234. *The Isolation of the Hitherto Unknown* anti-*Diazosulphonates in the Naphthalene Series, with Improved Preparations of* 2- *and* 4-*Nitro- and* 4-*Chloro*-1-*naphthylamine.*

By Herbert H. Hodgson and Donald Bailey.

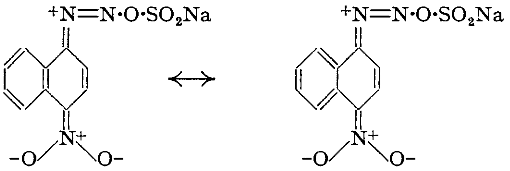
Naphthalene-α- and -β-*anti*-diazosulphonates, which Hantzsch and Schmiedel failed to identify among the reaction products from diazotised α- and β-naphthylamine with alkali sulphites, have now been prepared, and in addition the *anti*-diazosulphonates from 4-nitro- and 4-chloro-1-naphthylamine have also been isolated. The corresponding four *syn*-diazosulphonates, which are really diazo-sulphites, decompose far more rapidly than the benzene analogues, and by a two-way mechanism, to give the corresponding symmetrical azo-compound on the one hand and the *anti*-diazosulphonate on the other. The order of ***instability*** of these naphthalene diazo-sulphites is 4-chloro $>$ α- and β- $>$ 4-nitro-, and can be accounted for on resonance grounds.

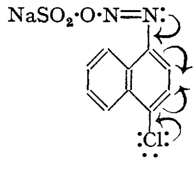
Hantzsch and Schmiedel (*Ber.*, 1897, **30**, 81) first prepared their so-called *syn*-sulphonates in the naphthalene series from α- and β-naphthylamine by the action of alkali sulphites on their diazonium salts. The *anti*-forms were not realised by these authors, because they believed that the *syn*-forms changed completely into 1 : 1′- and 2 : 2′-azonaphthalene respectively. This formation of symmetrical azo- from diazo-compounds was subsequently the subject of a patent by Lange (D.R.-P., 78225) in which the reaction of a diazonium salt with an alkali sulphite was carried out in the presence of acetic acid.

Recently a paper by Hodgson and Marsden (*J.*, 1943, 470) has provided conclusive evidence that Hantzsch's stereochemical conception of *syn*- and *anti*-diazosulphonates in the benzene series was fundamentally wrong, and that the alleged *syn*-geometrical isomerides were actually diazosulphites, whereas the alleged *anti*-forms were the true diazosulphonates. Since Hodgson and Marsden (*loc. cit.*) found that the unstable sulphites (alleged *syn*-forms) could never be obtained pure but were always mixed with their relatively stable *anti*-sulphonate isomerides into which they passed rapidly, it appeared probable that the naphthalene analogues would behave in like manner, and that stable *anti*-diazosulphonates could be prepared in the naphthalene series also.

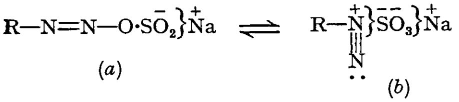
It is now shown that Hantzsch's alleged 1- and 2-naphthalene-*syn*-diazosulphonates experience a very rapid two-way conversion, *viz.*, (1) into the 1 : 1′- and 2 : 2′-azonaphthalene respectively, and (2) into the non-coupling 1- and 2-naphthalenediazosulphonates, so that the anti-*diazosulphonates* which Hantzsch failed to detect are actually found to possess a stable existence. These naphthalene-*anti*-diazosulphonates are red-brown substances, whereas the isomeric covalent sulphites (alleged *syn*-sulphonates) are yellow, and their presence and composition have been established by oxidation with bromine to diazonium salts which then couple with β-naphthol to give the corresponding 1- and 2-naphthaleneazo-β-naphthol. 4-Nitro-1-naphthalenediazonium chloride has also been found to give a more stable diazosulphite than the unsubstituted diazotised naphthylamines above, especially when treated with sodium sulphite in neutral solution, and this sulphite changes much more slowly (3 hours) than the corresponding unsubstituted naphthalenediazosulphites (a few seconds) into a mixture of 4 : 4′-dinitro-1 : 1′-azonaphthalene and *sodium* 4-*nitronaphthalene*-1-*diazosulphonate*. In like manner, 4-chloro-1-naphthylamine gives a mixture of 4 : 4′-dichloro-1 : 1′-azonaphthalene and *sodium* 4-*chloronaphthalene*-1-*diazosulphonate* in neutral solution, the transition from the sulphite being much the most rapid of the four diazonium salts examined.

