Tetrahedron Vol. 48, No. 37, pp. 8127-8142, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Cyclic Meso-ionic Heterocycles. Part 24.[1] The Reaction of 1,2–Dithiolium-4-olates with Aniline. The Formation of 11–Phenylbenz[*b*]indeno[2,1-*e*]-1,4-thiazine[#]

Christopher G. Newton, W. David Ollis,* and Graham P. Rowson

Department of Chemistry, The University, Sheffield S3 7HF, UK

Margaret J. Hamor and Thomas A. Hamor

School of Chemistry, The University of Birmingham,
Edgbaston, Birmingham B15 2TT, UK

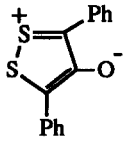
(*Received in USA* 13 *August* 1992)

Abstract: Reaction of the type B meso-ionic heterocycle 3,5-diphenyl-1,2-dithiolium-4–olate (**1**) with aniline yields *N*-phenyl-(3-phenyl-1-phenylimino-inden-2-yl)-amine (**10**) and 11-phenylbenz[*b*]indeno[2,1–*e*]-1,4-thiazine (**12**). Mechanistic investigations establish that the 3–phenylindenylamine (**10**) is an intermediate in the formation of the tetracyclic 1,4–thiazine (**12**).

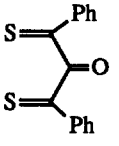
Meso-ionic heterocycles are associated with two main types, type A and type B.[2] The chemistry of type A meso-ionic heterocycles (representatives of 60 classes are known[3]) is far more extensive than that of type B meso-ionic heterocycles (representatives of 13 classes are known[3]). Type A meso-ionic heterocycles exhibit a wide range of different types of reaction which are generally understood.[4] In contrast, the investigation of type B meso-ionic heterocycles is much less extensive and general features of the mechanisms of their reactions have not yet been identified.[4] 1,2-Dithiolium-4-olates are type B meso-ionic heterocycles and their reaction with aniline is unexpectedly complex. We now report a detailed investigation of the reaction between 3,5–diphenyl-1,2-dithiolium-4-olate (**1**) and aniline.

Dedicated to Professor Charles W. Rees in celebration of his outstanding contributions to, and enthusiasm for, heterocyclic chemistry.

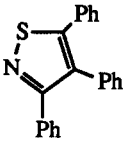
Now that it has been recognised that meso-ionic heterocycles are conjugated heterocyclic mesomeric betaines isoconjugate with even non-alternant hydrocarbon dianions,[4] we shall follow the proposal[4] that they should no longer be represented by a dipolar formulation indicated by a positive sign within a circle and a negative charge associated with the exocyclic substituent. In this and subsequent papers in this series, meso-ionic heterocycles of type A and type B will be represented by appropriately selected dipolar structures.[4] Thus type B 3,5-diphenyl-1,2-dithiolium-4-olate is represented by the dipolar structure **1**. This dipolar structure **1** could be associated with the valence isomer **2**, but crystal structure determination establishes the structure **1** in the solid state [S–S distance 2.005Å].[5,6] It is, however, possible that the covalent valence isomer **2** might be associated with chemical reactions of this compound.



1



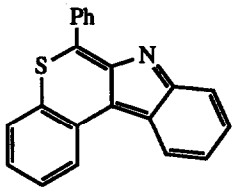
2



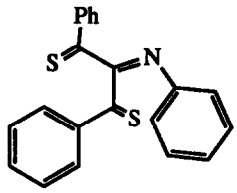
3

The reaction of 3,5-diphenyl-1,2-dithiolium-4-olate (**1**) with boiling aniline was reported to give a blue compound, mp 168–170°C (88% yield) which was formulated as 3,4,5-triphenylisothiazole (**3**).[7] In our view,[2] the blue colour of this compound was certainly not in accord with the properties of isothiazoles.[8] A substance with the formulation **3** would be predicted to be colourless and this was subsequently confirmed by its synthesis (*vide infra*). However, the real problem presented by the formulation of the blue compound as 3,4,5-triphenylisothiazole (**3**) was the requirement that the formation of 3,4,5-triphenylisothiazole (**3**) from the 1,2-dithiolium-4-olate (**1**) and aniline would have to involve an unprecedented (N → C) phenyl migration.

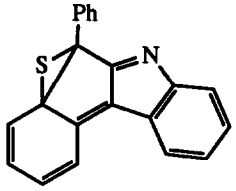
In our hands, the reaction between 3,5-diphenyl-1,2-dithiolium-4-olate (**1**) and boiling aniline (4 h) gave a blue compound, mp 169–170°C (~50% yield) which was obviously identical with that described previously.[7] However, its molecular formula, $C_{21}H_{13}NS$, which was established by analysis and its mass spectrum, clearly excluded the proposed structure **3** ($C_{21}H_{15}NS$). The structure **4** was initially considered for the blue compound because this had the required molecular formula ($C_{21}H_{13}NS$), and a reasonable pathway for its formation from the mono-anil **5** by electrocyclisation and extrusion of sulphur could be visualised. The mono-anil **5** could be regarded as an acceptable intermediate in this pathway because the mono-anil **5** could have been derived from the valence isomer **2** of the reactant **1**.



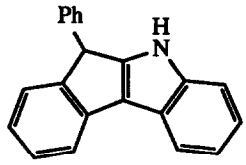
4



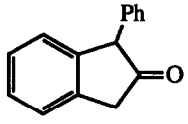
5



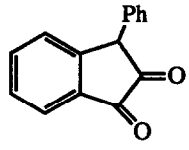
6



7



8



9

Support for the formula **4** for the blue compound ($C_{21}H_{13}NS$) was provided by its Raney nickel desulphurisation which yielded the indole derivative **7**. A reasonable route for the desulphurisation of the blue compound **4**, which requires ring contraction of the six-membered sulphur-containing ring in the precursor **4** giving the five-membered carbocyclic ring, could involve the thiirane **6** as a valence isomer of the precursor **4**.

The constitution of the desulphurisation product **7** was firmly established by synthesis. Fischer indole cyclisation of the phenylhydrazone of 1–phenylindan-2-one (**8**)[9] by heating (170°C; 5 min) with zinc chloride yielded the indole derivative **7**.

