Dyes and Pigments 9 (1988) 427–442

A New Synthesis of 'Three-Branched' Diazaphenothiazine Dyes*

Charles O. Okafor & Uche C. Okoro

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

(Received 4 January 1988; accepted 22 February 1988)

ABSTRACT

A new and unequivocal synthesis of a 'three-branched' azaphenothiazine heterocycle is described. The parent compound, 15,16-dithia-3,5,10,12-tetraazabenzo[h]pentaphene was obtained by mononitration of pyridin-4[1H]-one and thiation with P_2S_5 to give 3-nitropyridine-4[1H]-thione. Base-catalysed condensation of this compound with 2,3-dichloro-1,4-naphthoquinone gave 2,3-bis(3-nitro-4-pyridylthio)-1,4-naphthoquinone which, on reduction with tin(II) chloride and glacial acetic acid, gave the parent compound, a purple–red dye. Also reported is the synthesis of a new angular diazaphenothiazine, 9-bromo-6-chloro-8,11,12-triazabenz[a]anthracen-5-one. Their intense colorations, ease of preparation in good yields and ready reduction with $Na_2S_2O_4$ and reoxidation by atmospheric oxygen make these compounds good vat dyes. These purple–red dyes and their derivatives were also found to be good colorants for paper, plastic, paint, ink, soap, polish, rubber, candle and cosmetic products.

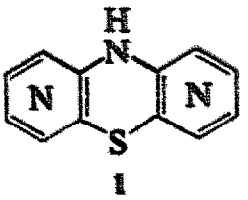
1 INTRODUCTION

The usefulness of phenothiazine derivatives as drugs,[1,2] pesticides,[3] antioxidants in lubricants and fuel,[4–6] and as dyes and pigments[7] has long been recognised. Although the chemistry of the linear azaphenothiazines (1)

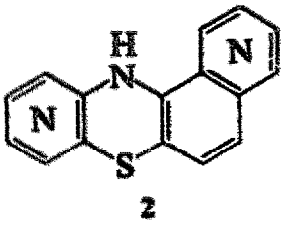
* Abstracted in part from the Ph.D thesis of U. C. Okoro, University of Nigeria, Nsukka, Nigeria, 1988.

Dyes and Pigments 0143-7208/88/$03·50

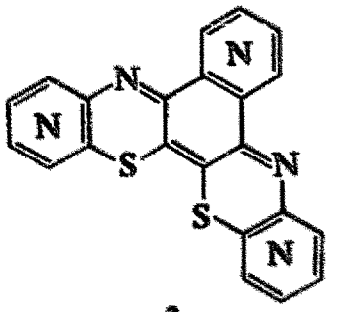
is now fairly well developed,[7–9] the 'angular' (two-branched) (2) and 'three-branched' systems (3) remain relatively under-studied in spite of their reported uses in medicine,[10] agriculture[11] and industry.[12–17]



1

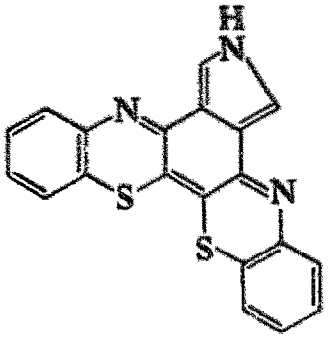


2

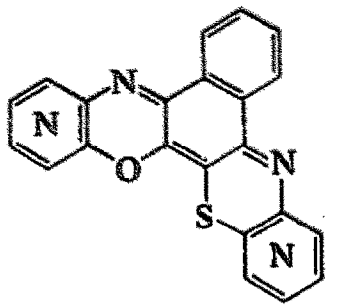


3

Only recently the first aza-analogue, pyrrolo[3,4-*a*][1,4]benzothiazino-[3,2-*c*]phenothiazine (4) was reported by some Japanese workers.[18] Subsequently, we reported the first synthesis of three-branched diaza-[19] and triaza-benzo[*a*]benzoxazinophenothiazine[20] heterocycles of type 5,



