New Dyes based on 3-Aryl-Benzo- and -Naphtho-1,4-thiazines

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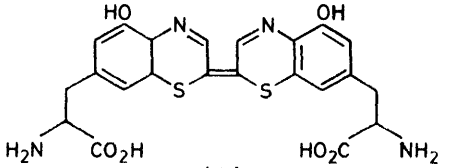
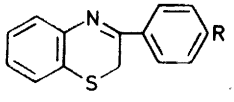
3-Aryl-2*H*-1,4-benzothiazines have been converted into cyanine dyes by condensing their hydroperchlorates with aldehydes, and into azo-compounds by coupling with reactive diazonium salts. The azo-compounds were also obtained by condensing arylglyoxal hydrazonyl bromides with *o*-aminothiophenol; they exist predominantly in their tautomeric hydrazone forms. 2-Amino-3-mercapto-1,4-naphthoquinone condenses with ω-bromoacetophenones to form 3-aryl-3,4-dihydro-3-hydroxy-2*H*-naphtho[2,3-*b*]-1,4-thiazine-5,10-quinones. Attempts to dehydrate these carbinolamines gave a variety of products. Oxidation of the phenyl analogue with iodosobenzene diacetate led to acetoxylation at C-2 by an indirect Pummerer oxidation.

THE identification [1] of the natural trichochrome pigments [*e.g.* (1)], and the synthesis [2] of the parent compound incorporating the new chromophore, suggested that the 1,4-benzothiazine system might form the basis of new dyes of possible commercial interest. Relatively little work [3] has been done in this area, and we describe in this paper some modifications of 3-aryl-2*H*-1,4-benzothiazines which lead to coloured compounds.



(1)

The benzothiazines (2; R = OMe and NO_2) were prepared by condensing the sodium salt of *o*-aminothiophenol with the appropriate ω-bromoacetophenone followed by rapid work-up to avoid oxidative dimerisation.[4a] Using the slower procedure of ref. 4*b* a monomeric benzothiazine (2; R = OMe) was isolated on only one occasion despite many attempts. That the compounds are the 2*H*-tautomers follows from the presence of a 2-proton singlet † in their n.m.r. spectra at δ *ca.* 3.5. This is consistent with previous work on (2; R = Me, Cl, Br) [4b] although (2; R = H) is said [5,6] to exist in solution as a tautomeric mixture of the 2*H*- and 4*H*-isomers. However the evidence is unconvincing; in particular no n.m.r. signal is reported for the vinyl proton of the 4*H*-tautomer which should be seen upfield from the aromatic proton resonances. An attempt [6] to separate the isomers gave the dimer (4; R = H). Several 3-aryl-2-cyanobenzothiazines have been assigned [7] the 4*H*-isomeric structure but without supporting evidence, possibly following an earlier unsupported suggestion.[8] The original 'preparations' [9] of (2; R = H), using the above method, actually gave the dimer (4; R = H) as did that of Finar and Montgomery.[10] 3-Aryl-2*H*-1,4-benzothiazines in general are very prone to autoxidative dimerisation, especially in polar solvents [5] (it can be effected deliberately by oxygenation in acid solution [11]), and we found it very difficult to avoid even when air was excluded. The *p*-tolyl derivative (2; R = Me) is particularly easily dimerised and we only obtained the monomer on one occasion.[12] Again, on repeating the preparation of the 3-*o*-hydroxyphenyl derivative (3) exactly as described [13] we also isolated the corresponding 2,2′-dehydro-dimer in 12% yield; (3) exists in the chelated form shown (δ_{OH} 14.74) but the dimer was too insoluble for n.m.r. purposes.



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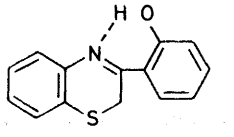

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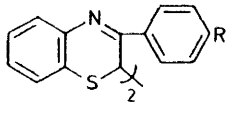

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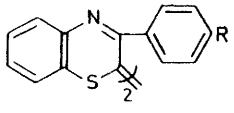


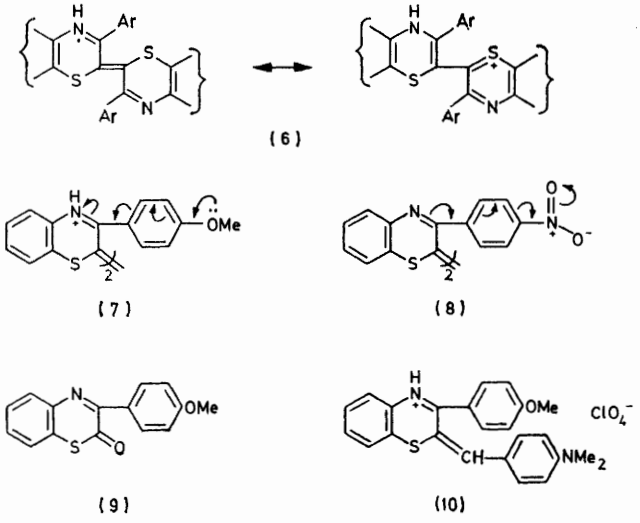
(5)

Following the method of Fujii [14] we obtained the 2,2′-dimers (4; R = OMe and NO_2) by oxidising the corresponding monomers with hot ethanolic picric acid, although (4; R = OMe) was sometimes obtained on attempted crystallisation of the monomer from methanol. In the mass spectra of the dimers (4; R = OMe and NO_2) the highest peak corresponds to $M^+ - 2$ again reflecting the ease of dehydrogenation, while for the 2,2′-dimer of (3) the highest peak is found at $M^+ - 4$. Oxidation of the monomers (2) with chloranil [15] gave the $\Delta^{2,2'}$-bibenzothiazines (5; R = OMe and NO_2) while further oxidation of (4; R = OMe) with DDQ also afforded (5; R = OMe). T.l.c. showed that (5; R = OMe) was a mixture of a red and a yellow compound, presumably the *cis* and *trans* forms by comparison with (5; R = Br, Cl, and Me).[15] Isolation of the two forms was not possible as they rapidly interconverted at room temperature. The red dinitro-dimer (5; R = NO_2)

† Unchanged at −40 °C.

exists in one form only (t.l.c.) which, by analogy,[15] is the *cis*-isomer. The visible spectra of the $\Delta^{2,2'}$-bibenzothiazines (5) undergo a large bathochromic shift in acid solution on formation of the mesomeric cation (6) [*ca.* 145 nm for (5; R = Br, Cl)].[15] However, the shift for (5; R = OMe) is reduced to 120 nm while (5; R = NO_2) shows no shift on acidification. The former can be attributed to competing conjugation from the methoxy-group (7) while the latter is probably due to the reduced basicity of the imino-nitrogen arising from the *p*-nitro-group (8).

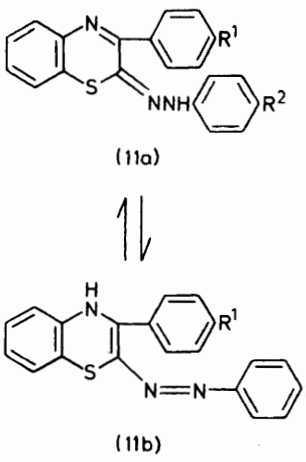
A minor product from the oxidation of (2; R = OMe) with chloranil was the thiolactone (9) [ν_{CO} 1 633 cm^{-1}, $M^+ - CO$ (100%)]. The structure was confirmed by a Sarett [16] oxidation of (2; R = OMe) which is known [17]

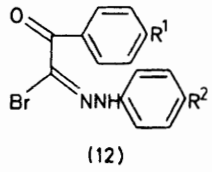


to convert chromens to coumarins. The major product from that oxidation was actually 2-(*p*-methoxyphenyl)-benzothiazole, and it was subsequently found that (9) could be converted into the thiazole merely by refluxing in methanol [decarbonylation [18] of (9; H in place of OMe) was effected at 300 °C].

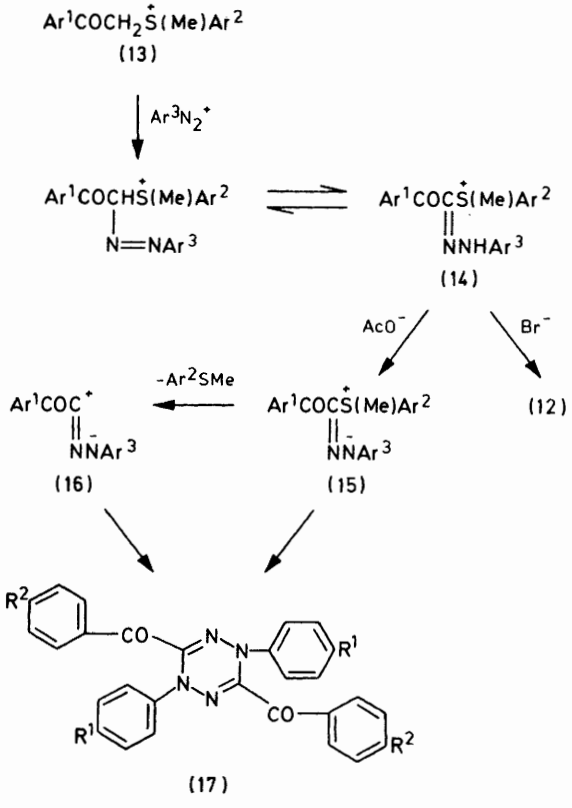
Cyanine Dyes.—Russian workers [3b] have shown that *N*-methyl-2*H*-1,4-benzothiazines will condense with aromatic aldehydes to form cyanine dyes. The methylene group of (2; R = OMe) would not condense with aldehydes under neutral or alkaline conditions but reaction occurred in acetic acid using the hydroperchlorate. Condensation with *p*-dimethylaminobenzaldehyde and *p*-dimethylaminocinnamaldehyde gave the intensely blue and green perchlorates (10) and (10; =CH–CH=CH in place of =CH), respectively ($\lambda_{max.}$ 588 and 646 nm). The free bases are orange.

