Diaminobenzobisthiazoles and Related Compounds

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In the preparation of benzobisthiazoles from *m*- and *p*-phenylenediamines by thiocyanation or by ring closure of derived thioureas the linear tricyclic compound is usually the major or the only product. 3,6-Diamino-1,2-phenylene di(hydrogen thiosulphate) (the so-called *p*-phenylenediamino-2,5-bisthiosulphuric acid) is the 2,3-isomer and correction is required to structures assigned to its derivatives, *e.g.*, the diaminophenylenedithiol, the bisdiazosulphide, and certain benzobisthiazoles. Formation of fused thiazole rings in derivatives of 2-naphthylamine and 6-aminoquinoline occurs in the 1- and 5-positions respectively.

2-Aminobenzothiazole derivatives are usually prepared by thiocyanation of arylamines with an unsubstituted *o*-position, or by ring-closure of arylthioureas, *e.g.*, by treatment with bromine. Treatment of *m*- and *p*-phenylenediamines by these methods could give either linear [(I) and (II)] or angular [(III) and (IV)] tricyclic compounds, and it was expected, by analogy with the formation of phenanthrolines, that the angular configuration would be preferred.

Stephens and Wibberley [1] attributed the structure (I; $R^1 = R^2 = NH_2$, $X = Y = H$) to a compound obtained by the action of potassium cyanide on 3,6-diamino-1,2-phenylene di(hydrogen thiosulphate) made by oxidising *p*-phenylenediamine in the presence of thiosulphate ions. The structure (V) assigned to this compound by Green and Perkin [2] has never been questioned although it rests only on analogy with the usual addition reactions of *p*-benzoquinone derivatives.

The diaminobenzobisthiazole (I; $R^1 = R^2 = NH_2$, $X = Y = H$) and the corresponding bismethylamino-derivative, which was obtained by the action of methyl isothiocyanate on 3,6-diamino-1,2-phenylene di(hydrogen thiosulphate) differed from the compounds obtained by the cyclisation of *p*-phenylenebisthiourea and 1,4-bis-*N'*-methylthioureidobenzene. Characterisation of these compounds was difficult because of their high and indefinite melting or decomposition points, but the ultraviolet absorption spectra of the hydrochlorides showed characteristic differences (Figures 1 and 2). Compounds with unequivocally linear and angular structures (I) and (III), ($R^1 = R^2 = NHMe$, $X = Y = Me$) were made from 2,5- and 2,3-dimethyl-*p*-phenylenediamines, respectively. Their absorption spectra (Figure 3) clearly showed that the products of cyclisation of *p*-phenylenebisthioureas are linear and the compounds from 3,6-di-

[1] F. F. Stephens and D. G. Wibberley, *J. Chem. Soc.*, 1950, 3336.
[2] A. G. Green and A. G. Perkin, *J. Chem. Soc.*, 1903, **83**, 1201.

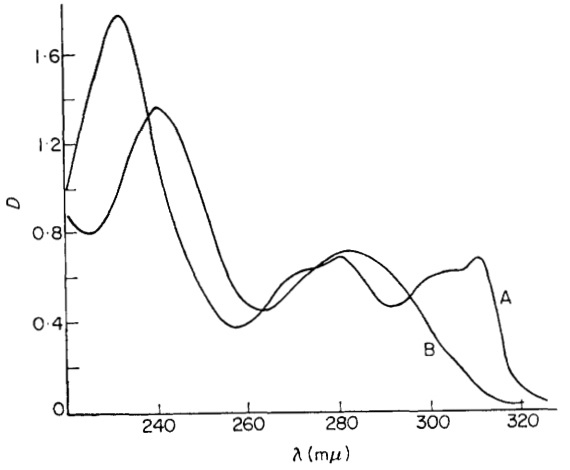


FIGURE 1 Absorption spectra of (A) 2,6-diaminobenzo-[1,2-*d*:4,5-*d*′]bisthiazole (I; $R^1 = R^2 = NH_2$, X = Y = H) and (B) 2,7-diaminobenzo[1,2-*d*:4,3-*d*′]bisthiazole (III; $R^1 = R^1 = NH_2$, X = Y = H), 1 mg. % in 0·1N-hydrochloric acid

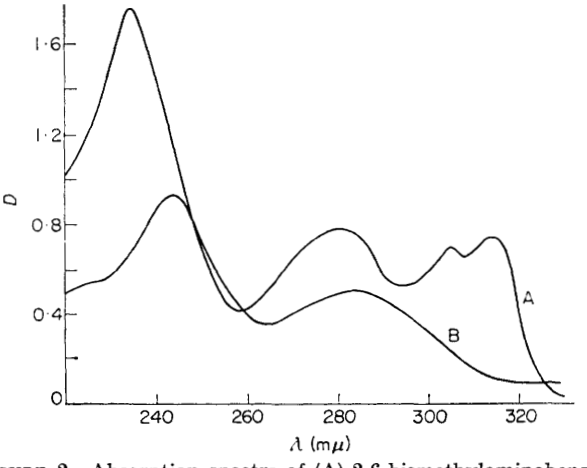


FIGURE 2 Absorption spectra of (A) 2,6-bismethylaminobenzo-[1,2-*d*:4,5-*d*′]bisthiazole (I; $R^1 = R^2 = NHMe$, X = Y = H) and (B) 2,7-bismethylaminobenzo[1,2-*d*:4,3-*d*′]bisthiazole (III; $R^1 = R^2 = NHMe$, X = Y = H), 1 mg. % in 0·1N-hydrochloric acid

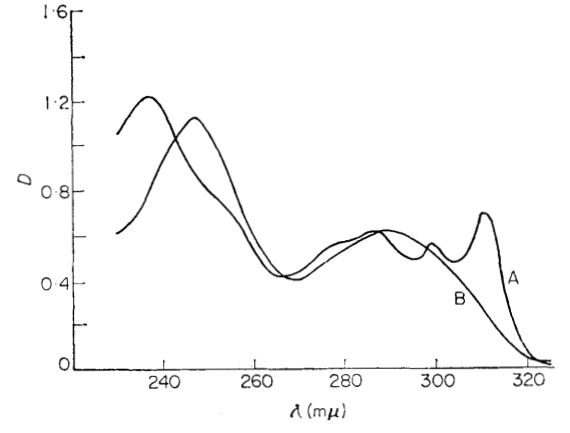
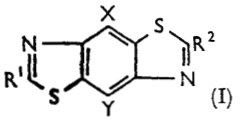
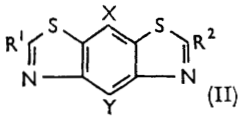


FIGURE 3 Absorption spectra of (A) 4,8-dimethyl-2,6-bismethylaminobenzo[1,2-*d*:4,5-*d*′]bisthiazole (I; $R^1 = R^2 = NHMe$, X = Y = Me) and (B) 4,5-dimethyl-2,7-bismethylaminobenzo[1,2-*d*:4,3-*d*′]bisthiazole (III; $R^1 = R^2 = NHMe$ X = Y = Me), 1 mg. % in 0·1N-hydrochloric acid

amino-1,2-phenylene di(hydrogen thiosulphate) belong to the angular series. 3,6-Diamino-1,2-phenylene dihydrogen thiosulphate must therefore be the 2,3-compound (VI), and the accepted structures of this compound and its derivatives are incorrect. Among these derivatives are several benzobisthiazoles.[1-3] Grandolini and his


(I)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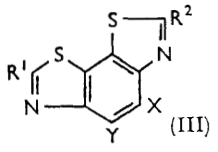
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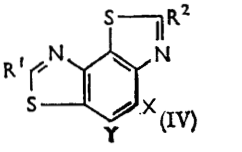
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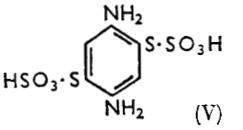
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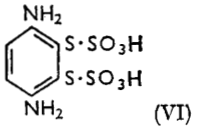
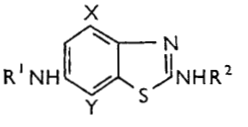
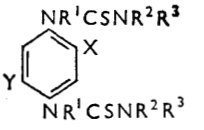

