acetate eluent system, to yield crystalline (I) in a very high yield ( $\geq 95 \%$ ). We have tested this reaction with various solvents (THF, $\mathrm{CH}_{3} \mathrm{CN}$ and DMF) and hydrochlorides of different amino esters, viz. glycine ethyl ester, L-valine methyl ester, L-alanine ethyl ester and L-phenylalanine methyl ester. N -(Boc)thioacetamide was prepared as described in the literature (Lee et al., 1998).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. A least-squares refinement, based
on $|F|^{2}$ of all reflections, was carried out with the program MoPro (Jelsch et al., 2005) using the ELMAM2 electrondensity database (Domagała et al., 2012). In this approach, scale factors, atomic positions and displacement parameters for all atoms were varied, but a multipolar charged-atom model was applied until convergence. The $\mathrm{H}-X$ distances were constrained to the standard values in neutron diffraction studies (Allen \& Bruno, 2010). The anisotropic displacement parameters of hydrogen atoms were constrained to the values obtained from the SHADE3 server (Madsen \& Hoser, 2014). Two subsets of the molecule ( $O$-t-butyl moiety and the rest of the molecule) were used as input to the SHADE3 program to obtain better estimations of the $U_{\text {ani }}(\mathrm{H})$ displacement parameters. The use of a transferred multipolar atom model allowed the reduction of $R(F)$ to $4.6 \%$ and $w R_{2}\left(F^{2}\right)$ to $7.2 \%$, compared to $6.1 \%$ and $11.8 \%$, respectively, for the neutralspherical atom model, as refined in MoPro. The r.m.s. residual electron density was likewise reduced from 0.042 to $0.034 \mathrm{e}^{-3}$.

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Table 4
Experimental details.

| Crystal data |  |
| :--- | :--- |
| Chemical formula | $\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NO}_{3}$ |
| $M_{\mathrm{r}}$ | 159.18 |
| Crystal system, space group | Monoclinic, $P 2_{1} / n$ |
| Temperature $(\mathrm{K})$ | 293 |
| $a, b, c(\AA)$ | $6.0404(6), 8.6114(7), 17.6110(17)$ |
| $\beta\left({ }^{\circ}\right)$ | $98.771(9)$ |
| $V\left(\AA^{3}\right)$ | $905.35(15)$ |
| $Z$ | 4 |
| Radiation type | Mo $\mathrm{K} \alpha$ |
| $\mu\left(\mathrm{mm}^{-1}\right)$ | 0.09 |
| Crystal size $(\mathrm{mm})$ | $0.15 \times 0.1 \times 0.08$ |
|  |  |
| Data collection |  |
| Diffractometer | Bruker Kappa CCD |
| Absorption correction | - |
| No. of measured, independent and | $2405,2059,1627$ |
| $\quad$ observed $[I>2 \sigma(I)]$ reflections |  |
| $R_{\text {int }}$ | 0.035 |
| $(\text { sin } \theta / \lambda)_{\text {max }}\left(\AA \AA^{-1}\right)$ | 0.650 |
|  |  |
| Refinement |  |
| $R\left[F^{2}>2 \sigma\left(F^{2}\right)\right], w R\left(F^{2}\right), S$ | $0.034,0.072,1.00$ |
| No. of reflections | 2059 |
| No. of parameters | 139 |
| No. of restraints | 31 |
| H -atom treatment | Only H-atom coordinates refined |
| $\Delta \rho_{\text {max }}, \Delta \rho_{\text {min }}\left(\mathrm{e} \AA \AA^{-3}\right)$ | $0.16,-0.17$ |

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXS97 (Sheldrick, 2008) and MoPro (Jelsch et al., 2005).
d'Action Culturelle (SCAC) de l'Ambassade de France en Mauritanie for financial support.

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## supporting information

# Synthesis, crystal structure and Hirshfeld surface analysis of tert-butyl $N$-acetylcarbamate 

Aly Dawa El Mestehdi, Moctar Abba, Mohamed Lemine El Housseine, Abderrahmane Ould Hadou, Aliou Hamady Barry, Brahim Ould Elemine, Christian Jelsch and Mohamed Gaye<br>\section*{Computing details}

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: MoPro (Jelsch et al., 2005); molecular graphics: MoPro (Jelsch et al., 2005); software used to prepare material for publication: MoPro (Jelsch et al., 2005).

