Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Red Colouring Photochromic 6′-Substituted Spiroindolinon Aphth[2,1-b][1,4]Oxazines

M. Rickwood [a] , S. D. Marsden [a] , M. E Ormsby [a] , A. L. Staunton [a] , D. W. Wood [a] , J. D. Hepworth [b] & C. D. Gabbutt [b]

[a] Pilkington PLC., Pilkington Technology Centre, Hall Lane , Lathom, Ormskirk, Lancashire, England , L40 5UF

[b] Dept. of Chemistry , University of Central Lancashire , Preston, England , PR 1 2TQ

Published online: 24 Sep 2006.

To cite this article: M. Rickwood , S. D. Marsden , M. E Ormsby , A. L. Staunton , D. W. Wood , J. D. Hepworth & C. D. Gabbutt (1994) Red Colouring Photochromic 6′-Substituted Spiroindolinon Aphth[2,1-b][1,4]Oxazines, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 17-24, DOI: 10.1080/10587259408037780

To link to this article: http://dx.doi.org/10.1080/10587259408037780

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 17–24
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

RED COLOURING PHOTOCHROMIC 6'-SUBSTITUTED SPIROINDOLINONAPHTH[2,1-*b*][1,4]OXAZINES.

M. RICKWOOD, S.D. MARSDEN, M.E ORMSBY, A.L. STAUNTON, and D.W. WOOD.
Pilkington PLC., Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, Lancashire, England, L40 5UF

and

J.D. HEPWORTH and C.D. GABBUTT
Dept. of Chemistry, University of Central Lancashire, Preston, England, PR1 2TQ.

Abstract Electron donating/withdrawing substituents and electronegative centres have been successfully employed in substantially widening the range of photo-generated colours available in the spiroindolinonaphthoxazine class of photochromic materials.

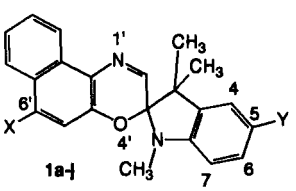
INTRODUCTION

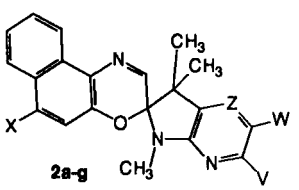
Of the many classes of organic photochromics[1] that have been evaluated for use in variable transmission filters, i.e. ophthalmics, and in absorption-reflectance articles such as textiles, spiroindolinonaphth[2,1-*b*][1,4]oxazines (SINO)[1-2] have proven to be one of the most useful. The relative utility of this class of materials is primarily due to their ability to impart good colouration to a polymer/host, and to still retain a relatively good photo-fatigue resistance. In recent years the interest in spirooxazine photochromics has been further intensified by the discovery and development of the hyperchromic 6'-amino substituted SINOs (e.g. **1a**) by Pilkington PLC[3]. However, despite recent advances these materials are limited in their potential usage, by their very small colour range, approximately 570-620nm for a given polymer/solvent host. It is therefore the aim of this group to extend the photo-generated colour range of SINOs beyond the currently available blues and to produce red colouring SINOs.

EXPERIMENTAL

6'-Amino spiroindolinonaphth[2,1-*b*][1,4]oxazines **1a-h** and **2a**, see Figure 1, were formed from the condensation of the respective 2-methyleneindoline (**3a-c** and **7a**) with 4-amino-1-nitroso-2-naphthol (**11a**, **b** and **e-h**). The latter being formed in situ from the reaction of 1-oximino naphthoquinone **12b**, tautomer of **12a** (see Scheme 3 and 4;

