NN'-*Diarylthioureas and Related Compounds of Potential Biological Interest.*

By Ng. Ph. Buu-Hoï, Ng. D. Xuong, and Ng. H. Nam.

[Reprint Order No. 5978.]

A large number of new *NN'*-diarylthioureas and similar sulphur compounds has been synthesised for testing for tuberculostatic activity and inhibitory properties against influenza virus. The preparation of *p*-alkoxyanilines, aryl *iso*thiocyanates, and a series of aminonaphthaquinones and 1-arylpyrroles was also investigated.

Thiourea and its derivatives are tuberculostatic. Thiourea itself possesses a slight but definite activity *in vitro*, which is enhanced by appropriate substitution, as in allylthiourea (Jouin and Buu-Hoï, *Ann. Inst. Pasteur*, 1946, **72**, 580), and especially in *p*-aminobenzenesulphonylthiourea (Mayer, *Chem. Abs.*, 1941, **36**, 5199; Jouin and Buu-Hoï, *loc. cit.*), but *NN'*-diarylthioureas failed to reveal significant activity *in vitro*; this group was not therefore investigated further. Interest in these compounds has recently revived with the discovery of outstanding tuberculostatic properties in *NN'*-di-(*p*-*n*-butoxyphenyl)thiourea and related compounds (Mayer, Eisman, and Konopka, *Proc. Soc. Exp. Biol.*, 1953, **82**, 769; Huebner *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 2274), and this activity has been confirmed in a series of new *NN'*-diarylthioureas (Buu-Hoï and Xuong, *Compt. rend.*, 1953, **237**, 498). Further, 4 : 4'-dialkoxythiocarbanilides have been found active against human leprosy (Buu-Hoï, *Internat. J. Leprosy*, 1954, **22**, 16), and certain diarylthioureas and related sulphur compounds against influenza-virus infections in mice (Buu-Hoï, Gley, Xuong, and Bouffanais, *Compt. rend.*, 1954, **238**, 2582).

These findings prompted the preparation of a wide series of new thiourea derivatives for biological testing with regard to these various activities. Some features concerning their preparation are worth mention. Symmetrical *NN'*-diarylthioureas were most conveniently obtained by Hugershof's method (*Ber.*, 1899, **32**, 2246), involving the heating of a primary arylamine with carbon disulphide and sulphur in ethanol. Aryl *iso*thiocyanates used in the preparation of unsymmetrical *NN'*-diarylthioureas were found, at variance with the literature (cf. Guillaumin, "Traité de Chimie organique de Grignard," Masson, Paris, 1939, vol. XIV, p. 348), to be readily accessible by an extension of the Werner reaction (*J.*, 1891, **59**, 399) involving a brief heating of symmetrical *NN'*-diarylthioureas with acetic anhydride. Condensation of the aryl *iso*thiocyanates with a variety of primary arylamines was readily effected in high yields, except in the case of *p*-nitroaniline, which gave no condensation product with aryl *iso*thiocyanates or carbon disulphide under the conditions of the Hugershof reaction. *p*-Aminobenzenesulphonamide, however, readily gave 4 : 4'-disulphonamidothiocarbanilide, a substance briefly mentioned in a patent (Dyson, B.P. 517,682) as being obtained in the reaction of *p*-sulphonamidophenyl *iso*thiocyanate with *p*-aminobenzenesulphonamide; condensation of the last with various aryl *iso*thiocyanates afforded a series of unsymmetrical thioureas bearing the *p*-sulphonamidophenyl radical. An interesting failure of a primary arylamine to condense with aryl *iso*thiocyanates was encountered with *o*-trifluoromethylaniline; this could clearly

be attributed to steric hindrance (cf. Buu-Hoï, Royer, and Hubert-Habart, *Rec. Trav. chim.*, 1954, **73**, 188), as *p*-trifluoromethylaniline readily underwent the reaction. Heterocyclic amines such as aminopyridines and 2-aminothiazole showed the same reactivity as aromatic amines. 2-Aminopyrimidine proved unreactive.

