# 89. *The Structures of Hantzsch's Isomeric Diazocyanides.*

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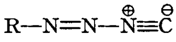
The chemical evidence upon which Hodgson and Marsden recently proposed that Hantzsch's *syn*- and *anti*-diazocyanides are related as *iso*- and *n*-cyanides respectively is shown as equivocal and not incompatible with the view that these substances are geometrically isomeric cyanides. Recorded dipole moments and refractivity data are also against Hodgson's hypothesis.

Infra-red spectra are now described of *syn*- and *anti*-*p*-chloro-, -*p*-bromo-, and -*p*-nitrobenzen diazocyanides, together with those of the two known 4 : 4′-diphenylbisdiazocyanides. Frequencies associated with cyanide, rather than *iso*cyanide, groups occur as common features throughout. Thus further support is provided for Hantzsch's formulations.

Between 800 and 900 cm.$^{-1}$, a regular peculiarity of the spectra of each isomeric pair of benzene derivatives is noted; this, when applied to the diphenylbisdiazocyanides, indicates that the allotment of configurations made earlier (by dipole-moment evidence) is probably correct.

The proposition that Hantzsch's *syn*- and *anti*-diazocyanides would be more appropriately represented as structural (I and II), than as geometrical (III and IV), isomers was recently discussed by Hodgson and Marsden (*J.*, 1944, 395). Their argument falls into three sections.

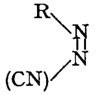


$R{-}N{=}N{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}$

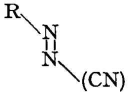
(I.)

$R{-}N{=}N{-}C{\equiv}N$

(II.)



(III.)



(IV.)

First, they state that the recorded reactions of these substances (" Die Diazo Verbindungen ", Hantzsch and Reddelien, 1921; " Organic Chemistry of Nitrogen ", Sidgwick and Taylor, Oxford, 1937; " The Chemistry of the Diazo-Compounds and Their Technical Applications ", Saunders, London, 1936) are in general " 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 ".

Secondly, they state that Le Fèvre and Vine's dipole-moment data (*J.*, 1938, 431) " are, in a broad qualitative way, not really antagonistic to the structural formulation. . . . Resonance will probably account for numerical details ". Thirdly, they describe new applications of the Grignard reagent to this problem, and then state that " 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 . . ."

*Comments on Hodgson and Marsden's Three Arguments.*—(1) *General chemistry of diazocyanides.* We are not convinced that Hodgson and Marsden (*loc. cit.*) have drawn the only possible conclusion from their review of the older literature on the diazocyanides. Such properties as relative speeds of coupling, ionisation, etc., do not, we submit, necessitate the possession by *syn*-compounds of the readily broken N–N bond, and by *anti-* of the more stable C–N link.

Similar, although less marked, contrasts are often shown by geometrical isomers. The oximes present the most relevant analogies, in that they frequently show notable differences in stability, particularly as derivatives; *e.g.*, the reactivities of the acetylated aldoximes under hydrolysis (Hantzsch, *Ber.*, 1891, **24**, 13; Wentworth and Brady, *J.*, 1920, **117**, 1045). With the parent substances, when these differences are great, only one form is known (particularly with aryl oximes, Brady and Dunn, *J.*, 1914, **105**, 821, 2409; 1915, **107**, 1858; 1916, **109**, 667; Wentworth and Brady, *loc. cit.*; Brady, Cosson, and Roper, *J.*, 1925, **127**, 2427; Brady and Bennett, *J.*, 1927, 894); when they are less, it is sometimes possible to interchange the forms by the action of light (Ciamician and Silber, *Ber.*, 1902, **35**, 4128; 1903, **36**, 4268; Brady and Klein, *J.*, 1927, 874). The isomeric oximes have different dissociation constants (Brady and Goldstein, *J.*, 1926, 1918).

Above all, the existence of azobenzene in *cis-* and *trans*-forms, both fully examined chemically and physically (Hartley, *J.*, 1938, 633; Le Fèvre and Hartley, *J.*, 1939, 531; Robertson, *J.*, 1939, 232; de Lange, Robertson, and Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398), clearly shows that geometrical isomerism about the $-N{=}N-$ system *is* possible. Moreover the properties of the two azobenzenes, although dissimilar in many features, are quite in harmony with recorded knowledge of geometrical isomerism, and—where comparison is reasonable—have close analogies in the diazocyanides (Hartley; Le Fèvre and Vine, *locc. cit.*).

We conclude, therefore, that geometrical isomerism need not be excluded on general grounds.

