448. *Some Benziminazole Derivatives.*

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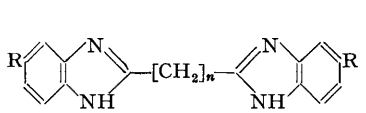
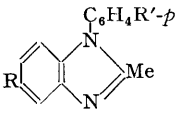
Some polymethylenebisbenziminazoles, phenyl-substituted benziminazoles, and alkyl- and chloroalkyl-benziminazoles have been synthesised during studies of the evaluation of the biological potentialities of this dicyclic ring system.

Our interest in the benziminazole ring system arose during collateral studies carried out in these Laboratories on the preparation of glycosyl derivatives of benziminazole with animal-protein-factor activity (see Mamalis, Petrow, and Sturgeon, *J. Pharm. Pharmacol.*, 1950, **2**, 491 *et seq.*). We have, therefore, prepared certain compounds related to specific chemotherapeutic types with the object of obtaining further information on the biological potentialities of this dicyclic nucleus.

(i) *Polymethylenebisbenziminazoles.*—Attempts to simulate the amœbicidal properties of emetine with simple synthetic compounds led to the discovery that biological activity of this type is often associated with polymethylenediamine derivatives (Pyman, *Rep. Brit. Assoc.*, 1937, **107**, 57; Goodson, Garvin, Goss, Kirby, Lock, Neal, Sharp, and Solomon, *Brit. J. Pharmacol.*, 1943, **3**, 49; Hall, Mahboob, and Turner, *J.*, 1950, 1842). We have, therefore, prepared a series of polymethylenebis-2-benziminazoles of type (I; R = H; n = 2—6, 8, or 10) employing Shriner and Upson's method (*J. Amer. Chem. Soc.*, 1941, **63**, 2277) whereby *o*-phenylenediamine is condensed with the appropriate dibasic acid in 4N-hydrochloric acid. Nitration of these compounds gave the polymethylenebis-5-nitrobenziminazoles (I; R = NO_2), which were reduced catalytically to the corresponding amino-derivatives, isolated as the hydrochlorides. The constitution assigned to the latter compounds was confirmed by the independent synthesis of (I; R = NH_2; n = 4) from adipobis-2 : 4-dinitroanilide and of (I; R = NH_2; n = 5) from pimalobis-2 : 4-dinitroanilide by reduction and ring closure.

Attempts to convert compounds of type (I; R = NH_2) into the corresponding polymethylenebis-5-cyanobenziminazoles by the Sandmeyer reaction proved unsuccessful. An alternative route to these compounds, whereby the dibasic acid is condensed with 4-cyano-1 : 2-phenylenediamine, gave (I; R = CN; n = 4 and 8) with adipic and sebacic acids. Conversion into the corresponding amidines, however, was not feasible in view of the very low yields obtained.


(I)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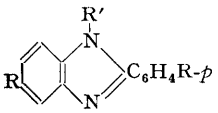
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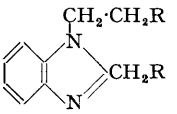
(IV)

(ii) *Phenyl-substituted Benziminazoles.*—The general resemblance in structural outline between 1-phenylbenziminazole (cf. II) and phenanthridine led us to undertake the preparation of compounds analogous to the trypanocidal phenanthridinium compounds of Morgan, Walls, and their collaborators (*J.*, 1931 *et seq.*). Some analogous work has since been reported by Bower, Stephens, and Wibberley (*J.*, 1950, 3341), who observed that 5(6)-amidino-2-*p*-amidinophenylbenziminazole, the preparation of which had likewise been undertaken independently by ourselves, showed marked activity against *T. equiperdum*.

The 2-methyl-1-phenylbenziminazoles (II) were prepared from the corresponding 2-aminodiphenylamine derivatives by Phillips's method (*J.*, 1929, 2820). Hydrogenation of nitro-groups was best effected by employing Raney nickel in ethanolic solution. Conversion into quaternary metho-salts was achieved in the usual manner. 5-Amino-1-*p*-aminophenyl-2-methylbenziminazole (II; R = R′ = NH_2), prepared in this way, was converted into the methochloride hydrochloride hydrate *via* the corresponding diacetyl derivative (II; R = R′ = NHAc), but had no trypanocidal action. Rather surprisingly attempts to convert the related 5-acetamido-1-*p*-acetamidophenylbenziminazole into the quaternary salt proved unsuccessful. The isomeric 1-methyl-2-phenylbenziminazoles (III), prepared by reaction of the *N*-methyl-*o*-phenylenediamines with the appropriate benzaldehyde derivative, are cyclised in boiling acetic acid. 1-Methyl-5-nitro-2-*p*-nitrophenylbenziminazole (III; R = NO_2, R′ = Me) readily passed into the quaternary salt. Reaction of 5-acetamido-2-*p*-acetamidophenyl-1-methylbenziminazole (III; R = NHAc, R′ = Me) with methyl iodide under various conditions, however, failed to give analytically pure material. The 1-phenyl-2-(substituted phenyl)-benziminazoles (III; R′ = Ph) were prepared by reaction of 2-aminodiphenylamines with the acyl chloride in boiling xylene. Reduction of 5-nitro-2-*p*-nitrophenyl-1-phenylbenziminazole (III; R = NO_2, R′ = Ph) gave the corresponding diamino-derivative, which was converted into the diacetyl derivative, and thence into 5-amino-2-*p*-aminophenyl-1-phenylbenziminazole methochloride dihydrochloride hydrate. Unfortunately, none of these compounds showed activity against *T. equiperdum*.

A second group of 2-arylbenziminazoles was prepared from 5-iodo- and 3 : 5-di-iodo-*o*-

phenylenediamine by reaction with 4-hydroxy-3-iodobenzaldehyde, 4-hydroxy-3 : 5-di-iodobenzaldehyde, and *p*-nitrobenzaldehyde. The compounds obtained are listed in Table 3, and were prepared for tests against *E. histolytica*.

(iii) *Alkyl- and Chloroalkyl-benziminazoles.*—As the growth-promoting properties of vitamin B_{12} are shared by some of its simple degradation products, and in particular by 5 : 6-dimethylbenziminazole (Emerson, Brink, Holly, Koniuszy, Heyl, and Folkers, *J. Amer. Chem. Soc.*, 1950, **72**, 3084), it seemed likely that certain structural analogues of the latter compound might function as metabolite inhibitors of vitamin B_{12} and thus be of interest in tumour chemotherapy (see also Holly, Peel, Cahill, and Folkers, *ibid.*, 1951, **73**, 332; Antaki and Petrow, *J.*, 1951, 2873). In selecting types suitable for examination, we have adopted the view expressed by Beaven, Holiday, Johnson, Ellis, Mamalis, Petrow, and Sturgeon (*J. Pharm. Pharmacol.*, 1949, **1**, 957) that both the glycosylbenziminazole fragment of vitamin B_{12} and riboflavin arise from a common biogenetic precursor, and that those alterations which effect conversion of riboflavin into a metabolite inhibitor are likewise effective in the present series (Antaki and Petrow, *loc. cit.*).