All the thioureas described possess chelating properties towards heavy metals, and most show tuberculostatic activity *in vitro* to some extent; a link between these two properties has been suggested (cf. Buu-Hoï, Xuong, Binon, and Nam, *Compt. rend.*, 1952, **235**, 329). Results of biological tests will be reported elsewhere; one of the most active compounds found was 4-ethyl-4'-*iso*pentyloxythiocarbanilide.

The preparations of several arylamines were improved in the course of this work; their condensation products with 2 : 3-dichloro-1 : 4-naphthaquinone and chloranil (cf. Buu-Hoï, Royer, and Eckert, *Rec. Trav. chim.*, 1952, **71**, 1059), and the 1-aryl-2 : 5-dimethylpyrroles obtained with acetonylacetone (cf. Buu-Hoï, *J.*, 1949, 2882), were prepared for characterisation.

Experimental [with E. Lescot, jun.]

The numerous *products* are tabulated. Unless otherwise stated, those for which no analysis is given are already known; all the others are new. Ligroin had b. p. 100—120°).

Preparation and Characterisation of p-*Alkyl- and* p-*Alkoxy-anilines.*—*p*-Alkylanilines were

Table 1.

(a) *Unsymmetrical substituted thiocarbanilides.*

Thiocarbanilide	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
4-Bromo-4'-fluoro-	177°	$C_{13}H_{10}N_2SBrF$	47·8	3·0	48·0	3·0
4-Bromo-4'-chloro-	202	$C_{13}H_{10}N_2SBrCl$	45·5	2·8	45·6	2·9
4-Bromo-2'-chloro-	198	$C_{13}H_{10}N_2SBrCl$	45·2	3·0	45·6	2·9
4-Bromo-4'-*iso*butoxy-	198	$C_{17}H_{19}ON_2SBr$	53·6	5·2	53·8	5·0
4-Bromo-2' : 5'-dimethoxy-	137	$C_{15}H_{15}O_2N_2SBr$	49·0	4·1	49·0	4·0
4-Bromo-4'-*n*-heptyloxy-	183—184	$C_{20}H_{25}ON_2SBr$	56·8	5·8	57·0	5·9
4-Bromo-4'-dimethylamino-	208	$C_{15}H_{16}N_3SBr$	51·1	4·8	51·4	4·5
4-Bromo-2'-phenyl-	178	$C_{19}H_{15}N_2SBr$	59·3	3·9	59·5	3·9
4-Bromo-4'-hydroxy-	196	$C_{13}H_{11}ON_2SBr$	48·1	3·7	48·2	3·4
4-Ethoxy-4'-methyl-	142	$C_{16}H_{18}ON_2S$	67·0	6·3	67·1	6·2
4-Methoxy-4'-methyl-	161	$C_{15}H_{16}ON_2S$	66·0	6·1	66·1	5·8
4-Methyl-4'-*n*-propoxy-	142	$C_{17}H_{20}ON_2S$	67·7	6·5	68·0	6·6
4-Methyl-4'-*iso*pentyloxy-	135	$C_{19}H_{24}ON_2S$	69·4	7·3	69·5	7·3
4-*iso*Butoxy-4'-methyl-	152	$C_{18}H_{22}ON_2S$	68·5	7·1	68·7	7·0
2-Methoxy-4'-methyl-	149	$C_{15}H_{16}ON_2S$	66·0	6·0	66·1	5·8
2 : 5-Dimethoxy-4'-methyl	128	$C_{16}H_{18}O_2N_2S$	63·7	5·8	63·5	5·9
2-Ethoxy-4'-methyl-	156	$C_{16}H_{18}ON_2S$	67·1	6·3	67·1	6·2
4-*n*-Butoxy-4'-methyl-	139	$C_{18}H_{22}ON_2S$	68·6	7·3	68·7	7·0
4-Methyl-4'-(3-phenylpropoxy)-	130	$C_{23}H_{24}ON_2S$	73·3	6·3	73·4	6·3
4-Ethyl-3'-methyl-	98	$C_{16}H_{18}N_2S$	70·8	6·8	71·1	6·6
2-Ethyl-4'-methyl-	182	$C_{16}H_{18}N_2S$	71·0	6·8	71·1	6·6
4 : 2' : 3'-Trimethyl-	156	$C_{16}H_{18}N_2S$	70·8	6·5	71·1	6·6
4-Methoxy-2' : 3'-dimethyl-	183	$C_{16}H_{18}ON_2S$	66·8	6·0	67·1	6·2
4-Bromo-4'-methoxy-	202	$C_{14}H_{13}ON_2SBr$	49·7	3·9	49·8	3·8
2-Chloro-4'-methoxy-	173	$C_{14}H_{13}ON_2SCl$	57·2	4·5	57·4	4·4
4-Fluoro-4'-methoxy-	172	$C_{14}H_{13}ON_2SF$	60·8	5·0	60·8	4·7
2 : 4'-Dimethoxy-	161	$C_{15}H_{16}O_2N_2S$	62·2	5·4	62·4	5·5
2-Ethoxy-4'-methoxy-	157	$C_{16}H_{18}O_2N_2S$	63·3	6·1	63·5	5·9
4 : 2' : 5'-Trimethoxy-	149	$C_{16}H_{18}O_3N_2S$	60·0	5·8	60·3	5·6
4-Arsono-4'-methyl-	d. *ca.* 262 *	$C_{14}H_{15}O_3N_2SAs$	45·4	3·8	45·9	4·0
4-Hydroxy-4'-methoxy-	198	$C_{14}H_{14}O_2N_2S$	61·1	5·2	61·3	5·1
4-Butoxy-4'-methoxy-	164	$C_{18}H_{22}O_2N_2S$	65·1	6·6	65·4	6·6
4-*iso*Butoxy-4'-methoxy-	161	$C_{18}H_{22}O_2N_2S$	65·6	6·5	65·4	6·6
4-Methoxy-4'-*iso*pentyloxy-	155	$C_{19}H_{24}O_2N_2S$	66·1	7·0	66·2	6·9
4-Methoxy-4'-(3-phenylpropoxy)-	154	$C_{23}H_{24}O_2N_2S$	70·5	6·4	70·4	6·1
4-Ethoxy-2' : 5'-dimethoxy-	149	$C_{17}H_{20}O_3N_2S$	61·3	6·2	61·4	6·0
4-Ethoxy-2'-methoxy-	129	$C_{16}H_{18}O_2N_2S$	63·4	6·0	63·5	5·9
4-Ethoxy-4'-(3-phenylpropoxy)-	147	$C_{24}H_{26}O_2N_2S$	70·6	6·6	70·9	6·4
4-Ethoxy-4'-hydroxy-	196	$C_{15}H_{16}O_2N_2S$	62·3	5·8	62·4	5·5
2-Chloro-4'-ethoxy-	191	$C_{15}H_{15}ON_2SCl$	58·4	5·0	58·7	4·8
4-Ethoxy-3' : 4'-dimethyl-	122	$C_{17}H_{20}ON_2S$	68·1	6·9	68·0	6·6

