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**AROMATIC DIAZO AND AZO COMPOUNDS LXIV¹.
NEW AMINO COMPOUNDS AND NEW AZO DYES
BASED ON NAPHTHO[2,1-*d*]OXAZOLE**

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In memory of Dr. Ing. Z.J. Allan, Dr.Sc.

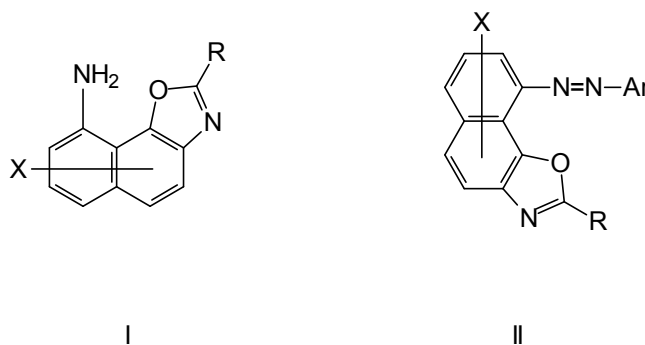
*The paper is focused on innovation of a chemical process leading to new amino compounds of structural formula **I** and their application to preparation of new azo dyes **II**. The procedure of preparation of the key derivative is presented. This derivative is aminonaphthoxazoledisulfonic acid **III**, which is used in syntheses of a number of azo dyes belonging to various technological and application categories. In this way, a chemically new class of azo dyes, containing the naphtho[2,1-*d*]oxazole skeleton in their molecules, was established.*

¹ LXIII: Collect. Czech Chem Commun. **30**, 1197 (1965).

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Introduction

Our previous paper [1] described the invention of isomerization and dehydration cyclization in which acyl group RCO– undergoes intramolecular rearrangement from the 8-amino group to 2-amino group in a 2,8-diaminonaphthalene-1-ol derivative and subsequent ring closure giving new amino compounds of structural formula **I**. Compounds **I** can be used in syntheses of azo dyes **II**,



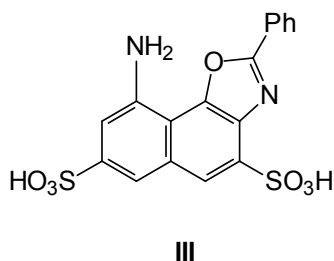
where

R means an unsubstituted or substituted aryl group of benzene or naphthalene series or a heteroaryl group, as the case may be,

Ar means a residue of simple or difunctional azo coupling component that can undergo not only azo coupling reaction but also diazotization,

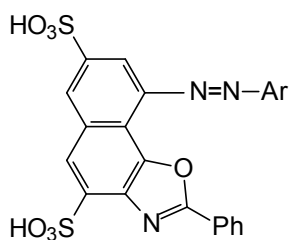
X means a substituent in remaining positions of the naphthalene nucleus.

This paper represents continuation to development of the original topic and involves a selection and practical applications of derivatives of the new amino compound **I**. In this respect the key derivative appeared to be 9-amino-2-phenylnaphtho[2,1-*d*]oxazole-4,7-disulfonic acid (**III**).



This compound can safely be diazotized with sodium nitrite in acid medium. The obtained diazonium salt is sufficiently stable and can easily be used in azo coupling reaction. This procedure provides a new class of naphthoxazole azo dyes that can be utilised in various areas of industrial applications, such as dyeing of textiles and plastics. In this respect, the aminonaphthoxazoledisulfonic acid **III** appears to be a versatile intermediate, which is documented by the following groups of naphthoxazole dyes.

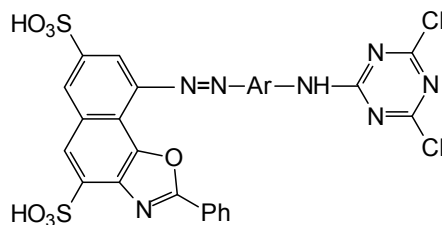
Naphthoxazole Monoazo Dyes of General Formula IV



IV

where Ar means the residue of the azo coupling component.

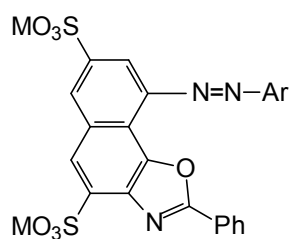
Naphthoxazole Dichlorotriazine Reactive Azo Dyes of General Formula V



V

where Ar means the bivalent residue of azo coupling component.

