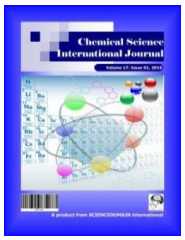

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# Novel Imidazole and Dibenzothiophene-dioxide Containing Tetracyclic Systems

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***Authors' contributions***

*This work was carried out in collaboration between all authors. Author M. Maisuradze designed the study, wrote the protocol and the first draft of the manuscript. Authors EK, MA and NG managed the synthesis part of the study. Authors GP and ST managed the analysis of the study. All authors read and approved the final manuscript.*

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## ABSTRACT

The aim of the current work is synthesis of new heterocyclic teratacyclic condensed systems that combine dibenzothiophenedioxide and imidazole in one molecule. The dibenzothiophene was taken as an initial compound and by consistent expansion were connected the imidazole cycles. As a result two new tetratacyclic systems 3H-imidazole[4,5-b]dibenzothiophene-5,5dioxide and 3H-imidazole[4,5-a] dibenzothiophene-5,5dioxide were produced. The spectral property of obtained systems were investigated.

*Keywords: Tetrtacyclic systems; synthesis; dibenzothiophene dioxide; imidazole.*

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## 1. INTRODUCTION

Antimicrobial resistance has become a serious global threat to public health, agriculture and economy. It significantly reduces or diminishes the effectiveness of prevention or treatment of infectious diseases, which also compromises the outcome of a broad range of medical treatment, such as cancer treatment and surgery. In April 2014, the World Health Organization (WHO) released an extensive global report, stating "very high rates of resistance have been observed in bacteria that cause common health-care associated and community-acquired infections (e.g. urinary tract infection, pneumonia) in all WHO regions". In September 2014, the US published the *National Strategy for Combating Antibiotic Resistant Bacteria*, emphasizing the importance of strategic and technical development to combat this ever-increasing threat.

Thus the creation of new compounds and their antimicrobial activities investigation become very principal. The creation of the biologically active composites based on heterocyclic compounds is one of the primary routes in the study of new drugs. Materials including heterocyclic particles quantitatively classify the top in the arsenal of medicaments (60% - above). Since the development of new drug is significant chemical modification of a studied biologically active molecules in one molecule that can increase activity of the new molecule and enlarge the spectrum of its pharmacological effect. This paper includes the merger into a alone molecule of physiologically active fragments, such as dibenzothiophene on the one hand and imidazole on the other hand. Each of these compounds is designated by high antifungal and antiviral activities [1-9].

## 2. MATERIALS AND METHODS

### 2.1 Materials and Apparatus

Chemicals and solvents used were of analytical grade and did not need any more purification. The melting points ($^0$C) of the compounds were determined by the open tube capillary method. The purity of the compounds was determined using thin layer chromatography (TLC). The infrared (IR) spectra were determined using infrared spectrophotometer, while elemental analysis using elemental analyzers by combustion in a stream of oxygen. The $^1$H Nuclear Magnetic Resonance (NMR) spectra were determined in DMSO with TMS as standard using a 400 MHz instrument. The mass-spectra were determined using Cromatomas-spectrometer "Clarus 500-MS" in a stream of helium;

### 2.2 Synthesis of Dibenzothiophene-5,5-dioxide (2). {see [10]}

White needle-like crystals; M=216; $C_{12}H_8O_2$; Yield: 95,3%. $T_{m.p.}$=231ºC, Lit. $T_{m.p.}$=232-233ºC. TLC – Chloroform/Ethyl acetate -3/1.

### 2.3 Synthesis of 3-Nitrodibenzo-thiophene-5,5-dioxide (3). {see [10]}

Yellow crystals; M = 261; $C_{12}H_7NO_4S$; Yield: 13 g, 94%; $T_{mp.}$=264ºC; Liter. $T_{mp.}$=265-266$^O$C; [16] . TLC – Chloroform/Ethyl acetate -3/1

