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New Non-linear Polycyclic Azaphenothiazine Dyestuffs

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ABSTRACT

*The synthesis of some new angular and Y-shaped azaphenothiazine ring systems from simple heterocyclic compounds is described. 3-Nitration of pyridin-4[1H]-one (**7**) followed by reduction and thiation with P_2S_5 gave 3-aminopyridine-4[1H]-thione (**10**) in good yields. Reaction of product **10** with 2,3-dichloro-1,4-naphthoquinone (**12**) gave a red dyestuff, 6-chloro-7-thia-10,12-diazabenz[a]anthracen-5-one (**13**) having a new angular azaphenothiazine ring system. Two facile methods were also proposed for the synthesis of 15,16-dithia-1,5,10-triazabenzo[h]pentaphene (**26**) from 3-aminopyridine-2[1H]-thione (**25**, R = H) and 2-aminothiophenol. The purple pigment **26**, R = H is the parent compound of this Y-shaped azaphenothiazine. Reduction of these dyestuffs (**13** and **26**) and their derivatives led to loss of colour which reappeared on exposure to atmospheric oxygen. This property makes them applicable as vat dyes. Additionally they were found to be good colorants for soap, candle, polish, paint and plastic materials.*

1 INTRODUCTION

The chemistry and applications of phenothiazine and its derivatives[1,2] have received considerable attention within the last century. Studies were initially centred on the side-chain derivatives which were used in medicine, agriculture and industry as drugs,[1–6] pesticides,[7] dyes and pigments,[8,9]

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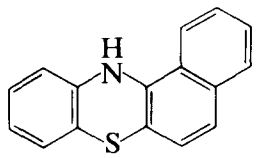
polymerization indicators[10] and antioxidants in grease and fuels.[11-13] More recently, attention has been focused on the branched,[14] aza-,[15,16] oxa-[17] and thia-analogues[16,18] in a continued search for products with better qualities.

Although benzo[a]phenothiazine (**1**), the prototype of the branched or angular phenothiazines, was first reported by Kym[19] nearly a century ago, its chemistry[14] has remained very poorly developed compared to that of



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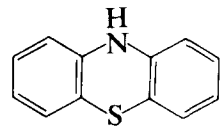

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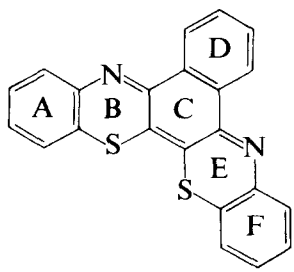
phenothiazine (**2**)[1,2,15] discovered a few years later by Bernthsen.[20] Even less attention has been given to the two-branched phenothiazine ring systems, the prototype of which is benzo[a][1,4]benzothiazino[3,2-c]-phenothiazine (**3**).[21,22] Whereas all four isomeric monoazaphenothiazines have been reported,[15] only two isomeric angular monoazaphenothiazine ring systems of type (**4**)[23,24] are known. In the more complex two-branched ring systems, we have recently synthesized some novel heterocycles of types **5** and **6** and the parent ring compounds of these Y-shaped heterocyclic structures.[25-27] We further describe here the successful synthesis of some novel heterocyclic ring systems in these series, the angular and Y-shaped heterocyclic compounds.



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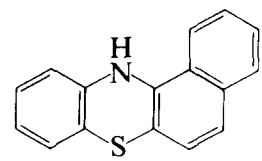

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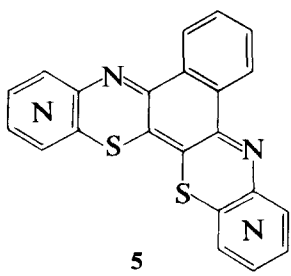

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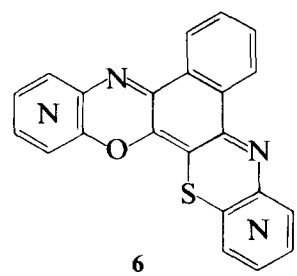

