

## Research Article

# Synthesis, Characterization, Thermochromism, and Photochromism of Aromatic Aldehyde Hydrazone Derivatives

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The Schiff bases N-(5-phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (**1**), N-(4'-chloro-5-phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (**2**), and N-(4'-nitro-5-phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (**3**) were synthesized. These compounds were characterized by using IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS. The photochromism of the compounds was investigated by IR and UV-visible spectrometry which is time variable under irradiation of 254 nm UV light. The thermochromism of the compounds was studied using temperature-variable IR, UV-visible spectrometry, TG, and differential scanning calorimetry (DSC). The results suggested that compound **2** showed thermochromism properties and compounds **2** and **3** displayed photochromism properties. The relationship between the substituents species and photochromic or thermochromic properties of these compounds was revealed as well.

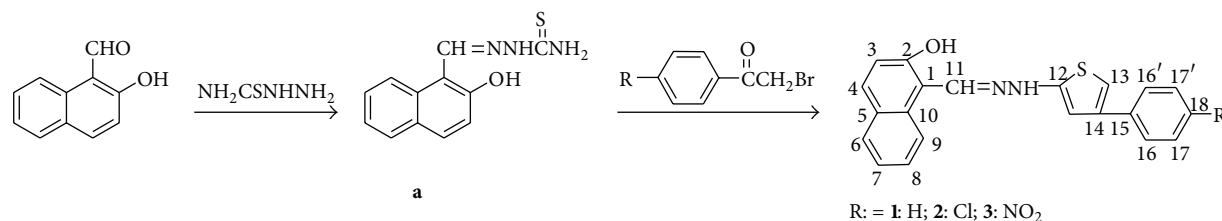
## 1. Introduction

Of the many Schiff bases, o-hydroxynaphthaldehydehydrazone had been found to be unique classes of Schiff bases with reversible thermochromism, photochromism, and other interesting properties. It was known that Schiff bases experience reversible phototransformations or thermal transformations between two forms, in particular, between enol-imine form and keto-amine form [1]. The tautomerism of the Schiff bases played an important role in their photochromic and thermochromic characteristics [2, 3]. When heated or receiving ultraviolet radiation, the hydrogen atom of the O-H or N-H transferred and attached to the N atom of C=N or O atom of C=O (Scheme 2) leading to  $\pi$ - $\pi$  charge transfer. The tautomerization between enol-imine and keto-amine achieved by proton migrating thermally or through irradiation induction, so orthohydroxyl played an important part on both thermochromism and photochromism of such Schiff bases [4, 5]. A link between molecular planar structures and thermochromism or photochromism has been proposed [6, 7]. Planarity of the molecule made it possible for the proton to transfer with small energy requirement [8, 9]. Substituents on the aromatic ring might also have an influence on the proton transfer [10, 11].

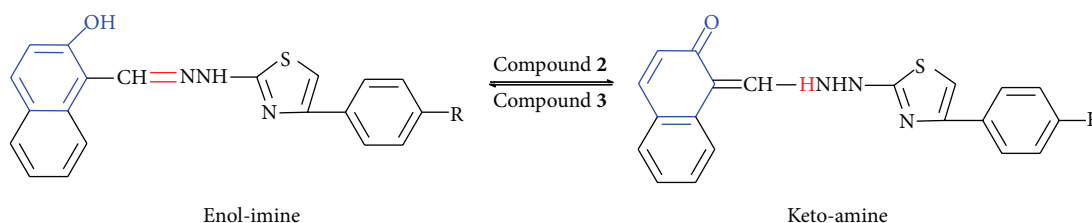
In this study, three Schiff bases (**1**–**3**) were synthesized (Scheme 1). The thermochromism or photochromism of the compounds were also studied. The results suggested that although the compounds (**1**–**3**) were all o-hydroxyl Schiff bases, compound **1** showed no thermochromism or photochromism, so o-hydroxyl was not the only factor work for the thermochromic or photochromic properties; the substituent species on the phenyl ring had great effect on such properties.

## 2. Experimental

**2.1. Materials and Methods.** All the required chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and were used without further purification. Melting points of the compounds were determined on SGWX-4 digital micromelting point apparatus. FT-IR spectra were recorded on a Thermo Scientific System 2000 FT-IR spectrometer. NMR spectra were recorded on AVANCE III NMR spectrometer in deuterated DMSO with TMS as an internal standard at 300 MHz for <sup>1</sup>H and for 75 MHz for <sup>13</sup>C. LC mass spectra were recorded on SHIMADZU, LCMS-2020 MS instrument with resolution >40000 FWHM. The UV-visible spectra



SCHEME 1



SCHEME 2: Tautomerism of aromatic aldehyde hydrazones.

were measured using a TU-1901 ultraviolet spectrophotometer. DSC analysis was performed by a DZ3335 differential scanning calorimeter (DSC) and TG analysis was detected by a STA449-F5TAQ600 analyzer. ZF-6 UV-light analyzer (254 nm, 365 nm) was used as the radiation source.

