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Synthesis of New Benzothiazinophenoxazine Ring Systems

Charles O. Okafor, Mabel U. Akpuaka* & Ihesinachi A. Eluwa

Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria

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ABSTRACT

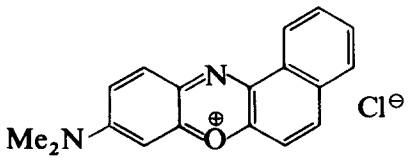
*New dyestuffs derived from new heterocyclic ring systems have been synthesized. The parent heterocycle, dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine was prepared in one case from 2-aminothiophenol, 1-phenylazo-2-naphthol (Solvent Yellow 14) and 2,3-dichloro-1,4-naphthoquinone. Also synthesized were two monoaza analogues and one diaza analogue. Nitration and sulphonation reactions of the parent heterocycle gave the mononitro and sulpho derivatives. The toxicities (as LD_{50}) and fastness properties of these dyes were also evaluated. They were found to be satisfactory as disperse dyes for polyester and nylon and were also useful for the colouration of soaps, plastics and waxes.*

1 INTRODUCTION

Phenoxazine is the base structure of an important group of dyes[1–6] for textiles and plastics. Two prototype dyes in these series are Meldola Blue (C.I. Basic Blue 6) (**1**)[7] and Gallocyanine (C.I. Mordant Blue 10) (**2**);[8] they have been commercially produced since 1879 and 1881, respectively.

Interest in these dyes was further boosted by the discovery by different workers that phenoxazine derivatives were responsible for the colouration in the eyes, wings and cuticles of certain insects and for the pigmentation in

* Present address: Department of Science Technology, Institute of Management and Technology, Enugu, Nigeria.



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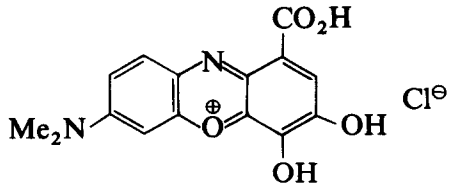

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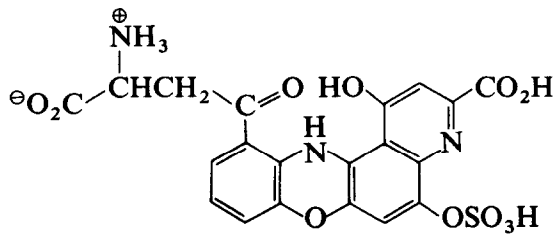
certain fungi. As examples, Ommatin D (**3**)[9-11] and Rhodommatin (**4**)[9-11] are, respectively, red-brown and brown pigments isolated from the cuticles of the blowflies *Calliphora erythrocephala, Musca domestica* and *Vanessa urticae.*



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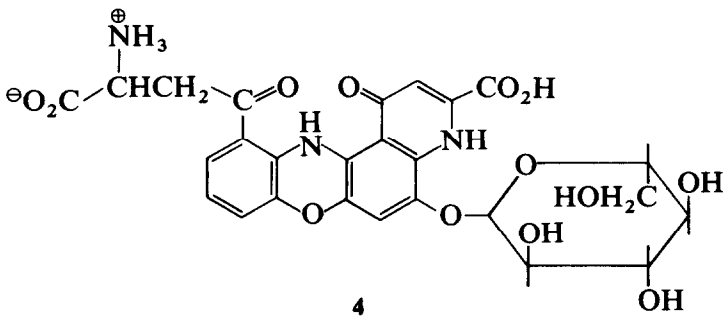

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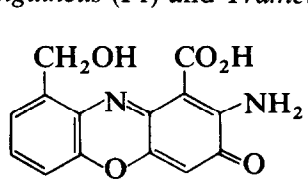
The red pigment, cinnabarine (**5**),[12-15] was isolated from the red wood-rotting fungi, *Coriolus sanguineus* (Fr) and *Trametes cinnabarina.*



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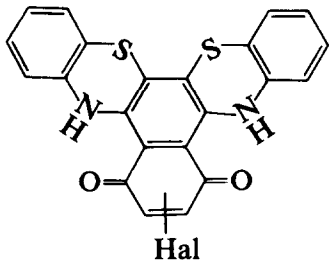
Recently, Matsuoka has pointed out the use of derivatives of the sulphur analogue, phenothiazine, in the electronic industry as key chemicals which absorb light quite efficiently. Examples are the Y-shaped[16] and Z-shaped[17] phenothiazino-quinone dyes, **6** and **7**.



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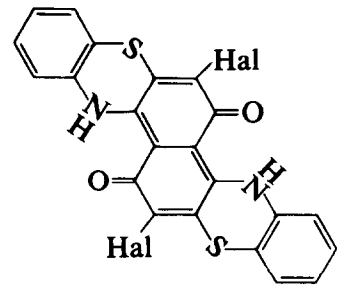

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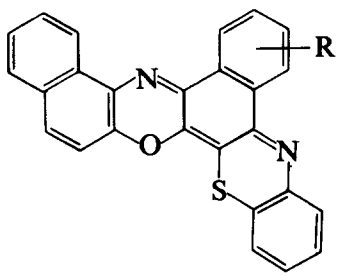
These dyes and pigments were derived from either the phenoxazine[5,11] or phenothiazine[16-19] ring structure. The authors now report a synthesis of new heterocyclic ring systems obtained by a fusion of phenoxazine and phenothiazine rings, leading to new Y-shaped benzoxazinophenothiazine dyes of types **8** and **9**.



