

218. *The Structures of Hantzsch's Isomeric Diazocyanides. A Reaffirmation of the Structural as opposed to the Geometrical Viewpoint, with a Critical Review of the Properties of the Alleged cis-Azobenzene.*

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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 upheld as being of fundamental importance for the solution of the structural problem. It is emphasised that chemical analogies are against the geometrical hypothesis and in favour of a structural isomerism. Physical data require that the compound examined shall retain its structure during the examination, whereas the identical sets of data recently published by Le Fèvre and by Sutherland indicate interconversion from the unstable to the stable forms of the diazocyanides before the recorded measurements. The structure assigned to the alleged *cis*-azobenzene is not in harmony with many of the properties of this compound, and its analogy with the *syn*-diazocyanides is denied.

HODGSON and MARSDEN (*J.*, 1944, 395) have already submitted considerable chemical evidence in favour of the *isonitrile* and the nitrile structure for Hantzsch's aryl *syn*- and *anti*-diazocyanides, respectively. The above paper followed one (*J.*, 1943, 470) in which Hantzsch's *syn*- and *anti*-diazosulphonates were claimed to possess sulphite and sulphonate structures respectively, and subsequently (*J.*, 1945, 207) chemical evidence was submitted for the structural isomerism of Hantzsch's *syn*- and *anti*-diazoates. Recently, however, Anderson, Le Fèvre, and Savage (*J.*, 1947, 445) have expressed their view that Hodgson and Marsden's chemical evidence for the *syn*- and *anti*-diazocyanides is equivocal and not incompatible with the hypothesis of geometrical isomerism, while they assert that recorded dipole moments and refractivity data are also against Hodgson's conclusions. A second paper by Anderson, Bedwell, and Le Fèvre (*J.*, 1947, 457) dealing with magnetic optical rotatory powers and diamagnetic susceptibilities is also submitted in support of their geometrical viewpoint. Further, an investigation of the vibration spectra of 4-bromo- and 2:4:6-tribromo-benzenediazocyanides by Sheppard and Sutherland (*J.*, 1947, 453) is claimed to prove conclusively that these isomers cannot be related as *isocyanide* and cyanide but are both cyanides. These claims are now examined.

The Original Objective of the Oxime Analogy.—It is perhaps of interest to recall that Hantzsch's work in this field had the primary and initially the only purpose of establishing the structures of the diazoates, which were distinguished by the ability of one of them to couple immediately with phenols and amines and of the other to resist coupling. For the purpose, Hantzsch made

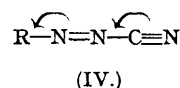
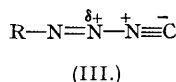
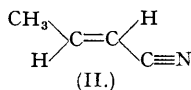
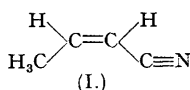
use of the geometrical analogy with the oximes, whose *syn*- and *anti*-forms (later proved by Meisenheimer and Lange, *Ber.*, 1924, 57, 282, to have the opposite configurations assigned to them by Hantzsch) seemed to furnish an appropriate parallel. Hantzsch thus reared the whole of his theory upon the fundamental proposition that the difference between the oximes and the diazo-compounds was merely the substitution of nitrogen for carbon, and that the series of so-called normal and *iso*-diazo-compounds must be derived from two isomeric diazohydroxides.

Energy States of the Alleged Geometrical Isomers.—According to Saunders ("The Aromatic Diazo-Compounds", Arnold, 1936, p. 185), the *anti*-form must be at a lower energy level than the *syn*-form, and this has been confirmed by Le Fèvre and Vine (*J.*, 1938, 431), who report the heat evolved in the transformation of *p*-bromobenzene *syn*- to *anti*-diazocyanide as 21—22 kcal./mole, *i.e.*, of the same order as the difference in bond energies between the N-N and the C-N bond. The rapidity of transformation of *syn*- to *anti*-compounds by heat has been stressed by previous investigators (cf. Hantzsch and Schultz, *Ber.*, 1895, 28, 666; Le Fèvre and Vine, *loc. cit.*; Hodgson and Marsden, *loc. cit.*). Moreover, Hodgson and Marsden doubted whether Hantzsch had ever been in possession of a pure *syn*-sulphonate or *syn*-cyanide. This rapidity of transformation readily explains the physical data assembled by Hantzsch, as well as the identity of the absorption spectra as found by Dobbie and Tinkler (*J.*, 1905, 87, 276) for the *syn*- and *anti*-sulphonates and for the *syn*- and *anti*-cyanides. In contrast, the absorption spectrum of Hantzsch's diazonium cyanide was quite different (cf. Hantzsch and Lifschitz, *Ber.*, 1912, 45, 3011). Notwithstanding these facts, Saunders (*op. cit.*, p. 195) comments that the only unchallenged item (of this great controversy) is the spectroscopic evidence, and that this must tell heavily on the credit side of Hantzsch's account, whereas in fact the evidence could not be more definite against him.