4



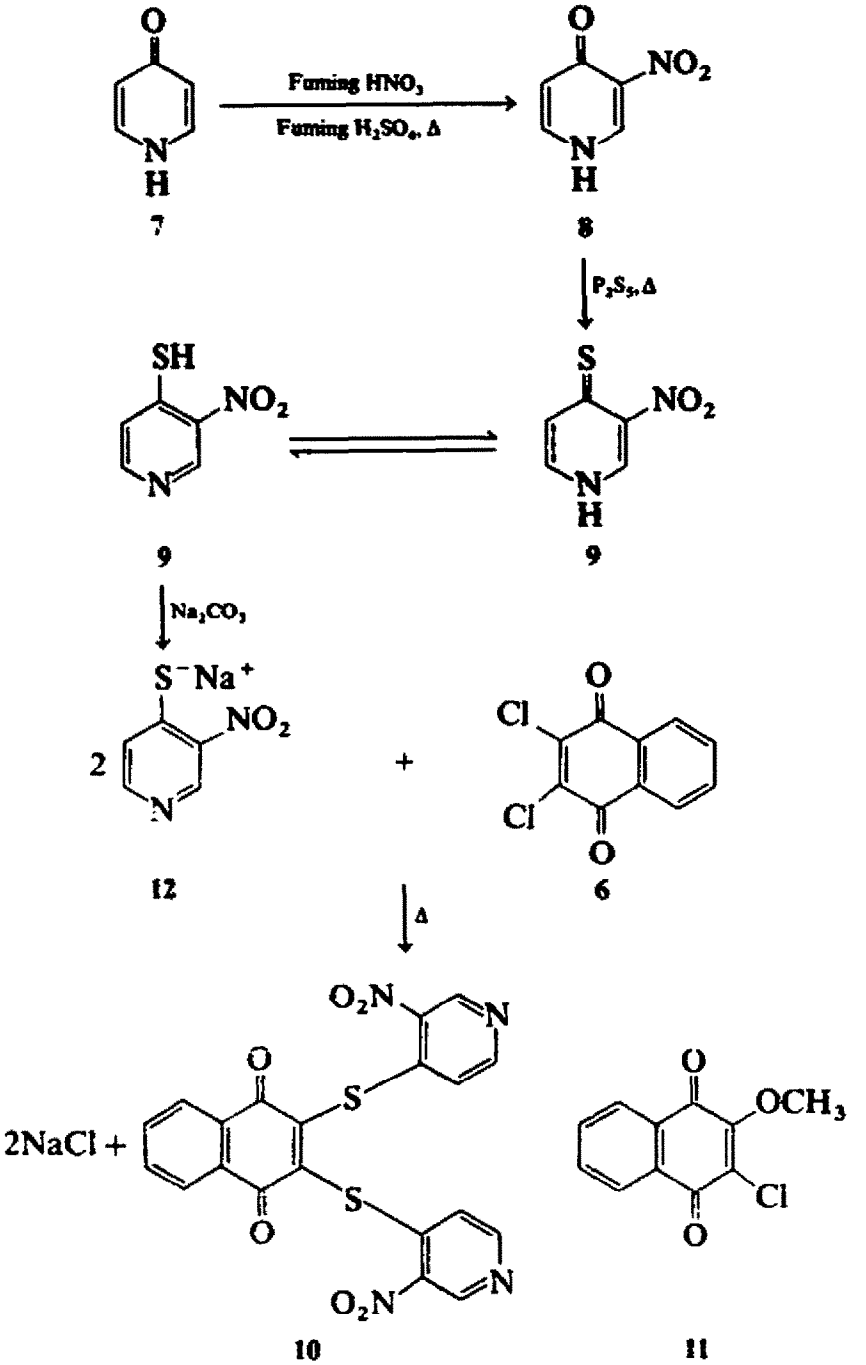
5

Compounds 5 were obtained by reacting 2,3-dichloro-1,4-naphthoquinone (6) with the appropriate *o*-aminophenol in a basic medium followed by treating the resulting angular azaphenoxazine with an alkaline solution of the *o*-aminothiol under strong heat. We have now found an alternative route to compounds 5 in which the oxazino oxygen atom has been replaced with sulphur.

2 RESULTS AND DISCUSSION

Pyridin-4[1*H*]-one (7) was converted to the 3-nitro derivative (8) by the action of mixed fuming nitric acid and 65% oleum at reflux temperature. Thiation with phosphorus pentasulphide gave 3-nitropyridine-4[1*H*]-thione (9) in good yields. By refluxing a mixture of compound (9) with 2,3-

dichloro-1,4-naphthoquinone (**6**) in a non-aqueous alkaline medium, a product identified as 2,3-bis(3-nitro-4-pyridylthio)-1,4-naphthoquinone (**10**) was obtained in excellent yield. It was earlier shown that a similar reaction with the less nucleophilic sodium methoxide gave the mono-ether, 2-chloro-3-methoxy-1,4-naphthoquinone (**11**), due to an observed decrease in the



7 **8** **9** **9** **12** **6** **10** **11**

Scheme 1

reactivity of the second halogen of compound **6** after the removal of the first.[19] However, with the highly nucleophilic mercaptide salt, **12**, the dithioether, **10**, was formed with relative ease (Scheme 1). Compound **10** is a brownish–purple crystalline solid, reasonably stable in air. Microanalysis and spectroscopy agreed with the assigned structure.

Product **10** is formed by a nucleophilic attack of two moles of the mercaptide ion **12**, on compound **6** leading to the loss of two chloride ions.

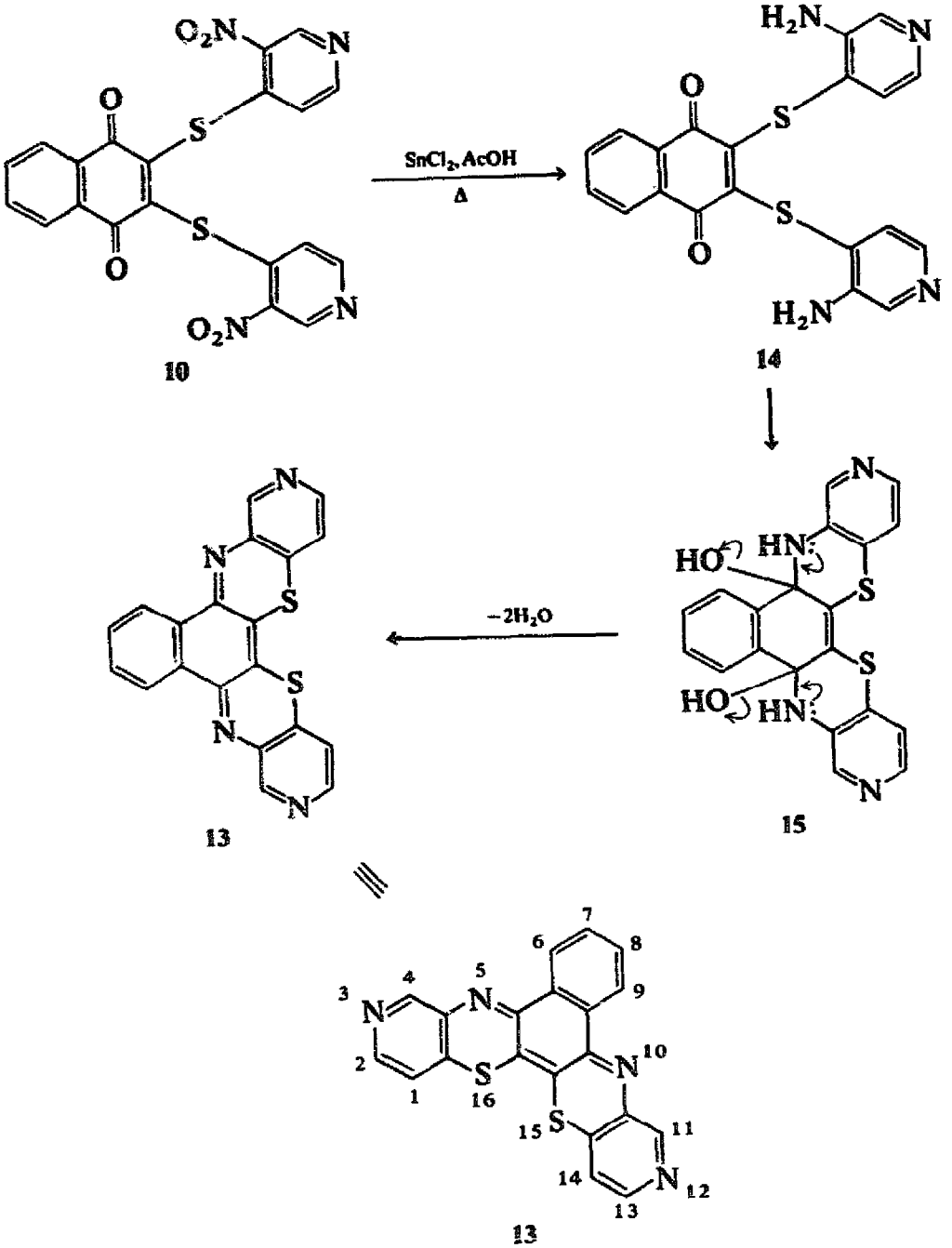
Reduction of compound **8** with stannous chloride in glacial acetic acid gave a deep purple high-melting solid, **A**. Elemental analysis was in agreement with the formula $C_{20}H_{10}N_4S_2$. The infrared spectrum showed the absence of amino and nitro groups. The shift in the visible maximum absorption band from 495 nm to 508 nm is in agreement with the three-branched hexacyclic structure **13** having an extended conjugative system (Scheme 2). Confirmatory evidence for the assigned structure **13** was provided by the mass spectrum.

