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**SYNTHESIS AND CHARACTERIZATION OF DIBENZOTHIOPHENE AND
PHENOTHIAZINE DERIVATIVES FOR ORGANIC OPTOELECTRONIC
DEVICES**

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Abbreviations

Ar	- Argon atmosphere
CDCl ₃	- deuterated chloroform
d	- doublet
DCM	- dichloromethane
dd	- double doublet
ddd	- double double doublet
DMF	- N,N- dimethylformamide
DMSO- <i>d</i> ₆	- deuterated dimethyl sulfoxide
H : EtAc	- Hexane : Ethyl acetate mixture (eluent)
J	- coupling constant
M	- molecular weight
m	- multiplet
MHz	- mega hertz
MS	- Mass spectroscopy
NBS	- N-Bromosuccinimide
Pd ₂ (dba) ₃	- Tris(Dibenzylideneacetone)dipalladium(0)
ppm	- parts per million
s	- singlet
t	- triplet
t-Bu) ₃ P	- tri- <i>tert</i> -butylPhosphine
td	- triplet doublet
THF	- tetrahydrofuran
TLC	- Thin-layer chromatography
TMS	- trimethylsilane [(CH ₃) ₃ SiH]
δ	- chemical displacement

1. Abstract

A family of benzothiophene and phenothiazine derivatives have been synthesized and characterized by ^1H NMR and mass spectroscopy.

Oxidation, Bromination, Alkylation and Iodination reactions have been carried out from 4,4-diphenylbromine, dibenzothiophene and phenothiazine using convergent synthesis according to yields and facilities of each reaction. The introduction of reactive functional groups as iodine and bromine in each case and alkyl chain for increase the solubility have been the main objectives of this project.

3,7-diiodobenzothiophene-S,S-dioxide, 3,7-dibromobenzothiophene-S,S-dioxide and 3,7-dibromo-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide are the target π -conjugated compounds which exhibit good charge transport properties according to viewed items.

These aromatic compounds have been synthesized with good yields and used as starting compounds for the performance of Ullmann coupling and Buchwald–Hartwig amination reactions in order to try to obtain the last phenyl compounds which will be used for the manufacturing of optoelectronic devices.

2. Objective

The main aim of this project is the synthesis of aromatic compounds derived from dibenzothiophene and phenothiazine, which will be the starting materials for the synthesis of organic compounds for optoelectronic devices.

The introduction of new functional groups by conventional chemistry ways, the study of the reactions conditions and yields as well as the characterization of these products by ^1H NMR and mass spectroscopy, have been carried out with the purpose to find the best synthetic routes.

3. Introduction

Phenothiazine and dibenzothiophene derivatives were synthesized and characterized in research group laboratory of Polymer Chemistry and Technology department of Kaunas University of Technology during February and June 2014.

This department is especially dedicated to the synthesis and study of organics semiconductors for optoelectronic applications, the cationic (photo)polymerization and (photo)cross-linking of electroactive monomers as a tool for the preparation of the layers for optoelectronic devices .

They are working in the field of synthesis and studies of organic electroactive materials, mainly organic semiconductors. They have been collaborating with big industrial companies such as „Imation“ and „Samsung Electronics“. The members of the group have published ca. 100 papers in the international scientific journals. They also co-authored ca. 50 patents and published patent applications of USA, Europe and Japan. The group has developed a number of effective organic charge-transporting materials.



Picture 1. Members of Polymer Chemistry and Technology Department of KTU

4. Literature review

An organic light-emitting diode (OLED) is a special type of light-emitting diode (LED).

OLED displays have attracted a lot of attention due to their many advantages such as fast response time, wide viewing angle, higher contrast ratio, and very thin structure. In 1978, Tang and Van Slyke of Kodak Company reported OLEDs based on small organic molecules by thermal vacuum deposition [2] and in 1990, at Cambridge University, Friend et al. reported OLEDs based on solution-processed semiconducting polymers [3].

These two pioneering works made a breakthrough in the OLED areas, and since then lots of papers on this subject were published. According to the materials used for OLEDs, OLEDs can be divided into two types: small-molecular OLEDs and polymer light-emitting diodes (PLEDs).

Generally, an OLED refers to small-molecular OLED.

A small-molecular OLED consists of one organic layer or multiple organic layers between two electrodes. The one organic layer device is called a single layer device. Thus, the organic material must serve all the three main functions: electron transport, hole transport and emission. In this case, the injection rates of both carriers should be almost equal for high efficiency. Otherwise, the surplus electrons or holes will not recombine, which results in low operation efficiency [3].

The simple structure of OLED is illustrated in Figure 1. The simplest OLED structure consist an anode (ITO), a hole transporting layer, an electron transporting layer with emitting function, and cathode [1]. In order to reduce the driving voltage and improve the efficiency of the OLED, the hole injection layer and electron injection layer have been introduced.

When a voltage is applied across the OLED, the charged carriers (holes and electrons) are injected from the anode and cathode into the adjacent organic layers, respectively.

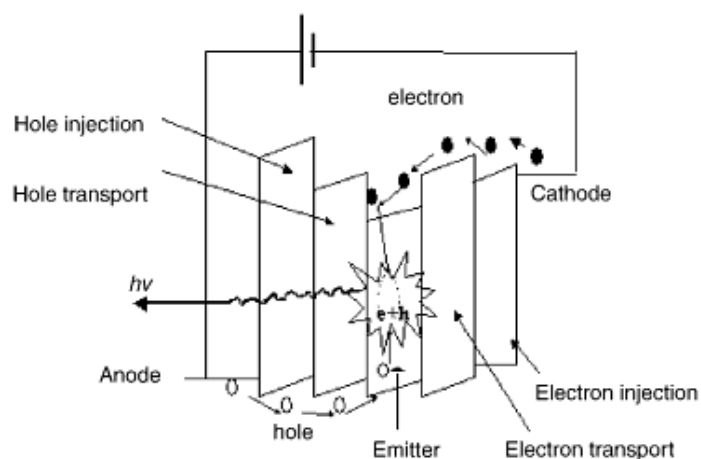


Figure 1. OLED structure

Traveling through the injection materials and transporting materials, the carriers with opposite polarity recombine in the emitting layer and generate the “exciton”. An exciton is essentially a molecule in the excited state. Is the relaxation of the exciton who leads to photon emission.

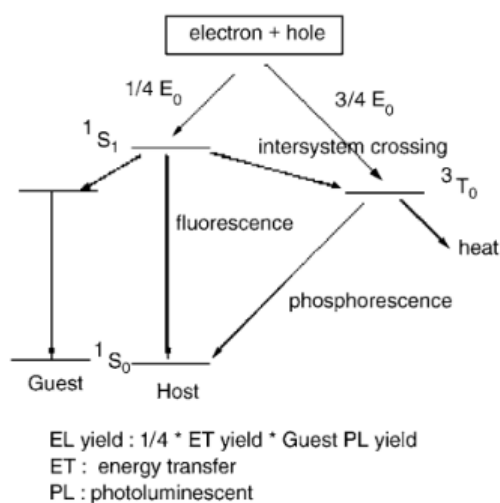


Figure 2. Hole-electron recombination and energy distribution

When the carriers with opposite polarity recombine they produce excitons. By means of the electroluminescent mechanism, there are four excited microstates of the exciton. One is the antisymmetry spin hybrid ($s=0$, singlet), and the other three are symmetry spin hybrids ($s=1$, triplet). According to the selection rule, only relaxation from the singlet excited state to the ground state is in general allowed. The fallowed relaxation that produces a photon is called fluorescence (see figure 2).

Relaxation from excited states to the ground state is forbidden in the selection rules. However, when spin orbital coupling occurs, this kind of relaxation can still take place, and is called phosphorescence [1].

The device performance of OLEDs depends on the charge balance of the injected holes and the electrons as well as the exciton confinement in the device. As π -conjugated emissive materials often exhibit better hole injection and transport than electrons, the charge balance of an OLED device is often optimized.

