

Self-coupling of Diazotised 1-Amino-8-hydroxynaphthalene-3,6-disulphonic Acid

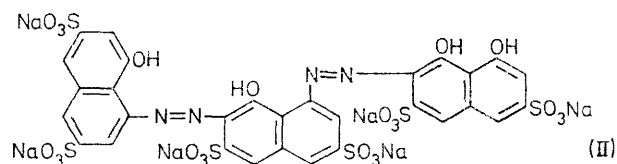
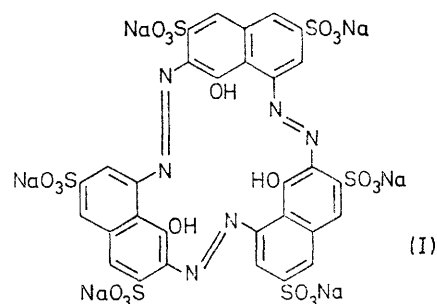
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Calcichrome, the product formed by the self-coupling of diazotised 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid, is shown to be 2,8,8'-trihydroxy-1,1'-azonaphthalene-3,6,3',6'-tetrasulphonic acid (III; $R^1 = H$, $R^2 = OH$).

THE self-coupling of diazotised 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid was first described in an early German patent¹ in which improbable structures were suggested for the azo-compound formed. West and Close² found the compound to be a specific colorimetric reagent for calcium for which purpose it has been introduced under the name Calcichrome. These authors advanced the possible structure (I) on spatial considerations, remarking that the structure accounted for the presence of three ionisable protons in the molecule. Lukin *et al.* dismissed structure (I) and postulated structure (II) for the reagent on the basis of colorimetric reactions of allied compounds.³ Structure (II) has since found general acceptance. In these postulations, however, analytical evidence pertinent to the structure of the compound is lacking.

Elemental analysis, on material prepared by minor variation on the methods due to previous authors,^{2,3} coupled with titrimetric determination of the azo-linkage, clearly indicates the presence of 20 carbon, 2 nitrogen, and 4 sulphur atoms for each azo-linkage and thus resolves the structure into a simple naphthalene-azo-naphthalene derivative. The n.m.r. spectrum of the substance shows the proton composition to be seven aromatic protons, arranged in four rings as three pairs and a single proton, and three labile protons, all hydrogen bonded. These data fit structure (III; $R^1 = H$, $R^2 = OH$). Synthetic proof of this structure

has been obtained by coupling diazotised 1-amino-8-*p*-tolylsulphonyloxynaphthalene-3,6-disulphonic acid at low pH with 7-amino-1-hydroxynaphthalene-3,6-disulphonic acid to yield (III; $R^1 = SO_2 \cdot C_6H_4 \cdot Me$, $R^2 = NH_2$). This compound on mild hydrolysis loses the

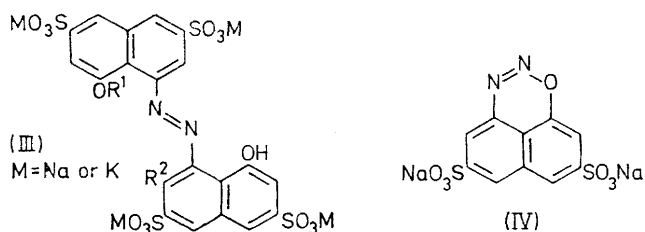


O-p-tolylsulphonyl group to yield (III; $R^1 = H$, $R^2 = NH_2$), but under more vigorous conditions undergoes further hydrolysis with replacement of the amino-group by a hydroxy-group to yield (III; $R^1 = H$, $R^2 = OH$); this latter compound is identical with Calcichrome.

¹ D.R.P. 92,012.

² R. A. Close and T. S. West, *Talanta*, 1960, **5**, 221.

³ A. M. Lukin, K. A. Smirnova, and B. Zavarikhina, *Zhur. analit. Khim.*, 1963, **18**, 444.



In the self-coupling of diazotised 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (III; $R^1 = H$, $R^2 = OH$) arises by a novel variation of the reaction described by Suckfull and Dittmer⁴ in which a diazonium salt reacts with a *syn*-diazotate under alkaline conditions. Nitrogen is eliminated and an azo-compound containing an additional hydroxy-group located *ortho* to the azo-linkage is formed. The mechanism of this reaction has been discussed by Zollinger and his co-workers.⁵ The internal diazo-oxide (IV) which is formed from 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid under the acid diazotisation conditions presumably functions as the *syn*-diazotate, reacting with the normal diazonium salt as it is formed from (IV) under alkaline conditions to yield (III; $R^1 = H$, $R^2 = OH$). In this product the hydroxy-group introduced during the course of the reaction occupies the 2-position.

