# **127.**—*Evidence for the Sulphite and Sulphonate Structures of Hantzsch's Potassium Benzene*-syn- *and* -anti-*diazosulphonates.*

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Hantzsch's potassium benzene-*syn*- and -*anti*-diazosulphonates couple with diazotised *p*-nitroaniline, giving products for which his stereochemical formulæ do not account. The *syn*-compound behaves like a sulphite, $R{\cdot}N{:}N{\cdot}O{\cdot}SO_2K$, but the *anti*-compound is best represented as a sulphonate, $R{\cdot}N{:}N{\cdot}SO_3K$. Hantzsch's potassium benzene-*syn*-diazosulphonate is a mixture of his so-called *syn*- and *anti*-isomerides, wherein the *syn*- is rapidly converted into the *anti*-form, behaviour which accounts for the identity of his spectroscopic and conductometric data. The *syn*-(sulphite) forms of potassium and sodium *p*-nitrobenzenediazosulphonates have been prepared.

In his discussion of Hantzsch's theory of the constitution of the diazo-compounds Saunders states ("The Aromatic Diazo-Compounds and their Technical Applications," London, **1936**, p. 188) that, if the theory is correct, it follows that every diazo-compound can exist in three isomeric forms, *viz.*, diazonium, *syn*- and *anti*-diazotates. Hantzsch was not able to cite any cases to prove his theory conclusively, but he sought chief support from three classes of compounds, *viz.*, the diazocyanides, the diazobenzenesulphonic acids, and the diazo-sulphonates. $Ar{\cdot}N{:}N{\cdot}SO_3K$. Evidence is now presented which proves that Hantzsch's stereochemical conception of *syn*- and *anti*-diazosulphonates is fundamentally wrong.

The diazosulphonates are known only in the two modifications of *syn*- and *anti*-forms, Saunders stating (*op. cit.*, p. 190) that no substance having the properties to be expected of a diazonium salt of sulphurous acid has been discovered to complete the family of isomers. In this respect, the stabilised compounds of diazonium salts with naphthalene- and other sulphonic acids must be either diazonium sulphites or diazo-sulphites, the colourless members probably having the former constitution. The following facts were the basis for Hantzsch's assertion that the two modifications above were stereoisomers: (1) The more deeply coloured *syn*-isomer had the power to couple with β-naphthol, and on standing in solution changed into the stable form, which did not couple and must therefore belong to the series usually termed *anti*. (2) Conductometric determinations showed the salts of both series to dissociate in solution into two ions, the *syn*-salt in addition giving evidence of hydrolytic dissociation. (3) A similarity of absorption spectra.

Bamberger (*Ber.*, 1894, **27**, 2586, 2930) suggested that the properties of the diazosulphonates, *viz.*, oxidation by iodine, coupling power, and decomposition by acids with liberation of sulphur dioxide, could just as well be explained by the sulphite formula $Ph{\cdot}N{:}N{\cdot}O{\cdot}SO_2K$, whereas the *anti*-diazosulphonates, which were non-reactive with iodine and did not couple, could be assigned the sulphonate formula, $Ph{\cdot}N{:}N{\cdot}SO_3K$, *i.e.*, with the azo-nitrogen attached to the sulphur atom. Claus (*J. pr. Chem.*, 1894, **50**, 239) reached the same conclusion, assuming normal potassium sulphite to be $KO{\cdot}SO_2K$. Saunders (*op. cit.*, p. 195) observes that the only unchallenged item is the spectroscopic evidence, which is in favour of Hantzsch. The alternative suggested by Blomstrand and Bamberger, that the normal *syn*-diazosulphonates were diazonium compounds $Ar{\cdot}\overset{\oplus}{N}{:}N\}\overset{\ominus}{S}\overset{\ominus}{O}_3\overset{\oplus}{K}$, was discounted by Hantzsch on the grounds that they should give three ions in aqueous solution (whereas only two were found) and that the solution should be colourless or nearly so, in conformity with the colours of benzenediazonium salts generally, whereas they are red. It has now been found that the *syn*-form cannot be obtained pure but is always mixed with the *anti*-isomeride, into which it passes rapidly; the spectroscopic evidence of identity of form therefore receives an obvious explanation.

