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Synthesis, Characterization and Crystal Structure of 2,3,6-Trichloro-5-(trichloromethyl)pyridine

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2,3,6-Trichloro-5-(trichloromethyl)pyridine (TCTCMP) was synthesized from 2-chloro-5-chloromethyl pyridine (CCMP) through two-steps chloridization using chlorine as chlorizating agent. Initially, 2-chloro-5-chloromethyl pyridine was chloridized for 8 h at reflux conditions in the presence of ultraviolet and transformed into 2-chloro-5-(trichloromethyl)pyridine (CTCMP), then CTCMP was chloridized for 6 h at 175 °C with WCl_6 as catalyst. The product was characterized by FT-IR, NMR and elemental analysis. The crystal structure of TCTCMP was investigated using X-ray diffraction and SHELXTL97 software and the result indicated that TCTCMP crystallized in the orthorhombic system, space group *Pbcm* with a = 8.3100(17), b = 17.018 (3), c = 7.3160(15) Å, V = 1034.6 (4) $Å^3$; Z 4.

Keywords: 2,3,6-Trichloro-5-(trichloromethyl)pyridine, Synthesis, Crystal structure.

INTRODUCTION

The importance of polychloropyridines derivatives as pharmaceutical and agricultural intermediates has been well established[1]. Some polychloropyridines derivatives had been reported for the preparation of herbicides, medicines, fungicides and insecticides, *etc*[2,3]. For example, 2-chloro-5-chloromethylpyridine could be used for synthesis of herbicide [4,5], 2-chloro-5-trichloromethyl pyridine is a useful compound in the preparation of medicines and herbicides[6].

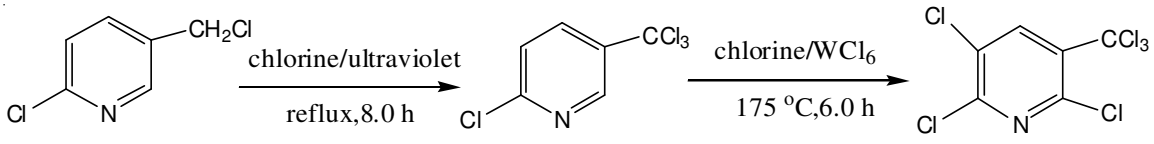
2,3,6-Trichloro-5-(trichloromethyl)pyridine (TCTCMP, I), as one of polychloropyridines compounds, could be utilized for the synthesis of different chemicals that have important application in the preparation of pesticide, such as 2,3,6-trichloro-5-(trifluoromethyl)pyridine and 2,5-dichloro-3-(trifluoromethyl) pyridine[7], *etc*. (**I**) could be prepared from polychlorinated β-picolines through gas-phase chlorination or β-(trichloromethyl)pyridines through catalytic chlorination with Lewis acid as catalyst[8,9]. Herein, we report the synthesis of (**I**) from 2-chloro-5-chloromethyl pyridine. Meanwhile, the crystal structure of (**I**) also was investigated. The synthesis of 2,3,6-trichloro-5-(trichloromethyl)pyridine presented as **Scheme-I**.

EXPERIMENTAL

2-Chloro-5-chloromethyl pyridine was supplied by Well Chemical Co. Ltd of Jiangsu (Yancheng, People's Republic of China), its mass content is 97.3 % determined by GC. Chlorine gas was purchased from Dahe Chlor-Alkali Chemical Industry Co. Ltd of Jiangsu (Yancheng, People's Republic of China), its mass content is 99.5 %. All other chemicals were of reagent grade and used without purification as received.

Fourier transform infrared (FT-IR) spectrum was recorded with KBr pellets on a Nicolet Nexux FT-IR 670 spectrometer. Sixteen scans at a resolution of 4 cm^{-1} were averaged and referenced against air. ^1H NMR spectrum was obtained with Bruker AV-500 spectrometer at 500.13 MHz and measured in $CDCl_3$ solution at 30 ± 0.5 °C. The sample was dissolved in a 5 mm diameter tube at a concentration of *ca* 20 mg/mL. X-ray diffraction was performed on a Bruker APEXII CCD diffractometer. Mass spectrum of (**I**) was analyzed using Trace DSQ GC/MS (Thermo Electron Co., USA).

