106. *Evidence for the* iso*Nitrile and Nitrile Structures of Hantzsch's Aryl* syn- *and* anti-*Diazocyanides.*

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Hantzsch's aryl *syn*- and *anti*-diazocyanides exhibit differences of chemical reactivity which are accounted for by *iso*nitrile and nitrile structures, *i.e.*, the presence of N–N and N–C bonds in the molecule. Analogy between the *syn*-cyanides and *iso*cyanates is found to be very close. The conversion of the non-coupling *p*-nitrobenzenediazocarbonamide (with its stable C–N bond) by reaction with bromine into an *N*-bromocarbonamide, which will then couple with α- or β-naphthylamine in non-aqueous media, as also with β-naphthol in aqueous-alcoholic and alkaline solution, indicates that the Hofmann reaction has occurred, and that the resulting intermediate diazocyanate with its easily ruptured N–N bond will now couple. The formation of *syn*-cyanides in mineral acid medium finds a parallel in the formation of diazoamino-compounds in acid media of similar strength. The ready rupture of the N–N bond is in accord with chemical experience generally.

It was obvious when Hantzsch put forward his stereochemical views on the diazohydroxides, diazosulphonates, and diazocyanides, that the great and many chemical differences between the *syn*- and *anti*-compounds were not readily accounted for by mere differences of configuration in space which the fallacious comparison of these compounds with the stereoisomeric oximes had involved. According to Sidgwick (" The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 418), the strongest evidence for Hantzsch's point of view was derived from the study of the diazosulphonates and diazocyanides, and this is to be found in " Die Diazo-Verbindungen " (Hantzsch and Reddelien, 1921), in " The Chemistry of the Diazo-Compounds and Their Technical Applications " (Saunders, 1936), and in papers by Le Fèvre and Vine (J., 1938, 431) and by Stephenson and Waters (J., 1939, 1796).

Recently, however, it was shown by Hodgson and Marsden (J., 1943, 470) that Hantzsch's *syn*- and *anti*-diazosulphonates are not geometrical but structural isomers, *viz.*, diazosulphites and diazosulphonates, respectively, and such a result calls for a re-examination of the position with respect to the *syn*- and *anti*-diazocyanides, despite the apparent confirmation of the stereochemical theory for the structures of these compounds by recent data from dipole-moment measurements (cf. Le Fèvre and Vine, *loc. cit.*).

Stephenson and Waters (*loc. cit.*) ascribe the great chemical reactivity of the *syn*-cyanides in ionising solvents to their partial ionisation, and it is noteworthy that in certain of their decompositions the odour of *iso*nitriles is prevalent. This last fact indicates that the cyanide ion can form a covalent union at its nitrogen atom, and therefore it is reasonable to infer that a like combination can occur between the nitrogens of the cyanide and the diazonium ions when a diazonium salt is treated with potassium cyanide in slightly acid solution. Actually, the addition always results in the formation of a yellow compound initially, which, if the reaction is conducted below −5° persists and the yellow *syn*-cyanide results, whereas if the temperature is above 0° the yellow colour quickly changes through yellow-orange to orange-red and then to red when the stable *anti*-cyanide is formed. In some cases, such as those of *o*- and *p*-chloro- and *p*-bromo-aniline, mixtures of *syn*- and *anti*-diazocyanides are formed above 0° but complete isomerisation takes place when Le Fèvre and Vine's procedure is followed (*loc. cit.*). These experiments support the view of these authors that the *syn*-cyanide is first produced, followed by conversion into the *anti*-isomeride.

One of the difficulties attending the acceptance of the stereoisomerism of the *syn*- and *anti*-diazosulphonates was the ease of coupling of the *syn*-compounds, *i.e.*, the ease of rupture of the bond between the diazo-nitrogen and the $-SO_3Na$ group in the *syn*-, and its impossibility under reasonable conditions in the *anti*-configuration. This difficulty is insurmountable if N–S bonds are postulated in both cases, but the problem receives immediate solution when the difference between the isomerides is ascribed to the ready rupture of an N–O bond in the *syn*- and the non-rupture of an N–S bond in the *anti*-compound. Complete analogies were to be found in the labile diazo-oxides and the stable diazo-sulphides. A similar difficulty arises when a C–N bond is postulated for both *syn*- and *anti*-diazocyanides, whereas the chemical evidence receives adequate explanation when the *syn*-compounds are held to possess the readily ruptured N–N bond, and the *anti*-diazocyanides the stable C–N link. Further, the difference in bond energies between these two links is 28 kg.-cals./mol. (cf. Pauling, " The Nature of the Chemical Bond," 1940, p, 53), which is of the same order as the 21—22 kg.-cals./mol. reported for the heat of transformation of *p*-bromobenzene-*syn*- into -*anti*-diazocyanide (Le Fèvre and Vine, *loc. cit.*). Also, Stephenson and Waters's experiments (*loc. cit.*), in which the *syn*-cyanide instantly reacts with silver nitrate, find a parallel in the formation of Prussian-blue when the *syn*-cyanide (but not the *anti*-cyanide) is treated successively with sodium hydroxide, ferrous sulphate, hydrochloric acid, and ferric chloride. Analogies are to be found of the readily ruptured N–N link in the diazoamino-compounds and in the transformations of hydrazo-compounds into benzidines and semidines. The fact that the *syn*-cyanide requires to be formed in weakly acid solution also finds a parallel in the care with which diazotisation must be conducted, even in mineral acid solution, in order to avoid formation of diazoamino-compounds which have comparable, and in the case of *pp*′-dinitrodiazoaminobenzene superior, stability to the *syn*-diazocyanides in mineral acid of similar concentration.

