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NOTE

Solid-State Synthesis and Thermochromism of Salicylidene Dinitrophenylhydrazine Derivatives

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Two salicylidene dinitrophenylhydrazine compounds (**1** and **2**) were synthesized by solid-state reaction of (2,4-dinitrophenyl)hydrazine with 2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde at room temperature, respectively. Their structures were characterized by elemental analysis, ESI-MS and IR and thermochromism properties were investigated by differential scanning calorimetry spectra. The results exhibited that both **1** and **2** displayed significant colour changes relying on temperature, which can be ascribed to the structural transformation between enol and keto forms in the solid state. This transformation may benefit from the intramolecular hydrogen bond and proton H-transfer.

Keywords: Solid-state reaction, Thermochromism, Schiff base, Intramolecular hydrogen bond.

At present, organic thermochromic materials have become a hot topic due to low toxicity, high sensitivity and special functionality [1-4]. Among numerous materials, Schiff base compounds containing the general C=N group [5,6], wherein N atom with lone pair electrons can derive important biological and chemical implications. Schiff bases would undergo hydrogen atom tautomerism between enol and keto forms depending on the temperature, which results in special chromic properties [7,8]. As a result, it is meaningful to prepare novel Schiff base derivatives especially using solid state reaction at room temperature. In this paper two salicylidene dinitrophenylhydrazine derivatives **1** and **2** were synthesized by solid-state grinding method. Their structures were confirmed by IR, ESI-MS and elemental analysis and thermochromism characteristics were also performed through differential scanning calorimetry (DSC) method.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. (2,4-Dinitrophenyl)hydrazine, 2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Aladdin Industrial Corporation. ESI-MS were recorded using a Waters Micromass ZQ-4000 spectrometer. C, H, N elemental analyses were performed on a Vario-EL. DSC spctra was obtained on a Netzsch DSC200 F3 maia.

General procedure: compounds **1** and **2** were prepared according to the solid-state grinding method. At room temperature, (2,4-dinitrophenyl)hydrazine (1.98 g, 10 mmol) and corresponding aromatic aldehyde (10 mmol) were carefully grinded in an agate mortar for 2 h in a fuming hood. Raw products were recrystallized by acetone to give targeted compounds, as shown in Fig. 1. Compound **1**: Yield 80 %. m.p.: 282.97 °C. ESI-MS: *m/z* 301.0 $[M-H]^+$. IR (KBr, cm^{-1}): 3432 (-OH), 3270 (-NH), 1617 (-C=N-), 1588 and 1514 (-C=C-), 1330 (-C-N-). Anal. calcd. for **1** ($C_{13}H_{10}N_4O_5$): C, 51.66; H, 3.33; N, 18.54. Found: C, 51.69; H, 3.39; N, 18.49. Compound **2**: Yield 79 %. m.p.: > 300 °C. ESI-MS: *m/z* 351.1 $[M-H]^+$. IR (KBr, ν_{max}, cm^{-1}): 3436 (-OH), 3275 (-NH), 1615 (-C=N-), 1589 and 1515 (-C=C-). 1330 (-C-N-) Anal. calcd. for **2** ($C_{60}H_{68}N_6BBrF_2$): C, 71.91; H, 6.84; N, 8.40. Found: C, 71.85; H, 6.87; N, 8.38.

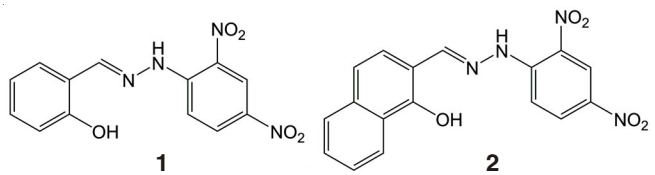

Fig. 1. Structures of two Schiff bases **1** and **2**

Two Schiff bases were placed in the micromelting point instrument to observe the colour changes along with increased temperature. According to Fig. 2, compound **1** displays an insignificant colour change from orange-red to red at about 306 °C, whilst compound **2** shows an obvious thermochromism from orange to purplish at approximate 300 °C. The difference might originate from structure distinction in the intramolecular hydrogen bond of type O-H···N, which is formed between hydrogen