### 2.4 Synthesis of 3-Aminodibenzothio-phen-5,5-dioxide (4)

10 g (0.038 mole) 3-nitrodibenzothiophene-5,5-dioxide (3) was mixed with 460 ml 96% ethanol and add 70 ml 31% hydrochloric acid. 23 g doze of zinc dust was added while boiling and stirring. Yellow reaction area eventually became transparent red. The reaction took 40-45 minutes. Reaction area was filtered, added water and the red precipitation was obtained. The precipitation was filtered and orange filtrate was processed with 40% solution of sodium alkali and was filtrated again. The amine from the filtrate was extracted with ethyl acetate. After ethylacetate evaporation was obtained 3-Aminodibenzothiophene-5,5-dioxide (4). After crystallization with 96% ethyl alcohol yellow color crystals were appeared. M=231; $C_{12}H_9NO_2S$; TLC -chloroform. Yield: 7.76g, 88.1%; $T_{mp.}$=256-258$^O$C; Lit. $T_{mp.}$=259-260$^O$C [11].

### 2.5 Synthesis of 3–Acetamido-dibenzithiophene-5,5-dioxide (5)

1.1g (0.0047 mole) of 3-aminodibenzo-thiophene-5,5-dioxide (4) was added 68.75 ml (0.3 mole) of glacial acetic acid and boiled under stirring condition. The drops of 0.75 ml (0.03 mole) acetic anhydride was added and beige-yellow color crystals was precipitated. The mixture was kept at stirring and boiling conditions for 30 minutes, was hotly filtered and washed

with water up neutral reaction. Then was dried at room temperature and crystallized with ethanol. TLC–Ethyl acetate/Ether–3/1. Yields: 1.4g, 95.2%; $T_{m.p.}$=317-319$^{O}$C; M=273. Anal. Calc. For. $C_{14}H_{11}NO_3S$; C- 61.52; H- 4.06; N- 5.12; S- 11.73%. Found: C- 61.50; H- 4.08; N- 5.13; S- 11.72%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3440 (NH);3245 ($CH_3$ ); 1704(C=O); 1550(CN); 1157($SO_2$) . $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.07 (3H, s, $J$= 2.09, CH-3), 7.50 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.33. $J_{8,5,}$=0.91, $J_{6,8,}$=0.91, H-6), 7.56(1H, bs, NH),7.61(1H, m, $J_{7,5}$=1.11, $J_{7,6}$=7.53, $J_{7,8}$=7.73, $J_{7,5}$=2.23, H-7), 7.71(1H, m, $J_{5.6}$=7.73, $J_{5,7}$=1.11, $J_{5,8}$=0.63, H-5), 7.83(1H, m, $J_{8,5}$=0.63, $J_{8,7}$=7.73, H-8), 8.02(1H, m, $J_{9,3}$=0.91, $J_{9,1}$=2.33, H-9), 8.17(1H, d, $J_{1,3}$=0.91, H-1), 8.53(1H, d, $J_{3,1}$=2.33, $J_{3,9}$=0.91, H-3). m/z: 273.05 (100.0%), 274.05 (16.2%), 275.04 (4.5%), 275.05 (1.9%)

## 2.6 Synthesis of 2-Nitro-3-acetamido-dibenzithiophene-5,5-dioxide (6)

2g (0.007 mole) 3-acetamidodibenzothiophene-5,5-dioxide (5) was placed in three-neck flask (that is equipped with stirring appliance, drop funnel and thermometer) and was added 32 ml (0.7 mole) glacial acetic acid. Then was added mix of sulfur acid and nitric acid (1.57 ml $H_2SO_4$, d=1.84 and 5.1 ml $HNO_3$; d=1.5) at stirring conditions and 60-70$^{O}$C temperature for 15 minutes. The reaction mass was moved into glacial glass and reddish crystals was precipitated. The precipitation was filtrated, washed, dried and crystallized into the ethyl acetate. TLC - Chloroform/Ethyl acetate -1/1. Yields: 1.8g, 78.3%; $T_{m.p.}$=292-293$^{O}$C; M=318. Anal. Calc.For. $C_{14}H_{10}N_2O_5S$; C-52.83; H- 3.17; N- 8.80; S- 10.07 %; Found: C- 52.82; H-3.17; N-8.83; S-10.08%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3440 (NH); 3245 ($CH_3$); 1700(C=O); 1535(CN); 1532 ($NO_2$); 1140($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.24 (3H, s, $J$= 2.10, CH-3), 7.50 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.00, H-6), 7.60(1H, m, $J_{7,5}$=1.00, $J_{7,8}$=7.75, H-7), 7.70(1H, m, $J_{5,8}$=0.63, H-5), 7.98(1H, m, $J_{8,6}$=1.00, H-8), 8.74(1H, d, $J_{3,9}$=0.71, H-3), 8.81(1H, m, H-9), 10.31(1H, bs, NH). m/z: 318.03 (100.0%), 319.03 (16.7%), 320.03 (4.8%), 320.04 (2.1%)