(VI)

co-workers[4] reported n.m.r. spectra in agreement with the now disputed structures of the benzobisthiazoles (I; $R^1 = R^2 = NHAc$, X = Y = H), (I; $R^1 = R^2 = Me$, X = Y = H), and (I; $R^1 = R^2 = Ph$, X = Y = H),[2] but in these cases the n.m.r. method is unreliable since single (two proton) peaks rather than AB quartets are shown by symmetrical 1,2,3,4-tetra-substituted benzene derivatives such as (III) or (VI), and even by some unsymmetrical benzobisthiazoles of type (IV).[5]

The diaminobenzobisthiazoles obtained by thiocyanation of *p*-phenylenediamine and 2,6-diaminobenzothiazole (VII; $R^1 = R^2 = H$) were mixtures of (I) and (III) ($R^1 = R^2 = NH_2$, X = Y = H); the spectra indicated a preponderance of angular isomer in the first case and linear isomer in the second. Cyclisation of a number of *p*-phenylenebisthioureas of the general formula (VIII) gave linear compounds (I). The dichloro-compound (X; $R^1 = R^2 = H$, $R^3 = Me$) resisted

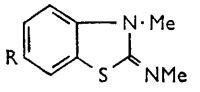

(VII) X = Y = H
(IX) X = Y = Cl


(VIII) X = Y = H
(X) X = Y = Cl

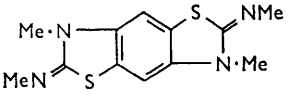
attempts to bring about ring closure, and thiocyanation of 2,5-dichloro-*p*-phenylenediamine gave only 2,6-diamino-4,7-dichlorobenzothiazole (IX; $R^1 = R^2 = H$). It has

[3] G. Barnikow, *Z. Chem.*, 1966, **9**, 342.
[4] G. Grandolini, A. Ricci, A. Martani, and F. delle Monache, *J. Heterocyclic Chem.*, 1966, **3**, 302.
[5] G. Grandolini, A. Ricci, A. Martani, and T. Mezzetti, *J. Heterocyclic Chem.*, 1966, **3**, 299.

been stated [6] that reaction of *NN'*-dialkyl-*N*-arylthioureas with bromine affords 3-alkyl-2-alkylimino-2,3-dihydrobenzothiazole derivatives, but no experiment confirming this statement appears to have been described. The u.v. absorption spectrum of 2,3-dihydro-3-methyl-2-methyliminobenzothiazole (XI; R = H) has been published [7] without other details of this compound or of its preparation. It was found that *NN'*-dimethyl-*N*-phenylthiourea was, in fact, cyclised to (XI; R = H) by bromine, and this compound was nitrated to give the 6-nitro-derivative (XI; R = NO_2). The n.m.r. spectrum of this nitro-derivative in deuteriochloroform solution showed multiplets at τ 3·14 (J = 8·5 c./sec.), 1·85 (J = 8·5, 2·0 c./sec.), and 1·76 (J = 2·0 c./sec.) for the three aromatic protons, indicating that the nitro-group was at position 5 or 6. Addition of trifluoroacetic acid to the solution to protonate the molecule caused a greater downfield shift of the doublet at τ 3·1 (0·72 p.p.m.) than of the other multiplets (0·36 and 0·42 p.p.m.). It may be argued that the proton showing the greatest downfield shift is the one *o*- to the nitrogen atom in the ring, and that the nitro-group must therefore be at position 6. Attempts to prepare this compound by ring-closure of *NN'*-dimethyl-*N*-*p*-nitrophenylthiourea with bromine or sulphuryl chloride were unsuccessful. The bisthiourea (VIII; $R^1 = R^3$ = Me, R^2 = H) treated with bromine gave 2,3,6,7-tetrahydro-3,7-dimethyl-2,6-di(methylimino)benzo[1,2-*d*:4,5-*d'*]bisthiazole (XII) which had an absorption spectrum characteristic of the linear series.



(XI)



(XII)

By thiocyanation of *m*-phenylenediamine with dichlorourea and ammonium thiocyanate Lichosherstov and Petrov [8] obtained 1,3-diaminobenzene-4-thiocyanate and -4,6-dithiocyanate, and Finzi and Grandolini [9] showed that the latter compound was cyclised by acid to 2,6-diaminobenzo[1,2-*d*:5,4-*d'*]bisthiazole (II; $R^1 = R^2 = NH_2$, X = Y = H). Thiocyanation of *m*-phenylenediamine or of 2,5-diaminobenzothiazole with cupric thiocyanate in acetic acid or with sodium thiocyanate and bromine gave the cyclic compound (II) directly, and it was also obtained by reduction of 1,3-dinitrobenzene-4,6-dithiocyanate in acid solution. Ring closure of *m*-phenylenebisthioureas with bromine gave linear benzobisthiazoles, *e.g.*, (II; $R^1 = R^2$ = NHMe, X = H, Y = H or Me) unless the parent *m*-phenylenediamine was substituted in the 4-position, when the angular compounds (IV; R^1 and $R^2 = NH_2$ or NHMe, X = Me, Cl, or MeO, Y = H) were obtained. The linear and angular compounds showed differences in u.v. absorption spectra like those found in the *p*-phenylenediamine derivatives (Figure 4). Spectroscopic data [10] on benzobisthiazoles [(I)—(IV)] in which R^1 and R^2 are hydrogen or alkyl do not show such clear differences.

Unsymmetrically substituted benzobisthiazoles were obtained by ring closure of 2-amino-5-alkyl- or 2-amino-6-alkyl-thioureidobenzothiazoles, *e.g.*, (VII; R^1 = Alkyl·NH·CS–) and (XI; R = Alkyl·NH·CS·NH–), both linear and angular isomers being produced. The methyl and ethylthioureido-compounds gave predominantly the linear compounds and isolation of the angular isomers was difficult. 2-Amino-6-isopropylthioureidobenzothiazole gave mainly (I; $R^1 = NH_2$, $R^2 = NHPr^i$, X = Y = H), but 2-amino-6-n-propylthioureidobenzothiazole gave an appreciable proportion of the angular compound (III; $R^1 = NH_2$, $R^2 = NHPr^n$, X = Y = H). A linear compound was obtained by cyclisation of 1-ethylthioureido-4-methylthioureidobenzene.

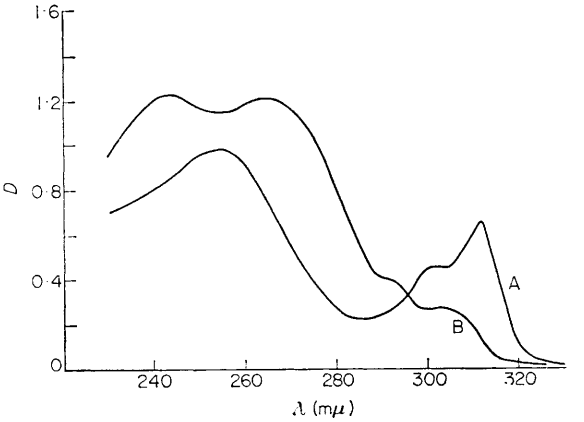


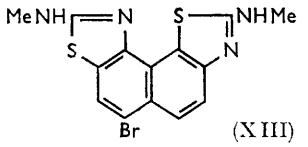
FIGURE 4 Absorption spectra of (A) 4-methyl-2,6-bismethylaminobenzo[1,2-*d*:5,4-*d'*]bisthiazole (II; $R^1 = R^2$ = NHMe, X = H, Y = Me) and (B) 4-methyl-2,7-bismethylaminobenzo-[1,2-*d*:3,4-*d'*]bisthiazole (IV; $R^1 = R^2$ = NHMe, X = Me, Y = H), 1 mg. % in 0·1N-hydrochloric acid

Reaction of methylisothiocyanate with *o*-phenylenediamine, benzidine, and 1,5-, 1,7-, 2,6-, and 2,7-diaminonaphthalene gave bisthioureas which were cyclised to bisthiazole compounds by treatment with bromine. The structures of the first three cyclic compounds were not in doubt, and the 2,6- and 2,7-naphthalene derivatives had n.m.r. spectra (AB quartets for the aromatic protons) which indicated that ring-closure had occurred in the adjacent α-positions. Cyclisation of the 1,7-naphthalene derivative was accompanied by nuclear bromination, and the n.m.r. spectrum of the product was consistent with the most probable structure (XIII).

