# Chemistry

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Structural formulas I–V

Figure 1: Structural formulas I–V

## Abstract

## Full Text

Chemistry

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# Polarographic Reduction and Infrared Spectra of Some *o*-Hydroxyazo Dyes

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For the purpose of a comparative spectral study, we synthesized a series of *o*-hydroxyazo dyes that contained carbazole residues either in the diazo component, or in the azo component, or in both simultaneously. In addition, the corresponding derivatives of *p*- and *m*-aminodiphenylamine and *p*- and *m*-aminodiphenyl were synthesized as model substances.

For a long time and up to the present, the structure of *o*-hydroxyazo dyes has been under discussion. For *o*-hydroxyazobenzene, evidence was adduced for the azo structure (1) I, while for 1-phenylazonaphthol-2 a quinone hydrazone structure II was proposed (2).

Ideas have been put forward concerning the presence of a dipolar ion III in the molecules of these compounds (3). I. Ya. Postovskii and I. F. Vladimirtsev (4), on the basis of data from polarographic reduction and IR spectra, explained the peculiarities in the properties of *o*-hydroxyazo dyes of the naphthalene series by the formation of a system with a hydrogen bond, owing to the lesser leveling of double bonds in the naphthalene ring IV.

Having at our disposal a number of new representatives of the class of 1-arylazonaphthol-2, for several compounds possessing sufficient solubility for this purpose, we carried out polarographic reduction and a study of the IR spectra, with the aim of obtaining an additional characterization of the structural features of substances of this type, and also of elucidating the influence of the structure of the diazo component, including a carbazole-containing one, on the ability of these compounds to be reduced at the dropping mercury electrode. For this purpose the azo dyes were reduced on a Heyrovský micropolarograph. The supporting electrolyte was a buffer solution containing 75% alcohol by volume, 0.1 N in $CH_3COOH$ and $CH_3COONa$, with pH 6.2. The concentration of azo compounds was $0.25 \cdot 10^{-4}$ mol/l–$1 \cdot 10^{-4}$ mol/l. The sensitivity of the galvanometer was equal–

was $8 \cdot 10^{-9}$ ampere. The capillary characteristic varied within the limits 1.82—1.77 $mg^{2/3} \cdot sec^{-1/2}$. The IR spectra were recorded on an IKS-14 spectrophotometer in the region 2.5—4 $\mu$ with a LiF prism in dioxane and dimethylformamide solution, and also in Vaseline oil, and in the region 5.8—10 $\mu$ with a NaCl prism in Vaseline oil.

The results of the polarographic reduction and the characteristic frequencies are given in Table 1.

As is seen from the data of Table 1, for all the studied *o*-hydroxy azo dyes the half-wave potentials lie within the range −0.35 to −0.57 V. If these values of the half-wave potentials are compared with $\varepsilon_{1/2}$ for compound V, which has an obviously quinonehydrazone structure and a half-wave potential equal to −0.22 V, then the conclusion suggests itself that, under the conditions of polarographic reduction, all the 1-arylazonaphthols-2 listed in Table 1 have an azo structure.

The shift of the half-wave potentials for the *o*-hydroxy compounds of the naphthalene series studied by us toward negative values, in comparison with the *o*-hydroxy compounds of the benzene series (−0.43 to −0.56 V and −0.30 to −0.35 V, respectively ([5])), indicates that for all the compounds, except that indicated in Table 1 as No. 14 ($\varepsilon_{1/2} = -0.34$ V), the assumption of the formation of a strong ring with a hydrogen bond is valid.

Comparing the obtained values of $\varepsilon_{1/2}$ with the half-wave potential for the simplest representative of this class of compounds (1-phenylazo-naphthol-2, No. 1 in Table 1), the following observations can be made.

The *p*-diphenylamino azo derivative (No. 2) has a half-wave potential shifted toward negative values, evidently because of the electron-donor effect of the phenylamino group, whereas the electron-acceptor *p*-phenyl residue in compound No. 6 exhibits the opposite effect and facilitates reduction of the azo group at the dropping mercury electrode. In the corresponding meta derivatives (Nos. 8 and 9, Table 1) a similar effect, as should have been expected, is not manifested, and $\varepsilon_{1/2}$ is shifted here only slightly toward negative values.

