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The crystal structure of *tert*-butyl (*tert*-butoxy (oxo)methyl)(5-bromo-2-fluorophenyl)carbamate, $C_{16}H_{21}BrFNO_4$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.12 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.30 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	27.5°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16818, 4042, 0.070
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2964
$N(\text{param})_{\text{refined}}$:	214
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.08101(3)	0.81476(3)	0.58939(2)	0.04502(11)
C1	0.3921(3)	0.8979(2)	0.42197(13)	0.0292(5)
C2	0.3234(3)	0.9940(2)	0.45152(14)	0.0355(6)
H2	0.340062	1.076508	0.437809	0.043*
C3	0.2302(3)	0.9693(2)	0.50120(14)	0.0341(6)
H3	0.181823	1.034684	0.522026	0.041*
C4	0.2077(3)	0.8490(2)	0.52044(13)	0.0300(6)
C5	0.2778(3)	0.7528(2)	0.49093(13)	0.0279(5)
H5	0.261873	0.670364	0.504914	0.034*
C6	0.3705(3)	0.7771(2)	0.44132(13)	0.0255(5)
C7	0.6006(3)	0.6850(2)	0.41793(13)	0.0255(5)
C8	0.8118(3)	0.6303(2)	0.35852(13)	0.0274(5)
C9	0.8979(3)	0.5643(3)	0.42365(15)	0.0410(7)
H9A	0.894427	0.612586	0.467917	0.062*
H9B	1.001889	0.554221	0.416835	0.062*
H9C	0.853401	0.483138	0.428497	0.062*
C10	0.8156(3)	0.5585(3)	0.28890(15)	0.0436(7)
H10A	0.776612	0.475392	0.293908	0.065*
H10B	0.918678	0.553225	0.279876	0.065*
H10C	0.754100	0.600504	0.247865	0.065*
C11	0.8665(4)	0.7603(2)	0.35220(19)	0.0516(8)
H11A	0.801829	0.802593	0.312344	0.077*
H11B	0.968892	0.758609	0.341994	0.077*
H11C	0.864358	0.804168	0.398140	0.077*
C12	0.3515(3)	0.5923(2)	0.36673(12)	0.0249(5)
C13	0.3585(3)	0.3850(2)	0.31694(13)	0.0274(5)
C14	0.3485(3)	0.4322(2)	0.23974(13)	0.0380(6)
H14A	0.272467	0.496823	0.230819	0.057*

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Abstract

$C_{16}H_{21}BrFNO_4$, monoclinic, $P2_1/n$ (no. 14), $a = 9.0896(4)$ Å, $b = 10.8609(4)$ Å, $c = 18.5637(8)$ Å, $\beta = 99.5050(10)^\circ$, $V = 1807.47(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0382$, $wR_{\text{ref}}(F^2) = 0.0900$, $T = 170$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H14B	0.321398	0.364389	0.205282	0.057*
H14C	0.445328	0.466018	0.233036	0.057*
C15	0.4763(3)	0.2860(2)	0.33381(15)	0.0366(6)
H15A	0.572708	0.318384	0.325491	0.055*
H15B	0.448732	0.214923	0.301932	0.055*
H15C	0.483684	0.260663	0.384949	0.055*
C16	0.2108(3)	0.3409(2)	0.33509(17)	0.0422(7)
H16A	0.222608	0.320647	0.387170	0.063*
H16B	0.178193	0.267511	0.306085	0.063*
H16C	0.135920	0.406058	0.323750	0.063*
F1	0.48272(17)	0.92160(13)	0.37289(8)	0.0397(4)
N1	0.4438(2)	0.67936(17)	0.40917(11)	0.0274(4)
O1	0.22729(19)	0.61699(14)	0.33802(10)	0.0335(4)
O2	0.41940(17)	0.48426(13)	0.36872(8)	0.0259(4)
O3	0.65003(18)	0.63117(15)	0.36273(9)	0.0317(4)
O4	0.67210(18)	0.73847(15)	0.46857(9)	0.0303(4)

Source of material

5-Bromo-2-fluoroaniline (5 g, 26.31 mmol) was dissolved in THF (80 mL) at room temperature, followed by di-*tert*-butyl dicarbonate (17.23 g, 78.94 mmol) and dimethylaminopyridine (0.32 g, 2.63 mmol) in order. Then mixture reacted under stirring at room temperature for 12 hours. Subsequently, the mixture was poured into water and extracted with ethyl acetate. The organic phase was dehydrated with anhydrous sodium sulfate and concentrated at reduced pressure to afford a yellow solid. The crude mixture was purified by silica gel column chromatography, eluted with petroleum ether to give a white solid (6.45 g, yield 62.80%). ¹H NMR (400 MHz, CDCl₃) δ [ppm] 7.40 (ddd, *J* = 8.8, 4.3, 2.5 Hz, 1H), 7.33 (dd, *J* = 6.7, 2.5 Hz, 1H), 7.00 (t, *J* = 9.1 Hz, 1H), 1.43 (s, 18H). Crystals were grown in hexane at room temperature.

Experimental details

All hydrogen atoms were placed in geometrically calculated positions. The *U*_{iso} values of the hydrogen atoms were set to 1.5 *U*_{eq}(C_{methyl}) and 1.2 *U*_{eq}(C_{aryl}).

Comment

Some carbamates are of significant interest in medicine, organic synthesis and fine chemicals. They can participate in the synthesis of aniline derivatives as EP2 agonists useful in treating glaucoma [5]. At the same time, they can also be used for electrolyte solution of nonaqueous secondary batteries [6]. In addition, it can be chemoselectively and efficiently deprotected in high yields using a catalytic agent to afford the corresponding mono-BOC-protected amine [7], which is an intermediate for the preparation of antiviral agents [8], glycogen phosphorylase inhibitors [9] and antagonists of gonadotropin releasing hormone (GnRH) [10].

There is one molecule in the asymmetric unit (see the figure). The phenyl moiety connects the two *tert*-butoxycarbonyl groups *via* a nitrogen atom, respectively. All bond lengths and angles in the crystal structure are within the normal range [11]. The values of the selected torsion angles C(1)-C(6)-N(1)-C(7), C(1)-C(6)-N(1)-C(12), C(5)-C(6)-N(1)-C(7) and C(5)-C(6)-N(1)-C(12) are 57.15°, −117.80°, −123.31° and 61.74°, respectively. The crystal structure shows that the intermolecular packing is stabilized by weak hydrogen bonds and the van der Waals forces.

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