Temperature appears to be of prime importance in bringing about the transformation of *syn*- into *anti*-diazocyanide, which takes place fairly rapidly with the *p*-nitro- and the *p*-chloro-benzene derivative, even in ethereal solution at about 0°.

When the *o*- and *p*-chloro-, *o*- and *p*-bromo-, and *p*-nitro-*syn*- and -*anti*-benzenediazocyanides are treated with methylmagnesium iodide in dry ether, orange-red complexes are formed, the *anti*- having a deeper red colour than the *syn*-complex, and subsequent decomposition of these complexes by iced 2N-sulphuric acid gives acetaldehyde from the *syn*- but not from the *anti*-complexes. To ensure that no *syn*-diazocyanide remained unisomerised in the experiments with the *anti*-compounds, since *o*-chloro- and *o*-bromo-benzene-*syn*-diazocyanides isomerise slowly, all the isomerisations were separately carried out in benzene solution according to Le Fèvre and Vine's directions (*loc. cit.*) before reaction with the Grignard reagent in dry ethereal solution. The yields of acetaldehyde, as determined by the 4-nitro- and the 2 : 4-dinitro-phenylhydrazones, were of the order of 20%, and we are of opinion that some isomerisation of *syn*- to *anti*-compound takes place before the formation of the complex since the *anti*- appeared to be formed rather more rapidly than the *syn*-complexes. Ths reaction with the Grignard reagent finds an analogy in the *iso*nitriles, which also give aldehydes under like conditions (cf. Sidgwick, *op. cit.*, p. 319), but the *anti*-diazocyanides when treated with phenylmagnesium bromide yield eventually considerable amounts of carbylamine, which suggests that the initial complex may be a mixture and contain a component of structure NR:N·C(MgBr):NPh, which in the subsequent decomposition might be expected to give phenyl *iso*nitrile. On analogy also, the m. p.'s of the *syn*-diazocyanides are lower than those of the *anti*-isomerides and so correspond with the lower b. p.'s of the organic *iso*cyanides than of the isomeric nitriles, and the ready ability of the *syn*-diazocyanides to form double compounds with metallic cyanides finds a parallel in the similar double-cyanide formation by organic *iso*cyanides. This property of forming double cyanides is lacking in the *anti*-diazocyanides. The course of the Grignard reactions with the *syn*-diazocyanides would therefore appear to be best represented by the following sequence of stages based on the assumption of an *iso*nitrile structure :

$$C_6H_4R{\cdot}N{:}N{\cdot}\overset{+}{N}\vdots\overset{-}{C} + MgIMe \longrightarrow C_6H_4R{\cdot}N{:}N{\cdot}N{:}CMe{\cdot}MgI \xrightarrow{\text{Hydrolysis}} C_6H_4R{\cdot}N{:}N{\cdot}N{:}CHMe \xrightarrow[\text{hydrolysis}]{\text{Further}} CH_3{\cdot}CHO$$

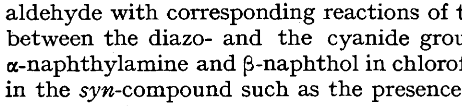
The ease of resonance of the non-polar nitrile structure has been pointed out by Stephenson and Waters (*loc. cit.*) as comparable with that of azobenzene, and this is shown by the deep red colour of the *anti*-diazocyanides which is similar to that of azobenzene, whereas the presence of the dipolar *iso*nitrile group in the *syn*-diazocyanide, with the consequent electronic strain imposed on the molecule, would account for the yellow colour of these compounds when formed initially. We suggest that the orange colours reported for the solid *syn*-diazocyanides provide evidence that a certain amount of isomerisation has taken place, a circumstance perhaps reflected in their low m. p.'s. Such isomerisation is so prone to take place, particularly in those compounds on which Hantzsch based his theory, that he must always have been dealing with a mixture of the two isomerides as in the case of his *syn*-diazosulphonates.