R = H, NO_2, SO_3H

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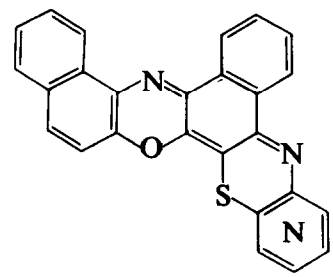

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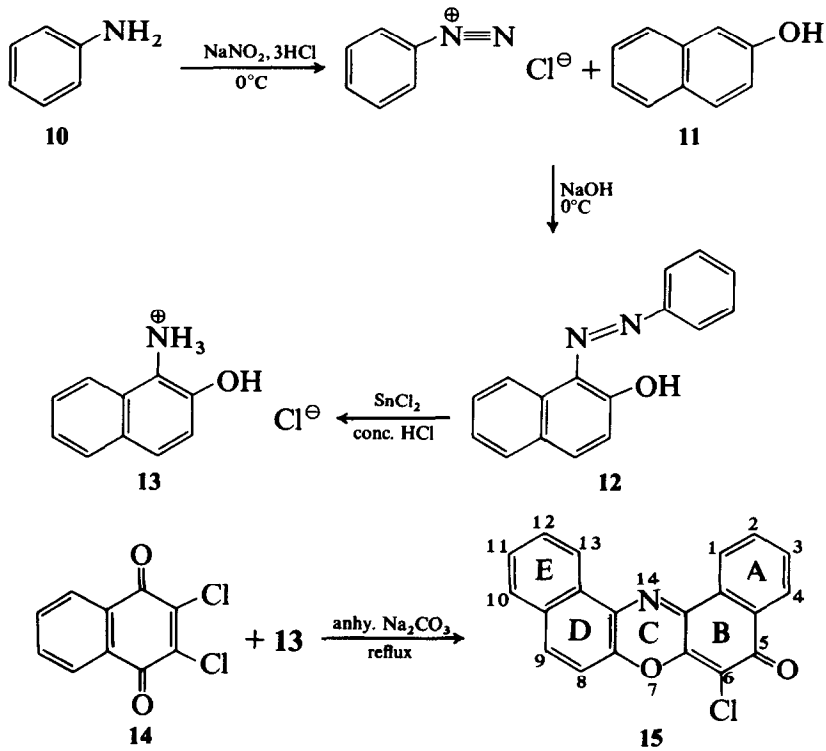
2 RESULTS AND DISCUSSION

2.1 Synthesis of the parent heterocycle

Diazotization of aniline (**10**) followed by coupling with 2-naphthol (**11**) in dilute sodium hydroxide at 0°C gave an excellent yield of 1-phenylazo-2-naphthol (Sudan I, Solvent Yellow 14, C.I. 12055) (**12**).[20] Reduction with tin(II) chloride in concentrated hydrochloric acid yielded 1-amino-2-naphthol hydrochloride (**13**) also in an excellent yield. Compound **13** is a white crystalline material which is very sensitive to light and quickly turns black on keeping overnight.[21,22] It was therefore used immediately in the next stage of the synthesis.

Condensation of 2,3-dichloro-1,4-naphthoquinone (**14**) and 1-amino-2-naphthol hydrochloride (**13**) in the presence of excess anhydrous sodium

carbonate gave a purple-red solid after purification by column chromatography and recrystallization from aqueous *N,N*-dimethylformamide. Microanalysis was in agreement with the molecular formula $C_{20}H_{10}NO_2Cl$. The infrared spectrum showed no NH band, and the presence of a carbonyl band at 1650 cm^{-1}. The strong visible absorption at 484 nm (ε_{max} 23 205) was commensurate with an extended conjugated system. The data are in agreement with the pentacyclic structure **15**. ^{1}H-NMR provided further evidence for this structure. The multiplet between δ 7·75 and 8·35 (8H) was assigned to the aromatic protons in rings A and E, while the downfield pair of doublets at δ 9·0 (J = 10·8 Hz) and δ 9·07 (J = 10·8 Hz) were assigned to the aromatic protons at C-9 and C-8, respectively. The product of the reactions was therefore 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (Scheme 1).