## 2.7 Synthesis of 2-Amino-3–acetamido-dibenzothiophene-5,5-dioxide (7)

Compound (7) was synthesized similarly as 3-aminodibenzothiophene-5,5-dioxide (4). TLC – Chloroform/Ethyl acetate/Ether – 1/3/1. Yields: 0.8g, 80%; Dark yellow crystals; $T_{m.p.}$=264-265$^{O}$C; M=288. Anal. Calc. For. $C_{14}H_{12}N_2O_3S$; C-58.32; H-4.20; N- 9.72; S-11.12 %. Found: C-58.30; H-4.21; N- 9.72; S-11.10%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3440 (NH); 3300 ($NH_2$); 3240 ($CH_3$ ); 1700(C=O); 1530(CN); 1150($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.01 (3H, s, $J$= 2.09, CH-3), 4.59(2H, s,NH-2), 6.29(1H, bs, NH),.7.50 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.00, H-6), 7.53(1H, m, $J_{7,5}$=1.11, $J_{7,8}$=7.75, H-7), 7.63(1H, m, $J_{5,8}$=0.63, H-5), 7.81(1H, m, $J_{8,5}$=0.63, H-8), 8.04(1H, d, $J_{3,9}$=0.71, H-3), 8.06(1H, m, H-9). m/z: 288.06 (100.0%), 289.06 (16.2%), 290.05 (4.5%), 290.06 (1.9%).

## 2.8 Synthesis of 2,3-Diamino-dibenzithiophene-5,5-dioxide (8)

0.6g (0.002 mole) 2-amino-3-acetamido-dibenzothiophene-5,5-dioxide (7) was added into 20 ml ethanol and 5g KOH dissolved in 20 ml water. It was kept at stirring and boiling conditions for 30 minutes. Dark yellow crystals were filtrated, washed until neutral reaction and dried. Then it was crystallized in Ethyl acetate. TLC – Benzene/Ethyl acetate – 3/1. Yields: 0.46g, 78%; $T_{m.p.}$=243-246$^{O}$C; M 246; Anal. Calc. For. $C_{12}H_{10}N_2O_2S$; C- 58.52; H-4.09; N,-11.37; S-13.02 %. Found: C- 58.50; H-4.10; N-11.37; S-13.01%.IR (KBr) $\nu_{max}$(cm$^{-1}$): 3400, 3300 ($NH_2$); 1150($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 4.57(2H, s, NH-2), 7.50(1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.00, H-6), 7.53(1H, m, $J_{7,5}$=1.11, $J_{7,8}$=7.75, H-7), 7.67(1H, m, $J_{8,5}$=0.63, $J_{8,7}$=7.75, H-8), 7.70(1H, m, $J_{5,8}$=0.63, H-5), 7.76(1H, s, $J_{9,3}$=0.71, H-9). m/z: 246.05 (100.0%), 247.05 (14.0%), 248.04 (4.5%), 248.05 (1.4%).

## 2.9 Synthesis of 2-Nitrodibenzothiophene (9), 2- Aminodibenzothiophene (10) and 2- Acetaminodibenzothiophene (11){see [12]}

The compounds 9, 10 and 11 were synthesyzed according to refference [12].

## 2.10 Synthesis of 2- Acetamidodibenzo-ithiophene-5,5-dioxide (12)

6g (0.024 mole) 2–acetamidodibenzo-thiophene (11) was mixed in 100 ml glacial acetic acid and then heated. 30 ml of hydrogen peroxide with drops was added at the boiling and stirring conditions and white colored crystals were precipitated. The reaction area was sustained under boiling and stirring processes for 1 hour and was added 10 ml of hydrogen peroxide and

