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Crystal structure and thermodynamic properties of myclobutanil

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ABSTRACT

Myclobutanil is a high-efficiency, low toxicity and wide spectrum triazole fungicide. Its crystal structure was characterised by single-crystal X-ray diffraction, which belongs to monoclinic system with space group $P2_1/c$. The molecules are linked by weak hydrogen bonds and halogen bond to from a 3D structure. This is the main reason for its low melting point. The specific molar heat capacity ($C_{p,m}$) of myclobutanil was determined by a continuous C_p mode of micro-calorimeter and theoretical calculation, and the $C_{p,m}$ of myclobutanil was 362.78 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at $T = 298.15$ K.

1. Introduction

Myclobutanil ($C_{15}H_{17}N_4Cl$; CASRN: 88671-89-0), chemically named α-butyl-α-(4-chlorophenyl)-1*H*-1,2,4-triazole-1-propane nitrile, is a high-efficiency, low toxicity and wide spectrum triazole fungicides [1]. It is used in control of Ascomycetes, Fungi Imperfecti and Basidiomycetes on a wide variety of crops [2,3]. For example, it used for a foliar treatment to control the scab in apples and pears; powdery mildew in apples, pears, stone fruit, vines, cucurbits and ornamentals; rust in ornamentals, stone fruit and perennial grasses grown for seed; and various diseases in wheat; it also used for a seed treatment to control the seed- and soil-borne diseases in crops such as barley, wheat maize, cotton and rice.

In this paper the crystal structure of myclobutanil was reported. The specific molar heat capacity ($C_{p,m}$) of myclobutanil was determined by continuous C_p mode of micro-calorimeter and theoretical calculation.

2. Experimental

2.1. Materials

Myclobutanil was obtained from Jiangsu Greenscie Chemical Co., Ltd. The colourless single crystal of myclobutanil (CCDC 907765) was obtained by recrystallisation from absolute ethyl alcohol. The mass fraction purity of single crystal of myclobutanil was measured by high performance liquid chromatography (HPLC type Shimadzu LC-10AT, infusion pump type LC-10ATvp, detector type SPD-10Avp, the mobile phase is acetonitrile and water with 60% (*V*/*V*)) and found to be above 0.999 (Table 1). The melting point of single crystal of myclobutanil was measured by microscopic melting point measuring instrument (type X-5, Beijing Tech Instrument Co., Ltd) at $T = 343.45 \pm 0.23$ K. This melting point falls within the temperature range of (338.15–348.37) [4–6] (Table 2), the purity of myclobutanil, the heating rate and the accuracy of instrument are important factors affecting the deviation of melting point.

2.2. Crystal structure determination

The crystal structure of myclobutanil was determined by single crystal X-ray diffraction. The data collection was performed on a Bruker Smart Apex CCD X-ray diffractometer (Bruker, Germany) with highly oriented graphite crystal monochromated Mo Kα radiation ($\lambda = 0.071073$ nm) using ω and φ scans mode at room temperature. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using the SADABS program [7]. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 with the SHELXTL-97 program [8]. All non-hydrogen atoms were obtained from the difference Fourier map and refined with atomic anisotropic thermal parameters. The hydrogen atoms were added according to the theoretical models. The details of data collection and refinement are given in Table 3.

2.3. Heat capacity determination

The $C_{p,m}$ of myclobutanil was determined by a continuous C_p mode from $T = (283.15$ to $333.15)$ K at a heating rate of 0.15 $K{\cdot}min^{-1}$

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Table 1
Provenance and mass fraction purity of the materials used in this study. HPLC is the high performance liquid chromatography.

Compound	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
Myclobutanil	Jiangsu Greenscie Chemical Co., Ltd	>0.95	Recrystallization	>0.999	HPLC
Naphthalene	Aladdin	>0.997			

Table 2
The references and experimental value of melting point for myclobutanil at pressure 101.3 kPa.[a] Ref. is the reference. Exp is the experimental.

	Ref. [4]	Ref. [5]	Ref. [6]	Exp. value
Melting point/K	338.15	344.05	348.37	343.45(0.23)[b]

[a] Standard uncertainty u is $u(p) = 1$ kPa.
[b] Standard uncertainty.

Table 3
Crystal data and structure refinement parameters for myclobutanil at pressure 101.3 kPa.[a]

Empirical formula	$C_{15}H_{17}N_4Cl$
CCDC number	907765
Formula weight	288.78
Temperature/K	296(2)
Crystal dimension/mm	0.38 × 0.30 × 0.25
Crystal system	Monoclinic
Space group	$P2_1/c$
a/nm	1.3242(0.0002)[b]
b/nm	0.85175(0.00014)[b]
c/nm	1.5118(0.0002)[b]
α/°	90
β/°	114.706(0.002)[b]
γ/°	90
V/nm^3	1.5491(0.0004)[b]
Z	4
Density, calculated/g·cm^{-3}	1.238(0.001)[b]
μ/mm^{-1}	0.243
F(000)	608
θ ranges/°	2.81–26.60
H	−13 to 15
K	−6 to 10
L	−17 to 18
Reflections collected	7432
R_{int}	0.0267
Data/restraints/parameters	2753/0/182
Goodness-of-fit on F^2	1.038
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0392, 0.1029
R_1,wR_2 indices (all data)	0.0467, 0.1095
Largest difference peak and hole/e·nm^{-3}	1.66 × 10^5, −230 × 10^5

