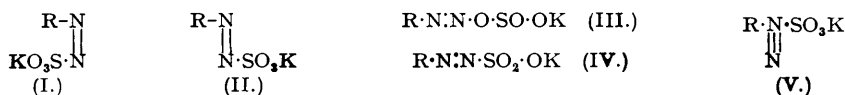## 92. *Hantzsch's Isomeric Diazosulphonates.*

By H. C. Freeman and R. J. W. Le Fèvre.

Much of the evidence recorded hitherto on the formulation of the diazo-sulphonates is inconclusive. Alkali salts of ten pairs (five not previously described) of isomeric diazosulphonic acids have therefore been prepared. Exposure of aqueous solutions to sunlight causes the production of the unstable from the stable forms accompanied by some irreversible decomposition. Thermal changes in the dark proceed in the direction : unstable $\longrightarrow$ stable. Small differences of λ and ε are found between the ultra-violet spectra of the members of each pair. The belief that their absorptions are identical is thus demonstrably incorrect. Attempts to make kinetic and other physical measurements are described. Of the structural (Bamberger, Hodgson; sulphite–sulphonate) and the configurational (Hantzsch; *cis-trans*-sulphonates) explanations for this series of isomers, the latter is preferred.

As is well known (cf. Sidgwick's " Organic Chemistry of Nitrogen," Oxford, 1942, p. 418; Saunders, " The Aromatic Diazo-Compounds and Their Technical Applications," 1949, p. 147), Hantzsch (*Ber.*, 1894, **27**, 1702, 1726, 2099; cf. also Hantzsch and Reddelien, " Die Diazo-Verbindungen," Stuttgart, 1921) regarded the various pairs of isomeric compounds isolable from diazonium salts and alkali sulphites in aqueous solution as cases (with the metallic diazoates

$$
\begin{array}{llll}
\text{R-N} & \text{R-N} & \text{R·N:N·O·SO·OK (III.)} & \text{R·N·SO}_3\text{K} \\
\text{KO}_3\text{S·N} & \text{N·SO}_3\text{K} & \text{R·N:N·SO}_2\text{·OK (IV.)} & \text{N} \\
\text{(I.)} & \text{(II.)} & & \text{(V.)}
\end{array}
$$

and diazocyanides) where the –N=N– unit may adopt a *cis-* or *trans-*configuration, as indicated by (I) and (II). Acrimonious controversy followed this suggestion. Attack came particularly from Bamberger (*Ber.*, 1894, **27**, 2582, 2930) who—while not disputing the possibility of

E E

geometrical isomerism about the azo-group—supported an explanation already mentioned by Hantzsch himself (*ibid.*, p. 2099), namely, that in these cases the differences are structural, the unstable and stable forms being respectively sulphites (III) and sulphonates (IV). Blomstrand and others (*J. pr. Chem.*, 1896, **53**, 169; 1897, **55**, 481) together with —at one stage—Bamberger (*Ber.*, 1895, **28**, 225, 444) wrote the stable varieties as diazosulphonates (IV) and their labile modifications as (V), but for reasons mentioned by Sidgwick (*op. cit.*, p. XIII; cf. also p. 417) such a formulation is unacceptable to-day

Hantzsch based his views mainly on those properties which appeared common to the three groups of isomeric diazo-compounds [diazocyanides, metallic diazoates, and diazo-sulphonates]. In each, one form coupled with alkaline solutions of phenols, decomposed with evolution of nitrogen, and was characterised by instability, and in these respects was in contrast to a second form which did not couple and was stable in conditions (*e.g.*, exposure to air, drying, etc.) where the first decomposed. However, Bamberger (*loc. cit.*; *Ber.*, 1895, **28**, 225, 444) and Claus (*J. pr. Chem.*, 1894, **50**, 239) contended that just those differences which distinguished the labile diazo-hydrates, -cyanides, and -sulphonates from their stable isomers, eliminated any probability of geometrical isomerism. In modern terms, these authors thought that mere alteration of bond directions could not be responsible for such great changes in chemical reactivity. Hantzsch (*Ber.*, 1895, **28**, 676) reiterated his original thesis. In a further paper with Schmiedel (*Ber.*, 1897, **30**, 71) he summarised his views. Geometrical isomerism involving $N{=}N$ linkages, was to him just as real as that with $C{=}C$, with the reservation that nitrogen atoms were less reactive than carbon atoms.

Hodgson and Marsden (*J.*, 1943, **470**; cf. also Hodgson and Bailey, *J.*, 1948, 1183) have recently revived Bamberger's suggestion that the relationship is constitutional and not configurational. It is of interest therefore to consider the arguments supporting the sulphite formula.

Hantzsch (*Ber.*, 1894, **27**, 2099) was incorrect in claiming that isomerism of the type $R{\cdot}SO_3K \rightleftharpoons RO{\cdot}SO_2K$ was not found elsewhere. Bamberger (*loc. cit.*) was able to quote many examples to the contrary, and Warlitz had demonstrated a sulphite–sulphonate rearrangement involving $C{-}O \longrightarrow C{-}S$, but Hantzsch and Schmiedel (*loc. cit.*) denied that this was analogous to $-N_2{-}O \longrightarrow -N_2{-}S$.

The labile isomers decolorised iodine and permanganate and gave sulphur dioxide with acids. Bamberger regarded this as conclusively in favour of the sulphite structure. Since, however, the aqueous solution of the isomer did not dissolve silver chloride, he was forced to make the reservation that the compound was actually a " complex sulphite." Hantzsch drew attention to this, and emphasised that it was not made clear why " complex sulphites " differed from ordinary sulphites (*loc. cit.*, 1894, p. 3527). He found, further, that the sulphite reactions were not instantaneous, but delayed, *e.g.*, benzene *syn*-diazosulphonates precipitated barium sulphite only on prolonged storage. In this and other respects these salts were like the double salts of mercury with alkali sulphites—salts shown by Barth (*Z. physikal. Chem.*, 1892, **9**, 195) to be sulphonates and not salts of sulphurous acid; *e.g.*, $Hg(SO_3K)_2$, which exhibited " delayed " sulphite reactions, gave the ions $Hg(SO_3)_2^-$ and $2K^+$ in solution and was neutral.

Hodgson's recent contributions to the subject (*loc. cit.*; *J.*, 1948, 1096) have been based on the assumption (supported by analogy) that the $N{-}S$ bond is always more stable than the $N{-}O$ bond; for instance, it is claimed that Hantzsch's *anti*-diazosulphonate (whose structure is not questioned) retains its $N{-}S$ bond during the reactions : $Ar{\cdot}N_2{\cdot}SO_3K \longrightarrow Ar{\cdot}N_2{\cdot}SO_3{\cdot}N_2{\cdot}Ar' \longrightarrow Ar{\cdot}N_2{\cdot}SO_3K + (\beta)C_{10}H_7O{\cdot}N_2{\cdot}Ar'$, while the *syn*-diazosulphonate evidently contains the weaker $N{-}O$ link, since a parallel treatment proceeds : $Ar{\cdot}N_2{\cdot}O{\cdot}SO_2K \longrightarrow Ar{\cdot}N_2{\cdot}O{\cdot}SO_2{\cdot}N_2Ar' \longrightarrow Ar{\cdot}N_2{\cdot}(\beta)C_{10}H_7O$ (where Ar $=$ Ph, Ar' $= p\text{-}NO_2{\cdot}C_6H_4$). In fact, some $Ar'{\cdot}N_2{\cdot}(\beta)C_{10}H_7O$ is also isolated, because—in Hodgson's view—the initial *syn*-preparation always contains the *anti*-isomer requisite for the first of the two reactions just written.

Hodgson (*J.*, 1948, 1097) further states that, in general, compounds with $\cdot N_2{\cdot}SR$ bonds (*e.g.*, $Ar{\cdot}N{:}N{\cdot}SR$, where SR $=$ SMe, SAr', or SO_2R) will not couple with alkaline β-naphthol, but the *syn*-diazosulphonates do so; hence, it is argued, they do not possess the $N{-}S$ link, but are diazosulphites.

The relevance of kinetic and spectral data was realised half a century ago. The first measurements of the stabilities and rates of isomerisation of the isomers were made by Bamberger (*loc. cit.*, p. 2930), who used the results to support his allegations that Hantzsch had never investigated or analysed a pure labile compound. The figures which he obtained, from titrations of the excess of iodine in a solution into which he had placed freshly-precipitated labile compound, indeed tended to show a high degree of conversion of the labile into the stable isomer within a matter of minutes of the formation of the sample.