Method A) with a secondary amine (**9a, b** and **e-h**). This reaction has not been fully investigated but is believed to involve an initial nucleophilic attack by a secondary amine (e.g. **9a**) at the 4-position of **12b**. Oxidation of the resulting transitory species **13** yields **9a, b** and **e-h**. The general synthetic scope of Method A is extremely limited and can be used only for the synthesis of SINOs with relatively simple 6'-amino substituents (e.g. **1b**). The limited utility of Method A is further reduced by the unreative nature of the electronegative 2-methyleneindolines (**3b, c** and **7a-d**) under discussion. This reduced nucleophilicity combined with the apparent short life time of the preformed 4-amino-1-nitroso-2-naphthols, as formed in situ, results in little or no product. An alternative method offering much greater utility, was devised for the synthesis of 6'-Substituted spiroindolinonaphth[2,1-b][1,4]oxazines **1a, b, i, j** and **2b-g** and spironaphthoxazines in general, see Scheme 2 and 4; Method B. This method uses pre-formed 4-substituted-1-nitroso-2-naphthols (**11**) which can then be reacted with 2-methyleneindolines (**3** and **7**) at elevated temperatures and extended reaction times relative to those used in Method A. The crucial pre-formed 4-substituted-1-nitroso-2-naphthols (**11a-d**) are formed from the reaction of hydroxylamine hydrochloride with 4-substituted-1,2-naphthoquinone (**10a-d**); see Scheme 2. The latter, except for 4-methoxy-1,2-naphthoquinone (**10d**) which is reported in the literature[4], are formed by reacting sodium 1,2-naphthoquinone-4-sulphonate (**8**) with the corresponding amino or imino bases. By way of an example the synthesis of 4-tetramethylguanidino-1-nitroso-2-naphthol (**11c**) is covered in detail; see Scheme 2.





1	X	Y
a	Indolino	H
b	Piperidino	H
c	Piperidino	Cl
d	Piperidino	CF_3
e	Morpholino	H
f	Aziridino	H
g	Diethylamino	H
h	Perhydroindolino	H
i	Methoxy	H
j	Tetramethylguanidino	H

2	X	Z	W	V
a	Piperidino	CH	H	H
b	Piperidino	N	H	H
c	Tetramethylguanidino	N	H	H
d	Tetramethylguanidino	CH	CF_3	H
e	Methoxy	CH	CF_3	H
f	Methoxy	N	H	H
g	Methoxy	CCF_3	H	CF_3

FIGURE 1 Structural formulae of 6'-substituted spiroindolinonaphthoxazines.

Of the 2-methyleneindoline derivatives (**3a-c** and **7a-d**) used in the synthesis of the 6'-substituted photochromics, **3a-b** are commercially available and **3c** and **7a** are reported in the literature. The synthesis of 2-methyleneindoline derivatives **7b-d** are unreported but

are exemplified here by way of a detailed synthesis of **7b**; see Scheme 1.

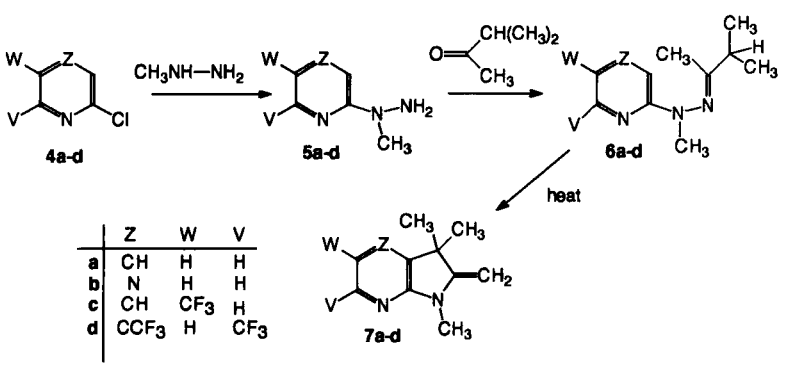
As an example of the general synthetic route, the synthesis of **1a** using Method A and B is outlined in detail in Scheme 4.

3	a	b	c
Y	H	Cl	CF_3

FIGURE 2 Structural formulae of 2-methylene-1,3,3-trimethylindolines (**3a-c**)

2-Methylene-1,3,3-trimethyl-4,7-diazaindoline (**7b**). A mixture of 51.9g (0.45 mol) of 2-chloropyrazine (**4b**) and 24.6g (0.53 mol) of methyl hydrazine was stirred at room temperature for 3 hours. The resulting yellow solid was treated with aqueous 5M NaOH to basify to pH 11 and extracted with ethyl acetate. The combined extracts were dried and evaporated to yield an orange oil which was purified by flash-chromatography over silica with diethyl ether to afford a 1-methyl-1-(pyraz-2-yl) hydrazine (**5b**) as an orange oil. Yield 58.4%.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 8.37 (d, 1H, H-3); 7.81 (m, 1H, H-5); 7.62 (d, 1H, H-6); 3.90 (bs, 2H, NH_2); 3.12 (s, 3H, NCH_3).