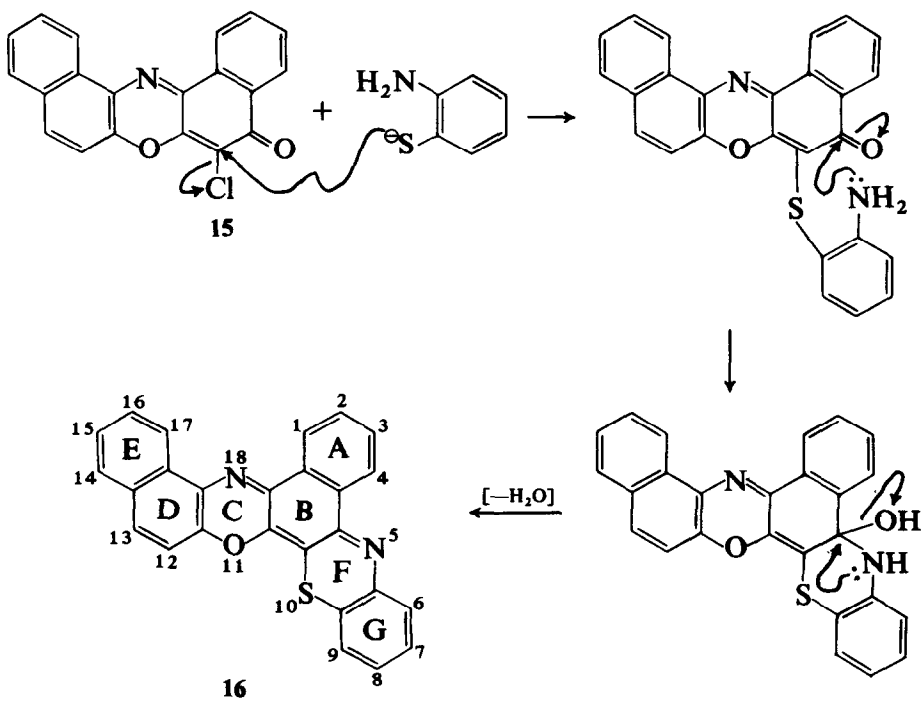


Scheme 1

Since compound **15** contains reactive chloro and carbonyl groups, it was thought desirable to extend further the conjugation by condensing it with 2-aminophenol and 2-aminothiophenol. No reaction took place with 2-aminophenol, in accord with previous observations that the reactivity of the chloro group in 2,3-dichloro-1,4-naphthoquinone is drastically reduced by the removal of one of them.[23] With the more reactive 2-aminothiophenol, no

reaction occurred under reflux conditions in methanol, benzene and pyridine. However, in nitrobenzene at 210–211°C, a violet pigment was isolated in 82% yield. Elemental analysis of the product was in agreement with the molecular formula $C_{26}H_{14}N_2OS$. Infrared, ultraviolet–visible and NMR spectra were in agreement with the heptacyclic Y-shaped structure (**16**). In the NMR spectrum, the aromatic hydrogens in rings A, E and G appeared as a multiplet between δ 7·30 and 8·06, while the protons in C-13 and C-12 appeared, respectively, at δ 8·82 and 8·89 ($J = 10{\cdot}8$ Hz).

The formation of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) probably proceeds by initial mercaptide attack on the 6-position of compound **15**, resulting in the loss of the halogen atom. This is followed by nucleophilic attack of the carbonyl carbon centre by the amino group, resulting in cyclization. Elimination of water under alkaline conditions led to the formation of **16** (Scheme 2).

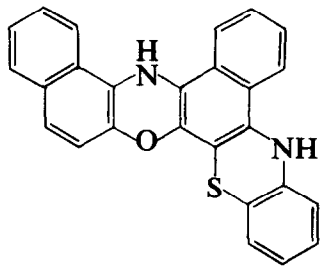


Scheme 2

Dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) is a violet pigment. Due to its insolubility in most common solvents its application as a dye is limited in spite of its high molar absorptivities at 560 and 600 nm; it was successfully applied as a disperse dye (see Section 2.6).

Reduction with sodium hydrosulphite led to loss of the violet colouration due to the formation of the dihydro product **17**. This compound quickly

reverted in the presence of oxygen to the dehydropigment **16**. The conversion of **17** to **16** was accelerated by the addition of oxidizing agents such as hydrogen peroxide. These reactions indicate that pigment **16** may be applicable as a vat dye.



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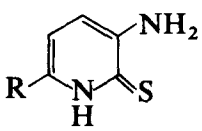
2.2 Synthesis of the monoaza analogues

Replacement of the 9-CH with a nitrogen atom, leading to the 9-aza analogue of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) was achieved by condensing 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) with 3-aminopyridine-2[1H]-thiones (**18**)[24–27] as described for dibenzo[*a,j*]-[1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) using nitrobenzene as solvent. These reactions led to the new heterocyclic ring system, identified as 11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (**19**). Its derivatives were similarly synthesized from the appropriate starting compounds.



