

SELECTIVE ORGANIC REACTIVE FOR DETERMINATION OF SEVERAL HEAVY METALS FROM DIFFERENT MATERIALS

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ABSTRACT

The research regarding the synthesis and characterization of tiobis-β-naphthol have established that it can be used as an efficient analytical reactive for separating through extraction the heavy metals in watery environments.

These studies have been presented in the CALIST program.

KEYWORD: organic reagents, heavy metals, residual waters

1. General

The practical and theoretical interest attached to the organic reactants is reflected by the large number of researchers which have focused their attention to this field and also by the significant contribution of this class of compounds to the development of the analytical chemistry. Due to the importance and advantages of the organic reactants, the studies carried out in this paper have been oriented so as to extend their scope of application.

The synthesis and critical approach of the literature to the chemistry of tiobis-β-naphthol and its derivatives have highlighted the theoretical and practical importance of the tiobisphenol due to their reactivity and possibilities of use in various fields especially as analytical reactant. In spite of this, only one application of tiobisphenol is known, namely reactant to gravimetrically determine the copper.

Tiobisphenol are organic combinations having the general formula R₂S, hypothetically generated from sulphide hydrogen by substituting the hydrogen atoms with phenol radicals. When R = - C₁₀H₆ - OH, tiobisphenol is formed.

The researches carried out under the CALIST program have significantly contributed to both the synthesis and characterization of tiobis-β-naphthol so as to make it usable as analytical reactant. Thus, the items below have been approached :

- synthesis and purification of the reactant;
- the study of the electronic spectra UV-VIS and IR
- solubility in different solvents

- the dissociation constant, identification reactions and reactivity with respect to some metal ions

The researchers have shown that the tiobis-β-naphthol can be used as efficient reactive in the extraction of some heavy metals from watery environment.

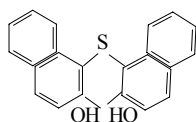
2. Synthesis of tiobis-β-naphthol

In order to obtain the tiobis-β-naphthol through a fast synthesis and from available substances a comparative study of the various preparation methods described by the literature has been carried out. To prepare the reactant, Tassinari's method has been chosen as amended by Kulkarni and Jadhov: sulphuration of the β-naphthol with sulphide dichloride as using as solvent the ethyl anhidru ether, a method which has been completed by the authors

Purity was found by melting point determination and elementary chemical analysis performance. Carbon and hydrogen were determined by gravimetric method using instruments for elementary analysis made by Knobloch.

The sulphide has been determined by desaggregation of the tiobis-β-naphthol in a nickel crucible with a mixture of anhidru sodium carbonate and sodium peroxide; from the melt dissolved into distilled water and further acidulated by HCl and barium sulphide has been precipitated to be subsequently filtered, dried, calcinated and weighted.

The elementary analysis of the tiobis-β-naphthol, with the chemical formula



is given in Table 1.

The melting point is 216 °C and the color is white.

Table 1

Chemical analysis, %	C	H	S
Calculated	75,45	4,40	10,07
Found	75,21	4,22	10,00

In order to highlight the spectral properties and make clear the reactivity if the tiobis-β-naphthol under different conditions, the synthesis of dehidrotiobis-β-naphthol and the tiobis-β-naphthol isomer has been performed with the melting point of 156°C (isosulphide). The clarifications were necessary in order to use the tiobis-β-naphthol as analytical reactant

3. Electronic UV-VIS spectra

In order to characterize the initial reactants, to clarify the development of the used reactions and to subsequently compare the newly sintered substances, the UV-VIS spectra were recorded. To identify the UV absorption bands, the specific absorptions of the β-naphthol, taken as reference term, were taken into account acc to fig.1.

In Table 2 the position and intensity of the absorption bands peaks characteristic to the studied compounds.