The 5-chloro-, 5-chloro-6-methyl-, 6-chloro-, 6-chloro-7-methyl-, 5 : 6-dichloro-, 5 : 7-dichloro-, and 5-bromo-benziminazoles given in Table 5 were prepared by standard methods from the corresponding *o*-nitroanilines (Table 4). The latter, in turn, were obtained from 1 : 4-dichloro-2-nitrobenzene, 2-chloro-4 : 5-dinitrotoluene, 4-chloro-1 : 2-dinitrobenzene, 6-chloro-2 : 3-dinitrotoluene, 1 : 2-dichloro-4 : 5-dinitro-, 3 : 5-dichloro-1 : 2-dinitro-, and 1 : 4-dibromo-2-nitrobenzene and the appropriate amine in ethanolic solution. *N'*-Substituted 4 : 5 : 6-trichloro-1 : 2-phenylenediamines failed to undergo conversion into benziminazoles when heated with formic acid.

A novel type of " nitrogen mustard " (IV; R = Cl) has also been obtained in these studies. Treatment of *N*-2'-hydroxyethyl-*o*-phenylenediamine with glycollic acid gave 1-2'-hydroxyethyl-2-hydroxymethylbenziminazole (IV; R = OH), converted into (IV; R = Cl) by thionyl chloride. The corresponding 5-chloro-, 5-chloro-6-methyl-, 6-chloro-, 5 : 6-dichloro-, 5 : 7-dichloro-, and 5-bromo-analogues were also prepared (see Table 7).

During biological studies of the chlorinated benziminazoles listed in Table 4, Dr. S. W. F. Underhill and his staff (Physiological Department) observed that certain compounds showed spasmolytic action of the peripheral musculotropic type when injected intravenously into mice. 5 : 6-Dichloro-1-methylbenziminazole, in particular, caused a mephenesin-like paralysis lasting 24 hours. We, therefore, prepared further compounds of this type and later extended the work to include some 1-(2 : 3-dihydroxypropyl) derivatives and their quaternary salts. Preparation of the latter was facilitated by the symmetrical distribution of charge in glyoxalinium compounds of this type. Thus 5 : 6-dichloro-1-(2 : 3-dihydroxypropyl)-3-methylbenziminazolinium chloride was more readily prepared by treating 5 : 6-dichloro-1-methylbenziminazole with α-monochlorohydrin at 160° than by direct quaternisation of the 1-(2 : 3-dihydroxypropyl) derivative. Reaction of 5 : 6-dichloro-1-methylbenziminazole with decamethylene dibromide afforded an analogue of the paralysing drug " Decamethonium iodide " (Organe, Paton, and Zaimis, *Lancet*, 1949, I, 21).

Experimental

M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.

Decamethylenebis-2-benziminazole (I; R = H; *n* = 10).—Decamethylene-1 : 10-dicarboxylic acid (1·1 g.), *o*-phenylenediamine (900 mg.), and 4N-hydrochloric acid were heated under gentle reflux at 135° for 5 hours. After cooling, the dihydrochloride which had separated was collected and basified, and the product crystallised from ethanol. *Decamethylenebis-2-benziminazole* formed needles, m. p. 298—299° (Found : C, 76·6; H, 8·1; N, 14·9. $C_{24}H_{30}N_4$ requires C, 77·0; H, 8·1; N, 14·9%). The dihydrochloride formed crystals, m. p. 261—263°. The remaining members of the series (*n* = 2—6 and 8) were prepared essentially as described by Shriner and Upson (*loc. cit.*).

Decamethylenebis-5-nitro-2-benziminazole Dihydrate (I; R = NO_2; *n* = 10).—Decamethylenebis-2-benziminazole (4·69 g.), dissolved in concentrated sulphuric acid, was treated at 0° with mechanical stirring with potassium nitrate (3·62 g.) added in portions, stirring being continued for a further 2 hours. The mixture was poured on crushed ice, the precipitated sulphate (5·77 g.;

m. p. 255—256°) collected, and the nitro-base liberated with aqueous ammonia and crystallised from aqueous ethanol.

The *compounds* (I; R = NO_2) listed in Table 1 were prepared in the same way.

TABLE 1. *Polymethylenebis-5-nitro-2-benziminazoles* (I; R = NO_2).

		Found, %				Required, %			Yield,	
n	M. p.	C	H	N	Formula	C	H	N	%	Remarks
2	289—290°	49·9	3·4	22·0	$C_{16}H_{12}O_4N_6,2H_2O$	49·5	3·4	21·6	77	Needles
3	165	55·9	3·9	23·2	$C_{17}H_{14}O_4N_6$	55·7	3·8	23·0	69	Plates
4	263	56·4	3·9	22·5	$C_{18}H_{16}O_4N_6$	56·8	4·2	22·1	80	Rosettes
5	208	53·7	4·5	19·7	$C_{19}H_{18}O_4N_6,2H_2O$	53·1	5·1	19·7	87	Needles [1]
6	248—249	54·8	5·1	18·4	$C_{20}H_{20}O_4N_6,2H_2O$	54·1	5·4	18·9	78	Needles
8	136	59·9	5·2	19·3	$C_{22}H_{24}O_4N_6$	60·5	5·5	19·3	93	Needles

[1] Crystallised from aqueous 2-methoxyethanol.

Ethylenebis-5-amino-2-benziminazole (I; R = NH_2; *n* = 2).—Ethylenebis-5-nitro-2-benziminazole (2 g.) in 2-methoxymethanol (100 ml.) was reduced catalytically at room temperature in the presence of Raney nickel. After removal of the catalyst the solution was treated with concentrated hydrochloric acid (4 ml.), and the precipitated *tetrahydrochloride* washed with ethanol and dried.

The *compounds* (I; R = NH_2) listed in Table 2 were prepared in the same way.

TABLE 2. *Tetrahydrochlorides of polymethylenebis-5-amino-2-benziminazoles* (I; R = NH_2).

		Found, %				Required, %			Yield,
n	M. p.	C	H	N	Formula	C	H	N	%
2	345°	43·8	4·6	18·7	$C_{16}H_{20}N_6Cl_4$	43·8	4·6	19·2	85
3	>300	45·7	4·9	18·2	$C_{17}H_{22}N_6Cl_4$	45·1	4·9	18·6	81
4	>300	46·6	4·5	18·8	$C_{18}H_{24}N_6Cl_4$	46·6	4·3	18·0	86
5	>300	47·5	5·7	17·4	$C_{19}H_{26}N_6Cl_4$	47·5	5·4	17·5	62
6	>345	48·6	5·7	17·5	$C_{20}H_{28}N_6Cl_4$	48·6	5·7	17·0	73
8	324—325	48·8	6·4	16·9	$C_{22}H_{32}N_6Cl_4$	48·6	6·4	16·7	86

Fumarobis-o-nitroanilide, pale yellow needles (83%) (from dioxan), m. p. 283° (Found: C, 53·4; H, 3·2; N, 15·7. $C_{16}H_{12}O_6N_4$ requires C, 53·9; H, 3·3; N, 15·7%), separated on cooling a mixture of *o*-nitroaniline (9·2 g.), fumaroyl chloride (5·1 g.), and dry benzene (50 ml.) which had been heated under reflux until evolution of hydrogen chloride had ceased.