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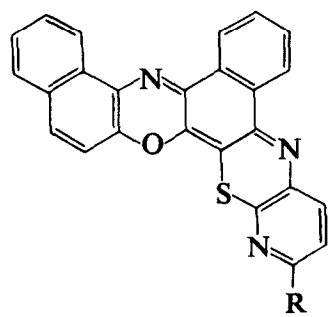
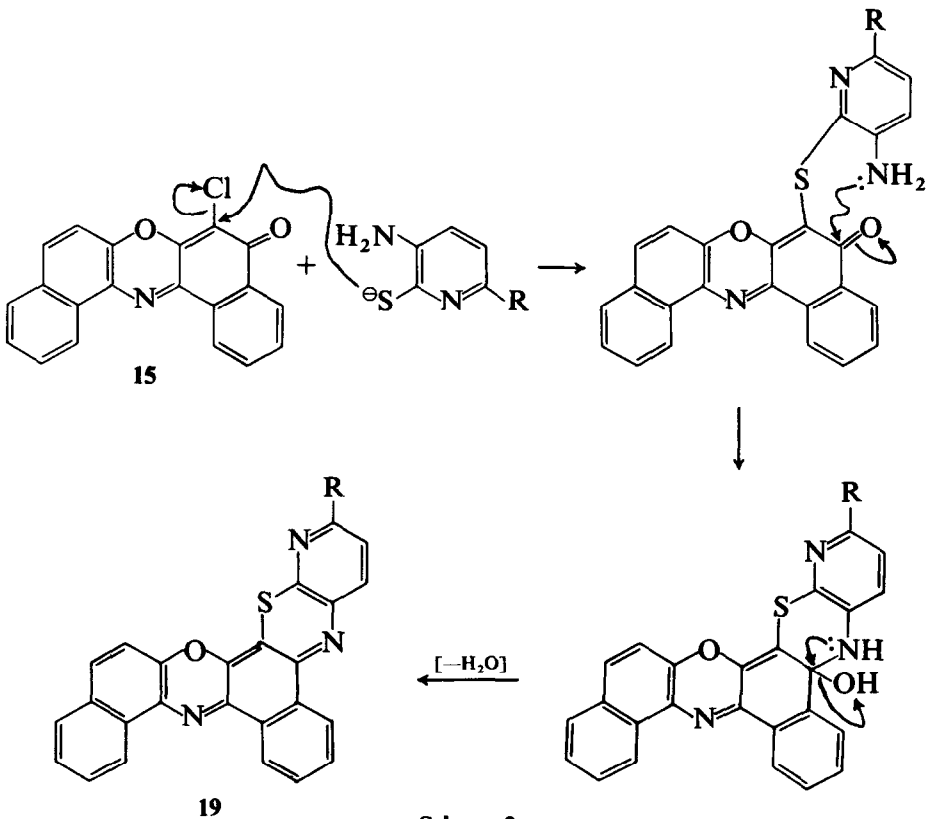


R = H, Cl, OMe

19

These compounds are high melting violet-blue pigments which are stable to air and light but lose their colour on refluxing with sodium hydrosulphite. They are, however, reconverted to the original quinoid forms, **19**, on exposure to air (oxygen), making them potentially applicable as vat dyes.

The formation of these products proceeds by nucleophilic attack of the mercaptide ion on the 6-carbon centre of compound **15**, followed by cyclization and loss of water as was described for dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) (Scheme 3).

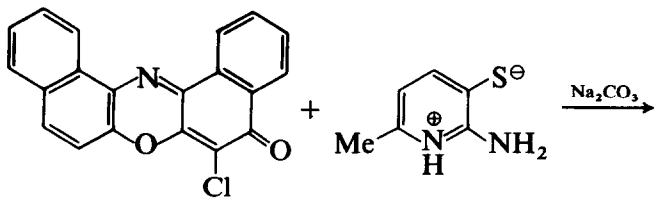


Scheme 3

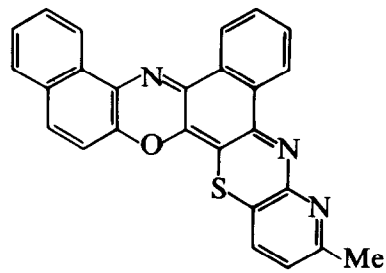
As a further extension of the chemistry of these Y-shaped polycyclic benzothiazinophenoxazine pigments, the synthesis of the new heterocyclic system, 11-oxa-10-thia-5,6,18-triazadibenzo[*a,r*]pentaphene (**20**), isomeric with structure **19**, was also carried out. Pyrolytic reaction of compound **15** with an alkaline solution of 2-amino-6-methyl-3-pyridinethiol (**21**)[28] gave a purple-blue pigment which was identified as 7-methyl-11-oxa-10-thia-5,6,18-triazadibenzo[*a,r*]pentaphene (**20**).

2.3 Synthesis of the diaza analogue

Similar reaction of compound **21** with 4,5-diaminopyrimidine-6-thiol (**22**)[29,30] gave a further new heterocyclic system, viz. the dark violet, 6-amino-11-oxa-10-thia-5,7,9,18-tetraazadibenzo[*a,r*]pentaphene (**23**). The



15 21



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heptacyclic structure was assigned to it by analysis and spectroscopy. Loss of the carbonyl band in compound **15** in the infrared spectrum and the shift of the visible band from 484 nm to 516, 560 and 600 nm are good evidence for the assigned structure.

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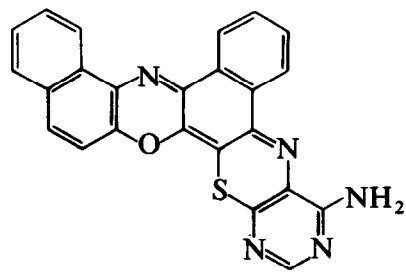

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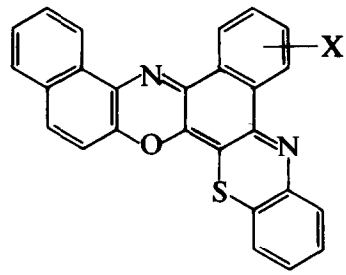
Further confirmation of the structure of this product was obtained from the ^{1}H-NMR spectrum which showed the aromatic protons as a multiplet between δ 7·40 and 8·50, the protons at C-12 and C-13 appearing at δ 8·92, while the singlet at δ 9·10 was assigned to the C-8 proton. The 6-NH_2 protons were buried in the aromatic multiplet between δ 7·40 and 8·50.

