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Short Note

tert-Butyl Carbazate (*N*-Boc-Hydrazine)

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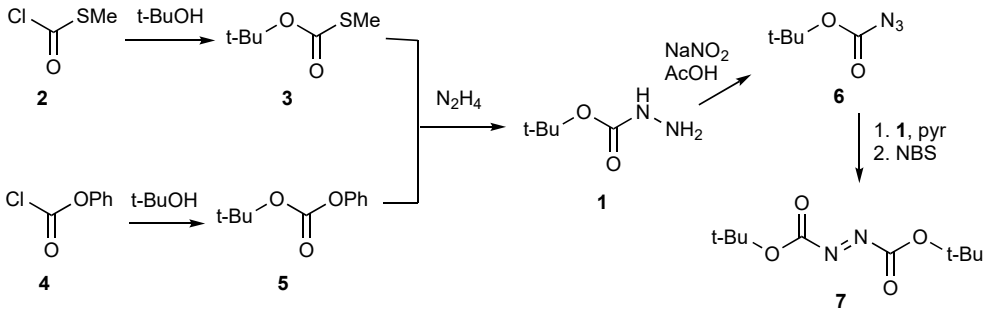
Abstract: The X-ray structure of the title compound was determined for the first time. There are four independent molecules that form a repeat unit packed in the crystal in alternating pairs with orthogonal orientation and further joined into infinite chains by hydrogen bonding.

Keywords: X-ray structure; hydrogen bonding

1. Introduction

The simple compound *tert*-butyl carbazate or *N*-tert-butoxycarbonylhydrazine **1** (Scheme 1) was first reported in 1957 [1] and is currently available from a number of commercial suppliers. Reliable methods have been published for its preparation either from MeS–C(=O)–Cl **2** via MeS–C(=O)–Ot-Bu **3** [2] or from PhO–C(=O)–Cl **4** via PhO–C(=O)–Ot-Bu **5** [2]. It has found a number of applications, including diazotisation to form *tert*-butyl azidoformate **6** [3], which is useful to introduce the "Boc" protecting group, and also by reaction between **6** and **1** followed by oxidation, to form di-*tert*-butyl azodiformate or di-*tert*-butyl azodicarboxylate **7** [4].



Scheme 1. Preparation and reactions of compound **1**.

Despite its importance, the structure of this simple compound in the solid state does not seem to have been investigated in detail before, perhaps due, in part, to its low melting point of 41–42 °C and the consequent difficulty in obtaining suitable crystals. We describe in this paper the X-ray structure determination of compound **1**.

2. Results

Crystals suitable for diffraction were obtained from the inner surface of a commercial bottle (Lancaster Synthesis), which had been stored for >5 years allowing for slow sublimation. The resulting structure (Figure 1, Supplementary Materials) shows no fewer than four independent molecules. Although these are rather similar, there are significant differences in some bond lengths and angles (Table 1). In a previous study on X-ray structures of tri- and tetraacylhydrazines [5], it was found that the planes defined by the groups at either end of the N–N bond were essentially perpendicular. For this compound, with just one non-H substituent, we might expect the two hydrogens of the NH_2 group to be evenly

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oriented on either side of the plane defined by H–N–N (Figure 2), but as shown in the final row of Table 1, the deviation from this situation varies from 21–27°.

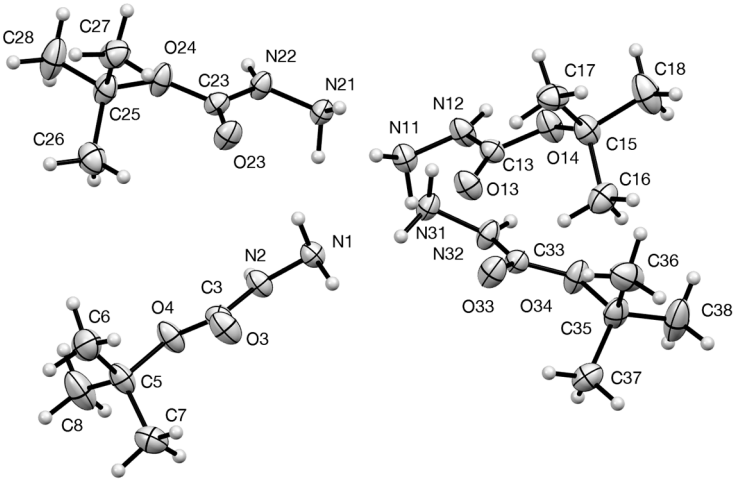

Figure 1. Molecular structure of **1**, showing the four independent molecules with anisotropic displacement ellipsoids drawn at the 50% probability level and the numbering system used.