Compound **13** is therefore 15,16-dithia-3,5,10,12-tetra-azabenzo[*h*] pentaphene. It is a new hexacyclic heterocyclic ring system as well as the parent compound of this new heterocycle. Its production from compound **10** proceeds by initial reduction of the nitro group followed by nucleophilic attack of the amino groups on the carbonyl carbons and eventual elimination of water.

Because of the potential of this compound as a dyestuff, substituted derivatives were also prepared. 3,5-Dinitropyridin-4[1*H*]-one (**16**) was obtained by further nitration of compound **8** with mixed fuming nitric and sulphuric acids at 130–140°C. Alternatively, direct dinitration of 4-pyridone (**7**)[21] with the same acids could be carried out satisfactorily at 95–100°C followed by allowing the temperature to rise to 130–140°C. Treatment with phosphorus pentasulphide led to 3,5-dinitropyridine-4[1*H*]-thione (**17**) in a good yield. Reaction with 2,3-dichloro-1,4-naphthoquinone (**6**) readily gave 2,3-bis(3,5-dinitro-4-pyridylthio)-1,4-naphthoquinone (**18**) which, on reduction and cyclisation, led to an excellent yield of 1,14-diamino-15,16-dithia-3,5,10,12-tetra-azabenzo[*h*]pentaphene (**19**, R = H). Acylation with acetyl chloride gave the diacetyl derivative (**19**, R = CH_3CO) (Scheme 3).

These three-branched diazaphenothiazines **13** and **19** were readily reduced by refluxing with sodium hydrosulphite to give the dihydro-products, **22**, R = H, NH_2. These compounds could not be isolated in the pure state because of their ease of oxidation by atmospheric oxygen to the starting imino-quinoid systems, **13** and **19**, which have extended conjugative systems and hence are more stable. This property makes them applicable as vat dyes.

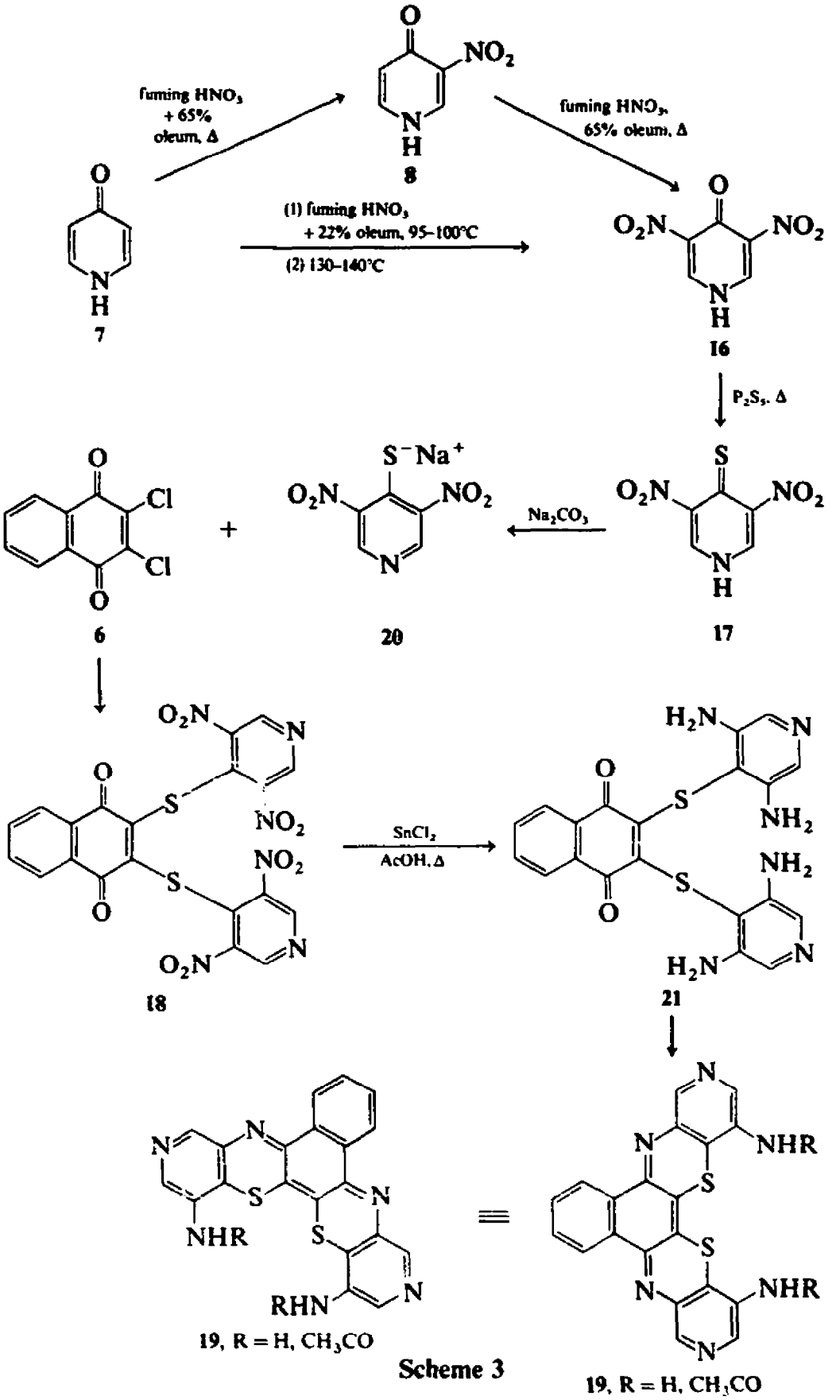
Bromination of 2-aminopyrazine (**23**) with bromine in glacial acetic acid gave 2-amino-3,5-dibromopyrazine (**24**). In brominations carried out in a