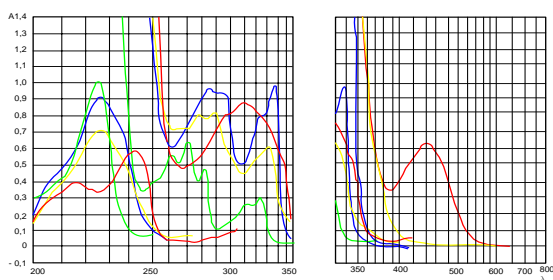
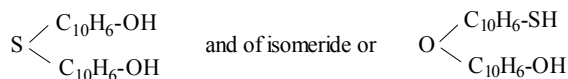


Fig. 1. Electronic absorption spectra UV-VIS

— tiobis-β-naphthol — isosulphide
 — β-naphthol — dehydrosulphide

The UV VIS absorption spectra of the tiobis-β-naphthol, represented by chemical formula



is similar to the β-naphthol absorption spectrum.

Table 2. Position and intensity of the peaks of the absorption bands

compound		β-naphthol	isosulphide	tiobis-β-naphthol	dehydrosulphide
E	λ max [nm]	225	225	225	216
	ε [l·mol ⁻¹ ·cm ⁻¹]	100000	71000	91000	38500
K	λ max [nm]	-	-	-	242
	ε [l·mol ⁻¹ ·cm ⁻¹]	-	-	-	59000
B	λ max [nm]	272	278	284	312
	Δ λ	-	6	10	40
	ε [l·mol ⁻¹ ·cm ⁻¹]	6440	8180	9700	8800
R	λ max [nm]	328	333	336	444
	Δ λ	-	6	9	117
	ε [l·mol ⁻¹ ·cm ⁻¹]	3000	6200	9900	636

With all three substances the three types of bands characteristics to the substituted aromatic compounds are to be found. The peaks of the absorption bands E, due to the transitions, π → π* are located at 225 nm. Since transition is high, the band is of high intensity, decreasing from β-naphthol to isosulphide.

The bands of type benzenoidic – B, datorate tot unor tranziții π → π*, specific to the aromatic nucleus, have the peaks situated within the range 272 – 282 nm. They are of low intensity and therefore they are forbidden. Since on the aromatic nuclei of the naphthalene auxochrome groups +E, having non participating electron pairs (-S, -OH, -O-, -SH) are inserted, possible transitions n → π* occur which

form radical bands R with absorption peaks within the range 327–336 nm. Representing auxochrome groups +E, they are capable of interacting by conjugation $p \rightarrow \pi$ with the electrons π of the aromatic nuclei. Thus, the sulphide of the β -naphthol causes a bathochrome displacement to the maximum of the bands B and R, simultaneously with a general effect of hyper-chrome. The fine structure of the bands almost disappears. The bathochrome activity of the substituting element is even more obvious when the hetero-atom is less electronegative, which means it has more flexible non-participating electrons. The bathochrome influence increases from iso-sulphide to di- β -naphthol, the bridging hetero-atom playing an important role. The dehydrosulphide features a characteristic electronic absorption spectrum. When $\lambda = 242$ nm, the absorption peak belonging to the conjugated band occurs-K of high intensity, accounted for by the existence of an unsaturated group which can be conjugated with the electrons π of the aromatic nucleus; ea se datorează unor tranziții $\pi \rightarrow \pi^*$. The radical band, because of the transition n

$\rightarrow \pi^*$ of the quinone group >C=O , appears displaced to the visible area, featuring an absorption peak of $\lambda = 444$ nm.

4. The IR spectra

The IR spectra for tiobis- β -naphthol were studied to examine their molecular structure and also to serve as reference for the comparison with other IR spectra of the derivative compounds and isolated in solid state. Thus information could be gathered with respect to the nature of their chemical bonds. The IR spectra fall within the range $400\text{--}4000\text{ cm}^{-1}$, in solid state with substances included into the potassium bromide on a Spectrometer Specord.

The IR absorption spectra are interpreted according to the literature, the specific bands being allocated according to the structure β -naphthol, tiobis- β -naphthol, dehydrosulphide and isosulphide (fig 2,3).

