

Short Note

tert-Butyl *N*-Hydroxycarbamate (*N*-Boc-Hydroxylamine)

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Abstract: The X-ray structure of the title compound has been determined for the first time. This features ribbons formed by two parallel chains of molecules joined by C=O...H-N hydrogen bonding, which are then cross-linked by C=O...H-O hydrogen bonds. The structure is compared to those of closely related compounds.

Keywords: X-ray structure; hydrogen bonding; *N*-acylhydroxylamines

1. Introduction

The simple compound *tert*-butyl *N*-hydroxycarbamate or *N*-*tert*-butoxycarbonylhydroxylamine **1** (Figure 1) was first reported in 1959 [1] and has proven to be useful in a number of recent applications, including the generation of *t*-Boc-N=O for use as a Diels Alder dienophile [2]. Such simple multifunctional compounds have the potential to form a wide range of interesting hydrogen bonding patterns in the solid state, and similar compounds such as the corresponding carbamate **2** [3], *N*-pivaloylhydroxylamine **3** [4] and *tert*-butyl carbamate **4** [5,6] have all been reported to show such patterns, as have a range of *N*-acylhydroxylamines such as **5** [7] and **6–9** [8]. We describe here the X-ray structure determination of compound **1**.



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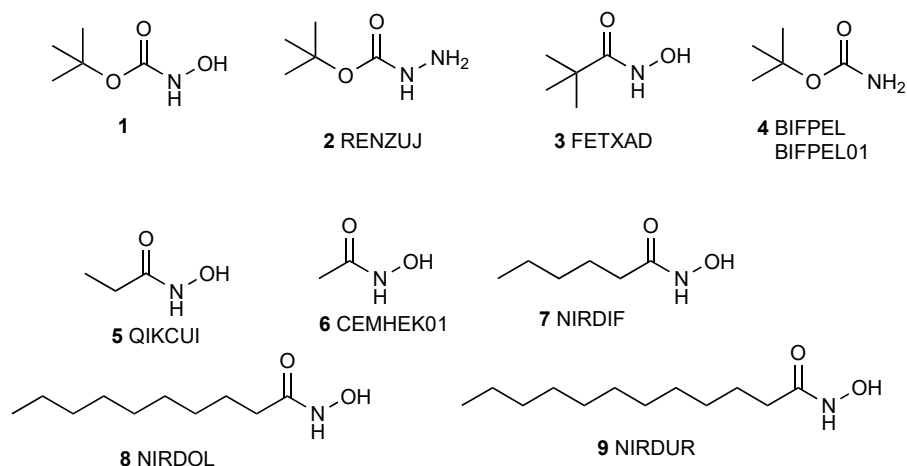


Figure 1. Structure of compound **1** and similar crystallographically characterised compounds with CSD RefCodes.

2. Results

The compound was prepared using a method from the literature [9] involving the reaction of hydroxylamine hydrochloride, potassium carbonate and di-*tert*-butyl dicarbonate. It had physical and NMR data (see Supplementary Materials) in agreement with published values [9]. Crystals suitable for diffraction were obtained by recrystallisation from hexane. The resulting molecular structure (Figure 2) shows fairly conventional bond lengths and angles. The *N*-hydroxycarbamate functionality is quite accurately planar with a torsion

angle O(1)–C(1)–N(1)–(O3) of $+2.1(2)^\circ$. In fact, this is characteristic of the compounds of Figure 1 with none having a corresponding torsion angle above 12° (Table 1).

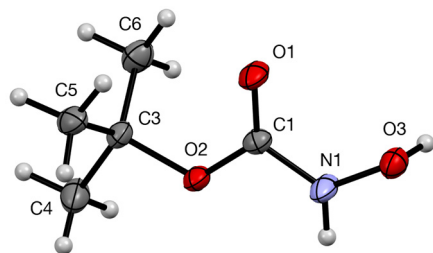


Figure 2. Molecular structure of **1** with anisotropic displacement ellipsoids drawn at 50% probability level and the numbering system used.

Table 1. Torsion angles in **1** and similar compounds.

Compound	Torsion Angle(s) O=C–NH–OH ^a (°)	Ref.
1	+2.1(2)	This work
2	−9.5(3), +10.4(3), −4.5(3), +11.9(3)	[3]
3	−0.6(2)	[4]
5	−8.5(2), −6.5(2), −1.6(2)	[7]
6	−4.8(2), −8.2(2)	[8]
7	−9.1(5)	[8]
8	−8.5(6)	[8]
9	−8.7(5)	[8]

^a O=C–NH–NH₂ for **2**.

