SYNTHESIS AND CHARACTERISATION OF REACTIVE DYES FROM QUINAZOLINONE DERIVATIVES AND THEIR COLOUR ASSESSMENT ON COTTON FABRIC

By

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DEPARTMENT OF POLYMER AND TEXTILE ENGINEERING,
FACULTY OF ENGINEERING,
AHMADU BELLO UNIVERSITY, ZARIA,
NIGERIA.

OCTOBER, 2021.

DECLARATION

I declare that the work in this dissertation entitled “**Synthesis and characterisation of Reactive Dyes from Quinazolinone Derivatives and their Colour Assessment on Cotton Fabric”** has been carried out by me in the Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria. The information derived from literature has been duly acknowledged in the text and a list of references is provided. No part of this project was previously presented for another degree or diploma at this or any other institution.

Oserueme Timothy ILEVBAOJE		
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CERTIFICATION

This project dissertation entitled “**SYNTHESIS AND CHARACTERISATION OF REACTIVE DYES FROM QUINAZOLINONE DERIVATIVES AND THEIR COLOUR ASSESSMENT ON COTTON FABRIC”** by Oserueme Timothy ILEVBAOJE meets the regulation governing the award of the degree of Master of Science in Colour Chemistry and Technology of the Ahmadu Bello University, Zaria, and is approved for its contribution to scientific knowledge and literary presentation**.**

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DEDICATION

This dissertation is dedicated to God Almighty.

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ABSTRACT

A series of monoazo reactive dyes with quinazolinone moiety were synthesised starting with the synthesis of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one from 2-amino-4,5-dimethoxybenzoic acid and fusing with different di-amino compounds to give dye intermediates A, B and C; 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (A), 4-amino-4'-(6,7-dimethoxy-4-oxo-2-phenylquinazolin-3(4*H*)-*yl*)-[1,1'-biphenyl]-2,2'-disulfonic acid (B), and 3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (C) which were diazotised at 0-5℃, followed by azo coupling with cyanurated H-acid, gamma acid and J-acid as coupling components. All the reactive dyes and intermediates were characterised by their percentage yield, UV-Visible spectroscopy, FT-IR spectroscopy, and GC-MS techniques. The UV-visible spectrophotometric investigation of the synthesised dyes was carried out in DMF, methanol and water with different dielectric constants to obtain the absorption maxima, molar extinction coefficients and solvatochromic effects of the dyes. The synthesised reactive dyes were applied on cotton fabric 2% shade with a liquor ratio of 50:1 and the percentage exhaustion and fixation of the dyes were found to be reasonably good and acceptable in the range 82 – 91% and 66 – 78%, respectively. The dyeings of all the dyes on cotton fabric gave moderate to good light fastness (3-4), good to very good wash fastness (3-4) and fair to very good fastness to perspiration (2-4). The dyes gave colours ranging from purple, red to pink shades, with a good degree of levelness. This indicates that the dyes were covalently bonded to the fabric.

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CHAPTER ONE

1.0 INTRODUCTION

Dyes that are based on heterocyclic ring systems are known to possess high tinctorial power with outstanding fastness properties (Patel and Patel, 2011a). Some azo dyes have been prepared from amino heterocyclic compounds and azo dyes prepared by using selected quinazoline derivatives as coupling components have also been described (Modi *et al*., 1993). Dyes based on quinazolinone ring system have been reported as being useful on natural and synthetic fibres and 4-oxoquinazoline have been used in the synthesis of azo dyes and reactive dyes (Bhatti and Seshadri, 2004). Improvement in the structure of reactive dye by the selection of chromogens and a variety of reactive groups has led to increased use of reactive dyes (Renfrew and Taylor, 1990; Abeta *et al*., 1984).

Compounds having fused heterocyclic systems like 4(3*H*)-quinazolinone and their derivatives are known to possess good pharmacological activities and are also used as intermediates in the dyestuff industry. The dyes containing heterocyclic moiety like quinazolinone have been found to give a wide range of colour shades (yellow to red to greenish-blue) with very good depth and levelness on fabrics and also showed excellent brightness and good fastness properties like sublimation, washing and light as well as high thermal stability (Patel and Patel, 2011b).

There are many different classes of dyes and azo dyes are certainly one of the most important classes. About half of the dyes used in industry today are azo dyes. Azo dyes have the basic structure, $Ar-N=N-Ar^1$, where Ar and Ar^1 are two aromatic groups. Synthetic azo dyes are extensively used in textile dyeing, paper printing, colour photography, pharmaceutical, food, cosmetics, and other industries (Zollinger, 2003). Among them, the textile industry is a major consumer. Their preparation procedure is by the classic diazotization and coupling reactions, which are very simple and of low cost. In recent years, several heterocyclic and non-heterocyclic compounds are extensively used in azo dye chemistry for textile and non-textile applications (Katritzky and Rees, 1984). These dyes are now marketed to produce a full range of azo dyestuffs without the use of colourants based on hetero-aromatic diazo components. Most of the heterocyclic dyes are derived from the diazo components consisting of six-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring. The dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong colour shades when applied on synthetic and natural fibres (Agho *et al.*, 2017).

Reactive dyes are a coloured compound which has a suitable group capable of forming a covalent bond between the dye ion or molecule and the substrate. Improvement in the structure of reactive chromogens, selection and a large number of reactive groups led to increased use of reactive dyes (Gorensek *et al*., 1995). Reactive dyes with two reactive groups give a higher fixation yield than dyes with one reactive group because if one of the two dye-fibre bonds are hydrolysed, the other one is left for fixation. The presence of the *s*-triazine structure in the dye molecule improves their dyeing ability and possibility for application (Patel *et al.*, 2015).

Dyeing using reactive dyes have recently led to increased demands on the quality of dyeing and the profitability of the dyeing process. Consequently, there is still a demand for novel reactive dyes which have improved properties, especially in respect to the application (Tandama and Bello, 2017). Reactive dyes which have adequate substantivity and at the same time good ease of washing out of the non-fixed portions are required for dyeing. They should furthermore have a good tinctorial yield and high reactivity, and dyeings having high degrees of fixation should be produced (Patel and Patel, 2009).

The possibility of forming a covalent bond between dyes and fibres had long been attractive to dye chemists since attachment by physical adsorption or mechanical obstruction had the disadvantage of either low wash fastness or high cost. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high fastness because covalent bonds are the strongest known binding forces between molecules. s-Triazine based chemicals have been applied variously in the manufacture of polymers, dyes, drugs, explosives, pesticides and commodity chemicals. Theoretical and experimental studies on these chemicals have been widely carried out and the s-triazine ring has been shown to be an important conjugated heterocycle whose electronics properties are expected to show suitable differences from those of benzene due to the alternate replacement of -CH- group by nitrogen atoms (Patel *et al.*, 2003).

Reactive dyes are now a major group of dyes, though a late entry into the family of synthetic dyes, which has attained commercial status. There is no slackening of activity in this field as seen from a lot of patent specifications and several ranges which continue to appear in the market. Hot-brand reactive dyes have been widely considered due to their fixation yield on various fibres. Patel have also synthesised bis-azo reactive dyes by diazotization of 4,4'-diaminobenzanilide with various cyanurated coupling components, assessing their dyeing performance on silk, wool and cotton fibres, which showed fair to very good lightfastness and very good to excellent washing and rubbing fastness (Patel *et al*., 2003).

In general, reactive dyes are the only textile colourants designed to bond covalently with the substrate on application. These dyes are can be applied by exhaust and continuous dyeing method to achieve relatively high wash fastness on different fibres due to the formation of a covalent bond during the fixation process (Patel *et al*., 2014). They are used for the dyeing and printing of cellulose and to a lesser extent polyamide fibre. They are valued for their brilliance and variety of hue, versatility, and high wet fastness profiles.

1.1 Statement of Research Problem

Commercial dyes have always been used for various applications in areas such as textiles, paints, paper and leather. Most of these dyes are being imported into the country, placing a huge demand on the nation’s economy. To reduce the burden of this importation, it has become necessary to explore new areas in a bid to commence the production of these vital chemicals.

Despite the obvious advantages associated with reactive dyes, there is a major problem of loss of potential dye-fibre interaction due to competing hydrolytic pressure which manifests itself in reduced dye fixation level, and general incomplete utilisation of the colour which is both uneconomical and give rise to an associated effluent problem.

It is hoped that these deficiencies will be mitigated using reactive dyes with two chlorine reactive moieties per molecule to improve dye fixation levels, and this will lead to dyeings with an increase in the percentage exhaustion of the dye and the amount of dye that will remain unfixed will be reduced, thereby reducing the environmental pollution of the unabsorbed dyes.

Recently, the use of heterocycles in dye synthesis is gaining wide popularity among researchers. The heterocycles are being contemplated to eventually replace benzenes in dye synthesis. But whether the heterocycles can be employed in the synthesis of acid and reactive dyes remains to be seen.

1.2 Justification of the Study

There is still a demand for novel reactive dyes with improved properties. The demand for reactive dyes is due to their excellent characteristics such as brilliant shades, excellent wet fastness of dyeing and simple dyeing operations which have increasingly been accepted within the industry.

There is a substantial linkage between fixation levels and the number of reactive groups per molecule of a dye. Usually, a dye with more than one reactive moiety per molecule will generally give an improved fixation level. Dichlorotriazinyl reactive dyes contain two replaceable (reactive) chlorine atoms which make them more reactive and are usually applied at lower temperatures than monochlorotriazinyl reactive dyes. With the incorporation of heterocycles, substantivity of the dye is meant to increase, and hence, improve the degree of exhaustion and fixation of the dyes.

Dyes based on the quinazoline ring system have also been reported as being useful on natural and synthetic fibres and 4-oxoquinazolines have been used in the synthesis of azo dyes and reactive dyes. A series of reactive dyes were synthesised to evaluate their stability for dyeing cotton fabrics.

1.3 Aim and Objectives

1.3.1 Aim

To synthesise and characterise some quinazolinone based derivatives of monoazo reactive dyes and to assess their dyeing properties on cotton fabric.

1.3.2 Objectives

The aim will be achieved through the following objectives:

I. Synthesis of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one from 2-amino-4,5-dimethoxybenzoic acid.

II. Synthesis of dye intermediate with quinazolinone ring from 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one.

III. Diazotization and coupling of the dye intermediate with several cyanurated coupling components to produce monoazo reactive dyes containing quinazolinone ring.

IV. Characterisation of the synthesised dyes and intermediate using UV-Visible spectrophotometry, FTIR and GC-MS.

V. Application of the synthesised dyes on cotton fabric and the assessment of fastness to washing, light and perspiration of the dyeings on cotton fabric.

1.4 Scope of This Study

This work is limited to the synthesis of intermediates, their diazotization, and the coupling of these diazo components to cyanurated H-acid, J-acid, and Gamma acid. It also includes the purification, characterisation, and application of the resulting reactive dyes on cotton fabric.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Synthetic Dyes

A dye is a coloured organic compound that absorbs light strongly in the visible region and can firmly attach to the fibre by chemical and physical bonding between a group of the dye and a group on the fibre. To be of commercial importance, a dye should be fast to light, rubbing and washing. Colour and dye have always played an important role in the life of man from time immemorial. Preparation of a colour and dyeing of cloth date back to antiquity (Iqbal, 2008).

The human race has made use of colour since prehistoric times, colours used were derived from natural resources. The dyes used to colour clothing were commonly extracted either from botanical sources, including plants, trees, roots, seeds, nuts, fruit skins, berries, and lichens or from animal sources such as crushed insects and molluscs (Orna, 2013).

At the same time, during this period, research in organic colour chemistry developed new directions, as a result of the opportunities presented by the emergence of a range of applications in new technologies, demanding new types of colourants. These colourants have commonly been termed functional dyes because the applications require the dyes to perform certain functions beyond simply providing colour.

Synthetic textile dyes are exclusively organic compounds, and in relative historical terms, their origin is much more recent. Textile materials were coloured exclusively with natural dyes until the mid-nineteenth century (Bechtold and Mussak, 2009). Since most of natural dyes are rather unstable, the dyeing produced in the very early days tended to be quite fugitive, for example to washing and light. Over the centuries, however, dyeing procedures, generally quite complex, using a selected range of natural dyes were developed that could give reasonable quality dyeing on textile fabrics. Since natural dyes generally have a little direct affinity for textile materials, they were usually applied together with compounds known as mordants, which were effective fixing agents.

Metal salts, for example of aluminium, iron, tin, chromium, or copper, were the most widely used mordants. They function by forming metal complexes of the dyes within the fibre. These complexes were insoluble and hence more resistant to washing processes. These agents not only improve the fastness properties of the dye but also in many instances were essential to developing the intensity and brightness of the colours produced by the natural dyes. Some natural organic materials, such as tannic and tartaric acids, may also be used as mordant (Christie, 2015).

The foundation of the synthetic dye industry is universally attributed to Sir William Henry Perkin on account of his discovery in 1856 of a purple dye that he originally gave the name Aniline Purple, but which was later to become known as Mauveine (Holme, 2006). Perkin was a young enthusiastic British organic chemist who was carrying out research not aimed initially at dyes but rather at developing a synthetic route to quinine, the antimalarial drug. Malaria was a devastating condition at the time and natural quinine, a product often in short supply and expensive, was the most effective treatment. His objective in one set of experiments was to attempt to prepare synthetic quinine from the oxidation of allyltoluidine, but his attempts to this end proved singularly unsuccessful. With hindsight, this is not too surprising given our current knowledge of the complex hetero alicyclic structure of quinine. As an extension of this research, he turned his attention to the reaction of the simplest aromatic amine, aniline, with the oxidizing agent, potassium dichromate. This reaction gave a black product which might have seemed rather unpromising to many chemists, but from which Perkin discovered that a low yield of a purple dye could be extracted with organic solvents. The role of dyes found in nature almost always extends beyond the need to provide colour, familiar examples of which include solar energy harvesting in photosynthesis and the mechanism of visual perception (Christie, 2015).

During the several years following the discovery of Mauveine, research activity in dye chemistry intensified especially in Britain, Germany, and France (Fox, 1987). For the most part, chemists concentrated on aniline as the starting material, adopting a largely empirical approach to its conversion into coloured compounds, and this resulted in the discovery, within a very short period, of several other synthetic textile dyes with commercial potential. The term ‘Aniline Dyes’ was for many decades synonymous with synthetic dyes (Johnston, 2008).

2.2 Colour and Chemical Constitution

The absorption of electromagnetic radiations in the UV and visible regions by a molecule causes electronic excitation and an electron moves to a higher electronic energy level from a lower. A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, $C=C$, $C\equiv C$, $C=O$, $C\equiv N$, $N=N$, NO_2, etc. If a compound absorbs light in the visible region (400–800 nm), only then it appears coloured. Thus, a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region (Gangani, 2006).

Dyes may be classified according to either their chemical structure or method of application. In many cases, a particular chemical class includes dyes of several application classes, and similarly, a particular application class may include dyes of varied chemical types (Benkhaya *et al.*, 2017).

2.3 Azo Dyes

The chemistry involved azo dyes reaction was unclear until 1866, when Kekule proposed correctly that the products have aryl rings linked through a –N=N– unit, called an azo group; hence, the dyes containing this functional groups are termed the azo dyes. The reaction of nitrous acid with Ar-NH_2 (where Ar represents an aryl groups gives Ar-NN^+, an aryldiazonium ion, which readily couples with anilines or phenols to furnish azo compounds (Bello, 1995).

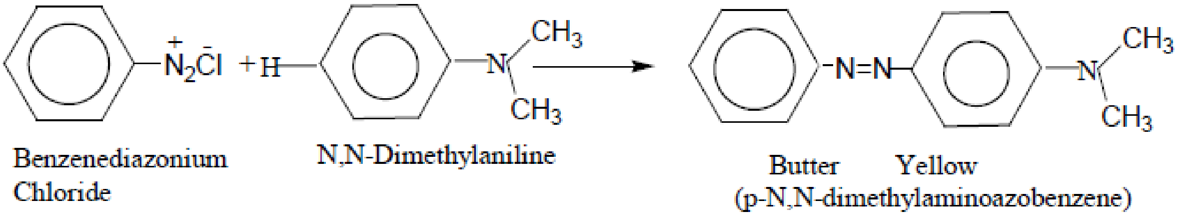
The azo dyes represent the largest and the most important group of dyes. They are characterised by the presence of one or more azo groups (–N=N–), which form bridges between two or more aromatic rings. The study of azo dyes has also been of great value in the development of theoretical organic chemistry (Gordon and Gregory, 1983). Preparation of azo dyes involves the following two steps.

Step 1. Conversion of primary aromatic amines into diazonium compounds by treatment with sodium nitrite in excess hydrochloric acid (diazotisation).

$$ArNH_2 + NaNO_2 + 2HCl \longrightarrow ArN_2^+Cl^- + H_2O$$

A primary aromatic amine A diazonium compound

Step 2. Coupling of diazonium compounds with phenols, naphthols, or other aromatic amines. Coupling with phenols and naphthols is carried out in basic solution; coupling with amines is carried in acid solution. Scheme 2.1 is a typical reaction between a diazonium component and a coupling component.



Scheme 2.1: Coupling reaction of an azo dyes

The reaction shown in scheme 2.1 are carried out at low temperatures (0 – 5℃) because diazonium compounds are usually unstable. In the resulting dyes, an aromatic system joined to the azo group is the chromophore, and the hydroxyl group or amino group is an auxochrome. There may be more than one azo group present in the dye molecule and thus one speaks of mono azo, disazo, trisazo. tetrakisazo and polyazo dyes according to whether there are one, two, three, four or more azo group present in the dye molecule (Chatwal, 2009).

Diazotisation of both amino group of m-phenylenediamine followed by coupling with more of the diamine gives Bismark brown, a major component I the first successful disazo dyes i.e. a dye with two azo groups. In 1884, a conjugated disazo dye, congo red, made by coupling 4-sulfo-1-napnthylamine with bisdiazotised benzidine, was found to dye cotton by simple immersion of the fabric in a hot aqueous bath of the dye. Congo red was the first dye to be known as a direct dye; today it is used as a pH indicator (Shore, 2002).

The -OH group and $-NH_2$ groups direct the coupling to the ortho and para sites, and the directive effects are pH-dependent. In alkaline media, coupling is directed by the -OH group, whereas $-NH_2$ group direct coupling in weakly acidic medium.

