

## Synthesis and Characterization of a New Heterocyclic Azo Pigment (Sintesis dan Pencirian Pigmen Azo Heterosiklik Baru)

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### ABSTRACT

*A new heterocyclic coupling agent has been produced from the reaction of maleic anhydride and p-aminophenol, namely N-(4-hydroxyphenyl)maleimide. The coupling agent underwent azo coupling reaction with aromatic amine, which is p-aminophenol to produce a new heterocyclic azo pigment. The pigment was then subjected to solubility, hiding power and light fastness test. Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet/Visible (UV/Vis) Spectroscopy, and Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ) were used to obtain the characteristics and structural features of the pigment.*

*Keywords: Aromatic amine; heterocyclic azo pigment; N-(4-hydroxyphenyl)maleimide*

### ABSTRAK

*Satu agen gandingan heterosiklik baru iaitu, N-(4-hydroxyphenyl)maleimide telah dihasilkan melalui tindak balas antara malik anhidrida dan p-aminofenol. Agen gandingan tersebut kemudian melalui tindak balas gandingan azo dengan amina aromatik, iaitu p-aminofenol untuk menghasilkan pigmen azo heterosiklik baru. Ujian keterlarutan, keupayaan menutupi warna substrak dan ujian tahan luntur cahaya dilakukan terhadap pigmen. Spektroskopi Inframerah (FTIR), Spektroskopi Ultraungu/Nampak (UV/Vis), dan Spektroskopi Resonans Magnetik Nuklear ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ) digunakan untuk mengenalpasti struktur dan ciri-ciri pigmen.*

*Kata kunci: Amina aromatik; N-(4-hydroxyphenyl)maleimide; pigmen azo heterosiklik*

### INTRODUCTION

Azo compounds are an important class of organic colorants which consist of at least a conjugated chromophore azo (-N=N-) group in association with one or more aromatic or heterocyclic system (Abrahart 1968; Bindu et al. 2000). They are capable of providing high intensity color and have reasonably good technical properties, including light and weather fastness and resistance to solvents and water (Christie 2001). It has been known for many years that azo compounds are the most widely used class of dyes due to their versatility in various fields such as the dyeing of textile fiber, the coloring of different materials, coloured plastics, biological-medical studies and advanced applications in organic synthesis (Catino & Farris 1985; Fadda et al. 1994; Kocaokutgen & Gumrukcuoglu 1995; Hartman et al. 1991; Law et al. 1994; Peters & Chisowa 1993; Tanaka et al. 1984; Venkataraman 1970).

In this past twenty years, heterocyclic coupling agents received a great deal of attention because of their excellent properties which are light fastness, good substantivity, good migration and have a very brilliant shade. Pyrazolones, iminopyrazolones, pyridones, pyrimidine are some of them (Schwander 1982). Manuela et al. (2009) reported that heterocyclic azo dyes derived from 5-N,N-dialkylamino-2,2'-bithiophene couplers could be used as thermally stable, solvatochromic probes which therefore find applications in electro-optical devices and sensors. Lee et

al. (2003) attempted to synthesize a range of temporarily solubilized disperse dyes which have a wider variety of colour by using the aromatic heterocyclic compounds such as pyridone and indole as coupling components. They claimed that the light fastness of the dyes was moderate and all the other fastness results were good to excellent. Furthermore, it has been reported that addition-curable phenolic resins functionalized with phenylmaleimide-system has improved the thermal characteristics and give good mechanical performance to composites. They are desirable for application in composites for thermo-structural applications (Bindu et al. 2000; Yang et al. 2007).

This paper reports the synthesis, characteristics and properties of the new heterocyclic coupling agent and the pigment obtain by the coupling of p-aminophenol with N-(4-hydroxyphenyl)maleimide.

### MATERIALS AND METHODS

#### MATERIALS

Maleic anhydride (MA), p-aminophenol (PAP), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 98%, concentrated hydrochloric acid (HCl) 37%, sodium hydroxide (NaOH), dimethylformamide (DMF), di-phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), sodium nitrite ( $\text{NaNO}_2$ ), isopropanol and glacial acetic acid were purchased from

Sigma-Aldrich, Switzerland. All the chemicals were used as received without further purification.