The sequence of instability of the above four diazosulphites is: 4-chloro- > unsubstituted > 4-nitro-, and an explanation based on resonance is suggested as follows. In the case of 4-nitronaphthalene-1-diazosulphite, the resonance of the nitro-group with the naphthalene nucleus will increase the number of resonance structures (10 for the α-acid, 9 for the β-unsubstituted compounds) to 20, while there will also be the two quinonoid resonance structures, bringing the total to 22. This increase in the number of structures of the 4-nitronaphthalene-1-diazosulphite hybrid over the 1- and 2-naphthalenediazosulphites corresponds to an increase in resonance energy with a consequent increase in stability. In the case of the 4-chloronaphthalene-1-diazosulphite, however, there will still be the 10 structures of the unsubstituted compound, but the resonance effect of the chlorine atom will be opposed to that of the diazo-nitrogen, thereby reducing the contribution of those structures which involve a separation of charge. In consequence, the 4-chloronaphthalene-1-diazosulphite will be less stable than any of the other diazosulphites mentioned.



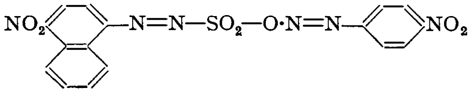


In aqueous solution these diazosulphites (*a*) are probably in equilibrium with their diazonium isomerides (*b*), since Hantzsch and Reddelien (" Die Diazo-Verbindungen ", 1921, p. 50) found that the aryl-*syn*-diazosulphonates afforded ions of the diazonium sulphite in solution, whence the diazo-form (*a*) subsequently isomerises to the *anti*-diazosulphonate (cf. Hodgson and Marsden, *loc. cit.*), and the diazonium form (*b*) decomposes to give the symmetrical azo-compound by the mechanism of Hodgson, Nicholson, and Turner (*J.*, 1944, 15) in which the diazo- and aryl radicals, $R{-}\ddot{N}{=}\ddot{N}\cdot$ and ·R, combine. The naphthalenediazosulphites decompose much more rapidly than their benzene analogues, with the consequence that the main product is the symmetrical azo-compound, whereas in the benzene series the main product is the *anti*-sulphonate. It was this rapidity of transformation to azo-compound that caused Hantzsch and Schmiedel to miss finding the *anti*-diazosulphonates in the decompositions of naphthalene-1- and -2-diazosulphites (*syn*-sulphonates).



$$\mathrm{R{-}N{=}N{-}O{\cdot}\overset{-}{S}O_2\}\overset{+}{Na}} \rightleftharpoons \mathrm{R{-}\underset{\underset{\cdot\cdot}{\overset{|||}{N}}}{\overset{+}{N}}\}\overset{--}{SO_3}\}\overset{+}{Na}}$$

(*a*) (*b*)



