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New Heterocyclic Compounds From Butadienyl Sulfanes and Thiols†

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2-Chloroethyl-pentachlorobutadienyl-sulphide reacts with some heterocyclic thiols (7-mercapto-4-methylcoumarin, 2-mercaptobenzimidazole derivatives *etc*.) in water-ethanol mixture in the presence of sodium hydroxide to give the new heterocyclic thioethers. New 2-(4-(2-chloro-ethylthio)-1,2,3,4-tetrachlorobuta-1,3-dienylthio)ethanol compound was obtained from the reaction of 1,4-*bis*(2-hydroxyethylthio)-1,2,3,4-tetrachloro-1,3-butadiene with $SOCl_2$ in pyridine. The structures of the new compounds were characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, MS and fluorescence spectrophotometry.

Keywords: Thioethers, Heterocyclic compounds, Benzimidazole, Coumarin, Nicotinicacid, Benzothiazole, Fluorescence property.

INTRODUCTION

Coumarin derivatives are important for their well-known biological activity[1-4]. There has been a continuous interest in the synthesis[5] of coumarin derivatives. The heteroaryl coumarine having activity as leukotriene biosynthesis inhibitors are useful as antiasthamic, antiallergic, antiinflammatory and cytoprotective agents.

They are also useful in treating angina, cerebral spasm, glomerular nephritis, hepatitis, endotoexamia and allograft rejection and in preventing the formation of atherosclerotic plaques[6]. The certain coumarin derivatives have particularly advantageus properties as optical whitening and/or brightening agent of polyamide, polyester, acrylic and other synthetic fibres[7,8].

Materials containing a coumarine component have been useful in many fields due to their characteristics of high emission yield, excellent photo-stability and extended spectral range, such as fluorescent images, non-linear optical materials, liquid crystals and fluorescent labels for fluorescence energy transfer experiments[9]. Their fluorescence properties have also been used as an advantage for the biochemical assay of enzymes[10]. The biological activities of coumarins and mercaptobenzoxazoles are well known and include antiviral, anticonvulsant, antimicrobial, antibacterial, anticancer and anti-HIV properties[11,12].

The 2-mercaptobenzimidazole derivatives are useful as medicine such as an antihyperlipemic agent or antiarteriosclerotic agent and also useful as an addivite for silver halide photosensitive materials liquid crystals and the like[13].

The 2-mercaptobenzimidazoles different biological activities (bacteriostatic, insecticidal, anthelminthic, antiinflammatory, antipyretic, antidepressant, analgetic, antihistaminic, antiallergic, antihypoxant, antiulcerous, antiischaemic, antiarrithmic activity, *etc*.) is known in the literature[14].

There have been patented many different S-substituted 2-mercaptobenzimidazoles with antiulcerous activity, some of them omeprezol, lansoprazol are used in clinical practice.

Thioethers are involved in the synthesis of specific classes of compounds including agricultural chemicals[15-17], pharmacological drugs[18,19], chemical resistant polymers[20,21] and rubber antioxidant[22,23]. Alkyl and heterocyclic sulphides exhibit pharmacological activity, germicidal properties[24] *e.g*., some unsymmetrical sulphides exhibit antioxidant activity[25].

The reaction of hexachloro-1,3-butadiene (**1**) with some thiols in DMF, DMSO and EtOH has been reported[26-28]. Some thioethers were obtained from the reaction of hexachloro-1,3-butadiene with methanethiol in EtOH. In an US Patent is reported, that these compounds exhibit biological activity[29].

The aim of this work was to synthesize new unsatured sulfanes containing a heterocyclic component(benzimidazole, coumarine *etc*.) and to determine their structures.

EXPERIMENTAL

Melting points were measured on Büchi B-540 capillary apparatus and were uncorrected. IR spectra (cm^{-1}) were recorded on an FTIR spectrometer Shimadzu IR Prestige 21 model Diamond, ATR method. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova spectrometer at 499.83 MHz for ^{1}H and 125.48 MHz for ^{13}C by using $CDCl_3$ as solvent and

†This paper is dedicated to the Prof. Dr. Cemil Ibis (retired in 2013).

TMS as internal standard. Mass spectra were obtained on a hybrid triple quadrupole linear ion trap mass spectrometer (4000 QTRAP, ABSciex). The 4000 QTRAP was operated in the triple quadruple mass spectrometer mode using an electrospray ionization (ESI) source. Elemental analyses (C, H, S) were conducted using the Thermo Finnigan Flash EA 1112 elemental analyzer; their results were found to be in good agreement (± 0.2 %) with the calculated values. Fluorescence spectra were run on a Varian Cary Eclipse Fluorescence spectrophotometer. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size 63-200 μm). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). All chemicals were reagent grade and were used without further purification. Moisture was checked by the glass apparatus using $CaCl_2$ drying tubes.