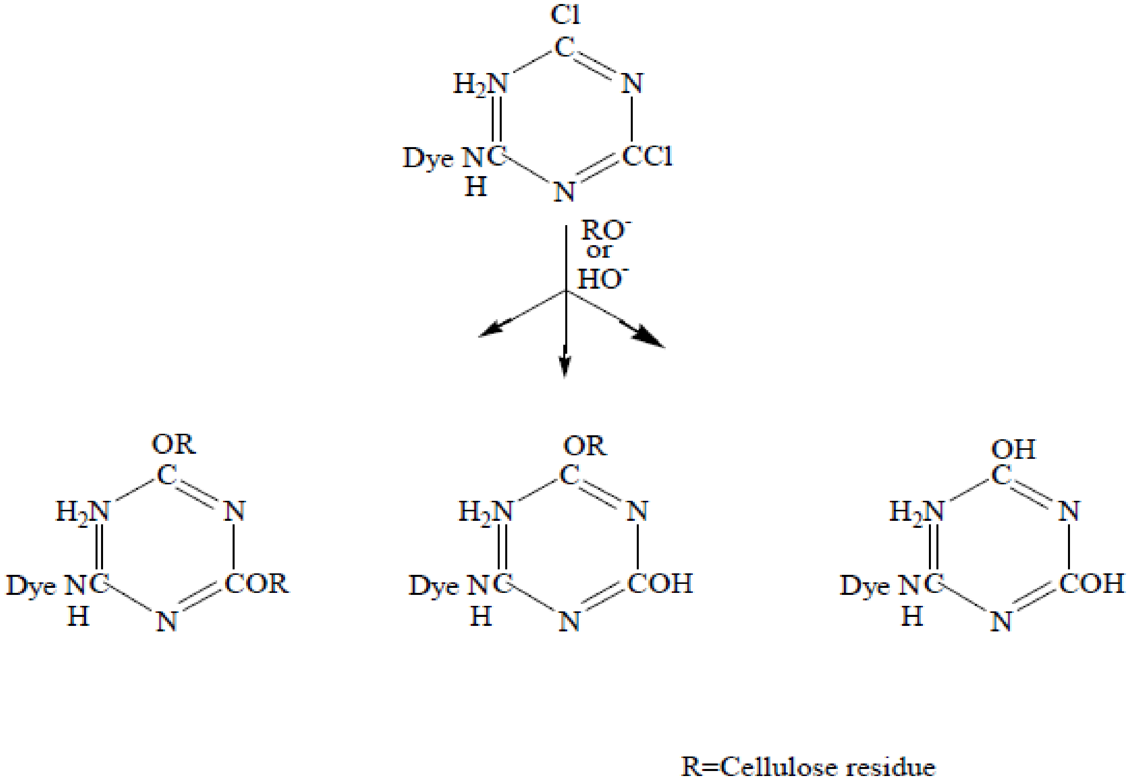
Azo dyes became the most important commercial colorants because of their wide colour range, good fastness properties, and tinctorial strength, which is twice that of the anthraquinones, the most second important group of dyes. Azo dyes are easily prepared from many readily available, inexpensive compounds and meet the demands of a wide range of end uses (David and Geoffrey, 1994).

2.4 Reactive dyes

A reactive dye, according to a useful definition by Rys and Zollinger, is a coloured compound that has a suitable group enable of forming a covalent bond between a carbon atom of a hydroxyl, an amine or a mercapto group respectively of the substrate. They point out that this definition excludes mordant dyes and 1:1 chromium azo dye complex, which are used in dyeing protein fibres, may form covalent bonds between the metal ion and nucleophilic groups of the fibre (Iqbal, 2008).

Reactive dyes are a highly successful class of modern synthetic dyes due to their wide shade gamut, their flexibility in application and the excellent fastness properties they offer when dyes on cotton fabric, wool, silk and regenerated cellulosic fibres. Reactive dyes may be loosely defined as chromophores which contains pendant groups capable of forming covalent bonds with nucleophilic sites in fibrous substrates. provided these covalent bonds are stable to conditions encountered in laundering then the wash fastness properties of the colouration will be outstanding (Mohammed *et al*., 2014)

The idea that the establishment of a covalent bond between dye and substrate would result in improved wash fastness compared with that of ordinary dye-substrate systems where weaker forces were operative is an old one. Attempts were made by various dye firms from about 1906 onwards to achieve this aim but it was not until 1956 that the first successful reactive dyes, the Procions, were introduced by ICI for the dyeing and printing of cellulose fibres, following the work of Rattee and Stephen from 1954 onwards (Panda, 2016). The invention consisted in the synthesis of dyes containing a reactive group, the 2,4,6–dichlorotriazinylamino group which has two labile chlorine atoms activated by the electron-withdrawing action of the three *N* atoms, and the devising of dyebath conditions, which, while bringing about the formation of a covalent bond, were mild enough to avoid serious damage to the fibre. The dyeing was carried out at ordinary temperatures, fixation being brought about by the addition of sodium bicarbonate, thus raising the pH (Panda, 2016). The reaction with cellulose may be represented as nucleophilic substitution by the attaching species RO^{-}or $OH^{-}$where R = cellulose moiety as shown.

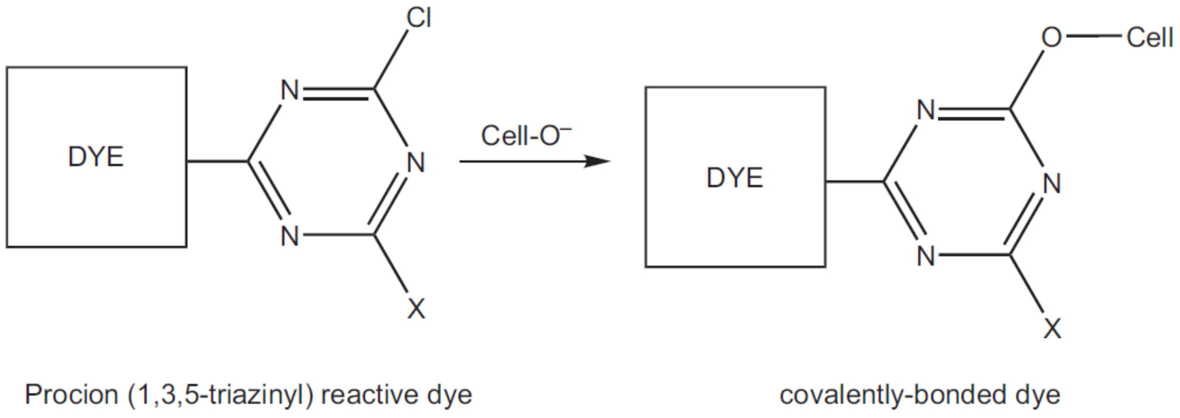


Scheme 2.2: Reactive dyes on cellulose

Attach by OH^{-}, derived from the water of the dyebath, occurs simultaneously, but that of cellulose onion predominates since the dye is absorbed by the cellulose fibres and the dye-substrate reaction is therefore facilitated. It is necessary to remove hydrolysed unfixed dye through soaping and washing otherwise inferior fastness to wet treatment results (Arslan-Alaton, 2003).

As time progressed, the strategies adopted in dye and pigment research evolved from the early approaches based largely on empiricism and involving the synthesis and evaluation of large numbers of products, to a more structured approach involving more fundamental studies of chemical principles. For example, attention turned to the reaction mechanisms involved in the synthesis of dyes and pigments and to the interactions between dye molecules and textile fibres. Probably the most notable advance in textile dyeing in the twentieth century, which arguably emerged from such fundamental investigations, is the process of reactive dyeing. Reactive dyes contain functional groups that, after application of the dyes to certain fibres, can be linked covalently to the polymer molecules that make up the fibres, and this gives rise to dyeings with superior wash fastness compared with the more traditional dyeing processes. Dyes that contain the 1,3,5-triazinyl group, discovered by ICI in 1954, were the first successful group of fibre-reactive dyes. The introduction of these products to the market as Procion dyes by ICI in 1956, initially for application to cellulosic fibres such as cotton, proved to be a rapid commercial success (Renfrew and Taylor, 1990).

The chemistry involved when Procion dyes react with the hydroxyl groups present on cellulosic fibres under alkaline conditions involves the aromatic nucleophilic substitution process outlined in scheme 2.3, in which the cellulose anion is the effective nucleophile.



Scheme 2.3: Reaction of procion dyes with cellulosic fibres

The chlorotriazinyl reactive dyes are by far the most important class and have proved a serious rival to the vat dyes as regards wash-fastness and in other ways. The main chromogens employed are azo, metal-azo, anthraquinone and phthalocyanine systems. The question of cotton substantivity is an important one. It should be high enough to ensure a high ‘fixation yield but at the same time, a substantivity of the unfixed, hydrolysed dye should be low enough to permit easy removal by soaping and rinsing to ensure maximum fastness to wet treatments in the finished dyeing (Deng *et al.*, 2000).

Reactive dyes are the youngest and most important dye class for cellulosic materials. The reactive dyes offer a wide range of dyes with varying shades, fastness, and cost with high brilliancy, easy applicability and reproducibility. However good pretreatment of the material is a prerequisite. The colour yield and brilliancy of shades are enhanced significantly by mercerisation. Unlike vat dyes, most of the reactive dyes are not fast to chlorine bleaching. Reactive dyes are water-soluble anionic dye purposefully designed to have low substantivity to facilitate the removal of hydrolysed dye by simple soaping and rinsing (Mahapatra, 2016).

2.5 Quinazolinones

According to Dianat *et al.*, (2016), quinazolinones are live nitrogen-containing heterocyclic compounds. In 1869, Griess prepared the first quinazoline derivative, 2-cyano-3, 4-dihydro-4–oxoquinazolinone, by the reaction of cyanogens with anthranilic acid. Griess externally recognised the bicyclic nature of the product, which he called bicyano–amido benzene and used it until 1885 when the structure was known with some certainty. Weddige carried out systematic quinazoline synthesis following the observation that the formyl and acetyl derivatives of anthranilamide lost water on heating. He correctly interpreted this as a cyclisation reaction and was the first to realise the possibility of tautomerism in the oxoquinazolines. The preparation of parent quinazoline comes many years later in 1895, when Bischler and Lang obtained it by decarboxylation of the 2-carboxy derivatives. A more satisfactory synthesis of quinazoline was subsequently devised by Gabriel who studied its properties and those of its derivatives in greater detail (Rajput and Mishra, 2012).

2.6.1 Numbering system of quinazolinone

The nomenclature of the quinazolinone ring system is as follows.

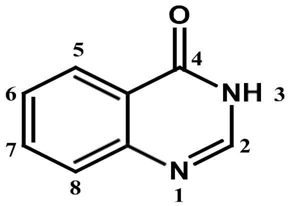
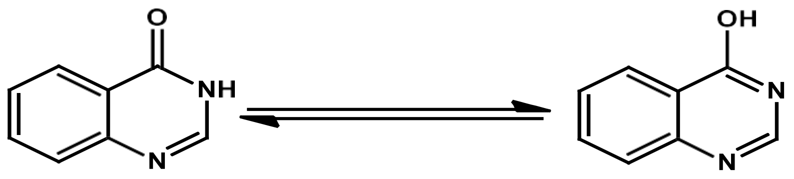


Figure 2.1: Quinazolinone ring

Quinazolinone is also known as phenmiazine, benzylene-amidine, 1,3- diazanaphthalene or benzo-1,3-diazine or 5,6-benzo-pyrimidine. The term phenmiazine was used by Wildman. The numbering shown in the structure was suggested by Paal and Busch and is one of remarkable use.

The quinazoline having a hydroxyl group in 2- or 4- position forms a distinct class and are tautomeric with the corresponding keto dihydroxy quinazoline, while 4–hydroxyquinazoline exists as an equilibrium mixture of (b) in which form (a) is the most stable as shown in scheme 2.4.



(a) (b)

Scheme 2.4: Tautomeric effect of quinazolinone ring

The 4–hydroxyquinazolinone tautomeric with 4-keto-3, 4-dihydro-quinazoline, is commonly named as 4(3*H*)-quinazoline is also the familiar name used for the system. Today, the name 4-quinazoline has been universally accepted for 4-keto-3,4–dihydroquinazoline (Tiwary *et al*., 2015).

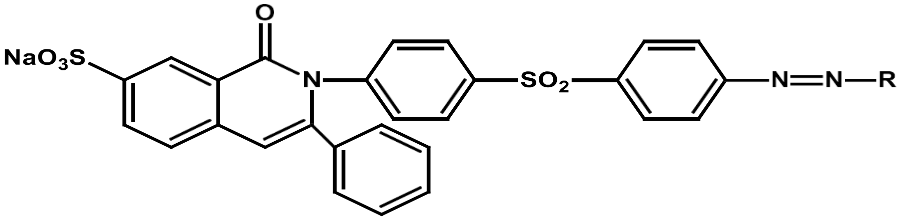
2.6.2 Synthesis of quinazolinone

The majority of the synthetic route of 4-quinazolinone essentially proceeds from anthranilic acid or its derivatives. Several methods may be classified into different categories according to the type of components undergoing condensation.

2.6.3 Chromophoric potential of the 4(3*H*)-quinazolinone

The first commercial synthetic dye, Mauveine, discovered by Perkin in 1856 was also heterocyclic. Since that time, the contribution of heterocyclic derivatives to colour chemistry has been considerable. The quinazoline nucleus is the key component of some coloured products. The following literature shows the important role of the 4(3*H*)-quinazolinone ring as a chromophore.

Patel and Patel (2010) synthesised hot brand heterocyclic mono azo reactive dyes by coupling of diazotized 2-phenyl-3{4'- [(4"-aminophenyl) sulphonyl] phenyl}-quinazoline-4(3*H*)-one-6-sulphonic acid with various 2-chloro-4-nitro anilino cyanurated coupling components. Their dyeing performance on silk, wool, and cotton has been assessed.



Where **R** = various 2-chloro-4-nitro anilino cyanurated coupling components

Figure 2.6: General structure of dye with quinazolinone ring

Patel and Patel (2011b) have also synthesised some novel quinazolinone based monoazo reactive dyes by coupling of diazotized 3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2-phenyl quinazolin-4(3*H*)-one with various p-chloro anilino cyanurated coupling components. These dyes gave good dyeing performance and fastness properties.

Patel *et. al*., (2015) have also synthesised monoazo reactive dyes based on 4-oxo-2-phenyl- 4*H*-3,1-benzoxazine and their dyeing performance on various fibres. Their dyeing performance on silk, wool and cotton fibres has been assessed. These dyes were found to give a variety of colour shades with very good depth and levelness on the fibres. Exhaustion and fixation of these dyes are very good in order. The wash fastness and rubbing fastness of synthesis dyes are also good to excellent indicate the good penetration and affinity of these dyes to the fabric.

2.6. Chemistry of Cotton Fibre

Cotton, the seed hair of plants of the genus *Gossypium*, is the purest form of cellulose readily available in nature. It has many desirable fibre properties making it an important fibre for textile applications. Cotton is the most important of the raw materials used in textile industry. The cotton fibre is a single biological cell with a multilayer structure (David and Geoffrey, 1994). The layers in the cell structure are from the outside of the fibre to the inside, cuticle, primary wall, secondary wall and lumen. These layers are different structurally and chemically. The primary and secondary walls have different degrees of crystallinity, as well as different molecular chain orientations (Wolfe and Audra, 2008). The cuticle composed of wax, proteins and pectins, is 2.5% of the fibre weight and is amorphous. The primary wall is 2.5% of the fibre weight, has a crystallinity index of 30% and is composed of cellulose. The secondary wall is 91.5% of the fibre weight has a crystallinity index of 70% and is composed of cellulose. The lumen is composed of protoplasmic residues (Christie, 1999).

Cotton fibres have a fibrillar structure. The whole cotton fibre contains 88 to 96.5% of cellulose, the rest are non-cellulosic polysaccharides constituting up to 10% of the total fibre weight. The primary wall in mature fibres is only 0.5-1µm thick and contains about 50% of cellulose. Non-cellulosic constituents consist of pectins, fats and waxes, protein and natural colourants. The secondary wall, containing about 92-95% cellulose, is built of concentric layers with altermatic shaped twists. The layers consist of densely packed elementary fibrils, organised into micro fibrils and macro fibrils. They are held together by strong hydrogen bonding bonds. The lumen forms the centre of the fibres. Cotton is composed almost entirely of the polysaccharide cellulose. Cotton cellulose consist of crystalline fibrils varying in complexity and length and connected by less organised amorphous regions with an average ratio of about two-thirds crystalline and one-third non-crystalline material, depending on the method of determination.

The chemical composition of cellulose is simple, consisting of anhydro-glucose units joined by β-1,4-glucosidic bonds to form linear polymeric chains. The chain length, or degree of polymerisation (DP), of a cotton cellulose molecule represents the number of anhydro-glucose units connected together to form the chain molecule. Degree of polymerisation of cotton may be as high a 14000, but it can be easily reduced to 1000-2000 by different purification treatments with alkali (Fierz-David, 1949). The crystalline regions probably have a degree of polymerisation of 200 to 300. Correspondingly, the molecular weight of cotton usually lies in the range of 50,000-1,500,000 depending on the source of the cellulose. The individual chains adhere to each other along their length n=by hydrogen bonding and van der Waals forces. The physical properties of the cotton fibre as a textile material, as well as its chemical behaviour and reactivity, are determined by arrangements of the cellulose molecules with respect to each other and to the fibre axis (Christie, 1999).

2.7. Dyeing Methods

Dyeing of reactive dyes, as in the case of many other classes of dyes, can be carried out by batch dyeing process and continuous dyeing process.

2.7.1 Dyeing with M-brand dyes

These are cyanuric chloride-based reactive dyes, highly reactive and generally employed under exhaust method at 30–40°C and pad-batch method. These dyes possess brilliancy in shades with high colour fastness to washing and light. These fibre-reactive dyes are easy to dyeing with high consistency of shades (Ezeribe *et al*., 2014).

Following are the pad-batch method:

(a) Pad-batch method (soda ash with M brand dyes or soda ash + bicarbonate with M brand dyes etc.).

(b) Pad-dry-thermofix method (bicarbonate + M dyes).

(c) Pad-dry-wash-method (bicarbonate + M dyes).

(d) Pad-steam method (bicarbonate + M dyes).

2.7.2 Dyeing with H-brand dyes

These H-brand reactive dyes contain brilliant shades of high fastness on cellulosic fabric. These dyes are less reactive so require more severe conditions of fixation. The extent of dye-fibre reaction and the ultimate discharge of unfixed dye vary widely with the type of reactive group and the dyeing technology used (Khatri *et al.*, 2015).