* d. = decomp.

TABLE 1. (*Continued.*)

Thiocarbanilide	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
3-Chloro-4′-ethoxy-	133°	$C_{15}H_{15}ON_2SCl$	58·8	4·8	58·7	4·8
4-Bromo-4′-ethoxy-	179	$C_{15}H_{15}ON_2SBr$	51·1	4·1	51·2	4·2
4-Dimethylamino-4′-ethoxy-	197	$C_{17}H_{21}ON_3S$	64·4	6·5	64·7	6·6
4-Ethoxy-4′-fluoro-	172	$C_{15}H_{15}ON_2SF$	62·0	5·4	62·0	5·1
4-Chloro-4′-ethoxy-	189	$C_{15}H_{15}ON_2SCl$	58·3	5·0	58·7	4·8
4-Ethoxy-2′-phenyl-	144	$C_{21}H_{20}ON_2S$	72·3	6·0	72·4	5·7
4 : 3′ : 4′-Trimethyl-	134	$C_{16}H_{18}N_2S$	71·0	6·5	71·1	6·6
2-Chloro-4′-methyl-	184	$C_{14}H_{13}N_2SCl$	60·5	4·8	60·7	4·7
3-Chloro-4′-methyl-	138	$C_{14}H_{13}N_2SCl$	60·4	4·7	60·7	4·7
4-*n*-Heptyloxy-2′ : 4′-dimethyl-	124	$C_{22}H_{30}ON_2S$	71·1	8·2	71·3	8·1
4-Dimethylamino-2′ : 4′-dimethyl-	155	$C_{17}H_{21}N_3S$	68·0	7·3	68·2	7·0
2 : 4-Dimethyl-4′-(3-phenylpropoxy)-	115	$C_{24}H_{26}ON_2S$	73·6	6·6	73·8	6·6
4-Fluoro-2′ : 4′-dimethyl-	131	$C_{15}H_{15}N_2SF$	65·6	5·5	65·5	5·4
2-*tert.*-Butyl-	190	$C_{17}H_{20}N_2S$	71·5	7·1	71·8	7·0
2-*tert.*-Butyl-2′-ethoxy-	172	$C_{19}H_{24}ON_2S$	69·6	7·5	69·5	7·3
4-Bromo-2-*tert.*-butyl-	187	$C_{17}H_{19}N_2SBr$	56·0	5·5	56·1	5·2
4-Fluoro-4′-hydroxy-	179	$C_{13}H_{11}ON_2SF$	59·4	4·1	59·5	4·1
4-Fluoro-3′-methyl-	125	$C_{14}H_{13}N_2SF$	64·5	5·1	64·6	5·0
4-Fluoro-2′-phenyl-	163	$C_{19}H_{15}N_2SF$	70·5	4·6	70·8	4·6
4-Methyl-4′-sulphonamido-	234	$C_{14}H_{15}O_2N_3S_2$	52·2	4·5	52·3	4·6
2-Chloro-4′-fluoro-	189	$C_{13}H_{10}N_2SClF$	55·3	3·6	55·6	3·5
4-*iso*Butoxy-4′-fluoro-	179	$C_{17}H_{19}ON_2SF$	64·0	5·9	64·1	5·9
3-Chloro-4′-fluoro-	136	$C_{13}H_{10}N_2SClF$	55·3	3·3	55·6	3·5
4-Dimethylamino-4′-fluoro-	193—194	$C_{15}H_{16}N_3SF$	62·4	5·4	62·2	5·5
4-Chloro-4′-fluoro-	169	$C_{13}H_{10}N_2SClF$	55·5	3·8	55·6	3·5
4-Fluoro-2′ : 5′-dimethoxy-	161	$C_{15}H_{15}O_2N_2SF$	58·6	5·0	58·8	4·9
4-Fluoro-4′-*n*-heptyloxy-	162	$C_{20}H_{25}ON_2SF$	66·3	7·1	66·6	6·9
4-Fluoro-4′-(3-phenylpropoxy)-	139	$C_{22}H_{21}ON_2SF$	69·2	5·3	69·4	5·5
4-Chloro-4′-*n*-propoxy-	189	$C_{16}H_{17}ON_2SCl$	59·8	5·4	60·0	5·3
4-(3-Phenylpropoxy)-4′-*n*-propoxy-	143	$C_{25}H_{28}O_2N_2S$	71·3	6·8	71·4	6·6
4-Fluoro-4′-*n*-propoxy-	178	$C_{16}H_{17}ON_2SF$	63·0	5·4	63·1	5·5
4-Dimethylamino-4-*n*-propoxy-	156	$C_{18}H_{23}ON_3S$	65·3	7·1	65·6	6·9
4-Hydroxy-4′-*n*-propoxy-	198	$C_{16}H_{18}O_2N_2S$	63·8	5·8	63·5	5·9
4-*iso*Butoxy-4′-*n*-propoxy-	175	$C_{20}H_{26}O_2N_2S$	67·0	7·2	67·0	7·2
4-*n*-Pentyloxy-4′-*n*-propoxy-	167	$C_{21}H_{28}O_2N_2S$	67·4	7·4	67·7	7·5
4-*n*-Heptyloxy-4′-*n*-propoxy-	162	$C_{23}H_{32}O_2N_2S$	68·8	8·2	69·0	8·0
4-Bromo-4′-*n*-butoxy-	189	$C_{17}H_{19}ON_2SBr$	53·5	5·0	53·8	5·0
4-*n*-Butoxy-4′-fluoro-	168	$C_{17}H_{19}ON_2SF$	64·0	6·0	64·1	5·9
4-*n*-Butoxy-4′-(3-phenylpropoxy)-	149	$C_{26}H_{30}O_2N_2S$	72·0	6·8	71·8	6·9
4-*n*-Butoxy-4′-hydroxy-	186	$C_{17}H_{20}O_2N_2S$	64·2	6·4	64·5	6·3
4-*n*-Butoxy-4′-trifluoromethyl-	186	$C_{18}H_{19}ON_2SF_3$	58·5	5·1	58·6	5·1
4-Chloro-4′-*iso*pentyloxy-	186	$C_{18}H_{21}ON_2SCl$	62·0	6·1	61·9	6·0
4-Fluoro-4′-*iso*pentyloxy-	171	$C_{18}H_{21}ON_2SF$	64·7	6·4	65·0	6·3
4-*n*-Heptyloxy-4′-*iso*pentyloxy-	121	$C_{25}H_{36}O_2N_2S$	69·8	8·2	70·0	8·4
4-*iso*Pentyloxy-4′-(3-phenylpropoxy)-	132	$C_{27}H_{32}O_2N_2S$	72·0	7·2	72·3	7·1
4-Hydroxy-4′-*iso*pentyloxy-	158	$C_{18}H_{22}O_2N_2S$	65·3	6·5	65·4	6·6
4-Hydroxy-4′-*n*-pentyloxy-	172	$C_{18}H_{22}O_2N_2S$	65·1	6·5	65·4	6·6
4-Dimethylamino-4′-*n*-pentyloxy-	142	$C_{20}H_{27}ON_3S$	67·0	7·8	67·2	7·5
4-*iso*Butoxy-4′-*n*-pentyloxy-	143	$C_{22}H_{30}O_2N_2S$	68·0	7·5	68·3	7·7
4-Chloro-4′-*n*-pentyloxy-	172	$C_{18}H_{21}ON_2SCl$	61·7	6·3	61·9	6·0
4-Fluoro-4′-*n*-pentyloxy-	168	$C_{18}H_{21}ON_2SF$	64·8	6·1	65·0	6·3
4-*iso*Butoxy-2′-phenyl-	145	$C_{23}H_{24}ON_2S$	73·5	6·5	73·4	6·3
4-Dimethylamino-2′-phenyl-	174	$C_{21}H_{21}N_3S$	72·3	6·1	72·6	6·0
4-Hydroxy-2′-phenyl-	168	$C_{19}H_{16}ON_2S$	70·9	5·1	71·2	5·0
4-Chloro-2′-phenyl-	191	$C_{19}H_{15}N_2SCl$	67·0	4·5	67·3	4·4
4-*n*-Heptyloxy-2′-phenyl-	123	$C_{26}H_{30}ON_2S$	74·7	7·4	74·6	7·1
2-Phenyl-4′-(3-phenylpropoxy)-	131	$C_{28}H_{26}ON_2S$	76·7	6·0	76·7	5·9
4-Fluoro-	194	$C_{13}H_{11}N_2SF$	63·2	4·5	63·4	4·4
4-Fluoro-4′-methyl-	179	$C_{14}H_{13}N_2SF$	64·5	5·0	64·6	5·0
4-Fluoro-2′-methoxy-	121	$C_{14}H_{13}ON_2SF$	61·0	5·0	60·8	4·7
2-Ethoxy-4′-fluoro-	134	$C_{15}H_{15}ON_2SF$	62·0	5·2	62·0	5·1
4-Ethyl-	129	$C_{15}H_{16}N_2S$	70·2	6·5	70·3	6·2
4-Ethyl-4′-methyl-	155	$C_{16}H_{18}N_2S$	71·3	6·5	71·1	6·6
4-Ethyl-4′-methoxy-	163	$C_{16}H_{18}ON_2S$	67·0	6·2	67·1	6·2
4-Ethoxy-4′-ethyl-	158	$C_{17}H_{20}ON_2S$	67·8	6·9	68·0	6·6
2-Ethoxy-4′-ethyl-	148	$C_{17}H_{20}ON_2S$	67·8	6·6	68·0	6·6
4-Ethyl-4′-*iso*pentyloxy-	138	$C_{20}H_{26}ON_2S$	70·0	7·6	70·1	7·6
4-Bromo-4′-ethyl-	198	$C_{15}H_{15}N_2SBr$	53·3	4·3	53·7	4·4
4-Ethyl-2′ : 4′-dimethyl-	119	$C_{17}H_{20}N_2S$	71·5	7·2	71·8	7·0
4-Ethyl-2′ : 3′-dimethyl-	172	$C_{17}H_{20}N_2S$	71·8	7·3	71·8	7·0
4-Ethyl-4′-*n*-propoxy-	154	$C_{18}H_{22}ON_2S$	68·5	7·1	68·7	7·0