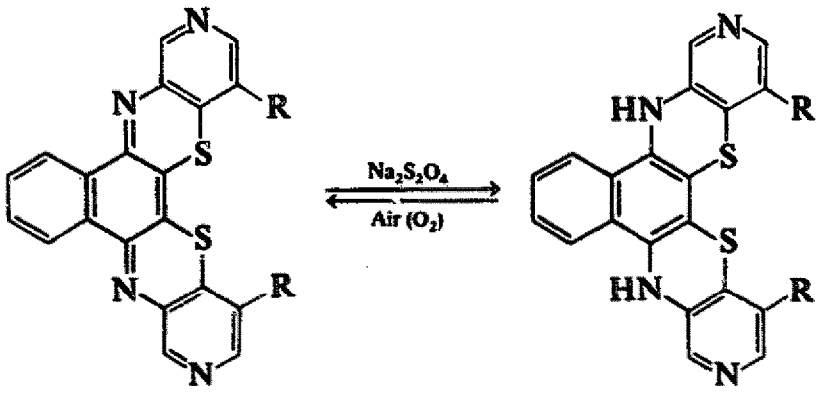
10 14 15 13 13

(compound A)

Scheme 2


fuming HNO3 + 65% oleum, Δ
fuming HNO3, 65% oleum, Δ
(1) fuming HNO3 + 22% oleum, 95–100°C
(2) 130–140°C
P2S5, Δ
Na2CO3
SnCl2
AcOH, Δ
NHR
RHN
19, R = H, CH3CO
19, R = H, CH3CO

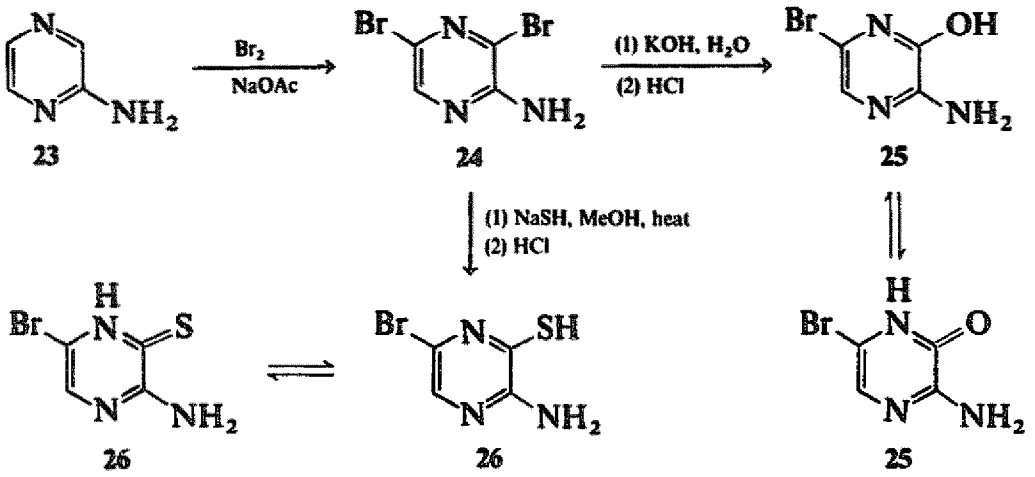
Scheme 3



13, R = H
19, R = NH_2

22, R = H, NH_2

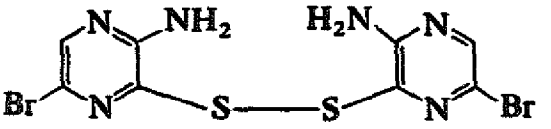
mixture of pyridine and chloroform, compound **24** was obtained together with 2-amino-5-bromopyrazine and 2-amino-3-bromopyrazine.[22] Because of the high reactivity of pyrazine derivatives with nucleophilic reagents, displacement of bromine in bromopyrazines by hydroxyl and mercapto groups proceeds with relative ease. Thus, the reaction of compound **24** with potassium hydroxide and sodium hydrosulphide gave 2-amino-5-bromo-pyrazin-3[4*H*]-one (**25**) and 2-amino-5-bromopyrazine-3[4*H*]-thione (**26**)[23,24] respectively (Scheme 4).



Scheme 4

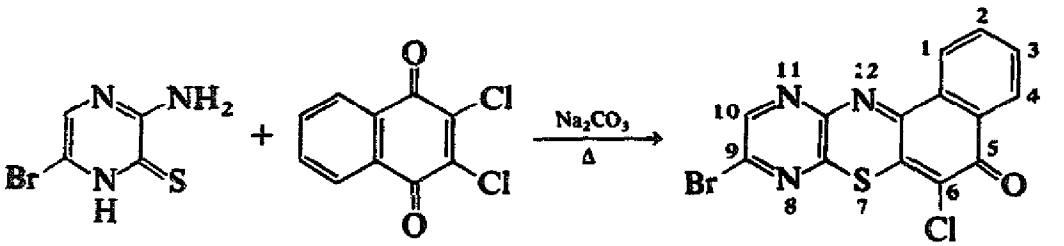
The reaction of 2-amino-5-bromopyrazin-3[4*H*]-one (**25**) with 2,3-dichloro-1,4-naphthoquinone (**6**) in the presence of anhydrous sodium carbonate was unsuccessful due to the low nucleophilic power of the hydroxide ion. However, with the more nucleophilic mercaptide salt of compound **26**, two solid products, **B** and **C**, were isolated. The lower-melting solid **B** was shown by microanalysis and spectroscopy to be 3-(2-amino-5-

bromopyrazinyl)disulphide, **27**. It was probably formed by air oxidation of the 2-amino-5-bromopyrazine-3[4*H*]-thione (**26**).



27 (compound **B**)

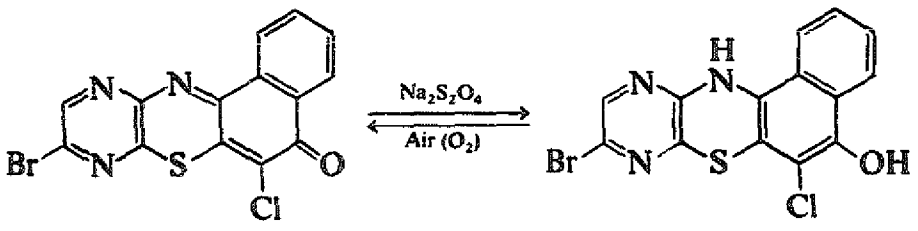
Microanalysis and spectroscopic study of the high-melting solid (**C**) were in agreement with the non-linear tetracyclic structure **28** which we have assigned to this product. Thus compound **28** is 9-bromo-6-chloro-8,11,12-triazabenz[*a*]anthracen-5-one, the first angular 1,4-diazaphenothiazine ring system.