These dyes are suitable for:

(a) Exhaust method.

(b) Pad-batch method.

(c) Semi-continuous methods.

(d) Continuous methods.

2.7.3. Dyeing with ME reactive dyes

These reactive dyes are most suitable at low temperatures (60–65℃) for high exhaust purposes and the pad-batch method. These are structurally different dyes from conventional dyes containing higher grade wet fastness, i.e., perspiration fastness, light fastness, washing fastness, dry and wet crocking fastness, chlorine and peroxide washing fastness, etc. The high degree of exhaustion and fixation rate is another merit point to accelerate excellent levelling properties. They have better alkali stability and reproducibility behaviour (Taylor, 2000).

2.7.4. Dyeing with HE reactive dyes

These dyes are identified for their extraordinary wet colour fastness along with cost-saving compared to conventional reactive dyes. These dyes are suitable for cellulose-blended fabric too. It facilitates quick rinsing and soaping to save time factor. They yield batch-to-batch consistency. Dyeing can be controlled with salt and temperature before alkali. These dyes are less sensitive to Glauber salt, time and temperature besides their level dyeing results. These are specially made for exhaust dyeing style at 80 to 90°C (Mahapatra, 2016).

2.7.5. Dyeing with Vinyl Sulfone reactive dyes

These dyes chemically react with the hydroxyl group of cellulose and form a firm covalent linkage in presence of alkali. These dyes are employed by the exhaust and pad batch process. Such dyes possess a poor affinity for cellulosic fibre in absence of salt and alkali. For this reason, these dyes are most suitable for the pad-batch method due to their high solubility even in presence of alkali. Similarly, substantivity can be increased by the addition of Glauber’s salt or common salt and alkali for making the dyestuff well suitable for all types of conventional dyeing machines.

Reactive dyeing is now the most important method for the colouration of cellulosic fibres. Reactive dyes can also be applied on wool and nylon; in the latter case, they are applied under weakly acidic conditions. Reactive dyes have a low utilisation degree compared to other types of dyestuff, since the functional group also bonds to water, creating hydrolysis. Many other reactive groups have been introduced into the reactive dye (Chatwal, 2009).

2.7.6 Dyeing mechanism of reactive dye

The dyeing mechanism of material with reactive dye takes place in three stages:

1. Exhaustion of dye in presence of electrolyte or dye absorption.

2. Fixation under the influence of alkali.

3. Wash off the unfixed dye from the material surface.

2.7.6.1 *Dye absorption*

When fibre is immersed in dye liquor, an electrolyte is added to assist the exhaustion of dye. Here NaCl is used as the electrolyte. This electrolyte neutralises absorption. So, when the textile material is introduced to dye liquor, the dye is exhausted onto the fibre.

2.7.6.2 *Fixation*

Fixation of dye means the reaction of a reactive group of dye with terminal –OH or $–NH_2$ group of fibre and thus forming a strong covalent bond with the fibre and thus forming a strong covalent bond with the fibre. Improvements in dye fixation efficiency result in significant reductions in the amount of unfixed dye in dyeing effluent. This is an important phase, which is controlled by maintaining proper pH by adding alkali. The alkali used for this creates proper pH in the dye bath and do as the dye-fixing agent (Ezeribe *et al.*, 2014).

2.7.6.3 Wash-off

As the dyeing is completed, a good wash must be applied to the material to remove extra and unfixed dyes from the material surface. This is necessary for level dyeing and good wash-fastness. It is done by a series of hot wash, cold wash and soap solution wash. At the same time, the commercial mixtures can have improved dyeing properties and reduced sensitivity to dyeing variables such as temperature and pH. In turn, it can improve dye fixation efficiency. (Khatri *et al.*, 2015).

2.7.7. Application method

These are three application procedures available:

(1) Discontinuous method.

(2) Continuous method.

(3) Semi-continuous method.

Reactive dyes are widely used for dyeing cellulose fibres and fabrics because of their economical dyeing's and simple dyeing operating. The newer types of reactive dyes offer quite reasonable and accepted levels of wet and other fastness properties coupled with cost advantages. These dyes have made vat dyes practically non-existent. Reactive dyes generally offer a wide range of bright colours, excellent performance, strong applicability, appealing hue and good performance on cellulosic fibres. Reactive dyes have received excellent market acceptability, especially for cellulosic fibre/fabrics. The global share of reactive dyes production is estimated to be 20–30% of the total dyestuff production. They are ranked first for application on cellulosic. But ordinary reactive dyes have a poor utilisation rate (poor exhaustion) mostly in the range of 60–65%. The rate of re-dyeing is high which increases the cost and total delivery time. The existing processes are not only time-consuming but associated with high-energy consumption and a huge amount of wastewater that is a lot more difficult to treat (Mahapatra, 2016).

2.7.8 Properties of reactive dyes

1. Reactive dyes are anionic dyes used for dyeing cellulose, protein and polyamide fibres.
2. Reactive dyes are found in powder, liquid and print paste form.
3. During dyeing, the reactive group of this dye forms a covalent bond with fibre polymer and becomes an integral part of the fibre.
4. Reactive dyes are soluble in water.
5. They have very good light fastness with a rating of about six (6). The dyes have a very stable electron arrangement and can protect against the degrading effect of ultra-violet rays.
6. Textile materials dyed with reactive dyes have a very good wash fastness rating. Reactive dye gives brighter shades and has moderate rubbing fastness.
7. The dyeing method of reactive dyes is easy. It requires less time and low temperature for dyeing.
8. Reactive dyes are comparatively cheap.
9. Reactive dyes have good perspiration fastness with a rating of 4–5.
10. Reactive dyes have good perspiration fastness.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials and Reagents

Hydrochloric acid

Sodium hydroxide

Sodium nitrite

Acetic acid

Benzoyl chloride

2-Amino-4,5-dimethoxybenzoic acid (Ak Scientific 98%)

4,4'-diamino-[1,1'-biphenyl]-2,2'-disulfonic acid

4,4'-sulfonyldianiline (Sigma Aldrich, 97%)

Benzene-1,4-diamine (Sigma Aldrich, 98%)

Pyridine

Sodium bicarbonate

Sodium carbonate

Sodium chloride

Chloroform

Ethanol

Sulphamic acid

Dimethylformamide (DMF)

Distilled water

H acid (Sigma Aldrich, 90%)

J acid (Sigma Aldrich, 90%)

Gamma acid (Sigma Aldrich, 90%)

Cyanuric chloride (Sigma Aldrich, 99%)

Acetone

Starch iodide paper

Cotton fabric

3.2 Equipment

Equipment that were used in this research include:

CARY 300 UV – Visible Spectrophotometer model Agilent technology,

FTIR – 8400S Fourier transform infra-red spectrophotometer,

GC-MS – Agilent 19091S-433HP-5M,

Melting point apparatus,

Hot plate/Magnetic stirrer,

Electronic weighing balance,

Electric oven.

3.3 Methods

3.3.1 Synthesis of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one

2-amino-4,5-dimethoxybenzoic acid (39.41g, 0.2mol) was dissolved in pyridine (100ml) and stirred. Thereafter, benzoyl chloride (23.22ml, 0.2mol) was added dropwise with constant stirring to the solution, maintaining the temperature near 0-5°C for one hour. The reaction mixture was stirred for another one hour at room temperature (32℃) until a solid product was obtained. At the end of the reaction, the solid mass obtained was filtered, washed with saturated sodium bicarbonate solution to remove unreacted acid, and finally washed with water, dried and recrystallised from pure ethanol. The percentage yield was calculated and the melting point determined.

3.3.2 Synthesis of dye intermediate (A): 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one

Benzene-1,4-diamine (2.16g, 0.02mol) and 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (5.66g, 0.02mol) were dissolved in pyridine (40ml) and heated under reflux for 9h under anhydrous reaction conditions and thereafter was allowed to cool at room temperature (32℃). The reaction mixture was then treated with ice-cooled dilute hydrochloric acid (10%) and stirred. A solid product precipitated out and was filtered off and washed with water to remove any adhered pyridine. It was dried under a vacuum and recrystallised from ethanol. The percentage yield was calculated and the melting point determined.

3.3.3 Synthesis of dye intermediate (B): 4-amino-4'-(6,7-dimethoxy-4-oxo-2-phenylquinazolin-3(4*H*)-*yl*)-[1,1'-biphenyl]-2,2'-disulfonic acid

4,4'-diamino-[1,1'-biphenyl]-2,2'-disulfonic acid (3.44g, 0.01mol) and 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2.83g, 0.01mol) was dissolved in pyridine (40ml) and heated under reflux for 9h under anhydrous reaction conditions thereafter allowed to cool at room temperature (32℃). The reaction mixture was treated with ice-cooled dilute hydrochloric acid (10%) and stirred. A solid product precipitated out, which was filtered off and washed with water to remove any adhered pyridine. It was dried under a vacuum and recrystallised from ethanol. The percentage yield was calculated and the melting point determined.

3.3.4 Synthesis of dye intermediate (C): 3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one

4,4'-sulfonyldianiline (4.69g, 0.02mol) and 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (5.66g, 0.02mol) were dissolved in pyridine (40ml) and heated under reflux for 9h under anhydrous reaction conditions and thereafter was allowed to cool at room temperature (32°C). The reaction mixture was then treated with ice-cooled dilute hydrochloric acid (10%) and stirred. A solid product precipitated out and was filtered off and washed with water to remove any adhered pyridine. It was dried under a vacuum and recrystallised from ethanol. The percentage yield was calculated, and the melting point determined.

3.3.5 Diazotization of intermediate A

3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (Intermediate A) (0.75g, 0.002mol) was dissolved in water (60ml), and hydrochloric acid (10ml, 0.008 mol) was added dropwise to the suspension formed and stirred, thereafter it was gradually heated up to form a clear solution and then the solution was cooled to 0-5°C in an ice bath. A solution of $NaNO_2$ (0.6g) in water (4ml) previously cooled to 0°C, was added for 5min with stirring. The stirring was also continued for an hour, maintaining the same temperature, for diazotization to occur. A clear diazo solution of A at 0– 5°C was obtained and used for the subsequent coupling reaction.

3.3.6 Diazotization of intermediate B

4-amino-4'-(6,7-dimethoxy-4-oxo-2-phenylquinazolin-3(4*H*)-*yl*)-[1,1'-biphenyl]-2,2'-disulfonic acid (3.05g, 0.005mol) was dissolved in water (60ml), and hydrochloric acid (20ml, 0.015mol) was added dropwise to the suspension formed and stirred thereafter it was gradually heated up to till a clear solution was formed and then the solution was cooled to 0–5°C in an ice bath. A solution of $NaNO_2$ (0.6g) in water (4ml) previously cooled to 0°C, was added for 5min with stirring. The stirring was also continued for an hour, maintaining the same temperature, for diazotization to occur. A clear diazo solution B at 0-5°C was obtained and used for the subsequent coupling reaction.

3.3.7 Diazotization of intermediate C

3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (Intermediate C) (1.026g, 0.002mol) was dissolved in water (60ml), and hydrochloric acid (10ml, 0.008mol) was added dropwise to the suspension formed and stirred, thereafter it was gradually heated up to form a clear solution and then the solution was cooled to 0–5°C in an ice bath. A solution of $NaNO_2$ (0.6g) in water (4ml) previously cooled to 0°C, was added for 5min with stirring. The stirring was also continued for an hour, maintaining the same temperature, for diazotization to occur. A clear diazo solution of C at 0– 5°C was obtained and used for the subsequent coupling reaction.

3.3.8 Preparation of coupling components

H-acid (3.19g, 0.01mol) was dissolved in water (15ml) at pH 7.5, using 20% (w/v) Na_2CO_3. A solution of cyanuric chloride (1.85g, 0.01mol) was stirred in acetone (25ml) at a temperature of 0-5°C and was added dropwise to the stirred H-acid solution at 0-5°C. After 10min, the solution was adjusted to a neutral pH by adding 20% (w/v) Na_2CO_3, and the reaction was continued for about 4 hours at 0-5°C to obtain a clear solution. The cyanurated H-acid solution thus obtained was used for coupling.

The same procedure and conditions were used for other coupling components, J-acid and Gamma acid.

3.3.9 Synthesis of dye 1A

To an ice-cold and stirred solution of cyanurated H-acid (4.67g, 0.01mol), a freshly prepared diazo solution (Intermediate A) (1.87g, 0.005mol) was added dropwise for 15min. The pH was maintained at 7.5–8.5 by simultaneous addition of sodium carbonate solution (10% w/v), and stirring was continued for 4h, maintaining the temperature below 5°C.

The reaction mixture was heated to 60°C and sodium chloride was added until the dye was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v) and dried.

Using the above procedure, other reactive dyes 2A and 3A were synthesised using various cyanurated coupling components i.e. J-acid and Gamma acid respectively (Patel & Patel, 2011a).

3.3.10 Synthesis of dye 1B

To an ice-cold and stirred solution of cyanurated H-acid (4.67g, 0.01mol), a freshly prepared diazo solution (Intermediate B) (3.05g, 0.005mol) was added dropwise for 15min. The pH was maintained at 7.5–8.5 by simultaneous addition of sodium carbonate solution (10% w/v), and stirring was continued for 4h, maintaining the temperature below 5°C.

The reaction mixture was heated up to 60°C and sodium chloride was added until the dye was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v) and dried.

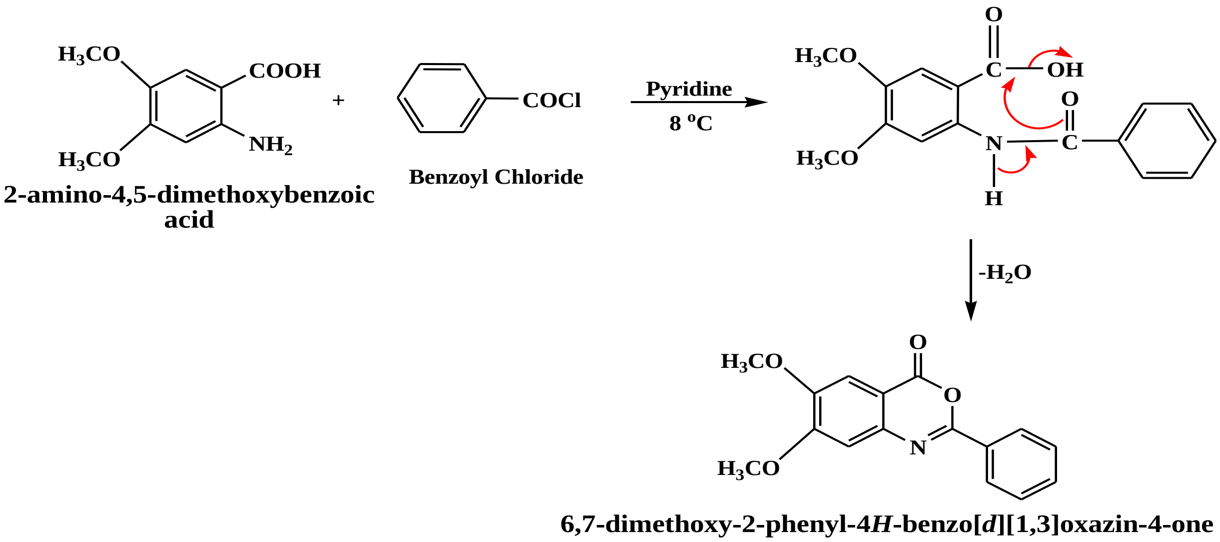
Using the above procedure, other reactive dyes 2B and 3B were synthesised using various cyanurated coupling components i.e. J-acid and Gamma acid respectively.

3.3.11 Synthesis of dye 1C

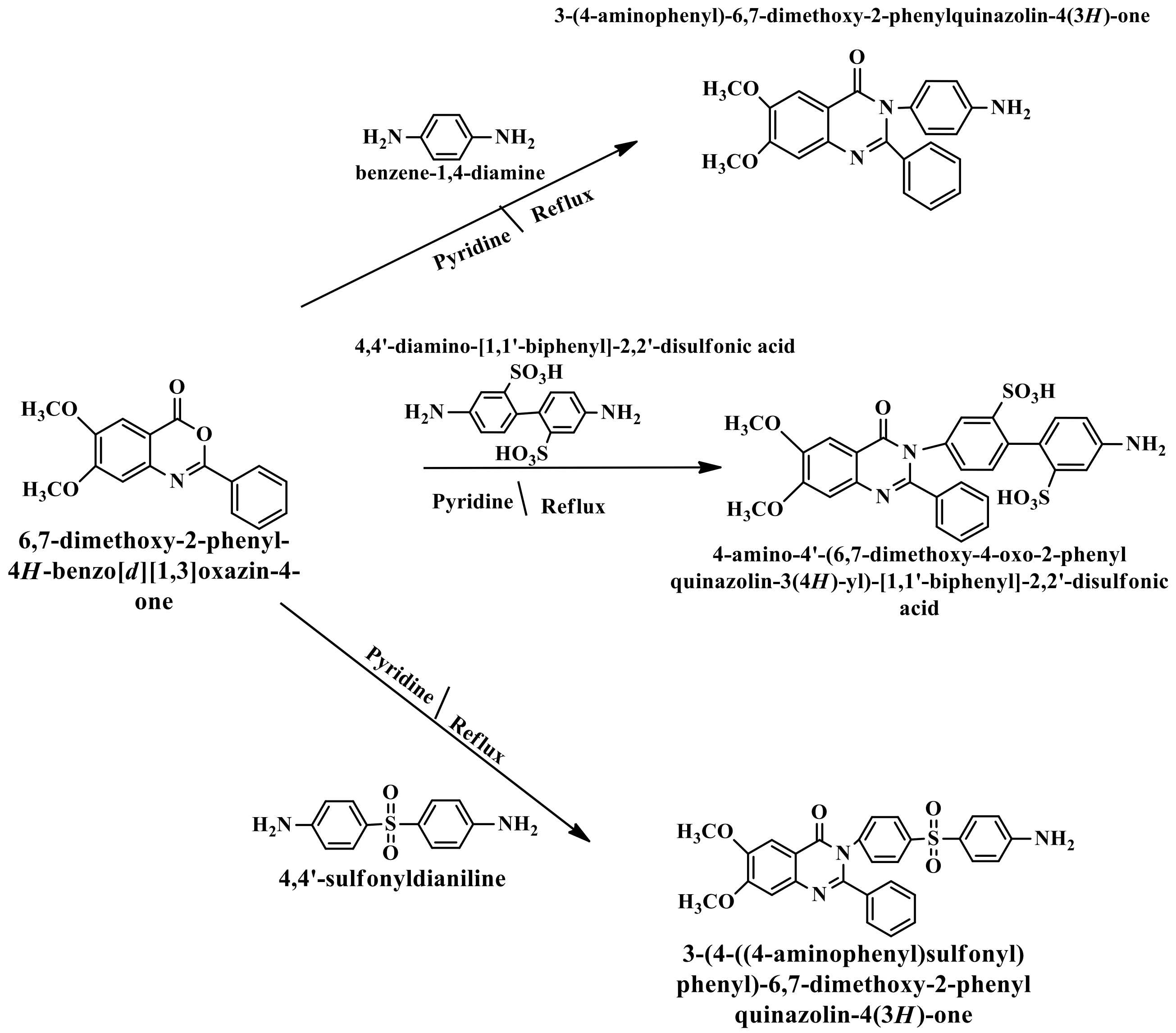
To an ice-cold and stirred solution of cyanurated H-acid (4.67g, 0.01mol), a freshly prepared diazo solution (Intermediate C) (2.57g, 0.005mol) was added dropwise for 15min. The pH was maintained at 7.5–8.5 by simultaneous addition of sodium carbonate solution (10% w/v), and stirring was continued for 4h, maintaining the temperature below 5°C.