Ethylenebis-2-benziminazole dihydrochloride dihydrate, needles (from ethanol), m. p. >330° (Found: C, 55·0; H, 4·9; N, 15·7; Cl, 19·9. $C_{16}H_{12}N_4,2HCl,2H_2O$ requires C, 54·7; H, 4·6; N, 15·9; Cl, 20·2%), was obtained by reduction of the foregoing compound (4 g.) in hot dioxan (150 ml.) with Raney nickel and hydrogen, followed by reaction with 5N-alcoholic acid under reflux for 2 hours.

Adipobis-4-cyano-2-nitroanilide, prepared by heating adipoyl chloride (from 2 g. of acid) with 4-cyano-2-nitroaniline (4·1 g.) (Stephens and Bower, *J.*, 1950, 1724) at 190° for 1 hour, separated (57%) from 2-ethoxyethanol in yellow crystals, m. p. 221—222° (Found: C, 54·6; H, 3·9; N, 19·4. $C_{20}H_{16}O_6N_6$ requires C, 55·0; H, 3·7; N, 19·3%).

Tetramethylenebis-5-cyano-2-benziminazole dihydrochloride was prepared by catalytic reduction of the foregoing compound (1 g.) in hot 2-ethoxyethanol (150 ml.) in the presence of Raney nickel, followed by addition of concentrated hydrochloric acid (5 ml.) to the filtrate and reaction on the steam-bath for 1 hour. It formed brownish crystals, m. p. 203° (Found: C, 57·7; H, 5·0; N, 20·2. $C_{20}H_{16}N_6,2HCl$ requires C, 58·1; H, 4·4; N, 20·3%). The corresponding base *dihydrate* was obtained from aqueous ethanol as a white powder, m. p. 260—261° (Found: C, 64·3; H, 5·2; N, 22·0. $C_{20}H_{16}N_6,2H_2O$ requires C, 63·9; H, 5·3; N, 22·4%).

Octamethylenebis-5-cyano-2-benziminazole crystallised from aqueous ethanol as needles (42%), m. p. 145° (Found: C, 71·8; H, 6·4; N, 21·1. $C_{24}H_{24}N_6$ requires C, 72·7; H, 6·1; N, 21·2%).

Pimelobis-2 : 4-dinitroanilide, prepared (55%) by heating pimeloyl chloride (from 8·15 g. of acid) and 2 : 4-dinitroaniline (18·3 g.) at 170—180° for 1 hour, crystallised from 2-ethoxyethanol in yellow needles, m. p. 188° (Found: C, 46·2; H, 4·0; N, 16·5. $C_{19}H_{18}O_{10}N_6$ requires C, 46·5; H, 3·7; N, 17·1%). Attempts to convert this compound into the corresponding bis-5-aminobenziminazole derivative proved unsuccessful.

2-Methyl-5-nitro-1-phenylbenziminazole methosulphate, prepared from 2-methyl-5-nitro-1-phenylbenziminazole (Phillips, *J.*, 1929, 2820), formed needles, m. p. 210° (decomp.) (Found: C, 50·3; H, 4·5; N, 11·1; S, 8·4. $C_{16}H_{17}O_6N_3S$ requires C, 50·7; H, 4·5; N, 11·1; S, 8·4%).

The *methochloride* formed clusters of needles, m. p. 182° (decomp.), from 5N-hydrochloric acid (Found : C, 50·3; H, 5·0; N, 11·7. $C_{15}H_{14}O_2N_3Cl,3H_2O$ requires C, 50·3; H, 5·6; N, 11·7%).

5-*Amino*-2-*methyl*-1-*phenylbenziminazole methochloride hydrochloride trihydrate*, obtained by treatment of 5-acetamido-2-methyl-1-phenylbenziminazole (Phillips, *loc. cit.*) with methyl sulphate, followed by 5N-hydrochloric acid, formed needles, m. p. 190° (decomp.) (Found : C, 49·5; H, 6·0; N, 11·4; Cl, 18·6. $C_{15}H_{17}N_3Cl_2,3H_2O$ requires C, 49·4; H, 6·3; N, 11·5; Cl, 19·5%).

2 : 4′-*Bisacetamido*-4-*nitrodiphenylamine* crystallised from ethanol as yellow needles, m. p. 236° (Found : C, 58·5; H, 4·9; N, 17·3. $C_{16}H_{16}O_4N_4$ requires C, 58·7; H, 4·9; N, 17·1%).

1-p-*Aminophenyl*-2-*methyl*-5-*nitrobenziminazole* (II; R = NO_2, R′ = NH_2), prepared by heating 2 : 4′-bisacetamido-4-nitrodiphenylamine (12 g.) with 4N-hydrochloric acid (120 ml.) for 40 minutes, followed by basification, formed needles (66%), m. p. 190° from ethanol (Found : C, 62·0; H, 4·5; N, 20·4. $C_{14}H_{12}O_2N_4$ requires C, 62·7; H, 4·5; N, 20·9%). The *acetyl* derivative formed needles (from ethanol), m. p. 198° (Found : C, 62·0; H, 4·5; N, 18·0. $C_{16}H_{14}O_3N_4$ requires C, 62·0; H, 4·5; N, 18·1%).

5-*Amino*-1-p-*aminophenyl*-2-*methylbenziminazole* (II; R = R′ = NH_2), prepared by catalytic reduction of the foregoing compound over Raney nickel, formed needles, m. p. 230°, from ethanol (Found : C, 70·6; H, 6·0; N, 22·7. $C_{14}H_{14}N_4$ requires C, 70·6; H, 5·9; N, 23·5%). The *diacetyl* derivative formed needles, m. p. 220°, from aqueous ethanol (Found : N, 17·2. $C_{18}H_{18}O_2N_4$ requires N, 17·4%).

1-p-*Aminophenyl*-2-*methyl*-5-*nitrobenziminazole methochloride hydrochloride tetrahydrate* formed hygroscopic needles (from water), m. p. >300° (Found : N, 12·8; Cl, 15·9. $C_{15}H_{16}O_2N_4Cl_2,4H_2O$ requires N, 13·1; Cl, 16·7%).

5-*Amino*-1-p-*aminophenyl*-2-*methylbenziminazole methochloride dihydrochloride pentahydrate* formed hygroscopic needles (from water) decomposing at 200° (Found : C, 40·6; H, 5·9; N, 11·5. $C_{15}H_{17}N_4Cl,2HCl,5H_2O$ requires C, 39·9; H, 6·4; N, 12·4%).

