Crystal structure of *N*-dichloroacetyl-3-methyl-6,8-dichloro-3,4-dihydro-2*H*-1,4-benzoxazine, $C_{11}H_9Cl_4NO_2$

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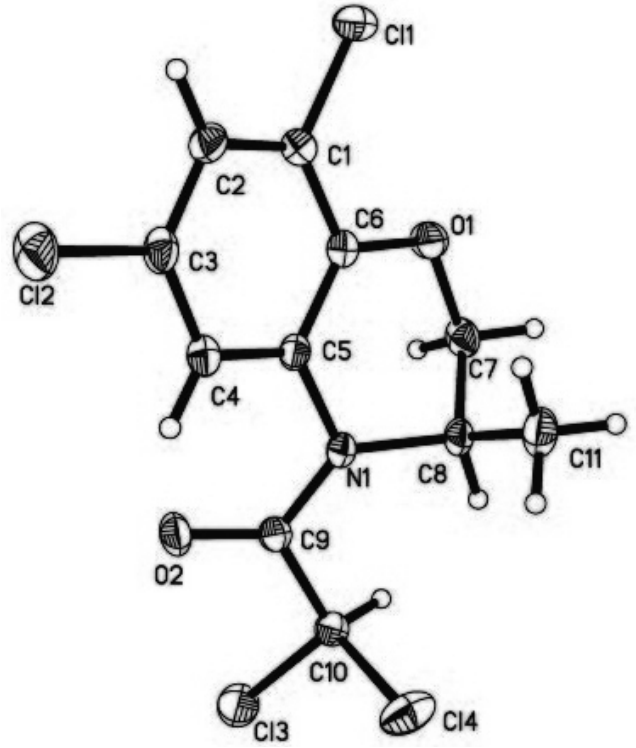

Abstract

$C_{11}H_9Cl_4NO_2$, monoclinic, $P2_1/c$ (no. 14), a = 11.995(2) Å, b = 11.831(2) Å, c = 9.798(2) Å, β = 108.65(3)°, V = 1317.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0374, $wR_{ref}(F^2)$ = 0.1050, T = 293 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.19×0.20×0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.89 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12641, 3018
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2538
$N(param)_{refined}$:	164
Programs:	DIAMOND [10], SHELX [11]

Source of material

Dichloroacetyl chloride (17.6 mmol) was added slowly in the mixture containing 3-methyl-6,8-dichloro-3,4-dihydro-2*H*-1,4-benzoxazine (14 mmol), Na_2CO_3 (15.2 mmol), and benzene (25 mL). The system was stirred at room temperature for 2h and *TLC* monitored. Then the mixture was rinsed, and the organic phase was dried over anhydrous magnesium sulfate. Benzene was removed under vacuum. The crude product was collected as white solid in 48% yield, and recrystallized from ethanol and light petroleum.

Experimental details

The C–H atoms were then constrained to an ideal geometry, with C–H distances of 0.93-0.98 Å. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}(C_{methyl})$ and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}(C)$.

Discussion

Benzoxazine derivatives have attracted widespread attention due to their broad applications in agriculture [1–3]. Moreover, benzoxazines were useful compounds as starting materials for the synthesis of larger structures with valuable biological activities [4–6]. *N*-Dichloroacetyl benzoxazines were used as herbicide safeners [7, 8]. This contribution is a continuation of our work to prepare and characterize *N*-dichloroacetyl-3-methyl-3,4-dihydro-1,4-benzoxazine through *O*-alkylation, reduction, cyclization and acylation reactions [9]. The title molecule is composed of two planar rings, and it is obvious that benzene plane and oxazine ring plane were almost in the same plane with dihedral angle of 9.32(6)°. The torsion angles of N1–C7–C8–N2 was 60.3(2)°, showing a half-chair conformation. Obviously there is a large conjunctive effect between O1, benzene ring, N1, C9–O2 [C=O], which resulted in the shorter bond length than the typical C–N bond length and C–O bond length. In the crystal, molecules are stablized by weak C–H···O hydrogen bonds and van der Waals forces.

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.0051	1.1949	0.5343	0.048
H(4)	4*e*	0.2885	0.9918	0.6294	0.039
H(7A)	4*e*	0.1439	0.9774	0.0221	0.045
H(7B)	4*e*	0.1135	0.8849	0.1193	0.045
H(8)	4*e*	0.3160	0.8993	0.1824	0.040
H(10)	4*e*	0.3575	0.7518	0.2678	0.040
H(11A)	4*e*	0.2976	1.1291	0.2500	0.074
H(11B)	4*e*	0.3361	1.0871	0.1200	0.074
H(11C)	4*e*	0.4168	1.0643	0.2784	0.074

