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Thermodynamic properties of diniconazole and hexaconazole

Biao Yan [a,*], Hong-Ya Li [a], Jing Gao [a], Ai-Min Wang [a], Guo-Yu Ren [a], Yan-Jun Li [a], Hai-Xia Ma [b,*]

[a] School of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Low Metamorphic Coal Clean Utilization, Yulin University, Yulin 719000, PR China
[b] School of Chemical Engineering, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, PR China

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ABSTRACT

Diniconazole and hexaconazole are wide spectrum triazole fungicides with high-efficiency and low toxicity. The specific molar heat capacity ($C_{p,m}$) of diniconazole and hexaconazole were determined by a continuous C_p mode of micro-calorimeter and theoretical calculation, their $C_{p,m}$ values at T = 298.15 K were 381.72 J K^{-1} mol^{-1} and 364.66 J K^{-1} mol^{-1}, respectively. The $C_{p,m}$ value of diniconazole is higher than that of hexaconazole at temperature from T = (283.15 to 353.15) K.

1. Introduction

Triazole fungicides are used for many different types of plants including field crops, fruit trees, vegetables and turf. These fungicides are highly effective for many different fungal diseases, especially for Ascomycetes, Fungi Imperfecti and Basidiomycetes [1]. The triazole fungicides can inhibit a specific enzyme, C14-demethylase, which plays an important role in sterol production. Sterols, such as ergosterol, are required for membrane structure and function, making them essential for the development of functional cell walls. Therefore, these fungicides result in abnormal fungal growth and eventually death [1].

Diniconazole ($C_{15}H_{17}N_3Cl_2O$, CASRN: 83657-24-3, shown in Fig. 1), chemically named (*E*)-(RS)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pent-1-en-3-ol, it's mode of action is systemic fungicide with protective and curative action. Diniconazole is used to control the leaf and ear diseases (*e.g.* powdery mildew, septoria, fusarium, smuts, bunt, rusts, scab, *etc.*) in cereals; powdery mildew in vines; powdery mildew, rust, and black spot in roses; leaf spot in peanuts; sigatoka disease in bananas; uredinales in coffee; and also used in fruit, vegetables, and other ornamentals.

Hexaconazole ($C_{14}H_{17}N_3Cl_2O$; CASRN: 79983-71-4, shown in Fig. 2), chemically named (RS)-2-(2,4-dichlorophenyl)-1-(1H-1,2,4-triazol-1-yl)hexan-2-ol, it is a systemic fungicide used to control many fungi particularly Ascomycetes and Basidiomycetes, and also used to control the powdery mildew, halo spot, take all, smut, leaf blight, glume blight, scald and rust in wheat; sheath blight, smut, false smut, blast, phyllosticta leaf blight and leaf scald in rice; spot, smut, rust, rot and scad in corn; spot, smut, sheath blight and seedling blight in sorghum; rust, spot and blight in peanut; and also used in grape, banana and pepper.

In this paper the specific molar heat capacity ($C_{p,m}$) of diniconazole and hexaconazole were determined by a continuous C_p mode of micro-calorimeter and theoretical calculation.

2. Experimental

2.1. Materials

Diniconazole and hexaconazole were obtained from Jiangsu Yencheng Limin Chemical Co., Ltd, and the colourless single crystals were obtained by recrystallization from absolute ethyl alcohol. The mass fraction purity of single crystal of diniconazole and hexaconazole were 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)), detailed information is provided in Table 1. The cell parameters of single crystal of diniconazole and hexaconazole were 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 (λ = 0.071073 nm) using ω and φ scans mode at room temperature, detailed information is provided in Table 2. The diniconazole and hexaconazole were racemate according to reference [2,3].

* Corresponding authors.
E-mail addresses: yanbiaoly@foxmail.com (B. Yan), mahx@nwu.edu.cn (H.-X. Ma).

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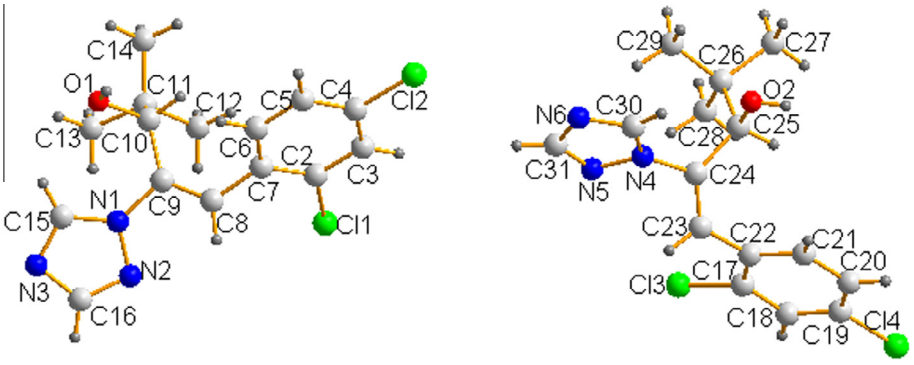

Fig. 1. Molecular structure of S-diniconazole.