Sodium 4-nitronaphthalene-1-*anti*-diazosulphonate readily reacts with diazotised *p*-nitroaniline to form a compound, as with the *anti*-diazosulphonates of the benzene series (cf. Hodgson and Marsden, *loc. cit.*), and this compound on reaction with alkaline β-naphthol gives a precipitate of *p*-nitrobenzeneazo-β-naphthol, leaving sodium naphthalene-1-*anti*-diazosulphonate in solution, from which it may be recovered intact or, after oxidation with bromine, as a diazonium salt which then couples with β-naphthol to give 4-nitronaphthalene-1 : 1′-azo-2′-naphthol. It follows, therefore, that the very stable N–S link of the original anti-structure remains intact during the coupling reaction. The corresponding reaction of diazotised *p*-nitroaniline with the sodium 4-nitronaphthalene-1-diazosulphite (Hantzsch's *syn*-compound), which was carried out as quickly as possible after the addition of sodium sulphite to 4-nitronaphthalene-1-diazonium chloride, afforded a solid which reacted with alkaline β-naphthol to give a mixed precipitate of 4-nitronaphthalene-1 : 1′-azo-2′-naphthol and *p*-nitrobenzeneazo-β-naphthol; the filtrate from this mixture when oxidised with bromine water also coupled with alkaline β-naphthol to give a mixture of the same azo-naphthols. These results, in contrast to the former unique data, indicate that the diazosulphite is changing to the diazosulphonate immediately after formation and in an exactly analogous manner to the phenomena obtained in the benzene series (cf. Hodgson and Marsden, *loc. cit.*).

An improved preparation of 4-chloro-1-naphthylamine, and a modified procedure for the separation of the 2- and 4-nitro-1-naphthylamines from the mixture given by the nitration of aceto-1-naphthalide, are described.

EXPERIMENTAL.

Action of Sodium Sulphite on Diazotised α-Naphthylamine.—A stirred hot solution of α-naphthylamine (3·6 g.) in hydrochloric acid (10 c.c., *d* 1·18) and water (10 c.c.) was chilled to 0°, ice (20 g.) added, and the fine suspension treated as rapidly as possible with one of sodium nitrite (2 g.) in water (10 c.c.), the mixture kept for 10 minutes, filtered, rapidly neutralised to Congo-red with calcium carbonate, and mixed immediately with a solution of crystallised sodium sulphite (6 g.) and sodium carbonate (1 g.) in water (25 c.c.). An orange-yellow precipitate of sodium naphthalene-1-diazosulphite (Hantzsch's *syn*-sulphonate) forthwith separated, and, if filtered off rapidly and washed at 0°, it coupled with alkaline *β*-naphthol to give 1-naphthaleneazo-*β*-naphthol (which gave a deep violet colour with concentrated sulphuric acid). When the mixture, however, continued to be stirred at 0°, it changed in a short time to a red-brown colour with evolution of nitrogen, and the solid portion then no longer reacted with alkaline *β*-naphthol. After the evolution of nitrogen had ceased, the mixture, which had been kept at 0° for *ca.* 10 minutes, was diluted with an equal volume of water and filtered; the precipitate, after being thoroughly washed with water until no more had dissolved, was 1 : 1′-azonaphthalene, and the filtrate, which did not couple with alkaline *β*-naphthol or ethyl-alcoholic *β*-naphthylamine, did so after being made just acid to Congo-red, freed from any excess nitrous acid with urea, and treated with bromine water until a slight excess was present as denoted by starch–potassium iodide paper, to give 1-naphthaleneazo-*β*-naphthol (0·65 g.), which crystallised from glacial acetic acid in red needles, m. p. and mixed m. p. with authentic specimen 229—230° (Meldola and Hanes, *J.*, 1894, **65**, 837, give m. p. 229—230°), and gave a violet colour with concentrated sulphuric acid. The 1 : 1′-azonaphthalene crystallised from glacial acetic acid in red needles, m. p. 198° (Nietzki and Goll, *Ber.*, 1885, **18**, 298, give m. p. 190°). The solution above thus contained, originally, the sodium naphthalene-*anti*-1-diazosulphonate, and another batch was evaporated to dryness on the water-bath, the residue extracted with hot ethanol, and the anti-*diazosulphonate* precipitated from the filtered extract by the addition of ether; the red-brown solid so obtained was purified by a repetition of the ethanol–ether treatment and could be recrystallised from water (Found : Na, 8·7. $C_{10}H_7O_3N_2SNa$ requires Na, 8·9%). When dissolved in water, the solution would not couple with alkaline *β*-naphthol but did so after treatment with bromine water as above.

