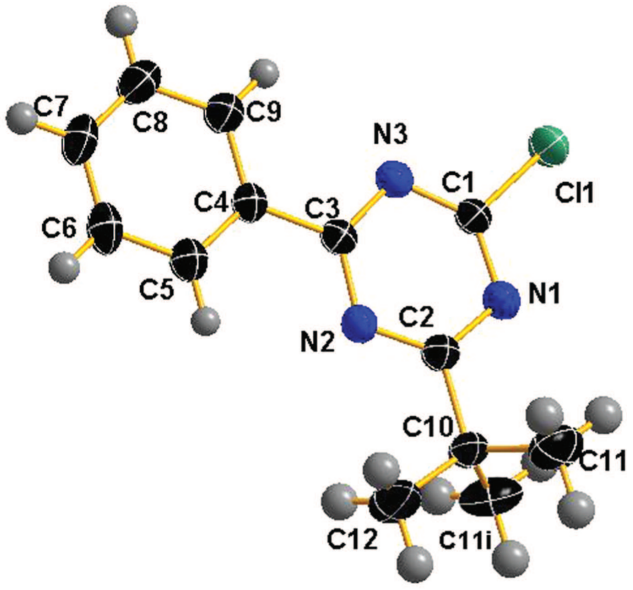
Xiao Song, Zhishu Tang*, Zhenyu Zuo and Jinao Duan*

The crystal structure of 2-(*tert*-butyl)-4-chloro-6-phenyl-1,3,5-triazine, $C_{13}H_{14}Cl_1N_3$



https://doi.org/10.1515/ncrs-2017-0386
Received March 7, 2018; accepted June 6, 2018; available online June 21, 2018

Abstract

$C_{13}H_{14}Cl_1N_3$, orthorhombic, *Pma*2 (no. 28), $a = 6.7623(2)$ Å, $b = 21.1431(6)$ Å, $c = 8.8708(2)$ Å, $Z = 4$, $V = 1268.31(6)$ Å^3, $R_{gt}(F) = 0.0362$, $wR_{ref}(F^2) = 0.0969$, $T = 200(2)$ K.

CCDC no.: 1563248

One of two crystallographically independent molecules of the asymmetric unit of the title structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding authors: Zhishu Tang,** College of Pharmacy, Shaanxi University of Chinese Medicine, Xi'an, Shaanxi, 712046, P.R. China, e-mail: tzs6565@163.com; **Jinao Duan,** College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023, P.R. China, e-mail: dja@njutcm.edu.cn
Xiao Song: College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023, P.R. China; and College of Pharmacy, Shaanxi University of Chinese Medicine, Xi'an, Shaanxi, 712046, P.R. China
Zhenyu Zuo: College of Pharmacy, Shaanxi University of Chinese Medicine, Xi'an, Shaanxi, 712046, P.R. China

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.15 × 0.12 × 0.10 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178Å)
μ:	2.50 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	68.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14980, 2537, 0.068
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2324
$N(param)_{refined}$:	215
Programs:	Bruker programs [1], SHELX [2]

Source of material

Under the atmosphere of N_2, to the solution of 1,3,5-triazine (18.44 g, 0.1 mol) in tetrahydrofuran (100 mL) was added the solution of PhMgBr in Et_2O (1 mol/L, 110 mL) dropwise at 258 K. The mixture was stirred for 2 h then quenched with 5 mL of water. The solvent was evaporated to get a yellow solid which was purified by silica gel chromatograph to afford 2-phenyl-4,6-dichloro-1,3,5-triazine (17.41 g, yield 77%). Under the atmosphere of N_2, to the solution of 2-phenyl-4,6-dichloro-1,3,5-triazine (11.30 g, 0.05 mol) in tetrahydrofuran (100 mL) was added the solution of t-butMgBr in Et_2O (1 mol/L, 55 mL) dropwise at 273 K. Then CuI (95.25 mg, 0.5 mmol) was added to the reaction system. The mixture was stirred and warmed to room temperature. After half an hour, the reaction was quenched with 5 mL of water. The solvent was evaporated to get a yellow solid which was purified by silica gel chromatograph to afford the title compound (8.05 g, yield 65%). ^{1}**HNMR**: 8.56 ppm (2*H*, d, $J = 8$ Hz), 7.62 ppm (1*H*, t, $J = 8$ Hz), 7.54 ppm (2*H*, t, $J = 8$ Hz), 1.48 ppm (9*H*,s). Crystals were obtained from an petroleumether/ethyl acetate mixture (1:1, v:v) by slow evaporation at room temperature.