Table 1. Comparison of selected geometric parameters between the 4 independent molecules of **1** (Å, °).

n=	—	1	2	3
N(n1)–N(n2)	1.409(2)	1.409(2)	1.413(2)	1.413(2)
N(n2)–C(n3)	1.341(2)	1.342(2)	1.347(2)	1.337(2)
C(n3)=O(n3)	1.218(2)	1.216(2)	1.219(2)	1.217(2)
C(n3)–O(n4)	1.345(2)	1.344(2)	1.340(2)	1.348(2)
O(n4)–C(n5)	1.472(2)	1.473(2)	1.476(2)	1.468(2)
N(n1)–N(n2)–C(n3)	121.80(15)	121.53(15)	121.10(15)	121.69(15)
N(n2)–C(n3)–O(n3)	124.29(17)	124.01(17)	124.04(17)	124.67(17)
N(n2)–C(n3)–O(n4)	109.74(15)	109.88(15)	109.90(15)	109.81(15)
O(n3)–C(n3)–O(n4)	125.95(16)	126.10(17)	126.02(16)	125.48(17)
C(n3)–O(n4)–C(n5)	120.45(14)	120.20(14)	120.70(14)	120.57(14)
N(n1)–N(n2) twist [a]	21.3	23.8	24.8	26.8

[a] 0.5 × | |N(n2)H–N(n2)–N(n1)–N(n1)H_A | — | N(n2)H–N(n2)–N(n1)–N(n1)H_B | |.

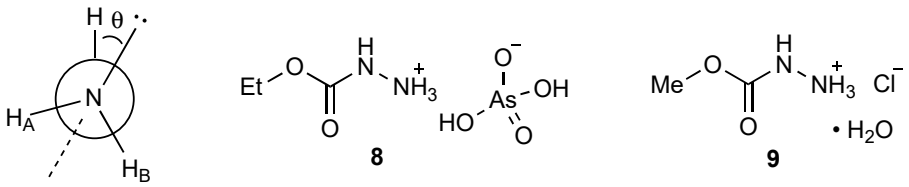

Figure 2. Definition of the twist angle for **1** and the structure of the comparison compounds **8** and **9**.

Taking a wider view of the crystal structure (Figure 3), the four independent molecules are arranged together in approximately rectangular units with the polar NH_2 groups in the middle and the non-polar *tert*-Bu groups on the outside. These then fit into a regular pattern with a pair of such units aligned one way surrounded on all four sides by four pairs of units aligned at right angles and vice versa.

In addition to this, all molecules form infinite chains along the direction of the *a* axis by C=O to N–H hydrogen bonding to neighbouring molecules of their own type only (Figure 4). The hydrogen bonding parameters (Table 2) are slightly different for each of the four independent molecules, but all are well within the normal ranges for an amide.

