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7-AMINO-2-NAPHTHOL-4-SULPHO ACID: SYNTHESIS AND CHARACTERISTICS

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7-AMINO-2-NAPHTHOL-4-SULPHO ACID: SYNTHESIS AND CHARACTERISTICS

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7-Amino-2-naphthol-4-sulpho acid was obtained and for the first time characterized.

Key words: 7-Amino-2-naphthol-4-sulpho acid

INTRODUCTION

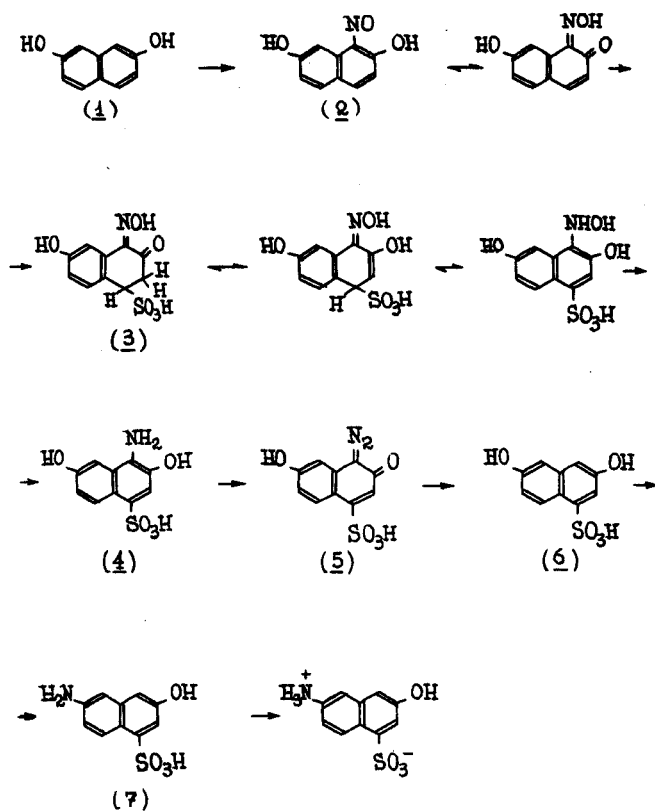
The last century marked the development of the chemistry of azo dyes and the subsequent search of their intermediates, the synthesis and properties of aminonaphtholsulpho acids being characterised by particularly intense research. Such acids allow to obtain azo dyes with high affinity to fibres, with bright and stable colours. Besides, in naphthalene fragments, those dyes have auxochromes that can be further modified chemically. For instance, acylation of amino group by cyanurotrichloride allows to pass from 'simple' azo dyes to 'active' ones, which form chemical bonds with cellulose hydroxy groups. Understandably, virtually all possible combinations of amino, hydroxy, and sulpho groups were therefore tested, in the sense of their arrangement in the naphthalene nucleus. Today, the repertory of intermediates from this series contains γ -acid (2-amino-8-naphthol-6-sulpho acid), I-acid (2-amino-5-naphthol-7-sulpho acid), M-acid (1-amino-5-naphthol-7-sulpho acid), Chicago-S-acid (1-amino-8-naphthol-4-sulpho acid), Echt-acid (1-amino-2-naphthol-4-sulpho acid), B-acid (6-amino-2-naphthol-4-sulpho acid) and others.¹ We managed to obtain yet another, previously undescribed, acid from this set of intermediates, viz. 7-amino-2-naphthol-4-sulpho acid, which may be tentatively called Z-acid.

This article describes the synthesis of Z-acid, gives evidence on its structure, and characterises the azo dyes obtained on its basis. The publication is dedicated to the memory of S. V. Bogdanov, my teacher.