Synthesis: We synthesized 2-chloroethyl-pentachlorobutadienyl-sulphide (**1**) from the reaction of 1,2,3,4,4-pentachloro-1-(2-hydroxyethylthio)-1,3-butadiene with $SOCl_2$ in pyridine[27].

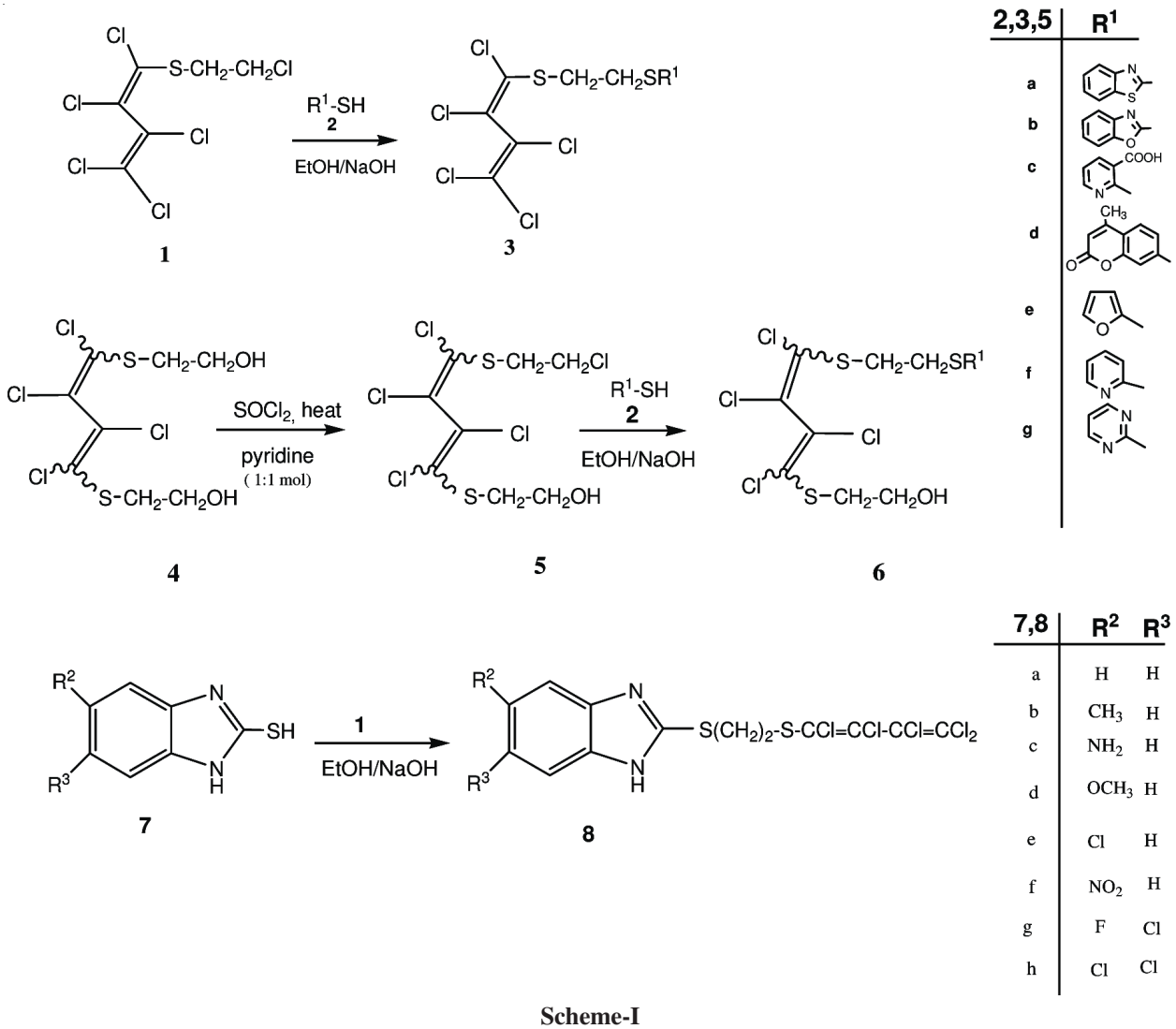
New 2-(4-(2-chloro-ethylthio)-1,2,3,4-tetrachlorobuta-1,3-dienylthio)ethanol compound (**5**) was obtained from the reaction of 1,4-*bis*(2-hydroxyethylthio)-1,2,3,4-tetrachloro-1,3-butadiene (**4**) with $SOCl_2$ (1 equiv.) in pyridine (1 equiv.).