(2) *Dipole moments of diazocyanides.* Le Fèvre and Vine (*loc. cit.*) did not allude to the possibility of a cyanide–*iso*cyanide relationship when discussing their results. Fortunately, the required dipole-moment data exist to enable this point to be examined. The figures shown in Table I were recorded by Poltz, Steil, and Strasser (*Z. physikal. Chem.*, 1932, *B*, **17**, 155—160), Wolfe and Strasser (*ibid.*, 1933, *B*, **21**, 389), and Hammick, New, Sidgwick, and Sutton (*J.*, 1930, 1876). It will be noted that the moment of phenyl cyanide is only slightly greater than that of phenyl *iso*cyanide. Electron-diffraction and spectroscopic studies (Brockway, *J. Amer. Chem. Soc.*, 1936, **58**, 2516; Gordy and Pauling, *ibid.*, 1942, **64**, 2952; Badger and Bauer, *ibid.*, 1937, **59**, 303) have indicated that $CH_3$·NC is a linear molecule to within 20°. All this, together with the fact (New and Sutton, *J.*, 1932, 1415) that 1 : 4-di*iso*cyanobenzene has a vanishingly small moment, justifies a view that the vectors arising from the cyanide and *iso*cyanide groups resemble one another in magnitude and direction and lie closely along the axis of the single links, Ar–CN and Ar–NC, in the two sets of compounds.

TABLE I.

| Benzene derivative. | Moment, D. | Phenyl cyanide derivative. | Moment, D. | Phenyl *iso*cyanide derivative. | Moment, D. |
|---|---|---|---|---|---|
| Me | 0·4 | *p*-Me | 4·37 | *p*-Me | 3·96<br>3·98 * |
| Cl | 1·55 | *p*-Cl | 2·51 | | |
| Br | 1·52 | *p*-Br | 2·64 | *p*-Cl | 2·08<br>2·07 * |
| $NO_2$ | 3·90 | *p*-$NO_2$ | <0·7<br>0·66 * | | |
| CN | 3·94 | | | | |
| NC | 3·53 | | | | |

* Figures from Hammick, New, Sidgwick, and Sutton (*loc. cit.*).

Now such a similarity of $\mu_{CN}$ and $\mu_{NC}$ means that the latter could be inserted into Le Fèvre and Vine's reasoning in place of the former. It is, therefore, clear that vectorial analysis of experimentally obtained values will not alone decide whether, if these compounds *are cis-* and *trans*-forms, the carbon and nitrogen atoms occur as the *iso*cyanide group in the former series and/or as the cyanide group in the latter.

However, although not explicity stated, Hodgson and Marsden's reference to Orton's paper indicates their acceptance of an extended *trans-* or linear configuration throughout, with the essential difference between the isomers being the possession of normal and *iso*-groups in the stable or labile forms respectively. Such a proposal can be easily tested, since in each case both members of the isomeric pairs (*a*) might be expected to have *roughly* the same moment, or (*b*), if their moments are not equal, show an approximate constancy of inequality throughout all the known examples. Reference to Table II makes it clear that neither of these forecasts is fulfilled.

TABLE II.

| Diazobenzene cyanide derivative. | Dipole moments found : labile form. | stable form. | Differences, $\mu_{\text{labile}} - \mu_{\text{stable}}$. |
|---|---|---|---|
| 4-Chloro- | 2·93 | 3·73 | −0·80 |
| 4-Bromo- | 2·91 | 3·78 | −0·87 |
| 4-Nitro- | 2·04 | 1·47 | −0·57 |
| 2 : 4 : 6-Tribromo- | 2·5 | 4·0 | +1·5 |

We conclude, therefore, that dipole moment data can eliminate a structural hypothesis in which both forms are *trans*.

(3) *The Grignard reactions.* The isolation of aldehydes is represented by Hodgson and Marsden as follows :

$$C_6H_4R{\cdot}N{:}N{\cdot}\overset{+}{N}{:}\overset{-}{C} + MgIMe \xrightarrow{Et_2O} C_6H_4R{\cdot}N{:}N{\cdot}N{:}CMe{\cdot}MgI \xrightarrow{\text{Hydrolysis}}$$

$$C_6H_4R{\cdot}N{:}N{\cdot}N{:}CHMe \xrightarrow[\text{hydrolysis}]{\text{Further}} CH_3{\cdot}CHO$$

and the analogy with the corresponding reactions of *iso*cyanides is advanced to support their allotment of this structure to (CN) groups in the *syn*-series.

Alternative possibilities are not discussed—notably the possible relevance of the observation by Stephenson and Waters (*J.*, 1939, 1796) that ethereal solutions of the *syn*-diazocyanides undergo purely catalytic decompositions by copper powder to aromatic *cyanides*, the corresponding hydrogen-substituted products, *and acetaldehyde.* The last-named could, therefore, have arisen in Hodgson's experiments from the solvent and be without significance to his main thesis.

These crucial Grignard reactions are recorded rather briefly, yields of acetaldehyde from methylmagnesium iodide greater than 20% on the weight of *syn*-diazocyanide taken are not claimed, and the identification of the aldehydes, from either methylmagnesium iodide or phenylmagnesium bromide, as their nitro- or dinitro-phenylhydrazones, is asserted without descriptive detail. For the important case of acetaldehyde this procedure is especially unsound in view of the uncertainty of melting point and suspected polymorphism of its 2 : 4-dinitrophenylhydrazone (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955; Cameron and Storrie, *J.*, 1934, 1330; Ingold, Pritchard, and Smith, *ibid.*, p. 79; Bryant, *J. Amer. Chem. Soc.*, 1933, **55**, 3201; Campbell, *Analyst*, 1936, **61**, 391; Allen and Richmond, *J. Org. Chem.*, 1937, **2**, 222; Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758). Further, we have found that the dinitrophenylhydrazones of the simpler aldehydes and ketones do not greatly depress one another's m. p.s (cf. Brandstatter, *Mikrochem.*, 1944, **32**, 33) so that mixed m. p. determinations (if these were used) could not have been relied upon to establish identity. Extinction angles under the polarising microscope, however, can be usefully applied in the matter.

