

SYNTHESIZATION OF β -NAFTOLORANGE, AN AZO DYE WITH SUPERIOR PURITY

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Abstract

Azo dyes are a class of synthetic organic compounds that have wide use in the chemical industry. In the past only natural dyes were used for the dyeing of materials, obtained from plant or animal organisms, now the cultivation of plants has decreased because the synthetic substances much cheaper and much more varied in color and shades have developed.

In this paper we synthesized an azo dye, β -naftolorange, by a simple method of diazotating sulphanilic acid with sodium nitrite in the presence of hydrochloric acid and coupling with β -naftol. The resulting azocolor can be used in industry as a colouring substance because, from the analyses carried out, FTIR and calcination, it has been shown to have superior purity.

Keywords: azodyes, organic compounds, β -naftolorange, diazotating, coupling

INTRODUCTION

Azo dyes are natural or synthetic colored organic substances that have azo bond structure as chromophore group responsible for color production. In addition to azo bound -N=N-, chromophore groups can also be the nitroso -N=O groups and nitro -NO₂ groups. The dye in order to be able to color the materials on which they are applied, such as: textile fibers, food, medicines, cosmetics, etc. must also contain in structure auxochrome groups, that darken or intensify the color of the dye. Auxochromic groups in structure of azocolorants can be: amino-NH₂, hydroxylphenolic or its alkylated derivatives Ar-OH, Ar-OR (Banu et al., 2010, Neîțescu, 2015, Sahar, Manal, 2012, Marian et al., 2011).

Azo dyes are the most widespread and the most used dyes in almost all industries because they are the largest class of organic dyes, accounting for over 70% of world dye production. They have many advantages: have a low purchase price, the method by which they are obtained is simple, are not sensitive to temperature, light and oxygen (Dan et al, 2018, Allam et al., 2011, Farah et al, 2011).

Although azo dyes are of particular interest to the food industry, many studies show that when they enter the body, products resulting from

metabolism can affect people's health. The age categories most affected by these dyes are children, pregnant women and elderly that can cause them: allergies, intolerance, respiratory disorders, reproductive disorders, hyperactivity, carcinogenic effects, after long consumption (Parneli et al., 2014, Gültekin, Doguc, 2013, Sulekova et al., 2016, Orănescu, 2008).

IR spectrometry is a simple method, important for analytical chemistry and not only, frequently used to determine the functional groups in the structure of organic / medicinal substances, to identify pure compounds or to detect the presence of specific impurities in a substance (Muntean, Bojiță, 2004, Bojiță et al., 2003, Munajad, Subroto, 2018, Peyne et al., 2017, Wang et al., 2016, Ozgenc et al., 2017).

In this paper we synthesized by a diazotization and coupling reaction an azo dye, then we determined the reaction yield, we analyzed the structure of the compound using the FTIR method and the purity of synthesized product using the calcination method.

MATERIALS AND METHODS

MATERIALS

Sulphanilic acid or p-aminobenzenesulfonic acid and β -naphthol (Sigma-Aldrich), sodium hydroxide (Elemental SRL), sodium nitrite and sodium chloride (Silver Chemicals), hydrochloric acid (Chemical Company), 25 mm ultrapure filter paper PN1250025, FTIR 7800 PG Instruments spectrometer, Nabertherm calcination furnace, Binder ED 56 9010-0333 oven.

METHODS

5 g of sulfanylic acid are dissolved in 12.5 mL of 2 N NaOH, stirring continuously until complete dissolution. A solution containing 2 g NaNO_2 in 25 mL 4N HCl is added over it. The solution is prepared under a niche because when adding hydrochloric acid over the sodium nitrite, a lot of yellow nitrous vapors are released. After mixing to the two solutions, a thick suspension of p-diazobenzenesulphonic acid is formed, which is added dropwise with stirring to a solution of sodium β -naphtholate formed by dissolving 4 g of β -naphthol in 50 mL of 2N NaOH, at room temperature. The azo dye is immediately formed, which can be seen in the form of yellow-orange sheets.