Hantzsch (*loc. cit.*, p. 3527) repeated these experiments, and by suitable corrections of Bamberger's methods showed that his own specimens of *syn*-diazosulphonate were 96% pure. (For instance, Hantzsch mixed his diazo-solution and sulphite solution rapidly, to minimise isomerisation; Bamberger had performed the addition gradually. Hantzsch used N/100-iodine solutions for his estimations, to assist the speedy dissolution and reaction of the labile solid; Bamberger had used N/10-solutions, giving him a smaller volume and hence slower rate of solution and thus of reaction.)

Hantzsch and Schmiedel (*loc. cit.*) continued these analyses, and also used the same procedure to follow the speeds of isomerisation with alkyl- and halogen-substituted benzene derivatives. Qualitative observations were also found practicable by naphthol-coupling. The results indicated that alkyl and nitro-substituents increased the velocity; halogen substituents had the reverse effect. The darker the colour of the *syn*-form, the greater its instability seemed to be. The isomerisation, it should be noted, appeared not to be a first-order process.

Despite Hantzsch's measurements of the decomposition rates of his labile isomers, and the recorded high purity of his specimens, Hodgson and Marsden have concluded that the " *syn* "-compound is " always mixed with the *anti*-isomeride, into which it passes rapidly." This assertion, repeated in Hodgson's 1948 papers, is based on reactions similar to those just mentioned.

Hantzsch early pointed out (1894) that both the labile and the stable isomers of the diazo-sulphonates were coloured, the labile member of each pair having the deeper colour, yet all diazonium salts of colourless anions were colourless; this meant that the diazosulphonates could not be salts of SO_3^{--}. Bamberger (*loc. cit.*, p. 2930) at once objected on the grounds that the colour of the diazosulphonates, with N:N·S, could not be compared with that of other diazo-compounds, such as the cyanides, with N:N·C. In any case, he wrote, the relation between colour and chemical structure was still too little known to be used as an argument; *e.g.*, the yellow lead iodide and the colourless potassium iodide were " analog constituirt und dennoch optisch verschieden." Hantzsch (1894) at once retorted that Bamberger had referred to the solid iodides; their *solutions* were both colourless. He continued with a description of cryoscopic measurements, which showed that *both* the *syn*- and the *anti*-diazosulphonates were dissociated into *two* ions. Hence any formulæ which *necessitated* dissociation into three ions, *viz.*, $Ar·N_2^+$, SO_3^{--}, and K^+, could be excluded. This was taken as evidence against the sulphite formula. Incidentally, the occurrence of only two ions formally disposes of the Blomstrand–Strecker–Erlenmeyer " phenylazonium " structure (V) for the labile isomer : according to modern theory, (V) can be modified only to $Ar·\overset{+}{N}:N\ SO_3^{--}\ K^+$, a diazonium salt with three ions.

Finally, Dobbie and Tinkler (*J.*, 1905, **87**, 273) and Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) have produced spectroscopic data favouring the structural identity hypotheses. The graphs in the second paper (the earlier measurements were less accurate and more restricted in range) particularly, show the similarities between the ultra-violet and the visible absorption bands of diazosulphonate pairs

This spectroscopic evidence remained unchallenged until recently. Hodgson *et al.* maintain that it is anomalous for compounds of distinctly different colours, chemical stabilities, and energy contents to give almost identical absorption spectra. This is actually a modern variation of Bamberger's theme—that compounds so different could not be geometrical isomers. Further, Hodgson argues that the depth of colour in the diazosulphonates is in reverse order to that in the diazocyanides, *viz.*, in the sulphonates the labile isomer, but in the cyanides the stable isomer has the deeper colour. This, it is claimed, destroys the analogy between the two groups of compounds.

As already mentioned, Hodgson and Marsden (1943) have concluded that the labile forms are always accompanied by a variable proportion of the *anti*-isomers. For this reason, Hodgson's diagnosis that Hantzsch's absorption spectra were identical because they were spectra of the same material, namely, the stable isomer, cannot be dismissed, since it is clear that a considerable fraction of the labile isomer might have isomerised in the time required for the older techniques of absorption spectroscopy available to Hantzsch and his collaborators.

Present Work.—At the outset, therefore, it seemed to us that the formulation of the diazo-sulphonates still remained a problem lacking sufficient *agreed* observational data for its resolution. We decided accordingly : (*a*) to prepare representative examples of this class, (*b*) to note their behaviour towards daylight, (*c*) to investigate the similarities of ultra-violet and visual spectra recorded for various of these isomers, and (*d*) to seek any measurable differences in properties between the aqueous solutions of the forms, and if possible thereby to study the rates of inversion and attempt to ascertain the energies of activation involved.

(*a*) *Isomers Examined.*—The following diazosulphonates have been prepared during the present investigation :

Diazosulphonic acid.	Forms isolated.
Benzene-	K and Na salts
o-Chlorobenzene-	Free acid, Na, K, and Ag salts
p- ,, ...	K and Na salts
o-Iodobenzene-	K salts
p- ,, ...	K salts
2 : 4-Di-iodobenzene-	K salts
2 : 4 : 6-Tribromobenzene-	K salt (one form only)
p-Nitrobenzene-	K salt (one form only)
Diphenyl-2-	K salts
,, -4-	K salts
Diphenyl-4 : 4'-bis-	K salts

No signs of the third, theoretically possible, variety of the diphenylbisdiazosulphonates have been obtained (compare Brown, Le Fèvre, and Whittem, *J.*, 1950, 185).

Five of the above pairs do not appear in the literature. Labile forms are known for at least 12 of the following 46 diazosulphonates, whose parental types include : Benzene (27 examples; Hantzsch *et al.*, *loc. cit.*; Riedel, " Friedländer," **3**, 922; Fischer and Kuzel, *Annalen*, 1883, **221**, 274; Altschul, *Ber.*, 1892, **25**, 1843; Stollé, *Ber.*, 1912, **45**, 2680; Franzen and Schmidt, *J. pr. Chem.*, 1917, **96**, 15; Perkin and Rubinstein, *J.*, 1926, 357; Hall and Gibbs, *J. Amer. Chem. Soc.*, 1927, **49**, 433; Desai, Mehta, and Thosar, *J. Soc. Dyers Col.*, 1938, **54**, 371), naphthalene (4 examples; Hantzsch and Schmiedel, *Ber.*, 1897, **30**, 80; Bamberger, Böcking, and Kraus, *J. pr. Chem.*, 1923, **105**, 251; Hodgson and Bailey, *J.*, 1948, 1183), diphenylamine (3 examples; Zitscher and Seidenfaden, U.S.P. 1,897,410), azobenzene (1 example; Tröger and Puttkammer, *Ber.*, 1907, **40**, 209), and benzeneazonaphthalene (11 examples; Tröger *et al.*, *Arch. Pharm.*, 1917, **255**, 1; *J. pr. Chem.*, 1926, **113**, 268; 1927, **114**, 269). Other examples occur in the technical literature.

In general, the behaviour of the various diazosulphonates was found to correspond to that expected from the literature. The decomposability of the labile isomers varied; for example, the *p*-nitrobenzene derivative began to deteriorate even on the filter-paper, while the halogenated or diphenyl compounds could be kept overnight on a porous tile in a dark vacuum desiccator at 0° with little or no decomposition.

Rough qualitative tests were carried out by means of naphthol coupling to determine the relative rates of isomerisation of the labile into the stable forms. The halogenated benzene derivatives were found to isomerise with rates of approximately the same order, *e.g.*, 1% solutions of the labile *o*-chloro-, *o*-iodo-, and *p*-iodo-benzenediazosulphonates failed to couple with alkaline β-naphthol after 2, 3, and 1 hours at 25°, respectively. It was noted, in anticipation of some spectroscopic observations to be mentioned later, that a solution of the labile *o*-chlorobenzene derivative, when kept at 0°, still coupled strongly after 3 hours.

Since good storage quality of labile isomer seems generally to be accompanied by slow rate of isomerisation (*Ber.*, 1897, **30**, 71), it was surprising to find that the relatively permanent diphenyldiazosulphonates isomerised extremely rapidly, all naphthol coupling of a 2% solution of each of them ceasing within 10 minutes of dissolution; the bisdiazosulphonate gave a heavy precipitate of the *anti*-isomer on standing for this short period.

