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Synthesis of Benzimidazo-[1,2-*a*]-quinolines: Fluorescent Disperse Dyes

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ABSTRACT

*The paper describes the synthesis of 7-diethylaminobenzimidazo-[1,2-*a*]-quinoline-3-carbonitrile (a highly fluorescent yellow compound) and its reduction to the formyl derivative. Styryl derivatives of the formyl compound gave attractive orange to pink-red dyeings on polyester. Oxidative cyanation of benzimidazo-[1,2-*a*]-quinoline-3-carbonitrile gave the red dinitrile. Absorption–emission spectra of the synthesised dyes were recorded.*

INTRODUCTION

During the course of our research work various heterocyclic fluorophoric systems have been generated to provide access to a range of fluorescent whiteners and fluorescent disperse dyes.[1–5] In this paper we report the synthesis of some fluorescent disperse dyes based on the fused heterocycle benzimidazo-[1,2-*a*]-quinolines.

RESULTS AND DISCUSSIONS

The reaction of a salicylaldehyde derivative (**1**) with benzimidazole-2-acetonitrile (**2**) in the presence of an organic base (Knoevenagel reaction)

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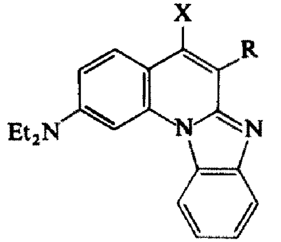
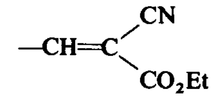
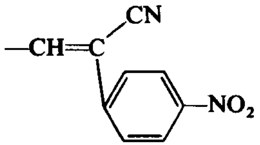
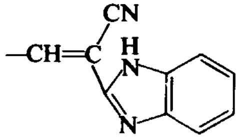
TABLE 1
Physical and Spectral Data



Compound	*R*	*X*	*Molecular formula*	*m.p. (°C)*	*Crystal-lisation solvent*	*Yield (%)*	*Absorption maximum DMF (nm)*	log *E*	*E_m maximum DMF (nm)*	*Solvent*	*PMR data*
10	CN	H	$C_{20}H_{18}N_4$	195	EtOH	75	448	4·6	461	$CDCl_3$	1·3 δ (*t*, 6H, CH_3), 3·2 δ (*q*, 4H, CH_2), 6·5 δ (*d*, 1H, 6-position), 7·0–7·5 δ (*m*, 4H, aromatic), 7·6 δ (*s*, 1H, 3-position), 7·8–7·9 δ (*m*, 2H, 5- and 8-position)
11	CHO	H	$C_{20}H_{19}N_3O$	220	C_6H_6	63	440	4·5	493	$CDCl_3$	1·3 δ (*t*, 6H, CH_3), 3·25 δ (*q*, 4H, CH_2), 6·6 δ (*d*, 1H, 6-position), 7·0–8·1 δ (*m*, 7H, Ar), 8·6 δ (*s*, 1H, CHO)

14	CN	CN	$C_{21}H_{17}N_5$	192–193	PhCl	83	—	4·1	—	—	—
13a	 $-CH{=}C(CN)CO_2Et$	H	$C_{25}H_{24}N_4O_2$	190	PhCl	70	453	4·3	499	$CDCl_3$	1·2 δ (*m*, 9H, CH_3), 3·5 δ (*q*, 4H, CH_2), 4·3 δ (*q*, 2H, CH_2 of ester function), 6·7 δ (*d*, 1H, 6-position), 7·0–8·0 δ (*m*, 6H, Ar), 8·7 δ (*s*, 1H, 4-position), 9·1 δ (*s*, 1H, CH proton)
13b		H	$C_{28}H_{23}N_5O_2$	265	PhCl	78	520	4·6	585 537	TFA	1·0 δ (*t*, 6H, CH_3), 3·5 δ (*q*, 4H, CH_2), 6·5 δ (*s*, 1H, 6-position), 7·2–8·0 δ (*m*, 10H, Ar), 8·5 δ (*s*, 1H, 4-position), 8·7 δ (*s*, 1H, CH)
13c		H	$C_{29}H_{24}N_6$	222	PhCl/DMF	82	512	3·9	550	—	—

