

145. *The Associating Effect of the Hydrogen Atom. Part IX. The N-H-N Bond. Virtual Tautomerism of the Formazyl Compounds.*

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On the grounds of their physical properties and the isolation of chelate metallic derivatives (see next paper), the formazyl compounds are assigned an internally co-ordinated (hydrogen-bond) structure, which accounts for their virtual tautomerism. Three pairs of alleged isomers are shown to be, in fact, three single individuals; a fourth pair, though not re-examined, probably permits of similar simplification.

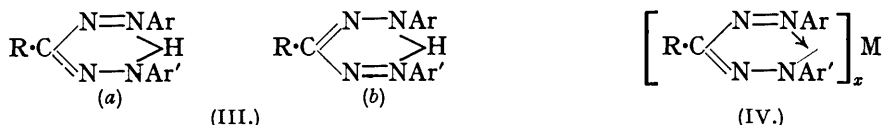
THE nomenclature and structure of the formazyl derivatives are given unusual prominence in the introduction to Beilstein's Handbuch (4th Edn., Vol. XVI, pp. 4—6), and from this and the subsequent details of individual compounds it is evident that the question of their structure is somewhat confused.

The formazyls are usually prepared by the coupling of a diazonium compound with an aldehydarylhydrazone, and it would appear that two isomeric formazyls are capable of synthesis by the schemes :



In practice, however, it is fairly generally agreed that (I) and (II) are identical, and v. Pechmann (*Ber.*, 1895, **28**, 876) suggested that the case is one of virtual tautomerism, and that (I) and (II) bear the same relationship as the tautomers of the amidines and those of the diazoamino-compounds. This means that the imino-hydrogen atom represented as permanently attached to a specific nitrogen atom in (I) and (II) is not, in fact, so attached, but is alternately bound to the two nitrogen atoms as indicated in the tautomeric equilibrium (I) \rightleftharpoons (II). That this view of the tautomerism of the formazyls is not universally accepted is evident from the isolation, subsequent to v. Pechmann's publication, of a number of pairs of alleged isomers with structures corresponding to (I) and (II).

In the course of developing a new classification of tautomeric systems (Hunter, *Chem. and Ind.*, 1941, **60**, 32), it was deemed desirable to re-examine the structure of the formazyls. It appeared possible that their virtual tautomerism might be attributable to an internally co-ordinated structure such that the tautomeric (imino-) hydrogen atom forms a hydrogen bond with one of the azo-nitrogen atoms. That it is favourably situated to do this is evident from formula (III), in which *a* and *b* are the two components of the



resonance hybrid. This formulation would explain satisfactorily not only the identity of the product obtained by the two routes (I) and (II), but also the alternative products of hydrolytic and reductive fission cited by v. Pechmann and Runge (*Ber.*, 1894, **27**, 1696) as evidence of the virtual tautomerism of the formazyl compounds.

Examination of the formazyls shows that they do indeed possess a chelate structure, a conclusion based on the following evidence.

1. A series of metallic derivatives has been prepared from the formazyls by replacement of the imino-hydrogen atom by 1 equiv. of metal. From their properties (see next paper) these derivatives are typically chelate, and must be formulated as (IV; M = *x*-valent metal). This is taken to be very strong evidence for a similar structure in the parent hydrogen compounds.

2. In spite of their high molecular weights (*e.g.*, diphenylformazylbenzene = 300), the formazyls are remarkably soluble in organic solvents. In contrast, *p*-benzeneazobenzaldehydphenylhydrazone (isomeric with diphenylformazylbenzene), the constitution of which precludes a chelate structure, is very sparingly soluble (Freundlich, *Compt. rend.*, 1902, **134**, 1360).

3. Measurement of molecular weight of the formazyls over a range of concentration in benzene solution reveals that they are substantially unimolecular. This must be due to internal satisfaction of the donor (azo-nitrogen) and acceptor (imino-hydrogen) centres. Cases of substituted arylhydrazones where such internal satisfaction is not structurally possible, and thus resulting in molecular association, have been quoted in Part V (J., 1940, 166).

The above explanation of the virtual tautomerism of the formazyl compounds would be gravely inadequate without some re-examination of the pairs of alleged isomers, mentioned above, corresponding to the structures (I) and (II). So far as we are aware, there have been four such pairs reported, details of which are contained in the following table.

Structure claimed.	M. p.	Authors.
NPh·N·CPh·N·NH·C ₁₀ H ₇ (α)	168°	Fichter and Schiess, <i>Ber.</i> , 1900, 33 , 751
NHPh·N·CPh·N·N·C ₁₀ H ₇ (α)	173	
NPh·N·CPh·N·NH·C ₁₀ H ₇ (β)	150	Fichter and Frohlich, <i>Z. Farb. Text. Chem.</i> , 1903, 2 , 251
NHPh·N·CPh·N·N·C ₁₀ H ₇ (β)	172	
NPh·N·CPh·N·NH·C ₆ H ₄ Br(<i>p</i>)	191	Busch and Schmidt, <i>J. pr. Chem.</i> , 1931, 131 , 182
NHPh·N·CPh·N·N·C ₆ H ₄ Br(<i>p</i>)	189	
NPh·N·CPh·N·NH·C ₆ H ₄ SO ₃ Na(<i>p</i>)	ca. 135	Fichter and Schiess, <i>loc. cit.</i>
NHPh·N·CPh·N·N·C ₆ H ₄ SO ₃ Na(<i>p</i>)	ca. 165	