RESULTS AND DISCUSSION

1. Synthetic Sequence

The synthetic sequence is shown in Scheme 1. The starting compound was 2,7-dihydroxynaphthalene (1), transformed into 1-nitroso-2,7-dihydroxynaphthalene (2) described by Clausius.² It reacts with an equimolecular amount of sodium bisulphite to yield a bisulphite compound (3). The reaction involves the use of



Scheme 1

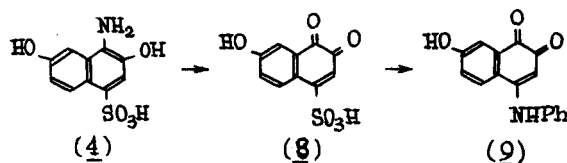
pyridine (small amount) and 37% sodium bisulphite solution. When recalculated to 100%, the yield of sodium salt of bisulphite compound (3) amounts to 75–80% of the starting compound (1).

The compound (3) is soluble in water and stable in neutral and acid media; in alkali, it decomposes into equimolecular amounts of bisulphite and nitrosodihydroxy naphthalene (2). In acetic acid, the derivative (3) reacts, splitting off water, with phenyl hydroxylamine and semicarbazide. In this case, phenylhydrazones and semicarbazones are formed with good yields. The i.r. spectrum of the bisulphite derivative (3) (potassium salt) measured in a KBr tablet, contains a very intense carbonyl absorption band at 1717 cm^{-1} . When reduced by tin chloride or bisulphite, in acid medium, this derivative yields 1-amino-2,7-dihydroxy-naphthalene-4-sulpho acid (4), quite similar to that described by Böniger,³ who obtained acid (4) by reducing a nitroso compound (2) with sulphurous acid without isolation and characterization of the bisulphite derivative (3). Given that only the solution colour can be used to compare the samples (4) in various media (see Experimental), the structure of substance (4) had to be proven chemically, and Section 2a is devoted to this. Aminosulpho acid (4) was subsequently transformed into a diazo compound (5), which eliminates nitrogen in glucose alkali solution to give 2,7-dihydroxy-naphthalene-4-sulpho acid (6) as sodium salt (yield 96%). The target product (7)

was obtained with the yield of 50%, from dihydroxysulpho derivative (6) by heating it in water-ammonia solution of ammonium sulphite. Section 2b provides evidence on the product structure (7).

2. Structural Evidence

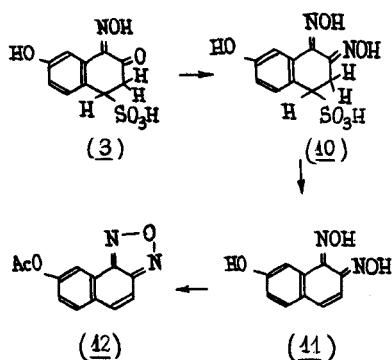
a. *1-Amino-2,7-dihydroxynaphthalene-4-sulpho acid*. Oxidation of this acid (4) results in 7-hydroxy-1,2-naphthoquinone-4-sulpho acid (8), which gives 7-hydroxy-4-phenylamino-1,2-naphthoquinone (9) when treated with aniline, Scheme 2. This



Scheme 2

naphthoquinone was obtained by Böniger from the same compound (4); hence, the inference about 1,2,4-alternation of NH_2 , OH and SO_3H groups in acid (4) has to be a subject of an additional proof.

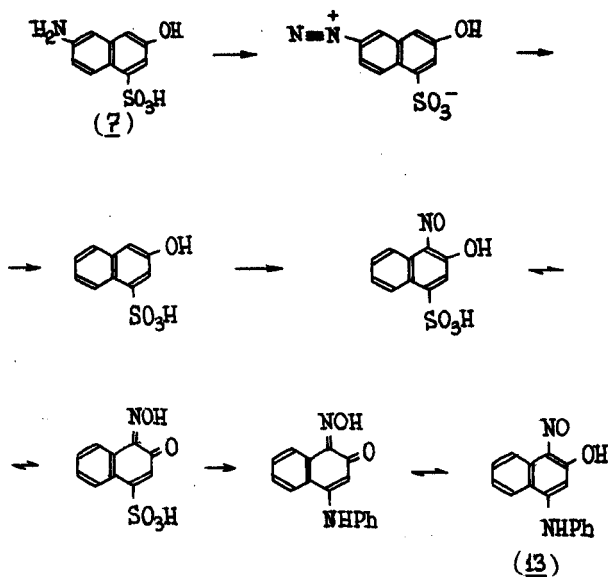
The presence of carbonyl and hydroxy groups in nucleus sites 2 and 7 is predetermined by the structure of the starting product (1). The ortho arrangement of two carbonyl groups follows from Scheme 3, in accord with which the bisulphite