Action of Sodium Sulphite on Diazotised β-Naphthylamine.—A hot solution of *β*-naphthylamine (3·6 g.) in hydrochloric acid (10 c.c., *d* 1·18) and water (30 c.c.) was chilled rapidly to 0°, and the finely divided precipitate of the hydrochloride was treated at 0° as quickly as possible with a solution of sodium nitrite (2 g.) in water (10 c.c.), and the mixture was then neutralised with calcium carbonate and treated with sodium sulphite as above. The immediate bright yellow precipitate (Hantzsch's *syn*-compound) changed in a few seconds to a fawn colour with a violent evolution of nitrogen. After the mixture had been kept at 0° for 5 minutes, it was stirred with an equal volume of water and filtered; the crude solid 2 : 2′-azonaphthalene crystallised from chloroform in dark red prisms, m. p. 204° (Hantzsch and Schmiedel, *loc. cit.*, give m. p. 204°). The filtrate, which did not couple with alkaline *β*-naphthol or with ethyl-alcoholic *β*-naphthylamine, did so after cautious addition of bromine water to give 2-naphthaleneazo-*β*-naphthol, which crystallised from glacial acetic acid in red-brown needles, m. p. and mixed m. p. with authentic specimen, 178—179° (Meldola and Hanes, *loc. cit.*., give m. p. 178—179°) and gave a red-violet colour with concentrated sulphuric acid. The red-brown *sodium naphthalene-2-diazosulphonate* was obtained like its isomeride above (Found : Na, 8·7%).

Experiments with 4-*Nitro*-1-*naphthylamine*.—(a) *Sodium* 4-*nitronaphthalene*-1-*diazosulphite* (*Hantzsch's* syn-*sulphonate*). The amine (4·7 g.) was stirred with hydrochloric acid (10 c.c., *d*, 1·18) and ice (20 g.), and treated as rapidly as possible at 0° with sodium nitrite (2 g.) dissolved in water (10 c.c.) (the efficiency of this method of diazotisation was *ca.* 60% by nitrometer test), when most of the paste went into solution; after 30 minutes, water (10 c.c.) was added, the mixture filtered, the filtrate neutralised with calcium carbonate, and a solution of crystallised sodium sulphite (5 g.) and sodium carbonate (0·5 g.) in water (20 c.c.) added as rapidly as possible at 0°. The immediate orange-yellow precipitate of sodium 4-nitronaphthalene-1-diazosulphite, which then coupled with alkaline β-naphthol, gradually darkened to a red-brown solid during 3 hours with very gradual evolution of nitrogen, after which it no longer coupled with alkaline β-naphthol; it was then a mixture of sodium 4-nitronaphthalene-1-diazosulphonate and 4 : 4′-dinitro-1 : 1′-azonaphthalene, since it also gave a brilliant blue colour with concentrated sulphuric acid. The orange-yellow precipitate from a second experiment was completely soluble in water to form a solution which evolved sulphur dioxide when treated with mineral acids, decolorised iodine, and coupled with alkaline β-naphthol to give 4-nitronaphthalene-1 : 1′-azo-2′-naphthol which crystallised from nitrobenzene in dark purple needles, m. p. 262—263° (Hodgson, Nicholson, and Turner, *loc. cit.*, give m. p. 258°), and gave with concentrated sulphuric acid a purple colour, with alcoholic potassium hydroxide a violet colour, and with acetone followed by sodium hydroxide a scarlet colour, which changed to blue. This solution of the sodium 4-nitronaphthalene-1-diazosulphite. on standing, deposited 4 : 4′-dinitro-1 : 1′-azonaphthalene, which crystallised from nitrobenzene in red needles, m. p. 334° (Hodgson, Nicholson, and Turner, *loc. cit.*, give m. p. 334°), and the filtrate then coupled with alkaline β-naphthol only after cautious oxidation with bromine water to give 4-nitronaphthalene-1 : 1′-azo-2′-naphthol (identified as above), while it no longer behaved like the solution of a sulphite.