Charge carriers, that is, hole and electron, for organic materials corresponds to the cation and anion radicals of a molecule. It has generally been accepted that charge transport in organic disordered systems, for example, polymers and molecularly dispersed polymers, takes place by a hopping process. That is, charge transport in organic disordered systems is understood as a sequential redox process over molecules; electrons are sequentially transferred from the anion radical of a molecule to the neutral molecule through the lowest unoccupied molecular orbital (LUMO) for electron transport, and electrons are sequentially transferred from a neutral molecule to its cation radical through the highest occupied molecular orbital (HOMO) for hole transport [5].

Many studies about new organic compounds for OLED shown that it is possible to obtain single layer organic optoelectronic devices due to the capability of those organic compounds to have in the same structure the hole and electron transporting properties. This is the main reason which this project try to synthesize the starting compounds for the synthesis of targets with this important characteristics.

Therefore, multifunctional emissive materials with dipolar character, which transport holes and electrons more or less equally, may be used to simplify the fabrication and structure of a multilayer device. This approach has been widely investigated to correct the charge imbalance in molecular emissive materials by means of incorporating electron affinitive substituents such as diary amine functional groups into dibenzothiophene and phenothiazine as central cores [6].

5. Measurements

^1H NMR spectra were taken at 400 MHz and 750 MHz with Varian Unity Inova spectrometer using chloroform- d and $\text{DMSO-}d_6$ as solvents, and tetramethylsilane (TMS) as internal standard.

Mass spectra were obtained by SQ2 detector (Waters, USA). Positive electrospray ionization was used to ionize the samples.

^1H NMR results have been interpreted by MestreNova program.

6. Materials

Commercially available reagents were supplied by Aldrich Chemical Co. Starting compounds 4,4-dibromodiphenyl **1** and dibenzothiophene **3** and phenothiazine **12**, solvents and catalysts were used without further purification.

6.1. Solvents

Table 1. All solvents used during the experimentation with the respective proprieties

Solvent	Molecular formula	Molecular Mass (g/mol)	Density (g/L)	Boiling point (°C)	Purity %
Acetone	$\text{C}_3\text{H}_6\text{O}$	58,08	0,791	56	99,9
Carbon Tetrachloride	CCl_4	153,82	1,594	76-77	99,85
Chloroform	CHCl_3	119,38	1,492	60,5-61,5	99,9
Chloromethane	CH_3Cl	50,49	0,742	-23,8	99,5
Dichloromethane	CH_2Cl_2	84,93	1,325	39,8-40,0	99,9
Ethanol	$\text{C}_2\text{H}_6\text{O}$	46,07	0,816	78,3	95,0
Ethylacetate	$\text{C}_4\text{H}_8\text{O}_2$	88,11	0,902	76,5-77,5	99,8
Glacial Acetic Acid	$\text{C}_2\text{H}_4\text{O}_2$	60,05	1,049	117-118	99,7
Hexane	C_6H_{14}	86,18	0,659	69	95,0
Methanol	CH_4O	32,04	0,791	64,7	99,9
o-Dichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$	147,00	1,306	178-180	98,5
Petroleum ether			0,661	50-70	
Sulfuric Acid	H_2SO_4	98,08	1,840	290	96,5
Tetrahydrofuran	$\text{C}_4\text{H}_8\text{O}$	72,11	0,889	65-67	99,9
Toluene	C_7H_8	92,14	0,865	110-111	99,75
N,N-Dimethylformamide	$\text{C}_3\text{H}_7\text{ON}$	73,09	0,944	153	
Deuterated Chloroforms	CDCl_3	120,38	1,500	60,9	99,0
Dimethylsulfoxide (DMSO – d_6)	$\text{C}_2\text{H}_6\text{OS}$	78,13	1,100	189	99,5

6.2. Catalysts

Table 2. All the catalysts with the respective proprieties.

Catalyst	Molecular formula	Molecular Mass (g/mol)	Density (g/L)	Boiling point (°C)	Purity %
Tetrabutylammonium Hydrogensulfate	C ₁₆ H ₃₇ NO ₄ S	339,53			97
Tris(Dibenzylideneacetone)dipalladium(0)	C ₅₁ H ₄₂ O ₃ Pd ₂	915,72			97
Tri-<i>tert</i>-butylPhosphine	C ₁₂ H ₂₇ P	202,32	0,834	102-103	98

6.3. Reagents

Table 3. All reagents used during the experimentation with the respective proprieties.

Reagent	Molecular formula	Molecular Mass (g/mol)	Density (g/L)	Boiling point (°C)	Purity %
18-Crown-6	C ₁₂ H ₂₄ O ₆	264,32			99,0
2-Ethylhexylbromide	C ₈ H ₁₇ Br	193,12	1,086	75-77	94,0
4,4'-Dibromobiphenyl	C ₁₂ H ₈ Br ₂	312,00		355-360	97,5
4,4'-Dimethoxydiphenylamine	C ₁₄ H ₁₅ NO ₂	229,27			98,5
Copper powder	Cu	63,55	8,94	2567	99,9
Dibenzothiophene	C ₁₂ H ₈ S	184,26		332-333	97,5
Diphenylamine	C ₁₂ H ₁₁ N	169,22		302	99,0
Hydrogen Peroxide	H ₂ O ₂	34,01	1,11	150,2	30,0
Iodic acid	HIO ₃	175,91	4,62		99,5
Iodine	I ₂	253,81	4,93	184	99,8
N-bromosuccinimide	C ₄ H ₄ BrNO ₂	177,98	2,09	339	99,0
Phenothiazine	C ₁₂ H ₉ NS	199,27		371	98,0
Potassium Carbonate anhydrous	K ₂ CO ₃	138,21	2,43		99,9
Potassium Hydroxide	KOH	56,11	2,12	1327	85,0
Potassium <i>tert</i>-Butoxide solution 1M	C ₄ H ₉ OK	112,21	0,902		
Sodium Hydrogen carbonate	NaHCO ₃	84,01	2,20		99,9
Sodium sulfate anhydrous	Na ₂ SO ₄	142,04	2,68	1429	99,0
Sodium sulfite	Na ₂ SO ₃	126,04	1,56		98,0
Sodium <i>tert</i>-Butoxide	C ₄ H ₉ ONa	96,10			99,9
Chlorosulfonic Acid	HSO ₃ Cl	116,52	1,75	151-152	99,0

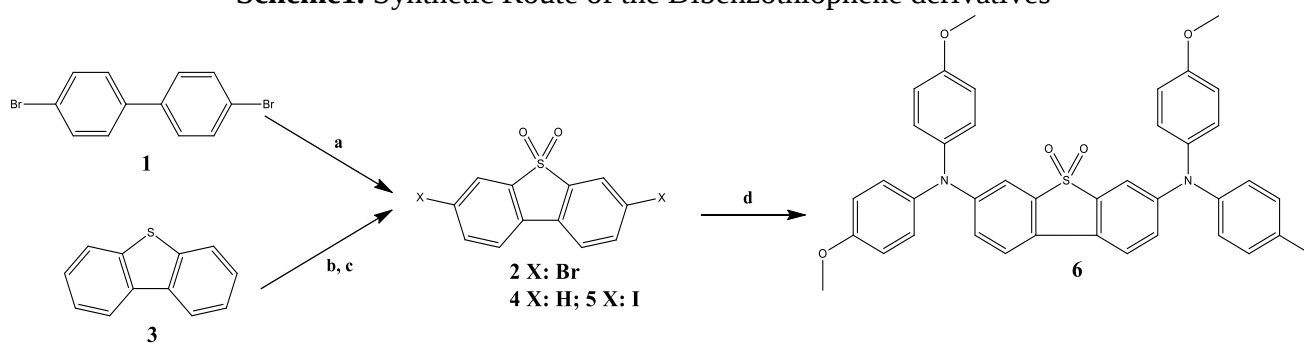
7. Experimental section

7.1. Dibenzothiophene derivatives

7.1.1. Synthesis of 3,7-bis(bis(4-methoxyphenyl)amino)dibenzothiophene 5,5-dioxide (6)

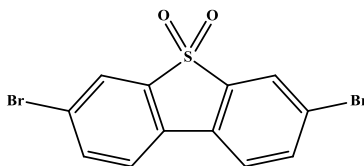
The general synthetic routes to the derivative compounds are outlined in Scheme 1.