Synthesis of 2,3,6-trichloro-5-(trichloromethyl)pyridine: 2-Chloro-5-chloromethyl pyridine (100 mmol) was dissolved by carbon tetrachloride and heated to the refluxing temperature



Scheme-I: Route for the synthesis of 2,3,6-trichloro-5-(trichloromethyl)pyridine

and the chlorine gas was poured into the reaction mixture in the presence of ultraviolet. After 8 h, the carbon tetrachloride was recovered by distillation. WCl_6 (2 g) was added into the residual material of distillation and stirred adequately, then the reaction mixture was heated to 175 °C and reacted with chlorine gas at this temperature for 6 h. After these procedure, the reactant was separated using vacuum distillation and the distillation cut of 120-124 °C/10 mmHg and 130-134 °C/10 mmHg was collected respectively. The temperature of the distillation cut of 130-134 °C/10 mmHg was cooled to lower than 5 °C for the formation of raw 2,3,6-trichloro-5-(trichloromethyl)pyridine. After filtration, the fine compound (**I**) was obtained by recrystallization of the filter residue using 1,2-dichloroethane as solvent and active carbon as decolorant. Crystals of (**I**) that suitable for X-ray diffraction were obtained by slow evaporation of 1,2-dichloroethane solution of (**I**).

X-ray crystallography: A colorless block-like crystal of compound (I) grown in 1,2-dichloroethane with dimensions of 0.30 mm × 0.20 mm × 0.20 mm was used for structural determination. Diffraction data were collected on a Bruker APEXII CCD diffractometer by using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods with SHELXS-97 and refined on the F^2 by full-matrix least-squares method with SHELXL-97. All non-hydrogen atoms were refined anisotropically.

RESULTS AND DISCUSSION

Identification of resonance in the spectra: The FT-IR, ^{1}H NMR and GC-MS spectra of purified TCTCMP were presented in Figs. 1-3, respectively.

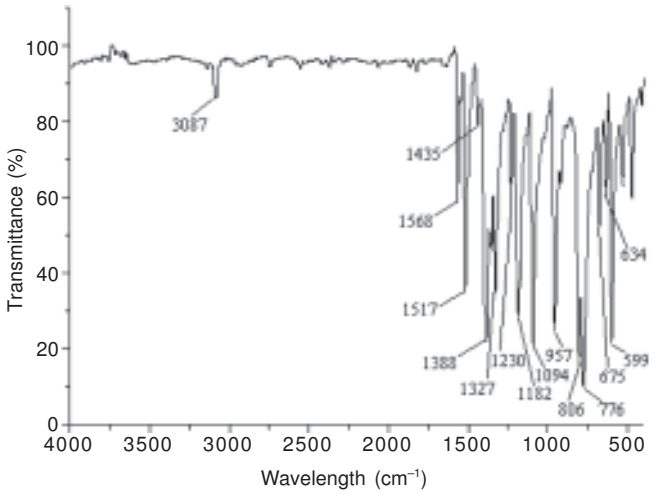


Fig. 1. FT-IR spectrum of TCTCMP

In the FT-IR spectrum of purified TCTCMP, the absorption bands at 3087 cm^{-1} was assigned to νC-H of pyridine ring, 1568, 1517, 1435 and 1388 cm^{-1} were ascribed to ν(C-C) of pyridine ring, 1327 and 1230 cm^{-1} were assigned to ν(C=N), 1182 and 1094 cm^{-1} were assigned to ν(C-Cl) of pyridine ring, 957 cm^{-1} was assigned to ν(C-H) pyridine ring, 806, 776 and 675 cm^{-1} were assigned to γ(C-Cl) of CCl_3.

In the ^{1}H NMR of TCTCMP, the peak at 8.54 ppm was ascribed to the proton of pyridine ring and 7.26 ppm was ascribed to the H of residual proton of $CDCl_3$.

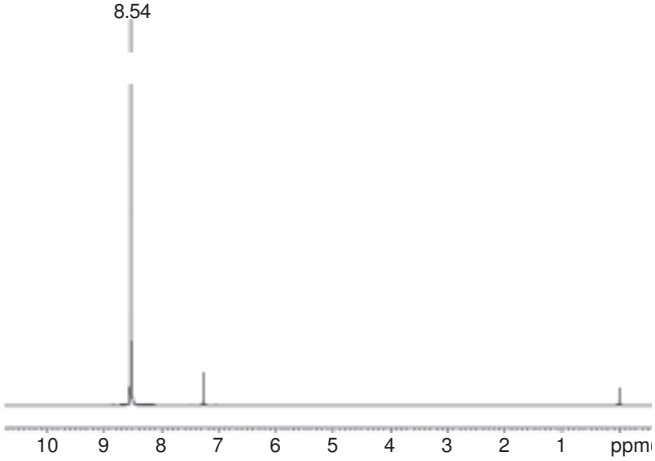


Fig. 2. ^{1}H NMR spectrum of TCTCMP

In the GC spectrum, peak at 9.75 minute ascribed to the TCTCMP. In the MS spectrum, the existence of seven peaks at right end showed six chlorine in the compound (**I**), *m/z* 296.84 was ascribed to molecular ion peak (M^+), *m/z* 298.86 was the isotopic peak of *m/z* 296.84, *m/z* 261.83 was ascribed to M^+-Cl peak.