The reaction mixture was heated to 60°C and sodium chloride was added until the dye was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v) and dried.

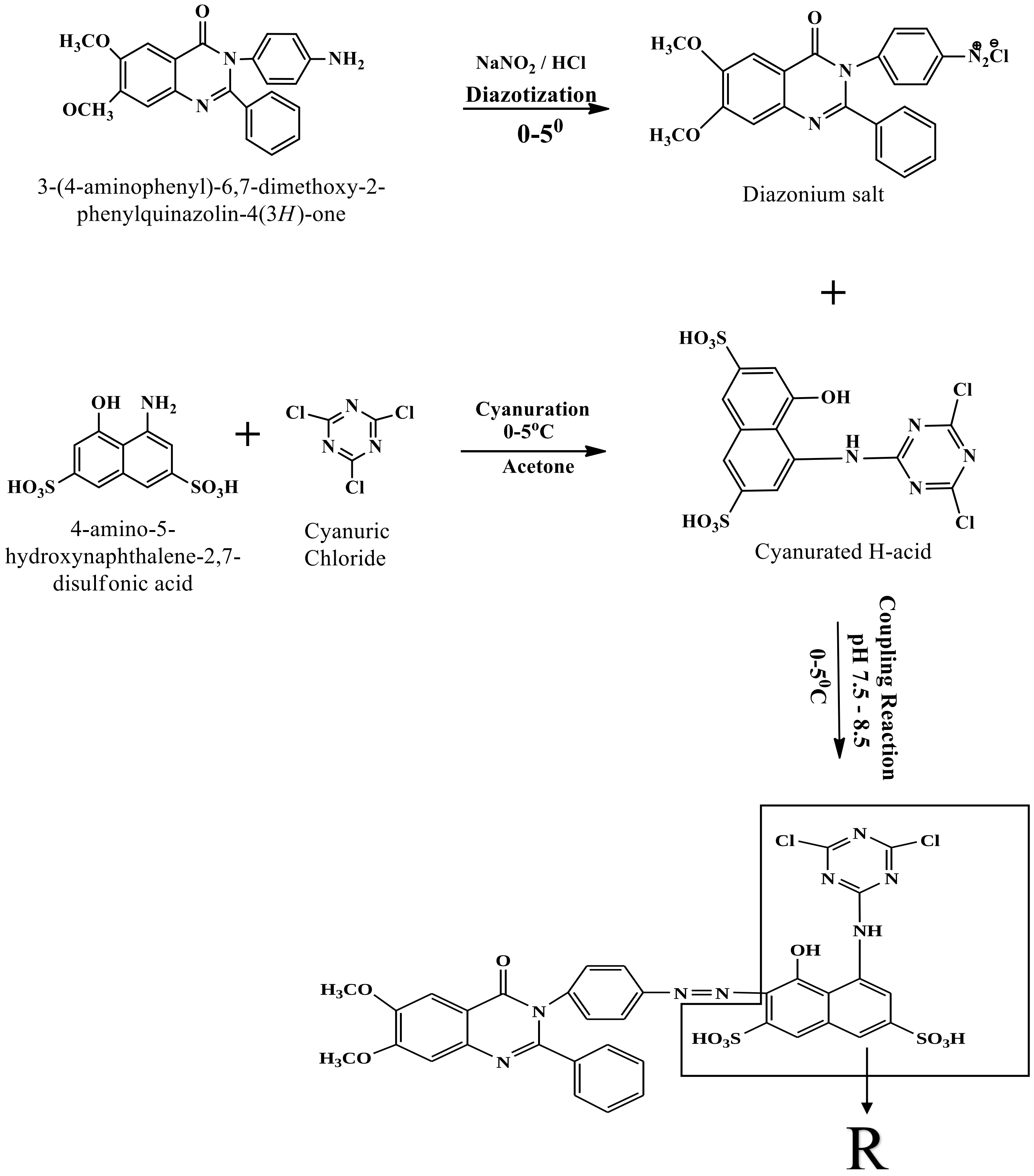
By the above procedure, other reactive dyes 2C and 3C were synthesised using various cyanurated coupling components i.e. J-acid and Gamma acid respectively.



Scheme 3.1: Preparation of quinazolinone ring

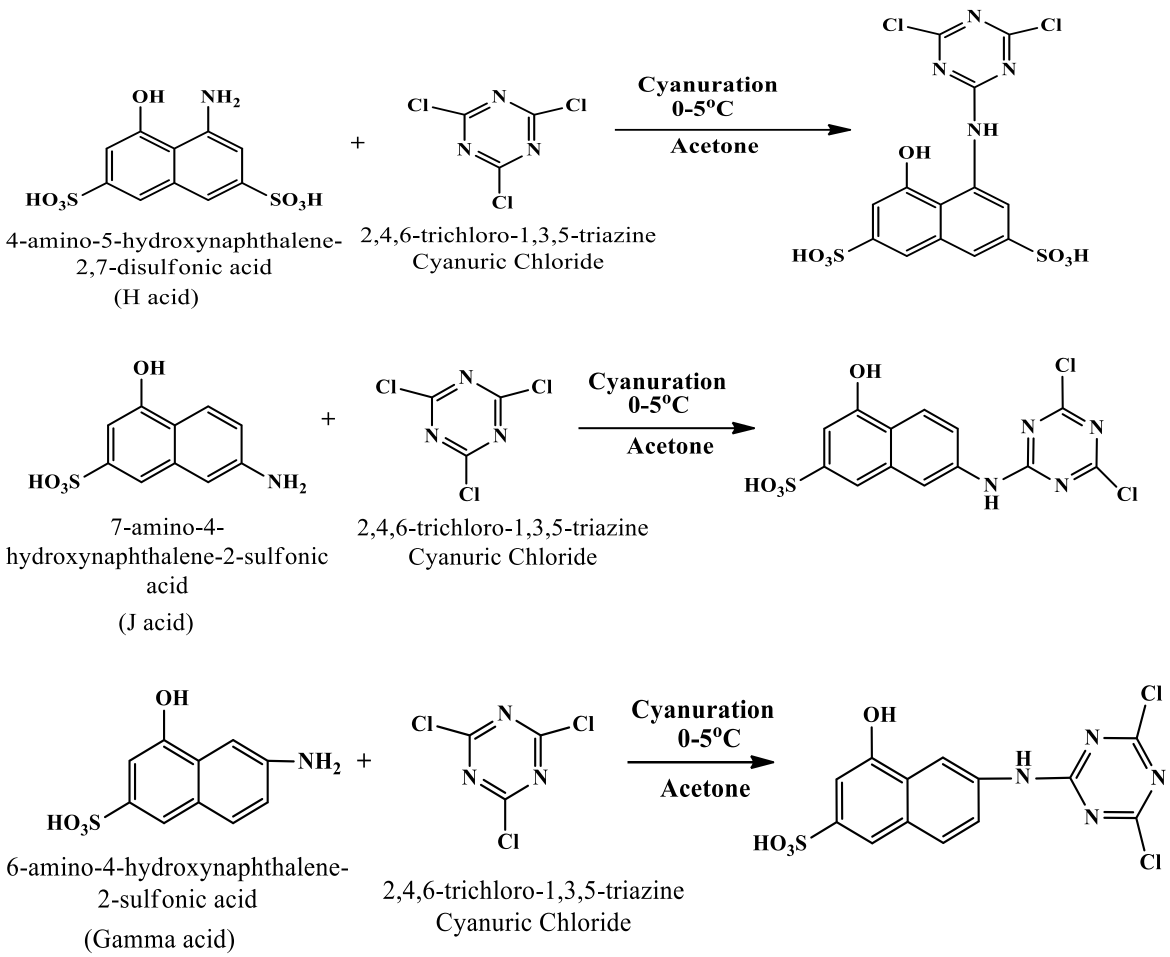


Scheme 3.2: Synthesis of intermediates A, B, C



Where R=Various cyanurated coupling components

Scheme 3.3: Diazotization and coupling reactions



Scheme 3.4: Cyanuration of coupling components

3.4 Percentage Yield

The percentage yield of the intermediates and the dyes were determined using the equation (1): (Musa *et al*., 2011).

$$\%Yield = \frac{MP}{MMP} \bigg/ \frac{MR}{MMR} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where MP is the mass of product

MMP is the molar mass of the product

MR is the mass of reactant

MMR is the molar mass of reactant

$$\%\text{yield} = \frac{Actual\ mass\ of\ product}{Theoretical\ mass\ of\ the\ product} \times 100 \qquad \ldots\ldots\ldots\ldots (2)$$

3.5 Determination of Melting Point

Melting points of the intermediates and the dyes were determined by the open capillary method using melting point apparatus are expressed in degree centigrade (°C) and are uncorrected. A small amount of the dyes and intermediate was filled into a capillary each and placed into the apparatus. The melting point of each was obtained by consistently focusing on the apparatus as it gradually heats in the tube.

3.6 Recrystallisation

The synthesised intermediates and dyes were purified by recrystallisation using different solvents based on the principle of recrystallisation. The intermediate (4.66g) was dissolved in an amount of the suitable solvents (30ml of Ethanol) heated up till it was completely dissolved, thereafter it was cooled under the ice to obtain a pure crystal. The crystal was collected by filtration, washed thoroughly with water and dried.

3.7 Spectroscopic Analysis

3.7.1 UV-Visible spectroscopy

The visible absorption spectra were determined using CARY 300 UV-visible spectrophotometer model Agilent technology. The wavelength of maximum absorption was determined using dye solutions in water, DMF, methanol, methanol plus hydrochloric acid.

3.7.2 Fourier transform infra-red (FT-IR) spectroscopy

The functional groups present in the intermediates were confirmed by infra-red spectroscopy using FTIR-8400S Fourier transform infrared spectrophotometer. All absorption bands are expressed in cm^{-1}.

3.7.3 Gas chromatography-mass spectrometry (GC-MS)

A mass spectrometry (MS) technique showing the plot of relative ion abundance versus mass-to-charge ratio(m/z) as recorded by the spectrometer, GC-MS – Agilent 19091S-433HP-5M, Federal University of Technology, Akure, was used to determine the molecular mass of the compounds (Silverstein and Webster, 1997).

3.8 Determination of the Molar Extinction Coefficient of Synthesised Dyes

The molar extinction coefficient (ε) is a constant for each molecule at any given wavelength, representing the absorbance of a 1cm thickness of a medium containing 1 mole of the absorbing substance per litre (Giles, 1974). ε was calculated using the relationship in equation (3).

$$\varepsilon = \frac{A}{Cl} \qquad \text{……………………………………………………………………} (3)$$

where (ε) = extinction coefficient

A = Absorbance

C = Concentration

L = path length

3.9 Dyeing of Cotton Fabric

Stock solution (1%) of each dye was prepared, a liquor ratio of 50:1 and 2% shade on the weight of fabric (o.w.f) were used (Shenai, 1973). The volume required from each stock solution was calculated using equation (4).

$$V = \frac{P \times W}{C} \qquad \text{……………………………………………………………………} (4)$$

where P = Percentage shade

W = Weight of fabric

C = percentage concentration

The fabric was introduced into the dyebath at 30°C and the temperature was raised to 70°C, over 30 min. at 2°C/min. Soda ash (Na_2CO_3) solution (10% v/v) was added to bring about fixation and the dyeing continued for additional 50min at the same temperature. The material was then removed, rinsed with cold water and dried.

3.9.1 Dye exhaustion and fixation

According to Modi *et al*., (1993) dye bath exhaustion can be assessed by spectrophotometric evaluation of the exhaust liquors. Dye exhaustion was determined by measuring the absorbance of the dye bath at the wavelength of the maximum absorption. The bath was sampled before and after dyeing. The absorbance of the diluted dye solution was measured at λ_{max} of the dye and the percentage dye bath exhaustion (%E) for each substrate was calculated using equation (5) (Choi *et al.*, 2008).

The percentage dye exhaustion for each dye was obtained from the dye optical density before dyeing (OD_1) and the corresponding optical density (OD_2) after dyeing using the expression in equation (5).

$$\%E = \frac{OD_1 - OD_2}{OD_1} \times 100 \qquad \text{……………………………………………} (5)$$

The term fixation ratio refers to the ratio of the amount of dye absorbed (which is covalently bonded to the fibre) to the hydrolysed dye on the surface of the fabric.

The percentage fixation was obtained by considering the optical density (ODs) of the dye stripped from the fabric using 10% Acetic acid. This gave relative fixation calculated through the use of the expression in equation (6).

$$\%F = \frac{OD_1 - OD_2 - OD_S}{OD_1 - OD_S} \times 100 \qquad \text{……………………………………………} (6)$$

where OD_1 = optical density of the dye before dyeing

OD_2 = optical density of the dye after dyeing

OD_s = optical density after stripping

3.10 Fastness Properties Test

3.10.1 Fastness to washing

The wash fastness tests were carried out using Gyro Wash- model no. 315/4/97/4023
ISO wash fastness test no. 3, under the following conditions:

Soda ash 2g/l

Soap 5g/l

Liquor ratio 50:1

Temperature 60°C

Time 30mins

Each dyed sample of cotton fabric was sandwiched between a piece of undyed cotton fabric to make a composite specimen and subjected to the wash fastness test. The composite specimens were separately agitated in a 100ml beaker containing the soap solution, plus other additives as prescribed above under the specified conditions of liquor ratio, temperature, and time. (Kamel *et al.,* 2009)

The composite specimens were then removed, rinsed and the components separated and dried. The change in colour of the dyed specimens and the staining of the adjacent cloths were assessed with the appropriate grey scale.

3.10.2 Fastness to light

The colour fastness to light was carried out according to standard method using Sun Test CPS - model no. 55007.

This test measures the resistance to fading of dyed textile when exposed to daylight. A small piece of the dyed fabric (0.25g) is cut and mounted on pattern cards (Blue Wool Scale). The test sample was exposed to light for 72 hours, after which the sample was removed and compared to the original unexposed samples. The colour changes were assessed by using a 'Blue Wool Reference Standard'.

3.10.3 Fastness to perspiration

This test measures the resistance of the colour of textile fabrics of all kinds to perspiration in all forms. Perspiration was carried out under acidic and alkaline solutions (Kamel *et al.*, 2009).

Acidic solution: sodium chloride (NaCl 5g/l), disodium hydrogen orthophosphate dehydrates ($Na_2HPO_4.2H_2O$ 2.5 g/L), histidine monohydrochloride monohydrate ($C_6H_9O_2N_3HCl.H_2O$ 0.5g/L), brought to pH 5.5 with 0.1N sodium hydroxide (NaOH) in a liquor ratio of 20:1.

Alkaline solution: sodium chloride (NaCl 5g/l), disodium hydrogen orthophosphate dehydrates ($Na_2HPO_4.2H_2O$ 2.5 g/L), histidine monohydrochloride monohydrate ($C_6H_9O_2N_3HCl.H_2O$ 0.5g/L), brought to pH 8 with 0.1N sodium hydroxide (NaOH) in a liquor ratio of 20:1

Procedure

A composite sample was made by sandwitching the dyed sample measuring 5x5cm between two pieces of un-dyed bleached cotton fabric measuring 5x5cm. The composite specimen was thoroughly wetted in the solution at room temperature (32℃) for 30mins. After 30mins, the composite specimen was removed from the solution and the composite sample was placed between two glass plates measuring 7.5x6.5cm under a force of 4.5kg. The apparatus containing the treated composites was then placed in a perspirometer at 37 + 2°C for 4 hours. The specimens were removed from the perspirometer and dried at 22℃. The change in colour of the specimen and the staining of the adjacent white cloth were assessed using grey scale.

CHAPTER FOUR

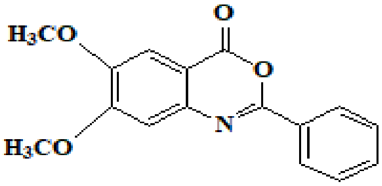
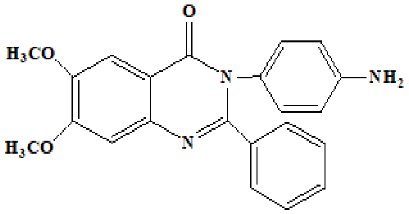
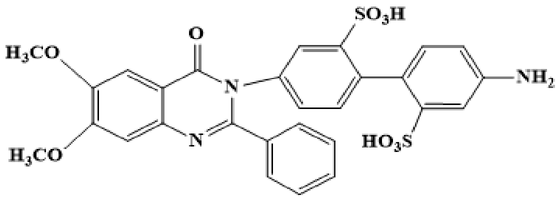
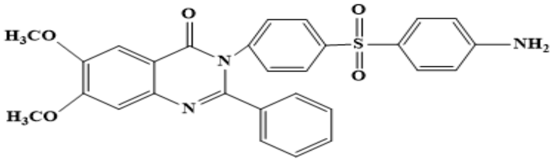
4.0 RESULTS AND DISCUSSION

4.1 Synthesis of Intermediates

4.1.1 Synthesis of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one (Intermediate 3H)

6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one was synthesised to give a white crystal solid after recrystallisation from ethanol as showed in the reaction scheme 3.1. the percentage yield and melting point was found to be 78% and 225-227°C, respectively, as shown in Table 4.1.