## tert-Butyl $N$-acetylcarbamate

## Crystal data

$\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NO}_{3}$
$M_{r}=159.18$
Monoclinic, $P 2_{1} / n$
Hall symbol: -P 2 yn
$a=6.0404$ (6) Å
$b=8.6114$ (7) $\AA$
$c=17.6110$ (17) $\AA$
$\beta=98.771(9)^{\circ}$
$V=905.35(15) \AA^{3}$
$Z=4$

## Data collection

Bruker Kappa CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD scans
2405 measured reflections
2059 independent reflections

## Refinement

Refinement on $F^{2}$
Least-squares matrix: full
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.034$
$w R\left(F^{2}\right)=0.072$
$S=1.00$
2059 reflections
139 parameters
31 restraints
$F(000)=344$
$D_{\mathrm{x}}=1.168 \mathrm{Mg} \mathrm{m}^{-3}$
Mo $K \alpha$ radiation, $\lambda=0.71073 \AA$
Cell parameters from 4200 reflections
$\theta=2.4-28.6^{\circ}$
$\mu=0.09 \mathrm{~mm}^{-1}$
$T=293 \mathrm{~K}$
Block, colorless
$0.15 \times 0.1 \times 0.08 \mathrm{~mm}$

1627 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.035$
$\theta_{\text {max }}=27.5^{\circ}, \theta_{\text {min }}=2.6^{\circ}$
$h=-7 \rightarrow 7$
$k=0 \rightarrow 11$
$l=0 \rightarrow 22$

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined
$w=1 /\left[4.4^{*} \sigma^{2}\left(F_{0}{ }^{2}\right)\right]$
$(\Delta / \sigma)_{\max }=0.002$
$\Delta \rho_{\text {max }}=0.16$ e $\AA^{-3}$
Extinction correction: Isotropic Gaussian
$\Delta \rho_{\min }=-0.17$ e $\AA^{-3}$
Extinction coefficient: 0.51132

## Special details

Refinement. Refinement of $\mathrm{F}^{2}$ against reflections. The threshold expression of $\mathrm{F}^{2}>2 \operatorname{sigma}\left(\mathrm{~F}^{2}\right)$ is used for calculating Rfactors $(\mathrm{gt})$ and is not relevant to the choice of reflections for refinement. R -factors based on $\mathrm{F}^{2}$ 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 ( $\boldsymbol{A}^{2}$ )

|  | $x$ | $y$ | $z$ | $U_{\mathrm{iso}} * / U_{\mathrm{eq}}$ |
| :--- | :--- | :--- | :--- | :--- |
| O1 | $0.38211(11)$ | $0.355396(15)$ | $0.40123(4)$ | $0.05484(14)$ |
| O2 | $0.63464(12)$ | $0.29985(8)$ | $0.32233(4)$ | $0.06801(17)$ |
| O3 | $0.73388(12)$ | $-0.08048(8)$ | $0.46784(4)$ | $0.06574(16)$ |
| N1 | $0.57479(13)$ | $0.14069(8)$ | $0.42246(5)$ | $0.05046(16)$ |
| H1 | $0.474(2)$ | $0.1271(16)$ | $0.4629(7)$ | 0.08754 |
| C5 | $0.54053(15)$ | $0.27070(10)$ | $0.37571(5)$ | $0.04754(17)$ |
| C6 | $0.73373(15)$ | $0.02549(11)$ | $0.42216(6)$ | $0.05121(18)$ |
| C1 | $0.30097(15)$ | $0.50254(10)$ | $0.36327(6)$ | $0.05446(18)$ |
| C7 | $0.89889(19)$ | $0.03248(14)$ | $0.36770(7)$ | $0.0716(3)$ |
| H7A | $1.0210(16)$ | $-0.0607(14)$ | $0.3829(8)$ | 0.10454 |
| H7B | $0.9899(18)$ | $0.1427(14)$ | $0.3755(9)$ | 0.11089 |
| H7C | $0.818(2)$ | $0.0353(17)$ | $0.3076(6)$ | 0.11503 |
| C4 | $0.18467(19)$ | $0.46831(14)$ | $0.28329(7)$ | $0.0740(3)$ |
| H4A | $0.3039(17)$ | $0.4270(16)$ | $0.2468(6)$ | 0.10880 |
| H4B | $0.106(2)$ | $0.5761(14)$ | $0.2597(8)$ | 0.11611 |
| H4C | $0.0505(16)$ | $0.3836(15)$ | $0.2852(8)$ | 0.11411 |
| C3 | $0.4904(2)$ | $0.61607(13)$ | $0.36559(8)$ | $0.0758(2)$ |
| H3A | $0.578(2)$ | $0.6274(16)$ | $0.4245(8)$ | 0.11708 |
| H3B | $0.419(2)$ | $0.7310(12)$ | $0.3505(9)$ | 0.12094 |
| H3C | $0.6142(17)$ | $0.5881(15)$ | $0.3283(7)$ | 0.10779 |
| C2 | $0.1345(2)$ | $0.55587(15)$ | $0.41419(8)$ | $0.0822(3)$ |
| H2A | $0.0073(16)$ | $0.4648(14)$ | $0.4127(9)$ | 0.11714 |
| H2B | $0.054(2)$ | $0.6620(14)$ | $0.3891(8)$ | 0.12347 |
| H2C | $0.232(2)$ | $0.5828(17)$ | $0.4703(7)$ | 0.12492 |
|  |  |  |  |  |