All compounds gave satisfactory elemental analysis.

gives the coumarin derivative (**4**). This reaction proceeds via the intermediate *o*-hydroxy styryl derivative (**3**), the hydroxyl group of which cyclises on the nitrile function under the reaction conditions to yield 7-diethylamino-3-benzimidazolyl coumarin (**4**). A patent[6] describes the reaction of 2-methoxy benzaldehydes (**5**) with benzimidazole-2-acetonitrile (**2**) followed by subsequent cyclisation of the resulting styryl derivatives (**6**) to obtain benzimidazo-[1,2-*a*]-quinolines (**7**), which are reported to be fluorescent brighteners for polyesters. It was therefore thought interesting to react 4-diethylamino-2-methoxybenzaldehyde (**8**) with benzimidazole-2-acetonitrile (**2**) and then to effect cyclisation of the —NH function of the imidazole ring on the carbon carrying the methoxyl group, thus giving 7-diethylaminobenzimidazo-[1,2-*a*]-quinoline-3-carbonitrile (**10**). Such a compound would be expected to possess good fluorescence due to the conjugation between the diethylamino function and the nitrile group at the 3-position.

Thus the reaction of 4-diethylamino-2-methoxybenzaldehyde (**8**) with benzimidazole-2-acetonitrile (**2**) gave the intermediate (**9**) in good yields. The subsequent cyclisation of this compound (**9**) at high temperature in *o*-dichlorobenzene in the presence of piperidine acetate as catalyst gave a highly fluorescent yellow compound. The structure of this compound was established as **10** by its elemental analysis, mass spectrum (M^+ at $M/e = 314$), IR spectrum (2220 cm^{-1}—CN) and its PMR spectrum (absence of OCH_3 protons indicating cyclisation). The tetracyclic compound (**10**) showed intense fluorescence and gave a greenish yellow fluorescent dyeing on polyester.

In order to extend the range of compounds of this type, it seemed feasible to reduce the nitrile group to the aldehyde, thus providing access to the styryl dyes (**13**). Reduction of 7-diethylamino-benzimidazo-[1,2-*a*]-quinoline-3-carbonitrile (**10**) using the Raney Ni–formic acid method[7] at reflux gave satisfactory yields of the formyl derivative (**11**). The structure of **11** was based on its elemental analysis, IR spectrum (absence of nitrile absorption at CN, presence of carbonyl peak at 1670 cm^{-1}), PMR spectrum (see Table 1) and its chemical properties (reaction with 2,4-dinitrophenyl-hydrazine to yield the hydrazone). Compound **11** was reacted with ethyl cyanoacetate, 4-nitrobenzylcyanide and with benzimidazole-2-acetonitrile to yield the respective styryl dyes (**13a–c**) in good yields. These were orange to red compounds giving fluorescent dyeings on polyester. The structures of styryl derivatives **13a–c** were based on their elemental analysis, IR spectrum (CN—2220 cm^{-1}) and their PMR spectrum (see Table 1).

It has been shown[8] that 3-substituted coumarins undergo oxidative cyanation at the 4-position, providing a strong bathochromic shift without much increase in the molecular weight. In an earlier communication[5] we have reported on an extension of this concept. It was anticipated that compound **10** would also behave analogously, leading to the dicyano compound **14**. The cyanation of **10** according to the usual procedure (NaCN–DMF, Br_2) gave the deep red compound **14**. However, 7-diethylamino benzimidazo-[1,2-*a*]-quinoline-3,4-dicarbonitrile (**14**) did not behave efficiently as a dyestuff for polyester due to its instability under the high-temperature dyeing conditions. Table 1 gives the absorption–emission data of the synthesised compounds. Though the styryl derivatives **13a–c** showed good fluorescence properties and gave attractive orange to pink red shades on polyester, fastness to light and sublimation were generally poor.