The observations reported in the early papers of Hantzsch and Bamberger having thus been submitted to a brief confirmatory review, with extension of their experiments to a number of new compounds, some attention was paid to the more recent evidence submitted by Hodgson and Marsden (1943). In particular, it was desired to repeat these authors' preparations of complexes derived from *syn*- and *anti*-diazosulphonates and diazotised amines, since the quantitative data of their paper seemed incomplete. (For instance, no indication is given of the *yield* of complex in any of the five reactions with which Hodgson and Marsden deal.) It was found impossible, however, to carry out the necessary estimations, owing to the instability of the complex formed; *e.g.*, that from *o*-chlorobenzene-*syn*-diazosulphonate and diazotised *p*-nitroaniline decomposed vigorously—even on being sucked semi-dry on the filter-paper—in a manner reminiscent of the more unstable of the labile diazosulphonates.

Despite the fact that Hodgson and Marsden place great reliance both on naphthol coupling and on diazonium-complex formation as showing the extremely rapid transformation of labile into stable isomerides, their recorded proportion of *anti*-isomer in a fresh sample of the labile modification (" 78% being a typical amount " of *anti*-isomer in a fresh, unwashed preparation)

seems very large when compared with the results of Hantzsch and Schmiedel's parallel experiments (*Ber.*, 1897, **30**, 71) using iodometric titrations of the *syn*-form. It is therefore to be regretted that Hodgson *et al.* do not record the relative quantities of the isomers as found, *e.g.*, by estimation of the naphthol-coupling products from the complex of benzene-*syn*-diazosulphonate with diazotised *p*-nitroaniline. In any case, there is no evidence that this complex itself does not isomerise, and that the conclusions drawn from its heterogeneous composition do not in fact relate at least partly to processes taking place *after* the formation of the complex.

A further criticism may be levelled against this work, particularly in view of the unassailability which Hodgson has claimed for the deductions made from it (cf. *J. Soc. Dyers Col.*, 1943, **59**, 271). The formation of the diazosulphonate–diazonium salt complexes was limited—by the instability of most of them—to those derived from the *syn*-diazosulphonates from aniline and *p*-nitroaniline. The use of these substances as test compounds is unfortunate, inasmuch as Hantzsch and Schmiedel reported that the *p*-nitroaniline derivative (whose decomposability we have already noted above) was even more unstable than that from aniline. Hantzsch, in 1894 (*Ber.*, **27**, 3527) as well as in his later paper with Schmiedel and in his spectroscopic observations with Lifschitz (*Ber.*, 1912, **45**, 3011), chose, *e.g.*, the halogen-substituted benzenediazosulphonates as more amenable to experiment than the unsubstituted compound.

In the work to be described below, the relatively stable *o*-chloroaniline derivatives have been used.

(*b*) *Effect of Light on Diazosulphonates.*—It has been known for 60 years (Feer, D.R.-P. 53,455, 1889; "Friedländer," **2**, 558) that diazosulphonates undergo changes on exposure to light, and become capable of coupling with phenols. Feer's work, however, was directed towards photographic applications; moreover, it took place before the discovery of isomerism among diazo-compounds.

Desai, Mehta, and Thosar (*J. Soc. Dyers Col.*, 1938, **54**, 371) regarded the process occurring when stable diazosulphonates were exposed to light as a production of the *syn*-isomers. Their measurements—intended also to determine the rates of conversion—were carried out by iodometric titrations, weighing an azo-compound formed on naphthol coupling, and by periodic observations of pH. References to their results will be made below.

The behaviour of diazosulphonates in light has a bearing also on the theoretical problem of their isomerism. If the isomerism is geometrical, then interconversion of the isomers in light will not be unexpected; if the isomers are related as sulphite to sulphonate, then no equivalent photochemical transformation would appear to have been discovered, and the effect of light—if any—might be a decomposition of the stable isomer.

Photochemical transformations of *cis-trans*-isomers are well-known. *trans*-Stilbene is converted into the *cis*-isomer (Smakula, *Z. physikal. Chem.*, 1934, *B*, **25**, 90; cf. Rollefson and Burton, " Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, 1939, 248), *trans*-azobenzene gives a photochemical equilibrium mixture with the *cis*-form (*J.*, 1938, 633), and a similar equilibration has been found for the diazocyanides (*J.*, 1938, 633, 1796, 1878). These cases are of interest in the present instance, since we believe their geometrical isomerism to be established, and since they possibly have in common a non-planar configuration for their less stable isomers (see p. 426).

For the diazocyanides, Stephenson and Waters (*J.*, 1939, 1796) and others (cf. *Chem. and Ind.*, 1948, 158, 432, 732, 782) have concluded that (i) stable diazocyanides are converted photochemically and reversibly into their labile forms; (ii) unstable diazocyanides in alcoholic solution are in tautomeric equilibrium with diazonium cyanides—since silver cyanide is rapidly precipitated with silver nitrate—and (iii) that neutral solutions of the labile varieties give self-coupling products, consequent upon apparent hydrolyses during which hydrogen cyanide is liberated. It is obvious that, if a similar reversible photochemical change can be shown for the diazosulphonates, the case for the analogy between the two types of isomers will be strengthened.

As to (i), during the course of the present experiments, indications were obtained that the process investigated by Desai *et al.* is in fact reversible, with the reservation (cf. iii, below) that complications are introduced by the great decomposability of the labile isomers; and as to (ii), aqueous solutions of the unstable diazosulphonates with silver nitrate do give precipitates of silver sulphite.
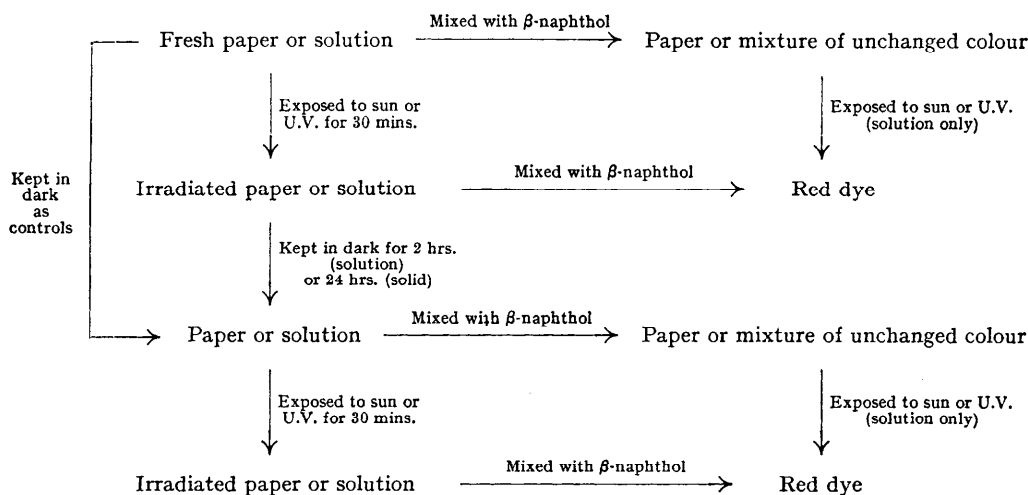
Thus, naphthol coupling being used to show the presence or absence of a labile isomer in solution, a solution of potassium or sodium *o*-chlorobenzene-*anti*-diazosulphonate—which initially did not react with alkaline β-naphthol—was divided, part being kept in the dark for reference. On exposure to sunlight or ultra-violet light for 15—30 minutes, the diazosulphonate solution gave a distinct red colour with the naphthol. A sample of the irradiated solution not

used for the coupling, if left in the dark for some hours, gradually lost its power to couple. On re-irradiation, coupling products could again be obtained; and so on.

Similarly, in repetition of the work of Desai and his co-workers, the diazosulphonate and naphthol solutions were mixed before irradiation, and the precipitation, after 10—15 minutes, of a red dye was observed. Simultaneously with all these experiments, control tests were conducted with solutions in darkened test-tubes; in no case was coupling observed with an unirradiated solution, while it could always be observed after exposure to light.

A parallel series of tests was conducted with the solid *anti*-diazosulphonate : filter-papers were soaked in a solution of *anti*-salt, and dried in an oven. The test for *syn*-isomer was performed by placing a drop of alkaline β-naphthol solution on the paper. In the case of papers which had not been exposed to strong light, or which had lain in a dark place for some hours, no red coloration was obtained. Papers exposed to sun or ultra-violet light gave a strong red colour. In this case, too, blanks were run, *e.g.*, half of each paper was masked with black paper during the irradiation, and tested with naphthol at the same time as the irradiated half. Reversibility of the reaction was shown as in the case of the solution experiments, the only apparent difference between the solid and the solution reactions being the comparative slowness of recovery of the former—24 hours was the order of magnitude of the time required for an irradiated paper to lose its coupling ability, compared with 2 hours for the solution.