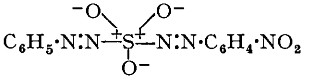
*The Coupling of Diazotised* p-*Nitroaniline with Potassium Benzene*-anti-*diazosulphonate*.—On Hantzsch's assumption that the potassium salt has the N–S link, the product formed by coupling with diazotised *p*-nitroaniline must have formula I*a* or *b*:

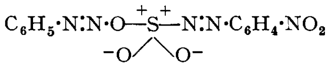
(I*a*.) $C_6H_5{\cdot}N{:}N{\cdot}SO_2{\cdot}O{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$ $C_6H_5{\cdot}N{:}N{\cdot}S\overset{\ominus}{O}_3\}\overset{\oplus}{N}_2{\cdot}C_6H_4{\cdot}NO_2$ (I*b*.)

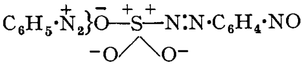
This compound, which is readily formed and sufficiently stable when moist at 0° for subsequent reaction, couples readily with β-naphthol to give *p*-nitrobenzeneazo-β-naphthol, leaving benzene-*anti*-diazoniumsulphonate in solution, from which it may be recovered intact or, after oxidation, as a diazonium salt, which then couples with β-naphthol to give benzeneazo-β-naphthol. It follows, therefore, that the N–S link of the original *anti*-structure remains intact during the coupling reaction.

*The Composite Character of Potassium Benzene*-syn-*diazosulphonate*.—The *syn*-salt made according to the directions of Hantzsch (*loc. cit.*) is of variable composition and cannot be obtained free from the *anti*-isomeride. Washing with water, or even keeping in a moist state on the filter, rapidly brings about conversion of the *syn*- into the *anti*-form, as shown by change of colour from orange-red to yellow and deterioration in coupling power with alkaline β-naphthol (Bamberger, *Ber.*, 1894, **27**, 2930, records that analyses of the *syn*-compounds are rendered untrustworthy by rapid decomposition and molecular change). Moreover, Hantzsch's observation that the *syn*-compound reacts with copper sulphate with evolution of nitrogen is in accord with the sulphite formula, since conversion into benzenediazonium sulphate will be brought about and followed by decomposition by the cuprous salt thereby produced; on the other hand, copper sulphate only produces a green coloration with the *anti*-isomeride.

*The Coupling of Diazotised* p-*Nitroaniline with Potassium Benzene*-syn-*diazosulphonate*.—When the mixture which has been termed the *syn*-compound is coupled with diazotised *p*-nitroaniline, a precipitate (A) is formed which couples with alkaline β-naphthol to form a mixture (B) of benzeneazo-β-naphthol and *p*-nitrobenzeneazo-β-naphthol, since on reduction (B) yields both aniline and *p*-phenylenediamine (identified by conversion into *p*-benzoquinone). The so-called *syn*-compound is therefore a mixture. Again, oxidation of the filtrate from (B) affords a mixture (C) of benzeneazo-β-naphthol and *p*-nitrobenzeneazo-β-naphthol, derived from the so-called *anti*- and *syn*-isomerides respectively in the original mixture. These experiments also show that in the so-called *syn*-compound the diazotised *p*-nitroaniline combines at the sulphur atom to form an N–S link and does not form a diazonium salt, otherwise the whole of the *p*-nitrobenzeneazo-component in mixture (A) would have been combined with β-naphthol in mixture (B), and (C) would have consisted of benzeneazo-β-naphthol only. If the *syn*-salt had the Hantzsch formula, the product with diazotised *p*-nitroaniline would be formulated as in (II), which is not possible on modern electronic theory. The formula of the product of the *syn*-compound with diazotised *p*-nitroaniline is therefore best represented by (III*a*); (III*b*), however, is not excluded. In either event the Hantzsch *syn*-structure with its N–S link is impossible, and the sulphite structure, which explains the experimental facts, must be preferred.


(II.)

(III*a*.)



(III*b*.)

*Formation of the Potassium* (*or Sodium*) p-*Nitrobenzene*-syn-*diazosulphonate*.—Hantzsch and Borghaus (*Ber.*, 1897, **30**, 89) state that the stable *anti*-form only is given by the nitrodiazobenzenes, but it has now been found that, when neutral *p*-nitrobenzenediazonium chloride is treated with potassium or sodium sulphite, a labile compound is formed which couples with alkaline β-naphthol, is oxidised by iodine, liberates sulphur dioxide with mineral acids, and couples with diazotised *p*-nitroaniline to form a complex which in turn couples with alkaline β-naphthol to form *p*-nitrobenzeneazo-β-naphthol in amount equivalent to half the total *p*-nitroaniline involved. The filtrate therefrom, when oxidised, affords *p*-nitrobenzeneazo-β-naphthol in amount corresponding to the other half of the *p*-nitroaniline. The labile compound, therefore, is analogous to the so-called *syn*-diazosulphonate from aniline.

