

## SYNTHESIZATION OF $\beta$ -NAFTOLORANGE, AN AZO DYE WITH SUPERIOR PURITY

Frenț Olimpia-Daniela\*, Dejeu Ioana-Lavinia\*, Tunduc Ioana\*\*,  
Zbârcea Claudia\*\*\*, Marian Eleonora\*

\*University of Oradea, Faculty of Medicine and Pharmacy, 1 December Square, Oradea, Romania

\*\*pharmacist

\*\*\*Secondary School "Mrs. Oltea", Oradea, Romania

E-mail: [ioana.dejeu@gmail.com](mailto:ioana.dejeu@gmail.com), [daniela.olimpia@yahoo.com](mailto:daniela.olimpia@yahoo.com)

### 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,  $\beta$ -naftolorange, by a simple method of diazotating sulphanilic acid with sodium nitrite in the presence of hydrochloric acid and coupling with  $\beta$ -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,  $\beta$ -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 -NO<sub>2</sub> 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-NH<sub>2</sub>, hydroxylphenolic or its alkylated derivatives Ar-OH, Ar-OR (Banu et al., 2010, Neițescu, 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  $\beta$ -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  $\text{NaNO}_2$  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  $\beta$ -naphtholate formed by dissolving 4 g of  $\beta$ -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  $\beta$ -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  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  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),  $\eta$  = yield.

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

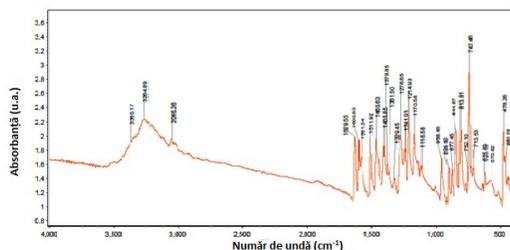


Fig.1. FTIR spectrum of  $\beta$ -naphthol on the 4000 – 400  $\text{cm}^{-1}$

Table 1.

Wave number, vibration intensity and vibrational attributions of  $\beta$ -naftol

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

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  $470.01\text{ cm}^{-1}$ , while the stretching vibration of the same link occurs at  $1378.85\text{ cm}^{-1}$  and the intensity is low. The deformation vibration of the C-C-O bond occurs at  $742.46\text{ cm}^{-1}$  and the stretching vibration of the same link occurs at  $1276.65\text{ cm}^{-1}$ .

Stretching vibrations due to the aromatic ring occur in several wave numbers:  $958.45\text{ cm}^{-1}$  (average),  $1329.45\text{ cm}^{-1}$  (poor),  $1465.63\text{ cm}^{-1}$  (average),  $1600.63\text{ cm}^{-1}$  (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  $1214.93\text{ cm}^{-1}$ . Two other high-intensity vibrations are due to tensile vibrations of the C-C-O bound at  $1276.65\text{ cm}^{-1}$  and C=C bound at  $1511.92\text{ cm}^{-1}$ .

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

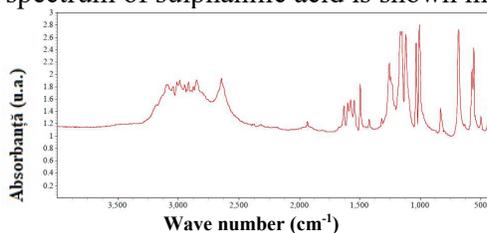


Fig. 2. FTIR spectrum of sulphanilic acid in the range  $4000 - 400\text{ cm}^{-1}$

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

The sulfanilic acid spectrum can be interpreted taking into account structure of organic compound, which contains a benzene nucleus, sulfonic and amino groups. Thus in addition to the vibrations characteristic of the benzene nucleus, deformation and stretching vibrations of the functional groups that are grafted on the benzene nucleus will appear. Deformation vibrations in plane of the C-C ( $431.98\text{ cm}^{-1}$ ), CH ( $559.26\text{ cm}^{-1}$ ), NH ( $686.53\text{ cm}^{-1}$ ) bonds and deformation vibration off-plane of the CH ( $825.36\text{ cm}^{-1}$ ) bonds are vibrations that find at small wave numbers in FTIR spectrum. The tensile vibrations of aromatic ring occur at  $1008.59\text{ cm}^{-1}$  of high intensity and at  $1600.63\text{ cm}^{-1}$  of low intensity. Three vibrations of very high intensity are those due to the tensile vibrations of the C-CN bonds ( $1033.66\text{ cm}^{-1}$ ), S=O bond ( $1120.44\text{ cm}^{-1}$ ) and NH bond ( $1155.15\text{ cm}^{-1}$ ) (Sonibare et al, 2010).