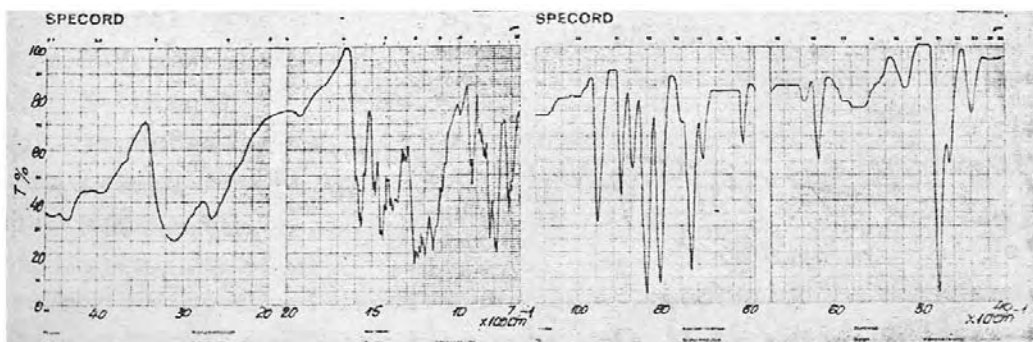


Fig. 2. IR spectrum of β -naphthol.

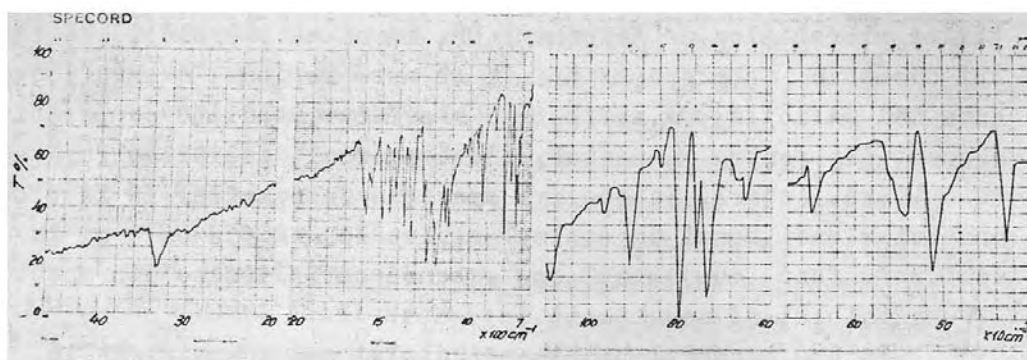


Fig. 3. IR spectrum of tiobis- β -naphthol.

The valence vibration frequency of the hydroxyl group (ν OH) looks like a well defined band with $\lambda = 3365\text{ cm}^{-1}$, for tiobis- β -naphthol and $\lambda = 3240\text{ cm}^{-1}$ for isosulphide; since the dehydrosulphide has no OH groups, it has no absorption either in the range $3000\text{--}3600\text{ cm}^{-1}$. The tiobis- β -naphthol and its isomer, by position α

containing electron donor atoms able to form hydrogen bonds with the hydroxyl group from position β has, in addition to the free ν OH bands corresponding to the associated hydroxyl of lower frequency ($\lambda = 3330\text{ cm}^{-1}$ and $\lambda = 3230\text{ cm}^{-1}$ respectively). In the range $1000\text{--}1250\text{ cm}^{-1}$ an intense valence vibration ν C-OH occurs, situated at

$\lambda=1190\text{ cm}^{-1}$ for tiobis- β -naphthol and $\lambda=1195\text{ cm}^{-1}$ for isosulphide.

The bands of the C-S bond are presented in the area $600 - 700\text{ cm}^{-1}$ range, of low intensity. Since with the aromatic compounds, due to the Ch deformation vibration outside the aromatic ring, identification becomes more and more difficult, allocation taking into account the absorbtions for the β -naphthol, tiobis- β -naphthol, dehydrosulphide and isosulphide.

Thus in the IR spectrum a band of $\lambda = 650\text{ cm}^{-1}$ peak becomes obvious with the tiobis- β -naphthol and with the dehydrosulphide with $\lambda = 652\text{ cm}^{-1}$, bands which are absent in the spectrum of the β -naphthol and isosulphide.