2.4 Nitration and suphonation reactions of the new heterocycle (16)

The purple-red coloured 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**), λ_{max} at 484 nm, was, in the above syntheses, converted to a series of violet-blue products, **16**, **19**, **20** and **23**. Further bathochromic shifts were achieved by nitration using potassium nitrate and concentrated sulphuric acid. Thus, nitration of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine gave a green product (**24**), melting above 300°C; microanalysis data indicated a

molecular formula $C_{26}H_{13}N_3SO_3$, in accord with a mononitrated derivative. It is of interest to note that on nitration the λ_{max} is shifted from 600 to 660 nm.



24 (X = NO_2)
25 (X = SO_3Na)

Sulphonation of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) with 65% fuming sulphuric acid at 120–130°C for 3 h gave a green product which had λ_{max} at 650 nm. This product was soluble in water and was isolated in an impure form as the sodium salt (structure **25**). Further studies are in progress to ascertain the nitration and sulphonation positions.

2.5 Determination of LD_{50} for three pigments

The toxicities (as LD_{50}) of three representative pigments in these series were determined using mice. The prototype dye, dibenzo[*a,j*][1,4]benzothiazino-[3,2-*c*]phenoxazine (**16**), has an LD_{50} value of 292 mg/kg of mice (i.p.). The

TABLE 1
Visible Absorption Maxima and Shades of Colour on Different Fabrics

Dye	λ_{max} (*nm*)	ε_{max}	*Polyester*	*Nylon*	*Cotton*
15	484	23 205	Red	Pink	Red
16	560 600	23 869 22 613	Bluish grey	Brilliant blue	Purple
19, R = Cl	556 600	8 245 6 900	Purple	Deep purple	Purple
19, R = OMe	560 602	8 209 8 030	Violet	Purple	Purple
23	560 602	10 475 9 024	Blue	Dark blue	Light violet
24	660	23 390	Brilliant green	Green	Light greenish blue

aza analogue, 8-chloro-11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (**19**, R = Cl), has an LD_{50} of 363 mg/kg and that of **15** was 279 mg/kg. These reasonably high values show that the pigments are relatively safe if used externally.

2.6 Application of the new pigments

Although these compounds are essentially pigments, they were also found to be applicable as disperse dyes, giving satisfactory colouration of polyester and nylon. Table 1 gives the λ_{max} of the dyes and the hues obtained.

3 EXPERIMENTAL

Melting points were determined with a Fisher–Johns apparatus and are uncorrected. UV and visible spectra were recorded on a Pye-Unicam SP 8000 spectrophotometer, using *N,N*-dimethylacetamide (DMAC) as solvent. IR spectra (KBr discs) were obtained on a Perkin Elmer 137 or on a Digilab FTS-40 ^{1}H-NMR spectra were determined on a Bruker AM 360 spectrophotomer in d_6-dimethyl sulphoxide using TMS as internal standard unless otherwise stated. Reactions were monitored using TLC on Silica Gel. Products were purified by column chromatography on aluminium oxide 90 (Merck, 70–230 mesh ASTM) using DMF or DMAC as the eluting solvent unless otherwise stated.

3.1 1-Phenylazo-2-naphthol (12)

1-Phenylazo-2-naphthol (Sudan 1, Solvent Yellow 14, C.I. 12055) was prepared by a modification of the previously described[29] method which involved tests to ensure that sodium nitrite was only slightly in excess.

A mixture of aniline (7·44 g, 80 mmol) and concentrated hydrochloric acid (18 ml) was stirred whilst cooling to 0°C. A cooled solution of anhydrous sodium nitrite (5·94 g 86 mmol) in water (30 ml) was added dropwise with stirring whilst maintaining the temperature of the reaction below 5°C. The addition of sodium nitrite solution was completed in 1 h. The diazonium liquor was then stirred for a further 30 min below 5°C and then stirred into a solution of 2-naphthol (11·52 g, 80 mmol) in sodium hydroxide (7·2 g, 180 mmol) in water (30 ml). The liquor was then stirred below 5°C for 30 min; the red product was filtered and recrystallized from benzene or glacial acetic acid to yield 1-phenylazo-2-naphthol (**12**) (19·25 g, 97% yield) as glistening red crystals after treatment with activated charcoal; m.p. 131–132°C; λ_{max} (nm) (ε in benzene): 418 (17 050), 476 (21 390); IR (KBr): 3480 (OH), 1628,

1604, 1560, 1510, 1455, 1395, 1320, 1260(d), 1207, 1145, 984, 900, 840, 752, 684 cm^{-1}.

3.2 Reduction of 1-phenylazo-2-naphthol

To a boiling solution of 1-phenylazo-2-naphthol (4·96 g, 20 mmol) in methylated spirit (50 ml) was added a solution of anhydrous tin(II) chloride (10 g, 53 mmol) in concentrated hydrochloric acid (300 ml). After heating for 2 h at 90–95°C, the pale brown solution was cooled in an ice-salt bath and the product collected as a grey-white crystalline solid. It was recrystallized from a hot water (charcoal) containing a few drops of stannous chloride solution (made by dissolving equal weights of stannous chloride and concentrated hydrochloric acid) to reduce atmospheric oxidation.