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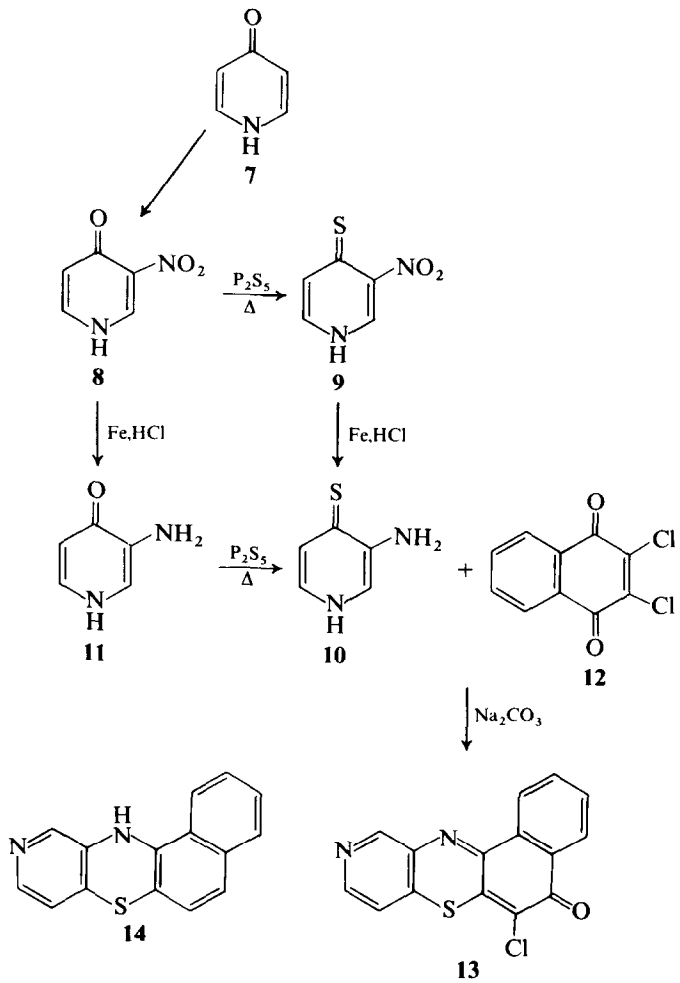
2 RESULTS AND DISCUSSION

Mononitration of pyridin-4[1H]-onc (**7**) with mixed nitric and sulphuric acids gave 3-nitropyridin-4[1H]-one (**8**).[28] Compound **8** was converted to 3-nitropyridine-4[1H]-thione (**9**) by treatment with phosphorus pentasulphide. Reduction of this product with iron and concentrated hydrochloric acid gave 3-aminopyridine-4[1H]-thione (**10**) which was also obtained by reduction of 3-nitropyridin-4[1H]-one (**8**) to the 3-amino derivative (**11**) before thiation with phosphorus pentasulphide (Scheme 1).

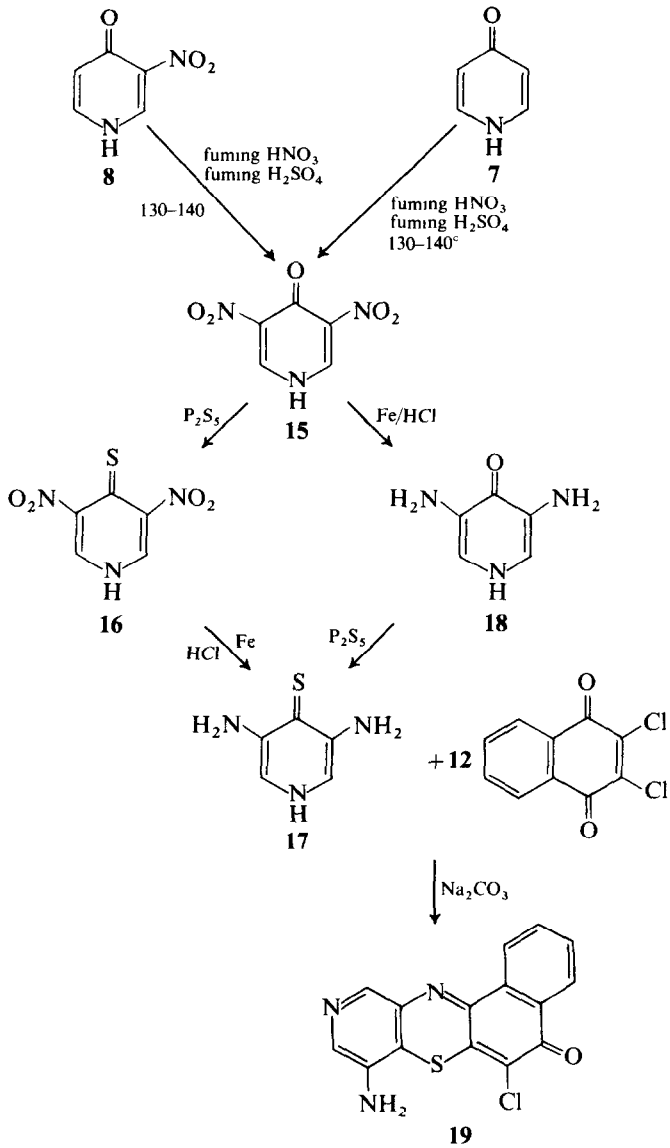
By heating a stoichiometric mixture of 2,3-dichloro-1,4-naphthoquinone (**12**) and 3-aminopyridine-4[1H]-thione (**10**) in the presence of anhydrous sodium carbonate, a red solid was isolated. From its microanalysis



Scheme 1

and spectroscopy, it was identified as 6-chloro-7-thia-10,12-diazabenz[a]-anthracen-5-one (**13**), a derivative of the new angular azaphenothiazine heterocycle.

