

## Quinones. Part 11.<sup>1</sup> The Reaction of *o*-Aminothiophenol with *o*-Benzo- and *o*-Naphtho-quinones: A New Route to 1*H*-Phenothiazin-1-ones

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1*H*-Phenothiazin-1-ones can be obtained by the condensation of *o*-aminothiophenol with 3,5-di-*t*-butyl- and 3-*t*-butyl-5-phenyl-*o*-benzoquinones. In the absence of large blocking groups the phenothiazinones are unstable. A methyl group at C-4 leads *via* the quinone-methide tautomer, to formation of a spiro-dimer the crystal structure of which was determined by *X*-ray analysis. By further reaction with *o*-aminothiophenol, 1*H*-phenothiazin-1-ones yield triphenodithiazines (benzothiazinophenothiazines).

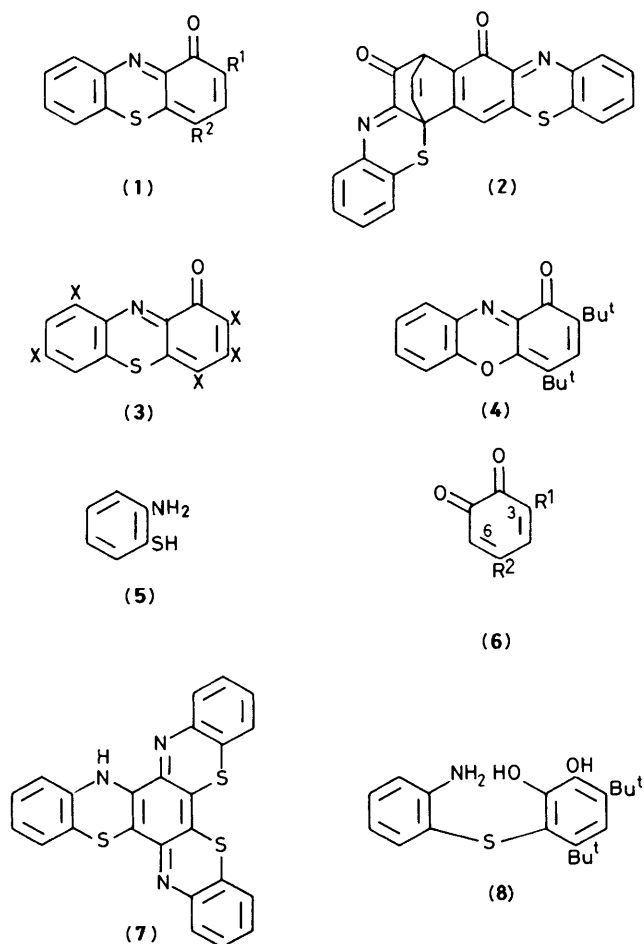
*o*-Naphthoquinones do not form benzo-1*H*-phenothiazin-1-ones with *o*-aminothiophenol. The parent compound yields 4-hydroxy-3*H*-benzo[*a*]phenothiazin-3-one by initial thiol addition at C-4 followed by rearrangement.

Very little is known of *o*-quinoneimines and in the particular case of the 1*H*-phenothiazin-1-one system (1) we are aware of only one publication<sup>2</sup> in the literature. The Roumanian workers<sup>2</sup> obtained compound (1; R<sup>1</sup> = R<sup>2</sup> = H) by oxidation of 1-hydroxyphenothiazine in dilute solution with lead(IV) oxide or silver(II) oxide in inert solvents followed by rapid evaporation of the deep blue solution. The parent compound (1; R<sup>1</sup> = R<sup>2</sup> = H) is unstable and very prone to dimerisation, even in the solid state, forming structure (2) by Diels-Alder cycloaddition and subsequent aromatisation and oxidation. The dimer (2) still retains the 1*H*-phenothiazin-1-one system and is stable. The halogenated monomers (3; X = Cl and Br) are also relatively stable; the polychloro compound (3; X = Cl) can be crystallised from dimethylformamide and melts without dimerisation although, surprisingly, (3; X = Br) dimerises in boiling *o*-dichlorobenzene.<sup>2</sup> However it seems that bulky groups in the quinonoid ring of compound (1) are necessary to prevent cycloaddition as exemplified by the stable oxygen analogue (4).<sup>3</sup> As we were interested in the blue to green colours of these *o*-quinoneimines ( $\epsilon$  values were not reported<sup>2,3</sup>) we sought a more flexible method of synthesis.

We chose to approach (1) by condensation of *o*-aminothiophenol (5) with suitably substituted *o*-benzoquinones (6). Thiols tend to react<sup>4</sup> with *o*-benzoquinones at C-6 rather than C-4 or C-5, and that was encouraged by blocking positions 3 and 5. In any case bulky groups are essential to control the reaction. For example, although we never used *o*-benzoquinone itself we found that *o*-chloranil condensed with *o*-aminothiophenol to form a multitude of compounds from which only the trithiazine (7)<sup>5</sup> (or the *o*-isomer) and 2,2'-diaminobiphenyl disulphide were isolated.

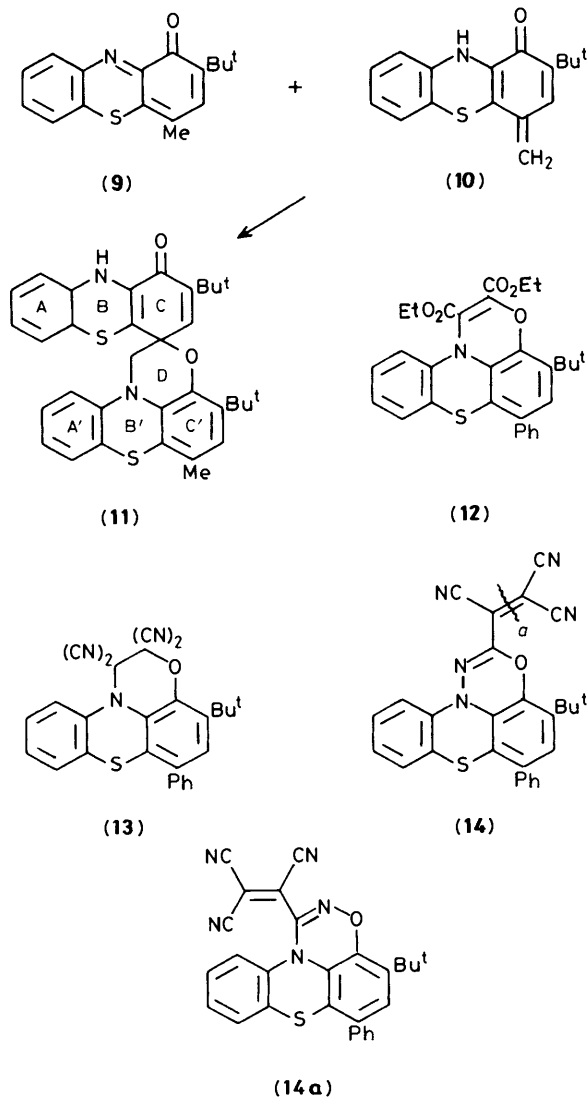
On addition of *o*-aminothiophenol to 3,5-di-*t*-butyl-1,2-benzoquinone the solution was decolourised immediately [formation of (8)]; further addition of iron(III) chloride then gave a deep blue-violet solution from which the stable phenothiazinone (1; R<sup>1</sup> = R<sup>2</sup> = Bu<sup>t</sup>) could be isolated as blue-black crystals [ $\lambda_{\max}$ , 630 nm ( $\epsilon$  3 385)]. The phenyl analogue (1; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph) was obtained similarly from 5-phenyl-3-*t*-butyl-1,2-benzoquinone. Obviously phenyl and *t*-butyl groups are large enough to prevent phenothiazinone (1) dimerisation but a methyl group is not.

For example, reaction of 5-methyl-3-*t*-butyl-1,2-benzoquinone with *o*-aminothiophenol followed by treatment with iron(III) chloride yielded a blue solid, assumed to be the phenothiazinone (1; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Me) on the basis of its



$\lambda_{\max}$ . at 635 nm. The base peak in the mass spectrum occurred at  $m/z$  566 indicating that dimerisation had occurred either on the probe or before the spectrum was run. The blue solid decomposed in *ca.* 30 min at room temperature and was not obtained pure. When warmed in toluene several compounds were formed of which the major product was a red crystalline compound,  $M^+$  566. On the grounds of colour and solubility, this red dimer was not of type (2). The <sup>1</sup>H n.m.r. spectrum

revealed the presence of two different *t*-butyl groups but only one methyl group. In addition there is a 2 H doublet centred at  $\delta$  4.21. When the spectrum was first run at 100 MHz the latter signal was not resolved and appeared as a broadened singlet, and on that basis it was difficult to propose a structure. The problem was therefore resolved by X-ray crystallography which established the spiro structure (11) for the red dimer. This means that the *o*-quinoneimine (9) had reacted in the tautomeric form (10), the dimer (11) being formed by cycloaddition of the exocyclic methylene group of (10) to the



heterodiene system of (9). As Diels–Alder additions to the N=C–C=O system appear to be quite rare<sup>6</sup> we explored the reaction further using (1; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph) and obtained adducts (12) and (13) using diethyl acetylenedicarboxylate and tetracyanoethylene (TCNE) respectively. Unexpectedly, tetracyanoethylene (TCNE) also behaved as a nitrile dienophile and yielded a second adduct which appears to be (14). This is supported by mass spectral and i.r. evidence but the compound was too insoluble for n.m.r. studies. The major fragment ion at  $m/z$  409 corresponds to fragmentation at *a* in (14). Examination of models suggests that the alternative structure (14a) (or its *cis*-isomer) is most improbable on steric grounds. A bis-adduct [from TCNE and 2 × (1; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph)] would also fit