**2.2. General Procedure for the Synthesis of Aromatic Aldehyde Hydrazone Derivatives.** To a 250 mL three-neck round flask containing 182 mg (2 mmol) of aminothiourea in 25 mL ethanol (80%), 344 mg (2 mmol) of 2-hydroxy-1-naphthaldehyde was dissolved in 20 mL absolute ethanol. Then 2 mL of glacial acetic acid was added. The resulting mixture was magnetically stirred and refluxed for 4 hours. The solution was poured into a beaker and laid in ice baths for 2 hours to precipitate. The solid was recrystallized from ethanol-DMF (volume ratio, 1:1) and dried at 40 °C; 461 mg golden yellow solid (yield: 94%) was obtained. The solid was 2-hydroxy-1-naphthaldehydethiosemicarbazone (**a**).

245 mg (1 mmol) of compound **a** was dissolved in 25 mL absolute ethanol, and 199 mg (1 mmol)  $\alpha$ -bromoacetophenone or 244 mg (1 mmol) 2-bromo-4'-chloroacetophenone or 245 mg (1 mmol)  $\alpha$ -bromo-4-nitroacetophenone in 10 mL ethanol was added, respectively.

The reaction mixture was refluxed for 30 minutes. The mixture became clear in a moment. Five minutes later, a great deal of solid appeared. Solid (compound **1**, **2**, or **3**) was obtained after suction filtration and recrystallized with ethanol-DMF (volume ratio, 1:1).

### 2.3. Spectral Data

***N*-(5-Phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (1).** 250 mg, yield 72.6%, bright yellow solid, m.p. 200–202 °C. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3320 ( $\nu_{\text{O-H}}$ ), 3111 ( $\nu_{\text{N-H}}$ ), 3073, 2971 (stretching vibration of Ar-H and thiazole-H, resp.), 1619 ( $\nu_{\text{C=N}}$ ), 1611, 1581, 1491, 1480 (Ar; thiazole ring), 1409, 1349 (rocking vibration of Ar-H and thiazole-H, resp.), 1319 ( $\nu_{\text{C-OH}}$ ), 756, 733 (out-of-plane ring bending vibration of

Ar-H and thiazole-H, resp.);  $^1\text{H NMR}$  (DMSO- $d_6$ , 300 MHz, ppm)  $\delta$ : 12.29 (s, 1H, OH), 11.02 (s, 1H, N-H), 8.97 (s, 1H, H-C=N), 8.74–8.71 (d, 1H, thiazole-H), 7.89–7.86 (t, 4H, naphthalene-H), 7.62–7.57 (m, 1H, naphthalene-H), 7.46–7.43 (d, 1H, naphthalene-H), 7.41–7.40 (d, 2H, benzene-H), 7.37–7.30 (m, 2H, benzene-H), 7.25–7.22 (d, 1H, benzene-H).  $^{13}\text{C-NMR}$  (75 MHz, DMSO- $d_6$ , ppm):  $\delta$  168.2 ( $\text{C}_{12}$ ), 156.9 ( $\text{C}_2$ ), 150.5 ( $\text{C}_{11}$ ), 141.8 ( $\text{C}_{14}$ ), 134.8 ( $\text{C}_{13}$ ), 132.4 ( $\text{C}_{15}$ ), 131.5 ( $\text{C}_{18}$ ), 129.3 ( $\text{C}_{17}$ ,  $\text{C}_{17'}$ ), 129.1 ( $\text{C}_{16}$ ,  $\text{C}_{16'}$ ), 128.6 ( $\text{C}_1$ ), 128.2 (d,  $J = 86.3$ ,  $\text{C}_5$ ,  $\text{C}_{10}$ ), 126.1 ( $\text{C}_4$ ), 123.9 ( $\text{C}_3$ ), 123.4 ( $\text{C}_6$ ), 118.7 ( $\text{C}_9$ ), 110.6 ( $\text{C}_7$ ), 103.61 ( $\text{C}_8$ ); ESIMS calculated for  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{OS}$ : 345.42, found  $m/z = 346.10$  [ $\text{M}+\text{H}$ ] $^+$ ,  $m/z = 368.10$  [ $\text{M}+\text{Na}$ ] $^+$ ,  $m/z = 344.05$  [ $\text{M}-\text{H}$ ] $^+$ .

