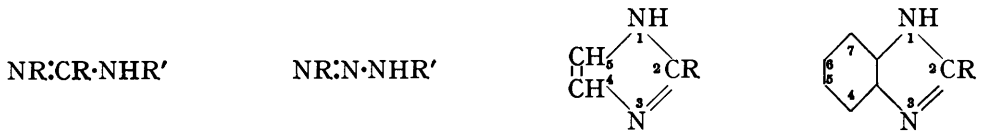
139. *The Associating Effect of the Hydrogen Atom. Part VIII. The* N–H–N *Bond. Benziminazoles, Glyoxalines, Amidines, and Guanidines.*

By Louis Hunter and John A. Marriott.

Measurement of molecular weight of amidines and related substances has been made in naphthalene solution over a range of concentration, and evidence has been adduced indicating molecular association through N–H–N bonds in those compounds possessing an unsubstituted imino-group. From the large factors of association exhibited by the glyoxalines and benziminazoles, it would appear that the N–H–N bond is neither so weak nor so rare as has hitherto been supposed. The strength of the bond is evidently enhanced in compounds of tautomeric character, and the virtual tautomerism of the types mentioned in the title is explained as a resonance phenomenon.

The formal resemblance between amidines (I) and diazoamino-compounds (II) is only weakly reflected in their chemical properties owing to the dominating influence of the azo-group. The two classes are, however, closely similar in exhibiting virtual tautomerism, *i.e.*, one substance shows all the chemical properties to be expected of the equilibrium $NR{:}X{\cdot}NHR' \rightleftharpoons NHR{\cdot}X{:}NR'$ (X = CR or N). The virtual tautomerism of the diazoamino-compounds having been connected with their associated character (Hunter, J., 1937, 320), it seemed desirable to examine the molecular condition of the amidines in order to discover whether their tautomeric behaviour is accompanied by a parallel molecular association.

Although amidines possessing a free imino-hydrogen atom (as in I) proved to be slightly more associated than those without (*e.g.*, NR:CR·NRR'), the differences between these two types of amidine were found to be far less marked than is the case in the diazoamino-compounds (*loc. cit.*) and other compounds described in previous parts of this series. In contrast, the glyoxalines (III) and the benziminazoles (IV), which can be regarded as



(I.) (II.) (III.) (IV.)

cyclic amidines, are found to be very strongly associated provided the imino-group remains unsubstituted; their *N*-substituted derivatives, on the contrary, are unassociated. It would appear, then, that association in these compounds is a hydrogen-bond phenomenon, and evidence is given for the belief that the bond involves a N–H–N bridge between the imino-group of one molecule and the tertiary nitrogen atom of another. The markedly superior tendency to associate in the glyoxalines and benziminazoles when compared with the amidines is probably connected with the more pronounced acid character of the former compounds; the belief is very generally held (Buswell, Rodebush, and Roy, *J. Amer. Chem. Soc.*, 1938, **60**, 2239; Pauling, " The Nature of the Chemical Bond," Cornell, 1940, pp. 287, 307) that the tendency to form hydrogen bonds is the stronger the more acidic is the nature of the hydrogen atom concerned.

Independent support of the evidence provided by molecular association is indicated in the very striking melting-point relationships between the glyoxalines and benziminazoles and their *N*-substituted derivatives (Table I). Although no close connexion between molecular complexity and melting point has been formulated, the unusually large reductions of melting point caused by substituting the 1-position of these compounds constitute strong suspicion of considerable complexity in the unsubstituted compounds.

Except in so far as the molecules of the substances examined are held together by hydrogen bonds, no conclusion can be drawn from the molecular-weight evidence as to the type of polymers formed. The form of the molecular-weight curves is such as to

TABLE I.

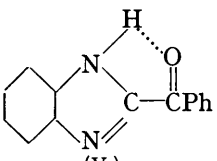
	M. p.		M. p.
Glyoxaline	90°	4 : 5-Diphenyl-2-*iso*propylglyoxaline	246°
1-Methylglyoxaline	liquid	4 : 5-Diphenyl-1-methyl-2-*iso*propylglyoxaline	97
1-Ethylglyoxaline	liquid	Benziminazole	170
1-Phenylglyoxaline	13	1-Methylbenziminazole	61
1-α-Naphthylglyoxaline	62	1-Phenylbenziminazole	97
2-Methylglyoxaline	139	2-Methylbenziminazole	175
1 : 2-Dimethylglyoxaline	liquid	1 : 2-Dimethylbenziminazole	111
4 : 5-Diphenylglyoxaline	228	2-Phenylbenziminazole	290
4 : 5-Diphenyl-1-methylglyoxaline	158	1 : 2-Diphenylbenziminazole	112
		2-Phenyl-1-benzylbenziminazole	133

indicate little or no falling off of the association factor with increasing concentration, and it would appear that chain polymers are the most probable. Indeed, except for some of the simpler amidines, cyclic dimers of the type suggested for the diazoamino-compounds (Hunter, *loc. cit.*) would be sterically impossible. Whatever form the molecular association takes, however, it appears likely that the virtual tautomerism of the amidines, glyoxalines, and derivatives is closely connected with it; *i.e.*, that the alternative attachment of the tautomeric hydrogen atom to one nitrogen atom or the other gives rise to a resonance hybrid showing all the properties of the virtually tautomeric mixture (for full discussion see Hunter, *Chem. and Ind.*, 1941, **60**, 32).

