

## FOURIER TRANSFORM INFRARED AND PROTON NUCLEAR MAGNETIC RESONANCE ANALYSIS OF SAMPLED QUINOLINEDIONES AND EFFECTS OF MORDANTS ON THEIR DYESTUFF PROPERTIES

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### ABSTRACT

Structural identification and new application of synthesized compounds have been a viable pursuit in organic chemistry. In this work, Fourier Transform Infrared (FT-IR) and Proton Nuclear Magnetic Resonance (Hnmr) spectroscopies were used to measure quinolinediones. FT-IR and Hnmr provided useful ways for identification of the compounds. Characteristic Infrared absorptions for quinolinediones such as  $750\text{ cm}^{-1}$  (C-X);  $1215\text{ cm}^{-1}$  (C-N);  $1650\text{ cm}^{-1}$  (C=O), among others, were observed and characteristic proton-proton coupling constants for quinolinediones, 4.7/7.9, among others and chemical shifts were observed. Quinolinediones produced excellent colours on cotton fabrics, food, petroleum jelly and illicit gin, with most enhanced binding when used with  $\text{FeSO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  mordants in both light and wash fastness. Alum also showed good fastness to mild soap. Varied excellent colours were imparted on the quinolinediones: 6,7-dibromo-5,8-quinolinedione imparted lemon green colour on starchy food; orange colour on petroleum jelly and brown colour on illicit gin while 6,7-dichloro-5,8-quinolinedione imparted brownish milk colour on starchy food and light yellow colour on petroleum jelly and illicit gin. FT-IR and Hnmr are therefore recommended as being sufficient for structural elucidation of quinolinediones and their derivatives. Quinolinediones are also recommended as good dyes and colourants, which will be consequent upon further studies about the toxicological effects.

**Keywords:** Dyes, dyestuff, FT-IR, Hnmr, mordants, Quinolinediones

### Introduction

The biological activities, which include among others, antimalaria, antifungal and antibacterial properties of quinolinediones are already being explored as several activities of the compounds against different microbes have appeared in literature (Ryu and Kim, 1994; Behforouz and Merriman, 1997; Keyari *et al.*, 2013 and Porter *et al.*, 1972).

Our group has focused on successful synthesis of the derivatives of quinolinediones (Egu *et al.*, 2015 and Egu *et al.*, 2016), verifying their structures using spectroscopic analysis. The place of structural elucidation in chemistry, particularly organic chemistry cannot be overemphasized. Reason being that target molecule preparation must be justified

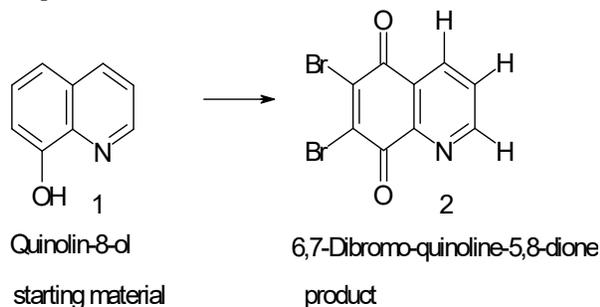
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so as to avoid mere speculation. Functional group and proton identification provides very useful information about a product. This is very much so about quinolinedione where some functional groups and protons present in the starting materials are absent in the products.



**Figure 1:** Synthesis of 6,7-dibromo-5,8-quinolinedione

The pyridine ring is present in both starting material and product. Pyridines possess characteristic proton-proton coupling constants which can be helpful in the measurement of target molecules.

Quinolonediones are conjugated, suggesting them to be potential dyes. A dye is a coloured substance that has an affinity to the substrate to which it is being applied. Application is generally in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber (Booth, 2000). Mordants are known to bind dyes on fabrics by forming a coordination complex with the dye, making it attach to the fabric (Rushikesh *et al*, 2016).

This report seeks to reveal the suitability and sufficiency of FT-IR and Hnmr spectroscopies in measuring synthesized quinolinediones and to investigate effects of different mordants on dyestuff properties of sample quinolinediones.

## Materials and Methods

### General

The NMR spectra were recorded on Bruker DPX 400. Chemical shifts are reported in ppm values relative to TMS as an internal standard. S09Chem 211 IR spectroscopy was used.

### Preparation of dye solution

The dye sample (1 g) was weighed into a beaker and little amount of water was added to make it into paste

form after which it was made up to 100 ml with water at 50 °C. The solution was heated for 5 mins to aid proper dissolution of the dye sample. It was then cooled. (Osabohien and Ukponwan, 2002)

### Preparation of the dye bath

From the dye solution already prepared, 25 ml was measured into a beaker and was made up to 100 ml with water.