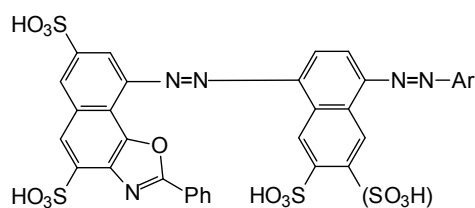
Water-insoluble Naphthoxazole Azo Dyes of General Formula VI



VI

where Ar has the same meaning as in formula IV, M is a lake-forming element, usually Ca, Ba and Mg.

From among other naphthoxazole dyes based on the diazo component III we can mention a more complex disazo dye VII.

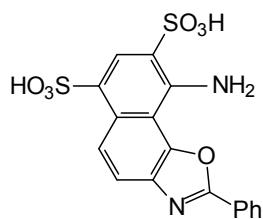


VII

This type of disazo dye with linear and/or planar structure belongs to the category of the so-called substantive (direct) dyes applicable to direct dyeing of natural materials, such as cotton and cellulose. The first two steps of synthesis of the disazo dye **VII** are diazotization of compound **III** and subsequent azo coupling reaction with 8-aminonaphthalene-2-(or 3)-sulfonic acid (the so-called Cleve acids). The resulting monoazo dye contains a primary amino group that can be diazotized, and the obtained diazonium compound is submitted to azo coupling reaction with Ar-H to give the disazo dye **VII**. If the coupling component Ar-H is one of the Cleve acids again, the last two steps can be repeated to obtain a trisazo dye. It is also possible to use the end amino group of the monoazo (or disazo) dye in other ways, e.g., the reaction with phosgene leads to *N,N'*-disubstituted urea (dye-NH-CO-NH-dye), or the reaction with cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) can lead to replacement of one, two or even all three chlorine substituents by the residues of aminoazo dye to give a cold reactive dye, hot reactive dye or substantive dye, respectively.

The below-given text presents an improved way of preparation of 9-aminonaphtho[2,1-*d*]oxazole derivatives according to patent [2]; these derivatives are useful not only in the field of organic dyes but also in other areas, such as syntheses of fluorescent brighteners and pharmaceuticals (they are not derivatives of the hazardous naphthalene-2-amine). The improvement consists in replacement of the 2-azo derivatives of the respective components by 2-nitroso derivatives, which eliminates rather laborious purification: removal of reduction products from both the intermediates and final products. It was found out [3] that addition of tin(II) chloride in the phase of isomerization and ring closure (this concerns only the reduction with dithionite) has not only anti-oxidizing effect but acts also as an inhibitor preventing acid hydrolysis of amino group in the naphthalene component. Thus this addition stimulates the process and improves the end product quality.

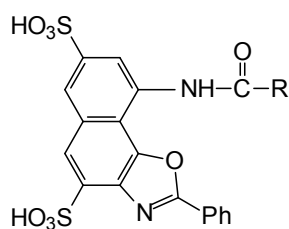
The intramolecular rearrangement of acyl group (mentioned above) can be generalized to all simple *peri*-benzoylamino(hydroxy)naphthalenesulfonic acids and those substituted in the benzoyl residue. Among them, 4-benzoylamino-5-hydroxynaphthalene-1,3-disulfonic acid and/or its 6-amino derivative appear interesting. The above-described transformation of this disulfonic acid gives 9-amino-2-phenylnaphtho[2,1-*d*]oxazole-6,8-disulfonic acid (**VIII**).



VIII

This compound has an interesting feature: a sulfonic acid group in *ortho*-position with respect to amino group. In accord with existing experience, it can be expected that the azo dyes prepared from this aminonaphthoxazolesulfonic acid will exhibit (due to the *ortho*-position of azo group and sulfonic acid group) better utility value, particularly increased daylight fastness.

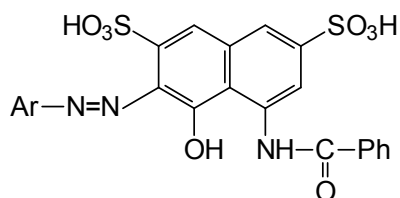
Another utilization of the rearrangement and dehydration cyclization can be seen in the preparation and examination of properties of various derivatives of not only naphthoxazolesulfonic acid **III** but also other aminonaphthoxazolesulfonic acids, such as, e.g., compounds **IX**,



IX

in which R means either 2,4-diaminophenyl group or 2-hydroxy-3-naphthyl group. Both these compounds can undergo azo coupling reaction as well as diazotization reaction, which applies to the 2,4-diaminophenyl derivative (*de facto* a derivative of benzene-1,3-diamine).

