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**SYNTHESIS OF 2,3-DITHIOFENIL DERIVATIVES OF PYRROL  
ON THE BASIS OF 2,2'-THIONINE**

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*It is known that pyrrole and its derivatives are a part of many important natural compounds. Polymeric semiconductors also were obtained on the basis of 2,5-dithienyl-pyrrole electropolymerization and its derivatives. The work deals with the synthesis of 2,3-dithiophenyl-1H-pyrroles by the reaction of 2,2'-thionine with various enamines.*

**Keywords:** pyrrol, 2,2'-thionine, pyrrole derivative, 2,3-dithiophenyl-1H-pyrroles, enamines

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### INTRODUCTION

Pyrrol and its derivatives hold a specific place between the five-membered heterocyclic compounds [1,2]. It is known that the pyrrol ring is a part of the composition of many important physiologically active natural organic compounds - chlorophyll, hemoglobin, vitamin B12, Crisprine A, Lettowainthine, Lamellarin D. Note that interest in pyrrole compounds is based on their antibacterial, antimicrobial, antidiabetic, etc. properties.

At present, a five-membered optical active pyrrole derivative "Lipitor" is the most widely used drug to decrease the amount of cholesterol in the blood [4].

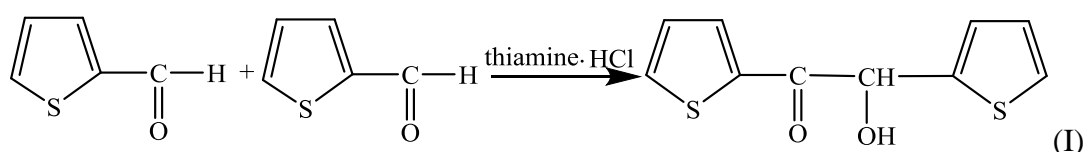
Compounds containing porphyrin, phthalocyanine and BDP (bordipyrrolometane dyes) fragments which are synthesized on the basis of pyrrole are indispensable specific materials for preparation of sensors and photonstylators in the optical electronics and electrical industry [5,6]. Recently, many

articles have been devoted to the synthesis and electrolysis of 2,5-dithiophene derivatives of pyrroles in the production of semiconductor polymers. Due to the effect of weak electric current these polymers change colors into red, green, and blue and thus play a crucial role in the development of internet and television technology [7,8].

The main objective of the article is to study the synthesis and structure of derivatives of the 2,3-dithiophene especially as there is no sufficient information about the subject in the literature.

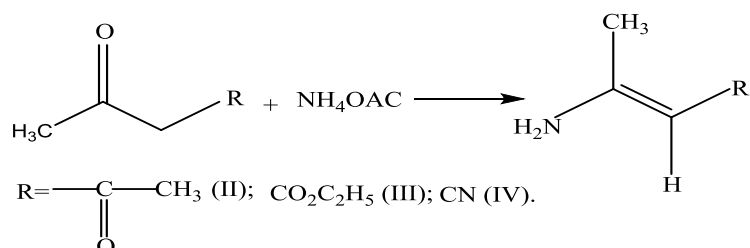
The 2,3-dithiophene of pyrrole is obtained from the condensation of 2,2'-thionine with various enamins at high temperature.

Thiophene-2-aldehyde was synthesized in the presence of the 2,2'-thionine thiamine hydrochloride catalyst by using the known method in the literature.