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

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| O1 | $0.0660(4)$ | $0.0489(4)$ | $0.0515(4)$ | $0.0085(3)$ | $0.0150(3)$ | $0.0127(3)$ |
| O2 | $0.0786(5)$ | $0.0669(5)$ | $0.0644(5)$ | $0.0061(4)$ | $0.0300(4)$ | $0.0184(3)$ |
| O3 | $0.0745(5)$ | $0.0484(4)$ | $0.0771(5)$ | $0.0077(3)$ | $0.0204(4)$ | $0.0162(3)$ |
| N1 | $0.0599(5)$ | $0.0439(4)$ | $0.0495(5)$ | $0.0021(3)$ | $0.0144(3)$ | $0.0091(3)$ |
| H1 | 0.09872 | 0.08344 | 0.09180 | 0.02741 | 0.05087 | 0.03885 |
| C5 | $0.0539(5)$ | $0.0441(5)$ | $0.0456(5)$ | $-0.0003(4)$ | $0.0107(4)$ | $0.0056(4)$ |
| C6 | $0.0573(5)$ | $0.0430(5)$ | $0.0533(5)$ | $-0.0001(4)$ | $0.0083(4)$ | $0.0024(4)$ |
| C1 | $0.0592(5)$ | $0.0460(5)$ | $0.0551(5)$ | $0.0050(4)$ | $-0.0011(4)$ | $0.0103(4)$ |
| C7 | $0.0720(7)$ | $0.0747(7)$ | $0.0731(7)$ | $0.0168(6)$ | $0.0274(6)$ | $0.0133(6)$ |
| H7A | 0.09887 | 0.10412 | 0.11797 | 0.04100 | 0.04001 | 0.02395 |


| H7B | 0.08822 | 0.09468 | 0.16018 | -0.00028 | 0.05229 | 0.03275 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| H7C | 0.14423 | 0.13621 | 0.06953 | 0.04903 | 0.03193 | 0.00590 |
| C4 | $0.0757(7)$ | $0.0794(8)$ | $0.0597(7)$ | $-0.0079(6)$ | $-0.0129(5)$ | $0.0126(6)$ |
| H4A | 0.12776 | 0.13382 | 0.06263 | 0.00285 | 0.00747 | 0.00354 |
| H4B | 0.11933 | 0.11272 | 0.10174 | 0.01287 | -0.02973 | 0.03707 |
| H4C | 0.09893 | 0.11674 | 0.11538 | -0.03490 | -0.01984 | 0.00269 |
| C3 | $0.0723(7)$ | $0.0514(6)$ | $0.0968(9)$ | $-0.0083(5)$ | $-0.0096(6)$ | $0.0110(6)$ |
| H3A | 0.11467 | 0.09511 | 0.12396 | -0.01659 | -0.03780 | -0.00724 |
| H3B | 0.11702 | 0.05611 | 0.17940 | -0.00332 | -0.01031 | 0.02819 |
| H3C | 0.08755 | 0.09430 | 0.14362 | -0.01523 | 0.02433 | 0.02842 |
| C2 | $0.0844(8)$ | $0.0751(8)$ | $0.0889(9)$ | $0.0249(6)$ | $0.0193(6)$ | $0.0046(7)$ |
| H2A | 0.09735 | 0.11323 | 0.15160 | 0.01562 | 0.05342 | 0.02003 |
| H2B | 0.12561 | 0.09416 | 0.15181 | 0.05340 | 0.02495 | 0.01964 |
| H2C | 0.15392 | 0.13217 | 0.08898 | 0.04922 | 0.01950 | -0.01800 |