Discussion of Hantzsch's Data.—When Hantzsch was challenged as to the diazonium character of the *syn*-sulphonates, he was quick to reply with the visual colour argument, *viz.*, that benzenediazonium salts are colourless, whereas the *syn*- and *anti*-compounds are highly coloured. It is incredible, therefore, that such outstanding differences in visual colour, *viz.*, that the *syn*- and *anti*-sulphonates are red- and yellow-orange respectively, while in contrast the *syn*- and *anti*-cyanides are yellow and red respectively, should not have been seriously considered by Hantzsch, especially when he obtained identity of absorption spectra and then proceeded to argue therefrom for the geometrical isomerism of these compounds. It is of great interest, therefore, that Hantzsch and Reddelien record ("Die Diazo-Verbindungen", 1921, p. 50) that the *syn*-diazosulphonates have a tendency in aqueous solution to afford ions of the diazonium sulphite, and, although not stated, it would appear that Hantzsch's view of the mechanism of transformation of *syn*- to *anti*-sulphonate is *via* the diazonium sulphite; since the formation of the *syn*-sulphonate must be from diazonium and sulphite ions initially, it is surely reasonable to conclude from Hantzsch's experiment that the diazo-sulphite and not the sulphonate is formed originally, and is, in fact, the alleged *syn*-sulphonate. When the original papers of Hantzsch were examined, no record whatever could be found to indicate that, at the conclusion of the physical experiments, the conditions of the compounds investigated were ever tested to ascertain whether any transformations had taken place or not. It would have been a simple matter for Hantzsch *et al.* to have found whether the final compound coupled or not, and thereby to have established quantitatively the extent, if any, of the change from *syn*- to *anti*-sulphonate or cyanide. It is irrational to argue diversity of structure from identity of test, and the writer reaffirms his former standpoint that the data are for the *anti*-compounds alone.

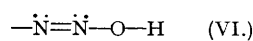
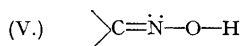
The Paper by Sheppard and Sutherland (*loc. cit.*)—The outstanding feature of this investigation is the almost complete identity of the "finger-prints" for the pairs of *syn*- and *anti*-isomers examined. No better experimental evidence could have been given that the substances were identical, *i.e.*, that transformation had taken place from *syn*- to *anti*-form in each case. The specimens examined were prepared elsewhere, and no time is stated for the interval between preparation and measurement. Further, no temperatures are given, no experiments are recorded to show that the compounds had remained unchanged either before or after the experiments, and no preliminary investigation of the effect of infra-red radiation on these remarkable compounds was made. It is the Hantzsch situation over again. Moreover, in the discussion from analogy, alkyl and aryl cyanides are compared with their isomeric *isocyanides*, so that in the former case a C-C bond connects the CN group with the rest of the molecule, and, in the latter case, a C-N bond is concerned; in none of the diazocyanides is a C-C bond in question. The analogies, therefore, are not as complete as these authors have asserted, and for the $R-N \equiv N - \overset{+}{N} - \overset{-}{N}C$ structure, *i.e.*, for an N-N bond, no analogies are given. This matter of

an irrelevant C-C bond runs throughout Sutherland's discussion, e.g., for *cis*- and *trans*-crotonitrile (I) and (II), and for the conjugation of the C≡N bond with the N=N bond he has to rely on his own prediction. The fact that the CN frequency is in exactly the same



position in all the diazocyanides is, in the author's opinion, very strong evidence that *anti*-forms are present throughout. With regard to the prediction for diazoisocyanides, the fact appears to have been ignored that this is a case of Pauling's "like adjacent charges" (III) ("The Nature of the Chemical Bond", 1940, pp. 109, 210), in which resonance is feeble, as shown by the yellow colour of the compounds as well as by their instability (ease of coupling), whereas in the nitrile compounds where resonance is facile (IV), the colours are deep red, and coupling prevented. Sutherland's statement, therefore, that the spectroscopic evidence against the isocyanide theory can be regarded as overwhelming, is at least very premature; neither has Sutherland proved conclusively, as he asserts, that Hantzsch's diazocyanides are *both* cyanides.