Further nitration of compound **8** gave a good yield of 3,5-dinitropyridin-4[1H]-one (**15**) which was also obtained directly[29] by refluxing at 130–140° for 24 h. Thiation with phosphorus pentasulphide gave 3,5-dinitripyridine-4[1H]-thione (**16**). These pyridin-4[1H]-ones (**8** and **15**) were successfully



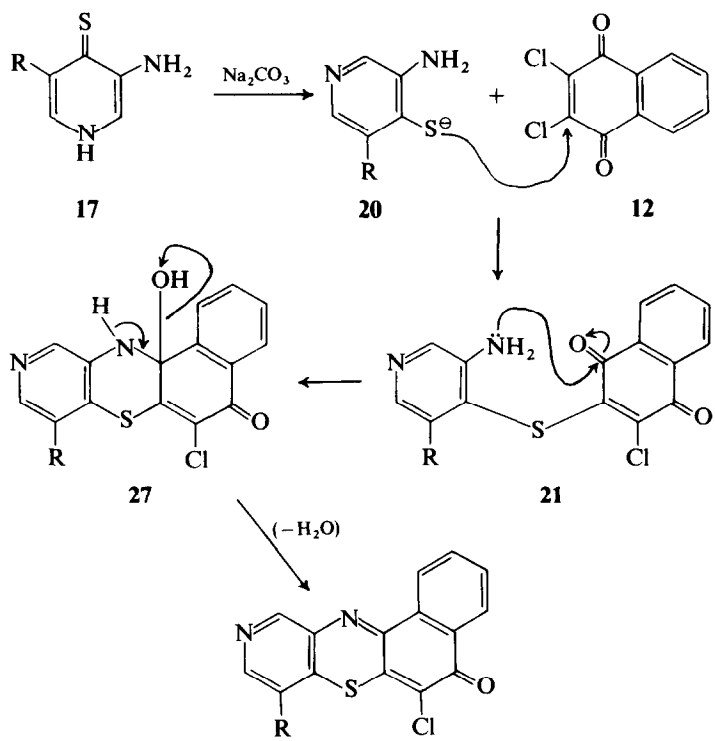
Scheme 2

thiated with phosphorus pentasulphide in agreement with Castle's observation that the conversion of heterocyclic phenols to the corresponding thiols with phosphorus pentasulphide can be achieved only when the phenolic hydroxyl group attached to the ring is tautomeric with its keto form.[30,31]

Compound **16** was converted to the 3,5-diamino derivative **17** by reduction with iron and concentrated hydrochloric acid. Alternatively, compound **15** may first be reduced with iron and concentrated hydrochloric acid to 3,5-diaminopyridin-4[1H]-one (**18**) before reaction with phosphorus pentasulphide to yield 3,5-diaminopyridine-4[1H]-thione (**17**). Compounds **15**, **16** and **17** also exist in equilibrium with their enol and thioenol forms, with the keto and thioketo forms predominating.

Base-catalysed condensation of compound **17** with the dichloronaphthoquinone, **12**, gave an excellent yield of a brilliant purple dye identified as 8-amino-6-chloro-7-thia-10,12-diazabenz[a]anthracen-5-one (**19**) (Scheme 2).

The formation of the angular phenothiazines **13** and **19** from 2,3-dichloro-1,4-naphthoquinone **12** and the appropriate aminopyridinethione in

