



## NOTE

### Synthesis of a Novel X-Type Chromophore with Two Imidazole Groups Under Microwave Irradiation

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A novel series of asymmetric X-type chromophore, which bears two imidazole groups, were designed and synthesized in two steps at high yields under microwave irradiation. All of the chromophores were characterized by <sup>1</sup>H NMR and IR spectra. The organic compound shows better thermal stability due to the molecular structure introduced by the imidazole heterocycle.

**Key Words:** X-Type chromophore, Imidazole, Synthesis, Microwave irradiation.

As an important member of the five-membered ring heterocycles, imidazole moiety is present in a wide range of naturally occurring molecule<sup>1</sup>. The biological importance of the imidazole ring system has made it a common structure in numerous nature compounds, such as fungicides, herbicides, plant growth regulators and therapeutic agents<sup>2</sup>. Besides, heterocyclic imidazole derivatives show unique chemical and physical properties<sup>3</sup> because they contain imidazole heterocycle which has better thermal stability. The intense interest in imidazole derivatives is due especially to their applications as linear, non-linear optical materials<sup>4</sup> and blue-emitting materials<sup>5</sup>.

Microwave-assisted organic synthesis (MAOS) has had a significant impact on synthetic chemistry. The wide applicability of microwave irradiation in chemical reaction enhancement is due to the high reaction rate with formation of cleaner products and operational simplicity<sup>6</sup>. Reductions in reaction time, increases in yield and suppression of side product formation have been described for microwave conditions relative to conventional thermal heating<sup>7</sup>. In this work, a novel series of asymmetric X-type chromophore, which bears two imidazole groups, were synthesized at moderate yields under microwave irradiation and the final products are isolated directly by filtration.

Solvents and reagents were obtained commercially and used as received. Infrared spectra were recorded using a Bruker Tensor-27 spectrometer using KBr pellets and reported as cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra were obtained in DMSO-*d*<sub>6</sub> on a Bruker

300 MHz spectrometer using TMS as the internal standard, chemical shifts ( $\delta$ ) are given in ppm.

#### General procedure for the synthesis of compounds 1 and 3

**Synthesis of compound 1:** A mixture of phenanthraquinone 2.1 g (10 mmol), 3.9 g ammonium acetate (50 mmol) and terephthalaldehyde 4.0 g (30 mmol) in 50 mL acetic acid was irradiated in a microwave synthesizer for 15 min monitored by TLC. The reaction mixture was neutralized with aqueous ammonia and the crude product was collected and recrystallized from nitrobenzene, 70 % yield, m.p. 315-317 °C. IR (KBr pellet,  $\nu_{\max}$ , cm<sup>-1</sup>): 3442, 1678. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\text{H}}$  13.77(s, 1 H), 8.82-9.10 (d, *J* = 8.2 Hz, 2H), 8.51-8.63 (m, 4H), 8.41-8.61 (d, *J* = 8.2 Hz, 2H), 7.81 (s, 2 H), 6.80 (s, 2 H).

**Compound 3:** m.p. 236-237 °C. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>) 695, 1605, 1696, 3051; <sup>1</sup>H NMR: H 7.38-7.56 (m, 12H), 8.00-8.03 (d, *J* = 8.1 Hz, 2H), 8.29-8.32 (d, *J* = 8.1 Hz, 2H), 10.03 (s, 1H), 12.96 (brs, 1H) ppm.

**General procedure for the synthesis of target chromophores 2a-2c and 4a-4b:** A mixture of compound 1 3.2 g (10 mmol), 3.9 g ammonium acetate (50 mmol) and 1,2-diketone (10 mmol) in 20 mL acetic acid was irradiated in a microwave synthesizer for 20 min monitored by TLC. After cooling to 50 °C the resulting solid was filtered, washed with cold methanol and dried to give the pure target compound.

**Compound 2a:** IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 842, 1481, 1615, 1655, 3059; <sup>1</sup>H NMR: H 7.28-7.75 (m, 14H), 8.31-8.33 (d, *J* = 7.4 Hz, 2H), 8.57 (s, 2H), 8.58-8.61 (m, 2H), 8.84-8.87 (m, 2H), 12.84 (brs, 1H), 13.50 (brs, 1H) ppm.

