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Synthesis of New Fluorescent Dyes from 6-Methoxy-1-chloro-3,4-Dihydronaphthalene-2-Carboxaldehyde*

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ABSTRACT

The synthetic utility of the Vilsmeier reagent to generate new precursors for condensed heterocycles has been extended to the synthesis of some new fluorescent compounds. 6-Methoxy-1-chloro-3,4-dihydronaphthalene-2-carboxaldehyde was used to synthesise new benzimidazo-[1,2-a]-quinolines, quinazolines, thienylbenzimidazole, benzo-[h]-quinolines, benz-[g]-indazoles and isothiazole derivatives. The efficacy of the aldehyde derivative was further extended to synthesise strongly fluorescent pyrano, imino-thiopyrano and exocyclic dicyano derivatives. The compounds were characterised by IR, ^{1}H-NMR and visible absorption–emission spectra; they were also applied to polyester as fluorescent dyes and their properties evaluated.

INTRODUCTION

The Vilsmeier reaction has been extensively utilised to generate a variety of precursors for the synthesis of condensed heterocycles, and a large number of fluorescent coumarin and quinoline derivatives for polyester and polyamide have thus been prepared.

The application of the Vilsmeier reaction has been extended to arylmethyl ketones,[1] lactams[2] and acetanilides,[2] to prepare the respective chloraldehydes, which were subsequently reacted with various bifunctional derivatives to give new heterocyclic systems.

* Abstracted in part from the PhD Tech. thesis of R. Rajagopal, University of Bombay, India, 1989.

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This paper describes the utility of the chloroaldehyde, 6-methoxy-1-chloro-2-formyl-3,4-dihydronaphthalene (**1**), in the synthesis of a number of new heterocyclic derivatives.