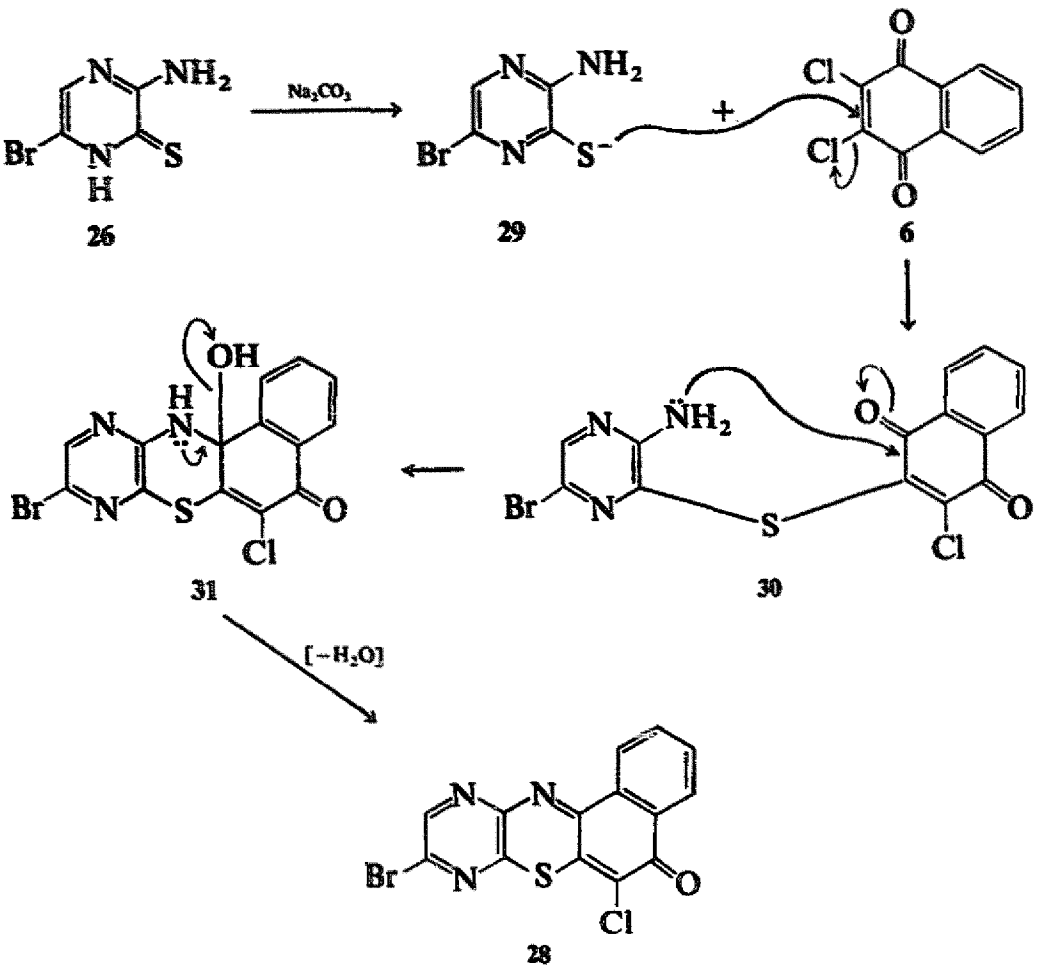
26 **6** **28** (compound **C**)

Product **24** was probably formed by an initial nucleophilic attack of the dichloronaphthoquinone (**6**) by the mercaptide ion **29** leading to the formation of the diaryl sulphide **30**. Cyclisation takes place by the condensation of the amino group with the carbonyl group in the naphthoquinone moiety. In so doing, water is eliminated, resulting in the formation of 9-bromo-6-chloro-8,11,12-triazabenz[*a*]-anthracen-5-one (**28**) (Scheme 5).

Compound **28** is an intensely coloured solid owing to its extended conjugative system. It is stable to air oxidation but easily loses its colour on refluxing with sodium hydrosulphite due to the formation of 9-bromo-6-chloro-12*H*-8,11,12-triazabenz[*a*]anthracen-5-ol (**32**). This product could not however be isolated in the pure form as it readily reverted to the iminoquinone form **28** due to air oxidation. This property makes the dye **28** applicable as a vat dye to textile materials.



28 **32**



Scheme 5

Derivatives of these ring compounds, **13** and **28**, were also found to be good colorants for soap, paint, ink, candle, plastic, rubber, polish and cosmetic products.

3 EXPERIMENTAL

3.1 General

Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Ultraviolet and visible spectra were recorded on a Pye–Unicam SP 8000 spectrophotometer using matched 1 cm quartz cells. The solvent was MeOH and the absorption maxima are given in nanometers (nm); the figures in parentheses are ε values. Infrared spectra were obtained on a Perkin–Elmer Model 137 spectrophotometer using KBr discs unless

otherwise stated. ^{1}H-NMR spectra were determined on a Varian Associates T-60 instrument. Chemical shifts are reported on the δ scale relative to tetramethylsilane (TMS) used as an internal standard. The letters br, s, d, t, q, sh and m are used to indicate broad, singlet, doublet, triplet, quartet, shoulder and multiplet respectively. The mass spectra were obtained on an AE1 MS-9 double-focusing mass spectrometer at 70 eV. All products were purified by column chromatography on alumina eluting with benzene–chloroform mixture before recrystallisation.

3.2 3-Nitropyridin-4[1*H*]-one, 8

This compound was prepared as previously reported except that 65% oleum instead of 20% oleum was used, this giving a more satisfactory synthesis. M.p. 280–281°C (lit. m.p. 278–279°C).

3.3 3-Nitropyridine-4[1*H*]-thione, 9

Pyridine (200 ml), dried over potassium hydroxide pellets, was gradually added with cooling and stirring over 0·5 h to a mixture of 3-nitropyridin-4[1*H*]-one (20·0 g, 143 mmol) and crushed phosphorus pentasulphide (61·3 g, 276 mmol) (external ice cooling). The mixture was stirred for a further half-hour and then refluxed at 118°C for 8 h with stirring.

