Crystal structure of 1-benzamido-2-chloro-1-(4-methylphenyl)-2-nitro-propane, $C_{17}H_{17}ClN_2O_3$

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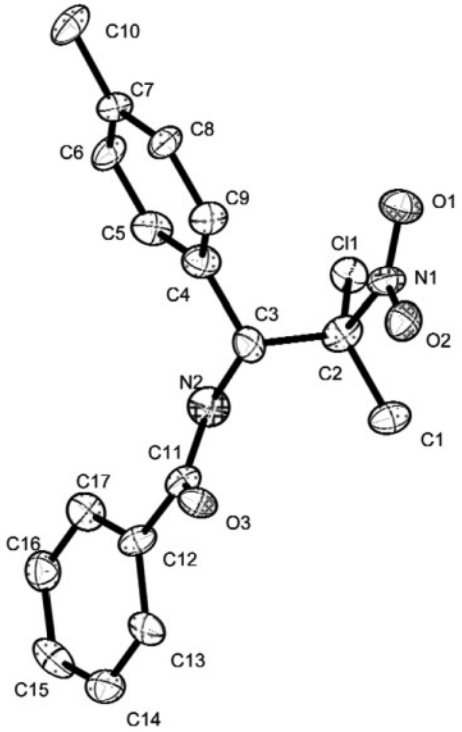

Abstract

$C_{17}H_{17}ClN_2O_3$, monoclinic, *Cc* (no. 9), a = 17.390(9) Å, b = 21.12(1) Å, c = 9.734(5) Å, β = 112.113(6)°, V = 3312.1 Å^3, Z = 8, $R_{gt}(F)$ = 0.0445, $wR_{ref}(F^2)$ = 0.1035, T = 291 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.24×0.26×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.46 cm^{-1}
Diffractometer, scan mode:	Bruker Smart Apex CCD, φ and ω
$2\theta_{max}$:	51.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8790, 4292
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3912
$N(param)_{refined}$:	419
Programs:	SHELX [17]

Source of material

A dry vial was charged with (*E*)-1-(4-methylphenyl)-2-nitro-propene (177 mg), benzamide (242 mg), K_2CO_3 (454 mg), $Ni(OAc)_2$ (35 mg), 4 Å molecular sieves (500 mg), *N*-chloro-succinimide (400 mg, 3.0 mmol) and CH_2Cl_2 (5.0 ml) with nitrogen atmosphere. The resulting mixture was stirred at room temperature for 48h and the reaction was then quenched with saturated aqueous Na_2SO_3 (5.0 mL) solution. The precipitates were filtered off and washed with ethyl acetate (3×10 ml). The combined organic phases were washed with brine and dried with anhydrous sodium sulfate. The organic solution was concentrated and purified via flash chromatography with ethyl acetate and petroleum ether (*v*/*v*, 1:4) as the eluent to give the title compound as white solid (225 mg) in the yield of 68 %. Colourless crystals were obtained by slow evaporation from ethyl acetate solution.

Discussion

1,2-Haloamines are important building blocks in organic, bioorganic and medicinal chemistry [1–7], which can be converted to aziridines [8–9], dehydroamino acids [10] and other compounds [2–7] via intra and intermolecular substitution reactions. Because the carbon- nitrogen and carbon-halogen bonds can be effectively formed in a single process [11], the aminohalogenation of α,β-unsaturated functionalized olefins has become one of the most efficient method to get 1,2-haloamines derivatives. Several α,β-unsaturated functionalized olefins, such as α,β-unsaturated carboxylic esters, ketones, nitriles, methylenecyclopropanes and vinylidenecyclopropanes, have been used as the olefins substrates of aminohalogenation [11], and in these aminohalogenation processes the substituted sulfonamides were mainly used as nitrogen sources. Recently, α,β-unsaturated nitros are also found to be good olefins substrates of aminohalogenation [12–14], and many reagents, such as *N*,*N*-dichloro-*p*-tolylsulfonamide, and many others have been used as the halogen /nitrogen sources. Interestingly, in the aminohalogenation of α,β-unsaturated nitros, the amino functionality is added onto the β-position of nitro group and the halo functionality is added onto the α-position, while the amino functionality is normally added onto the α-position and the halo functionality is added onto the β-position of the substrates connecting groups such as ester, ketone or nitrile [11]. In the compound *N*-(2-chloro-2-nitro-1-phenylpropyl)-4-methylbenzene-sulfonamide, the α-carbon of the substrate was fully chlorinated [12]. However, the aminohalogenation reactions of (*E*)-1-(4-methylphenyl)-2-nitro-propene with combination of *N*-chlorosuccinimide and aryl formamides as nitrogen / halogen sources was not been well documented. So, we synthesized the title compound as a part of this study in order to elucidate the conformation and configuration of this product. The bond lengths and an-gles in the title structure are in good agree with expected values [15]. The dihedral angle between the O1–N1–O2 plane and the C4C9 benzene ring is 43.2(2)°. While the dihedral angle between the O3–N2–O4 plane and the C6–C11 benzene ring is 38.4(3)°. For 1-(2-chloro-1-(4-chlorophenyl)-2-nitro- propyl)pyrrolidine-2,5-dione [16], the torsion angles are significantly different.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*a*	0.0944	–0.0164	0.4487	0.043
H(1B)	4*a*	0.0278	0.0056	0.5112	0.043
H(1C)	4*a*	0.1117	–0.0241	0.6179	0.043
H(3)	4*a*	0.2159	0.0564	0.4756	0.029
H(5)	4*a*	0.3114	0.1285	0.8264	0.034
H(6)	4*a*	0.3725	0.2272	0.8640	0.031
H(8)	4*a*	0.2741	0.2599	0.4261	0.031
H(9)	4*a*	0.2134	0.1606	0.3879	0.027
H(10A)	4*a*	0.4218	0.3189	0.6717	0.050
H(10B)	4*a*	0.3668	0.3392	0.7601	0.050
H(10C)	4*a*	0.3332	0.3476	0.5875	0.050
H(13)	4*a*	0.3087	–0.1526	0.5991	0.028
H(14)	4*a*	0.3855	–0.2287	0.7656	0.038
H(15)	4*a*	0.4669	–0.2004	1.0055	0.044
H(16)	4*a*	0.4743	–0.0955	1.0812	0.039
H(17)	4*a*	0.3949	–0.0179	0.9147	0.035