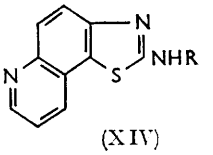
6-Thioureidoquinoline and 6-methylthioureidoquinoline when treated with bromine gave the thiazoloquinolines (XIV; R = H or Me), the structures of which were confirmed by their n.m.r. spectra. The amino-

[6] J. M. Sprague and A. H. Land, "Heterocyclic Compounds," Wiley, New York, 1957, vol. 5, p. 582.
[7] J. Goerdeler and E. R. Erbach, *Chem. Ber.*, 1962, **95**, 1637.
[8] M. W. Lichosherstov and A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1933 [3], **65**, 183.
[9] C. Finzi and G. Grandolini, *Gazzetta*, 1959, **89**, 2543.
[10] C. Finzi and G. Grandolini, *Gazzetta*, 1959, **89**, 2551; A. Fravolini, G. Grandolini, and G. Monzali, *Ann. Chim.* (*Italy*), 1964, **54**, 80.

compound (XIV; R = H) was also obtained from 2,6-diaminobenzothiazole by the Skraup reaction.



(XIII)



(XIV)

Many of these diaminobenzobisthiazoles had considerable potency in preventing an inflammatory reaction in conventional biological tests, *e.g.*, kaolin arthritis and carrageenin granuloma in rats. The effects, however, were attributable to leucopenia and not to a useful and specific anti-inflammatory action. The most active of the compounds (II; $R^1 = NH_2$, $R^2 = NHMe$, X = Y = H) had a moderate inhibitory effect on the growth of the Walker 256 tumour in rats, but had a negligible effect on sarcoma 180 in mice.

EXPERIMENTAL

Arylthioureas.—In general the arylthioureas were prepared (A) by reaction of an arylamine with an alkylisothiocyanate or (B) by reaction of an arylisothiocyanate or di-isothiocyanate with ammonia or an alkylamine. The reactants were boiled under reflux in ethanol for 0·5—1 hr., or warm solutions in ethanol or pyridine were mixed and set aside for 1—2 days at room temperature, the solvent then being evaporated if the product had not crystallised. The products are listed below, the preparative method being shown in parentheses.

N-*Methyl*-N′-p-*nitrophenylthiourea*, (A) or (B), cream microcryst. from aqueous 2-ethoxyethanol, m. p. 211—213° (Found: C, 46·0; H, 4·6; N, 19·6; S, 15·4. $C_8H_9N_3O_2S$ requires C, 45·5; H, 4·3; N, 19·0; S, 15·2%). The n.m.r. spectrum was in agreement with the proposed structure. Hunter and Parken [11] obtained yellow prisms of m. p. 183—184° by method (B).

NN′-*Dimethyl*-N-p-*nitrophenylthiourea*, (A), yellow prisms from ethanol, m. p. 112—113° (Found: C, 47·8; H, 4·9; N, 18·7. $C_9H_{11}N_3O_2S$ requires C, 48·0; H, 4·9; N, 18·7%).

NN-*Dimethyl*-N′-p-*nitrophenylthiourea*, (B), needles from ethanol, m. p. 177—179° (Found: C, 48·1; H, 4·7; N, 18·9%). The n.m.r. spectrum was consistent with the proposed structure. The reported m. p. is 124—126°,[12] but no proof of the identity of the compound is given in the abstract.

N-p-*Acetamidophenyl*-N′N′-*dimethylthiourea*, (B), needles from ethanol, m. p. 203—204° (Found: C, 55·7; H, 6·5; N, 17·3. $C_{11}H_{15}N_3OS$ requires C, 55·7; H, 6·3; N, 17·7%).

N-3-*Amino*-2-*methylphenyl*-N′-*methylthiourea*, (A), (isolated as a by-product in the preparation of the bisthiourea) prisms from ethanol, m. p. 180—181° (Found: N, 20·8. $C_9H_{13}N_3S$ requires N, 21·5%).

1,3-*Bis*-N′-*methylthioureidobenzene*, (A), needles from acetic acid, m. p. 171—173° (Found: N, 21·5. $C_{10}H_{14}N_4S_2$ requires N, 22·05%).

1,3-*Bis*-N′N′-*dimethylthioureidobenzene*, (B), needles from ethanol, m. p. 221—223° (Found: C, 50·7; H, 6·5; N, 19·6. $C_{12}H_{18}N_4S_2$ requires C, 51·1; H, 6·4; N, 19·9%).

1,3-*Bis*-NN′-*dimethylthioureidobenzene*, (A), microcryst. prisms from ethyl acetate–light petroleum, m. p. 157—159° (Found: C, 51·5; H, 6·7; N, 19·9%).

1,3-*Bis*-N′-*ethylthioureidobenzene*, (A), platelets from ethanol, m. p. 188—189° (Found: N, 20·0%).

1,3-*Bis*-N′N′-*diethylthioureidobenzene*, (B), prisms from ethanol, m. p. 143—145° (Found: C, 57·0; H, 7·9; N, 16·2. $C_{16}H_{26}N_4S_2$ requires C, 56·8; H, 7·7; N, 16·7%).

1,3-*Bis*-N′-*n-propylthioureidobenzene*, (A), crystals from ethyl acetate, m. p. 149—151° (Found: C, 51·3; H, 7·4; N, 17·0. $C_{14}H_{22}N_4S_2,H_2O$ requires C, 51·2; H, 7·3; N, 17·1%).

1,3-*Bis*-N′-*isopropylthioureidobenzene*, (A), platelets from ethanol, m. p. 159—160° (Found: C, 53·8; H, 7·1. $C_{14}H_{22}N_4S_2$ requires C, 54·2; H, 7·1%).

1,3-*Bis*-N′N′-*pentamethylenethioureidobenzene*, (B), prisms from ethanol, m. p. 177—179° (Found: N, 15·4. $C_{18}H_{26}N_4S_2$ requires N, 15·5%).

1,4-*Bis*-N′-*methylthioureidobenzene*, (A), microcryst. from dimethylformamide, m. p. 242—244° (decomp.) (Found: N, 21·6. $C_{10}H_{14}N_4S_2$ requires N, 22·05%).

1,4-*Bis*-N′N′-*dimethylthioureidobenzene*, (B), microcryst. from dimethylformamide, m. p. 253—254° (decomp.) (Found: C, 51·1; H, 6·9; N, 20·0. $C_{12}H_{18}N_4S_2$ requires C, 51·1; H, 6·4; N, 19·9%).

1,4-*Bis*-NN′-*dimethylthioureidobenzene*, (A), needles from dimethylformamide, m. p. 225—227° (Found: C, 51·3; H, 6·7; N, 19·9%).

1-N′-*Ethylthioureido*-4-N′-*methylthioureidobenzene*, (A), microcryst. from dimethylformamide–ethanol (1 : 3), m. p. 222—224° (Found: C, 49·9; H, 6·0; N, 20·7. $C_{11}H_{16}N_4S_2$ requires C, 49·2; H, 6·0; N, 20·9%).