However, as expected, it is the pattern of interactions formed by hydrogen bonding that is more interesting. Each carbonyl oxygen is hydrogen bonded to the N–H and O–H of two separate adjacent molecules, resulting in a ribbon structure featuring a series of ten-membered rings (Figure 3, Table 2). The molecules are linked in two parallel chains by C=O⋯H–N bonding and these are then cross-linked by C=O⋯H–O hydrogen bonds, giving a graph set description of $C(4)R^2_3(10)$ [10].

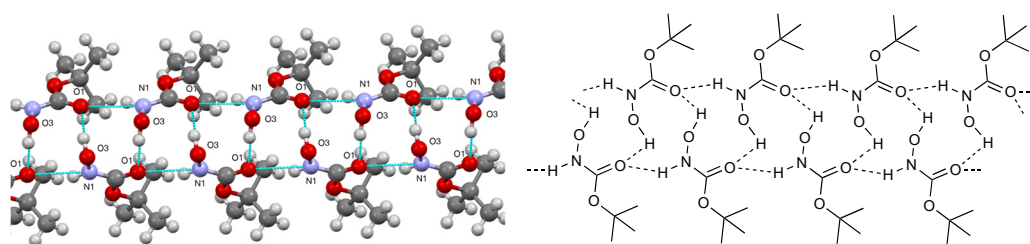


Figure 3. Hydrogen bonding pattern in **1** viewed along the *b*-axis and schematic representation.

Table 2. Hydrogen bonding parameters for **1** (Å, °).

	D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A	Ref.
1	N(1)–H(1)⋯O(1)	0.88(1)	2.17(1)	2.976(1)	152(1)	This work
1	O(3)–H(3)⋯O(1)	0.93(1)	1.87(1)	2.772(1)	161(1)	This work
3	N(1)–H(1)⋯O(1)	0.82(3)	2.01(3)	2.810(2)	164(2)	[4]
3	O(2)–H(2)⋯O(1)	0.91(2)	1.74(2)	2.647(2)	171(2)	[4]

Among the related compounds shown in Figure 1, the structure is most similar to that of *N*-pivaloylhydroxylamine **3** [4]. This also features a ribbon with each carbonyl oxygen hydrogen-bonded to the N–H and O–H of two separate molecules (Figure 4,

Table 2). However, the important distinction is that, while **1** has the two chains of molecules aligned in parallel, in **3**, they are antiparallel, and the structure can be viewed as a series of $R^2_2(10)$ dimers formed by $C=O\cdots H-O$ bonding, which are then joined in the chain by the $C=O\cdots H-N$ bonding, resulting in a first-order network of $C(4)R^2_2(10)$ and a second-order network of $R^2_4(10)$ [10].

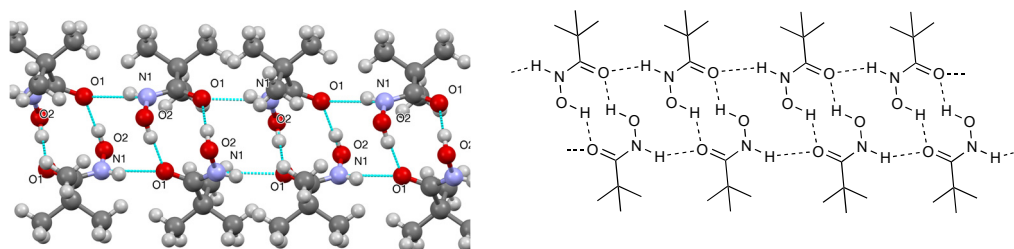


Figure 4. Hydrogen bonding pattern in **3** viewed along the *b*-axis and schematic representation.

Although it is not obvious from Figure 3, the ribbons of hydrogen-bonded molecules of **1** are not planar, but distinctly V-shaped. The angle between the mean planes defined by O(2), C(1), O(1), N(1) and O(3) of molecules on the two sides of the ribbon is $62.62(4)^\circ$. A view of the unit cell along the *a*-axis shows how the hydrogen-bonded chains of molecules are aligned in a zig-zag pattern (Figure 5).