Scheme1. Synthetic Route of the Dibenzothiophene derivatives*



* Conditions: (a) CHCl_3 , HSO_3Cl , $<50^\circ\text{C}$; (b) CH_3COOH , H_2O_2 , 115°C ; (c) CH_3COOH , I_2 , HIO_4 , 100°C ; (d) Ullmann coupling reaction¹.

3,7-dibromo-dibenzothiophene-S,S-dioxide (2) [7]



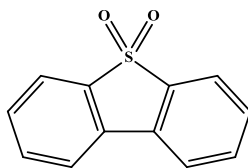
4,4-Dibromodiphenyl **1** (2 g, 6.41 mmol) was dissolved in chloroform (18 mL) in a two-necked round bottom flask. Sulfonic chloride acid 1.14 mL (2 g 17.16 mmol) was added slowly to solution stirred and heated under 50°C during the addition. The color of the mixture darkens as more excess reagent is added. After the addition, the mixture was cooling till room temperature and stirred for 6h more. The reaction was monitoring by TLC using $\text{H} : \text{EtAc}$ (v/v 5:1) as eluent. When TLC showed that the reaction has completed, the mixture was poured very slowly into ice-water and stirred.

After the ice has melted, the mixture was neutralized with hydrogen sodium carbonate NaHCO_3 , the formed solid was filtered and recrystallized from acetic acid.

Final white needles, 0.80g was obtained with yield 34% $M = 374,05 \text{ g/mol}$, $(\text{C}_{12}\text{H}_6\text{Br}_2\text{O}_2\text{S})$

¹ Irina, P, B .; Andrei, V, C.: Coordination Chemistry Reviews 248 (2004) 2337–2364.

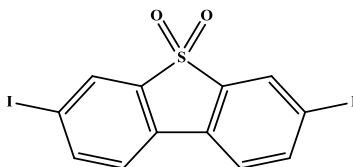
Dibenzothiophene-S,S-dioxide (4) [8]



To a stirred solution of dibenzothiophene **3** (5 g, 27 mmol) in 25 mL of acetic acid was added Hydrogen peroxide 8 mL (9 g, 270 mmol) by addition funnel increasing the temperature till 115 °C. The reactions was followed by TLC using as eluent a mixture of H: EtA (v/v 1:1). After 48h under reflux, the mixture was cooled to room temperature, and the solid filtrated and washed with water.

Final yellow light needles, 4.52g was obtained with yield 77%. M 216,26 g/mol, (C₁₂H₈O₂S)

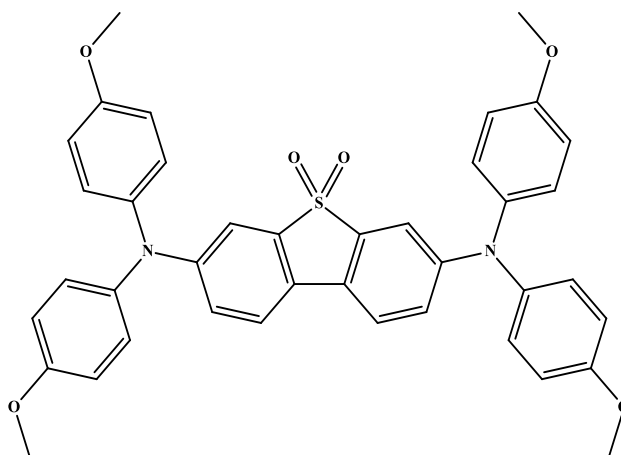
3,7-diiodobenzothiophene-S,S-dioxide (5) [8]



In a two-necked round bottom flask was dissolved dibenzothiophene-S,S'-dioxide **4** (0.5 g, 1.34 mmol), in acetic acid (10 mL), water (1 mL), concentrated sulfuric acid (1 mL), added iodine (0.41 g, 1.61 mmol), iodic acid (0.37 g, 1.61 mmol) and heated at 100 °C for 48h under vigorously stirred conditions. After, the mixture was cooled to room temperature and poured into water and extracted with dichloromethane. The combined dark purple organic layer was decolorized by sodium sulfite, washed with water and dried with sodium sulfate anhydrous, filtered and evaporated to dryness. The product was purified by column chromatography using as eluent a mixture solvent of petroleum ether: dichloromethane (v/v 1:1).

Final white needles, 0.93g was obtained with yield 86% M 468,05 g/mol, (C₁₂H₆I₂O₂S)

3,7-bis(bis(4-methoxyphenyl)amino)dibenzothiophene-5,5-dioxide (6)



This target compound was obtained by an improved Ullmann coupling reaction 0.1g (0.2 mmol) of 3,7-Diiodobenzothiophene S,S' dioxide **5**, 0.1g (0.45 mmol) 4,4'-Dimetoxidiphenylamine and 0.037g (0.14 mmol) 18-crown-6 were dissolved in 5mL of o-Dichlorobenzene under inert atmosphere and increasing the temperature till 100°C. After 0.22g (1.6 mmol) of K₂CO₃ was added onto the mixture and the temperature was increasing slowly till 150°C. At this temperature 0.051g (0.8 mmol) copper powder was added and the temperature increasing till 200°C. The reaction was finished after 48h.

Then, copper and inorganic salts were removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and finally the product purified by column using gradient of polarity an eluent a mixture of Hexane/Ethylacetate.

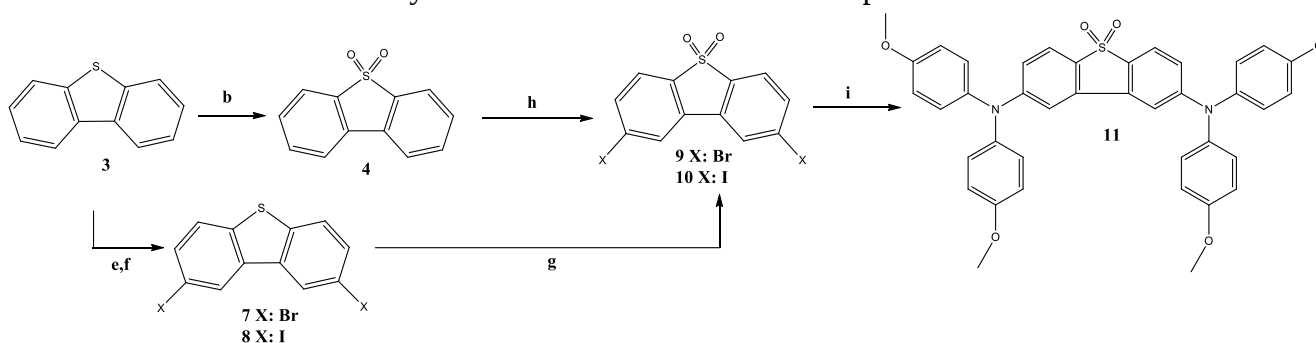
Chromatography column using gradient of polarity is necessary when the TLC shows many closely spaced spots which can't be separated by only one kind of eluent. In this case is usually to start from an eluent less polar and step by step increase the polarity of the eluent. In this experiment was used first a mixture of Hexane/Ethylacetate (v:v = 50:1) after (v:v = 20:1), then (v:v = 10:1), (v:v = 8:1) and finally (v:v = 5:1).

This reaction was performed using as starting compound 3,7-diiodobenzothiophene-S,S'.dioxide **2** using the same procedure but the result was the same, the final compound was not obtained according to it characterization.

7.1.2. Synthesis of 2,8-bis(bis(4-methoxyphenyl)amino)dibenzothiophene-5,5-dioxide (11)

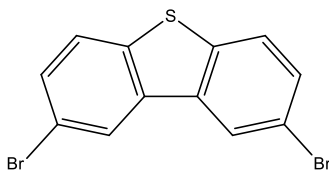
The general synthetic routes to the derivative compounds are outlined in Scheme 2.

Scheme 2. Synthetics Routes of the dibenzothiophene derivative^{*}



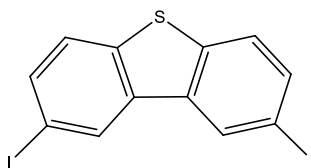
^{*}Conditions: (e) CHCl_3 , NBS ; (f) I_2 , HIO_4 , AcOH <50 °C overnight ; (h) CHCl_3 , NBS (g) CH_3COOH , H_2O_2 , 115°C

2,8-dibromodibenzothiophene (7) [7]



To a solution of dibromodibenzothiophene **3** (1 g, 54,3 mmol) in 20mL chloroform was added two equivalents of NBS (1,93 g 10,9 mmol) and stirred during 24h at room temperature. After the mixture was cooled to room temperature and TLC was performed in order to reveal if the reaction was completed. Unfortunately the TLC shown any change compared with the starting compound, therefore the bromination reaction by NBS did not occur.