Scheme 3

compound (3), when treated with hydroxylamine, gives dioxime (10), and under the influence of alkalis turns into 7-hydroxy-1,2-naphthoquinone dioxime (11). The latter proved similar to the one described by Nietsky and Knapp.⁴ Boiling it in acetic anhydride gives rise to 7-acetoxy-naphtho-1,2-furazan (12), which was identified with an authentic sample obtained independently.⁴ The final stage in the proof is connected with the presence of a sulpho group in site 4, and is outlined in Section 2b.

b. *7-Amino-2-naphthol-4-sulpho acid*. The structure of acid (7) was chemically proven by Scheme 4 through diazotization of the compound (7) and elimination



Scheme 4

of the diazo group to obtain 2-naphthol-4-sulpho acid; when treated with nitrous acid, the latter yielded 1-nitroso-2-naphthol-4-sulpho acid, which was, in turn, converted to 4-phenylamino-1-nitroso-2-naphthol (13) identified with the sample obtained by counter synthesis.⁵ The above-mentioned evidence on the structure of the target product (7) was corroborated independently in a crystal chemical study of its monohydrate by X-ray diffraction analysis.

Crystal structure of this monohydrate was described by us in a separate paper,⁶ and the same work also gives evidence of its molecular geometry. Significantly, it also establishes the presence of group OH in site 2 of the naphthalene nucleus, of group SO_3^- in site 4, and group NH_3^+ in site 7, see Scheme 1.

3. *Trial Azo Dyes Based on 7-Amino-2-Naphthol-4-Sulpho Acid (Protected by Soviet Inventor's Certificate⁷)*

Z-acid (7) was used as an azo component, either as such or in the form of an acetyl derivative; in the latter case, the obtained dyes were hydrolysed. Orthanilic acid, 4-toluidine-2,5-disulpho acid, 4-aminoanisole-2-sulpho acid, and 2-naphthylamine-4,8-disulpho acid were used as diazo components. In all the cases, the azo coupling referred to the hydroxy group at site 1 of the naphthalene nucleus. After removal of acetyl protection, the amino group was acylated with cyanurotrichloride; as a result, an 'active' form of azo dye containing a cyanurodichloride fragment was used to dye cotton or staple fibre. The dyed material was obtained and described colouristically by Abramova and Gryzlova.⁷ The dyes (orange or red) are highly

resistant to soapy solution and sweat; their affinities to fibre are high; their photostabilities are satisfactory and may be raised by selecting a corresponding diazo component.

EXPERIMENTAL

1-Nitroso-2,7-dihydroxynaphthalene (2). 18% Hydrochloric acid (197 g) was introduced at 0° for 1.5–2 h under the level of the solution of 95% sodium nitrite (22.8 g, 0.314 mol 100%), 95% sodium hydroxide (25.26 g, 0.6 mol 100%), water (825 ml) and 2,7-dihydroxynaphthalene (48 g, 0.3 mol, m.p. 186.5–187.5° from water; dimethyl ester, m.p. 136.5–137°, from MeOH). After stirring for 3 h at 0°, the mass was left for 12 h at 25°. The dark red residue was then filtered, washed with water till neutral reaction, and thoroughly suspended in water (75 ml) with pyridine (0.75 ml) and 34.1% sodium bisulphite (83 g). The mixture was stirred for 2 h at 10°, and then for additional 2 h at 25°. The resultant solution was filtered and added to the filtrate 43% sodium hydroxide solution (61.5 g). After 15 min of shaking, it was added to cooled 5% hydrochloric acid (800 ml). The resultant red precipitate was then filtered, washed with cold water and dried in vacuum.