### Dyeing

The material to be dyed (2 g) was first weighed and scoured with soap before placing in the dye bath to allow proper penetration of the dye liquor into the fibre to ensure uniform and even dyeing (Sharma, 2011).

The fabric after been scoured and rinsed in water was introduced into the dye bath solution and dyeing commenced for 30 mins at 60 °C, after which the fabric was removed and oxidised in air for 10 mins, and then rinsed in cold water to remove any loose dye particle that might have adhered to the fabric. The fabric was then air dried and tested for fastness properties. The fabrics were mordanted by introducing the scoured fabric into 2 % solution of potassium dichromate, Alum, stannous chloride and iron sulphate for 30 mins at 60 °C after which the fabrics were then dyed in the dye bath for 30mins at 60 °C. The fabric was air dried and tested for fastness properties.

### Fastness Properties

#### Light Fastness

One set of the dyed fabrics was exposed to sunlight for one week and the other set was kept in a polyethene, away from light for one week (Osabohien and Ukponwan, 2002). The two sets were rated on grey scale (Osabohien and Ukponwan, 2002).

#### Wash Fastness

The dyed fabrics were made into two sets. One set of the fabric was washed in mild soap while the second set in a strong soap. The washed fabrics were compared with the unwashed ones on a grey scale (Nkeoye, 1987 and Akpuaka, *et al.*, 2007).