The solvent was removed by vacuum distillation. Crushed ice (30 g) was added to the residue and the mixture heated on a water bath to remove hydrogen sulphide. When the evolution of hydrogen sulphide ceased, the resulting liquor was filtered hot. The filtrate was brought to near-boiling and treated with activated charcoal. The filtrate was treated with concentrated hydrochloric acid which brought the pH down to 1. The resulting solution was chilled in a refrigerator for two days. The solid that separated was collected by filtration and recrystallised from aqueous ethanol (Norit A) to give 3-nitropyridine-4[1*H*]-thione **9** (13·4 g, 60%) as yellow plates, m.p. > 240°C (dec.); UV λ_{max}(MeOH) 263 nm (ε 7401), 358 (10 573); IR (KBr) ν_{max} 1533, 1333 cm^{-1} (NO_2); ^{1}H-NMR (DMSO-d_6) δ 8·33 (1H, s, 2-H), 8·00 (2H, s, 5-H, 6-H), 6·70 (1H, s, br, SH). Found: C, 38·4; H, 2·7; N, 18·0; S, 20·5. Calcd. for $C_5H_4N_2O_2S$: C, 38·5; H, 2·6; N, 17·95; S, 20·5%.

3.4 2,3-Bis(3-nitro-4-pyridylthio)-1,4-naphthoquinone, 10

Benzene (30 ml) and *N*,*N*-dimethylformamide (DMF) (3 ml) were added to a mixture of powdered 3-nitropyridine-4[1*H*]-thione (**9**) (3·43 g, 22 mmol) and anhydrous sodium carbonate (2·12 g, 20 mmol), and the mixture was heated at 60°C for 20 min. 2,3-Dichloro-1,4-naphthoquinone (**6**) (2·27 g, 10 mmol)

was then added to the hot mixture. A reddish-brown coloration was immediately observed. The mixture was refluxed at 80°C for 90 min.

At the end of the reflux period, the resulting mixture was cooled and poured into water (200 ml) to dissolve inorganic materials. The brown residue was filtered and recrystallised from aqueous DMF to give 3·82 g (82% yield) of 2,3-bis(3-nitro-4-pyridylthio)-1,4-naphthoquinone (**10**) as an orange–brown powder, m.p. 245–246°C (dec); UV-V λ_{max}(MeOH) 264 (ε 9398), 313 (8026), 495 nm (5566); IR (KBr) ν_{max} 1640 (C=O), 1495, 1340 cm^{-1} (NO_2); ^{1}H-NMR (DMSO-d_6) δ 8·80 (2H, s, 2-Hs of pyridine rings), 7·98 (4H, s, 5-H and 6-Hs of pyridine rings), 9·92 (4H, m, phenyl Hs); MS *m/e* (relative intensity) 466 (100%, M^+), 468 (37·8%, M + 2). Found: C, 51·4; H, 2·1; N, 12·2; S, 13·6. Calcd. for $C_{20}H_{10}N_4S_2O_6$: C, 51·5; H, 2·15; N, 12·0; S, 13·7%).

3.5 15,16-Dithia-3,5,10,12-tetra-azabenzo[*h*]pentaphene, 13

Glacial acetic acid (20 ml) was added to a stirred mixture of stannous chloride decahydrate (11·06 g, 49 mmol) and 2,3-bis(3-nitro-4-pyridylthio)-1,4-naphthoquinone (**10**) (0·93 g, 2 mmol) and the mixture heated on a steam bath. A yellowish–brown precipitate was initially formed after about 10 min. Heating was continued for 2·5 h, during which time the precipitate dissolved with formation of a dark red solution.

The solution was cooled to room temperature and then chilled for 24 h. It was filtered and the residue collected and treated with DMF, boiled and filtered hot (Norit). A little cold water was added to the DMF extract and the solution cooled. The resulting crystalline material was collected by filtration. It was oven-dried to give 15,16-dithia-3,5,10,12-tetra-azabenzo[*h*]pentaphene (**13**) (0·70 g, 95% yield) as a purple–red powder, m.p. > 360°C (dec.); UV-V λ_{max}(MeOH) 263 (ε 18 972), 340 (14 128, 508 nm (10 764); IR (KBr) ν_{max} 1640 cm^{-1} (C=N); ^{1}H-NMR (DMSO-d_6) δ 8·07 (m, aromatic Hs); MS *m/e* (relative intensity) 370 (100%, M^+), 372 (35%, M + 2). Found: C, 65·0; H, 2·65; N, 15·0; S, 17·4. Calcd. for $C_{20}H_{10}N_4S_2$: C, 64·9; H, 2·7; N, 15·1; S, 17·3%).

3.6 3,5-Dinitropyridin-4[1*H*]-one, 16

Method A. Nitration of 4-pyridone, 7

This compund was prepared from 4-pyridone (**7**), fuming nitric acid (*d* 1·50) and 22% oleum as previously described[21] except that after stirring at 95–100°C for 24 h, the condenser was removed before the temperature could rise beyond 100°C. Refluxing was maintained at 130–140°C for another 24 h.

Method B. Nitration of 3-nitropyridin-4[1H]-one, **8**

22% Oleum (30 ml) was added dropwise over 30 min at 0°C to 3-nitropyridin-4[1*H*]-one (14·0 g, 100 mmol) (external ice–salt cooling). To the stirred slurry was then added, dropwise, fuming nitric acid (*d* 1·50, 33 ml) with constant stirring, ensuring the temperature of the mixture never rose beyond 30°C. After addition was complete, the mixture was stirred with cooling for a further half-hour to avoid a rapid rise in temperature.

The mixture was then stirred at 95–100°C for 3 h. At the end of the reflux period, the condenser was removed and the temperature allowed to rise and maintained between 130 and 140°C for 24 h.

The mixture was then cooled in an ice–salt mixture and neutralised with concentrated ammonia. The deep yellow solid which separated was filtered and recrystallised from boiling water (Norit) to give deep yellow glistening needles of 3,5-dinitropyridin-4[1*H*]-one (**16**) (14·43 g, 78% yield), m.p. 338–339°C (lit.[21] m.p. > 300°C.

3.7 3,5-Dinitripyridine-4[1*H*]-thione, 17

Pyridine (250 ml) (dried over potassium hydroxide pellets) was gradually added with stirring and cooling over 30 min to a mixture of 3,5-dinitropyridin-4[1*H*]-one (**16**) (27·75 g, 150 mmol) and crushed phosphorus pentasulphide (64·2 g, 289 mmol) (external ice–salt cooling). The mixture was stirred for a further 20 min and then heated at 120°C for 8 h with stirring.