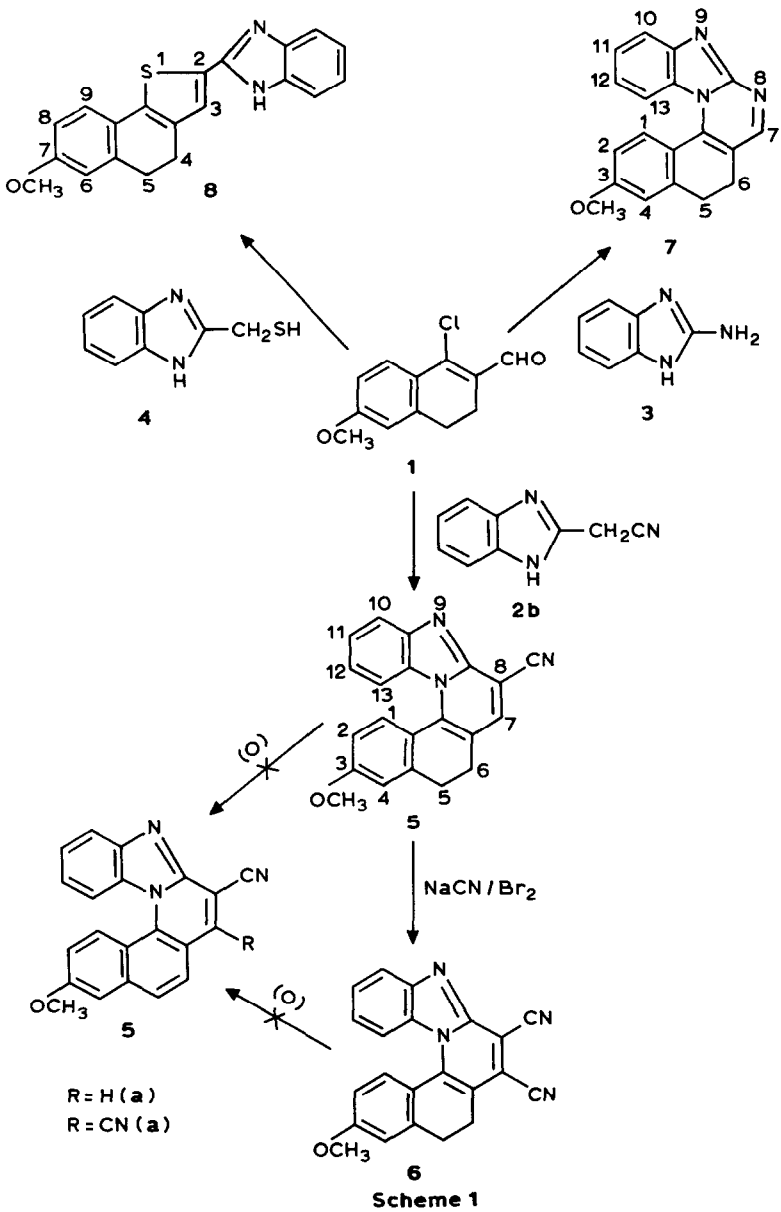
RESULTS AND DISCUSSIONS

Vilsmeier reaction of 6-methoxy-1-tetralone yielded **1**.[3] Reaction with benzimidazo-2-acetonitrile (**2b**) in dimethylformamide yielded the benzimidazo-[1,2-*a*]-benzo-[*h*]-quinoline derivative, **5**, which exhibited a greenish-yellow fluorescence and gave brilliant-yellow shades on polyester (Scheme 1). Moeckli[4] has reported the cyanation at the 4-position of coumarin derivatives containing an electron-withdrawing group at the 3-position. The condensed derivative **5**, which contains the cyano group, is related to the 3-cyano coumarins and was thus expected to undergo nucleophilic attack by the cyanide ion. Gokhale and Seshadri[1] have previously reported the cyanation of similar bezimidazo quinoline derivatives.

Cyanation of **5** was carried out by treatment with sodium cyanide and then with bromine at low temperature. The dicyano derivative isolated, **6**, was characterised by IR and ^{1}H-NMR spectra, the latter not showing the low field proton singlet at δ 8·1 (C-7) because of the cyanation at that position. It exhibited a greenish-yellow fluorescence and dyed polyester in bright yellow-orange shade. Physical and spectral data of compounds **5** and **6** are given in Table 1.

Oxidation of the nitrile derivative, **5**, and of the dinitrile derivative, **6** to the naphthalene derivatives, **5a** and **6a**, could not be effected under the usual conditions for this reaction. Reaction of **1** with 2-aminobenzimidazole (**3**) under basic conditions yielded the benzimidazo-[1,2-*a*]-benzo-[*h*]-quinazoline derivative, **7**, which was characterised by IR and ^{1}N-NMR spectra; the low field proton at δ 8·6 (C-7) is due to the protonation of the benzimidazolyl nitrogen atom when trifluoracetic acid was used with $CDCl_3$ as solvent. A new synthesis of benzimidazolyl-thieno derivative was effected, starting from 2-chloromethyl-1*H*-benzimidazole, which was prepared from *o*-phenylenediamine and monochloracetic acid. This was then converted to 2-mercaptomethyl-1*H*-benzimidazole (**4**), which offered a new route to the benzimidazolyl-thieno derivative. Reaction of **1** with **4** in dimethylformamide under basic conditions yielded the 2-thienylbenzimidazole derivative, **8**. Characterisation data of compounds **7** and **8** are given in Table 1.

The chloroaldehyde, **1**, was reacted with cyanoacetamide (**2e**) and cyanoacetanilide (**2c**) to yield the respective benzo-[*h*]-quinoline derivatives,



Scheme 1

9a and **9b** (Scheme 2). The isothiazole derivative, **10**, was prepared by reacting **1** with sulphur and aqueous ammonium in dimethylformamide, and the fused indazole derivatives, **12a** and **12b**, were prepared by reacting **1** with arylhydrazines (**11a** and **11b**). Characterisation data of these compounds are given in Table 1.