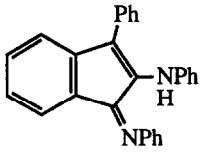
The influence of reaction conditions upon the yield of the isolated blue compound was then examined in order to explore the possible role of the mono-anil **5** as the putative intermediate in the formation of the blue compound **4**. When the reaction between the 1,2-dithiolium-4-olate (**1**) and boiling aniline was carried out under a stream of nitrogen then the yield of the blue product was rather variable, even under the same conditions of time and temperature. This was attributed to the loss of hydrogen sulphide from the reaction mixture, but it was not clear how this could influence the yield of the blue compound if the intermediate **5** was transformed to the product **4**. However, it was then found that consistently high yields (> 80%) of the blue compound were obtained when the reaction between the 1,2-dithiolium-4-olate (**1**) and aniline was carried out in a sealed tube.

The stoichiometry of the reaction could have been associated with the following equation:

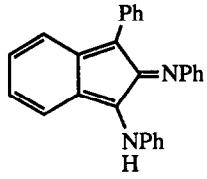
$$C_{15}H_{10}OS_2 + PhNH_2 \rightarrow C_{21}H_{13}NS + H_2O + H_2S$$

Measurement of the yield of hydrogen sulphide was made by weighing the precipitated cupric sulphide when the effluent gases were passed through aqueous cupric acetate and nitrogen gas was bubbled through the reaction mixture in an open system. The yield of hydrogen sulphide in terms of the above equation was 114%, clearly indicating that some additional reactions were involved. Furthermore, the reaction of 3,5-diphenyl-1,2-dithiolium-4-olate (**1**) with aniline gave two coloured products – the blue compound ($C_{21}H_{13}NS$) and a maroon compound ($C_{27}H_{20}N_2$). The following experiments indicated that the maroon compound ($C_{27}H_{20}N_2$) was the genuine intermediate in the formation of the blue compound ($C_{21}H_{13}NS$). We had therefore encountered a remarkable sequence where the precursor **1** containing ***two*** sulphur atoms was transformed into the final product containing ***one*** sulphur atom *via* an intermediate containing ***no*** sulphur atoms.

The role of the maroon compound as an intermediate in the formation of the blue compound was demonstrated by the following experiments: (i) 3,5-diphenyl-1,2-dithiolium-4-olate (**1**) and boiling aniline gave only the maroon compound (32% yield) after a short period (10 min), (ii) the maroon compound and boiling aniline containing sulphur gave the blue compound (74% yield), (iii) the maroon compound and boiling aniline containing sulphur and hydrogen sulphide gave the blue compound (86% yield), and (iv) the formation of the blue compound in the reaction of the 1,2-dithiolium-4-olate (**1**) and aniline is suppressed by the thiophile, triphenylphosphine, and only the maroon compound is obtained. These results indicated that consideration of the constitution of the maroon compound could be a useful prelude to the elucidation of the constitution of the blue compound.

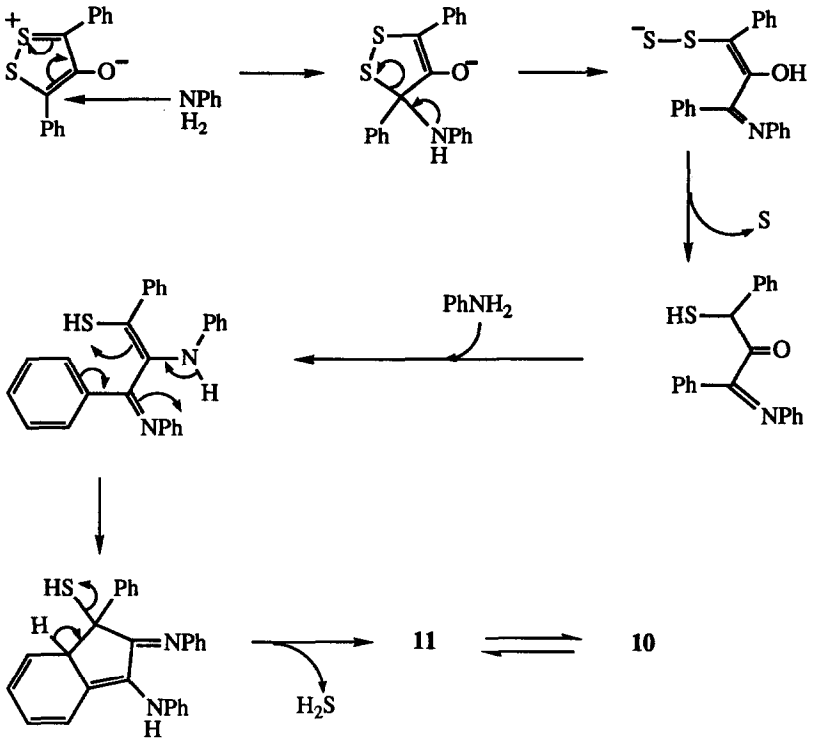


10



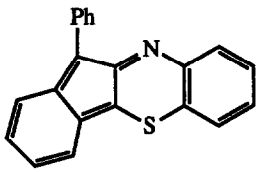
11

Two constitutional formulae **10** and **11**, which were related as tautomers, could be considered for the maroon compound on the basis of its formation [experiment (i), see above] and its molecular formula, $C_{27}H_{20}N_2$. Furthermore, a reasonable mechanism for the formation of either of these structures **10** or **11** could be envisaged (Scheme 1): these structures were confirmed when the maroon compound was produced (83% yield) by a rational synthesis by heating 3-phenylindan-1,2-dione (**9**)[10] with aniline. A decision between the two possible constitutions **10** or **11** was not possible on chemical evidence, but a crystal structure determination firmly established that the maroon compound had the tautomeric structure **10** in the solid state.