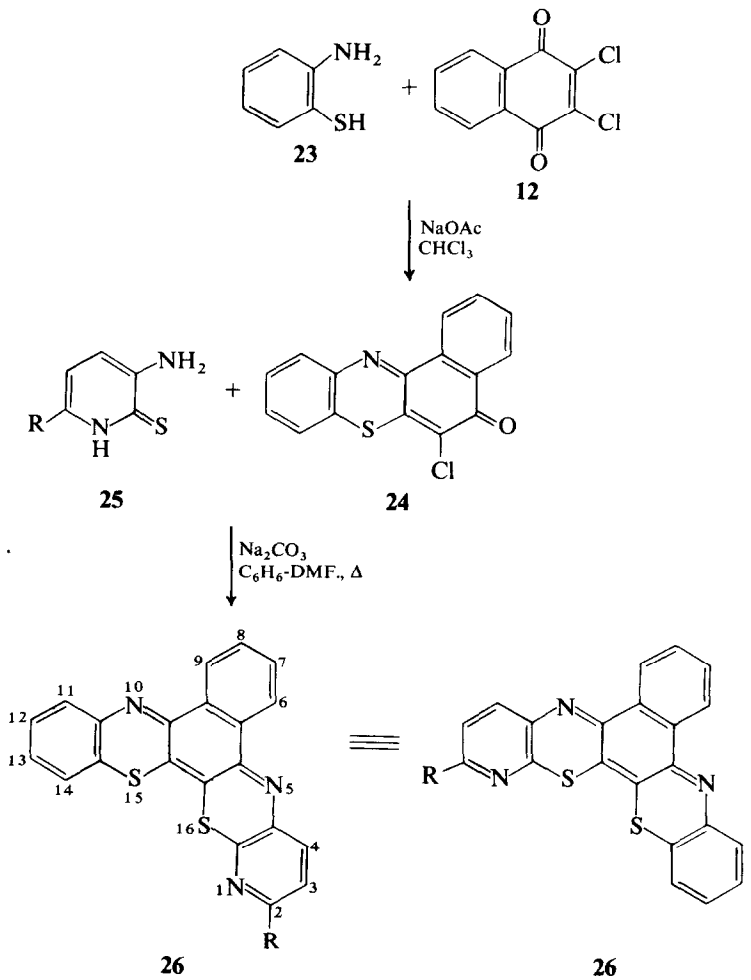


13, R = H
19, R = NH_2

Scheme 3

alkaline media probably proceeds by an initial nucleophilic attack of the hydrogen sulphide ion (**20**) on compound **12**. The resulting diaryl sulphide (**21**) can then undergo an internal condensation leading to the loss of water and the formation of the cyclized product (Scheme 3).

To produce the two-branched azaphenothiazines, 2,3-dichloro-1,4-naphthoquinone (**12**) was condensed with 2-aminothiophenol (**23**) in the presence of anhydrous sodium carbonate or sodium acetate. A near quantitative yield of the purple dye, 6-chlorobenzo[a]phenothiazin-5-one (**24**), was obtained. Further reaction of this product with an alkaline solution of an equimolar amount of 3-aminopyridine-2[1H]-thione **25**, R = H under strong heat gave a dark purple-red solid melting above 300°. Microanalysis and spectroscopy are in agreement with structure **26**, R = H. This dye is



23 **12** **25** **24** **26** **26**

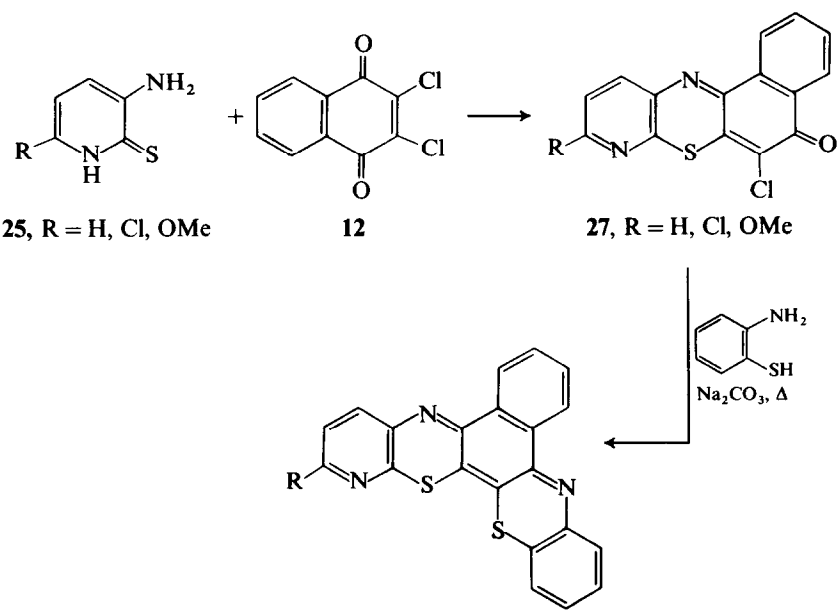
Scheme 4

therefore 15,16-dithia-1,5,10-triazabenzo[h] pentaphene (**26**, R = H) (Scheme 4).

Compound **26**, R = H was also obtained by condensing 6-chloro-7-thia-8,12-diazabenz[a]anthracen-5-one **27**, R = H with 2-aminothiophenol (**23**) in the presence of anhydrous sodium carbonate. 2-Substituted derivatives (**26**) were prepared from substituted 3-aminopyridine-2[1H]-thiones (**25**), 2,3-dichloro-1,4-naphthoquinone (**12**) and 2-aminothiophenol **23** as shown in Scheme 5.

When these dyes, **13**, **19** and **26**, were refluxed with sodium dithionite, the colours were discharged giving yellow-orange colorations. The reduced products were unstable in air due to autooxidation by atmospheric oxygen and regeneration of the original intensely coloured iminoquinoid compounds **13**, **19** and **26** (Scheme 6). The absence of intense colorations in compounds **28** and **29** is due to the loss of extended conjugation inherent in the iminoquinoid compounds **13**, **19** and **20**.