***N*-(4'-Chloro-5-phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (2).** 277 mg, yield 73%, gray purple crystal, m.p. 302–304 °C. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3333 ( $\nu_{\text{O-H}}$ ), 3112 ( $\nu_{\text{N-H}}$ ), 2921, 2851 (stretching vibration of Ar-H and thiazole-H, resp.), 1629 ( $\nu_{\text{C=N}}$ ), 1600, 1580, 1560, 1490 (Ar; thiazole ring), 1469, 1419 (rocking vibration of Ar-H and thiazole-H, resp.), 1399 ( $\nu_{\text{C-OH}}$ ), 779, 739 (out-of-plane ring bending vibration of Ar-H and thiazole-H, resp.).  $^1\text{H NMR}$  (DMSO- $d_6$ , 300 MHz, ppm)  $\delta$ : 12.27 (s, 1H, OH), 10.94 (s, 1H, N-H), 8.96 (s, 1H, H-C=N), 8.77–8.74 (s, 1H, thiazole-H), 7.92–9.86 (t, 4H, naphthalene-H), 7.62–7.57 (t, 1H, naphthalene-H), 7.50–7.48 (d, 1H, naphthalene-H), 7.44–7.42 (d, 1H, benzene-H), 7.40–7.37 (d, 2H, benzene-H), 7.25–7.22 (d, 1H, benzene-H), 706 ( $\nu_{\text{C-Cl}}$ ).  $^{13}\text{C-NMR}$  (75 MHz, DMSO- $d_6$ , ppm):  $\delta$  173.0 ( $\text{C}_{18}$ ), 161.6 ( $\text{C}_{12}$ ), 154.6 ( $\text{C}_2$ ), 146.5 ( $\text{C}_{11}$ ), 138.6 ( $\text{C}_{14}$ ), 137.3 ( $\text{C}_{13}$ ), 137.1 ( $\text{C}_{17}$ ,  $\text{C}_{17'}$ ), 136.3 ( $\text{C}_{16}$ ,  $\text{C}_{16'}$ ), 134.0 ( $\text{C}_{15}$ ), 133.8 ( $\text{C}_1$ ), 133.4 ( $\text{C}_5$ ), 132.9 ( $\text{C}_{10}$ ), 132.5 ( $\text{C}_4$ ), 128.6 ( $\text{C}_3$ ), 128.1 ( $\text{C}_6$ ), 123.5 ( $\text{C}_9$ ), 115.3 ( $\text{C}_7$ ), 109.1 ( $\text{C}_8$ ). ESIMS calculated for  $\text{C}_{20}\text{H}_{14}\text{N}_3\text{OSCl}$  379.86, found  $m/z = 380.00$  [ $\text{M}+\text{H}$ ] $^+$ ,  $m/z = 378.00$  [ $\text{M}-\text{H}$ ] $^+$ ,  $m/z = 402.05$  [ $\text{M}+\text{Na}$ ] $^+$ .

***N*-(4'-Nitro-5-phenylthiazole-2-yl)-2-hydroxynaphthaldehydehydrazone (3).** 306 mg, yield 78.4%, shallow orange crystal, m.p. 257–259 °C. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3309 ( $\nu_{\text{O-H}}$ ), 3118 ( $\nu_{\text{N-H}}$ ),

2921, 2851 (Ar-H, thiazole-H), 1619 ( $\nu_{C=N}$ ), 1601, 1580, 1499, 1469 (Ar; thiazole ring), 1521, 1330 (stretching vibration of the nitro group), 1439, 1419 (rocking vibration of Ar-H or thiazole-H), 1371 ( $\nu_{C-OH}$ ), 777, 746 (out-of-plane ring bending vibration of Ar-H and thiazole-H, resp.).  $^1\text{H-NMR}$  (DMSO- $d_6$ , 300 MHz, ppm)  $\delta$ : 12.36 (s, 1H, OH), 10.89 (s, 1H, N-H), 8.96 (s, 1H, H-C=N), 8.82–8.80 (d, 1H, thiazole-H), 8.32–8.29 (d, 2H, naphthalene-H), 8.16–8.13 (d, 2H, naphthalene-H), 7.89–7.86 (d, 2H, naphthalene-H), 7.77 (s, 1H, benzene-H), 7.62–7.57 (t, 1H, benzene-H), 7.42–7.37 (t, 1H, benzene-H), 7.25–7.22 (d, 1H, benzene-H).  $^{13}\text{C-NMR}$  (75 MHz, DMSO- $d_6$ , ppm)  $\delta$ : 168.6 ( $C_{18}$ ), 156.9 ( $C_{12}$ ), 149.1 ( $C_2$ ), 146.7 ( $C_{11}$ ), 141.9 ( $C_{14}$ ), 141.0 ( $C_{13}$ ), 132.5 ( $C_{17}$ ,  $C_{17'}$ ), 131.5 ( $C_{16}$ ,  $C_{16'}$ ), 129.3 ( $C_{15}$ ), 128.7 ( $C_1$ ), 128.2 ( $C_5$ ), 126.9 ( $C_{10}$ ), 124.6 ( $C_4$ ), 123.9 ( $C_3$ ), 123.7 ( $C_6$ ), 118.6 ( $C_9$ ), 110.6 ( $C_7$ ), 108.6 ( $C_8$ ); ESIMS calculated for  $C_{20}H_{14}N_4O_3S$  390.42, found  $m/z = 391.10$   $[\text{M}+\text{H}]^+$ ,  $m/z = 388.95$   $[\text{M}-\text{H}]^+$ ,  $m/z = 413.25$   $[\text{M}-\text{Na}]^+$ .