Compound **1** reacts with the reaction of thiols **2a-g** in water-ethanol mixture in the presence of sodium hydroxide to give the new heterocyclic thioethers **3a**-**3g**, respectively. 5-(2-(4-(2-Hidroxyethylthio)-1,2,3,4-tetra-chlorobuta-1,3-dienyl)-sulfanyl)ethylsulfanyl)-4-methyl-coumarin (**6d**) was obtained from the reaction of compound **5** with 7-mercapto-4-methyl-coumarin (**2d**) (**Scheme-I**).

Preperation of unsatured sulfanes containing heterocyclic component

General procedure: 0.314 g (0.97 mmol) of 2-chloroethyl-penta-chlorobutadienyl-sulphide (**1**) in 25 mL of ethanol and 0.164 g (0.97 mmol) of 2-mercaptobenzothiazole (**2a**) in 25 mL of ethanol were mixed and 0.05 g NaOH in 15 mL of water was added at room temperature. The mixture was stirred for 48 h. Then chloroform (100 mL) was added to the reaction mixture. The organic layer was separated, washed with water (4 × 30 mL) and dried with $MgSO_4$. The solvent was eveporated and the residue was purified by column chromatography on silica gel with hexane as eluent. Compounds **3a-g**, **6d**, **8a-h** synthesized in the same way.

Synthesis of 2-(2-pentachlorobuta-1,3-dienylsulfanyl-ethylsulfanyl)benzothiazole (3a): Compound **3a** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide



Scheme-I

(0.314 g, 0.97 mmol) and 2-mercaptobenzothiazole (**2a**) (0.164 g, 0.97 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3a: Yield: 0.284 g (66 %); oil. R_f = 0.85 (hexane). IR (film): ν_{max} = 2985, 2970 cm^{-1} (C-H), 1555, 1600 (C=C). ^1H NMR ($CDCl_3$): δ = 7.53-8.01 ppm (m, 4H,Ar-H), 3.27-4.41 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$):δ = 28.2, 36.5, 97.3, 112.0, 116.0, 120.1, 124.2, 126.7, 128.9, 136.0, 139.7, 144.7, 147.1. $C_{13}H_8Cl_5S_3N$ (451.67): calcd. (%) C, 34.57; H, 1.79; N 3.10; S 21.29. Found (%) C, 34.15; H, 1.76; N 3.12; S 21.87. MS (*m/z*): 451.87$[M]^+$.

Synthesis of 2-(2-pentachlorobuta-1,3-dienylsulfanyl-ethylsulfanyl)benzoxazol (3b): Compound **3b** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercaptobenzoxazole (**2b**) (0.236 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3b: Yield: 0.156 g (23 %); oil. R_f = 0.87 (hexane). IR (film): ν_{max} = 2995, 2980 cm^{-1} (C-H), 1565, 1615 (C=C). ^1H NMR ($CDCl_3$):δ = 7.53-8.01 ppm (m, 4H, Ar-H), 3.27-4.41 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 28.7, 36.5, 110.6, 119.1, 120.1, 123.8, 124.2, 124.8, 126.7, 136.0, 141.5, 151.9, 165.0. $C_{13}H_8Cl_5S_2ON$ (435.61): calcd. (%) C, 35.84; H, 1.85; N 3.22; S 14.72. Found (%) C, 35.93; H, 1.82; N 3.44; S 14.89.

Synthesis of 2-(2-pentachlorobuta-1,3-dienylsulfanyl-ethylsulfanyl)nicotinic acid (3c): Compound **3c** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercaptonicotinic acid (**2c**) (0.24 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3c: Yield: 0.311 g (46 %); oil. R_f = 0.82 (Hexane). IR (film): ν_{max} = 3490 cm^{-1} (OH), 3050 (C-H), 1730 (C=O), 1540, 1590 (C=C). ^1H NMR ($CDCl_3$): δ = 11.03 ppm (s, 1, OH), 6.50-7.19 (m, 3H, Ar-H), 3.21- 4.06 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 28.7, 36.8, 119.3, 120.1, 124.2, 124.6, 126.7, 136.0, 137.2, 151.5, 159.9, 169.3. $C_{12}H_8Cl_5S_2O_2N$ (439.597): calcd. (%) C, 32.78; H, 1.83; N 3.19; S 14.58. Found (%) C, 32.85; H, 1.96; N 3.67; S 14.65.

Synthesis of 4-methyl-7-(2-pentachlorobuta-1,3-dienylsulfanyl-ethylsulfanyl)coumarine (3d): Compound **3d** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 7-mercapto-4-methylcoumarin (**2d**) (0.30 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3d: Yield: 0.398 g (54 %); oil. R_f = 0.73 (hexane). IR (film): ν_{max} = 2853,2952, (C-H), 1717 (C=O), 1547, 1590 (C=C). ^1H NMR ($CDCl_3$): δ = 6.50-7.19 (m, 3H, Ar-H), 6.23 (s, 1H, CH), 3.07-4.12 (m, 4H, CH_2), 2.42 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 19.4, 28.7, 36.8, 112.5, 116.0, 118.7, 120.1, 123.5, 124.2, 126.7, 127.0, 135.9, 136.0, 150.3, 152.7, 160.8. $C_{16}H_{11}Cl_5S_2O_2$ (476.658): calcd. (%) C, 40.32; H, 2.32; S 13.45. Found (%) C, 40.41; H, 2.66; S 13.82.

