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Temperature induced reversible polymorphic phase transformations in a bis-hydrazone compound

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ABSTRACT

Two reversible polymorphic phase transformation of 2,3-butanedione, 2,3- bis[4,4′-bis(diethylamino) benzophenone hydrazone] (**DEBH**) have been identified in DSC experiment. Topotactic phase transformation of three polymorphs has been observed in variable temperature Single Crystal X-ray Diffraction experiment. The reversible phase transformation of bulk material has been confirmed by Powder X-ray diffraction study.

1. Introduction

Polymorphism has been the subject of intense research over the past decades due to its importance in pharmaceutical and other specialty industry [1–4]. Polymorphism is nuisance to design new materials with desired properties. However, research in polymorphism remain very interesting because it assists in understanding the kinetic of crystal nucleation, molecular recognition and crystal growth [5–10]. According to the most accepted definition of polymorphism, it is a phenomenon of having at least two different crystal structures of same chemical compound [11,12].

Crystallization in different solvents is the most common methods for preparation of different polymorphs of a compound, although many other methods are known [13–17]. In this regard, solid-to-solid phase transformation induced by external stimuli is very convenient method to prepare polymorphs [18–20]. Polymorphic phase transformation is very interesting subject to study, because this helps in understanding the kinetic and thermodynamic stability of different polymorphs of a compound [21–23]. In addition, study of polymorphic phase transformation is very much necessary in specialty chemical industry in order to recognize the storage and stability condition of different polymorphs. Although polymorphic phase transformation of various organic compounds through Single Crystal to Single Crystal (SCSC) process have been reported [24–29], SCSC transformation in organic materials is very much challenging because simultaneous and cooperative movement of constituent atoms or molecules leads to the appreciable loss of single crystallinity. In many cases, solid to solid phase transformation occurs topotactically, where the single crystal disintegrates due to external stimuli [30] However, in topotactic transformation definite relationship has been observed between the crystal structure of mother crystal and daughter crystal [31–33]. Here, we have reported topotactic polymorphic phase transformations of three polymorphs of a bis-hydrazone compound, **DEBH** (Scheme 1). These transformations are completely temperature dependent and occur reversibly. The reversible phase transformation has been first identified in DSC experiment and confirmed by variable temperature Single Crystal X-ray Diffraction (SCD) and Powder X-ray Diffraction (PXRD) experiments.

2. Experimental

2.1. Synthesis and crystallization of *DEBH*

Compound **DEBH** was synthesized by slightly modified literature reported procedure [34]. Molecular structure has been confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, $CDCl_3$): δ7.638 (d, 4H), δ7.202 (d, 4H), δ6.672 (d of d, 8H), 3.444 (quartet, 16H), δ2.208 (s, 6H), δ1.229 (t, 24H).

DEBH has been crystallized by slow evaporation method. Dissolving this compound in almost all common solvents available in our laboratory generate exclusively the crystals of **Form-I**.

Single crystal of **Form-IV** has been prepared by melting of the as-synthesized material of **DEBH** followed by cooling and reheating at 140 °C in DSC instrument. Heating of the as-synthesized material

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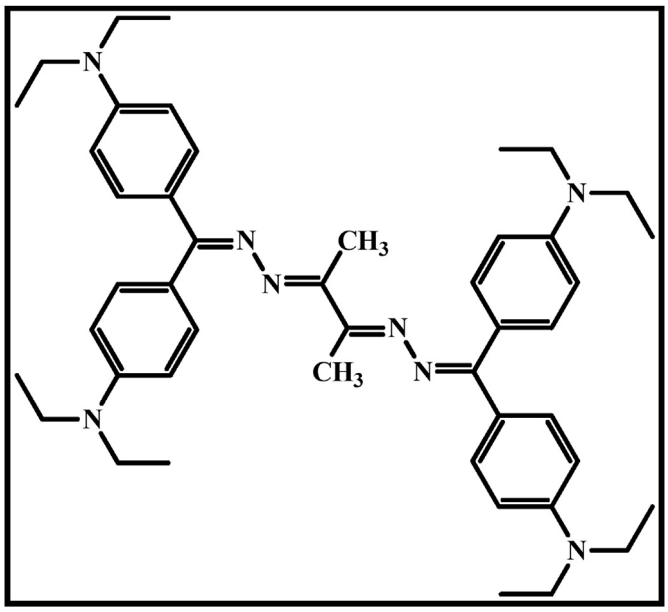

Scheme 1. Molecular structure of 2,3-butanedione, 2,3- bis[4,4′-bis(diethylamino) benzophenone hydrazone] (**DEBH).**

till 250 °C does not change the chemical nature of the compound during synthesis of **Form-IV.** This has been confirmed by NMR and mass spectroscopy (See Fig S17 and S18).