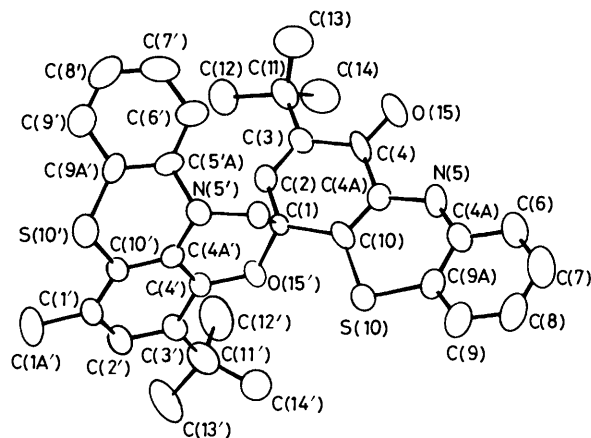
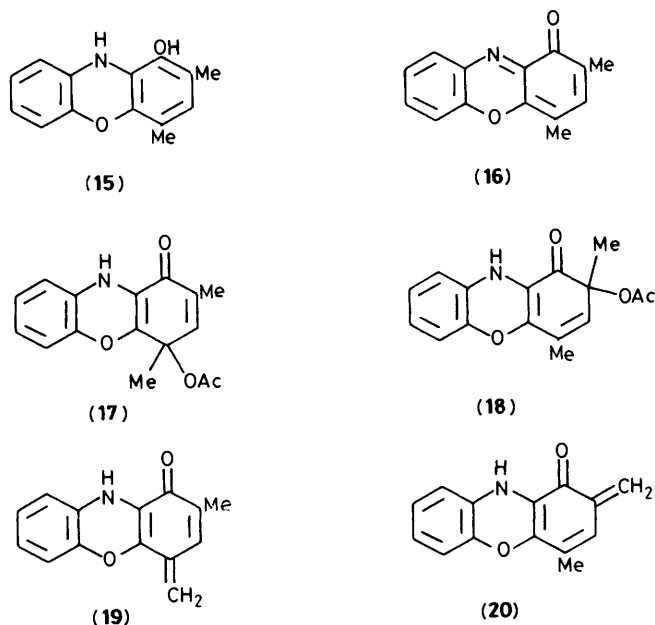


Figure. X-ray molecular structure of compound (11)

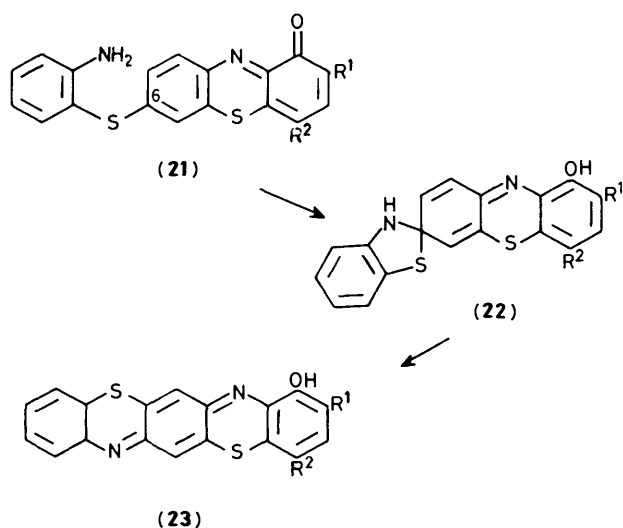
the available evidence and would account better for the colour and insolubility, but the molecular ion ( $M^+$ , 818) could not be detected by either f.d. or f.a.b. mass spectrometry.

The instability of (1; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Me) recalls an earlier failure<sup>7</sup> to convert the phenoxazine (15) into the dimethylphenoxazinone (16). The product obtained by oxidation with iron(III) chloride in acetic acid was structure (17) or (18) which could be formed by addition of acetic acid either to (16) or possibly to one of the quinonemethide tautomers (19) or (20).



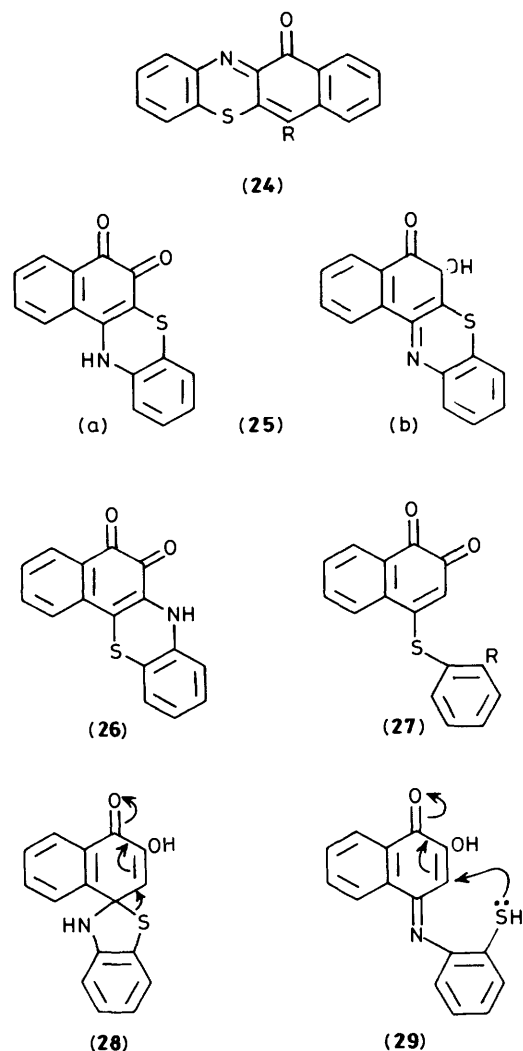
The reaction of 3-methyl-5-*t*-butyl-1,2-benzoquinone with *o*-aminothiophenol was more complex than the others and the blue phenothiazinone (1; R<sup>1</sup> = Me, R<sup>2</sup> = Bu<sup>t</sup>) was not isolated. The main violet product was difficult to purify but spectral evidence suggested that it was derived from the quinone and 2 mol equiv. of thiol. The experiment was therefore repeated with addition of a further 1 mol equiv. of *o*-aminothiophenol at the 'blue stage', followed by treatment with iron(III) chloride. The major violet product was isolated by chromatography. After being kept in chloroform solution for 3 days it underwent further change to form a less polar violet compound, C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>OS<sub>2</sub>, in low yield, which appears to be the triphenodithiazine (23; R<sup>1</sup> = Me, R<sup>2</sup> = Bu<sup>t</sup>). The <sup>1</sup>H n.m.r. spectrum

shows signals for a hydroxyl, one methyl and one *t*-butyl group, four contiguous aromatic protons, and three isolated aromatic protons. Irradiation of the methyl protons sharpened the 1 H singlet at  $\delta$  7.01. The visible spectrum ( $\lambda_{\text{max}}$ , 530sh, 565 nm) shifted in acid solution to  $\lambda_{\text{max}}$ , 614, 672, 736 nm, both curves showing a close resemblance to those of the parent triphenodithiazine (benzothiazinophenothiazine). The analogous compound (**23**;  $R^1 = R^2 = \text{Bu}^t$ ) was obtained in the same manner from 3,5-di-*t*-butyl-1,2-benzoquinone (**6**;  $R^1 = R^2 = \text{Bu}^t$ ), and the analogue (**23**;  $R^1 = \text{Bu}^t$ ,  $R^2 = \text{Ph}$ ) was prepared starting from (**1**;  $R^1 = \text{Bu}^t$ ,  $R^2 = \text{Ph}$ ) and *o*-aminothiophenol. The formation of triphenodithiazines (**23**) from phenothiazinones (**1**) suggests that the reaction proceeds by nucleophilic attack at C-6 to give (**21**) (after reoxidation), which is probably the main constituent of the initial violet product. On being kept in chloroform solution (**21**) is apparently converted into (**23**) presumably by further nucleophilic attack at C-6 (**22**) followed by rearrangement and oxidation. Evidence for such a rearrangement in another context is provided below.



Extension of the 1*H*-phenothiazin-1-one synthesis to *o*-naphthoquinones seemed attractive as the resulting benzo derivative (**24**;  $R = \text{OEt}$ ) is known<sup>8</sup> and appears to be stable. However on reaction of *o*-naphthoquinone with *o*-aminothiophenol no blue compound could be detected, and the product isolated was the red thiazinone (**25**). The same compound was obtained by reaction of *o*-aminothiophenol with 3-chloro-1,2-naphthoquinone, and with 3-chloro-2-hydroxy-1,4-naphthoquinone and it appears to be identical with the thiazinone derived previously<sup>9</sup> from *o*-aminothiophenol and 2-hydroxy-1,4-naphthoquinone. These synthetic methods suggest that the product is compound (**25**) rather than (**26**) which was confirmed by desulphurisation with Raney nickel to give 4-anilino-1,2-naphthoquinone. The thiazinone (**25**) can exist in two tautomeric forms. When prepared in the cold the keto form (**25a**) ( $\nu_{\text{max}}$ , 3 460, 3 320, 1 690, and 1 640  $\text{cm}^{-1}$ ) separates. When dissolved in methanol it rapidly enolises, the initial pale yellow solution ( $\lambda_{\text{max}}$ , 319, 357sh nm) changing to red ( $\lambda_{\text{max}}$ , 510 nm) in a few minutes. Crystallisation of (**25a**) from hot solvent yields the enol (**25b**).