The Papers by Anderson, Le Fèvre, and Savage, and by Anderson, Bedwell, and Le Fèvre (loc. cit.).—In the preamble to the first paper, justice is not done to the arguments of Hodgson and Marsden (loc. cit.), inasmuch as Le Fèvre's dipole-moment data are not given the prominence suggested, while the foundational experimental evidence based on the behaviour of N-C and N-N bonds is *completely ignored* by Le Fèvre. The example of a diazo-carbonamide, R·N:N·CO·NH₂, was chosen by Hodgson and Marsden as typical, since this compound resists fission of its N-C bond by coupling agents. When the carbonamide is converted into an isocyanate, R·N:N·NCO, by the Hofmann or the Lossen reaction, coupling immediately becomes possible, since the N-C bond has now been changed to an N-N bond. Instead, Le Fèvre *et al.* focus their criticism on the Grignard experiments, which after all constitute contributory data only, since their failure would not invalidate the main argument in the slightest degree. Le Fèvre *et al.* also state that such properties as relative speeds of coupling, ionisation, etc., do not necessitate the possession by *syn*-compounds of the readily broken N-N bond and by *anti*-compounds of the more stable C-N link, while similar, although less marked, contrasts are often shown by geometrical isomers. The author emphatically asserts that the difference between the immediate coupling of the *syn*-compounds and its absence with *anti*-compounds is not to be described as a relative speed of coupling, and that no differences between geometrical isomers, a long list of which is cited by Le Fèvre, can even compare with this remarkable difference of immediate scission at the link between the diazo- and the cyanogen groups in the case of the *syn*-compounds. Moreover, the author refuses to accept an analogy between a saturated carbon bonded to an unsaturated nitrogen, as in the oximes (V), and two



unsaturated nitrogens of the diazo-group in the diazo-compounds (VI), and he asserts that there is no similarity in the sense of the present discussion between oximes and diazo-compounds. Finally, the alleged existence of azobenzene in *cis*- and *trans*-forms is used as evidence by Le Fèvre *et al.* for the possibility of geometrical isomerism about the $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{N}}$ -system, whereas when *cis*-azobenzene was claimed to have been discovered the analogy with the *syn*-diazocyanides was invoked in its favour. In view of the fact that many of the properties exhibited by the alleged *cis*-azobenzene are anomalous, the author had always refused to believe in its existence until more unequivocal evidence was forthcoming. These anomalies will be discussed later, but meanwhile, the author objects to *cis*-azobenzene being invoked to establish the possibility of existence of *syn*-diazocyanides and *vice versa*.

In their second set of comments on dipole moments, Le Fèvre *et al.* repeat the analogies of Sutherland where the cyanides have all C-C bonds and the isocyanides all C-N links; nowhere is an N-N link quoted. Instead, it is stressed that the moment of phenyl cyanide is only slightly greater than that of phenyl isocyanide, an argument irrelevant to the whole issue. It is true that in the dipole-moment data differences appear between the *syn*- and the *anti*-forms, but Le Fèvre's arguments are based on the unique and constant structures of the *syn*-compounds, whereas the methods of preparation cited in the papers by Le Fèvre *et al.* indicate mixtures to have been obtained; otherwise, what is meant by the statement "By the following modification . . . greatly improved specimens of the unstable forms are obtained", and again, "materials with melting points as high as ever previously recorded"? The author is convinced

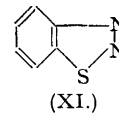
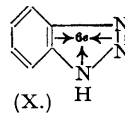
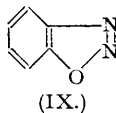
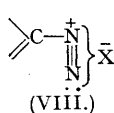
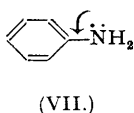
from the renewal of his experimental work in this field that, not only had Hantzsch always worked with impure specimens of *syn*-diazosulphonates and cyanides, but that Le Fèvre *et al.* have given no proof whatever that in the cases of their *syn*-diazocyanides were they really ever in possession of unique compounds.

