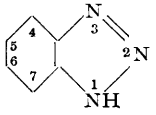
76. *The Associating Effect of the Hydrogen Atom. Part X. The* N–H–N *Bond. The Constitution of the Benztriazoles.*

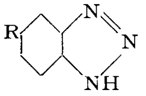
By Thomas G. Heafield and Louis Hunter.

On the evidence of cryoscopic measurement of molecular weight in naphthalene solution, benztriazoles possessing a free imino-hydrogen atom are shown to be strongly associated. Substitution of aryl or acyl groups for the imino-hydrogen atom completely checks association. Benztriazoles of the former type are therefore assigned a hydrogen-bond structure (N–H–N) in which any of the three nitrogen atoms can act as an electron donor. Correlation between this behaviour and the tautomeric character of the benztriazoles is made.

The tautomeric character of the pyrazoles (Hayes and Hunter, J., 1941, 1) and the iminazoles (Hunter and Marriott, *ibid.*, p. 777) having been connected with their hydrogen-bond structure, it was expected that a similar cause might account for the tautomerism of the benztriazoles. The virtual tautomerism of these compounds is now accepted (Ingold and Piggott, J., 1923, **123**, 1469), for the equivalence of the 5- and the 6-position (see I) has been established by chemical means (Griess, *Ber.*, 1882, **15**, 1878; Zincke and Helmert, *Annalen*, 1896, **291**, 313).



(I.)



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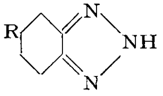
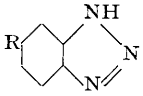


(III.)



(IV.)

Analogy with the diazoamino-compounds might suggest that the tautomeric hydrogen atom of the benztriazoles would reside alternately on the 1- and the 3-nitrogen atom (see I); but consideration of their structural formula shows that the latter compounds possess wider tautomeric possibilities than the former owing to the additional possibility that the benz-nucleus could assume an *o*-quinonoid structure, thus allowing the mobile hydrogen atom to be attached to any of the three nitrogen atoms (II $\rightleftharpoons$ III $\rightleftharpoons$ IV).* That all these tautomers contribute to the structure of the benztriazoles is indicated by the work of Krollpfeiffer *et al.* (*Annalen*, 1935, **515**, 113; *Ber.*, 1938, **71**, 596), who show that alkylation results in the simultaneous formation of 1-, 2-, and 3-alkyl derivatives. It is probable, however, that the tautomer (III) makes only a small contribution to the structure, since both chemically and physically (*idem, ibid.*; v. Auwers, *Ber.*, 1938, **71**, 604) the parent benztriazoles resemble their 1 (or 3)- much more closely than their 2-alkyl derivatives.

By measurement of molecular weight of a number of benztriazoles in naphthalene solution over a range of concentration, these compounds are shown to fall into two distinct classes (see figure). Those possessing an unsubstituted imino-hydrogen atom are highly associated, the factor of association increasing rapidly with rising concentration; but those in which the imino-hydrogen atom is replaced (whether in the 1-, 2-, or 3-position) by aryl or acyl groups are substantially unimolecular over the same concentration range. These results are interpreted, as in previous parts of this series, as indicating molecular association through N–H–N bonds in all those compounds possessing an unsubstituted imino-group. The association being regarded as a resonance phenomenon, the unperturbed structures contributing to the polymer hybrid will possess properties hitherto attributed to the separate tautomers. Such a mechanism will satisfactorily explain the molecular association of the benztriazoles on the one hand, and their tautomeric character on the other (Hunter, *Chem. and Ind.*, 1941, **60**, 32).