At the outset we repeated Hodgson and Marsden's directions many times and confirmed the formation of acetaldehyde in ethyl ether as a medium. The yield (as dinitrophenylhydrazone), slightly improved by omitting the 15 mins.' boiling (*loc. cit.*, p. 398, line 8 of Experimental), was always impure, and only showed the correct properties after several crystallisations. At least one of the accompanying derivatives, *viz.*, acetone 2 : 4-dinitrophenylhydrazone, has been separated from the total crude product.

We have also examined the interaction of methylmagnesium iodide with various of the *syn*-diazocyanides in anisole or *iso*amyl ether. Dinitrophenylhydrazones were obtained in small amounts. These we failed to resolve into pure components although, in cases where amyl ether was used, experimental evidence indicated the final presence of a derivative of *iso*valeraldehyde.

Nevertheless, both Hodgson's experiments and ours can easily be understood if, following Stephenson and Waters (*loc. cit.*), the *syn*-diazocyanides undergo fission, even momentarily in solution to give two neutral free radicals :

$$R{\cdot}N_2{\cdot}CN \longrightarrow R{\cdot}N_2{\cdot} + {\cdot}CN$$

followed, *e.g.*, by

$$OEt_2 + {\cdot}CN \longrightarrow HCN + {\cdot}C_2H_4{\cdot}OEt$$

and eventually

$$HCN + MgIMe \longrightarrow \text{etc.} \longrightarrow CH_3{\cdot}CHO$$

It is true that Stephenson and Waters demonstrated this type of fission in the presence of copper; they emphasised, however, the fact that the metal was completely unaffected. With other diazo-compounds, *e.g.*, benzene*iso*diazoacetate (Waters, *J.*, 1937, 113), analogous decompositions, *in which acetaldehyde is also produced from ethyl ether*, took place spontaneously at ordinary temperatures *without* a catalyst being necessary. Many reactions other than the above can also occur (cf. Waters, *loc. cit.*; Grieve and Hey, *J.*, 1934, 1797; Hey and Waters, *Chem. Revs.*, 1937, **21**, 169) and may easily explain low yields of aldehydes and the formation of large amounts of nitrogenous tars in the present work.

The simultaneous production of acetone during these Grignard reactions could either be effected *via* a simple double decomposition :

$$R{\cdot}N_2{\cdot}CN + MgIMe \longrightarrow R{\cdot}N_2{\cdot}MgI + Me{\cdot}CN \xrightarrow[\text{etc.}]{\text{MgIMe,}} COMe_2$$

or—Grignard reagents themselves being a fruitful source of free radicals (Hey, *Ann. Reports*, 1940, **37**, 285; 1944, **41**, 181)—the intermediate methyl cyanide could be formed directly :

$$Me{\cdot} + {\cdot}CN \longrightarrow MeCN.$$

We conclude, therefore, that Hodgson and Marsden's Grignard reactions do not necessitate an *iso*cyanide structure for the *syn*-diazocyanides.

*Recorded Physical Evidence bearing on the Problem.*—Apart from the dipole-moment measurements already mentioned, refractometric data indicate a definite conclusion. Le Fèvre and Vine (*loc. cit.*, p. 433), observing that the *stable* member of each pair of diazocyanides had the *greater* molecular refraction, commented that this was the relationship common throughout geometrical isomerism, a fact which supported the idea that the *syn-* and *anti*-forms are *cis-* and *trans-*, respectively. The structural hypothesis (I and II) was not mentioned.

The actual refractions (Table III) can be considered *vis-à-vis* the values for known cyanides and *iso*cyanides, *e.g.*, Ph·CN, $[R_L]_D$ = 31·62 c.c.; Ph·NC, $[R_L]_D$ = 32·32 c.c. (these figures evidently are not much affected by conjugation between the substituent and the aromatic nucleus since similar differences occur with aliphatic derivatives, *e.g.*, Et·CN, $[R_L]_\alpha$ = 15·71 c.c.; Et·NC, $[R_L]_\alpha$ = 16·45 c.c.). Von Auwers (*Ber.*, 1927, **60**, 2137) summarises the matter by quoting $[R_L]_D$ group refractions as 5·415 c.c. for the cyanide group; 6·136 for the *iso*cyanide group. Formulæ of type (I) and (II) would therefore require the refractions of the unstable varieties to be greater than their stable (*trans-*) isomers. Experiment demonstrates the reverse order.