These observations may be summarised as below :

```
                              Mixed with β-naphthol
    ┌─── Fresh paper or solution  ───────────────────────→  Paper or mixture of unchanged colour
    │                    │                                               │
    │                    │ Exposed to sun or                            │ Exposed to sun or U.V.
    │                    │ U.V. for 30 mins.                            │ (solution only)
    │                    ↓                                               ↓
Kept in                                    Mixed with β-naphthol
dark       Irradiated paper or solution  ────────────────────────→   Red dye
as
controls                │
                        │ Kept in dark for 2 hrs.
                        │ (solution)
                        │ or 24 hrs. (solid)
                        ↓
                                          Mixed with β-naphthol
    └───→ Paper or solution  ──────────────────────────→  Paper or mixture of unchanged colour
                        │                                               │
                        │ Exposed to sun or                            │ Exposed to sun or U.V.
                        │ U.V. for 30 mins.                            │ (solution only)
                        ↓                                               ↓
                                          Mixed with β-naphthol
       Irradiated paper or solution  ──────────────────────→   Red dye
```

The various attempts to find measurable differences in properties between the isomeric diazosulphonates were accompanied by parallel measurements on irradiated solutions of the *anti*-isomer. The details of these attempts, which were largely unsuccessful, are given on p. 423. At this stage the most relevant measurements were those of the pH of solutions before and after irradiation.
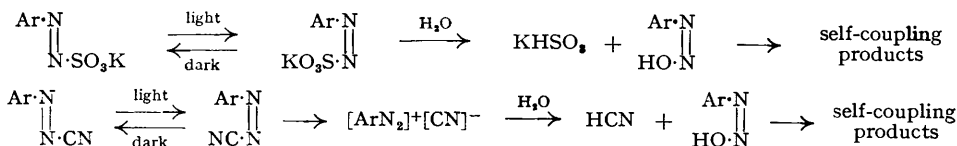
Desai *et al.* (*loc. cit.*) carried out the first measurements of pH of irradiated solutions, and found the pH to fall during irradiation; *e.g.*, a M/200-solution of *o*-chlorobenzene-*anti*-diazosulphonate of original pH $6 \cdot 02$ assumed a nearly constant pH of $2 \cdot 5$ after 90 minutes' irradiation by sunlight. This change was attributed to hydrolytic dissociation of the *syn*-compound. Although we have verified these results, the above explanation cannot be accepted; for, as reported on p. 423, the fresh *syn*-compound did not show a correspondingly lower pH than the pure *anti*-compound, the pH of an isomerising solution remaining approximately constant.

The following is a typical set of our observations : the pH of a solution of *o*-chlorobenzene-*anti*-diazosulphonate, measured before and after irradiation, showed a decrease in pH; after the cessation of illumination, however, a return to the original pH did not occur; instead, the pH decreased further for a certain period of time, until it finally became constant. On further irradiation another decrease in pH was observed.

At the same time, a smell of sulphur dioxide was noticed during and after every irradiation. These two facts—the fall in pH and liberation of sulphur dioxide—seem most easily explained along the lines proposed by Stephenson and Waters (*loc. cit.*) for the diazocyanides, with the exception that—since a form $[RN_2]^+[SO_3K]^-$ is unlikely—no analogue of the diazonium cyanide

intervenes as such, but the alkali sulphonate proceeds to suffer irreversible hydrolysis of the type which Raschig's potassium hydrazinodisulphonate (prepared from chlorosulphonic acid, pyridine, and hydrazine sulphate) underwent when treated with alkali-lye : $N_2H_2(SO_2 \cdot OK)_2 + 2KOH \longrightarrow$ $N_2 + 2K_2SO_3 + 2H_2O$. It is notable that, in this case, Raschig obtained no nitrogen or sulphite at ice temperatures, when—he suggested—dihydroxyhydrazine was present as an unstable intermediate (for references, see Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., 1928, VIII, pp. 682, 683).

We therefore propose the following scheme, written for comparison above that of Stephenson and Waters for the diazocyanides :—

$$
\begin{array}{c}
\underset{N \cdot SO_3K}{\overset{Ar \cdot N}{\|}}
\quad \underset{dark}{\overset{light}{\rightleftarrows}} \quad
\underset{KO_3S \cdot N}{\overset{Ar \cdot N}{\|}}
\quad \overset{H_2O}{\longrightarrow} \quad
KHSO_3 + \underset{HO \cdot N}{\overset{Ar \cdot N}{\|}}
\quad \longrightarrow \quad
\begin{array}{c}\text{self-coupling}\\\text{products}\end{array}
\end{array}
$$

$$
\begin{array}{c}
\underset{N \cdot CN}{\overset{Ar \cdot N}{\|}}
\quad \underset{dark}{\overset{light}{\rightleftarrows}} \quad
\underset{NC \cdot N}{\overset{Ar \cdot N}{\|}}
\quad \longrightarrow \quad
[ArN_2]^+[CN]^-
\quad \overset{H_2O}{\longrightarrow} \quad
HCN + \underset{HO \cdot N}{\overset{Ar \cdot N}{\|}}
\quad \longrightarrow \quad
\begin{array}{c}\text{self-coupling}\\\text{products}\end{array}
\end{array}
$$

In this way the fall in pH during illumination appears to be due to the decomposition following hydrolytic dissociation.

Further, the steady decomposition of the *syn*-isomer in photo-equilibrium with the stable form is implicit in the results of Desai *et al.*, who found that the proportion of *syn*-isomer in a continuously illuminated solution reached a maximum, then decreased. It appears that the proportion of *syn*- relative to *anti*- may not have changed, but that the total quantity of
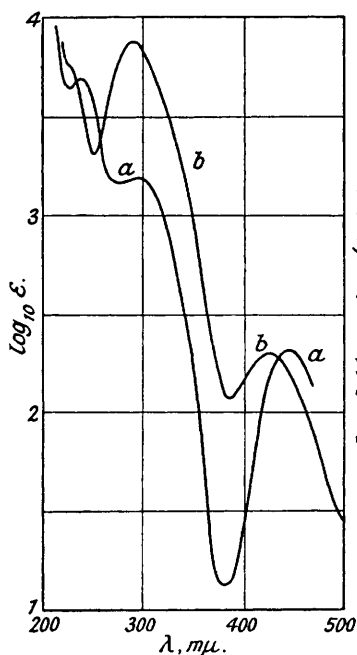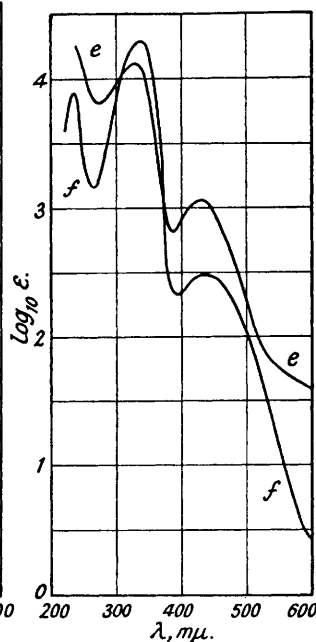
FIG. 1. FIG. 2. FIG. 3.

(undecomposed) diazosulphonate may have decreased. Only by having the naphthol present in the solution during irradiation were the Indian authors able to obtain a steady increase in the amount of azo-compound precipitated ; this experiment, however, involved continuous removal of the *syn*-isomer as it was formed.

As an adjunct to the general investigation of these photochemical reactions, the behaviour of the free *o*-chlorobenzenediazosulphonic acid was examined. This substance, in aqueous solution, decomposed at once on being irradiated, and no evidence of a second isomer could be obtained. It is mentioned here because the evolution of sulphur dioxide during its decomposition parallels the same process in the decomposition of the labile sodium salt.

(c) *Ultra-violet and Visible Absorption Spectra.*—Hodgson *et al.* have attacked the spectroscopic evidence produced by Dobbie and Tinkler (*J.*, 1905, **87**, 273) and Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) from both the technical and the theoretical points of view. In particular, they consider it unreliable because the solutions used for the absorption spectra of the labile diazosulphonates were not tested at the end of the measurements to prove that transformation of the *anti*-diazosulphonates had not taken place. From our own experience we admit at once that Hantzsch's spectrum of, *e.g.*, what he thought was *o*-chlorobenzene-*syn*-diazosulphonate must have been that of a mixture of the two isomers. Accordingly, it seemed desirable that any re-examination of the diazosulphonate question should include a repetition of the spectroscopic work.