EXPERIMENTAL

Calcichrome.—2N-Sodium nitrite solution (250 ml.) was added during 15 min. to a suspension of the monosodium salt of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (171 g.) in water (1 l.) and concentrated hydrochloric acid (50 ml.) below 5°. A trace of excess of nitrous acid was destroyed with a few drops of sulphamic acid solution and the suspension was slowly added, below 20°, to 10N-sodium hydroxide solution (225 ml.). After 3 hr., the precipitate was filtered off, dissolved in boiling water (1 l.), and the filtered solution was acidified with concentrated hydrochloric acid (50 ml.). The precipitated Calcichrome (104 g.) gave deep purple crystals of the tetrasodium salt (from water) [Found: C, 30.4; H, 2.2; N, 3.5; S, 16.3%; *M* (by titanous estimation), 788. Calc. for $C_{20}H_{10}N_2Na_4O_{15}S_4 \cdot 3H_2O$: C, 30.2; H, 2.0; N, 3.5; S, 16.15%; *M*, 792.]

2-Amino-8-hydroxy-8-*p*-tolylsulphonyloxy-1,1'-azonaphth-

alene-3,6,3',6'-tetrasulphonic Acid.—The disodium salt of 1-amino-8-*p*-tolylsulphonyloxynaphthalene-3,6-disulphonic acid (103.4 g.) in water (1 l.) was acidified below 5° with concentrated hydrochloric acid (50 ml.) and diazotised with 2N-sodium nitrite solution (100 ml.); excess of nitrous acid was destroyed after 10 min. with a few drops of sulphamic acid solution. The monosodium salt of 2-amino-8-hydroxynaphthalene-3,6-disulphonic acid (68.4 g.) was added to the solution and the whole was stirred for 22 hr. below 5°; the pH of the reaction was maintained between 2.5 and 3.0 with potassium acetate solution. Potassium acetate (2 kg.) in water (2 l.) was added to the filtered solution and the precipitated azo-compound was filtered off, dissolved in water (1 l.), and reprecipitated with potassium acetate (1 kg.) in water (1 l.). The tetrapotassium salt was washed with ethanol and was obtained as a deep ruby red powder (Found: C, 31.0; H, 3.0; N, 3.8; S, 15.0%. Calc. for $C_{27}H_{17}K_4N_3O_{16}S_4 \cdot 5H_2O$: C, 31.0; H, 2.6; N, 4.0; S, 15.3%).

2-Amino-8,8'-dihydroxy-1,1'-azonaphthalene-3,6,3',6'-tetrasulphonic Acid.—The foregoing azo-compound (43 g.) was stirred for 5 hr. at 20°, and then for 20 min. at 40° with N-sodium hydroxide solution (50 ml.); sodium hydrogen carbonate (50 g.) was then added to the mixture. The precipitated tetrasodium salt of the dihydroxy-azo-compound formed purple crystals (16.5 g.) from water [Found: C, 29.6; H, 2.3; N, 5.3; S, 15.6%; *M* (by titanous estimation), 800. Calc. for $C_{20}H_{11}N_3Na_4O_{14}S_4 \cdot 4H_2O$: C, 29.7; H, 2.35; N, 5.2; S, 15.8%; *M*, 809].

2,8,8'-Trihydroxy-1,1'-azonaphthalene-3,6,3',6'-tetrasulphonic Acid.—The tetrapotassium salt of 2-amino-8-hydroxy-8'-*p*-tolylsulphonyloxy-1,1'-azonaphthalene-3,6,3',6'-tetrasulphonic acid (25 g.) after 1 hr. at 90° in sodium hydroxide solution (250 ml.) was cooled below 50° and sodium hydrogen carbonate (150 g.) was added to it. Sodium chloride (100 g.) was added to the precipitate in water (1 l.) and concentrated hydrochloric acid (50 ml.) at 60°. The precipitated tetrasodium salt (12.5 g.) formed deep purple crystals from water [Found: C, 30.4; H, 2.5; N, 3.5; S, 16.3%; *M* (by titanous estimation), 798] $C_{20}H_{10}N_2Na_4O_{15}S_4 \cdot 3H_2O$ requires C, 30.2; H, 2.0; N, 3.5; S, 16.15; *M*, 792). The chromatographic behaviour and i.r. spectrum of this compound were identical with those of the sample of Calcichrome described above.

[9/1743 Received, October 14th, 1969]

⁴ F. Suckfull and H. Dittmer, *Chimia (Switz.)*, 1961, **15**, 137.

⁵ M. Christen, L. Funderbuck, E. A. Halevi, G. E. Lewis, and H. Zollinger, *Helv. Chim. Acta*, 1966, **49**, 1376.