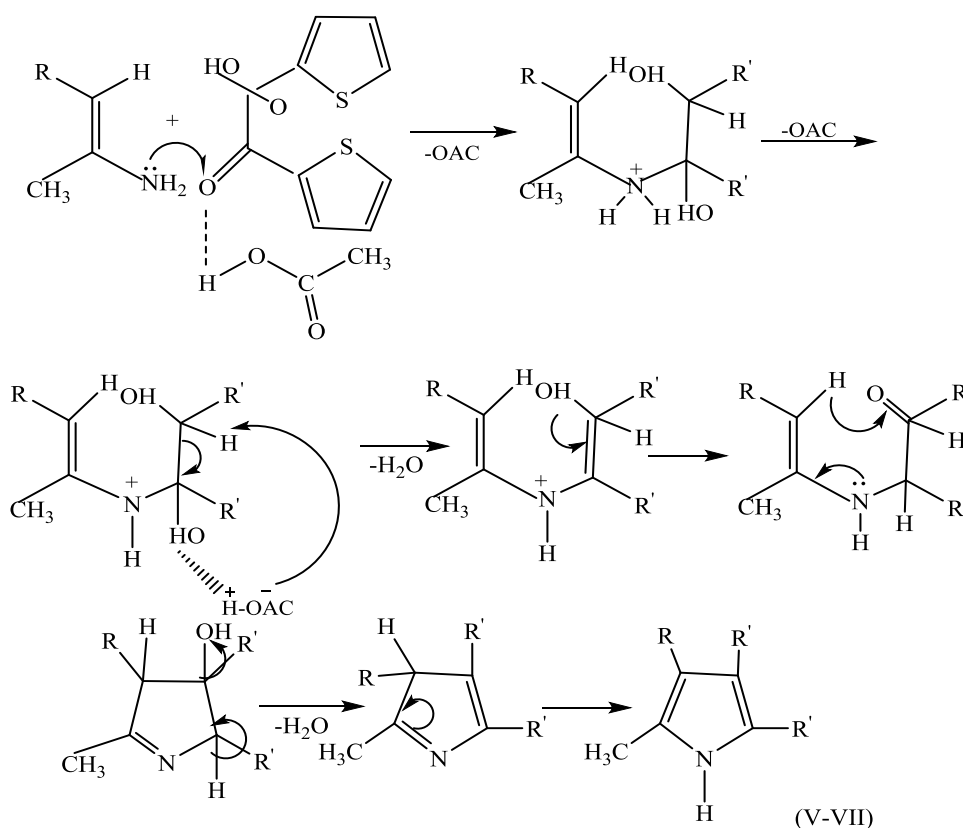
The structure of this substance was proved with  $H^1$ -NMR spectroscopy. Two doublets was detected at 4.35 and 6.0 pp.m for the CH-OH fragment. Six protons of two thiophene rings was detected at 4.35 and 6.0

pp.m chemical shift as singlet and doublet peaks. The three enamins that we used as starting materials were also synthesized according to the following scheme [9].



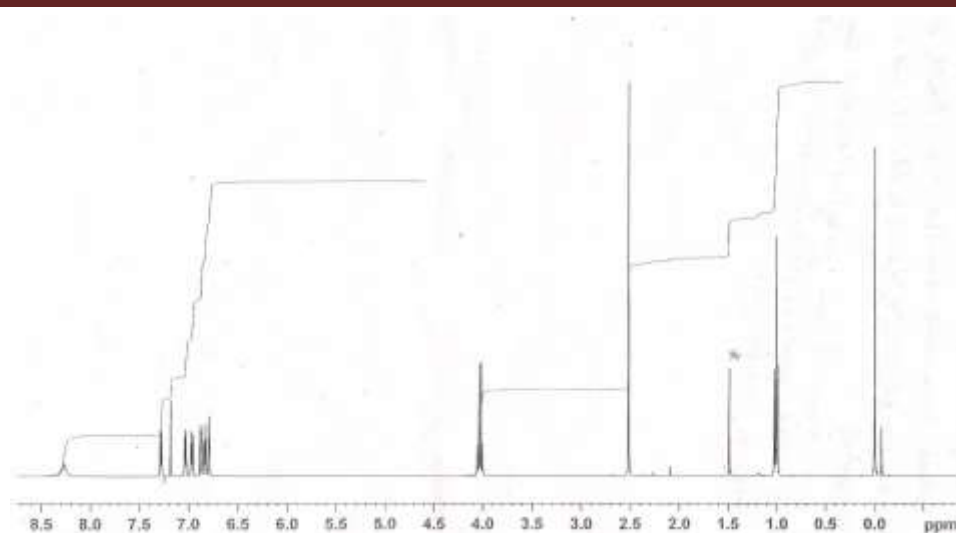
The structure and purity of the synthesized enamines (II-IV) were explored by the NMR-spectroscopy and the TLC method. The 2,3-

dithiophene derivatives of the pyrolyte were synthesized by condensation of 2,2'-thionine with enamines at 140 ° C in acetic acid.