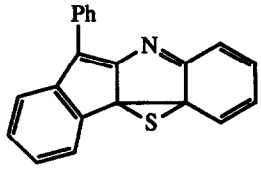


SCHEME 1. Mechanism for the formation of the maroon compound (**10**)

The established constitution **10** for the maroon compound then raised the interesting question how the maroon compound **10** could possibly function as an intermediate in the formation of the blue compound **4** [experiments (ii) and (iii) above]. No reasonable mechanism could be proposed for this transformation (**10** → **4**), but these considerations did lead to the examination of a new constitution **12** for the blue compound which was still compatible with the experimental result that Raney nickel desulphurisation of the blue compound gave the indole derivative **7**. The new constitution **12** for the blue compound could be associated with the thiirane **13** as a valence isomer and this on desulphurisation could lead to the indole derivative **7**.

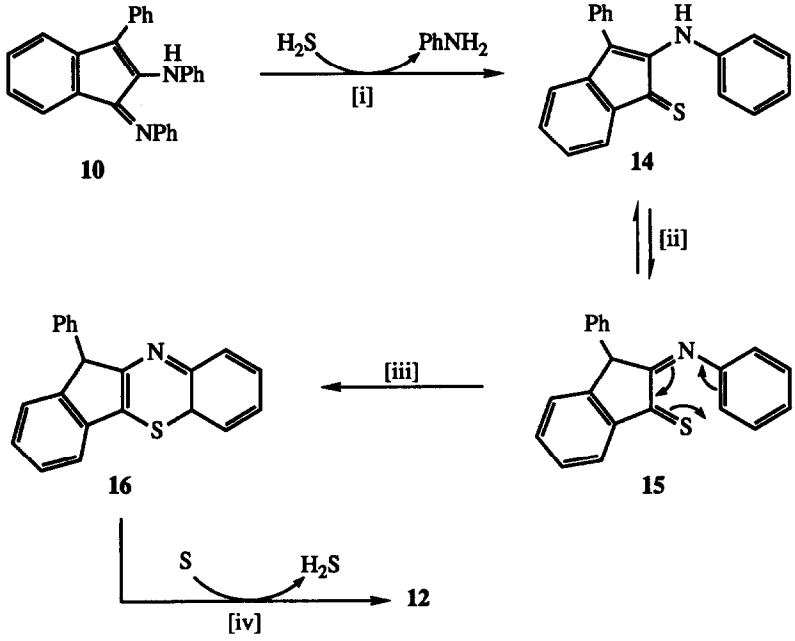


12



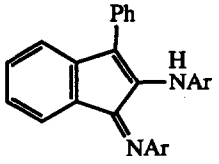
13

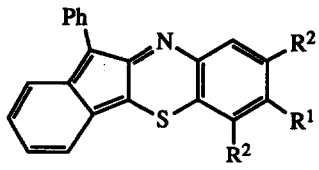
A possible mechanism (Scheme 2) for the transformation of the maroon compound **10** to the blue compound **12** was now considered. This mechanism involved (i) the acceptable transformation of the anil **10** to the thioketone **14** by hydrogen sulphide, (ii) the tautomerisation (**14** → **15**), (iii) the novel 6π–electrocyclic reaction (**15** → **16**), and (iv) dehydrogenation by sulphur yielding the blue compound **12**. The hydrogen sulphide generated in step (iv) could be utilised in step (i). This proposal was compatible with the high yield (89%) of the blue compound which was obtained when the reaction between the 1,2–dithiolium-4-olate (**1**) and aniline was carried out in a sealed tube.



SCHEME 2. A possible mechanism for the transformation of the maroon compound (**10**) to the blue compound (**12**)

Support for Scheme 2 was apparently provided by a study of the reaction between the 1,2-dithiolium-4–olate (**1**) and various substituted anilines. *p*-Toluidine yielded the compounds **17** and **20**, 3,5–dimethylaniline yielded compound **21**, whereas 2,6–dimethylaniline yielded only compound **19**.





17 Ar = 4-methylphenyl

18 Ar = 3,5-dimethylphenyl

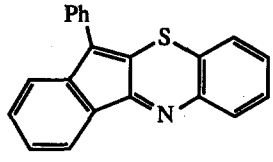
19 Ar = 2,6-dimethylphenyl

20 R^1 = Me, R^2 = H

21 R^1 = H, R^2 = Me

However, support for the 6π-electrocyclic reaction (**15**, arrows) postulated in Scheme 2 was not provided by the following experiments. The transformation **10** → **12** was not observed when the maroon compound **10** was heated with sulphur and hydrogen sulphide either in the inert solvents, toluene or xylene, or in *N,N*-dimethylaniline. Aniline appeared to be an essential reactant. Furthermore, the reaction of aniline with sulphur yielding *o*-aminothiophenol and derived products is a well-established process.[11,12] Thus Scheme 2 could be replaced by a simpler sequence in which aniline and sulphur give *o*-aminothiophenol which could then react with the maroon compound **10** giving the blue compound **12** directly.

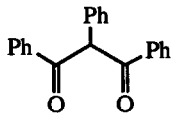
This mechanistic proposal was firmly supported by the following results. The maroon compound **10** and *o*-aminothiophenol in boiling aniline yielded the blue compound **12** (89%). Similarly, 3-phenylindan-1,2-dione (**9**) and *o*-aminothiophenol in boiling xylene also yielded the blue compound **12** (83%). It is interesting to note that the transformations **10** → **12** and **9** → **12** are regiospecific and the formation of the regio-isomer **22** containing two benzenoid rings was not detected.



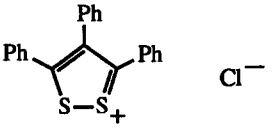
22

Our interest in this problem[2] was generated by the report[7] that the reaction of 3,5-diphenyl-1,2–dithiolium-4-olate (**1**) and aniline yielded a ***blue*** compound formulated as 3,4,5-triphenylisothiazole (**3**). This compound has been synthesised and it is ***colourless***. 1,3,5-Propan-1,3-dione (**23**)[13] and phosphorus

pentasulphide yielded 3,4,5-triphenyldithiolium chloride (**24**) which, with ammonia in boiling ethanol,[8] gave 3,4,5-triphenylisothiazole (**3**) as colourless needles, mp 215–216°C.