Azo Dyes.—Benzo-1,4-thiazine azo-compounds, not known hitherto, have been prepared by two methods. Coupling (2; R = OMe) with diazotised *p*-nitroaniline and diazotised methyl *p*-aminobenzoate in aqueous methanolic sodium acetate readily gave the azo-dyes (11; R^1 = OMe, R^2 = NO_2), and (11; R^1 = OMe, R^2 = CO_2Me), respectively, but the reaction is limited to



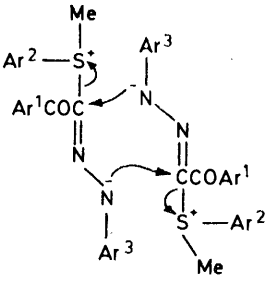


the more reactive diazonium salts. In the second method the azo-coupling was effected at an earlier stage in the formation of the hydrazonyl bromides (12) which were then condensed with the sodium salt of *o*-aminothiophenol to give the azo-compounds (11; R^1 = H, R^2 = H, OMe, and NO_2). The hydrazonyl bromides (12; R^1 = R^2 = H; R^1 = H, R^2 = OMe; and R^1 = R^2 = OMe) were prepared [19,20] by converting aryl phenacyl sulphides into the corresponding methyl sulphonium bromides (13) which were coupled with a diazonium salt (Scheme 1). However, attempted preparation of (12; R^1 = H, R^2 = NO_2; R^1 = OMe, R^2 = NO_2; R^1 = R^2 = NO_2) under the same conditions



SCHEME 1

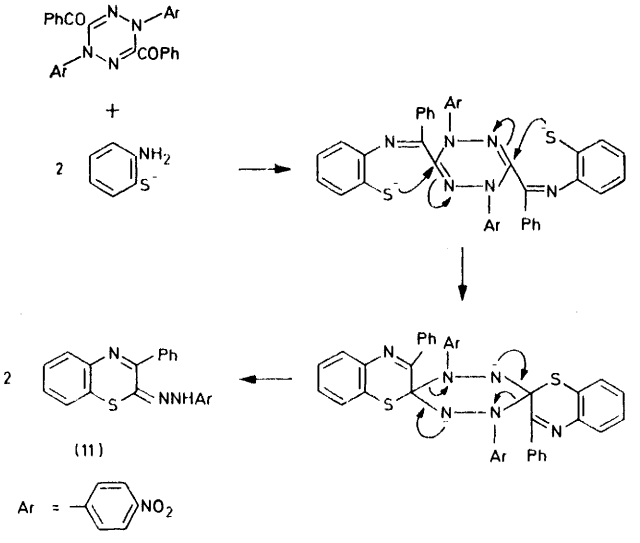
led to the formation of the 1,2,4,5-tetrazines (17; R^1 = NO_2, R^2 = H, OMe, NO_2) in low yield. This has been observed before [20,21] and may be attributed to the removal of a proton from the intermediate sulphonium hydrazone (14) by base (acetate) to form the zwitterion (15) which either cyclises as shown (18), or loses aryl methyl sulphide to produce a 1,3-dipole (16) which then dimerises. All the tetrazines isolated were derived from the *p*-nitrophenylhydrazones [14; Ar^3=$C_6H_4NO_2$-(*p*)]. The *p*-nitro-group would favour tetrazine formation in preference to formation of hydrazonyl bromide



(18)

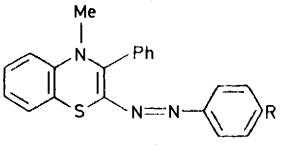
both by increasing the acidity of the NH proton in (14), and by stabilisation of the 1,3-dipole (16) if formed.

Another member of the benzothiazine 'azo' series (11) was obtained from one of the tetrazines thus providing further confirmation of the *s*-tetrazine structure (*cf.* ref. 20). Condensation of the tetrazine (17; R^1 = NO_2, R^2 = H) with the sodium salt of *o*-aminothiophenol gave (11; R^1 = H, R^2 = NO_2) which must proceed as shown in Scheme 2.



SCHEME 2

The 'azo' compounds (11) are written as an equilibrium mixture but only (11; R^1 = H, R^2 = OMe) provided evidence for the presence of two tautomers. This compound moved as two spots on t.l.c. and each spot, after elution, ran again as two compounds. Further, the u.v. absorption curves, measured in five different solvents at the same concentration, formed an isosbestic point. To determine which isomer predominated comparison was made with the azo-compounds (19; R = H, and OMe) prepared by condensing *o*-*N*-methylaminothiophenol with the hydrazonyl bromides (12; R = H and OMe). As the Table shows,



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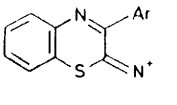

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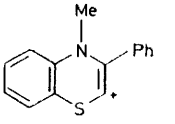

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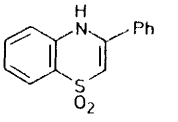


(22)

(23a) (23b)

the preferred tautomer is the hydrazone form (11a). Some further support is provided by the mass spectra of the compound (11). These all include a strong peak for M^+ — ArNH (20) except for (13; R^1 = H, R^2 = OMe) where it is weak, while in the spectra of (19) it is replaced by a fragment ion M^+ — N=NAr (21) which is the base peak.

Two azo-compounds of type (23) were also prepared from the benzothiazine *SS*-dioxide (22). This compound, obtained by reductive cyclisation of *o*-nitrophenyl phenacyl sulphone with phosphinic acid and palladium black, exists exclusively in the 4*H*-tautomeric form (δ *ca.* 6.2, =CH–) like other members of the series,[22] in contrast to the 2*H*-1,4-benzothiazines (2). It coupled only with the more reactive diazonium salts to give (23; R = NO_2 and CO_2Me). Only one tautomeric form was observed in each case but we have no decisive evidence in favour of (a) or (b).

Visible absorption of compounds (11) and (19)

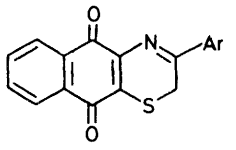
Compound (11) R^1	R^2	$\lambda_{max.}$ * nm (log ε)
OMe	NO_2	417 (4.38)
OMe	CO_2Me	408 (4.19)
H	NO_2	430 (4.38)
H	H	426 (4.09)
H	OMe	438 (4.02)
Compound (19)		
R = H		505 (4.17)
R = OMe		506 (4.25)

* In EtOH.

Quinones.—Another way to introduce colour into the benzothiazine system is to convert the aromatic ring into a quinone. For convenience we initially attempted

to synthesise the naphthothiazinequinone system (24) which appeared to be readily accessible by condensing 2-amino-3-mercapto-1,4-naphthoquinone with ω-bromoacetophenones. In the event the compounds isolated were the carbinolamines (25) (more accurately vinylogous carbinolamides). The mass spectra of (25; R = H, OMe, NO_2) all showed initial fragmentation with loss of water and subsequent loss of sulphur.

It is possible that the condensation reactions do yield the anhydro-form (24), as in the 3-aryl-2*H*-1,4-benzo-



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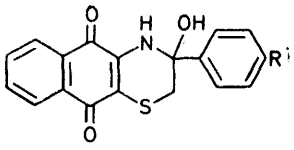

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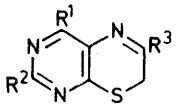

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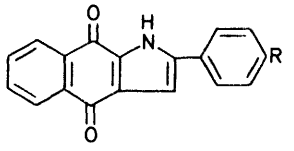

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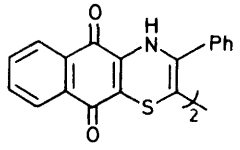

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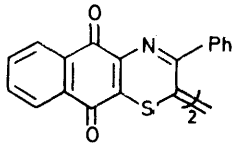

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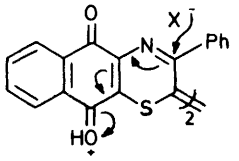


(30)

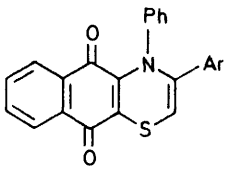
thiazine preparations described above, but rehydration would occur readily as the unsaturated system, C=N–C=C–C=O, thus formed, would be very nucleophilic. Russian workers [23] have observed that in the preparation of pyrimidino-2*H*-1,4-thiazines (26) the reaction may stop at the carbinolamine stage according to the substituents present. Stirring the carbinolamines (25) with acid-washed silica or alumina or a trace of toluene-*p*-sulphonic acid in dry solvents, appeared to effect dehydration (as judged by colour changes) but the anhydro-products could not be isolated. Treating (25; R = H) in cold methanol with a drop of hydrochloric acid gave the *O*-methyl derivative (25; R = H, OMe in place of OH).