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}
C(1)	4*a*	0.0862(3)	0.0021(2)	0.5321(4)	0.039(2)	0.022(2)	0.024(2)	–0.003(2)	0.011(2)	0.001(1)
C(2)	4*a*	0.1258(2)	0.0685(2)	0.5621(4)	0.037(2)	0.030(2)	0.014(2)	–0.006(2)	0.011(1)	–0.006(1)
C(3)	4*a*	0.2173(2)	0.0694(2)	0.5732(3)	0.022(2)	0.029(2)	0.015(2)	0.004(2)	0.001(1)	0.000(1)
C(4)	4*a*	0.2574(2)	0.1342(2)	0.6025(4)	0.033(2)	0.025(2)	0.022(2)	0.002(2)	0.008(2)	–0.002(1)
C(5)	4*a*	0.3043(3)	0.1548(2)	0.7458(4)	0.037(2)	0.026(2)	0.020(2)	0.004(2)	0.009(2)	0.001(1)
C(6)	4*a*	0.3403(2)	0.2144(2)	0.7680(4)	0.026(2)	0.025(2)	0.019(2)	–0.008(2)	0.001(1)	–0.004(1)
C(7)	4*a*	0.3293(2)	0.2561(2)	0.6497(3)	0.027(2)	0.017(2)	0.018(2)	–0.001(1)	0.008(1)	–0.000(1)
C(8)	4*a*	0.2817(2)	0.2339(2)	0.5072(4)	0.026(2)	0.021(2)	0.027(2)	–0.007(1)	0.006(1)	–0.002(1)
C(9)	4*a*	0.2455(2)	0.1738(2)	0.4836(3)	0.031(2)	0.024(2)	0.009(1)	–0.001(2)	0.003(1)	–0.002(1)
C(10)	4*a*	0.3661(3)	0.3213(2)	0.6690(4)	0.035(2)	0.031(2)	0.026(2)	–0.015(2)	0.002(2)	–0.002(2)
C(11)	4*a*	0.2932(2)	–0.0302(2)	0.6278(4)	0.027(2)	0.021(2)	0.024(2)	–0.005(1)	0.008(1)	–0.004(1)
C(12)	4*a*	0.3437(2)	–0.0775(2)	0.7425(4)	0.032(2)	0.019(2)	0.021(2)	–0.006(2)	0.014(1)	–0.001(1)
C(13)	4*a*	0.3412(2)	–0.1413(2)	0.6960(4)	0.028(2)	0.025(2)	0.027(2)	0.005(2)	0.023(2)	0.002(1)
C(14)	4*a*	0.3874(3)	–0.1867(2)	0.7954(4)	0.035(2)	0.024(2)	0.043(2)	–0.001(2)	0.025(2)	0.002(2)
C(15)	4*a*	0.4364(3)	–0.1696(2)	0.9389(5)	0.035(2)	0.037(2)	0.040(2)	0.017(2)	0.016(2)	0.010(2)
C(16)	4*a*	0.4405(3)	–0.1067(2)	0.9849(4)	0.026(2)	0.037(2)	0.030(2)	0.001(2)	0.006(2)	–0.003(2)
C(17)	4*a*	0.3929(3)	–0.0599(2)	0.8848(4)	0.032(2)	0.032(2)	0.023(2)	0.003(2)	0.010(2)	0.003(2)
Cl(1)	4*a*	0.11600(5)	0.10049(4)	0.72305(8)	0.0300(5)	0.0306(4)	0.0194(4)	–0.0003(4)	0.0158(3)	–0.0082(3)
N(1)	4*a*	0.0773(2)	0.1116(1)	0.4301(3)	0.033(2)	0.019(1)	0.028(2)	0.001(1)	0.001(1)	–0.004(1)
N(2)	4*a*	0.2628(2)	0.0200(2)	0.6763(3)	0.038(2)	0.036(2)	0.011(1)	0.002(2)	0.010(1)	–0.000(1)
O(1)	4*a*	0.0569(2)	0.1647(1)	0.4502(3)	0.041(2)	0.026(1)	0.034(1)	0.006(1)	0.009(1)	0.001(1)
O(2)	4*a*	0.0623(2)	0.0882(1)	0.3065(3)	0.029(1)	0.033(1)	0.023(1)	–0.002(1)	0.006(1)	0.001(1)
O(3)	4*a*	0.2792(2)	–0.0387(1)	0.4938(3)	0.032(2)	0.023(1)	0.022(1)	0.006(1)	0.013(1)	–0.0024(9)

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