TABLE 1. (*Continued.*)

Thiocarbanilide	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
4-Ethyl-4'-*iso*propoxy-	134°	$C_{18}H_{22}ON_2S$	68·5	7·3	68·7	7·0
4-Bromo-3'-fluoro-6'-methoxy-	152	$C_{14}H_{12}ON_2SBrF$	47·0	3·1	47·3	3·3
4-*n*-Butoxy-4'-ethyl-	144	$C_{19}H_{24}ON_2S$	69·5	7·2	69·5	7·3
4-*iso*Butoxy-4'-ethyl-	146	$C_{19}H_{24}ON_2S$	69·6	7·6	69·5	7·3
4-Ethyl-4'-fluoro-	168	$C_{15}H_{15}N_2SF$	65·4	5·4	65·6	5·4
4-Chloro-4'-ethyl-	197	$C_{15}H_{15}N_2SCl$	61·6	5·2	61·9	5·1
4-*n*-Propyl-	126	$C_{16}H_{18}N_2S$	71·0	6·6	71·1	6·6
4-Methyl-4'-*n*-propyl-	131	$C_{17}H_{20}N_2S$	71·6	7·0	71·8	7·0
4-Methoxy-4'-*n*-propyl-	164	$C_{17}H_{20}ON_2S$	67·9	6·6	68·0	6·6
4-Methoxy-4'-sulphonamido-	232—234	$C_{14}H_{15}O_3N_3S_2$	49·5	4·2	49·8	4·4
2-Methoxy-4'-*n*-propyl-	129	$C_{17}H_{20}ON_2S$	68·1	6·5	68·0	6·6
4-Ethoxy-4'-*n*-propyl-	166	$C_{18}H_{22}ON_2S$	68·5	7·1	68·7	7·0
2-Ethoxy-4'-*n*-propyl-	161	$C_{18}H_{22}ON_2S$	68·4	7·2	68·7	7·0
4-*iso*Pentyloxy-4'-*n*-propyl-	138	$C_{21}H_{28}ON_2S$	70·8	8·0	70·7	7·8
4-Bromo-4'-*n*-propyl-	187	$C_{16}H_{17}N_2SBr$	54·7	5·0	55·0	4·8
2 : 4-Dimethyl-4'-*n*-propyl-	129	$C_{18}H_{22}N_2S$	72·6	7·5	72·4	7·3
2-Phenyl-4'-*n*-propyl-	143	$C_{22}H_{22}N_2S$	76·5	6·2	76·3	6·3
4-*n*-Propoxy-4'-*n*-propyl-	168	$C_{19}H_{24}ON_2S$	69·6	7·6	69·5	7·3
4-*iso*Propoxy-4'-*n*-propyl-	155	$C_{19}H_{24}ON_2S$	69·4	7·5	69·5	7·3
4-*n*-Butoxy-4'-*n*-propyl-	157	$C_{20}H_{26}ON_2S$	70·0	7·5	70·1	7·6
4-*iso*Butoxy-4'-*n*-propyl-	159	$C_{20}H_{26}ON_2S$	70·2	7·6	70·1	7·6
4-Fluoro-4'-*n*-propyl-	157	$C_{16}H_{17}N_2SF$	66·6	6·0	66·6	5·9
4-Chloro-4'-*n*-propyl-	177	$C_{16}H_{17}N_2SCl$	62·8	5·5	63·0	5·5
4-*n*-Butyl-	144	$C_{17}H_{20}N_2S$	71·7	7·2	71·8	7·0
4-*n*-Butyl-4'-methyl-	137	$C_{18}H_{22}N_2S$	72·3	7·5	72·4	7·3
4-*n*-Butyl-4'-methoxy-	169	$C_{18}H_{22}ON_2S$	68·4	7·1	68·7	7·0
4-*n*-Butyl-2'-methoxy-	121	$C_{18}H_{22}ON_2S$	68·5	7·2	68·7	7·0
4-*n*-Butyl-4'-ethoxy-	159	$C_{19}H_{24}ON_2S$	69·4	7·2	69·5	7·3
4-*n*-Butyl-2'-ethoxy-	138	$C_{19}H_{24}ON_2S$	69·2	7·1	69·5	7·3
4-*n*-Butyl-4'-*iso*pentyloxy-	132	$C_{22}H_{30}ON_2S$	71·3	8·2	71·3	8·1
4-*n*-Butyl-4'-*n*-propoxy-	167	$C_{20}H_{26}ON_2S$	70·2	7·6	70·1	7·6
4-*n*-Butyl-4'-*iso*propoxy-	138	$C_{20}H_{26}ON_2S$	70·2	7·8	70·1	7·6
4-*n*-Butoxy-4'-*n*-butyl-	161	$C_{21}H_{28}ON_2S$	70·4	7·9	70·7	7·8
4-*iso*Butoxy-4'-*n*-butyl-	151	$C_{21}H_{28}ON_2S$	70·7	7·8	70·7	7·8
4-*n*-Butyl-4'-fluoro-	162	$C_{17}H_{19}N_2SF$	67·4	6·4	67·5	6·2
4-*n*-Butyl-4'-chloro-	174	$C_{17}H_{19}N_2SCl$	64·2	5·8	64·0	5·9
4-Bromo-4'-*n*-butyl-	181	$C_{17}H_{19}N_2SBr$	56·0	5·0	56·1	5·2
4-Fluoro-4'-*n*-heptyl-	158	$C_{20}H_{25}N_2SF$	69·5	7·5	69·7	7·2
4-Chloro-4'-*n*-heptyl-	167	$C_{20}H_{25}N_2SCl$	66·3	6·8	66·5	6·9
4-Bromo-4'-*n*-heptyl-	176	$C_{20}H_{25}N_2SBr$	59·4	6·1	59·2	6·1
4-Ethoxy-4'-sulphonamido [a]	246	$C_{15}H_{17}O_3N_3S_2$	—	—	—	—
4-*n*-Heptyl-4'-methyl	129	$C_{21}H_{28}N_2S$	74·0	8·5	74·1	8·2
4-Ethoxy-4'-*n*-heptyl-	151	$C_{22}H_{30}ON_2S$	71·3	8·3	71·3	8·1
4-*n*-Heptyl-4'-*n*-propoxy-	156	$C_{23}H_{32}ON_2S$	71·7	7·9	71·8	8·0
4-*n*-Heptyl-4'-*iso*propoxy-	136	$C_{23}H_{32}ON_2S$	71·6	8·0	71·8	8·0
4-*n*-Butoxy-4'-*n*-heptyl-	151	$C_{24}H_{34}ON_2S$	72·5	8·5	72·3	8·5
4-*iso*Butoxy-4'-*n*-heptyl-	116	$C_{24}H_{34}ON_2S$	72·2	8·6	72·3	8·5
4-*n*-Heptyl-4'-*iso*pentyloxy-	112	$C_{25}H_{36}ON_2S$	72·9	8·7	72·8	8·4
4-Ethyl-4'-*n*-propyl-	139	$C_{18}H_{22}N_2S$	72·3	7·5	72·4	7·3
4-*n*-Butyl-4'-*n*-propyl-	164	$C_{20}H_{26}N_2S$	73·5	8·0	73·6	7·9
4-*n*-Heptyl-4'-*n*-propyl-	138	$C_{23}H_{32}N_2S$	74·7	8·8	75·0	8·6
4-*n*-Butyl-4'-ethyl-	138	$C_{19}H_{24}N_2S$	72·9	7·9	73·0	7·6
4-*n*-Butyl-4'-*n*-heptyl-	140	$C_{24}H_{34}N_2S$	75·4	8·9	75·3	8·8
2-Methylthio-	189	$C_{14}H_{14}N_2S_2$	61·5	5·0	61·2	5·1
4-Methyl-2'-methylthio-	204	$C_{15}H_{16}N_2S_2$	62·6	5·8	62·5	5·5
3-Methyl-2'-methylthio-	174	$C_{15}H_{16}N_2S_2$	62·4	5·6	62·5	5·5
2-Methylthio-4'-*n*-propyl-	183	$C_{17}H_{20}N_2S_2$	64·3	6·2	64·5	6·3
4-*n*-Butyl-2'-methylthio-	179	$C_{18}H_{22}N_2S_2$	65·1	6·6	65·4	6·6
4-Ethoxy-2'-methylthio-	202	$C_{16}H_{18}ON_2S_2$	60·0	5·5	60·3	5·6
2-Methylthio-4'-*n*-propoxy-	204	$C_{17}H_{20}ON_2S_2$	61·3	6·2	61·4	6·0
2-Methylthio-4'-*iso*propoxy-	144	$C_{17}H_{20}ON_2S_2$	61·2	6·1	61·4	6·0
4-*n*-Butoxy-2'-methylthio-	194	$C_{18}H_{22}ON_2S_2$	62·1	6·3	62·4	6·3
4-*iso*Butoxy-2'-methylthio-	207	$C_{18}H_{22}ON_2S_2$	62·2	6·2	62·4	6·3
2-Methylthio-4'-*iso*pentyloxy-	189	$C_{19}H_{24}ON_2S_2$	63·0	6·9	63·3	6·6
4-Fluoro-2'-methylthio-	217	$C_{14}H_{13}N_2S_2F$	57·2	4·6	57·5	4·4
4-Chloro-2'-methylthio-	225	$C_{14}H_{13}N_2S_2Cl$	54·1	4·2	54·4	4·2
4-Bromo-2'-methylthio-	228	$C_{14}H_{13}N_2S_2Br$	47·5	3·8	47·5	3·6
2-Methylseleno-	196	$C_{14}H_{14}N_2SSe$	52·1	4·1	52·3	4·3

[a] No m. p. available in the literature for this compound (Ganapathi, *J. Indian Chem. Soc.*, 1938, **15**, 255; *Proc. Indian Acad. Sci.*, 1940, **11**, *A*, 298).

TABLE 1. (*Continued.*)