For the isomer of the tiobis- β -naphthol an absorbtion band was identified at $\lambda = 2500\text{ cm}^{-1}$ featuring a much lower intensity than that of the -OH group which is characteristic to the valence vibration $\nu\text{ S-H}$.

With iso- and dehydrosulphide, there appear the vibrations specific to the absorbtions $\nu_{\text{C-O-C}}$ assimilated with $\lambda = 1240\text{ cm}^{-1}$ and $\lambda = 1220\text{ cm}^{-1}$ respectively and absorbtions $\nu_{\text{C-O-C}}$ simmilar with $\lambda = 1060\text{ cm}^{-1}$ and $\lambda = 1020\text{ cm}^{-1}$ (less intense than the first).

The appearance of the carbonyl group with the oxidation compound of the tiobis- β -naphthol is accounted for by the presence in the IR spectrum of a band which is intense at $\lambda = 1650\text{ cm}^{-1}$, allocated to the valence vibration $\nu_{\text{C=O}}$.

The study of the UV-VIS and IR spectra carried out for the first time on the tiobis- β -naphthol of the oxidation product-dehydrotiobis- β -naphthol and its isomer - isosulphide - have enabled the identification of the functional groups, in compliance with the structure proposed for these compounds.

5. Solubility of the tiobis- β -naphthol

The literature only provides qualitative indications on the solubility of the tiobis- β -naphthol in some usual solvents. To determine different possibilities of using this substance in the analytical chemistry, its solubility was determined in a number of 27 solvents of different types. Determinations were made at $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$. By using the solvent classification system acc to the donor-acceptor properties, we get the data in table 3.

The tiobis- β -naphthol is slightly soluble in protophiles and amphiprotos, such as cetones and esthers ; it is very little soluble in alcohols, ether or glacial acetic acid. The lowest solubility is to be found with the aprotic solvents. It is insoluble in formic acid and ordinary gasoline.

At the same time, solvents do influence the electronic spectra.

Table 3.

Solvent	Solubility (g/l)
A. Protolitici	
a. Protofilii	
Dimethyl formamide	293,7
1-4 Dioxan	192,0
b. Amfiprotici	
- Ketone	
Acetone	97,5
Metiletilcetonă	98,0
Metil-npropilcetonă	71,9
Acetil-acetonă	48,0
- Esters	
Acetat de etil	98,3
Acetat de n-butil	22,4
- Alcoolii	
Methanol	9,0
Ethanol	8,0
N-propane	9,8
N-butane	5,3
Izobutanol	7,1
- Nitroderivați	
Nitrometan	1,3
Nitrobenzen	14,4
- Eteri	
Ether ethylic	9,5
c. Protogeni	
Acid formic	-
Acetic acid	5,4
B. Aprotici	
Phenyl methane	5,5
Chloroform	5,9
O-xylene	1,9
Carbon dusulphide	1,2
Benzene	1,1
Ligroină	0,7
Eter de petrol	0,4
Tetraclorură de carbon	0,5
Gas	-

Thus both the position and shape of the absorbtion peaks along with the UV-VIS spectra band intensity are influenced by the solvent polarity. The positions of the absorbtion band peaks recorded for tiobis- β -naphthol in three solvents of different polarities are given in table 4.

Table 4. Influence of solvents on the absorbtion band peaks of the tiobis- β -naphthol

Solvent	Dielectric constant	transition	
		$\pi \rightarrow \pi^*$ $\lambda\text{ max}$	$n \rightarrow \pi^*$ $\lambda\text{ max}$
n-heptan		281,7	333,3
Ethylic alcohol	24,3	283,6	336,0
Methylic alcohol	32,6	285,6	338,0

Under the solvent action, a positive solvent – chromatic effect is visible with both types of transition; the bathochrome displacement, with an increased solvent polarity, is low. Usually, the absorption band corresponding to the transitions of type $\pi \rightarrow \pi^*$ move bathochromally when the solvent polarity increases; the excited state is more polar than the fundamental state as it is strongly stabilized by a polar solvent (the energy required for the electronic transition decreases).