A complete precipitation is made if a saturated NaCl solution is added. Filter on filter paper and then wash the azo dye with cold water. After filtration and washing, the β -naphtholorange obtained is dried in an oven at 40 °C for 6 hours until the mass of product remains constant. Weigh the mass of dye obtained and calculate the efficiency of diazotisation and coupling reaction.

FTIR spectrometric determinations of the base compounds and the final compound were performed at the spectral range 4000-400 cm^{-1} with a resolution of 2 cm^{-1} and KBr was used for pelleting. A calcination furnace with a heating range of 30-3000° C was used to determine the purity of the synthesized azo dye.

RESULTS AND DISCUSSIONS

After obtaining the azo dye, the reaction yield is calculated according to the formula:

$$\eta = \frac{m_p \times 100}{m_t}$$

m_p = practical mass (how much i got), m_t = theoretical mass (as I used), η = yield.

After replacing the values obtained in the formula, a good yield of 82.5% was obtained. The spectra of sulphanilic acid, β -naphthol and dye obtained were further analysed. Figure 1 shows the spectrum of β -naphthol and table 1 shows wave numbers, vibration intensity and vibrational attributions of β -naphthol.

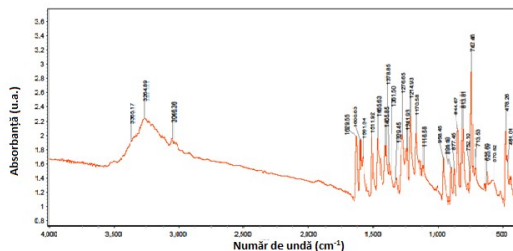


Fig.1. FTIR spectrum of β -naphthol on the 4000 – 400 cm^{-1}

Table 1.

Wave number, vibration intensity and vibrational attributions of β -naftol

| Wave number (cm^{-1}) | Vibration intensity | Vibrational attribution |
|----------------------------------|---------------------|---|
| 470.01 | Great | Deformation of the aromatic δ_{C-C} bond in the plane |
| 742.46 | Great | Deformatin in the plane of the connection δ_{C-C-O} |
| 813.81 | Great | Deformatin in the plane of the connection δ_{C-H} |
| 844.67 | Great | Out-of-plane deformation of the connection γ_{C-H} |
| 958.45 | Average | Vibration of the aromatic/naphthalnic ring |
| 1170.58 | Great | Stretching vibration ν_{C-O} of the phenolic hydroxyl group |
| 1214.93 | Very large | Stretching vibration ν_{C-O} of the phenolic hydroxyl group |
| 1276.65 | Great | Link stretching vibration ν_{C-C-O} |
| 1329.45 | Poor | Vibration of the aromatic/naphthalnic ring |
| 1378.85 | Poor | Aromatic stretching vibration ν_{C-C} |
| 1405.80 | Average | Vibration of the deformation of the link δ_{O-H} |
| 1465.63 | Average | Vibration of the aromatic/naphthalnic ring |
| 1511.92 | Great | Link stretching vibration ν_{C-C} |
| 1581.34 | Average | Vibration of deformation δ_{O-H} of the absorbed water |
| 1600.63 | Great | Vibration of the aromatic/naphthalnic ring |
| 1629.55 | Great | Stretching vibration ν_{O-H} of the absorbed water |
| 3046.36 | Poor | Aromatic stretching vibration ν_{C-H} |
| 3264.89 | Great | Vibration of the phenolic link ν_{O-H} |

It should be noted that in small wave numbers, the spectral bands correspond to the deformation of some links, while for the same links, the spectral bands corresponding to the stretching vibrations found in larger wave numbers. This is possible because the energy needed to change the amplitude of a deformation vibration is less than the energy needed to change the amplitude of a stretching vibration. Thus, the deformation of the aromatic C-C bond appears as a high-intensity vibration at 470.01 cm^{-1} , while the stretching vibration of the same link occurs at 1378.85 cm^{-1} and the intensity is low. The deformation vibration of the C-C-O bond occurs at 742.46 cm^{-1} and the stretching vibration of the same link occurs at 1276.65 cm^{-1} .

Stretching vibrations due to the aromatic ring occur in several wave numbers: 958.45 cm^{-1} (average), 1329.45 cm^{-1} (poor), 1465.63 cm^{-1} (average), 1600.63 cm^{-1} (great).