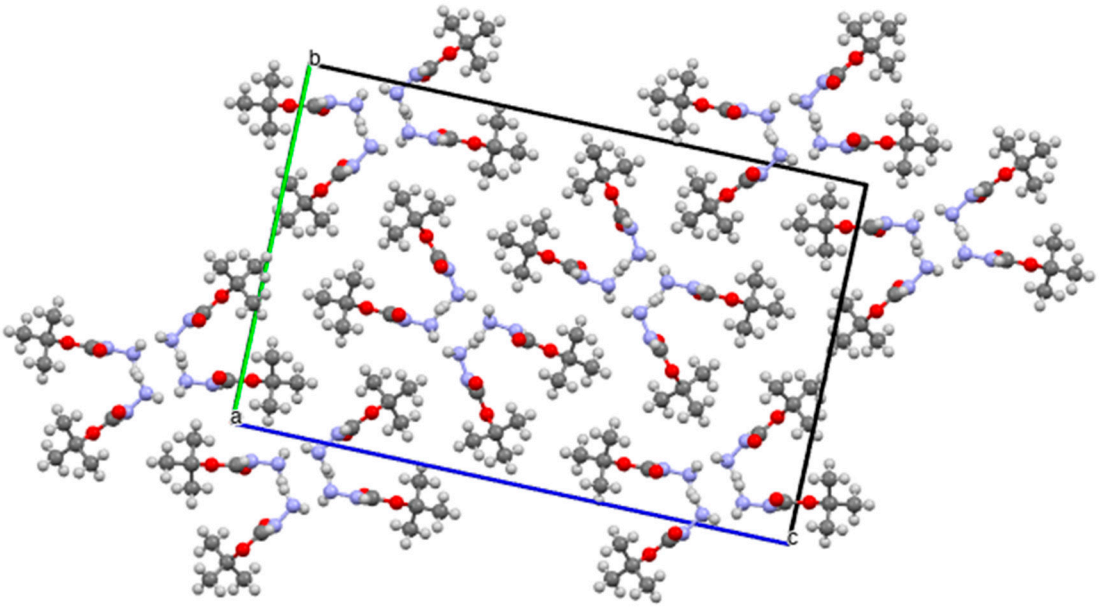

Figure 3. Packing pattern of sets of four independent molecules, showing orthogonal pairs and the 16 molecules within the unit cell viewed along the *a* axis.

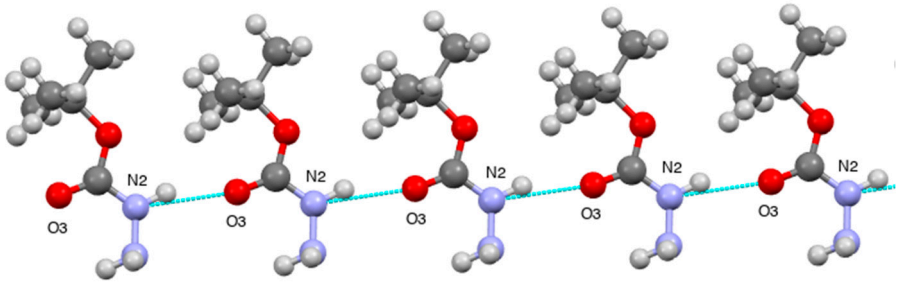

Figure 4. Hydrogen-bonding pattern within one chain of molecules.

We were only able to locate two previous X-ray structures in the Cambridge Structural Database (CSD) [6] containing simple alkyl carbazates, and these are both ionic salts (Figure 2). The ethyl carbazate arsenic acid salt **8** (CCDC ref. code. HALCOO) also shows an exactly similar pattern of hydrogen bonding [7], and its parameters are included in Table 2, showing stronger and more linear bonding as compared to **1**. The methyl carbazate hydrochloride hydrate **9** (CCDC ref. Code IFURAD), in contrast, shows a more complex pattern with C=O bonding to NH_3^+ hydrogens, which are also hydrogen bonded to the water of hydration [8].

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

	D—H . . . A	D—H	H . . . A	D . . . A	D—H . . . A	Ref.
1	N(2)–H(2) . . . O(3)	0.975(14)	2.033(11)	2.945(2)	154.8(17)	This work
1	N(12)–H(12) . . . O(13)	0.976(11)	2.067(10)	2.975(2)	154.1(17)	This work
1	N(22)–H(22) . . . O(23)	0.975(14)	2.040(11)	2.943(2)	153.2(17)	This work
1	N(32)–H(32) . . . O(33)	0.975(12)	2.036(10)	2.961(2)	157.6(19)	This work
8	N–H . . . O	0.93(11)	1.84(11)	2.763(6)	172(10)	[7]

In summary, we obtained the X-ray crystal structure of *tert*-butyl carbazate for the first time and found the molecule to exist, when viewed along the *a* axis, in rectangular groups of four independent molecules with slightly different molecular dimensions. These are then further arranged in pairs, which pack alternately with two orthogonal orientations.

All molecules are then additionally joined in infinite chains along the *a* axis by hydrogen bonding between the C=O and H–N-C=O.

3. Experimental Procedure

The structure was determined on a Rigaku XtalLAB P200 diffractometer using graphite-monochromated Mo Kα radiation λ = 0.71075 Å.

Crystal data for $C_4H_{12}N_2O_2$: M = 132.16 g mol^{-1}, colourless prism, crystal dimensions 0.15 × 0.03 × 0.03 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 5.1435(6), b = 19.122(3), c = 29.686(5) Å, β = 92.773(4) °, V = 2916.3(8) Å^3, Z = 16, D_{calc} = 1.204 g cm^{-3}, T = 173 K, $R1$ = 0.0502, $Rw2$ = 0.1141 for 4484 reflections with $I > 2\sigma(I)$, and 385 variables, R_{int} 0.0559, goodness of fit on F^2 1.148. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2087799. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures. The structure was solved by direct methods and refined by full-matrix least squares against F^2 (SHELXL Version 2018/3 [9]).

Supplementary Materials: The following are available online: cif and check-cif files for **1**.

Author Contributions: A.M.Z.S. 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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Data Availability Statement: The X-ray data are at CCDC as stated in the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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