Nucleophiles normally attack *o*-naphthoquinones at C-4 and we checked that by reaction of the parent compound with aniline and with *p*-thiocresol to give, respectively, the 4-anilino and 4-*p*-tolylthio derivatives; both yielded 2-hydroxy-1,4-naphthoquinone on hydrolysis. As thiols are more reactive



nucleophiles<sup>10</sup> than amines it would be expected that *o*-aminothiophenol would attack *o*-naphthoquinones at C-4 through the thiol function, leading to (**26**) rather than (**25**) as the final product. As compound (**26**) is not obtained a rearrangement must occur, and evidence for this was obtained as follows. Reaction of *o*-nitrothiophenol with *o*-naphthoquinone gave the nitroquinone (**27**;  $R = \text{NO}_2$ ) which was reduced<sup>11</sup> to the amine (**27**;  $R = \text{NH}_2$ ) with tin(II) chloride-sodium borohydride. After neutralisation the mixture was shaken with chloroform to give a violet-red extract which yielded the thiazinone (**25b**). Thus the liberated amine (**27**;  $R = \text{NH}_2$ ) must effect an intramolecular nucleophilic addition at C-4 to form the spiro intermediate compound (**28**) which probably undergoes a dienone-phenol rearrangement, as indicated or, less likely, the ring opens to form (**29**) and then cyclises to give (**25**) after oxidation.

The formation of blue thiazinones of type (**24**) should be favoured if C-4 is blocked in the starting *o*-naphthoquinone which would enforce reaction at C-3 but an attempt to test this using 4-phenyl-1,2-naphthoquinone was negative. 3-Phenyl-1,2-naphthoquinone reacted normally at C-4 with aniline and with *p*-thiocresol but no definite product could be isolated from the reaction with *o*-aminothiophenol. The 3- and 4-phenyl-1,2-naphthoquinones used for these experiments were obtained by direct phenylation of 1,2-naphthoquinone using benzene and palladium acetate,<sup>12</sup> the 3-phenyl isomer being the major product. Previously only the 4-phenyl isomer was isolated.<sup>12</sup>

## Experimental

M.p.s. were determined on a Kofler block. I.R. spectra were recorded with a Perkin-Elmer 197 spectrophotometer and u.v. spectra with a Perkin-Elmer 402 instrument.  $^1\text{H}$  N.m.r. spectra were measured at 220 MHz on a Perkin-Elmer R34 spectrometer using tetramethylsilane as internal reference, and  $^{13}\text{C}$  spectra on a Bruker WH 360 instrument at 90 MHz. Mass spectra were obtained using an A.E.I. MS 30 mass spectrometer at 70eV. Silica gel grade 62 (Grace) was used for dry column chromatography.

**Reaction of 5-Methyl-3-*t*-butyl-1,2-benzoquinone (6) with *o*-Aminothiophenol (5).**—A solution of *o*-aminothiophenol (5) (0.35 g, 2.8 mmol) in ethanol (10 ml) was added, with stirring, to 5-methyl-3-*t*-butyl-1,2-benzoquinone (6) (0.5 g, 2.8 mmol) in ethanol (20 ml). After 5 min *M*-iron(III) chloride (20 ml) was added to the colourless solution which became deep blue. Stirring was continued for 30 min when the mixture was extracted with chloroform, and the extract dried ( $\text{MgSO}_4$ ) rapidly and evaporated under reduced pressure. The residue was passed down a column of dry silica in chloroform. The major blue band yielded an unstable blue solid regarded as (1;  $\text{R}^1 = \text{Bu}^t$ ,  $\text{R}^2 = \text{Me}$ ) (0.5 g, 63%);  $\lambda_{\text{max.}}(\text{CHCl}_3)$  630 nm;  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 640  $\text{cm}^{-1}$ ;  $m/z$  (%) 566 (100), 285 (100), 283 ( $M^+$ , 40), 271 (35), 270 (34), 256 (10), and 255 (10). Without delay, the blue compound (0.5 g) in toluene (20 ml) was heated on a steam-bath for 5 min, the blue solution turning to red-brown. Removal of solvent left an oil which was chromatographed in chloroform on a column of dry silica. The main red band yielded the *spiro dimer* (11) which separated from light petroleum (b.p. 60–80 °C) as red plates, m.p. 155–157 °C (85 mg, 17%) (Found: C, 72.2; H, 6.3; N, 5.0; S, 11.45.  $\text{C}_{34}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_2$  requires C, 72.1; H, 6.0; N, 4.95; S, 11.3%;  $\lambda_{\text{max.}}(\text{CHCl}_3)$  267, 297sh, 320sh and 415 nm (log  $\epsilon$  4.50, 4.03, 3.72, and 3.37);  $\nu_{\text{max.}}(\text{KBr})$  3 363 and 1 647  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.07 (9 H, s,  $\text{Bu}^t$ ), 1.32 (9 H, s,  $\text{Bu}^t$ ), 2.30 (3 H, s, Me), 4.21 (2 H, dd,  $J$  15 Hz,  $\text{CH}_2$ ), 6.72 (1 H, s, exch. with  $\text{D}_2\text{O}$ , NH), and 6.56–7.10 (10 H, m, ArH + 3-H);  $m/z$  (%) 566 ( $M^+$ , 1), 285 (100), and 283 (22), 270 (37).

**Reaction of 3-Methyl-5-*t*-butyl-1,2-benzoquinone (6) with *o*-Aminothiophenol (5).**—A solution of *o*-aminothiophenol (5) (625 mg, 5 mmol) in ethanol (10 ml) was added slowly, with stirring, to 3-methyl-5-*t*-butyl-1,2-benzoquinone (6) (895 mg, 5 mmol) in ethanol (10 ml). After 10 min *M*-iron(III) chloride (20 ml) was added and the resulting blue solution stirred for 15 min, when further *o*-aminothiophenol (625 mg, 5 mmol) in ethanol (10 ml) was added, followed by *M*-iron(III) chloride (20 ml). After being stirred for 30 min the solution was extracted with chloroform and the extract washed well with water (slightly acidic), dried ( $\text{MgSO}_4$ ), and evaporated. The complex mixture was partially purified by chromatography in chloroform on a column of dry silica, followed by p.l.c. to isolate the major violet product. This was not obtained in a pure form but when kept in chloroform for 3 days a less polar violet compound developed which was separated on a column of dry silica in chloroform. Crystallisation from chloroform–methanol yielded 1-hydroxy-2-methyl-4-*t*-butyl[1,4]benzothiazino[2,3-*b*]phenothiazine (23;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Bu}^t$ ) as violet needles, m.p. 249–251 °C (311 mg, 15%) (Found: C, 68.3; H, 5.0; N, 6.8; S, 15.8%;  $M^+$ , 404.1018.  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$  requires C, 68.35; H, 5.0; N, 6.9; S, 15.9%;  $M$ , 404.1017);  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH}, 1:4)$  285, 325, 530sh, and 565 nm (log  $\epsilon$  4.42, 4.31, 4.37, and 4.47);  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH--HCl})$  281, 336, 614, 672, and 736 nm (log  $\epsilon$  4.37, 4.42, 4.17, 4.34, and 4.25); (the parent benzothiazino[2,3-*b*]phenothiazine shows  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH}, 1:4)$  512sh and 557 nm;  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH--HCl})$  597sh, 650, 707nm);  $\nu_{\text{max.}}(\text{KBr})$  3 410 and 1 500  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.12 (1 H, br s, OH), 7.39 (1 H, br d,  $J$  8 Hz, 8-H), 7.17 (1 H, dt,  $J$  2 and 8 Hz, 9-

H), 7.08 (1 H, dt,  $J$  2 and 8 Hz, 10-H), 7.05 (1 H, dd,  $J$  2 and 8 Hz, 11-H), 7.01 (1 H, s, 3-H), 6.86 and 6.78 (each 1 H, s, 6-H and 13-H) 2.19 (3 H, s, Me), and 1.44 (9 H, s,  $\text{Bu}^t$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  150.64(s), 149.07(s), 145.16(s), 141.64(s), 135.07(s), 133.05(s), 132.24(s), 131.36(d), 129.77(d), 129.01(s), 127.79(d), 127.63(d), 124.70(d), 122.23(s), 121.43(d), 121.18(d), 119.84(s), 117.98(s), 35.38(s), 29.96(q), and 15.51(q) {the spectrum of the parent benzothiazino[2,3-*b*]phenothiazine is 148.94(s), 141.47(s), 132.55(s), 131.54(d), 128.08(d), 127.67(d), 124.77(d), 122.52(s), 122.30(d)};  $m/z$  (%) 406 (57), 404 ( $M^+$ , 63), 389 (100), 374 (11), 348 (14), and 287 (15) (the m.s. of the parent compound shows 320 ( $M^+ + 2$ , 21) and 318 ( $M^+$ , 100). The acetate ( $\text{Ac}_2\text{O}$ –pyridine) formed dark violet crystals with a metallic sheen, m.p. 239–241 °C (methanol–chloroform) (Found:  $M^+$ , 466.1160.  $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$  requires  $M$ , 446.1122);  $\lambda_{\text{max.}}(\text{CHCl}_3)$  290, 300, 532, and 571 nm;  $\nu_{\text{max.}}(\text{KBr})$  1 750  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.45–7.06 (5 H, m, 3-H + 8-H to 11-H), 6.88 and 6.74 (each 1 H, s, 6-H and 13-H), 2.43 (3 H, s, Me), 2.22 (3 H, s, OAc), and 1.54 (9 H, s,  $\text{Bu}^t$ );  $m/z$  (%) 448 (74), 446 ( $M^+$ , 43), 406 (54), 404 (77), 390 (46), 389 (100), and 43 (55).