Table 4.1: Physical properties of the dye intermediates

Intermediate	**Structure**	**Molecular Formula**	**Molecular Weight (g/mol)**	**Melting Point (℃)**	**Yield (%)**
3[H]		$C_{16}H_{13}NO_4$	283	225-227	78
A		$C_{22}H_{19}N_3O_3$	373	237-239	62
B		$C_{28}H_{23}N_3S_2O_9$	609	235-237	55
C		$C_{28}H_{23}N_3SO_5$	513	227-229	65

Intermediate 3[H] (6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one) has an infra-red (IR λ_{max} cm^{-1} Appendix A1) spectrum that shows absorption at 1751 this is due to the C=O stretch. The signal at 1612 indicates C=N stretch. The signal at 3071 is attributed to the C-H stretch. The signal 1273 shows the (C-O) stretch, as shown in Table 4.2.

The mass spectrum (Figure 4.1) analysis showed a molecular ion [M^+] at m/z 281 which agrees with the formula mass 283$gmol^{-1}$.

4.1.2 Synthesis of 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (intermediate A)

6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one was refluxed with Benzene-1,4-diamine to obtain intermediate (A) in the presence of pyridine, as shown in the reaction scheme 3.2. The melting points and other physical properties are shown in Table 4.1.

4.1.3 Synthesis of 4-amino-4'-(6,7-dimethoxy-4-oxo-2-phenylquinazolin-3(4*H*)-*yl*)-[1,1'-biphenyl]-2,2'-disulfonic acid (intermediate B)

6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one was refluxed with 4,4'-diamino-[1,1'-biphenyl]-2,2'-disulfonic acid to obtain intermediate B, in the presence of pyridine, as shown in the reaction scheme 3.2.

4.1.4 Synthesis of 3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (intermediate C)

6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one was refluxed with 4,4'-sulfonyldianiline to obtain intermediate C, in the presence of pyridine, as shown in the reaction scheme 3.2.

Table 4.2: FT-IR spectra of the dye intermediates

Intermediate	**FT-IR (KBr):** $\boldsymbol{v}\ (\boldsymbol{cm^{-1}})$
3[H]	1751 (C=O), 1612 (C=N), (C-O-C), 3071 (C-H), 1273 (C-O)
A	1728 (C=O), 1620 (C=N), 3394 (N-H), 3063 (C-H), 1280 (C-O)
B	1612 (C=O), 1512 (C=N), 1388 (S=O), 3363 (N-H), 3140 (C-H), 1157 (C-O)
C	1743 (C=O), 1620 (C=N), 1373 (S=O), 3456 (N-H), 3171 (C-H), 1280 (C-O)

4.1.5 Gas chromatography-mass spectra (GC-MS) fragment of intermediates.

The plot of relative ion abundance against mass-to-charge ration(m/z) as recorded by the spectrometer showing the peaks including the parent ion versus their relative concentration as electron beam in the mass spectrometer bombard each substance under investigation as positive ion fragments are shown in Table 4.3 and Figures 4.1 – 4.4.

Table 4.3 Mass spectra values of the synthesised dye intermediates

Code	**Molecular formula**	**Calculated mass(m/z)**	**Experimental mass(m/z)**
3[H]	$C_{16}H_{13}NO_4$	283	281
A	$C_{22}H_{19}N_3O_3$	373	375
B	$C_{28}H_{23}N_3S_2O_9$	609	599
C	$C_{28}H_{23}N_3SO_5$	513	514

Intermediate (A) has the yield and the melting point of 62% and 237-239°C, respectively. The infra-red (IR $vmax\ cm^{-1}$Appendix A2) spectrum shows absorption at 1728 which is due to C=O stretch. The signal at 1620 indicates C=N stretch. The signal 3394 shows the N-H stretch. The signal at 3063 is attributed to the C-H stretch. The signal 1280 is due to C-O stretch, as shown in Table 4.2

The mass spectrum (Figure 4.2) analysis showed a molecular ion [M^+] at m/z 375 which is in agreement with the formula mass 373gmol^{-1}.

Intermediate (B) has the yield and melting point of 55% and 235-237°C, respectively. The infra-red (IR $vmax\ cm^{-1}$ Appendix A3) spectrum shows absorption at 1612 which is responsible for C=O stretch. The signal at 1512 is due to the C=N stretch. The signal at 1388 indicates S=O stretch. The signal at 3363 is attributed to the N-H stretch. The signal at 3140 is due to the C-H stretch. The signal 1157 indicates the C-O stretch, as shown in Table 4.2

The mass spectrum (Figure 4.3) analysis showed a molecular ion [M^+] at m/z 599 which is in agreement with the formula mass 609gmol^{-1}.

Intermediate (C) has the yield and melting point of 65% and 227-229°C, respectively. The infra-red (IR $vmax\ cm^{-1}$ Appendix A4) spectrum shows absorption at 1743 which is due to C=O stretch. The signal at 1620 is due to the C=N stretch. The signal 1373 is due to the S=O stretch. Signal 3456 indicate the N-H stretch. The signal at 3171 is attributed to the C-H stretch. The signal 1280 shows the C-O stretch, as seen in Table 4.2

The mass spectrum (Figure 4.4) analysis showed a molecular ion [M^+] at m/z 514 which is in agreement with the formula mass 513gmol^{-1}.

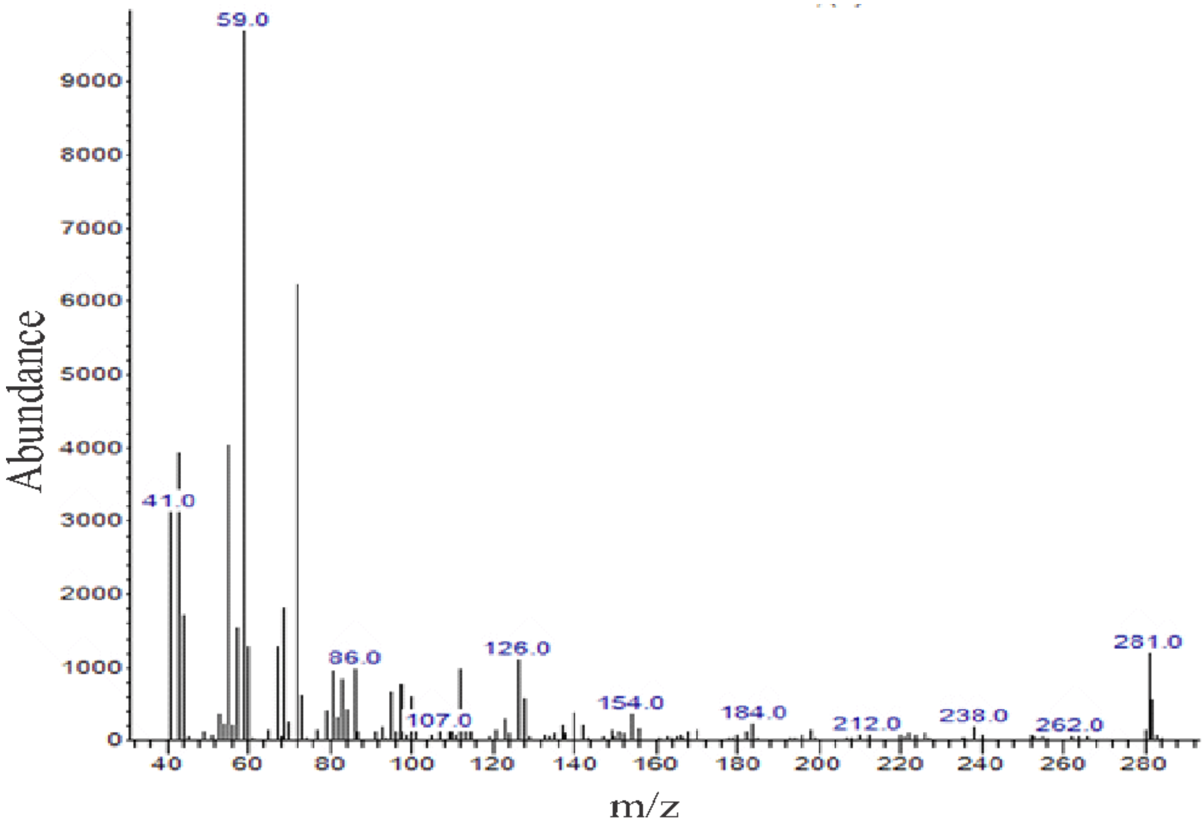


Figure 4.1: Gas chromatography–mass spectroscopy (GC-MS) spectrum of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one

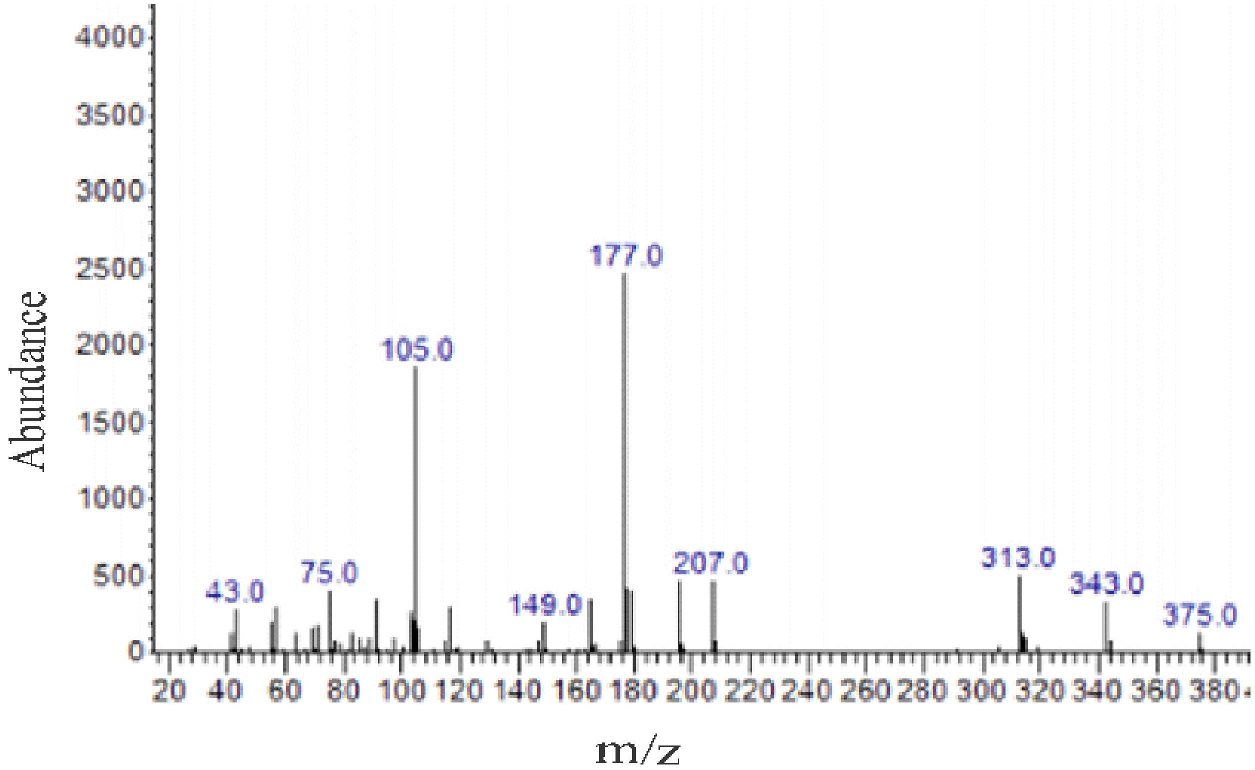


Figure 4.2: Gas chromatography–mass spectroscopy (GC-MS) spectrum of 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one

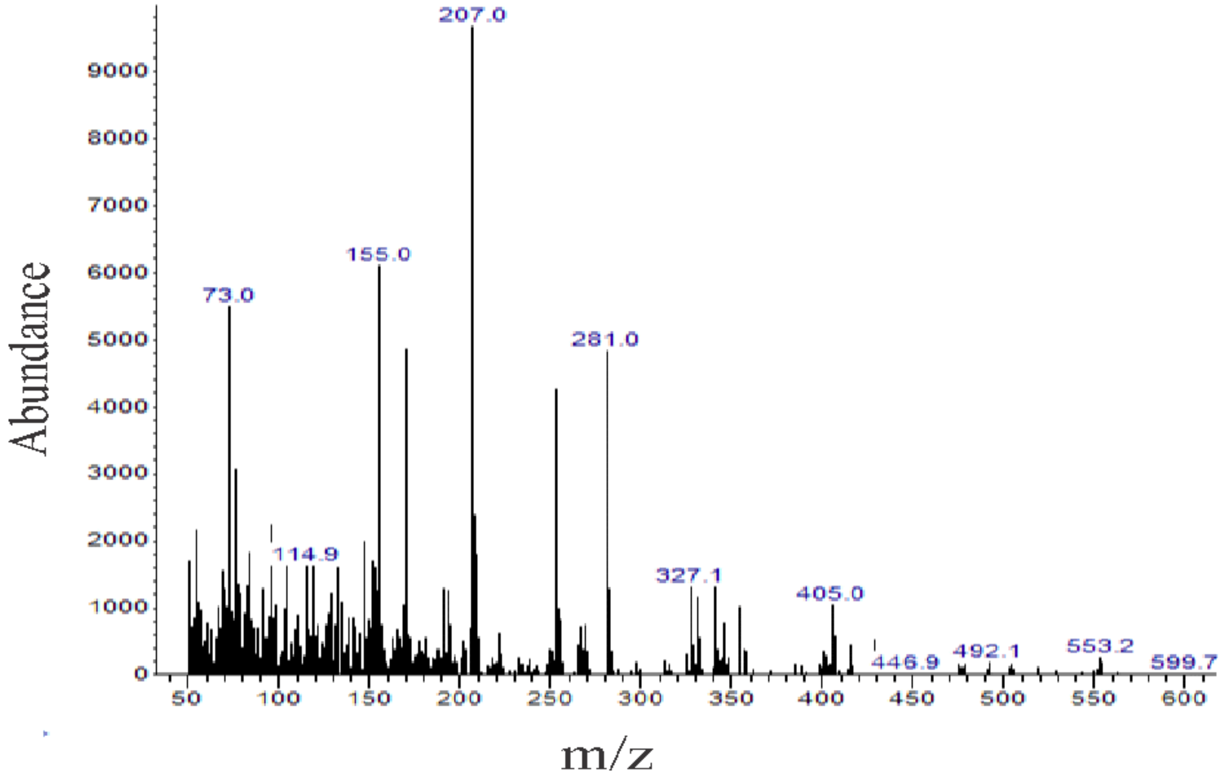


Figure 4.3: Gas chromatography–mass spectroscopy (GC-MS) spectrum of 4-amino-4'-(6,7-dimethoxy-4-oxo-2-phenylquinazolin-3(4*H*)-yl)-[1,1'-biphenyl]-2,2'-disulfonic acid

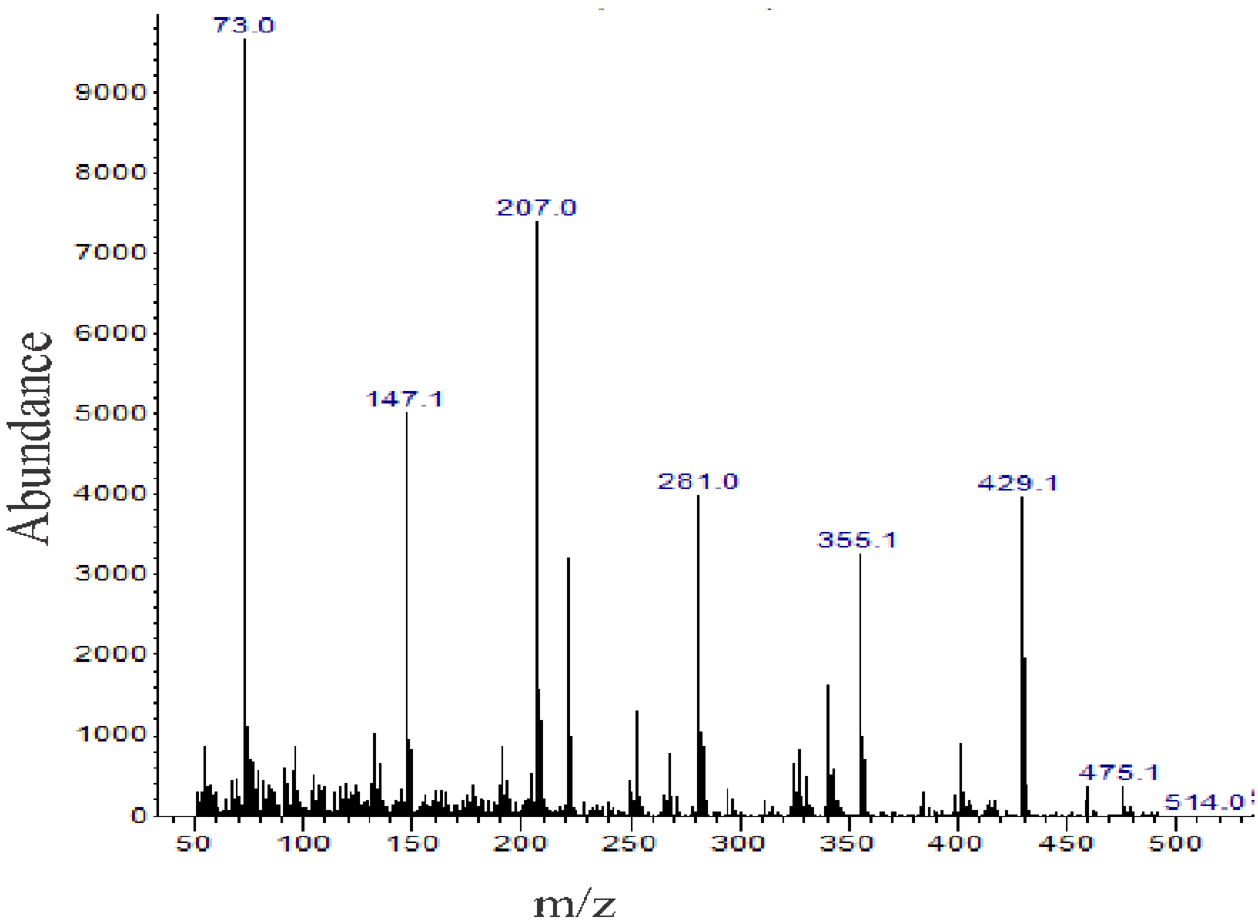


Figure 4.4: Gas chromatography–mass spectroscopy (GC-MS) spectrum of 3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one

The mass spectrum is presented as a vertical bar graph in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion as show in Figures 4.1 – 4.4. The most intense ion is assigned an abundance of 100, and it is referred to as the based peak. Most of the ions formed in a mass spectrometer have a single charge, so the m/z value is equivalent to mass itself. Mass spectrometer easily distinguishes ions differing by only a single atomic mass unit, and thus provides completely accurate values for the molecular mass of a compound. The highest mass ion in a spectrum is usually considered to be the molecular ion (M), and the lower mass ions are fragments from the molecular ion. The nature of the fragments often provides a clue to the molecular structure (Manfred *et al*., 1997).

