Refinement of the crystal structure of 1-chloromethyl-nitrobenzene, $C_7H_6ClNO_2$, *at 200 K*

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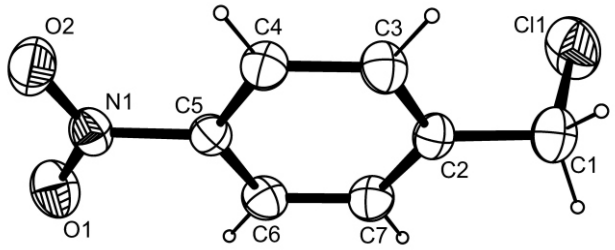

Abstract

$C_7H_6ClNO_2$, orthorhombic, $P2_12_12_1$ (no. 19), a = 4.745(2) Å, b = 6.412(3) Å, c = 24.781(8) Å, V = 754.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.090, T = 200 K.

Source of material

The compound was obtained upon photodecarboxylation of 4-nitro-phenylacetic acid in the presence of *tert*-butylhypochlorite and iodine according to a published procedure [1].

Experimental details

Carbon-bound H atoms were placed in calculated positions with d(C—H) = 0.99 Å for the methylene group and d(C—H) = 0.95 Å for aromatic carbon atoms and were included in the refinement in the riding model approximation with U(H) = 1.2 U_{eq}(C). The Flack parameter is –0.03(9).

Discussion

4-Nitrobenzyl chloride is a versatile and easily-available synthon for the production of various carboxylic acid and amine derivatives bearing the *para*-nitrobenzyl moiety. Many of these compounds are interesting mono- or multidentate ligands for the complexation of transition metals. To allow comparative studies, it seemed of interest to determine the molecular and the crystal structure of the title compound at low temperature. Until now, the structure was only deposited as a *private communication* or determined at room temperature [3,4]. The structure of 4-nitrobenzyl bromide has been reported earlier [5].

In the title crystal structure, intracyclic angles ∠C–C–C cover a range from 118.32(14)-122.44(15)° with the biggest angle found on the C atom bonded to the nitro group. The smallest angles are found on both C atoms in *ortho* position to the nitro-group-bearing C atom.

The nitro group is nearly in plane with the phenyl ring. The least-squares planes defined by the respective atoms enclose an angle of 2.6(3)°. The chlorine atom, on the other hand, is not in plane with the phenyl ring. In comparison to the metrical data determined at room temperature [4], the O–N–C–C dihedral angles are found at slightly smaller values (about 2.3° instead of 2.4°) while the respective Cl–C–C–C dihedral angles adopt slightly bigger values (about 84.2° instead of 83.8°). In the crystal structure, C–H···O contacts whose range falls by more than 0.2 Å below the sum of van-der-Waals radii of the atoms participating in them are present. Taking into account only the shortest contacts – which are formed between one of the H atoms of the methylene group and one of the O atoms of the nitro group – the molecules are connected to chains along [110]. In terms of graph-set analysis [6,7], the descriptor for these contacts on the unitary level is $C_1^1(8)$. Although π stacking is not a prominent feature in the crystal structure, N–O···π interactions can be observed for both O atoms of the nitro group. The corresponding O···Cg distances were found at 3.446(2) Å and 3.822(2) Å, respectively.

Table 1. Data collection and handling.

Crystal:	colourless platelet, size 0.338 × 0.489 × 0.530 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.49 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3912, 1869
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1773
$N(param)_{refined}$:	100
Programs:	SHELXS-97, SHELXL-97 [8], ORTEP-3 [9], Mercury [10], PLATON [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*a*	1.0845	0.7687	0.1856	0.047
H(1B)	4*a*	1.0249	0.5739	0.1466	0.047
H(3)	4*a*	0.6566	0.5939	0.0796	0.039
H(4)	4*a*	0.3251	0.7915	0.0318	0.037
H(6)	4*a*	0.4161	1.2623	0.1401	0.041
H(7)	4*a*	0.7491	1.0631	0.1875	0.041

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4*a*	0.7489(1)	0.54855(9)	0.22421(2)	0.0724(4)	0.0624(3)	0.0485(3)	0.0037(3)	–0.0029(3)	0.0232(2)
O(1)	4*a*	0.0757(3)	1.3408(2)	0.06999(5)	0.0509(8)	0.0358(6)	0.0488(7)	0.0155(6)	0.0024(6)	–0.0027(6)
O(2)	4*a*	0.0155(3)	1.0861(2)	0.01425(5)	0.0444(7)	0.0430(7)	0.0440(7)	0.0063(6)	–0.0129(6)	0.0002(6)
N(1)	4*a*	0.1292(3)	1.1651(2)	0.05338(5)	0.0304(6)	0.0321(6)	0.0325(6)	0.0044(6)	0.0041(5)	0.0041(6)
C(1)	4*a*	0.9350(4)	0.6784(3)	0.17040(7)	0.0385(9)	0.0448(9)	0.0342(8)	0.0074(8)	–0.0028(7)	0.0002(7)
C(2)	4*a*	0.7304(4)	0.8079(2)	0.13863(6)	0.0269(7)	0.0334(7)	0.0267(6)	0.0027(7)	0.0012(6)	0.0008(5)
C(3)	4*a*	0.6064(4)	0.7290(3)	0.09203(6)	0.0357(8)	0.0306(7)	0.0302(7)	0.0067(6)	0.0008(6)	–0.0052(6)
C(4)	4*a*	0.4107(3)	0.8453(3)	0.06357(6)	0.0327(7)	0.0311(7)	0.0285(7)	0.0022(7)	–0.0010(6)	–0.0052(6)
C(5)	4*a*	0.3427(3)	1.0420(2)	0.08253(6)	0.0244(6)	0.0270(6)	0.0287(6)	0.0004(6)	0.0032(5)	0.0009(6)
C(6)	4*a*	0.4651(4)	1.1263(3)	0.12811(7)	0.0375(8)	0.0283(7)	0.0356(8)	0.0015(6)	0.0010(7)	–0.0062(6)
C(7)	4*a*	0.6614(4)	1.0076(3)	0.15614(7)	0.0376(8)	0.0353(8)	0.0300(7)	–0.0002(7)	–0.0033(6)	–0.0057(6)

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