A vibration of very high intensity is represented by the stretch vibration of the C-O link in the phenolic hydroxyl group that occurs at the wave number 1214.93 cm^{-1} . Two other high-intensity vibrations are due to tensile vibrations of the C-C-O bound at 1276.65 cm^{-1} and C=C bound at 1511.92 cm^{-1} .

The FTIR spectrum of sulphanilic acid is shown in Figure 2.

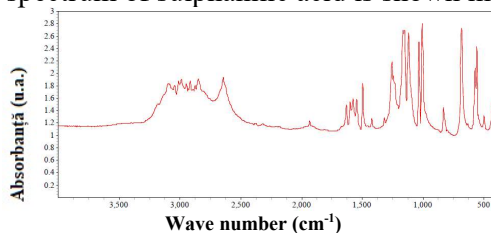


Fig. 2. FTIR spectrum of sulphanilic acid in the range $4000 - 400\text{ cm}^{-1}$

Spectral bands in FTIR of sulphanilic acid are shown in table 2.

Table 2.

Wave number, vibration intensity and vibrational attributions of the sulphanilic acid spectrum

| Wave number (cm^{-1}) | Vibration intensity | Vibrational attribution |
|----------------------------------|---------------------|---|
| 431.98 | Small | Deformation vibration in the plane δ_{C-C} |
| 559.26 | Average | Deformation vibration in the plane δ_{C-H} |
| 686.53 | Great | Deformation vibration in the plane δ_{N-H} |
| 825.36 | Small | Out-of-plan deformation vibration γ_{C-H} |
| 1008.59 | Great | Vibration of the stretching of the aromatic ring |
| 1033.66 | Great | Stretch vibration of the link ν_{C-N} |
| 1120.44 | Great | Stretch vibration of the link ν_{S-O} |
| 1155.15 | Great | Stretch vibration of the link ν_{N-H} |
| 1257.36 | Average | Stretch vibration of the link ν_{C-N} |
| 1496.49 | Average | Deformation vibration in the plane δ_{O-H} from water absorbed |
| 1546.63 | Small | Stretch vibration of the link ν_{C-C} |
| 1577.49 | Small | Deformation vibration in the plane δ_{O-H} from water absorbed |
| 1600.63 | Small | Vibration of the aromatic ring |
| 1628.91 | Small | Deformation vibration in the plane δ_{O-H} from water absorbed |
| 2642.00 | Small | Stretch vibration of the link ν_{O-H} from water absorbed |
| 2848.35 | Small | Stretch vibration of the link ν_{C-H} |
| 2989.12 | Small | Stretch vibration of the link ν_{C-H} |
| 3093.26 | Small | Stretch vibration of the link ν_{C-H} |

In the FTIR spectrum of sulphanilic acid can also be found deformation vibrations in the plane of the OH bonds (1496.49 cm^{-1} , 1577.49 cm^{-1}) and tensile vibrations of the OH bond (1628.91 cm^{-1} , 2642.00 cm^{-1}) from the water absorbed from atmosphere. The tensile vibrations of the C-H bonds have low intensity and are found at large wave numbers (2848.35 cm^{-1} , 2989.12 cm^{-1} , 3093.26 cm^{-1}) (Xi et al., 2019, Rudyk et al., 2019).

Spectral bands in the FTIR spectrum of β -naphtholorange are assigned according to table 3.

Table 3

Wave number, vibration intensity and vibrational attributions of β -naftolorange

| Wave number (cm ⁻¹) | Vibration intensity | Vibrational attribution |
|---------------------------------|---------------------|---|
| 480.19 | Small | Deformation vibration in the plane δ_{C-C} |
| 575.81 | Small | Deformation vibration in the plane δ_{C-H} |
| 698.11 | Small | Deformation vibration in the plane δ_{N-H} |
| 825.36 | Small | Out-of-plan deformation vibration γ_{C-H} |
| 1008.59 | Great | Vibration of the stretching of the aromatic ring |
| 1033.66 | Average | Stretch vibration of the link ν_{C-C-N} |
| 1118.51 | Great | Stretch vibration of the link ν_{S-O} |
| 1174.44 | Average | Stretch vibration of the link ν_{C-O} from O^-Na^+ |
| 1474.19 | Small | Deformation vibration in the plane δ_{O-H} |
| 1511.92 | Average | Stretch vibration of the link $\nu_{C=C}$ |
| 1570.23 | Small | The deformation vibration in the plane of the water absorbed |
| 1600.63 | Small | Vibration of the aromatic ring |
| 1619.91 | Small | Deformation vibration in the plane δ_{O-H} from water absorbed |
| 3056.34 | Small | Stretch vibration of the link ν_{C-H} |
| 3369.03 | Small | Stretch vibration of the phenolic link ν_{O-H} |