The absorptions of *o*-chlorobenzene-*syn*- and -*anti*-diazosulphonates were therefore recorded, by means of a Beckman Photoelectric Spectrophotometer, model DU. They are shown diagrammatically in Fig. 1, curves *a* and *b*, respectively. In keeping with Hodgson's suggestions, two precautions were taken. To prevent or, at least, to minimise the isomerisation during the process of spectroscopic examination, the freshly precipitated *syn*-diazosulphonate was dissolved (after brief but thorough drying on a porous tile) in distilled water at 0°. The solution was kept in an ice-bath, and for each point on the absorption curve the spectrophotometer cell was filled with fresh solution from the bulk. The process of filling the cell, replacing it in the instrument, and taking the reading took about 30 seconds. To confirm that the spectrum obtained was indeed that of the labile isomer, reference was made to naphthol-coupling experiments (see above) with a solution kept under similar conditions.

Although the spectra of the two isomers show quite clearly that the compounds are different, yet they show equally clearly the similarity to which Hodgson has taken exception. In Fig. 2, curves *c* and *d*, Hantzsch and Lifschitz's spectra have been redrawn on a similar scale to those of Fig. 1. Comparison of the two figures indicates the inherent correctness of the earlier curve for the *anti*-isomeride; curve *c* is in agreement with a spectrum (not shown here) of the *syn*-solution used for Fig. 1 after it had been kept for one hour at 2—5°.

If the spectra of Fig. 1 are further compared with the absorption spectra of isomers whose geometrical isomerism is highly probable, the general similarity throughout becomes apparent. As an example, the spectra of the two *p*-chlorobenzenediazocyanides are reproduced (Fig. 3) from Le Fèvre and Wilson (*J.*, 1949, 1106). Other compounds, whose geometrical isomers show absorption curves reminiscent of Figs. 1—3, include azobenzene (*J.*, 1938, 431; 1939, 1316), stilbene (*Z. physikal. Chem.*, 1931, *A*, **155**, 353) and (in some respects) the oximes (*J.*, 1933, 1037).

The feature of these pairs of spectra which is most striking is that in each case the isomers absorb at roughly the same wave-lengths but with different intensities. This is evident from the following summary :

Absorption * of :

Compound.	Solvent.	cis-.	trans-.	Ref.
Azobenzene	C₆H₆	430 (3·1), *ca.* 300 (3·6)	450 (2·7), 330 (4·3)	*J.*, 1938, 431.
	CHCl₃	438 (3·1), 324 (4·2)	445 (2·5), 319 (4·3)	*J.*, 1939, 1316.
Stilbene	C₆H₆	280 (3·5), *ca.* 220 (3·7)	264 (3·8), 226 (3·5)	*Z. physikal. Chem.*, 1931, *A*, **155**, 353.
p-Chlorobenzene-diazocyanide	Et₂O	432 (3·1), 330 (4·1)	438 (2·5), 338 (4·3)	*J.*, 1949, 1106.
o-Chlorobenzene-diazosulphonate	H₂O	448 (2·3), 300 (3·2), 238 (3·7)	428 (2·3), 292 (3·9), 228 (3·8)	

* λ_{max} in mμ., and $\log_{10} \varepsilon_{max}$. (in parentheses).

With the information just recorded we were able to obtain more evidence concerning the nature of the photochemical process discussed in Section (*b*) above. Owing to the lability of the irradiation product, an accurate determination of the spectrum after illumination was not made, since it was thought that what was required was an indication of the *changes* caused by irradiation. Accordingly, the solutions of *anti*-isomer were irradiated for varying periods, and after each the spectrum was quickly scanned (observations of the absorption curves were made at 50 or 100 mμ. intervals, the solutions were briefly re-illuminated, and another set of observations was made, starting at the opposite end of the absorption curves).

The curves in Fig. 4 were obtained by examining a solution (M/5000) of the *anti*-isomer of *o*-chlorobenzenediazosulphonate after 10 (curve *b*), 20 (curve *c*), and 45 (curve *d*) minutes' irradiation at 50 cm. from a mercury-vapour lamp. The solution was the same as that used for the curves in Fig. 1, and the absorption curve of the unirradiated solution is represented in Fig. 4 by curve *a* (broken line). The following comments can be made :

Curve b. Irradiation for 10 minutes has caused a change of absorption in the direction to be expected for a conversion of the *anti-* into the *syn*-isomer (cf. curve *a*, Fig. 1). The absorption at 290 mμ. has decreased in extinction value, while the extinction at 250 mμ. has shown an increase.

Curve c. After 20 minutes, there has been a reversal of the trend at 250 mμ.—the extinction has returned almost to its original value—while the band at 290 mμ. has widened considerably; a new band appears at 275 mμ., and the 300 mμ. band of the *syn*-diazosulphonate spectrum is evident.

Curve d. After 45 minutes, the original spectrum has disappeared; one band only is apparent (the band at 420 mμ. having also disappeared, although not shown in this figure).

Observations on the re-conversion of the *syn-* into the *anti*-isomer were next attempted, each of the above solutions being re-examined after 24 hours, during which they were not exposed to light. As an example of the type of result, Fig. 5 shows the spectrum of a solution exposed for 20 minutes to sunlight (curve *c*); the absorption of the " recovered " solution is shown in curve *f*.

FIG. 4.　　　　　　FIG. 5.
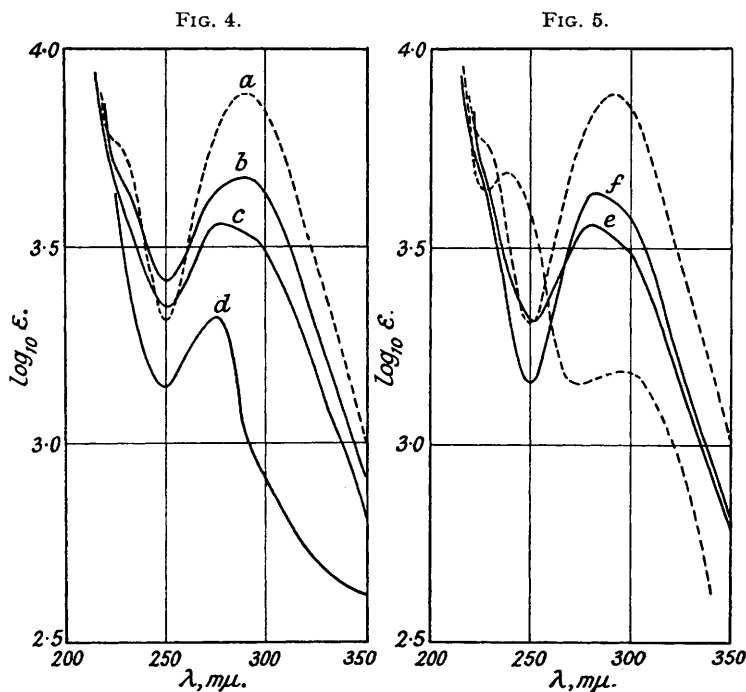
In addition, the absorptions of the *syn-* and the *anti*-isomers have been reproduced (broken lines). The resemblance, except for a slight widening of the main band, between curve *f* and the curve of the *anti*-diazosulphonate is apparent; the lowering of the extinction value, which is approximately uniform along the whole curve, is in agreement with the postulated partial decomposition of the irradiation product. Further, a solution irradiated for 10 minutes showed an even greater recovery of its original properties; while one irradiated for 45 minutes displayed an extremely small tendency towards recovery.

From the spectroscopic evidence, as well as from the known reactions of the labile diazo-sulphonates, it seems not unreasonable to claim that the analogy between the diazocyanides and sulphonates extends beyond spectral details and obvious chemical relationships. In each case the isomers seem not only to be related similarly, but are interconvertible in a fashion common to both; moreover, the labile isomer may undergo hydrolysis and subsequent decomposition. The likelihood of the photo-reaction's being *only* a decomposition—occurring possibly in the surface layer of the solution—seems to be remote, since the spectroscopic evidence shows that *some* return to the original composition does take place.