It might be argued that differences obtained for other physical properties such as dipole moment, etc., and ascribed by the author to mixtures of *cis*- and *trans*-, should also affect the absorption spectra, but this would depend on the relative amounts of each isomeride present, and on the sensitiveness of the test. It must be realised that the various quantitative experiments of Le Fèvre and Sutherland were not carried out simultaneously or even standardised, and that no one has yet stated the actual amount of the *syn*-compound present in any of its preparations; apparently Le Fèvre unwarrantably assumes his starting material to be 100% pure (cf. Le Fèvre and Vine, *loc. cit.*, who deduce the rates of isomerisation of *cis*- to *trans*-diazocyanides from dipole-moment data in benzene at 25°, *i.e.*, of compounds prepared at or below -10°, which are very unstable at 0°, and isomerise spontaneously at *ca.* 50°). In actual fact, therefore, the starting compound must have been a mixture, and this would account for the rate of isomerisation being sufficiently slow to enable its measurement at 25°.

The Grignard Reactions.—In all Hodgson and Marsden's experiments the ether used was first tested by hydrazone formation with 4-nitro- and 2:4-dinitro-phenylhydrazine for the presence of any acetone or aldehyde as impurity, since the former is a possibility *ab initio* and the latter by slow oxidation during long storage. It is of course possible that a *syn*-cyanide can oxidise ethyl ether to acetaldehyde just as diazonium salts oxidise ethyl alcohol to this aldehyde, especially as the *syn*-diazocyanides behave in many respects like diazonium salts (cf. Stephenson and Waters, *J.*, 1939, 1796), and a diazonium structure would probably have been assigned to them long ago but for their pronounced colour and sparing solubility in water. The oxidation of alcohol by diazonium salts, however, is usually carried out under boiling conditions and over a time period much greater than that involved in these Grignard reactions, whereas the oxidation, if any, of ether by the *syn*-diazocyanides is not only more difficult than that of alcohol, but in addition would have to take place at 0° and during a few minutes. Hodgson and Marsden (*loc. cit.*) attributed their low yields (maximum 20%) of acetaldehyde to the rapid change of *syn*- to *anti*-diazocyanide, probably accelerated by the Grignard reagent itself, since in most cases no yields at all were obtained; and this circumstance is suggested for the failure of Le Fèvre in the benzaldehyde experiments. In the latter case, where phenylmagnesium bromide is used in place of methylmagnesium iodide, Le Fèvre should have obtained a measurable yield of acetaldehyde just as in the other experiments, since it is attributed by him to the oxidation of the ether by the *syn*-cyanide, whereas he reports practically no yield at all. The author maintains that Le Fèvre *et al.* have in nowise proved that the acetaldehyde reported by Hodgson and Marsden, and confirmed by them, did not come mainly from the interaction of the Grignard reagent with the *syn*-cyanide and subsequent decomposition of the complex formed. Finally, the same objection as was made earlier against the experiments of Hantzsch and of Sutherland must be made against all the physical measurements recorded for the unstable *syn*-cyanides—some of them at 20° and 25°—for substances which have to be prepared below -10°. In fact, the most unstable of Hantzsch's *syn*-cyanides are dealt with as though their stability was in no doubt whatever, while calculations are based on the same irrelevant analogies for cyanides and isocyanides possessing C-C and C-N bonds respectively.

An Argument for the Structural Viewpoint based on Analogy.—The strength of the C-N bond and its resistance to fission is an outstanding feature of all compounds in which it occurs, and, where resonance is possible, as in (VII), the bond is even strengthened. Only under conditions involving high temperatures and pressures can this bond be broken, *e.g.*, in alkyl and aryl isocyanides and nitro-, nitroso-, and amino-compounds. Further, when a halogen is *ortho*- or *para*- to a nitro-group in a benzene or naphthalene derivative, it is the halogen which is displaced by anionoid reagents, *i.e.*, the C-Cl and not the C-N bond is ruptured. On the other hand, in such compounds as R·N·N·CH₃, R·N·N·C₆H₅, R·N·N·CO·NH₂, and R·N·N·CN (*anti*), no coupling occurs with alkaline β-naphthol; it is only in diazonium salts (VIII) that the bond is readily broken, and in these cases the simultaneous evolution of the nitrogen molecule is also necessary. The author does not accept the free-radical hypothesis of Hey and Waters for the decomposition of diazo-compounds in aqueous solution, which he considers to be unnecessary, and his reasons for this standpoint have already been given (Hodgson, this vol., p. 348). In fact, the only examples of a ruptured C-N bond without attendant complex decompositions are in the alleged *syn*-diazocyanides. On the other hand, all the diazo-compounds with N-O bonds couple immediately with alkaline β-naphthol, *e.g.*, C₆H₅·N·N·OH, C₆H₅·N·N·O·CH₃,