In the present work, measurements have been made cryoscopically in naphthalene solution over a range of concentration. Conclusions as to molecular association have been made, as in previous parts of this series, by comparison of the slopes of the molecular weight–concentration curves; a steep curve is taken to indicate molecular association, and a flat or gently sloped curve non-association. By comparing the slopes of these curves for substances of similar constitution, errors arising from departures from the ideal laws are very much diminished. The more important results obtained for each class of compound examined are set out below.

Benziminazoles (Figs. 1—4).—Benziminazoles unsubstituted in position 1 are all highly associated, but association is checked completely by replacement of the imino-hydrogen atom by alkyl or aryl groups (Figs. 1 and 2), by acyl or carbethoxy-groups (Fig. 2), or by amino-groups (Fig. 3). The solubility of the benziminazoles runs roughly parallel with this behaviour : those having a free imino-hydrogen atom are, with few exceptions, sparingly soluble in hydrocarbon solvents, whereas the reverse is true of the *N*-substituted derivatives.

Numerous examples have been recorded in previous parts of this series (J., 1938, 375, 1034; 1939, 484; 1940, 166) of the engagement of the hydrogen atom responsible for molecular association in chelate ring-formation, with consequent suppression of molecular association. Similar results are now observed in the benziminazole series. Thus, 2-benzoylbenziminazole (V; Fig. 3), although slightly more associated than its 1-substituted isomer (IV; H = COPh), is considerably less associated than any of the benziminazoles with an unsubstituted 1-position. It would appear that the majority of its molecules possess an internally chelate (N–H–O) structure, as indicated in (V). Its phenylmethylhydrazone (VI) is similar in being only weakly associated, no doubt on account of the formation of an internal N–H–N bond. In view of the failure of 2-benzeneazoglyoxaline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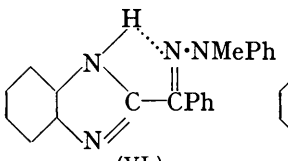
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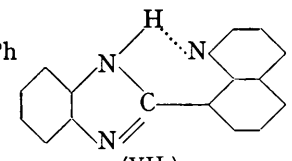
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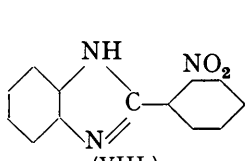
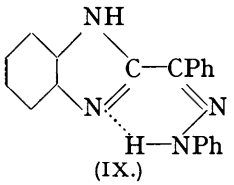
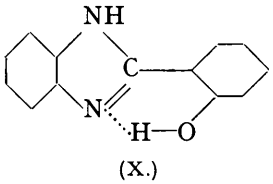

(VIII.)

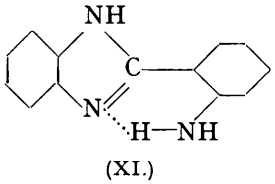
(see p. 780) to achieve a similar type of chelation, the possibility cannot be entirely excluded that the greatly reduced degree of association found in (VI) may be due to the steric

disposition of the phenylmethylhydrazone group in a manner such as to lead to interference with the smooth functioning of intermolecular N–H–N bonds. The somewhat restricted solubility in naphthalene of (V) (about 6·5%) and (VI) (about 5%) would seem to give support to the molecular-weight evidence that a certain proportion of their molecules are associated by the ordinary benziminazole mechanism. On the other hand 2-(8′-quinolyl)benziminazole (VII), by its high solubility in naphthalene and its relatively flat association–concentration curve (Fig. 3), shows unmistakable signs of possessing a chelate structure. 2-*o*-Nitrophenylbenziminazole (VIII; Fig. 4) is highly associated and therefore not chelate.

The behaviour of the phenylhydrazone (IX) of 2-benzoylbenziminazole is specially noteworthy. This compound is completely unassociated (Fig. 3), is at least three times as soluble in naphthalene as either 2-benzoylbenziminazole (V; m. p. 210°) or its phenylmethylhydrazone (VI; m. p. 223°), and has a melting point (184°) lower than either. Indeed, it is so completely different from these compounds that we ascribe to it a six-membered chelate structure involving a N–H–N bond, the greater stability of which, by comparison with the five-membered systems in (V) and (VI), would account for the very high proportion of its molecules being unassociated. It will be observed that the unimolecular state of this compound is attributed, not to the replacement of its iminazole hydrogen atom, or even to its involvement in chelate ring-formation, but to the engagement of the tertiary nitrogen atom of the iminazole nucleus in co-ordinate ring-formation. That this can equally well result in checking association is borne out by other examples. For instance, both 2-*o*-hydroxyphenyl- (X) and 2-*o*-aminophenyl-benziminazole (XI) are


(IX.)

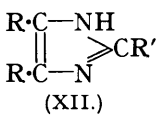

(X.)

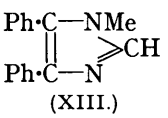

(XI.)

substantially unimolecular (Fig. 4). Indeed, (X) is a unique example of a compound possessing two highly associating groups (hydroxyl and iminazole) which, by virtue of their mutual satisfaction within the molecule, result in the suppression of intermolecular hydrogen bonds. Another example (XIV) of similar type is quoted in the next section.

