66. *The Azo-group as a Chelating Group. Part II. The Structure of the Diazoamino-compounds.*

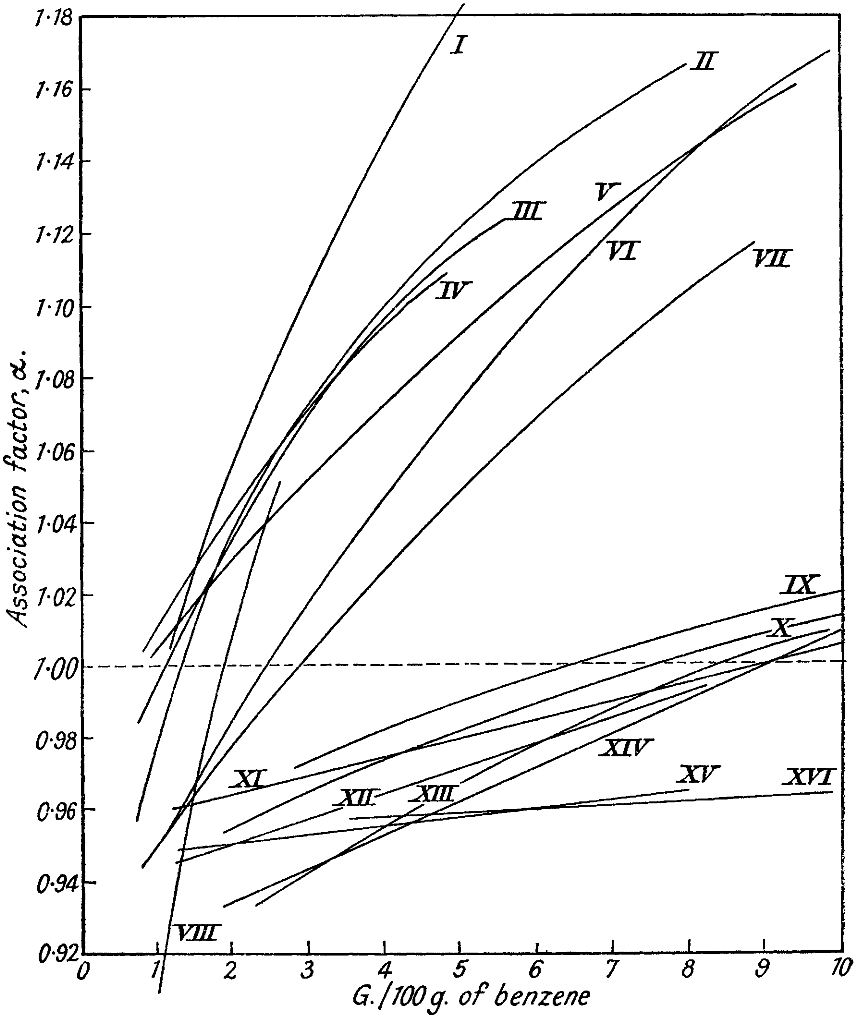
By Louis Hunter.

The constitution of the diazoamino-compounds, since their discovery by Griess (*Annalen*, 1862, **121**, 258), has presented an unsolved problem. The fundamental difficulty is the fact, originally revealed by Griess (*Ber.*, 1874, **7**, 1618), that the unsymmetrical compounds are capable of synthesis by interaction between a diazonium salt and a primary amine by the two alternative routes :

$$R{\cdot}N_2X + R'{\cdot}NH_2 \longrightarrow R{\cdot}N_3H{\cdot}R' \longleftarrow R{\cdot}NH_2 + R'{\cdot}N_2X$$

Similarly, fission of the compound so prepared (*e.g.*, by acids) usually results in the formation of all four possible products. Attempts to decide for each individual diazoamino-compound whether it possesses the formula $R{\cdot}N{:}N{\cdot}NHR'$ or $R{\cdot}NH{\cdot}N{:}NR'$ have, in most cases, led to conflicting results (for summary of evidence, see Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," pp. 131 *et seq.*, 1936). It is now fairly generally agreed that the unsymmetrical diazoamino-compounds are chemically homogeneous, and that the case is one of "virtual tautomerism" (von Pechmann, *Ber.*, 1895, **28**, 869; Ingold and Piggott, J., 1922, **121**, 2381).