$C_6H_5 \cdot N \cdot N \cdot O \cdot CO \cdot CH_3$ [and the diazo-oxides if they are assumed to have the formula (IX)]; similarly all the chain diazo-compounds with N-N bonds couple immediately under appropriate

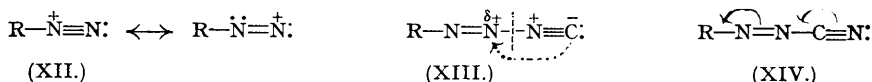


conditions, e.g., $C_6H_5 \cdot N \cdot N \cdot NH \cdot C_6H_5$, $C_6H_5 \cdot N \cdot N \cdot N \cdot CO$, and diazoimino-compounds, but the ring compounds such as (X) do not, though here we have an example of benzene-like stability produced by the existence of an aromatic sextet [cf. Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions", Institute of Chemistry, 1932, p. 10]. Further, all the diazo-compounds with N-S bonds will not couple, e.g., $C_6H_5 \cdot N \cdot N \cdot SO_3Na$ (*anti*), $C_6H_5 \cdot N \cdot N \cdot S \cdot CH_3$, $C_6H_5 \cdot N \cdot N \cdot S \cdot C_6H_5$, $C_6H_5 \cdot N \cdot N \cdot SO_2R$ and (XI), with the single exception of the alleged *syn*-sulphonates, e.g., $C_6H_5 \cdot N \cdot N \cdot SO_3Na, K$ (*syn*). The *syn*-sulphonates and *syn*-cyanides thus stand out as the *sole* exceptions of their respective classes, so that evidence for their existence should be overwhelming, especially in view of the great anomaly. The alleged *syn*-sulphonates, however, have been shown beyond doubt to be sulphites (Hodgson and Marsden, *loc. cit.*), so that now the *syn*-diazocyanides stand alone.

The Validity of the Infra-red Spectra.—The evidence for the existence of *syn*-diazocyanides depends upon an absolute proof of the presence in them of the $>N-C \equiv N$ group. It is obvious that two compounds which differ so much that their visual colours are yellow and red, respectively, must be in very different states of internal strain (cf. Saunders, *op. cit.*), and therefore should exhibit other outstanding differences in properties, including spectra whether visual or otherwise. Germane to this standpoint is a paper by Sutherland and Thompson (*Trans. Faraday Soc.*, 1945, 41, 175), wherein it is stated (in italics) that "the infra-red spectrum of a chemical compound is probably the most characteristic property of that compound"; and (again in italics): "In principle, however, no two molecules other than a pair of optical isomers can have an exactly similar array of frequencies, and although two closely related molecules may have several absorption bands at identical wave-lengths, we may expect to find some spectral region in which differences can be found. In this sense the infra-red spectrum is a fingerprint of the molecule, and with structural isomers of relatively simple molecules, as well as with highly complex organic structures, this spectrum may well be the most characteristic physical property of the compound." Again (*ibid.*, p. 207), Le Fèvre asks "whether two molecules which are structurally identical but spatially different might have infra-red spectra at least as unlike as are the visible and ultra-violet spectra for such compounds", and in reply Thompson (*ibid.*, p. 208) states: "although information about the spectra of *cis*- and *trans*-isomers is accumulating, I do not think that we are yet in a position to predict on theoretical grounds how the spectra should differ, except perhaps in some simple cases. The mathematical treatment of complex molecules is not at present very satisfactory, mainly because little is known about the force fields in such molecules."