TABLE III.

| Diazobenzene cyanide derivative. | | 4-Cl. | 4-Br. | 4-NO$_2$. | 2-Br. | 2 : 4-Br$_2$. | 2 : 4 : 6-Br$_3$. |
|---|---|---|---|---|---|---|---|
| $[R_L]_D$ value | Stable form ......... | 48·0 | 52·3 | 48·6 | 51·6 | 58·64 * | 68 |
| | Unstable form ...... | 46·1 | 49·9 | 44·7 | 47·2 | 56·59 * | 64 |

(Data from Le Fèvre and Vine, *loc. cit.*, and Bruhl, *Ber.*, 1896, **29**, 2907—the latter are asterisked.)

Spectroscopic and conductometric (Hantzsch, *Ber.*, 1900, **33**, 2177) information is also available. Neither is very helpful. Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) and Le Fèvre and Vine (*loc. cit.*) have reported absorption spectra in the visible and the near ultra-violet region, but their findings do not add to the evidence for either view. This might be expected since, where the cyanide–*iso*cyanide question is concerned, Wolf and Strasser (*Z. physikal. Chem.*, 1933, *B*, **21**, 389) have found that the phenyl, *p*-tolyl, and *p*-chlorophenyl cyanides and *iso*cyanides show no remarkable spectrum differences in hexane or heptane between 2200 and 2850 A., while *apropos* geometrical isomerism, it is well known that the spectra of such isomerides need not be dissimilar.

It seemed to us that important results might be achieved by the use of longer wave-lengths; this followed, since Dadieu (*vide* Hibben, " The Raman Effect and its Chemical Application ") has found certain notable differences between the Raman spectra of isomeric nitriles and *iso*cyanides—differences which are appropriately detected in the related infra-red spectra (see below). The remainder of the present paper is chiefly concerned with observations arising from this point.

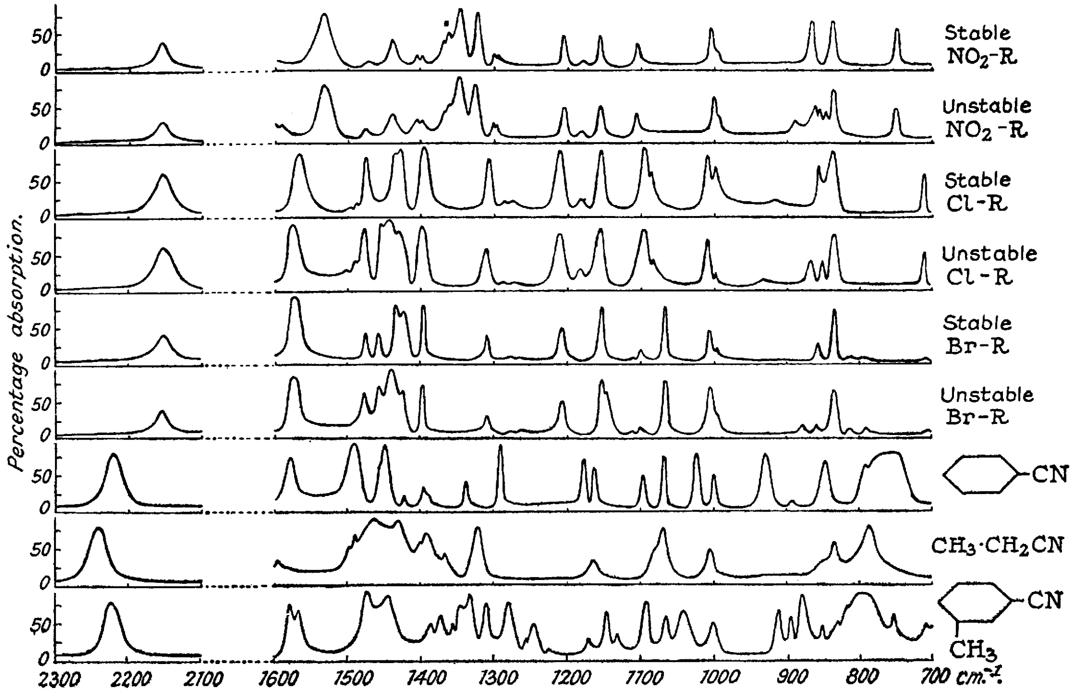
*Infra-red Absorption Spectra of Isomeric Diazocyanides.*—These have been measured over the range 4—14 μ by using the Hilger Infra-red Prism Spectrometer as a single-beam instrument with photographic recording. The rock-salt prism was of the 30° Littrow type, and the instrument incorporated a Hilger–Schwarz vacuum thermopile.

The spectrometer was calibrated in the region 6—14 μ by using the absorption bands of ammonia, water, and carbon dioxide, as described by Oetjen, Chao-Lan Kao, and Randall (*Rev. Sci. Instr.*, 1942, **13**, 515); in that from 3—5 μ, by using liquid benzene, and applying the benzene absorption frequencies given by Bailey, Hall, Ingold, and Thompson (*J.*, 1931, 931).

The cyanides were examined in solution in carbon tetrachloride and carbon disulphide from 4 to 12 and 12 to 14 μ, respectively. Solutions were prepared by mixing an excess of the compound with the solvent in the dark, and filtering the solution into a rock-salt cell, having a thickness of about 0·1 mm. In addition to the diazo-cyanides, the absorption spectra of phenyl, *m*-tolyl, and ethyl cyanides were determined. The spectra are reproduced in Figs. 1 and 2.