### 3. Results and Discussion

#### 3.1. Thermochromism

**3.1.1. IR Spectroscopic and TG Studies.** The color of compound **2** changed from gray purple to brown after being heated to 229°C and restored the original color after cooling. To investigate the thermochromism of the compounds thoroughly, KBr tablets of **1–3** were heated to certain temperatures on the electric hot plate; then the IR spectra were measured promptly. The IR spectra of **2** were shown in Figure 1(a). Compound **2** had the characteristic stretching band of hydroxyl group (O-H) at 3333  $\text{cm}^{-1}$ . When compound **2** was heated to 140°C, the absorption peak intensity of hydroxyl group absorption peak decreased partly the result of a conversion of the hydroxyl group to the carbonyl group (Scheme 2). When the temperature reached 200°C, the band almost disappeared. When compound **2** was heated to 60°C, a small absorption peak appeared at 1763  $\text{cm}^{-1}$ . This was due to the stretching vibration of the carbonyl of the keto-amine, which was produced from enol-imine of compound **2** on heating [12–14].

In fingerprint region (Figure 1(b)), small new absorption peaks appeared at 756  $\text{cm}^{-1}$  and 695  $\text{cm}^{-1}$ , while the peak at 652  $\text{cm}^{-1}$  diminished. All of these changes were ascribed to the bending vibration of the C-H bond of the losing aromaticity ring of the keto-amine [12–14].

Figure 2 was the TG curve of compound **2**. The TG curve suggested that there was a loss weight in the beginning of the test. The loss weight had relations to the loss of the crystal water in the molecule. Because the band of crystal water in IR spectra overlapped that of hydroxyl group, the reduction of the intensity at 3333  $\text{cm}^{-1}$  in Figure 1(a) was about more than the loss of crystal water. Similar intensity changes could be observed in Figure 7. By photoirradiation, the absorption peak intensity at 3333  $\text{cm}^{-1}$  of unheated compound **2** became smaller gradually without the loss of crystal water. So the intensity decreased partly because of the tautomerism and Figure 4 confirmed the discussion as

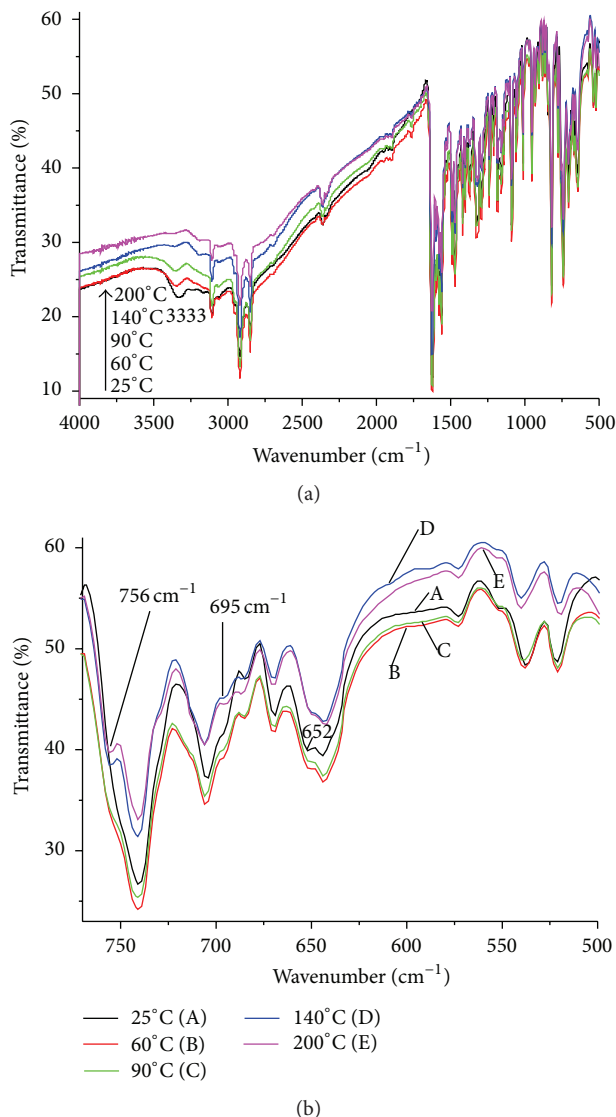


FIGURE 1: The IR spectra of compound **2** on heating in the whole spectra range investigated (a) and in the narrowed range (b).

well. The band at 3333  $\text{cm}^{-1}$  in Figure 1(a) almost disappeared when temperature rose to 200°C. It was still the result of the loss of the crystal water and tautomerism. All the crystal water lost at this moment and maybe most enol-imine form of compound **2** changed to enol-amine form.

When the temperature rose to 337°C, compound **2** lost weight again because it started to decompose.