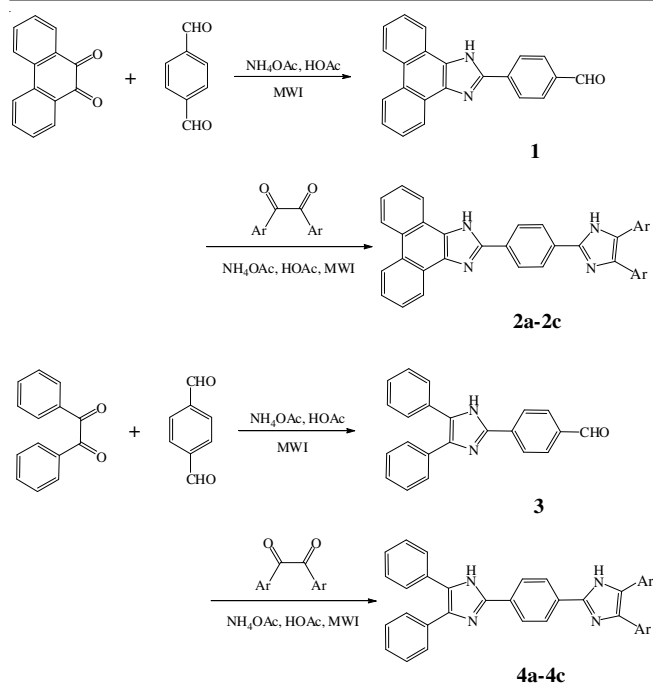


Fig. 1. Synthetic scheme for X-type chromophores

TABLE-1  
STRUCTURE AND YIELD OF CHROMOPHORES

Entry	Product	Ar	Yield (%)
1	<b>2a</b>	Phenyl	71
2	<b>2b</b>	4-Chlorophenyl	76
3	<b>2c</b>	2-Furyl	72
4	<b>4a</b>	4-Chlorophenyl	80
5	<b>4b</b>	2-Furyl	73

**Compound 2b:** IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 830, 1496, 1614, 3442;  $^1\text{H NMR}$ : H 7.43-7.75 (m, 14H), 8.28-8.31 (d,  $J = 7.6$  Hz, 2H), 8.42-8.44 (d,  $J = 7.6$  Hz, 2H), 8.60 (s, 2H), 8.87 (s, 2H), 12.95 (brs, 1H), 13.51 (brs, 1H) ppm.

**Compound 2c:** IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 844, 1481, 1616, 3421;  $^1\text{H NMR}$ : H 6.62 (s, 1H), 6.69 (s, 1H), 6.70 (s, 1H), 6.81 (s, 1H), 6.82 (s, 1H), 7.87 (m, 6H), 8.31-8.34 (d,  $J = 8.2$  Hz, 2H), 8.44-8.44 (d,  $J = 8.2$  Hz, 2H), 8.44-8.64 (m, 2H), 8.84-8.90 (t,  $J = 9.3$  Hz, 4H), 13.05 (brs, 1H), 13.55 (brs, 1H) ppm.

**Compound 4a:** IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 831, 1498, 1637, 3441;  $^1\text{H NMR}$ :  $\delta_{\text{H}}$  7.43-7.75 (m, 14H), 8.28-8.31 (d,  $J = 7.5$  Hz, 2H), 8.42-8.44 (d,  $J = 7.5$  Hz, 2H), 8.60 (s, 2H), 8.87 (s, 2H), 12.95 (brs, 1H), 13.51 (brs, 1H) ppm. IR (KBr  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 845, 1486, 1602, 3060;  $^1\text{H NMR}$ : H 6.60 (s, 1H), 6.69 (s, 1H), 6.79 (s, 1H), 6.99 (s, 1H), 7.26-7.56 (m, 7H), 7.74 (s, 1H), 7.85 (s, 1H), 8.21 (s, 1H), 12.77 (brs, 1H), 12.93 (brs, 1H) ppm.

**Compound 4b:** IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 845, 1486, 1602, 3060;  $^1\text{H NMR}$ :  $\delta_{\text{H}}$  6.60 (s, 1H), 6.69 (s, 1H), 6.79 (s, 1H),

6.99 (s, 1H), 7.26-7.56 (m, 7H), 7.74 (s, 1H), 7.85 (s, 1H), 8.21 (s, 1H), 12.77 (brs, 1H), 12.93 (brs, 1H) ppm.

Aldehydes **1** and **3** were prepared through Debus reaction under microwave irradiations with better yields than under the traditional condition. In the second step reaction, the high reaction yield is primarily due to the insolubility of the target chromophores in the acetic acid medium, which in turn causes rapid precipitation of the products, shifting the reaction equilibrium to the right. The structures of **2a-2c** and **4a-4c** were characterized by IR and  $^1\text{H NMR}$ . The  $^1\text{H NMR}$  data showed two proton signal in the region  $\delta$  12.77-13.61 ppm for NH of the imidazole ring. In the infrared spectra, the N-H bands appeared at 3060-3442  $\text{cm}^{-1}$ . High thermal stability is an important feature of dyes in order to be usable in applications, melting points of all compounds are beyond 300  $^{\circ}\text{C}$ , showing relatively high thermal stability.

## Conclusion

In summary, a general microwave-assisted synthesis of asymmetric X-type chromophores containing two imidazole groups is developed. In addition to its speed and simple setup, the reaction is high yielding.

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