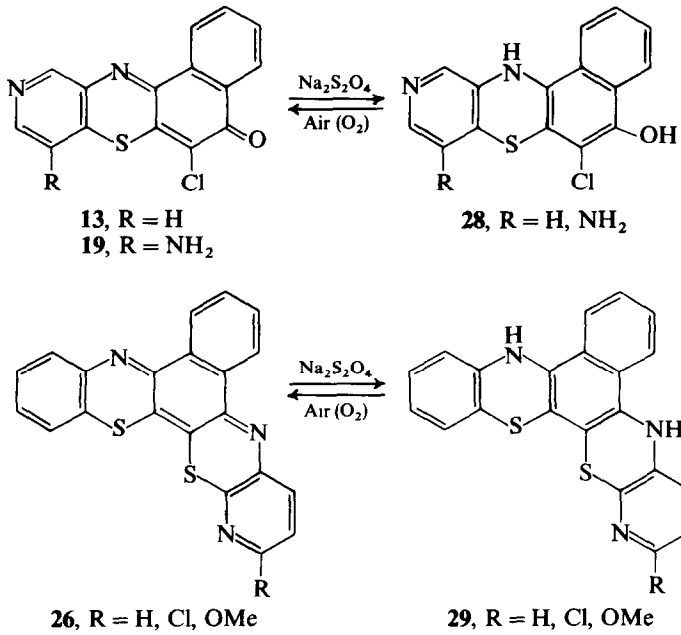
The presence of a halogen atom in C-6 of compounds **13** and **19** and an additional NH_2 group in C-8 of compound **19** would be expected to have a marked influence on the electronic absorption spectra of these compounds and also to result in their potential use as dyes. The presence of the amino group at C-8 in compound **19**, R = NH_2 causes a bathochromic shift in the visible absorption maximum as well as a marked increase in the intensity.



25, R = H, Cl, OMe **12** **27**, R = H, Cl, OMe

26, R = H, Cl, OMe

Scheme 5



Scheme 6

Polyester materials dyed with compounds **13**, **19** and **26** acquired red, purple and purple-red colorations, respectively, which were fast to sunlight and washing. Their intense colorations and good fastness to soap and sunlight, coupled with their ease of production, make them good dyes for textiles. Additionally their insolubility in most common solvents renders them of interest as pigments for paints, varnishes, plastics, ink and cosmetics.

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 methanol and the absorption maxima (ε_{max}) are given in nm. Infrared spectra were obtained on a Perkin-Elmer Model spectrophotometer using KBr discs unless otherwise stated. ^{1}H-NMR spectra were determined on a Varian Associates (Palo Alto, California, USA) T-60 instrument. Chemical shifts are reported on the δ scale relative to tetramethylsilane (TMS) used as an internal standard. 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 aluminium oxide 90 (Merck, Rahway, New Jersey, USA,

70-230 mesh ASTM) eluting with benzene-ethyl acetate before recrystallization in the specified solvent.

3.2 3-Nitropyridin-4[1H]-one (8)

This compound was prepared from pyridin-4[1H]-one (**7**) by modification of the previously described method.[28]

Pyridin-4[1H]-one (**7**) (9·5 g, 100 mmoles) was placed in a flask immersed in a freezing mixture of ice and isopropanol. 22% Oleum (16·5 ml), precooled to 0°, was added during half an hour with gentle stirring. Fuming nitric acid (d, 1·50, 20 ml) was then added slowly, ensuring that the temperature of the reaction mixture did not exceed 30°. After the addition was complete, the mixture was stirred for a further half hour (below 30°C) and was then heated at 95–98° for $2\frac{1}{2}$ h. The solution was then cooled and poured into crushed ice (200 g) which was also cooled in a freezing mixture. The resulting mixture was partially neutralized with concentrated ammonia and resultant precipitate was filtered and recrystallized from boiling water (activated charcoal) to give yellow microneedles of 3-nitropyridin-4[1H]-one (**8**) (11·9 g, 85% yield); m.p. 280–281°; literature m.p. 278–279°.[28]

3.3 3-Nitropyridine-4[1H]-thione (9)

This compound was prepared in 63% yield as previously described[25] except that the phosphorus pentasulphide was ground to a powder to facilitate dissolution in the reaction solvent.

3.4 3-Aminopyridine-4[1H]-thione (10)

3-Aminopyridine-4[1H]-thione was prepared by modification of a previously described method for 3-aminopyridin-4[1H]-one hydrochloride.[18]

Iron powder (20 g) was added in small portions to a warm (40°) stirred suspension of 3-nitropyridine-4[1H]-thione (**9**) (11·08 g, 71 mmoles) in water (100 ml) containing concentrated hydrochloric acid (5 ml). When the initial reaction had subsided, further iron powder (5·0 g) was added and the mixture heated for $1\frac{1}{2}$ h on a water bath. The resulting dark suspension was filtered hot and the filtrate treated with excess concentrated hydrochloric acid and evaporated to a small bulk. On cooling, a solid product separated; this was filtered and recrystallized (twice) from aqueous ethanol (activated charcoal) to give creamy yellow crystals of 3-aminopyridine-4[1H]-thione (**10**) (5·73 g, 64% yield); m.p. > 300° (dec); λ_{max} 257 (3780), 343 nm (1449); ν_{max} 3420 (d, NH_2). Found: C, 47·81; H, 4·70; N, 22·13; S, 25·55. Calcd for $C_5H_6N_2S$: C, 47·62; H, 4·76; N, 22·22; S, 25·40.