Further attempts to dehydrate (25) to (24) by heating gave other products. Thus heating (25; R = H) at 280 °C *in vacuo* led to extrusion of sulphur and loss of water to form the indolequinone (27; R = H) which has been prepared [24] previously by thermolysis of 2-azido-3-styryl-1,4-naphthoquinone. The methoxy-analogue (27; R = OMe) was derived similarly while the nitro-compound (27; R = NO_2) could only be obtained, in poor yield, by heating with copper bronze. Heating the quinone (25; R = H) in higher boiling solvents (mesitylene, dimethylformamide, or dimethyl sulphoxide) gave either recovered starting material or an intractable mixture but in boiling acetic acid a nearly quantitative yield of the dimer (28) was obtained. Evidently dehydration to (24) is followed by oxidative dimerisation either self-induced or effected by air. That the dimer is in the 4*H*-tautomeric form is evident from the i.r. [ν_{NH} 3 365 cm^{-1}] and n.m.r. (no methine signal) spectra and may be attributed to the presence of the conjugated system Ph–C=C–C=C–Ph. A Dreiding model indicated that intramolecular hydrogen bonding would be negligible. The highest peak in the mass spectrum of (28) is attributed to $M^+ - S$ with the base peak at *m/e* 544 ($M^+ - 2S$); an unexpected ion at *m/e* 562 corresponds to $M^+ - CH_2S$. Oxidation of (28) with silver oxide gave the violet $\Delta^{2,2'}$-dimer (29) which ran as two compounds in t.l.c., presumably *cis*- and *trans*-isomers, but they could not be isolated. In contrast to analogous dimers, discussed above, this compound showed a bathochromic shift of the visible spectrum in acid solution. This may be attributed to protonation on a carbonyl group and nucleophilic attack at C-3 (and 3'?) [see (30)]. In the mass spectrum of (29) both M^+ and $M^+ - S$ are base peaks but $M^+ - 2S$ (542) is much weaker than $M^+ - 2S + 2H$ (544).

In view of our inability to isolate naphtho-2*H*-1,4-thiazine-quinones of type (24) we attempted to synthesise a 4*H*-thiazine of type (31). Condensation of 2-anilino-3-mercapto-1,4-naphthoquinone with ω-bromoacetophenone did not lead to (31; Ar = Ph) or the corresponding carbinolamine but gave only the uncyclised product (32) (ν_{NH} 3 250 cm^{-1}, no ν_{HO}, ν_{CO} 1 682 cm^{-1}, δ_{CH_2} 4.06). On heating in methanol containing a drop of hydrochloric acid cyclisation did occur but the product was nitrogen-free and we regard it as the oxathian-quinone (33) which is consistent with the spectroscopic and analytical data. Presumably the anilinoquinone (32) is hydrolysed to the corresponding hydroxyquinone followed by cyclisation to the hemiacetal (33; OH in place of OMe), and further reaction with methanol in the presence of acid to give (33).

Other variations of (24) which might permit the isolation of a stable compound are the sulphoxides (34) or the corresponding sulphones. In an approach to (34) the quinone (25; R = H) was oxidised with iodosobenzene diacetate [25] in acetic acid but unexpectedly the product obtained was the quinone (35) showing n.m.r. signals for ethoxy- and acetoxy-groups, and –NH– proton and a methine proton at δ 6.16. In the mass spectrum the base peak falls at *m/e* 293 ($C_{17}H_{11}NO_2S$, *i.e.* $M^+ -$ EtOH $- CH_2CO - CO$) which we attribute to the ion (36). The appearance of the acetoxy-group at C-2 is evidently the result of a Pummerer rearrangement the

unusual feature being that the reaction starts with a sulphide rather than a sulphoxide, the first step being formation of the sulphonium acetate (37). The ethoxy-



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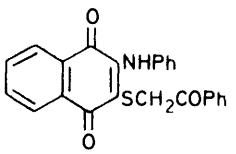

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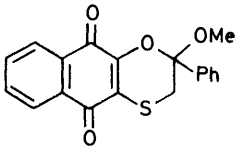

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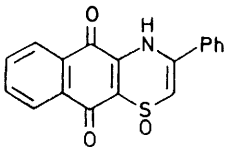

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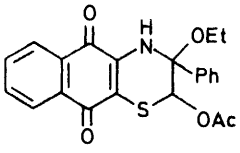
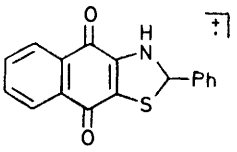
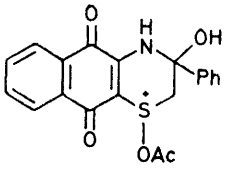


(35)



(36)



(37)

group in the product (35) arises from the ethanol in the chloroform used in chromatographic purification.

EXPERIMENTAL

U.v. and n.m.r. spectra were measured for solutions in ethanol and deuteriochloroform, respectively, and i.r. spectra for KBr discs unless otherwise stated. Merck Kieselgel 100 (70—230 mesh) was used for dry column chromatography.

3-(p-*Methoxyphenyl*)-2H-1,4-*benzothiazine* (2; R = OMe).—*o*-Aminothiophenol (1.25 g) was added to a solution prepared from sodium (0.23 g) and ethanol (20 ml), and, after 15 min, ω-bromo-*p*-methoxyacetophenone (2.28 g) in ethanol (25 ml) was added. The *benzothiazine* precipitated almost immediately. It crystallised from 80% ethanol as pale yellow needles, m.p. 98—100 °C (2.4 g, 94%) (Found: C, 70.4; H, 5.2; N, 5.3; S, 12.8. $C_{15}H_{13}NOS$ requires C, 70.6; H, 5.1; N, 5.5; S, 12.55%); $\lambda_{max.}$ 234sh, 275, 309, 323, 351sh nm (log ε 4.19, 4.20, 4.10, 4.10, and 3.96); δ 3.52 (2 H, s, CH_2), 3.80 (3 H, s, OMe), 6.94 (2 H, d, *J* 9 Hz, H-3′ and -5′), 7.02—7.52 (4 H, m, ArH), and 7.95 (2 H, d, *J* 9 Hz, H-2′ and -6′); *m/e* 255 (M^+, 100%), 240 (9), and 121 (7). The benzothiazinium perchlorate was prepared by heating the benzothiazine (2; R = OMe) (2.0 g) in boiling ethanol (30 ml) containing 60% perchloric acid (1.5 g) for 2 h. After filtration the *salt* separated on cooling to form yellow needles, m.p. 159—161 °C (from ethanol) (1.95 g, 93%) (Found: C, 50.5; H, 3.9; Cl, 10.2; N, 3.6; S, 8.7. $C_{15}H_{14}ClNO_5S$ requires C, 50.6; H, 3.9; Cl, 10.0; N, 3.9; S, 9.0%).

3-(p-*Nitrophenyl*)-2H-1,4-*benzothiazine* (2; R = NO_2).—The above reaction was repeated using ω-bromo-*p*-nitroacetophenone (2.43 g). After stirring for 3 h the mixture was evaporated *in vacuo* leaving an oil which, in chloroform, was passed down a column of dry silica to give a solid which gave the *benzothiazine* as pale yellow plates, m.p. 120—122 °C (decomp.) (from ethanol) (1.14 g, 52%) (Found: C, 62.2; H, 3.5; N, 10.4; S, 11.6. $C_{14}H_{10}N_2O_2S$ requires C, 62.2; H, 3.7; N, 10.4; S, 11.9%); $\lambda_{max.}$ 240, 274, 304, and 347 nm (log ε 4.37, 4.27, 4.13, and 4.02); δ 3.60 (2 H, s, CH_2), 7.04—7.56 (4 H, m, ArH), 8.20 (4 H, dd, *J* 9 Hz, H-2′, -3′, -5′, and -6′); *m/e* 270 (M^+, 100%), 224 (18), 223 (28), and 121 (25).

3-p-*Tolyl*-2H-1,4-*benzothiazine* (2; R = Me).—The above reaction was repeated with ω-bromo-*p*-methylacetophenone (2.12 g). After stirring overnight the mixture was evaporated *in vacuo* leaving a dark yellow oil which was dissolved in chloroform and passed down a column of dry silica. The yellow oil obtained slowly solidified. Crystallisation from methanol gave the benzothiazine as yellow needles, m.p. 54—55 °C (lit.,[11] 53—55 °C) (1.8 g, 75%); δ 2.38 (3 H, s, CH_3), 3.54 (2 H, s, CH_2), 6.9—7.6 (6 H, m, ArH), and 7.86 (2 H, d, *J* 8 Hz, H-2′ and -6′); *m/e* 239 (M^+, 20%), 238 (100), 223 (11), and 121 (3).

2,2′-*Bi*(3-*aryl*-2H-1,4-*benzothiazine*)*s*.—(*a*) (4; R = OMe). 3-(*p*-Methoxyphenyl)-2*H*-1,4-benzothiazine (1.3 g) and picric acid (1.17 g) were heated in refluxing ethanol (40 ml) for 30 min. The *dimer* crystallised on cooling as yellow needles, m.p. 219—221 °C (from xylene) (1.0 g, 78%) (Found: C, 71.0; H, 4.8; N, 5.6; S, 12.5. $C_{30}H_{24}N_2O_2S_2$ requires C, 70.9; H, 4.7; N, 5.5; S, 12.6%); $\lambda_{max.}$ ($CHCl_3$) 250, 277, 303, 340, and 361 nm (log ε 4.35, 4.36, 4.27, 4.14, and 4.10); δ(C_5D_5N, 100 °C) 3.71 (6 H, s, OMe), 4.49 (2 H, s, >CH−), 6.90 (4 H, d, *J* 9 Hz, H-3′, -3″ and H-5′, -5″), 6.98—7.74 (8 H, m, ArH), 7.82 (4 H, d, *J* 9 Hz, H-2′, -2″ and H-6′, -6″), *m/e* 508 (M^+, <0.1%), 506 (<0.3), 255 (35), 254 (100), 240 (5), 223 (7), 106 (13), and 91 (45). By analogy, this dimer is probably the *meso* form.[11]

(*b*) (4; R = NO_2) was obtained similarly. It crystallised from xylene as yellow needles, m.p. 245—247 °C (0.23 g, 86%) (Found: C, 62.4; H, 3.4; N, 10.3; S, 12.1. $C_{28}H_{18}N_4O_4S_2$ requires C, 62.5; H, 3.3; N, 10.4; S, 11.9%); $\lambda_{max.}$ ($CHCl_3$) 254, 269sh, 304, and 359 nm (log ε 4.42, 4.38, 4.26, and 4.08); δ(C_5D_5N) 4.57 (2 H, s, >CH−), 6.9—7.9 (8 H, m, ArH), and 7.95 and 8.16 (each 4 H, d, *J* 9 Hz, $C_6H_4NO_2$); *m/e* 538 (<0.1%), 536 (M^+, <0.3%), 270 (32), 269 (100), 223 (71), and 91 (10). Only one form of the dimer was detected, presumably the *meso*.[11]