Yield: 47.5 g (84%, recalculated to dihydroxynaphthalene). After crystallisation from alcohol, the substance had the form of long rosy plates.

Found %: C 63.22, H 3.76, N 7.38. $C_{10}H_7NO_3$.

Calc. %: C 63.46, H 3.73, N 7.40.

Bisulphite compound of 1-nitroso-2,7-dihydroxynaphthalene (3). The above conditions were used to dissolve in aqueous solution of sodium bisulphite a moist 1-nitroso-2,7-dihydroxynaphthalene paste obtained at nitrosation of 2,7-dihydroxynaphthalene (48 g). The resultant solution was filtered and saturated at 25° with sodium chloride (20% of volume). The precipitate was filtered after 20 h and washed with 14% sodium chloride, alcohol and ether.

Yield: 67 g of white substance (content 97.83%) or 77% of theoretical, calculated for dihydroxynaphthalene.

The bisulphite compound was purified by precipitating it from the aqueous solution with an equal volume of alcohol at 10°, and then recrystallized twice from seventy-fold volume of 85% alcohol. The pure sample crystallized in colourless plates. The aqueous solution of the sample yielded a blue-green precipitate while treating it with green vitriol and soda. Titrimetric analysis of bisulphite compound: 0.2 g was dissolved in water (100 ml), then 40% sodium hydroxide solution (5 ml) was added and the mixture was stirred for 15 min. Water (1.500 ml) and then 35% hydrochloric acid (10 ml) were added and the aliquot part of obtained yellow solution was titrated with 0.1 N iodine solution.

Found %: N 4.74, S 10.81, M 292.5 (iodometrically). $C_{10}H_8NO_6SNa$.

Calc. %: N 4.77, S 10.93, M 293.2.

1-Amino-2,7-dihydroxynaphthalene-4-sulpho acid (4). a. A warm (40°) solution of 95% tin chloride (10.6 g, 0.45 mol, 100%), 35% hydrochloric acid (17.7 ml) and water (11.8 ml) was poured in 1 h into the suspension of 3.12 g of 94% bisulphite compound of 1-nitroso-2,7-dihydroxynaphthalene (0.001 mol, 100%) in 22 ml water. The mixture was boiled for 30 min; hydrogen sulphide was evolved. The cooled suspension was filtered, and the gray precipitate washed on a filter with ice water, alcohol and ether. The yield amounted to 2.15 g. The substance was dissolved in hot water containing sodium acetate and separated from a small tin sulphide residue by filtration. Cooling of the filtrate resulted in long white grayish needles which, after filtration and drying in vacuum, weighed 2.03 g (yield 70% of theoretical).

b. Moist paste of 1-nitroso-2,7-dihydroxynaphthalene, obtained from 2,7-dihydroxynaphthalene (48 g), was thoroughly suspended in water (75 ml) with pyridine (0.75 ml) and 89 g (67 ml) 34.1% sodium bisulphite. The mixture was stirred for 2 h at 10°, and then for an additional 2 h at 25°. The resultant solution was filtered, added to a filtrate of 34.1% sodium bisulphite solution (67 ml) and 35% hydrochloric acid (135 ml). The tightly sealed mixture was left for 24 h at 25°. The condensed mass was then filtered, and the residue washed on a filter with cold water and dried in vacuum at 70°. The yield amounted to 65–70 g (75–80% of the theoretical recalculated for dihydroxynaphthalene). To purify the substance, water (700 ml) containing calcinated soda (18.2 g) and 34.1% sodium bisulphite solution (70 ml) was dissolved; the resultant solution was stirred with coal, filtered and cooled, and 35% hydrochloric acid was added thereto till acid reaction of the medium. The resultant precipitate was filtered, washed with cold water and dried in vacuum at 70°. Yield of purified substance: 60–63 g.

