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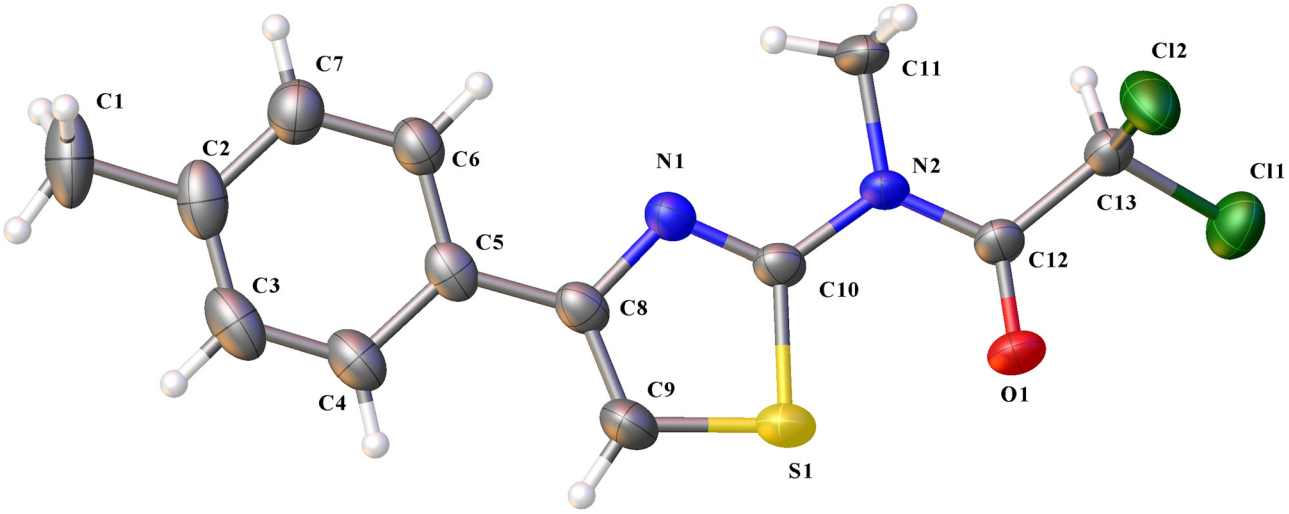
Crystal structure of 2,2-dichloro-*N*-methyl-*N*-(4-*p*-tolylthiazol-2-yl)acetamide, $C_{13}H_{12}Cl_2N_2OS$



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Abstract

$C_{13}H_{12}Cl_2N_2OS$, orthorhombic, $Pna2_1$ (no. 33), a = 30.2415(19) Å, b = 6.0253(4) Å, c = 7.8933(6) Å, V = 1438.27(17) Å^3, Z = 4, $R_{gt}(F)$ = 0.0428, $wR_{ref}(F^2)$ = 0.1046, T = 285 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.15 × 0.13 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.59 mm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω scans
θ_{max}, completeness:	27.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27472, 3288, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3231
$N(param)_{refined}$:	173
Programs:	Bruker,[1] Olex2,[2,3] SHELX[4]

1 Source of material

The title compound was synthesized according to literature with slight modification.[5,6] A solution was formed consisting of 5.76 mmol (1.23 g) of 2-bromo-4′-methylacetophenone, 5.49 mmol (0.56 g) of triethylamine and 25 mL of ethanol. *N*-methylthiourea (0.92 g, 5.49 mmol) was added to the mixture by drops followed by heated to reflux. After the reaction was completed, the solvent was removed by rotary evaporation. The obtained substance was dissolved in dichloromethane, then washed three times with saturated salt water, dried over anhydrous sodium sulfate, and filtered, and the solvent was then evaporated under reduced pressure to yield intermediate (*N*-methyl-4-*p*-tolylthiazol-2-amine). The intermediate (1.02 g, 5.00 mmol) and triethylamine (1.52 g, 15.00 mmol) were added to 30 mL of acetonitrile. Subsequently, dichloracetyl chloride (1.47 g, 10.00 mmol) was added dropwise with stirring at room temperature for 2.00 h. After removing the solvent by rotary evaporation, the product was purified *via* column chromatography on silica gel (petroleum ether: EtOAc = 10:1, *v*/*v*). Crystals of the title compound were obtained by using a mixed solvent of EtOAc and petroleum ether at room temperature.

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2 Experimental details

The structures was solved by direct methods with the SHELXS program.[4] All hydrogen atoms were placed in geometrically calculated positions and constrained to ride on their parent atoms.

3 Comment

N-dichloroacetamides herbicide safeners have generated considerable commercial interest and research activity for their application to crops to alleviate the injury from herbicides.[7,8] Thiazole derivatives, due to their unique physiological activities, are extensively utilized in the development of active small molecules for applications in pesticides and pharmaceuticals.[9–13] In view of the principle of fragment splicing,[14] the thiazole derivative and dichloroacetyl were spliced together to design and synthesize novel potential 2-dichloroacetyl thiazole derivatives herbicide safeners.

Single-crystal structure analysis revealed that the title compound belongs to orthorhombic system, The space group type is $Pna2_1$. Bond lengths and angles are all in normal ranges.[15,16] There is only a drug molecule in the asymmetric unit (see the Figure). Obviously, there is π–π conjugation effect in amide moiety, which cause shorter N(2)–C(12) (1.360(3) Å) bond than the normal N–C (1.47 ~ 1.50 Å). Besides, the torsion angle of N(1)–C(8)–C(5)–C(4) and N(1)–C(8)–C(5)–C(6) are 175.3(3)° and −5.0(3)°, respectively, which indicate the benzene ring and thiazole ring are almost coplanar. The torsion angles of N(1)–C(10)–N(2)–C(12) and S(1)–C(10)–N(2)–C(12) are 176.9(3)° and −2.1(3)°, respectively, so the carbon atom C(12) and thiazole ring are almost coplanar. Weak intermolecular C–H···O and C–H···Cl hydrogen bonds are founded.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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