The solvent was removed by vacuum distillation. Crushed ice (400 g) was added to the residue and the mixture heated over a water bath to remove hydrogen sulphide. When the evolution of hydrogen sulphide gas ceased, the resulting mixture was filtered hot. The filtrate was brought to near boiling and treated with activated charcoal. Acidification with concentrated hydrochloric acid led to a brown precipitation when the pH was 1.

The solid product was filtered by and further product was obtained by chilling the filtrate overnight and filtering. The combined proudct was recrystallised from aqueous ethanol (Norit A) to yield 3,5-dinitropyridine-4[1*H*]-thione (**17**) (17·8 g, 59% yield) as an orange powder, m.p. 200–201°C; UV λ_{max}(MeOH) 264 (ε 6317), 354 nm (10 481); IR (KBr) ν_{max} 2580 (w, SH), 1335 cm^{-1} (s, NO_2); ^{1}H-NMR (DMSO-d_6) δ 8·20 (1H, s, br, 1-NH), 7·55 (2H, s, 2-H, 6-H); MS *m/e* (relative intensity) 174 (27%, M − HCN), 201 (100%, M^+). Found: C, 29·9; H, 1·6; N, 21·0; S, 15·8. Calcd. for $C_5H_3N_3O_4S$: C, 29·85; H, 1·5; N, 20·9; S, 16·0%.

3.8 2,3-Bis(3,5-dinitro-4-pyridylthio)-1,4-naphthoquinone, 18

A mixture of 3,5-dinitropyridine-4[1*H*]-thione (**17**) (8·84 g, 44 mmol), benzene (42 ml) and DMF (6 ml) was stirred at 65°C for 15 min. 2,3-Dichloro-1,4-naphthoquinone (**6**) (4·54 g, 20 mmol) was then added. An immediate dark-red coloration was observed. The mixture was refluxed for 2 h and then poured into water (250 ml) to remove inorganic salts.

The product was filtered and recrystallised from aqueous DMF (Norit A) to afford 2,3-bis(3,5-dinitro-4-pyridylthio)-1,4-naphthoquinone (**18**) (8·0 g, 80% yield) as an orange–brown powder; m.p. > 300°C (dec); UV-V λ_{max}(MeOH) 262 (ε 5638), 283 (14 873), 319 (12 858), 504 nm (9730); IR (KBr) ν_{max} 1635 (s, C=O), 1342 cm^{-1} (s, NO_2); ^{1}H-NMR (DMSO-d_6)) δ 8·90 (4H, s, pyridine Hs), 7·90 (4H, m, phenyl Hs); MS *m/e* (relative intensity) 502 (21%, M − 2HCN), 528 (14%, M − CO), 556 (100%, M^+). Found: C, 43·0; H, 1·6; N, 15·0; S, 11·4. Calcd. for $C_{20}H_8N_6O_{10}S_2$: C, 43·2; H, 1·4; N, 15·1; S, 11·5%.

3.9 1,14-Diamino-15,16-dithia-3,5,10,12-tetra-azabenzo[*a*]pentaphene, 17, R = H

Acetic acid (23 ml) was added gradually to a mixture of stannous chloride dihydrate (7·2 g, 32 mmol) and 2,3-bis(3,5-dinitro-4-pyridylthio-1,4-naphthoquinone (**18**) (1·0 g, 1·8 mmol). The mixture was heated on a steam bath for 5 h, during which period all the yellowish–brown precipitate that formed dissolved, giving a purple–red solution. The reaction mixture was chilled for 24 h, filtered and the residue treated with DMF. The slurry was boiled, filtered and the filtrate treated with activated charcoal. Addition of water to the filtrate gave 1,14-diamino-15,16-dithia-3,5,10,12-tetra-azabenzo[*h*]pentaphene (**19**, R = H) (0·65 g, 90% yield); m.p. > 360°C; UV-V λ_{max}(MeOH) 265 (ε 28 364), 341 (16 944), 510 nm (17 456); IR (KBr) ν_{max} 3400 (m, NH_2), 1650 cm^{-1} (s, C=N); ^{1}H-NMR (DMSO-d_6) δ 8·32 (8H, m, aromatic Hs), 7·93 (4H, br, 1-NH_2, 14-NH_2); MS *m/e* (relative intensity) 336 (17%, M − 2S), 368 (23%, M − S), 373 (28%, M − HCN), 400 (100%, M^+). Found: C, 60·2; H, 3·0; N, 20·9; S, 15·8. Calcd. for $C_{20}H_{12}N_6S_2$: C, 60·0; H, 3·0; N, 21·0; S, 16·0%.

3.10 2-Amino-3,5-dibromopyrazine, 24

This compound was prepared from 2-aminopyrazine (**23**) (9·5 g, 100 mmol) as described previously[23] except that equally satisfactory results were obtained using 12 ml of bromine instead of 16 ml.

3.11 2-Amino-5-bromopyrazin-3[4*H*]-one, 25

A mixture of 2-amino-3,5-dibromopyrazine (**24**) (6·33 g, 25 mmol) potassium hydroxide (7·0 g, 125 mmol) and water (300 ml) was refluxed for 12 h. During this period the organic materials dissolved. Activated charcoal was added and the slurry boiled for 15 min and filtered. The residue was discarded and the filtrate cooled and neutralized with 4M-hydrochloric acid to near pH 5. The acidic mixture was chilled when yellowish-white crystals of 2-amino-5-bromopyrazin-3[4*H*]-one (**25**) (4·0 g, 84% yield) separated. Since it is insoluble in most solvents, the analytical sample was further purified by dissolution in 3M-KOH, boiling and treatment with activated charcoal. On filtering and cooling the filtrate, the pure product separated. It was collected by filtration and washed several times with hot water; m.p. > 300°C (dec); UV λ_{max}(MeOH) 250 (ε 7030), 326 nm (7600); IR (KBr) ν_{max}3410 (2-NH_2), 1684 cm^{-1} (C=O); ^{1}H-NMR (DMSO-d_6) δ 7·0 (1H, s, 6-H), 6·63 (2H, br, s, 2-NH_2); MS *m/e* (relative intensity) 189 (98·2%, M^+), 191 (100%, M + 2). Found: C, 25·4; H, 2·1; N, 22·0; Br, 42·0. Calcd. for $C_4H_4N_3BrO$: C, 25·3; H, 2·1; N, 22·1; Br, 42·1%.