	Z	W	V
a	CH	H	H
b	N	H	H
c	CH	CF_3	H
d	CCF_3	H	CF_3

SCHEME 1 Representation of synthetic pathway for the formation of azaindoline (**7a, c** and **d**) and diazaindoline (**7b**) intermediates.

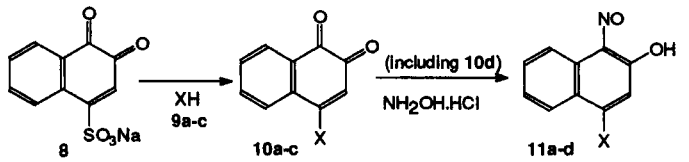
A solution of 45.0g (0.36 mol) of **5b** and 34.7g (0.40 mol) of 3-methyl-2-butanone in 90 ml of toluene was heated under reflux and nitrogen, with constant water removal, for 24 hours. The resulting solution was evaporated and the residue flash-chromatographed over silica with diethyl ether/hexane (1:10 V:V) to afford 3-methyl-2-butanone 1-methyl-1-(pyraz-2-yl) hydrazone (**6b**) as a orange oil. Yield 46%.

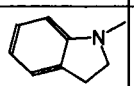
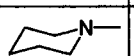
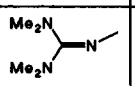
^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 8.07 (m, 2H, H-5 and H-3); 7.90 (d, 1H, H-6); 3.17 (s, 3H, NCH_3); 2.70 (sept., 1H, CH); 1.95 (s, 3H, CH_3); 1.20 (d, 6H, $2xCH_3$).

55.0g (0.29 mol) of **6b** was stirred under a nitrogen atmosphere and heated to 250°C for 2 hours. The dark residue was purified by flash-chromatography over silica with ether to yield **7b** as an orange oil. Yield 24%.

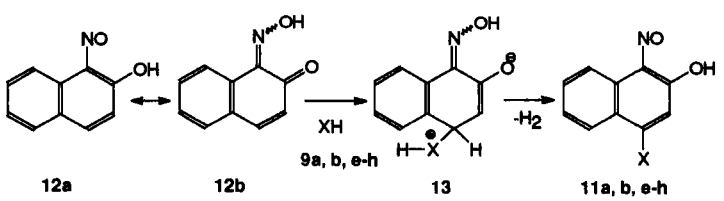
^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 7.72 (d, 1H, H-5); 7.62 (d, 1H, H-6); 4.08 (dd, 2H, CH_2); 3.12 (s, 3H, NCH_3); 1.33 (s, 6H, 2xCH_3). Intermediates **7a, c** and **d** (Scheme 1) were synthesised using this synthetic method.

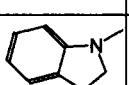
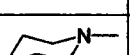
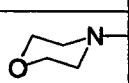
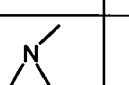
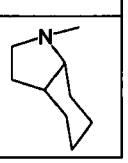
4-Tetramethylguanidino-1-nitroso-2-naphthol (**11c**). A solution of 2.60g (0.01 mol) of sodium 1,2-naphthoquinone-4-sulphonate (**8**) in 50 ml of water was treated in one portion with 1.62g (0.014 mol) of tetramethylguanidine (**9c**) and stirred at room temperature for 3 hours. The orange solution was extracted with chloroform (3 x 50 ml) and the combined extracts dried and evaporated to yield 4-Tetramethylguanidino-1,2-naphthoquinone (**10c**) as an orange solid; m.p. 174-6°C. Yield 24%.



9, 10 and 11	a	b	c	d
X				OMe

SCHEME 2 Representation of synthetic Method B for the formation of 4-substituted nitrosonaphthols and structural formulae of same.