(*d*) *Miscellaneous Physical Properties of the Isomers.*—The *cis*-isomers both of azobenzene and of the diazocyanides are the denser form (*J.*, 1938, 431; 1939, 531; 1947, 445; 1949, 333).

Since preliminary experiments by naphthol coupling had shown the speed of interconversion of the diazosulphonates to be high, direct density determinations on solutions of the labile and stable salts were not attempted; instead, however, the dilatometric technique found convenient by Le Fèvre and Northcott (*J.*, 1949, 2235) was applied. Although reproducible results were difficult to obtain, the density differences between isomers were evidently small, since no marked change of volume was observed during the spontaneous isomerisations.

Observations of pH were made in the hope that they would either reveal a difference in structure between the isomers or provide a means of following the interconversion rates. Solutions of the separate isomers were not examined, but in order to ensure that the concentrations of the species being compared were equal, measurements were always started on the labile variety, and followed through during the isomerisation process.

Solutions of about 1% concentration and a Leeds and Northrup pH meter being used, no significant changes in pH were noted during the isomerisation (as stated above however, a fully isomerised solution *did* show a distinct fall in pH when irradiated. The cause in these circumstances cannot therefore be the interconversion of the isomers, and our deduction that decomposition as well as interconversion occurs, is supported).

Behind these experiments was the expectation that the degrees of hydrolysis, and therefore the pH's of the solutions of the related sodium salts, would depend on the strengths of their parent acids. Information concerning the relative strengths of sulphurous and sulphonic acids appears to be lacking, although in general sulphonic acids are strong acids, with dissociation constants greater than 10^{-1} (Branch and Calvin " Theory of Organic Chemistry," Prentice-Hall, 1941, Chapter XI). We have been unable to find any measurements for the corresponding sulphurous acids. The relation between the acid strengths of geometrical isomers has, however, received some attention (*op. cit.*). Often a *cis*-carboxylic acid isomer has the greater strength, but this is not unequivocally so, the dissociation constants of the isomers of, *e.g.*, 2-methylbut-1-ene-1-carboxylic acid being approximately equal. We doubt, therefore, whether we should have expected a difference if the diazosulphonates are geometrical isomers. The presumption, however, is that, were one of them a sulphite, this fact would have affected our pH measurement.

In parallel to the tests just mentioned, we have examined the conductivities of isomerising solutions, using the conventional A.C. bridge method (see, *e.g.*, Glasstone, " Introduction to Electrochemistry," Van Nostrand, 1942, 35). No reproducible changes of conductivity were recorded; in some cases a rise occurred, but continued far longer (3·5—4 hours) than the time known to be required for complete isomerisation. Similar increases in conductivity resulted from irradiation of the stable salt in solutions. Since these phenomena were also noted *after* cessation of illumination (occasionally, production of bubbles of gas on the electrodes was seen) they were ascribed to decomposition.

In view of the sensitivity of Blake's radio-frequency conductivity apparatus (*Chem. and Ind.*, 1946, 48; *J. Sci. Instr.*, 1945, **22**, 174; 1947, **24**, 77, 101) several diazosulphonate solutions, as well as some of the free *o*-chlorobenzenediazosulphonic acid, prepared *via* the silver salt, were examined by it, but no clearer indications than by ordinary procedures were obtained.

The above experience left only one possible method (spectrophotometry) with which to study the kinetics of the spontaneous (thermal) interconversions. Absorption measurements against time at a single wave-length of several isomerising solutions were therefore made. In no case were the data obtained compatible with first-order equations—a conclusion in agreement with the findings, *via* the iodine titration technique, of Hantzsch and Schmiedel (*Ber.*, 1897, **30**, 71), and not unexpected if labile diazosulphonates are in fact capable of simultaneous rearrangement and decomposition.

Conclusions.—The following statements may be based upon the above evidence from experiment : (1) The absorption spectra of isomeric diazosulphonates show similarities and differences of the same type and degree as do those of related diazocyanides, azobenzenes, etc. (2) On exposure of the stable diazosulphonates—either as solids or aqueous solutions—to ultra-violet or sun-light, at least partial conversion into the labile form occurs. (3) This interconversion is reversible, the degree of recovery of an irradiated solution towards its original state being reduced by slow decomposition of the labile isomer, the chemical decomposability of which seems to be increased by light. (4) Between aqueous solutions of members of a given pair there are no notable differences of density, pH, or conductivity.

The above points, in general, add to the analogies between diazo-compounds and a number of non-azo-molecules whose geometrical relationship is not in dispute. No instance of a reversible photochemical " sulphonate to sulphite " rearrangement has yet been observed, although the *decomposing* action of light on aqueous diazonium compounds has often been

noticed (cf. De Jonge, Dijkstra, and Braun, *Rec. Trav. Chim.*, 1948, **67**, 328; 1949, **68**, 430, for some recent examples). For these reasons we prefer Hantzsch's configurational explanation to Bamberger and Hodgson's structural one.

Configuration and Reactivity.—We now refer to the differences of reactivity between the pairs of compounds which we consider to be geometrically related. In an earlier paper (*J.*, 1947, 445) similar instances from oxime chemistry were cited. Two other examples that appear relevant are : (*a*) that *cis*-stilbene is decomposed without rearrangement to yield unidentified products, under conditions where the *trans*-isomer is unaffected (Smakula, *Z. physikal. Chem.*, 1934, *B*, **25**, 90; cf. Rollefson and Burton, *op. cit.*, p. 248), and (*b*) that *cis*-azobenzene with 10N-solutions of the three common mineral acids produces an unidentified yellow substance, whereas *trans*-azobenzene does not do so even on exposure to sunlight.

Between stilbene and azobenzene there is a measure of stereochemical analogy. In both cases the molecules can achieve a *cis*-configuration only at the expense of the coplanarity of the aromatic rings and the C=C or N=N systems. In particular, the repulsion between the *o*-hydrogen atoms in the *cis*-arrangement of azobenzene requires the two Ar rings to be twisted out of the C–N=N–C plane by 50°. This distortion (evidence for which has come from Robertson's X-ray data, *J.*, 1939, 232; *Proc. Roy. Soc.*, 1939, **171**, *A*, 398) is responsible for a reduction in the resonance between the central double bonds and the rings, leading immediately to an explanation for the greater potential energy of the *cis*-isomer compared with the *trans*-. Similar conclusions have been reached from considerations of scale drawings in other chemical problems (cf. Sidgwick, *Ann. Reports*, 1932, **29**, 64; Calderbank and Le Fèvre, *J.*, 1949, 1462).

<div align="center">

FIG. 6.

*Benzene-*syn-*diazosulphonate.*

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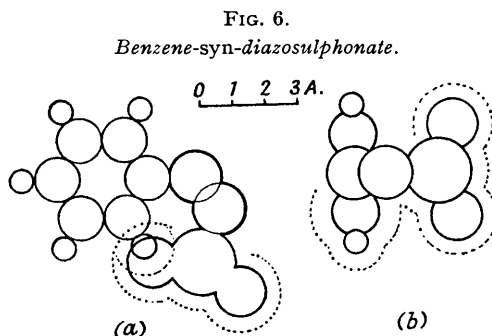
Figs. 6(*a*) and (*b*) represent the *cis*-configuration of the molecule $C_6H_5 \cdot N \colon N \cdot SO_3K$. It has been assumed that (1) the N=N–S system is coplanar with the benzene ring, and that (2) the SO_3 group is tetrahedral (Pauling, " Nature of the Chemical Bond," Cornell, 1942, 240) about the sulphur atom and rotates freely about the N–S axis (the oxygen atoms are shown in the two extreme lateral positions which define the cross-section of the path swept out by the three atoms). The heavy lines represent atomic radii as follows (Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205; Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37) : C(aromatic) = 0·70, H = 0·37, N = 0·70, S = 1·04, O = 0·74 A. The broken lines around some atoms denote Stuart's " Wirkungsradien " (*Z. physikal. Chem.*, 1935, *B*, **27**, 350). The nitrogen valency angles have been taken as 125° for the *cis*-form and 121° for the *anti*-form (from azobenzene). The S–O distance has been taken to be 1·50 A., the value for the distance in the sulphate ion; it has thus almost certainly been underestinated (normal S–O distance = 1·70 A.). In the absence of information regarding the method of fixation of the water molecule essential for the existence of the *syn*-isomer, no account has been taken of water of crystallisation in constructing the diagrams. The argument which follows seems reasonable, no matter what the position of the water molecule in the solid compound; certainly, no doubts arise from this direction as far as properties in solution are concerned.