2,2′-*Bi*-[(3-o-*hydroxyphenyl*)-2H-1,4-*benzothiazine*]. —3-(*o*-Hydroxyphenyl)-2*H*-1,4-benzothiazine was prepared from *o*-aminothiophenol (1.25 g) as described [13] to afford yellow needles, m.p. 117—118 °C (lit.,[13] 115—116 °C) (0.98 g, 41%); $\lambda_{max.}$ 277, 323sh, and 374 nm (log ε 4.11, 3.82, and 3.94); δ 3.71 (2 H, s, CH_2), 6.8—7.7 (16 H, m, ArH), and 14.74 (1 H, s, OH). The material insoluble in 80% ethanol was crystallised from xylene to give the *dimer* as yellow needles, m.p. >300 °C (0.28 g, 12%) (Found: C, 70.3; H, 4.1; N, 6.05; S, 13.3. $C_{28}H_{20}N_2O_2S_2$ requires C, 70.3; H, 3.8; N, 5.9; S, 13.4%); $\lambda_{max.}$ ($CHCl_3$) 252sh, 268, 290sh, 347, and 392 nm (log ε 4.20, 4.32, 3.98, 3.99, and

4.05); *m/e* 480 (M^+, <0.3%), 476 (<0.3%), 241 (63), 240 (100), 224 (8), 223 (8), 211 (18), 208 (22), and 170 (5.5).

$\Delta^{2,2'}$-*Bi*-[(3-p-*methoxyphenyl*)-2H-1,4-*benzothiazine*] (5; R = OMe).—(*a*) 3-(*p*-Methoxyphenyl)-2*H*-1,4-benzothiazine (0.37 g) and chloranil (0.714 g) were heated in dioxan (20 ml) at 60 °C for 4 h. After removal of solvent the residue, in chloroform, was shaken successively with aqueous sodium hydrogensulphite, 2M-sodium hydroxide, and water, dried, and evaporated. Chromatography in chloroform on a dry column of silica gel gave (i) 3-(p-*methoxyphenyl*)-1,4-*benzothiazin*-2-*one* (9) as yellow needles, m.p. 127—129 °C (from methanol) (52 mg, 13%) (Found: C, 67.1; H, 4.4; N, 4.9; S, 11.6%; M^+, 269.051 1. $C_{15}H_{11}NO_2S$ requires C, 66.9; H, 4.1; N, 5.2; S, 11.9%; *M*, 269.051 0); $\lambda_{max.}$ 234 and 366 nm (log ε 4.16 and 3.66); $\lambda_{max.}$ 1 633 cm^{-1}; δ 3.87 (3 H, s, OMe), 6.97 (2 H, d, *J* 8 Hz, H-3′ and H-5′), 7.44 (3 H, m, ArH), 7.93 (1 H, m, ArH), and 8.25 (2 H, d, *J* 8 Hz, H-2′ and H-6′); *m/e* 269 (M^+, 9%), 241.056 3 ($C_{14}H_{11}NOS$ requires 241.056 1), 226 (25), and 198 (20); and (ii) the *dimer* (5; R = OMe), red needles, m.p. 218—220 °C (0.29 g, 78%) (Found: C, 71.2; H, 4.4; N, 5.4; S, 13.0. $C_{26}H_{22}N_2O_2S_2$ requires C, 71.1; H, 4.3; N, 5.5; S, 12.7%); $\lambda_{max.}$ 217, 266, 310sh, 368, and 464 nm (log ε 4.27, 4.23, 3.89, 3.82, and 3.39); $\lambda_{max.}$ (EtOH–HCl) 217, 266, 335, 424, and 584 nm (log ε 4.24, 4.15, 3.81, 3.79, and 3.27); δ 3.89 (6 H, s, OCH_3), 7.15 (12 H, m, ArH), and 7.88 (4 H, m, ArH); *m/e* 506 (M^+, 100%), 473 (5), 399 (3), 372 (14), 265 (6), 253 (6), 240 (5), 222 (5), and 151 (100). T.l.c. showed a red and a yellow spot.

(*b*) 2,2′-Bi-(3-*p*-methoxyphenyl)-2*H*-1,4-benzothiazine (136 mg) and DDQ (61 mg) were heated in refluxing dioxan for 30 min. Work-up as in (*a*) gave identical red needles, m.p. 218—220 °C (120 mg, 88%).

$\Delta^{2,2'}$-*Bi*-[3-(p-*nitrophenyl*)-2H-1,4-*benzothiazine*] (5; R = NO_2).—3-(p-Nitrophenyl)-2*H*-1,4-benzothiazine (0.27 g) was oxidised with chloranil as above. The dimer crystallised from benzene as red needles, m.p. 248—250 °C (0.2 g, 78%) (Found: C, 62.7; H, 3.0; N, 10.2; S, 11.6. $C_{28}H_{16}N_4O_4S_2$ requires C, 62.7; H, 3.0; N, 10.5; S, 11.9%); $\lambda_{max.}$ 216, 269, 308sh, 362, and 500 nm (log ε 4.36, 4.22, 4.05, 3.91, and 3.37); δ 7.35 (12 H, m, ArH), and 7.94 (4 H, m, ArH); *m/e* 536 (M^+, 100%), 370 (18), 341 (5), 268 (16), 223 (10), and 222 (10).

3-(p-*Methoxyphenyl*)-1,4-*benzothiazin*-2-*one* (9). —3-(*p*-Methoxyphenyl)-2*H*-1,4-benzothiazine (0.29 g) was added to chromic anhydride (76 mg) in pyridine (5 ml). After stirring for 4 h at 55 °C the mixture was poured into water giving a precipitate which was chromatographed in chloroform on a dry column of silica to give (i) 3-(*p*-methoxyphenyl)-1,4-benzothiazin-2-one, yellow needles, m.p. 127—129° (35 mg, 12%), identical with that described above; (ii) 2-(*p*-methoxyphenyl)benzothiazole, needles, m.p. 110—113 °C (from methanol) (lit.,[26] 115 °C) (85 mg, 28%) (Found: C, 69.6; H, 4.6; N, 5.9; S, 13.2. Calc. for $C_{14}H_{11}NOS$: C, 69.7; H, 4.6; N, 5.8; S, 13.3%); δ 3.84 (3 H, s, OMe), 6.96 (2 H, d, *J* 9 Hz, H-3′ and H-5′), 7.2—7.9 (4 H, m, ArH), and 8.00 (2 H, d, *J* 9 Hz, H-2′ and H-6′); *m/e* 241 (M^+, 100%), 226 (32), 198 (28), 135 (5), and 108 (5).

2-(p-*Methoxyphenyl*)*benzothiazole*.—A solution of 3-(*p*-methoxyphenyl)-1,4-benzothiazin-2-one (30 mg) in methanol (10 ml) was refluxed for 30 min and evaporated to dryness. The residue crystallised from methanol as needles, m.p. 110—113 °C (25 mg, 95%), identical with those obtained above.

2-(p-*Dimethylaminobenzylidene*)-3-(p-*methoxyphenyl*)-2H-1,4-*benzothiazine*.—A solution of 3-(*p*-methoxyphenyl)-2*H*-1,4-benzothiazinium perchlorate (200 mg) and *p*-dimethylaminobenzaldehyde (83 mg) in acetic acid was heated to boiling for 2 min. On cooling the intensely blue solution, ether (10 ml) was added to give a precipitate of the required perchlorate (11) which crystallised from ethanol as small blue needles, m.p. 129—134 °C (190 mg, 70%); $\lambda_{max.}$ ($CHCl_3$) 262, 293sh, 359, 427, and 580 nm (log ε 4.32, 4.06, 4.44, 4.28, and 4.47). The salt (100 mg) in chloroform (20 ml) was stirred vigorously with 2M-sodium hydrogencarbonate (20 ml) until the blue organic phase turned orange (*ca.* 30 min). Work-up gave the *dimethylaminobenzylidene* derivative as orange needles, m.p. 140—142 °C (from methanol) (75 mg, 97%) (Found: C, 74.5; H, 5.9; N, 7.5; S, 8.5. $C_{24}H_{22}N_2OS$ requires C, 74.6; H, 5.7; N, 7.3; S, 8.3%); $\lambda_{max.}$ ($CHCl_3$) 264, 344, and 425 nm (log ε 4.25, 4.32, and 3.94); δ 3.00 (6 H, s, NMe_2), 3.85 (3 H, s, OMe), 6.71 (2 H, d, *J* 9 Hz, ArH), 6.9—7.5 (9 H, m, ArH + –CH=), and 7.81 (2 H, d, *J* 9 Hz, ArH); *m/e* 386 (M^+, 100%), 371 (1.5), 355 (1.5), and 253 (<0.3).

2-(p-*Dimethylaminocinnamylidene*)-3-(p-*methoxyphenyl*)-2H-1,4-*benzothiazine*.—The above reaction was repeated with *p*-dimethylaminocinnamaldehyde (98 mg) giving an intensely green solution. The required perchlorate (12) crystallised from ethanol as small blue-green needles, m.p. 150—156 °C (210 mg, 73%); $\lambda_{max.}$ ($CHCl_3$) 253, 277, 312sh, 388, 464, and 646 nm (log ε 4.34, 4.36, 4.22, 4.37, 4.10, and 4.55). The free *base*, orange needles, had m.p. 150—151.5 °C (from methanol) (83 mg, 84%) (Found: C, 75.4; H, 5.8; N, 6.8; S, 7.9. $C_{26}H_{24}N_2OS$ requires C, 75.5; H, 5.8; N, 6.8; S, 7.8%); $\lambda_{max.}$ ($CHCl_3$) 256sh, 273, 374, and 455 nm (log ε 4.29, 4.31, 4.35, and 4.25); δ 2.97 (6 H, s, NMe_2), 3.86 (3 H, s, OMe), 6.44—7.60 (13 H, m, ArH + =CH–CH=CH), and 7.75 (2 H, d, *J* 9 Hz, ArH); *m/e* 412 (M^+, 100%), 397 (5), 206 (5), and 134 (4).