5-Amino-1-*p*-chlorophenyl-2-methylbenziminazole, prepared by reduction of the corresponding 5-nitro-derivative (m. p. 228°; cf. Fries, *Annalen*, 1927, **454**, 121, who gives m. p. 210°), crystallised from aqueous ethanol as needles, m. p. 170° (Found : C, 64·8; H, 4·8; N, 16·7; Cl, 14·0. Calc. for $C_{14}H_{12}N_3Cl$: C, 65·1; H, 4·7; N, 16·3; Cl, 13·8%).

2-*p*-Acetamidophenylbenziminazole separated from aqueous ethanol in small, pale yellow needles, m. p. 309° (Found: C, 66·9; H, 5·9; N, 15·6. Calc. for $C_{15}H_{13}ON_3,H_2O$: C, 66·9; H, 5·6; N, 15·6%). Attempts to convert this compound into its quaternary salt failed.

1-*Methyl*-2-p-*nitrophenylbenziminazole Methiodide.*—The product obtained by heating 1-methyl-2-*p*-nitrophenylbenziminazole (4 g.) and methyl iodide (10 ml.) in methanol (10 ml.) for 3 hours at 120° was extracted with boiling water (500 ml.) leaving the *methoperiodide*, small brown plates, m. p. 182° (Found : C, 28·6; H, 2·4; N, 6·3; I, 57·7. $C_{15}H_{14}O_2N_3I_3$ requires C, 27·7; H, 2·2; N, 6·5; I, 58·7%), from ethylene glycol. The aqueous filtrate, on cooling, deposited the *methiodide*, yellow needles, m. p. 297° (decomp.) (Found : C, 45·9; H, 3·6; N, 10·4. $C_{15}H_{14}O_2N_3I$ requires C, 45·6; H, 3·6; N, 10·6%).

1-*Methyl*-5-*nitro*-2-p-*nitrophenylbenziminazole methosulphate* crystallised from methanol–ethyl acetate in small prisms, m. p. 280° (Found : C, 45·6; H, 3·9; N, 13·1; S, 7·5. $C_{16}H_{16}O_8N_4S$ requires C, 45·3; H, 3·8; N, 13·2; S, 7·5%). The *methobromide* formed pale yellow needles, m. p. 255° (Found : C, 45·9; H, 3·4; N, 14·7; Br, 21·3. $C_{15}H_{13}O_4N_4Br$ requires C, 45·8; H, 3·3; N, 14·3; Br, 20·4%). The *methochloride* crystallised from ether–ethanol in needles, m. p. 242° (decomp.) (Found : C, 52·1; H, 3·5; N, 15·9; Cl, 10·4. $C_{15}H_{13}O_4N_4Cl$ requires C, 51·6; H, 3·8; N, 16·1; Cl, 10·2%).

5-*Acetamido*-2-p-*acetamidophenyl*-1-*methylbenziminazole hemihydrate*, formed by reducing 1-methyl-5-nitro-2-*p*-nitrophenylbenziminazole (5 g.) in ethanol (200 ml.) in the presence of Raney nickel and acetylating the product, crystallised from aqueous methanol as plates, m. p. 264—265° (Found: C, 65·7; H, 5·9; N, 16·8. $C_{18}H_{18}O_2N_4,\frac{1}{2}H_2O$ requires C, 65·3; H, 5·7; N, 16·9%).

5-*Amino*-2-p-*aminophenylbenziminazole trihydrochloride* was obtained by treating a suspension of 5-nitro-2-*p*-nitrophenylbenziminazole in hot methanol (160 ml.) with a solution of stannous chloride dihydrate (37·5 g.) in methanol (30 ml.) and concentrated hydrochloric acid (20 ml.), added portionwise, followed by 5 minutes' heating on the water-bath and precipitation by concentrated hydrochloric acid (100 ml.). It formed small glistening plates (4 g.), m. p. >320° (Found : C, 46·4; H, 4·2; N, 16·4; Cl, 32·3. $C_{13}H_{12}N_4,3HCl$ requires C, 46·8; H, 4·5; N, 16·8; Cl, 32·6%).

5-*Acetamido*-2-p-*acetamidophenylbenziminazole hemihydrate* was obtained (6·5 g.) by treating

TABLE 3.

Benziminazole	M. p.	Found, % C	H	N	I	Formula	Required, % C	H	N	I	Remarks
5-Iodo-2-methyl-	220°	37·2	3·0	10·9	48·9	$C_8H_7N_2I$	37·2	2·7	10·9	49·2	Yellow needles
5 : 7-Di-iodo-2-methyl-	257	25·3	1·7	7·1	65·8	$C_8H_6N_2I_2$	25·0	1·5	7·1	66·1	Cream needles
2-(*p*-Hydroxy-*m*-iodophenyl)-	248	46·8	2·7	8·1	38·0	$C_{13}H_9ON_2I$	46·4	2·7	8·3	37·8	
2-(*p*-Hydroxy-*m*-iodophenyl)-1-methyl-5-nitro-	232	43·2	2·5	11·0	32·5	$C_{14}H_{10}O_3N_3I$	42·5	2·6	10·6	32·1	
2-(*p*-Hydroxy-*m*-iodophenyl)-5-iodo-	187	33·4	2·0	5·3	55·6	$C_{13}H_{18}ON_2I_2$	33·8	1·7	6·0	55·0	
2-(*p*-Hydroxy-*m*-iodophenyl)-5 : 7-di-iodo-	190	—	—	4·6	64·8	$C_{13}H_7ON_2I_3$	—	—	4·7	64·8	Pale yellow needles
5 : 7-Di-iodo-2-(*p*-nitrophenyl)-	295	31·8	1·4	8·6	51·7	$C_{13}H_7O_2N_3I_2$	31·8	1·4	8·6	51·7	Yellow needles
2-(*p*-Aminophenyl)-5 : 7-di-iodo-	143	34·0	2·2	9·1	—	$C_{13}H_9N_3I_2$	33·8	1·9	9·1	—	Needles
2-(4-Hydroxy-3 : 5-di-iodophenyl)-	193	33·6	1·5	5·7	54·3	$C_{13}H_8ON_2I_2$	33·8	1·7	6·1	55·0	Pale brown needles
2-(4-Hydroxy-3 : 5-di-iodophenyl)-5 : 7-di-iodo-	193	21·3	0·9	4·0	71·1	$C_{13}H_6ON_2I_4$	21·8	0·8	3·9	71·1	Pale yellow needles
2-*p*-Hydroxyphenyl-5 : 7-di-iodo-	230	34·5	2·4	5·7	—	$C_{13}H_8ON_2I_2$	33·8	1·7	6·1	—	Cream needles
2-(4-Hydroxy-3 : 5-di-iodophenyl)-5-iodo-	200	26·7	1·2	4·3	65·9	$C_{13}H_7ON_2I_3$	26·5	1·2	4·7	64·8	Pale yellow needles
4-*p*-Dimethylaminophenyl-5 : 7-di-iodo-	158	36·3	2·7	8·0	52·7	$C_{15}H_{13}N_3I_2$	36·8	2·7	8·6	51·9	,, ,,
1-*p*-Iodophenyl-2-methyl-5-nitro- (HCl)	216	40·5	2·7	8·9	—	$C_{14}H_{10}O_2N_3I$,HCl	40·5	2·7	10·0	—	Yellow needles