**Reaction of 3,5-Di-*t*-butyl-1,2-benzoquinone (6) with *o*-Aminothiophenol (5).**—(a) *o*-Aminothiophenol (5) (600 mg, 4.8 mmol) in ethanol (20 ml) was added to 3,5-di-*t*-butyl-1,2-benzoquinone (6) (1.0 g, 4.5 mmol) in ethanol (20 ml). After 5 min *M*-iron(III) chloride (50 ml) was added to the colourless solution which was stirred for 30 min. The blue mixture was then worked up as before by chloroform extraction, column chromatography on dry silica, and p.l.c. on silica in chloroform–ethyl acetate (99:1). The 2,4-di-*t*-butyl-1H-phenothiazin-1-one (1;  $\text{R}^1 = \text{R}^2 = \text{Bu}^t$ ) crystallised from methanol–chloroform as black rods, m.p. 141 °C (486 mg, 33%) (Found: C, 73.8; H, 7.2; N, 4.1; S, 9.5%;  $M^+$ , 325.1487.  $\text{C}_{20}\text{H}_{23}\text{NOS}$  requires C, 73.9; H, 7.1; N, 4.3; S, 9.8%;  $M$ , 325.1498);  $\lambda_{\text{max.}}(\text{CHCl}_3)$  247, 312, 351sh, and 630 nm (log  $\epsilon$  3.98, 3.93, 3.84, and 3.53);  $\nu_{\text{max.}}(\text{KBr})$  1 630  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.97 (1 H, m, 9-H), 7.35 (4 H, m, ArH + 3-H), and 1.44 and 1.31 (each 9 H, s,  $\text{Bu}^t$ );  $m/z$  (%) 325 ( $M^+$ , 100), 310 (30), 295 (12), 282 (10), 254 (10), and 253 (9).

(b) *o*-Aminothiophenol (5) (1.25 g, 10 mmol) in ethanol (20 ml) was added to 3,5-di-*t*-butyl-1,2-benzoquinone (6) (2.0 g, 9 mmol) in ethanol (20 ml) and the mixture was stirred for 10 min. *M*-Iron(III) chloride (30 ml) was then added when the solution became deep blue-violet. Further *o*-aminothiophenol (1.25 g, 10 mmol) was added after a few minutes followed by more *M*-iron(III) chloride (20 ml). The solution was then stirred for 1 h and worked up as before to allow isolation of a major violet band by dry column chromatography. This product was kept in chloroform (30 ml) for 3 days and again chromatographed on dry silica in chloroform. The main violet component yielded 1-hydroxy-2,4-di-*t*-butylbenzothiazinophenothiazine (23;  $\text{R}^1 = \text{R}^2 = \text{Bu}^t$ ) as dark violet needles, m.p. 245–247 °C (931 mg, 23%) (Found: C, 69.9; H, 5.7; N, 6.4; S, 14.4%;  $M^+$ , 446.1487.  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{OS}_2$  requires C, 69.9; H, 5.8; N, 6.3; S, 14.4%;  $M$ , 446.1486);  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH}, 1:9)$  286, 324, 528sh, and 564 nm (log  $\epsilon$  4.44, 4.35, 4.43, and 4.52);  $\lambda_{\text{max.}}(\text{CHCl}_3\text{--MeOH--HCl})$  283, 338, 620, 670, and 735 nm (log  $\epsilon$  4.40, 4.42, 4.25, 4.40, and 4.32);  $\nu_{\text{max.}}(\text{KBr})$  3 410, 1 600, 1 578, 1 595, and 1 574  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.38 (1 H, br d,  $J$  8 Hz, 8-H), 7.23–7.05 (4 H, m, ArH), 6.86 and 6.78 (each 1 H, s, 6-H and 13-H), and 1.45 and 1.40 (each 9 H, s,  $\text{Bu}^t$ ) (OH not observed);  $m/z$  (%) 448 (54), 446 ( $M^+$ , 93), 431 (100), 415 (19), 403 (30), and 389 (20).

**Reaction of 5-Phenyl-3-*t*-butyl-1,2-benzoquinone (6) with *o*-Aminothiophenol (5).**—*o*-Aminothiophenol (5) (360 mg, 2.8 mmol) in ethanol (20 ml) was added to 5-phenyl-3-*t*-butyl-1,2-benzoquinone (6) (600 mg, 2.45 mmol) in ethanol (20 ml). After 10 min *M*-iron(III) chloride (50 ml) was added. The intense blue solution was stirred for 30 min, and then extracted with

chloroform and worked up as above. The major blue component was separated on a column of dry silica in chloroform and crystallised from chloroform-methanol to give the *t*-butylphenylphenothiazin-1-one (**1**; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph) as black plates, m.p. 200–202 °C (500 mg, 58%) (Found: C, 76.5; H, 5.7; N, 4.3; S, 9.4%; M<sup>+</sup>, 345.1177. C<sub>22</sub>H<sub>19</sub>NOS requires C, 76.5; H, 5.6; N, 4.1; S, 9.3%; M, 345.1187; λ<sub>max</sub>(CHCl<sub>3</sub>) 310 and 645 nm (log ε 4.15 and 3.58); ν<sub>max</sub>(KBr) 1 633 cm<sup>-1</sup>; δ<sub>H</sub>(CDCl<sub>3</sub>) 7.97 (1 H, m, 9-H), 7.55–7.10 (8 H, m, ArH), 7.10 (1 H, s, 3-H), and 1.34 (9 H, s, Bu<sup>t</sup>); m/z (%) 345 (M<sup>+</sup>, 100), 330 (10), 315 (9), 302 (8), 287 (7), and 286 (7).

**Reaction of 4-Phenyl-2-*t*-butyl-1H-phenothiazin-1-one with *o*-Aminothiophenol (**5**).—***o*-Aminothiophenol (**5**) (50 mg) in ethanol (10 ml) was added to a stirred solution of the phenothiazinone (**1**; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph) (50 mg, 0.15 mmol) in chloroform (5 ml) and ethanol (10 ml). The blue solution became colourless immediately. After 5 min iron(III) chloride (50 ml) was added to produce a deep blue-violet solution which was stirred for 45 min and then extracted with chloroform. The dried (MgSO<sub>4</sub>) extract was left for 3 days and then chromatographed on a column of dry silica in chloroform. The main violet component afforded the benzothiazinophenothiazine (**23**; R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = Ph) which separated from chloroform-methanol as dark violet micro-crystals, m.p. 268–269 °C (14 mg, 21%) (Found: M<sup>+</sup>, 466.1174. C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>OS<sub>2</sub> requires M, 466.1173; λ<sub>max</sub>(MeOH-CHCl<sub>3</sub>, 4:1) 278, 328sh, and 564 nm (log ε 4.31, 3.93, and 4.20); λ<sub>max</sub>(MeOH-CHCl<sub>3</sub>-HCl) 281, 335, 615sh, 670, and 734 nm (log ε 4.46, 4.34, 4.15, 4.30 and 4.24); ν<sub>max</sub>(KBr) 3 260 and 1 498 cm<sup>-1</sup>; n.m.r.—too insoluble; m/z (%) 468 (59), 466 (M<sup>+</sup>, 100), 451 (84), and 423 (5). This compound was also obtained directly from 5-phenyl-3-*t*-butyl-1,2-benzoquinone (**6**) and excess of *o*-aminophenol (**5**) (yield 15%).

**Cycloaddition Reactions of 4-Phenyl-2-*t*-butyl-1H-phenothiazin-1-one.**—(a) *With diethyl acetylenedicarboxylate.* The phenothiazinone (**1**) (100 mg, 0.29 mmol) and the diester (60 mg, 0.35 mmol) were heated in boiling chlorobenzene (5 ml) for 24 h. The solvent was removed under reduced pressure and the residue was purified by repeated p.l.c. on silica in chloroform-light petroleum (b.p. 60–80 °C) (3:2). Elution of a yellow band, followed by evaporation, left a gum which was triturated with hexane. The resulting solid separated from aqueous ethanol to give the adduct (**12**) as small yellow crystals, m.p. 152–154 °C (58 mg, 40%, allowing for recovered phenothiazinone) (Found: C, 69.6; H, 5.8; N, 3.0; S, 6.1%; M<sup>+</sup>, 515.1765. C<sub>30</sub>H<sub>29</sub>NO<sub>5</sub>S requires C, 69.9; H, 5.7; N, 2.7; S, 6.2%; M, 515.1766; λ<sub>max</sub>(CHCl<sub>3</sub>) 276, 304sh, and 404 nm (log ε 4.31, 3.95, and 3.53); ν<sub>max</sub>(KBr) 1 720 and 1 640 cm<sup>-1</sup>; δ<sub>H</sub>(CDCl<sub>3</sub>) 7.50–6.90 (10 H, m, ArH), 4.3 (4 H, m, 2 × CH<sub>2</sub>), 1.35 (9 H, s, Bu<sup>t</sup>), and 1.32 and 1.16 (each 3 H, t, J 7 Hz, 2 × Me); m/z 515 (M<sup>+</sup>, 100), no fragments > m/z 100 and > 5%.