This gave pure white needles of 1-amino-2-naphthol hydrochloride (**13**) (2·41 g, 62% yield); m.p. 254–255°C (Ref. 22, m.p. 255°C). The product was unstable in the presence of light and turned black on storage. It was therefore used immediately in the next stage of the synthesis.

3.3 6-Chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (15)

To a solution of 1-amino-2-naphthol hydrochloride (3·91 g, 20 mmol) in chloroform (50 ml) was added anhydrous sodium carbonate (3·18 g, 30 mmol), followed by DMF (4 ml). The mixture was warmed for 15 min and to it was added a solution of 2,3-dichloro-1,4-naphthoquinone (4·54 g, 20 mmol) (**14**) in chloroform (50 ml) and the mixture was refluxed for 3 h.

Chloroform was distilled off and water was added to the slurry to dissolve sodium carbonate and sodium chloride residues. The purple-brown product was filtered and boiled in acetone (40 ml) to remove unreacted 2,3-dichloro-1,4-naphthoquinone. The deep purple-red product was chromatographed on an alumina column eluting with toluene–ethyl acetate (2:1) and was finally recrystallized from aqueous DMF (Norit) to give glistening purple-red crystals of 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (4·10 g, 62% yield); m.p. 284–286°C; UV-V (DMAC) λ_{max} (nm) (ε): 285 (16 812), 295 (16 575), 376 (61 649), 396 (63 936), 484 (23 205); IR (KBr): ν_{max} 1650 cm^{-1} (C=O); ^{1}H-NMR (DMSO-d_6) δ: 9·05 (d, J = 10·8 Hz, 8H), 8·98 (d, J = 10·8 Hz, 9H), 8·33–7·67 (m, H1, H2, H3, H4, H10, H11, H12, H13). Analysis calculated for $C_{20}H_{10}NO_2Cl$: C 72·40, H 3·02, N 4·22, Cl 10·71. Found: C 72·53, H 3·08, N 4·20, Cl 10·57.

3.4 Dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (16)

2-Aminothiophenol (2·50 g, 20 mmol) and anhydrous sodium carbonate (3·18 g, 30 mmol) were heated in nitrobenzene (80 ml) to 100°C for about

15 min. 6-Chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (6·63 g, 20 mmol) was added and the mixture stirred at 180–200°C for 11 h, during which time, the colour changed from yellow through blood-red to violet.

Nitrobenzene was removed by vacuum distillation (to near dryness); water–methanol (5:2) (140 ml) was added and the mixture cooled. The dark violet solid was filtered and purified by column chromatography on alumina using toluene–ethyl acetate (2:1) as the eluent. Further purification by crystallization from aqueous DMF gave brilliant violet crystals of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) (6·60 g, 82% yield); m.p. >300°C; UV-V (DMAC) λ_{max} (nm) (ε): 280 (11 432), 376 (6156), 394 (6533), 560 (23 869), 600 (22 613); IR (KBr): ν_{max} 1585 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ: 7·30–8·06 (m, aromatic H in rings A, E and G), 8·82 (d, J = 10·8 Hz, 13H), 8·89 (d, J = 10·8 Hz, 12H). Analysis calculated for $C_{26}H_{14}N_2OS$: C 77·61, H 3·48, N 6·97, S 7·96. Found: C 77·75, H 3·36, N 7·10, S 7·88.

3.5 Reduction of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (16) with $Na_2S_2O_4$

To a solution of the violet coloured dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) (4·02 g, 10 mmol) in DMF (250 ml) was added sodium hydrosulphite (6·96 g, 40 mmol) and the mixture was then heated for 3 h at 160–170°C.

The resulting brown coloured solution was then poured into an ice-cold solution of sodium hydrosulphite (6·96 g, 40 mmol) in water (200 ml), the slurry stirred and filtered.

During the filtration, the reduced dye was re-oxidized by atmospheric oxygen to the starting dye, with regeneration of the original violet colour. On isolation of this product it was found by melting point, UV-V, IR and ^{1}H-NMR spectroscopy to be identical to the starting compound **16**.

3.6 3-Amino-6-chloropyridine-2[1H]-thione (18), R = Cl

This compound was prepared by the conversion of 3-amino-6-chloropyridine to 2-amino-5-chlorothiazolo[5,4-*b*]pyridine followed by base-catalysed hydrolysis as described previously.[24,25]

3.7 3-Amino-6-methoxypyridine-2[1H]-thione (18), R = OMe

3-Amino-6-methoxypyridine-2[1H]-thione (**18**, R = OMe) was prepared in excellent yield by the conversion of 3-amino-6-methoxypyridine to 2-amino-

5-methoxythiazolo[5,4-*b*]pyridine followed by base-catalysed hydrolysis as described previously.[24]

3.8 3-Aminopyridine-2[1H]-thione (18), R = H

This compound was prepared by reaction of 3-amino-2-chloropyridine with sodium hydrosulphide in propylene glycol as described previously.[26,27]

3.9 8-Chloro-11-oxa-10-thia-5,9,18-triazabenzo[*a,r*]pentaphene (19), R = Cl

A mixture of 3-amino-6-chloropyridine-2[1H]-thione (**18**, R = Cl) (1·605 g, 10 mmol) and anhydrous sodium carbonate (3·18 g, 30 mmol) in nitrobenzene (60 ml) was warmed to 100°C for 15 min. 6-Chlorodibenzo[*a,j*]-[1,4]phenoxazin-5-one (**15**) (3·32 g, 10 mmol) was added and the mixture heated at 190–200°C for 21 h.