1-*Bromo*-2-*phenylglyoxal* 1-(p-*Methoxyphenyl*)*hydrazone* (12; R^1 = H, R^2 = OMe).—Phenacyl phenyl sulphide [27] (23 g) was heated with dimethyl sulphate (12.5 g) at 100 °C for 30 min giving a gelatinous product to which potassium bromide (12 g) in water (30 ml) was added to precipitate the methyl phenacyl phenyl sulphonium bromide which was collected, washed, and dried. To a solution of the sulphonium bromide (15 g) and sodium acetate (37 g) in 50% aqueous methanol (230 ml), a freshly prepared equivalent quantity of aqueous *p*-methoxybenzene diazonium sulphate was added. The *hydrazone* precipitated immediately, and was crystallised from ethanol as yellow needles, m.p. 136—138 °C (lit.,[21] 141 °C) (11.7 g, 76%) (Found: C, 53.9; H, 4.0; Br, 23.7; N, 8.5. Calc. for $C_{15}H_{13}BrN_2O_2$: C, 54.2; H, 3.9; Br, 24.0; N, 8.4%); δ 3.76 (3 H, s, OMe), 6.95 (4 H, dd, *J* 9 Hz, ArH), 7.45 (3 H, m, ArH), 7.96 (2 H, dd, *J* 9 and 2 Hz), and 8.62 (1 H, s, NH); *m/e* 334 (M^+, 16%), 332 (M^+, 18), 252 (2), 122 (100), and 105 (100).

1-*Bromo*-2-(p-*methoxyphenyl*)*glyoxal* 1-(p-*Methoxyphenyl*)-*hydrazone* (12; R^1 = R^2 = OMe).—Thiophenol (16.5 g) was added to sodium methoxide (8.1 g) in methanol (35 ml) at 0 °C, followed by a solution of ω-bromo-*p*-methoxyacetophenone (34.4 g) in methanol (50 ml). The precipitated *sulphide* was collected after 30 min and crystallised from methanol as needles, m.p. 79—81.5 °C (3.5 g, 90%) (Found: C, 69.9; H, 5.5; S, 12.5. $C_{15}H_{14}O_2S$ requires C, 69.8; H, 5.4; S, 12.4%); δ 3.87 (3 H, s, OMe), 4.24 (2 H, s, CH_2), 6.94 (2 H, d, *J* 9 Hz, ArH), 7.16—7.52 (5 H, m, ArH), and 7.93 (2 H, d, *J* 9 Hz, ArH). The sulphide was converted into the *p*-methoxyphenacyl methyl phenyl

sulphonium bromide which was coupled with *p*-methoxybenzenediazonium sulphate as above. The *hydrazone* crystallised from carbon tetrachloride–light petroleum (1 : 2, v/v) as yellow needles, m.p. 119—121 °C (23%) (Found: C, 52.9; H, 4.1; Br, 21.9; N, 7.4. $C_{16}H_{15}BrN_2O_3$ requires C, 52.9; H, 4.1; Br, 22.0; N, 7.7%); δ 3.79 and 3.89 (each 3 H, s, OMe), 7.0 (6 H, m, ArH), 8.05 (2 H, d, *J* 9 Hz, ArH) and 8.52 (1 H, s, NH); *m/e* 364 (M^+, 0.6%), 362 (0.6), 282 (1.5), 135 (100), 122 (4), and 107 (4).

3-*Phenyl*-2-*phenylhydrazono*-2H-1,4-*benzothiazine* (11a; $R^1 = R^2 = H$).—To a solution of *o*-aminothiophenol (0.31 g) in ethanol (10 ml) containing sodium ethoxide (0.17 g) was added 1-bromo-2-phenylglyoxal 1-phenylhydrazone [20] (0.76 g) in ethanol (10 ml). The mixture was stirred for 30 min and left overnight. Addition of water precipitated the *product* which was crystallised from ethanol as yellow needles, m.p. 142—144 °C (0.69 g, 84%) (Found: C, 73.1; H, 4.5; N, 12.6; S, 9.7. $C_{20}H_{15}N_3S$ requires C, 72.9; H, 4.5; N, 12.7; S, 9.7%); $\lambda_{max.}$ (MeOH) 249, 282, 318, and 426 nm (log ε 4.22, 4.29, 4.26, 4.09); δ 6.8—7.7 and 7.8—8.1 (total 15 H, m, ArH + NH); *m/e* 329 (100%), 237 (25), 224 (5), 211 (79), 134 (5), 108 (25), and 105 (7).

2-(p-*Methoxyphenylhydrazono*)-3-*phenyl*-2H-1,4-*benzothiazine* (11a; $R^1 = H$, $R^2 = OMe$).—The preceding preparation was repeated using 1-bromo-2-phenylglyoxal 1-(*p*-methoxyphenyl)hydrazone (0.83 g). The *product*, which separated overnight, crystallised from ethanol as yellow needles, m.p. 138—140.5 °C (0.65 g, 72%) (Found: C, 70.2; H, 4.8; N, 11.8; S, 8.9. $C_{21}H_{17}N_3OS$ requires C, 70.2; H, 4.7; N, 11.7; S, 8.9%); $\lambda_{max.}$ 235, 280sh, 308, 335sh, and 438 nm (log ε 4.24, 4.16, 4.18, 4.06, and 4.02); δ 3.74 (3 H, s, OMe), 6.87 (4 H, dd, *J* 9 Hz, ArH), 7.04—7.72 and 7.8—8.2 (total 10 H, m, ArH + NH); *m/e* 359 (M^+, 100%), 237 (4.5), 212 (11), and 122 (100); t.l.c. showed the presence of two tautomers; isosbestic point (EtOH, $CHCl_3$, Et_2O, $C_4H_8O_2$, C_6H_{12}) at $\lambda_{max.}$ 340 nm (log ε 3.99).

3-(*p*-*Methoxyphenyl*)-2-(p-*nitrophenylhydrazono*)-2H-1,4-*benzothiazine* (11a; $R^1 = OMe$, $R^2 = NO_2$).—To 3-(*p*-methoxyphenyl)-2*H*-1,4-benzothiazine (0.5 g) and sodium acetate (1.6 g) in 25% aqueous methanol (30 ml) was added a freshly prepared equivalent quantity of aqueous *p*-nitrobenzenediazonium sulphate. The precipitate crystallised from methanol to give the *hydrazone* as orange needles, m.p. 241—242 °C (0.49 g, 60%) (Found: C, 62.4; H, 4.0; N, 13.7; S, 8.2. $C_{21}H_{16}N_4O_3S$ requires C, 62.4; H, 4.0; N, 13.9; S, 7.9%); $\lambda_{max.}$ ($CHCl_3$) 257, 282, 353sh, and 417 nm (log ε 4.26, 4.21, 4.17, and 4.38); δ([$^2H_6$]DMSO) 3.86 (3 H, s, OMe), 7.03, 7.25, 7.92, and 8.12 (each 2 H, d, *J* 9 Hz, ArH), and 7.2—7.6 (4 H, m, ArH); *m/e* 404 (M^+, 100%), 267 (75), 254 (50), 241 (67), 226 (22), 210 (5), and 198 (22).

2-(p-*Methoxycarbonylphenylhydrazono*)-3-(p-*methoxyphenyl*)-2H-1,4-*benzothiazine* (11a; $R^1 = OMe$, $R^2 = CO_2Me$).—The above reaction was repeated using *p*-methoxycarbonylbenzenediazonium sulphate. The *product* crystallised from methanol as dark yellow needles, m.p. 144—146 °C (0.27 g, 65%) (Found: C, 66.0; H, 4.7; N, 9.9; S, 7.7%. $C_{23}H_{19}N_3O_3S$ requires C, 66.2; H, 4.55; N, 10.1; S, 7.7%); $\lambda_{max.}$ 257, 285, 329, and 408 nm (log ε 4.22, 4.25, 4.37, and 4.19); δ([$^2H_6$]DMSO) 3.78 and 3.85 (each 3 H, s, OMe), 7.04, 7.22, 7.82, and 7.92 (each 2 H, d, *J* 9 Hz, ArH), 7.2—7.7 (4 H, m, ArH), and 10.18 (1 H, s, exchanges, NH); *m/e* 417 (M^+, 100%), 267 (35), 241 (35), 226 (8), 198 (5), and 135 (16).

2-(p-*Nitrophenylhydrazono*)-3-*phenyl*-2H-1,4-*benzothiazine* (11a; $R^1 = H$, $R^2 = NO_2$).—*o*-Aminothiophenol (152 mg) was added to sodium ethoxide (83 mg) in ethanol (10 ml) followed by 3,6-dibenzoyl-1,4-dihydro-1,4-bis-(*p*-nitrophenyl)-1,2,4,5-tetrazine (17; $R^1 = NO_2$, $R^2 = H$) (see below) (325 mg) in ethanol (60 ml), and the mixture was stirred overnight. Dilution with water gave the *hydrazone* which crystallised from methanol as orange needles, m.p. 221—224 °C (105 mg, 23%) (Found: 64.2; H, 3.7; N, 14.8; S, 8.7. $C_{20}H_{14}N_4O_2S$ requires C, 64.2; H, 3.7; N, 15.0; S, 8.6%); $\lambda_{max.}$ 225, 250, 282, 346sh, and 430 nm (log ε 4.41, 4.31, 4.28, 4.03, and 4.38); δ([$^2H_6$]DMSO) 7.21 and 8.10 (each 2 H, d, *J* 9 Hz, ArH), 7.3—8.0 (10 H, m, ArH + NH); *m/e* 374 (M^+, 100%), 237 (40), 224 (4), 211 (79), and 108 (10).