We therefore suggest that the association of the benztriazoles possessing a free imino-hydrogen atom is the result of hydrogen bonds linking the 1- and the 3-nitrogen atoms in separate molecules (a mechanism we

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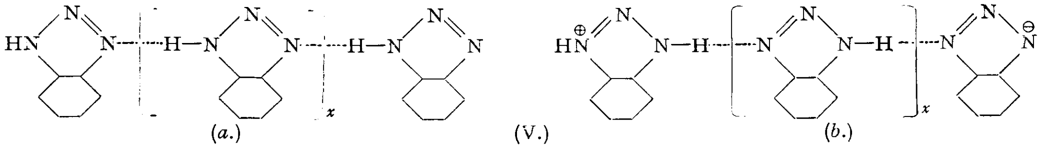
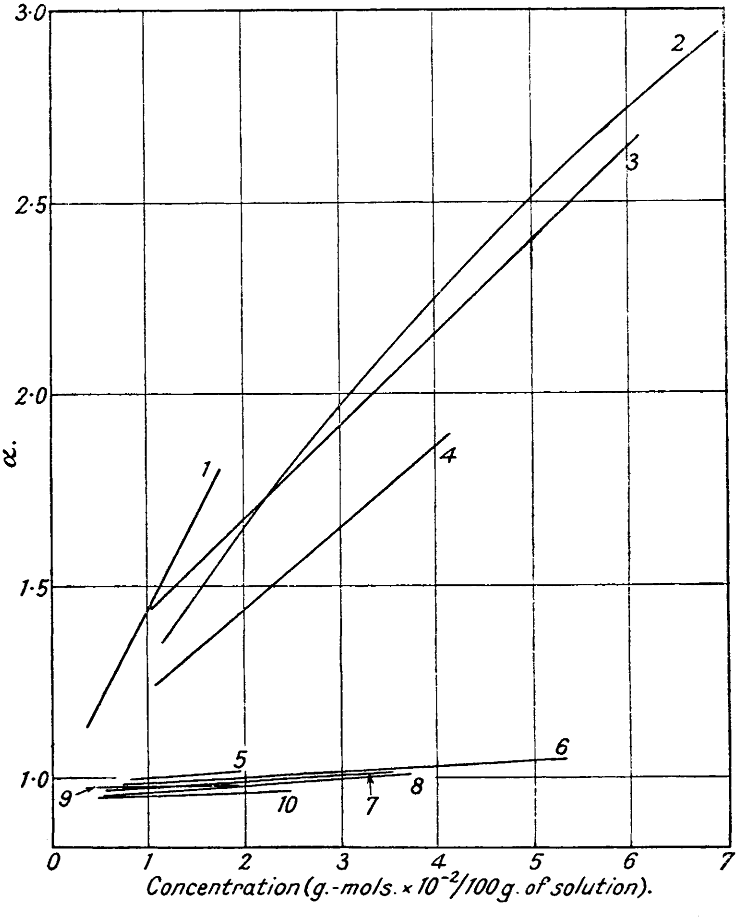
* In spite of the uncertain location of the hydrogen atom, it is conventional to number the benztriazole nucleus (I) as though the imino-group were fixed in a position adjacent to the benzene nucleus.

shall denote as " 1 : 3-association "), with a lesser contribution from polymers linked by hydrogen bonds involving the 1- and the 2-nitrogen atoms in separate molecules (" 1 : 2-association "), a system which has been shown to prevail in the pyrazole and indazole series (Hayes and Hunter, *loc. cit.*). There seems to be no valid reason why 1 : 2- and 1 : 3-association should not occur simultaneously within the same polymer. The type of polymer cannot be deduced from the measurements; chain polymers seem most probable, although it is noteworthy that almost strainless models of a cyclic dimer involving 1 : 2-association, and a cyclic trimer involving 1 : 3-association, can be constructed. A chain polymer containing $x + 2$ molecules involved in 1 : 3-association is illustrated in (V), in which (*a*) and (*b*) are unperturbed structures of the resonance hybrid.



(V.)



The sharp distinction between benztriazoles according to whether their imino-group is substituted or not extends to other physical properties besides association. For example, those of unsubstituted type, although sparingly soluble in hydrocarbon solvents, are invariably soluble in water, a property attributable to the formation of a hydrogen bond with the oxygen atom of the solvent water. The difference in solubility of the two classes in hydrocarbons is well illustrated by a comparison between αβ-naphthatriazole, which was too sparingly soluble in naphthalene for molecular-weight measurement, and its 2-phenyl derivative, or even 1-phenylbenztriazole, both of which are readily soluble in naphthalene in spite of having considerably higher molecular weights. Moreover, in the few cases in which boiling points are recorded, the replacement of the imino-hydrogen atom in the benztriazoles results in a very great reduction in boiling point in spite of the rise in molecular weight; melting point is similarly affected. These properties are all taken as an indication of the readiness of the imino-hydrogen atom to take part in hydrogen-bond formation.