23



24

EXPERIMENTAL

General experimental details are given in Part 21.[14]

Reaction of 3,5-*Diphenyl*-1,2-*dithiolium*-4-*olate* (**1**) *with Aniline. Formation of* N-*Phenyl*-(3-*phenyl*-1-*phenyliminoinden*-2-*yl*)-*amine* (**10**) *and* 11-*Phenylbenz*[b]*indeno*[2,1-e]-1,4-*thiazine* (**12**). — [a] A suspension of 3,5-diphenyl-1,2-dithiolium-4-olate[7] (3.5 g) in aniline (250 ml) was heated under reflux in an atmosphere of nitrogen (4 h). The aniline was removed under reduced pressure and the residue fractionated by preparative TLC (chloroform–light petroleum, 1:3) giving two fractions. Fraction 1 yielded N-*phenyl*-(3-*phenyl*-1-*phenyliminoinden*-2-*yl*)-*amine* (R_f 0.75) (0.86 g, 18%) as dark maroon needles, mp 178–179°C from light petroleum, bp 80–100°C (Found: C, 87.1; H, 5.7; N, 7.4; $M^{+\bullet}$, 372. $C_{27}H_{20}N_2$ requires C, 87.1; H, 5.4; N, 7.5%; *M*, 372); λ_{max} 267, 373, and 518 nm (ε 28430, 9130, and 8920); υ_{max} (KBr) 3315, 1645, 1620, 1590, 1515, and 1450 cm^{-1}; δ_H 6.2–7.5 (m, Ar–H). Fraction 2 yielded 11-*phenylbenz*[b]*indeno*[2,1-e]-1,4-*thiazine* (R_f 0.70) (2.3 g, 58%) as dark blue needles, mp 169–170°C from ethanol (Found: C, 80.9; H, 4.5; N, 4.4; S, 10.5; $M^{+\bullet}$, 311. $C_{21}H_{13}NS$ requires C, 81.1; H, 4.2; N, 4.5; S, 10.3%; *M*, 311); λ_{max} 255, 300, 360, 376, and 540 nm (ε 25660, 29540, 9330, 7780, and 2490); υ_{max} (KBr) 1615, 1605, 1585, 1530, 1490, 1460, 1440, and 1430 cm^{-1}; δ_H 7.2–8.25 (m, Ar–H).

(b) *Sealed tube experiment.* — 3,5-Diphenyl-1,2-dithiolium-4-olate (1 g) and aniline (20 ml) were sealed in a glass tube in an atmosphere of nitrogen and the tube was heated at 200°C (4 h). Aniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3) giving 11-phenylbenz[*b*]indeno[2,1–*e*]-1,4-thiazine (R_f 0.70) (1.02 g, 89%).

(c) *Entrapment of evolved gases.* — A suspension of 3,5-diphenyl-1,2-dithiolium-4-olate (500 mg) in aniline (25 ml) was heated under reflux (4 h) and a stream of nitrogen was passed through the solution. The escaping gases were passed into an aqueous solution of copper(II) acetate. The precipitated copper(II) sulphide was collected and dried (200 mg, 114%). The aniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3) giving two fractions. Fraction 1 yielded *N*-phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (R_f 0.75) (99 mg, 14%). Fraction 2 yielded 11-phenylbenz[*b*]indeno[2,1–*e*]-1,4-thiazine (R_f 0.70) (297 mg, 52%), mp 169–170°C.

(d) *Influence of reaction time.* — A suspension of 3,5-diphenyl-1,2-dithiolium-4-olate (0.5 g) in aniline (25 ml) was heated under reflux (10 min) giving *N*-phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (0.22 g, 32%).

(e) *Influence of triphenylphosphine.* — A solution of 3,5-diphenyl-1,2-dithiolium-4-olate (500 mg) and triphenylphosphine (1 g) in aniline (30 ml) was heated under reflux in an atmosphere of nitrogen (4 h) yielding *N*-phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (209 mg, 30%).

Reactions of N-*Phenyl*-(3-*phenyl*-1-*phenyliminoinden*-2-*yl*)-*amine* (**10**). (a) *With sulphur in aniline.* — *N*-Phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (150 mg) and sulphur (25 mg) in aniline (15 ml) were heated under reflux (24 h). A further portion of sulphur (25 mg) was added and heating continued (24 h). The aniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform), giving 11-phenylbenz[*b*]indeno[2,1-*e*]-1,4-thiazine (R_f 0.67) (92 mg, 74%).

(b) *With hydrogen sulphide and sulphur in aniline.* — *N*-Phenyl-(3-phenyl-1-phenyliminoinden-2–yl)-amine (500 mg) and sulphur (80 mg) in aniline (20 ml) were heated under reflux (3.5 h) and hydrogen sulphide was passed through the mixture. The aniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3), giving 11–phenylbenz[*b*]indeno[2,1–*e*]-1,4-thiazine (R_f 0.70) (360 mg, 86%).

(c) *With hydrogen sulphide and sulphur in various solvents.* — *N*-Phenyl-(3-phenyliminoinden-2-yl)-amine (150 mg) and sulphur (25 mg) were dissolved in the appropriate solvent (40 ml) and hydrogen sulphide was passed through the reaction mixture during the period of heating under reflux. The reactions were monitored by TLC (chloroform). No reaction occurred in toluene (7 h) or xylene (7 h). A complex mixture of products was formed in *N,N*-dimethylaniline (4 h).

(d) *With 2-aminothiophenol in aniline.* — *N*-Phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (500 mg) and 2-aminothiophenol (0.2 ml) in aniline (25 ml) were heated under reflux (4 h), evaporated under diminished pressure, and the residue fractionated (medium pressure liquid chromatography, eluant methylene chloride–light petroleum, 1:3) giving three fractions. Fraction 1 yielded starting material (45 mg, 9%). Fraction 2 yielded a mixture of starting material (8 mg) and 11-phenylbenz[*b*]indeno-[2,1-*e*]-1,4-thiazine (13 mg). Fraction 3 yielded 11-phenylbenz[*b*]indeno-[2,1–*e*]-1,4-thiazine (319 mg, 76%).