In the case of 1-carbazolylazo-naphthols-2, the character of the influence is determined by the position of the azo group in the carbazole molecule. The 3-aminocarbazole derivative (No. 3) has a value of $\varepsilon_{1/2}$ shifted toward negative values to the same extent as it is shifted in the case of the *p*-azodiphenylamino derivative. The 2-aminocarbazole derivative (No. 7) is an analog of the *p*-aminodiphenylamine derivative (No. 6) and has the same value of the half-wave potential as the latter. N-Alkylation of the carbazole residue changes scarcely at all the half-wave potentials of the corresponding carbazole derivatives (compare Nos. 3, 4, and 5).

In compounds Nos. 10, 11, 12, 13, in which the azo component is not $\beta$-naphthol but $\beta$-hydroxynaphthoic acid or its phenylamide (azotol A), an additional influence on the reducibility of the azo group is exerted by the amide or carboxyl group located in the naphthalene nucleus in the *o*-position to the hydroxyl. Despite its meta position relative to the azo group, the amide group, and especially the carboxyl group, weakens the hydrogen bond between the hydrogen of the hydroxyl and the nitrogen atom of the azo group, and also exerts an inductive electron-withdrawing influence on the azo group, which facilitates reduction of compounds Nos. 10, 11, 12, and especially compound No. 13 at the dropping mercury electrode.

On the basis of a comparison of the polarographic-reduction data with literature data ([4],[5] ), in general an azo structure may be assumed for compounds Nos. 10, 11, 12, 13, as well as for compounds Nos. 2—9.

As is seen from the data of Table 1, the infrared spectra do not give a clear answer regarding the structure of the compounds studied. Probably, because of the presence of strong intermolecular and intramolecular hydrogen bonds in the molecules of the compounds studied, in the solid state in the region 2.5—4 $\mu$ it is not possible to detect characteristic frequencies for the OH group or the NH group.

**Table 1**

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(1)$, V | $C$, mol/l | $I/d$, $\mu$A | Absorption bands characteristic for group –N=N– | Absorption bands characteristic for group –OH |
|---|---|---|---|---|---|---|---|
| 1 | Structural formula shown: phenyl-N=N-hydroxy-naphthyl | –0,52 | – | $0{,}25 \cdot 10^{-4}$ | 0,156 | | |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(1)$, V | $C$, mol/l | $I/d$, $\mu$A | Absorption bands characteristic for group –N=N– | Absorption bands characteristic for group –OH |
|---|---|---|---|---|---|---|---|
| 2 | Structural formula shown: phenyl-NH-phenylene-N=N-hydroxy-naphthyl | –0,55 | –0,02 | $0{,}25 \cdot 10^{-4}$ | 0,16 |  | 3426 $cm^{-1}$ |
| 3 | Structural formula shown: carbazolyl-N=N-hydroxy-naphthyl, carbazole N–H | –0,55 | –0,03 | $0{,}25 \cdot 10^{-4}$ | 0,116 | 1616 $cm^{-1}$ |  |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(1)$, V | $C$, mol/l | $I/d$, $\mu$A | Absorption bands characteristic for group –N=N– | Absorption bands characteristic for group –OH |
|---|---|---|---|---|---|---|---|
| 4 | Structural formula shown: N-methylcarbazolyl-N=N-hydroxy-naphthyl | –0,54 | –0,02 | $0{,}25 \cdot 10^{-4}$ | 0,12 |  | 3426 $cm^{-1}$ |
| 5 | Structural formula shown: N-$(CH_2CH_2CN)$carbazolyl-N=N-hydroxy-naphthyl | –0,56 | –0,04 | $0{,}25 \cdot 10^{-4}$ | 0,124 |  |  |
| 6 | Structural formula shown: biphenyl-N=N-hydroxy-naphthyl | –0,48 | +0,04 | $0{,}25 \cdot 10^{-4}$ | 0,296 | 1622 $cm^{-1}$ | 3460 $cm^{-1}$ |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(1)$, V | $C$, mol/l | $I/d$, $\mu$A | Absorption bands characteristic for group –N=N– | Absorption bands characteristic for group –OH |
|---|---|---|---|---|---|---|---|
| 7 | Structural formula shown: carbazolyl-N=N-hydroxy-naphthyl, carbazole N–H | –0,50 | +0,027 | $0{,}25 \cdot 10^{-4}$ | 0,146 | 1614 $\text{cm}^{-1}$ | |
| 8 | Structural formula shown: phenyl-NH-phenylene-N=N-hydroxy-naphthyl | –0,51 | +0,01 | $0{,}25 \cdot 10^{-4}$ | 0,14 | 1613 $\text{cm}^{-1}$ | |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(1)$, V | $C$, mol/l | $I/d$, $\mu$A | Absorption bands characteristic for group –N=N– | Absorption bands characteristic for group –OH |
|---|---|---|---|---|---|---|---|
| 9 | Structural formula shown: biphenyl-N=N-hydroxy-naphthyl | −0,51 | +0,01 | $0{,}25 \cdot 10^{-4}$ | 0,172 | 1620 $\text{cm}^{-1}$ | 3440 $\text{cm}^{-1}$ |