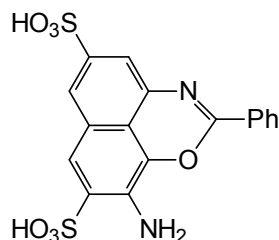
In this context we should refer to the paper [4] dealing with structural analysis of tar-derived dyes. This study describes, *inter alia*, the reduction of azo dye **X**,



X

i.e. the azo coupling product obtained from 4-benzoylamino-5-hydroxynaphthalene-2,7-disulfonic acid (*N*-benzoyl-H-acid). It was found out that the reduction of

this dye with tin(II) chloride and hydrochloric acid gives, instead of the expected 6-amino-4-benzoylamino-5-hydroxynaphthalene-2,7-disulfonic acid (the so-called “azo-coupled” *N*-benzoyl-H-acid), the cyclization product of the assigned structure of amino-*peri*-naphthoxazine **XI**.



XI

Subsequent, more detailed study of reduction of the mentioned type of azo dyes with tin(II) chloride showed [1] that the reduction decomposition of the molecule is accompanied by rearrangement of acyl group and subsequent dehydration cyclization. Again it can be stated that this process of structural and chemical transformation in the series of 8-acylaminonaphthalene-1-ols is rather general: it concerns simple as well as more complex derivatives having hydroxy and acylamino groups at the positions 1,8 (*peri*) of naphthalene skeleton.

Experimental

Preparation of 9-Amino-2-phenylnaphtho[2,1-*d*]oxazole-4,7-disulfonic Acid (**III**)³

4-Benzoylamino-5-hydroxynaphthalene-2,7-disulfonic acid (*N*-benzoyl-H-acid) (0.1 gmol) is dissolved in 850 ml water with added sodium bicarbonate. The slightly alkaline solution is mixed with 80-90 ml standard solution of hydrochloric acid ($c[\text{HCl}] = 2.5 \text{ mol l}^{-1}$), and after cooling to the temperature of 0 °C, 40 ml standard solution of sodium nitrite ($c[\text{NaNO}_2] = 2.5 \text{ mol l}^{-1}$) is continuously added with stirring. The formed nitroso derivative is precipitated from the hot mixture after addition of 200 g sodium chloride, the precipitated solid is collected by suction of the warm slurry, and the filter cake is washed with 10% NaCl solution. The obtained paste (ca 170 g) of 4-benzoylamino-5-hydroxy-6-nitrosophthalene-2,7-disulfonic acid is mixed with 600 ml water, and the slightly alkaline solution is reduced with a solution of sodium dithionite at the temperature of 45-50 °C. After the reduction is finished, the reaction mixture is acidified with acetic acid, and the precipitated 6-amino derivative is collected by suction in the form of a paste which is processed further. It is mixed with water, treated with hydrochloric

³ Modified procedure according to patent [2].

acid and 50 ml 20 % solution of tin(II) chloride, and heated to the temperature of 80-95 °C until the isomerization reaction and dehydration ring closure are finished. The formed 9-amino-2-phenylnaphtho[2,1-*d*]oxazole-4,7-disulfonic acid (**III**) is isolated (yield ca 86 % of theory, referred to the mol. mass of 420.39) and used further. It can be diazotised directly or indirectly with sodium nitrite, and the obtained diazonium salt can be used for azo coupling reaction. The dyes synthesised in this way are described below.

If the reduction of the 6-nitroso derivative is carried out with tin(II) chloride in hydrochloric acid medium at the temperature of 45-50 °C and with subsequent boiling, the naphthoxazolesulfonic acid **III** is obtained directly, which means that the reduction is accompanied by isomerization and followed by ring closure.

The described procedure of preparation of naphthoxazolesulfonic acid applies to all 9-amino derivatives of naphtho[2,1-*d*]oxazole described in the previous paper [1]. All the derivatives prepared and defined so far are characterised by undergoing easy and safe diazotization and also by intense fluorescence, which makes them applicable to preparation of fluorescent brighteners. Inclusive of naphthoxazolesulfonic acid **III** this generally applies to the derivatives of 9-aminonaphthoxazole which are presented in Table 1 of the mentioned study [1].

Naphthoxazole Monoazo Dyes of General Formula **IV**

Below presented are examples of naphthoxazole monoazo dyes obtained by various syntheses and covering almost the whole gamut of dyes usable for dyeing wool and silk from acid bath.