In β -naphtholorange spectrum, most vibrations are found encountered in FTIR spectra of the reactants, less tensile vibrations of the N-H bond, a bond that has partially disappeared. Thus, the stretching vibration of the N-H bond from 1155.15 cm⁻¹ and the stretching vibrations of the C-H bond from large wave numbers (2642.00, 2848.35 and 2989.12 cm⁻¹) disappear. However at 698.11 cm⁻¹ the deformation vibration is found in δ_{C-C-O} plane, even if its intensity is very low. This could be explained by the fact that reaction product is not completely pure, it may present sulfanilic acid as traces / impurities.

The rest of vibrations that occur in spectrum of the reaction product are vibrations characteristic of covalent bonds. One can also notice the δ_{C-C-O} deformation vibration, vibration that occurs at 752.19 cm⁻¹, has low intensity, unlike β -naphthol spectrum, where vibration intensity was very high. A vibration that decreases in intensity is ν_{C-O} , a vibration that occurs at 1174.44 cm⁻¹. Also, the presence in the β -naphtholorange spectrum of the deformation vibration in the δ_{H-O} plane, even if it has a very low intensity, can also lead to idea that the reaction product is also impure with β -naphthol. There are two other vibrations whose intensity has decreased, the tensile vibration of C-H bond (3056.34 cm⁻¹) and the tensile vibration of phenolic O-H bond, probably trace / impurity in the reaction product.

Presence of azo bond, -N=N-, can only be observed in color of the synthesized azo dye, because bond does not show infrared vibration.

Determination of purity of the synthesized azo dye could be performed by calcining a small amount in a calcination furnace. The calcination was carried out for 90 minutes and temperature reached by the oven was 1000 °C. The sample taken was dried in an oven at 80 °C for 60 minutes to remove water that was absorbed in the synthesis step, then triturated until a very fine

powder was obtained. The analysis was performed in triplicate. By calcining the samples, an amount of ash remained, which consists of metal oxides (Na_2O) contained in azo dye.

Amount of samples taken to be calcined and amount of ash remaining after calcination are given in Table 4.

Table 4.

Data obtained when calcination of the naftolorange

| Sample/Mass | Crucible mass naked (g) | Calcinating sample mass (g) | Crucible mass + sample (g) | Sodium oxide mass resulting from calcination $m_{\text{Na}_2\text{O}}(\text{g})$ | Mass of sodium oxide found in the calcinating sample (g) | Sample purity (%) |
|-------------|-------------------------|-----------------------------|----------------------------|--|--|---------------------|
| (1) | (2) | (3) | (4) = (2)+(3) | (5) | (6) | (7) = (5) x 100/(6) |
| P1 | 19.7316 | 1.2885 | 21.0201 | 0.2088 | 0.2147 | 97.25 |
| P2 | 19.4768 | 1.3258 | 20.8026 | 0.2133 | 0.2209 | 96.56 |
| P3 | 18.5489 | 1.4256 | 19.9745 | 0.2301 | 0.2376 | 96.88 |

Analysis of purity of the azo dye using the calcination method has led to conclusion that synthesized β -naphtholorange has a relatively good purity for the reaction product to be used for industrial purposes ($96.90 \pm 0.35 \%$).

CONCLUSIONS

Azo dyes are natural organic or synthetic coloured substances containing the azo group and having the ability to colour the materials on which they are applied. Synthesis of the β -naphtholorange by the diazotation and coupling reaction had a relatively good yield and was demonstrated using FTIR spectrophotometry. Determination of purity of the synthesized azo dye has shown that it has good purity, so it can be used for industrial purposes.

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