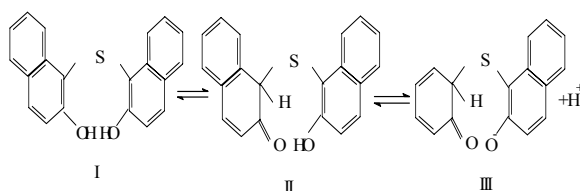
The hydrogen bonds between the solute and the solvent also affect the shape of the electronic spectra. The protic solvents easily form hydrogen bonds with the atoms containing non-participating electrons. That is why the bands corresponding to transitions $n \rightarrow \pi^*$ are affected by the protic solvents. The formation of hydrogen bonds causes the absorption bands to move bathochromally to the molecules where the dipole moment of the excitation state is higher than the dipole moment of the fundamental state.

6. Determining of tiobis- β -naphthol dissociation constant

It is important to know the value of the analytical reactant dissociation constant in order to better understand the structure of the organic molecule and be able to predict their chemical behavior for analysis purpose.

In order to determine the dissociation constant the spectro-photometric method was used.

The tiobis- β -naphthol dissociation could be represented as follows:



Structure III, proposed for the dissociated form of the tiobis- β -naphthol is accounted for by the aspect of the absorption spectrum in UV-VIS (Fig. 4). From the spectrum it is visible the existence of an absorption peak, at $\lambda = 244$ nm, which might be assigned to a band K ($\pi \rightarrow \pi^*$), which is further due to an unsaturated group conjugated with the electrons π of the aromatic nucleus. With the dehydro-di- β -naphthol monosulfura (Fig.1), band K features an absorption peak at $\lambda = 242$ nm. The radical band R looks a little displaced for tiobis- β -naphthol at pH = 13 toward higher wave lengths, $\lambda_{\max} = 362$ nm. Therefore, to determine the acid dissociation constant the simplified Comar method can be used. For the measurement purpose, those wave lengths have been chosen where only the reactive dissociated form is absorbing. From fig 4 it

can be seen then, from $\lambda = 370$ nm, the tiobis- β -naphthol dissolved into etilic or metilic alcohol, at pH<7 features no absorption.

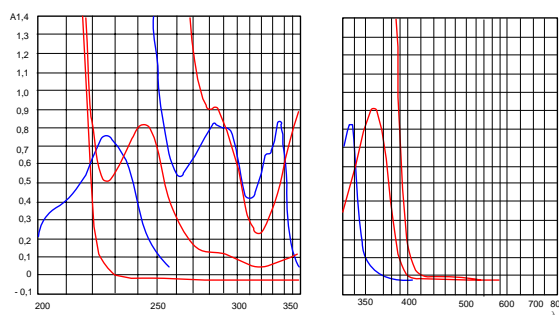


Fig. 4. Electronic absorption spectra UV-VIS at tiobis- β -naphthol
 — etilic alcohol solvent
 — pH=13

The reactant, dissolved into a NaCl solution, with pH=13 at the same concentration features absorption at $\lambda = 420$ nm. From the above reasons, measurements have been carried out at $\lambda_1 = 400$ nm and respectively $\lambda_2 = 410$ nm. A number of solutions of constant reactant concentration have been prepared, equal to 10^{-3} mol/l and different values of the pH; the absorbances at the chosen wave lengths have been measured. Assuming that the reactant dissociates with a monobase acid, acc to the scheme $HR = H^+ + R^-$, then its dissociation constant shall take the values :

$$K_{HR} = \frac{[H^+] \cdot x}{c - x} \quad (1)$$

Where:

- [H] = concentration of the hydrogen ions;
- x - balance concentration of the reactant dissociation;
- c - total concentration of the reactant.

Acc. to the light absorption law, the sum of the reactant dissociated and non-dissociated absorbances is:

$$A = \varepsilon_{HR} \cdot l (c - x) + \varepsilon_{R^-} \cdot l \cdot x \quad (2)$$

Where:

- ε_{HR} și ε_{R^-} – molar coefficients of HR and R^- absorption respectively
- l – making.