9 and 11	a	b	e	f	g	h
X					-NEt2	

SCHEME 3 Representation of synthetic Method A for the in situ formation of 4-substituted nitrosonaphthols, and structural formulae of same.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 8.08-7.45 (m, 4H, H-aromatic); 5.29 (s, 1H, H-3); 2.96 (s, 6H, 2xNCH_3). The 4-aminonaphthoquinone intermediates **10a** (m.p. 160°C (decomp.), yield 56%; dark purple blue solid) and **10b** (m.p. 132-4°C; yield 55%; red/purple solid) see Scheme 2, were synthesised using this method. The 4-methoxy-1,2-naphthoquinone **10d** (m.p. 187-91°C) is not synthesised using this method but was synthesised using a previously been reported method[4].

A solution of 4.0g (0.015 mol) of **10c** in 50 ml of absolute ethanol was treated in one portion with 1.26g (0.08 mol) of hydroxylamine hydrochloride and stirred at room temperature for 3 days. The mixture was evaporated, treated with water, extracted with dichloromethane, and the combined extracts evaporated to yield an orange solid/gum. Purification by trituration with diethyl ether afforded 4-tetramethylguanidino-1-nitroso-2-naphthol (**11c**) as an orange solid; m.p. 142-4°C. Yield 8%.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 18.70 (bs, 1H, OH); 8.30 (d, 1H, H-8) 8.15 (d, 1H, H-6); 7.58-7.49 (m, 2H, aromatic); 5.14 (s, 1H, H-3); 2.94 (s, 6H, 2xNCH_3). The 4-substituted nitrosonaphthols intermediates **11a** (m.p. 166-72°C, yield 37%; copper-red solid), **11b** (m.p. 135-7°C; yield 8%; orange brown solid) and **11d** (m.p. 163-4°C. yield 30%; yellow solid), see Scheme 2, were synthesised using this method.

6'-Indolino-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (**1a**).
Method A.

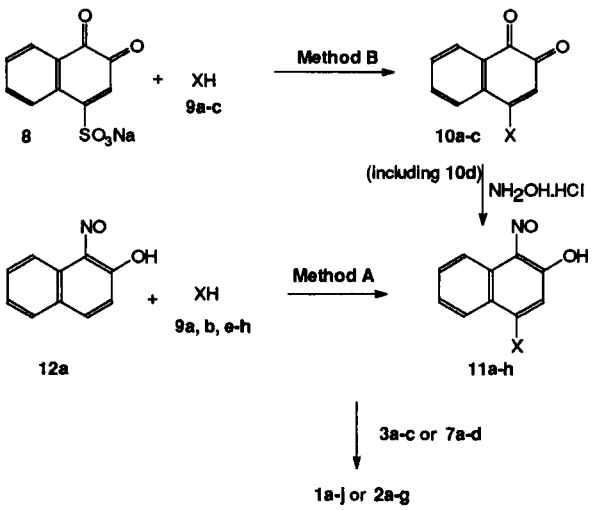
A solution of 86.5g (0.50 mol) of 1-nitroso-2-naphthol (**12**) in 650 ml of methanol was heated to reflux and treated in one portion with a solution of 120g (1.0 mol) of indoline (**9a**) in 100 ml of methanol. The resulting solution was heated under reflux for 10 minutes and then treated, over the course of 1 minute, with a solution of 86.5g (0.05 mol) of 1,3,3-trimethyl-2-methyleneindoline (**3a**) in 250 ml of methanol. The resulting dark solution was refluxed for a further 1 hour, concentrated, and the residue washed with acetone to afford **1a** as a yellow solid; m.p. 253-5°C. Yield 9%.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 8.59 (d, 1H, H-10'); 7.95 (d, 1H, H-7'); 7.69 (s, 1H, H-2'); 7.62-6.29 (m, 10H, aromatic); 6.93 (s, 1H, H-5'); 3.93 (m, 2H, NCH_2); 3.17 (m, 2H, CH_2Ar); 2.77 (s, 3H, NCH_3); 1.36 (s, 6H, 2x3-CH_3). 6'-Amino substituted spirooxazine photochromics **1b** (m.p. 238-9°C; Yield 17%; white solid), **1c** (220-22°C; 2%; yellow solid), **1d** (213°C; 3%; grey solid), **1e** (196°C; 15%; white solid), **1f** (168-70°C; 3%; grey solid), **1g** (138-9°C; 7%; brown solid), **1h** (238-9°C; 0.5%; brown/yellow solid); and **2a** (209-11°C; 2%; pale brown solid), were synthesised.