Finally, potassium *p*-nitrobenzene-*anti*-diazosulphonate couples with diazotised aniline to form a complex, which reacts with alkaline β-naphthol to form only benzeneazo-β-naphthol, and the filtrate therefrom is oxidised to give *p*-nitrobenzeneazo-β-naphthol only, the exclusive results indicating that the initial *anti*-structure has been preserved in the complex.

*Conclusions*.—(1) Hantzsch's *syn*-formula for potassium benzene-*syn*-diazosulphonate cannot be correct, since the sulphur atom cannot be covalently attached to both diazo-groups in the various complexes described. (2) A sulphite formula correctly accounts for all the reactions, and this may be either $C_6H_5\cdot N{:}N\cdot O\cdot SO_2K$ or $C_6H_5\cdot\overset{+}{N}_2\}\overset{-}{O}\cdot SO_2K$ or an equilibrium mixture of both. (3) The *anti*-formula of Hantzsch is valid, and is in accord with the general behaviour of sulphonates. (4) The ready transformation in aqueous solution of the *syn*- into the *anti*-form is accounted for on the sulphite–sulphonate formulation by facile fission of the N–O link (as shown by coupling), which is favoured by the greater stability of quadricovalent sulphur (cf. the stable ·N:N·S· group in the diazo-sulphides with the far less stable ·N:N·O· group in those diazo-oxides whose constitution is beyond doubt) (cf. also recent work by Kenyon *et al.* on analogous isomerisations of sulphinic esters to sulphones). (5) The original view of Bamberger and Claus is more reasonable than that of Hantzsch in the light of modern chemical theory; *e.g.*, it is improbable that stereoisomeric structures in the *syn*-form contain an N–S link so unstable that fission occurs in the presence of alkaline phenols or naphthols, or even with the latter in the presence of sodium acetate, whereas in the *anti*-configuration this N–S link resists such rupture. (6) The colour of the sulphite (*syn*-compound) is in favour of a covalent N–O link. (7) The complexes prepared from both the *syn*- and the *anti*-isomerides by coupling with diazotised amine probably contain both structures. They are all very unstable with the exception of the one from potassium benzene-*anti*-diazosulphonate and diazotised *p*-nitroaniline, which may be dried at room temperature.

## EXPERIMENTAL.

*The Coupling of Diazotised* p-*Nitroaniline with Potassium Benzene*-anti-*diazosulphonate*.—The *anti*-compound, prepared from aniline (9·3 g.) according to the directions of Hantzsch (*loc. cit.*), was salted out with brine and air-dried; it did not couple with alkaline *β*-naphthol. It was dissolved in water (200 c.c.), the solution filtered, and ice (50 g.) added, followed by a solution of *p*-nitrobenzenediazonium chloride (from 13·8 g. of *p*-nitroaniline) which had been neutralised with calcium carbonate. The yellow crystalline precipitate formed was collected, washed with ice-water (1500 c.c.) until free from diazonium salt, and stirred into *β*-naphthol (20 g.) dissolved in a slight excess of sodium hydroxide solution; the *p*-nitrobenzeneazo-*β*-naphthol formed had m. p. 237°, and 250° after recrystallisation from acetic acid. The remaining solution on air oxidation (slowly, or more rapidly by bubbling), or on addition of potassium chromate, or on neutralisation with dilute nitric acid, addition of alcohol to dissolve precipitated *β*-naphthol and then of lead nitrate, gave benzeneazo-*β*-naphthol, m. p. 125°, and m. p. 131° after recrystallisation.

*Reactions of Potassium Benzene*-syn-*diazosulphonate*.—(a) *With β-naphthol.* The unfiltered mixture of *syn*- and *anti*-compounds prepared according to the directions of Hantzsch (*loc. cit.*) from aniline (4·65 g.) was immediately treated with excess of alkaline *β*-naphthol, benzeneazo-*β*-naphthol (9·6 g.) being precipitated in amount corresponding to a ratio of 77·5% of *syn*- and 22·5% of *anti*-compound. A delay of only 15 minutes between preparation and coupling caused a decrease in the amount of *syn*-compound to 33%.