1-Amino-2,7-dihydroxynaphthalene-4-sulpho acid (**4**) was dissolved in aqueous solution of soda with blue-green colouring; the resultant solutions were subsequently diluted to produce blue fluorescence.

Found %: C 47.02, H 3.61, N 5.29, S 12.57. $C_{10}H_9NO_5S$.

Calc. %: C 47.01, H 3.55, N 5.49, S 12.56.

Found H_2O (dried at 100° over P_2O_5) 12.45%. $C_{10}H_9NO_5S \cdot 2H_2O$.

Calc. %: H_2O 12.37.

7-Hydroxy-1,2-naphthoquinone-4-sulpho acid (8). 1-Amino-2,7-dihydroxynaphthalene-4-sulpho acid (1.85 g, 0.0063 mol) was dissolved in cold water (15 ml) containing calcinated soda (0.7 g), and concentrated hydrochloric acid (2 ml) was rapidly added to the resultant solution, and then, at 0° in 1 h, a mixture of water (4.5 ml) and 95% sodium nitrite (0.85 g) was added thereto. The orange residue of ammonium salt of 7-hydroxy-1,2-naphthoquinone-4-sulpho acid was filtered after standing for 18 h, and subsequently washed with cold (10°) water; after drying in air, the residue weighed 1.48 g. The filtrate was saturated with potassium chloride (12% of volume) and, after 18 h, filtered to obtain small red needles of potassium chloride of quinone sulpho acid. The latter, after washing with alcohol, ether and drying in air, weighed 0.09 g. Ammonium salt, obtained from the reaction, was transferred to potassium salt after solvating it in water and saturating the solution with potassium chloride, the yield 1.44 g. The total yield of potassium salt was 1.53 g (77.5% of the theoretical). After crystallization from water, the substance had the form of cherry-red elongated plates.

Found %: C 38.76, H 2.50, S 10.29, H_2O (100° , P_2O_5) 6.11. $C_{10}H_6O_6SK \cdot H_2O$.

Calc. %: C 38.70, H 2.60, S 10.33, H_2O 5.81.

7-Hydroxy-4-phenylamino-1,2-naphthoquinone (9). A solution of anhydrous potassium salt of 7-hydroxy-1,2-naphthoquinone-4-sulpho acid (0.12 g, 0.0004 mol) was stirred for 3 h at 25° with aniline water (15 ml, 0.006 mol aniline). The red residue was separated from the light yellow solution by filtration, and after washing with water and drying in vacuum it weighed 0.11 g (yield 98.3% of theoretical). The substance crystallized from alcohol in the form of light red needles which decomposed at about 240° .

Found %: N 5.27. $C_{16}H_{11}NO_3$.

Calc. %: N 5.28.

Carbonyl derivatives of bisulphite compound of 1-nitroso-2,7-dihydroxy-naphthalene. a. Phenyl hydrazone. A suspension of hydrochloric salt of phenyl hydrazine (1.6 g, 0.0111 mol) and crystalline sodium acetate (4.62 g, 0.034 mol) in water (5 ml) was added to a solution of sodium salt of bisulphite compound of 1-nitroso-2,7-dihydroxynaphthalene (3.02 g of 94% sample or 0.0097 mol of 100%) in water (25 ml). This resulted in a solution, from which a grayish-white residue shortly starts to precipitate. The sediment was filtered after 20 h of standing at 25° ; the resultant mass, after washing with alcohol and ether, and subsequent drying in air, amounted to 4.12 g (yield 93% of theoretical). After recrystallization from a twenty-fold volume of water heated to 60° , large triangular golden-yellow plates were obtained. The aqueous solutions of bisulphite compound gradually reddened at addition of alkali, and at boiling with alkali a cherry-red colour was instantly developed. The same colour was formed when alkali was added to the solution, priorly boiled with hydrochloric acid.