### Results and Discussion

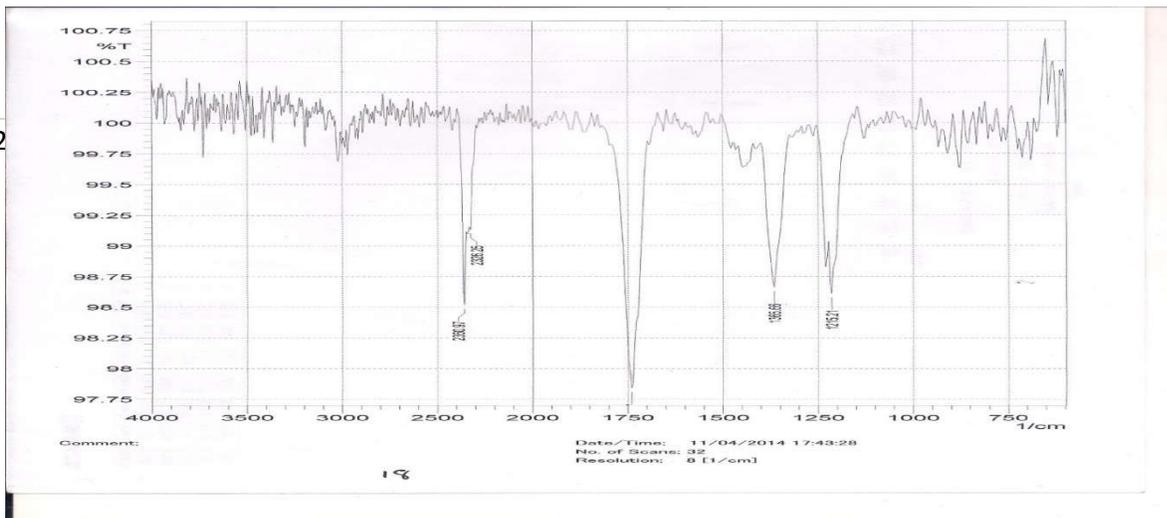


Figure 2: IR spectra of 7-bromo-6-phenylaminoquinoline-5,8-dione

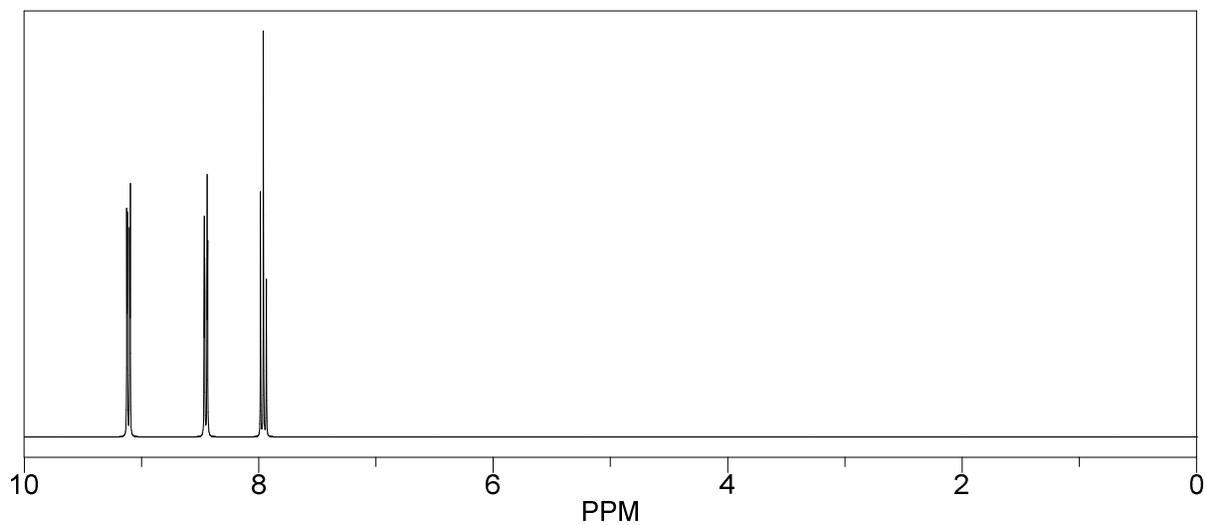
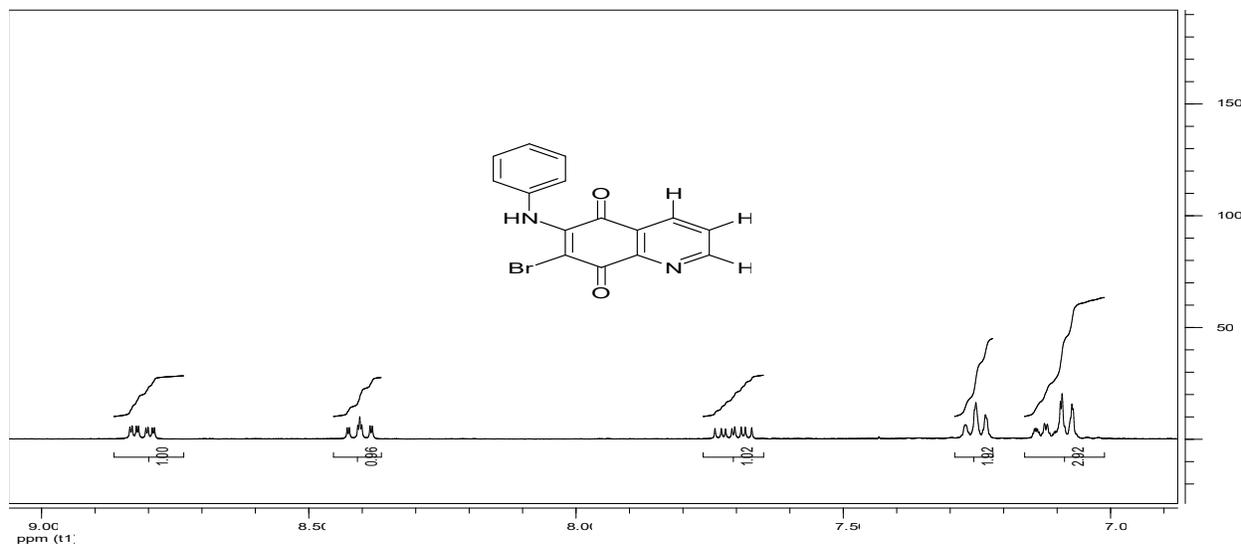


Figure 3: <sup>1</sup>H NMR spectra of 6,7-dibromoquinoline-5,8-dione



**Figure 4:**  $^1\text{H}$ nmr spectra of 7-bromo-6-phenylaminoquinoline-5,8-dione

**Table 1:** Recorded characteristic peaks of FT-IR spectrum of 7-bromo-6-phenylaminoquinoline-5,8-dione

S/No	Structure	Literature value( $\text{cm}^{-1}$ )	Observed value( $\text{cm}^{-1}$ )	Inference
1		800-600	750	C-X
2		1350-1000	1215.21	C-N
3		1690-1640	1650	C=N
4		3500-3100	3000	N-H
5		1800-1600	1750	C=O

Literature value obtained from Loharet *al*, 2016

**Table 2:** Characteristic proton-proton coupling constant for quinolinedione

Proton	Chemical Shift	Coupling Constants (Hz)	
H <sub>B</sub>	7.9	4.7	7.9
H <sub>C</sub>	8.5	1.6	7.9
H <sub>A</sub>	9.0	1.7	4.7

**Table 3:** Colour/Solubility

Sample	Colour of Sample	Colour in solution (aqueous)	Solubility		
			Cool	Warm	Ethanol
7-chloroquinoline-5,8-dione	Brown	Brown	Soluble	Soluble	Soluble
6,7-dichloroquinoline-5,8-dione	Yellow	Yellow	Insoluble	Sparingly soluble	Soluble