Method B.

A solution of 5.80g (0.20 mol) of 4-indolino-1-nitroso-2-naphthol (**11a**) and 3.46g (0.020 mol) of 1,3,3-trimethyl-2-methyleneindoline (**3a**) in 100 ml of 1,4-dioxane was heated under reflux for 21 hours. The resulting purple solution was evaporated to dryness and the residue purified by flash-chromatography over silica with diethyl ether/hexane (1:7 V:V) to give 5.56g of **1a**, as a green gum/solid, which was further treated by washing with acetone to give **1a** as yellow solid; m.p. 255-57°C; Yield 58%. Using a similar synthetic method the 6'-substituted spirooxazine photochromics **1b** (m.p. 238-9°C; Yield 30%; white solid), **1i** (m.p. 181-2°C; yield 70%; pale brown solid), **1j** (m.p. 175-9°C; yield 7%; brown solid), **2b** (Yield 10%; dark orange gum), **2c** (Yield 6%; dark

orange gum); **2d** (yield 3%; brown gum/solid), **2e** (m.p. 161-5°C; yield 20%; grey solid), **2f** (m.p. 164-5°C; yield 12%; light brown solid); and **2g** (m.p. 147-51°C; yield 2%; white solid) were synthesised.



SCHEME 4 Representation of synthetic routes A and B used to produce 6'-substituted spiro[1,2-b][1,4]naphthoxazines **1a-j** and **2a-g**.

Sample preparation. The photochromic properties of spironaphthoxazines **1a-j** and **2a-g** were evaluated in both toluene and an aliphatic thermoset polyurethane. The latter was produced by a direct casting process[5]. The comparative photochromic **14a**, see Figure 3, is reported in the literature and is commercially available[6].

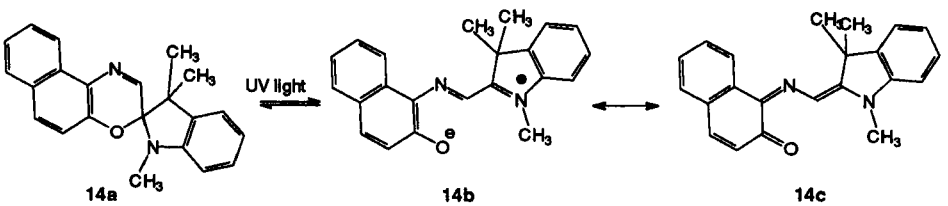


FIGURE 3 Comparative spironaphthoxazine photochromic showing photo-activated open/coloured resonance forms.

Physiochemical characterisation and photochromic evaluation. ^{1}H NMR spectra were recorded on a Brüker 250 MHz. Melting points were determined on a Du Pont 9900 Differential Scanning Calorimeter with a DSC 910 cell. U.V./visible absorbance maxima were measured on a Hewlett Packard 8452A Diode Array Spectrophotometer. The photochromic test samples were activated under solar simulation using a 1 KW Xenon arc lamp filtered to Air Mass 2[7].

RESULTS AND DISCUSSION

Upon activation by ultra-violet light, or by sunlight spironaphthoxazines (e.g. **14a**; Figure 3) are known to undergo a reversible heterolytic scission of the carbon(spiro)-oxygen bond of the oxazine ring (**14a**↔ **14b**↔**14c**)[1-2]. This is followed by a number of extremely fast (i.e. 10^{-9}-10^{-12} S^{-1}) bond rearrangements[8], resulting in the formation of the chromorphoric species (e.g.**14b** ↔ **14c**) that are responsible for the photo-generated colours. Although the nature of the photo-generated coloured species is unknown, evidence[1-2] tentatively supports a charge separated form lying somewhere between the two extremes of the fully charged separated zwitterionic (**14b**) and the fully conjugated (**14c**) forms. Through the use of substituents, and their effect upon these resonance forms, the activated colour can be altered either hypsochromically or bathochromically. The effect of a variety of substituents/groups upon the activated colour of SINOs is summarised in Table 1. The results show that the absorbance range of these materials, in polyurethane (PU) and in toluene can now be hypsochromically shifted (blue shift) by as much as 95nm in polyurethane and 104nm in toluene, with respect to comparative SINO **14a**. All results are discussed relevant to polyurethane except where specifically stated.