After such emphatic pronouncements in January, 1945, Le Fèvre *et al.* and Sheppard and Sutherland then present in July 1946 what really amount to identical fingerprints for sets of alleged *syn*- and *anti*-isomers of which the *syn*- have to be prepared at -10° , and, in some compounds at least, commence to change into the *anti*-isomers forthwith. Even the identity of the fingerprint of the probably more stable tribromobenzene-*syn*-diazocyanide with that of its isomer cannot be claimed as supporting evidence for the very unstable *p*-nitro- and *p*-chloro-benzene-*syn*-diazocyanides; on the contrary the identities of the fingerprints for compounds which are known to isomerise spontaneously at 0° (Le Fèvre, *loc. cit.*) and below 0° (Hantzsch, *loc. cit.*), invalidate the conclusions which their investigators have drawn. It is reasonable, therefore, not only on grounds of analogy, but also because it accounts for all the chemical properties of the alleged aryldiazo-*syn*-cyanides, that their general formula should be, $R \cdot N \equiv N \cdot N \equiv \bar{C}$. It is also germane to the issue that in the cases of all the compounds which on Hantzsch's theory should be capable of geometrical isomerism, e.g., $R \cdot N \cdot N \cdot O \cdot CH_3$ (especially in view of the stress laid by Hantzsch, Saunders, Le Fèvre, and others on oxime analogy), $R \cdot N \cdot N \cdot S \cdot CH_3$, $R \cdot N \cdot N \cdot SO_2R$, and $R \cdot N \cdot N \cdot NHR$, not a single one can be obtained in two forms, and that the only cases claimed are the *syn*-sulphonates (now proved to be non-existent) and the *syn*-cyanides. It is therefore incredible that, in view of the enormous relative stability of the *anti*-sulphonates and *anti*-cyanides, a mere angular difference should produce such remarkable changes in chemical properties and in visual spectra.

The Mode of Formation of the Aryldiazoisonitriles.—This may be envisaged as follows : on addition of potassium cyanide to the solution of the diazonium salt the cyanide anion will approach the diazonium kation (XII) at the nitrogen in accord with the approach of diazo-compounds to aniline, since the nitrogen atom has less affinity for a negative charge than carbon; the diazoisonitrile (XIII) will thereby be formed initially, but will immediately commence to undergo a redistribution of electrical charge so that the N-N link becomes exceedingly weak from the presence of like positive charges on its members, and forthwith



commences to isomerise into the more stable diazocyanide (XIV), whose stability is greatly enhanced by the facile resonance that will now occur. During the *isonitrile* stage, it is obvious that immediate coupling can occur with suitable reagents, but that in the cyanide condition coupling is now prevented. In the formation of the diazosulphites (*syn*-sulphonates) it is clear that the approach of the sulphite anion must be at an oxygen atom, and to give a sulphite initially.

There now remains the analogy with *cis*-azobenzene quoted by Le Fèvre *et al.* to show that geometrical isomerism about the $\text{N}=\text{N}$ -system is possible.

A Critical Discussion of Some of the Properties of the Alleged cis-Azobenzene.—Since the geometrical isomerism of compounds containing the azo-group is restricted to that of *cis*- and *trans*-azobenzene (hereinafter referred to as *cis* and *trans*) the evidence for its existence *must be unequivocal*. The following discussion will show, however, that a double compound of azoxybenzene and hydrazobenzene exhibits far more convincingly many of the reactions given by *cis*. The data singled out for discussion are as follows :

(1) Ease of conversion of *cis* to *trans* is paralleled by ease of reaction between hydrazobenzene and azoxybenzene to give *trans*. Evaporation in a vacuum of an ice-cold chloroform solution of *cis* is sufficient to bring about some conversion into *trans*. Photochemical formation of *cis* from *trans* in the presence of water (Hartley, *J.*, 1938, 633) lends support to the view of an oxidation-reduction reaction for production of azoxy- and of hydrazo-benzene. Irradiation of absolutely dry ligroin solutions of *trans* in absence of air afforded no *cis*, whereas when water was present a deepening of colour resulted, indicating the formation of *cis*; this colour was discharged by desiccating agents such as anhydrous sodium sulphate with re-formation of *trans*. Contrary to these results, Hartley and Le Fèvre (*J.*, 1939, 531) have concluded that solutions in benzene of *cis* and of *trans* separately when illuminated by sunlight each give an equilibrium mixture containing 22% of *cis*; no compounds were isolated from these *trans* experiments, and whether the experiments were conducted in absence of air is not stated.