Experimental details

The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Discussion

1,3,5-Triazine derivatives are important intermediates which were widely used in drug development, pesticide research, chemical materials and catalytic application, due to its

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.250000	0.71123(5)	1.41697(10)	0.0471(3)
N1	−0.250000	0.66798(16)	1.1436(4)	0.0369(8)
N2	−0.250000	0.55879(16)	1.0871(4)	0.0342(8)
N3	−0.250000	0.59247(17)	1.3425(4)	0.0337(8)
C1	−0.250000	0.65043(18)	1.2865(5)	0.0330(8)
C2	−0.250000	0.61896(19)	1.0459(5)	0.0355(9)
C3	−0.250000	0.54733(18)	1.2360(4)	0.0307(8)
C4	−0.250000	0.48098(18)	1.2860(5)	0.0322(8)
C5	−0.250000	0.4322(2)	1.1796(5)	0.0392(10)
H5	−0.250000	0.441954	1.075116	0.047*
C6	−0.250000	0.3698(2)	1.2257(6)	0.0463(11)
H6	−0.250000	0.336897	1.152811	0.056*
C7	−0.250000	0.3551(2)	1.3770(6)	0.0468(12)
H7	−0.250000	0.312133	1.408149	0.056*
C8	−0.250000	0.4029(2)	1.4836(6)	0.0490(12)
H8	−0.250000	0.392480	1.587801	0.059*
C9	−0.250000	0.4659(2)	1.4393(5)	0.0402(10)
H9	−0.250000	0.498505	1.512914	0.048*
C10	−0.250000	0.6356(2)	0.8796(5)	0.0410(10)
C11	−0.4336(6)	0.6765(2)	0.8475(4)	0.0662(10)
H11A	−0.429089	0.714704	0.909757	0.099*
H11B	−0.553170	0.652291	0.871417	0.099*
H11C	−0.435345	0.688360	0.740698	0.099*
C12	−0.250000	0.5773(3)	0.7819(6)	0.084(2)
Cl2	−0.250000	0.20354(5)	1.14771(11)	0.0488(4)
N4	−0.250000	0.08493(16)	1.0723(4)	0.0332(8)
N5	−0.250000	0.05119(16)	0.8158(4)	0.0330(7)
N6	−0.250000	0.16102(16)	0.8735(4)	0.0354(7)
C13	−0.250000	0.14331(19)	1.0165(4)	0.0330(8)
C14	−0.250000	0.11263(18)	0.7758(5)	0.0329(8)
C15	−0.250000	0.04038(18)	0.9650(4)	0.0307(8)
C16	−0.250000	−0.02651(18)	1.0143(5)	0.0313(8)
C17	−0.250000	−0.07472(19)	0.9077(5)	0.0372(9)
H17	−0.250000	−0.064532	0.803370	0.045*
C18	−0.250000	−0.1374(2)	0.9523(6)	0.0432(10)
H18	−0.250000	−0.170019	0.878681	0.052*
C19	−0.250000	−0.1527(2)	1.1049(6)	0.0447(11)
H19	−0.250000	−0.195758	1.135843	0.054*
C20	−0.250000	−0.1054(2)	1.2097(5)	0.0465(11)
H20	−0.250000	−0.115859	1.313849	0.056*
C21	−0.250000	−0.0420(2)	1.1667(5)	0.0394(9)
H21	−0.250000	−0.009616	1.240954	0.047*
C22	−0.250000	0.12908(19)	0.6090(5)	0.0368(9)
C23	−0.4284(9)	0.1696(4)	0.5768(5)	0.115(3)
H23A	−0.548881	0.144632	0.591296	0.172*
H23B	−0.422628	0.184785	0.472452	0.172*
H23C	−0.429579	0.205900	0.645614	0.172*
C24	−0.250000	0.0713(4)	0.5126(8)	0.144(6)
H12A	−0.368(5)	0.5518(16)	0.805(3)	0.215*
H12B[a]	−0.253(5)	0.5897(9)	0.6756(13)	0.215*
H24A	−0.367(5)	0.0460(16)	0.535(3)	0.215*
H24B[a]	−0.250(5)	0.0840(9)	0.4066(14)	0.215*