Fig. 6(*a*) provides an explanation for the instability and reactivity of the labile diazo-sulphonate, assumed as a *syn*-form of the stable *anti*-isomer shown in Fig. 7. It is clear, even without invoking the Wirkungsradien, that steric interference prevents the molecule from assuming the planar structure of Fig. 6(*a*). In Fig. 6(*b*) an end-view of the same molecule [*i.e.*, 6(*a*) seen by looking at it in the plane of the paper from the right edge of the page] has been drawn. The N=N–S system has, however, been turned by 90° about the C–N axis, thus bringing it into a plane perpendicular to the benzene ring. Inspection of this diagram shows the

possibility of the existence of a *syn*-molecule in this state. Measurement of the minimum angle through which the N꞊N–S plane must be turned from the coplanar condition of Fig. 6(*a*) to avoid the steric hindrance yields a result of 70—50°, according to the extent to which the Stuart radii are considered. This angle of minimum distortion is of the same order as that reported by Robertson *et al.* for *cis*-azobenzene.

It is of interest that no steric factors would enter the discussion, if the labile isomer had the *anti*-diazosulphite structure advocated by Bamberger and Hodgson. Purely for the purpose of comparison, one of the possible configurations of the *syn*-diazosulphite is drawn in Fig. 8 (this formula was first mentioned—and rejected on the same grounds as the *anti*-diazosulphite— by Hantzsch). On the basis of Fig. 8 the *syn*-diazosulphite is not impossible on steric grounds. In the configuration shown, smaller repulsive inter-action is indicated ; some of the altern-ative positions of the SO_2 group, obtained by rotation of the $O \cdot SO_2$ about the N–O link, would be accompanied by steric interference with the *o*-hydrogen atom.

Finally, because of the other analogies between the diazosulphonates and diazocyanides, the same metrical process has been applied to the *syn*-isomer of benzenediazocyanide (Fig. 9). The diagram shows the likelihood of repulsion between the –C꞊N group and the *o*-hydrogen atom, leading to probable non-coplanarity of the benzene ring and the N꞊N–CN system. The necessary deviation from the coplanar condition seems to be smaller than for the corresponding sulphonate ; this observation is compatible with the known decreased instability and velocity of isomerisation of the diazocyanides relatively to the sulphonates.

These speculations also lead to a possible reason for the existence of only one of the two

Fig. 7.	Fig. 8.	Fig. 9.
*Benzene-*anti*-diazosulphonate.*	*Benzene-*syn*-diazosulphite.*	*Benzene-*cis*-diazocyanide.*
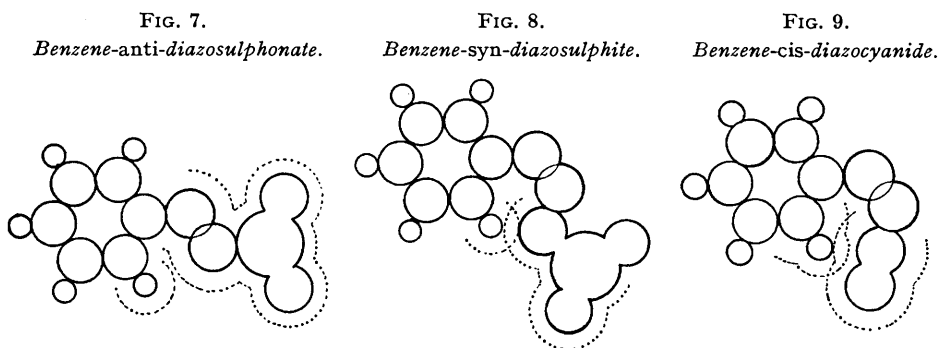
predicted isomers of 2 : 4 : 6-tribromobenzenediazosulphonate. This isomer has the stability of the *anti*-diazosulphonates, together with the coupling ability of the *syn*-isomers. It is not impossible—though it requires experimental proof—that the form which is isolated is an unusually stable *syn*-isomer, whose stability is ascribable to the same causes as the generally increased stability of halogenated diazosulphonates, and whose isomerisation by rotation about the N–N bond is prevented sterically (analogously to the hindered racemisation of some 2 : 2′ : 6 : 6′-substituted diphenyls). It is relevant that the isomerisation of 2 : 4 : 6-tribromo-benzenediazocyanide has an exceptionally low reaction-rate constant (*J.*, 1949, 944).

It can therefore be concluded by purely theoretical considerations that, if the labile isomers of the diazo-sulphonates and -cyanides exist in *syn*-configurations, then their molecules are non-planar. In such distorted species, the conjugation of the –N꞊N– bond with the aromatic ring will be reduced, and instability of the *syn*- relatively to the *anti*-isomers is predictable.

EXPERIMENTAL.

Preparation of Diazosulphonates.—In general, the amine (0·1 g.-mol.) was diazotised in 5N-hydrochloric acid (30 ml.) at 0—5° by sodium nitrite (0·1 g.-mol.). The diazo-solution was stirred into an ice-cold solution of sodium sulphite crystals (0·1 g.-mol.) and sodium carbonate (0·35 g.-mol.) in water (150 ml.). The precipitated *syn*-diazosulphonate was filtered off after being washed with three 10-ml. quantities of iced water. With benzidine, it was found necessary to dissolve the amine in the minimum of alcohol before precipitating the hydrochloride from the hot alcoholic solution. The diazotisation then proceeded smoothly.

Some difficulty was experienced in repeating the preparation of potassium 2 : 4 : 6-tribromobenzenedi-azosulphonate (cf. *Ber.*, 1901, **34**, 3338). Instead of isolating the solid diazonium salt before preparing the diazosulphonate, it was better first to diazotise 2 : 4 : 6-tribromoaniline (0·02 g.-mol.) in 18N-sulphuric acid (25 ml.) by adding a solution of potassium nitrite (0·02 g.-mol.) at 10°, and then to mix the filtered diazo-solution with a cold solution of potassium sulphite (0·02 g.-mol.) and potassium carbonate (0·24 g.-mol.) in water (50 ml.).

In every case, the diazo-solution was treated with a small quantity of urea to remove excess of nitrous acid, and was filtered before addition to the sulphite–carbonate mixture.

The stable diazosulphonates were prepared by warming saturated solutions of the unstable isomers, and were recrystallised from hot water. 2 : 4 : 6-Tribromobenzenediazosulphonate was unchanged by this treatment. Sodium *o*-chlorobenzene-*syn*-diazosulphonate consisted of orange needles, which could be dried on a porous tile and kept in a darkened vacuum desiccator over phosphoric oxide at 0° for 1—2 days (Found, for Na-salt : N, 10·81. After 24 hours : N, 11·00. Calc. for $C_6H_4O_3N_2ClSNa,H_2O$: N, 10·75%). *o*-Chlorobenzene-*anti*-diazosulphonate was obtained in yellow needles (Found : N, 11·5. Calc. for $C_6H_4O_3N_2ClSNa$: N, 11·55%).

Potassium 2 : 4 : 6-tribromobenzenediazosulphonate retained its ability to couple slowly with β-naphthol even after its solution had been boiled (a small amount of brown decomposition product being removed by filtration).

The colours of the five pairs of diazosulphonates prepared for the first time were as follows :

Diazosulphonate.	Unstable form.	Stable form.	Diazosulphonate.	Unstable form.	Stable form.
o-Iodobenzene- ...	Bright orange	Yellow	Diphenyl-2-	Yellow-orange	Yellow
p-Iodobenzene- ...	Brown	Yellow-orange	Diphenyl-4-	Orange	Yellow
Diphenyl-4 : 4-bis-	Bright red	Yellow-orange			

Preparation of o-Chlorobenzenediazosulphonic Acid.—The yellow silver salt was precipitated from a solution of the stable sodium diazosulphonate with silver nitrate; after recrystallisation from hot water, it was treated with the calculated quantity of hydrochloric acid. Filtration of the precipitated silver chloride yielded a yellow solution of the diazosulphonic acid; the solid acid was obtained by slow evaporation of the solution under vacuum. Solutions of this compound decomposed on exposure to strong light.