Example 1

Sodium salt of 9-amino-2-phenylnaphtho[2,1-*d*]oxazole-4,7-disulfonic acid (22.1 parts) is diazotized by indirect method: 3.5 parts of sodium nitrite is added at the temperature of 10-15 °C, and the formed suspension of finely crystalline diazonium compound is used in the azo coupling reaction with aqueous solution of 17.4 parts of 8-hydroxynaphthalene-1,6-disulfonic acid with addition of 11 parts of sodium bicarbonate. After the azo coupling reaction is finished, the formed dye is precipitated by addition of sodium chloride, collected by suction and dried. Wool fibres are dyed with this product from a bath acidified with formic acid producing a brilliant red hue. The dyeing has very good fastness to light, water, washing and perspiration.

Example 2

The suspension of diazotised naphthoxazolesulfonic acid prepared in the same way as in Example 1 is mixed at the temperature of 10-15 °C with a fine suspension of 10.8 parts of acetoacet-*o*-anisidide, and the mixture is alkalized with 11 parts of sodium bicarbonate. After the azo coupling reaction is finished, the reaction mixture is heated to the temperature of 80 °C, the dye is precipitated with sodium chloride and collected by suction. The product is a yellow paste of virtually uniform azo dye, which gives a canary yellow hue on wool fibres. The dyeing has high fastness to light, water, washing and perspiration.

Example 3

The suspension of diazotised naphthoxazolesulfonic acid prepared in the same way as in Example 1 is mixed with 20 parts of 3-aminoacetanilide sulfate, and the mixture is treated with 200 volume parts of 20 % aqueous solution of sodium acetate. After 24 hours of azo coupling reaction at the temperature of 15-22 °C, the reaction mixture is heated to the temperature of 95 °C, and the dye is precipitated by addition of sodium chloride; it is isolated from cold slurry by suction and dried. It dyes wool from slightly acidic bath giving a reddish orange hue. The dyeing has high fastness to light and very good fastness to water.

Example 4

The suspension of diazotised naphthoxazolesulfonic acid prepared in the same way as in Example 1 is neutralized and added to a solution of 12.3 parts of 6-aminonaphthalene-2-sulfonic acid (sodium salt) with addition of 25 parts of crystalline sodium acetate. After 18-hour stirring, the red-brown precipitate of the dye is collected by suction, washed with 10 % solution of sodium chloride and dried. It dyes wool from acidic bath giving a red hue.

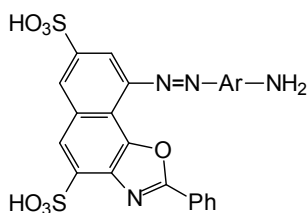
Table I presents further examples of naphthoxazole monoazo dyes prepared from naphthoxazolesulfonic acid **III**. From among the naphthoxazole monoazo dyes presented in Table I, the combination in example 16 is interesting, because it gives violet hue on wool, which is rare with monoazo dyes. This is assisted also by the bathochromic effect of the heterocycle attached to naphthalene nucleus, which manifests itself as early as diazotization: the obtained diazonium salt has a striking yellow colour hue.

Table I Naphthoxazole monoazo dyes prepared from naphthoxazoledisulfonic acid **III**

Example	Azo coupling component	Colour hue on wool
5	acetoacetanilide	greenish yellow
6	acetoacet- <i>o</i> -anisidide	brilliant yellow
7	2-naphthol	red
8	4-hydroxynaphthalene-1-sulfonic acid	bluish red
9	3-hydroxynaphthalene-2,7-disulfonic acid	bordeaux
10	6-hydroxynaphthalene-1,3-disulfonic acid	red
11	8-hydroxyquinoline	yellowish brown
12	3-aminonaphthalene-2,7-disulfonic acid	red
13	6-aminonaphthalene-1,3-disulfonic acid	yellowish red
14	6-aminonaphthalene-1-sulfonic acid	yellowish red
15	4-acetylamino-5-hydroxynaphthalene-2,7-disulfonic acid	reddish violet
16	4-benzoylamino-5-hydroxynaphthalene-2,7-disulfonic acid	violet
17	1-phenyl-3-methylpyrazol-5-one	orange

Naphthoxazole Dichlorotriazine Reactive Azo Dyes of General Formula **V**

The first step of preparation of these azo dyes consists in azo coupling reaction of diazotized naphthoxazoledisulfonic acid **III** with amino component to give aminoazo dye **XII**,

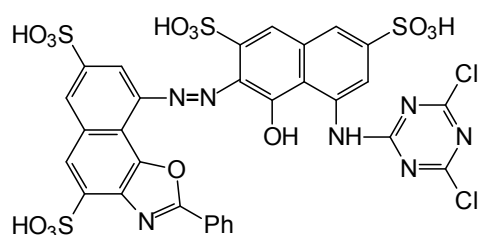


XII

where Ar means a bivalent residue of component with free amino group. In the second step of synthesis, the obtained dye **XII** is condensed with 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride).