Geometric parameters ( $A,{ }^{\circ}$ )

| O1-C5 | 1.3344 (11) | C7-H7A | 1.0950 |
| :---: | :---: | :---: | :---: |
| $\mathrm{O} 1-\mathrm{C} 1$ | 1.4808 (9) | C7-H7B | 1.0950 |
| O2-C5 | 1.1970 (11) | C4-H4C | 1.0950 |
| O3-C6 | 1.2164 (11) | C4-H4A | 1.0950 |
| N1-C5 | 1.3864 (12) | C4-H4B | 1.0950 |
| N1-C6 | 1.3811 (12) | C3-H3C | 1.0950 |
| N1-H1 | 1.013 (8) | C3-H3B | 1.0950 |
| C6-C7 | 1.4868 (15) | C3-H3A | 1.0950 |
| C1-C3 | 1.5009 (14) | $\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 1.0950 |
| C1-C4 | 1.5042 (15) | C2-H2B | 1.0950 |
| C1-C2 | 1.5170 (16) | C2-H2A | 1.0950 |
| C7-H7C | 1.0950 |  |  |
| C5-O1-C1 | 121.38 (6) | H7C-C7-H7B | 104 (1) |
| C5-N1-C6 | 128.22 (7) | H7A-C7- H 7 B | 107.3 (8) |
| C5-N1-H1 | 117.3 (7) | $\mathrm{C} 1-\mathrm{C} 4-\mathrm{H} 4 \mathrm{C}$ | 110.1 (7) |
| C6-N1-H1 | 114.4 (7) | $\mathrm{C} 1-\mathrm{C} 4-\mathrm{H} 4 \mathrm{~A}$ | 111.0 (6) |
| $\mathrm{O} 1-\mathrm{C} 5-\mathrm{O} 2$ | 126.91 (8) | C1-C4-H4B | 107.6 (6) |
| $\mathrm{O} 1-\mathrm{C} 5-\mathrm{N} 1$ | 106.93 (7) | H4C-C4-H4A | 111 (1) |
| $\mathrm{O} 2-\mathrm{C} 5-\mathrm{N} 1$ | 126.15 (7) | $\mathrm{H} 4 \mathrm{C}-\mathrm{C} 4-\mathrm{H} 4 \mathrm{~B}$ | 107.3 (10) |
| O3-C6-N1 | 117.82 (7) | H4A-C4-H4B | 110 (1) |
| O3-C6-C7 | 121.61 (8) | $\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{C}$ | 115.4 (7) |
| N1-C6-C7 | 120.57 (8) | C1-C3-H3B | 108.2 (6) |
| $\mathrm{O}-\mathrm{C} 1-\mathrm{C} 3$ | 110.28 (7) | C1-C3-H3A | 109.8 (7) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 4$ | 109.28 (7) | H3C-C3-H3B | 109 (1) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 2$ | 101.29 (7) | H3C-C3-H3A | 108.3 (10) |
| C3-C1-C4 | 113.48 (8) | H3B-C3-H3A | 105 (1) |
| C3-C1-C2 | 110.99 (9) | $\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 106.5 (7) |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2$ | 110.85 (9) | C1-C2-H2B | 107.8 (8) |
| C6-C7-H7C | 112.4 (7) | C1-C2-H2A | 107.1 (7) |
| C6-C7-H7A | 107.8 (6) | $\mathrm{H} 2 \mathrm{C}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | 109.3 (10) |