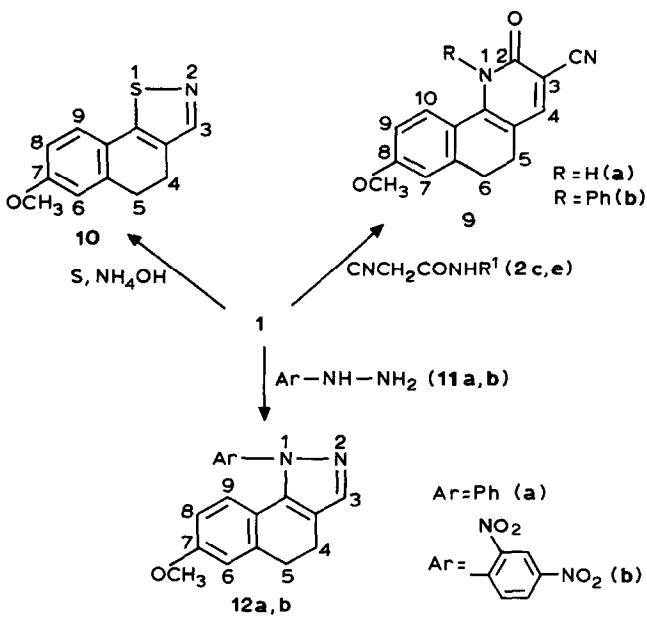
Newer synthetic routes to pyrano- and imino-thiopyrano derivatives were

TABLE 1
Physical and Spectral Data of Compounds

Compound	*Molecular formula*[a]	*Melting point* (°C)	*Yield* (%)	*Visible absorption–emission data*[b]			^{1}*H-NMR spectral data*[c]
				Absorption max (*nm*)	(*log* ε)	*Emission max* (*nm*)	
5	$C_{21}H_{12}N_3O$	212[d]	65	438	4·1	516	2·7 [s, 4H, —$(CH_2)_2$]; 3·7 [s, 3H, —OCH_3]; 6·5 [d, 1H, C-2]; 6·7 [s, 1H, C-4]; 6·9–7·3 [m, 3H, C-10, 11, 12]; 7·6 [d, 2H, C-1, 13]; 7·9 [s, 1H, C-7]
6	$C_{22}H_{11}N_4O$	225[d]	50	440	4·3	462	2·8 [s, 4H, —$(CH_2)_2$]; 3·8 [s, 3H, —OCH_3]; 6·6 [d, 1H, C-2]; 6·7 [s, 1H, C-4]; 7·0–7·4 [m, 2H, C-10, 11, 12]; 7·7 [d, 2H, C-1, 13]
7	$C_{19}H_{15}N_3O$	215[d]	45	320	4·0	410	3·0 [s, 4H, —$(CH_2)_2$]; 4·0 [s, 3H, —OCH_3]; 6·8 [d, 1H, C-2]; 6·95 [s, 1H, C-4]; 7·1–7·5 [m, 3H, C-10, 11, 12]; 7·9 [d, 2H, C-1, 13]; 8·2 [s, 1H, C-7]

8	$C_{20}H_{16}N_2OS$	190[d]	40	380	3·9	436	2·9 [s, 4H, —$(CH_2)_2$]; 3·9 (s, 3H, —OCH_3]; 6·7 [d, 2H, C-6, 8]; 7·2–8·0 [m, 5H, C-9 and four aromatic protons of benzimidazolyl ring]; 8·1 [s, 1H, C-3]
9a	$C_{15}H_{12}N_2O_2$	285[d]	80	404	4·2	460	2·8 [s, 4H, —$(CH_2)_2$]; 3·8 [s, 3H, —OCH_3]; 6.7 [d, 2H, C-7, 9]; 7·6 [d, 2H, C-10 and one —NH proton]; 8·3 [s, 1H, C-4]
9b	$C_{21}H_{16}N_2O_2$	223[d]	55	396	3·9	500	—
10	$C_{12}H_{11}NSO$	85[e]	45	320	3·9	430	—
12a	$C_{18}H_{16}N_2O$	155[d]	55	410	4·1	480	—
12b	$C_{18}H_{14}N_4O_5$	206[d]	70	412	4·5	436	2·8 [s, 4H, —$(CH_2)_2$]; 3·8 [s, 3H, —OCH_3]; 6·6 [d, 2H, C-6, 8]; 7·4–7·7 [d, 2H, C-9 and one aromatic proton]; 8·9 [d, 1H *ortho* to —NO_2]; 8·4 [s, 1H, C-3]; 8·9 (s, 1H, and on aromatic proton between —NO_2 groups)

[a] All components showed satisfactory elemental analysis ±0·3%.
[b] Methanol.
[c] $CDCl_3$ and trifluoracetic acid.
[d] Solvent of crystallisation: dimethylformamide.
[e] Solvent of crystallisation: dimethylformamide–ethanol.