The ease of rupture of the N–N bond is also shown in the facile coupling of the diazo*iso*cyanates, NR:N·NCO. Both *syn*- and *anti*-*p*-nitrobenzenediazocyanides on hydrolysis give the same diazocarbonamide (Hantzsch and Schulze, *Ber.*, 1895, **28**, 666), $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, which is a relatively stable substance and does not couple with alkaline β-naphthol, thereby indicating the resistance to rupture of the C–N bond. When, however, this carbonamide is treated with bromine in a dry, neutral solvent such as chloroform or benzene, or in glacial acetic acid, an orange-red substance is precipitated, which is probably a perbromide since it rapidly loses bromine in the air, and changes to a comparatively stable yellow *substance* whose analysis and chemical behaviour correspond to $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NHBr,HBr$. This *N*-bromocarbonamide when added to a solution of α- or β-naphthylamine in chloroform or benzene rapidly couples to give *p*-nitrobenzeneazo-α- or -β-naphthylamine, but will not do so with a chloroform or benzene or absolute alcoholic solution of β-naphthol. If, however, aqueous-alcoholic β-naphthol is employed, and of course alkaline β-naphthol, coupling occurs at once to give *p*-nitrobenzeneazo-β-naphthol.

The mechanism of the naphthylamine couplings with the *N*-bromocarbonamide undoubtedly involves that of the well-known Hofmann rearrangement (*Ber.*, 1882, **15**, 407), whereas the coupling with β-naphthol requires intermediate hydrolysis of the *N*-bromocarbonamide to the hydroxamic acid, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH{\cdot}OH$, followed by the Lossen rearrangement (*Annalen*, 1872, **161**, 347). In both cases the formation of a diazo*iso*cyanate with its weak N–N link must precede coupling. The fact that the naphthylamine couplings take place in a medium where hydrolysis is precluded, affords evidence against the diazonium ion coupling theory of Wistar and Bartlett (*J. Amer. Chem. Soc.*, 1941, **63**, 413) and Hauser and Breslow (*ibid.*, p. 418), and in favour of the polarisation theory (cf. Hodgson, *J. Soc. Dyers Col.*, 1942, **58**, 228). It is of interest that both acetamide (Hofmann, *loc. cit.*) and benzamide (Laurent, Gmelin's " Handbuch der Organischen Chemie," 1848—1870, **3**, 115) form labile compounds with bromine without apparent replacement of hydrogen, whereas such replacement has undoubtedly occurred in the *p*-nitrobenzenediazo-*N*-bromocarbonamide, since free bromine is not evolved from it, whereas it reacts with water partly to regenerate the unbrominated carbonamide and partly to form the hydroxamic acid which undergoes the Lossen rearrangement and so gives a compound, *viz.*, the *iso*cyanate, which has coupling properties. In addition, a labile compound with bromine, such as those described by Laurent and Hofmann, could hardly be expected to couple with β-naphthol in aqueous alcohol. Further evidence of the reactivity of the diazo*iso*cyanates is afforded by the formation of 4 : 4′-dinitrodiazoaminobenzene when neutral *p*-nitrobenzenediazonium sulphate is treated with potassium cyanate and the mixture kept overnight, the almost quantitative yield indicating that the *p*-nitrobenzenediazo*iso*cyanate first formed must have decomposed intermediately to give *p*-nitroaniline which has then reacted with unchanged diazonium sulphate to give the diazoamino-compound. That an *iso*cyanate is formed has an analogy in the production of phenyl *iso*cyanate when benzenediazonium salts react with potassium cyanate (Gattermann and Canzler, *Ber.*, 1890, **23**, 1225; 1892, **25**, 1086), and in the striking fact that only the *iso*cyanates are known of the two possible series of esters of cyanic acid. All our attempts to isolate a diazocyanate or *iso*cyanate by treating neutral *p*-nitrobenzenediazonium chloride with potassium or silver cyanate were frustrated by the facile decomposition of the resulting diazo-compound. An attempt to crystallise the *N*-bromocarbonamide from ethyl alcohol afforded *p*-bromobenzene, showing that the hot alcohol had brought about the Hofmann rearrangement, and that the resulting diazo*iso*cyanate had reacted with the liberated hydrobromic acid in the usual manner.