The first three of these pairs have been thoroughly investigated (see Experimental), and there seems little doubt that the lower-melting compound of each pair is in reality an impure form of the higher-melting compound, and that in fact only one substance exists. The last pair was not re-examined, since it was not expected that a satisfactory method of proving the identity of these sodium sulphonates could be devised. Nevertheless, the original authors' distinction between the alleged isomers rests solely on differences in very doubtful melting points, and on slightly different shades of dyeing silk or wool. It is significant that both so-called isomers undergo cyclisation to yield the same phenylbenztriazine (Fichter and Schiess, *loc. cit.*), whereas if they were different individuals one would be expected to yield the triazine sulphonate.

EXPERIMENTAL.

The first three pairs of alleged isomers (see table) were prepared by the alternative schemes outlined in (I) and (II), the products being shown to be identical.

Phenyl- α -naphthylformazylbenzene.—(a) *By coupling α -naphthalenediazonium chloride with benzaldehydephenylhydrazone.* Benzaldehyde (10.6 g.) and phenylhydrazine (10.8 g.) were mixed in a small quantity of alcohol, warmed for a short time, and diluted with alcohol to 1 l. The diazonium salt solution was prepared from α -naphthylamine (14.3 g.), hydrochloric acid (50 c.c.), and sodium nitrite (8 g.) in water. The two solutions were run at equivalent rates with mechanical stirring into a solution of sodium hydroxide (45 g.) in the minimum of water, diluted with alcohol (300 c.c.). The mixture was kept overnight, and the crude formazyl compound was then separated, and crystallised whilst still moist from aqueous acetone (charcoal). It formed brownish-purple microcrystals with a green reflex from chloroform-alcohol; m. p. 170—171°.

(b) *By coupling benzenediazonium chloride with benzaldehyde- α -naphthylhydrazone.* This preparation gave some difficulty, owing chiefly to the relative insolubility of the hydrazone, and partly to the tendency for the diazonium salt to couple at positions other than the methine hydrogen atom. As a result, the product is frequently an oil which slowly solidifies, and this fact undoubtedly accounts for the mistaken identity of the substance prepared by Fichter and Schiess (*loc. cit.*). The method finally adopted was as follows. Benzaldehyde- α -naphthylhydrazone (17 g.) in alcohol (800 c.c.) was mixed with a solution of sodium hydroxide (20 g.) in the least amount of water diluted with alcohol (200 c.c.). To the cooled and stirred mixture was slowly added a solution of benzenediazonium chloride prepared from aniline (7 g.). After standing overnight, the resulting solid was filtered off and recrystallised from benzene. A black insoluble portion, m. p. 188°, formed about one-third of the total, and was not further examined; the main bulk of the formazyl compound was recrystallised many times from benzene-alcohol, and finally from acetone-water. It formed a purple solid with a greenish reflex; m. p. 170°.

The identity of the substances produced in methods (a) and (b) was shown by the fact that they yielded identical metallic derivatives (see next paper), and that mixed m. p.'s on three intermediate compositions all lay between 170° and 171°.

Phenyl- β -naphthylformazylbenzene.—(a) *By coupling β -naphthalenediazonium chloride with benzaldehydephenylhydrazone.* The crude product (m. p. 158°) was repeatedly recrystallised from acetone-water and chloroform-alcohol, yielding a purple-brown microcrystalline solid, m. p. 170°.

(b) *By coupling benzenediazonium chloride with benzaldehyde- β -naphthylhydrazone.* After six recrystallisations from chloroform-alcohol the product formed a purple-brown crystalline solid with a green reflex, m. p. 169—170°.

The identity of these two products was confirmed by the derivation of identical metallic compounds (see next paper), and by the sharpness of the m. p.'s of three intermediate mixtures, all lying between 169° and 170°.

Phenyl-p-bromophenylformazylbenzene.—(a) *By coupling benzenediazonium chloride with benzaldehyde-p-bromophenylhydrazone.* The product formed a greenish-purple, crystalline solid, m. p. 188°.

(b) *By coupling p-bromobenzenediazonium chloride with benzaldehydephenylhydrazone.* The product crystallised from chloroform-alcohol as a purple-brown solid, but when crystallised from acetone-water it had a greenish reflex; m. p. 187°.

The identity of these two substances was shown as in the foregoing cases, the m. p.'s of three intermediate mixtures all lying between 187° and 188°.

Molecular-weight Data.—The unimolecular state of the formazyl derivatives is deduced from cryoscopic measurements in benzene solution on the following three compounds.

Diphenylformazylbenzene (Calc.: *M*, 300).

G. of solute/100 g. of benzene	0.80	2.12	3.39	4.63
Apparent molecular weight	284	297	292	299

Phenyl-*p*-tolylformazylbenzene (Calc.: *M*, 314).

G. of solute/100 g. of benzene	0.68	2.01	3.31	4.56	5.79
Apparent molecular weight	290	305	297	308	316

Phenyl-*p*-methoxyphenylformazylbenzene (Calc.: *M*, 330).

G. of solute/100 g. of benzene	0.67	2.00	3.28	4.76	6.01
Apparent molecular weight	340	339	332	339	347

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