Experiments on Stability, β-Naphthol Coupling, etc.—The solid sodium or potassium unsubstituted and *p*-nitro-benzenediazosulphonates (*syn*) decomposed within 5—30 minutes of formation. The other *syn*-diazosulphonates could usually be preserved for varying lengths of time on porous tiles, the slow deterioration being evident from a gradual darkening of colour. On some occasions, however, sudden decompositions occurred, with the evolution of heat and fumes, the residue being a dark brown, viscous mass. This type of decomposition was completely unpredictable, but was noted whenever the solid was washed with dehydrating solvents (alcohol–ether) and when mechanical impurities were present. These observations, as also the analyses, are in accord with Hantzsch's statement that the labile isomers decomposed when deprived of their one molecule of water of crystallisation.

For several solid *syn*-compounds (sodium salts), where sudden decomposition did not occur, the relative stabilities were compared by naphthol coupling. The solids, kept on porous tiles in a dark place, were tested occasionally, the formation of a dye with alkaline naphthol being the obvious criterion for the presence of *syn*-isomer. The following were typical periods (in hours), at the end of which the compounds mentioned still showed appreciable naphthol-coupling ability :

o-Chlorobenzene-*syn*-diazosulphonate	48
o- and *p*-Iodobenzene-*syn*-diazosulphonates	72
Diphenyl-4 : 4′-bis-*syn*-diazosulphonate	12
Diphenyl-2- and -4-*syn*-diazosulphonates	6—8

The rates of isomerisation of several sodium diazosulphonates were submitted to a similar qualitative comparison. A 1—2% solution of the *syn*-isomer of each pair was kept at room temperature in a dark place. 1-Ml. portions were removed at 10-minute intervals and mixed with 1 ml. of alkaline 1% β-naphthol solution. When only a faint orange colour was noticed for two consecutive tests, the isomerisation was assumed complete. Typical times for complete isomerisation were :

o-Chlorobenzenediazosulphonate	2·5 hrs. (1% soln.)
o-Iodobenzenediazosulphonate	3 hrs. (1% soln.)
p-Iodobenzenediazosulphonate	0·8 hr. (1% soln.)
Diphenyl-4 : 4′-bisdiazosulphonate	*ca.* 10 mins. (2% soln.)
Diphenyl-2-diazosulphonate	*ca.* 10 mins. (2% soln.)
Diphenyl-4-diazosulphonate	*ca.* 10 mins. (2% soln.)

With sodium *o*-chlorobenzenediazosulphonate, a parallel experiment was conducted, with the solution at 0°. This solution still showed a coupling activity after 3 hours, comparable with its original activity.

Action of Light on Sodium o-Chlorobenzene-anti-diazosulphonate.—(i) *Solution.* A 2% solution in distilled water was prepared from the solid. In each of the following tests, 1 ml. of this solution (A) was ultimately tested with 1 ml. of a solution (B) of 2% β-naphthol and 2% potassium hydroxide in water.

(*a*) Fresh (A) gave an orange colour with (B); the mixture was kept in the dark as standard. (*b*) (A), kept in the dark for 2 hours, gave the same colour with (B) as initially. (*c*) (A), exposed for 30 minutes to sunlight, gave a red colour with (B), the first mixture being used as standard for comparison. (*d*) (A), exposed for 30 minutes to ultra-violet radiation from a quartz mercury-vapour lamp, gave a red colour with (B). (*e*) A mixture of (A) and (B) exposed to sunlight gave a red precipitate within 15 minutes. (*f*) A mixture of (A) and (B) exposed to ultra-violet light gave a red precipitate within 15 minutes. (*g*, *h*) (A), exposed to sunlight or ultra-violet light respectively for 30 minutes, then kept in the dark for some hours, gave the same colour with (B) as unexposed (A). (*i*, *j*) Mixtures of (A) and (B) from (*g* and *h*), exposed to sunlight, gave a red precipitate as in (*e*).

(ii) *Solid.* Six strips of filter-paper were soaked in a fresh 2% solution of *o*-chlorobenzene-*anti*-diazosulphonate, and were dried in the oven at 85°. Each paper in turn was treated by one of the methods shown below, and was then tested by moistening with alkaline 2% β-naphthol solution, (B). (*a*) Freshly-dried paper : no colour with (B). (*b*) Paper kept in the dark for 2 hours : no colour with (B). (*c*) Paper exposed to sunlight for 30 minutes : bright orange colour with (B). (*d*) Paper exposed to ultra-violet light for 30 minutes : bright orange colour with (B). (*e*, *f*) Papers exposed to sunlight and ultra-violet light respectively for 30 minutes : small pieces when tested gave a colour with (B). Papers then kept dark for 12 hours still gave a faint orange colour with (B). After 24 hours, no colour was observed. (*g*, *h*) Pieces of the papers from (*e*) and (*f*), which had not been tested with (B), were re-exposed to sunlight for 30 minutes and then gave a bright colour with (B).

The solution-tests were also carried out with the iodobenzenediazosulphonates, with identical results.

Spectroscopic Examination.—Spectra were recorded by means of a Beckman Photoelectric Quartz Spectrophotometer, Model DU. In all cases, M/5000-solutions were prepared by suitable dilutions of more concentrated initial solutions; so as to minimise errors due to differences in concentration from one solution to another, a single solution was used throughout one complete set of absorption curves.

A solution of freshly precipitated sodium *o*-chlorobenzene-*syn*-diazosulphonate, which had been dried for about 5 minutes by thorough grinding on a porous tile, was prepared in distilled water at 0°. This solution was kept in an ice–salt bath, and the spectrum of the *syn*-isomer was recorded : for each wave-length of observation, the cell was re-filled with fresh solution from the bulk. On completion of the readings, a repetition of some of the early readings showed only an insignificant change. During *ca.* 1·25 hours, however, significant isomerisation had taken place.

After 20 hours at room temperature in the dark, the solution was re-examined, and an absorption curve for the *anti*-diazosulphonate was obtained. This coincided within very small limits with a separate curve obtained from a solution of recrystallised *anti*-isomer.

The absorption curves of the various irradiated solutions were obtained with less rigorous precautions against isomerisation than were used in the case of the *syn*-diazosulphonate. Readings were taken at 100-mμ. intervals, and after every 2 or 3 readings, the bulk of the solution was re-irradiated for 15 seconds before the cell was re-filled. Here again the method was justified by the results, a check at the first wave-lengths recorded revealing small changes at the end of the observations; the absorption curves of irradiated solution were not meant to be recorded in detail, generalities being sufficient to support the theory advanced. The solution used for irradiation was the one obtained by isomerisation of the solution used for the *syn*-absorption curve.

An exploratory experiment was conducted, in which the optical density ($D = \log I_0/I$) at 286 mμ. was plotted against time, for a solution " recovering " after irradiation. Temperature control was not attempted, and the concentrations calculated from the readings did not correspond to those for first-order kinetics. With regard to irradiated solutions, no matter how short the period of illumination—15 seconds was the minimum time used—the solution never returned to its original absorption.

The absorption curves above 400 mμ. were also obtained from solutions examined on a Hardy General Electric Recording Spectrophotometer (at the National Standards Laboratory, C.S.I.R.O., Sydney); the extinctions recorded for *syn*- and *anti*-diazosulphonates and an irradiated solution were higher than those obtained with the Beckman instrument, but were similarly related.

Absorptiometric Examination of Thermal syn- *to* anti-*Change of Sodium* o-*Chlorobenzene Derivatives.*—A 0·001M-solution of freshly precipitated and tile-dried sodium *o*-chlorobenzene-*syn*-diazosulphonate in distilled water was kept in a thermostat at 20°; the water in the latter was dyed red to prevent stray photochemical effects. Samples were taken at 3—5-minute intervals, and their absorptions measured at once with a Hilger Spekker Photoelectric Absorptiometer, model H454. Water was found to be a suitable reference liquid. The solutions were examined in a 1-cm. cell, a Wood's glass filter and mercury-vapour lamp being used to isolate the 3560·1 A. line. The instrument had previously been calibrated with the *anti*-diazosulphonate, giving, with this salt, a linear plot of concentration against scale-reading for the light used. A similar relation had to be assumed for the *syn*-isomer. The results could not be reconciled with first-order kinetics. The first-order velocity constants (*k*) calculated are shown below. A check was made to ensure that exposure of the solution to the ultra-violet light of the instrument for the duration of a reading had no effect on the result.

t (mins.)	1	4	7	10	14	17	24·5
k_{20} (mins.$^{-1}$)	0·787	0·822	0·833	0·648	0·528	0·533	0·518
t (mins.)	29	33·5	39	45	62	81	106
k_{20} (mins.$^{-1}$)	0·438	0·398	0·342	0·337	0·297	0·282	0·343

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