(b) *With tetracyanoethylene.* The phenothiazinone (**1**) (110 mg, 0.32 mmol) and tetracyanoethylene (80 mg, 0.64 mmol) were heated in boiling chlorobenzene (30 ml) for 1.5 h. After removal of the solvent under reduced pressure the residue was separated into starting material (ca. 50%) and two new compounds by repeated p.l.c. on silica in chloroform-light petroleum (b.p. 60–80 °C) (3:2). (i) The adduct (**13**) crystallised from chloroform-methanol as minute orange plates, m.p. 291 °C (12 mg, 16%, allowing for recovered starting material) (Found: C, 71.2; H, 4.0; S, 6.8%; M<sup>+</sup>, 473.1322. C<sub>28</sub>H<sub>19</sub>N<sub>5</sub>OS requires C, 70.8; H, 4.0; S, 6.8%; M, 473.1310; λ<sub>max</sub>(CHCl<sub>3</sub>) 264, 283sh, and 458 nm (log ε 4.48, 4.13, and 4.22); ν<sub>max</sub>(KBr) 2 220, 1 610, 1 575, and 1 515 cm<sup>-1</sup>; δ<sub>H</sub>(CDCl<sub>3</sub>) 8.04 (1 H, d, J 8 Hz, 9-H), 7.60–7.0 (9 H, m, ArH), and 1.42 (9 H, s, Bu<sup>t</sup>); m/z (%) 473 (M<sup>+</sup>, 100), 458 (29), and 431 (39). (ii) The adduct (**14**) separated from chloroform-methanol as dark violet microcrystals, m.p.

> 300 °C (10 mg, 13%) (Found: C, 73.6; H, 4.8; N, 10.4; S, 7.9%; M<sup>+</sup>, 473.1306. C<sub>28</sub>H<sub>19</sub>N<sub>5</sub>OS requires C, 73.3; H, 4.7; N, 10.3; S, 7.8%; M, 473.1310; λ<sub>max</sub>(CHCl<sub>3</sub>) 271, 317sh, 330, 345sh, and 564 nm (log ε 4.49, 4.52, 4.58, 4.48, and 4.68); ν<sub>max</sub>(KBr) 2 200 and 1 500 cm<sup>-1</sup>; n.m.r.—too insoluble; m/z (%) 473 (13), 409.1250 (C<sub>25</sub>H<sub>19</sub>N<sub>3</sub>OS requires 409.1249, 95), 394 (100), 366 (30), 354 (20). When this reaction was repeated in refluxing chlorobenzene (5 ml) for 5 h the adduct (**14**) was obtained in 58% yield (based on starting material consumed) with only a trace of (**13**).

**6-Hydroxy-5H-benzo[*a*]phenothiazin-5-one (**25b**)**—(a) A solution of 3-chloro-1,2-naphthoquinone (0.62 g, 3.2 mmol) and *o*-aminothiophenol (**5**) (0.4 g, 3.2 mmol) in ethanol (20 ml) was stirred at room temperature for 1 h. The orange solution was evaporated under reduced pressure and the residue was crystallised from ethanol to give the benzophenothiazinone as dark red needles, m.p. 270–272 °C (lit.<sup>9</sup> 267–269 °C) (0.52 g, 58%) (Found: C, 68.9; H, 3.3; N, 4.7; S, 11.3%. Calc. for C<sub>16</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 68.8; H, 3.2; N, 5.0; S, 11.5%; λ<sub>max</sub>(MeOH) 253, 273sh, 329, 353, and 510 nm (log ε 3.55, 3.44, 3.27, 3.27, and 3.01); ν<sub>max</sub>(KBr) 3 260, 1 614, and 1 590 cm<sup>-1</sup>; m/z (%) 279 (M<sup>+</sup>, 100), 251 (20), and 223 (9).

(b) Reaction (a) was repeated using 3-chloro-2-hydroxy-1,4-naphthoquinone (100 mg) to yield (**25b**), m.p. 270–272 °C (92 mg, 69%) identical with those obtained above.

(c) To a solution of *o*-naphthoquinone (325 mg, 2 mmol) in ethanol (10 ml) and chloroform (10 ml), *o*-aminothiophenol (**5**) (265 mg, 2 mmol) in ethanol (10 ml) was added. The mixture was stirred for 45 min after which orange-brown crystals (224 mg, 40%) of (**25a**) were collected; λ<sub>max</sub>(MeOH) 259, 319, and 357sh nm; ν<sub>max</sub>(KBr) 3 320, 3 260, 1 690, and 1 640 cm<sup>-1</sup>; m/z (%) 279 (M<sup>+</sup>, 100), 251 (20), 223 (9), and 160 (23). Crystallisation from a large volume of ethanol gave dark red needles, m.p. 270–272 °C of (**25b**) identical with those described in (a).

(d) To a stirred solution of 4-*o*-nitrophenylthio-1,2-naphthoquinone (50 mg, 0.16 mmol) in ethanol (75 ml) at 65 °C was added stannous chloride dihydrate (165 mg). After 5 min sodium borohydride (20 mg) in ethanol (10 ml) was added, dropwise, over 10 min and stirring was continued for 30 min. The reaction was then quenched by addition of water, and the mixture neutralised with 0.2M sodium hydroxide and extracted (× 3) with chloroform (which became violet) to yield the phenothiazinone (**25b**) as dark red needles, m.p. 270–272 °C (from ethanol) (40 mg, 89%) identical with those obtained in (a).

**4-*o*-Nitrophenylthio-1,2-naphthoquinone (**27**; R = NO<sub>2</sub>).**—*o*-Nitrothiophenol (0.43 g, 3.48 mmol) in chloroform (25 ml) was added to a stirred solution of *o*-naphthoquinone (0.5 g, 3.16 mmol) in methanol (50 ml) and chloroform (25 ml) at 4 °C, during 10 min. The mixture was left to warm to room temperature overnight. The precipitate was collected and washed with chloroform, and a further amount was obtained by concentrating the filtrate under reduced pressure. Crystallisation of the combined solids from a large volume of ethanol gave the required quinone as orange-brown needles, m.p. 218–220 °C (decomp.) (0.79 g, 80%) (Found: C, 61.95; H, 3.0; N, 4.4; S, 10.4%. C<sub>16</sub>H<sub>9</sub>NO<sub>4</sub>S requires C, 61.75; H, 2.9; N, 4.5; S, 10.3%; ν<sub>max</sub>(KBr) 1 697 and 1 645 cm<sup>-1</sup>; δ<sub>H</sub>(CDCl<sub>3</sub>) 8.15 (1 H, d, J 2 Hz, 8-H), 8.05 (1 H, dd, J 5 and 2 Hz, 3'-H), and 7.81–7.56 (6 H, m, ArH). On addition of sodium hydroxide (25 mg) in water (0.5 ml) to (**27**; R = NO<sub>2</sub>) (100 mg) in cold ethanol (100 ml) the solution became red-violet immediately. After 2 min M hydrochloric acid (50 ml) was added and the suspension was extracted with chloroform. The product was chromatographed on silica (CHCl<sub>3</sub>-MeOH; 99:1) to give, besides *o*-nitrothiophenol and the disulphide, 2-hydroxy-1,4-naphthoquinone,

**Table 1.** Fractional atomic co-ordinates ( $\times 10^4$ ) for compound (11) with estimated standard deviations in parentheses (e.s.d.s)

Atom	x	y	z
C(1)	0 626(5)	7 399(5)	2 557(5)
C(1A)	0 278(5)	6 572(6)	1 354(5)
C(2)	1 061(6)	6 758(6)	3 547(6)
C(3)	2 163(6)	6 811(6)	4 009(6)
C(4)	3 039(6)	7 668(7)	3 584(7)
C(4A)	2 640(6)	8 518(6)	2 838(6)
N(5)	3 526(5)	9 406(6)	2 680(6)
C(5A)	3 388(6)	10 073(7)	1 762(7)
C(6)	4 374(7)	10 685(8)	1 414(8)
C(7)	4 266(9)	11 407(9)	0 545(9)
C(8)	3 196(9)	11 543(8)	-0 002(8)
C(9)	2 218(8)	10 912(7)	0 307(7)
C(9A)	2 309(6)	10 209(6)	1 190(6)
S(10)	1 012(2)	9 520(2)	1 631(2)
C(10)	1 516(6)	8 459(6)	2 424(6)
C(11)	2 587(6)	6 129(7)	5 011(6)
C(12)	1 561(7)	5 376(8)	5 395(7)
C(13)	3 337(8)	5 276(9)	4 539(8)
C(14)	3 240(8)	7 008(9)	6 089(7)
O(15)	4 079(5)	7 682(6)	3 835(6)
C(1')	-3 660(5)	5 769(6)	2 011(6)
C(1A')	-4 876(6)	5 013(8)	1 738(7)
C(2')	-3 444(6)	6 863(6)	2 745(6)
C(3')	-2 349(6)	7 602(6)	3 057(6)
C(4')	-1 445(5)	7 159(6)	2 565(6)
C(4A')	-1 626(5)	6 075(6)	1 814(5)
N(5')	-0 702(4)	5 633(5)	1 344(4)
C(5A')	-0 591(6)	4 448(6)	1 451(5)
C(6')	0 465(7)	4 109(7)	1 795(6)
C(7')	0 490(8)	2 925(8)	1 886(7)
C(8')	-0 497(9)	2 077(8)	1 632(8)
C(9')	-1 549(8)	2 399(7)	1 270(7)
C(9A')	-1 597(6)	3 592(6)	1 169(6)
S(10')	-2 903(2)	3 980(2)	0 594(2)
C(10')	-2 741(5)	5 360(6)	1 533(6)
C(11')	-2 154(7)	8 762(7)	3 926(8)
C(12')	-1 333(9)	8 656(10)	5 054(8)
C(13')	-3 274(8)	9 013(10)	4 331(11)
C(14')	-1 664(7)	9 825(7)	3 361(9)
O(15')	-0 353(3)	7 894(4)	2 853(4)