boiled for 30 minutes again. The mixture was leaved for 24 hours and filtrated and crystallizing in ethanol. It was obtained white crystals of 2-Acetamidodibenzithiophene-5,5dioxide. TLC - Chloroform/Ethyl acetate – 3/1. Yields: 5g, 73.6%; $T_{m.p.}$=272-274$^{O}$C. M 273; Anal. Calc.For. $C_{14}H_{11}NO_3S$; C- 61.52; H-4.06; N-5.12; ; S-11.73; %. Found: C-61.50; H-4.05; N-5.11; S-11.71%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3445 (NH); 3235 ($CH_3$ ); 1700(C=O); 1555(CN); 1157($SO_2$) . $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.09 (3H, s, $J$= 2.09, CH-3),6.98 (1H, d, $J_{2,3}$=8.60, H-2),7.50 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.12, H-6), 7.67(1H, m, $J_{7,5}$=1.11, $J_{7,8}$=7.73, H-7), 7.82(1H, m, $J_{8,5}$=0.63, $J_{8,6}$=1.12, $J_{8,7}$=7.75, H-8), 7.86(1H, m, $J_{5,7}$=1.11, H-5), 7.89(1H, d, $J_{3,2}$=8.60, $J_{3,9}$=0.71, H-3), 8.46(1H, m, $J_{9,2}$=2.13, $J_{9,3}$=0.71, H-9), 9.87(1H, bs, NH). m/z: 273.05 (100.0%), 274.05 (16.2%), 275.04 (4.5%), 275.05 (1.9%);

## 2.11 Synthesis of 1-Nitro-2-acetamido-dibenzothiofene-5,5-dioxide (13)

5g (0.018 mole) 2 – acetamidodibenzo-thiophene-5.5 dioxide (12) was dissolved in 100 ml glacial acetic acid and then was added drops of 16 ml nitric acid (d=1.5). The temperature of 30$^{O}$C grades was kept. This mixture was allowed to cool and poured into ice water. The Lemon-yellow crystals was filtered, washed by water, dried and crystallized in 96% ethanol. TLC – Chloroform/Ethyl acetate – 1/1; Yields: 4.16 g, 72.7%; $T_{m.p.}$=256-258$^{O}$C. M 318; Anal. Calc. For. $C_{14}H_{10}N_2O_5S$; C-52.83; H-, 3.17; N- 8.80; S-10.07 %. Found: C- 52.80; H-3.20; N- 8.82; S-10.08%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3445 (NH);3250 ($CH_3$ ); 1710(C=O); 1540 (CN); 1530 ($NO_2$); 1145 ($SO_2$).$^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.26 (3H, s, $J$= 2.09, CH-3),7.49 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.05, H-6),7.74 (1H, d, $J_{2,3}$=8.60, H-2),7.80(1H, m, $J_{7,5}$=1.13, $J_{7,8}$=7.77, H-7), 7.83(1H, m, $J_{8,5}$=0.63, $J_{8,6}$=1.05, $J_{8,7}$=7.76, H-8), 8.01(1H, m, $J_{5,8}$=0..63, H-5), 8.22(1H, d, H-3), 10.31(1H, bs, NH). m/z: 318.03 (100.0%), 319.03 (16.7%), 320.03 (4.8%), 320.04 (2.1%).

## 2.12 Synthesis of 1-amino-2-acetamido-dibenzothiophene-5,5-dioxide (14)

3.8g (0.012 mole) of 1-nitro-2-acetamidodiben-zothiophene (13) was mixed with 142 ml 96% ethanol. Rene/Ni catalyst in small portions was added while boiling and stirring. Then drops of 6 ml hydrazine hydrate were added. Reaction area became transparent. The reaction took two more hours. Reaction area was filtered and cold. The precipitation was filtered, washed up to neutral area and dried at room temperature. Whitish-violate crystals were obtained. TLC – Benzene/Ethyl acetate – 3/1. Yields: 2.7g, 75%; $T_{m.p.}$=282-283$^{O}$C. M 288.32; Anal. Calc.For. $C_{14}H_{12}N_2O_3S$; C-58.32; H-4.20; N- 9.72; S-11.12%. Found: C- 58.30; H- 4.22; N- 9.72; S-11.15%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3445 (NH); 3310 ($NH_2$); 3240 ($CH_3$ ); 1710(C=O); 1530(CN); 1155($SO_2$) . $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 2.03 (3H, s, $J$= 2.09, CH-3), 4.50(2H, NH-2) 6.21(1H, bs, NH), 6.92 (1H, d, $J_{2,3}$=8.60, H-2),7.02(1H, d, H-3), 7.42 (1H, m, $J_{6,5}$=7.75, $J_{6,7}$=7.55. $J_{6,8,}$=1.00, H-6),7.51(1H, m, $J_{8,5}$=0.62, $J_{8,6}$=1.00, $J_{8,7}$=7.75, H-8), 7.65(1H, m, $J_{7,5}$=1.11, H-7), 7.84(1H, m, $J_{5,6}$=7.75, $J_{5,7}$=1.11, H-5), m/z: 288.06 (100.0%), 289.06 (16.2%), 290.05 (4.5%), 290.06 (1.9%).