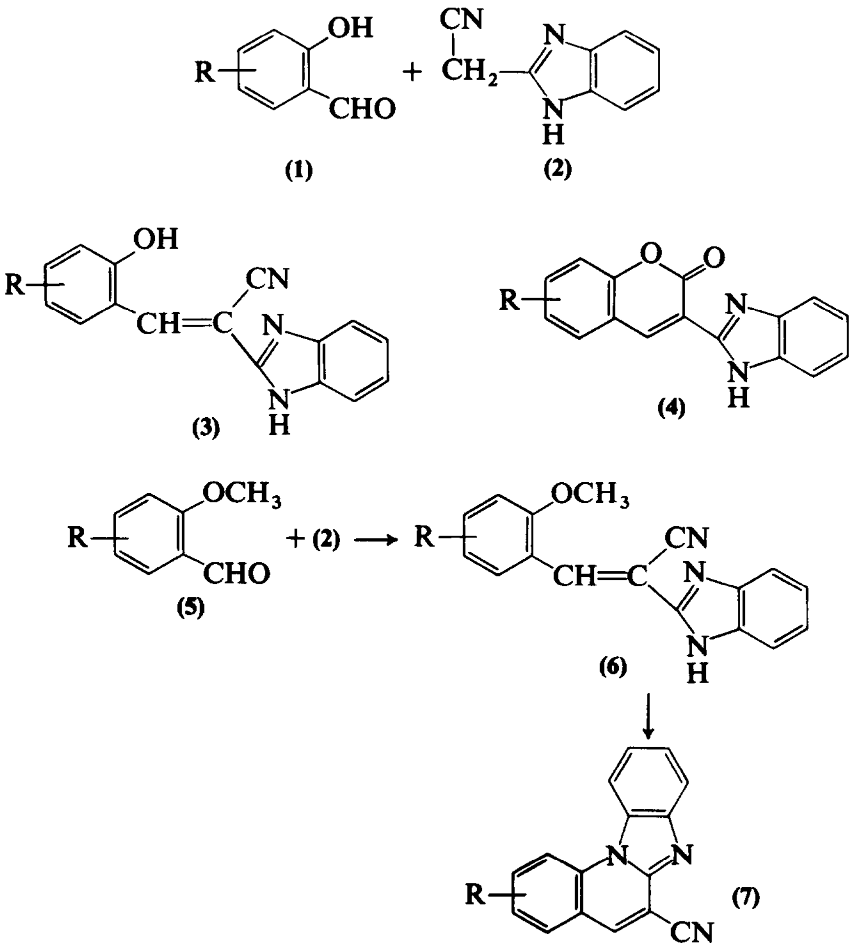


Chart 1

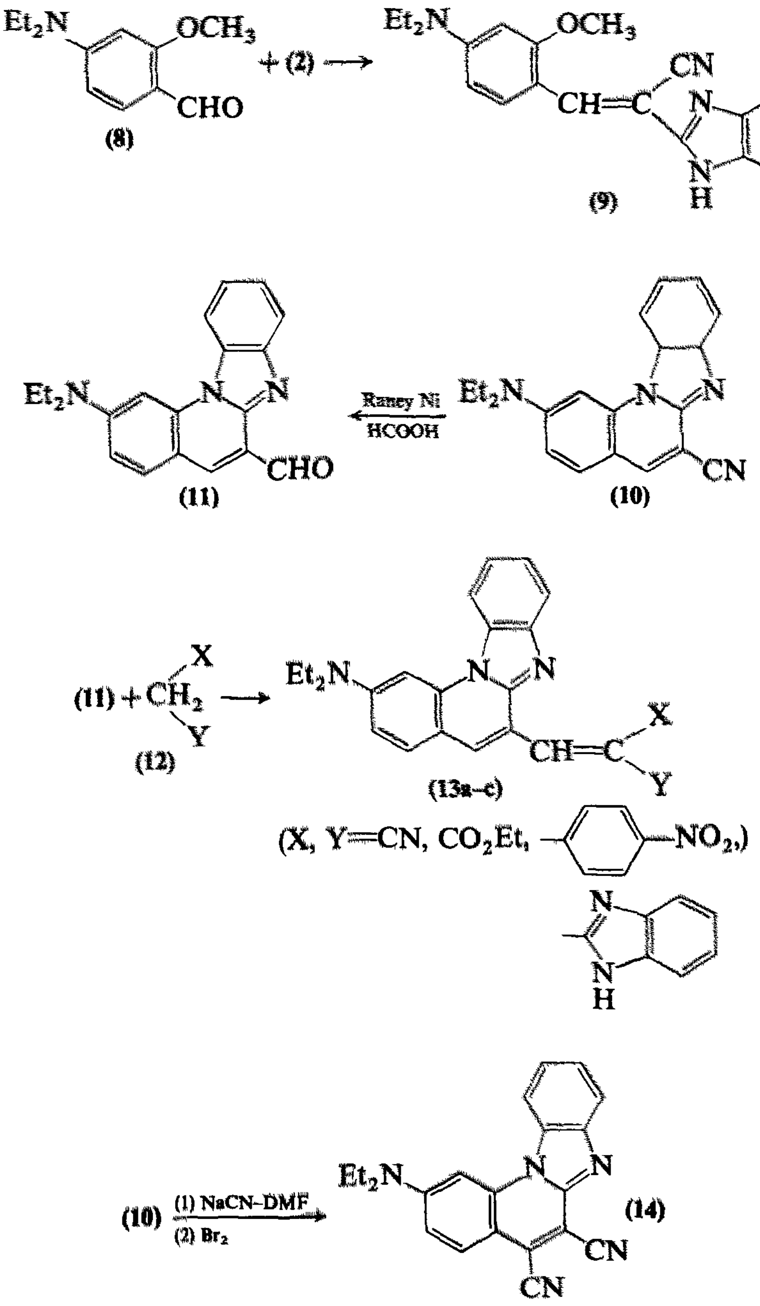

Et$_2$N
OCH$_3$
CHO
(8)
+ (2)
CN
CH=C
N
N
H
(9)
Raney Ni
HCOOH
(11)
CHO
(10)
CN
(11) + CH$_2$
X
Y
(12)
(13a–c)
CH=C
(X, Y=CN, CO$_2$Et, NO$_2$,)
(10)
(1) NaCN–DMF
(2) Br$_2$
(14)

Chart 2

EXPERIMENTAL PROCEDURE

All melting points are uncorrected. Infra-red spectra were recorded in Nujol mull on a Perkin–Elmer 397 spectrophotometer, PMR spectra on a Varian EM-360L spectrophotometer using TMS as internal standard and mass spectra on a Varian Mat CH-7 spectrometer.

4-Nitrobenzylcyanide,[9] benzimidazole-2-acetonitrile (**2**),[10] 4-diethylaminosalicylaldehyde (**1**—R = NEt_2)[11] were prepared by the usual methods. The reaction of 4-diethylaminosalicylaldehyde with dimethyl sulphate in alkali (10%) using standard methylation procedures at 40–50°C gave 4-diethylamino-2-methoxy benzaldehyde (**8**), m.p. 85°C, in 85% yield.