A solution of the sulphite prepared as above from 4-nitro-1-naphthylamine (4·7 g.) was stirred at 0° with a solution of *p*-nitrobenzenediazonium chloride (from 2 g. of *p*-nitroaniline) which had been neutralised with calcium carbonate, and the yellow precipitate which immediately formed was collected and washed with ice-water (1—1½ l.) until free from diazonium salt, as tested for by β-naphthol-coupling of the filtrate; it was then stirred into a solution of β-naphthol (2·5 g.) in 2% aqueous sodium hydroxide (slight excess) to give a mixture of 4-nitronaphthalene-1 : 1′-azo-2′-naphthol and *p*-nitrobenzeneazo-β-naphthol, m. p. 160°. The filtrate from the precipitate of azo-compounds was oxidised with bromine water and again coupled with alkaline β-naphthol to give a mixture, m. p. 172°, of the same azo-naphthols as above. This experiment indicated that the sodium 4-nitronaphthalene-1-diazosulphite above was mixed with the isomeric diazosulphonate as in the analogous benzene compounds (cf. Hodgson and Marsden, *loc. cit.*).

(b) *Sodium* 4-*nitronaphthalene*-1-*diazosulphonate*. A sample of the sodium 4-nitronaphthalene-1-diazosulphite was prepared as above and the mixture allowed to stand for 3 hours; the separated solids were then filtered off and stirred with water (200 c.c.), again filtered off, and the two filtrates combined. A red-brown solution of the *sodium* 4-*nitronaphthalene*-1-*diazosulphonate* was thus obtained which did not couple with alkaline β-naphthol but did so after oxidation with bromine water to give 4-nitronaphthalene-1 : 1′-azo-2′-naphthol (identified as above). The sodium salt was also isolated as for the analogous naphthalenediazosulphonates as an orange-red solid (Found : Na, 7·4. $C_{10}H_6O_5N_3SNa$ requires Na, 7·6%).

Coupling of Sodium 4-*Nitronaphthalene*-1-*diazosulphonate*.—(a) *With diazotised aniline*. The sodium salt (from 4·7 g. of 4-nitro-1-naphthylamine) was made into a paste with water, and then diluted to a fine suspension which was then stirred with a solution of benzenediazonium chloride that had been previously neutralised with calcium carbonate; rapid decomposition immediately ensued with formation of a black tar.

(b) *With diazotised* p-*nitroaniline* (*from* 2 g.) *made neutral with calcium carbonate*. A yellow precipitate resulted, which was filtered off, washed with ice-water (1—1½ l.) until free from diazonium salt, and then stirred into a solution of β-naphthol (5 g.) in 2% aqueous sodium hydroxide (slight excess); *p*-nitrobenzeneazo-β-naphthol *only* separated and was filtered off; it crystallised from glacial acetic acid, m. p. and mixed m. p. with authentic specimen, 250°. The filtrate above was just acidified at 0° (ice), the precipitated β-naphthol filtered off, and the filtrate oxidised carefully with bromine water; it then again coupled with alkaline β-naphthol, this time to give 4-nitronaphthalene-1 : 1′-azo-2′-naphthol which crystallised from nitrobenzene in dark purple needles, m. p. and mixed m. p. with authentic specimen, 262—263°.