Example of Preparation

The azo dye prepared in alkaline medium by the azo coupling reaction of diazotized naphthoxazolesulfonic acid **III** and 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (H-acid) is, with or without isolation, condensed at the temperature of 0-10 °C with a stoichiometric amount or slight excess of 2,4,6-trichloro-1,3,5-triazine (either powder or solution in inert water-miscible organic solvent). The resulting dichlorotriazine dye is isolated and after addition of stabiliser finalised by means of fluid drying. Chemically, the product is sodium salt of monoazo dye with four sulfonic groups **XIII**.



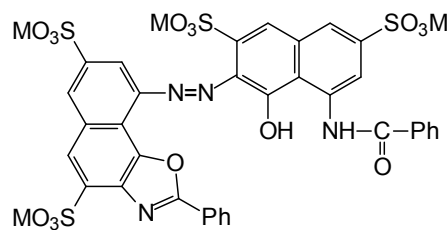
XIII

Dichlorotriazine naphthoxazole azo dyes of general formula **V** are prepared in analogous way when the H-acid used in the above example is replaced by amino components of benzene or naphthalene series, such as 3-aminoanisole, 3-aminophenol, 3-aminophenetole, 3-aminotoluene, 3-aminoacetanilide etc. From the naphthalene series we can mention naphthalene-1-amine, 8-aminonaphthalene-2-(or 3)-sulfonic acids (the so-called Cleve acids), 7-amino-4-hydroxynaphthalene-2-sulfonic acid, 4-amino-5-hydroxynaphthalene-1,3-disulfonic acid, and 8-amino-4-hydroxynaphthalene-2-sulfonic acid.

The given dichlorotriazine naphthoxazole azo dyes belong to the category of azo dyes that form covalent bond with the substrate; the dyeing thus possesses the maximum fastness properties to water and washing.

Water-insoluble Naphthoxazole Azo Dyes of General Formula **VI**

Also this group of azo dyes, the so-called azo lakes, is based on a single starting intermediate, namely the mentioned naphthoxazolesulfonic acid **III**. An example of this class is the monoazo dye with four sulfonic acid groups converted into suitable salt - formula **XIV**.



XIV

The symbol M means $\frac{1}{2}$ Ca and the preparation is performed as follows: 0.1 g/mol 9-amino-2-phenylnaphtho[2,1-*d*]oxazole-4,7-disulfonic acid is diazotized in indirect way with sodium nitrite, and the obtained suspension of finely crystalline diazonium compound is used in the azo coupling reaction in the presence of sodium bicarbonate with aqueous solution of sodium salt of 4-benzoylamino-5-hydroxynaphthalene-2,7-disulfonic acid (*N*-benzoyl-H-acid). The formed azo dye is isolated and then, in solution of fine suspension, it is allowed to react with calcium chloride solution at the temperature of 80-100 °C. The resulting calcium(II) azo lake is isolated, dried and then transformed into granules or fine powder as requested. It is also possible to mention other azo lakes, e.g., magnesium(II) and barium(II) ones or their mixtures, or an arbitrary mixture of lake-forming reagents can be adopted.

Naphthoxazole azo lakes belong to the class of highly valued organic pigments which are suitable for dyeing plastics: they neither diffuse nor migrate from the dyed substrate. In this respect they are comparable with the considerably more expensive pigments based on condensation azo dyes.

Conclusion

The invention of isomerization and dehydration cyclization in the series of 1-acylamino-8-hydroxynaphthalene (*peri*-acylaminonaphthol) means an improvement in the chemistry of organic compounds. It enables broadly-founded basic research in several areas of organic chemistry, primarily in the field of organic dyes, particularly azo dyes: in this branch this invention establishes a new group of intermediates and a new class of azo dyes derived from naphtho[2,1-*d*]oxazole. Other areas in which the mentioned invention of isomerization and cyclization is applicable involve the studies of pharmaceuticals and in particular the field of intensely fluorescing compounds that are suitable for preparation of fluorescent brighteners.

Acknowledgements

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References

- [1] Mužík F.: *Collection of Czechoslov. Chem. Commun.* **30**, 559-572 (1965).
- [2] Mužík F.: CZ patent No. 118 725 (1966).
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- [4] Mužík F.: *Collection of Czechoslov. Chem. Commun.* **25**, 2831-2840 (1960).