For the particular case of (2), for $\varepsilon_{HR} = 0$, we get:

$$x = \frac{A}{\varepsilon_{R^-} \cdot l} \quad (3)$$

By introducing x in the dissociation constant equation, we get a two-unknown value relation K_{HR} and ε_R^- :

$$K_{HR} = \frac{[H^+] \frac{A}{\varepsilon_R^- \cdot l}}{c - \frac{A}{\varepsilon_R^- \cdot l}} \quad (4)$$

Solving this equation by means of two series of measurements, we shall have:

$$K_{HR} = \frac{A^i [H]^i - A^K [H]^K}{A^K - A^i} \quad (5)$$

$$\varepsilon_R^- = \frac{A^i A^K ([H]^i - [H]^K)}{c l (A^i [H]^i - A^K [H]^K)} \quad (6)$$

As presented in Table 5, $pK_{HR} = 10,25$, complies satisfactorily with $pK_{HR} = 10,12$ determined potentiometrically.

Table 5. Results obtained from the spectrophotometric measurement of the dissociation constant

pH	H ⁺	A ₄₀₀	A ₄₁₀	K _{HR} 400 nm	K _{HR} 410 nm
10,92	1,20·10 ⁻¹¹	0,840	0,292	5,12·10 ⁻¹¹	4,10·10 ⁻¹¹
10,80	1,59·10 ⁻¹¹	0,800	0,272		
10,90	1,26·10 ⁻¹¹	0,830		7,53·10 ⁻¹¹	
10,80	1,59·10 ⁻¹¹	0,800			
Average $K_{HR} = 5,58 \cdot 10^{-11}$ $pH_{HR} = 10,25$					

As a conclusion, the tiobis-β-naphthol is a low mono-base acid with the acid dissociation constant of $K_{HR} = 6,59 \cdot 10^{-11}$ and $pK_{HR} = 10,18$.

7. Identification of tiobis-β-naphthol

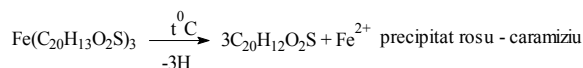
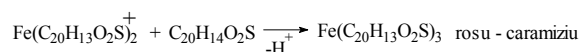
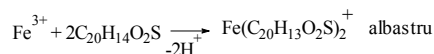
The use of tiobis-β-naphthol in various domains asks for new determination and identification methods. Thus the original oxidation method is proposed for the purpose of this study.

The oxidation reaction of the dehydro-di-β-naphthol is characteristic for the tiobis-β-naphthol and makes use of the ferric nitrogen as oxidant.

The reaction takes place as follows: the tiobis-β-naphthol dissolved into ethylic alcohol is treated with a concentrated ferric nitrogen solution. Initially a blue compound is obtained which turns into red upon heating, colors characteristic for the complex combinations with charge transfer, made up of tiobis-β-naphthol and ion Fe (III) according to the ratio

Fe: HR=1:2 and Fe: HR=1:3 respectively. Upon boiling, the redox process is completed resulting in red – orange abundant precipitate. The isolated precipitate flushed in much water and purified by glacial acetic acid results in a fine crystalline light-red powder which does not contain any Fe, and having the 159°C.

The elementary and spectral analysis in the range UV-VIS indicates that dehydrosulphide has been obtained:



8. Conclusions

The synthesis of the new reactant (tiobis-β-naphthol) as well as the latest researches on solubility, the dissociation constant, the original identification method and the UV- VIS and IR studies bring about important contributions to the tiobis-β-naphthol structure.

The tiobis-β-naphthol having groups of (-S-) and (-OH-) situated in suitable positions features high reactivity being able to form a donor-acceptor bond with some metals.

The tiobis-β-naphthol may be used for selective determination of several metals like: Cu²⁺, Hg²⁺, Mn²⁺, Pb²⁺ etc. from different materials as: ore, rocks, used water etc.

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