It has been shown by Gordy and Williams (*J. Chem. Physics*, 1935, **3**, 664; 1936, **4**, 85), who studied various organic cyanides and corresponding *iso*cyanides, that the absorption frequency due to the CN valency vibration, occurring at about 2250 cm.$^{-1}$ (4·45 μ) for the cyanides, was shifted by about 100 cm.$^{-1}$ to a lower frequency for the *iso*cyanides. This result was confirmed by Badger and Bauer (*J. Amer. Chem. Soc.*, 1937, **59**, 303) in their examination of the absorption spectra of methyl cyanide and *iso*cyanide. Hibben (*op. cit.*, p. 280) has summarised the evidence obtained from numerous investigations of the Raman spectra of organic and inorganic cyanides and *iso*cyanides. Here, again, a similar shift of 100 cm.$^{-1}$ is obtained when comparing an *iso*cyanide with the corresponding cyanide. We would therefore expect that, if ν were the absorption frequency measured for any cyanide, where ν may lie roughly between the limits 2100—2250 cm.$^{-1}$ depending on the homopolar nature of the R–CN linking (Hibben, *op. cit.*, p. 454), the frequency would be approximately ν — 100 for the corresponding *iso*cyanide.

FIG. 1.



(R=-$C_6H_4$·N:N·CN).

The spectra now recorded for methyl cyanide, *m*-tolyl cyanide, and phenyl cyanide show agreement with the frequency values obtained by previous authors. All pairs of diazocyanides examined have a common frequency, measured as 2160 cm.$^{-1}$.* This may be assigned to the

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* The estimation of frequencies in the region 4·5 μ is not very precise when using a rock-salt prism and a cam which covers the whole spectral region 1—5 μ on a 12″ photographic record. Since the measurements now recorded were completed, a special cam has been constructed which " spreads out " the spectrum in the region 4·5 μ, so that greater accuracy in frequency determination is possible. A value of 2187 cm.$^{-1}$ has now been obtained for the CN " stretching " frequency by a re-examination of the two forms of 4-bromobenzenediazocyanide. This is in excellent agreement with the value found by Sheppard and Sutherland (this vol., p. 453).

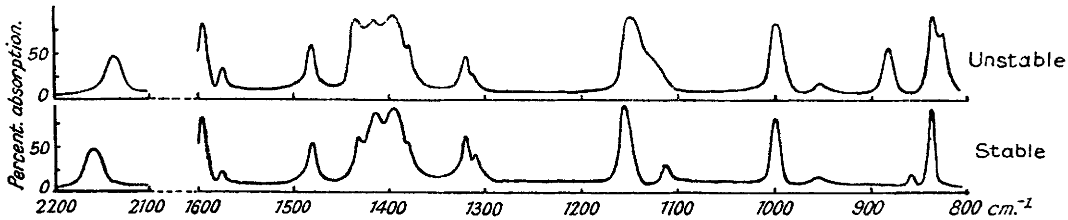
CN valency vibration. The important point is that there is no relative shifting of this frequency for any of the pairs now investigated—a fact which is substantially in favour of a cyanide form throughout.

Further evidence in support of this is the almost identical forms of the absorption spectra of any one pair of isomers in the range 1600—700 cm.$^{-1}$—where Badger and Bauer (*loc. cit.*) found distinct differences for methyl cyanide and *iso*cyanide (frequencies 1417, 1370, 1040, and 917 cm.$^{-1}$ for the cyanide, and 1456, 1414, 1041, and 928 cm.$^{-1}$ for the *iso*cyanide).

Barnes, Liddel, and Williams (*Ind. Eng. Chem.*, 1943, **15**, 659) summarise infra-red spectra of some 19 cyanides, including the following of interest to the present paper. Cyanamide and its allyl derivatives, *cis-* and *trans*-β-ethylacrylonitriles, and *cis-* and *trans*-crotononitriles all show strong absorption between 1400 and 1500 cm.$^{-1}$. Such bands are well known (compare Hibben, *op. cit.*, pp. 272, 294) to be associated with the CH and $^{-}N{\equiv}N^{-}$ groups. The complexity observed is therefore reasonably to be expected.

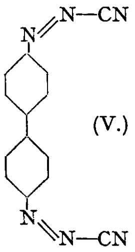
Before our spectrometer was available, specimens of the 2 : 4 : 6-tribromobenzenediazocyanides (provided by Dr. F. B. Kipping) and of the 4-bromobenzenediazocyanides (prepared by us) were kindly examined in chloroform, carbon disulphide, and nujol solutions by Dr. G. B. B. M. Sutherland on his double-beam instrument at Cambridge. His results are reported elsewhere (this vol., p. 453). They are in accord with our work in that the appropriate pairs show similarity, and other features, in satisfactory agreement with Figs. 1 and 2.

FIG. 2.