The mass spectrum of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one gave mass to charge ratio (m/z) of 41, 59, 86, 126, 154, 184, 212, 262 and parent 281 representing molecular ion (M) and the corresponding positively charge fragments of $C_3H_5^+$, $C_4H_{10}^+$, $C_5H_{10}O^+$, $C_8H_{13}O^+$, $C_{11}H_8N^+$, $C_{11}H_6NO^+$, $C_{12}H_6NO_3^+$, $C_{16}H_8NO_3^+$, $C_{16}H_{13}NO_4^+$ are shown, respectively, in Figure 4.1.

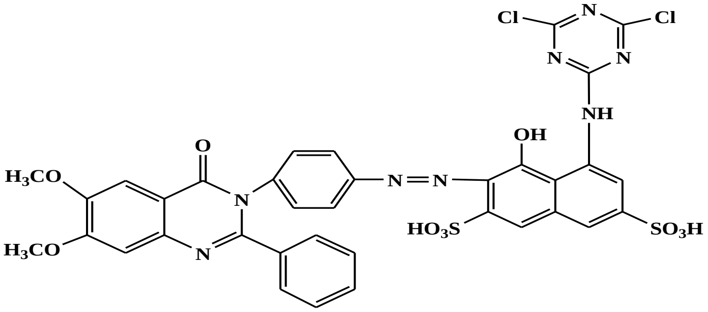
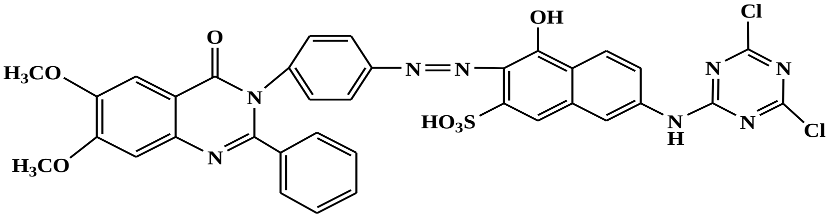
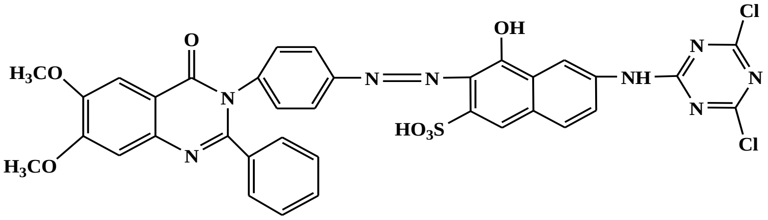
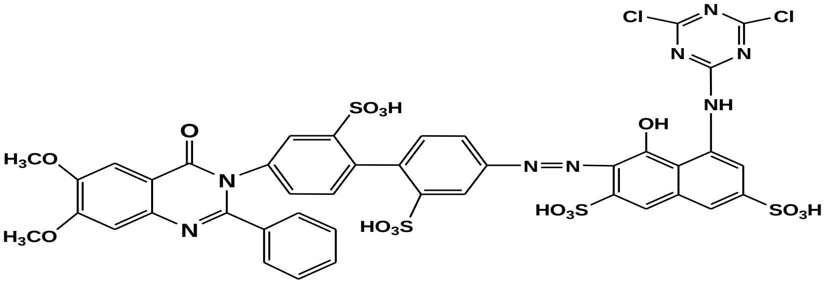
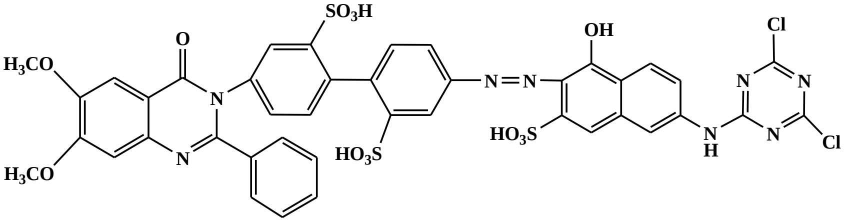
The mass spectrum of 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one (intermediate A) gave mass to charge ratio (m/z) of 43, 75, 105, 149, 177, 207, 313, 343 and parent 375 representing molecular ion (M) and the corresponding positively charge fragments of $C_2H_4O^+$, $C_6H_5^+$, $C_6H_6N_2^+$, $C_8H_9N_2O^+$, $C_{10}H_{12}N_2O_2^+$, $C_{13}H_9N_2O^+$, $C_{20}H_{15}N_3O^+$, $C_{21}H_{17}N_3O_2^+$, $C_{22}H_{19}N_3O_3^+$, are shown, respectively, in Figure 4.2.

The mass spectrum of 3-(4-((4-aminophenyl)sulfonyl)phenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (intermediate C) gave mass to charge ratio (m/z) of 73, 147, 207, 281, 355, 429, 475, and parent 514 representing molecular ion (M) and the corresponding positively charge fragments of $C_6H_5^+$, $C_8H_7N_2O^+$, $C_{10}H_9N_2O_3^+$, $C_{16}H_{13}N_2O_2^+$, $C_{22}H_{16}N_2O_3^+$, $C_{24}H_{22}N_3SO_3^+$, $C_{26}H_{23}N_3SO_4^+$, $C_{28}H_{23}N_3SO_5^+$ are shown, respectively, in Figure 4.3.

4.2 Synthesis of Dyes

The various dyes 1A, 2A, 3A, 1B, 2B, 3B, 1C, 2C and 3C were successfully synthesised using diazotization and coupling reactions and the structures and properties are shown in Tables 4.4 and 4.5.

Table 4.4: Structures of the synthesised dyes

Dye No	Structure
1A	
2A	
3A	
1B	
2B	

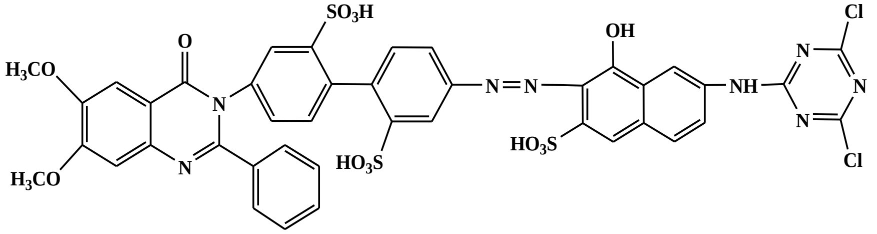
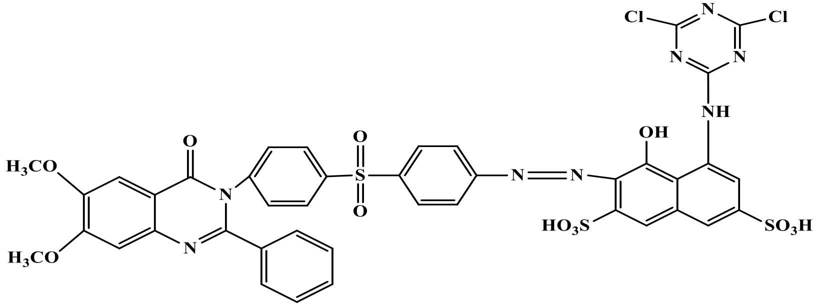
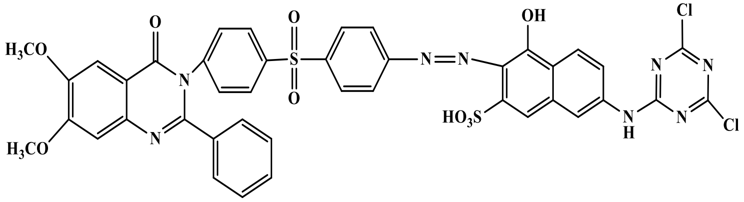
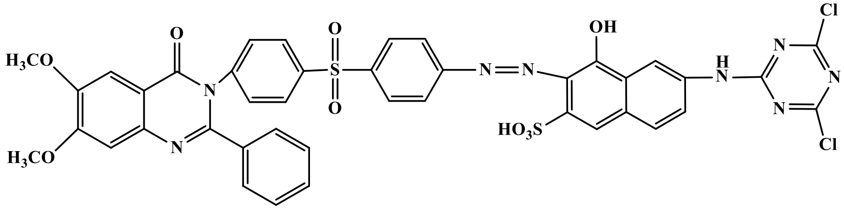
3B	H3CO H3CO O N N SO3H HO3S N=N OH HO3S NH N N N Cl Cl
1C	Cl N Cl N N NH OH H3CO H3CO O N N O S O N=N HO3S SO3H
2C	H3CO H3CO O N N O S O N=N OH HO3S N H Cl N N N Cl
3C	H3CO H3CO O N N O S O N=N OH HO3S H N N N N Cl Cl

Table 4.5: Physical properties of synthesised dyes

Dye	**Molecular Formula**	**Molecular Weight (g/mol)**	**Melting Point °C**	**Yield %**	**Physical Appearance (Colour)**
1A	$C_{35}H_{24}N_8Cl_2O_{10}$	787	310-312	76	Light purple
2A	$C_{35}H_{24}N_8Cl_2O_7$	739	290-293	85	Purple
3A	$C_{35}H_{24}N_8Cl_2O_7$	739	347-350	90	Light pink
1B	$C_{41}H_{28}N_8S_4Cl_2O_{16}$	1087	319	80	Light pink
2B	$C_{41}H_{28}N_8S_3Cl_2O_{13}$	1007	340-344	74	Deep pink
3B	$C_{41}H_{28}N_8S_3Cl_2O_{13}$	1007	278-280	65	Deep pink
1C	$C_{41}H_{28}N_8S_3Cl_2O_{12}$	991	310-312	89	Light pink
2C	$C_{41}H_{28}N_8S_2Cl_2O_9$	959	303-306	92	Yellowish pink
3C	$C_{41}H_{28}N_8S_2Cl_2O_9$	959	280-283	90	Yellowish pink

4.3 Visible Absorption Spectra of the Synthesised Dyes

The visible absorption spectra of the dyes were measured in water, dimethylformamide (DMF) and methanol. The results are shown in Table 4.7.

Table 4.6: Wavelength of maximum absorption and molar extinction coefficient of the dyes

Dye No.	ε_{max} in DMF $\times 10^4 lmol^{-1}cm^{-1}$	**H_2O λ_{max}(nm)**	**DMF λ_{max}(nm)**	**Methanol λ_{max}(nm) a**	**Methanol + HCl λ_{max}(nm) b**	**Change in λ_{max}(nm) (b-a)**
1A	2.92	529	527	524	528	+4
2A	2.79	533	535	533	529	-4
3A	2.92	521	516	514	510	-4
1B	0.62	535	531	532	536	+4
2B	1.14	495	496	487	495	+8
3B	1.06	508	506	494	508	+14
1C	0.33	525	526	504	535	+31
2C	0.78	480	461	488	503	+15
3C	1.15	512	509	509	514	+5

Absorbance is the measure of the amount of light absorbed. The visible absorption properties were measured in water, dimethylformamide (DMF) methanol and methanol + HCl. The results is summarised in Table 4.7. The colour of the reactive monoazo dyes depends on the nature of both the diazo and coupling component. The wavelength of the maximum absorption of the quinazolinone based dyes ranges from 470 to 540 in water, 460 to 550 in DMF, 470 to 540 in methanol and 490 to 540 in methanol + HCl.

The molar extinction coefficient (ε) of the dyes was calculated based on the concentration in dimethylformamide (DMF) as a solvent and are also listed in Table 4.7.

The λ_{max} shifts in solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent. The measurement of λ_{max} in methanol, water and DMF showed that the λ_{max} of the intramolecular charge transfer bonds exhibits a marked red shift on transfer from non-polar to polar solvent. This behaviour indicates that the polar excited states of the synthesised dyes are stabilised by polarisation interaction forces as the polarisability of the solvent is increased.

The molar extinction coefficient was calculated based on the concentrations of the dyes in DMF as a solvent. The molar extinction coefficient, also is a measure of the light absorbed by a compound in solution, which was calculated for each dye. From the results in Table 4.7, it can be observed that dyes 1A, 2A, 3A possess high molar extinction coefficient and appear bright on the substrate. This may be attributed to the fact that they transmit light in comparison to others and therefore have more narrow absorption bands with sharp peaks compared to others (Mclaren 1983). The higher the molar extinction coefficient value of the dyes implies the possibility for more electronic transition.

4.3.1 Solvent effect on the UV-Vis spectra (solvatochromism)

Solvatochromism is due to various solute-solvent interactions in both the ground state and excited states. Effect of solvent polarity on the maximum absorption wavelength of dyes i.e. the ability of a chemical substance to change colour due to change in solvent polarity was studied. With the increase in polarity of the solvent, the absorption maximum is shifted to a longer wavelength (Marini *et al*., 2010).

Solvatochromism is observed in many dyes due to the difference in solvation of the ground state and the first excited state of the light absorbing molecule. On increasing solvent polarity, the ground state molecule stabilises better by solvation than the excited state molecule, this effect is called blue shift or negative solvatochromism or hypsochromic shift, while on increasing solvent polarity, dye molecule stability increases in excited state rather than ground state, this effect is called red shift or positive solvatochromism or bathochromic shift (Patel and Patel, 2012).

The bathochromic shift observed on changing to a more polar solvent suggests that the dye molecule has a more polar excited state than the ground state and this will lower the energy of the transition. Thus, the energy difference between the ground and the excited states is reduced leading to a bathochromic shift of the visible band. On the other hand, those dyes with hypsochromic shift (negative solvatochromism) mean that the dyes molecules have a more polar ground state than the excited state.

The visible absorption spectra of all the dyes in pure solvents of different dielectric constants via water, DMF and methanol, were recorded and shown in Table 4.7 showed that the bands were observed in the region 480-535 nm in water, 461-535 nm in DMF, 488-533 nm in methanol.

The bathochromic shift (positive solvatochromism) was observed in water relative to DMF and methanol. as a result of the increase in the solvent polarity because of the increase in the dielectric constant of water relative to DMF and methanol. This positive solvatochromism is observed in dyes 1A, 3A, 1B, 3B and. 3C. These results suggest that the excited state in these dyes were more polar than the ground state. The hypsochromic shift (negative solvatochromism) occurring in water-related to DMF and methanol. This effect is observed in dyes 2A, 2B, 1C and 2C. The negative solvatochromism observed is due to the solute-solvent interaction through intermolecular hydrogen bond formation between water and lone pair of electrons of a secondary amino nitrogen atom.

4.3.2 Effects of acid on visible absorption band

The effect of drops of acid on the visible absorption band which could decrease or increase the maximum absorption wavelength is referred to as halochromism. It is also referred to as colour change which occurs on the addition of acid (or base or salt) to a solution of a compound into a coloured one. When 0.1 M HCl was added to the dye solution in methanol, dye 1A, 1B, 2B, 3B, 1C, 2C and 3C showed a bathochromic shift (positive halochromism). This showed that these dyes exist in the cationic form in an acidic methanolic solution. Dyes 2A and 3A show negative halochromism on the effects of acids in the dye solution in methanol, this may be due to an electron-withdrawing strength of the substituent, if the electron-withdrawing strength of the substituent is sufficiently high, negative halochromism can be observed.

4.4 Infra-red Spectra of the Synthesised Dyes

IR spectroscopy is often used to identify structures because functional groups give rise to the characteristic bands both in terms of intensity and position (frequency) as shown in Table 4.6.

Table 4.7 FT-IR spectra of the dyes

Dye No.	**FT-IR (KBr):** $v\ (cm^{-1})$
1A	1651 (C=O), 1443 (-N=N-), 3402 (O-H), 1203 (C-N), 3279 (N-H), 3047,2931 (C-H aromatic, aliphatic), 864 (C-Cl)
2A	1736 (C=O), 1443 (-N=N-), 3463 (O-H), 1204 (C-N), 3279 (N-H), 1350 (S=O), 3187 2924 (C-H aromatic, aliphatic), 787 (C-Cl)
3A	1728 (C=O), 1574 (-N=N-), 3449 (O-H), 1195 (C-N), 3279 (N-H), 1365 (S=O), 3047,2931 (C-H aromatic, aliphatic), 748 (C-Cl)

1B	1728 (C=O), 1451 (-N=N-), 3449 (O-H), 1211 (C-N), 3279 (N-H), 1371 (S=O), 3055, 2924 (C-H aromatic, aliphatic), 864 (C-Cl)
2B	1735 (C=O), 1450 (-N=N-), 3557 (O-H), 1203 (C-N), 3271 (N-H), 1342 (S=O), 3047, 2924 (C-H aromatic, aliphatic), 840 (C-Cl)
3B	1743 (C=O), 1450 (-N=N-), 3518 (O-H), 1204 (C-N), 3279 (N-H), 1327, 1126 (S=O), 3048, 2768 (C-H aromatic, aliphatic), 880 (C-Cl)
1C	1743 (C=O), 1496 (-N=N-), 3425 (O-H), 1227 (C-N), 3279 (N-H), 1304, 1026 (S=O), 3048, 2924 (C-H aromatic, aliphatic), 849 (C-Cl)
2C	1743 (C=O), 1543 (-N=N-), 3402 (O-H), 1204 (C-N), 3233 (N-H), 1335, 1126 (S=O), 3048, 2778 (C-H aromatic, aliphatic), 810 (C-Cl)
3C	1751 (C=O), 1543 (-N=N-), 3525 (O-H), 1204 (C-N), 3279 (N-H), 1319, 1119 (S=O), 3133, 2793(C-H aromatic, aliphatic), 880(C-Cl)

Dye 1A has the yield and melting point of 76% and 310-312°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A5) spectrum shows absorption at 3047 and 2931 which is due to C-H stretch for aromatic and aliphatic. The signal at 1651 is due to the C=O stretch. The signal at 1443 is responsible for -N=N- stretch. The signal at 3402 indicates O-H stretch. The signal at 1203 is due to the C-N stretch. The signals 3279 and 864 are attributed to N-H and C-Cl stretch.