[a]Occupancy: 0.5.

especial pharmacological activities, biological activities [3, 4], photoelectric properties [5] and catalytic properties. Because of these advantages, the synthesis of new triazine derivatives have drawn more attentions in recent years [6]. As an important unit, tertiary butylgroup was widely used in constructing efficient chiral ligands or chiral catalysts, due to its large steric stabilisation. So, 2-(*tert*-butyl)-4-chloro-6-phenyl-1,3,5-triazine was firstly synthesized using 1,3,5-triazine as starting material. This derivative can be used to synthesize many important chiral ligands by substitution reactions with chiral sulfamide, chiral sulfenamide, chiral amine, chiralphosphine and so on.

This title crystal structure consists of the $C_{13}H_{14}ClN_3$ molecules, in which all bond lengths are in normal ranges. There are two cystallographically independent molecules in the asymmetric unit. In one of independent molecule, the bond length of C1—Cl1 and C10—C11 are 1.730(4) Å and 1.538(5) Å respectively. The bond length of C1—N1 is 1.320(5) Å, which is shorter than C7—C8 1.383(7) Å. The angle of C1—N1—C2 = 113.6(3)° is smaller than that of C4—C5—C6 = 120.3(4)°. There are π-π stacking interactions between the adjacent molecules in different layer. The distance between the adjacent aromatic rings in different layers is less than 3.5 Å, which is within normal range [7]. No classical hydrogen bonds were observed as following: C5—H5···N2 (d(H5···N2) = 2.47 Å), C6—H6···Cl2 (d(H6···Cl2) = 2.82 Å), C17—H17···N5 (d(H17···N5) = 2.45 Å) and C23—H23C···N6 (d(H23C···N6) = 2.54 Å).

Acknowledgements: We acknowledge the supports by Key project of Shaanxi Provincial Education Department (17JS029), Natural Science Basic Research Program of Shaanxi(2017JM8070). China Postdoctoral Science Foundation funded project(2016M602994).

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2012).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. Sect.C: **27** (2015) 3–8.
3. Sharma, A.; Ghabbour, H.; Khan, S. T.; Torre, B. G.; Albericio, F.; El-Faham A.: Novelpyrazolyl-s-triazine derivatives, molecular structure and antimicrobial activity. J. Mol. Struct. **1145** (2017) 244–253.
4. Xiao, Y.; Jin, B.; Peng, R.; Zhao, J.; Liu, Q.; Chu, S.; Synthesis, characterization and properties of a new energetic salt 2,4-

diamino-6-methyl-1,3,5-triazine dinitramide. J. Mol. Struct. **1146** (2017) 417–423.
5. Wang, T.; Sun, H.; Lu, T.; Bridgmohan, C. N.; Li,F.; Liu, D.; Hu , W.; Li, W.; Zhou, X.; Wang, L.: Dissociation exists in *s*-triazine based donor-accepter organic systemsby photo-induced electron transfer. Dyes. Pigments. **139** (2017) 264–273.
6. Wang, K.; Tang , Y.; Jiang, Q.; Lan,Y.; Huang, H.; Liu , D.; Zhong, C.: A thiophene-containing covalent triazine-based framework with ultramicropore for CO_2 capture. J. Energy Chem. **26** (2017) 902–908.
7. Deng, L.; Liu, H.; Li, S.: Crystal structure of 4-(chloromethyl)-3-nitrobenzoic acid, $C_8H_6ClNO_4$. Z. Kristallogr. NCS **232** (2017) 647–648.