| C6-C7-H7B | 109.1 (7) |
| :---: | :---: |
| H7C-C7-H7A | 115.8 (9) |
| O1-C5-N1-C6 | -174.66 (12) |
| $\mathrm{O} 1-\mathrm{C} 5-\mathrm{N} 1-\mathrm{H} 1$ | 4 (1) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{C}$ | 71.1 (8) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~B}$ | -166.1 (9) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~A}$ | -51.6 (9) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 4-\mathrm{H} 4 \mathrm{C}$ | 55.5 (7) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 4-\mathrm{H} 4 \mathrm{~A}$ | -67.8 (7) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 4-\mathrm{H} 4 \mathrm{~B}$ | 172.1 (9) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | 66.4 (7) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | -176.4 (7) |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | -59.4 (7) |
| $\mathrm{O} 2-\mathrm{C} 5-\mathrm{O} 1-\mathrm{C} 1$ | 0.45 (12) |
| $\mathrm{O} 2-\mathrm{C} 5-\mathrm{N} 1-\mathrm{C} 6$ | 5.90 (14) |
| $\mathrm{O} 2-\mathrm{C} 5-\mathrm{N} 1-\mathrm{H} 1$ | -175 (1) |
| O3-C6-N1-C5 | -179.23 (13) |
| $\mathrm{O} 3-\mathrm{C} 6-\mathrm{N} 1-\mathrm{H} 1$ | 2 (1) |
| O3-C6-C7- 77 C | 121.4 (9) |
| O3-C6-C7-H7A | -7.4 (8) |
| O3-C6-C7-H7B | -123.6 (8) |
| N1-C5-O1-C1 | -178.99 (12) |
| N1-C6-C7-H7C | -58.8 (8) |
| N1-C6-C7-H7A | 172.4 (8) |
| N1-C6-C7-H7B | 56.1 (8) |


| $\mathrm{H} 2 \mathrm{C}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | $117(1)$ |
| :--- | :--- |
| $\mathrm{H} 2 \mathrm{~B}-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | $108.8(10)$ |
| $\mathrm{H} 1-\mathrm{N} 1-\mathrm{C} 6-\mathrm{C} 7$ | $-178(1)$ |
| $\mathrm{C} 5-\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 3$ | $-60.18(11)$ |
| $\mathrm{C} 5-\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 4$ | $65.21(11)$ |
| $\mathrm{C} 5-\mathrm{O} 1-\mathrm{C} 1-\mathrm{C} 2$ | $-177.77(12)$ |
| $\mathrm{C} 5-\mathrm{N} 1-\mathrm{C} 6-\mathrm{C} 7$ | $1.01(14)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{C}$ | $-51.9(7)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~B}$ | $70.9(7)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~A}$ | $-174.6(9)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | $-177.8(9)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | $-60.5(7)$ |
| $\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | $56.4(8)$ |
| $\mathrm{H} 4 \mathrm{~A}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3$ | $56(1)$ |
| $\mathrm{H} 4 \mathrm{~A}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2$ | $-179(1)$ |
| $\mathrm{H} 4 \mathrm{~B}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3$ | $-64(1)$ |
| $\mathrm{H} 4 \mathrm{~B}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2$ | $61(1)$ |
| $\mathrm{H} 4 \mathrm{C}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 3$ | $179(1)$ |
| $\mathrm{H} 4 \mathrm{C}-\mathrm{C} 4-\mathrm{C} 1-\mathrm{C} 2$ | $-55(1)$ |
| $\mathrm{C} 3-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{C}$ | $-50.7(7)$ |
| $\mathrm{C} 3-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~B}$ | $66.5(8)$ |
| $\mathrm{C} 3-\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2 \mathrm{~A}$ | $-176.5(8)$ |
| $\mathrm{H} 3 \mathrm{~A}-\mathrm{C} 3-\mathrm{C} 1-\mathrm{C} 2$ | $60(1)$ |
| H3B-C3-C1-C2 | $-55(1)$ |
| H3C-C3-C1-C2 | $-177(1)$ |

Hydrogen-bond geometry ( $A,{ }^{\circ}$ )

| $D — \mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C} 4 — \mathrm{H} 4 A \cdots \mathrm{O} 2$ | 1.10 | 2.48 | $3.0651(14)$ | 112 |
| $\mathrm{C} 3 — \mathrm{H} 3 C \cdots \mathrm{O} 2$ | 1.10 | 2.49 | $2.9928(15)$ | 107 |
| $\mathrm{~N} 1 — \mathrm{H} 1 \cdots \mathrm{O} 3{ }^{\mathrm{i}}$ | $1.01(1)$ | $1.92(1)$ | $2.9285(11)$ | $173(1)$ |

Symmetry code: (i) $-x+1,-y,-z+1$.