The above elucidation of the structure of the benztriazoles will provide some explanation of the physical and chemical behaviour of closely allied compounds. For instance, in certain other tautomeric cyclic nitrogenous systems in which unexpectedly large reductions in b. p. and m. p. are caused by replacing the imino-hydrogen atom (as in 1 : 2 : 3- and 1 : 2 : 4-triazoles, and in tetrazoles), their tautomeric character is probably attributable to molecular association by N–H–N bonds. Further, the abnormal physical properties of hydrazoic acid (Audrieth, *Chem. Reviews*, 1934, **15**, 180) and its associated character (Hantzsch, *Ber.*, 1933, **66**, 1349) are almost certainly indications of a hydrogen-bond structure.

EXPERIMENTAL.

The solvent naphthalene was the specially purified product for cryoscopic use obtained from the British Drug Houses. The following new compound was prepared.

4 : 6-*Dimethylbenztriazole.*—Noelting and Thesmar (*Ber.*, 1902, **35**, 636) described but did not characterise a white precipitate formed by the action of sodium nitrite on an acetic acid solution of *m*-xylylene-4 : 5-diamine. This diamine (1 mol.), in a slight excess of dilute sulphuric acid, was treated with aqueous sodium nitrite (1 mol.) until excess of nitrous acid was indicated by starch–potassium iodide paper. The black tar which separated was dried in a vacuum desiccator, and distilled under reduced pressure (b. p. 200°/*ca.* 16 mm.). The yellow distillate solidified in the receiver, and crystallised from xylene as buff micro-crystals, m. p. 183°, of the *monohydrate* (Found : C, 59·0; H, 6·4; N, 25·0; loss on heating, 10·0. $C_8H_3N_3,H_2O$ requires C, 58·2; H, 6·7; N, 25·4; H_2O, 10·9%). The anhydrous triazole had m. p. 190°.

Data.—In the following table concentrations are expressed as g.-mols. × 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. For reasons explained in previous parts of this series, conclusions as to molecular association are based, not on the absolute values of α, but on the slope of the association–concentration curves.

	Concn.	*M.*	α.
Benztriazole (119) (Curve 3)	0·81	172	1·44
	1·59	182	1·53
	2·33	211	1·77
	3·47	245	2·06
	4·62	283	2·32
	6·08	319	2·68
5-Methylbenztriazole (133) (Curve 2)	1·13	180	1·36
	1·93	217	1·63
	3·70	285	2·14
	5·00	333	2·50
	6·95	394	2·96
4 : 6-*Dimethylbenztriazole* (147) (Curve 1)	0·36	167	1·14
	0·91	197	1·34
	1·72*	266	1·81
5-Chlorobenztriazole (153·5) (Curve 4)	1·00	193	1·26
	1·70	208	1·36
	2·77	246	1·61
	4·12*	292	1·90
1-Phenylbenztriazole (195) (Curve 6)	0·73	192	0·99
	1·85	192·5	0·99
	3·10	201	1·03
	5·34	206	1·06

	Concn.	*M.*	α.
1-Acetylbenztriazole (161) (Curve 8)	0·54	154·5	0·96
	1·60	158	0·98
	2·80	160	0·99
	3·70	164	1·02
1-Benzoylbenztriazole (223) (Curve 9)	0·73	220	0·99
	1·18	224	1·00
	1·58	218	0·98
	2·24	220	0·99
1-Acetyl-5-methylbenztriazole (175) (Curve 7)	0·44	171	0·98
	1·08	173·5	0·99
	1·61	174	1·00
	2·22	175	1·00
	2·92	176	1·01
	3·54	178	1·01
2-*p*-Tolyl-5-methylbenztriazole (223) (Curve 5)	0·80	222	1·00
	1·12	226	1·01
	1·45	222	1·00
	1·95	226	1·02
2-Phenyl-$\alpha\beta$-naphthatriazole (245) (Curve 10)	0·49	228	0·96
	0·89	239	0·98
	1·15	238	0·97
	1·75	246	1·00
	2·48	237	0·97

* Solute separates at higher concentrations.

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