TABLE 6. 1-2′-*Chloroethyl*-2-*chloromethylbenziminazole hydrochlorides.*

Substituents	M. p.	Description	Found, % N	Cl	Formula	Required, % N	Cl	Solvent *
None	176—177° †	White needles	10·6	40·3	$C_{10}H_{10}N_2Cl_2$,HCl	10·5	40·1	*b*
5-Chloro-	194 †	Needles	9·1	46·6	$C_{10}H_9N_2Cl_3$,HCl	9·3	47·3	*a*
5-Chloro-6-methyl-	204—209 †	,,	8·8	42·9	$C_{11}H_{10}N_2Cl_3$,HCl	8·5	42·8	*a*
6-Chloro-	>290	,,	9·3	46·2	$C_{10}H_9N_2Cl_3$,HCl	9·3	47·3	*b*
5 : 6-Dichloro-	190—192 †	,,	8·3	52·7	$C_{10}H_8N_2Cl_4$,HCl	8·1	53·1	*b*
5 : 7-Dichloro-	182—183°	,,	8·2	50·0	$C_{10}H_8N_2Cl_4$,HCl,H_2O	8·0	50·4	*a*
5-Bromo-	188—190 †	,,	7·8 ‡	—	$C_{10}H_9N_2Cl_2Br$	8·1 ‡	—	*b*

* (*a*) Ethanol. (*b*) Ethanol–light petroleum. † With decomp. ‡ Found : C, 34·3; H, 3·0. Required : C, 34·8; H, 2·9%.

TABLE 7. 1-2′-*Chloroethyl- and chloromethyl-benziminazole hydrochlorides.*

Benziminazole hydrochlorides	M. p.	Description	Found, % N	Cl	Formula	Required, % N	Cl	Solvent *
5-Chloro-2-chloromethyl-1-methyl-	301—302° †	Tablets	11·1	—	$C_9H_8N_2Cl_2$,HCl	11·1	—	*a*
5-Chloro-1-2′-chloroethyl-	174—175	Needles	11·4	42·1	$C_9H_8N_2Cl_2$,HCl	11·1	42·2	*b*
5-Chloro-1-2′-chloroethyl-6-methyl-	180—181	Prisms	10·4	40·1	$C_{10}H_{10}N_2Cl_2$,HCl	10·6	40·1	*c*
6-Chloro-2-chloromethyl-1-methyl-	315—317 †	Cream prisms	11·4	—	$C_9H_8N_2Cl_2$,HCl	11·1	—	*a*
6-Chloro-1-2′-chloroethyl-	197—198	Prisms	10·7	40·2	$C_9H_8N_2Cl_2$,HCl,$\frac{1}{2}H_2O$	10·7	40·7	*b*
5 : 7-Dichloro-1-2′-chloroethyl-	202—204	Needles	10·2	—	$C_9H_7N_2Cl_3$,HCl	9·8	—	*b*

* (*a*) Ethanol. (*b*) Ethanol–light petroleum. (*c*) Ethanol–ether. † With decomp.

TABLE 4.

N-Substituents	M. p.	Description	Found, % N	Found, % Cl	Formula	Required, % N	Required, % Cl	Solvent *
4-Chloro-2-nitroanilines.								
n-Butyl	30—31°	Orange prisms	11·1	—	$C_{10}H_{13}O_2N_2Cl,H_2O$	11·3	—	*b*
Benzyl	68	Orange needles	—	13·7	$C_{13}H_{11}O_2N_2Cl$	—	13·5	*d*
2′-Hydroxyethyl	104—105	,,	12·5	—	$C_8H_9O_3N_2Cl$	12·9	—	*a*
4-Chloro-5-methyl-2-nitroanilines.								
Ethyl	125—126	Orange needles	12·4	—	$C_9H_{11}O_2N_2Cl,H_2O$	12·1	—	*a*
n-Propyl	67—68	,,	11·9	—	$C_{10}H_{13}O_2N_2Cl$	12·2	—	*a*
*iso*Propyl	90—92	,,	12·1	—	$C_{10}H_{13}O_2N_2Cl$	12·2	—	*a*
n-Butyl	42—43	Orange leaflets	11·8	—	$C_{11}H_{15}O_2N_2Cl$	11·5	—	*a*
Benzyl	110—101	Orange needles	10·0	—	$C_{14}H_{13}O_2N_2Cl$	10·1	—	*a*
2′-Hydroxyethyl	171—172	Vermilion needles	11·9	—	$C_9H_{11}O_3N_2Cl$	12·1	—	*e*
2′-Hydroxy-*n*-propyl	137—138	Orange needles	10·9	13·7	$C_{10}H_{13}O_3N_2Cl,H_2O$	10·7	13·5	*a*
2′ : 3′-Dihydroxy-*n*-propyl	166	,,	11·2	14·2	$C_{10}H_{13}O_4N_2Cl$	10·8	13·6	*a*
5-Chloro-2-nitroanilines.								
*iso*Propyl	43—44	Orange plates	12·9	16·7	$C_9H_{11}O_2N_2Cl$	13·0	16·6	*b*
n-Butyl	28	Orange-yellow needles	12·0	—	$C_{10}H_{13}O_2N_2Cl$	12·2	—	*b*
Benzyl	100—101	Orange needles	10·7	—	$C_{13}H_{11}O_2N_2Cl$	10·7	—	*a*
2′-Hydroxyethyl	114—115	Red plates	13·4	—	$C_8H_9O_3N_2Cl$	12·9	—	*a*
2′ : 3′-Dihydroxy-*n*-propyl	155—156	Golden leaflets	—	15·1	$C_9H_{11}O_4N_2Cl$	—	14·4	*a*
5-Chloro-6-methyl-2-nitroanilines.								
Ethyl	58—59	Orange needles	13·2	—	$C_9H_{11}O_2N_2Cl$	13·0	—	*a*
Benzyl	54	Orange prisms	10·0	12·9	$C_{14}H_{13}O_2N_2Cl$	10·1	12·9	*a*
2′-Hydroxyethyl	75	Yellow needles	12·2	—	$C_9H_{11}O_3N_2Cl$	12·1	—	*c*
4 : 5-Dichloro-2-nitroanilines.								
Methyl	148	Orange needles	12·5	—	$C_7H_6O_2N_2Cl_2$	12·5	—	*a*
Ethyl	120	,,	11·7	—	$C_8H_8O_2N_2Cl_2$	11·9	—	*a*
n-Propyl	84—85	,,	11·2	—	$C_9H_{10}O_2N_2Cl_2$	11·2	—	*a*
Benzyl	104	Yellow needles	9·4	—	$C_{13}H_{10}O_2N_2Cl_2$	9·4	—	*a*
Phenyl	96	Orange plates	9·3	—	$C_{12}H_8O_2N_2Cl_2$	9·9	—	*a*
2′ : 3′-Dihydroxy-*n*-propyl	142	Yellow plates	9·9	—	$C_9H_{10}O_4N_2Cl_2$	10·0	—	*a*
4 : 5 : 6-Trichloro-2-nitroanilines.								
Methyl	72—73	Orange-yellow needles	11·1	41·3	$C_7H_5O_2N_2Cl_3$	11·0	41·6	*a*
Benzyl	65—66	Orange-red needles	9·0	31·6	$C_{13}H_9O_2N_2Cl_3$	8·5	32·1	*a*
2′-Hydroxyethyl	104—105	Yellow needles	—	37·2	$C_8H_7O_3N_2Cl_3$	—	37·3	*b*
4-Bromo-2-nitroanilines.			N	Br		N	Br	
Ethyl	92	Orange needles	11·6	32·5	$C_8H_9O_2N_2Br$	11·4	32·7	*a*
n-Propyl	41	Red prisms	10·9	31·5	$C_9H_{11}O_2N_2Br$	10·8	31·6	*a*
*iso*Propyl	98	Orange rods	10·6	30·7	$C_9H_{11}O_2N_2Br$	10·8	31·6	*a*
Benzyl	94	Orange-red blades	9·3	26·3	$C_{13}H_{11}O_2N_2Br$	9·1	26·1	*a*
2′-Hydroxyethyl	90—91	Yellow needles	10·8	31·4	$C_8H_9O_3N_2Br$	10·7	30·7	*b*
2′ : 3′-Dihydroxy-*n*-propyl	102—103	Orange-yellow needles	10·1	28·2	$C_9H_{11}O_4N_2Br$	9·6	27·5	*c*