Whatever be the structure of the diazoamino-compounds, however, that of their *N*-substituted derivatives is beyond dispute, for two different isomers R′·N:N·NRR″ and R·N:N·NR′R″ can in all cases be readily synthesised. In the present investigation measurements have been made of the molecular weights of diazoamino-compounds in benzene solution, and the results clearly show that, although substances of formula $R{\cdot}N_3H{\cdot}R'$ are associated in solution, those of formula $R'{\cdot}N_3{\cdot}RR''$ are of normal molecular weight. The data are in the tables, and when plotted graphically (see figure), the results indicate a wide divergence of type between *N*-substituted and unsubstituted diazoamino-compounds. The curves due to the former (curves IX—XVI) lie for the most part slightly below the line indicating normal molecular weight; those of the latter (curves I—VIII) lie above, and are invariably steeply sloped, indicating a rapidly rising degree of association with increasing concentration. *pp*′-Diethoxydiazoaminobenzene (curve VIII) is very abnormal in showing an apparent dissociation in dilute solution, but the slope of the curve is such as clearly to indicate that, were it possible to obtain a more concentrated solution, it would undoubtedly show considerable association. That the abnormality is not due to the presence of alkoxy-groups is shown by the fact that it is not shared by *N*-substituted diazoamino-compounds containing methoxy-groups (curves X and XV).



Unsubstituted diazoamino-compounds.

Figures in parenthesis indicate the normal molecular weight; *M* is the apparent molecular weight. Concentrations are given as g./100 g. of benzene; α is the association factor.

	Concn.	*M*.	α.		Concn.	*M*.	α.
Diazoaminobenzene (197) (Curve VI)	1·07	188·0	0·954	*p*-Methyldiazoaminobenzene (211) (Curve V)	0·93	211·9	1·004
	2·54	198·8	1·010		2·91	220·7	1·046
	4·68	209·6	1·064		4·68	229·4	1·086
	8·10	222·5	1·130		7·44	238·2	1·130
	9·88	230·1	1·168		9·31	244·9	1·160
op′-Dimethyldiazoaminobenzene (225) (Curve III)	0·77	222·0	0·986	*mp*′-Dimethyldiazoaminobenzene (225) (Curve II)	0·70	215·9	0·959
	2·26	235·1	1·045		1·77	231·5	1·030
	3·93	245·9	1·093		3·28	243·1	1·080
	5·55	252·1	1·120		5·46	254·2	1·130
					7·97	261·8	1·163
pp′-Dimethyldiazoaminobenzene (225) (Curve IV)	0·78	225·6	1·003	*pp*′-Dimethoxydiazoaminobenzene (257) (Curve I)	1·17	258·2	1·005
	2·79	239·6	1·065		2·64	283·0	1·101
	4·75*	247·6	1·100		4·03	294·5	1·146
oo′-*Dimethoxydiazoaminobenzene* (257) (Curve VII)	0·76	242·4	0·943		5·90	307·2	1·195
	2·26	252·8	0·984		7·14	318·4	1·239
	3·84	263·0	1·024	*pp*′-Diethoxydiazoaminobenzene (285) (Curve VIII)	0·67	236·0	0·828
	5·56	270·8	1·054		1·21	261·8	0·919
	7·57	281·4	1·095		1·69	276·2	0·969
	8·72	286·9	1·116		2·56*	299·0	1·050