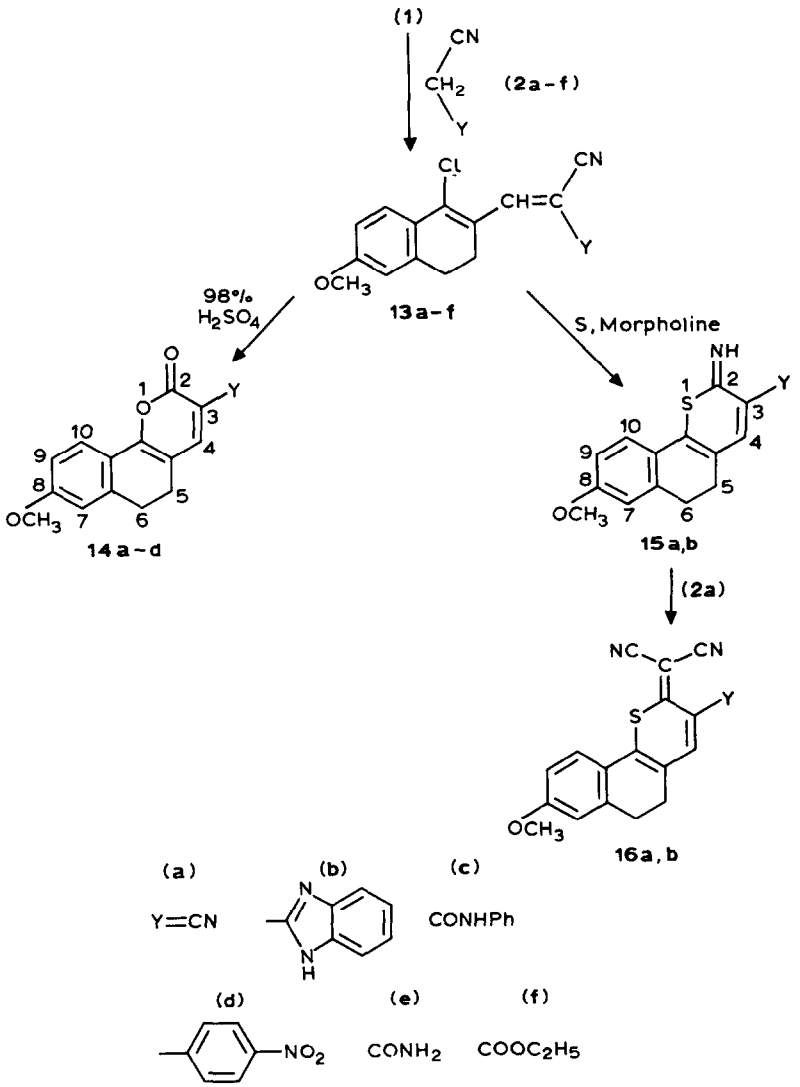
Scheme 2

attempted, starting from the methylene derivatives, **13a–f** (Scheme 3). Thus, reaction of **1** with various acetonitrile derivatives (**2a–f**) gave the respective methylene derivatives (**13a–f**), characterisation data of which are given in Table 2.

The derivatives **13a–d** were treated with concentrated sulphuric acid to effect hydrolysis of the chloro group and subsequent cyclisation to the pyrano derivatives, **14a–d**, which showed a greenish-yellow fluorescence in daylight. Characterisation data of the pyrano derivatives are given in Table 3.