Glyoxalines (Fig. 5).—The high solubility of glyoxaline (III; R = H) in water and in other donor solvents, together with the very great reduction of melting point caused by substitution in its 1-position (Table I), is strong presumptive evidence of electron-accepting tendencies in its imino-hydrogen atom. In spite of this, we scarcely anticipated the extremely high degree of association actually found in naphthalene solution, or the steepness of its association–concentration curve (Curve 1). Although the factors of association found for this substance and for its 2 : 4 : 5-trimethyl derivative (Curve 2) cannot be accepted literally, they do indicate a most unusually high state of polymerisation. That this is due in some measure to the conjugated structure of the glyoxalines is shown by the much reduced association exhibited by lysidine (2-methyl-4 : 5-dihydroglyoxaline; Curve 7), in which the conjugation is absent, although the imino-hydrogen atom remains.

Of the *C*-substituted glyoxalines investigated, 4 : 5-diphenyl- (XII; R = Ph, R′ = H), 4 : 5-diphenyl-2-methyl- (XII; R = Ph, R′ = Me), and 2 : 4 : 5-triphenyl-glyoxaline (XII; R = R′ = Ph) had rather limited solubilities in naphthalene, but in spite of this the slopes of the realisable portions of their curves are still considerable, and only slightly less than


(XII.)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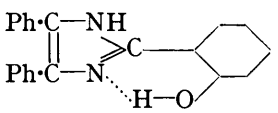
(XIV.)

those of the simpler glyoxalines. That the properties of these compounds are largely due to the possession of an unsubstituted 1-position is indicated by the behaviour of 4 : 5-di-

phenyl-1-methylglyoxaline (XIII); this compound is completely unassociated (Curve 9), and is at least ten times as soluble in naphthalene as either its 2-methyl isomer (XII; R = Ph, R′ = Me) or its lower homologue 4 : 5-diphenylglyoxaline. This striking result affords convincing proof that association in the glyoxalines, as with the benziminazoles, is dependent on the presence of a free imino-hydrogen atom.

KEY TO FIGS. 1—8.

FIG. 1.

1 = Benziminazole.
2 = 2-Methylbenziminazole.
3 = 2-Ethylbenziminazole.
4 = 2-*n*-Propylbenziminazole.
5 = 2-*iso*Propylbenziminazole.
6 = 1 : 2-Dimethylbenziminazole.
7 = 2-Phenyl-1-benzylbenziminazole.

FIG. 2.

1 = 2 : 5-Dimethylbenziminazole.
2 = 2-*n*-Butylbenziminazole.
3 = 2-*iso*Butylbenziminazole.
4 = 2-Benzylbenziminazole.
5 = 1-Carbethoxybenziminazole.
6 = 1-Benzoylbenziminazole.

FIG. 3.

1 = 2-Methyl-β-naphthiminazole.
2 = 2-Benzoylbenziminazolephenylmethylhydrazone.
3 = 2-Benzoylbenziminazole.
4 = 1-Phenylamino-2-phenyl-β-naphthiminazole.
5 = 2-Benzoylbenziminazolephenylhydrazone.
6 = 2-(8′-Quinolyl)benziminazole.
7 = 1-*p*-Tolylamino-2-phenyl-6-methylbenziminazole.

FIG. 4.

1 = 2-*o*-Nitrophenylbenziminazole.
2 = 2-*o*-Hydroxyphenylbenziminazole.
3 = 2-*o*-Aminophenylbenziminazole.

FIG. 5.

1 = Glyoxaline.
2 = 2 : 4 : 5-Trimethylglyoxaline.
3 = 4 : 5-Diphenylglyoxaline.
4 = 4 : 5-Diphenyl-2-methylglyoxaline.
5 = 2 : 4 : 5-Triphenylglyoxaline.
6 = 2-Benzeneazoglyoxaline.
7 = Lysidine (2-methyl-4 : 5-dihydroglyoxaline).
8 = 2-*o*-Hydroxyphenyl-4 : 5-diphenylglyoxaline.
9 = 4 : 5-Diphenyl-1-methylglyoxaline.

FIG. 6.

1 = *N*-Phenyl-*N*′-*p*-tolylacetamidine.
2 = *NN*′-Diphenylacetamidine.
3 = *N*-Phenyl-*N*′-*m*-tolylacetamidine.
4 = *N*-Phenyl-*N*′-*o*-tolylacetamidine.
5 = N-*Phenyl*-N′-*β-naphthylacetamidine*.
6 = *NN*′-Diphenylpropionamidine.
7 = *NN*′-Di-*m*-tolylacetamidine.
8 = *NN*′-Di-*o*-tolylacetamidine.
9 = Triphenylacetamidine.
10 = NN′-*Diphenyl*-N-*methylacetamidine*.
11 = *NN*-Diphenyl-*N*′-*p*-tolylacetamidine.
12 = NN-*Diphenyl*-N′-*o-tolylacetamidine*.

FIG. 7.