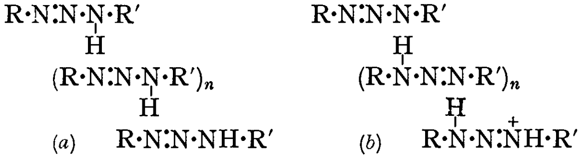
N-*Substituted diazoamino-compounds.*

1-*p*-Tolyl-3 : 3-dimethyltriazen (163) (Curve XII)	1·27	154·3	0·947	1-m-*Tolyl*-3-*phenyl*-3-*methyltriazen* (225) (Curve XI)	1·27	216·3	0·961
	3·59	156·7	0·961		3·39	218·5	0·971
	5·23	159·1	0·976		6·00	220·5	0·980
	8·14	162·0	0·994		8·21	224·2	0·997
					10·73	226·5	1·007
1-p-*Bromophenyl*-3 : 3-*dimethyltriazen* (228) (Curve XIII)	2·33	213·0	0·934	1-p-*Bromophenyl*-3-*phenyl*-3-*methyltriazen* (290) (Curve IX)	2·98	279·6	0·964
	5·48	222·0	0·974		4·09	286·5	0·988
	7·86	227·2	0·996		6·10	290·0	1·000
	9·90	229·8	1·008		8·37	293·7	1·013
					10·62	296·1	1·021
1-p-*Bromophenyl*-3-*phenyl*-3-*benzyltriazen* (366) (Curve XVI)	3·51	351·5	0·960	*p*-Bromophenylazopiperidine (268) (Curve XIV)	1·96	250·4	0·934
	5·41	349·6	0·955		4·94	257·9	0·962
	7·66	350·7	0·958		7·78	264·2	0·986
	9·89	354·1	0·968		10·34	270·7	1·010
1-o-*Methoxyphenyl*-3-*phenyl*-3-*methyltriazen* (241) (Curve XV)	1·32	228·6	0·948	1-p-*Methoxyphenyl*-3-*phenyl*-3-*methyltriazen* (241) (Curve X)	1·88	229·9	0·954
	2·81	229·0	0·950		4·51	237·2	0·984
	4·40	231·8	0·962		7·37	240·3	0·997
	7·77	232·0	0·963		10·66	244·7	1·015

* The substance was not sufficiently soluble for measurements to be made at higher concentrations.

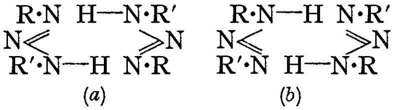
It is clear from these results that the association of substances of formula $R\cdot N_3H\cdot R'$ is due to the presence of the imino-hydrogen atom, and it seems reasonable to attribute it to hydrogen-bond formation; *i.e.*, adjacent molecules are held together by sharing the imino-hydrogen atom, the alternative point of attachment probably being at one of the azo-nitrogen atoms. The molecular-weight measurements give no information as to the extent of the association, and there are two types of polymer possible, *viz.*, open-chain, of the kind suggested for water and other hydroxy-compounds (*Ann. Reports*, 1934, **31**, 42) and for quinhydrone (Foz and Palacios, *Anal. Fis. Quim.*, 1932, **30**, 421), or cyclic, for which, on steric grounds, the most probable form is dimeric. It is possible that in solution both types of polymer are present.

By using the newer concept of hydrogen bonds (Sidgwick, *Ann. Reports*, 1933, **30**, 112) it at once becomes apparent that the association of the diazoamino-compounds probably has an intimate bearing on their tautomeric behaviour. The following formulæ depict the extreme forms (*a*) and (*b*) due to hydrogen resonance in an open-chain polymer (I) and in a cyclic polymer (II). Such a formulation implies that the imino-hydrogen atoms are attached alternately to nitrogen atoms in adjacent molecules, with a consequent rearrangement of valency linkings within the remainder of the molecule. It is probable that in the undissolved condition the diazoamino-structure is represented by either (I) or (II) or some variant of these. In solution, however, partial dissociation occurs, each extreme resonance state giving rise to a different unimolecular form; *i.e.*, (I*a*) and (II*a*) dissociate into



$$\begin{array}{ll}\mathrm{R{\cdot}N{:}N{\cdot}\underset{|}{N}{\cdot}R'} & \mathrm{R{\cdot}N{:}N{\cdot}\overset{-}{N}{\cdot}R'}\\ \quad\mathrm{H} & \quad\mathrm{H}\\ \mathrm{(R{\cdot}N{:}N{\cdot}\underset{|}{N}{\cdot}R')_n} & \mathrm{(R{\cdot}N{\cdot}N{:}N{\cdot}R')_n}\\ \quad\mathrm{H} & \quad\mathrm{H}\\ (a)\ \mathrm{R{\cdot}N{:}N{\cdot}NH{\cdot}R'} & (b)\ \mathrm{R{\cdot}\overset{+}{N}{\cdot}N{:}NH{\cdot}R'}\end{array}$$

(I.)



(*a*) (*b*)

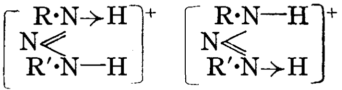
(II.)