3.12 Reaction of 2-amino-5-bromopyrazine-3[4*H*]-thione, 26, with 2,3-dichloro-1,4-naphthoquinone, 6

Sodium carbonate (1·06 g, 10 mmol) was added to 2-amino-5-bromopyrazine-3[4*H*]-thione (**26**) (1·03 g, 5 mmol) in 50 ml of chloroform and the slurry refluxed for 15 min. 2,3-Dichloro-1,4-naphthoquinone (**6**) (1·14 g, 5 mmol) was added and the mixture refluxed for 6 h. The solvent was removed by distillation and the residue taken up in acetone, boiled and filtered. The residue (C) was retained.

To the acetone filtrate was added some water and the mixture was heated to boiling. Activated charcoal was added and the slurry again boiled for 3 min and filtered. The residue was discarded. From this filtrate, glistening creamy-white microcrystals of 3-(2-amino-5-bromopyrazinyl) disulphide (**27**) (0·3 g) were collected; m.p. 121–122°C; UV λ_{max}(MeOH 253 (ε 10064), 278 (11 368), 326 nm (2143); IR (KBr) ν_{max} 3400 cm^{-1} (2-NH_2); MS *m/e* (relative intensity) 410 (100%, M^+). Found: C, 23·6; H, 1·3; N, 20·3; S, 15·6; Br, 39·1. Calcd. for $C_8H_6N_6Br_2S_2$: C, 23·4; H, 1·5; N, 20·5; S, 15·6; Br, 39·0%.

The original residue (A) was boiled in water and filtered hot. The aqueous filtrate was discarded and the residue crystallised from DMF–acetone–water mixture after treatment with activated charcoal to yield 9-bromo-6-chloro-8,11,12-triazabenz[*a*]anthracen-5-one (**28**) (0·90 g, 48% yield) as a red microcrystalline powder; m.p. > 200°C (dec); UV λ_{max}252 (ε 18 132), 277 (15 373), 360 nm (5781); IR (KBr) ν_{max}1680 cm^{-1} (s, C=O); ^{1}H-NMR

(DMSO-d_6) δ 8·60 (4H, m, 1-H, 2-H, 3-H and 4-H), 7·50 (1H, s, 10-H); MS *m/e* (relative intensity) 377 (67%, M^+), 379 (92%, M + 2). (Found: C, 44·6; H, 1·4; N, 11·0; Br, 21·3; Cl, 9·3; S, 8·4. Calcd. for $C_{14}H_5N_3BrClOS$: C, 44·4; H, 1·3; N, 11·1; Br, 21·1; Cl, 9·4; S, 8·5%.

3.13 Reduction of the dyes 13, 19 and 28 with $Na_2S_2O_4$

To an acetone solution of the dye was added four molar equivalents of sodium hydrosulphite and the mixture heated under reflux for 2 h, during which time the dye lost its colour, being reduced to the dihydro derivative.

The solution was poured into an ice-cold solution of another four molar equivalents of sodium hydrosulphite in 150 ml of water. The slurry was stirred and filtered. In the process, the reduced dye became re-oxidised to the starting dye resulting in the regeneration of the original colour and isolation of a product which was characterised as the starting dye.

ACKNOWLEDGEMENTS

This work was supported by Grant No. 00134/76 from the Senate Research Grants Committee of the University of Nigeria, Nsukka. The authors wish to thank Professor C. Galeffi of Istituto Superiore di Sanita, Rome, for part of the microanalysis and mass spectra. Grateful acknowledgement is also extended to Mr A. Imo of the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow and now of these Laboratories. Other technical assistance of Mrs Patricia Agwuna, Messrs F. U. Ekezie, O. O. Ibe, N. Igwe and M. Onyishi is also deeply appreciated.

REFERENCES

1. Massie, S. P., *Chem. Rev.*, **54**, (1954), 797.
2. Bodea, C. & Silberg, I. *Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky & A. J. Boulton, Academic Press, New York, 1968, pp. 321–460.
3. Campbell, F. L., Sullivan, W. N., Smith, L. E. & Haller, H. L., *J. Econ. Entomol.*, **27** (1934), 1176.
4. Elliot, J. S. & Edwards, E. (Castrol Ltd), British Patent 860675 (8 February 1961); *Chem. Abstr.*, **55** (1961), 15913a.
5. Murphy, C. M. & Sanders, C. E., *Petroleum Refiner*, **26** (1947), 479.
6. West, H. L., *J. Inst. Petroleum*, **34** (1948), 774.
7. Okafor, C. O., *Dyes and Pigments*, **7** (1986), 249.
8. Okafor, C. O., *Int. J. Sulfur Chem.*, **6B** (1971), 237.
9. Okafor, C. O., *Phosphorus and Sulfur*, **4** (1978), 79.

10. Gozsy, B. & Kato, L., *Arch. Intern. Pharmacodynamie*, **128** (1960), 75; *Chem. Abstr.*, **55** (1961), 8664.
11. Tozer, T. N., Tuck, L. D. & Cymerman-Craig, J., *J. Med. Chem.*, **12** (1969), 294.
12. Ueno, Y., Shiraki, H., Koshitani, J. & Yoshida, Y., *Synthesis* (1980), 313.
13. Woods, H. A. & Bollinger, L. C. (Shell Development Co.), US Patent 2 813 828 (19 November 1957); *Chem. Abstr.*, **52** (1958), 4977d.
14. Burford, B. L. & Kauder, O. S. (Argus Chemical Corp.), Belgian Patent 665 496 (16 December 1965); *Chem. Abstr.*, **64** (1966), 19902c.
15. Okafor, C. O., Okerulu, I. O. & Okeke, S. I., *Dyes and Pigments*, **8** (1987), 11.
16. Van Allen, J. A., Reynolds, G. A. & Maier, D. P., *J. Org. Chem.*, **34** (1969), 1691.
17. Agarwal, N. L. & Mital, R. L., *J. Chem. Eng. Data*, **20** (1975), 199.
18. Nanya, S., Tange, T., Maekawa, E. & Ueno, Y., *J. Heterocyclic Chem.*, **23**, (1986), 1267.
19. Okafor, C. O., *Tetrahedron*, **42** (1986), 2771.
20. Okafor, C. O., *Tetrahedron*, **44** (1988), 1187.
21. Okafor, C. O., *J. Org. Chem.*, **32** (1967), 2006.
22. Sato, N. J., *J. Heterocyclic Chem.*, **19** (1982), 673.
23. Okafor, C. O., *Dyes and Pigments*, **6** (1985), 405.
24. Kruger, S. & Mann, F. G., *J. Chem. Soc.* (1955), 2755.