#### SYNTHESIS OF N-(4-HYDROXYPHENYL)MALEIMIDE

PAP (0.15 mol, 16.37 g) and MA (0.15 mol, 14.71 g) were dissolved separately into 50 mL of DMF to yield solution A and B, respectively. Solution B was added into solution A by mean of dropping method to get solution C. Solution C was stirred for 2 h at 20°C in a water bath. P<sub>2</sub>O<sub>5</sub> (12.0 g) (as a catalyst) was dissolved in 10 mL of H<sub>2</sub>SO<sub>4</sub> and 70 mL of DMF. The mixture was slowly added into solution C by using dropping funnel and was stirred for 2 h at 70°C. The mixture was kept chilled in the ice bath and poured into cold water. A precipitate formed and was filtered, repeatedly washed with distilled water. It was then recrystallized from hot iso-propanol and dried in an oven at 65°C for 24 h until fully dried.

#### PREPARATION OF PIGMENT

Pure PAP (0.01 mol, 0.93 g) was dissolved in 3 mL of concentrated HCl and 3 mL of water to yield solution A and cooled at 5°C in an ice bath. NaNO<sub>2</sub> (0.01 mol, 0.69 g) was dissolved in 10 mL water at 5°C (solution B). Solution A was added into solution B at 5°C by drop wise method and kept stirred. The mixture was then slowly added into N-(4-hydroxyphenyl)maleimide (0.01 mol, 1.89 g), which was dissolved in 20 mL of 10% NaOH at 5°C. The mixture was kept chilled in the ice bath and stirred continuously for 10 min. The precipitate formed was filtered and recrystallized from glacial acetic acid, washed with methanol to eliminate the acetic acid and dried in an oven at 65°C for 24 h.

#### CHARACTERIZATION

The materials (MA, PAP), N-(4-hydroxyphenyl)maleimide and the pigment were characterized using a Nicolet Fourier Transform infrared spectroscopy (FT-IR) instrument for functional group assignment. The FT-IR spectra were recorded by high-purity dried potassium bromide (KBr) powder at room temperature. The coupling agent and the pigment then subjected to UV/Vis Spectroscopy and Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR) to confirm their characteristics and structural features.

The pigment was mixed with polyester and methyl ethyl ketone peroxide (MEKP) as a curing agent, while cobalt naphtenate as an accelerator. The paint was coated on a black and white patterned card (opacity chart) with thickness of 90 µm. The cured film was exposed to the day light for light fastness testing. The hiding power of the pigment was observed by coating the mixture of the pigment and polyester on the opacity chart and left to cure at room temperature for 24 h.

#### RESULTS AND DISCUSSION

Figure 1 shows three different IR spectra representing MA, PAP and N-(4-hydroxyphenyl)maleimide. For MA,

the most characteristic anhydride bands (-C=O) can be seen at 1890.89 cm<sup>-1</sup>. The exact position of these bands is slightly dependent on the nature of the sample as well as the solvent used (Trivedi & Culbertson 1982). Apart from these absorption bands, the presence of -CH=CH- and -C-O-C- are observed at 3058.63 cm<sup>-1</sup> and 1262.95 cm<sup>-1</sup>, respectively.

FT-IR spectrum of PAP shows the absorption due to the -OH group is visible at 3176.21 cm<sup>-1</sup>. The most characteristic bands are -NH<sub>2</sub> (primary amines) can be seen at 3340.29 and 3280.15 cm<sup>-1</sup>, as well as aromatic ring which appeared at 1616.27 cm<sup>-1</sup>.

Meanwhile, N-(4-hydroxyphenyl)maleimide consist of combination characteristic from MA which is carboxylic group (-C=O) at 1702.94 cm<sup>-1</sup>, alkenes group (-CH=CH-) at 3119.30 cm<sup>-1</sup> and characteristic from PAP which is hydroxyl group (-OH) at 3481.99 cm<sup>-1</sup>. The OH is substituted at the benzene ring at 832.91 cm<sup>-1</sup>. Thus, it is clearly proved that MA and PAP was undergone a reaction.

On the other hand, the FT-IR spectrum (Figure 2) indicates that the azo pigment has successfully undergone the azo coupling reaction, as can be seen from the absorption by the azo functional group (-N=N-) in the 1630-1575 cm<sup>-1</sup> region. An *o*-substituted amine group attached to the benzene ring yields absorption in the 750-775 cm<sup>-1</sup> region of the spectrum.