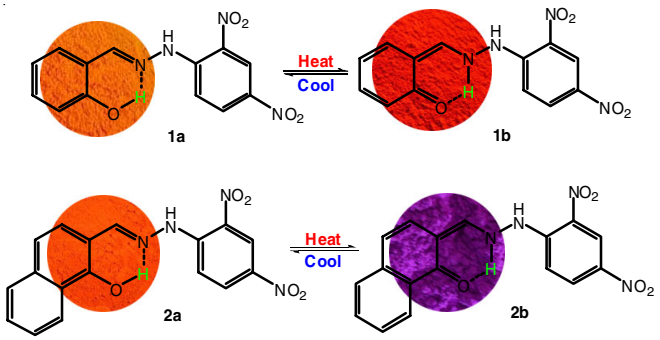

Fig. 2. Reversible thermochromism and tautomerism pathways of compounds **1** and **2**

atom of OH group and nitrogen atom of the imine group [9]. As well-known, H-transfer mechanism resulting from hydrogen bonding is prominently attributable to thermochromism behaviour [10,11].

This discussions can be identified from their IR spectra at room temperature. As shown in Fig. 3, the vibration peak at 3432 cm^{-1} with respect to OH group is very weak and difficult-to-observe for compound **1**, while this corresponding peak at 3436 cm^{-1} is relatively strong and broad for **2**. It can be speculated that most H atoms have transferred from the OH group to the imine N atoms for **1** at room temperature, as depicted in Fig. 2 [12]. Namely, keto form **1b** is predominant compared to phenol form **1a** in the tautomerism. As a result, significant thermochromism was not observed with a rise of temperature. On the contrary, compound **2** exhibits a broad infrared vibration band at 3436 cm^{-1}, indicating that the H atom of OH group does not transfer at 25 °C. This transfer process can be stimulated by heating-up and naphthol form **2a** resultantly develops keto structure **2b**. Interestingly, the original colour can recover with the temperature decreasing to ambient 25 °C. Reversible thermochromism characterizations should be ascribed to the transition between enol and keto forms [8,13].

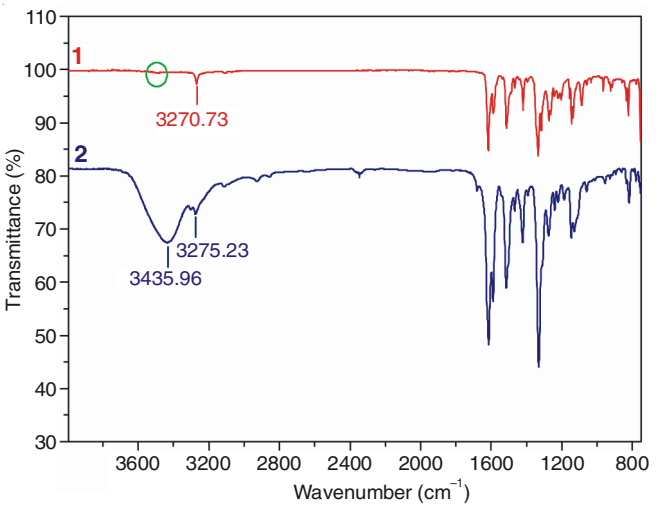

Fig. 3. Partial IR spectra of compounds **1** and **2**

To elaborate the phase transition in thermochromism, DSC analysis was carried out for two Schiff base derivatives **1** and **2**. The experimental temperature increased from 50 to 350 °C by the step of 5 °C and then the temperature decreased to room temperature 25 °C. DSC spectra illustrates an obvious endo-thermic and exothermic peak for two compounds, separately. In the case of compound **1**, the sharp endothermic peak at 256.7 °C can be ascribed to the melting peak, which is prior to the big and broad exothermic band with respect to the novel crystalline peak. This is the reason why thermochromic features of **1** have been found. Interestingly, the melting peak for **2** was not examined, but a dramatic shoulder-peak at 300.2 °C exists inferior to the main crystalline band, indicating the phase transition of **2a** to a more stable **2b** [14,15]. It suggests that the melting process does not occur in the re-crystalline transition process of Schiff base derivative **2**.

Conclusion

In summary, two salicylidene dinitrophenylhydrazine derivatives **1** and **2** were constructed by solid-state grinding and their thermochromic properties were investigated by IR and DSC techniques. As results showed, H-transfer mechanism originated from intramolecular hydrogen binding should account for the reversible thermochromism characterizations. The transition between enol and keto forms determines the colour changes along with the temperature change. Functional films based on both compounds are under way.

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