* (*a*) Ethanol. (*b*) Aqueous ethanol. (*c*) Ethanol–light petroleum. (*d*) Light petroleum. (*e*) 2-Ethoxyethanol.

TABLE 5.

Substituents	M. p.	Description	Found, % N	Found, % Cl	Formula	Required, % N	Required, % Cl	Solvent *
5-Chlorobenziminazoles.								
1-Methyl-, hydrochloride	243—245°	White needles	13·8	—	$C_8H_7N_2Cl,HCl$	13·8	—	*d*
1 : 2-Dimethyl-, hydrochloride	277	,,	12·9	—	$C_9H_9N_2Cl,HCl$	12·9	—	*a*
1-*n*-Butyl-, picrate	185—186	Yellow needles	16·2	—	$C_{11}H_{13}N_2Cl,C_6H_3O_7N_3$	16·0	—	*h*
2-Hydroxymethyl-	210	Grey needles	15·3	—	$C_8H_7ON_2Cl$	15·3	—	*b*
1-Methyl-2-hydroxymethyl-	181—182	Leaflets	14·3	18·4	$C_9H_9ON_2Cl$	14·2	18·1	*b*
1-2′-Hydroxyethyl-	83—84	Needles	13·0	17·2	$C_9H_9ON_2Cl,H_2O$	13·1	16·6	*b*
1-2′-Hydroxyethyl-2-hydroxymethyl	150—151	,,	12·3	15·3	$C_{10}H_{11}O_2N_2Cl$	12·3	15·6	*b*
5-Chloro-6-methylbenziminazoles.								
1-Methyl-, hemihydrate	114—115	Needles	14·8	18·7	$C_9H_9N_2Cl,\frac{1}{2}H_2O$	14·7	18·7	
1-Methyl-, hydrochloride	255—260	Prismatic needles	12·5	32·6	$C_9H_9N_2Cl,HCl$	12·9	32·7	*a*
1-Methyl-, picrate	274—275 †	Yellow needles	16·8	—	$C_9H_9N_2Cl,C_6H_3O_7N_3$	17·1	—	*h*
1-Methyl-, methiodide	255 †	Prismatic needles	8·2	—	$C_{10}H_{12}N_2ClI,H_2O$	8·0	—	*a*
1-Methyl-, methochloride	220—221 †	Needles	10·7	—	$C_{10}H_{12}N_2Cl_2,H_2O$	11·1	28·0	*a*
1-Ethyl-	87	Cream needles	14·3	—	$C_{10}H_{11}N_2Cl$	14·4	18·2	*g*
1-*n*-Propyl-	63—64	White plates	13·5	16·9	$C_{11}H_{13}N_2Cl$	13·4	17·0	*g*
1-*n*-Propyl-, hydrochloride	93—95	Prismatic needles	11·0	27·4	$C_{11}H_{13}N_2Cl,HCl,H_2O$	10·7	27·0	*d*
1-*n*-Propyl-, picrate	198	Yellow needles	15·7	—	$C_{11}H_{13}N_2Cl,C_6H_3O_7N_3$	16·0	—	*h*
1-*iso*Propyl-, picrate	257	Yellow leaflets	15·7	7·9	$C_{11}H_{13}N_2Cl,C_6H_3O_7H_3$	16·0	8·1	*h*
1-*n*-Butyl-, picrate	197—199	Yellow needles	15·2	—	$C_{12}H_{15}N_2Cl,C_6H_3O_7N_3$	15·5	—	*h*
1-Benzyl-	155—156	Needles	11·0	13·9	$C_{15}H_{13}N_2Cl$	10·9	13·8	*b*
1-2′-Hydroxyethyl-	155—156	White needles	13·1	16·4	$C_{10}H_{11}ON_2Cl$	13·3	16·8	*b*
1-2′-Hydroxyethyl-2-hydroxymethyl-	149—151	,,	11·6	14·5	$C_{11}H_{13}O_2N_2Cl$	11·6	14·8	*b*
1-(2 : 3-Dihydroxypropyl)-	140	Prisms	12·4	—	$C_{11}H_{13}O_2N_2Cl$	11·6	—	*c*
1-(2 : 3-Dihydroxypropyl)-, 3-methiodide	188	,,	7·4	—	$C_{12}H_{16}O_2N_2ClI$	7·3	—	*a*
1-(2 : 3-Dihydroxypropyl)-, 3-methochloride	239	Needles	9·9	24·2	$C_{12}H_{16}O_2N_2Cl_2$	9·6	24·4	*a*
3-(2 : 3-Dihydroxypropyl)-, 1-methochloride	236—237 †	,,	9·2	23·3	$C_{12}H_{16}O_2N_2Cl_2,H_2O$	9·1	23·0	*d*
6-Chlorobenziminazoles.								
1 : 2-Dimethyl-	158	Needles	15·6	—	$C_9H_9N_2Cl$	15·5	—	*f*
1-Ethyl-, hydrochloride	211—213	Prisms	12·8	32·9	$C_9H_9N_2Cl,HCl$	12·9	32·7	*d*
1-Ethyl-, picrate	236—237	Yellow needles	17·2	—	$C_9H_9N_2Cl,C_6H_3O_7N_3$	17·1	—	*h*
1-*iso*Propyl-, hydrochloride	194—196	Needles	11·5	28·1	$C_{10}H_{11}N_2Cl,HCl,H_2O$	11·3	28·5	*d*
1-*iso*Propyl-, picrate	211	Yellow needles	16·3	—	$C_{10}H_{11}N_2Cl,C_6H_3O_7N_3$	16·5	—	*h*
1-*n*-Butyl-, hydrochloride	178—179	Needles	11·0	27·2	$C_{11}H_{13}N_2Cl,HCl,H_2O$	10·6	27·0	*i*
1-*n*-Butyl-, picrate	147	Yellow needles	16·2	—	$C_{11}H_{13}N_2Cl,C_6H_3O_7N_3$	16·0	—	*a*
1-Benzyl-	137—138	Needles	11·9	15·0	$C_{14}H_{11}N_2Cl$	11·5	14·6	*b*
1-Methyl-2-hydroxymethyl-	180—182	White prisms	13·9	—	$C_9H_9ON_2Cl$	14·2	—	*a*
1-2′-Hydroxyethyl-	146	Needles	14·6	—	$C_9H_9ON_2Cl$	14·2	—	*b*
1-2′-Hydroxyethyl-2-methyl-	171	White needles	13·2	16·9	$C_{10}H_{11}ON_2Cl$	13·3	16·8	*b*
1-(2 : 3-Dihydroxypropyl)-	156—157	Needles	12·5	15·7	$C_{10}H_{11}O_2N_2Cl$	12·3	15·7	*c*
1-(2 : 3-Dihydroxypropyl)-, 3-methiodide	172—173	,,	7·5	—	$C_{11}H_{14}O_2N_2ClI$	7·6	—	*c*
1-2′-Hydroxyethyl-2-hydroxymethyl-	178—179	,,	11·6	14·6	$C_{10}H_{11}O_2N_2Cl,H_2O$	11·5	14·5	*b*