UV/Vis spectrum of the coupling agent is shown in Figure 3. Azo functional group (-N=N-) usually give its absorption wavelength at range from 350 nm-370 nm. However, from the result (Table 1), we could not see the absorption. This is due to tautomerism of the pigment. Rao et al. (1967) studied the effect on solvent on keto-enol equilibria and found that the polar and proton donor solvents, which can stabilized the carbonyl group by dipolar association or hydrogen bonding and it will decrease the magnitude of the enolization. As a result, the predominant group (keto) will give a shorter wavelength.

Nuclear Magnetic Resonance Spectroscopy: <sup>1</sup>H-NMR (Figure 4) shows that there are four peaks from 6.31 ppm to 6.58 ppm proved that the alkenes group proton, (H-C=C-H) is present in the structure and also appearance of the aromatic proton, (H-C=C-H) from the peaks at 6.78 ppm to 7.48 ppm. <sup>13</sup>C-NMR spectrum of N-(4-hydroxyphenyl) maleimide (Figure 5) shows that the following peaks are the characteristic of the structure; 170.79 ppm (C=O), 157.44 ppm (C-N), 134.37 ppm (-C=C-, alkenes) and 128.23 ppm (-C=C-, aromatic).

#### MELTING POINT

The melting point of the coupling agent is 182-184°C while pigment is 210-212°C. It is due to the presence of the hydroxyl group. It will form a hydrogen bonding with the nearest hydrogen and will increase the stability of the compound. Melting point is used to determine the purity of a compound. An impure compound will give a lower melting point. From the result, it is estimate that the

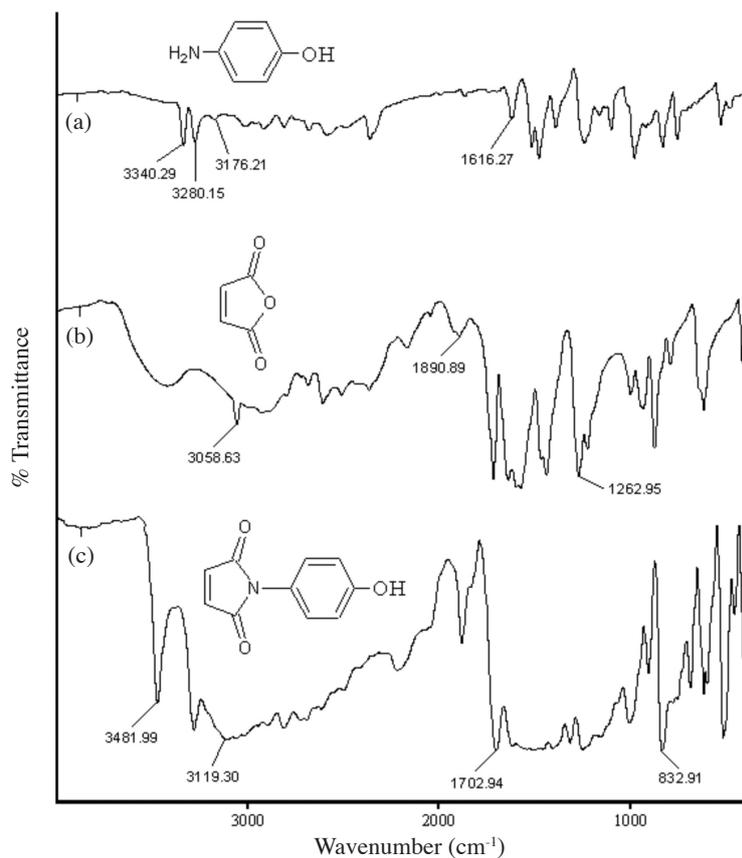


FIGURE 1. FT-IR spectra of (a) *p*-aminophenol, (b) maleic anhydride and (c) N-(4-hydroxyphenyl)maleimide