1 = *N*-Phenyl-*N*′-methylbenzamidine.
2 = *NN*′-Diphenylbenzamidine.
3 = *N*-Phenyl-*N*′-*o*-tolylbenzamidine.
4 = *N*-Phenyl-*N*′-*m*-tolylbenzamidine.
5 = *N*-Phenyl-*N*′-*p*-tolylbenzamidine.
6 = Triphenylbenzamidine.

FIG. 8.

1 = *NN*′-Diphenylguanidine.
2 = *NN*′*N*″-Triphenylguanidine.
3 = *NNN*′*N*″-Tetraphenylguanidine.

An attempt to engage the imino-hydrogen atom of the glyoxaline nucleus in chelate ring-formation by substituting a suitable electron-donor group in a position adjacent to it was not successful in suppressing the association. For instance, 2-benzeneazoglyoxaline is sparingly soluble in naphthalene and highly associated, and there seems little doubt that no chelate ring is in fact formed. On the other hand, a comparison between 2 : 4 : 5-triphenylglyoxaline (XII; R = R′ = Ph, Curve 5) and 2-(*o*-hydroxyphenyl)-4 : 5-diphenylglyoxaline (XIV; Curve 8) shows that the latter, by its higher solubility and its flat curve, is rightly ascribed a chelate structure.

In conclusion, it should be stated that the tautomeric character of the glyoxalines (and therefore the equivalence of the 4- and the 5-position) is well authenticated, with the single exception of the reported isolation of 2 : 4- and 2 : 5-diphenylglyoxalines (Burtles and Pyman, J., 1923, **123**, 361). These authors do not give very convincing evidence of the isomeric relationship of this pair, and there seems little doubt that, in reality, they are polymorphs (see Weidenhagen and Hermann, *Ber.*, 1935, **68**, 1957).

Amidines (Figs. 6 and 7).—Although they were at first the primary object of this investigation, the amidines, probably by reason of their basic character, exhibit molecular association far inferior to that of either the benziminazoles or the glyoxalines. Indeed, had it not been for an examination of these cyclic analogues, the association of the amidines might have escaped recognition. However, when their association factors are plotted on a very much enlarged scale, the slopes of the association–concentration curves

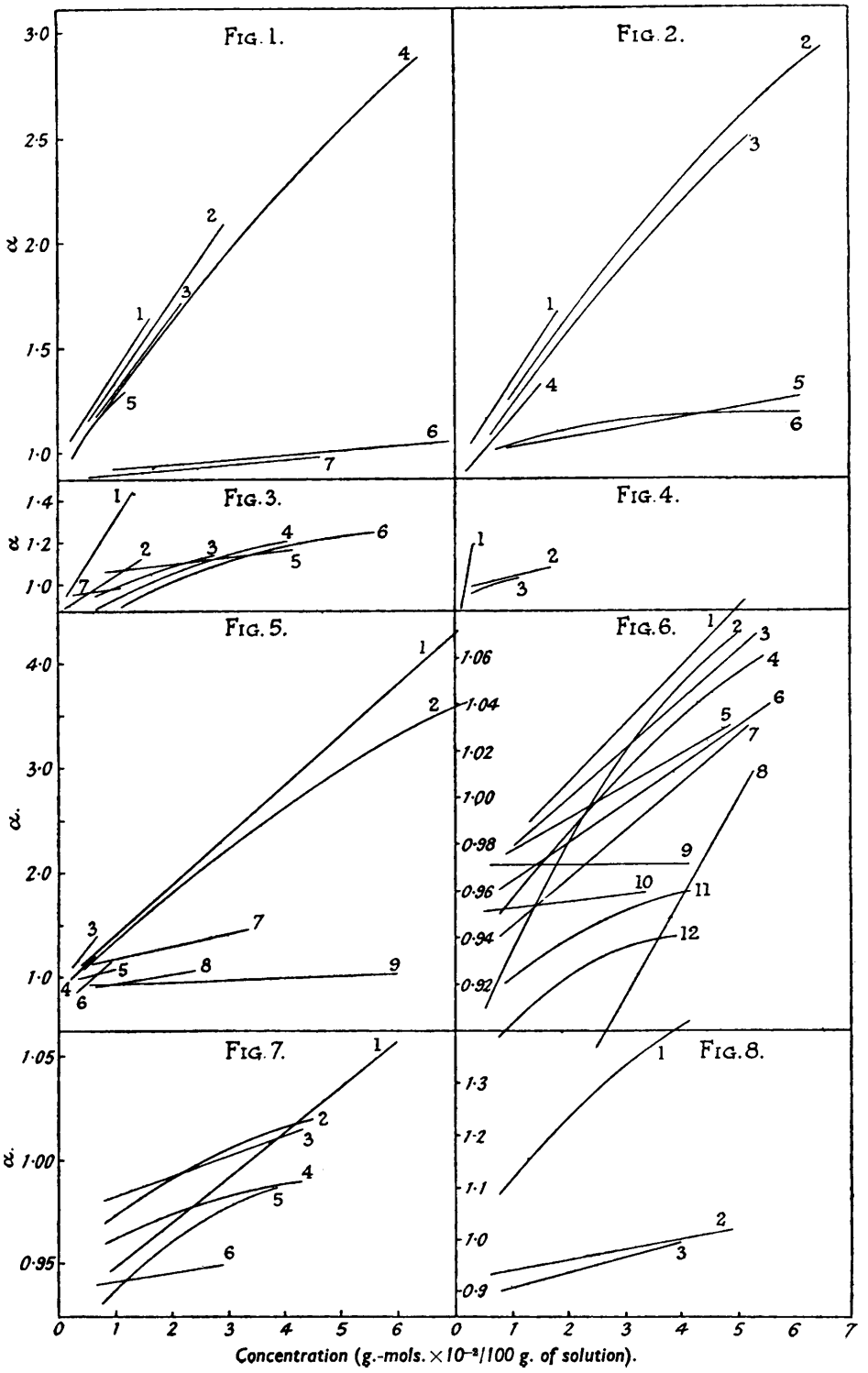
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.
Concentration (g.-mols. × 10⁻²/100 g. of solution).