1,4-*Bis*-N′-*ethylthioureidobenzene*, (A) and (B), prisms from ethanol, m. p. 209—210° (Found: C, 50·7; H, 6·5; N, 19·0. $C_{12}H_{18}N_4S_2$ requires C, 51·1; H, 6·4; N, 19·9%).

1,4-*Bis*-N′N′-*diethylthioureidobenzene*, (B), needles from ethanol, m. p. 182—184° (Found: C, 56·9; H, 7·5; N, 16·2. $C_{16}H_{26}N_4S_2$ requires C, 56·8; H, 7·7; N, 16·7%).

1,4-*Bis*-N′-*n-propylthioureidobenzene*, (B), leaflets from pentanol, m. p. 202—203° (Found: N, 17·7. $C_{14}H_{22}N_4S_2$ requires N, 18·1%).

1,4-*Bis*-N′-*isopropylthioureidobenzene*, (A) and (B), needles from ethanol, m. p. 207—209° (Found: C, 54·7; H, 7·2. $C_{14}H_{22}N_4S_2$ requires C, 54·2; H, 7·1%).

1,4-*Bis*-N′N′-*di-n-heptylthioureidobenzene*, (B), platelets from ethanol, m. p. 158—159° (Found: N, 8·7. $C_{36}H_{66}N_4S_2$ requires N, 9·0%).

1,4-*Bis*-N′N′-*pentamethylenethioureidobenzene*, (B), prisms from ethanol, m. p. 217—219° (Found: N, 15·2. $C_{18}H_{26}N_4S_2$ requires N, 15·5%).

1,4-*Bis*-N′-(2-*diethylaminoethyl*)*thioureidobenzene*, (B), prisms from ethanol, m. p. 193—195° (Found: C, 55·3; H, 8·3; N, 19·1. $C_{20}H_{36}N_6S_2,0{\cdot}5H_2O$ requires C, 55·4; H, 8·5; N, 19·4%).

1,4-*Bis*-N′-(4-*diethylaminobutyl*)*thioureidobenzene*, (B), waxy, microscopic crystals from benzene, m. p. 163—164° (Found: C, 59·9; H, 9·2; N, 17·0. $C_{24}H_{44}N_6S_2$ requires C, 60·0; H, 9·2; N, 17·5%).

2,4-*Bis*-N′-*methylthioureidotoluene*, (A), microcrystals from aqueous acetic acid, m. p. 168—169° (with effervescence, solidifying and re-melting at 183—185°) (Found: N, 20·6. $C_{11}H_{16}N_4S_2$ requires N, 20·9%).

2,6-*Bis*-N′-*methylthioureidotoluene*, (A), prisms from ethanol, m. p. 208—209° (Found: N, 20·9%).

1-*Chloro*-2,4-*bis*-N′-*methylthioureidobenzene*, (A), leaflets

[11] R. F. Hunter and E. R. Parken, *J. Chem. Soc.*, 1934, 1175.
[12] Pint-Lin Ho, Hua-Chêng Yang, and Su-Nan Fang, *Acta. Chim. Sinica*, 1960, **26**, 1 (*Chem. Abs.*, 1961, **55**, 18,635).

from ethanol, m. p. 184—186° (Found: C, 41·5; H, 4·5; N, 19·8. $C_{10}H_{13}ClN_4S_2$ requires C, 41·6; H, 4·5; N, 19·4%).

1-*Methoxy*-2,4-*bis*-N′-*methylthioureidobenzene*, (A), microcrystalline needles from ethanol, m. p. 177—179° (Found: C, 46·0; H, 5·4; N, 18·8; S, 21·4. $C_{11}H_{16}N_4OS_2$ requires C, 46·5; H, 5·6; N, 19·7; S, 22·5%).

1,2-*Dimethyl*-3,6-*bis*-N′-*methylthioureidobenzene*, (A), platelets from pyridine, m. p. 226—227° (Found: C, 51·2; H, 6·2; N, 20·4. $C_{12}H_{18}N_4S_2$ requires C, 51·1; H, 6·4; N, 19·9%).

1,4-*Dimethyl*-2,5-*bis*-N′-*methylthioureidobenzene*, (A), microcrystalline powder from dimethylformamide, m. p. 238—240° (Found: N, 19·5%).

1,4-*Dichloro*-2,5-*bis*-N′-*methylthioureidobenzene*, (A), leaflets from ethanol, m. p. 216—217° (Found: N, 17·1. $C_{10}H_{12}Cl_2N_4S_2$ requires N, 17·4%).

4,4′-*Bis*-N′-*methylthioureidobiphenyl*, (A), needles from acetic acid, m. p. 315—317° (softening at 245—250°, but melting when dipped in a bath at 250° and re-melting at 314°) (Found: C, 58·1; H, 5·6; N, 17·2. $C_{16}H_{18}N_4S_2$ requires C, 58·2; H, 5·5; N, 17·0%).

1,5-*Bis*-N′-*methylthioureidonaphthalene*, (A), grey prisms from dimethylformamide, m. p. 244—245° (Found: N, 18·3. $C_{14}H_{16}N_4S_2$ requires N, 18·4%).

1,7-*Bis*-N′-*methylthioureidonaphthalene*, (A), platelets from ethanol, m. p. 209—210° (Found: C, 55·0; H, 5·5; N, 17·8. $C_{14}H_{16}N_4S_2$ requires C, 55·3; H, 5·3; N, 18·4%).

2,6-*Bis*-N′-*methylthioureidonaphthalene*, (A), grey needles from dimethylformamide, m. p. 242—243° (Found: C, 55·8; H, 5·5; N, 18·0%).

2,7-*Bis*-N′-*methylthioureidonaphthalene*, (A), grey leaflets from aqueous acetic acid, m. p. 200—201° (Found: C, 54·9; H, 5·5; N, 18·2%).

6-N′-*Methylthioureidoquinoline*, (A) and (B), cream prisms from ethanol, m. p. 182—183° (Found: N, 19·6. $C_{11}H_{11}N_3S$ requires N, 19·4%).

2-*Amino*-5-N′-*methylthioureidobenzothiazole*, (A), prisms from 2-ethoxyethanol, m. p. 220—221° (Found: C, 45·6; H, 4·6; N, 23·1. $C_9H_{10}N_4S_2$ requires C, 45·4; H, 4·2; N, 23·5%).

2-*Amino*-6-N′-*methylthioureidobenzothiazole*, (A), microcrystalline from aqueous dimethyformamide, m. p. 238—240° (Found: C, 45·1; H, 4·3; N, 23·0; S, 26·2. $C_9H_{10}N_4S_2$ requires C, 45·4; H, 4·2; N, 23·5; S, 26·9%).

2-*Amino*-6-N′-*ethylthioureidobenzothiazole*, (A), microcrystalline from ethanol, m. p. 212° (decomp.) (Found: C, 47·8; H, 4·9; N, 21·5. $C_{10}H_{12}N_4S_2$ requires C, 47·6; H, 4·8; N, 22·2%).

2-*Amino*-6-N′-*n-propylthioureidobenzothiazole*, (A), leaflets from ethanol, m. p. 214° (Found: N, 20·7. $C_{11}H_{14}N_4S_2$ requires N, 21·05%).

2-*Amino*-6-N′-*isopropylthioureidobenzothiazole*, (A), microcrystalline from ethanol, m. p. 209—210° (Found: N, 20·6%).

2-*Dimethylamino*-6-N′-*methylthioureidobenzothiazole*, (A), hexagonal plates from ethanol, m. p. 207—208° (Found: C, 49·9; H, 5·2; N, 20·9. $C_{11}H_{14}N_4S_2$ requires C, 49·6; H, 5·25; N, 21·05%).

3-*Methyl*-2-*methylimino*-6-N′-*methylthioureido*-2,3-*dihydrobenzothiazole*, (A), needles from ethanol, m. p. 237—238° (decomp.) (Found: C, 50·0; H, 5·8; N, 20·4%).