**3.1.2. The DSC Measurement.** The DSC curves of compounds **1–3** were shown in Figure 3. Compound **2** exhibited three endothermic peaks at 229°C, 303°C, and 343°C, respectively. The first endothermic peak at 229°C corresponded to color change temperature; the second and the third endothermic peak corresponded to the melting point and decomposition temperature, respectively. The results further confirmed that compound **2** showed thermochromism. The melting point

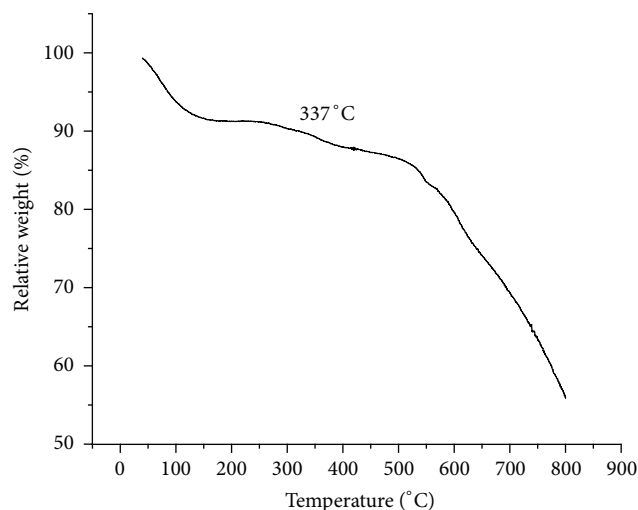


FIGURE 2: The TG curve of compound 2.

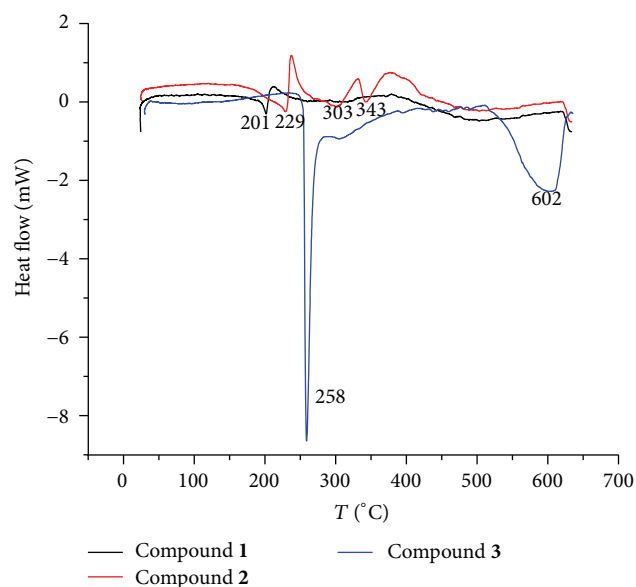


FIGURE 3: The DSC curves for compounds 1–3.

peaks for compounds 1 and 3 were 201°C and 258°C, respectively. There was another endothermic peak at 602°C for compound 3 which was a decomposition peak.

**3.1.3. UV-Visible Spectroscopic Studies.** The UV-visible spectra of orthohydroxylated Schiff bases existing mainly as enol-imine structure indicated the presence of bands at <400 nm. However, the compounds existing as either keto-amine or mixture of enol-imine/keto-amine forms showed a new band at >400 nm [15]. Photochromism or thermochromism was the phenomenon of chromatic change due to the reversible photoisomerization or thermomerization between the two tautomers which showed different absorption bands and absorbance changes of the bands [16–20].

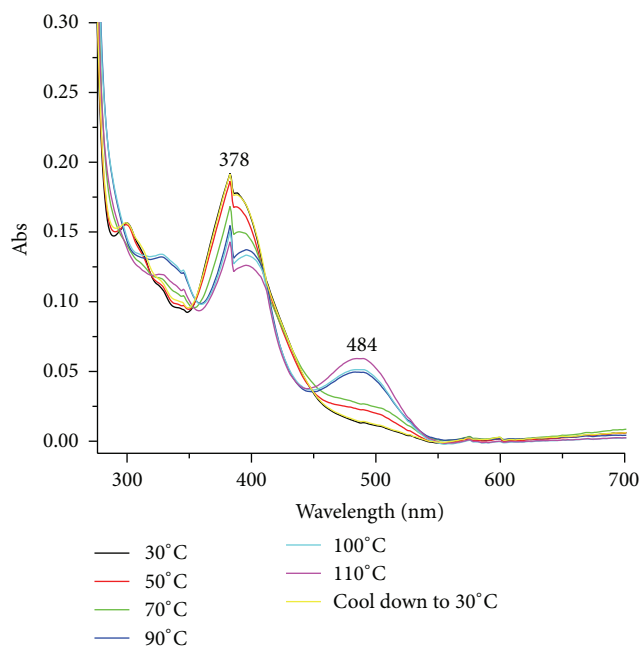


FIGURE 4: The UV-vis spectra of compound 2 on heating.