A new route to the synthesis of imino-thiopyrano derivatives from the methylene derivatives involved reaction of **13a–b** with sulphur and morpholine in ethanol to yield the imino-thiopyrano derivatives, **15a–b**. These were characterised by IR and ^{1}H-NMR; the low field singlet at δ 8·9 (C-4) could be due to protonation of the imino nitrogen atom in the presence of trifluoracetic acid. Reaction of the imino coumarin with malononitrile (**2a**) to give the exocyclic dicyano derivatives, **16a** and **16b**, has been studied by Wolfgang and Horst.[5] On this basis, reaction of the imino-thiopyrano derivatives, **15a** and **15b**, with **2a** under non-basic conditions gave **16a** and **16b**. Characterisation data of the imino-thiopyrano derivatives and the exocyclic dicyano derivatives are given in Table 3.

The fluorescent derivatives were applied to polyester using high-



Scheme 3

temperature dyeing techniques. The benzimidazo-[1,2-*a*]-quinoline derivatives, **5** and **6**, gave dyeings with good light-fastness (4–5), pick-up (4) and sublimation-fastness (3). The benz-[*g*]-indazole, **12b**, and the methylene derivatives, **13a–f**, had moderate dyeing properties. The other compounds gave dyeings, having poor light- and sublimation-fastness. Relevant data is shown in Table 4.

TABLE 2
Physical and Spectral Data of Methylene Derivatives (**13a–f**)

Compound	*Molecular formula*[a]	*Melting point* (°C)	*Yield* (%)	*Visible absorption–emission data*[b]			^{1}*H-NMR spectral data*[c]
				Absorption max (nm)	(*log ε*)	*Emission max (nm)*	
13a	$C_{15}H_{11}N_2OCl$	198[d]	60	424	4·3	—	—
13b	$C_{21}H_{16}N_3OCl$	140[d]	50	440	4·2	—	2·9 [s, 4H, —$(CH_2)_2$]; 3·9 [s, 3H, —OCH_3]; 6·75 [d, 2H, C-5, 7]; 7·6–8·3 [—, 5H, C-8 and 4H of benzimidazolyl ring]; 8·85 [s, 1H, C-3]
13c	$C_{21}H_{17}N_2O_2Cl$	170[e]	60	380	4·1	—	—
13d	$C_{20}H_{16}N_2O_3Cl$	240[d]	68	410	4·0	—	—
13e	$C_{15}H_{13}N_2O_2Cl$	168[d]	68	410	4·0	—	—
13f	$C_{17}H_{16}NO_3Cl$	148[e]	555	416	4·6	—	—

[a] All compounds showed satisfactory elemental anslysis ±0·3%.
[b] Methanol.
[c] $CDCl_3$ and trifluoracetic acid.
[d] Solvent of crystallisation: dimethylformamide.
[e] Solvent of crystallisation: dimethylformamide–ethanol.

TABLE 3

Physical and Spectral Data of Pyrano, Imino-Thiopyrano and Exocyclic-Dicyano Compounds

Compound	*Molecular formula*[a]	*Melting point* (°C)	*Yield* (%)	*Visible absorption–emission data*[b]			^{1}*H-NMR spectral data*[c]
				Absorption max (nm)	*(log)*	*Emission max (nm)*	
14a	$C_{15}H_{13}NO_3$	320[d]	45	430	3·9	470	—
14b	$C_{21}H_{16}N_2O_3$	275[d]	35	440	3·8	500	2·9 [s, 4H, —$(CH_2)_2$]; 3·9 [s, 3H, —OCH_3]; 6·7 [d, C-7, 9]; 7·3–7·9 [m, 5H, C-10 and 4H of benzimidazolyl ring]; 8·1 [s, 1H, C-4]
14c	$C_{21}H_{17}NO_4$	295[d]	30	420	3·9	450	—
14d	$C_{20}H_{16}NO_5$	305[d]	48	428	4·5	446	—
15a	$C_{15}H_{12}N_2SO$	120[e]	50	416	4·1	490	—
15b	$C_{21}H_{17}N_3SO$	202[d]	40	430	3·9	528	2·9 [s, 4H, —$(CH_2)_2$]; 3·9 [s, 3H, —OCH_3]; 6·7 [d, 2H, C-7, 9]; 7·2–8·2 (—, 5H, C-10 and 4H of benzimidazolyl ring]; 8·7 (s, 1H, C-4]
16a	$C_{18}H_{11}N_3SO$	260[f]	42	390	4·0	450	—
16b	$C_{24}H_{16}N_4SO$	310[f]	55	472	4·2	510	—

[a] All compounds showed satisfactory analysis ±0·3%.
[b] Methanol
[c] $CDCl_3$ and trifluoracetic acid.
[d] Solvent of crystallisation: dimethylformamide.
[e] Solvent crystallisation: dimethylformamide–ethanol.
[f] Solvent of crystallisation: chlorobenzene.