**Table 2.** Bond lengths (Å) for compound (11) with e.s.d.'s in parentheses

C(1)-C(1A)	1.525(8)	C(11)-C(14)	1.510(11)
C(1)-C(2)	1.507(9)	C(1')-C(1A')	1.527(10)
C(1)-C(10)	1.518(9)	C(1')-C(2')	1.379(10)
C(1)-O(15')	1.437(7)	C(1')-C(10')	1.406(9)
C(1A)-N(5')	1.452(8)	C(2)-C(3')	1.403(9)
C(2)-C(3)	1.328(9)	C(3')-C(4')	1.414(9)
C(3)-C(4)	1.494(10)	C(3')-C(11')	1.516(10)
C(3)-C(11)	1.544(10)	C(4')-C(4A')	1.382(9)
C(4)-C(4A)	1.471(10)	C(4')-O(15')	1.398(7)
C(4)-O(15)	1.224(9)	C(4A')-N(5')	1.423(8)
C(4A)-N(5)	1.392(9)	C(4A')-C(10')	1.410(9)
C(4A)-C(10)	1.339(9)	N(5')-C(5A')	1.409(9)
N(5)-C(5A)	1.387(10)	C(5A')-C(6')	1.392(10)
C(5A)-C(6)	1.402(11)	C(5A')-C(9A')	1.387(10)
C(5A)-C(9A)	1.395(10)	C(6')-C(7')	1.383(12)
C(6)-C(7)	1.383(14)	C(7')-C(8')	1.366(13)
C(7)-C(8)	1.376(14)	C(8')-C(9')	1.383(14)
C(8)-C(9)	1.383(13)	C(9')-C(9A')	1.401(11)
C(9)-C(9A)	1.378(11)	C(9A')-S(10')	1.746(7)
C(9A)-S(10)	1.786(7)	S(10')-C(10')	1.758(7)
S(10)-C(10)	1.745(7)	C(11')-C(12')	1.533(12)
C(11)-C(12)	1.530(11)	C(11')-C(13')	1.527(12)
C(11)-C(13)	1.524(12)	C(11')-C(14')	1.529(12)

**Table 3.** Valency angles ( $^\circ$ ) for compound (11) with e.s.d.'s in parenthesis

C(2)-C(1)-C(1A)	112.1(5)	C(10)-C(1)-C(1A)	108.6(5)
O(15')-C(1)-C(1A)	109.3(5)	N(5')-C(1A)-C(1)	112.4(5)
C(10)-C(1)-C(2)	112.1(5)	O(15')-C(1)-C(2)	109.2(5)
C(3)-C(2)-C(1)	125.9(6)	O(15')-C(1)-C(10)	105.3(5)
C(4A)-C(10)-C(1)	120.4(6)	S(10)-C(10)-C(1)	116.9(4)
C(4')-O(15')-C(1)	118.2(4)	C(4A')-N(5')-C(1A)	112.6(5)
C(5A')-N(5')-C(1A)	123.1(5)	C(4)-C(3)-C(2)	116.8(6)
C(11)-C(3)-C(2)	124.8(6)	C(11)-C(3)-C(4)	118.2(6)
C(4A)-C(4)-C(3)	119.0(6)	O(15)-C(4)-C(3)	122.0(7)
C(12)-C(11)-C(3)	110.6(6)	C(13)-C(11)-C(3)	109.3(6)
C(14)-C(11)-C(3)	109.7(6)	O(15)-C(4)-C(4A)	119.0(7)
N(5)-C(4A)-C(4)	113.6(6)	C(10)-C(4A)-C(4)	121.7(6)
C(10)-C(4A)-N(5)	124.5(6)	C(5A)-N(5)-C(4A)	121.6(6)
S(10)-C(10)-C(4A)	122.6(5)	C(6)-C(5A)-N(5)	119.1(7)
C(9A)-C(5A)-N(5)	123.2(7)	C(9A)-C(5A)-C(6)	117.6(7)
C(7)-C(6)-C(5A)	120.5(8)	C(9)-C(9A)-C(5A)	121.1(7)
S(10)-C(9A)-C(5A)	120.5(5)	C(8)-C(7)-C(6)	121.2(9)
C(9)-C(8)-C(7)	118.7(8)	C(9A)-C(9)-C(8)	120.8(8)
S(10)-C(9A)-C(9)	118.4(6)	C(10)-S(10)-C(9A)	101.3(3)
C(13)-C(11)-C(12)	107.4(7)	C(14)-C(11)-C(12)	108.2(6)
C(14)-C(11)-C(13)	111.6(6)	C(2')-C(1')-C(1A')	120.3(6)
C(10')-C(1')-C(1A')	120.9(6)	C(10')-C(1')-C(2')	118.9(6)
C(3')-C(2')-C(1')	123.8(6)	C(4A')-C(10')-C(1')	119.4(6)
S(10')-C(10')-C(1')	123.2(5)	C(4')-C(3')-C(2')	115.7(6)
C(11')-C(3')-C(2')	121.2(6)	C(11')-C(3')-C(1')	122.9(6)
C(4A')-C(4')-C(3')	122.4(6)	O(15')-C(4')-C(3')	116.3(5)
C(12')-C(11')-C(3')	108.7(7)	C(13')-C(11')-C(3')	111.9(7)
C(14')-C(11')-C(3')	111.3(7)	O(15')-C(4')-C(4A')	121.3(5)
N(5')-C(4A')-C(4')	121.6(6)	C(10')-C(4A')-C(4')	119.8(6)
C(10')-C(4A')-N(5')	118.5(6)	C(5A')-N(5')-C(4A')	117.4(5)
S(10')-C(10')-C(4A')	117.4(5)	C(6')-C(5A')-N(5')	123.3(6)
C(9A')-C(5A')-N(5')	116.9(6)	C(9A')-C(5A')-C(6')	119.7(6)
C(7')-C(6')-C(5A')	119.3(7)	C(9')-C(9A')C(5A')	119.8(7)
S(10')-C(9A')-C(5A')	120.1(5)	C(8')-C(7')-C(6')	121.5(8)
C(9')-C(8')-C(7')	119.7(8)	C(9A')-C(9')-C(8')	119.8(8)
S(10')-C(9A')-C(9')	119.9(6)	C(10')-S(10')-C(9A')	97.8(3)
C(13')-C(11')-C(12')	106.6(8)	C(14')-C(11')-C(12')	110.9(7)
C(14')-C(11')-C(13')	107.4(7)		

m.p. 192 °C (decomp.) (ethanol) (45 mg, 80%) identical with authentic material.

**4-(*p*-Tolylthio)-1,2-naphthoquinone.**—A solution of *o*-naphthoquinone (100 mg, 0.63 mmol) and *p*-thiocresol (79 mg, 0.63 mmol) in methanol (15 ml) was stirred in the cold for 10 min, and then evaporated under reduced pressure. The residue was purified by p.l.c. on silica (chloroform) and crystallised from methanol to give the tolylthioquinone as orange needles, m.p. 206–209 °C (lit.,<sup>14</sup> 203–205 °C) (130 mg, 74%) (Found: C, 72.9; H, 4.3; S, 11.1%. Calc. for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub>S: C, 72.9; H, 4.3; S, 11.4%)  $v_{\max}$  (KBr) 1 699 and 1 645 cm<sup>-1</sup>; 8.22–7.18 (8 H, m, ArH), 5.89 (1 H, s, 3-H), and 2.45 (3 H, s, Me);  $m/z$  (%) 282 (8), 280 ( $M^+$ , 3) 252 (100), 224 (80), 129 (24), 101 (38), 91 (13) and 75 (17). The quinone, in methanol, was hydrolysed by addition of *m* sodium hydroxide. After 15 min in the cold, work-up yielded 2-hydroxy-1,4-naphthoquinone as yellow needles, m.p. 192–194 °C (decomp.) (MeOH) identical (mixed m.p., t.l.c.) with authentic material.