(b) *The composite character of Hantzsch's* syn-*compound.* The orange-red *syn*-potassium salt, removed as rapidly as possible after formation, was thoroughly pressed (but not washed, since this only served to convert the *syn*- into the *anti*-form), and then coupled with alkaline $\beta$-naphthol. The precipitate of benzeneazo-$\beta$-naphthol was removed, and the filtrate oxidised as above; a further precipitate of benzeneazo-$\beta$-naphthol was then obtained derived from the *anti*-isomeride present in the initial orange-red crystals. However rapid the manipulation, there was always a substantial amount of *anti*-compound present (78% being a typical amount).

(c) *Coupling of a mixture of sodium benzene*-syn- *and* -anti-*diazosulphonates with diazotised* p-*nitroaniline.* Aniline (9·3 g.) was diazotised at 0° in dilute hydrochloric acid and the solution was neutralised with calcium carbonate, filtered, and added to crystallised sodium sulphite (25·2 g.) in water (50 c.c.); the mixture was kept at 0° for 15 minutes and then added to neutralised *p*-nitrobenzenediazonium chloride (from 13·8 g. of *p*-nitroaniline) in water (250 c.c.). The precipitated orange-yellow crystalline (plates) complex was rapidly washed with ice-water (1500 c.c.) until free from diazonium salt and then coupled with alkaline $\beta$-naphthol. The precipitate of benzeneazo- and *p*-nitrobenzeneazo-$\beta$-naphthol, m. p. 216°, was removed, and the filtrate oxidised as above, a mixture of the same azo-$\beta$-naphthols being obtained, m. p. 170°. Both mixtures, when reduced with zinc dust in boiling aqueous-alcoholic suspension, gave aniline (removed by steam-distillation) and *p*-phenylenediamine (by oxidation of the residual liquor with ferric chloride).

*The Coupling of Diazotised Aniline with Sodium* p-*Nitrobenzene*-anti-*diazosulphonate.*—A mixture at 0° of *p*-nitrobenzenediazonium chloride (from *p*-nitroaniline, 13·8 g.) in the minimum of water (150 c.c.) with a saturated solution of sodium sulphite (25·2 g.) and anhydrous sodium carbonate (6 g.) was kept for 90 minutes; it then no longer coupled with alkaline $\beta$-naphthol. Sodium chloride was added, and the yellow precipitate of sodium *p*-nitrobenzene-*anti*-diazosulphonate collected, washed with brine, dried (*ca.* 50% yield), and redissolved in water (150 c.c.), and the solution filtered and treated with neutral benzenediazonium chloride (from 4·65 g. of aniline). The yellowish-brown amorphous precipitate obtained, which was moderately stable when moist at 0°, was washed free from diazotised aniline and coupled with alkaline $\beta$-naphthol. The precipitated benzeneazo-$\beta$-naphthol (m. p. 126°, and 131° after recrystallisation from acetic acid) was removed; the filtrate, when oxidised as above, gave a precipitate of *p*-nitrobenzeneazo-$\beta$-naphthol, m. p. 246°, and 250° after recrystallisation from acetic acid.

*Sodium* p-*Nitrobenzene*-syn-*diazosulphonate coupled with Diazotised Aniline.*—A solution of crystallised sodium sulphite (25·2 g.) was added to one of neutral *p*-nitrobenzenediazonium chloride (from 13·8 g. of *p*-nitroaniline) (total vol., 300 c.c.), and the mixture kept at 0° for 90 minutes, then treated with neutral benzenediazonium chloride (from 9·3 g. of aniline) (vol., 200 c.c.) at 0°. The orange crystalline (plates) precipitate was washed at 0° with ice-water (2 l.) until the filtrate no longer coupled with alkaline $\beta$-naphthol, and then stirred with excess of alkaline $\beta$-naphthol. The mixture of benzeneazo- and *p*-nitrobenzeneazo-$\beta$-naphthols formed (m. p. 162—165°) was removed; the filtrate on oxidation gave a similar precipitate (m. p. 170°). Both precipitates afforded aniline and *p*-phenylenediamine on reduction.

*Sodium* p-*Nitrobenzene*-syn-*diazosulphonate coupled with Diazotised* p-*Nitroaniline.*—This complex, prepared as described above, was obtained as a thick orange-yellow precipitate, which was washed free from the excess of diazotised *p*-nitroaniline. A portion of it was treated with excess of alkaline $\beta$-naphthol; the precipitated *p*-nitrobenzeneazo-$\beta$-naphthol (5·2 g.) had m. p. 246°. From the filtrate, after oxidation, a further precipitate of the same compound was obtained (5·0 g.), m. p. 246°. Both precipitates, crystallised from glacial acetic acid, gave pure *p*-nitrobenzeneazo-$\beta$-naphthol, m. p. 250°.

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