3.5 3-Aminopyridin-4[1H]-one hydrochloride (11 . HCl)

3-Aminopyridine-4[1H]-one (**11**) was obtained as the hydrochloride salt in 72% yield by reduction of 3-nitropyridin-4[1H]-one (**8**) with iron and concentrated hydrochloride as described for 3-aminopyridine-4[1H]-thione (**10**). The product was isolated as the hydrochloride salt since the free base decomposed readily giving a dark brown oil. 3-Aminopyridin-4[1H]-one hydrochloride (**11** . HCl) separated as glistening creamy white microneedles, m.p. 227–228° (decomposes); λ_{max} 264 (2285), 306 nm (1051); ν_{max} 3320 (d, 3-NH_2), 1660 cm^{-1} (C=O).

3.6 Reaction of 3-aminopyridin-4[1H]-one (11) with P_2S_5

A mixture of 3-aminopyridin-4[1H]-one hydrochloride (**11** . HCl) (4·31 g, 29 mmoles) powdered phosphorus pentasulphide (17·0 g) and pyridine (110 ml) dried over potassium hydroxide was refluxed at 114° for 6 h with constant stirring. The solvent was removed by vacuum distillation. Crushed ice (150 g) was added to the solid concentrate and the mixture heated on a water bath to remove hydrogen sulphide. When the evolution of hydrogen sulphide ceased, the resulting slurry was filtered hot and the filtrate brought to near boiling. The hot mixture was treated with activated charcoal and filtered. The pH of the filtrate was brought down to 1 by addition of concentrated hydrochloric acid and the mixture was then chilled for 5 days and filtered. The residue was recrystallized from aqueous ethanol (activated charcoal) to give creamy yellow microneedles of 3-aminopyridine-4[1H]-thione (**10**) (2·0 g, 55% yield); m.p. > 300° (dec). The product was identical to the product obtained by reduction of 3-nitropyridine-4[1H]-thione (see Section 3.4).

3.7 6-Chloro-7-thia-10,12-diazabenz[a]anthracen-5-one (13)

A mixture of 3-aminopyridine-4[1H]-thione (**10**) (0·5 g, 4 mmoles), anhydrous sodium carbonate (1·0 g), benzene (25 ml) and *N*,*N*-dimethylformamide (DMF) was heated at 60° for 15 min with stirring. 2,3-Dichloro-1,4-naphthoquinone (**12**) (0·91 g, 4 mmoles) was then added and the resulting mixture refluxed for $4\frac{1}{2}$ h. The mixture was then cooled and poured into water (100 ml) to remove inorganic materials. The residue was filtered, washed with cold acetone and then with water, and finally recrystallized from a large volume of acetone (activated charcoal) to afford the red dye, 6-chloro-7-thia-10,12-diazabenz[a]anthracen-5-one, **13**, R = H (1·17 g, 98% yield); m.p. > 300°, λ_{max} 309 (11344), 442 nm (8372); ν_{max} 1670 cm^{-1} (C=O); ^{1}H-NMR (DMSO-d_6) 7·82 (m, aromatic Hs); mass

spectrum *m/e* 253 (M-S-CO, 18%), 281 [M − S, 23%], 313 [M^+, 100%], 315 [M + 2, 34%]. Found: C, 60·46; H, 2·21; N, 9·53; Cl, 12·00; S, 10·63. Calcd for $C_{15}H_7N_2ClOS$: 60·30; H, 2·35; N, 9·38; Cl, 11·89; S, 10·72.

3.8 3,5-Dinitropyridin-4[1H]-one (15)

This compound was prepared by the nitration of pyridin-4[1H]-one (**7**) with a mixture of fuming nitric acid (d, 1·50) and 22% oleum at 130–140° as previously described.[29] When the reaction was carried out at 95–100° mononitration took place and the product was 3-nitropyridin-4[1H]-one (**8**).

3.9 3,5-Dinitropyridine-4[1H]-thione (16)

3,5-Dinitropyridine-4[1H]-thione was prepared by the reaction of 3,5-dinitropyridin-4[1H]-one (**15**) with phosphorus pentasulphide as previously described.[25]

3.10 3,5-Diaminopyridine-4[1H]-thione (17) (Method A)

This compound was prepared from 3,5-dinitropyridine-4[1H]-thione (**16**) using the conditions reported (Section 3.4) for 3-aminopyridine-4[1H]-thione (**10**); m.p. 246–247°, λ_{max} 242 (4348), 347 nm (3936); ν_{max} 3320 (d, NH_2), 2620 (w, SH), 1640 (C=N), 1250 cm^{-1} (C=S); δ 8·17 (2H, s, 2-H, 6-H), 7·90 (4H, br, 3-NH_2, 5-NH_2). Found: C, 42·76; H, 5·04; N, 29·70; S, 22·72. Calcd for $C_5H_7N_3S$: C, 42·55; H, 4·96; N, 29·79; S, 22·70.