Benzothiazoles.—2,5-*Diaminobenzothiazole*. Iron (pin dust) (115 g.), water (800 c.c.) and conc. hydrochloric acid (115 c.c.) were heated to boiling with vigorous stirring and treated during 20 min. with 2,4-dinitrophenylthiocyanate (24 g.) dissolved in ethanol (250 c.c.). The mixture was stirred vigorously and boiled under reflux for 1 hr., made alkaline with sodium carbonate, and filtered while hot. 2,5-Diaminobenzothiazole (6 g.; m. p. 175—177°) crystallised on cooling, and concentration of the mother-liquor afforded a further 6·5 g. of material. Reduction of 2,4-dinitrophenylthiocyanate with stannous chloride [13] gave inferior yields.

6-*Acetamido*-2-*methylaminobenzothiazole*. *N*-*p*-Acetamidophenyl-*N*′-methylthiourea (11·15 g.) in chloroform (100 c.c.) was stirred at room temperature and treated dropwise with bromine (8 g.) in chloroform (20 c.c.). The mixture was stirred and boiled under reflux 1 hr. and the solid perbromide was filtered off when cold, suspended in hot water (100 c.c.), and reduced with sulphur dioxide. Addition of an excess of ammonia to the aqueous solution precipitated 6-*acetamido*-2-*methylaminobenzothiazole* (8·1 g.), prisms, m. p. 270—276° (from pyridine) (Found: C, 54·3; H, 4·5; N, 18·9. $C_{10}H_{11}N_3OS$ requires C, 54·2; H, 5·0; N, 19·0%).

6-*Amino*-2-*methylaminobenzothiazole*. 6-Acetamido-2-methylaminobenzothiazole (33·2 g.) was boiled under reflux with 5N-sulphuric acid (300 c.c.). After 10 min. the solution was filtered and made alkaline with sodium hydroxide to precipitate 6-*amino*-2-*methylaminobenzothiazole* (26·5 g.) platelets, m. p. 204—206° (from ethanol) (Found: C, 53·5; H, 4·8; N, 22·4. $C_8H_9N_3S$ requires C, 53·6; H, 5·0; N, 23·5%).

2-*Dimethylamino*-6-*nitrobenzothiazole*. 2-Dimethylaminobenzothiazole (15 g.) was added in small portions to well cooled (<5°) nitric acid (75 c.c.; *d* 1·5) with stirring, and 10 min. after the last addition the mixture was poured into ice–water (500 g.). The precipitated solid was collected and the solution was made alkaline with sodium hydroxide to precipitate a second crop. The combined products were digested with hot water made alkaline with ammonia and the material (16·8 g.) was crystallised from benzene, to give the product (10·75 g.), m. p. 201—202° (Found: N, 19·1. Calc. for $C_9H_9N_3O_2S$: N, 18·8%). This compound has previously been made from 2-chloro-6-nitrobenzothiazole.[14]

6-*Amino*-2-*dimethylaminobenzothiazole*. 2-Dimethylamino-6-nitrobenzothiazole (15 g.) in ethanol (250 c.c.) was hydrogenated over Raney nickel at s.t.p. Evaporation of the solution to small bulk afforded the diamine (9·6 g.), prisms, m. p. 148—149° (from ethanol) (lit.,[15] m. p. 144—145°) (Found: C, 56·5; H, 5·8; N, 21·3. Calc. for $C_9H_{11}N_3S$: C, 56·0; H, 5·7; N, 21·8%).

3-*Methyl*-2-*methylimino*-2,3-*dihydrobenzothiazole*. *NN*′-Dimethyl-*N*-phenylthiourea (35 g.) in chloroform (300 c.c.) was stirred at room temperature and treated dropwise with bromine (29·8 c.c.) in chloroform (120 c.c.). The mixture was stirred and boiled under reflux for 30 min., and when cold the solid product was collected, washed with chloroform, and heated with 20% sodium bisulphite solution (600 c.c.). The aqueous solution was made alkaline with sodium hydroxide to precipitate a crude product (32·3 g.), m. p. 64—65°, which was filtered off and extracted with hot benzene. Evaporation of the benzene yielded 3-*methyl*-2-*methylimino*-2,3-*dihydrobenzothiazole* (30 g.), prisms from

[13] H. A. Müller, *Z. Farbenindustrie*, 1906, **5**, 357.
[14] W. Scott and G. W. Watt, *J. Org. Chem.*, 1937, **2**, 148.
[15] T. Takahashi, J. Shibasaki, and J. Okada, *J. Pharm. Soc. Japan*, 1951, **71**, 41 (*Chem. Abs.*, 1951, **45**, 7110).

light petroleum, m. p. 66—67° (Found: C, 60·9; H, 5·5; N, 15·7. $C_9H_{10}N_2S$ requires C, 60·7; H, 5·6; N, 15·7%).

3-Methyl-2-methylimino-6-nitro-2,3-dihydrobenzothiazole. 3-Methyl-2-methylimino-2,3-dihydrobenzothiazole (30 g.) nitrated under the same conditions as 2-dimethylaminobenzothiazole gave the *nitro-compound* (30·7 g.), yellow needles from benzene, m. p. 228—229° (Found: C, 48·3; H, 3·9; N, 18·3. $C_9H_9N_3O_2S$ requires C, 48·4; H, 4·0; N, 18·8%).

6-Amino-3-methyl-2-methylimino-2,3-dihydrobenzothiazole. The foregoing nitro-compound (28 g.) hydrogenated over Raney nickel in ethanol at s.t.p. afforded the *amine* (16·1 g.) as platelets, m. p. 185°, from ethanol (Found: C, 56·1; H, 5·5; N, 21·6. $C_9H_{11}N_3S$ requires C, 56·0; H, 5·7; N, 21·8%).

2,6-Diamino-4,7-dichlorobenzothiazole. 2,5-Dichloro-*p*-phenylenediamine (17·7 g.) and sodium thiocyanate (32·4 g.) were stirred with glacial acetic acid (250 c.c.) and treated during 50 min. with bromine (32 g.) in acetic acid (20 c.c.) with cooling so that the temperature did not exceed 14°. The mixture was stirred for 2 hr. longer, and the orange solid was collected and extracted with hot water (5 × 80 c.c.). Basification of the aqueous extracts afforded a sticky solid which was crystallised from 2N-hydrochloric acid (carbon) to give the *dihydrochloride* (5·5 g.), microscopic prisms, m. p. 266—268° (Found: C, 26·6; H, 2·4; N, 13·4; S, 10·3. $C_7H_5Cl_2N_3S,2HCl,0·5H_2O$ requires C, 26·6; H, 2·5; N, 13·3; S, 10·1%).

2-Aminothiazolo[4,5-f]quinoline. (*a*) 6-Quinolylthiourea 9·2 g.) in chloroform (100 c.c.) was stirred and treated dropwise withbromine (6·5 c.c.) in chloroform (50 c.c.). The mixture was stirred and boiled under reflux for 30 min., and the solid was collected, washed with chloroform and dissolved by warming in 40% aqueous sodium bisulphite (100 c.c.). The filtered solution was treated with ammonia to precipitate the *thiazoloquinoline* (7·5 g.) which crystallised from pentanol as microscopic prisms, m. p. 287—289° (Found: C, 59·0; H, 3·5; N, 19·5. $C_{10}H_7N_3S$ requires C, 59·7; H, 3·5; N, 20·9%). The *dihydrochloride* formed yellow prisms, m. p. 307—308° (Found: C, 43·2; H, 3·2; N, 15·0. $C_{10}H_7N_3S,2HCl$ requires C, 43·8; H, 3·3; N, 15·3%).