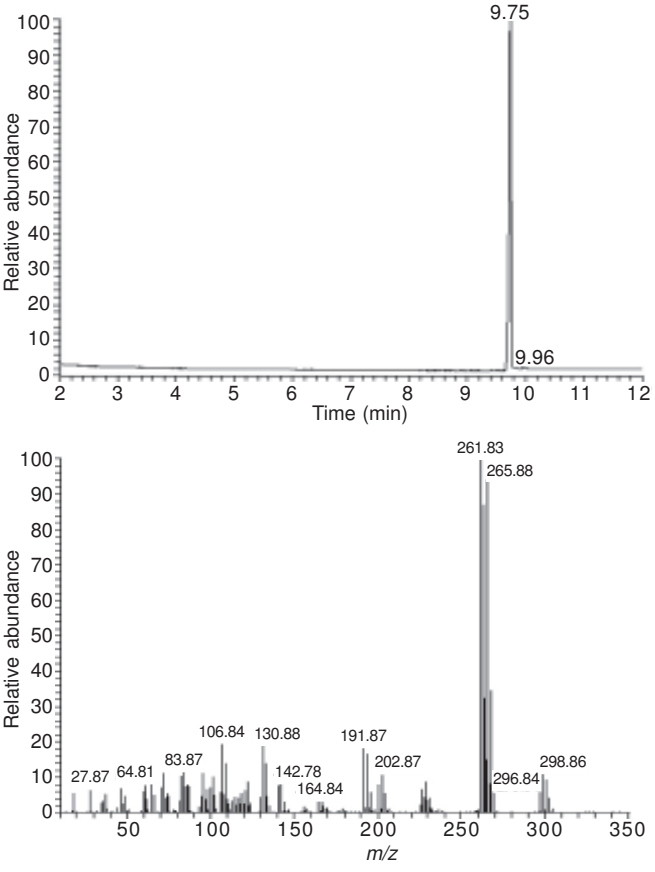


Fig. 3. GC-Mass spectrum of TCTCMP

The crystal configuration of TCTCMP was confirmed by X-ray structural analysis. Experimental details for X-ray data collection were presented in Table-1 and the geometric parameters for compound (**I**) were listed in Table-2. Molecular structure and packing plot of TCTCMP were showed in Figs. 4 and 5, respectively.

According to the data from X-ray crystallographic analysis, compound (**I**) crystallized in a *Pbcm* space group of the orthorhombic system. The only H atom was positioned geometrically and constrained to ride on C1 with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. A weak intramolecular C–H···Cl contacts were observed and hydrogen-bond geometry for compound (I) was listed in Table-3. Unit cell parameters: a = 8.3100(17), b = 17.018 (3), c = 7.3160(15) Å, V = 1034.6(4) $Å^3$; Z = 4.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPOUND (I)

ITEM	Data or Description
Formula	$C_6H\ Cl_6N$
Formula weight	299.78
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcm
a (Å)	8.3100(17)
b (Å)	17.018(3)
c (Å)	7.3160(15)
Volume ($Å^3$)	1034.6(4)
Z	4
Calculated density (g/cm^3)	1.925
Absorption coefficient (mm^{-1})	1.607
F(000)	584
Crystal size (mm)	0.30 × 0.20 × 0.20
Theta range for data collection (°)	2.39 to 25.39
Reflections collected / unique	1985/1033 [R(int) = 0.0633]
Completeness to theta = 25.39 (%)	99.9
Max. and min. transmission	0.7393 and 0.6442
Refinement method	Full-matrix least-squares on F
Data / restraints / parameters	1033 / 0 / 77
Goodness-of-fit on F^2	1.005
Final R indices [I>2σ(I)]	R1 = 0.0398, wR2 = 0.1107
R indices (all data)	R1 = 0.0558, wR2 = 0.1234
Largest diff. peak and hole (e. $Å^{-3}$)	0.26 and -0.39

TABLE-2
GEOMETRIC PARAMETERS FOR COMPOUND (I)

