Crystal structure of 1-(benzyloxy)urea, $C_8H_{10}N_2O_2$

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Abstract

$C_8H_{10}N_2O_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 12.456(3)$ Å, $b = 5.008(1)$ Å, $c = 13.681(4)$ Å, $\beta = 96.017(4)^\circ$, $V = 848.7$ Å³, $Z = 4$, $R_{\text{int}}(F) = 0.057$, $wR_{\text{ref}}(F^2) = 0.166$, $T = 296$ K.

Source of material

The title compound was synthesized by reaction of hydroxyurea (0.026 mol) with benzyl chloride (0.034 mol) in methanol (100 ml) in the presence of potassium hydroxide (0.034 mol). After refluxing for 13 h, the solution was distilled in the reduced pressure at 35 °C. The resulting crude solid was filtered and washed by trichloromethane, then recrystallized in acetone/trichloromethane (5:2, v/v), filtered and dried. Colorless needle-shaped single crystals of the title compound suitable for X-ray structure determination were obtained by slow evaporation of the mixed solvent acetone/*n*-hexane (9:11, v/v) at room temperature for one week (m.p. 140–142 °C).

Experimental details

H atoms were placed in calculated positions with $d(\text{C—H}) = 0.93$ (aromatic), 0.97 Å (methylene) and $d(\text{N—H}) = 0.86$ Å, and were refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C,N})$.

Discussion

In the title crystal structure, the conformations of the N—O and C=O bonds are *anti* to each other (figure, top), similar to that observed in 1-(2-fluorobenzyl)-1-(2-fluorobenzyloxy)urea [1], *N*-hydroxyurea [2–5], 1-hydroxy-1-methylurea and 1-hydroxy-3-methylurea [6]. The length of the carbonyl bond (C=O) in above hydroxyurea derivatives [2–6] is longer (> 1.25 Å), but the values observed in the title compound is in the normal range of 1.19–1.23 Å and obviously shorter (< 1.25 Å). This may be related with the hydroxyl group etherification, which suggests that the structure has not an H atom of hydroxyl group to form intramolecular hydrogen bonding with O2. The C—N bond lengths in the urea group (1.274(3)–1.326(3) Å, mean 1.300(3) Å) are longer than a typical C=N double bond (mean 1.269 Å), but shorter than a C—N single bond (mean 1.443(4) Å), indicating electron delocalization in the urea group [7]. The group N—(C=O)—N urea planar forms a dihedral angle of $71.5(2)^\circ$ with the benzyl group, and the N—O bonds are twisted by about 20° out of the N—(C=O)—N urea planes. In the crystal structure, molecules are linked into antiparallel chains running along [010] by intermolecular N—H...O hydrogen bonding (figure, bottom).

Table 1. Data collection and handling.

Crystal:	colourless needle, size $0.158 \times 0.411 \times 0.801$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	0.95 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, ϕ/ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4629, 1453
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1173
$N(\text{param})_{\text{refined}}$:	110
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(1A)	4e	0.2376	1.0445	1.0679	0.076
H(1B)	4e	0.2503	1.2966	1.0009	0.076
H(7)	4e	0.1055	0.7731	1.0108	0.115
H(6)	4e	0.0182	0.5614	0.8809	0.150
H(3)	4e	0.2954	1.1400	0.8215	0.102
H(5)	4e	0.0662	0.6487	0.7254	0.113
H(4)	4e	0.2074	0.9271	0.6922	0.112
H(1)	4e	0.3680	0.6409	0.9926	0.063
H(2A)	4e	0.4599	0.9426	1.2365	0.066
H(2B)	4e	0.4050	1.1021	1.1539	0.066

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	4e	0.2619(2)	1.1055(6)	1.0066(2)	0.075(2)	0.051(2)	0.061(2)	0.011(1)	−0.017(1)	−0.003(1)
C(2)	4e	0.2072(2)	0.9724(5)	0.9271(2)	0.056(1)	0.050(2)	0.056(1)	0.009(1)	−0.015(1)	0.004(1)
C(7)	4e	0.1237(3)	0.7997(8)	0.9473(2)	0.102(2)	0.110(3)	0.071(2)	−0.038(2)	−0.024(2)	0.026(2)
C(6)	4e	0.0739(4)	0.681(1)	0.8728(3)	0.121(3)	0.131(4)	0.109(3)	−0.068(3)	−0.047(2)	0.029(3)
C(3)	4e	0.2393(3)	1.0227(8)	0.8299(2)	0.073(2)	0.112(3)	0.066(2)	−0.022(2)	−0.012(2)	0.003(2)
C(5)	4e	0.1052(3)	0.7341(8)	0.7781(3)	0.090(2)	0.095(3)	0.088(2)	−0.006(2)	−0.041(2)	−0.004(2)
C(4)	4e	0.1894(3)	0.9035(9)	0.7559(2)	0.088(2)	0.131(3)	0.057(2)	0.004(2)	−0.016(2)	−0.003(2)
O(1)	4e	0.3742(1)	1.0419(3)	1.0028(1)	0.068(1)	0.0375(9)	0.055(1)	−0.0016(7)	−0.0258(8)	0.0075(7)
N(1)	4e	0.3887(2)	0.7727(4)	1.0303(1)	0.073(1)	0.030(1)	0.047(1)	−0.0045(8)	−0.0257(9)	0.0001(8)
C(8)	4e	0.4358(2)	0.7452(4)	1.1169(2)	0.063(1)	0.031(1)	0.040(1)	−0.0040(9)	−0.0117(9)	0.0008(9)
O(2)	4e	0.4724(2)	0.5232(3)	1.1362(1)	0.093(1)	0.0291(9)	0.0467(9)	0.0027(8)	−0.0262(8)	−0.0001(6)
N(2)	4e	0.4333(2)	0.9545(4)	1.1760(1)	0.083(1)	0.033(1)	0.044(1)	0.0042(9)	−0.0213(9)	−0.0033(8)

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