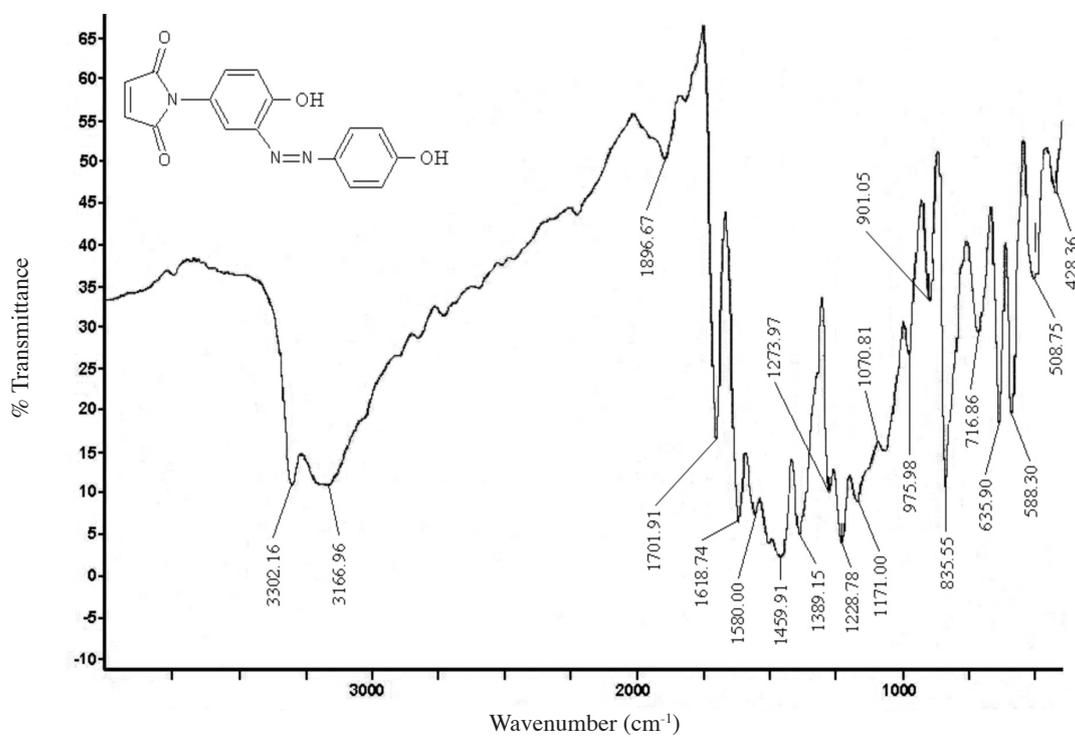


FIGURE 2. FT-IR spectrum of azo pigment

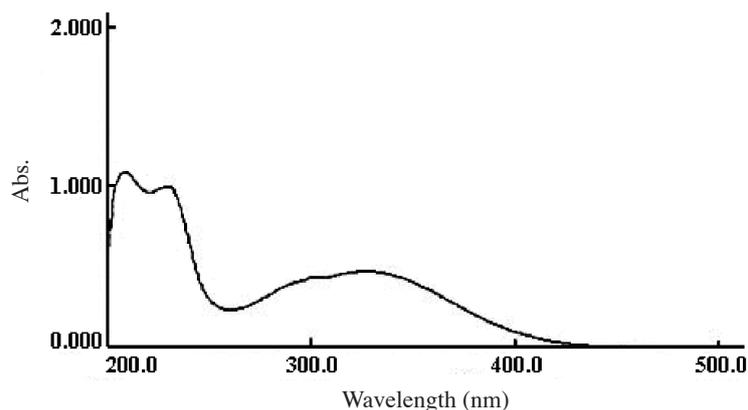
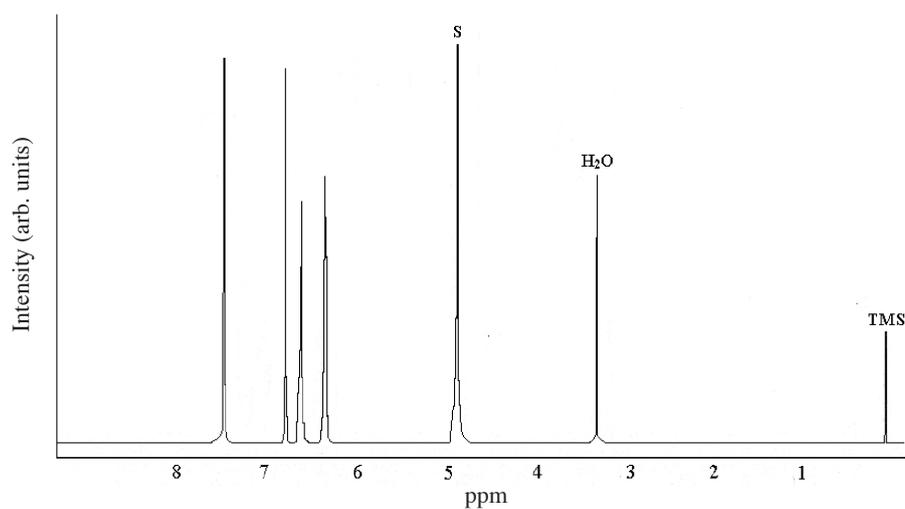