Experiments with 4-*Chloro*-1-*naphthylamine*.—The amine (2·2 g.) was stirred with hydrochloric acid (5 c.c., *d* 1·18), water (10 c.c.), and ice (10 g.), diazotised by rapid addition of sodium nitrite (1 g.) dissolved in water (5 c.c.), and the mixture kept for 30 mins., filtered, neutralised with calcium carbonate, and finally treated rapidly with a solution of crystallised sodium sulphite (3 g.) and sodium carbonate (0·25 g.) in water (10 c.c.). The bright yellow precipitate which separated immediately did not change colour on keeping, although there was a brisk evolution of nitrogen, and it appeared to be a mixture 4 : 4′-dichloro-1 : 1′-azonaphthalene and sodium 4-chloronaphthalene-1-diazosulphonate (Hantzsch's *anti*-compound) since there was no coupling with alkaline β-naphthol. After removal and stirring of the solid with water, the mixture was filtered. The filtrate coupled with alkaline β-naphthol only after oxidation with bromine water, when 4-*chloronaphthalene*-1 : 1′-*azo*-2′-*naphthol* was precipitated; this crystallised from nitrobenzene in dark red needles, m. p. 218—220° (Found : N, 8·6. $C_{20}H_{13}ON_2Cl$ requires N, 8·4%). The yellow solid *sodium* 4-*chloronaphthalene*-1-*diazosulphonate* was obtained as above (Found : Na, 7·6. $C_{10}H_6O_3N_2ClSNa$ requires Na, 7·86%).

4-*Chloro*-1-*naphthylamine*.—A solution of aceto-1-naphthalide (18·5 g.) in glacial acetic acid (60 c.c.) and hydrochloric acid (23 c.c., *d* 1·18) was cooled below 20° and treated gradually with a solution of sodium chlorate (6 g.) in water (25 c.c.), the temperature being kept below 50°. 4-Chloroaceto-1-

naphthalide partly separated, and the precipitation was completed by addition of water; the orange-yellow product (20 g.) was then collected and dried; it was hydrolysed by heating it with ethanol (100 c.c.) and 50% aqueous sulphuric acid (100 c.c.) for an hour, after which the crude sulphate of 4-chloro-1-naphthylamine was precipitated by adding the mixture to water, and recrystallised from dilute sulphuric acid (1 part acid of *d* 1·84 and 2 parts water). On basification of the sulphate crystals with ammonia and subsequent crystallisation from aqueous ethanol (charcoal), the 4-chloro-1-naphthylamine was obtained in very pale pink, almost colourless needles, m. p. 98° (Reverdin and Crépieux, *Ber.*, 1900, **33**, 682, give m. p. 98°).

Alternative Separation of 2- *and* 4-*Nitro*-1-*naphthylamine*.—After hydrolysis of the mixture of 2- and 4-nitroaceto-1-naphthalides obtained by the mononitration of aceto-1-naphthalide (for details see Hodgson and Walker, *J.*, 1933, 1205), the solid obtained by dilution with water of the hydrolysis mixture was removed and boiled with hydrochloric acid (500 c.c., *d* 1·18) and water (1 l.), and the mixture filtered; the dissolved 4-nitro-1-naphthylamine, m. p. 187—189°, separated from the filtrate on cooling, and on recrystallisation from glacial acetic acid (*ca.* 13 c.c. per g.) afforded yellow-brown needles, m. p. 193—194° (Hodgson and Walker, *loc. cit.*, give m. p. 193—194°). Further extractions with dilute hydrochloric acid as above gave decreasing amounts of a less pure amine, the m. p. of which finally reached 130—150°. The insoluble residue, which was mainly the 2-nitro-1-naphthylamine, was dissolved in glacial acetic acid (10 c.c. per g.), the solution filtered, and the base precipitated as sulphate by addition of sulphuric acid (5 c.c. per 100 c.c. solution); this was removed, washed with glacial acetic acid, and basified by water (m. p. 138—140°); it crystallised from glacial acetic acid or 90% formic acid in orange-yellow prisms, m. p. 143—144° (Hodgson and Walker, *loc. cit.*, give m. p. 143—144°). Alternatively, the material of m. p. 138—140° was dissolved in boiling dilute sulphuric acid (1 part acid of *d* 1·84 and 2 parts water), and the solution filtered and diluted with water until precipitation was complete; this gave orange crystals of 2-nitro-1-naphthylamine, m. p. 143—144°.

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