Figure 4 showed the UV-visible absorption spectra change of compound 2 on heating. The yellow DMF solution of compound 2 (concentration:  $1.0 \times 10^{-5}$  mol/L, path length: 1 cm) transformed to light orange. The intensity of the absorption peak at 378 nm decreased, and a new band appeared at 484 nm. The absorption peak intensity of the new band became greater with temperature rising. The heated solution was left to rest for enough time to cool down to room temperature, and the color of the solution came back to yellow. UV-visible absorption spectra were tested again. The result was showed in Figure 4 as well. The absorption curve of the cooled compound 2 was compared with that of the unheated compound 2 and they agreed well. These indicated that compound 2 had reversible thermochromism.

### 3.2. Photochromism

**3.2.1. UV-Visible Spectroscopic Studies.** Figures 5 and 6 showed the UV-visible absorption spectra changes of compounds 2 and 3 upon irradiation of 254 nm UV light, respectively. The yellow DMF solution of compound 2 (concentration:  $1.0 \times 10^{-5}$  mol/L, path length: 1 cm) transformed to pale orange under the UV light. The intensity of the absorption peak at 378 nm decreased and a new band appeared at 480 nm which kept increasing as the exposure time went on.

The orange red DMF solution of compound 3 transformed to orange yellow under the UV light (concentration:  $1.0 \times 10^{-5}$  mol/L, path length: 1 cm). Furthermore, the intensity of the absorption peak at 469 nm became smaller, while the absorption peak at 377 nm increased gradually. The changes of the absorption peaks of compounds 2 and 3 supported that the two compounds underwent tautomerism. Because the ratio of keto-amine form of compound 2 increased under UV irradiation, the absorbance of the peak

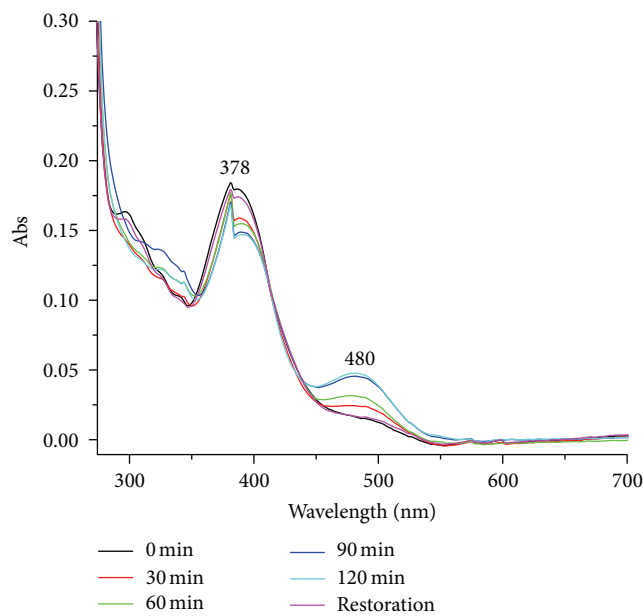


FIGURE 5: The UV-vis spectra of compound 2 after a period of exposure to UV light.

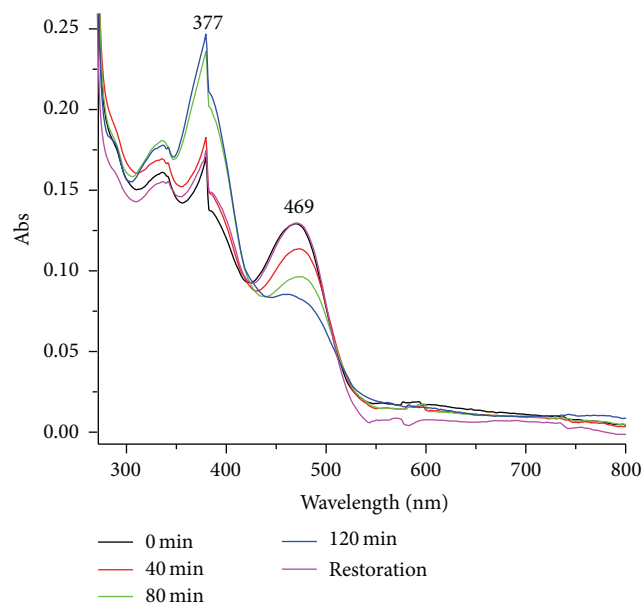


FIGURE 6: The UV-vis spectra of compound 3 after a period of exposure to UV light.

at greater than 400 nm increased. For the same reason, the ratio of the enol-imine form of compound 3 increased while the keto-amine decreased after irradiation of UV light [21].

The UV light was removed after the solutions exposure to it for two hours. The solutions were let to stand for 24 hours and the UV-visible spectra of the compounds were detected again. The spectra of the restored compounds 2 and 3 were also showed in Figures 5 and 6, respectively. The absorption curves were of close resemblance to the spectra of the compounds without irradiation with UV light.

