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The crystal structure of 4-bromobenzyl chloride, C_7H_6BrCl

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Abstract

C_7H_6BrCl , orthorhombic, $Pna2_1$ (no. 33), $a = 9.4506(7)$ Å, $b = 18.1015(10)$ Å, $c = 4.4418(3)$ Å, $V = 759.86(9)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0271$, $wR_{ref}(F^2) = 0.0558$, $T = 200(2)$ K.

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The molecular structure is shown in 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 (Sigma-Aldrich). Crystals suitable for the diffraction study were taken directly from the provided product and mounted under inert conditions to prevent rapid hydrolysis.

Experimental details

Carbon-bound atoms (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups) were included in

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.24 × 0.29 × 0.34 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.66 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	7312, 1807, 0.025
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1571
$N(param)_{refined}$:	235
Programs:	BRUKER [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

the refinement in the riding model approximation, with $U(H)$ set to 1.2 $U_{eq}(C)$.

The Flack parameter for this non-centrosymmetric structure refined to 0.049(15).

Comment

Benzene is among the most important synthons in chemistry. Via electrophilic substitution reactions a vast variety of functionalized derivatives is readily available. The interplay between activating and deactivating substituents as well as the competition and synergism between inductive and mesomeric effects allows for the seemingly endless functionalization of the respective archaetype hydrocarbon scaffold. The latter gives rise to a large toolbox of new synthons that can be applied for the production of dyes, medications, catalysts and ligands for novel coordination compounds. Several simple and fundamental derivatives of benzene are powerful and versatile reagents themselves and have entered the preparative chemist's toolbox decades ago. One notable example for the latter statement is benzylchloride which is readily available upon simple radical chlorination of toluene and whose status as a benzylic compound opens up a vast array of nucleophilic substitution reactions. During the preparation of a number of functionalized derivatives of boronic and borinic acids the title compound – which is commercially available – was used as a starting material. To prevent accidentally characterizing the title compound instead of the sought-after ligands and in continuation of our