2.2. Differential scanning calorimetric study

Differential scanning calorimetric studies have been performed by heat-cool-heat method on a Mettler Toledo DSC1 calorimeter with FRS5 DSC Sensor attached with HUBER TC100-MT chiller and STARe software V14.00. About 6 mg of as-synthesized compound **DEBH** was taken in 40 μL aluminum pan sealed with pierced lid. The sample was purged with a flow of dry nitrogen gas at 50 mL/min. The sample was first heated at the rate of 5 °C/min from 30 to 250 °C. In the second step, the sample was cooled at the rate of 10 °C/min from 250 °C to −80 °C. Finally, the sample was reheated from −80 °C to 250 °C at the rate of 5 °C/min. In the second experiment, sample was first heated at the rate of 5 °C/min from 30 °C to 160 °C. In the second step, the sample was cooled at the rate of 10 °C/min from 160 °C to −80 °C. Finally, the sample was reheated from −80 °C to 250 °C at the rate of 5 °C/min.

2.3. Variable temperature single crystal X-ray diffraction

Single crystal X-ray structures were collected on Bruker D8 Quest single crystal X-ray diffractometer equipped with a micro-focus anode (Mo) and a PHOTON 100 CMOS detector. A single crystal was glued to a thin glass fiber. The temperature of the crystal was controlled using an Oxford Cryosystream 800 Plus cryostat. The single-crystal data were initially recorded at 27 °C and then by heating the crystal successive datasets were collected at 127 °C and 167 °C. Reversibly by cooling the crystal the intensity data were collected at 107 °C and 27 °C. The data were integrated and scaled using the Bruker suite of programs [35]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-2014 [36]. All non-hydrogen host atoms were refined anisotropically and all hydrogen atoms were placed using calculated positions and riding models.

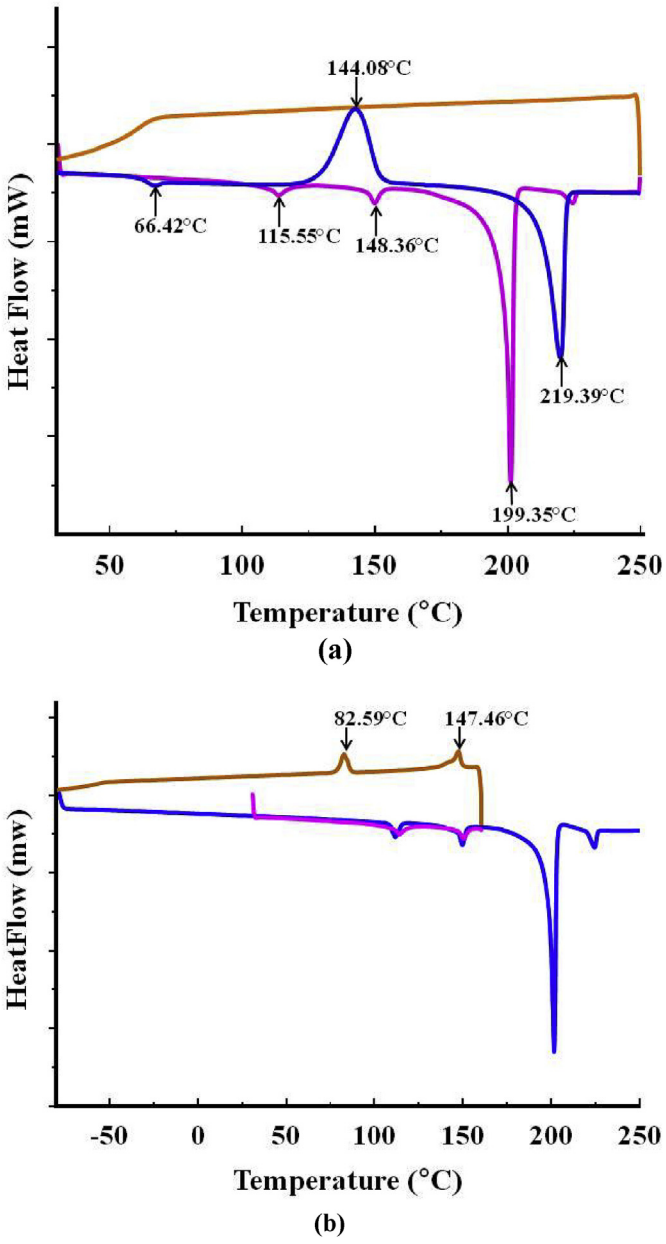

Fig. 1. DSC thermogram of as-synthesized material by heat-cool-heat method showing polymorphic phase transformation. Heating in first segment shown in pink color, cooling segment shown in orange color and blue color indicates reheating. Peak temperatures have been indicated by arrow. (a) Melting is shown in the first segment followed by cooling and then reheating; (b) DSC thermogram showing reversible polymorphic phase transformation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. Variable temperature X-ray powder diffraction

X-ray powder diffractograms were measured on PANalytical Empyrean X-ray diffractometer with CuK_α radiation, $\lambda = 1.54059$ Å) operating in Bragg-Brentano geometry. Powder sample was loaded in XRK 900 chamber from Anton Paar. Initially the pattern was recorded at 27 °C. Sample was heated at the rate of 10°/min and put isothermal condition for 5 min. Subsequently the data were recorded 127 °C and 167 °C by heating the sample. Similarly, the data were collected at 87 °C and 27 °C reversibly by cooling the sample at the rate of 10°/min. In each case, data were collected in