3,6-*Dibenzoyl*-1,4-*dihydro*-1,4-*bis*-(p-*nitrophenyl*)-1,2,4,5-*tetrazine* (17; $R^1 = NO_2$, $R^2 = H$).—To a solution of methyl phenacyl phenyl sulphonium bromide (7.5 g) and sodium acetate (18.5 g) in 50% aqueous methanol (110 ml) a freshly prepared equivalent of aqueous *p*-nitrobenzenediazonium sulphate was added. The dark red precipitate thus obtained crystallised from dimethylformamide to give the *tetrazine* as small red plates, m.p. 232—234 °C (0.51 g, 8%) (Found: C, 62.6; H, 3.7; N, 15.95. $C_{28}H_{18}N_6O_6$ requires C, 62.9; H, 3.5; N, 15.7%); $\lambda_{max.}$ ($CHCl_3$) 264 and 393 nm (log ε 4.39 and 4.28); $\nu_{max.}$ 1 670 cm^{-1}; *m/e* 534 (M^+, 18%) and 105 (100).

1,4-*Dihydro*-3,6-*bis*-(p-*methoxybenzoyl*)-1,4-*bis*-(p-*nitrophenyl*)-1,2,4,5-*tetrazine* (17; $R^1 = NO_2$, $R^2 = OMe$).—The above preparation was repeated with *p*-methoxyphenacyl methyl phenyl sulphonium bromide (2 g) to give the *tetrazine* as orange needles, m.p. 275—277 °C (20 mg, 1%) (Found: C, 60.8; H, 4.0; N, 14.0. $C_{30}H_{22}N_6O_8$ requires C, 60.6; H, 3.7; N, 14.1%); $\lambda_{max.}$ 254, 316, and 395 nm (log ε 4.34, 4.55, and 4.43); $\nu_{max.}$ 1 660 cm^{-1}; *m/e* 594 (M^+, 16%), 161 (16), and 136 (100).

1,4-*Dihydro*-3,6-*bis*-(p-*nitrobenzoyl*)-1,4-*bis*-(p-*nitrophenyl*)-1,2,4,5-*tetrazine* (17; $R^1 = R^2 = NO_2$).—*p*-Nitrophenacyl phenyl sulphide was prepared from ω-bromo-*p*-nitroacetophenone (36.6 g) as above; yellow needles, m.p. 99—101.5 °C (37.3 g, 91%) (Found: C, 61.4; H, 4.3; N, 5.1; S, 11.7. $C_{14}H_{11}NO_3S$ requires C, 61.5; H, 4.0; N, 5.1; S, 11.7%); δ 4.24 (2 H, s, CH_2), 7.26 (5 H, m, ArH), 8.01 and 8.21 (each 2 H, d, *J* 9 Hz, ArH); *m/e* 273 (M^+, 25%), 150 (9), 123 (100), 109 (3.5), and 104 (5.5). The sulphide was converted into phenyl *p*-nitrophenacyl sulphonium bromide, as above, and this was coupled with *p*-nitrobenzenediazonium sulphate as before to give the *tetrazine* which crystallised from dimethylformamide as small red plates, m.p. >300 °C (15 mg, 0.5%) (Found: M^+, 624.098 8. $C_{28}H_{16}N_8O_{10}$ requires *M*, 624.098 8); too insoluble for u.v.; $\nu_{max.}$ 1 677 cm^{-1}; *m/e* 624 (M^+, 18%), 448 (55), 150 (100), and 104 (35).

4-*Methyl*-3-*phenyl*-2-*phenylazo*-4H-1,4-*benzothiazine* (19; R = H).—*o*-*N*-methylaminothiophenol (140 mg) was added to sodium ethoxide (68 mg) in ethanol (5 ml), followed by 1-bromo-2-phenylglyoxal 1-phenylhydrazone (300 mg) in ethanol (10 ml). After stirring for 30 min the mixture was left overnight. The precipitate which deposited crystallised from ethanol to give the *azo-compound* as golden brown needles, m.p. 160.5—162 °C (310 mg, 90%) (Found: C, 73.4; H, 5.0; N, 12.0; S, 9.2. $C_{21}H_{17}N_3S$ requires C, 73.5; H, 5.0; N, 12.2; S, 9.3%); $\lambda_{max.}$ 232, 276sh, 315, and 505 nm (log ε 4.21, 4.11, 4.24, and 4.17); δ 3.13 (3 H, s, NMe), and 6.8—7.6 (14 H, m, ArH); *m/e* 343 (M^+, 100%), 238 (100), 236 (18), 226 (6), and 223 (25).

2-(p-*Methoxyphenylazo*)-4-*methyl*-3-*phenyl*-4H-1,4-*benzothiazine* (19; R = OMe).—The above preparation was repeated using 1-bromo-2-phenylglyoxal 1-(*p*-methoxyphenyl)hydrazone (332 mg). The *azo-compound* crystallised from ethanol as red-golden needles, m.p. 152—153 °C (350 mg, 94%) (Found: C, 70.6; H, 5.1; N, 11.3; S, 8.6. $C_{22}H_{19}N_3OS$ requires C, 70.8; H, 5.1; N, 11.3; S, 8.6%); $\lambda_{max.}$ 233, 273, 333, and 506 nm (log ε 4.29, 4.14, 4.28, and 4.25); δ 3.12 (3 H, s, NMe), 3.79 (3 H, s, OMe), and 6.7—7.7 (13 H, m, ArH); *m/e* 373 (M^+, 100%), 238 (100), 236 (18), 226 (22), and 223 (28).

o-*Nitrophenyl Phenacyl Sulphone*.—Phenacyl bromide (4.0 g) in methanol (10 ml) was added to a solution of sodium methoxide (0.86 g) and *o*-nitrothiophenol (2.5 g) in methanol (20 ml). The sulphide separated immediately and was crystallised from 80% acetic acid as yellow plates, m.p. 145—147 °C (lit.,[10] 146—147 °C) (3.2 g, 73%); ν_{CO} (Nujol) 1 675 cm^{-1}; δ([$^2H_6$]DMSO) 4.94 (2 H, s, CH_2); *m/e* 273 (M^+, 0.6%) and 105 (100). The sulphide (0.5 g) was suspended in acetic acid (5 ml) and acetic anhydride (1.5 ml) at 80 °C, and hydrogen peroxide (1.25 ml, 30%) was added, dropwise, maintaining the temperature at 70—80 °C. The solution was then heated on a steam-bath for 15 min, allowed to cool, and poured into water. The sulphone thus obtained was crystallised from 80% ethanol as needles, m.p. 136—137 °C (lit.,[10] 136.5—137.5°) (0.47 g, 77%); δ 5.26 (2 H, s, CH_2); *m/e* 259.042 8 ($M^+ - NO_2$ requires 259.042 9, 0.4%), and 105 (100).

o-*Nitrophenyl* p-*Methoxyphenacyl Sulphone*.—The above sulphide preparation was repeated using ω-bromo-*p*-methoxyacetophenone (2.29 g). The *sulphide* precipitated and was crystallised from 80% acetic acid as yellow needles, m.p. 107—109 °C (2.0 g, 82%) (Found: C, 59.2; H, 4.3; N, 4.5; S, 10.5. $C_{15}H_{13}NO_4S$ requires C, 59.4; H, 4.3; N, 4.6; S, 10.6%); δ([$^2H_6$]DMSO) 3.84 (3 H, s, OMe), 4.81 (2 H, s, CH_2), 7.05 and 8.02 (each 2 H, d, *J* 9 Hz, ArH), and 7.9—8.2 (total 4 H, m, ArH); *m/e* 303 (M^+, 0.1%), 135 (100), 121 (2), and 107 (3). The sulphide (0.5 g) was oxidised with hydrogen peroxide (1.25 ml, 30%) as before to give the *sulphone* which crystallised from 80% ethanol as pale yellow needles, m.p. 138—140 °C (0.42 g, 74%) (Found: C, 53.6; H, 3.8; N, 4.2; S, 9.3. $C_{15}H_{13}NO_6S$ requires C, 53.7; H, 3.9; N, 4.2; S, 9.6%); δ 3.86 (3 H, s, OMe), 5.18 (2 H, s, CH_2), 6.94 (2 H, d, *J* 9 Hz, ArH), and 7.6—8.3 (6 H, m, ArH); *m/e* 335 (M^+, 1%), 149 (6), 135 (100), and 121 (18).

p-*Nitrophenacyl* o-*Nitrophenyl Sulphone*.—*p*-Nitrophenacyl *o*-nitrophenyl sulphide was prepared as above from ω-bromo-*p*-nitroacetophenone (2.4 g). It crystallised from 80% acetic acid as yellow *needles*, m.p. 159—162 °C (2.2 g, 84%) (Found: C, 52.6; H, 2.8; N, 8.6; S, 10.2. $C_{14}H_{10}N_2O_5S$ requires C, 52.8; H, 3.1; N, 8.8; S, 10.1%); $\nu_{max.}$ 1 684 cm^{-1}; δ([$^2H_6$]DMSO) 5.00 (2 H, s, CH_2) and 7.3—8.5 (8 H, m, ArH); *m/e* 318 (M^+, 3%), 253 (8), 224 (67), 168 (11), 150 (100), 138 (100), 134 (6), 122 (13), 121 (14), 120 (14), 108 (13), and 104 (100). The sulphide (0.5 g) was oxidised with hydrogen peroxide as above to give the *sulphone* as pale yellow needles, m.p. 168—170° (from 80% ethanol) (0.4 g, 71%) (Found: C, 48.2; H, 2.7; N, 7.7; S, 8.9. $C_{14}H_{10}N_2O_7S$ requires C, 48.0; H, 2.9; N, 8.0; S, 9.1%); δ([$^2H_6$]DMSO) 5.67 (2 H, s, CH_2), and 7.8—8.4 (8 H, m, ArH); *m/e* 350 (M^+, 0.1%), 186 (4.5), 164 (10), 150 (100), 136 (35), 120 (11), and 104 (05).