Compounds (V-VII) were provided with  $H^1$  and  $C^{13}$  NMR spectroscopy. (VI) In the pyrrole spectrum  $CH_3$  protons of the  $CO_2C_2H_5$  fragment consist of triplet which were detected at 1pp.m ( $J = 7.0$  Hz), and  $CH_2$  protons at 4.04 pp.m ( $J = 7.0$ Hz) as a quartet. The methyl

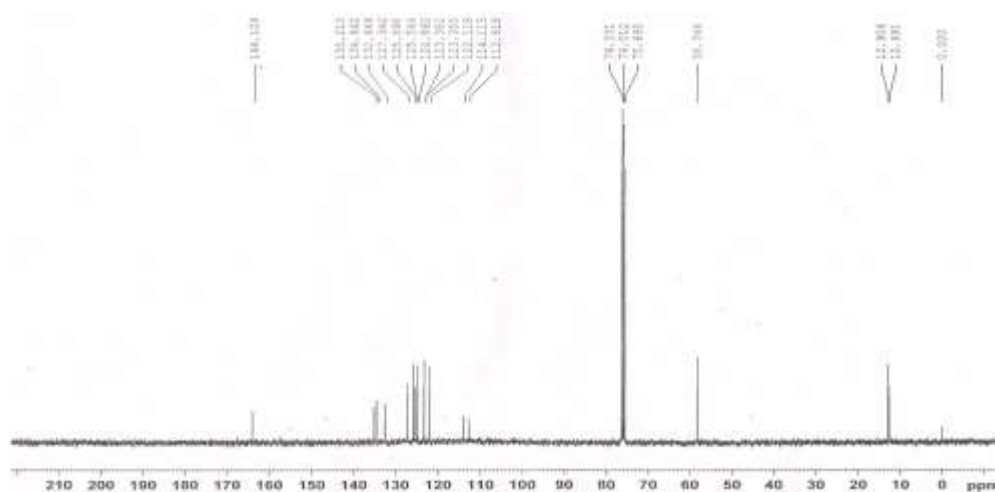
radical of the pyrrole ring was observed as a singlet at 2,5 pp.m , and proton NH was observed as wide peak at the 8.30 pp.m. The six protons of the two thiophenes were observed as a multiplet at 6.80- 7.30 pp.m. (Fig. 1).



**Figure 1.**  $^1\text{H}$  NMR spectroscopy of 2,3-dithiophene-4-ethylcarboxylate-5-methyl-1H-pyrrole

Pyrrole compound (VI) was also studied by  $^{13}\text{C}$  NMR spectroscopy. As seen in the spectrum (Picture 2), (5) compound contains 16 carbon atoms. Carbon atoms of pyrrole ring's and  $\text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CH}_3$  radicals were

observed at 12.90 and 12.69 ppm areas, but  $\text{OCH}_2$  carbon atom at 58.30 ppm. The carbon atom of  $\text{C}=\text{O}$  group's carbon atom was observed at 164.10 ppm weak area.



**Figure 2.**  $^{13}\text{C}$  NMR spectroscopy of 2,3-dithiophene-4-ethylcarboxylate-5-methyl-1H-pyrrole

$^{13}\text{C}$  NMR spectroscopy of the pyrrole and two thiophene rings was observed in the following area (m.h.): 112.18, 114.11, 122.12, 123.56,

123.83, 124.86, 125.54, 125.90, 127.34, 132.65, 134.66, 135.21.

(V-VII) pyrrole compounds were proved by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy

## EXPERIMENTAL PART

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy of the synthesized compounds were studied in the Bruker DPX400 ( $\text{CDCl}_3$ ) and their cleaning

was investigated by UV light ( $\lambda = 254\text{nm}$ ) on the thin layer.

**The synthesis of 2,2-thionine.**

Thiaminehydrochloride salt 1.68 (5mmol), 4.2 ml (30 mmol) triethylamine and 8.9 ml (100 mmol) thiophene 2-aldehyde were placed in 25 ml flask, then added to 30 ml anhydrousethyl, left it stirring under condenser for 24 h at the room temperature. At the end of the reaction the mixture was filtered and the precipitation washed through cold ethanol, then left it to dry.

Note that 10 q compound was obtained in the yield of 78 % (melting point 39°C)

$^1\text{H}$  NMR spectroscopy for ( $\text{CDCl}_3$ ):  $\delta$ , 4.35 d (CH), 6.0 d (OH), 6.90 d (1H), 7.10 m (2H), 4.40 d (1H), 7.70 dd (2H).