3.11 3,5-Diaminopyridin-4[1H]-one dihydrochloride (18.2HCl)

3,5-Dinitropyridin-4[1H]-one (**15**) (10·0 g, 54 mmoles) was suspended in water (100 ml) containing concentrated hydrochloric acid (10 ml). The mixture was warmed to 40° and iron powder (25 g) added portionwise over half an hour with constant stirring. When the initial reaction had subsided, further iron powder (5 g) was added and the mixture heated for 2 h on a water bath. The resulting dark-brown suspension was filtered hot and the filtrate treated with excess concentrated hydrochloric acid and evaporated to near dryness. The solution was cooled, filtered and the residue recrystallized from water (activated charcoal) to give 3,5-dinitropyridin-4[1H]-one dihydrochloride (**18**.2HCl) (9·5 g, 89% yield) as long brown needles, m.p. 280–281°; λ_{max} 236 (3784), 260 (2970), 304 (3773), 350 nm (1540); ν_{max} 3250 (br, $NH_3^{\oplus}$), 1675 cm^{-1} (C=O); 7·57 (2H, s, 2-H, 6-H), 6·60 (5H, b, 1-NH, 3-NH_2, 5-NH_2). Found: C, 30·22; H, 4·68; N, 21·42; Cl, 36·03. Calcd for $C_5H_9N_3Cl_2O$: C, 30·30; H, 4·55; N, 21·21; Cl, 35·86.

3.12 3,5-Diaminopyridine-4[1H]-thione (17) (Method B)

A mixture of 3,5-diaminopyridin-4[1H]-one dihydrochloride (10·0 g, 80 mmoles), ground phosphorus pentasulphide (21·5 g) and pyridine (150 ml) dried over potassium hydroxide pellets was refluxed with stirring for 8 h. The solvent was removed by vacuum distillation. Crushed ice (300 g) was added and the mixture heated on a water bath to remove hydrogen sulphide. When the evolution of hydrogen sulphide ceased, the resulting slurry was filtered hot and the filtrate brought to near boiling. It was then treated with activated charcoal and filtered. The filtrate was acidified with concentrated hydrochloric acid to pH 1 with cooling. The solution was chilled in a refrigerator for 3 days and the product collected by filtration. Recrystallization from aqueous ethanol (activated charcoal) afforded 3,5-diaminopyridine-4[1H]-thione (**17**) (5·0 g, 44% yield) as glistening yellowish green plates, m.p. 246–247°. Mixed melting-point determination with the previously produced product (method A Section 3.10) showed no depression; the ultraviolet, infrared and NMR spectra of both compounds were identical.

3.13 8-Amino-6-chloro-7-thia-10,12-diazabenz[a]anthracen-5-one (19)

A mixture of 3,5-diaminopyridine-4[1H]-thione (**17**) (0·71 g, 5 mmoles), anhydrous sodium carbonate (1·06 g, 10 mmoles) and benzene (30 ml) DMF 2 ml was warmed with stirring and maintained at 60° for 15 min.

2,3-Dichloro-1,4-naphthoquinone (**12**) (1·36 g, 6 mmoles) was then added and the mixture refluxed for $4\frac{1}{2}$ h. The resulting mixture was cooled, poured into 200 ml of water, stirred for 10 min and filtered. The dark-brown residue was washed with cold acetone and recrystallized from aqueous DMF. The crystalline material was further purified by column chromatography on alumina (Merck, 70–230 mesh ASTM) eluting with (1:10:10) DMF–benzeneacetone mixture. 8-Amino-6-chloro-7-thia-10,12-diazabenz[a]-anthracen-5-one (**19**) was collected as a purple crystalline powder (1·44 g, 92% yield); m.p. > 360°; λ_{max} 311 (15 786), 460 nm (11 196); ν_{max} 3350 (NH_2), 1652 cm^{-1} (C=O); 8·82 (1H, s, 11-H), 8·56 (1H, s, 9-H), 8·04 (2H, br, 8-NH_2), 7·83 (4H, m, 1-H, 2-H, 3-H, 4-H). Found: C, 57·40; H, 2·43; N, 13·49; Cl, 11·20; S, 10·40. Calcd for $C_{15}H_8N_3ClOS$: C, 57·42; H, 2·55; N, 13·40; Cl, 11·32; S, 10.21.