(2) Since *cis* has a dipole moment, its molecular weight of 179 in benzene (associating solvent) could be expected to be higher than that of 190 in acetic acid (dissociating solvent), whereas the opposite is the case (Hartley, *loc. cit.*), although the differences from 182 for azobenzene are small enough to be within experimental error from the standpoint of conversion to *trans* during the determinations.

(3) The red colour given by *cis* with concentrated sulphuric acid or hydrochloric acid is similar and peculiar to azoxybenzene, which has been ascribed by Wallach and Bellis (*Ber.*, 1880, 13, 528) to isomerisation of azoxy- to hydroxyazo-benzene. Since *trans* gives only a yellow solution in concentrated sulphuric acid, the origin of the red colour given by *cis* is more than difficult to explain in the absence of auxochromes.

(4) The greater solubility of *cis* than of *trans* in polar solvents is more reasonably accounted for by the above double compound. Hartley (*loc. cit.*) records a much higher solubility for *cis* than for *trans* in 0.5*N*- and in *N*-hydrochloric acid, although he argues, notwithstanding, that the *cis* is not much, if at all, more basic than the *trans*. On Swientoslawski's hypothesis (*Bull. Soc. chim.*, 1924, 35, 137; *Ber.*, 1929, 62, 2034; *Annalen*, 1931, 491, 273) that deformation of the azo-group should make it more acidic, *i.e.*, less prone to dissolve in acids (and this would also follow on electronic grounds), the greater solubility of *cis* in acids—or even Hartley's argument that the *cis* is not much, if at all, more basic than the *trans*—is evidence contrary to the hypothesis of a *cis*-structure.

(5) It is noteworthy that Cook (*J.*, 1938, 878) isolated what might be an azoxytoluene by long irradiation of *mm'*-azotoluene *in air*.

(6) Robertson (*J.*, 1939, 232) found that ordinary *trans*-azobenzene crystallised in the monoclinic system, that its X-ray spectrum was easily explained, and that two almost planar

centrosymmetrical molecules contributed to the asymmetrical unit. A quite different crystal structure was encountered with Hartley's *cis*-azobenzene, in that it was orthorhombic while the molecule had a two-fold axis but no centre of symmetry. To accommodate these results into a *cis*-azo-structure involved considerable ingenuity (cf. also Hampson and Robertson, *J.*, 1941, 409). Pauling (*op. cit.*, p. 221) writes in comment on the above data: "that steric interaction of the two rings in *cis* is so great that a coplanar configuration cannot be achieved since contact of the ortho-hydrogen atoms of the two rings prevents the molecule from assuming the coplanar configuration, and each phenyl group is rotated *ca.* 50° out of the coplanar orientation. Since coplanarity is an essential attribute of double-bond character, it is assumed that the amount of conjugation energy in *cis* is probably not greater than 2 or 3 kcal./g.-mol., and the difference in energy as determined by Hartley (*loc. cit.*) between *cis* and *trans* of 12 kcal./g.-mol. is taken as the conjugation energy for the *trans*-configuration". This considerable departure from coplanarity with consequent strain in the molecule should also be accompanied by an appreciable difference in its absorption spectrum from that of the *trans* isomer, but such is not the case, for while the *cis* absorbs more light at the blue end of the spectrum, there is no displacement of the visible band although the ultra-violet absorption band is shifted towards a higher frequency (Le Fèvre and Vine, *loc. cit.*, p. 438). This relatively small difference in light absorption, which, so far as visible light is concerned, is even contrary to what should be expected from a highly strained molecule (*i.e.*, less instead of more blue), is in striking contrast with the absorption spectra differences exhibited by other geometrical isomers. For example, in the case of *cis*- and *trans*-di-*p*-tolylethylene, where the *trans* is completely changed by sunlight to the *cis* in *ca.* 2 hours (Martin, Bett, Romans, and Tidridge, *Trans. Roy. Soc. Canada*, 1940, 34, 35), the *trans* is yellow with strong absorption at 4047 Å., whereas the *cis* is colourless and quite transparent at 4047—3660 Å., absorbing at 2536 Å. only slightly. On analogy, therefore, the almost complete absence of resonance in *cis*-azobenzene as compared with the facile resonance in *trans*-azobenzene should have been accompanied by very dissimilar absorption, and if the analogy with the *syn*-diazocyanides as adopted by Hartley and by Le Fèvre is pressed (cf. *J.*, 1947, 446), the visual colour should at least have been yellow whereas *cis*- is visually redder than the *trans*-azobenzene, and likewise the deepening of colour in the irradiation experiments, instead of lightening, is the qualitative test of the formation of *cis*-azobenzene. The analogies quoted by Le Fèvre and Vine (*loc. cit.*) are invalid, since the geometrically isomeric diazoates and diazo-sulphonates do not exist. Is it possible that *cis*- and *trans*-azobenzene are the only geometrical isomers in which the *more* strained member is *more* bathochromic than the practically unstrained isomer, since the contrary should be the case if the structure assigned to *cis*-azobenzene is correct? In the double-compound alternative above, the reddening of the yellow colour of the azoxybenzene component would be accounted for by relief of the strain imposed by its dipole through association with the anionoid hydrazobenzene.