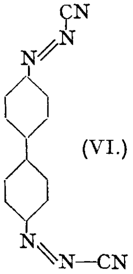


*Diphenyl-4 : 4′-bisdiazocyanides.*

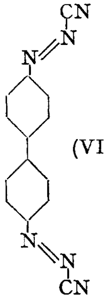
Diphenyl-4 : 4′-bisdiazocyanides should occur as three isomerides, (V), (VI), and (VII), on Hantzsch's formulations. Only two forms, however, are known (Euler, *Chem. Zentr.*, 1907, i, 1572; Le Fèvre and Vine, *J.*, 1938, 1878). They differ in stability and other properties. Owing to free rotation, dipole-moment measurements (Le Fèvre and Vine, *loc. cit.*) could only indicate the probability that the more stable isomer is (VII), *i.e.*, *trans-trans*. The other, therefore, might be *cis-trans* or *cis-cis*.



(V.)



(VI.)

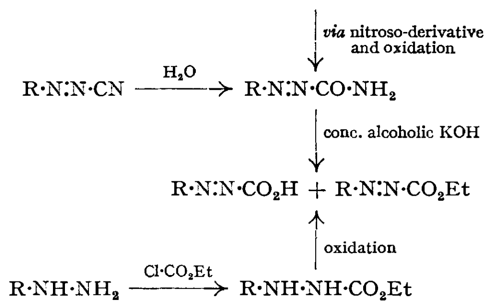


(VII.)

Such an allotment seems to be in agreement with the spectroscopic records now obtained and presented in Fig. 2. Passage from the stable to the unstable form seems to involve a shift in the CN frequency of about 15 cm.$^{-1}$. Such a small difference is only just outside the possible error of frequency determination in this spectral region, and is in any case insufficient to suggest an *iso*cyanide grouping in the unstable compound. Both forms therefore appear to contain cyanide groups only, and thus further support the conclusions above.

Inspection of Figs. 1 and 2 reveals that all the molecules containing *syn-* (*cis-*) configurations about the $^{-}N{\equiv}N^{-}$ group show a characteristic band system between the limits 800—900 cm.$^{-1}$, which does not occur with those possessing the *anti-* (*trans-*) arrangement. The curves of Fig. 2, by analogy, suggest that the stable diphenyl-4 : 4′-bisdiazocyanide does not contain a *cis*-azo-unit, *i.e.*, that it is correctly formulated as (VII). The unstable variety may, therefore, be either (V) or (VI). We have attempted to use the nearly quantitative precipitation of silver cyanide, noted by Stephenson and Waters (*loc. cit.*) as occurring between alcoholic solutions of *syn-* (not *anti-*) diazocyanides and silver nitrate, to effect a decision. The results (see Experimental) favour (V); (VI) is thus shown as the undiscovered member.

*Summary.*—From all the above physical considerations we conclude that in *syn-* and *anti-*diazocyanides the carbon and nitrogen atoms are *linked in the same manner*, most probably, as ·C⁝N. In case it might be urged that our work does not rigidly exclude the chance that the diazocyanides are geometrically isomeric *iso*cyanides, it should be mentioned that a number of reactions have been described in the literature from which the $^-$N, N, CN atomic sequence is *definitely* inferable, *e.g.*, the formation of imidocyanides and imidoethers with hydrogen cyanide and alcohols respectively, and of azo-carboxylic amides with water. Good examples (because they involve independent synthetic support) are the following (Widman, *Ber.*, 1895, **28**, 1925; Hantzsch and Schultze, *ibid.*, p. 670; Hantzsch and Danziger, *ibid.*, 1897, **30**, 2529):



## EXPERIMENTAL.

*Preparation of Diazocyanides.*—The directions of Le Fèvre and Vine (*loc. cit.*) were used in the cases of the chloro-, bromo-, and nitro-derivatives. For the 4 : 4′-diphenylbisdiazocyanides the following improved method was adopted. Benzidine (10 g.), in a mixture of alcohol (25 c.c.) and 10N-hydrochloric acid (34 c.c.), was diazotised with sodium nitrite (7·8 g.) in water (125 c.c.) at 10°. The resulting solution was filtered, and chloroform (100 c.c.) added. To the mixture, cooled in an ice-bath, a solution of potassium cyanide (8 g.) in water (50 c.c.) was added dropwise with vigorous mechanical stirring. The temperature was maintained at 0°. The pale orange 4 : 4′-diphenylbisdiazocyanide was formed immediately, and rapidly dissolved in the chloroform. Stirring was continued for a further 15 minutes, and the two layers were then separated. The aqueous layer was extracted several times with 10-c.c. portions of chloroform, the extracts being added to the original chloroform portion. After being washed several times with distilled water, the chloroform extract was dried ($Na_2SO_4$), diluted to twice its volume with light petroleum (b. p. 40—60°), and cooled to 0°. Light orange micro-needles of the labile form of 4 : 4′-diphenylbisdiazocyanide then separated; these, after collection, washing (light petroleum), and drying in a vacuum desiccator in the dark, had m. p. (with explosion) 97—98°.

The stable form of 4 : 4′-diphenylbisdiazocyanide was formed gradually from the labile form on standing in the light at room temperature, but better by boiling a solution of the latter form in light petroleum (b. p. >120°). It was isolated as maroon-coloured crystals, m. p. (with explosion) 208—209°.