## 2.13 Synthesis of 1,2-diaminodibenzothi-ophene -5,5-dioxide (15)

Compound (15) was synthesized similarly as 2,3-Diaminodibenzithiophene-5,5-dioxide (8).

Yields: 74%; $T_{m.p.}$=297$^{O}$C. M 246.28; Anal. Calc.For. $C_{12}H_{10}N_2O_2S$; C-58.52; H-4.09; N-11.37; S-13.02%. Found: C-58.50; H- 4.10; N-11.34; S-13.00 %. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3400-3300 ($NH_2$); 1150($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 4.53-4.56(2H, $NH_2$-1, $NH_2$-2), 6.08 (1H, d, $J_{2,3}$=8.30, H-2),7.13(1H, d, H-3), 7.42 (1H, m, $J_{6,5}$=7.73, $J_{6,7}$=7.53. $J_{6,8,}$=1.00, H-6),7.44(1H, m, $J_{8,5}$=0.63, $J_{8,7}$=7.75, H-8), 7.57(1H, m, $J_{7,5}$=1.11, $J_{7,6}$=7.53, H-7), 7.70(1H, m, H-5), m/z: 246.05 (100.0%), 247.05 (14.0%), 248.04 (4.5%), 248.05 (1.4%);

## 2.14 Procedure for the General Synthesis of Imidazolodibenzothiophene-5,5-dioxide

0.2 g diamine (0.007 mole) was placed in the three-necked flask (that is equipped with dropping funnel and reflux condenser) and added 1 ml (0.02 mole) of formic acid and 1 ml of 31% hydrochloric acid and suspension was boiled during 30 minutes. By adding of 50 ml water, obtained suspension was alkalized by ammonium hydroxide – till the ammonia odor appeared. Formed crystals were filtered, washed until neutral conditions, dried and crystallized in acetone. TLC- Ether/Hexane/Ethyl acetate – 5/1/3.

### 2.15 3H-imidazolo[4,5-b]dibenzothiophene-5,5-dioxide (16)

Yields: 0.17g, 82%; $T_{m.p..}$=225-227$^{O}$C; White yellowish crystals; M 256.28;Anal. Calc.For. $C_{13}H_8N_2O_2S$; C-60.93; H-3.15; N-10.93; S-12.51%. Found: C-60.90 H-3.12; N-10.90; S-12.48%. IR (KBr) $\nu_{max}$(cm$^{-1}$): 3410 (NH); 1155($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 7.50(1H, m, $J_{7,6}$=7.73, $J_{7,8}$=7.53, $J_{7,9}$=1.00 H-7), 7.63(1H, m, $J_{8,7}$=7.53, $J_{8,9}$=7.75, $J_{8,6}$=1.11, H-8), 7.80 (1H, m, $J_{6,9}$=0.63, H-6),7.88 (1H, m, $J_{9,8}$=7.75, H-9),7.99 (1H, d, $J_{10,4}$=0.91, H-10),8.42(1H, d, H-4), ),8.53 (1H, d, H-2), 7.70(1H, m, $J_{5,6}$=7.73, $J_{5,7}$=1.11, $J_{5,8}$=0.63, H-5), 10.20(1H,bs, NH). m/z: 256.03 (100.0%), 257.03 (15.7%), 258.03 (5.2%).