3.14 6-Chloro-benzo[a]phenothiazin-5-one (24)

This compound was prepared by modification of the previously described method.[22]

A mixture of 2-aminothiophenol (**23**) (1·25 g, 10 mmoles), chloroform (50 ml) and anhydrous sodium carbonate (2·12 g, 20 mmoles) was heated on a water bath with stirring. After 15 min, 2,3-dichloro-1,4-naphthoquinone (2·27 g, 10 mmoles) was added. The mixture was initially stirred at room temperature for half an hour and then refluxed for 3 h. The solvent was removed by distillation, water (300 ml) added to dissolve inorganic salts and the mixture filtered. The residue was purified by column chromatography and recrystallized from aqueous acetone (activated charcoal). 6-Chloro-benzo[a]phenothiazin-5-one (**24**) (2·83 g, 95% yield) was obtained as a purple microcrystalline powder, m.p. 233–234°; m.p. 232°.[22]

3.15 15,16-Dithia-1,5,10-triazabenzo[h]pentaphene (26, R = H)

To a mixture of 6-chloro-benzo[a]phenothiazin-5-one (**24**) (1·19 g, 4 mmoles) and 3-aminopyridin-2[1H]-thione[32] (**25**, R = H) (0·5 g, 4 mmoles) was added. Nitrobenzene (60 ml) and DMF (5 ml), followed by anhydrous sodium carbonate (0·43 g, 4·1 mmoles) were then added. The slurry was stirred at room temperature for 20 min and then refluxed for 16 h.

Nitrobenzene was distilled off after the reflux period. Water (500 ml) was then added and the dark-red slurry warmed to 60° for 15 min. It was filtered hot and the residue recrystallized from acetone (activated charcoal) to give the purple-red dye, 15,16-dithia-1,5,10-triazabenzo[h]pentaphene (**26**, R = H) (1·24 g, 84% yield); m.p. > 300°, λ_{max} 468 nm (13 258); ν_{max} 1650 cm^{-1} (C = N); *m/e* 369 (M^+, 100%). Found: C, 68·03; H, 3·06; N, 11·55; S, 17·30. Calcd for $C_{21}H_{11}N_3S_2$: C, 68·29; H, 2·98; N, 11·38; S, 17·35.

3.16 2-Chloro-15,16-dithia-1,5,10-triazabenzo[h]pentaphene (26, R = Cl)

This purple dye was prepared from 6-chloro-benzo[a]phenothiazin-5-one (**24**) and 3-amino-6-chloropyridine-2[1H]-thione[33] (**25**, R = Cl) in the presence of anhydrous sodium carbonate as was described for 15,16-dithia-1,5,10-triazabenzo[h]pentaphene (**26**, R = H) (Section 3.15); m.p. > 300°; λ_{max} 477 nm (22, 147); ν_{max} 1646 cm^{-1} (C=N); *m/e* 403 [M^+, 100%], 405 [M + 2, 37%]. Found: C, 62·36; H, 2·39; N, 10·60; S, 16·01; Cl, 8·66. Calcd for $C_{21}H_{10}N_3S_2Cl$: C, 62·45; H, 2·48; N, 10·41; S, 15·86; Cl, 8·80.

3.17 2-Methoxy-15,16-dithia-1,5,10-triazabenzo[h]pentaphene (26, R = OMe)

2-Methoxy-15,16-dithia-1,5,10-triazabenzo[h]pentaphene (**26**, R = OMe) was similarly prepared from 3-amino-6-chlorpyridine-2[1H]-thione[33] (**25**, R = OMe) and 6-chloro-benzo[a]phenothiazin-5-one (**24**) in the presence of

anhydrous sodium carbonate (as for **26**, R = H, Section 3.15); m.p. > 300°; λ_{max} 481 nm (16958); ν_{max} 1652 cm^{-1} (C = N); *m/e* 399 [M$^+$, 100%]. Found: C, 65·99; H, 3·34; N, 10·40; S, 15·87. Calcd for $C_{22}H_{13}N_3S_2O$: C, 66·17; H, 3·26; N, 10·53; S, 16·04.

3.18 Reactions of 9-substituted-6-chloro-7-oxa-8,12-diazabenz[a]anthracen-5-ones (27, R = H, Cl, OMe) with *o*-aminothiophenol (23)

The 9-substituted-6-chloro-7-oxa-8,12-diazabenz[a]anthracen-5-ones (**27**, R = H, Cl, OMe) required for these reactions were obtained as previously reported.[23] Base-catalysed condensations with 2-aminothiophenol (**23**) as described for 15,16-diathia-1,5,10-triazabenzo[h]pentaphene (**26**, R = H) gave products identical with the 15,16-dithia-1,5,10-triazabenzo-[h]pentaphenes, **26**, R = H, Cl, OMe described above.

3.19 Sodium dithionite reduction of the dyes (13, 19 and 26)

In a typical experiment, 6-chloro-7-thia-10,12-diazabenz[a]anthracen-5-one (**13**) (0·3 g, 1 mmole) was dissolved in 25 ml of acetone. Water (1 ml) was added, followed by sodium dithionite (0·7 g, 4 mmoles) and the mixture was refluxed for 3 h.

During this period, the originally blood-red solution became discoloured. It was poured into an ice-cold solution of sodium dithionite (0·7 g) in 150 ml of water, stirred and filtered. During the filtration process, the solution gradually changed to the colour of the starting compound **13**. The product that was isolated was identical with the starting compound, confirming that the reduced compound was oxidized to the starting quinoid compound **13** by atmospheric oxygen during the work-up stage.

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