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

The FTIR spectrum of  $\beta$ -naphtholorange is represented in figure 3.

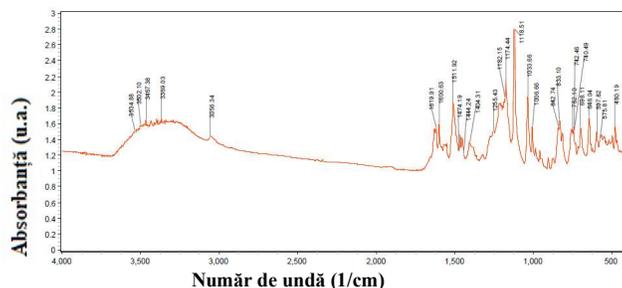


Fig. 3. FTIR spectrum of synthesized dye ( $\beta$ -naphtholorange) in the  $4000 - 400\text{ cm}^{-1}$

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

Table 3

Wave number, vibration intensity and vibrational attributions of  $\beta$ -naftolorange

Wave number (cm <sup>-1</sup> )	Vibration intensity	Vibrational attribution
480.19	Small	Deformation vibration in the plane $\delta_{C-C}$
575.81	Small	Deformation vibration in the plane $\delta_{C-H}$
698.11	Small	Deformation vibration in the plane $\delta_{N-H}$
825.36	Small	Out-of-plan deformation vibration $\gamma_{C-H}$
1008.59	Great	Vibration of the stretching of the aromatic ring
1033.66	Average	Stretch vibration of the link $\nu_{C-N}$
1118.51	Great	Stretch vibration of the link $\nu_{S-O}$
1174.44	Average	Stretch vibration of the link $\nu_{C-O}$ from $O^{Na^+}$
1474.19	Small	Deformation vibration in the plane $\delta_{O-H}$
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 $\delta_{O-H}$ from water absorbed
3056.34	Small	Stretch vibration of the link $\nu_{C-H}$
3369.03	Small	Stretch vibration of the phenolic link $\nu_{O-H}$

In  $\beta$ -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<sup>-1</sup> and the stretching vibrations of the C-H bond from large wave numbers (2642.00, 2848.35 and 2989.12 cm<sup>-1</sup>) disappear. However at 698.11 cm<sup>-1</sup> the deformation vibration is found in  $\delta_{C-C-O}$  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  $\delta_{C-C-O}$  deformation vibration, vibration that occurs at 752.19 cm<sup>-1</sup>, has low intensity, unlike  $\beta$ -naphthol spectrum, where vibration intensity was very high. A vibration that decreases in intensity is  $\nu_{C-O}$ , a vibration that occurs at 1174.44 cm<sup>-1</sup>. Also, the presence in the  $\beta$ -naphtholorange spectrum of the deformation vibration in the  $\delta_{H-O}$  plane, even if it has a very low intensity, can also lead to idea that the reaction product is also impure with  $\beta$ -naphthol. There are two other vibrations whose intensity has decreased, the tensile vibration of C-H bond (3056.34 cm<sup>-1</sup>) 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 ( $\text{Na}_2\text{O}$ ) 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  $\beta$ -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  $\beta$ -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.