The diazocyanides used throughout the present work were examined with a polarising microscope and are specified in Table IV.

2 : 4-*Dinitrophenylhydrazones for comparison.* The compounds in Table V were prepared and characterised by means of m. p. and behaviour to polarised light.

*Mixed M. ps.*—The m. ps. of intimate mixtures of acetaldehyde and acetone 2 : 4 dinitrophenylhydrazones, made by grinding, were as follows :

| $CH_3$·CHO deriv., % | 0 | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|
| M. p. | 126° | 115—117° | 109—112° | 108—110° | 107—109° | 108—110° |
| $CH_3$·CHO deriv., % | 60 | 70 | 80 | 90 | 100 | |
| M. p. | 111—113° | 120—123° | 135—137° | 150—152° | 166° | |

*Interaction of Grignard Solutions with* cis-*Diazocyanides.*—(a) *With* cis-p-*bromobenzenediazocyanide.* A large number of reactions were carried out using methylmagnesium iodide and phenylmagnesium bromide according to the directions of Hodgson and Marsden (*loc. cit.*). In some cases the 15 mins. boiling (*idem, loc. cit.*, p. 398) was omitted, with the result that the yield of 2 : 4-dinitrophenylhydrazone was slightly increased, and the mixture appeared to be less complex, since its m. p. was higher than the product otherwise obtained. M. p.s of the products were taken as " crude ", after two recrystallisations from alcohol, and in admixture with authentic specimens of the dinitrophenylhydrazones of acetaldehyde

TABLE IV.

| Diazocyanide. | | M. p. (obs.). | M. p. (Le F. and V.). | Extinction angle. | Solvent.* | Description. |
|---|---|---|---|---|---|---|
| *p*-$Cl\cdot C_6H_4\cdot N_2\cdot CN$ | *cis* | 29—30° | 29° | *ca.* 46° to length of crystal | *Y* cooled on slide | Long thin parallelograms. Acute crystal angle *ca.* 45° |
| | *trans* | 105 | 105 | *ca.* 43° to length | *Z* | Thin parallelograms. Acute crystal angle *ca.* 51° |
| *p*-$Br\cdot C_6H_4\cdot N_2\cdot CN$ | *cis* | 42—43 | 42—43 | *ca.* 20° to length or straight extinction | *Y* cooled | Imperfect needles. Angles indefinite |
| | *trans* | 132 | 132 | *ca.* 22° to length. | *Z* | Thin parallelograms. Crystal angle *ca.* 63° |
| *p*-$NO_2\cdot C_6H_4\cdot N_2\cdot CN$ | *cis* | 45—47 | 29—30 | 33° to length or straight ex tinction | *Y* cooled | Long thin needles. Angles indefinite |
| | *trans* | 86 | 86 | 34° to length or straight extinction | *Z* | Imperfect needles (longer and thinner habit than *cis*-form) |
| $(-C_6H_4\cdot N_2\cdot CN)_2$ | *labile* | 97—98 | 97 | All straight extinction | Pptd. from $CHCl_3$ with *Y* | Long imperfect needles. Angles indefinite |
| | *stable* | 208—209 | 208 | *ca.* 45° to length | *Z* | Long thin parallelograms. Crystal angle *ca.* 43° |

* *Y* = Light petroleum, b. p. 40—60°. *Z* = Light petroleum, b. p. >120°.

TABLE V.

| 2 : 4-Dinitrophenylhydrazone of : | Solvent. | M. p. (obs.). | M. p. (lit.).* | Description. | Extinction. |
|---|---|---|---|---|---|
| Formaldehyde | EtOH | 164—165° | 166° | Long yellow needles and plates. Acute crystal angle *ca.* 60° | *Needles.* Straight extinction.<br>*Plates.* *ca.* 37° to length |
| Acetaldehyde | ,, | 166 | 168 | Long yellow rectangular plates | (1) Straight extinction or (2) *ca.* 42° to length |
| *iso*Valeraldehyde | ,, | 122—123 | 123 | Crystallises from alcohol in two forms : (*a*) orange needles, (*b*) yellow plates | *Needles.* *ca.* 15° to length.<br>*Plates.* *ca.* 25° to length |
| Acetone | ,, | 126 | 126 | Yellow plates. Acute crystal angle 80° | *ca.* 30° to length |
| Mesityl oxide † | $C_6H_6$ | 202 | 203 | Carmine, micro-crystals. Indefinite under microscope | — |
| Benzaldehyde | ,, | 236 | 237 | Orange needles | Straight extinction |

* Campbell (*Analyst*, 1936, **61**, 391).

† Included in case mesityl oxide were formed by the action of dil. $H_2SO_4$ on any acetone occurring in the aqueous extract from the reactions between MgMeI and *cis*-diazocyanides.

and acetone. In addition, the dinitrophenylhydrazones were examined under the polarising microscope after recrystallisation. In general, they appeared to be mixtures of acetaldehyde and acetone dinitrophenylhydrazones. The usual m. p. obtained for the crude product was about 140—145°, which corresponded to between 80 and 85% of acetaldehyde in the mixtures. In one case (see Table VI), acetone 2 : 4-dinitrophenylhydrazone was obtained as a single substance. The traces of dinitrophenylhydrazone obtained from the reactions with phenylmagnesium bromide were too small to demonstrate the presence of the derivative of benzaldehyde. Our observations suggested that the acetaldehyde derivative was largely produced (see Table VI).

