Dyes and Pigments 3 (1982) 317–324

DISPERSE DYES DERIVED BY THE CONDENSATION OF HOMOPHTHALIMIDES AND 2-PYRIDONES WITH NAPHTHOSTYRIL AND ISATIN

N. R. AYYANGAR, R. J. LAHOTI and S. R. OTIV

National Chemical Laboratory, Pune 411008, India

(Received: 17 November, 1981)

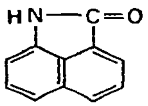
SUMMARY

Naphthostyril (1) *and isatin* (2) *were condensed with* N-*substituted homophthalimides* (4) *in the presence of phosphorus oxychloride to give violet to bluish violet disperse dyes* (5) *and* (7′), *which could be applied to polyester fibre. Similarly violet disperse dyes were obtained by the condensation of* N-*substituted 2-pyridones with isatin in the presence of phosphorus oxychloride. The spectroscopic properties in relation to the structural features of the dyes are discussed.*

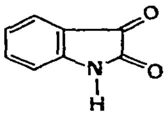
1. INTRODUCTION

Several patents describe cationic and disperse dyes derived from 1,8-naphtholactam, better known as naphthostyril (1).[1-6] It is generally converted into the 8-chloro derivative (3) by reacting with phosphorus oxychloride and then condensing with primary arylamines, compounds containing a reactive methylene group or other similar suitable intermediates. Thus reddish yellow dyes are obtained by the condensation of (3) with 2-aminobenzothiazole or benzoxazole-2-acetamide.[5,7] Its condensation with 6-methoxythioindoxyl results in a red dye[8] and with 2-cyano-4-nitroaniline it yields a brilliant yellow dye.[2] The condensation product of (1) with ethyl 5-pyrazolone-3-carboxylate has been reported in the *Colour Index* as C.I. Disperse Red 196 (C.I. 48310). It has good fastness properties. We have previously reported the synthesis of disperse dyes by the condensation of (1) with *N*-substituted 2-pyridone derivatives[9] to give reddish violet dyeings on polyester fibre. The shades were comparable with the one produced by using a 1:1 mixture of Resolin Red Violet FBL and Resolin Violet RL (C.I. Disperse Violets 31 and 28 respectively).

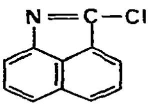
Dyes and Pigments 0143-7208/82/0003-0317/$02·75
Printed in Great Britain



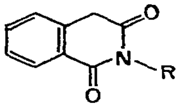
(1)



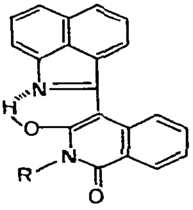
(2)



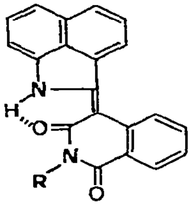
(3)



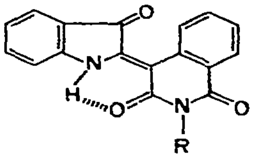
(4)



(5)

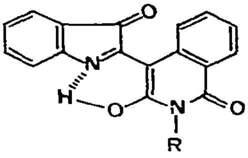


(6)

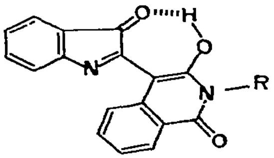


(7)

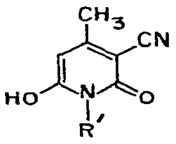
a. R , Ethyl
b. R , n-Butyl
c. R , β-Chloroethyl
d. R , β-Cyanoethyl
e. R , Cyclohexyl
f. R , Phenyl
g. R , p-Tolyl
h. R , p-Anisyl
i. R , 3-methoxy-4-methylphenyl
j. R , p-Chlorophenyl
k. R , p-Nitrophenyl



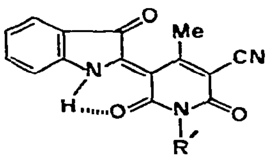
(7′)



(8)

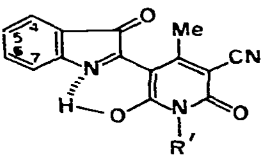


(9)

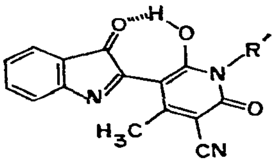


(10)

a. R′, Methyl ; b. R′, o-Tolyl



(10′)



(11)

We now wish to report the synthesis of violet to bluish violet disperse dyes (**5a–k**) by the condensation of (**1**) with homophthalimide derivatives (**4**) in the presence of phosphorus oxychloride in refluxing benzene. Similar condensations of isatin (**2**) with homophthalimides (**4c,e,f,i**) and 2-pyridones (**9a,b**) yielded violet disperse dyes (**7′c,e,f,i**) and (**10′a,b**).