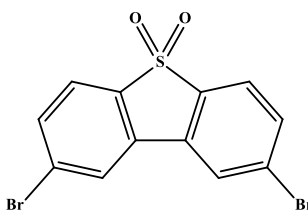
2,8-diiodobenzothiophene (8) [8]



In a double-necked round bottomed flask was dissolved dibenzothiophene **3** (1.84g, 10 mmol) in acetic acid (10 mL), water (1ml), concentrated sulfuric acid (1ml), was added iodine (2.54 g, 10 mmol), periodic acid (2.28 g, 10 mmol) and chloroform (10 mL) in three portions under vigorous magnetic stirred conditions and heated at 50 °C for overnight. After cooled to room temperature, the reaction mixture was poured into water and extracted with dichlorometane (3x 50 mL). The combined dark purple organic layer was decolorized with sodium sulfite, washed with water, dried with anhydrous magnesium sulfate, filtered and evaporated to dryness. Purification of the crude product by column chromatography using as eluent a mixture EtAc:H (v/v= 1:5).

The characterization of the product by ^1H NMR and MS showed that the iodination compound was not obtained.

2,8-dibromobenzothiophene-S,S-dioxide (9) [7]



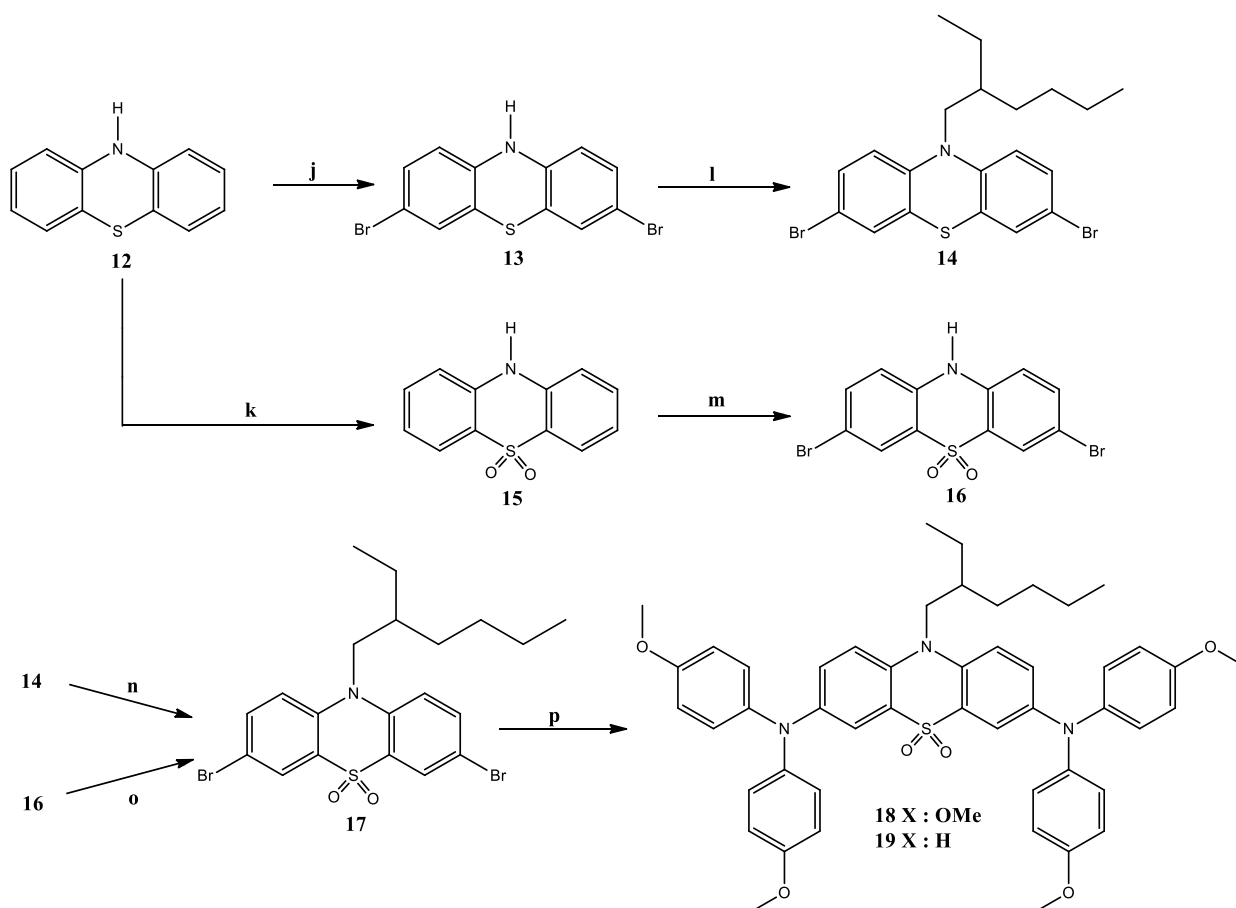
To a stirring solution of benzothiophene-S,S'-dioxide **4** (0.3 g, 0.8 mmol) in 10mL was added 2.1 equivalents of NBS (1 g 1.7 mmol) and stirred during 24h at room temperature. As well as in the bromination of dibenzothiophene **3**, the TLC, using H : EtAc (v/v 1:1) as eluent, revealed that the bromination by NBS did not take place.

7.2. Phenothiazine derivatives

7.2.1. Synthesis of 3,7-bis(bis(4-methoxyphenyl)amino)-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide (18)

The general synthetic routes to the derivative compounds are outlined in Scheme 3.

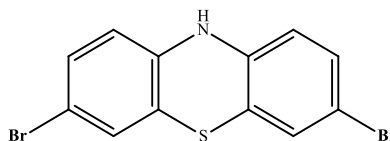
Scheme 3. Synthetic route of Phenothiazine derivative^{*}



^{*}Conditions: (j) THF, NBS, 24h >0°C; (k) CH₃COOH, H₂O₂ <50°C; (l) 2-Ethylhexylbromide, KOH, K₂CO₃, tetrabutylammonium hydrogensulphate; (m) THF, NBS, 24h >0°C; (n) CH₃COOH, H₂O₂ <50°C; (o) 2-Ethylhexylbromide, KOH, K₂CO₃, tetrabutylammonium hydrogensulphate; (p) Buchwald-Hartwig amination².

² Paul, T. A.; Robert, H. C.; Green chemistry- Homogeneous catalysis.

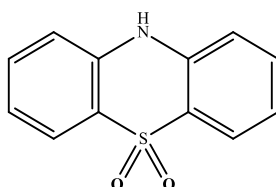
3,7-dibromo-10H-phenothiazine (13) [9]



To a solution of phenothiazine **12** (3 g, 15 mmol) in THF (30 mL) was added dropwise 2.2 equivalents of NBS (5.87 g 33 mmol) using dropping funnel during 1 hour and 30 minutes. During the addition the reaction was stirred and temperature was keeping under 0 °C in an ice bath for 24h. TLC showed the end of the reaction using EtAc:Hexane (v/v 1:4) as eluent. The product was purified by column chromatography (EtAc:Hexane v/v 1:8). Finally light green crystals were obtained and characterized by ^1H NMR.

Final brown viscous liquid, 2.5 g was obtained with 46.3% of yield M 357,06 g/mol, ($\text{C}_{12}\text{H}_7\text{Br}_2\text{NS}$)

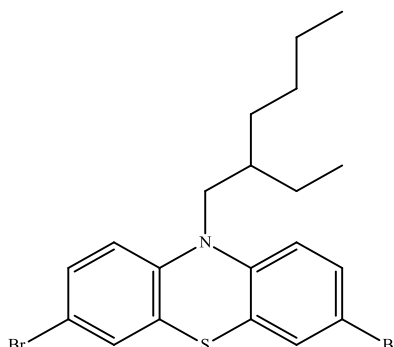
10H-phenothiazine-5,5-dioxide (15) [10]



1 g (5 mmol) of phenothiazine **12** was dissolved in 20 mL glacial acetic acid keeping the temperature at 45-50 °C. After 1.2 mL hydrogen peroxide was added dropwise onto the solution and stirred during 48h until the complete consumption by TLC monitoring. After the mixture was extracted with ethyl acetate and the brown product was dried using vacuum.