[a] Standard uncertainty u is $u(p) = 1$ kPa.
[b] Standard uncertainty.

on a Micro-DSCIII (Setaram, France) instrument with the sample mass of 210.18 mg at pressure 101.3 kPa. The micro-calorimeter was calibrated with α-Al_2O_3 (calcined), its mathematical expression was C_p/(J·K^{-1}·mol^{-1}) = 18.64804 + 2.039107 × 10^{-1} (T/K) from T = (283.15 to 333.15) K, the recommended equation is C_p/(J·K^{-1}·mol^{-1}) = −1.32506 × 10^8(T/K)$^{-3}$ + 4.54238 × 10^6(T/K)$^{-2}$ − 5.4755 99 × 10^4(T/K)$^{-1}$ + 2.574076 × 10^2 − 1.715032 × 10^{-1}(T/K) + 1.289 7189 × 10^{-4}(T/K)^2 − 4.60768 × 10^{-8}(T/K)^3 + 6.31755 × 10^{-12}(T/K)^4 from T = (273.15 to 2250) K [9] (Fig. 1). The difference between the experimental and recommended value are (−0.50 to 1.37) J·K^{-1}·mol^{-1} from T = (283.15 to 333.15) K, the standard uncertainty is ±0.45 J·K^{-1}·mol^{-1}, the relative standard uncertainty is ±0.51%.

2.4. Quantum chemical calculations

Single crystal structural data of myclobutanil were used in the theoretical calculations. The density functional theory (DFT) calculation was performed with the program package DMol^3 in Materials Studio (version 8.0) of Accelrys Inc. on a personal computer [10,11]. The generalised gradient approximation (GGA) with the

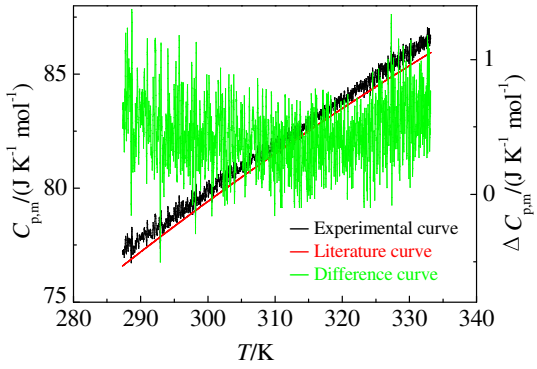

Fig. 1. Experimental/literature/difference curves of the $C_{p,m}$ of α-Al_2O_3.

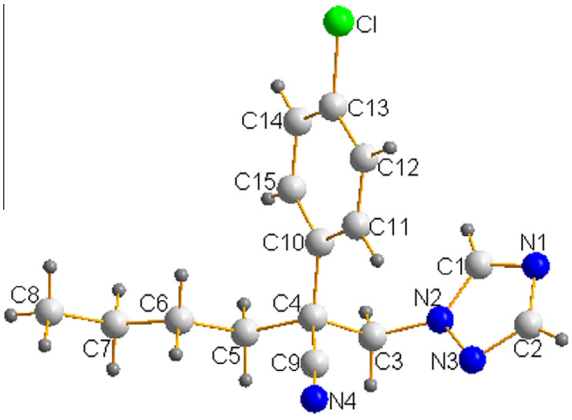

Fig. 2. Molecular structure of S-myclobutanil.

RPBE functional [12] and double-numerical quality basis set with polarisation functions (DNP) were used for all the atoms, the size of DNP is comparable to Gaussian 6-31G**. A thermal smearing of 2.0 × 10^{-3} hartree (Ha, 1Ha = 27.2114 eV) and a real-space cut off of 0.40 nm were adopted. For the numerical integration, the fine quality mesh size of the program was used. A 3 × 3 × 3 k-point sampling was applied in geometry optimisation [13–16]. The convergences of energy, gradient and maximal displacement were set as 10^{-5} Ha, 2.0 × 10^5 Ha cm^{-1} (2.0 × 10^{-2} Ha·nm^{-1}) and 5.0 × 10^{-4} nm, respectively. In addition, the frequency analysis [13–15] was performed to check if the stationary point was a potential minimum and to obtain thermodynamic properties at different temperatures under atmospheric pressure. The crystal data, input coordinates, final coordinates, vibrational frequencies and standard thermodynamic quantities for myclobutanil are listed in Tables S1–S5.

3. Results and discussion

3.1. Crystal structure

Single-crystal analysis shows the compound crystallises in monoclinic space group $P2_1/c$, with Z = 4. Myclobutanil is a chiral molecule (Fig. 2), R- and S-myclobutanil through hydrogen bond