Thiocarbanilide	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
4-Methyl-2′-methylseleno-	209°	$C_{15}H_{16}N_2SSe$	53·4	4·7	53·7	4·7
3-Methyl-2′-methylseleno-	176	$C_{15}H_{16}N_2SSe$	53·6	4·6	53·7	4·7
2-Methylseleno-4′-*n*-propyl-	182	$C_{17}H_{20}N_2SSe$	56·0	5·8	56·2	5·5
4-*n*-Butyl-2′-methylseleno-	178	$C_{18}H_{22}N_2SSe$	57·0	5·8	57·2	5·8
4-Ethoxy-2′-methylseleno-	207	$C_{16}H_{18}ON_2SSe$	52·5	5·2	52·6	4·9
2-Methylseleno-4′-*n*-propoxy-	203	$C_{17}H_{20}ON_2SSe$	53·5	5·1	53·8	5·2
2-Methylseleno-4′-*iso*propoxy-	151	$C_{17}H_{20}ON_2SSe$	53·7	5·3	53·8	5·2
4-*n*-Butoxy-2′-methylseleno-	195	$C_{18}H_{22}ON_2SSe$	54·6	5·8	54·9	5·5
4-*iso*Butoxy-2′-methylseleno-	198	$C_{18}H_{22}ON_2SSe$	54·8	5·8	54·9	5·5
2-Methylseleno-4′-*iso*pentyloxy-	189	$C_{19}H_{24}ON_2SSe$	56·2	5·7	56·0	5·8
4-Fluoro-2′-methylseleno-	221	$C_{14}H_{13}N_2SSeF$	49·2	4·1	49·5	3·8
4-Chloro-2′-methylseleno-	226	$C_{14}H_{13}N_2SSeCl$	47·0	3·5	47·2	3·6
4-Bromo-2′-methylseleno-	232	$C_{14}H_{13}N_2SSeBr$	41·7	3·1	42·0	3·2
4-Chloro-4′-fluoro-6-methoxy-	139	$C_{14}H_{12}ON_2SFCl$	53·8	4·0	54·1	3·8
4-Chloro-4′-fluoro-5′-methyl-	181	$C_{14}H_{12}N_2SFCl$	56·7	4·1	57·0	4·0
4-Chloro-5′-fluoro-4′-methoxy-	179	$C_{14}H_{12}ON_2SFCl$	54·0	4·1	54·1	3·8
3-Fluoro-6-methoxy-4′-methyl-	148	$C_{15}H_{15}ON_2SF$	62·2	5·2	62·0	5·1
4-Ethoxy-3′-fluoro-6′-methoxy-	163	$C_{16}H_{17}O_2N_2SF$	60·1	5·5	60·0	5·3
3-Fluoro-6-methoxy-4′-*iso*pentyloxy-	93	$C_{19}H_{23}O_2N_2SF$	63·2	6·1	62·9	6·3
4-Phenyl-	208	$C_{19}H_{16}N_2S$	75·2	5·5	75·0	5·2
4-Fluoro-4′-phenyl-	221	$C_{19}H_{15}N_2SF$	71·0	4·5	70·8	4·6
4-Bromo-4′-phenyl-	229	$C_{19}H_{15}N_2SBr$	59·2	4·0	59·5	3·9
4-*n*-Heptyl-4′-phenyl-	219	$C_{26}H_{30}N_2S$	77·5	7·4	77·6	7·4
4-Methoxy-4′-phenyl-	211	$C_{20}H_{18}ON_2S$	71·5	5·5	71·8	5·3
2-Methoxy-4′-phenyl-	223	$C_{20}H_{18}ON_2S$	71·6	5·6	71·8	5·3
4-Ethoxy-4′-phenyl-	226	$C_{21}H_{20}ON_2S$	72·3	5·5	72·4	5·7
2-Ethoxy-4′-phenyl-	232	$C_{21}H_{20}ON_2S$	72·1	5·9	72·4	5·7
4-*iso*Butoxy-4′-phenyl-	225	$C_{23}H_{24}ON_2S$	73·2	6·2	73·4	6·3
4-*iso*Pentyloxy-4′-phenyl-	195	$C_{24}H_{26}ON_2S$	74·1	6·5	73·8	6·6
2 : 4′-Diphenyl-	226	$C_{25}H_{20}N_2S$	78·8	5·4	78·9	5·2
2 : 5-Dichloro-	177	$C_{13}H_{10}N_2SCl_2$	52·2	3·4	52·5	3·3
2 : 5-Dichloro-4′-fluoro-	174	$C_{13}H_9N_2SFCl_2$	49·4	3·0	49·5	2·8
2 : 5-Dichloro-4′-chloro-	201	$C_{13}H_9N_2SCl_3$	46·8	2·9	47·0	2·7
4-Bromo-2′ : 5′-dichloro-	193	$C_{13}H_9N_2SCl_2Br$	41·1	2·2	41·4	2·3
2 : 5-Dichloro-4′-methyl-	162	$C_{14}H_{12}N_2SCl_2$	54·2	3·8	54·0	3·8
2 : 5-Dichloro-3′-methyl-	156	$C_{14}H_{12}N_2SCl_2$	53·7	3·6	54·0	3·8
2 : 5-Dichloro-4′-methoxy-	177	$C_{14}H_{12}ON_2SCl_2$	51·0	3·5	51·3	3·6
2 : 5-Dichloro-2′-methoxy-	154	$C_{14}H_{12}ON_2SCl_2$	51·2	3·6	51·3	3·6
2 : 5-Dichloro-4′-ethoxy-	172	$C_{15}H_{14}ON_2SCl_2$	52·8	4·3	52·7	4·1
2 : 5-Dichloro-4′-*n*-propoxy-	158	$C_{16}H_{16}ON_2SCl_2$	53·7	4·4	54·0	4·5
2 : 5-Dichloro-4′-*iso*propoxy-	151	$C_{16}H_{16}ON_2SCl_2$	54·1	4·3	54·0	4·5
4-*n*-Butoxy-2′ : 5′-dichloro-	145	$C_{17}H_{18}ON_2SCl_2$	55·0	5·0	55·2	4·8
4-*iso*Butoxy-2′ : 5′-dichloro-	161	$C_{17}H_{18}ON_2SCl_2$	55·1	4·6	55·2	4·8
2-Methoxy-5-methyl-	181	$C_{15}H_{16}ON_2S$	66·2	5·6	66·1	5·8
2-Methoxy-4′-fluoro-5-methyl-	142	$C_{15}H_{15}ON_2SF$	62·2	5·2	62·0	5·1
4-Chloro-2′-methoxy-5′-methyl-	153	$C_{15}H_{15}ON_2SCl$	58·4	4·9	58·7	4·8
4-Bromo-2′-methoxy-5′-methyl-	161	$C_{15}H_{15}ON_2SBr$	51·0	4·4	51·2	4·2
2-Methoxy-5 : 4′-dimethyl-	139	$C_{16}H_{18}ON_2S$	67·0	6·3	67·1	6·2
2-Methoxy-5 : 3′-dimethyl-	129	$C_{16}H_{18}ON_2S$	67·3	6·1	67·1	6·2

(*b*) *Symmetrical substituted thiocarbanilides.*

4 : 4′-Dichloro-2 : 2′-dimethoxy-	151—152°	$C_{15}H_{14}O_2N_2SCl_2$	50·3	4·0	50·4	3·9
2 : 3 : 2′ : 3′-Tetramethyl-	224	$C_{17}H_{20}N_2S$	71·5	7·3	71·8	7·0
4 : 4′-Di-*n*-heptyloxy-	155	$C_{27}H_{40}O_2N_2S$	71·1	8·9	71·0	8·7
2 : 2′-Diethoxy-	126	$C_{17}H_{20}O_2N_2S$	64·3	6·3	64·5	6·3
4 : 4′-Di-(3-phenylpropyloxy)-	159—160	$C_{31}H_{32}O_2N_2S$	75·1	6·3	75·6	6·4
2 : 2′-Diphenyl-	165—166	$C_{25}H_{20}N_2S$	79·1	5·5	78·9	5·2
4 : 4′-Di-*n*-propyl-	154	$C_{19}H_{24}N_2S$	—	—	—	—
4 : 4′-Di-*n*-butyl-	159	$C_{21}H_{28}N_2S$	—	—	—	—
4 : 4′-Di-*n*-heptyl-	152	$C_{27}H_{40}N_2S$	76·3	9·4	76·4	9·4
2 : 2′-Dimethylthio-	159	$C_{15}H_{16}H_2S_3$	56·0	5·3	56·2	5·0
2 : 2′-Dimethylseleno-	167	$C_{15}H_{16}N_2Se_2$	47·3	4·2	47·6	4·1
4 : 4′-Di*iso*propoxy-	142	$C_{19}H_{24}O_2N_2S$	66·3	7·1	66·2	6·9
2 : 2′-Di-*tert.*-butyl-	182	$C_{21}H_{28}N_2S$	74·3	8·3	74·1	8·2
4 : 4′-Disulphonamido-	d. *ca.* 248 *	$C_{13}H_{14}O_4N_4S_3$	—	—	—	—
2 : 2′-Dimethoxy-5 : 5′-dimethyl-	146	$C_{17}H_{20}O_2N_2S$	64·2	6·1	64·5	6·3
4 : 4′-Difluoro-	208	$C_{13}H_{10}N_2SF_2$	59·0	3·6	59·1	3·8
3 : 3′ : 4 : 4′-Tetrachloro-[b]	180—181	$C_{13}H_8N_2SCl_4$	42·3	2·2	42·6	2·1

[b] Dyson, George, and Hunter (*J.*, 1926, 3042) gave m. p. 144°

prepared free from *o*- and *m*-isomers by Beckmann rearrangement of the appropriate 4-alkylacetophenone oximes, and hydrolysis of the resulting *p*-alkylacetanilides. *p*-*n*-Propylaniline thus obtained had b. p. 229°, n_D^{23} 1·5428; the product prepared by alkylating aniline with *n*-propyl alcohol and zinc chloride (Francksen, *Ber.*, 1884, **17**, 1221) must have been impure, as the 4 : 4'-di-*n*-propylthiocarbanilide derived from it was reported to melt at 138°, whereas a pure sample was now found to melt at 154°. Pure *p*-*n*-butylaniline had b. p. 242°, n_D^{23} 1·5361; Reilly and Hickinbottom (*J.*, 1918, **113**, 983) gave b. p. 258—260°/750 mm. p-n-*Heptylaniline* was a pale yellow oil, b. p. 286°, n_D^{23} 1·5205 (Found: C, 81·5; H, 11·3. $C_{13}H_{31}N$ requires C, 81·7; H, 11·0%); Auger (*Bull. Soc. chim. France*, 1887, **47**, 50) gave b. p. 175°/10 mm. for an amine prepared by reduction of a nitro-*n*-heptylbenzene of unknown constitution.