Nitrobenzene was distilled *in vacuo*, methanol–water (3:10) was added and the mixture cooled overnight.

On filtration, a purple solid resulted. This was washed several times with 20 ml of benzene to remove unreacted starting compound. The dark purple residue was recrystallized from aqueous DMF after treatment with activated charcoal. Glistening bluish violet crystals of 8-chloro-11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (**19**, R = Cl) (1·34 g, 31% yield) were obtained; m.p. > 300°C; UV-V (DMAC) λ_{max} (nm) (ε): 343 (12 115), 500 (8918), 556 (8245), 600 (6899); IR (KBr): ν_{max} 1595 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ: 9·04 (d, J = 10·8 Hz, 12H), 8·97 (d, J = 10·8 Hz, 13H), 7·60–8·33 (m, the remaining 10 aromatic protons). Analysis calculated for $C_{25}H_{12}N_3SOCl$: C 68·57, H 2·74, N 9·60, S 7·31, Cl 8·11. Found: C 68·54, H 2·90, N 9·53, S 7·06, Cl 7·88.

3.10 8-Methoxy-11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (19) R = OMe

This pigment was prepared as described for 8-chloro-11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (**19**), R = Cl, except that the reflux period in nitrobenzene was 5·5 h. From 3-amino-6-methoxypyridine-2[1H]-thione (**18**, R = OMe) (1·56 g, 10 mmol) and 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (3·315 g, 10 mmol), 8-methoxy-11-oxa-10-thia-5,9,18-triazadibenzo-[*a,r*]pentaphene (**19**, R = OMe) (2·50 g, 58% yield) was obtained as brilliant violet crystals after crystallization from aqueous DMF; m.p. > 300°C; UV-V (DMAC) λ_{max} (nm) (ε): 277 (6946), 350 (6134), 394 (5503), 560 (8209), 600 (8029); IR (KBr): ν_{max} 1589 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ: 9·05 (d, J = 10·8 Hz, 12H), 9·00 (d, J = 10·8 Hz, 13H), 7·60–8·34 (m, the remaining 10

aromatic protons), 4·00 (s, 8OMe). Analysis calculated for $C_{26}H_{15}N_3SO_2$: C 72·06, H 3·46, S 7·39. Found: C 71·88, H 3·29, S 7·67.

3.11 11-Oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (19), R = H

Starting with 3-aminopyridine-2[1H]-thione (**18**, R = H) (1·25 g, 10 mmol) and 6-chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (3·315 g, 10 mmol), 11-oxa-10-thia-5,9,18-triazadibenzo[*a,r*]pentaphene (**19**, R = H) (1·49 g, 37% yield) was obtained as was described for 8-chloro-11-oxa-10-thia-5,9,18-triazadibenzo [*a,r*]pentaphene (**19**, R = Cl) except that the reflux period was 14 h in an oil bath. The product was a violet solid; m.p. > 300°C; UV-V (DMF) λ_{max} (nm) (ε): 275 (7212), 343 (6787), 480 (5144), 500 (4984), 550 (3871). Analysis calculated for $C_{25}H_{13}N_3OS$: C 74·44, H 3·23; N 10·42, S 7·94. Found: C 74·61, H 3·33, N 10·35, S 8·11.

3.12 2-Amino-6-methylpyridine-3-thiol (21)

2-Amino-6-methylpyridine-3-thiol (**21**) was prepared by the 3-thiocyanation of 2-amino-6-picoline followed by base-catalysed hydrolysis and acidification of the resulting 2-amino-3-thiocyano-6-picoline as previously described.[28]

3.13 7-Methyl-11-oxa-10-thia-5,6,18-triazadibenzo[*a,r*]pentaphene (20)

A mixture of 2-amino-6-methylpyridine-3-thiol (**21**) (1·40 g, 10 mmol) and anhydrous sodium carbonate (2·12 g, 20 mmol) in nitrobenzene (40 ml) was heated to 90°C for 15 min. 6-Chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (3·315 g, 10 mmol) was then added and the mixture heated with stirring at 190–200°C for 13 h.

The nitrobenzene was then distilled *in vacuo* and water (50 ml) and methanol (20 ml) added to the slurry, which was then stirred and cooled. On filtration, a purple solid was obtained. It was purified by column chromatography on alumina using petroleum ether (60–80°C) and acetone (2:1) as the eluent. The resulting purple solid was recrystallized from aqueous DMF to give 7-methyl-11-oxa-10-thia-5,6,18-triazadibenzo[*a,r*]-pentaphene (**20**) (1·40 g. 34% yield) as purple-blue crystals; m.p. > 300°C; UV-V (DMAC) λ_{max} (nm) (ε): 300 (12 325), 380 (7413), 485 (17 642), 600 (6486); IR (KBr): ν_{max} 1590 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ: 3·92 (s, 7CH_3), 7·45–9·04 (m, aromatic protons). Analysis calculated for $C_{26}H_{15}N_3OS$: C 74·82, H 3·60, N 10·07, S 7·67. Found: C 75·00, H 3·52, N 10·06, S 7·53.