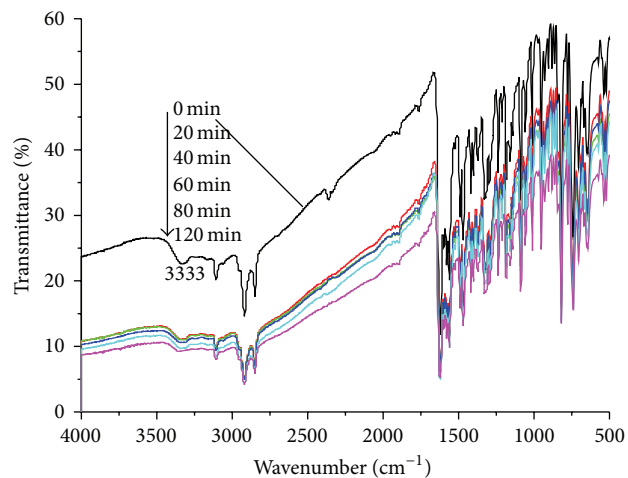


FIGURE 7: The IR spectra of compound 2 after a period of exposure to UV light.

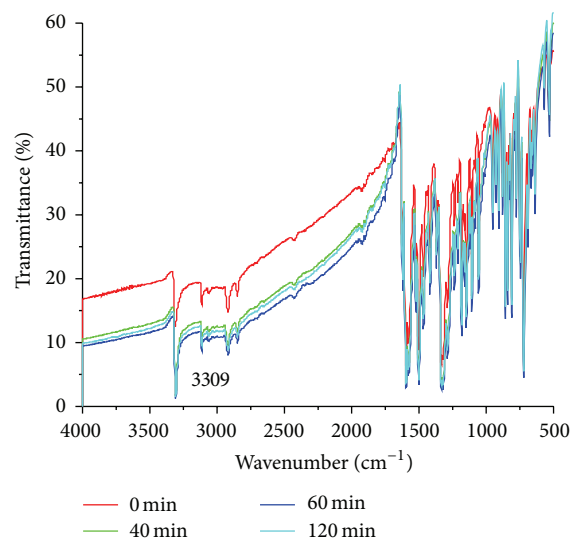


FIGURE 8: The IR spectra of compound 3 after a period of exposure to UV light.

Meanwhile, the color of the solutions was nearly back, so both of compounds 2 and 3 were reversible photochromic.

**3.2.2. IR Spectroscopic Studies.** The IR spectra of 2 and 3 were taken on each exposure time by the 254 nm UV light. The time-variable behavior of the IR spectra of compounds 2 and 3 exposure to UV light was shown in Figures 7 and 8, respectively. In Figure 7, The hydroxyl group (O-H) stretching band was observed at  $3333\text{ cm}^{-1}$  for compound 2. Upon irradiation with ultraviolet (UV) light, the intensity of the stretching band decreased. It was confirmed that the enol-imine form of compound 2 changed partially to keto-amine, while in Figure 8 the hydroxyl group (O-H) stretching band of compound 3 at  $3309\text{ cm}^{-1}$  became greater which confirmed that part of the keto-amine turned to enol-imine form when exposed to UV light.



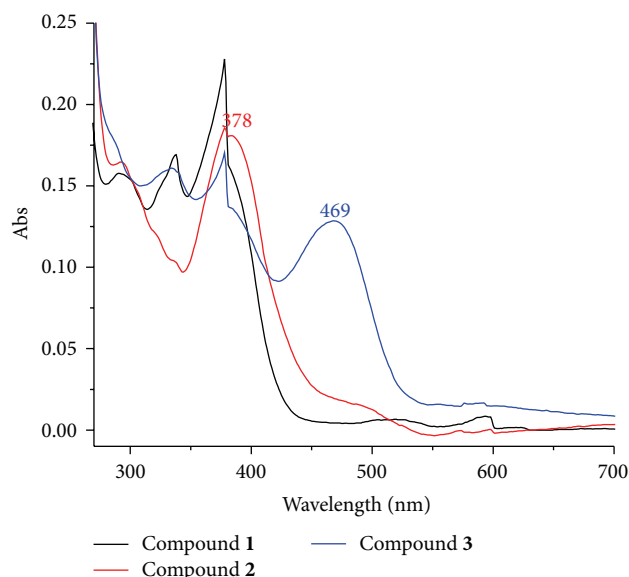


FIGURE 9: The UV-vis spectra of compounds 1, 2, and 3.

3.3. *The Effect of Substituents on Thermochromism or Photochromism.* Based on what had been discussed above, compounds 2 and 3 showed thermochromism and compound 2 exhibited photochromism, both phenomena being associated with an intramolecular proton transfer which led to the tautomerism between the enol-imine and the keto-amine [7]. But compound 1 had no similar properties. Orthohydroxyl was essential for the intramolecular proton transfer. Compounds 1, 2, and 3 were all orthohydroxyl Schiff bases and their structures were similar except for the difference in the substituents on the phenyl groups, so the substituent species effected the proton transfer as well.

Figures 9 and 10 were the UV-vis spectra of compounds 1–3 and those of the compounds exposure to the UV light for two hours, respectively. The results showed that compound 1 existed as enol-imine form and changed little after irradiation. Compound 2 existed as enol-imine form and transformed to keto-amine form, and the conversion ( $\alpha = (A\% - A_0\%) / A_0\%$ ;  $\alpha$  was conversion;  $A_0\%$  and  $A\%$  were the absorbance of a compound before and after irradiation by UV light) was nearly 11% at 378 nm. As for compound 3, the conversion of keto-amine to enol-imine was about 36% at 469 nm.