## REFERENCES

- Allam K. V., G.P. Kumar, 2011, Colorants the cosmetics for the pharmaceutical dosage forms, International Journal of Pharmacy and Pharmaceutical Sciences, 3, 20, 1-9
- Banu C., A. Stoica, N. Buțu, E. Bărășescu, D. Resmeriță, C. Vizireanu, C. Lungu, M. Jordan, 2010, Aplicații ale aditivilor și ingredientelor în industria alimentară, Ed. Asab București, 11-26-48-866
- Bojiță M., R. Săndulescu, L. Roman, R. Oprean, 2003, Analiza și controlul medicamentelor, vol. II, Editura Intelcredo Deva, 210-250
- Constantin D.N., 2015, Chimie organică, vol I, București
- Dan O. D., L. Vicaș, E. Marian, 2018, Impact of azo dyes on the body and their use in the food industry and pharmaceuticals, Analele Universității din Oradea, Fascicula: Protecția Mediului, 31, 22, 251-256
- Farah M., C. Drumond, J.K. Dorta, D.P. Oliveira, 2010, Azo dyes and their metabolites: does the discharge of the azo dye into water bodies represent human and ecological risks?, Advance in Treating Textile Effluent, DOI: 10.5772/19872, 1-24

7. Gültekin F., D.K. Doguc, 2012, Allergic and immunologic reactions to food additives, *Clinical Reviews In Allergy & Immunology*, 45, 1, 6–29
8. Marian E., T. Jurca, L. Vicas, I. Kacso, M. Miclaus, I. Bratu, 2011, Inclusion compounds of erythromycin with b-cyclodextrin, *Revista de Chimie*, 62, 11, 1065-1068
9. Munajad A., C. Subroto, 2018, Fourier transform infrared (FTIR) spectroscopy analysis of transformer paper in mineral oil-paper composite insulation under accelerated thermal aging, *Energies*, 11, 2, 364
10. Muntean D.L., M. Bojița, 2004, *Controlul medicamentelor. Metode spectrale, cromatografice și electroforetice de analiză*, Editura Medicală Universitară Iuliu Hațieganu, Cluj-Napoca, 98-130
11. Orănescu E., 2008, *Aditivi alimentari, necesitate și risc*, Ed. Agir, București, 3-46
12. Ozgenc O., S. Durmaz, S. Kuştaş, 2017, Chemical analysis of tree barks using ATR-FTIR spectroscopy and conventional techniques, *BioResources*, 12, 4, 9143-9151
13. Parnali C., M.M. Alvi, 2014, Excipients and active pharmaceutical ingredients, *Pediatric Formulations*, 347-361
14. Payne J., J. Gautron, J. Doudeau, E. Joussein, S. Rossignol, 2017, Influence of calcium addition on calcined brick clay based geopolymers: a thermal and FTIR spectroscopy study, *Construction and building materials*, 152, 794-803
15. Rudyk, R. A., M.A. Checa, C.A. Catalán, S.A. Brandán, 2019, Structural FT-IR, FT-Raman and ECD studies on the free base, cationic and hydrobromide species of scopolamine alkaloid, *Journal of Molecular Structure*, 1180, 603-617
16. Sahar S. A. S., Manal M.E.M.S., 2012, The effects of using color foods of children on immunity properties and liver, kidney on rats, *Food and Nutrition Sciences*, 3, 7, 897-904
17. Sonibare O.O., T. Haeger, S.F. Foley, 2010, Structural characterization of Nigerian coals by X-ray diffraction, Raman and FTIR spectroscopy, *Energy*, 35, 12, 5347-5353
18. Sulekova M., A. Hudák, M. Smrcova, 2016, The determination of food dyes in vitamins by RP-HPLC, *Molecules*, volume 21, 10, 1-8
19. Wang Q., J.B. Ye, H.Y. Yang, Q. Liu, 2016, Chemical composition and structural characteristics of oil shales and their kerogens using Fourier Transform Infrared (FTIR) spectroscopy and solid-state <sup>13</sup>C Nuclear Magnetic Resonance (NMR), *Energy & Fuels*, 30, 8, 6271-6280
20. Xi X., S. Jiang, W. Zhang, K. Wang, H. Shao, Z. Wu, 2019, An experimental study on the effect of ionic liquids on the structure and wetting characteristics of coal, *Fuel*, 244, 176-183