(*b*) 2,6-Diaminobenzothiazole (8·25 g.), glycerol (10 g.), sodium *m*-nitrobenzene sulphonate (15 g.), water (12·5 c.c.), and conc. sulphuric acid (15 c.c.) were stirred and boiled under reflux for 6 hr., and the cooled solution was diluted with water (50 c.c.) and filtered. The filtrate on treatment with sodium hydroxide gave a tar which was washed with water by decantation and was extracted with ethanol. Purification of the ethanol extract by chromatography (alumina) gave impure 2-aminothiazolo[4,5-*f*]quinoline (3 g.) which on crystallisation from pentanol or dilute hydrochloric acid afforded the base and dihydrochloride identical with the samples made by method (*a*).

2-Methylaminothiazolo[4,5-f]quinoline, prepared by bromination of 6-*N'*-methylthioureidoquinoline as in (*a*) above, formed cream needles from ethanol, m. p. 224—225° (Found: C, 61·4; H, 4·1; N, 19·5. $C_{11}H_9N_3S$ requires C, 61·4; H, 4·2; N, 19·5%).

Diaminobenzobisthiazoles.—The properties of the diaminobenzobisthiazoles are listed in Tables 1—4. Typical preparative methods were the following. (*a*) *p*-Phenylenebisthiourea (5 g.) in chloroform (100 c.c.) was stirred and treated dropwise, at room temperature, with bromine (6 c.c.) in chloroform (50 c.c.). The mixture was then stirred and boiled under reflux for 1 hr., hydrogen bromide being evolved. The yellow perbromide was collected when cold, washed with chloroform, and stirred with 20% aqueous sodium bisulphite solution (100 c.c.) at 80—90° until its colour was discharged. The solid was filtered off when cold and was extracted with boiling dilute hydrochloric acid (200 c.c.). Basification of the filtered extract with ammonia precipitated *2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole* (2·9 g.) which crystallised from acetic acid or from dimethylformamide as needles. On being heated under reflux with acetic anhydride in acetic acid the *diacetyl derivative* was obtained (see Table 1).

(*b*) 2-Amino-6-(*N'*-methylthioureido)benzothiazole (13·3 g.) in chloroform (100 c.c.) was stirred and treated dropwise with bromine (8·4 c.c.) in chloroform (40 c.c.). A large lump of solid which separated from the solution was removed, ground up and returned to the reaction vessel. The mixture was then boiled under reflux for 2 hr. The solid product was filtered off when cold, washed with chloroform, and freed from the excess of bromine by warming with 20% sodium bisulphite solution. The solid was dissolved in dilute hydrochloric acid and reprecipitated with sodium hydroxide, and the base was crystallised from 2N-hydrochloric acid. The first crop (m. p. 310—312°) gave on recrystallisation *2-amino-7-methylaminobenzo[1,2-d:4,3-d']bisthiazole dihydrochloride monohydrate* (1·3 g.), m. p. 322—324°. The mother-liquor on standing deposited *2-amino-6-methylaminobenzo[1,2-d:4,5-d']bisthiazole dihydrochloride dihydrate* (4·4 g.), m. p. >360° (when plunged in a bath at 330° this melted at 338°). In most experiments this separation of isomers was not achieved, the product being a mixture of m. p. 320—350°.

(*c*) *NN'*-Dimethyl-*p*-phenylenediamine (5·85 g.), sodium thiocyanate (13·84 g.), and glacial acetic acid (150 c.c.) were stirred and treated dropwise, below 15°, with bromine (4·4 c.c.) in acetic acid (10 c.c.). After the addition the mixture was stirred for 1·5 hr., and the solid product was collected and extracted with boiling dilute hydrochloric acid. The extract was treated with carbon and then with concentrated hydrochloric acid to precipitate *2,6-di-imino-3,7-dimethyl-2,3,6,7-tetrahydrobenzo[1,2-d:4,5-d']bisthiazole dihydrochloride hemihydrate* (0·4 g.).

(*d*) Dipotassium 3,6-diamino-1,2-phenylene dithiosulphate (10 g.) dissolved in hot water (100 c.c.) was boiled under reflux with methylisothiocyanate (4 g.). A pale yellow solid separated after 15 min., and after 1·5 hr. the solution was cooled and filtered. The solid (4·9 g.) was extracted with boiling dilute hydrochloric acid and the extract was treated with conc. hydrochloric acid to precipitate *2,7-bismethylaminobenzo[1,2-d:4,3-d']bisthiazole dihydrochloride.*

(*e*) Copper sulphate pentahydrate (50 g.) and sodium thiocyanate (33 g.) were ground together in a mortar, and to the black paste of cupric thiocyanate was added *m*-phenylene diamine (5·4 g.) in acetic acid (25 c.c.). The mixture was stirred until the cupric thiocyanate was largely decolourised, and was then heated on the steam-bath for 30 min., diluted with hot water (200 c.c.) and filtered. The insoluble residue was extracted with boiling dilute hydrochloric acid (2 × 300 c.c.), and the combined aqueous filtrates were basified with ammonia to precipitate 2,6-diaminobenzo[1,2-*d*:5,4-*d'*]-bisthiazole (3·5 g.) which crystallised from aqueous 2-ethoxyethanol or aqueous dimethylformamide as needles. The *diacetate* was obtained by crystallisation from glacial acetic acid and dihydrochloride from dilute hydrochloric acid. The base and the dihydrochloride were infusible

when heated slowly, but melting points could be obtained by dipping samples into a bath pre-heated almost to the required temperature. The same product was obtained by thiocyanation of 2,5-diaminobenzothiazole under the same conditions.

(*g*) 1,3-Bis-*NN'*-dimethylthioureidobenzene (5·6 g.) dissolved in chloroform (80 c.c.) was stirred and treated dropwise with freshly distilled, chlorine-free sulphuryl chloride (4 c.c.). The mixture was stirred at 55° for 2 hr., heated to the boil, and cooled. The solid product was collected,