### 2.16 3H-imidazolo[4,5-a]dibenzothiophene-5,5-dioxide (17)

Yields: 0,16g. 77%; $T_{m.p.}$=337$^{O}$C. Dark yellow crystals; M 256.28; Anal. Calc.For. $C_{13}H_8N_2O_2S$; C-60.93; H-3.15; N-10.93; S-12.51%. Found: C-60.94 H- 3.13; N-10.90; S-12.48%. IR (KBr) $\nu_{max}$ (cm$^{-1}$): 3400 (NH); 1150($SO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) (ppm): 7.55(1H, m, $J_{8,7}$=7.73, $J_{8,9}$=7.53, $J_{8,6}$=1.00, H-8), 7.85 (1H, m, $J_{9,8}$=7.53, $J_{9,7}$=1.11, $J_{9,10}$=7.75, H-9),7.89(1H, d, $J_{4,5}$=8.60, H-4), 7.91(1H, d, H-5), 8.04(1H, m, $J_{7,10}$=0.63. $J_{7,8}$=7.73, H-7), 8.14 (1H, m, $J_{10,7,}$=0.63, H-10),8.45 (1H, d, H-2),10.20(1H, bs,NH). m/z: 256.03 (100.0%), 257.03 (15.7%), 258.03 (5.2%).

## 3. RESULTS AND DISCUSSION

In our earlier studies were successfully obtained tetracyclic systems on the base of benzimidazole/benzotriazole and benzothiophene [12-16]. The present investigation aimed to synthesize teratacyclic systems where the tricycle system of thiophene-dioxide would be connected with imidazole cycles.

For the synthesis of tetracyclic systems is necessary obtaining of ortho-diamine compounds. Imidazole cycle connection site depends on amino-groups location. Our aim was to obtain 1,2- and 2.3 – diaminodibenzothiophene-5.5dioxide. As an initial compounds in both cases was taken dibenzothiophene (1) (Scheme 1). By oxygenation of compound (1) with hydrogen peroxide was obtained dibenzothiophene – 5.5 dioxide (2) [11]. By nitrating of compound (2) with nitric acid and sulfuric acid was obtained 3 – nitrodibenzothiophene – 5.5-dioxide (3). By the reduction of compound (3) with hydrochloric acid using zinc dust was obtained 3–aminodibenzothiophene (4). By acylation of compound (4) with acetic anhydride in acetic acid area was obtained 3–acetamidodibenzothiophene–5.5dioxide (5) and by its re-nitration with nitrating mixture: nitric acid/sulfuric acid was obtained 2- nitro-3-acetamidodibenzothiophene 5.5dioxide (6) that is reduction up to 2-amino-3–acetamidodibenzothiophene,-5.5 – dioxide (7) in hydrochloric acid using zinc dust. By hydrolyzing of compound (7) was obtained 2,3–diaminodibenzothiophene–5.5 dioxide (8) (Scheme 1).

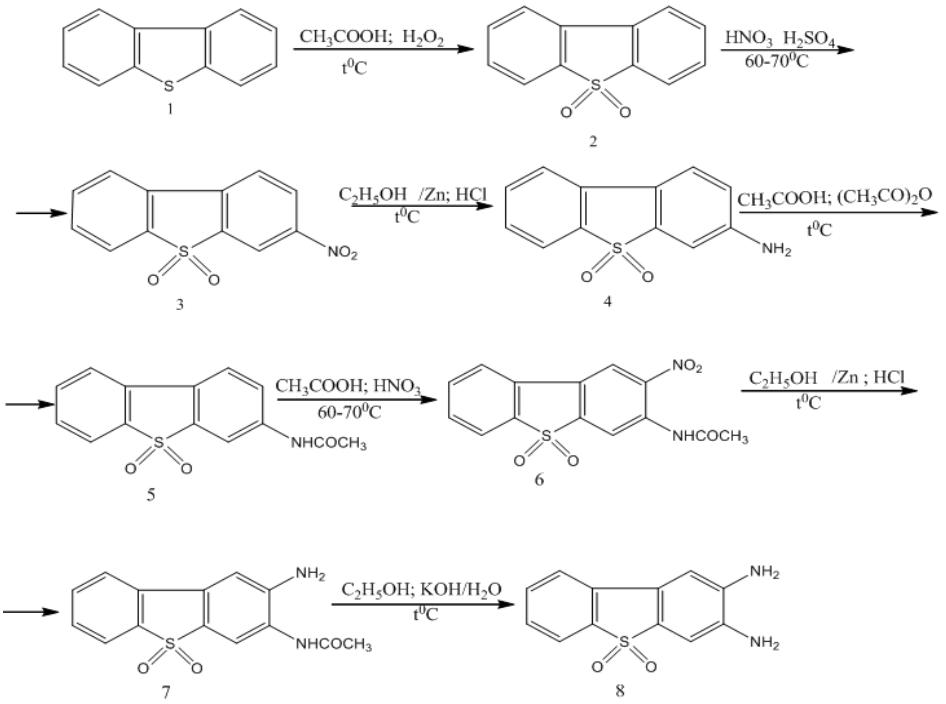
1,2-diaminodibenzothiophene-5,5-dioxide was obtained by following scheme: Dibenzothiophene (1) was used as starting compound. By its nitration with nitrating agent (nitric acid/sulfuric acid) was obtained 2–nitrodibenzothiophene (9) that was recovered up to 2–aminodibenzothiophene (10) with hydrazine hydrate and Nickel/Rene in ethanol area. By acylation of compound (10) with acidic anhydride in benzene area was obtained 2–acetamidodibenzothiophene (11) that was oxidized with hydrogen peroxide up to 2–acetamidodibenzothiophene–5.5 dioxide (12). By nitration of compound (11) with smoking nitric acid in acetic acid area was obtained 1–nitro,-2–acetamidodibenzothiophene –5.5 dioxide (13). It was recovered with hydrazine hydrate and nickel/Rene in ethanol area up to 1-amino,2–acetamidodibenzothiophene-5.5dioxide (14). By hydrolyzing of compound (14) with sodium hydroxide in ethanol area was obtained 1.2 – diaminodibenzothiophene–5.5dioxide (15) (Scheme 2).