TABLE 4
Dyeing Evaluation Data

Compound	*Light-fastness*	*Sublimation-fastness*	*Pick-up*	*Shade on polyester*[a]
5	5	2–3	4	Bright yellow
6	4	2–3	4	Yellowish orange
7[b]	1	2	1	Pale yellow
8[b]	1	1–2	1	Pale yellow
9a	2	4–5	1	Lemon yellow
9b	1	4	1–2	Pale yellow
10[b]	1	2	1	Pale brown
12a	1–2	3	1	Yellow
12b	3	2–3	4	Bright orange
13a	2–3	1–2	2	Bright yellow
13b	1–2	2–3	2	Bright yellow
13c	1–2	2–3	2	Bright yellow
13d	2	1–2	2	Bright yellowish orange
13e	1	1–2	2	Lemon yellow
13f	1	1	2	Lemon yellow
14a	1–2	2	1	Pale yellow
14b[b]	1–2	2–3	1	Yellowish orange
14c[b]	1	2	1	Yellow
14d	2	2	4	Bright yellow
15a	1	2–3	2	Creamish yellow
15b	1	2–3	2	Orange
16a	1	4	1	Pale reddish brown
16b	1	3–4	1	Brown

[a] Dyed by high-temperature high-pressure (HTHP) method.
[b] Compounds **7**, **8**, **10**, **14b** and **14c** underwent partial decomposition during HTHP dyeing.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 397 spectrophotometer in Nujol mull, visible absorption–emission spectra on a Kontron spectrophotometer, fluorescence spectra on an Aminco Bowman spectrophotofluorimeter and ^{1}H-NMR spectra on a Varian EM 360 L spectrophotometer using tetramethylsilane as external standard.

6-Methoxy-1-chloro-2-formyl-3,4-dihydronaphthalene (**1**),[3] benzimidazo-2-acetonitrile (**2b**),[6] 2-aminobenzimidazole (**3**),[7] 2-mercaptomethyl-benzimidazole (**4**),[8] cyanoacetamide (**2e**),[9] cyanacetanilide (**2c**)[10] and *p*-nitrobenzyl-cyanide (**2d**)[11] were prepared according to reported methods; malononitrile (**2a**) was a commercial sample.

*5,6-dihydro-3-methoxybenzimidazo-[1,2-*a*]-benzo-[*h*]quinoline-8-carbonitrile (***5***), 5,6-dihydro-3-methoxybenzimidazo-[1,2-*a*]-benzo-[*h*]-quinazoline (***7***) and 2-(4,5-dihydro-7-methoxynaphtho-[1,2-*b*]-thien-2-yl)-1*H*-benzimidazole (***8***).* A mixture of the chloraldehyde, **1** (1·11 g, 0·005 mol), and the appropriate 2-substituted benzimidazole derivative (**2b**, **3** or **4**; 0·005 mol) was refluxed in dimethylformamide (6 ml) in presence of pyridine (0·005 mol) for 4 h. After cooling and diluting with ethanol (5 ml), solid products precipitated. These were filtered and recrystallised from a dimethylformamide–ethanol mixture. Characterisation data of the compounds are given in Table 1.

*5,6-dihydro-3-methoxybenzimidazo-[1,2-*a*]-benzo-[*h*]-quinoline-7,8-dicarbonitrile (***6***).* Sodium cyanide (0·049 g, 0·001 mol) was added at 20°C to a solution of **5** (0·32 g, 0·001 mol) in dimethylformamide (3 ml). The reaction mixture was stirred at 20°C for 1 h, the temperature then lowered to 5°C and bromine (0·05 ml, 0·001 mol) added slowly. The mixture was allowed to stand at room temperature for 4 h before quenching into ice–water mixture (20 ml). The orange product was filtered, washed with ethanol and recrystallised from dimethylformamide. Characterisation data of the compound are given in Table 1.