An explanation of Pieroni's coupling reactions (*Gazzetta*, 1922, **52**, ii, 32) with his so-called azoxycarbonamides may be afforded by the above data, *viz.*, that the azoxycarbonamides, which were prepared from the diazocarbonamides by oxidation with hydrogen peroxide, are really the isomeric hydroxamic acids of formula $NR{:}N{\cdot}CO{\cdot}NH{\cdot}OH$ and not $NR{:}N{\cdot}CO{\cdot}NH_2$, and that with alkaline β-naphthol they undergo the Lossen rearrangement with subsequent coupling of the diazo*iso*cyanate and the β-naphthol; hydrolysis of the *iso*cyanate may of course take place before coupling, although direct coupling is recorded above in non-hydrolytic solvents. Incidentally, Oliveri-Mandalà (*Gazzetta*, 1922, **52**, i, 107) found that the oxidation of benzamide and toluamide by hydrogen peroxide gave the corresponding hydroxamic acid.

The great reactivity of the *syn*-diazocyanides is paralleled by the action of pyridine in promoting the coupling reaction (see numerous patents). One type of an azo-dye is made by coupling a diazo-compound with an aminonaphthalene, diazotising the amino-compound, coupling again, and so building up a chain of aromatic nuclei united by azo-links. This process cannot be continued indefinitely owing to the decreasing stability of the ever-enlarging diazo-compound, and difficulties are encountered which increase after the third repetition of the cycle. It would appear that the promoting action of the pyridine, whereby the above chain can be extended, is due to its reaction with the diazo-compound (*a*), an acetate in the usual examples, with formation of a kation (*b*), which will temporarily prevent decomposition of the unstable diazo-compound, but which, having like adjacent charges (cf. Pauling, *op. cit.*, pp. 109, 210), will subsequently decompose in contact with a molecule of the second amino-component to give an azo-compound. The ease and mechanism of coupling of the *syn*-diazocyanides which occurs in chloroform or alcoholic solution with α-naphthylamine or β-naphthol can also be attributed to the like adjacent charges, on the assumption that the *syn*-diazocyanides have the *iso*nitrile structure, $NR{=}N{-}\overset{+}{N}{\equiv}\overset{-}{C}{:}$.



Conclusions.—(1) Hantzsch's stereo-formulation of the aryl *syn*-diazocyanides will not explain (*a*) the formation of complexes with methylmagnesium iodide or phenylmagnesium bromide, in dry ethereal solution, leading eventually on hydrolysis to acetaldehyde and benzaldehyde, respectively, and the non-formation of an aldehyde with corresponding reactions of the *anti*-isomerides; (*b*) ionisation; (*c*) the ease with which the link between the diazo- and the cyanide group is ruptured in non-ionising solvents and also in coupling with α-naphthylamine and β-naphthol in chloroform and alcohol; (*d*) the great difference in colour, indicating strain in the *syn*-compound such as the presence of a dipole would confer; (*e*) the contrasting great stability of the *anti*-isomerides.

(2) Hantzsch's formulation of the *anti*-diazocyanides is correct and in accord with electronic demands. (3) The parallel behaviour of the diazo*iso*cyanates and the *syn*-diazocyanides is explained by the easy rupture of an N–N link, whereas the stability of the *anti*-diazocyanides and the diazocarbonamides is due to the resistance to rupture of a C–N link. (4) The colours of both *syn*- and *anti*-diazocyanides indicate covalent links between the diazo- and the $-\overset{+}{N}{\equiv}\overset{-}{C}{:}$ and $-C{\equiv}N{:}$ groups, respectively. (5) The ease of rupture of the N–N link is in accord with Pauling's theory of adjacent charges and of the inferior strength of the N–N compared with the

C–N link. (6) Chemical reactions in general are entirely in favour of Orton's view (J., **1903**, **83**, 796) that the *syn*- and *anti*-diazocyanides are the diazo*iso*nitriles and diazonitriles respectively.

(7) Le Fèvre and Vine's dipole-moment data (*loc. cit.*), which, with suitable assumptions, have been shown to support Hantzsch's views on the stereoisomerism of the *syn*- and *anti*-diazocyanides, are, in a broad qualitative way, not really antagonistic to the structural formulation. Since the halogenobenzene-*anti*-diazocyanides have greater resultant dipole moments than their *syn*-isomerides, this can be held to indicate a subtractive effect when the $-\mathrm{C{\equiv}N}\colon$ group is changed to the $-\overset{+}{\mathrm{N}}{\equiv}\overset{-}{\mathrm{C}}\colon$ group; when, therefore, the halogen is replaced by the nitro-group, as in the *p*-nitrobenzene-*syn*- and -*anti*-diazocyanides, with consequent reversal in sign of the mesomeric dipolar halogen to that of the dipolar nitro-group, a change in resultant effect in favour of the *syn*-isomerides is to be expected. Resonance will probably account for numerical details.