3.14 4,5-Diaminopyrimidine-6-thiol (22)

4,5-Diamino-6-hydroxypyrimidine was converted to 4,5-diaminopyrimidine-6-thiol (**22**) by reaction with phosphorus pentasulphide as reported previously.[29,30]

3.15 6-Amino-11-oxa-10-thia-5,7,9,18-tetraazadibenzo[*a,r*]pentaphene (23)

A mixture of 4,5-diaminopyrimidine-6-thiol (**22**) (1·42 g, 10 mmol) and anhydrous sodium carbonate (3·18 g, 30 mmol) in nitrobenzene (45 ml) was heated to 100°C for 15 min. 6-Chlorodibenzo[*a,j*][1,4]phenoxazin-5-one (**15**) (3·315 g, 10 mmol) was added and the mixture heated at 180–200°C for 25 h. The nitrobenzene was removed, water (100 ml) and methanol (30 ml) added and the mixture cooled overnight.

On filtration a dark purple solid was collected. The residue was washed several times with boiling toluene to remove any unreacted materials.

Purification by column chromatography on alumina, eluting initially with benzene–acetone (2:1) and later with DMF, gave a purple product. Crystallization from aqueous DMF gave dark violet crystals of 6-amino-11-oxa-10-thia-5,7,9,18-tetraazadibenzo[*a,r*]pentaphene (**23**) (0·88 g, 21% yield); m.p. >300°C; UV-V (DMAC) λ_{max} (nm) (ε): 335 (10 475), 374 (10 797), 396 (11 119), 516 (9669), 560 (10 475), 602 (9024); IR (KBr): ν_{max} 3440 (NH_2), 1613 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ: 9·14 (s, 8H), 8·90 (12H, 13H) 7·50–8·50 (m, 6NH_2 and the remaining 8 aromatic protons). Analysis calculated for $C_{24}H_{13}N_5OS$: C 68·74, H 3·10, N 16·71, S 7·64. Found: C 68·58, H 2·96, N 16·87, S 7·80.

3.16 Mononitration of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (16)

A mixture of dibenzo[*a,j*]benzothiazino[3,2-*c*]phenoxazine (**16**) (2·01 g, 5 mmol) and potassium nitrate (3·54 g, 30 mmol) was carefully added, a little at a time and with constant stirring to ice-cold concentrated sulphuric acid (40 ml). The temperature was maintained at 0°C throughout the addition and for a further 30 min, and the reaction mixture was then stirred at room temperature for 2·5 h when a greenish slurry resulted. The slurry was chilled overnight and added to ice-water (100 ml). The resulting brown suspension was made alkaline with concentrated ammonia when the green colouration reappeared. The mixture was filtered and the dark green residue collected. Recrystallization from aqueous DMF after treatment with activated charcoal gave a green solid (1·72 g, 77% yield), identified as the mononitro derivative (**24**) of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**); m.p. >300°C; UV-V (DMAC) λ_{max} (nm) (ε): 275 (4262), 340

(3483), 470 (11 767), 660 (23 390); IR (KBr): ν_{max} 1623 (C=N), 1531 (NO_2), 1368 cm^{-1} (NO_2); ^{1}H-NMR (DMSO-d_6) δ: 6·50–8·98 (m, aromatic protons). Analysis calculated for $C_{26}H_{13}N_3O_3S$: C 69·80, H 2·91, N 9·40, S 7·16. Found: C 69·65, H 3·04, N 9·23, S 7·40.

3.17 Sulphonation of dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (16)

Dibenzo[*a,j*][1,4]benzothiazino[3,2-*c*]phenoxazine (**16**) (2·01 g, 5 mmol) was cautiously added over 30 min to 65% oleum in an ice-bath maintained at 0°C. After the addition, the mixture was stirred at 0°C for 15 min, at room temperature for 30 min and then at 120–130°C for 3 h. The resulting green solution was allowed to cool overnight in a refrigerator. Ice-cold water (100 ml) was added, when the green colour changed to brown. On neutralizing with anhydrous sodium hydrogen carbonate, the green colour was regenerated, but no solid product precipitated out.

The solution was then saturated with sodium chloride, boiled and filtered hot. The filtrate was chilled overnight and filtered to yield a green solid (mixed with sodium chloride). This product was very soluble in water and had λ_{max}, in water, at 376, 394 and 650 nm.

4 CONCLUSIONS

The synthesis of one new pentacyclic phenoxazine ring system and four new Y-shaped heptacyclic benzothiazinophenoxazine heterocycles are described. Nitration and sulphonation of one of these compounds, dibenzo[*a,j*]-[1,4]benzothiazino[3,2-*c*]phenoxazine (**16**), gave intensely green coloured mononitro and monosulpho derivatives. The toxicities of these compounds as their LD_{50} were also determined and found to be reasonably high.

The compounds were found to have good fastness properties. They were applied as disperse dyes to polyester and nylon, as vat dyes for cotton and as colourants for soaps, plastics and waxes.

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