Desulphurisation of 11-*phenylbenz*[b]*indeno*[2,1–e]-1,4-*thiazine* (**12**). *Formation of* 5,6-*Dihydro*-6-*phenylindeno*[2,1-b]-*indole* (**7**). — 11-Phenylbenz[*b*]indeno[2,1-*e*]-1,4-thiazine (1 g) was added to a slurry of deactivated[15] Raney nickel (4 g) in ethanol (50 ml), and the mixture was heated under reflux (2 h). The mixture was filtered and the nickel was washed with hot ethanol (4 x 20 ml). The combined filtrates were evaporated and the residue crystallised from chloroform–light petroleum giving 5,6-dihydro-6-phenylindeno[2,1-*b*]-indole (0.63 g, 69%) as colourless needles, mp 175–177°C (Found: $M^{+\bullet}$, 281.1203. $C_{21}H_{15}N$ requires *M*, 281.1204; λ_{max} 250, 323, and 341 nm (ε 18500, 15800, and 9800); υ_{max} (KBr) 3395, 1600, 1500, 1490, 1450, 1440, 1385, and 1305 cm^{-1}; δ_H 4.9 (1H, s, C*H*Ph, 6.7–7.6 (13H, m, Ar–H), and 10.55 (1H, s, NH).

1-Phenylindan-2-one Phenylhydrazone. — 1-Phenylindan-2-one[9] (15 g) and phenylhydrazine (12 g) were heated with stirring at 100°C under nitrogen (1 h). The mixture was cooled to room temperature and ethanol (90%, 30 ml) was added. The solid was collected and recrystallised from ethanol (95%) giving *1-phenylindan-2-one phenylhydrazone* (17 g, 78%) as yellow needles, mp 129–130°C (Found: C, 84.5; H, 6.2; N, 9.4; $M^{+\bullet}$, 298. $C_{21}H_{18}N_2$ requires C, 84.5; H, 6.1; N, 9.4%; *M*, 298); λ_{max} 286 and 389 nm (ε 25750 and 660); υ_{max} (KBr) 3290, 1595, 1490, 1475, 1450, 1305, and 1230 cm^{-1}; δ_H 3.5 (2H, s, CH_2), 4.97 (1H, s, C*H*Ph), 6.7 (1H, s, NH), and 6.8–7.4 (14H, m, Ar–H).

5,6-Dihydro-6-phenylindeno[2,1–b]*indole* (**7**). — 1-Phenylindan-2-one phenylhydrazone (10 g) was finely ground with anhydrous zinc chloride (50 g) and the mixture was heated to 170°C (5 min) with stirring. The reaction was cooled, digested with water (200 ml) and concentrated hydrochloric acid (10 ml), filtered, and the solid extracted with hot chloroform, filtered, and the filtrate evaporated. Crystallisation of the residue from chloroform–light petroleum gave 5,6-dihydro-6-phenylindeno[2,1-*b*]-indole (4.98 g, 53%) as colourless needles, mp 176–177°C, identical with the desulphurisation product described above.

Reaction of 3-Phenylindan-1,2-dione (**9**) *with Aniline. Formation of* N *-Phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine* (**10**). — A solution of 3-phenylindan-1,2-dione[10] (1 g), aniline (2 ml), and toluene-*p*-sulphonic acid (15 mg) in xylene (30 ml) was heated under reflux under Dean–Stark conditions in an atmosphere of nitrogen (2.5 h). The xylene was evaporated under reduced pressure and the residue fractionated by preparative TLC giving *N*-phenyl-(3-phenyl-1-phenyliminoinden-2-yl)-amine (R_f 0.8) (1.4 g, 83%).

Reaction of 3,5-Diphenyl-1,2-dithiolium-4-olate (**1**) *with 4-Methylaniline. Formation of* N-(4-*Methylphenyl)-[3-phenyl-1-(4-methylphenyl)iminoinden-2-yl]-amine* (**17**) *and 3-Methyl-11-phenylbenz*[b]*indeno*[2,1-e]-1,4-*thiazine* (**20**). — A suspension of 3,5-diphenyl-1,2-dithiolium-4-olate (2 g) in 4-methylaniline (120 g) was heated at 180°C (4 h). The 4-methylaniline was evaporated under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3). Fraction 1 yielded N-(4-*methylphenyl*)-[3-*phenyl*-1-(4-*methylphenyl*)*iminoinden-2-yl*]-*amine* (R_f 0.73) (0.5 g, 17%) as maroon prisms, mp 156–157°C from light petroleum, bp 80–100°C (Found: $M^{+\bullet}$, 400.1951. $C_{29}H_{24}N_2$ requires *M*, 400.1949); λ_{max} 278, 382, and 522 nm (ε 27170, 11830, and 9010); υ_{max} (KBr) 3320, 1640, 1605, 1585, 1495, and 1440 cm^{-1}; δ_H 2.1 (3H, s, CH_3), 2.45 (3H, s, CH_3), and 6.4–7.3 (17H, m, Ar–H). Fraction 2 yielded 3-*methyl*-11-*phenylbenz*[b]*indeno*[2,1-e]-1,4-*thiazine* (R_f 0.68) (1.27 g. 53%) as dark blue needles, mp 218–219°C from ethanol (Found: C, 81.5; H, 4.9; N, 4.1; S, 10.0; $M^{+\bullet}$, 325. $C_{22}H_{16}NS$ requires C, 81.3; H, 4.7; N, 4.3; S, 9.9%; *M*, 325); λ_{max} 253, 312, 367, 374, and 540 nm (ε 13830, 23870, 14240, 8540, and 2390); υ_{max} (KBr) 1620, 1605, 1580, 1530, 1480, 1465, 1455, and 1435 cm^{-1}; δ_H 2.35 (3H, s, CH_3) and 7.1–8.25 (12H, m, Ar–H).

Reaction of 3,5-*Diphenyl*-1,2-*dithiolium*-4-*olate* (**1**) *with* 3,5-*Dimethylaniline. Formation of* 2,4-*Dimethyl*-11-*phenylbenz*[b]*indeno*[2,1–e]-1,4-*thiazine* (**21**). — A suspension of 3,5-diphenyl-1,2–dithiolium-4-olate (2 g) in 3,5-dimethylaniline (80 ml) was heated under reflux (4 h). The 3,5–dimethylaniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3) giving 2,4-dimethyl-11-phenylbenz[*b*]indeno[2,1–*e*]-1,4-thiazine (R_f 0.65) (1.34 g, 53%) as dark blue needles, mp 221–223°C from ethanol (Found: $M^{+\bullet}$, 339.1070. $C_{23}H_{17}NS$ requires *M*, 339.1081); λ_{max} 254, 319, 365, 383, and 538 nm (ε 25430, 16950, 7240, 8210, and 580); υ_{max} (KBr) 1612, 1605, 1585, 1530, 1490, 1470, and 1440 cm^{-1}; δ_H 2.02 (3H, s, CH_3), 2.25 (3H, s, CH_3), and 6.5–7.2 (11H, m, Ar–*H*).