Dye 2A has the yield and melting point of 85% and 290-293°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A6) spectrum shows absorption at 1736 which is due to C=O stretch. The signal at 1443 is attributed to -N=N- stretch. The signal at 3463 indicates the O-H stretch. The signals 1204 and 3279 is attributed to C-N and N-H stretch. The signal at 1350 is due to the S=O stretch. The signal at 3187 and 2924 is due to the C-H stretch for aromatic and aliphatic. The signal 787 is due to the C-Cl stretch.

Dye 3A has the yield and melting point of 90% and 347-350°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A7) spectrum shows absorption at 3047 and 2931 which is due to C-H stretch for aromatic and aliphatic. The signal at 1728 shows a C=O stretch. The signal at 1574 indicates a -N=N- stretch. The signal 3449 is responsible for the O-H stretch. The signals 1195 and 3279 is attributed to C-N and N-H stretch. The signal 1365 is due to the S=O stretch. The signal 748 is due to the C-Cl stretch.

Dye 1B the yield and melting point of 80% and 319°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A8) spectrum shows absorption at 1728 which indicate C=O stretch. The signal 1451 is responsible for -N=N- stretch. Signal 3449 indicate O-H stretch. The signal at 1211 is due to the C-N stretch. The signal 3279 is attributed to the N-H stretch. The signal at 1371 is due to the S=O stretch. The signal at 3055 and 2924 indicate C-H stretch for aromatic and aliphatic. The signal 864 is due to the C-Cl stretch.

Dye 2B has the yield and melting point of 74% and 340-344°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A9) spectrum shows absorption at 3047 and 2924 which is due to C-H stretch for aromatic and aliphatic. The signal at 1735 indicates the presence of a C=O stretch. The signal at 1450 is due to -N=N- stretch. The signal at 3557 is responsible for the O-H stretch. The signal at 1203 and 3271 indicate C-N and N-H stretch. The signal at 1342 is due to the S=O stretch. The signal 840 indicate a C-Cl stretch.

Dye 3B has the yield and melting point of 65% and 278-280°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A10) spectrum shows absorption at 1743 which is due to C=O stretch. The signal at 1450 indicates -N=N- stretch. The signal at 3518 is responsible for the O-H stretch. The signal 1204 is due to the C-N stretch. The signal 3279 is attributed to the N-H stretch. The signal 1327 and 1126 indicate S=O stretch. The signal at 3048 and 2768 correspond to the C-H stretch for aromatic and aliphatic. The signal at 880 is due to the C-Cl stretch.

Dye 1C has the yield and melting point of 89% and 310-312°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A11) spectrum shows absorption at 3048 and 2924 which is responsible for C-H stretch for aromatic and aliphatic. The signal at 1743 shows C=O stretch. The signal at 1496 indicates -N=N- stretch. The signal at 3425 is due to the O-H stretch. The signal at 1227 is attributed to the C-N stretch. The signal at 3279 indicates the N-H stretch. The signal 1304 and 1026 shows absorption for S=O stretch. The signal at 849 is due to the C-Cl stretch.

Dye 2C has the yield and melting point of 92% and 303-306°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A12) spectrum shows absorption at 1743 is due to C=O stretch. The signal at 1543 indicates -N=N- stretch. The signal 3402 is responsible for the O-H stretch. The signal at 1204 is due to the C-N stretch. The signal at 3233 shows absorption for the N-H stretch. The signal at 1335 and 1126 indicate S=O stretch. The signal 3048 and 2778 is attributed to C-H stretch for aromatic and aliphatic. The signal at 810 is due to the C-Cl stretch.

Dye 3C has the yield and melting point of 90% and 280-283°C, respectively, as shown in Table 4.5. The infra-red (IR $vmax\ cm^{-1}$ Appendix A13) spectrum shows absorption at 1751 is due to C=O stretch. The signal 1543 indicate -N=N- stretch. The signal 3525 is responsible for the O-H stretch. The signal at 1204 is attributed to the C-N stretch. The signal at 3279 is due to the N-H stretch. The signal at 1319 and 1119 shows S=O stretch. The signal at 3133 and 2793 is attributed to the C-H stretch for aromatic and aliphatic. The signal 880 is due to C-Cl stretch.

4.5 Dyeing

The reactive dyes were applied on cotton fabric in the dye bath condition with high percentage exhaustion and fixation, and the results are shown in Table 4.8.

Table 4.8: Exhaustion and fixation values of the reactive dyes on cotton

Dye	Colour	Exhaustion (%)	Fixation (%)
1A	Light purple	86	71
2A	Purple	89	69
3A	Light pink	84	67
1B	Light pink	86	70
2B	Deep pink	89	75
3B	Deep pink	87	73
1C	Light pink	90	72
2C	Yellowish pink	91	78
3C	Yellowish pink	82	66

From the results in Table 4.8, dyes 1A, 2A, 3A, 1B, 2B, 3B, 1C, 2C and 3C applied on cotton fabric gave percentage exhaustion of 86, 89, 84, 86, 89, 87, 90, 91 and 82%, respectively. The very good exhaustion of these dyes indicates good affinity for the fabric

The percentage fixation (% F) is the ratio of the amount of dye absorbed which is covalently bonded to the fibre. It can be observed from the results in Table 4.8, that the dyes gave percentage fixation range from 66 – 78% which indicate a good covalent bonding between the dye and the fibre

4.6 Fastness Tests

The wash, light and perspiration fastness of the dyed cotton fabric are presented in Table 4.9

Table 4.9: Fastness properties of the synthesised dyes

Dye	Washing Fastness		Light Fastness	Fastness to Perspiration	
	Colour change	staining		Acid	Alkaline
1A	3-4	4	4	4	4
1B	4	4	4	4	4
2A	4	3-4	3	2	4
2B	3-4	4	3	3	4
3A	4	4	4	4	3
3B	3-4	4	4	3	4
1C	3-4	4	3	4	3
2C	4	4	4	3	4
3C	3-4	4	3	3	4

4.6.1 Fastness to washing

Coloured fabric must withstand conditions that it may encounter during processing following colouration and its subsequent daily use. If the dye is not covalently bonded to the fabric, it may be lost during washing. Wash fastness properties of the synthesised dyes are generally moderate to very good for all dyes, as all the dyes fall between 3 and 5 as shown in Table 4.9. This is because the dyes containing reactive groups are compatible with the fibre and were covalently bonded with the reactive sites in the fibre. The fastness rating of 4, 4-5 shows that the binding forces between the dye and the fibre are strong. This means the formation of a covalent bond between the reactive sites in the dye and the fibre is relatively strong as there is little or no staining on the adjacent fabric. However, some exhibited good to moderate values of 3 - 4 on adjacent fabric due to poor uptake of the dye into the fibre.

4.6.2 Fastness to light

Lightfastness is the resistance of dyes to the effect of sun, heat and light energy. The light fastness was fair, moderate to fairly good, as the value ranges from 3 - 5 for all the dyes applied on cotton as seen in Table 4.9. The poor light fastness of 3 may be due to the poor planarity of the dyes. Many factors can affect light fastness, some of them are depth of shade, the presence of foreign substances and inherent photo-stability of the dye chromophore and how this stability is affected by the chemical nature of the fabric.

Generally, reactive dyes have moderate resistance to light. Also, darker depths of shades show good resistance to light whereas brighter/lighter shades of dyes show poor resistance to light. The electron mobility of dyes with brighter shade is high and so the electrons can easily move to the excited state causing breakage in the chromophore system of the dye which results in fading. This is attributed to good penetration and affinity of the reactive dyes to the fibres. The high light

fastness may be due to the higher attraction between dye and fibre and higher stability of resonance in the conjugated system (Patel and Patel, 2011c).

Additionally, factors that affect the colour fastness of textiles are internal and external. Internal factors may include the dye and the fibre type while external factors are products imposed by external forces or conditions.

4.6.3 Fastness to perspiration

The perspiration produced by the human body is a chemical fluid that can have adverse effects on a coloured fabric in regular contact with it. All perspirations contain common salt which can affect some dyes but can vary in acidity or alkalinity according to a particular individual (S.D.C, 1991). Two chemical solutions which approximate human perspiration was used, one being slightly acidic and the other being slightly alkaline (Nkeonye, 1993). The fastness to perspiration carried out in both acidic and alkaline solutions of histidine is summarised in Table 4.9.

All the dyes had a very good fastness to perspiration values between 3 and 5.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

Monoazo reactive dyes based on quinazolinone ring have been successfully synthesised using cyanurated H-acid, J-acid and Gamma acid as coupling components with good percentage yield ranging from 65 – 90%.

The diazo components were synthesised from 2-amino-4,5-dimethoxybenzoic acid as starting material and various reactions were carried out to obtain the diazo components containing quinazolinone ring before coupling to obtain the synthesised dyes.

The molar mass of the synthesised dyes was between 700 – 1100g/mol. The infra-red spectra showed functional groups of C=O, -N=N-, O-H, C-N, N-H, S=O, C-H for aromatic and aliphatic.

The intermediates and the dyes were purified by recrystallisation method and characterised using FT-IR, UV-Visible and mass spectroscopic techniques.

The UV-Visible spectrophotometric investigation of the synthesised dyes in different solvents was determined to obtain their absorption maxima, molar extinction coefficients and solvatochromic effects.

The synthesised dyes were applied on cotton fabric and gave a high percentage exhaustion range of 82 – 91% and a fixation rate ranging from 66 – 78% which indicate a strong covalent bond between the dye and the fibre.

The fastness properties (light, washing and perspiration) of the dyed samples were assessed and gave a good to very good results (3 - 5).

5.2 Conclusion

The diazotization of the synthesised quinazolinone intermediates followed by coupling with various cyanurated acid coupling components gave corresponding monoazo reactive dyes.

The presence of the triazine group of the dye molecules improves the exhaustion, fixation and fastness properties. Thus, the exhaustion and fixation of these dyes are very good (65 – 91%), this indicates that the dyes have good affinity and solubility for the fabric. The remarkable degree of levelness and brightness after washing indicates the good penetration and affinity of these dyes for the fabric.

The colour difference may be attributed to both nature and position of the substituent. The dyes gave a satisfactory performance of 65 – 91% for exhaustion and fixation on cotton fabric.

These dyes gave a wide range of fast shades like purple, orange, and pink shade on cotton fabric. This type of dye synthesis is generally convenient and economical for use. The dyeing performance of all dyes on cotton fabric gave moderate to good (3 - 4) light fastness, good to excellent (3 - 5) wash fastness and moderate to good (3 - 4) fastness to perspiration

The fastness properties to washing, light and perspiration of the dyes on cotton showed good to excellent (3 - 5) performance.

The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to cotton fabric.

5.3 Recommendation

Based on the results of this research, it is recommended that further work be carried out on the following areas:

1) ^{1}HNMR and ^{13}CNMR should be carried out to further confirm the structures of the synthesised intermediates and dyes.
2) The intermediates used in the synthesis can be subjected to other coupling components.
3) The antimicrobial properties of these dyes can also be investigated.

5.4 Contribution to Knowledge

From this research, new heterocyclic reactive dyes have been synthesised successfully from novel coupling components and intermediates of quinazolinone derivatives with a very good yield of up to 90%.

The new reactive dyes have 91% exhaustion when compared to existing commercial reactive dyes when applied on cotton fabric.

The synthesised dyes showed good build-up and very good wash fastness property rating of 4 when applied to cotton fabric.

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APPENDIX

Appendix A: Infra-Red Spectra of Synthesised Intermediate and Dyes

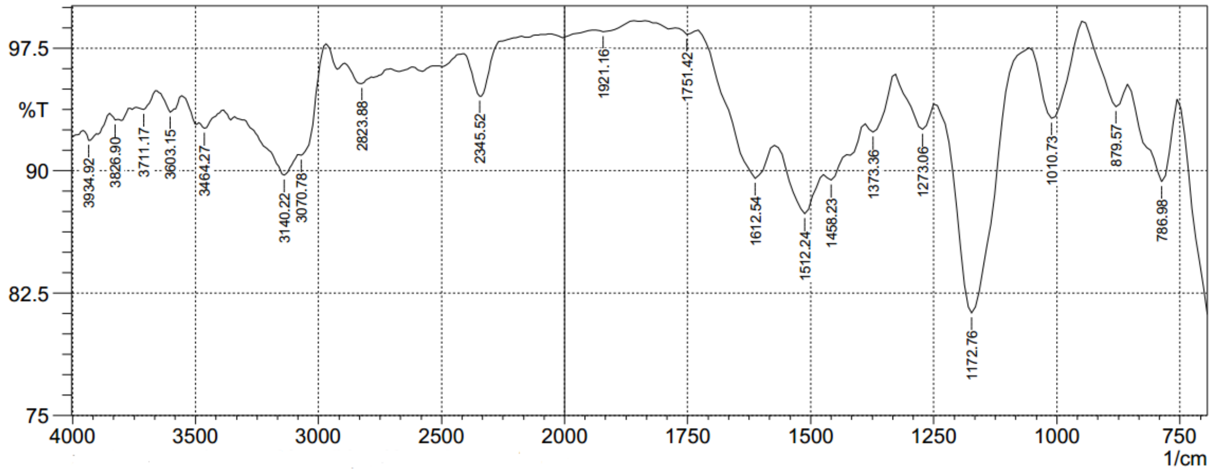

Figure A1: FTIR –spectrum of 6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxaxin-4-one