Found %: N 9.50, S 7.02. $C_{16}H_{14}N_3O_5SNa \cdot 4H_2O$.

Calc. %: N 9.23, S 7.04.

b. Semicarbazone. A solution of hydrochloric salt of semicarbazide (0.62 g, 0.00555 mol) and crystalline sodium acetate (1.5 g, 0.011 mol) in water (7 ml) was added to sodium salt of bisulphite compound of 1-nitroso-2,7-dihydroxynaphthalene (1.51 g of 94% sample or 0.00485 mol of 100%) in water (10 ml) and the resultant solution was kept for 24 h at 25° . It was subsequently cooled to 5° , and the resultant white residue filtered, washed with alcohol and ether, and dried in air. The yield amounted to 1.23 g (60% of theoretical). Recrystallization from three-fold volume of water heated to 60° allowed to obtain colourless rhombic plates. The aqueous solutions reddened very slowly in the presence of alkali; but alkalification of the aqueous solution previously boiled with hydrochloric acid caused instant cherry-red colouring.

Found %: C 31.39, H 4.50, N 13.21, S 7.54. $C_{11}H_{11}N_4O_6SNa \cdot 4H_2O$.

Calc. %: C 31.27, H 4.53, N 13.26, S 7.59.

c. Oxime (**10**). Hydrochloric hydroxylamine (2 g, 0.0289 mole) was added to a suspension of purified sodium salt of bisulphite compound of 1-nitroso-2,7-dihydroxynaphthalene (8 g of 96.2% sample or

0.0263 mol of 100%), crystalline sodium acetate (3.93 g, 0.0289 mol), and water (7.5 ml). The suspension turned into a brownish solution when heated to 65°, the temperature maintained for 1 h to isolate a white residue of bisulphite oxime sodium salt. The residue was filtered after being kept for 18 h at 25°, and then washed with alcohol and ether, and dried in air. The yield amounted to 5.95 g. A half volume of 35.5% hydrochloric acid was added at 15° to the filtrate, obtained after the residue separation from the reaction solution; this allowed to isolate the additional amount of the bisulphite derivative of 7-hydroxy-1,2-naphthoquinone dioxime (0.49 g). The total yield, calculated for the sodium salt of the bisulphite compound amounted to 6.54 g (72.5% of theoretical). At 30°, the sodium salt is dissolved in a three-fold water volume. Cooling of the solution to 5° led to a residue in the form of colourless rhombic plates. Aqueous solutions give a red-violet colour when treated with green vitriol and sodium acetate to subsequently become light orange when alkali is added. Alkaline solutions redden after standing.

Found %: C 34.90, H 3.70, N 8.25, S 9.19, H₂O (100°, P₂O₅) 10.52. C₁₀H₉N₂O₆Na · 2H₂O.

Calc. %: C 34.87, H 3.80, N 8.14, S 9.31, H₂O 10.47.

7-Hydroxy-1,2-naphthoquinone dioxime (11) and 7-acetoxy-1,2-naphthofurazan (12). Purified sodium salt of the bisulphite compound of 7-hydroxy-1,2-naphthoquinone dioxime (18.9 g, 0.055 mol) was dissolved in 10% solution of sodium hydroxide (110 ml), and the obtained orange solution was heated to 55° and subsequently cooled slowly to 5° to add 10% hydrochloric acid (185 ml). The isolated yellow precipitate was filtered and washed on a filter with cold water, and then dried in vacuum. The yield of 7-hydroxy-1,2-naphthoquinone dioxime (11) was 9.64 g (85% of theoretical). The substance was crystallized from 60% acetic acid in the form of yellow plates which decomposed at 186–186.4°. The substance decomposition temperature differed from that indicated in the literature⁴ (195°), but at boiling with a twenty-fold volume of acetic anhydride gave 7-acetoxynaphtho-1,2-furazan (12) with a melting point of 136.4–137.5° (from 50% alcohol; lit.⁴ m.p. 137°). The m.p. of the mixture (product obtained, together with an authentic sample) was 136.7–137.4°. The structure of 7-hydroxy-1,2-naphthoquinone dioxime (11) was also confirmed by elemental analysis.