Bond	Dist. (Å)	Bond	Dist. (Å)
N–C4	1.318 (6)	C2–C3	1.385 (8)
N–C3	1.321 (6)	Cl3–C4	1.739 (4)
Cl1–C2	1.724 (5)	Cl4–C6	1.774 (3)
C1–C2	1.381 (7)	C4–C5	1.400 (6)
C1–C5	1.381 (6)	Cl5–C6	1.783 (5)
C1–H1A	0.9300	C5–C6	1.519 (6)
Cl2–C3	1.719 (4)	C6–Cl4^{i}	1.774 (3)
Angle	**Data (°)**	**Angle**	**Data (°)**
C4–N–C3	118.0 (4)	N–C4–Cl3	112.7 (3)
C2–C1–C5	120.5 (4)	C5–C4–Cl3	122.2 (3)
C2—C1–H1A	119.7	C1–C5–C4	115.4 (4)
C5–C1–H1A	119.7	C1–C5–C6	121.1 (4)
C1–C2–C3	118.4(4)	C4–C5–C6	123.5 (4)
C1–C2–Cl1	119.6 (4)	C5–C6–Cl4	110.77 (18)
C3–C2–Cl1	122.0 (4)	C5–C6–Cl4^{i}	110.77 (18)
N–C3–C2	122.6 (4)	Cl4–C6–Cl4^{i}	109.2 (2)
N–C3–Cl2	116.0 (4)	C5–C6–Cl5	112.2 (3)
C2–C3–Cl2	121.4 (4)	Cl4–C6–Cl5	106.84 (17)
N–C4–C5	125.1 (4)	Cl4^{i}–C6–Cl5	106.84 (17)
C5–C1–C2–C3	0.0	C2–C1–C5–C6	180.0
C5–C1–C2–Cl1	180.0	N–C4–C5–C1	0.0
C4–N–C3–C2	0.0	Cl3–C4–C5–C1	180.0
C4–N–C3–Cl2	180.0	N–C4–C5–C6	180.0
C1–C2–C3–N	0.0	Cl3–C4–C5–C6	0.0
Cl1–C2–C3–N	180.0	C1–C5–C6–Cl4	119.32 (19)
C1–C2–C3–Cl2	180.0	C4–C5–C6–Cl4	–60.68 (19)
Cl1–C2–C3–Cl2	0.0	C1–C5–C6–Cl4^{i}	–119.32 (19)
C3–N–C4–C5	0.0	C4–C5–C6–Cl4^{i}	60.68 (19)
C3–N–C4–Cl3	180.0	C1–C5–C6–Cl5	0.0
C2–C1–C5–C4	0.0	C4–C5–C6–Cl5	180.0

Symmetry code: (i) x, y, –z+1/2.

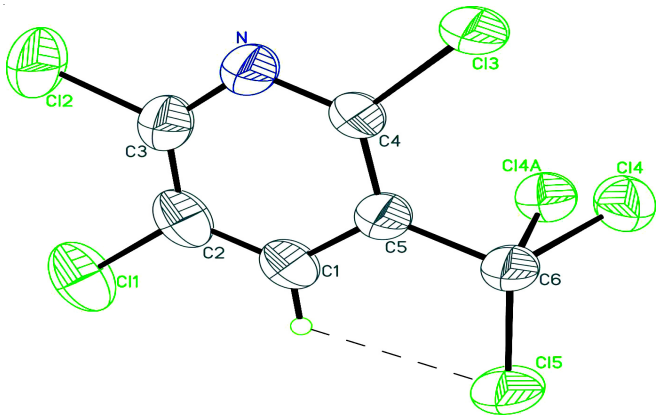


Fig. 4. General appearance of TCTCMP with the atoms represented by thermal vibration ellipsoids of 50 % probability

TABLE-3
HYDROGEN-BOND GEOMETRY FOR COMPOUND (I)

D—H···A	D—H	H···A	D···A	D—H···A
D—H···A	D—H	H···A	D···A	D—H···A

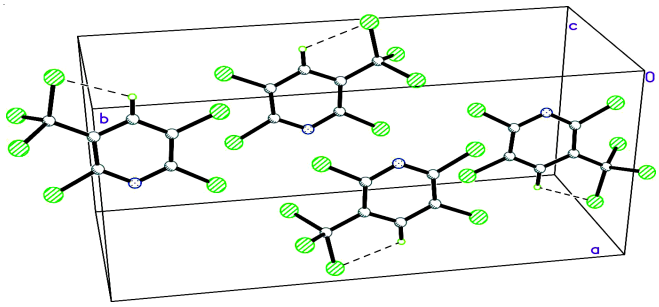


Fig. 5. Packing diagram for TCTCMP

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