Final brown viscous liquid, 0.80 g was obtained with 69% of yield M 231,27 g/mol, ($\text{C}_{12}\text{H}_9\text{NO}_2\text{S}$)

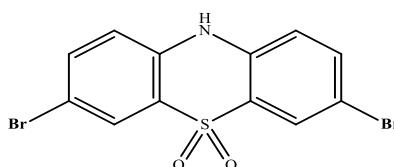
3,7-dibromo-10-(2-ethylhexyl)-phenothiazine (14) [11]



A round bottomed flask was charged with 3,7-dibromo-10H-phenothiazine **13** (0.5 g, 1.4 mmol) and dissolved in acetone 20 mL, stirred and heated till 65 °C under reflux. When the compound it dissolved, was added 0,4 mL (0,41 g, 2.1 mmol) 2-ethylhexylbromide and in three portions, 0.28 g potassium hydroxide and 0.7 g of K₂CO₃. A little amount of tetrabutylamonium hydrogensulphate catalyst was added into the mixture and stirred till TLC reveled the end of the alkylation. After the solution was extracted with ethyl acetate dried with sodium sulfate anhydrous and the solvent was evaporated obtaining a viscous product. This viscous product was purified by column chromatography using EtAc:H (v/v 1:5) .

Final brown viscous liquid, 0.23 g was obtained with 35 % of yield M 469,28 g/mol, (C₂₀H₂₃Br₂NS)

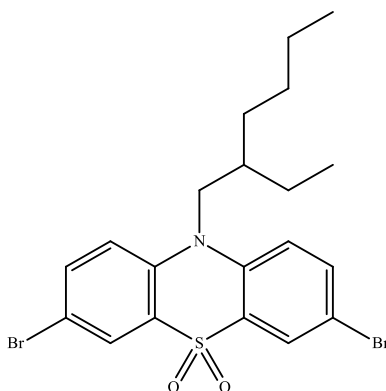
3,7-dibromo-10H-phenothiazine 5,5-dioxide (16) [10]



To a solution of 10H-phenothiazine 5,5-dioxide **15** (0.3 g, 0.8 mmol) in THF (3 mL) was added dropwise 2.2 equivalents of NBS (0.32 g 33 mmol) using dropping funnel for 1 hour. During the addition the reaction was stirred and temperature was

keeping under 0 °C in an ice bath for 24h. EtAc:H (v/v 1:1) as eluent was used for TLC which shown that the reaction did not take place.

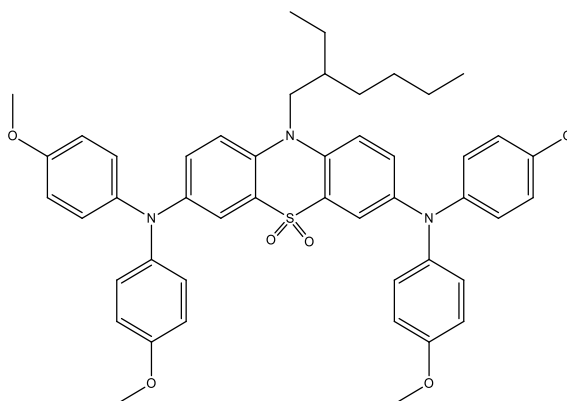
3,7-dibromo-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide (17) [11]



To a stirred solution of 3,7-dibromo-10-(2-ethylhexyl)-10H-phenothiazine **14** (0.72 g, 1.5 mmol) in 25 mL of acetic acid was added Hydroperoxide 0.45 mL (0.51 g, 15 mmol) by addition funnel increasing the temperature till 115 °C. The reactions was followed by TLC using as eluent a mixture of H: EtAc (v/v 1:1). After 48h under reflux, the mixture was cooled to room temperature, and the solid filtrated and washed with water. 1 g of brown viscous liquid mas obtained.

Final brown viscous liquid, 0.4 g was obtained with 52% of yield M 501,28 g/mol, (C₂₀H₂₃Br₂NO₂S)

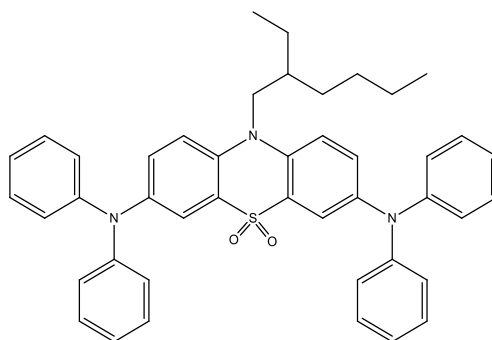
3,7-bis(bis(4-methoxyphenyl)amino)-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide (18) [12]



$\text{Pd}_2(\text{dba})_3$ (0.14 g, 0.15 mmol) and $(t\text{-Bu})_3\text{P}$ (0.13 g, 1.15 mmol) were dissolved under Ar in 20 mL of dry toluene and stirred for 10 minutes in room temperature in order to perform the catalyst of the Buchwald-Hartwingm reaction.

Then the mixture of 3,7-dibromo-10-(2-ethylhexyl)-phenothiazine 5,5-dioxide **17** (0.5 g, 1 mmol), 4,4'-dimethoxydiphenylamine (0.17 g, 0.77 mmol) and potassium *tert*-butoxide (0.13 g, 1.15 mmol) was dissolved in 50 ml of dry toluene and added to the flask where the catalyst is and the reaction mixture was heated at 90°C for 48h. After cooling the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine (1M NaOH solution). After being dried over MgSO_4 and filtered, the solvent was removed and a sample from the viscous residue was taken for preform TLC using as eluent a mixture of H: EtAc (v/v 5:1), which shown many spots and it was decided not to carry out column chromatography due to the difficulty to separate all the compounds from the reaction mixture.

3,7-bis(bis(4-methoxyphenyl)amino)-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide (19) [12]



The same procedure as described previously for the last compound was performed for introduces diphenylamine functional group into the dibenzothiophene core.

$\text{Pd}_2(\text{dba})_3$ (0.171 g, 0.19 mmol) and $(t\text{-Bu})_3\text{P}$ (0.038 g, 0.19 mmol) were dissolved under Ar atmosphere in 20 mL of dry toluene and stirred for 10 min in room temperature in order to perform the catalyst of the Buchwald-Hartwingm reaction. Then the mixture of 3,7-dibromo-10-(2-ethylhexyl)-phenothiazine 5,5-dioxide 17 (2.3 g, 4.8 mmol), and sodium *tert*-butoxide (0.69 g, 7.2 mmol) was dissolved in 50 mL of dry toluene and added to the flask where the catalyst was, and the reaction mixture was heated at 90°C for 48 h. After cooling the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine (1M NaOH solution). After being dried over MgSO_4 was filtered, the solvent was removed and a sample from the viscous residue was taken to perform TLC which, as in the previous reaction, shown many spots and it was decided not to carry out column chromatography due to the difficulty to separate all the compounds from the reaction mixture.

8. Results and discussions

The main ^1H NMR and MS of the obtained products are showed below.