Reaction of 3,5-*Diphenyl*-1,2-*dithiolium*-4-*olate* (**1**) *with* 2,6-*Dimethylaniline. Formation of* N-(2,6-*Dimethylphenyl*)-[3-*phenyl*-1-(2,6-*dimethylphenyl*)*iminoinden*-2-*yl*]-*amine* (**19**). — A suspension of 3,5-diphenyl-1,2-dithiolium-4-olate (2 g) in 2,6-dimethylaniline (80 ml) was heated under reflux (4 h). The 2,6-dimethylaniline was removed under reduced pressure and the residue was fractionated by preparative TLC (chloroform–light petroleum, 1:3) giving N-(2,6-*dimethylphenyl*)-[3-*phenyl*-1-(2,6–*dimethylphenyl*)*iminoinden*-2-*yl*]-*amine* (R_f 0.77) (1.18 g, 37%) as maroon prisms, mp 199–200°C from light petroleum, mp 80–100°C (Found: $M^{+\bullet}$, 428.2279. $C_{31}H_{28}N_2$ requires *M*, 428.2268); λ_{max} 274, 388, and 521 nm (ε 28110, 9520, and 8280); υ_{max} (KBr) 3295, 1660, 1620, 1590, 1500, 1485, and 1450 cm^{-1}; δ_H 2.1 (12H, s, 4 x CH_3) and 6.1–7.3 (15H, m, Ar–H).

Reaction of 3-*Phenylindan*-1,2-*dione* (**9**) *with* 2-*Aminothiophenol. Formation of* 11–*Phenylbenz*[b]*indeno*[2,1–e]-1,4-*thiazine* (**12**). — A solution of 3-phenylindan-1,2-dione[10] (1.0 g), 2–aminothiophenol (1.7 g), and toluene-*p*-sulphonic acid (15 mg) in xylene (30 ml) was heated under reflux in an atmosphere of nitrogen with a Dean–Stark water separator (20 min). The xylene was evaporated and the residue fractionated by preparative TLC (chloroform), giving 11-phenylbenz[*b*]indeno[2,1–*e*]-1,4–thiazine (R_f 0.8) (0.97 g, 69%).

3,4,5-*Triphenylisothiazole* (**3**) (With T. I. Richards). — A mixture of 1,2,3-triphenylpropan-1,3-dione[13] (0.9 g) and phosphorus pentasulphide (0.9 g) was heated at 160°C (15 min). The resulting dark brown solid was then heated under reflux in hydrochloric acid (60 ml, 0.1M) (3.5 h). The hot mixture was filtered and the filtrate cooled, yielding 3,4,5-triphenyl-1,2-dithiolium chloride (0.3 g, 27%) as yellow needles, mp 210–213°C (decomp); δ_H [$(CD_3)_2SO$] 6.5–6.8 (m, Ar–H). A solution of 3,4,5-triphenyl-1,2-dithiolium chloride (200 mg) in boiling ethanol (20 ml) was treated with a stream of ammonia (20 min). The reaction mixture was cooled and evaporated, and the residue crystallised from ethanol yielding 3,4,5–*triphenylisothiazole* (70 mg, 40%) as colourless needles, mp 215–216°C (Found: C, 80.6; H, 4.7; N, 4.5; S, 10.4; $M^{+\bullet}$, 313. $C_{21}H_{15}NS$ requires C, 80.5; H, 4.8; N, 4.5; S, 10.2%; *M*, 313); λ_{max} 236 and 281 nm (ε 22500 and 13300); υ_{max} (KBr) 3040, 1600, 1580, 1500, 1480, 1440, 1400, 1360, 1270, 1070, 1030, 910, 780, 760, 750, 725, 700, 690, and 680 cm^{-1}; δ_H 6.9–7.8 (m, Ar–H).

X-RAY STRUCTURAL DETERMINATION OF *N*-PHENYL-(3-PHENYL-1-PHENYLIMINOINDEN-2-YL)-AMINE (10)

Crystallographic Measurements. — The crystals were in the form of deep maroon needles. A crystal of dimensions 0.7 x 0.2 x 0.2 mm was set about the direction of elongation (*b*). Cell dimensions and intensity data were measured with a Stoe 2-circle, computer-controlled diffractometer using graphite monochromated Mo-*K*α radiation. Of 5407 reflections scanned within the range $0.1 < \sin\theta/\lambda < 0.65$ Å^{-1}, 2363 having $I > 2.5\sigma(I)$ were considered to be observed. The ω scan technique was used. For layers *h*0*l* and *h*1*l*, 120 counts of 1s at intervals of 0.01° were taken for each reflection, backgrounds being measured for 30s at each end of the scan. For reflections on layers 2-7 a variable scan range was used as described previously.[16] The intensities of four *h*0*l* reflections were remeasured at the end of each layer of data collection to monitor the stability of the system. There was no systematic variation of intensity with time.

Crystal Data. — $C_{27}H_{20}N_2$, $M = 372.5$. Monoclinic, $a = 20.78(1)$, $b = 6.13(1)$, $c = 31.44(2)$ Å, $\beta = 99.64(5)°$, $U = 3948.3$ Å^3, $Z = 8$, $D_c = 1.253$ g cm^{-3}, $F(000) = 1568$. Systematic absences: *hkl* when $h + k$ is odd, *h*0*l* when *l* is odd; space group *Cc* or *C*2/*c*. *C*2/*c* established as a result of this investigation. Mo-*K*α radiation, $\lambda = 0.71069$ Å; μ(Mo-*K*α) = 0.39 cm^{-1}.