TABLE 5 (*continued*).

Substituents	M. p.	Description	Found, % N	Found, % Cl	Formula	Required, % N	Required, % Cl	Solvent
6-Chloro-7-methylbenziminazoles.								
1-Ethyl-, hydrochloride	264	Needles	12·0	30·5	$C_{10}H_{11}N_2Cl,HCl$	12·1	30·7	*d*
1-Ethyl-, picrate	211—212	Yellow needles	16·2	8·8	$C_{10}H_{11}N_2Cl,C_6H_3O_7N_3$	16·5	8·4	*h*
1-2′-Hydroxymethyl-	186—187	Cream needles	13·0	16·2	$C_{10}H_{11}ON_2Cl$	13·3	16·8	*b*
1-2′-Hydroxyethyl-, hydrochloride	225	Needles	11·3	28·7	$C_{10}H_{11}ON_2Cl,HCl$	11·3	28·7	*d*
5 : 6-*Dichlorobenziminazoles.*								
1-Methyl-	174	Prisms	13·6	34·9	$C_8H_6N_2Cl_2$	13·9	35·3	*e*
1-Methyl-, methiodide	>270	White needles	7·8	—	$C_9H_9N_2Cl_2I$	8·2	—	*d*
1 : 2-Dimethyl-	200	Needles	12·9	33·2	$C_9H_8N_2Cl_2$	13·1	33·1	*e*
1 : 2-Dimethyl-, picrate	268	Lemon needles	15·8	—	$C_9H_8N_2Cl_2,C_6H_3O_7N_3$	15·8	—	*h*
1-Ethyl-	117—118	Plates	—	33·2	$C_9H_8N_2Cl_2$	—	33·1	*a*
1-Benzyl-	144	Needles	9·9	—	$C_{14}H_{10}N_2Cl_2$	10·1	—	*f*
1-Phenyl-	131—132	White needles	10·4	26·7	$C_{13}H_8N_2Cl_2$	10·4	27·0	*e*
2-Hydroxymethyl-	278 †	,,	13·1	33·0	$C_8H_6ON_2Cl_2$	12·9	32·7	*c*
2-Hydroxymethyl-1-methyl-	195	,,	11·9	30·4	$C_9H_8ON_2Cl_2$	12·1	30·7	*a*
1-2′-Hydroxyethyl-	162	Prisms	12·2	30·2	$C_9H_8ON_2Cl_2$	12·1	30·7	*c*
1-(2 : 3-Dihydroxypropyl)-	152—153	Needles	11·0	—	$C_{10}H_{10}O_2N_2Cl_2$	11·2	—	*e*
1-(2 : 3-Dihydroxypropyl)-, 3-methiodide	216	Arrowheads	7·7	—	$C_{11}H_{13}O_2N_2Cl_2I$	7·0	—	*a*
1-(2 : 3-Dihydroxypropyl)-, 3-methochloride	245—246	Needles	9·0	34·2	$C_{11}H_{13}O_2N_2Cl_3$	9·4	34·3	*a*
1-2′-Hydroxyethyl-2-hydroxymethyl	168	,,	10·1	—	$C_9H_{10}O_2N_2Cl_2,H_2O$	10·5	—	*b*
5 : 7-*Dichlorobenziminazoles.*								
1-Methyl-	137—138	Cream needles	13·5	34·1	$C_8H_6N_2Cl_2,\frac{1}{2}HO_2$	13·3	33·8	*f*
2-Methyl-	218—219	Needles	13·6	—	$C_8H_6N_2Cl_2$	13·9	—	*b*
2-Methyl-, hydrochloride	300 †	Leaflets	12·1	46·4	$C_8H_6N_2Cl_2,HCl$	12·4	47·0	*a*
2-Methyl-, picrate	262 †	Yellow needles	17·3	16·8	$C_8H_8N_2Cl_2,C_6H_3O_7N_3$	16·7	16·9	*a*
2-Hydroxymethyl-	210	Cream needles	12·6	32·5	$C_8H_6ON_2Cl_2$	12·9	32·7	*b*
1-2′-Hydroxyethyl-	152—153	Needles	12·3	31·7	$C_9H_8ON_2Cl_2$	12·1	31·7	*b*
1-(2 : 3-Dihydroxypropyl)-	180	Yellow needles	13·9	—	$C_{10}H_{10}O_2N_2Cl_2,C_6H_3O_7N_3$	14·3	—	*a*
1-2′-Hydroxyethyl-2-hydroxymethyl-	177—178	Needles	11·1	27·4	$C_{10}H_{10}O_2N_2Cl_2$	10·8	27·1	*b*
5-Bromobenziminazoles.			N	Br		N	Br	
1-Methyl-	86—87	Silver plates	13·2	—	$C_8H_7N_2Br$	13·3	—	*g*
1-Methyl-, picrate	264 †	Lemon needles	15·8	—	$C_8H_7N_2Br,C_6H_3O_7N_3$	15·9	—	*h*
1 : 2-Dimethyl-	137—138	Prisms	12·5	35·6	$C_9H_9N_2Br$	12·4	35·6	*e*
1-Ethyl-	55	Needles	12·4	35·4	$C_9H_9N_2Br$	12·4	35·6	*g*
1-Benzyl-	112	,,	9·7	—	$C_{14}H_{11}N_2Br$	9·8	—	*e*
1-2′-Hydroxyethyl-	92	Plates	11·2	—	$C_9H_9ON_2Br$	11·4	—	*f*
1-(2 : 3-Dihydroxypropyl)-	140	Prisms	10·0	29·3	$C_{10}H_{11}O_2N_2Br$	10·3	29·5	*c*
1-(2 : 3-Dihydroxypropyl)-, picrate	181	Yellow needles	—	16·2	$C_{10}H_{11}O_2N_2Br,C_6H_3O_7N_3$	—	16·0	*a*
1-2′-Hydroxyethyl-	144	Needles	10·4	29·6	$C_{10}H_{11}O_2N_2Br$	10·3	29·5	*c*

