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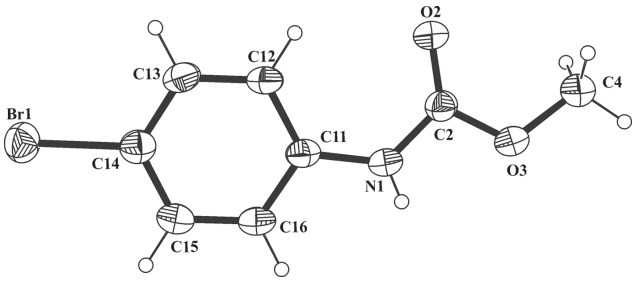
The crystal structure of methyl *N*-(4-bromophenyl) carbamate, $C_8H_8BrNO_2$



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Abstract

$C_8H_8BrNO_2$, orthorhombic, *Pbca* (no. 61), $a = 10.1313(3)$ Å, $b = 8.5416(4)$ Å, $c = 20.4597(7)$ Å, $V = 1770.53(12)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0394$, $wR_{ref}(F^2) = 0.1214$, $T = 296$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared by the following method: The mixture of cyanoacetic acid hydrazide (0.01 mol), 4-bromophenyl isocyanate (0.01 mole) and methanol (15 mL) was heated with reflux for 0.5 h. After cooling the solution, the precipitated compound was filtered and crystallized from methanol. Crystals were grown by slow evaporation of an ethanol solution.

Table 1: Data collection and handling.

Crystal:	Cubes, colourless
Size:	0.60 × 0.57 × 0.41 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	6.01 mm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω
$2\theta_{max}$, completeness:	68.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31984, 1615, 0.157
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1387
$N(param)_{refined}$:	113
Programs:	Bruker [1], SIR92 [2], SHELX [3], ORTEP, WinGX [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.05084(4)	0.21611(6)	0.75316(2)	0.0706(3)
O2	−0.00847(19)	−0.2979(3)	0.48416(11)	0.0610(6)
O3	0.18764(18)	−0.3619(4)	0.44039(12)	0.0735(7)
N1	0.1858(2)	−0.2062(3)	0.52492(15)	0.0579(7)
H1	0.256(5)	−0.221(5)	0.520(2)	0.087*
C2	0.1099(3)	−0.2891(4)	0.48368(14)	0.0514(7)
C4	0.1238(3)	−0.4590(5)	0.39248(18)	0.0788(11)
H41	0.1892	−0.5047	0.3643	0.118*
H42	0.0756	−0.5406	0.4141	0.118*
H43	0.0642	−0.3967	0.3670	0.118*
C11	0.1474(2)	−0.1122(4)	0.57745(14)	0.0492(6)
C12	0.0181(3)	−0.0686(4)	0.59023(16)	0.0584(7)
H12	−0.0499	−0.1041	0.5636	0.088*
C13	−0.0093(3)	0.0279(4)	0.64274(16)	0.0597(8)
H13	−0.0960	0.0567	0.6514	0.090*

[a]Occupancy: 0.854(7).

Experimental details

The N-bound H atom was located by difference Fourier synthesis and refined freely. The remaining H atoms were positioned geometrically and treated as riding on their parent C atoms with C—H distances of 0.96 Å (CH_3) and 0.93 Å (aromatic). All H atoms were refined with isotropic

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displacement parameters taken as $U_{iso}(H) = 1.5U_{eq}(C,N)$ in refinement procedure.

Discussion

The title compound was prepared as a part of our study on the synthesis of novel semicarbazide derivatives as potential antimicrobial agents [5]. We expected to receive 1-cyanoacetylo-4-(4-bromophenyl)semicarbazide in the reaction of cyanoacetic acid hydrazide, 4-bromophenyl isocyanate and methanol according to the literature data [6], but during the reaction methyl *N*-(4-bromophenyl)carbamate was obtained. We suppose that instead of the isocyanate reaction with the hydrazide, the isocyanate reacted with the methanol, which was the reaction medium giving the title compound.

The molecule is nearly planar with the mean planes of the benzene ring and carbamate group twisted relative to each other by an angle of 9.69(12)°. The bond lengths and angles have normal values and they are in good agreement with those observed in related structures of methyl *N*-(4-chlorophenyl)carbamate [7] and methyl *N*-(4-nitrophenyl)carbamate [8].

In the crystal structure of the title compound, molecules related by 2_1 symmetry axis are linked into chains parallel to [100] direction *via* N1—H1···O2^{i} hydrogen bonds [N1—H1 = 0.73(5) Å, H1···O2 = 2.39(5) Å, N1···O2 = 3.103(3) Å, N1—H1—O2 = 165(4)° and $^{i} = 1/2 + x, 1/2 - y, -z$]. Moreover, the molecules related by centre of inversion form dimers through non-classical, very weak C4—H42···O2^{ii} hydrogen bonds [C4—H42 = 0.96 Å, H42···O2 = 2.59 Å, C42···O2 = 3.471(4) Å, C4—H42—O2 = 153° and $^{ii} = 1 - x, 1 - y, -z$]. The combination of these two intermolecular motifs gives hydrogen bonding molecular planes parallel to (010) net plane.

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