TABLE 1

Benzo[1,2-*d*:4,5-*d'*]bisthiazoles

Name or structure	Method	Formula	M. p.	Found (%) C	H	N	Required (%) C	H	N	Spectroscopic data $\lambda_{max.}$ mμ ($10^{-3}\varepsilon$)
(I; $R^1 = R^2 = NH_2$, X = Y = H)	(*a*)	$C_8H_6N_4S_2$ $C_8H_6N_4S_2,2HCl,H_2O$	>350° >350	43·4 30·9	3·0 3·2	24·8 17·0	43·2 30·7	2·7 3·2	25·2 17·9	205 (15·7), 234 (37·4), 282 (12·4), 310 ~(11·2), 316 (12·5)
(I; $R^1 = NH_2$, R^2 = NHMe, X = Y = H)	(*b*)	$C_9H_8N_4S_2$ $C_9H_8N_4S_2,2HCl,2H_2O$	>350 >360	45·2 31·5	3·4 3·8	23·3 15·8	45·8 31·3	3·4 4·1	23·7 16·2	204 (8·7), 234 (21·5), 283 (8·4), 309 (7·3), 316 (7·73)
(I; $R^1 = R^2$ = NHMe, X = Y = H)	(*a*)	$C_{10}H_{10}N_4S_2,2HCl$	>350	36·9	3·7	17·1	37·15	3·7	17·3	235 (50·7), 280 (25·5), 305 (22·6), 315 (20·5)
(I; $R^1 = NH_2$, R^2 = NHEt, X = Y = H)	(*b*)	$C_{10}H_{10}N_4S_2,2HCl,0{\cdot}5H_2O$	310—312	35·7	3·5	16·9	36·1	3·9	16·9	203 (16·5), 234 (34·1), 282 (14·9), 305 (17·8), 315 (11·3)
2,3,6,7-*Tetrahydro*-2,6-*diimino*-3,7-*dimethylbenzo*-[1,2-*d*:4,5-*d'*]*bisthiazole*	(*c*)	$C_{10}H_{10}N_4S_2,2HCl,0{\cdot}5H_2O$	350	35·7	3·9	16·9				211 ~(16·2), 237 (33·3), 252 ~(30·9), 314 ~(22·2), 321 (25·7)
(I; R^1 = NHMe, R^2 = NHEt, X = Y = H)	(*a*)	$C_{11}H_{12}N_4S_2,2HCl,0{\cdot}5H_2O$	336—338	38·4	4·3	15·8	38·2	4·3	16·2	207 (12·2), 237 (30·3), 285 (12·8), 311 ~(11·0), 320 (11·5)
(I; $R^1 = NH_2$, $R^2 = NHPr^n$, X = Y = H)	(*b*)	$C_{11}H_{12}N_4S_2,2HCl$	300	39·5	3·9	16·0	39·2	4·1	16·6	199 (10·6), 232 (24·3), 279 (12·0), 299 ~(8·2) 311 (6·8)
(I; $R^1 = NH_2$, $R^2 = NHPr^i$, X = Y = H)	(*b*)	$C_{11}H_{12}N_4S_2,2HCl,H_2O$	284	37·8	4·7	15·2	37·2	4·5	15·8	206 (15·9), 237 (33·3), 285 (15·4), 308 (11·1), 318 (9·9)
(I; R^1 = NHMe, $R^2 = NMe_2$, X = Y = H)	(*b*)	$C_{11}H_{12}N_4S_2,2HCl,H_2O$	296—298	37·5	4·6	15·2				
2,3-*Dihydro*-3-*methyl*-6-*methylamino*-2-*methyliminobenzo*-[1,2-*d*:4,5-*d'*]*bisthiazole*	(*b*)	$C_{11}H_{12}N_4S_2,2HCl,2H_2O$	308—310	35·4	4·6	15·0	35·4	4·8	15·0	205 (10·3), 234 (27·6), 283 (10·6), 312 ~(10·25), 319 (11·1)
(I; $R^1 = R^2 = NMe_2$, X = Y = H)	(*a*)	$C_{12}H_{14}N_4S_2$	320—321	52·1	5·4	20·2	51·8	5·0	20·2	206 (15·0), 234 (41·2), 279 ~(16·5), 286 (17·8), 313 ~(18·9), 322 (208)
(XII)	(*a*)	$C_{12}H_{14}N_4S_2$ $C_{12}H_{14}N_4S_2,2HCl,3H_2O$	307—308 348—350	51·9 35·5	5·1 4·0	20·1 13·7	35·5	5·4	13·8	204 (16·2), 237 (31·5), 247 ~(16·4), 284 (11·2) 316 ~(12·4), 322 (14·1)
(I; $R^1 = R^2$ = NHEt, X = Y = H)	(*a*)	$C_{12}H_{14}N_4S_2$	312—313	52·1	4·8	19·7				205 (17·9), 235 (44·2), 286 (16·9), 313 ~(16·9), 320 (17·9)
(I; $R^1 = R^2$ = NHMe, X = Y = Me)	(*a*)	$C_{12}H_{14}N_4S_2$ $C_{12}H_{14}N_4S_2,2HCl$	>360 *ca.* 320	41·0	4·7	19·3 15·9	41·0	4·6	16·0	217 (21·0), 240 (34·5), 289 (17·2), 303 (15·5), 314 (20·5)
(I; $R^1 = R^2$ = NHAc, X = Y = H)		$C_{12}H_{10}N_4O_2S_2$	>360	47·0	3·7	18·3	47·1	3·3	18·3	
(I; $R^1 = R^2 = NHPr^n$, X = Y = H)	(*a*)	$C_{14}H_{18}N_4S_2$	273—275	55·4	6·0	18·3	54·9	5·9	18·3	200 (17·8), 230 (43·5) 280 (16·8), 309 ~(17·0), 314 (18·2)
(I; $R^1 = R^2 = NHPr^i$, X = Y = H)	(*a*)	$C_{14}H_{18}N_4S_2$	319—321	55·1	6·1	18·0				206 (18·5), 236 (44·7), 285 (17·2), 315 ~(17·8), 320 (19·0)
(I; $R^1 = R^2 =$ $NHCH_2CH_2NEt_2$, X = Y = H)	(*a*)	$C_{20}H_{32}N_6S_2$	222—224	56·9	7·5	19·0	57·1	7·6	20·0	205 (13·1), 238 (30·5), 289 (13·6), 310 ~(15·0), 320 (16·2)

(*f*) 1,3-Dinitro-4,6-dithiocyanobenzene (5 g.) was added to stannous chloride dihydrate (25 g.) dissolved in conc. hydrochloric acid (50 c.c.). The mixture was boiled under reflux for 2 hr. and was then cooled. The solid product was collected and extracted with boiling dilute hydrochloric acid, and the extract was basified with ammonia to precipitate 2,6-diaminobenzo[1,2-*d*:5,4-*d'*]bisthiazole (0·6 g.).

washed with chloroform, and dissolved in water with a little hydrochloric acid. The solution was treated with carbon and basified with ammonia to precipitate the *benzobisthiazole* which crystallised from pentanol as needles.

2,5-*Bismethylaminobenzo*[1,2-d:4,3-d']*bisthiazole*, from 1,2-bis-*N'*-methylthioureidobenzene with bromine [method (*a*)] or, better, with sulphuryl chloride [method (*g*)],

TABLE 2

Benzo[1,2-*d*:4,3-*d*′]bisthiazoles

Name or structure	Method	Formula	M. p.	Found (%) C	H	N	Required (%) C	H	N	Spectroscopic data $\lambda_{max.}$ mμ ($10^{-3}\varepsilon$)
(III; $R^1 = R^2 = NH_2$, X = Y = H)	Ref. 1	$C_8H_6N_4S_2$	>350°	42·6	3·0	25·6	43·2	2·7	25·2	204 (9·7), 221 (16·9), 243 (31·7), 286 (13·3)
		$C_8H_6N_4S_2$,2HCl	>350	32·6	2·9	19·9	32·55	2·7	19·0	
(III; $R^1 = NH_2$, R^2 = NHMe, X = Y = H)	(*b*)	$C_9H_8N_4S_2$,2HCl,H_2O	320—322	33·0	3·7	16·6	33·0	3·7	17·1	204 (12·8), 224 ~(16·8), 244 (27·8), 285 (15·2)
(III; $R^1 = R^2$ = NHMe, X = Y = H)	(*d*)	$C_{10}H_{10}N_4S_2$,2HCl,0·5H_2O	328—330	36·7	4·1	16·9	36·1	3·9	16·9	204 (11·9), 223 (15·5), 244 (29·7), 286 (16·3), 330 (2·4)
(III; $R^1 = NH_2$, R^2 = NHEt, X = Y = H)	(*b*)	$C_{10}H_{10}N_4S_2$,2HCl	310—312	37·0	3·6	17·3	37·15	3·7	17·3	202 (9·5), 221 (12·9), 243 (24·0), 285 (12·4)
(III; $R^1 = R^2$ = NHMe, X = Y = Me)	(*a*)	$C_{12}H_{14}N_4S_2$,2HCl	337—338	40·6	4·4	15·8	41·0	4·6	16·0	217 (19·8), 247 (26·5), 290 (14·2)
(III; $R^1 = R^2$ = NHAc, X = Y = H)		$C_{12}H_{10}N_4O_2S_2$,AcOH	>360	46·2	3·8	15·4	45·9	3·8	15·3	