$\mathrm{R{\cdot}N{:}N{\cdot}NH{\cdot}R'}$, and (I*b*) and (II*b*) into $\mathrm{R{\cdot}NH{\cdot}N{:}N{\cdot}R'}$. Such a view would lead us not only to accept, but indeed to expect, the mass of conflicting evidence for any static formulation of the diazoamino-compounds. There is obviously the possibility of numerous other less symmetrical variations of the two general types of polymer represented above. Whatever the actual dispositions of the constituent molecules within the polymers, however, they will one and all dissociate into mono-molecules which will show the properties of both $\mathrm{R{\cdot}N{:}N{\cdot}NH{\cdot}R'}$ and $\mathrm{R{\cdot}NH{\cdot}N{:}N{\cdot}R'}$.

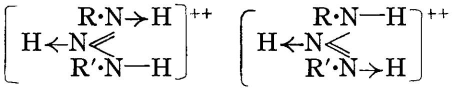
The dimeric form (II) is chosen as the most probable type of cyclic polymer on stereochemical grounds. The *trans*-configuration of diazoamino-compounds has long been accepted in explanation of their stability; and this, together with the 180° valency angle of the co-ordinated hydrogen atom (Sidgwick, *loc. cit.*, pp. 113—115), results in a practically strainless eight-membered ring (compare the dimeric form of carboxylic acids; Pfeiffer, " Organische Molekülarverbindungen," 2nd edn., 1927, pp. 122, 123; Sidgwick, *loc. cit.*).

With certain reagents the diazoamino-compounds react as though they possess a fixed and not a tautomeric constitution, and such reagents have been used diagnostically. For instance, their behaviour with phenyl *iso*cyanate led Goldschmidt and his co-workers (*Ber.*, 1888, **21**, 1016, 2557; 1905, **38**, 1096) to the conclusion that the imino-group is always attached to the more negative radical. On the other hand, the decomposition of diazoamino-compounds with ice-cold mineral acid led Dimroth and his co-workers (*Ber.*, 1905, **38**, 670; 1907, **40**, 2390) to the opposite conclusion. Such reactions find ready explanation as a preferential reaction of the diagnostic reagent with one of the unimolecular forms, the continuous removal of which ultimately results in the complete conversion of the less into the more reactive form.

The mild salt-forming properties of the diazoamino-compounds are probably attributable to a cause similar to that operating in their association, *viz.*, the tendency of the azo-nitrogen atoms to share electrons with, in this case, a hydrogen ion. These salts are very unstable, and may contain one or two (but never more) equivalents of acid to each molecule of diazoamino-compound, thus pointing to electron-donor properties only in the azo-nitrogen atoms. Formula (III) depicts the extreme states, due to hydrogen resonance, of the ion derived from a diazoamino-compound acting as a monoacid base, *e.g.*,



(III.)



(IV.)

$\mathrm{(Ph{\cdot}N_2{\cdot}NHPh)_2,H_2PtCl_6}$ (Griess, *Annalen*, 1862, **121**, 261), and formula (IV) the ion derived from a diazoamino-compound acting as a diacid base, *e.g.*, $\mathrm{(C_6H_4Me)_2N_3H,H_2PtCl_6}$ (Griess, *loc. cit.*, p. 277). It is doubtless the intermediate formation of ions of this structure which precedes the decomposition of the diazoamino-compound $\mathrm{R{\cdot}N_3HR'}$ by mineral acid into a mixture of diazonium salts ($\mathrm{R{\cdot}N_2X}$ and $\mathrm{R'{\cdot}N_2X}$) and amines ($\mathrm{R{\cdot}NH_2}$ and $\mathrm{R'{\cdot}NH_2}$).

EXPERIMENTAL.

Molecular weights were measured cryoscopically in benzene, the same Beckmann thermometer, and benzene from the same source being used for all the measurements. In view of the tendency to undergo decomposition in hot solvents which characterises certain diazoamino-compounds

(Earl, *Chem. and Ind.*, 1936, 192), special care was taken in their purification. Since the majority of the known *N*-substituted diazoamino-compounds are liquids, a number of new solid compounds have been synthesised for the purpose of this investigation.