2. RESULTS AND DISCUSSION

The use of *N*-substituted homophthalimides (**4**) as coupling components for the preparation of azo disperse dyes has been reported in the patent literature.[10–14] All such azo disperse dyes have yellow to orange hues. It is interesting to note that the disperse dyes obtained by the condensation of the *N*-substituted homophthalimides (**4**) or 2-pyridones (**9**) with naphthostyril (**1**) or isatin (**2**) have violet to bluish violet shades. The sublimation fastness of the dyes on polyester is given in Table 1. It can be seen that the substituents on the nitrogen of the homophthalimide moiety greatly influence the sublimation fastness properties. In general, the dyes show poor lightfastness (1 to 2) on polyester fibre.

The p.m.r. spectrum of (**5a**) in $CDCl_3$ shows multiplets in the region δ 6·8–8·2 (10H, aromatic protons, a quartet centred at 4·2 (2H, $C\underline{H}_2CH_3$) and a triplet at 1·33 (3H, $CH_2C\underline{H}_3$). The D_2O exchangeable hydroxyl proton appears as a broad

TABLE 1
ELECTRONIC SPECTRA AND SUBLIMATION FASTNESS PROPERTIES ON POLYESTER OF (**5a–k**), (**7′c,e,f,i**) AND (**10′a,b**)

Dye	*Electronic spectra in DMF*		*Sublimation fastness on polyester*	*Hue on polyester*
	λ_{max} (*nm*)	ε		
5a	525	24600	5	Violet
5b	530	21950	3–4	Violet
5c	530	19540	5	Violet
5d	530	13990	2	Violet
5e	530	23330	2–3	Violet
5f	525	21990	5	Violet
5g	525	24030	3–4	Violet
5h	525	23360	2–3	Violet
5i	525	16240	5	Violet
5j	530	23440	4–5	Violet
5k	525	19480	2–3	Violet
7′c	535	5040	2–3	Violet
7′e	530	5436	3–4	Violet
7′f	535	7330	3–4	Violet
7′i	530	6307	2–3	Violet
10′a	565	8615	2–3	Bluish violet
10′b	565	8615	2–3	Bluish violet

singlet at 11·86 ppm. The p.m.r spectra of the dyes (**5b–k**) in $CDCl_3$ follow a similar pattern to that of (**5a**) in the aromatic region.

The mass spectra of the dyes (**5a–k**) show strong molecular ions and their fragmentation patterns have similar characteristics. For example, in the mass spectrum of (**5b**), the molecular ion at *m/e* 368 is quite prominent. Loss of methyl and successive losses of methylene moieties from the molecular ion are indicated at *m/e* 353, 339, 325 and 311. Total loss of $NCH_2CH_2CH_2CH_3$ results in the fragment 296. The fragments at 269 and 241 are due to the successive losses of two C=O groups.

The i.r. spectrum of (**5a**) in carbon tetrachloride shows a chelated hydroxyl group at 3255 cm^{-1}; the carbonyl group appears at 1665 cm^{-1}. The hydroxyl absorption is not shifted at various dilutions and hence strong intramolecular hydrogen bonding is indicated. The dye (**5d**) shows a CN group at 2250 cm^{-1}. The i.r. spectra of other dyes (**5b–k**) had similar characteristics.

