Crystal Structure of 3-Chloro-4-(3,3-dichloroallyloxy)benzenamine

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The title compound, 3-chloro-4-(3,3-dichloroallyloxy)benzenamine, crystallizes in the orthorhombic space group *Pbca* with the following unit-cell parameters: $a = 5.5640(11)$, $b = 14.832(3)$, $c = 26.399(5)$ Å, $V = 2178.6(8)$ Å³. The crystal structure of this compound was solved by direct methods and refined to a final $R = 0.051$ for 1185 reflections with $I > 2\sigma(I)$. In the crystal packing, the molecules are linked via N-H...O and N-H...N hydrogen bonds.

(Received October 20, 2009; Accepted May 27, 2010; Published on web July 10, 2010)

The safe and effective use of insecticides to fight serious crop damage from harmful pests is an essential element in both the defense of the food supply and the prevention of disease transmission. Due to the ability of insects to rapidly develop resistance, the discovery of agents that act on new biochemical targets is an important tool for effective pest management. The title compound is a kind of aromatic organic intermediate that can be used for insecticides and pesticides.^{1,2} Herein we report on its synthesis and crystal structure.

The title compound (Fig. 1) was synthesized according to a traditional reduction reaction.³ A mixture consisting of 3.8 g (68 mmol) of iron powder, 0.24 g (6.8 mmol) of hydrochloric acid and 25 ml of water was placed in a 100 mL four-necked flask fitted with a condenser, a sealed stirrer and a thermometer reaching into the liquid. After heating to 353 K, then 7 g (24.5 mmol) of 2-chloro-1-(3,3-dichloroallyloxy)-4-nitrobenzene was added in several small portions with vigorous agitation to the reaction vessel. It was stirred further at 363–373 K for 5 h and then cooled. The mixture was treated with 3 g of sodium hydroxide and stirred for 1 h, then filtered by a vacuum. The filter cake was washed with four 50 ml portions of hot water. The filtrate was extracted with ethyl acetate. The organic layers were moved under reduced pressure, and the obtained target product 3-chloro-4-(3,3-dichloroallyloxy)benzenamine (5 g) as red solid. The yield reached 81.3%.

Its single crystal is suitable for X-ray structural analysis, and was obtained by slowly evaporating from methanol at room temperature for 4 days.

A red crystal having dimensions of $0.30 \times 0.30 \times 0.2$ mm³ was

Fig. 1 Chemical diagram of 3-chloro-4-(3,3-dichloroallyloxy)benzenamine.

chosen for X-ray diffraction studies. The experimental crystallographic details are given in Table 1. Measurements were made on a Enraf-Nonius CAD4 diffractometer equipped with graphite crystal monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares procedures on F^2 , using the program SHELXL-97.⁴ All H atoms were located with idealized geometry and were included during calculations using riding models.

Table 1 Crystal and experimental data

Chemical formula: C ₉ H ₈ Cl ₃ NO	
Formula weight = 252.51	
$T = 298$ K	
Crystal system: orthorhombic, <i>Pbca</i>	
Space group: <i>Pbca</i>	$Z = 8$
$a = 5.5640(11)$ Å	$\alpha = 90^\circ$
$b = 14.832(3)$ Å	$\beta = 90^\circ$
$c = 26.399(5)$ Å	$\gamma = 90^\circ$
$V = 2178.6(8)$ Å ³	
$D_x = 1.540$ g cm ⁻³	
Radiation: Mo K_α ($\lambda = 0.71073$ Å)	
Goodness of fit on F^2 : 1.004	
Data/restraints/parameters: 1973/0/127	
$\mu(\text{Mo } K_\alpha) = 0.81$ mm ⁻¹	
$F_{000} = 1024$	
Crystal size = $0.30 \times 0.30 \times 0.20$ mm	
Reflections collected/unique/with $[I > 2\sigma(I)]$: 1973/1973/1185	
θ range for data collection: 1.5 to 25.3°	
Final R indices $[I > 2\sigma(I)]$: $R1 = 0.0509$, $wR2 = 0.1086$	
$wR(F^2) = 0.125$	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.228$ e Å ⁻³	
$(\Delta\rho)_{\text{min}} = -0.245$ e Å ⁻³	
Measurement: Enraf-Nonius CAD4	
Program system: CAD4 Express	
Structure determination: SHELXS-97, SHELXL-97	
Refinement: full matrix	
CCDC deposition number: 750872	

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Table 2 Selected bond distances (Å) and angles (°)

C11-C1	1.696 (4)
C12-C1	1.708 (4)
C13-C5	1.725 (3)
O-C4	1.366 (4)
C1-C2	1.316 (5)
O-C3	1.415 (5)
N-C7	1.369 (4)
C4-O-C3	118.1 (3)
C2-C1-C11	123.8 (3)
C2-C1-C12	123.1 (3)
C11-C1-C12	113.0 (3)
O-C3-C2	109.4 (3)
O-C4-C9	125.1 (3)
O-C4-C5	117.2 (3)
C6-C5-C13	119.1 (3)
C4-C5-C13	119.9 (2)
N-C7-C6	121.4 (3)
N-C7-C8	121.5 (3)

Fig. 2 ORTEP structure of 3-chloro-4-(3,3-dichloroallyloxy)benzenamine showing 50% probability ellipsoids.

The selected bond lengths and bond angles are listed in Table 2. The fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters are presented in Table S1 (Supporting Information). As can be seen from Fig. 2, the structure consists of a substituted phenyl ring (C4-C9). The C1-C2 bond length of 1.267(3) Å conforms to the value for a double bond, while the N-C7 bond length of 1.369(4) Å conforms to the value for a single bond. The torsion angles, C1-C2-C3-O and N-C7-C8-C9, are 92.3(6) and 175.9(4)°, respectively.

In the crystals, the intermolecular hydrogen bonds (N-H0A...N and N-H0B...N) were observed to form a three-dimensional network (Fig. 3), which was effective for stabilization of the crystals. Additionally, the crystal packing is stabilized by intermolecular hydrogen-bond interactions (Table 3).

Acknowledgements

The authors wish to acknowledge the Center of Testing and

Fig. 3 Molecular packing diagram of 3-chloro-4-(3,3-dichloroallyloxy)benzenamine.

Table 3 Hydrogen-bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N-H0A...Ni	0.86	2.52	3.382(4)	175
N-H0B...Oii	0.86	2.58	3.275(4)	139

Symmetry codes: (i) $x+1/2, y, -z+1/2$; (ii) $-x-1/2, y-1/2, z$.

Analysis, Nanjing University, China, for the use of Enraf-Nonius CAD4 diffractometer.

Supporting Information

Table S1 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

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