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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}
C(1)	4*e*	0.0317(2)	1.1232(2)	0.3602(2)	0.0377(9)	0.0335(9)	0.0367(9)	0.0046(7)	0.0147(8)	0.0062(7)
C(2)	4*e*	0.0542(2)	1.1471(2)	0.5041(2)	0.050(1)	0.035(1)	0.042(1)	0.0074(8)	0.0260(9)	0.0009(8)
C(3)	4*e*	0.1517(2)	1.0982(2)	0.6024(2)	0.055(1)	0.0325(9)	0.0299(9)	–0.0010(8)	0.0207(8)	–0.0021(7)
C(4)	4*e*	0.2242(2)	1.0247(2)	0.5610(2)	0.0391(9)	0.0323(9)	0.0273(8)	–0.0016(7)	0.0128(7)	0.0012(7)
C(5)	4*e*	0.1998(2)	1.0003(2)	0.4146(2)	0.0323(8)	0.0301(9)	0.0280(8)	–0.0009(7)	0.0140(7)	0.0016(6)
C(6)	4*e*	0.1039(2)	1.0519(2)	0.3122(2)	0.0340(8)	0.0336(9)	0.0273(8)	–0.0009(7)	0.0122(7)	0.0016(7)
C(7)	4*e*	0.1470(2)	0.9595(2)	0.1199(2)	0.050(1)	0.039(1)	0.0242(8)	0.0038(8)	0.0122(8)	–0.0005(7)
C(8)	4*e*	0.2742(2)	0.9587(2)	0.2162(2)	0.0421(9)	0.038(1)	0.0261(8)	0.0040(8)	0.0184(7)	0.0038(7)
C(9)	4*e*	0.3197(2)	0.8323(2)	0.4356(2)	0.0324(8)	0.0368(9)	0.0252(8)	0.0024(7)	0.0092(7)	0.0006(7)
C(10)	4*e*	0.3976(2)	0.7606(2)	0.3714(2)	0.0339(8)	0.0369(9)	0.0304(8)	0.0033(7)	0.0113(7)	0.0004(7)
C(11)	4*e*	0.3369(2)	1.0700(2)	0.2162(2)	0.055(1)	0.052(1)	0.049(1)	–0.006(1)	0.028(1)	0.010(1)
Cl(1)	4*e*	–0.09035(5)	1.18098(5)	0.23245(6)	0.0465(3)	0.0539(3)	0.0476(3)	0.0194(2)	0.0158(2)	0.0081(2)
Cl(2)	4*e*	0.18423(6)	1.13073(5)	0.78455(5)	0.0918(5)	0.0537(3)	0.0316(3)	0.0123(3)	0.0252(3)	–0.0062(2)
Cl(3)	4*e*	0.42088(6)	0.62557(5)	0.45191(8)	0.0768(4)	0.0462(3)	0.0770(4)	0.0255(3)	0.0459(3)	0.0199(3)
Cl(4)	4*e*	0.53327(5)	0.83082(6)	0.39736(8)	0.0371(3)	0.0668(4)	0.0869(5)	–0.0044(2)	0.0254(3)	–0.0077(3)
N(1)	4*e*	0.2733(1)	0.9283(1)	0.3631(2)	0.0339(7)	0.0343(8)	0.0240(6)	0.0030(6)	0.0139(6)	0.0022(6)
O(1)	4*e*	0.0784(1)	1.0405(1)	0.1674(1)	0.0424(7)	0.0538(9)	0.0255(6)	0.0112(6)	0.0088(5)	0.0017(6)
O(2)	4*e*	0.3021(2)	0.8023(1)	0.5455(2)	0.071(1)	0.0494(9)	0.0358(7)	0.0203(8)	0.0299(7)	0.0143(6)

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References

1. Xue, N.; Zhou, Y. H.; Wang, G. W.; Miao, W. R.; Qu, J. P.: Syntheses and herbicidal activity of pyrazolyl benzoxazole derivatives. J. Heterocycl. Chem. **47** (2010) 15–21.
2. Macias, F. A.; Marin, D.; Oliveros-Bastidas, A.; Chinchilla, D.; Simonet, A. M.; Molinillo, J. M. G.: Isolation and synthesis of allelochemicals from gramineae: Benzoxazinones and related compounds. J. Agric. Food Chem. **54** (2006) 991–1000.
3. Tang, Z. L.; Chen, W. W.; Zhu, Z. H.; Liu, H. W.: Synthesis of 2,3-diaryl-3,4-dihydro-2*H*-1,3-benzoxazines and their fungicidal activities. J. Heterocycl. Chem. **48** (2011) 255–260.
4. Matsumoto, Y.; Tsuzuki, R.; Matsuhisa, A.; Masuda, N.; Yamagiwa, Y.; Yanagisawa, I.; Shibanuma, T.; Nohira, H.: Novel potassium channel activators. II. Synthesis and pharmacological evaluation of 3,4-dihydro-2*H*-1,4-benzoxazine derivatives: Modification of the aromatic part Chem. Pharm. Bull. **47** (1999) 971–979.
5. Largeron, M.; Lockart, B.; Pfeiffer, B.; Fleury, M. B.: Synthesis and in vitro evaluation of new 8-amino-1,4-benzoxazine derivatives as neuro- protective antioxidants. J. Med.Chem. **42** (1999) 5043–5052.
6. Sakami, S.; Kawai, K.; Maeda, M.; Aoki, T.; Fuji, H.; Ohno, H.; Ito, T.; Saitoh, A.; Nakao, K.; Izumimoto, N.; Matsuura, H.; Endo, T.; Ueno, S.; Natsume, K.; Nagase, H.: Design and synthesis of a metabolically stable and potent antitussive agent, a novel opioid receptor antagonist, TRK-851. Bioorg. Med. Chem. **16** (2008) 7956–7967.
7. Hatzios, K. K.; Burgos, N.: Metabolism-based herbicide resistance: regulation by safeners. Weed Sci. **52** (2004) 454–457.
8. Buono, D. D.; Scarponi, L.; Damato, R.: Benoxacor induction of terbuthylazine detoxification in Zea mays and Festuca arundinacea. J. Agric. Food Chem. **53** (2005) 2483–2488.
9. Fu, Y.; Xu, Z. Z.; Ye, F.: Synthesis and crystal structure of 4-dichloroacetyl-3-phenyl-3,4-dihyro-2*H*-1,4-benzoxazine. Asian J. Chem. **26** (2014) 2913–2915
10. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2i. Crystal Impact, Bonn, Germany 2012.
11. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.