(continued)

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(4)$, V | $C$, mol/l | $I_d$, $\mu$A | Absorption bands characteristic for the group –N=N– | Absorption bands characteristic for the group –OH |
|---|---|---|---|---|---|---|---|
| 10 | [[structural formula: biphenyl-N=N-substituted 2-hydroxy-3-naphthanilide fragment, with CONH-phenyl group]] | −0,43 | +0,09 | $1 \cdot 10^{-4}$ | 0,168 | | |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(4)$, V | $C$, mol/l | $I_d$, $\mu$A | Absorption bands characteristic for the group –N=N– | Absorption bands characteristic for the group –OH |
|---|---|---|---|---|---|---|---|
| 11 | [[structural formula: phenyl-NH-phenylene-N=N-substituted 2-hydroxy-3-naphthanilide fragment, with CONH-phenyl group]] | −0,51 | +0,01 | $0{,}5\cdot10^{-4}$ | 0,132 | | |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(4)$, V | $C$, mol/l | $I_d$, $\mu$A | Absorption bands characteristic for the group –N=N– | Absorption bands characteristic for the group –OH |
|---|---|---|---|---|---|---|---|
| 12 | [[structural formula: phenyl-NH-phenylene-N=N-substituted 2-hydroxy-3-naphthanilide fragment, with CONH-phenyl group; different position of the phenylamino substituent]] | −0,44 | +0,08 | $0{,}5 \cdot 10^{-4}$ | 0,138 | | |

| No. | Dye formula | $\varepsilon_{1/2}$, V | $\Delta\varepsilon = \varepsilon_{1/2}(n) - \varepsilon_{1/2}(4)$, V | $C$, mol/l | $I_d$, $\mu$A | Absorption bands characteristic for the group –N=N– | Absorption bands characteristic for the group –OH |
|---|---|---|---|---|---|---|---|
| 13 | [[structural formula: biphenyl-N=N-substituted 2-hydroxy-3-naphthoic acid fragment, with COOH group]] | −0,34 | +0,18 | $0{,}5 \cdot 10^{-4}$ | 0,152 | | |

In a solution of dioxane and dimethylformamide, for some of the compounds studied it is possible to detect, in the region 3425-3460 $\mathrm{cm}^{-1}$, an absorption characteristic of a hydroxyl with a strong hydrogen bond [6]. In the region of 1620 $\mathrm{cm}^{-1}$, almost all the compounds studied show a distinct absorption which, by analogy with the absorption found for 2-hydroxyazobenzene, 1-phenylazonaphthol-2, and 1-(p-methoxyphenylazo)-naphthol-2, may be assigned to the absorption characteristic of the azo group.

Thus, the study of the IR spectra of the investigated 1-arylazonaphthols-2 confirms their azo structure and the probability of hydrogen-bond formation.

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*Note: Figure translations are in progress. See original paper for figures.*