FIGURE 3. UV/Vis spectrum on N-(4-hydroxyphenyl)maleimide

TABLE 1. UV/Vis. Absorption and wavelength of pigment

Wavelength (nm)	Absorption	Component
326.5	0.3843	N=N
302.5	0.3531	C=O
230.5	0.8049	Ar-CN
210	0.8654	Ar-OH

\*Ar-CN (benzene substituted with CN);  
 Ar-OH (benzene substituted with OH);  
 Ar-CH<sub>3</sub> (benzene substituted with CH<sub>3</sub>)

FIGURE 4. <sup>1</sup>H-NMR spectrum of N-(4-hydroxyphenyl)maleimide

pigment has a good thermal stability (Patai 1978; Patton 1979).

#### LIGHT FASTNESS

It is necessary to make sure that the pigment particles were dispersed homogeneously before apply to the substrate. Non-homogeneous film and inconsistent thickness will result in different degree of scattering and absorption of light. After 3 weeks exposure in indoor, there was no

change in color, signifying that the pigment has good light fastness indoor. Meanwhile, 3 weeks exposure to day light showed only a slight changing color in the film. This indicated that the pigment has quite good light fastness. The pigment can exhibit tautomerism form, light fastness may improve due to the reduction in electron density at azo group by the hydrogen bonding which can reduce the sensitivity towards photochemical oxidation (Christie 2001; Willy et al. 2004).

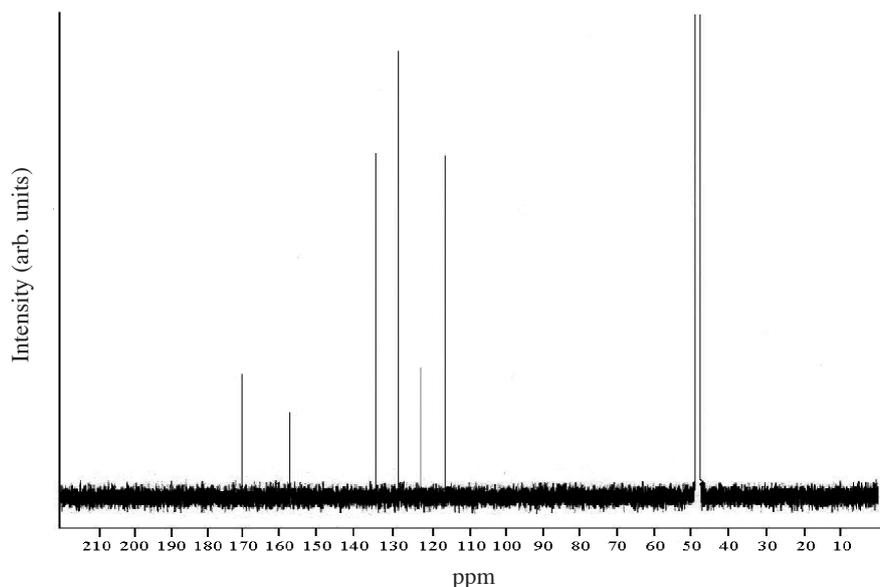


FIGURE 5.  $^{13}\text{C}$ -NMR spectrum of N-(4-hydroxyphenyl)maleimide

#### CONCLUSION

We have synthesized and characterized a new heterocyclic coupling agent (N-(4-hydroxyphenyl)maleimide) by the reaction of maleic anhydride and *p*-aminophenol. In a different stage, a new yellow heterocyclic azo pigment was produced by azo coupling reaction of N-(4-hydroxyphenyl)maleimide with aromatic amine, *p*-aminophenol. The pigment with melting point of 210–212°C and yield of 81% showed good solubility in polar solvent except water; which is the main properties of pigment. It also demonstrated that the pigment has good light fastness as well as good hiding power.

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