The p.m.r. spectra of the dyes (**7'c,e,f,i**) in $CDCl_3$ were similar to those of (**5a–k**) and account for the isatin moiety in place of the naphthostyril unit. The p.m.r. spectrum of the condensation product (**10'a**) obtained from isatin and *N*-methyl-2-pyridone (**9a**) in arsenic trichloride showed a two-proton multiplet at 7·57–7·94, which can be assigned to the C_4 and C_7 protons. Another two-proton multiplet at 7·3–7·5 can be assigned to the C_5 and C_6 protons. The *N*-methyl and *C*-methyl groups are seen at 3·34 and 2·7 respectively. The hydroxyl proton, exchangeable in D_2O, was observed at 10·58 (in DMSO). The i.r. spectrum of (**7'f**) shows chelated hydroxyl absorption as a broad peak at about 3350 cm^{-1}. The absorptions at 1700 and 1660 cm^{-1} are due to isatin carbonyl and homophthalimide carbonyl groups. The dye (**10'a**) shows chelated hydroxyl at 3125 and isatin and pyridone carbonyls at 1740 and 1650 cm^{-1} respectively. In the mass spectrum both (**7'c**) and (**10'a**) show the molecular ions as base peaks at *m/e* 352 and 293 respectively; their fragmentation patterns are as expected.

The absorption maxima and the intensity of absorption of all the dyes (**5a–k**), (**7'c,e,f,i**) and (**10'a,b**) in their electronic spectra are given in Table 1. The dyes obtained by the condensation of naphthostyril with 2-pyridones generally showed λ_{max} at 510 nm with ε in the range of 7467 to 8545 as reported by us earlier.[9] The dyes obtained by the condensation of naphthostyril with homophthalimides showed a distinct bathochromic effect with λ_{max} ranging from 525 to 535 nm, and a more than two-fold increase in the intensity of absorption. The dyes (**7'c,e,f,i**), although showing λ_{max} in the range 530–535 nm, had a lower intensity of absorption. The dyes (**10'a,b**) showed a further bathochromic shift to 565 nm with ε values of 8615. The alkyl or aryl substituents on nitrogen in the homophthalimides or 2-pyridones had very little effect on the absorption maxima.

It can be seen that the dyes obtained by the condensation of naphthostyril (**1**) with homophthalimides (**4**) have two possible tautomeric forms (**5**) and (**6**). However, the spectral studies as discussed above favour (**5**). Similarly the dyes from isatin and homophthalimides can be indicated as (7), (7′) and (8). The major contributions of (7′) are indicated on the basis of spectral data. The isatin and 2-pyridone condensation products can be represented by (**10′**) as a preferred structure. The alternative forms are (**10**) and (**11**).

3. EXPERIMENTAL

All melting points are uncorrected and are in °C. Visible spectra in DMF solutions were recorded on a UV–VIS 44069 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 221 spectrophotometer (ν_{max} in cm^{-1}). The p.m.r. spectra were recorded on a Varian T-60 spectrophotometer and the chemical shifts are cited on a δ (ppm) scale using TMS as internal reference. The mass spectra were obtained on a CEC21-110B mass spectrometer at minimum source temperature.

3.1. *8-[4′-(N-Ethylhomophthalimido)]-1-aza-acenaphthene* (**5a**)

Naphthostyril (0·01 mol; 1·93 g), *N*-ethyl homophthalimide (0·01 mol; 1·89 g) and phosphorus oxychloride (3 ml) were refluxed under stirring in benzene (25 ml) for 5 h. The benzene was then distilled off and the sticky product was poured on ice–water. The separated solid was filtered, collected and recrystallized from toluene to give (5a) as red needles (2·3 g; 68 %), m.p. 190° (dec). Analysis: Found (%): C, 77·2; H, 4·9; N, 7·8. Calculated for $C_{22}H_{16}N_2O_2$: C, 77·6; H, 4·7; N, 8·2.

The synthesis of other dyes were carried out similarly by using the typical procedure described above.

3.2. *8-[4′-(N-n-Butylhomophthalimido)]-1-aza-acenaphthene* (**5b**)

Crystallized from toluene in brown platelets (2·57 g; 70 %), m.p. 140°. Analysis: Found (%): C, 78·5; H, 5·2; N, 7·4. Calculated for $C_{24}H_{20}N_2O_2$: C, 78·3; H, 5·4; N, 7·6.

3.3. *8-[4′-(N-β-Chloroethylhomophthalimido)]-1-aza-acenaphthene* (**5c**)

Crystallized from toluene in violet amorphous powder (2·7 g; 72 %), m.p. 187° (dec). Analysis: Found (%): C, 70·18; H, 4·33; N, 7·98; Cl, 9·8. Calculated for $C_{22}H_{15}ClN_2O_2$: C, 70·85; H, 4·4; N, 7·5; Cl, 9·5.