Structure Analysis. — The structure was solved by direct methods with the SHELX 76 program.[17] Carbon and nitrogen atomic coordinates and anisotropic thermal parameters were refined by full-matrix least-squares calculations. Hydrogen atoms were located from a subsequent Fourier difference synthesis and refined isotropically. Least-squares refinement was continued until all calculated shifts were $< 0.1\sigma$ and *R* 6.64% for the 2363 observed amplitudes.*

Results and Discussion. — *X*-Ray structural determination firmly establishes the constitution **10** rather than the tautomeric constitution **11** for the maroon compound, mp 178-179°C. Figure 1 shows a stereoscopic view of the molecule and also indicates the atomic numbering scheme. Bond lengths and angles are listed in Table.

---

* Atomic coordinates and bond distances have been deposited at the Cambridge Crystallographic Data Centre.

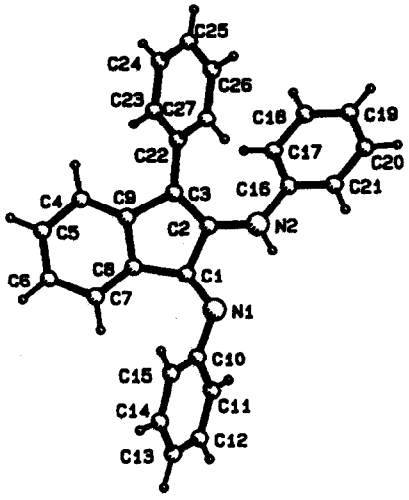


FIGURE 1.
A view of the maroon-3-phenylindenylamine **10**

The indene ring system, the two exocyclic nitrogen atoms, and phenyl carbon atoms C(10) and C(22) are coplanar to within ±0.1 Å. The amine hydrogen atom deviates by only 0.085 Å from this plane and phenyl carbon atom C(16) by 0.46 Å. The three bonds from the amine nitrogen, N(2)–C(2), N(2)–C(16), and N(2)–H[N] are approximately coplanar, the nitrogen atom being displaced by 0.085 Å from the plane of C(2), C(16), and H[N].

Bond lengths and angles generally agree well with accepted values,[18] although certain bonds in the phenyl rings appear to be significantly shorter than the accepted aromatic C–C length. This may, however, be due to the effect of thermal libration.

The imine nitrogen atom N(1) is not involved in conjugation either with the indene ring system or with the phenyl ring C(10)–C(15). Thus the lengths of bond C(1)–C(8) and C(1)–C(2) correspond to that of a single bond between sp^2–hybridised carbon atoms,[18,19] C(1)–N(1) has the length of a C=N double bond[18,20] and C(10)–N(1) that of a C(sp^2)–N(sp^2) single bond.

The amine nitrogen atom N(2) is involved in π-electron delocalisation as indicated by the short (1.378 Å) C(2)–N(2) single bond, the long (1.357 Å) C(2)–C(3) double bond, and the near–planar disposition of the bonds around N(2).

The distance between the amine hydrogen atom and the imine nitrogen is 2.34 Å. This distance is too great for significant hydrogen bonding to occur between the two nitrogen atoms, the H...N separation in N–H...N hydrogen bonding being typically 2.2 Å.[21] The N–H bond length (0.85 Å) is 0.16 Å shorter than the N–H bond in ammonia as determined by spectroscopic methods (such a shortening of bonds involving hydrogen atoms is a feature of the *X*-ray crystallographic method). If the amine hydrogen atom is moved to its "true" position, 1.01 Å from N(2), its distance from the imine nitrogen atom becomes slightly less, 2.30 Å. This is, however, still too great for strong intramolecular hydrogen bonding. The H[N]–N(2)...N(1) angle of 55° is also unfavourable for hydrogen bonding. Nevertheless, there appears to be an attractive force between the nitrogen atoms as shown by the distortion of the bond angles at C(1) and C(2).

TABLE

Molecular Dimensions

(a) Bond lengths (Å) with estimated standard deviations in parentheses

C(1) - C(2)	1.497(5)	C(22) - C(23)	1.404(5)
C(2) - C(3)	1.357(5)	C(23) - C(24)	1.386(7)
C(3) - C(9)	1.485(4)	C(24) - C(25)	1.366(7)
C(9) - C(4)	1.385(5)	C(25) - C(26)	1.369(7)
C(4) - C(5)	1.388(5)	C(26) - C(27)	1.384(6)
C(5) - C(6)	1.372(6)	C(27) - C(22)	1.380(5)
C(6) - C(7)	1.395(6)		
C(7) - C(8)	1.371(5)	C(4) - H(4)	0.97(4)
C(8) - C(9)	1.411(5)	C(5) - H(5)	0.96(4)
C(8) - C(1)	1.492(5)	C(6) - H(6)	0.96(3)
C(1) - N(1)	1.271(5)	C(7) - H(7)	0.95(4)
N(1) - C(10)	1.421(4)	C(11) - H(11)	0.95(4)
C(10) - C(11)	1.378(6)	C(12) - H(12)	0.93(5)
C(11) - C(12)	1.376(6)	C(13) - H(13)	0.98(4)
C(12) - C(13)	1.374(7)	C(14) - H(14)	0.95(4)
C(13) - C(14)	1.364(7)	C(15) - H(15)	0.97(4)
C(14) - C(15)	1.375(6)	C(17) - H(17)	0.93(3)
C(15) - C(10)	1.392(5)	C(18) - H(18)	0.90(4)
C(2) - N(2)	1.378(4)	C(19) - H(19)	0.90(4)
N(2) - C(16)	1.410(5)	C(20) - H(20)	0.97(4)
C(16) - C(17)	1.385(5)	C(21) - H(21)	0.95(3)
C(17) - C(18)	1.381(6)	C(23) - H(23)	0.98(3)
C(18) - C(19)	1.356(6)	C(24) - H(24)	0.96(5)
C(19) - C(20)	1.375(7)	C(25) - H(25)	0.92(5)
C(20) - C(21)	1.385(6)	C(26) - H(26)	0.97(4)
C(21) - C(16)	1.379(5)	C(27) - H(27)	1.01(4)
C(3) - C(22)	1.472(5)	N(2) - H[N]	0.85(5)

(continued)