3,7-dibromo-dibenzothiophene-S,S-dioxide (2)

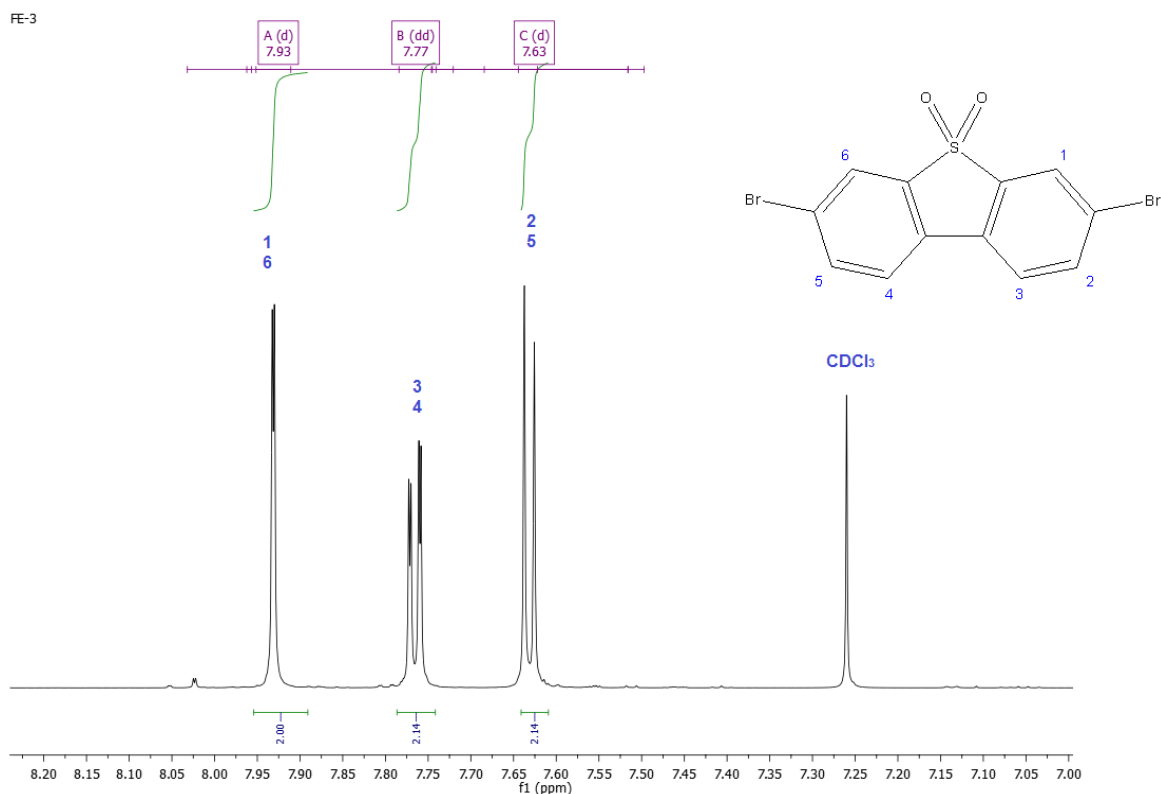


Figure 3. ^1H NMR (750 MHz, CDCl_3) $\delta(\text{ppm})$ spectra of **2** compound

^1H NMR of 3,7-dibromodibenzothiophene-S,S-dioxide **2** was performed in deuterated chloroform using 750MHz frequency apparatus. This symmetric molecule should show on the spectra three signals around the aromatic zone corresponding to three aromatic protons. These protons are coupled by spin-spin coupling. It involves the different magnetic environments that a specific proton feels due to the presence of other protons that are (generally) attached to adjacent carbons.

As in the spectra shows, all this three signals integrate two isochrones protons. First of all, there is a doublet at 7.93 ppm corresponding to 1 and 6 protons which coupling constant is 1,7 Hz , a double doublet at 7.77 ppm with 8.2 Hz orto constant coupling (J_{orto}) and 1.7 Hz J_{meta} corresponding to 3 and 4 protons. Protons 2 and 5 show a doublet at 7.63 Hz with a J_{orto} 8.2 Hz. Finally there is a solvent signal at 7.25 ppm.

Dibenzothiophene-S,S-dioxide (4)

FE-2

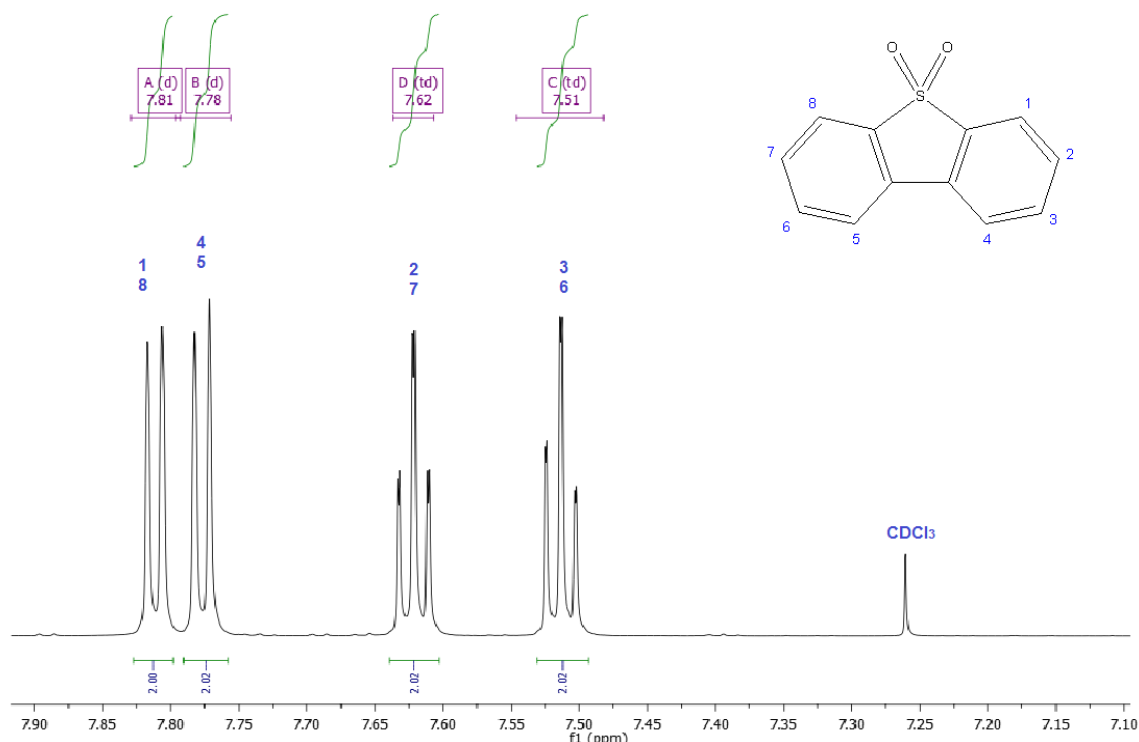


Figure 4. ^1H NMR (750 MHz, CDCl_3) $\delta(\text{ppm})$ spectra of **4** compound

^1H NMR of Dibenzothiophene-S,S-dioxide **4** was performed in deuterated chloroform using 750MHz frequency apparatus. This symmetric molecule should show on the spectrum four signals around the aromatic zone (7-9 ppm) corresponding to four aromatic protons. These protons are also coupled by spin-spin coupling with orto, para and meta coupling constants.

As it is expected to see in this spectrum at 7.81 ppm there is a doublet which integrates two protons corresponding to 1 and 8, with 7.6 Hz of J . The next signal is a doublet that belongs to 4 and 5 protons and appears at 7.78 ppm of displacement with 7.7 Hz of J .

2 and 7 protons show a triplet doublet at 7.62 ppm with a J_{orto} 7.60 Hz and J_{meta} 1.0 Hz. The last triplet doublet belongs to 3 and 6 protons which appear at 7.51 ppm of displacement, J_{orto} and J_{meta} in this case are 7.60, 0.8 Hz respectively.

Finally there is a solvent signal at 7.25 ppm.