Found %: C 58.95, H 4.10, N 13.82. C₁₀H₈N₂O₃.

Calc. %: C 58.82, H 3.95, N 13.73.

1-Diazo-2,7-dihydroxynaphthalene-4-sulpho acid (5). 10% Solution of green vitriol (5 ml) and 0.5 N solution of sodium nitrite (200 ml) were added to a suspension of dihydrate of 1-amino-2,7-dihydroxynaphthalene-4-sulpho-acid (28.5 g, 0.1 mol) in water (1,000 ml). The solution was stirred for 1 h at 25°, coal was then added and stirred for 20 min. After filtration, sodium chloride (20% of volume) was then added to the filtrate. The isolated sodium salt of the diazo compound (5) was subsequently filtered, washed with 10% solution of sodium chloride, and dried in vacuum. Filtration and washing are necessary to liberate the product of copper salts.

The yellow needles of the diazo compound weigh 35 g; the average content of the basic substance is 78%, and the yield is 95% of the theoretical, recalculated for 100% of the substance. The diazo compound contents in the reaction product were estimated by the amount of nitrogen liberated at boiling with cuprous chloride in hydrochloric acid.

2,7-Dihydroxynaphthalene-4-sulpho acid (6). A mixture of sodium salt of 1-diazo-2,7-dihydroxynaphthalene-4-sulpho acid (52 g of 74% sample or 0.135 mol of 100%) and glucose (13.8 g, 0.076 mol) in water (600 ml) was added at stirring to 10% solution of sodium hydroxide (100 g, 0.0725 mol) at 80° for 30 min. to result in a solution, from which nitrogen was continually liberated. This is followed by stirring for another 30 min under the same temperature, till the ending of nitrogen bubbling. The solution was then cooled, neutralized with hydrochloric acid and evaporated first on a boiling water bath and then in vacuum. The residue was purified by crystallization from an equal volume of water. The yield of pure sodium salt of 2,7-dihydroxynaphthalene-4-sulpho acid was 36.5 g or 96% of theoretical, calculated for crystallohydrate.

Elongated hexagonal plates. Brown colour with iron chloride.

Found H₂O (110°, P₂O₅) 7.78%. C₁₀H₇O₅Na · 1. 2H₂O.

Calc. H₂O 7.62%.

Found %: C 45.80, H 2.73, S 12.30. C₁₀H₇O₅Na.

Calc. %: C 45.81, H 2.69, S 12.23.

7-Amino-2-hydroxynaphthalene-4-sulpho acid (7). A mixture of sodium salt of 2,7-dihydroxynaphthalene-4-sulpho acid (60 g, 0.22 mol), 44% solution of ammonium sulphite (127 g, 0.48 mol) and 18%

solution of ammonia (30.5 g, 0.32 mol) was heated at 130° for 6 h in a rotating enamelled autoclave. Prior to the beginning of the process, the reaction mixture represented a suspension, and at the end of the process—a solution of red-brown colour. The obtained solution was filtered and acidified with hydrochloric acid to pH 7–8, blowing off the liberated sulphur dioxide with nitrogen. A yellowish-white residue precipitated which was separated by filtration, washed with cold water, and then dried in vacuum. The target product (7) yield was 26 g, or 50% of theoretical, recalculated for crystallohydrate.