**The synthesis of 2,3-dithiophene-4-acetoxy-5-methyl-1H-pyrrole (V).**

1q (0.1 mol) Fluorine-P, 2.24 q (0.1 mol) 2,2'-thionine and 3.08 q (0.4 mol) ammoniumacetate were placed in a 25 ml flask, then left it to reflux at the 140°C for 2 h. Upon completion, the mixture left it to remain at room temperature, then 30 ml ethylacetate was added, washed with water and 5%  $\text{NaHCO}_3$ . After that,  $\text{MgSO}_4$  used to dry water. Ethylacetate was evaporated and 2.15 q 75% liquid compound obtained. (V)

$^1\text{H}$  NMR spektroskopi for ( $\text{CDCl}_3$ ):  $\delta$ , 1.80 s ( $\text{CH}_3$ ), 2.50 s ( $\text{COCH}_3$ ), 6.80 d (2H, HC=), 6.90 s (1H, HC=), 7.00 m (2H, HC=), 7.30 d

(1H, HC=), 9.00 s (1H, NH).

$^{13}\text{C}$  ( $\text{CDCl}_3$ ): 14.47 ( $\text{CH}_3$ ), 30.00 ( $\text{CDCH}_3$ ), 113.97, 123.01, 123.67, 124.45, 126.89, 127.11, 127.36, 129.48, 133.57, 135.93, 136.32, 196.46 (C=O).

**The synthesis of 2,3-dithiophene-4-ethylcarboxylate-5-methyl-1H-pyrrole (VI).**

The same procedure was used for (VI) where 73% liquid was synthesized.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ , 1.00 t (3H,  $\text{CH}_3$ ,  $J=7\text{Hz}$ ), 2.50 s (3H,  $\text{CH}_3$ ), 4.00 Kv (2H,  $\text{COCH}_2$ ,  $J=7,00\text{Hz}$ ), 6.70-7.30 m (6H, HC=), 8.30 s (1H, NH).

$^{13}\text{C}$  ( $\text{CDCl}_3$ ): 12.59, 12.90, 58.34, 112.81, 114.11, 122.11, 123.35, 123.38, 124.86, 125.54, 125.89, 127.34, 132.64, 134.66, 135.21, 164.11 (C=O).

**The synthesis of 2,3-dithiophene-4-nitril-5-methyl-1H-pyrrole (VII)**

(1.7q) Pyrrole derivative (78%) (VII) was synthesized from the mixture of 2,2'-thionine (2.24q), 1-methyl, 2-amine acronitrile (0.68 g), ammonium acetate (3.08g) and 10 ml of vinegar acid by using the same procedure.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ , 2.40 s (3H,  $\text{CH}_3$ ), 6.90-7.20 m (6H, HC=), 8.80-8.90 m (1H, NH).

$^{13}\text{C}$  ( $\text{CDCl}_3$ ):  $\delta$ , 13.30, 93.94, 116.45, 122.81, 125.32, 125.85, 127.15, 127.33, 128.25, 129.05, 132.07, 133.46, 137.89, 138.06.

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### 2,2'-TİONİN ƏSASINDA 2,3-DİTİOFENİL PİRROL TÖRƏMƏLƏRİNİN SİNTEZİ

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*Pirrol və onun törəmələri vacib təbii birləşmələrin tərkibinə daxildir. Eyni zamanda 2,5-ditiənil-pirrol və onun törəmələri əsasında yarımkeçirici polimer pirrollar sintez olunub. İş 2,2'-tioninin müxtəlif enaminlərlə reaksiyası əsasında 2,3-ditiofenil-1H-pirrolların alınmasına həsr olunub.*

*Açar sözlər: pirrol, tionin, enamin, 2,3-ditiofenil-1H-pirrollar*

### СИНТЕЗ 2,3-ДИТИОФЕНИЛПРОИЗВОДНЫХ ПИРРОЛА НА ОСНОВЕ 2,2'-ТИОНИНА

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*Пиррол и его производные входят в состав многих важных природных соединений. На основе электрополимеризации 2,5-дителиенил-пиррола и их производных получены также полимерные полупроводники. Работа посвящена синтезу 2,3-дитиофенил-1H-пирролов реакцией 2,2'-тионина с различными енаминами.*

*Ключевые слова: пиррол, тионин, 2,3-дитиофенил-1H-пирролы, енамин*