Isomeric tetracyclic systems 3H-imidazole[4,5-b]dibenzothiophene-5,5dioxide (15) and 3H-imidazole[4,5-a]dibenzothiophene-5,5dioxide (16) were obtained from correspondent diamines (7) and (14) by condensation with formic acid at the presence of a catalytic amount of hydrochloric acid and the modified Phillips reaction conditions (Scheme 3).

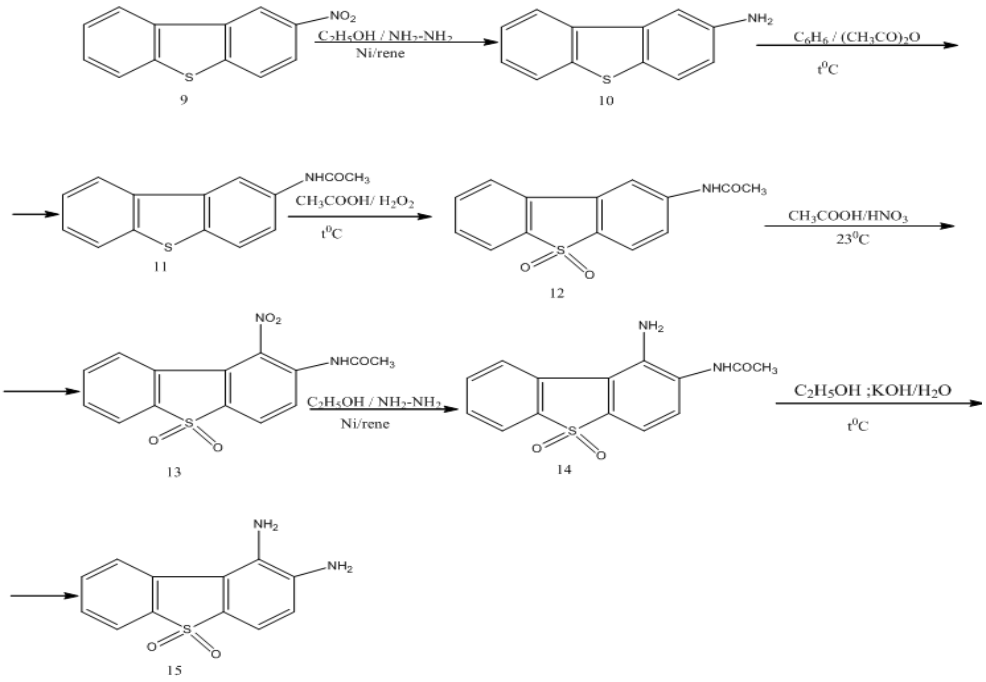
### 3.1 Spectroscopic Analysis

The originally synthesized compounds were tested by IR, 1H-PMR and mass-spectroscope methods and the chemical structure were confirmed $NH_2$ - groups signal of IR spectra of compounds (7), (8), (14) and (15) were observed