TABLE 2. NN'-*Disubstituted thioureas*, R·NH·CS·NHR'.

R'	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
R = 1-$C_{10}H_7$.						
p-Fluorophenyl-	185°	$C_{17}H_{13}N_2SF$	68·6	4·1	68·9	4·3
p-Chlorophenyl	192	$C_{17}H_{13}N_2SCl$	65·0	4·3	65·2	4·1
m-Chlorophenyl-	156	$C_{17}H_{13}N_2SCl$	65·1	4·1	65·2	4·1
2 : 5-Dichlorophenyl-	202	$C_{17}H_{12}N_2SCl_2$	58·3	3·4	58·7	3·4
3 : 4-Dichlorophenyl-	191	$C_{17}H_{12}N_2SCl_2$	58·5	3·5	58·7	3·4
p-Bromophenyl-	226	$C_{17}H_{13}N_2SBr$	56·3	3·5	56·6	3·6
p-Tolyl-	204	$C_{18}H_{16}N_2S$	74·0	5·5	73·9	5·4
2 : 4-Dimethylphenyl-	189	$C_{19}H_{18}N_2S$	74·7	6·0	74·5	5·8
p-Ethylphenyl-	173	$C_{19}H_{18}N_2S$	74·3	6·0	74·5	5·8
n-Propylphenyl-	168	$C_{20}H_{20}N_2S$	74·8	6·1	75·0	6·2
n-Butylphenyl-	164	$C_{21}H_{22}N_2S$	75·5	6·5	75·4	6·5
p-*n*-Heptylphenyl-	149	$C_{24}H_{28}N_2S$	76·5	7·6	76·5	7·4
p-Hydroxyphenyl-	208	$C_{17}H_{14}ON_2S$	69·0	4·8	69·3	4·7
p-Methoxyphenyl-	194	$C_{18}H_{16}ON_2S$	70·0	5·2	70·1	5·1
3-Fluoro-6-methoxyphenyl-	137	$C_{18}H_{15}ON_2SF$	66·0	4·8	66·2	4·6
2 : 5-Dimethoxyphenyl-	153	$C_{19}H_{18}O_2N_2S$	67·1	5·2	67·4	5·3
p-Phenetyl-	201	$C_{19}H_{18}ON_2S$	70·7	5·5	70·8	5·5
o-Phenetyl-	164	$C_{19}H_{18}ON_2S$	70·5	5·6	70·8	5·5
p-*n*-Butoxyphenyl-	157	$C_{21}H_{22}ON_2S$	72·2	6·5	72·0	6·2
p-*iso*Butoxyphenyl-	166	$C_{21}H_{22}ON_2S$	72·0	6·1	72·0	6·2
p-*iso*Pentyloxyphenyl-	163	$C_{22}H_{24}ON_2S$	72·3	6·8	72·2	6·5
p-3-Phenylpropoxyphenyl-	152	$C_{26}H_{24}ON_2S$	75·6	5·9	75·7	5·8
o-Methylthiophenyl-	178	$C_{18}H_{16}N_2S_2$	66·3	4·9	66·6	4·9
o-Methylselenophenyl-	174	$C_{18}H_{16}N_2SSe$	58·8	4·4	59·1	4·3
p-Dimethylaminophenyl-	189	$C_{19}H_{19}N_3S$	70·8	6·1	71·0	5·9
2-Naphthyl-	201	$C_{21}H_{16}N_2S$	76·5	5·0	76·8	4·8
5-Hydroxy-1-naphthyl-	219	$C_{21}H_{16}ON_2S$	73·0	4·5	73·2	4·6
4-Chloro-1-naphthyl-	212	$C_{21}H_{15}N_2SCl$	69·2	4·1	69·5	4·1
R = 2-$C_{10}H_7$.						
p-Fluorophenyl-	203	$C_{17}H_{13}N_2SF$	68·6	4·2	68·9	4·3
p-Chlorophenyl-	215	$C_{17}H_{13}N_2SCl$	65·0	4·2	65·2	4·1
2 : 5-Dichlorophenyl-	179	$C_{17}H_{12}N_2SCl_2$	58·7	3·7	58·7	3·4
p-Bromophenyl-	212	$C_{17}H_{13}N_2SBr$	56·3	3·6	56·6	3·6
p-Tolyl-	171	$C_{18}H_{16}N_2S$	73·6	5·5	73·9	5·4
2 : 4-Dimethylphenyl-	168	$C_{19}H_{18}N_2S$	74·2	6·0	74·5	5·8
p-Ethylphenyl-	183	$C_{19}H_{18}N_2S$	74·6	6·1	74·5	5·8
p-*n*-Propylphenyl-	179	$C_{20}H_{20}N_2S$	74·9	6·2	75·0	6·2
n-Butylphenyl-	179	$C_{21}H_{22}N_2S$	75·5	6·6	75·4	6·5
o-*tert*.-Butylphenyl-	200	$C_{21}H_{22}N_2S$	75·1	6·4	75·4	6·5
p-*n*-Heptylphenyl-	176	$C_{24}H_{28}N_2S$	76·6	7·4	76·5	7·4
p-Hydroxyphenyl-	224	$C_{17}H_{14}ON_2S$	69·0	4·9	69·3	4·7
p-Methoxyphenyl-	192	$C_{18}H_{16}ON_2S$	70·0	5·1	70·1	5·1
3-Fluoro-6-methoxyphenyl-	137	$C_{18}H_{15}ON_2SF$	66·0	4·8	66·2	4·6
2 : 5-Dimethoxyphenyl-	166	$C_{19}H_{18}O_2N_2S$	67·5	5·5	67·4	5·3
p-Phenetyl-	190	$C_{19}H_{18}ON_2S$	70·7	5·4	70·8	5·5
p-*iso*Butoxyphenyl-	179	$C_{21}H_{22}ON_2S$	71·8	6·4	72·0	6·2
p-*n*-Butoxyphenyl-	185	$C_{21}H_{22}ON_2S$	72·1	6·1	72·0	6·2
p-*n*-Heptyloxyphenyl-	176	$C_{24}H_{28}ON_2S$	73·3	7·3	73·4	7·1
p-3-Phenylpropoxyphenyl-	171	$C_{26}H_{24}ON_2S$	75·4	6·0	75·7	5·8
o-Methylthiophenyl-	205	$C_{18}H_{16}N_2S_2$	66·5	5·0	66·6	4·9
o-Methylselenophenyl-	210	$C_{18}H_{16}N_2SSe$	59·0	4·1	59·1	4·3
p-Dimethylaminophenyl-	172	$C_{19}H_{19}N_3S$	70·8	6·0	71·0	5·9
4-Diphenylyl-	242	$C_{23}H_{18}N_2S$	78·0	5·1	77·9	5·0
2-Diphenylyl-	192	$C_{23}H_{18}N_2S$	77·9	5·3	77·9	5·0
4-Chloro-1-naphthyl-	189	$C_{21}H_{15}N_2SCl$	69·2	4·3	69·5	4·1

TABLE 2. (*Continued.*)