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.52863 (15)	0.40516 (15)	0.76473 (17)	0.0618 (4)
C2	0.5373 (2)	0.3373 (2)	0.8852 (2)	0.0955 (7)
H2A	0.602527	0.275066	0.905995	0.143*
H2B	0.451652	0.302985	0.864812	0.143*
H2C	0.563527	0.389595	0.963441	0.143*
C3	0.6564 (3)	0.4691 (3)	0.7976 (4)	0.1295 (11)
H3A	0.728741	0.412841	0.828337	0.194*
H3B	0.672335	0.526404	0.869456	0.194*
H3C	0.650420	0.509189	0.716236	0.194*
C4	0.4893 (3)	0.3307 (2)	0.6404 (2)	0.0945 (7)
H4A	0.558053	0.272942	0.655477	0.142*
H4B	0.477248	0.380044	0.562836	0.142*
H4C	0.406965	0.290390	0.621608	0.142*
C7	−0.00964 (14)	0.75511 (15)	0.68634 (15)	0.0575 (4)
C8	0.06147 (18)	0.81784 (17)	0.82089 (17)	0.0696 (5)
H8A	−0.001432	0.864227	0.839283	0.104*
H8B	0.128511	0.869420	0.816858	0.104*
H8C	0.103285	0.760391	0.893454	0.104*
C9	−0.1066 (2)	0.66714 (19)	0.6889 (2)	0.0805 (5)
H9A	−0.180418	0.707761	0.693531	0.121*
H9B	−0.063860	0.616630	0.768449	0.121*
H9C	−0.138662	0.619613	0.606289	0.121*
C10	−0.0730 (2)	0.8400 (2)	0.5704 (2)	0.0873 (6)
H10A	−0.142392	0.883038	0.581133	0.131*
H10B	−0.110742	0.797090	0.484426	0.131*
H10C	−0.006851	0.894976	0.570410	0.131*
O1A ^a	0.43765 (13)	0.50715 (11)	0.73432 (17)	0.0555 (4)
O2A ^a	0.25815 (15)	0.40045 (13)	0.6966 (2)	0.0818 (6)
O3A ^a	0.2532 (2)	0.59567 (17)	0.6721 (3)	0.0692 (5)
O4A ^a	0.17181 (14)	0.57709 (12)	0.82467 (14)	0.0658 (4)
O5A ^a	0.09014 (15)	0.70265 (12)	0.64805 (14)	0.0541 (4)
C5A ^a	0.3147 (4)	0.4878 (3)	0.7046 (5)	0.0556 (6)
C6A ^a	0.1668 (3)	0.6206 (2)	0.7246 (4)	0.0499 (8)
O1B ^b	0.3916 (9)	0.4374 (9)	0.7597 (10)	0.066 (3)
O2B ^b	0.3397 (10)	0.5534 (10)	0.5778 (11)	0.077 (3)
O3B ^b	0.2003 (9)	0.5234 (8)	0.6676 (13)	0.078 (3)
O4B ^b	0.2330 (8)	0.7173 (7)	0.6996 (10)	0.061 (2)
O5B ^b	0.0433 (7)	0.6268 (7)	0.6669 (9)	0.052 (2)
C5B ^b	0.3226 (14)	0.5105 (14)	0.6679 (17)	0.050 (3)
C6B ^b	0.1670 (17)	0.6332 (14)	0.689 (3)	0.052 (6)
O1C ^c	0.413 (2)	0.486 (3)	0.676 (3)	0.040 (5)
O2C ^c	0.292 (3)	0.425 (3)	0.777 (4)	0.040 (5)
O3C ^c	0.262 (3)	0.601 (3)	0.666 (5)	0.040 (5)
O4C ^c	0.046 (2)	0.550 (3)	0.568 (3)	0.040 (5)
O5C ^c	0.1257 (18)	0.701 (3)	0.710 (4)	0.040 (5)
C5C ^c	0.312 (7)	0.488 (5)	0.702 (9)	0.040 (5)
C6C ^c	0.133 (2)	0.613 (3)	0.636 (4)	0.040 (5)

^aOccupancy: 0.851(3), ^bOccupancy: 0.122(2), ^cOccupancy: 0.027(2).

own studies into the structural aspects of core-halogenated derivatives of benzene [7–12], the crystallographic data for the substrate was sought. The molecular and crystal structure of benzylchloride [13] and several other core-halogenated

derivatives [14–16] including that of 1-bromo-4-(bromo-methyl)benzene [17] have been reported in the literature.

The title compound is the para-brominated derivative of benzylchloride. The C–Cl bond length of 1.806(5) Å as well as the C–Br bond length of 1.898(4) Å are in good agreement with the respective values apparent for similar connectivity patterns in compounds whose metrical parameters have been deposited with the Cambridge Structural Database [18]. Intracyclic C–C–C angles span a narrow range of 118.1(4)°–121.6(4)° with the smallest value apparent on the carbon atom bearing the chloromethylene substituent and the largest angle found on one of the carbon atoms directly in *ortho* position to this side-chain-bearing C atom. The side chain adopts an almost perpendicular conformation with regards to the aromatic system it is attached to as the least-squares planes as defined by the non-hydrogen atoms of the central phenyl ring on the one hand and the three heavy atoms of the C–CH₂–Cl motif enclose an angle of 89.1(4)°.

The crystal structure is almost devoid of intermolecular interactions. Apart from very weak dispersive Br...Cl interactions whose range falls just slightly below the sum of van-der-Waals radii of the atoms participating in them (with a distance of only 3.5544(11) Å the shortening is less than 0.1 Å) and no further intra- or intermolecular interactions are apparent. The absence of even π stacking – the shortest intercentroid distance between two centers of gravity measure at 4.442(3) Å – further explains the volatility and mucosa irritating properties of the compound.

The halogen-based contacts connect the molecules to chains along [1 0 1].

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