**Table 4:** Colour hue

Dye sample/Mordants	Colour on Fabric	Light Fastness	Wash Fastness	
			Detergent	Mild Soap
7-chloroquinoline-5,8-dione	Milk	1 – 2	1 – 2	2 – 3
CuSO <sub>4</sub>	Pale yellow	2 – 3	1 – 2	1 – 2
FeSO <sub>4</sub>	Yellow	3 – 4	2 – 3	3 – 4
SnCl <sub>2</sub>	Pale yellow	1 – 2	1 – 2	1 – 2
Alum	Pale yellow	2 – 3	2 – 3	3 – 4
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Yellow	3 – 4	2 – 3	3 – 4
6,7-dichloroquinoline-5,8-dione	Milk	2 – 3	2 – 3	3 – 4
CuSO <sub>4</sub>	Light milk	3 – 4	3 – 4	3 – 4
FeSO <sub>4</sub>	Yellow	3 – 4	3 – 4	2 – 3
SnCl <sub>2</sub>	Light pink	3 – 4	2 – 3	2 – 3
Alum	Light pink	2 – 3	3 – 4	2 – 3
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Light pink	4 – 5	4 – 5	4 – 5

**Key:** 1 – 2 = Poor; 2 – 3 = Fair; 3 – 4 = Good; 4 – 5 = Excellent

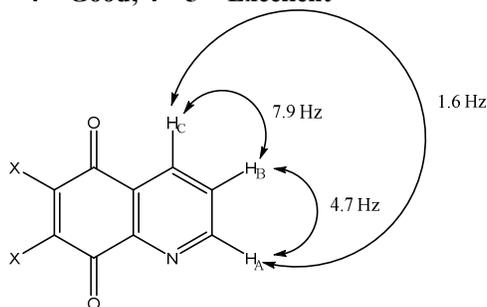
**Figure 5:** Proton-proton coupling constant

Table 1 shows that FT-IR spectrum of the quinolinedione is in agreement with its chemical structure since the characteristic bands for the functional groups- C-X, C=N, C-N, N-H and C=O were observed.

Figures 3 and 4 reveal the types and number of protons in the quinolinediones. The integration is an added evidence in revealing the number of protons. Table 2 also supplies characteristic proton-proton coupling constant to further confirm the retention of the pyridine ring in the product.

Table 3 displayed the colour of the sample as brown and yellow for 7-chloroquinoline-5,8-dione and 6,7-dichloroquinoline-5,8-dione respectively with 7-chloroquinoline-5,8-dione soluble in cold H<sub>2</sub>O, warm H<sub>2</sub>O and ethanol and 6,7-dichloroquinoline-5,8-dione only very soluble in ethanol.

The colour hue on fabric produced by the unmordanted and mordanted fabrics were excellent; 7-chloroquinoline-5,8-dione showed a milk colour with poor fastness to light and fair fastness to washing in mild soap. CuSO<sub>4</sub>, SnCl<sub>2</sub> and alum mordants displayed pale yellow colour, while FeSO<sub>4</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> showed yellow colour. FeSO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> mordants showed superiority to light fastness; FeSO<sub>4</sub>, alum and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> showed good fastness to mild soap. In detergent, FeSO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> displayed superiority to fastness (Table 4).

6,7-dichloroquinoline-5,8-dione produced a milk colour hue on the fabric with a good fastness property to washing in mild soap as very slight colour change was observed; the mordants CuSO<sub>4</sub> and FeSO<sub>4</sub> displayed light milk and yellow colour respectively. Light pink was imparted all through for alum, SnCl<sub>2</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> mordants respectively (Table 4).

Irrespective of the original colours of the dyes, they imparted varied excellent colours on the

substrates; 7-chloroquinoline-5,8-dione showed lemon green, orange and brown on starchy food, petroleum jelly and illicit gin respectively; 6,7-dichloroquinoline-5,8-dione exhibited brownish milk on pap and light yellow on petroleum jelly and illicit gin.

## Conclusion

This study has made it glaring that FT-IR and Hnmr spectra are capable of measuring quinolinediones. It is therefore recommended that FT-IR and Hnmr be accepted by researchers as sufficient enough for structural determination of quinolinedione and other related compounds.

From the results obtained, we recommend the use of these compounds in dye industries with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as the most efficient mordant. Their usage as colourants on substrates is also recommended, however, the toxicity of these compounds should be further studied.

## CONFLICT OF INTEREST

Authors have no any form of conflict of interest and no sponsors.

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