**4-Anilino-1,2-naphthoquinone.**—(a) *o*-Naphthoquinone (100 mg, 0.63 mmol) and aniline (59 mg, 0.63 mmol) were heated in refluxing methanol (15 ml) for 10 min. The solution was then evaporated, and the residue was crystallised from methanol to give the anilinoquinone as dark red needles, m.p. 244–245 °C (lit.,<sup>15</sup> 244 °C) (120 mg, 76%);  $v_{\max}$  (KBr) 3 320, 1 698, 1 598, and 1 584;  $m/z$  (%) 249 ( $M^+$ , 100), 220 (43), 203 (32), 193 (18), and 77 (36). To hydrolyse the quinone it was dissolved in concentrated

**Table 4.** Torsion angles (°) for compound (11) with e.s.d.'s in parentheses

C(2)-C(1)-C(1A)-C(1A)-N(5')	64.8(7)	C(10)-C(1)-C(1A)-N(5')	-170.8(5)
O(15')-C(1)-C(1A)-N(5')	-56.4(6)	C(1A)-C(1)-C(2)-C(3)	101.7(8)
C(10)-C(1)-C(2)-C(3)	-20.7(9)	O(15')-C(1)-C(2)-C(3)	-137.0(7)
C(1A)-C(1)-C(10)-C(4A)	-102.7(7)	C(1A)-C(1)-C(10)-S(10)	73.3(6)
C(2)-C(1)-C(10)-C(4A)	21.7(8)	C(2)-C(1)-C(10)-S(10)	-162.4(4)
O(15')-C(1)-C(10)-C(4A)	140.3(6)	O(15')-C(1)-C(10)-S(10)	-43.8(6)
C(1A)-C(1)-O(15')-C(4')	38.0(7)	C(2)-C(1)-O(15')-C(4')	-85.0(6)
C(10)-C(1)-O(15')-C(4')	154.5(5)	C(1)-C(1A)-N(5')-C(4A')	48.0(7)
C(1)-C(1A)-N(5')-C(5A')	-102.2(6)	C(1)-C(2)-C(3)-C(4)	5.9(10)
C(1)-C(2)-C(3)-C(11)	-179.0(6)	C(2)-C(3)-C(4)-C(4A)	9.1(10)
C(2)-C(3)-C(4)-O(15)	-170.7(7)	C(11)-C(3)-C(4)-C(4A)	-166.4(6)
C(11)-C(3)-C(4)-O(15)	13.8(11)	C(2)-C(3)-C(11)-C(12)	0.3(10)
C(2)-C(3)-C(11)-C(13)	118.3(8)	C(2)-C(3)-C(11)-C(14)	-118.9(8)
C(4)-C(3)-C(11)-C(12)	175.4(6)	C(4)-C(3)-C(11)-C(13)	-66.6(8)
C(4)-C(3)-C(11)-C(14)	56.1(8)	C(3)-C(4)-C(4A)-N(5)	168.9(6)
C(3)-C(4)-C(4A)-C(10)	-7.3(10)	O(15)-C(4)-C(4A)-N(5)	-11.3(10)
O(15)-C(4)-C(4A)-C(10)	172.5(7)	C(4)-C(4A)-N(5)-C(5A')	161.8(7)
C(10)-C(4A)-N(5)-C(5A')	-22.1(11)	C(4)-C(4A)-C(10)-C(1)	-9.1(10)
C(4)-C(4A)-C(10)-S(10)	175.2(5)	N(5)-C(4A)-C(10)-C(1)	175.0(6)
N(5)-C(4A)-C(10)-S(10)	-0.7(10)	C(4A)-N(5)-C(5A)-C(6)	-161.0(7)
C(4A)-N(5)-C(5A)-C(9A)	21.7(11)	N(5)-C(5A)-C(6)-C(7)	-176.6(8)
C(9A)-C(5A)-C(6)-C(7)	0.9(12)	N(5)-C(5A)-C(9A)-C(9)	178.0(7)
N(5)-C(5A)-C(9A)-S(10)	0.5(10)	C(6)-C(5A)-C(9A)-C(9)	0.6(11)
C(6)-C(5A)-C(9A)-S(10)	-176.9(6)	C(5A)-C(6)-C(7)-C(8)	-0.2(14)
C(6)-C(7)-C(8)-C(9)	-1.9(15)	C(7)-C(8)-C(9)-C(9A)	3.4(13)
C(8)-C(9)-C(9A)-C(5A)	-2.7(12)	C(8)-C(9)-C(9A)-S(10)	174.8(7)
C(5A)-C(9A)-S(10)-C(10)	-17.4(7)	C(9)-C(9A)-S(10)-C(10)	165.0(6)
C(9A)-S(10)-C(10)-C(1)	-158.1(5)	C(9A)-S(10)-C(10)-C(4A)	17.8(7)
C(1A)-C(1)-C(2)-C(3)	178.8(6)	C(10)-C(1)-C(2)-C(3)	-0.5(10)
C(1A)-C(1)-C(10)-C(4A')	-179.3(6)	C(1A)-C(1)-C(10)-S(10')	0.4(9)
C(2)-C(1)-C(10)-C(4A')	-0.0(9)	C(2)-C(1)-C(10)-S(10')	179.6(5)
C(1)-C(2)-C(3)-C(4)	0.1(10)	C(1)-C(2)-C(3)-C(11')	-176.4(7)
C(2)-C(3)-C(4)-C(4A')	0.7(9)	C(2)-C(3)-C(4)-O(15')	179.0(5)
C(11)-C(3)-C(4)-C(4A')	177.1(6)	C(11)-C(3)-C(4)-O(15')	-4.5(9)
C(2)-C(3)-C(11)-C(12')	114.7(8)	C(2)-C(3)-C(11)-C(13')	-2.7(10)
C(2)-C(3)-C(11)-C(14')	-122.9(7)	C(4)-C(3)-C(11)-C(12')	-61.5(9)
C(4)-C(3)-C(11)-C(13')	-179.0(7)	C(4)-C(3)-C(11)-C(14')	60.8(9)
C(3)-C(4)-C(4A)-N(5')	-178.9(6)	C(3)-C(4)-C(4A)-C(10')	-1.2(10)
O(15')-C(4)-C(4A)-N(5')	2.9(9)	O(15)-C(4)-C(4A)-C(10')	-179.4(5)
C(3)-C(4)-O(15)-C(1)	169.0(5)	C(4A)-C(4)-O(15)-C(1)	-12.6(8)
C(4)-C(4A)-N(5)-C(1A)	-21.5(8)	C(4)-C(4A)-N(5)-C(5A')	130.5(6)
C(10)-C(4A)-N(5)-C(1A)	160.8(6)	C(10)-C(4A)-N(5)-C(5A')	-47.2(8)
C(4)-C(4A)-C(10)-C(1')	0.8(9)	C(4)-C(4A)-C(10)-S(10')	-178.9(5)
N(5)-C(4A)-C(10)-C(1')	178.6(6)	N(5)-C(4A)-C(10)-S(10')	-1.1(8)
C(1A)-N(5)-C(5A)-C(6')	12.3(10)	C(1A)-N(5)-C(5A)-C(9A')	-166.3(6)
C(4A)-N(5)-C(5A)-C(6')	-136.5(7)	C(4A)-N(5)-C(5A)-C(9A')	44.9(8)
N(5)-C(5A)-C(6)-C(7')	179.5(7)	C(9A)-C(5A)-C(6)-C(7')	-2.0(11)
N(5)-C(5A)-C(9A)-C(9')	-179.2(6)	N(5)-C(5A)-C(9A)-S(10')	5.1(8)
C(6)-C(5A)-C(9A)-C(9')	2.1(10)	C(6)-C(5A)-C(9A)-S(10')	-173.6(5)
C(5A)-C(6)-C(7)-C(8')	0.8(13)	C(6)-C(7)-C(8)-C(9')	0.3(14)
C(7)-C(8)-C(9)-C(9A')	-0.2(13)	C(8)-C(9)-C(9A)-C(5A')	-1.0(11)
C(8)-C(9)-C(9A)-S(10')	174.7(7)	C(5A)-C(9A)-S(10)-C(10')	-41.6(6)
C(9)-C(9A)-S(10)-C(10')	142.8(6)	C(9A)-S(10)-C(10)-C(1')	-141.1(6)
C(9A)-S(10)-C(10)-C(4A')	38.6(6)		

sulphuric acid to which water was added, and the suspension then warmed on a steam-bath for 15 min. Work up gave 2-hydroxy-1,4-naphthoquinone, m.p. 192–194 °C (from methanol) identical with that described above.

(b) Raney nickel (0.25 g, B.D.H.) was added to 6-hydroxy-5H-benzo[*a*]phenothiazin-5-one (25b) (50 mg) in methanol (20 ml), and the mixture was refluxed for 20 h. After removal of the nickel the solution was evaporated *in vacuo* and the residue was crystallised from methanol to give 4-anilino-1,2-naphthoquinone as dark red needles, m.p. 244–245 °C (40 mg, 89%) identical with those described in (a).

**3- and 4-Phenyl-1,2-naphthoquinone.**—Following reference 12 a mixture of *o*-naphthoquinone (1.62 g) and palladium acetate

(1.0 g) in acetic acid (150 ml) and benzene (200 ml) was stirred at 80 °C under nitrogen for 16 h, and then evaporated under reduced pressure. The residue was passed down a column of silica in chloroform and the main red band was further separated by p.l.c. on silica gel in chloroform–benzene (1:1) (multiple development). The less polar orange-red band yielded 3-phenyl-1,2-naphthoquinone as red needles, m.p. 161–162 °C (lit.,<sup>16</sup> 156 °C) (from methanol) (36%);  $\nu_{\max}$  (KBr) 1 690 and 1 655  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.10 (1 H, d, *J* 8 Hz, 8-H), 7.70–7.35 (9 H, m, ArH + 4-H);  $m/z$  (%) 236 (26), 234 (*M*<sup>+</sup>, 6), 206 (100), 178 (30), and 76 (22). The more polar orange-yellow band afforded 4-phenyl-1,2-naphthoquinone, orange needles, m.p. 118–120 °C (lit.,<sup>17</sup> 120–121 °C) (from methanol) (12%);  $\nu_{\max}$  (KBr) 1 680 and 1 645  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.19 (1 H, dd, *J* 8