3.4. *8-[4′-(N-β-Cyanoethylhomophthalimido)]-1-aza-acenaphthene* (**5d**)

Crystallized from toluene in violet powder (2·5 g; 68 %), m.p. 198°. Analysis: Found (%): C, 75·3; H, 4·33; N, 10·87. Calculated for $C_{23}H_{15}N_3O_2$: C, 75·6; H, 4·1; N, 11·5.

3.5. *8-[4'-(N-Cyclohexylhomophthalimido)]-1-aza-acenaphthene* (5e)

Crystallized from toluene in violet plates with greenish lustre (2·6 g; 66%), m.p. 226°(dec). Analysis: Found (%): C, 79·22; H, 5·86; N, 7·1. Calculated for $C_{26}H_{22}N_2O_2$: C, 79·20; H, 5·88; N, 6·73.

3.6. *8-[4'-(N-Phenylhomophthalimido)]-1-aza-acenaphthene* (5f)

Crystallized from toluene in violet plates (2·7 g; 69%), m.p. 245°. Analysis: Found (%): C, 80·5; H, 4·4; N, 7·35. Calculated for $C_{26}H_{16}N_2O_2$: C, 80·4; H, 4·1; N, 7·2.

3.7. *8-[4'-(N-p-Tolylhomophthalimido)]-1-aza-acenaphthene* (5g)

Crystallized from toluene in violet amorphous powder (2·7 g; 68%), m.p. 205°. Analysis: Found (%): C, 80·2; H, 4·6; N, 7·3. Calculated for $C_{27}H_{18}N_2O_2$: C, 79·7; H, 4·6; N, 7·2.

3.8. *8-[4'-(N-p-Anisylhomophthalimido)]-1-aza-acenaphthene* (5h)

Crystallized from toluene in violet plates (2·9 g; 70%), m.p. 286°(dec). Analysis: Found (%): C, 77·9; H, 4·6; N, 7·0. Calculated for $C_{27}H_{18}N_2O_3$: C, 77·5; H, 4·3; N, 6·7.

3.9. *8-[4'-(N-3''-Methoxy-4''-methylhomophthalimido)]-1-aza-acenaphthene* (5i)

Crystallized from toluene in violet needles with greenish lustre (2·8 g; 65%), m.p. 235°. Analysis: Found (%): C, 77·3; H, 5·1; N, 6·25. Calculated for $C_{28}H_{20}N_2O_3$: C, 77·8; H, 4·6; N, 6·5.

3.10. *8-[4'-(N-p-Chlorophenylhomophthalimido)]-1-aza-acenaphthene* (5j)

Crystallized from toluene in violet needles with greenish lustre (3·0 g; 70%), m.p. 267°. Analysis: Found (%): C, 73·8; H, 3·8; Cl, 8·6; N, 6·5. Calculated for $C_{26}H_{15}ClN_2O_2$: C, 73·4; H, 3·85; Cl, 8·04; N, 6·2.

3.11. *8-[4'-(N-p-Nitrophenylhomophthalimido)]-1-aza-acenaphthene* (5k)

Obtained from toluene as a brown amorphous powder (2·8 g; 65%), m.p. 290° (dec). Analysis: Found (%): C, 72·3; H, 3·8; N, 9·3. Calculated for $C_{26}H_{15}N_3O_4$: C, 72·07; H, 3·7; N, 9·2.

3.12. *4'-(N-β-Chloroethylhomophthalimido)-2-indole indigo* (7'c)

Obtained from toluene as a violet amorphous powder (2·5 g; 70%), m.p. 240° (dec). Analysis: Found (%): C, 64·4; H, 3·4; Cl, 9·5; N, 7·8. Calculated for $C_{19}H_{13}ClN_2O_3$: C, 64·8; H, 3·7; Cl, 10·0; N, 8·0.

3.13. *4'-(N-Cyclohexylhomophthalimido)-2-indole indigo* (**7'e**)

Obtained from toluene as a violet amorphous powder (2·45 g; 66 %), m.p. 249° (dec). Analysis: Found (%): C, 74·4; H, 5·0; N, 7·2. Calculated for $C_{23}H_{20}N_2O_3$: C, 74·2; H, 5·4; N, 7·5.