TABLE 3

Benzo[1,2-*d*:5,4-*d*′]bisthiazoles

Name or structure	Method	Formula	M. p.	Found (%) C	H	N	Required (%) C	H	N	Spectroscopic data $\lambda_{max.}$ mμ ($10^{-3}\varepsilon$)
(II; $R^1 = R^2 = NH_2$, X = Y = H)	(*a*), (*e*), (*f*)	$C_8H_6N_4S_2$	325—326°	43·1	2·5	24·8	43·2	2·7	25·2	206 (16·2), 237 (27·2), 246 ~(23·4), 309 (12·0), 316 (14·2)
		$C_8H_6N_4S_2$,2AcOH	>360	41·6	3·9	16·8	42·1	4·1	16·4	
		$C_8H_6N_4S_2$,2HCl,H_2O	340—350	30·7	3·3	17·9	30·7	3·2	17·9	
(II; $R^1 = NH_2$, R^2 = NHMe, X = Y = H)	(*b*)	$C_9H_8N_4S_2$,2HCl,0·5H_2O	335	33·9	3·9	17·5	34·0	3·5	17·6	206 (17·4), 237 (30·0), 247 ~(26·2), 311 ~(14·4), 317 (16·2)
(II; $R^1 = R^2$ = NHMe, X = Y = H)	(*a*)	$C_{10}H_{10}N_4S_2$,2HCl	318—319	36·9	3·8	17·4	37·15	3·7	17·3	206 (11·3), 236 (23·2), 246 ~(19·9), 312 ~(11·6), 317 (13·0)
(II; $R^1 = R^2$ = NHMe, X = H, Y = Me)	(*a*)	$C_{11}H_{12}N_4S_2$	302—304	50·0	4·6	20·7	50·0	4·5	21·2	212 (15·9), 257 (21·2), 305 (9·6), 316 (14·1)
		$C_{11}H_{12}N_4S_2$,2HCl,2H_2O	303—304	35·9	4·5	14·8	35·4	4·8	15·0	
(II; $R^1 = R^2 = NMe_2$, X = Y = H)	(*a*)	$C_{12}H_{14}N_4S_2$	315—317	51·7	4·8	20·1	51·8	5·0	20·2	211 ~(16·2), 237 (33·3), 252 ~(30·9), 314 ~(22·2), 321 (25·7)
2,3,5,6-*Tetrahydro*-3,5-*dimethyl*-2,6-*bismethylimino*-*benzo*[1,2-*d*:5,4-*d*′]*bisthiazole*	(*a*), (*g*)	$C_{12}H_{14}N_4S_2$	250—252	51·9	4·9	19·6				216 ~(17·7), 241 (30·5), 250 (30·5), 315 ~(18·8), 320 (22·1)
(II; $R^1 = R^2$ = NHEt, X = Y = H)	(*a*)	$C_{12}H_{14}N_4S_2$	306—308	51·6	5·2	20·1				206 (5·9), 237 (33·8), 249 ~(28·2), 313 ~(18·9), 319 (21·5)
(II; $R^1 = R^2$ = NHPr^n, X = Y = H)	(*a*)	$C_{14}H_{18}N_4S_2$	251—253	54·3	6·0	17·6	54·9	5·9	18·3	206 (14·9), 236 (29·3), 249 ~(24·3), 313 ~(17·0), 318 (19·2)
(II; $R^1 = R^2$ = NHPr^i, X = Y = H)	(*a*)	$C_{14}H_{18}N_4S_2$	319—321	55·1	6·1	18·0				206 (17·3), 237 (33·8), 249 ~(27·1), 314 ~(19·4), 319 (22·2)
(II; $R^1 = R^2 = NEt_2$, X = Y = H)	(*a*)	$C_{16}H_{22}N_4S_2$	155—156	57·5	6·8	16·8	57·5	6·6	16·8	208 (13·2), 238 (26·8), 255 (22·7), 316 ~(19·6), 323 (22·6)

TABLE 4

Benzo[1,2-*d*:3,4-*d*′]bisthiazoles

Name or structure	Method	Formula	M. p.	Found (%) C	H	N	Required (%) C	H	N	Spectroscopic data $\lambda_{max.}$ mμ ($10^{-3}\varepsilon$)
(IV; $R^1 = R^2 = NH_2$, X = Cl, Y = H)	(*c*)	$C_8H_5ClN_4S_2$	>360°	37·1	2·3	20·5	37·5	2·0	21·9	
(IV; $R^1 = R^2 = NH_2$, X = Me, Y = H)	(*c*)	$C_9H_8N_4S_2$,2HCl	254—258	35·0	3·7	18·0	34·95	3·2	18·1	
(IV; $R^1 = R^2$ = NHMe, X = Cl, Y = H)	(*a*)	$C_{10}H_9ClN_4S_2$	313—314			19·6			19·7	
		$C_{10}H_9ClN_4S_2$,2HCl	284—285	33·2	3·3	15·6	33·6	3·1	15·7	
(IV; $R^1 = R^2$ = NHMe, X = Me, Y = H)	(*a*)	$C_{11}H_{12}N_4S_2$	267—268			21·2			21·2	205 (12·4), 244 (21·0), 207 (21·0), 295 (6·2), 309 (4·8)
		$C_{11}H_{12}N_4S_2$,2HCl,3H_2O	302—303	34·3	5·3	14·2	33·8	5·1	14·3	
(IV; $R^1 = R^2$ = NHMe, X = OMe, Y = H)	(*a*)	$C_{11}H_{12}N_4OS_2$,2HCl,2H_2O	246—247	33·7	4·7	13·5	33·1	4·5	14·0	

formed microscopic prisms, m. p. 315—316° from pyridine (Found: C, 47·9; H, 4·1; N, 21·5. $C_{10}H_{10}N_4S_2$ requires C, 48·0; H, 4·0; N, 22·4%).

The following were prepared by method (*a*). 2,7-*Bismethylaminonaphtho*[2,1-d:6,5-d′]*bisthiazole dihydrochloride*, m. p. 306—308° (Found: C, 40·4; H, 4·3; N, 13·6. $C_{14}H_{12}N_4S_2,2HCl,2{\cdot}5H_2O$ requires C, 40·2; H, 4·5; N, 13·4%).

2,7-*Bismethylaminonaphtho*[1,2-d:5,6-d′]*bisthiazole*, needles (solvated?) from acetic acid, became a powder at 100°, and sintered at 345°, m. p. *ca.* 360° [Found (dried at 100°): C, 55·2; H, 4·0; N, 18·3. $C_{14}H_{12}N_4S_2$ requires C, 56·0; H, 4·0; N, 18·7%].

2,9-*Bismethylaminonaphtho*[1,2-d:8,7-d′]*bisthiazole dihydrochloride*, m. p. 340° (Found: C, 41·2; H, 4·4; N, 13·7. $C_{14}H_{12}N_4S_2,2HCl,2H_2O$ requires C, 41·1; H, 4·4; N, 13·7%).

6(?)-*Bromo*-2,9-*bismethylaminonaphtho*[1,2-d:7,8-d′]*bisthiazole*, m. p. 255—256° (Found: C, 44·4; H, 2·9; N, 15·0. $C_{14}H_{11}BrN_4S_2$ requires C, 44·3; H, 2·9; N, 14·8%).

2,2′-*Bismethylamino*-6,6′-*dibenzothiazolyl dihydrochloride*, m. p. 360° (Found: C, 47·6; H, 4·4; N, 13·3. $C_{16}H_{14}N_4S_2,2HCl,0{\cdot}5H_2O$ requires C, 47·1; H, 4·2; N, 13·7%).

Thiocyanation of *p*-phenylenediamine with sodium thiocyanate and bromine [method (*c*)] or of 2,6-diaminobenzothiazole with cupric thiocyanate [method (*e*)] gave inseparable mixtures of linear and angular diaminobenzobisthiazoles.

1,3-*Dinitrobenzene*-4,6-*dithiocyanate*.[16]— 1,3-Dichloro-4,6-dinitrobenzene (23·7 g.) was added with stirring to a solution of sodium thiocyanate (17 g.) in acetone (60 c.c.). The mixture was stirred for 4 hr., and the solid was then filtered off, washed with a little acetone, slurried with water, and again filtered. The product (20·1 g.) was substantially pure, and formed pale yellow needles, m. p. 197—199° (Found: C, 34·1; H, 0·8; N, 19·8. Calc. for $C_8H_2N_4O_4S_2$: C, 34·0; H, 0·7; N, 19·8%).

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