show that they fall distinctly into the two expected classes, those having a free imino-hydrogen atom (as in I) being mildly associated, and those without (*i.e.*, *N*-trisubstituted amidines) being unassociated.

Although this is true of the acetamidines (I ; CR = CMe), the distinction between the two classes in the case of the benzamidines (I; CR = CPh) is not nearly so sharp, and becomes almost submerged in the general tendency (shown by all classes of associated compound) for the association factor to diminish with rise of molecular weight. However, the results expressed in Fig. 7 show that, even if there is no sharp division into two distinct classes, it is true to say that the benzamidines possessing a free imino-hydrogen atom give curves of greater slope than that in which this hydrogen is replaced by an aryl group.

Guanidines (Fig. 8).—By regarding guanidines (XV) as amino-derivatives of the amidines, we were led to examine the molecular condition of a few of these compounds in naphthalene solution. From the slope of the curve obtained (Fig. 8, Curve 1) for *NN'*-diphenylguanidine (XV; R = Ph) it is clear that this substance is highly associated, and it would seem, by analogy with the amidines and their cyclic analogues, that this association is again a hydrogen-bond phenomenon. Experimental proof of this by methods

$NR{:}C(NH_2)\cdot NHR$	$NHR\cdot C(NHR){:}NR'$	$NR{:}C(NHR)\cdot NHR'$
(XV.)	(XVI.)	(XVII.)

similar to those which have been applied to other compounds containing the N–H–N bond is not possible, for this would involve a comparison between guanidines possessing a free imino-hydrogen atom and those in which all five imino-hydrogen atoms have been replaced. Fig. 8 shows that even in the tri- and tetra-substituted guanidines the association–concentration curves have so diminished in slope as to warrant the inference that association is absent. Evidently the very large increase in molecular weight consequent on these numerous substitutions has the effect (as in other compounds) of overcoming any tendency to molecular association, and it therefore becomes impossible to distinguish this effect from that resulting from the replacement of the hydrogen atoms.

In view of the general similarity between guanidines and amidines, it is with some surprise that we note the reported isolation (Sieg and Dehn, *J. Amer. Chem. Soc.*, 1940, **62**, 3506) of a dozen pairs of isomeric *NN'N''*-trisubstituted guanidines corresponding to (XVI) and (XVII). Even if the mechanism of interchange of virtual tautomers advocated in the present series of papers (Hunter, *Chem. and Ind., loc. cit.*) were inoperative in the guanidines, their synthesis in the presence of mineral acid would surely give rise to a guanidinium ion, $NHR\cdot C(NHR){:}\overset{\oplus}{N}HR' \rightleftharpoons \overset{\oplus}{N}HR{:}C(NHR)\cdot NHR'$, common to both tautomers, and would thus effectively prevent any separation. Moreover, the thiourea method of synthesis of the substituted guanidines employed by Sieg and Dehn frequently leads, in our experience, to products obstinately retaining impurities.

In the following tables concentrations are expressed as g.-mols. $\times 10^{-2}/100$ g. of solution, the formula weights appearing in parentheses; *M* is the apparent molecular weight deduced according to the ideal-solution laws; and the association factor (α) is calculated as the ratio of *M* to the formula weight. The cryoscopic solvent is naphthalene. To avoid congestion in Fig. 6 a few of the amidine curves (as indicated in the tables) are omitted.

Fig. 1.	Concn.	*M*.	α.
Benziminazole (118) (Curve 1)	0·19	125	1·06
	0·51	141	1·195
	1·13	168	1·42
	1·66 *	195	1·65
2-Methylbenziminazole (132) (Curve 2)	0·54	152	1·15
	1·47	200	1·52
	2·17	236	1·79
	2·96 *	274	2·07

	Concn.	*M*.	α.
2-Ethylbenziminazole (146) (Curve 3)	0·775	173	1·185
	1·12	192	1·32
	1·45	210	1·44
	1·73	226	1·55
	1·96	238	1·63
	2·23 *	249	1·70

* Solute separates at higher concentrations.