Table VI summarises typical results obtained from various reactions with *cis*-*p*-bromobenzenediazocyanide (0·01 g.-mol. used throughout).

(b) *With the labile form of* 4 : 4′-*diphenylbisdiazocyanide.* An ethereal solution of this labile form (0·01 g.-mol.) was added slowly to methylmagnesium iodide (0·02 g.-mol.) in ether at 0°. A dark blue complex was formed immediately, which turned brown on decomposition with iced 2N-sulphuric acid. The aqueous layer was separated, filtered, and treated with 2 : 4-dinitrophenylhydrazine in 2N-sulphuric acid. The resulting dinitrophenylhydrazone (0·5 g.) was filtered off, recrystallised twice from alcohol,

TABLE VI.

| Grignard reagent. | Wt. (g.) and m. p. of crude dinitrophenylhydrazone. | M. p. after 2 recrystallisations from EtOH. | Mixed m. p. with acetaldehyde deriv. | Mixed m. p. with acetone deriv. | Appearance under polarising microscope, and extinction angle. |
|---|---|---|---|---|---|
| MgMeI ......... | 0·4; 135—137° | 148—149° | 149—150° | 122—126° | Long, yellow, rectangular plates. Straight extinction |
| MgMeI ......... | 0·3; 112—115 | 125 † | 114 | 125 | Yellow plates. Acute crystal angle *ca.* 80°. Extinction: 30° to length |
| MgMeI ......... | 0·34; 140—141 | 161—162 | 162 | 140—142 | Long, rectangular plates Straight extinction |
| MgMeI * ...... | 0·45; 140—143 | 161—162 | 162—163 | 132—135 | ,, ,, ,, |
| MgPhBr ...... | 0·10; 138—140 | 155—156 | 157—159 | — | ,, ,, ,, |
| MgPhBr * ... | 0·15; 142—145 | 157—159 | 158—159 | — | ,, ,, ,, |

* 15 Mins.' boiling omitted. † After 4 recrystallisations.

and examined under the polarising microscope. The crude product had m. p. 143—145°, raised after two recrystallisations to 148—150°. This, mixed with acetaldehyde dinitrophenylhydrazone, had m. p. 154—157°, and with the acetone derivative, 104—106°. Two varieties of crystals occurred, some with straight extinction and others with extinction at 40° to length (cf. acetaldehyde in Table V).

(c) *Reactions with methylmagnesium iodide in* iso*amyl ether and anisole.* The directions of Hodgson and Marsden (*loc. cit.*) were followed, solutions of methylmagnesium iodide and *cis*-*p*-bromobenzenediazocyanide in both *iso*amyl ether and anisole instead of ethyl ether being used. Orange-red complexes were again formed, and decomposed with iced 2N-sulphuric acid. On treating the aqueous extracts with 2 : 4-dinitrophenylhydrazine in 2N-sulphuric acid, no dinitrophenylhydrazone was formed. The ethereal layer from the reaction in *iso*amyl ether was distilled, and the first c.c. of the distillate was shaken with a solution of 2 : 4-dinitrophenylhydrazine in 2N-sulphuric acid. An orange precipitate was slowly formed. This was filtered off, recrystallised from alcohol, and examined as before. Distillation of the anisole layer produced no precipitate with 2 : 4-dinitrophenylhydrazine. The m. p. of the crude derivative was 85—89°, raised, after two recrystallisations, to 110—120°. The mixed m. p. with the acetaldehyde hydrazone was 98—102°, and that with the *iso*valeraldehyde derivative, 115—118°. The extinction angle was *ca.* 15° to the length (see Table V).

It thus appears that the dinitrophenylhydrazone obtained from the reaction in *iso*amyl ether is *not* the acetaldehyde derivative but mainly that of *iso*valeraldehyde. This is consistent with the view that the aldehydes produced arise either from the oxidation of the ether by the *cis*-compounds or from free radicals occurring in the ethereal solutions. The failure of the anisole solutions to produce any phenylhydrazone-forming product is not significant since oxidation of anisole would produce formaldehyde which would be too volatile for isolation and identification.

*Estimation of Silver Cyanide produced from the Labile Form of* 4 : 4′*-Diphenylbisdiazocyanide by Alcoholic Silver Nitrate.*—The labile form of the cyanide (0·036 g.) in a mixture of redistilled chloroform (20 c.c.) and absolute alcohol (80 c.c.) was added to an alcoholic solution of silver nitrate (1 g. in 25 c.c. of 80% alcohol). The precipitated silver cyanide was filtered off, washed successively with water, alcohol, and chloroform, dried and weighed. Yield 0·036 g., *i.e.*, 97% based on a *cis–cis*-configuration.

ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH, HANTS.

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