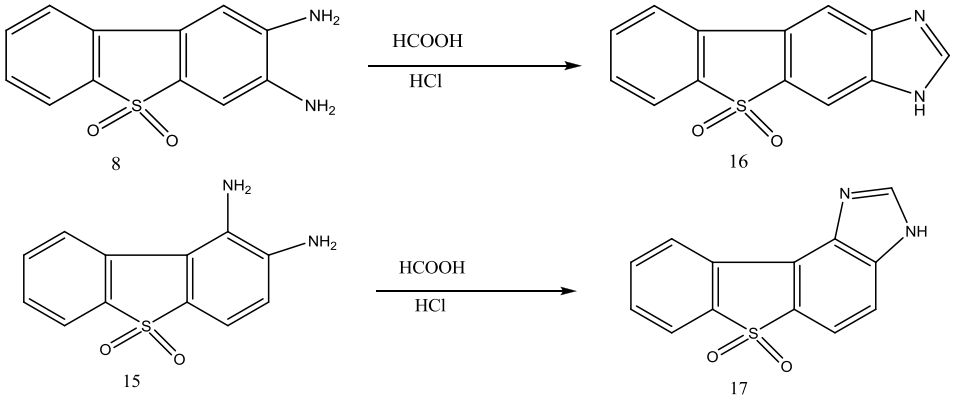
at 3400- 3300 $cm^{-1}$ area, NH- groups signal of IR spectra of compounds (5),(6), (7), (12), (13), (14) – were observed at 3440 $cm^{-1}$ area. $SO_2$-group signals of IR spectra of all the compounds were observed at 1157-1150 $cm^{-1}$ area. $CH_3$-group signals of IR spectra of compounds (5), (6), (7), (12), (13), (14) were observed at 3250 - 3235 $cm^{-1}$ area. C=O - group signals of IR spectra of compounds 5), (6), (7), (12), (13), (14) were observed at 1710 -1700 $cm^{-1}$ area. C=N-group signals of IR spectra of these substances also observed at 1555-1535 $cm^{-1}$ area.




**Scheme 1. Synthesis of 2,3 Diaminodibenzithiophene-5,5-dioxide**




**Scheme 2. Synthesis of 1,2-diaminodibenzothiophene-5,5-dioxide**




**Scheme 3. Synthesis of 3H-imidazolo[4,5- b]dibenzothiophene-5,5-dioxide (16) and 3H-imidazolo[4,5-a]dibenzothiophene-5,5-dioxide (17)**

2nd proton signal of (6), (7) and (8) compounds of 1H-PMR spectra, as well as, first proton absence of (13), (14) and (15) compounds confirms substituent's replacement at this location. At the same time $NH_2$ groups protons signals of (7), (8), (14) and (15) compounds arise in spectra. NH group protons signals of (5), (6), (7), (12), (13) and (14) compounds were observed.

NH groups protons signals of (16) and (17) compounds spectra were observed too. $J_{10,4}$ = 0.91 of compound (16) and $J_{4,5}$ = 8.60 in the case of compound (17) confirmed connection of imidazole cycle at appropriate location.

Mass spectroscopy data matches the molecular weights of synthesized compounds. 1H-PMR spectroscopy data also confirm the structure of obtained compounds.

## 4. CONCLUSION

The present investigation conducted to synthesize tetracyclic systems where the tricycle system of thiophene would be connected with two imidazole/triazole cycles. The goal was to synthesise tetracyclic heterocyclic condense compounds on the base of imidazole and dibenzothiopendioxide. 1,2- and 2,3-diaminodibenzotiophenedioxides have been used as initial compounds that were obtained after successive transformations of dibenzothiophene. 3H-imidazole[4,5-b]dibenzothiophene-5.5-dioxide and 3H-imidazole[4,5-a]dibenzothiophene-5.5 dioxide were obtained from diamines by condensation with hydrochloric acid at the presence of formic acid and Phillips reaction conditions. The originally synthesized compounds owing to antimicrobial action of their part cycles present fine starting form for receive many derivatives by entering various substituents.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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