TABLE 1

Absorbance maxima and absorbance shifts for substituted spiro[2,1-b][1,4]naphthoxazines relative to **14a** in Polyurethane (PU) and Toluene (Tol.).

	λ_{max} (PU)	$\Delta\lambda_{max}$ (PU)	λ_{max} (Tol.)	$\Delta\lambda_{max}$ (Tol.)
15a	605	0	582	0
1a	606	1	582	0
1b	578	-27	560	-22
1c	568	-37	-	-
1d	560	-45	-	-
1e	580	-25	-	-
1f	574	-31	-	-
1g	574	-31	-	-
1h	576	-29	-	-
1i	574	-31	-	-
1j	568	-37	530	-52

	λ_{max} (PU)	$\Delta\lambda_{max}$ (PU)	λ_{max} (Tol.)	$\Delta\lambda_{max}$ (Tol.)
15a	605	0	582	0
2a	540	-65	-	-
2b	526	-79	-	-
2c	516	-89	478	-104
2d	520	-85	-	-
2e	522	-83	-	-
2f	524	-81	-	-
2g	510	-95	498	-84

6'-Amino SINOs (e.g. **1b**) as well as exhibiting remarkable depths of photo-activated colouration[9] also, in general, show relatively large hypsochromic colour shifts. These absorbance shifts can be up to 30nm for 6'-substituents such as piperidino (e.g. **1b**) and morpholino (e.g. **1e**). An investigation of other amino substituents, of which only a few are discussed here, failed to yield substantially greater hypsochromic shifts than those already revealed. The mechanism whereby these primarily π-electron (lone-pair) donating, but also inductively electron withdrawing amino groups alter the absorbance maxima is not fully understood but is tentatively ascribed to their close proximity, at their point of

attachment, to the formal negative charge situated upon the oxygen (e.g. **13b**). An investigation of other substituents showed that alkoxy substituents (e.g. **1i**) and imino substituents (e.g. **1j**) imparted hypsochromic shifts of similar magnitude as 6'-aminos. The ability to affect even greater hypsochromic shifts solely through manipulation of the 6'-substituent does not appear to be possible.

Further absorbance shifts can be achieved by the use of electronegative groupings attached to the spiroindolino moiety, an effect reported by Crano et al. in a review [2] of SINOs. Chloro- and trifluoromethyl substituents at the 5-position of the spiroindolino moiety, as exemplified by **1c** and **1d**, affect hypsochromic shifts of the order of 10nm and 18nm relative to **1b**. A much larger shift of 38nm is achieved through the use of a nitrogen at the 7-position (**2a**), whilst an additional nitrogen centre at the 4-position (**2b**) causes an further shift of 14nm and therefore 52nm in total relative to **1b**. This additive effect is further evident when comparing **1i** and **1j** with their respective 4,7-diaza analogues **2f** and **2c**. Other SINOs with two electronegative grouping attached to the spiroindolino moiety (e.g. **1d** and **1e**), also show shifts of the order of 50nm. Further still, a SINO incorporating three electronegative centres, 4,6-bistrifluoromethyl-7-aza derivative **2g**, shows a shift of 64nm relative to **1i**, resulting in an absorbance maximum of 510nm and hence red photoactivated colouration.

REFERENCES

1. H. Dürr and H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier (1990).
2 C. B. McArdle, Applied Photochromic Polymer Systems, Blackie (1992).
3. M. Rickwood and J.D. Hepworth, US 4913544 for Pilkington PLC.
4. K. Ditrich et al., DE 3926747 for BASF A.-G.,
5. M. E. Ormsby et al. EP 294056 for Pilkington PLC.
6. Catalogue Handbook of Fine Chemicals, Aldrich, 32,254-7.
7. P. Moon, J. Franklin Inst., 583-617, 230, (1940).
8. F. Wilkinson et al., J. Chem. soc. Faraday Trans., 1511-17, 88(11), (1992).
9. C. D. Gabbutt et al., Chemistry of Functional Dyes Vol 2., ed. Z. Yoshida and Y. Shirota, Mita Press (Tokyo), 394-8 (1993).