3-*Phenyl*-4H-1,4-*benzothiazine* 1,1-*Dioxide* (22).—*o*-Nitrophenyl phenacyl sulphone (0.5 g) in methanol (10 ml) was reduced[28] by addition to a stirred suspension of palladium–charcoal (90 mg, 10%) in phosphinic acid (0.9 ml) and methanol (15 ml). The mixture was refluxed for 2½ h and the *benzothiazine dioxide* was collected on cooling, and crystallised from ethanol as needles, m.p. 271—274 °C (lit.,[22b] 276°) (0.36 g, 88%) (Found: C, 65.2; H, 4.2; N, 5.4; S, 12.5. $C_{14}H_{11}NO_2S$ requires C, 65.3; H, 4.2; N, 5.4; S, 12.5%); δ([$^2H_6$]DMSO) 6.25 (1 H, s, –CH=), 7.1—7.9 (9 H, m, ArH), and 10.75 (1 H, s, NH); *m/e* 257 (M^+, 45%), 193 (100), 155 (6) and 105 (7).

3-(p-*Methoxyphenyl*)-4H-1,4-*benzothiazine* 1,1-*Dioxide*.—The above preparation was repeated using *p*-methoxyphenacyl *o*-nitrophenyl sulphone (0.5 g). The *benzothiazine dioxide* crystallised from methanol as needles, m.p. 256—260 °C (0.26 g, 60%) (Found: C, 62.4; H, 4.7; N, 4.75; S, 11.2. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.5; N, 4.9; S, 11.15%); δ([$^2H_6$]DMSO) 3.82 (3 H, s, OMe), 6.18 (1 H, s, –CH=), 7.10 and 7.64 (each 2 H, d, *J* 9 Hz, ArH), 7.2—7.9 (4 H, m, ArH), and 10.65 (1 H, s, NH); *m/e* 287 (M^+, 100%), 223 (100), 208 (100), 193 (6), 180 (28), 152 (8), and 135 (6).

2-(p-*Nitrophenylazo*)-3-*phenyl*-4H-1,4-*benzothiazine* 1,1-*Dioxide* (23; R = NO_2).—To 3-phenyl-4*H*-1,4-benzothiazine 1,1-dioxide (50 mg) and sodium acetate (160 mg) in 50% aqueous methanol (20 ml) was added a freshly prepared equivalent quantity of aqueous *p*-nitrobenzenediazonium sulphate. After 3 h the *azo-compound* was collected and crystallised from ethanol as red needles, m.p. 269—272 °C (52 mg, 64%) (Found: C, 57.5; H, 4.0; N, 14.3; S, 7.6%; M^+, 406.073 2. $C_{20}H_{14}N_4O_4S$ requires C, 59.1; H, 3.45; N, 13.8; S, 7.9%; *M*, 406.073 4. Satisfactory analyses could not be obtained); $\lambda_{max.}$ 233, 274sh, 308sh, and 412 nm (log ε 4.36, 4.14, 3.99, and 4.43); $\nu_{max.}$ 3 500, 1 520, 1 334, and 1 150 cm^{-1}; *m/e* 406 (M^+, 45%), 244 (9), 228 (7), 211 (28), 205 (8), 195 (13), 179 (100), and 106 (53); too insoluble for n.m.r.

2-(p-*Methoxycarbonylphenylazo*)-3-*phenyl*-4H-1,4-*benzothiazine* 1,1-*Dioxide* (23; R = CO_2Me).—The above preparation was repeated using *p*-methoxycarbonylbenzenediazonium sulphate. The *azo-compound* crystallised from ethanol as red microneedles, m.p. 226—229 °C (55 mg, 66%) (Found: C, 62.7; H, 4.3; N, 10.3; S, 7.5. $C_{22}H_{17}N_3O_4S$ requires C, 63.0; H, 4.05; N, 10.0; S, 7.6%), $\lambda_{max.}$ 228, 266sh, 301sh, and 397 nm (log ε 4.32, 4.19, 4.02, and 4.43); $\nu_{max.}$ 3 300, 1 684, 1 283, and 1 151 cm^{-1}; δ 3.88 (3 H, s, OMe), 7.0—8.1 (14 H, m, ArH and NH); *m/e* 419 (M^+, 63%), 244 (28), 205 (18), 195 (22), 179 (100), and 105 (100).

3,4-*Dihydro*-3-*hydroxy*-3-*aryl*-2H-*naphtho*[2,3-b]-1,4-*thiazine*-5,10-*quinones*.—(*a*) (25; R = H). 2-Amino-3-chloro-1,4-naphthoquinone (1 g) in aqueous sodium hydrogen sulphide (25%, 3 g) and methanol (25 ml) were heated under reflux for 20 min. The solution became intense blue. After cooling, a solution of ω-bromoacetophenone (1.5 g) in methanol (15 ml) was added, a dark red precipitate forming immediately. It crystallised from methanol to give the *naphthothiazinequinone* as purple needles, m.p. >300 °C (1.45 g, 94%) (Found: C, 66.6; H, 4.0; N, 4.1; S, 9.7. $C_{18}H_{13}NO_3S$ requires C, 66.85; H, 4.0; N, 4.35; S, 9.9%); $\lambda_{max.}$ ($CHCl_3$) 287, 350sh, and 500 nm (log ε 4.33, 3.19, and 3.32); $\nu_{max.}$ 3 470, 3 330, 1 645, and 1 630 cm^{-1}; δ 2.93 (2 H, dd, *J* 12 Hz, CH_2), 3.42 (1 H, s, exchangeable, OH or NH), 6.69br (1 H, s, exchangeable, OH or NH), and 7.3—8.1 (9 H, m, ArH) {the CH_2 signal was a singlet (δ 2.98) in [$^2H_6$]DMSO}; *m/e* 323 (M^+, 6%), 305 (30), 273 (4), 218 (56), and 105 (100).

(*b*) (25; R = OMe) obtained similarly, gave purple *needles*, m.p. >300 °C (1.61 g, 95%) (Found: C, 64.5; H, 4.5; N, 4.1; S, 9.0. $C_{19}H_{15}NO_4S$ requires C, 64.6; H, 4.25; N, 4.0; S, 9.1%); $\lambda_{max.}$ ($CHCl_3$) 285, 352sh, and 500 nm (log ε 4.46, 3.31, and 3.44); $\nu_{max.}$ 3 440, 3 305, 1 670, and 1 633 cm^{-1}; δ 2.90 (2 H, dd, *J* 14 Hz, CH_2), 3.38 (1 H, s, exchangeable, OH or NH), 3.82 (3 H, s, OMe), 6.65 (1 H, s, exchangeable, OH or NH), 6.94 (2 H, d, *J* 9 Hz, ArH), 7.51 (2 H, d, *J* 9 Hz, ArH), and 7.6—8.1 (4 H, m, ArH) {the CH_2 signal is a singlet (δ 2.95) in [$^2H_6$]DMSO}; *m/e* 353 (M^+, 2.5%), 335 (13), 303 (5), 218 (4), 205 (3), 200 (3), and 135 (100).

(*c*) (25; R = NO_2) obtained similarly, gave purple *needles*, m.p. >300 °C (1.72 g, 97%) (Found: C, 58.9; H, 3.1; N, 7.3; S, 8.8%); $\lambda_{max.}$ ($CHCl_3$) 283, 303sh, and 492 nm (log ε 4.52, 3.31, and 3.34); $\nu_{max.}$ 3 350br and 1 665 cm^{-1}; δ([$^2H_6$]DMSO) 3.04 (2 H, dd, *J* 12 Hz, CH_2), 6.97 (1 H, s, exchangeable, OH or NH), 7.58 (1 H, s, exchangeable, OH or NH), 7.85 (4 H, m, ArH), and 7.75 and 8.22 (each 2 H, d, *J* 8 Hz, ArH); *m/e* 368 (M^+, 5.5%), 350 (18), 318 (25), 304 (3), 288 (7), 272 (4), 218 (100), 205 (8), 173 (9), 160 (5.5), 150 (13), and 104 (13).

3,4-*Dihydro*-3-*methoxy*-3-*phenyl*-2H-*naphtho*[2,3-b]-1,4-*thiazine*-5,10-*quinone*.—The quinone (28; R = H) (100 mg) in methanol (25 ml) was stirred with 12M-hydrochloric acid (1 drop) at room temperature for 1 h. The solvent was removed and the residue, in chloroform, was washed with aqueous sodium hydrogencarbonate, and water, and then dried and evaporated. Crystallisation from methanol gave the *methoxyquinone* as purple needles, m.p. 224—226 °C (80 mg, 79%) (Found: C, 67.3; H, 4.4; N, 3.9; S, 9.6. $C_{19}H_{15}NO_3S$ requires C, 67.6; H, 4.45; N, 4.15; S, 9.5%); $\lambda_{max.}$ ($CHCl_3$) 290, 355sh, and 520 nm (log ε 4.39, 3.08, and 3.33); $\nu_{max.}$ (KBr) 3 340, 1 645, and 1 635 cm^{-1}; δ 2.75 and 3.14 (each 1 H, d, *J* 12 Hz, CH_2), 3.19 (3 H, s, OMe), 6.65 (1 H, s, exchanges, NH), and 7.4—8.1 (9 H, m, ArH); *m/e* 337 (M^+, 13%), 305 (100), 292 (4.5), 277 (8), 273 (25), and 105 (13).