Fig. 1 (*contd.*)	Concn.	*M.*	*a.*
2-*n*-Propylbenziminazole (160) (Curve 4)	0·79	191	1·195
	1·24	213	1·33
	1·87	250	1·56
	2·64	293	1·83
	3·33	324	2·03
	4·20	371	2·32
	4·69	393	2·46
	5·28	418	2·62
	6·41	459	2·87
2-*iso*Propylbenziminazole (160) (Curve 5)	0·22	155	0·97
	0·60	185	1·15
	1·04 *	204	1·27
FIG. 2.			
2 : 5-Dimethylbenziminazole (146) (Curve 1)	0·24	150	1·03
	0·63	173	1·18
	0·93	188	1·28
	1·23	207	1·42
	1·46	225	1·54
	1·76 *	243	1·665
2-*n*-Butylbenziminazole (174) (Curve 2)	0·96	218	1·25
	1·94	282	1·62
	2·64	325	1·87
	3·34	363	2·085
	4·32	415	2·38
	5·48	469	2·69
	6·48	509	2·925
2-*iso*Butylbenziminazole (Curve 3)	0·635	188	1·08
	1·50	230	1·32
	2·615	305	1·75
	3·69	358	2·05
	4·51	407	2·34
	5·16 *	435	2·50
FIG. 3.			
2-Methyl-β-naphthiminazole (182) (Curve 1)	0·12	174	0·95
	0·27	188	1·03
	0·53	206	1·13
	0·75	220	1·21
	0·99	239	1·31
	1·30	259	1·42
2-Benzoylbenziminazole-phenylmethylhydrazone (326) (Curve 2)	0·17	290	0·89
	0·42	313	0·96
	0·68	324	0·99
	0·93	332	1·02
	1·18	348	1·07
	1·49 *	362	1·11
2-Benzoylbenziminazole (222) (Curve 3)	0·57	211	0·95
	1·43	229	1·03
	2·13	239	1·08
	2·73 *	252	1·14
1-Phenylamino-2-phenyl-β-naphthiminazole (335) (Curve 4)	0·57	294	0·88
	1·11	319	0·95
	1·72	344	1·03
	2·40	357	1·07
	3·32	379	1·13
	4·03	405	1·21
Fig. 4.			
2-*o*-Nitrophenylbenziminazole (239) (Curve 1)	0·10	210	0·88
	0·12	220	0·92
	0·17	234	0·98
	0·28 *	281	1·175
2-*o*-Aminophenylbenziminazole (209) (Curve 3)	0·235	200	0·96
	0·44	208	0·99
	0·80	211	1·01
	1·11 *	214	1·02
1 : 2-Dimethylbenziminazole (146) (Curve 6)	0·99	135	0·925
	1·86	136	0·93
	3·595	140	0·96
	4·49	144	0·99
	5·37	146	1·00
	6·00	149	1·02
	6·94	153	1·05
2-Phenyl-1-benzylbenziminazole (284) (Curve 7)	0·50	244	0·86
	1·28	261	0·92
	2·15	266	0·94
	2·86	270	0·95
	3·36	273	0·96
	3·94	276	0·97
	4·64	280	0·985
2-Benzylbenziminazole (208) (Curve 4)	0·21	186	0·89
	0·44	203	0·98
	0·70	222	1·07
	0·99	243	1·17
	1·25 *	257	1·23
1-Carbethoxybenziminazole (190) (Curve 5)	0·95	194	1·02
	1·83	201	1·06
	2·72	208	1·10
	3·94	220	1·16
	5·00	227	1·195
	6·17	244	1·28
1-Benzoylbenziminazole (222) (Curve 6)	0·71	225	1·01
	1·57	243	1·09
	2·31	251	1·13
	2·94	254	1·14
	3·49	255	1·15
	4·28	259	1·17
	5·05	257	1·16
	6·11	264	1·19
2-Benzoylbenziminazole-phenylhydrazone (312) (Curve 5)	0·81	333	1·07
	1·27	335	1·075
	1·74	333	1·07
	2·17	344	1·10
	2·78	355	1·14
	3·43	354	1·14
	4·14	365	1·17
2-(8′-Quinolyl)benziminazole (245) (Curve 6)	1·33	218	0·89
	2·10	250	1·02
	3·18	271	1·105
	4·06	284	1·16
	4·775	296	1·21
	5·56	306	1·25
1-*p*-Tolylamino-2-phenyl-6-methylbenziminazole (316) (Curve 7)	0·20	304	0·96
	0·40	298	0·94
	0·59	299	0·95
	0·74	311	0·98
	0·85	309	0·98
	1·02 *	312	0·985
2-*o*-Hydroxyphenylbenziminazole (210) (Curve 2)	0·36	208	0·99
	0·71	212	1·01
	1·06	219	1·04
	1·38	223	1·06
	1·68 *	227	1·08

* Solute separates at higher concentrations.

Fig. 5.	Concn.	*M.*	α.
Glyoxaline (68) (Curve 1)	0·40	77	1·13
	1·04	97	1·43
	1·69	120	1·76
	2·43	143	2·10
	3·72	187	2·75
	4·71	221	3·25
	5·93	257	3·78
	7·32	299	4·39
2 : 4 : 5-Trimethylglyoxaline (110) (Curve 2))	0·43	120	1·09
	1·01	145	1·32
	1·86	190	1·73
	2·84	238	2·17
	3·71	279	2·54
	5·36	337	3·07
	7·67	412	3·74
	9·92	474	4·31
	12·10	522	4·75
4 : 5-Diphenyl-2-methylglyoxaline (234) (Curve 4)	0·19	232	0·99
	0·38	253	1·08
	0·64 *	282	1·20
2-*o*-Hydroxyphenyl-4 : 5-diphenylglyoxaline (312) (Curve 8)	0·67	285	0·91
	1·12	299	0·96
	1·76	318	1·02
	2·41 *	327	1·05