Hammett parameters (paranitro: +0.778, para-Cl: +0.227, H: 0.0) were important basis for judging substituents effects on the reaction of benzene ring. For example, the alkalinity of p-nitroaniline was weaker than aniline due to the charge population on N atom being less and proton capacity weakened since the nitro group was a strong electron-withdrawing group. But p-nitroaniline and p-nitrophenylhydrazine were only alkaline which accept proton rather than lose proton.

But here it was evident that the molecule of compound 3 was a system containing several aryl rings and amino group was not isolated. If the proton on N atom could transfer, a double bond formed between the N atom and the neighboring C atom. Meanwhile, the unsaturated cyclic ketone

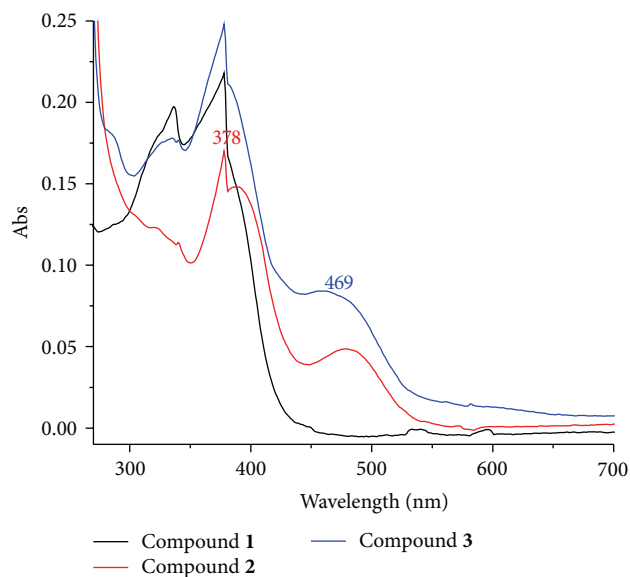


FIGURE 10: The UV-vis spectra of compounds 1, 2, and 3 exposure to UV light for 120 min.

changed to a much more stable benzene ring. Furthermore, the benzene ring and C=N formed conjugated system and the whole molecule became more stable. So the proton transfer could take place [20, 22–29].

The paranitro group made less charge population on N atom of amino group due to inductive effect and the shared electron pair deviate from H atom and turn to N atom which is advantageous to the hydrogen proton on N atom going away.

The substituent of compound 2 was a chlorine atom which was also an electron-withdrawing group. The compound tended to turn enol-imine into keto-amine form. Whatever the direction of the tautomerism, intramolecular proton in compounds 2 and 3 transferred more readily than compound 1.

## 4. Conclusion

Investigations of three naphthaldehyde hydrazone derivatives were conducted. It was found that not all of the o-hydroxyl Schiff bases exhibited thermochromism and photochromism. Compounds 1, 2, and 3 had similar structures, but the substituted species on phenyl ring were different. Compound 2 showed thermochromism and compounds 2 and 3 showed photochromism. As for compound 1, it showed no such properties. So the substituted species was a very important prerequisite in these properties. Results of UV-visible and IR analyses showed that compound 2 existed as enol-imine form. Heated to a certain temperature or exposed to UV light for a period of time, it partially transformed to keto-amine. Part of the keto-amine tautomer of compound 3 changed to enol-imine tautomer upon UV-light irradiation. Of these three compounds, the electron-withdrawing substituents on the benzene ring seemed to help the tautomerism.

## Additional Points

All additional information pertaining to characterization of the complexes using ESI-MS technique (Figures S1, S1', and S1'"; S4, S4', and S4'"; S7, S7', and S7'"), <sup>1</sup>H NMR (Figures S2, S5, and S8), and <sup>13</sup>C NMR (Figures S3, S3'; S6; and S9) is given in Supplementary Material available online at <http://dx.doi.org/10.1155/2016/8460462>.

## Competing Interests

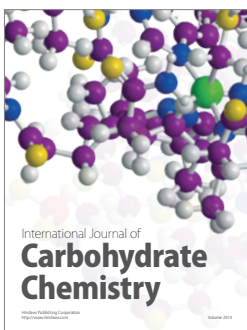
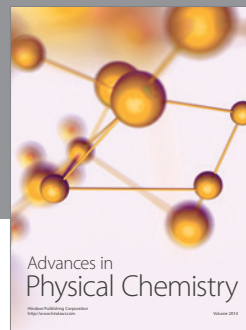
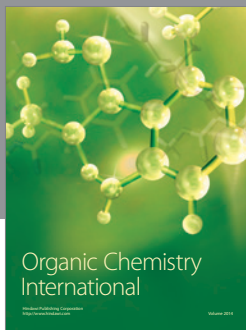
The authors declare that they have no competing interests.

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