*1,2,5,6-tetrahydro-8-methoxy-2-oxobenzo-[*h*]-quinoline-3-carbonitrile (***9a***) and 1,2,5,6-tetrahydro-8-methoxy-2-oxo-1-phenylbenzo-[*h*]-quinoline-3-carbonitrile (***9b***).* A mixture of **1** (0·001 mol) and **2e** or **2c** (0·001 mol) was refluxed in dimethylformamide) (5 ml) in the presence of pyridine (0.001 mol) for 3 h. On cooling, the solid was filtered and recrystallised from dimethylformamide. Characterisation data are given in Table 1.

*4,5-dihydro-7-methoxynaphth-[2,1-*d*]-isothiazole (***10***).* A mixture of **1** (1·11 g, 0·005 mol), sulphur (0·32 g, 0·01 mol) and 25% aqueous ammonium hydroxide (10 ml) was stirred in dimethylformamide (10 ml) at 70°C for 5 h. The reaction mixture was filtered hot, run into ice-cold hydrochloric acid, the pH adjusted to 7 and the red solid filtered and crystallised from alcohol. Characterisation data are given in Table 1.

*4,5-dihydro-7-methoxy-1-phenyl-1*H*-benz-[*g*]-indazole (***12a***) and 1-(2,4-dinitrophenyl)-4,5-dihydro-7-methoxy-1*H*-benz-[*g*]-indazole (***12b***).* A mixture of **1** (0·001 mol) and the appropriate arylhydrazine derivative, **11a** or **11b** (0·001 mol), was refluxed in dimethylformamide or ethanol in presence of acetic acid as catalyst for 3 h. On cooling, the products were filtered, washed ethanol, and recrystallised from dimethylformamide. Characterisation data are given in Table 1.

*(1-chloro-3,4-dihydro-6-methoxy-2-naphthalenyl)-methylene derivatives (***13a–f***).* A mixture of **1** (0·001 mol) and the respective acetonitrile derivative (**2a–f**; 0·001 mol) was refluxed in ethanol (10 ml) in the presence of piperidine.

The products which separated were filtered and recrystallised from a suitable solvent. Characterisation data are given in Table 2.

*5,6-dihydro-8-methoxy-2*H*-naphtho-[1,2-*b*]-pyran-2-one derivatives (***14a–d***).* The respective methylene derivative (**13a–d**; 0·001 mol) was treated with 98% sulphuric acid at 100–110°C for 3 h. The reaction mixture was then run into ice-cold water (25 ml) and the products filtered, washed free of acid, dried and recrystallised from dimethylformamide. Characterisation data are given in Table 3.

*5,6-dihydro-2-imino-8-methoxy-2*H*-naphtho-[1,2-*b*]-thiopyran-3-carbonitrile (***15a***) and 2-(5,6-dihydro-2-imino-8-methoxy-2*H*-naphtho-[1,2-*b*]-thiopyran-3-yl)-benzimidazole (***15b***).* A mixture of the appropriate methylene derivative (**13a** or **13b**); 0·001 mol), sulphur (0·001 mol) and morpholine (0·002 mol) was refluxed in ethanol (10 ml) for 4 h. The reaction mixture was then filtered hot and run into ice-cold hydrochloric-acid solution. The products were filtered, washed free of acid, dried and recrystallised from a suitable solvent. Characterisation data are given in Table 3.

*3-cyano-5,6-dihydro-8-methoxy-2*H*-naphtho-[1,2-*b*]-thiopyran-$\Delta^{2,\alpha}$-malononitrile (***16a***) and 3-(2-benzimidazolyl)-5,6-dihydro-8-methoxy-2*H*-naphtho-[1,2-*b*]-thiopyranmalononitrile (***16b***).* The appropriate imino-thiopyrano derivatives (**15a** or **15b**; 0·001 mol) was refluxed in dimethylformamide (5 ml) with **2a** (0·001 mol) for 4 h. The products were filtered, washed with ethanol and recrystallised from a suitable solvent. Characterisation data are given in Table 3.

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