	Concn.	*M.*	α.
4 : 5-Diphenylglyoxaline (220) (Curve 3)	0·20	242	1·10
	0·69 *	311	1·41
2 : 4 : 5-Triphenylglyoxaline (296) (Curve 5)	0·34	294	0·99
	0·50	297	1·00
	2·01 *	321	1·08
2-Benzeneazoglyoxaline (172) (Curve 6)	0·28	152	0·88
	0·53	173	1·01
	0·99 *	200	1·17
Lysidine (84) (Curve 7)	0·59	95	1·13
	1·27	100	1·19
	1·86	108	1·28
	2·78	115	1·37
	4·25	125	1·49
4 : 5-Diphenyl-1-methylglyoxaline (234) (Curve 9)	0·32	220	0·94
	0·77	217	0·93
	1·19	221	0·95
	1·53	220	0·94
	1·90	225	0·96
	2·90	228	0·975
	4·05	239	1·02
	4·90	236	1·01
	5·98	241	1·03

Fig. 6.			
N-Phenyl-*N'*-*p*-tolylacetamidine (224) (Curve 1)	1·33	222	0·99
	3·32	231	1·03
	4·46	237	1·06
	5·01	243	1·085
NN'-Diphenylacetamidine (210) (Curve 2)	0·54	191	0·91
	1·72	203	0·97
	2·69	210	1·00
	3·42	215	1·025
	4·21	220	1·05
	4·97	224	1·07
N-Phenyl-*N'*-*m*-tolylacetamidine (224) (Curve 3)	1·04	220	0·98
	1·84	221	0·99
	2·77	227	1·01
	3·67	232	1·04
	4·36	235	1·05
	5·34	239	1·07
N-Phenyl-*N'*-*o*-tolylacetamidine (Curve 4)	0·84	214	0·95
	1·65	219	0·98
	2·81	225	1·00
	3·555	229	1·02
	4·34	233	1·04
	5·44	237	1·06
N-*Phenyl*-N'-*β*-*naphthylacetamidine* (260) (Curve 5)	0·91	253	0·975
	1·69	257	0·99
	2·61	260	1·00
	3·33	262	1·01
	4·05	265	1·02
	4·80	268	1·03
NN'-Diphenylpropionamidine (224) (Curve 6)	0·75	216	0·96
	1·52	218	0·97
	2·51	222	0·99
	3·40	223	0·995
	4·54	228	1·02
	5·53	233	1·04
NN'-Di-*m*-tolylacetamidine (238) (Curve 7)	0·80	223	0·94
	1·56	226	0·95
	2·39	231	0·97
	3·21	235	0·99
	4·02	239	1·00
	5·17	246	1·03

Triphenylacetamidine (286) (Curve 9)	0·55	277	0·97
	2·05	276	0·96
	2·58	276	0·96
	3·34	278	0·97
	4·09	277	0·97
NN-Diphenyl-*N'*-*p*-tolylacetamidine (300) (Curve 11)	0·86	275	0·92
	1·50	278	0·93
	2·15	281	0·94
	2·91	286	0·95
	3·41	287	0·96
	4·07	287	0·96
NN-*Diphenyl*-N'-o-*tolylacetamidine* (Curve 12)	0·58	267	0·89
	1·32	274	0·91
	1·99	277	0·92
	2·64	282	0·94
	3·95	282	0·94
NN'-Di-*p*-tolylacetamidine (238) (Curve omitted)	0·89	223	0·94
	1·61	228	0·96
	2·49	233	0·98
	3·59	241	1·01
	4·23	244	1·03
	5·13	250	1·05
N-o-Tolyl-*N'*-*m*-tolylacetamidine (Curve omitted)	0·83	220	0·93
	1·81	227	0·95
	2·64	231	0·97
	3·29	235	0·985
	3·98	239	1·00
	4·44	241	1·01
	5·14	245	1·03
N-o-*Tolyl*-N'-p-*tolylacetamidine* (Curve omitted)	1·21	223	0·94
	1·86	225	0·95
	2·74	232	0·975
	3·59	237	0·995
	4·47	242	1·02
	5·46	247	1·04
N-m-*Tolyl*-N'-p-*tolylacetamidine* (Curve omitted)	0·89	224	0·94
	1·74	228	0·96
	2·54	230	0·97
	3·16	236	0·99
	3·83	239	1·00
	4·75	245	1·03

* Solute separates at higher concentrations.