* (*a*) Ethanol. (*b*) Aqueous ethanol. (*c*) Ethanol–light petroleum. (*d*) Ethanol–ether. (*e*) Benzene. (*f*) Benzene–light petroleum. (*g*) Light petroleum. (*h*) 2-Ethoxyethanol. (*i*) Acetone. † With decomp.

the foregoing compound (6·5 g.) with acetic acid (80 ml.) and acetic anhydride (30 ml.) for 40 minutes at room temperature, and had m. p. 358° (Found : C, 63·9; H, 5·3; N, 17·5. $C_{17}H_{16}O_2N_4,\frac{1}{2}H_2O$ requires C, 64·4; H, 5·4; N, 17·7%). Attempted methosulphonation of this compound proved unsuccessful.

5-*Amino*-2-p-*aminophenyl*-1-*phenylbenziminazole*, obtained by reducing the corresponding nitro-compound with hydrogen and Raney nickel in ethanol, formed needles, m. p. 265° (Found : C, 75·6; H, 5·4; N, 19·3. $C_{19}H_{16}N_4$ requires C, 76·0; H, 5·3; N, 18·7%). The diacetyl derivative crystallised from aqueous ethanol in plates, m. p. 207° (Found : N, 14·5. $C_{23}H_{20}O_2N_4$ requires N, 14·6%).

5-*Amino*-2-p-*aminophenyl*-1-*phenylbenziminazole methochloride dihydrochloride pentahydrate* separated from ethanol–ether in pale yellow hygroscopic crystals, m. p. 210° (decomp.) (Found : C, 47·2; H, 6·0; N, 10·7; Cl, 21·9. $C_{20}H_{19}N_4Cl,2HCl,5H_2O$ requires C, 46·7; H, 6·0; N, 10·9; Cl, 20·8%).

5-*Nitro*-1-p-*nitrobenzyl*-2-p-*nitrophenylbenziminazole*.—*p*-Nitrobenzaldehyde (20 g.) in hot glacial acetic acid (200 ml.) was added to 4-nitro-1 : 2-phenylenediamine (20 g.) in hot acetic acid (20 g.), and the mixture heated under reflux for 5 hours, after which acetic acid (450 ml.) was removed by distillation during 1 hour. After cooling, some 5-nitro-2-*p*-nitrophenylbenziminazole, m. p. 340°, was removed, and the filtrate diluted with water. The precipitated orange solid was dissolved by heating it with nitrobenzene (75 ml.) under reflux for 1½ hours, the solution cooled somewhat, and methanol added until crystallisation commenced. 5-*Nitro*-1-p-*nitrobenzyl*-2-p-*nitrophenylbenziminazole* was obtained in pale orange-yellow needles (11 g.), m. p. 256—258° (Found : C, 57·5; H, 2·8; N, 16·5. $C_{20}H_{13}O_6N_5$ requires C, 57·3; H, 3·1; N, 16·7%).

2-p-*Diethylaminophenylbenziminazole* crystallised from ethyl acetate–light petroleum in buff-coloured needles, m. p. 232° (Found : C, 76·8; H, 7·3; N, 15·4. $C_{17}H_{19}N_3$ requires C, 76·9; H, 7·2; N, 15·8%).

2-p-*Dimethylaminophenyl*-1-*methyl*-5-*nitrobenziminazole hydrochloride* separated from glacial acetic acid in crystals, m. p. 259° (Found : C, 57·9; H, 5·2. $C_{16}H_{16}O_2N_4,HCl$ requires C, 57·7; H, 5·2%).

2-p-*Diethylaminophenyl*-1-*methyl*-5-*nitrobenziminazole hydrochloride* separated from glacial acetic acid in crystals, m. p. 250° (Found : C, 59·9; H, 6·1; N, 15·6; Cl, 10·2. $C_{18}H_{21}O_2N_4Cl$ requires C, 59·9; H, 5·9; N, 15·5; Cl, 9·8%).

5-*Iodo*-1 : 2-*phenylenediamine*, prepared by reduction of 5-iodo-2-nitroaniline with hydrogen and Raney nickel, crystallised from ethanol in silvery platelets, m. p. 73° (Found : C, 30·7; H, 3·2; N, 11·8; I, 54·3. $C_6H_7N_2I$ requires C, 30·8; H, 3·0; N, 11·9; I, 54·3%).

3 : 5-*Di-iodo*-1 : 2-*phenylenediamine* crystallised from ethanol in needles, m. p. 112° (Found : C, 20·4; H, 1·4; N, 7·8; I, 69·7. $C_6H_6N_2I_2$ requires C, 20·0; H, 1·7; N, 7·8; I, 70·5%).

The iodinated *benziminazole* derivatives listed in Table 3 were prepared by standard methods. They were generally purified by crystallisation from ethanol, acetic acid, or aqueous acetic acid.

5-*Iodo*-2-*ketobenziminazoline*, prepared by treating 4-iodo-1 : 2-phenylenediamine (4 g.) with carbonyl chloride in toluene (30 ml. of 12·5%) for 3 hours on the water-bath, crystallised on cooling, and had m. p. 250° (Found : C, 31·8; H, 2·4; N, 11·3. $C_7H_5ON_2I$ requires C, 32·3; H, 1·9; N, 10·8%).

5 : 7-*Di-iodo*-2-*ketobenziminazoline* formed crystals, m. p. 230° (Found : C, 22·3; H, 1·0; N, 7·3; I, 64·9. $C_7H_4ON_2I_2$ requires C, 21·8; H, 1·0; N, 7·3; I, 65·8%).

Decamethylenebis-5 : 6-*dichloro*-3-*methyl*-1-*benziminazolinium Dibromide*.—Decamethylene dibromide (3 g.) and 5 : 6-dichloro-1-methylbenziminazole (5 g.) were heated together at 160° for 45 minutes. The melt solidified on cooling and the product was recrystallised from ethanol and ether, forming small prisms, m. p. 232° (decomp.) (Found : C, 44·3; H, 4·8; N, 7·9. $C_{26}H_{32}N_4Cl_4Br_2$ requires C, 44·4; H, 4·6; N, 8·0%).

Various Products.—For other *compounds* prepared by the methods outlined, see the attached Tables.

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