3,7-diiodobenzothiophene-S,S-dioxide (5)

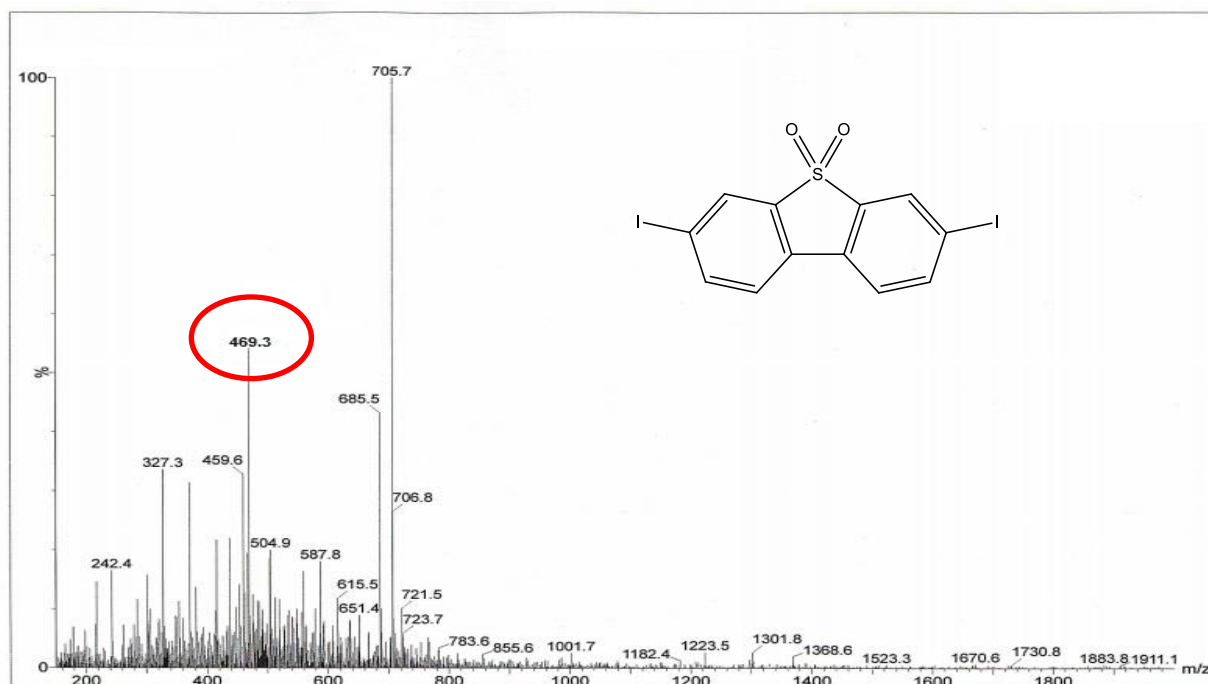


Figure 5. MS spectra of 5 compound

Chemical Formula: $C_{12}H_6I_2O_2S$

Molecular Weight: 468,3 g/mol

$m/z(\%) = 469.3 [M + H]^+$

The compound 3,7-diiododibenzothiophene-S,S-dioxide 5 was characterized only by MS. As it shows in this spectra, one of the main peak belong to the molecular weight plus 1. Normally, in this kind of synthesis, the product can be not pure therefore is not easy to interpret mass spectra. As it can see, the fact that one of the main peaks belong to the molecular weight of this compound it means that the typical fragmentation is given in a high percent.

3,7-dibromo-10H-phenothiazine (**13**)

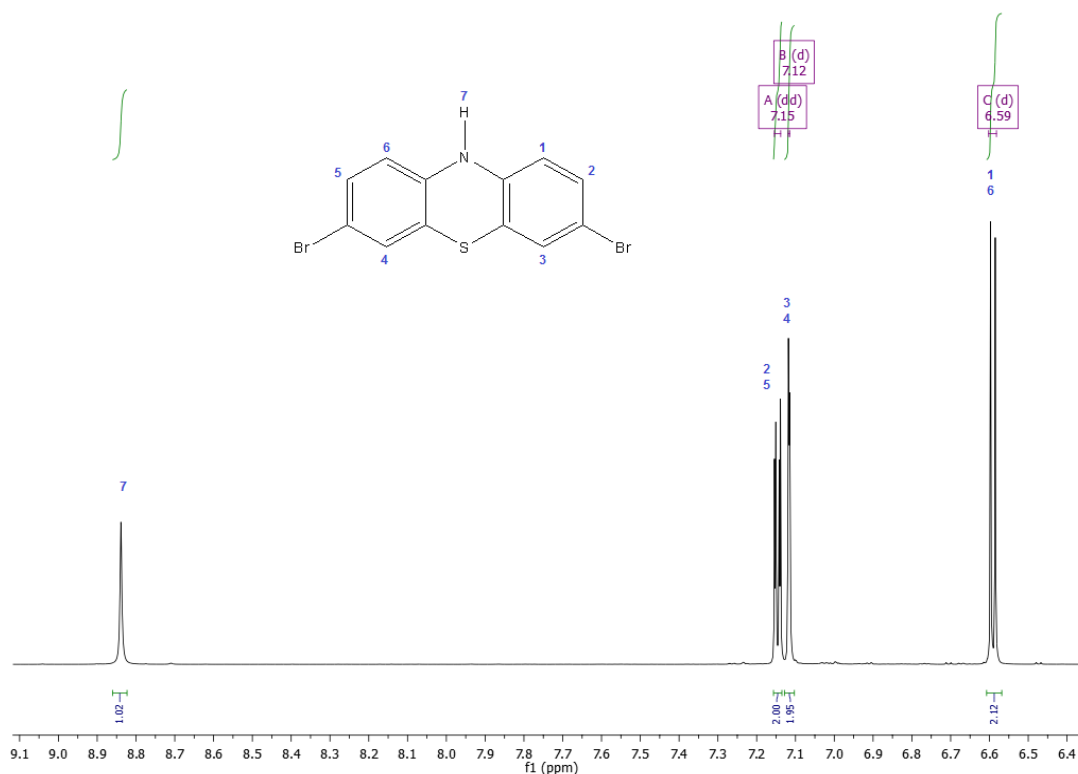


Figure 6. ¹H NMR (400 MHz, CDCl₃) δ(ppm) spectra of **13** compound

¹H NMR of 3,7-dibromo-10H-phenothiazine **13** was performed in DMSO-*d*₆ using 400 MHz frequency apparatus. This symmetric molecule should show on the spectrum four signals, three of which integrate two protons and appear around the aromatic zone (7-9 ppm) corresponding to six aromatic protons. These protons are also coupled by spin-spin coupling with orto and meta coupling constants.

As it is expected to see in this spectrum at 8.84 ppm there is a singlet which integrates one proton corresponding to nitrogen proton.

The next signal is a double doublet that appears at 7.15 ppm of chemical displacement and belongs to 2 and 5 which are coupled with protons in orto and meta. J_{orto} and J_{meta} are 8.5, 2.3 Hz respectively.

The protons 3 and 4 show a doublet at 7.12 ppm with a 2.2 Hz of J . The doublet at 6.59 ppm belongs to protons 1 and 6 with 8.5 Hz of J .

10H-phenothiazine 5,5-dioxide (15)

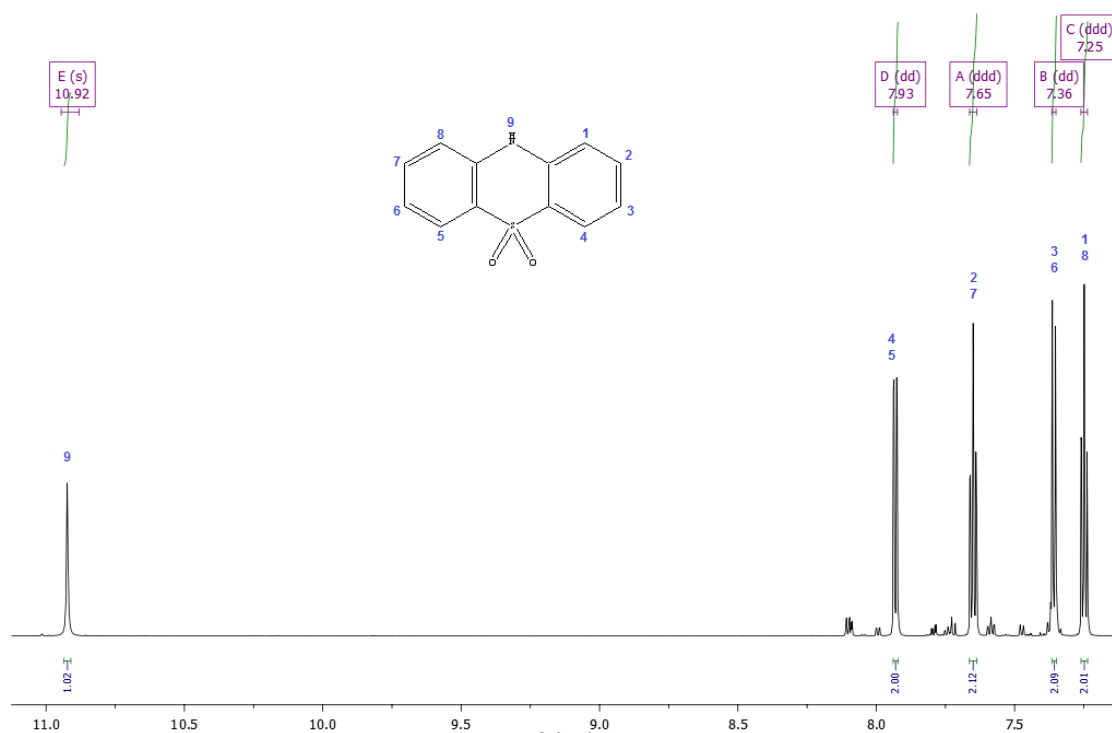


Figure 7. ^1H NMR (750 MHz, CDCl_3) $\delta(\text{ppm})$ spectra of **15** compound