Fig. 6 (*contd.*)	Concn.	*M.*	a.		Concn.	*M.*	a.
NN'-Di-*o*-tolylacetamidine (Curve 8)	1·91	205	0·86	*NN'*-Diphenylphenacetamidine (286) (Curve omitted)	0·87	257	0·90
	2·83	216	0·91		1·75	261	0·91
	3·56	224	0·94		2·34	266	0·93
	4·46	232	0·98		2·97	270	0·94
	5·22	240	1·01		3·58	273	0·95
					4·33	278	0·97
NN'-*Diphenyl*-N-*methylacetamidine* (224) (Curve 10)	0·59	212	0·95				
	1·06	212	0·95				
	2·55	212	0·95				
	3·26	215	0·96				
Fig. 7.							
N-Phenyl-*N'*-methylbenzamidine (210) (Curve 1)	0·91	199	0·95	*NN'*-Diphenylbenzamidine (272) (Curve 2)	0·77	263	0·97
	2·16	203	0·97		1·44	267	0·98
	2·92	208	0·99		2·07	267	0·98
	3·71	210	1·00		2·93	274	1·01
	4·37	213	1·02		3·53	274	1·01
	4·98	217	1·03		4·48	276	1·02
	5·91	222	1·055				
				N-Phenyl-*N'*-*o*-tolylbenzamidine (286) (Curve 3)	0·78	280	0·98
N-Phenyl-*N'*-*p*-tolylbenzamidine (Curve 5)	0·67	265	0·93		1·33	282	0·985
	2·00	274	0·96		2·44	285	1·00
	2·67	279	0·98		3·58	288	1·01
	3·50	282	0·985		4·30	290	1·015
	4·30	283	0·99				
				N-Phenyl-*N'*-*m*-tolylbenzamidine (Curve 4)	0·83	276	0·96
Triphenylbenzamidine (348) (Curve 6)	0·66	327	0·94		1·53	278	0·97
	1·21	329	0·945		2·15	280	0·98
	1·84	331	0·95		2·77	278	0·97
	2·30	331	0·95		3·36	281	0·98
	2·90	332	0·95		4·23	283	0·99
FIG. 8.							
NN'-Diphenylguanidine (211) (Curve 1)	0·70	230	1·09	*NN'N''*-Triphenylguanidine (287) (Curve 2)	0·55	271	0·94
	1·77	253	1·20		1·49	268	0·93
	2·38	267	1·27		2·24	275	0·96
	3·35	289	1·37		3·23	285	0·99
	4·14	299	1·42		4·04	286	1·00
					4·87	293	1·02
NNN'N''-Tetraphenylguanidine (363) (Curve 3)	0·76	327	0·90				
	1·41	329	0·91				
	1·97	342	0·94				
	2·85	350	0·965				
	3·79	359	0·99				

* Solute separates at higher concentrations.

EXPERIMENTAL.

The solvent naphthalene was the specially purified product for cryoscopic use, obtained from the British Drug Houses. The following new compounds were prepared in the course of the investigation.

N-*Phenyl*-N'-β-*naphthylacetamidine*, prepared from aceto-β-naphthalide and aniline by the method of Sidiki and Shah (*J. Univ. Bombay*, 1937, **6**, Part II, 132), was produced as an oil which slowly solidified in the ice-box. It crystallised from aqueous alcohol as small, yellowish crystals, m. p. 86° (Found: N, 10·6. $C_{18}H_{16}N_2$ requires N, 10·8%). NN'-*Diphenyl*-N-*methylacetamidine* was prepared similarly from acetanilide and methylaniline. The oily product was extracted with ether, dried, and fractionated. The fraction, b. p. 320—324°, slowly solidified in a desiccator as a white solid, m. p. 83° (Found: N, 12·8. $C_{15}H_{16}N_2$ requires N, 12·5%).

N-o-*Tolyl*-N'-p-*tolylacetamidine*, prepared from aceto-*p*-toluidide and *o*-toluidine, formed long white needles from alcohol, m. p. 143° (Found: N, 11·7. $C_{16}H_{18}N_2$ requires N, 11·8%). N-m-*Tolyl*-N'-p-*tolylacetamidine*, prepared from aceto-*m*-toluidide and *p*-toluidine, formed clusters of small white needles from aqueous alcohol, m. p. 79° (Found: N, 11·7%).

NN-*Diphenyl*-N'-o-*tolylacetamidine*, prepared from aceto-*o*-toluidide and diphenylamine, formed stout white needles from aqueous alcohol, m. p. 100° (Found: N, 9·5. $C_{21}H_{20}N_2$ requires N, 9·3%).

The following had m. p.'s differing from those given in the literature: *NN'*-Diphenylbenzamidine, m. p. 147° (lit. 144°); *N*-phenyl-*N'*-*p*-tolylacetamidine, m. p. 93° (lit. 90°). 4 : 5-Diphenyl-1-methylglyoxaline, prepared by methylation of 4 : 5-diphenylglyoxaline with methyl sulphate, formed large rhombs from aqueous alcohol, m. p. 158° (Found: N, 11·8.

Calc. : N, 12·0%); Pinner (*Ber.*, 1902, **35**, 4139) gives m. p. 147°. 2-*o*-Hydroxyphenylbenziminazole, white platelets, m. p. 233° (Found : N, 13·2. Calc. : N, 13·3%); Hübner and Mensching (*Annalen*, 1881, **210**, 345) give m. p. 222·5°. 2-*o*-Nitrophenylbenziminazole, prepared by the method of Weidenhagen (*Ber.*, 1936, **69**, 2263), formed pale yellow needles, m. p. 261° (Found : N, 17·2. Calc. : N, 17·6%). Weidenhagen gives m. p. 190—193°, but Walther and v. Pulawski (*J. pr. Chem.*, 1899, **59**, 261) give m. p. 263°.

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