Preparation of styryl derivative (9) from 4-diethylamino-2-methoxy benzaldehyde (8) and benzimidazole-2-acetonitrile (2)

A solution of 4-diethylamino-2-methoxybenzaldehyde (**8**) (4·14 g, 0·02 mol) and benzimidazole-2-acetonitrile (**2**) (3·14 g, 0·02 mol) in ethanol (15 ml) was refluxed in the presence of piperidine (0·1 ml) for 1 h. The crystalline yellow product which separated on cooling was filtered, washed with ethanol and dried. Yield of the styryl derivative (**9**) was 6·0 g (85%), m.p. 248–250°C (chlorobenzene).

Preparation of 7-diethylamino-benzimidazo-[1,2-*a*]-quinoline-3-carbonitrile (10)

*Cyclisation of **9***

To a suspension of **9** (3·6 g, 0·01 mol) in *o*-dichlorobenzene (10 ml) was added piperidine (1 ml) followed by acetic acid (0·5 ml). The reaction mixture was refluxed for 4–5 h (until the starting material was absent on TLC). The clear solution was cooled to room temperature and to it was added petroleum ether (60–80°C) (25 ml) to precipitate the product, which was filtered and dried. Yield of **10** was 2·5 g (75%), m.p. 195°C (ethanol); the IR spectrum showed absorption at 2220 cm^{-1} (CN). The PMR spectrum (Table 1) was in agreement with the assigned structure **10**.

Preparation of 7-diethylamino-benzimidazo-[1,2-*a*]-quinoline-3-carboxaldehyde (11)

*Reduction of **10***

To a stirred solution of **10** (3·32 g, 0·01 mol) in formic acid (5 ml, 85%) and water (10 ml) at 95–100°C was gradually added Raney Ni alloy (50:50) (10 g). The solution was stirred at this temperature for 0·5 h until the nitrile was absent (TLC). The hot solution was filtered and the Ni residue washed with hot water. The filtrate was cooled to room temperature and neutralised (pH 7) with dilute sodium hydroxide solution (10%). The sticky residue obtained was separated from the supernatant liquid and was washed with a little water by decantation and it solidified to a filterable solid on keeping overnight in water. The orange-yellow compound was filtered, washed with water, dried and recrystallised from benzene. Yield of **11** was 2·0 g (63%), m.p. 220°C; the IR spectrum showed absorption at 1670 cm^{-1} (—CHO) and absence of a peak at 2220 cm^{-1} (CN). The aldehyde was further characterised by its PMR spectrum (low field signal at 8·6, —CHO proton) and its reaction with active methylene compounds (**12**) to give the styryl derivatives (**13**).

Preparation of styryl dyes (13a–c) from 7-diethylaminobenzimidazo-[1,2-*a*]-quinoline-3-carboxaldehyde (11)

To a solution of the aldehyde (**11**) (3·17 g, 0·01 mol) in ethanol (10 ml) was added the appropriate active methylene compound (**12a–c**). The reaction mixture was refluxed for 2 h and the crystalline styryl derivatives (**13a–c**) which separated on cooling were filtered, washed with ethanol and dried. The yields, molecular formula, m.p., crystallisation solvents and the PMR spectrum of the derivatives are given in Table 1, which also gives the absorption–emission data of the dyes.

Preparation of 7-diethylamino-benzimidazo-[1,2-*a*]-quinoline-3,4-dicarbonitrile (14)

*Cyanation of **10***

To a suspension of 7-diethylaminobenzimidazo-[1,2-*a*]-quinoline-3-carbonitrile (**10**) (3·3 g, 0·01 mol) in dimethylformamide (10 ml) was added finely powdered sodium cyanide (1·4 g, 0·02 mol). A clear solution resulted on stirring at room temperature for 1 h, after which the reaction mixture was cooled to 0–5°C in an ice–salt bath and bromine (1·6 g, 0·01 mol) was added. The oxidation was then completed at room temperature (0·5 h). The cyanated red product (**14**) was isolated by adding to water. Yield was 3·0 g (83%), m.p. 192–193°C (PhCl); the IR spectrum showed absorption at 2220 cm^{-1} (CN). Details are given in Table 1.

ACKNOWLEDGEMENT

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