^1H NMR of 10H-phenothiazine-5,5-dioxide **15** was performed in $\text{DMSO}-d_6$ using 750MHz frequency apparatus. In this case it should show on the spectrum four signals around the aromatic zone (7-9 ppm) corresponding to four aromatic protons and one signal. These protons are also coupled by spin-spin coupling with ortho, para and meta coupling constants.

As it is expected to see in this spectrum at 7.93 ppm there is a double doublet which integrates two protons corresponding to 4 and 5, with J_{ortho} 8.0 Hz and J_{meta} 1.4 Hz.

The next signal is a double double doublet that belongs to 2 and 7 protons and appears at 7.65 ppm with J_{ortho} 8.5 Hz, J_{meta} 1.2 Hz and J_{para} 1.5 Hz.

3 and 6 protons show a double double doublet at 7.25 ppm with a J_{ortho} 7.9 Hz, J_{meta} 2.3 Hz and J_{para} 0.9 Hz.

A double doublet appears at 7.36 ppm and belongs to 3 and 6 protons J_{ortho} and J_{meta} in this case are 8.3, 0.4 Hz respectively.

Finally there is a singlet corresponding to the amino proton (9) at 10.92 ppm.

3,7-dibromo-10-(2-ethylhexyl)-phenothiazine (14)

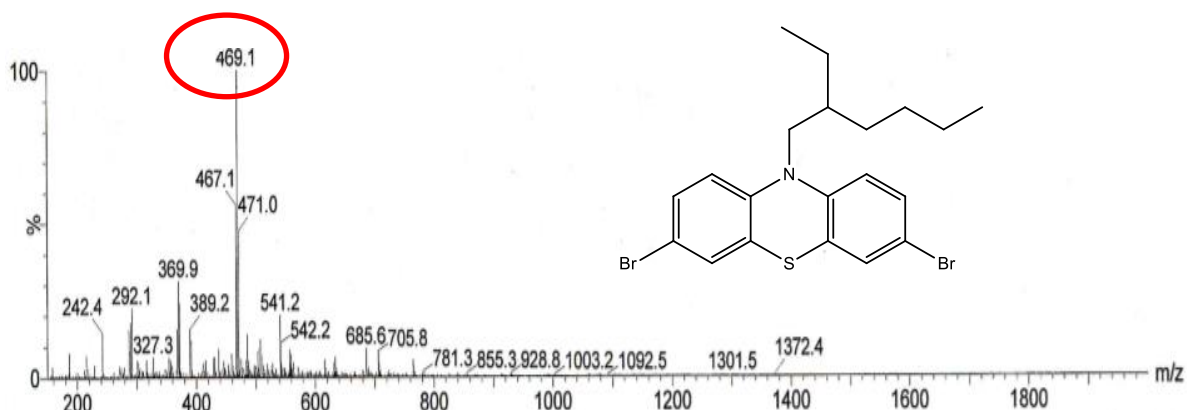


Figure 8. MS spectra of 14 compound

Chemical Formula: $C_{20}H_{23}Br_2NS$

Molecular Weight: 468,28 g/mol

$m/z(\%) = 469.1 [M + H]^+$

The compound 3,7-dibromo-10-(2-ethylhexyl)-phenothiazine **14** was characterized only by MS. As it shows in this spectra, the molecular peak correspond to the molecular weight plus 1, therefore it means that the expected product has been obtained.

7-dibromo-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide (17)

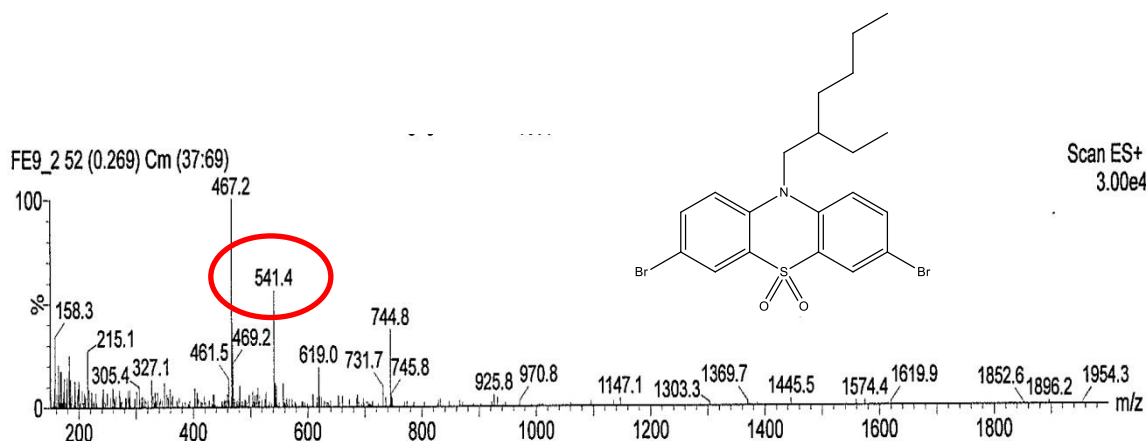


Figure 9. MS spectra of 17 compound

Chemical Formula: $C_{20}H_{23}Br_2NSO_2$

Molecular Weight: 501.28 g/mol

$m/z(\%) = 541.4 [M + Ar]^+$

The compound 7-dibromo-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide **17** was characterized only by MS. As it shows in this spectra, one of the main peak belong to the molecular weight plus 40 corresponding to Argon molecular weight.

9. Conclusions

- Phenothiazine and dibenzothiophene derivatives have been synthesized with different ways and different yields.
- 2,8-dibromobenzothiophene (7) was not obtained by bromination of benzothiophene with NBS. Probably would have been obtained by bromination with bromine, but due to the danger of the reaction, this was not attempted.
- 2,8-diiodobenzothiophene (8) also was not obtained by Iodination of benzothiophene with Iodine and periodic acid. Probably the reaction can occur if the Iodine is added by little portions and waiting till it dissolves in to the solvent. Also the presence of acid sulfuric can produce the oxidation of the product.
- The bromination using NBS of dibenzothiophene-S,S-dioxide and 10H-phenothiazine 5,5-dioxide to give 2,8-dibromobenzothiophene-S,S- dioxide (9) and 3,7-dibromo-10H-phenothiazine 5,5-dioxide (16) respectively, didn't take place.
- The following target compounds; 3,7-diiodobenzothiophene-S,S'-dioxide, 3,7-dibromobenzothiophene-S,S-dioxide and 3,7-dibromo-10-(2-ethylhexyl)-phenothiazine-5,5-dioxide, have been synthesized successfully and characterized by ^1H NMR and MS.
- The last phenil compounds were not obtained by Ullman and Buchwald-Hartwig coupling reactions, probably because of the many difficulties presented by this kind of catalytic reactions.
- These ways of synthesis should be performed in order to obtain the final compounds.

10. Acknowledgment

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SYNTHESIS AND CHARACTERIZATION OF DIBENZOTHIOPHENE AND PHENOTHIAZINE DERIVATIVES FOR ORGANIC OPTOELECTRONIC DEVICES by [Ei Ouahabi, Fátima Aušra Tomkeviien](#) is licensed under a [Creative Commons Reconocimiento-NoComercial-SinObraDerivada 4.0 Internacional License](#).

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