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Synthesis and spectroscopic studies of some naphthalimide based disperse azo dyestuffs for the dyeing of polyester fibres

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Abstract

A series of monoazo disperse dyestuffs derived from some naphthalimide derivatives were prepared. 4-Amino-*N*-methyl (alternatively *N*-ethyl, *N*-propyl, *N*-butyl) derivatives of naphthalimide were used as the diazo components and β-naphthol, *N*,*N*-diethyl-*m*-toluidine and *p*-aminoacetophenone constituted the coupling components.

The various 4-aminonaphthalimide derivatives mentioned above were all prepared by standard reactions from acenaphthene as the starting material. The reaction conditions were varied in order to obtain optimal yields for each stage of the preparation to obtain the corresponding 4-aminonaphthalimide derivative as the diazo component which was subsequently purified. The coupling components were purchased and were of analytical grade. Diazotisation and coupling reactions were carried out in order to obtain the final dyestuffs. Again maximal yields were sought after and the reaction conditions were varied accordingly.

The final dyestuffs were recrystallised in order to be attained in a purified form. The obtained dyestuffs and their corresponding intermediates were characterized by the use of elemental analysis, DSC, FTIR, H NMR, and UV–visible spectroscopic techniques.

Spectrophotometric investigations of the prepared dyestuffs in different solvents were carried out in order to obtain their absorption maxima, halochromic effects and various intensities. The dyestuffs were finally dyed on polyester fibres in order to investigate their dyeing properties and the obtainable colour gamut.

Keywords: Acenaphthene; 4-Aminonaphthalimide derivatives; Synthesis; Characterization; Disperse dyestuffs; Dyeing

1. Introduction

Pioneering work on naphthalimides and their derivatives has been researched to assess their role as intermediates for dyestuff preparation [1–5].

Other related compounds have also been investigated such as heterocyclic derivatives of naphthalimides, phenylazophthalimides and 1,8-naphthalic anhydrides [6,7]. These compounds have been considered for the preparation of disperse dyestuffs, dyestuffs for other polymer fibres, acid dyestuffs, dyestuffs for polymeric materials and dyestuffs capable of copolymerization.

Naphthalimides have been investigated in a number of ways to examine their use as intermediates for dyes to be applied on both synthetic and natural fibres as well as on other polymeric materials. Derivatives of *N*-methyl-naphthalimidoazobenzene have been utilized to produce a series of disperse dyestuffs in order to compare them with the analogous derivatives of phenylazobenzene by means of UV–visible absorption spectra in DMF [8]. Detailed investigation of the structure and properties of naphthalimide dyestuffs derived from pyrazolone have been carried out. The investigation examined the

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consequences of using the *N*-methyl and sulpho derivatives of aminonaphthalenes, 3- and 4-aminonaphthalimides as diazo components and derivatives of 1-phenyl-3-methylpyrazol-5-one as coupling components [9]. The fluorescent properties of naphthalic derivatives and their anhydrides have been discussed [10].

Aminonaphthalimides are known to produce yellow dyestuffs for synthetic polymer fibres [11]. The earliest industrial use of such compounds was Celliton Brilliant yellow FFACF (C.I. Disperse yellow 11, C.I. 56200), viz *N*-2,4-dimethylphenyl-4-amino-1,8-naphthalimide. Deficiencies in fastness properties, of these dyestuffs especially on polyester fibres, lead to the development of more satisfactory dyestuffs, e.g. derivatives of 7*H*-benzimidazo-[2,1-*a*]-benz-[*d*,*e*]-isoquinolin-7-one [11], naphthalene-1,4,5,8-tetra carboxylic acid [11], benzo-[*k*,*l*]-thioxanthene-3,4-dicarboxylic acid [11].

Phenylazo derivatives of 1,8-naphthalimides giving scarlet to bluish-red hues on synthetic polymer fibres can be obtained [6] by coupling 4-hydroxy-1,8-naphthalimides with diazotised arylamines. Diazotisation of 4-amino-1,8-naphthalimides, optionally substituted in the 3-position by nitro or halogeno groups, and coupling to arylamines will give red to blue disperse dyestuffs [6] and similar coupling to 2,6-dihydroxy-3-cyano-4-methylpyridine affords yellow pigments.

It has been reported [8] that benzeneazonaphthalimide dyestuffs prepared from 4-aminonaphthalimide have a very intense colour due to the polar forms which occur under normal conditions. The proportion of the different forms of the dyestuff structure depends on the type of dialkylamino group in the coupling component. Polyester fibres can be dyed with these dyestuffs to give reddish-blue shades, while the 3-isomers give orange hues.

It has been shown in the last decade investigations [9] that the use of diazo components such as 4-aminonaphthalimides have advantageous effects on the dyeing properties of the derived disperse azo dyestuffs. The presence of the naphthalimide system also leads to a deep and intense colour.

In general, the relationship between the colour and the structure of azo dyestuffs [12] is dependent on the polarization of the molecule, this being the result of the interaction between electron-acceptor and -donor groups at opposite ends of the conjugated bond system.

In the present study a series of the monoazo disperse dyestuffs have been obtained utilizing 4-amino-*N*-methyl (or alternatively, *N*-ethyl, *N*-propyl, *N*-butyl) naphthalimide as the diazo components and β-naphthol, *N*,*N*-diethyl-*m*-toluidine and *p*-aminoacetophenone as the coupling components. To this end, acenaphthene (as the starting material) was nitrated and further reacted by various unit processes such as oxidation, amination, reduction, diazotisation and coupling to obtain synthesized monoazo disperse dyestuffs. The dyestuffs were then purified and characterized together with their corresponding intermediates. The spectrophotometric properties of the prepared disperse dyestuffs in various solvents were examined. The absorption maxima of these dyestuffs, their halochromic effects, and their intensities have also been obtained.

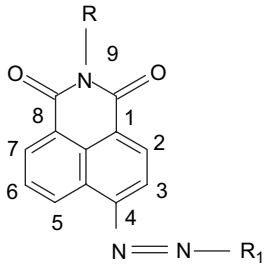

Fig. 1. General formula of the prepared mono azo disperse dyestuff, where R = CH_3, C_2H_5, C_3H_7, C_4H_9; R_1 = β-naphthol, *N*,*N*-diethyl-*m*-toluidine, *p*-aminoacetophenone.

The prepared dyestuffs were subsequently dyed on polyester fibres and finally their optical and dyeing properties; light fastnesses, wash fastnesses and sublimation fastnesses were determined.

General formula of the prepared monoazo disperse dyestuffs is given in Fig. 1.

2. Experimental

2.1. Materials

All compounds used in this study were of analytical grade unless otherwise stated.

2.2. Procedures

(i) Preparation of 5-nitroacenaphthene was carried out by the use of a modified method of Okazaki et al. [13].

(ii) Preparation of 4-nitro-1,8-naphthalic anhydride was carried out according to the method of Okazaki et al. [14].

(iii) Preparation of 4-nitro-*N*-methyl (or alternatively *N*-ethyl, *N*-propyl, or *N*-butyl)-1,8-naphthalimide and the subsequent reduction of the nitro group to an amino group was carried out according to a modified method of Dongwu and Alexiou [15,16].

(iv) The diazotisation of the prepared diazo components (i.e. 4-amino-*N*-methyl, or the alternative *N*-ethyl, *N*-propyl and *N*-butyl derivatives) were carried out by the nitrosylsulphuric acid procedure, and the coupling reaction with β-naphthol, *N*,*N*-dimethyl-*m*-toluidine and aminoacetophenone were carried out according to Peters and Wojciechowski [6,17].