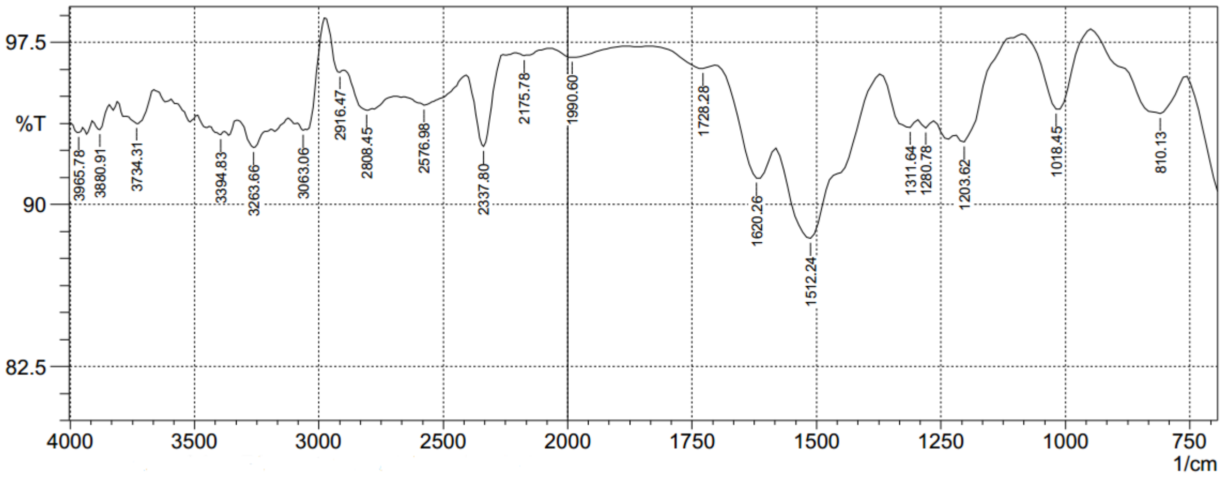

Figure A2: FTIR –spectrum of dye intermediate A

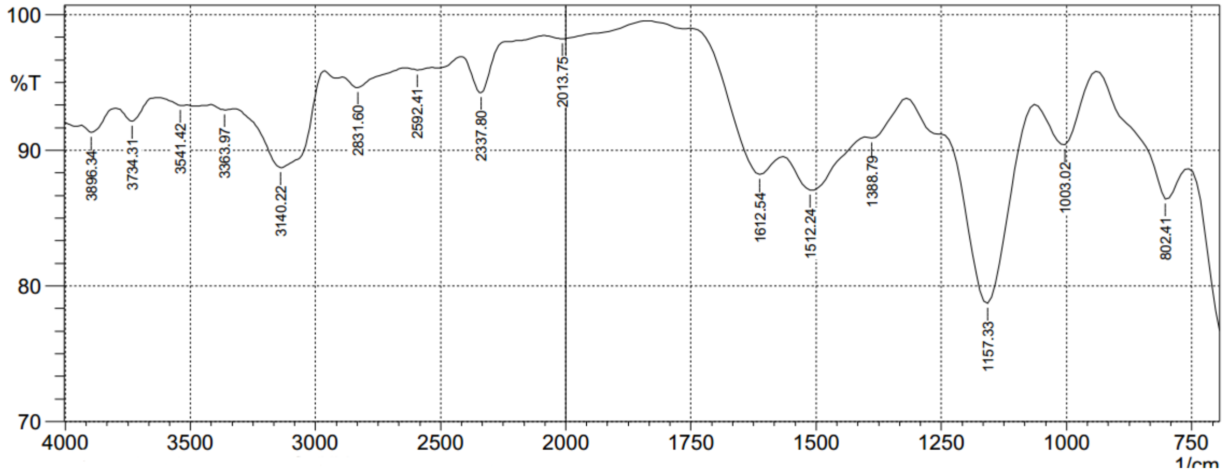

Figure A3: FTIR –spectrum of dye intermediate B

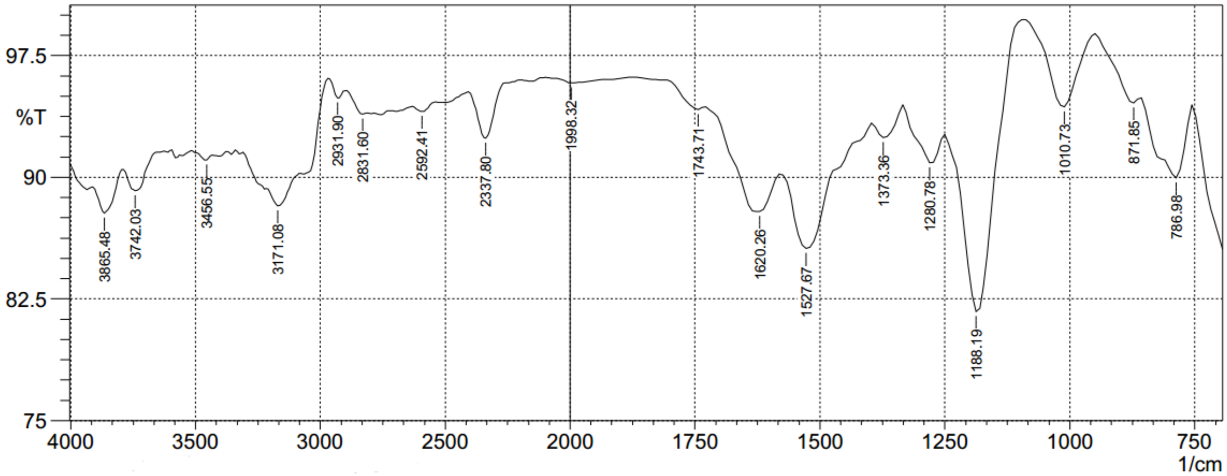

Figure A4: FTIR –spectrum of dye intermediate C

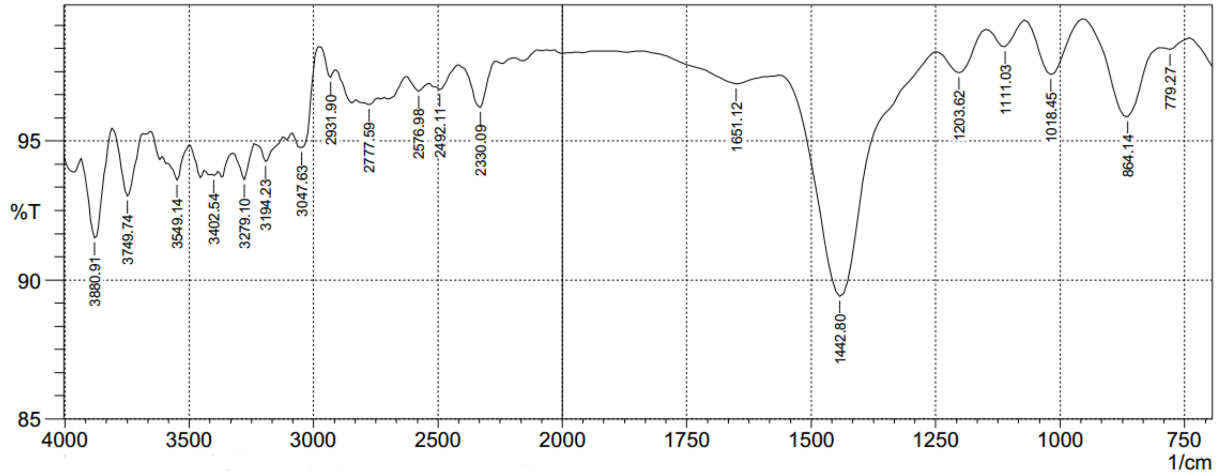

Figure A5: FTIR –spectrum of dye 1A

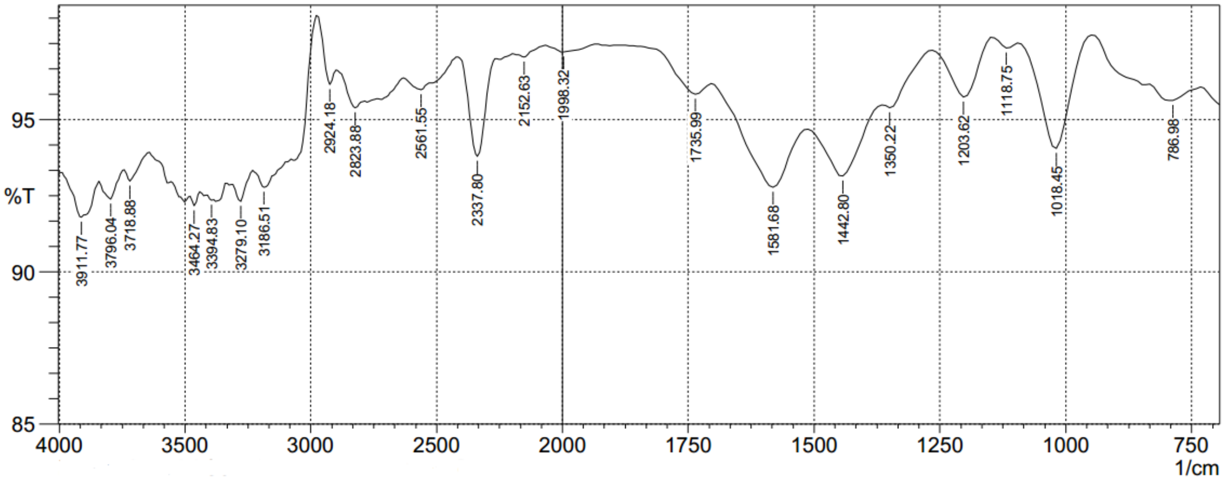

Figure A6: FTIR –spectrum of dye 2A

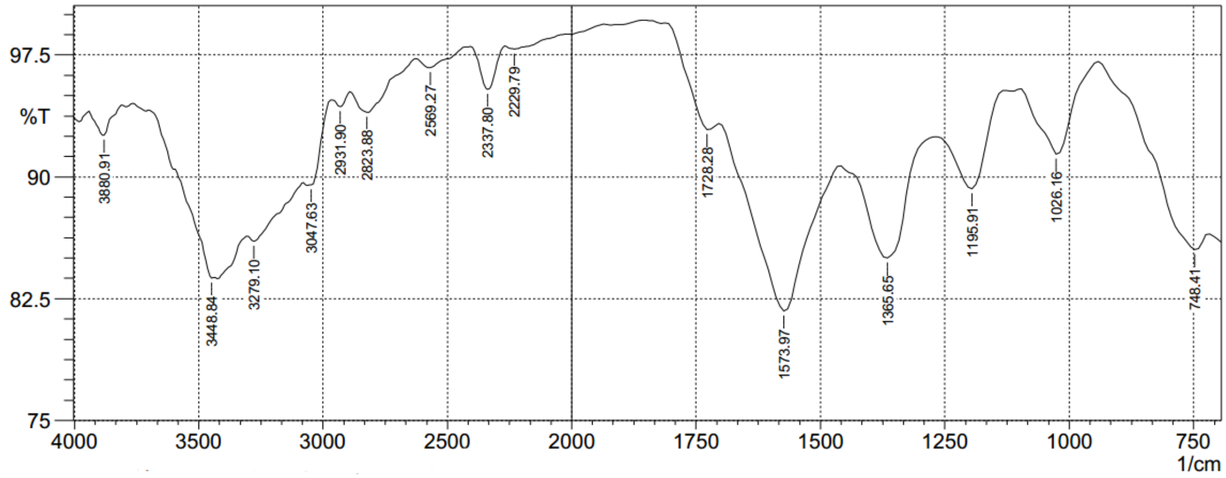

Figure A7: FTIR –spectrum of dye 3A

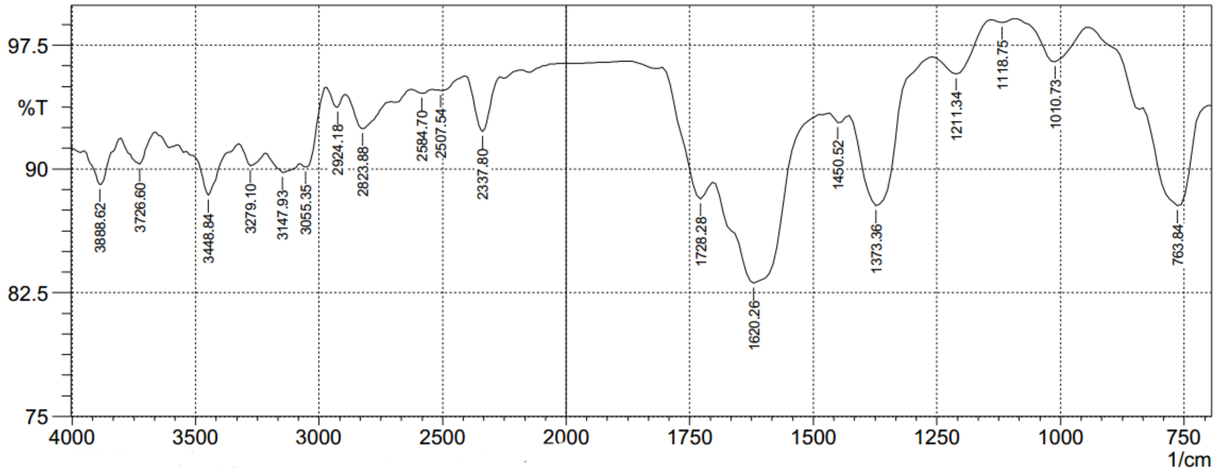

Figure A8: FTIR –spectrum of dye 1B

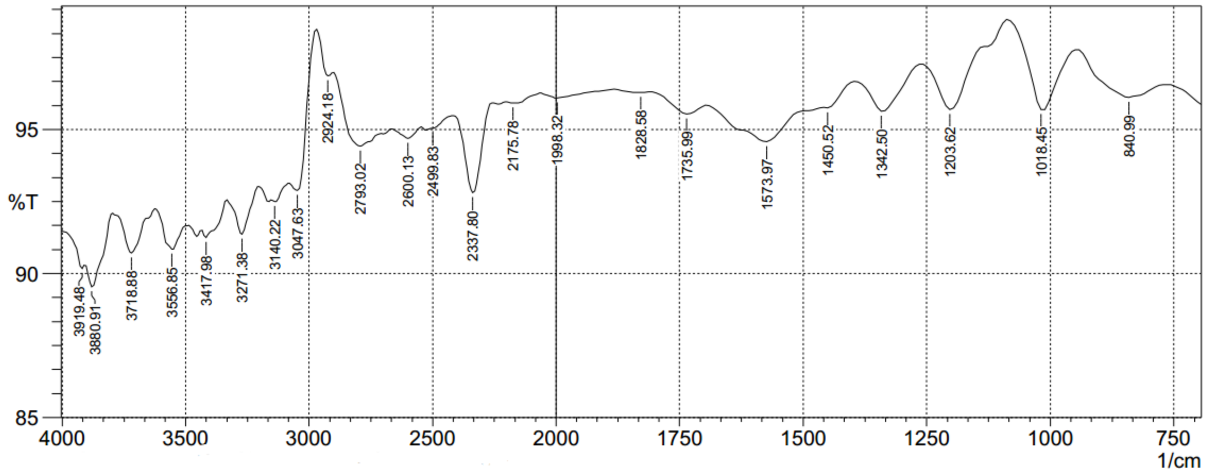

Figure A9: FTIR –spectrum of dye 2B

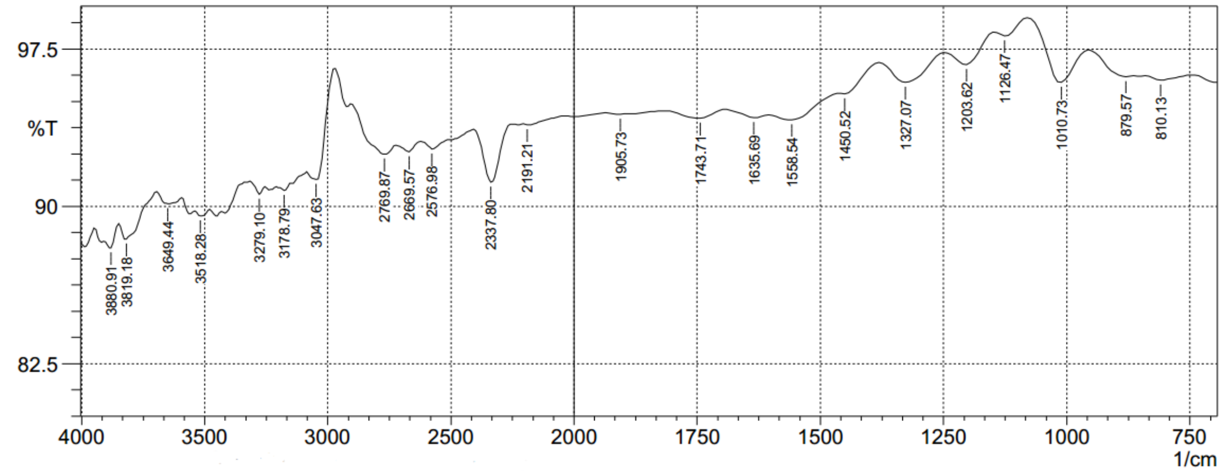

Figure A10: FTIR –spectrum of dye 3B

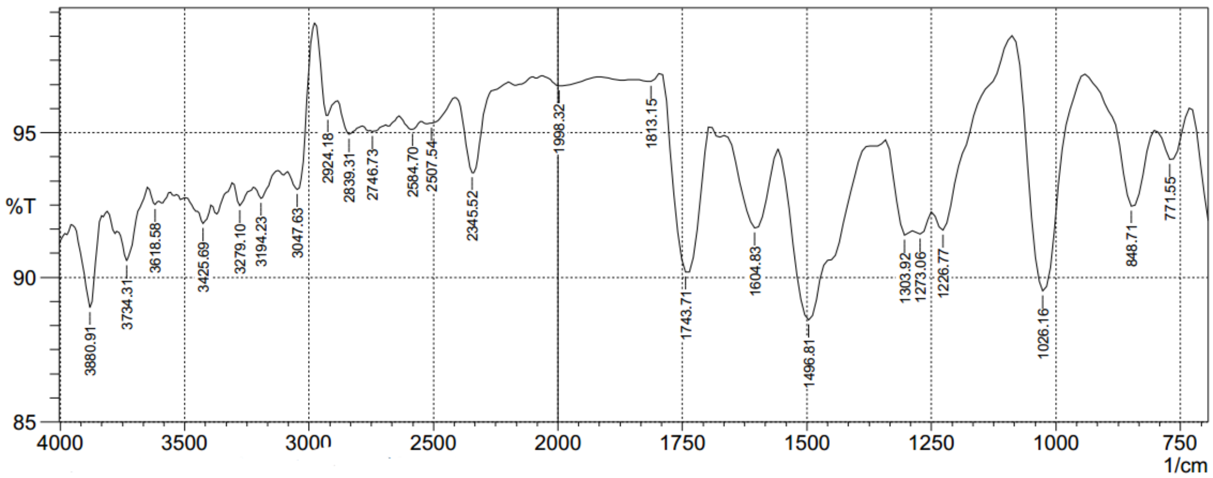

Figure A11: FTIR –spectrum of dye 1C

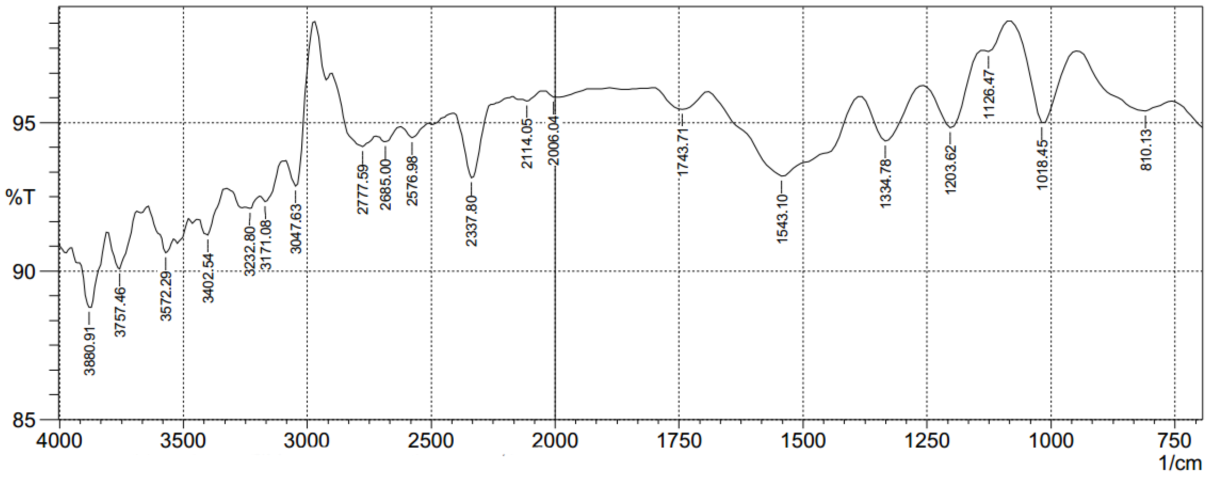

Figure A12: FTIR –spectrum of dye 2C

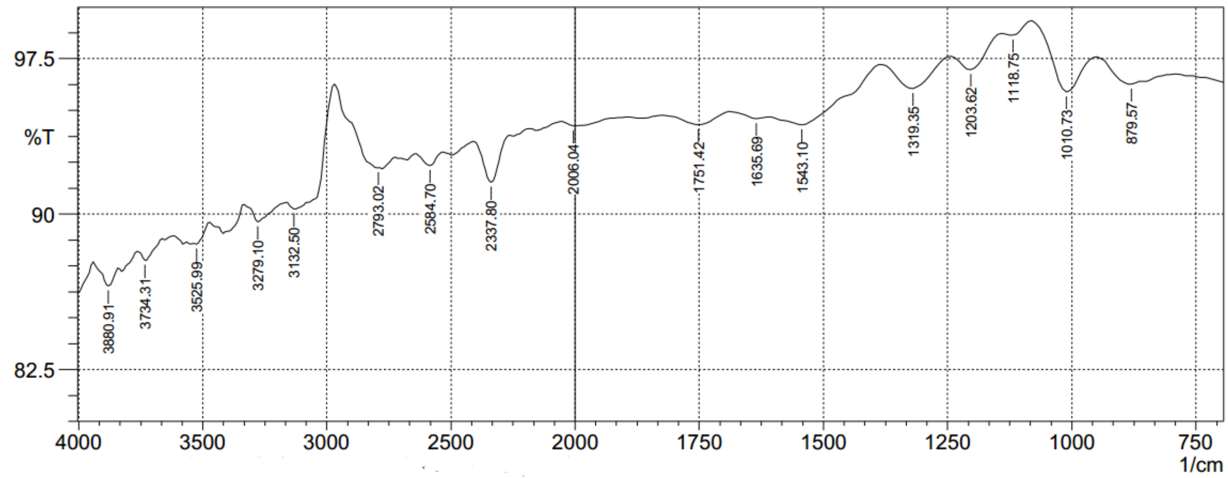

Figure A13: FTIR –spectrum of dye 3C