(b) Bond angles (°) with standard deviations in parentheses

C(8) - C(1) - C(2)	105.7(3)	C(12) - C(13) - C(14)	119.5(4)
C(2) - C(1) - N(1)	118.8(3)	C(13) - C(14) - C(15)	121.2(4)
C(8) - C(1) - N(1)	135.5(3)	C(14) - C(15) - C(10)	119.7(4)
C(1) - C(2) - C(3)	110.2(3)	C(17) - C(16) - N(2)	121.4(3)
C(1) - C(2) - N(2)	116.1(3)	C(21) - C(16) - N(2)	119.0(3)
C(3) - C(2) - N(2)	133.7(3)	C(17) - C(16) - C(21)	119.6(3)
C(2) - C(3) - C(9)	107.6(3)	C(16) - C(17) - C(18)	119.0(3)
C(2) - C(3) - C(22)	129.2(3)	C(17) - C(18) - C(19)	121.3(4)
C(9) - C(3) - C(22)	123.1(3)	C(18) - C(19) - C(20)	120.2(4)
C(9) - C(4) - C(5)	118.7(4)	C(19) - C(20) - C(21)	119.3(4)
C(4) - C(5) - C(6)	121.5(4)	C(20) - C(21) - C(16)	120.5(4)
C(5) - C(6) - C(7)	120.0(4)	C(23) - C(22) - C(3)	120.6(3)
C(6) - C(7) - C(8)	119.3(4)	C(27) - C(22) - C(3)	120.8(3)
C(7) - C(8) - C(9)	120.5(3)	C(23) - C(22) - C(27)	118.6(4)
C(7) - C(8) - C(1)	133.2(3)	C(22) - C(23) - C(24)	120.0(4)
C(1) - C(8) - C(9)	106.3(3)	C(23) - C(24) - C(25)	120.0(5)
C(8) - C(9) - C(4)	119.8(3)	C(24) - C(25) - C(26)	120.9(5)
C(4) - C(9) - C(3)	130.0(3)	C(25) - C(26) - C(27)	119.7(4)
C(8) - C(9) - C(3)	110.2(3)	C(26) - C(27) - C(22)	120.9(4)
C(11) - C(10) - N(1)	118.7(3)	C(1) - N(1) - C(10)	123.1(3)
C(15) - C(10) - N(1)	122.4(3)	C(2) - N(2) - C(16)	130.0(3)
C(11) - C(10) - C(15)	118.6(3)	C(2) - N(2) - H[N]	116.8(27)
C(10) - C(11) - C(12)	121.0(4)	C(16) - N(2) - H[N]	111.6(28)
C(11) - C(12) - C(13)	119.9(4)		

Angles C(2)–C(1)—N(1) and C(1)—C(2)—N(2) are each some 17° smaller than angles C(8)—C(1)—N(1) and C(3)—C(2)—N(2), respectively. The effect of this is that the N(1)...N(2) separation (2.72 Å) is considerably less than N(1)...C(7) (3.34 Å) or N(2)...C(22) (3.25 Å).

None of the intermolecular distances is shorter than the sum of the van der Waals radii of the atoms concerned.

Acknowledgements. — We thank the S. E. R. C. and the Ministry of Defence for support [to C. J. N. and G. P. R.] and the Leverhulme Trust for the award of an Emeritus Fellowship [to W. D. O.].

REFERENCES

1. Part 23. Newton, C. G.; Ollis, W. D.; Wright, D. E. *J. Chem. Soc., Perkin Trans 1*, **1984**, *75*.
2. Ollis, W. D; Ramsden, C. A. *Adv. Heterocycl. Chem.* **1976**, *19*, 1.
3. Newton, C. G.; Ramsden, C. A. *Tetrahedron*, **1982**, *38*, 2965; Ramsden, C. A. *Comprehensive Organic Chemistry* [edited by D. H. R. Barton and W. D. Ollis]; Pergamon Press: Oxford, **1979**, Volume 4, p. 1171.
4. Ollis, W. D.; Stanforth, S. P.; Ramsden, C. A. *Tetrahedron* **1985**, *41*, 2239.
5. Cannon, J. R.; Potts, K. T.; Raston, C. L.; Sierakowski, A. F.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 297.
6. Barillier, D. *Phosphorus, Sulphur and Related Elements* **1980**, *8*, 79.
7. Chinone, A.; Inouye, K.; Ohta, M. *Bull. Chem. Soc. Japan* **1972**, *45*, 213.
8. Slack, R.; Wooldridge, K. R. H. *Adv. Heterocycl. Chem.* **1965**, *4*, 107; Wooldridge, K. R. H. *ibid.* **1972**, *14*, 1; Pain, D. L., Peart, B. J.; Wooldridge, K. R. H. *Comprehensive Heterocyclic Chemistry* [edited by A. R. Katritzky and C. W. Rees]; Pergamon Press: Oxford, **1984**, Volume 16, p. 131.
9. Blomquist, A. T.; Moriconi, E. J. *J. Org. Chem.* **1961**, *26*, 3761.
10. Pfeiffer, P.; de Waal, H. L. *Annalen* **1935**, *520*, 185.
11. Hodgson, H. H. *J. Chem. Soc.* **1924**, 1855.
12. Moore, M. L.; Johnson, T. B. *J. Amer. Chem. Soc.* **1935**, *57*, 1287.
13. Beringer, F. M.; Forgione, P. S.; Yudis, M. D. *Tetrahedron*, **1960**, *8*, 49.
14. Part 21. Newton, C. G.; Ollis, W. D.; Podmore, M. L.; Wright, D. E. *J. Chem. Soc., Perkin Trans 1*, **1984**, 63.
15. Woodward, R. B.; Cava, M. P.; Ollis, W. D.; Hunger, A.; Daeniker, H. U.; Schenker, K. *Tetrahedron*, **1963**, *19*, 247.
16. Goodhand, N.; Hamor, T. A. *Acta Crystallogr. 1989, C45*, 1609.
17. Sheldrick, G. M. *SHELX 76 Program for Crystal Structure Determination*, University of Cambridge, **1976**.
18. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.
19. Cruickshank, D. W. J. *Tetrahedron*, **1962**, *17*, 155.
20. Lofthus, A. *Mol. Phys.* **1959**, *2*, 367.
21. Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, **1968**.