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The crystal structure of *para*-nitrobenzylbromide, $C_7H_6BrNO_2$ – A second polymorph and correction of 3D coordinates

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Abstract

$C_7H_6BrNO_2$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 4.7019(6)$ Å, $b = 6.4700(9)$ Å, $c = 25.283(4)$ Å, $V = 769.14(19)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0294$, $wR_{ref}(F^2) = 0.0671$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Merck). Crystals suitable for the diffraction study were taken directly from the provided product.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for

Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	$0.38 \times 0.12 \times 0.11$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	5.29 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.0° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6983, 1854, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1583
$N(\text{param})_{\text{refined}}$:	101
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

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	1.23357 (10)	0.04014 (6)	0.22432 (2)	0.04408 (15)
O1	0.5682 (6)	0.8376 (4)	0.06872 (10)	0.0376 (7)
O2	0.5052 (6)	0.5864 (4)	0.01375 (10)	0.0357 (7)
N1	0.6222 (7)	0.6632 (5)	0.05236 (12)	0.0275 (7)
C1	1.2296 (8)	0.3067 (5)	0.13533 (12)	0.0243 (7)
C2	1.1623 (8)	0.5066 (6)	0.15216 (14)	0.0297 (9)
H2	1.252854	0.562323	0.182576	0.036*
C3	0.9648 (8)	0.6240 (6)	0.12488 (13)	0.0271 (8)
H3	0.917248	0.759395	0.136447	0.033*
C4	0.8378 (7)	0.5399 (5)	0.08028 (13)	0.0230 (7)
C5	0.9028 (8)	0.3436 (6)	0.06217 (13)	0.0256 (8)
H5	0.814296	0.289823	0.031330	0.031*
C6	1.0993 (8)	0.2277 (5)	0.08992 (13)	0.0270 (8)
H6	1.146351	0.092666	0.078011	0.032*
C7	1.4360 (8)	0.1792 (6)	0.16603 (13)	0.0305 (8)
H7A	1.588254	0.268503	0.180481	0.037*
H7B	1.524724	0.074905	0.142606	0.037*

methylene groups) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

The compound was refined as a two-component inversion twin with a volume ratio of 94.4:5.6.

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Comment

Benzylic halogenides are versatile synthons in Organic Chemistry. Resonance effects greatly assist in displacing the halogen atom in the wake of nucleophilic substitution reactions [7]. A vast series of such derivatives bearing functional groups on the aromatic system has been synthesized and characterized over the last century. In continuation of our interest in the structural chemistry of halogenated derivatives of benzene [8–16] the molecular and crystal structure of the title compound were determined. While a structural analysis is apparent in the literature (ref. Code: WIQDUV) [17], the latter is plagued by two problems: first, the structure was determined based on powder diffraction data which precludes the anisotropic treatment of the atoms during the refinement procedure and – second – an inspection of the 3D coordinates reveals a number of questionable features such as an undulated aromatic system, involving the pertaining hydrogen atoms to create linear zig-zag patterns. Furthermore, the cell constants found in this study differ from the ones reported earlier [17]. The molecular and crystal structure of the chlorinated equivalent have been determined previously [18, 19].

The title crystal solution shows the presence of 4-nitrobenzylbromide. The C–Br bond length of 1.971(4) Å and the nearly equal N–O bond lengths of 1.226(4) and 1.228(4) Å are in good agreement with pertaining values found for other comparable compounds whose metrical parameters have been deposited with the Cambridge Structural Database [20]. Intracyclic C–C–C angles span a range of 118.6(3)°–122.3(3)° with the smaller value being present on both carbon atoms in *ortho*-position to the nitro group and the largest value on the carbon atom bearing the latter substituent. The least-squares planes as defined by the respective atoms of the nitro group and the non-hydrogen atoms of the bromomethyl group and its pertaining *ipso*-carbon atom enclose angles of 2.0(4)° and 84.8(3)°, respectively, with the first value being indicative of resonance involving the nitro group.

In the crystal, C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. These are established between one of the hydrogen atoms of the methylene group as well as one of the aromatic CH groups in *ortho*-position to the halogenated substituent and one of the oxygen atoms of the nitro group as acceptor. In terms of graph-set analysis [21, 22], the descriptor for these contacts is C₁¹(6)C₁¹(8) on the unary level. In total, the molecules are connected to chains along [110]. One could discuss a possible C–H···π interaction, however, the latter is characterized by an angle

deviating strongly from linearity. π-Stacking is not a prominent feature in the crystal structure of the title compound with the shortest distance found between two centers of gravity measured at 4.702(2) Å.

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