EXPERIMENTAL.

syn-Diazocyanides were prepared from *o*-chloro-, *p*-chloro-, *o*-bromo-, *p*-bromo-, and *p*-nitro-anilines by the procedure of Le Fèvre and Vine (*loc. cit.*), the temperature being kept at −10°. Above −5°, isomerisation appears to occur in all cases to a certain extent. The drying procedure before the treatment with the Grignard reagent was that described by Stephenson and Waters (*loc. cit.*). Isomerisation of the *syn*- to the *anti*-diazocyanides was carried out in benzene solution according to Le Fèvre and Vine (*loc. cit.*).

Reaction of the syn- *and* anti-*Diazocyanides with Methylmagnesium Iodide.*—A solution of the diazocyanide (0·02 g.-mol.) in dry ether was added gradually at 0° to methylmagnesium iodide (0·02 g.-mol.) prepared in dry ether. The orange complex was formed immediately, and after being kept at 0° for 15 mins., the mixture was boiled for 15 mins., cooled, and decomposed by 2N-sulphuric acid containing ice. The layers were separated, and the ethereal portion extracted several times with water, the extracts being added to the sulphuric acid portion; this mixture was filtered and treated (*a*) with 2 : 4-dinitrophenylhydrazine dissolved in 2N-sulphuric acid or (*b*) with 4-nitrophenylhydrazine hydrochloride dissolved in water. The resulting hydrazones from the *syn*-compounds were dried and weighed, then crystallised and identified as the hydrazone of acetaldehyde. *p*-Nitrobenzene-*syn*- and -*anti*-diazocyanides were also brought into reaction with phenylmagnesium bromide, and the benzaldehyde obtained from the *syn*-compound identified by conversion into the 2 : 4-dinitro- and 4-nitro-phenylhydrazones. The yields of acetaldehyde were about 20% on the weight of the *syn*-diazocyanide taken.

Bromination of p-*Nitrobenzenediazocarbonamide.*—A solution of the carbonamide (1 g.) (prepared according to Hantzsch and Schulze, *loc. cit.*) in glacial acetic acid (25 c.c.) was kept at 0—5° and treated with bromine (3 g.); at higher temperatures nitrogen was evolved immediately. After 2 hours, the crystalline, orange-red product, which had separated in needles, was filtered off, washed with chloroform, and dried on filter-paper. Bromine was evolved, and, after its cessation, a yellow crystalline compound remained (1·3 g.) which appeared to be the *hydrobromide* of p-*nitrobenzenediazo*-N-*bromocarbonamide*, m. p. *ca.* 81° (decomp.) (Found : Br, 45·5. $C_7H_5O_3N_4Br,HBr$ requires Br, 45·2%). The same sequence of products was obtained by bromination in chloroform. This *N*-bromocarbonamide (1 g.), when suspended in cold water (30 c.c.) and aerated for 1—1½ hours, regenerated some of the original *p*-nitrobenzenediazocarbonamide (0·2 g.), which was filtered off; when the filtrate was added to alkaline β-naphthol, *p*-nitrobenzeneazo-β-naphthol was precipitated. The coupling reactions of this *N*-bromocarbonamide are described on p. 396. When the *N*-bromo-compound (1 g.) was decomposed in the cold with 20% aqueous sodium hydroxide (20 c.c.), an immediate darkening in colour occurred with rapid evolution of nitrogen and carbon dioxide; the solution on acidification with acetic acid gave 4 : 4′-dinitrodiazoaminobenzene (0·25 g.), m. p. after recrystallisation from alcohol, and mixed m. p. with authentic specimen, 226° (Found : N, 24·5. Calc. : N, 24·4%).

A New Preparation of 4 : 4′-*Dinitrodiazoaminobenzene.*—*p*-Nitrobenzenediazonium sulphate (2 g.) was dissolved in water (7 c.c.), and the filtered solution mixed at 0° with powdered potassium cyanate (0·8 g.); an immediate evolution of nitrogen and carbon dioxide took place together with some lachrymatory substance, doubtless *p*-nitrobenzene *iso*cyanate. After the mixture had been kept for one hour, the light yellow precipitate of 4 : 4′-dinitrodiazoaminobenzene (1·7 g.) was filtered off and crystallised from alcohol; m. p. and mixed m. p. with authentic specimen, 226°.

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