R′	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
R = 2-pyridyl.						
p-Fluorophenyl-	178°	$C_{12}H_{10}N_3SF$	58·0	4·0	58·2	4·0
p-Chlorophenyl-	208	$C_{12}H_{10}N_3SCl$	54·3	3·8	54·6	3·7
p-Bromophenyl-	224	$C_{12}H_{10}N_3SBr$	46·4	3·2	46·6	3·2
p-Tolyl-	192	$C_{13}H_{13}N_3S$	64·0	5·5	64·1	5·3
m-Tolyl-	174	$C_{13}H_{13}N_3S$	64·2	5·3	64·1	5·3
2 : 4-Dimethylphenyl-	193	$C_{14}H_{15}N_3S$	65·0	6·0	65·3	5·8
p-*n*-Butylphenyl-	156	$C_{16}H_{19}N_3S$	67·3	6·8	67·3	6·6
p-Methoxyphenyl-	208	$C_{13}H_{13}ON_3S$	60·1	5·3	60·2	5·0
p-Phenetyl-	209	$C_{14}H_{15}ON_3S$	61·3	5·5	61·5	5·4
p-*n*-Propoxyphenyl-	171	$C_{15}H_{17}ON_3S$	62·8	6·2	62·7	5·9
p-*n*-Butoxyphenyl-	149	$C_{16}H_{19}ON_3S$	63·8	6·5	63·7	6·3
p-*iso*Pentyloxyphenyl-	146	$C_{17}H_{21}ON_3S$	64·4	6·7	64·7	6·6
2-Diphenylyl-	176	$C_{18}H_{15}N_3S$	70·5	5·1	70·8	4·9
1-Naphthyl-	236	$C_{16}H_{13}N_3S$	68·6	4·5	68·8	4·6
2-Naphthyl-	242	$C_{16}H_{13}N_3S$	68·5	4·3	68·8	4·6
R = 2-thiazolyl.						
p-Fluorophenyl-	181	$C_{10}H_8N_3S_2F$	47·3	3·1	47·4	3·1
p-Chlorophenyl-	204	$C_{10}H_8N_3S_2Cl$	44·3	3·1	44·5	2·9
p-Bromophenyl-	206	$C_{10}H_8N_3S_2Br$	38·0	2·8	38·2	2·5
p-Tolyl-	201	$C_{11}H_{11}N_3S_2$	53·1	4·7	53·0	4·4
2 : 4-Dimethylphenyl-	204	$C_{12}H_{13}N_3S_2$	54·6	4·7	54·7	4·9
p-*n*-Propylphenyl-	204	$C_{13}H_{15}N_3S_2$	56·5	5·3	56·3	5·4
p-Methoxyphenyl-	212	$C_{11}H_{11}ON_3S_2$	49·6	4·1	49·8	4·1
p-Phenetyl-	203	$C_{12}H_{13}ON_3S_2$	51·3	4·5	51·6	4·6
1-Naphthyl-	235	$C_{14}H_{11}N_3S_2$	59·0	3·5	58·9	3·8
2-Naphthyl-	232	$C_{14}H_{11}N_3S_2$	58·6	3·9	58·9	3·8
Various thioureas.						
NN′-Di-(1 : 2-dihydroindan-5-yl)-	127—128	$C_{19}H_{20}NS$	74·2	6·5	74·0	6·4
NN′-Di-(4-chloro-1-naphthyl)-	202	$C_{21}H_{14}N_2SCl_2$	63·3	3·6	63·4	3·5
N-(4-Chloro-1-naphthyl)-*N*′-*p*-fluorophenyl-	199	$C_{17}H_{12}N_2SClF$	61·5	3·5	61·8	3·6
N-(4-Chloro-1-naphthyl)-*N*′-2-diphenylyl-	198	$C_{23}H_{17}N_2SCl$	70·9	4·5	71·0	4·3
N-*p*-Butoxyphenyl-*N*′-(5-hydroxy-1-naphthyl)-	181	$C_{21}H_{22}O_2N_2S$	68·6	6·2	68·8	6·0
N-(6-Methyl-2-pyridyl)-*N*′-1-naphthyl-	212	$C_{17}H_{15}N_3S$	69·8	5·0	69·6	5·1
N-(6-Methyl-2-pyridyl)-*N*′-2-naphthyl-	252	$C_{17}H_{15}N_3S$	69·5	5·3	69·6	5·1
NN′-Di-2-thiazolyl-	260	$C_7H_6N_4S_3$	34·5	2·7	34·7	2·4

p-Alkyloxyanilines were prepared in good yields (75—90%) by refluxing for 4—6 hr. an ethanol solution of *p*-formamidophenol (1 mol.) and potassium hydroxide (1 mol.) with the appropriate alkyl bromide (1 mol.), and subsequent alkaline hydrolysis of the crude *p*-alkyloxyformanilide. The following amines were thus obtained: p-iso*Propoxyaniline*, pale yellow oil darkening rapidly on exposure to the air, b. p. 146—147°/15 mm., n_D^{18} 1·5471 (Found: C, 71·4; H, 8·5. $C_9H_{13}ON$ requires C, 71·5; H, 8·6%); *p*-*n*-propoxyaniline, n_D^{25} 1·5455; *p*-*n*-butoxyaniline, n_D^{28} 1·5398; *p*-*iso*butoxyaniline, b. p. 149—150°/15 mm.; *p*-*iso*pentyloxyaniline, n_D^{26} 1·5302; p-n-*pentyloxyaniline*, b. p. 175—176°/17 mm., n_D^{26} 1·5345 (Found: C, 73·5; H, 9·6. $C_{11}H_{17}ON$ requires C, 73·7; H, 9·5%); p-n-*heptyloxyaniline*, b. p. 202—204°/16 mm., shiny leaflets, m. p. 46—47° (from ligroin) (Found: C, 75·3; H, 10·2. $C_{13}H_{21}ON$ requires C, 75·4; H, 10·1%); p-3′-*phenylpropoxyaniline*, b. p. 234—236°/15 mm., colourless needles, m. p. 58° (from ligroin) (Found: C, 79·1; H, 7·4. $C_{15}H_{17}ON$ requires C, 79·3; H, 7·5%). *p*-Alkyloxyanilines have usually been prepared in low yields by reduction of the corresponding nitro-compounds (cf. Spiegel and Sabbath, *Ber.*, 1901, **34**, 1938; Gutekunst and Gray, *J. Amer. Chem. Soc.*, 1922, **44**, 1744), or by alkylation of *p*-benzylideneaminophenol and subsequent hydrolysis (Philipp, *Ber.*, 1892, **25**, 3248; Höchster Farbwerke, D.R.-P. 69,006).

Characterisation of the Amines.—Condensation of the amines (1 mol.) with acetonylacetone (1·5 mol.) was effected by refluxing the mixture for 30 min., and the 1-*aryl*-2 : 5-*dimethylpyrroles* formed (Table 3) were distilled *in vacuo*; the solid products were crystallised from methanol (the yields range from 90 to 100%). Table 4 records new 2-*arylamino*-3-*chloro*-1 : 4-*naphthaquinones*, obtained by briefly refluxing an ethanol solution of the arylamine (1 mol.), 2 : 3-dichloro-1 : 4-naphthaquinone (1 mol.), and sodium acetate (1 mol.); the precipitate obtained on

TABLE 3. N-*Substituted* 2 : 5-*dimethylpyrroles.*

N-Substituent	B. p./mm.	M. p.	*n*	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
p-*n*-Propoxyphenyl-	176°/13	47°	—	$C_{15}H_{19}ON$	78·5	8·5	78·6	8·2
p-*iso*Propoxyphenyl-	177/25	—	n_D^{52} 1·5485	$C_{15}H_{19}ON$	78·3	8·1	78·6	8·2
p-*iso*Butoxyphenyl-	179/14	45	—	$C_{16}H_{21}ON$	78·8	8·9	79·0	8·6
p-*n*-Butoxyphenyl-	186/13	39	—	$C_{16}H_{21}ON$	79·1	8·5	79·0	8·6
p-*iso*Pentyloxyphenyl-	189/13	—	$n_D^{19\cdot5}$ 1·4675	$C_{17}H_{23}ON$	79·0	9·1	79·3	8·9
p-*n*-Pentyloxyphenyl-	189—192/13	—	n_D^{21} 1·4557	$C_{17}H_{23}ON$	79·3	9·1	79·3	8·9
p-*n*-Heptyloxyphenyl-	222/15	—	n_D^{26} 1·4355	$C_{19}H_{27}ON$	79·9	9·3	80·0	9·4
p-3-Phenylpropoxyphenyl-	260/16	68—69	—	$C_{21}H_{23}ON$	82·3	7·6	82·6	7·5
o-Ethoxyphenyl-	158—160/13	—	$n_D^{19\cdot5}$ 1·5404	$C_{14}H_{17}ON$	78·0	7·9	78·1	7·9
p-*n*-Propylphenyl-	164/23	—	n_D^{25} 1·5479	$C_{15}H_{19}N$	84·7	8·8	84·5	8·9
p-*n*-Butylphenyl-	178/25	—	n_D^{24} 1·5426	$C_{16}H_{21}N$	84·5	9·5	84·5	9·2
p-*n*-Heptylphenyl-	208/25	—	n_D^{25} 1·5296	$C_{19}H_{27}N$	84·9	10·2	84·7	10·0
o-Methylthiophenyl-	—	91	—	$C_{13}H_{15}NS$	71·5	6·9	71·8	6·9