The substance is moderately soluble in hot water and almost insoluble in cold water. The aqueous solutions have pH 7 (i.e. internal salt formation between the amino- and sulphy groups takes place). Colourless rhombic prisms are crystallized from water. In passing light through the aqueous solutions it reveals blue fluorescence, and with iron chloride gives a blue colouring, which at standing turns into brown. In ammonium hydroxide, the solutions are colourless and do not fluoresce.

Found %: C 46.54, H 4.30, N 5.47, S 12.46, H₂O (105°, P₂O₅) 6.94. C₁₀H₉NO₄S · H₂O.

Calc. %: C 46.68, H 4.31, N 5.45, S 12.47, H₂O 7.00.

1-(Azobenzol-2-sulpho)-7-amino-2-naphthol-4-sulpho diacid. Acetic anhydride (2 ml) was added to a solution of 2.5 g 7-amino-2-naphthol-4-sulpho acid (calculated for 100%) in 1N soda solution (12 ml). The obtained solution was after 1 h neutralized with 25% ammonia solution and a suspension of 1-diazobenzol-2-sulpho acid was added at 2°. The diazo compound was prepared from orthonilic acid (1.7 g) (calculated for 100%) by the usual method and added in 40 min; pH 8.0 was maintained with the help of 25% ammonia solution. At this point and further, pH control was performed continually by using a low-temperature glass electrode in pair with a saturated calomel electrode. When the azo-coupling was stopped (stop of pH change, disappearance of diazo compound in a sample), the reaction mass (80 ml) was boiled at 60° with concentrated hydrochloric acid (16 ml) for 3 h. This led to removal of acetyl protection of the amino group. The suspension of the resultant aminoazo dye was cooled to 5° and filtered to yield 3.5 g of dye containing 92% of basic substance (mol. mass 423), yield 77% of theoretical, recalculated for orthonilic acid. When chromatographing both the solution after hydrolysis and the isolated dye (radial chromatogram developed on Filtrak 388-Red Ribbon paper with 1N soda solution) only one annular zone was found to have $R_f = 0.37$.

To obtain an 'active' dye, an aminoazo compound (1.9 g of 92% sample) was dissolved in water (50 ml) while adding soda and retaining the solution neutral; the solution was subsequently cooled to 0–2° and cyanurotrichloride (29 g of 98% sample) in acetone (9 ml) was then added. The pH was retained at 6.5 by addition of a soda solution. When the pH value stopped changing, the reaction mixture was kept for 20 min under the same temperature, the excess cyanurotrichloride was filtered. A dichloro-cyanuric derivative of the azodye was isolated after an addition of sodium chloride (10% of volume), at 0–3°. This yielded an orange-red paste (8.8–9.0 g), which was jammed with a mixture of mono-potassium phosphate (0.9 g) and disodium phosphate (0.5 g) and dried in vacuum at 70°.

Yield: 4.2–4.4 g dry dye; azo compound contents 52%.

Yield: 85–90% of theoretical, recalculated for 100% aminoazo dye.

In a sample with dye concentration equal to 51.71%, active chlorine was found to amount to 5.72%, which corresponded to dichloride with empirical formula C₁₉H₁₀N₆Cl₂O₂S₂Na₂. Calculated active chlorine, 5.96%.

Cotton and viscose fibres were dyed at 40° from aqueous solutions containing table salt and calcinated soda. Orange dyes with reddish tinge possess high degree of fixation; being ingrained, they are highly resistant to soapy solutions at 40 and 100° and to sweat. Photostabilities are satisfactory ones.

If the azo component (7) were to be combined with the same diazo compound without prior protection of the amino group, the resultant dye would have a noticeably more yellow tinge.

Dyes based on acetylated intermediate (7) were obtained when using as diazo components 4-toluidine-2,5-disulpho acid, 4-aminoanisole-2-sulpho acid, and 2-naphthylamine-4,8-disulpho acid by the procedure mentioned above. On cotton and staple fibres, the resultant 'active' dyes produced the following colours: orange with reddish tinge, red, and pink. Colouristic estimates were similar to those cited above.

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