2-*Arylbenzo*[f]*indole*-4,9-*quinones*.—(*a*) (27; R = H). 2,3-Dihydro-3-hydroxy-3-phenylnaphtho[2,3-*b*]-1,4-thiazine-5,10-quinone (35 mg) was heated at 280 °C and 0.05 mmHg for 1 h. The benzoindolequinone sublimed as red needles, m.p. >300 °C (lit.,[24] 304—305 °C) (18 mg, 60%) (Found: C, 79.1; H, 4.1; N, 4.9. Calc. for $C_{18}H_{11}NO_2$: C, 79.1; H, 4.0; N, 5.1%); $\lambda_{max.}$ ($CHCl_3$) 293, 345sh, and 440 nm (log ε 4.58, 3.41, and 3.66); $\nu_{max.}$ 3 270, 1 655, and 1 630 cm^{-1}; δ([$^2H_6$]DMSO) 7.19 (1 H, d, *J* 2 Hz, collapses to s on addition of CD_3OD, H-3) and 7.3—8.2 (10 H, m, ArH and NH); *m/e* 273 (M^+, 100%), 245 (6), 216 (4.5), 189 (6), and 114 (10).

(*b*) (27; R = OMe), obtained similarly, sublimed as red *needles*, m.p. >300 °C (23 mg, 54%) (Found: M^+, 303.089 3. $C_{19}H_{13}NO_3$ requires *M*, 303.089 5); $\lambda_{max.}$ ($CHCl_3$) 283sh, 307, 349sh, and 462 nm (log ε 4.20, 4.25, 3.38, and 3.68); δ([$^2H_6$]-DMSO) 3.89 (3 H, s, OMe), and 6.9—7.3 and 7.7—8.2 (total 11 H, m, ArH and NH); *m/e* 303 (M^+, 100%), 288 (71), and 260 (16).

(*c*) (27; R = NO_2), obtained similarly by heating with copper bronze at 300 °C and 0.05 mmHg for 1 h, sublimed as red *needles*, m.p. >300 °C (1.5 mg, 6%) (Found: M^+, 318.064 4. $C_{18}H_{10}N_2O_4$ requires *M*, 318.064 0); *m/e* 318 (M^+, 100%), 288 (32), 272 (32), 260 (5.5), 214 (8), and 189 (10).

2,2′-*Bi*-(3-*phenyl*-4H-*naphtho*[2,3-b]-1,4-*thiazine*)-5,5′,-10,10′-*diquinone* (28).—3,4-Dihydro-3-hydroxy-3-phenyl-2*H*-naphtho[2,3-*b*]-1,4-thiazine-5,10-quinone (250 mg) in acetic acid (15 ml) was heated under reflux for 10 min. The *dimer* crystallised on cooling and formed green needles, m.p. 285—286 °C (from acetic acid) (220 mg, 94%) (Found: C, 71.1; H, 3.4; N, 4.5; S, 10.7. $C_{36}H_{20}N_2O_4S_2$ requires C, 71.3; H, 3.3; N, 4.6; S, 10.5%); $\lambda_{max.}$ ($CHCl_3$) 257, 292, 372, and 570 nm (log ε 4.55, 4.53, 4.26, and 3.04); $\nu_{max.}$ 3 365, 1 655, and 1 633 cm^{-1}; δ(CF_3CO_2D) 7.4—8.8 (ArH); *m/e* 576.114 2 ($C_{36}H_{20}N_2O_4S$ requires 576.114 4; M^+ — S, 9%), 562.098 5 ($C_{35}H_{18}N_2O_4S$ requires 562.098 7; 5), 544.142 1 ($C_{36}H_{20}N_2O_4$ requires 544.142 3; 100), 467 (25), 305 (22), 273 (8), and 105 (100).

$\Delta^{2,2'}$-*Bi*-(3-*phenyl*-2H-*naphtho*[2,3-b]-1,4-*thiazine*)-5,5′,-10,10′-*diquinone*) (29).—Silver oxide (153 mg) was added to a solution of the above quinone (32) (200 mg) in dry tetrahydrofuran (50 ml), and the mixture was stirred for 2 h at room temperature. The intensely violet solution was filtered and evaporated, and the residue was chromatographed on a column of dry silica in chloroform to give the $\Delta^{2,2'}$-*dimer* which crystallised from 2-ethoxyethanol as dark violet needles, m.p. 287—290 °C (150 mg, 75%) (Found: C, 71.3; H, 3.0; N, 4.9; S, 10.65. $C_{36}H_{18}N_2O_4S_2$ requires C, 71.3; H, 3.0; N, 4.6; S, 10.6%); $\lambda_{max.}$ (dioxan) 275, 353sh, and 562 nm (log ε 4.53, 4.10, and 3.59); $\lambda_{max.}$ (dioxan–12M-HCl) 280, 353sh, and 518 nm (log ε 4.55, 4.25, and 3.66); $\nu_{max.}$ 1 670 and 1 640 cm^{-1}; δ ArH signals only; *m/e* 606 (M^+, 100%), 574 (100), 544.142 1 (71; $C_{36}H_{20}N_2O_4$ requires 544.142 2), 542.126 4 (18; $C_{36}H_{18}N_2O_4$ requires 542.126 7), 467 (21), 429 (21), 121 (8), 105 (13), and 104 (13). T.l.c. showed the presence of two isomers.

2-*Acetoxy*-3-*ethoxy*-3,4-*dihydro*-3-*phenyl*-2H-*naphtho*-[2,3-b]-1,4-*thiazine*-5,10-*quinone* (35).—3,4-Dihydro-3-hydroxy-3-phenyl-2*H*-naphtho[2,3-*b*]-1,4-thiazine-5,10-quinone (100 mg) was stirred with iodosobenzene diacetate (100 mg) in acetic acid for 1½ h, at room temperature. Evaporation and chromatography on a column of dry silica in chloroform gave the new *quinone* which crystallised from methanol as lustrous red needles, m.p. 150—152 °C (55 mg, 45%) (Found: C, 64.8; H, 4.6; N, 3.1; S, 7.9; M^+, 409.098 6. $C_{22}H_{19}NO_5S$ requires C, 64.55; H, 4.65; N, 3.4; S, 7.8%; *M*, 409.098 4); $\lambda_{max.}$ ($CHCl_3$) 295, 353sh, and 494 nm (log ε 4.31, 3.22, and 3.36); $\nu_{max.}$ 3 310, 1 735, and 1 662 cm^{-1}; δ 1.15 (3 H, t, *J* 7 Hz, CH_2CH_3), 1.72 (3 H, s, O_2CMe), 3.31 (2 H, q, *J* 7 Hz, CH_2CH_3), 6.16 (1 H, s, >CH–), 6.68br (1 H, s, exchangeable, NH), and 7.3—8.2 (9 H, m, ArH); *m/e* 409 (M^+, 11), 364.064 0 ($C_{20}H_{14}NO_4S$ requires 364.064 3; 18), 322 (5.5), 304 (6), 293.050 7 ($C_{17}H_{11}NO_2S$ requires 293.051 0; 100), 164 (5.5), and 105 (63).

2-*Anilino*-3-*phenacylthio*-1,4-*naphthoquinone* (32).—A suspension of 2-anilino-3-chloro-1,4-naphthoquinone (0.5 g) in aqueous sodium hydrogen sulphide (25%, 0.8 g) and methanol (20 ml) was stirred for 30 min at room temperature until an intense blue solution was obtained. Phenacyl bromide (0.59 g) in methanol (15 ml) was added, the mixture was stirred for 1 h, during which time it became red. The mixture was diluted with water, extracted with ether, and worked up by chromatography on dry silica in chloroform. The *phenacylthioquinone* crystallised from carbon tetrachloride as red needles, m.p. 129—131 °C (0.2 g, 28%) (Found: C, 72.1; H, 4.3; N, 3.45; S, 8.0. $C_{24}H_{17}NO_3S$ requires C, 72.2; H, 4.3; N, 3.5; S, 8.0%); $\lambda_{max.}$ ($CHCl_3$) 253, 285, 351, and 506 nm (log ε 4.24, 4.33, 3.55, and 3.48); $\nu_{max.}$ 3 250, 1 682, and 1 665 cm^{-1}; δ 4.06 (2 H, s, CH_2), and 6.7—8.2 (15 H, m, ArH and NH); *m/e* 399 (M^+,

8%), 381 (40), 365 (22), 336 (18), 294 (100), 281 (20), 260 (25), 249 (40), 204 (45), 121 (8), and 105 (100).

2,3-Dihydro-2-methoxy-2-phenylnaphtho[2,3-b]-1,4-*oxathiin-5,10-quinone* (33).—2-Anilino-3-phenacylthio-1,4-naphthoquinone (100 mg) in methanol (10 ml) was heated under reflux with 12M-hydrochloric acid (1 drop) for 6 h, taken to dryness, and the residue chromatographed on dry silica in chloroform. The new *quinone* crystallised from methanol as yellow needles, m.p. 215—217 °C (45 mg, 53%) (Found: C, 67.3; H, 4.0; S, 9.6%. $C_{19}H_{14}SO_4$ requires C, 67.5; H, 4.1; S, 9.5%); $\lambda_{max.}$ ($CHCl_3$) 275, 250sh, and 446 nm (log ε 4.31, 3.30, and 3.32); $\nu_{max.}$ 1 658 cm^{-1}; δ 3.14 (2 H, dd, *J* 13 Hz, CH_2), 3.18 (3 H, s, OMe), and 7.2—8.2 (9 H, m, ArH); *m/e* 338 (M^+, 75%), 306 (20), 290 (18), 278 (8), 206 (45), 175 (20), 133 (100), 121 (8), and 104 (84).

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