TABLE 4. 2-*Substituted* 3-*chloro*-1 : 4-*naphthaquinones.*

2-Substituent	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
p-*n*-Propylanilino-	141°	$C_{19}H_{16}O_2NCl$	69·8	4·6	70·0	4·9
p-*n*-Butylanilino-	139	$C_{20}H_{18}O_2NCl$	70·3	5·1	70·6	5·3
p-*n*-Heptylanilino-	124	$C_{23}H_{24}O_2NCl$	72·1	6·1	72·3	6·2
p-*n*-Propoxyanilino-	162	$C_{19}H_{16}O_3NCl$	66·8	4·6	66·7	4·6
p-*iso*Propoxyanilino-	176	$C_{19}H_{16}O_3NCl$	66·5	4·5	66·7	4·6
p-*n*-Butoxyanilino-	155	$C_{20}H_{18}O_3NCl$	67·2	5·2	67·5	5·0
p-*iso*Butoxyanilino-	181	$C_{20}H_{18}NCl$	67·5	5·1	67·5	5·0
p-*n*-Pentyloxyanilino-	147	$C_{21}H_{20}O_3NCl$	68·0	5·6	68·2	5·4
p-*iso*Pentyloxyanilino-	145	$C_{21}H_{20}O_3NCl$	68·3	5·5	68·2	5·4
p-*n*-Heptyloxyanilino-	136	$C_{25}H_{24}O_3NCl$	69·6	6·1	69·4	6·0
p-3-Phenylpropoxyanilino-	170	$C_{25}H_{20}O_3NCl$	72·0	4·9	71·8	4·7
3 : 4-Dichloroanilino- [a]	246	$C_{16}H_8O_2NCl_3$	54·1	2·5	54·4	2·2
2-Methoxy-5-methylanilino-	157	$C_{18}H_{14}O_3NCl$	65·8	4·2	65·9	4·2

[a] 2 : 5-Dichloroaniline did not give a normal condensation product.

TABLE 5. 2 : 5-*Disubstituted* 3 : 6-*dichloro*-1 : 4-*benzoquinones.*

2 : 5-Substituents	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
p-*n*-Propylanilino-	268°	$C_{24}H_{24}O_2N_2Cl_2$	64·7	5·5	65·0	5·4
p-*n*-Butylanilino-	264	$C_{26}H_{28}O_2N_2Cl_2$	66·0	5·9	66·2	5·9
p-*n*-Heptylanilino-	212	$C_{32}H_{40}O_2N_2Cl_2$	69·0	7·1	69·1	7·2
p-*n*-Propoxyanilino-	254	$C_{24}H_{24}O_4N_2Cl_2$	60·3	5·2	60·6	5·0
p-*iso*Propoxyanilino-	>300	$C_{24}H_{24}O_4N_2Cl_2$	60·5	4·8	60·6	5·0
p-*n*-Butoxyanilino-	248	$C_{26}H_{28}O_4N_2Cl_2$	61·9	5·4	62·0	5·5
p-*iso*Butoxyanilino-	278	$C_{26}H_{28}O_4N_2Cl_2$	62·2	5·5	62·0	5·5
p-*n*-Pentyloxyanilino-	241	$C_{28}H_{32}O_4N_2Cl_2$	63·1	6·3	63·3	6·0
p-*iso*Pentyloxyanilino-	262	$C_{28}H_{32}O_4N_2Cl_2$	63·3	5·9	63·2	6·0
p-*n*-Heptyloxyanilino-	234	$C_{32}H_{40}O_4N_2Cl_2$	65·1	7·0	65·4	6·8
p-3-Phenylpropoxyanilino-	228	$C_{36}H_{32}O_4N_2Cl_2$	68·7	5·0	68·8	5·1
3 : 4-Dichloroanilino- [a]	>320	$C_{18}H_8O_2N_2Cl_6$	43·1	1·9	43·4	1·6
2-Methoxy-5-methylanilino-	263	$C_{22}H_{20}O_4N_2Cl_2$	58·8	4·3	59·0	4·4

[a] 2 : 5-Dichloroaniline did not give a normal condensation product.

cooling was crystallised from ethanol. 2 : 5-*Bisarylamino*-3 : 6-*dichloro*-1 : 4-*benzoquinones*, similarly prepared from chloranil (1 mol.) and the appropriate arylamine (2 mol.), were recrystallised from ethanol or ethanol–pyridine; they are listed in Table 5 (yields : 80 to 98%).

Preparation of Aryl iso*Thiocyanates.*—A solution of the appropriate thiocarbanilide (1 mol.) in acetic anhydride (2 mol.) was gently refluxed for 10 min., the resulting mixture slowly fractionated *in vacuo*, and the *iso*thiocyanate, obtained in 80—90% yield, was redistilled; the new aryl *iso*thiocyanates are listed in Table 6.

Preparation of Disubstituted Thioureas.—(a) *Unsymmetrical thioureas.* A solution of equimolecular amounts of the appropriate arylamine and aryl *iso*thiocyanate in a few drops of ethanol was heated at 45—50° for some minutes; in most instances, the thiourea formed solidified immediately and was recrystallised from methanol, ethanol, or ethanol–benzene. In the case of *o*-substituted arylamines or aryl *iso*thiocyanate, the thiourea was formed more slowly,

TABLE 6. *Aryl* iso*thiocyanates.*

	B. p./mm.	n	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
p-*n*-Propylphenyl [a]	150°/15	$n_D^{22.5}$ 1·5942	$C_{10}H_{11}NS$	—	—	—	—
p-*n*-Butylphenyl	162/15	n_D^{23} 1·5880	$C_{11}H_{13}NS$	69·0	6·9	69·1	6·8
p-*n*-Heptylphenyl [b]	205—207/20	—	$C_{14}H_{19}NS$	72·3	8·0	72·1	8·1
p-*n*-Propoxyphenyl	174/15	n_D^{22} 1·6072	$C_{10}H_{11}ONS$	62·1	5·6	62·1	5·6
p-*iso*Propoxyphenyl	170/17	n_D^{19} 1·6056	$C_{10}H_{11}ONS$	62·2	5·8	62·1	5·6
p-*n*-Butoxyphenyl	190—191/16	n_D^{27} 1·5942	$C_{11}H_{13}ONS$	63·6	6·5	63·7	6·2
p-*n*-Pentyloxyphenyl	202—204/16	n_D^{27} 1·5726	$C_{12}H_{15}ONS$	65·0	7·0	65·1	6·7
p-*iso*Pentyloxyphenyl [c]	195—196/15	n_D^{25} 1·5802	$C_{12}H_{15}ONS$	65·2	6·9	65·1	6·7
p-Fluorophenyl	215	n_D^{26} 1·6116	C_7H_4NSF	54·8	2·6	54·9	2·6
2-Diphenylyl-	312/32	n_D^{26} 1·6162	$C_{13}H_9NS$	73·9	4·5	73·9	4·2
2 : 3-Dimethylphenyl [d]	146/13	n_D^{20} 1·6119	C_9H_9NS	—	—	—	—
2 : 4-Dimethylphenyl [e]	144—145/16	n_D^{28} 1·6102	C_9H_9NS	—	—	—	—

[a] Francksen (*loc. cit.*) gave b. p. 263°. [b] Solidified at room temperature to a fat-like mass. [c] Crystallised as long flat prisms, m. p. 42°, from ligroin. [d] Prepared by a different method by Dyson, George, and Hunter (*J.*, 1927, 440), who gave b. p. 262—263°/760 mm. [e] Prepared by Werner (*J.*, 1891, **59**, 405).

and with *o*-trifluoromethylaniline only the symmetrical thiourea corresponding to the aryl *iso*thiocyanate was isolated.

(b) *Symmetrical thioureas.* A mixture of the arylamine (2 mol.), sulphur (0·5 mol.), carbon disulphide (2 mol.), and ethanol was gently refluxed for 24 hr., the mixture obtained filtered, and the filtrate concentrated. The thiourea formed was recrystallised from methanol, ethanol, or ethanol–benzene; the yields range from 90 to 100%.

All these thioureas undergo thermal decomposition on prolonged heating below their m. p.s; the m. p.s therefore depend to a great extent on the speed of heating. This accounts for the wide discrepancies recorded at times in the literature. In the present work m. p.s were taken with a Maquenne block, and represent the point of instantaneous liquefaction.

DEPARTMENT OF ORGANIC CHEMISTRY,
THE RADIUM INSTITUTE, UNIVERSITY OF PARIS.

[*Received, December 18th*, 1954.]