**Table 5.** Displacement (Å) of atoms from various planes

(i)	C(5A') 0.02, C(6') -0.07, C(7') -0.06, C(8') 0.01, C(9') 0.07, C(9A') 0.06, N(5') 0.03, S(10') -0.01.
(ii)	C(1') 0.00, C(2') 0.00, C(3') 0.00, C(4') 0.00, C(4A') 0.02, N(5') -0.01, S(10') 0.00, C(10') 0.01.
(iii)	C(5A) 0.03, C(6) 0.00, C(7) -0.04, C(8) -0.04, C(9) 0.04, C(9A) 0.04, N(5) -0.01, S(10) 0.00.
(iv)	C(1) 0.23, C(2) -0.12, C(3) -0.16, C(4) 0.05, C(4A) 0.08, N(5) 0.03, S(10) -0.02, C(10) 0.07.
(v)	C(2) 0.02, C(3) -0.04, C(4) 0.04, C(4A) -0.02, C(10) 0.00, C(1) 0.29.
(vi)	C(1) -0.08, C(4') -0.06, C(4A') -0.04, N(5') 0.04, O(15') 0.05, C(1A) 0.58.
(vii)	C(4A') -0.01, C(5A') 0.01, C(9A') -0.01, C(10') 0.01, S(10') 0.65, N(5') 0.47.
(viii)	C(4A) 0.00, C(5A) -0.01, C(9A) 0.01, C(10) 0.00, S(10) -0.29, N(5) -0.21.
(ix)	C(1A) 0.00, C(4A') 0.00, C(5A') 0.00, N(5') 0.22.
(x)	H(5) 0.00, C(4A) 0.00, C(5A) 0.00, N(5) -0.20.

(Atoms in italics are not included in the derivation of the mean planes.)

and 2 Hz, 8-H), 7.78—7.29 (8 H), and 6.42 (1 H, s, 3-H);  $m/z$  (%) 236 ( $M^+ + 2$ , 18), 206 (100), 178 (78), and 76 (40).

**4-Anilino-3-phenyl-1,2-naphthoquinone.**—A mixture of 3-phenyl-1,2-naphthoquinone (100 mg) and aniline (0.5 ml) in methanol (10 ml) was refluxed for 10 min and then evaporated. The residue was purified by p.l.c. on silica in chloroform and the most polar component was crystallised from methanol to give the *anilinoquinone* as dark violet prisms, m.p. 220—222 °C (36 mg, 26%) (Found:  $M^+$ , 325.1120.  $C_{22}H_{15}NO_2$  requires  $M$ , 325.1103);  $\lambda_{\max}$  (CHCl<sub>3</sub>) 378 and 479 nm (log  $\epsilon$  3.48 and 3.58);  $\nu_{\max}$  (KBr) 3 340 and 1 682 cm<sup>-1</sup>;  $m/z$  (%) 327 (18), 325 ( $M^+$ , 100), 297 (22), 296 (42), 267 (23), and 77 (18). The anilino compound (10 mg) was dissolved in concentrated sulphuric acid (0.5 ml) to which water (5 ml) was added. The suspension was then heated on a steam-bath for 15 min (becoming yellow), cooled, and extracted with chloroform to give 2-hydroxy-3-phenyl-1,4-naphthoquinone identical (t.l.c., i.r., m.s.) with an authentic sample.

**3-Phenyl-4-p-tolylthio-1,2-naphthoquinone.**—*p*-Thiocresol (64 mg, 0.51 mmol) was added to 3-phenyl-1,2-naphthoquinone (60 mg, 0.26 mmol) in chloroform (5 ml) and methanol (5 ml). After 30 min the colourless solution was evaporated. The residue was applied to a silica plate and chromatographed in chloroform during which the quinol was oxidised to the desired *quinone*. Elution of the red band and crystallisation from chloroform-methanol gave red needles, m.p. 191—193 °C (40 mg, 44%) (Found: C, 77.25; H, 4.45; S, 8.95%.  $M^+ + 2$ , 358.1016.  $C_{23}H_{16}O_2S$  requires C, 77.5; H, 4.5; S, 9.0%;  $M^+ + 2$ , 358.1027);  $\lambda_{\max}$  (CHCl<sub>3</sub>) 339, 424, and 479sh nm (log  $\epsilon$  3.55, 3.62, and 3.54);  $\nu_{\max}$  (KBr) 1 670, 1 650, and 1 635 cm<sup>-1</sup>;  $m/z$  (%) 358 (23), 356 ( $M^+$ , 11), 328 (100), 295 (45), 205 (100), and 176 (45). The *p*-tolylthioquinone (15 mg) was refluxed for 5 h in methanol (5 ml) containing aniline (1 drop). Evaporation followed by p.l.c. gave 4-anilino-3-phenyl-1,2-naphthoquinone as dark violet crystals, m.p. 220—222 °C (from methanol) identical (t.l.c., m.s.) with those described above.

**Reaction of *o*-Chloranil with *o*-Aminothiophenol.**—A solution of *o*-chloranil (0.5 g, 2 mmol) and *o*-aminothiophenol (0.625 g, 5 mmol) in ethanol (25 ml) was stirred for 12 h, evaporated to dryness under reduced pressure and the residue passed down a

column of dry silica to give (i) the *trithiazine* (7), purple needles, m.p. > 300 °C (2-ethoxyethanol) (65 mg, 7.4%) (Found: C, 65.6; H, 3.3; N, 9.3; S, 21.6. Calc. for  $C_{24}H_{13}N_3S_3$  C, 65.6; H, 3.0; N, 9.6; S, 21.9%;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 267, 375, 537sh, and 576 nm (log  $\epsilon$  4.42, 4.37, 4.16, and 4.31);  $m/z$  (%) 439 ( $M^+$ , 100), 407(25), 375 (7), and 343 (3.5); (ii) 2,2'-diaminophenyl disulphide, m.p. 92—93 °C (lit.,<sup>18</sup> 93 °C) (0.25 g, 40%);  $m/z$  (%) 248 ( $M^+$ , 28) and 124 (100).

**Crystal Structure Determination of 6-Methyl-2',4-di-*t*-butyl-spiro{[1,4]oxazino[2,3,4-*k*l]phenothiazine-2(1H),4'(1'H)-phenothiazin}-1'-one (11).**—*Crystal data.*  $C_{34}H_{34}N_2O_2S_2$ ,  $M = 566.8$ , triclinic,  $a = 11.876(11)$ ,  $b = 11.492(10)$ ,  $c = 11.435(8)$  Å,  $\alpha = 97.72(6)$ ,  $\beta = 98.20(6)$ ,  $\gamma = 99.28(7)^\circ$ ,  $U = 1505$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.25$  g cm<sup>-3</sup>,  $F(000) = 600$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 1.69$  cm<sup>-1</sup>. Space group P $\bar{1}$ .

*Crystallographic measurements.* Intensity measurements were obtained from a Nicolet P3 automated diffractometer using monochromatized Mo- $K_\alpha$  radiation. Integrated relative intensities for 2 585 independent reflexions with  $2\theta < 50^\circ$  were measured by the  $\theta$ — $2\theta$  scan method; 1 912 reflexions had  $I > 3.0 \sigma I$ .

*Structure analysis.* The crystal structure was elucidated by direct methods using the 'MULTAN' programme.<sup>19</sup> Refinement of structural parameters were performed using the 'SHELX' programme.<sup>20</sup> The H atoms, observed on electron density maps, were constrained to 1.00(3) Å bond lengths, using full matrix least-squares refinement. Apart from H(5) the H atoms were allowed to ride on their attached carbon atoms; common isotropic temperature factors refined to 0.11 Å<sup>2</sup> for the methyl hydrogens and 0.06 Å<sup>2</sup> for the non-methyl hydrogens. The positional and anisotropic temperature factors for the non-H atoms were refined and convergence was reached at  $R = 6.1\%$ . The weighting scheme used in the final cycles of least-squares refinement was:  $w = 1/(\sigma^2 F_o + 0.004 72 F_o^2)$ .

Final positional parameters for non-hydrogen atoms are listed in Table 1: bond lengths, valency angles and torsion angles are given in Tables 2—4, respectively. Thermal parameters and final positional parameters for hydrogen atoms are available on request from the Cambridge Crystallographic Centre.\*

The molecular conformation of the dimer (Figure) shows the arrangement of the tricyclic thiazine moieties about the spiro carbon. Displacements of atoms from various planes are shown in Table 5. The phenothiazine system (rings A'B'C') is folded about the S,N axis with a dihedral angle of 133.7°. Similar folded configurations are found in other *N*-substituted phenothiazines such as 3-(2-methoxyphenothiazin-10-yl)-*N,N*,2-trimethylpropanamine<sup>21</sup> where the dihedral angle is 135.4°. There is also folding about the S,N axis in the phenothiazinone system (rings ABC) where the dihedral angle is 157.4°. However, there are distortions from co-planarity here as shown by plane (iv), Table 5. Comparable dihedral angles of 153.3° and 158.5° have been reported for the phenothiazine molecule.<sup>22,23</sup> In the current study both S and N atoms have been included in calculations of mean planes.

Rings A,A' and C' adopt planar conformations, rings C and D adopt distorted sofa conformations, and the thiazine rings adopt boat conformations. The geometry around the N atoms is similar in both rings (Table 5). The spiro planes C(1)C(1A)O(15') and C(1)C(2)C(10) are inclined at 90.4° and the tetrahedral angles around the spiro carbon vary from 105.3(5)–112.1(5)°. Similar values have been reported<sup>24</sup> around other spiran junctions.

\* See Instructions for Authors (1986), para. 5.6.3, in *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.



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