3.14. *4'-(N-Phenylhomophthalimido)-2-indole indigo* (**7'f**)

Obtained from toluene as a violet amorphous powder (2·5 g; 67 %), m.p. 224°. Analysis: Found (%): C, 75·2; H, 3·9; N, 7·6. Calculated for $C_{23}H_{14}N_2O_3$: C, 75·4; H, 3·8; N, 7·68.

3.15. *4'-(N-3″-Methoxyl-4″-methylphenylhomophthalimido)-2-indole indigo* (**7'i**)

Crystallized from toluene in violet needles (2·8 g; 69 %), m.p. 267° (dec). Analysis: Found (%): C, 73·02; H, 4·8; N, 6·4. Calculated for $C_{25}H_{18}N_2O_4$: C, 73·2; H, 4·4; N, 6·8.

3.16. *2-Indolo-[5'-(3'-cyano-1',4'-dimethyl-6'-hydroxypyrid-2'-one)]indigo* (**10'a**)

Isatin (1·47 g; 0·01 mol), pyridone (**9a**) (1·64 g; 0·01 mol) and phosphorus oxychloride (3 ml) were heated in chlorobenzene (50 ml) under stirring at 140 °C for 5 h. The chlorobenzene was distilled off and the residue was treated with ice water. The separated product was filtered and recrystallized from *o*-dichlorobenzene in violet needles (2·1 g; 80 %), m.p. 252°. Analysis: Found (%): C, 61·02; H, 4·28; N, 15·5. Calculated for $C_{16}H_{11}N_3O_3$: C, 61·57; H, 4·18; N, 15·97.

3.17. *2-Indolo-[5'-(3'-cyano-1'-o-tolyl-4'-methyl-6'-hydroxypyrid-2'-one)]indigo* (**10'b**)

Prepared as in the case of section 3.16 and recrystallized from *o*-dichlorobenzene in violet needles (2·88 g; 70 %), m.p. 293°. Analysis: Found (%): C, 71·1; H, 4·2; N, 11·6. Calculated for $C_{22}H_{15}N_3O_3$: C, 71·55; H, 4·06; N, 11·39.

ACKNOWLEDGEMENT

One of us (SRO) thanks the Council of Scientific and Industrial Research, New Delhi and the Director, National Chemical Laboratory, Pune for the award of a Junior Research Fellowship.

REFERENCES

1. D. R. BAER, in *Chemistry of synthetic dyes*, Vol. 4, ed. K. Venkataraman, p. 202, New York, Academic Press (1971).
2. Sumitomo Chemical Co. Ltd, Fr. Demande 2 005 697 (Japan Appl. 1968).
3. E. YAMADA, K. YAMAGUCHI and T. AKAMATSU (Sumitomo Chemical Co. Ltd), Ger. Offen. 1 931 798 (Japan Appl. 1968).
4. T. PADMANATHAN (American Cyanamid Co.), US Patent 3 687 972 (Appl. 1970).

5. H. Harnisch (Bayer AG), Ger. Offen. 2 309 612 (Appl. 1973).
6. A. Brack (Bayer AG), Ger. Offen. 2 341 657 (Appl. 1973).
7. A. Brack, H. Gleinig, R. Raue and H. Kleiner, Fr. Demande 1 388 599 (Ger. Appl. 1963).
8. K. Mix (Cassella Farbwerke Mainkur AG) Brit. Pat. 1 155 905 (Ger. Appl. 1967).
9. N. R. Ayyangar, R. J. Lahoti and D. R. Wagle, *Indian J. Chem.*, **17B**, 140 (1979).
10. E. Daubach, E. Schefczik and W. Schulte (BASF AG), Ger. Offen. 2 255 910 (Ger. Appl. 1972).
11. B. Fishwick, R. Hyde and N. Hughes (ICI), Brit. Pat. 1 435 516 (Ger. Appl. 1972).
12. A. H. Berrie, N. Hughes and E. Young (ICI), Ger. Offen. 2 130 991 (Ger. Appl. 1970).
13. E. Schefczik (BASF AG), Ger. Offen. 2 050 657 (Appl. 1970).
14. U. S. Rao, 'Studies in synthetic dyes', Ph.D. Thesis, Bombay University (1980).