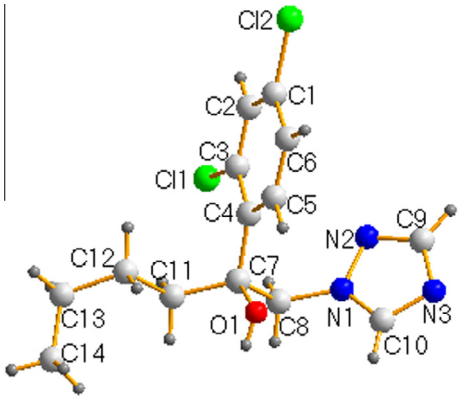

Fig. 2. Molecular structure of S-hexaconazole.

Table 2
The references and experimental values of cell parameters for diniconazole and hexaconazole under atmospheric pressure. Ref. is the reference. Exp. is the experimental.[a]

Cell parameters	Diniconazole		Hexaconazole	
	Exp.	Ref. [2]	Exp.	Ref. [3]
a/nm	0.72324 (0.00014)	0.72321 (0.00015)	1.0911 (0.0002)	1.0895 (0.0006)
b/nm	2.0260(0.0003)	2.0248(0.0004)	1.1012 (0.0002)	1.1006 (0.0006)
c/nm	2.2473(0.0003)	2.2449(0.0005)	1.3617 (0.0002)	1.3595 (0.0008)
β (°)	96.079(0.002)	96.072(0.002)	106.554 (0.003)	106.526 (0.009)
Z	8	8	4	4
Density/ g cm^{-3}	1.323(0.001)	1.326(0.001)	1.331(0.001)	1.335(0.002)
Temperature/K	296(2)	296(2)	296(2)	293(2)

[a] Standard uncertainties *u* are *u*(*p*) = 1 kPa.

2.2. Heat capacity determination

The $C_{p,m}$ of diniconazole and hexaconazole was determined by a continuous C_p mode from T = (283.15 to 353.15) K at a heating rate of 0.15 K min^{-1} on a Micro-DSCIII (Setaram, France) instrument under atmospheric pressure, the sample mass was 329.28 mg and 313.36 mg, respectively. The micro-calorimeter was calibrated with α-Al_2O_3 (calcined), its mathematical expression was C_p/(J K^{-1} mol^{-1}) = 18.82369 + 2.033349 × 10^{-1} (T/K) from T = (283.15 to 353.15) K, and the recommended equation is C_p/(J K^{-1} mol^{-1}) = −1.32506 × 10^8 (T/K)$^{-3}$ + 4.54238 × 10^6 (T/K)$^{-2}$ − 5.475599 × 10^4 (T/K)$^{-1}$ + 2.574076 × 10^2 − 1.715032 × 10^{-1} (T/K) + 1.2897189 × 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 [4] (Fig. 3). The difference between the experimental and recommended value are (−0.50 to 1.59) J K^{-1} mol^{-1} from T = (283.15 to 353.15) K, and the standard uncertainty is ±0.63 J K^{-1} mol^{-1}, the relative standard uncertainty is ±0.55%.

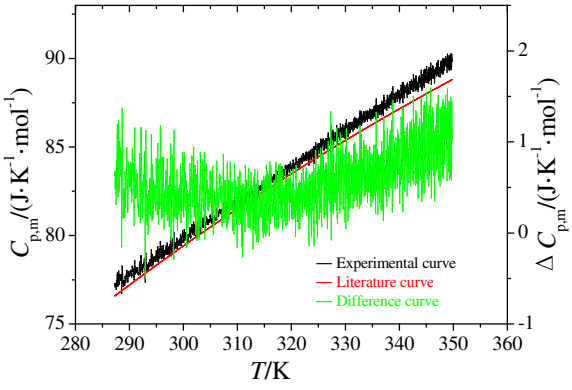

Fig. 3. Experimental/literature/difference curves of the $C_{p,m}$ for α-Al_2O_3.

2.3. Quantum chemical calculations

Single crystal structural data of diniconazole [2] and hexaconazole [3] 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 [5,6]. The generalised gradient approximation (GGA) with the RPBE functional [7] 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.

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
Diniconazole	Jiangsu Yencheng Limin Chemical Co., Ltd	>0.95	Recrystallization	>0.9996	HPLC
Hexaconazole	Jiangsu Yencheng Limin Chemical Co., Ltd	>0.95	Recrystallization	>0.9995	HPLC