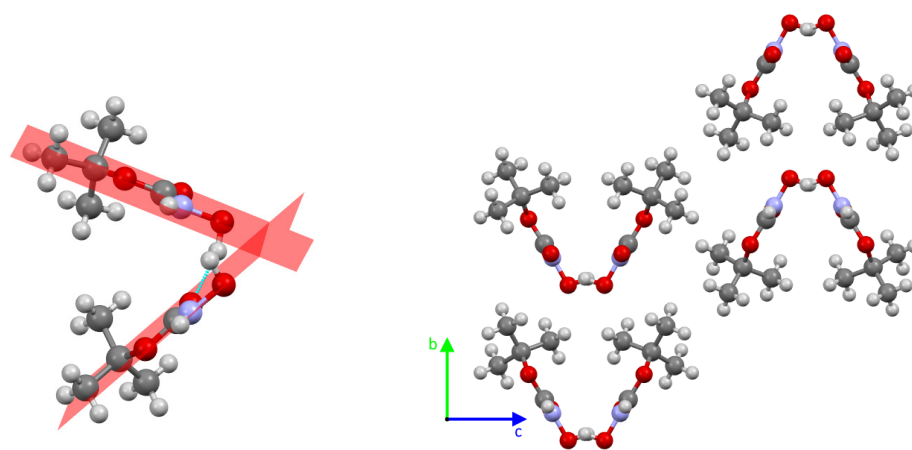


Figure 5. V-shaped end view and unit cell of **1** viewed along the *a*-axis, showing the packing of hydrogen-bonded ribbons.

By comparison, the remaining compounds identified in Figure 1 show an interesting variety of hydrogen bonding patterns. For *tert*-butyl carbazate **2**, there are four independent molecules joined in a rectangular array by $N\cdots H-N$ (NH_2) interactions, and these units are then joined in infinite chains by the $C=O\cdots H-N$ (NH) hydrogen bonding [3]. For *tert*-butyl carbamate **4**, we have simple $R^2_2(8)$ dimers [5,6]. *N*-Propionylhydroxylamine **5** has three independent molecules and six separate hydrogen bonding interactions [7], and *N*-acetylhydroxylamine **6** has two independent molecules with five separate hydrogen bonding interactions [8], resulting, in each case, in highly complex three-dimensional networks. In contrast, the longer chain analogues *N*-hexanoyl-, *N*-decanoyl- and *N*-dodecanoylhydroxylamine **7–9** all form two-dimensional layers with a central region formed by only two hydrogen bonding interactions and an outer hydrophobic region accommodating the hydrocarbon chains [8].

In summary, we obtained the X-ray crystal structure of *tert*-butyl *N*-hydroxycarbamate for the first time and found the molecules to exist, when viewed along the *b*-axis, in cross-linked parallel chains with each carbonyl oxygen hydrogen bonded to both NH and OH of adjacent molecules. These then pack in a zig-zag pattern when viewed along the *a*-axis.

3. Experimental Section

NMR spectra were obtained for ^1H at 500 MHz and for ^{13}C at 125 MHz using an AV-III instrument (Bruker, Billerica, MA, USA). Spectra were run at 25 °C on solutions in CDCl_3 with internal Me_4Si as the reference. Chemical shifts are reported in ppm to high frequency of the reference. The melting point measurement was made on a Reichert hot-stage microscope (Reichert, Vienna, Austria).

Compound **1** was prepared using the literature method [9] as colourless crystals, mp 49–51 °C (ref. [9] 51 °C). δ_{H} (500 MHz) 1.475 (9H, s), 7.13 (1H, br s) and 7.24 (1H, br s); δ_{C} (125 MHz) 158.9 (C=O), 82.2 (C) and 28.2 (3CH₃)—good agreement with ref. [9].

X-ray diffraction data for compound **1** were collected at 125 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P200 diffractometer (Cu K α radiation ($\lambda = 1.54187 \text{ \AA}$), Tokyo, Japan). Data were collected and processed (including correction for Lorentz, polarisation and absorption) using CrysAlisPro [11]. The structure was solved by dual-space methods (SHELXT) [12] and refined by full-matrix least-squares against F^2 (SHELXL-2019/3) [13]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model, except for the hydrogen atoms on N1 and O3, which were located from the difference Fourier map and refined isotropically subject to distance restraint. All calculations were performed using the Olex2 interface [14].

Crystal data for $\text{C}_5\text{H}_{11}\text{NO}_3$, $M = 133.15 \text{ g mol}^{-1}$, colourless plate, crystal dimensions $0.21 \times 0.12 \times 0.02 \text{ mm}$, orthorhombic, space group Pbc a (No. 61), $a = 5.22500(10)$, $b = 13.6564(2)$, $c = 19.5261(2) \text{ \AA}$, $V = 1393.28(4) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.270 \text{ g cm}^{-3}$, $T = 125 \text{ K}$, $R1 = 0.0328$, $Rw2 = 0.0829$ for 1392 reflections with $I > 2\sigma(I)$ and 92 variables, $R_{\text{int}} 0.0283$, goodness of fit on F^2 1.069. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2290327. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>.

Supplementary Materials: The following are available online, ^1H and ^{13}C NMR spectra, cif and check-cif files for **1**.

Author Contributions: D.K.S. prepared the compound; D.B.C. and A.P.M. collected the X-ray data and solved the structure; R.A.A. designed the study, analysed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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