(7) Finally, it is of great interest to find that the surprisingly large value of 12 kcal./g.-mol. found, and so commented upon, by Hartley for the conversion of solid *cis*- at 21° to solid *trans*- at 21° is of the same order as that for the heat of reaction between azoxy- and hydrazo-benzene when computed from their published (Beilstein) heats of combustion at constant pressure, namely, 10.7 kcal. per g.-mol. of *trans*-azobenzene formed. Further, with respect to analytical data, the following are the calculated percentage values for the elements in azobenzene and (in parentheses) for the double compound: C, 79.1 (75.4); H, 5.5 (5.75); N, 15.4 (14.7); from which it is obvious that only the value for carbon is discriminating, and conversion even in part would bring this value within the limits of experimental error.

It follows, therefore, that weighty evidence exists against the structure assigned to the alleged *cis*-azobenzene, and since it and the *syn*-diazocyanides are the only examples left of geometrical isomerism about the $\text{-}\ddot{\text{N}}=\ddot{\text{N}}\text{-}$ system, further data of an unequivocal character must be forthcoming to establish the validity of the geometrical hypothesis in these cases. Meanwhile, the author adheres to his original view that the *syn*-diazocyanides are isonitriles, and that the structure of *cis*-azobenzene has not been unequivocally established.

Conclusions.—(1) The data of Le Fèvre *et al.* (*loc. cit.*) and of Sheppard and Sutherland (*loc. cit.*) are challenged on the ground that no tests appear to have been made to prove that interconversion of *syn*- to *anti*- during the course of the experiments had *not* taken place. The identity of the spectroscopic data for both isomers is a convincing proof of identity of compound, particularly in view of their facile interconversion; in any event it is no evidence of the similarity of geometrically isomeric forms.

(2) In a compound so highly strained as the alleged *syn*-diazocyanide, wherein rupture of the C-N link occurs with the greatest ease as in coupling with phenols and amines, compared with

the *anti*-isomer which resists coupling, other marked differences should also exist, notably in their spectra; *e.g.*, the visual colours being different, why should the visual spectra be alike if interconversion had not taken place?

(3) Irrelevant analogies are given by the above authors for the interpretation of their data, and the real analogies that C-N and N-S bonds universally resist rupture, whereas N-O and N-N bonds split readily, are now emphasised.

(4) In view of the ephemeral character of the compounds discussed, it would appear that chemical is of far more importance than physical evidence for the problem in hand.

(5) The properties of the alleged *cis*-azobenzene are in many respects so anomalous that doubt must be expressed as to its *cis*-azo-structure.

(6) To formulate the isomeric diazocyanides as *both* cyanides with a C-N link, is to accept a structure for one of them (the yellow one) whose chemical behaviour contradicts it. The author therefore adheres to the *isonitrile* structure, $\text{R}-\text{N}=\text{N}^+-\text{N}^-\equiv\text{C}$, for these very reactive compounds.

The experimental work alluded to in the section dealing with *cis*-azobenzene was carried out during 1938—1940 in collaboration with Drs. W. Davey and E. Marsden. Adverse climatic conditions during the succeeding summers have prevented further work despite frequent attempts. The author, however, feels that the present occasion requires a statement of his views, since the analogy of *cis*-azobenzene with the *syn*-diazocyanides has recently been stressed.

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