Diazoaminobenzene, crystallised rapidly from alcohol, formed pale yellow plates, m. p. 99°. *p*-Methyldiazoaminobenzene, crystallised similarly, formed yellow needles, m. p. 90°.

op′-Dimethyldiazoaminobenzene requires special care in purification, since considerable amounts of the isomeric *p*-tolueneazo-*o*-toluidine are formed during its preparation. It was obtained first from benzene and ligroin as an undoubted mixture melting sharply at 109°. Repeated crystallisation from the same solvents ultimately raised the m. p. to 117—118°. It formed long, straw-yellow, silky needles.

mp′-Dimethyldiazoaminobenzene crystallised from benzene and ligroin in bright yellow, silky needles, m. p. 96°. *pp*′-Dimethyldiazoaminobenzene, crystallised rapidly from alcohol, formed yellow needles, m. p. 116°.

oo′-*Dimethoxydiazoaminobenzene* was prepared in the usual way by diazotising *o*-anisidine in dilute hydrochloric acid, and adding an equivalent quantity of *o*-anisidine dissolved in hydrochloric acid, followed by an excess of aqueous sodium acetate under mechanical stirring. The oil first formed rapidly solidified, and was filtered off, washed, and crystallised whilst still moist from alcohol. Rapid cooling of the alcoholic solution was necessary to minimise decomposition. The product formed pale yellow leaflets, m. p. 97° (Found: N, 16·2. $C_{12}H_{15}O_2N_3$ requires N, 16·3%).

pp′-Dimethoxydiazoaminobenzene, crystallised repeatedly from benzene and ligroin, formed liquorice-yellow prisms, m.p. 100°. *pp*′-Diethoxydiazoaminobenzene crystallised from benzene in orange prisms, m.p. 119—120°.

1-*p*-Tolyl-3 : 3-dimethyltriazen formed large, sweet-smelling, colourless plates from alcohol, m. p. 50—51°.

3-*Phenyl*-1-m-*tolyl*-3-*methyltriazen.*—A solution of *m*-toluidine (1 mol.) in hydrochloric acid was diazotised at 0°. During thorough mechanical stirring a solution of methylaniline (1 mol.) in hydrochloric acid was added, followed by an excess of aqueous sodium acetate; this precipitated an orange-coloured oil which soon solidified. The resulting yellow solid was filtered off, washed with water, and crystallised from alcohol. It formed bright yellow leaflets, m. p. 67° (Found: N, 19·0. $C_{14}H_{15}N_3$ requires N, 18·7%).

1-p-*Bromophenyl*-3 : 3-*dimethyltriazen.*—*p*-Bromoaniline was diazotised at 0° in hydrochloric acid solution with sodium nitrite, until the starch–iodide reaction was just positive. An excess of cooled, saturated, aqueous sodium acetate was then added to remove mineral acidity, followed by aqueous dimethylamine solution until the whitish precipitate no longer formed. The pale buff-coloured solid was then filtered off, washed, and crystallised whilst still moist from alcohol. It formed pale buff prisms, m. p. 62·5°, having the sickly sweet odour common to most aryldimethyltriazens (Found: N, 18·3; Br, 34·8. $C_8H_{10}N_3Br$ requires N, 18·4; Br, 35·1%).

1-p-*Bromophenyl*-3-*phenyl*-3-*methyltriazen*, prepared from diazotised *p*-bromoaniline and methylaniline, crystallised from alcohol in orange flakes, m. p. 82° (Found: N, 14·3; Br, 27·4. $C_{13}H_{12}N_3Br$ requires N, 14·5; Br, 27·6%).

1-p-*Bromophenyl*-3-*phenyl*-3-*benzyltriazen*, prepared from diazotised *p*-bromoaniline and *N*-benzylaniline, crystallised from alcohol in long, silky, orange needles, m. p. 111—112° (Found: N, 11·6; Br, 21·4. $C_{19}H_{16}N_3Br$ requires N, 11·5; Br, 21·8%).

p-Bromophenylazopiperidine formed pale orange leaflets from alcohol, m. p. 55° (Found: Br, 29·7. Calc.: Br, 29·8%).

1-o-*Methoxyphenyl*-3-*phenyl*-3-*methyltriazen*, prepared from diazotised *o*-anisidine and methylaniline, crystallised from alcohol in thick, deep yellow prisms, m. p. 97—98° (Found: N, 17·3. $C_{14}H_{15}ON_3$ requires N, 17·4%).

1-p-*Methoxyphenyl*-3-*phenyl*-3-*methyltriazen*, prepared from *p*-anisidine as above, crystallised from alcohol in brilliant yellow, silky needles, m. p. 61° (Found: N, 17·4. $C_{14}H_{15}ON_3$ requires N, 17·4%).

Grateful acknowledgment is made to Professor C. K. Ingold, F.R.S., and the referees for their helpful assistance.

UNIVERSITY COLLEGE, LEICESTER.

[*Received, November 5th, 1936.*]