Synthesis of 2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl-methyl)furan (3e): Compound **3e** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-furanmethanethiol (**2e**) (0.18 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3e: Yield: 0.22 g (35 %); oil. R_f = 0.74 (hexane). IR (film): ν_{max} = 2945 (C-H), 1550, 1610 (C=C). ^1H NMR ($CDCl_3$): δ = 5.88-7.21 (m, 3H, Ar-H), 3.11-3.55 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 29.0, 31.9, 33.1, 105.7, 110.6, 120.1, 123.8, 131.5, 136.0, 141.2, 152.5. $C_{11}H_9Cl_5S_2O$ (398.587): calcd. (%) C, 33.15; H, 2.28; S 16.08. Found (%) C, 33.64 H, 2.45; S 16.22.

Syntheis of 2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)pyridine (3f): Compound **3f** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercaptopyridine (**2f**) (0.17 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3f: Yield: 0.342 g (57 %); oil. R_f = 0.77 (hexane). IR (film): ν_{max} = 3005 (C-H), 1530, 1590 (C=C). ^1H NMR ($CDCl_3$): δ = 8.48-7.09 (m, 4H, Ar-H), 3.27-3.60 (m, 4H, CH_2) ^{13}C NMR ($CDCl_3$):δ = 29.2, 36.8, 119.0, 120.1, 121.4, 123.8, 131.5, 135.7, 136.0, 149.3,159.9. $C_{11}H_8Cl_5S_2N$ (395.587): calcd. (%) C, 33.40; H, 2.04; N, 3.54; S 16.21. Found (%) C, 33.74 H, 2.27; N, 3.76; S 16.98.

Synthesis of 2-(2-pentachloro-buta-1,3-dienylsul-fanyl-ethylsulfanyl)pyrimidine (3g): Compound **3g** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercaptopyrimidine (**2g**) (0.18 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

3g: Yield: 0.37 g (59 %); oil. R_f = 0.71 (hexane). IR (film): ν_{max} = 2980 (C-H), 1545**,** 1600 (C=C ^1H NMR ($CDCl_3$): δ = 8.70-7.17 (m, 3H, Ar-H), 3.27-3.60 (m, 4H, CH_2) .^{13}C NMR ($CDCl_3$): δ = 29.2, 36.8,116.8, 120.1, 123.8, 131.5, 136.0, 156.1, 168.1. $C_{10}H_7Cl_5S_2N_2$ (396.574): calcd. (%) C, 30.29; H, 1.78; N, 7.06; S 16.17. Found (%) C, 30.69; H, 1.87; N, 7.29; S 16.72.

Synthesis of 2-(4-(2-chloro-ethylthio)-1,2,3,4-tetra-chlorobuta-1,3-dienylthio)ethanol (5): To a solution of the compound **4** (1 equiv.) in pyridine (1 equiv.) was added dropwise thionyl chloride (1 equiv.). The reaction mixture was strirred at room temperature for 1 h and then refluxed for an additional 1 h. After, cooling water (50 mL) was added. The reaction mixture was then extracted with $CHCl_3$ (100 mL). The organic layerwas washed with 35 mL of aqueous NaOH (5 %), with water (4 × 30 mL) and then dried over $MgSO_4$. The solvent was eveporated and the residue was purified by column chromatography on silica gel with hexane as eluent.

5: Yield: 0.30 g (48 %); oil. R_f = 0.85 (Hexane). IR (film): ν_{max} = 3490 (OH), 2985, 3000 (C-H), 1545, 1620 (C=C). ^1H NMR ($CDCl_3$): δ = 3.06-4.20 (m, 8H, CH_2), 2.0 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 30.4, 32.6, 42.6, 61.2, 120.1, 136.0. $C_8H_9Cl_5S_2O$ (362.55): calcd. (%) C, 26.50; H, 2.50; S 17.69. Found (%) C, 26.02; H, 2.41; S 17.76.

Synthesis of 5-(2-(4-(2-hidroxyethylthio)-1,2,3,4-tetra-chlorobuta-1,3-dienyl)sulfanyl)ethylsulfanyl)-4-methyl-coumarin) (6d): Compound **6d** was synthesized from 2-(4-(2-chloro-ethylthio)-1,2,3,4-tetrachlorobuta-1,3-dienylthio)-ethanol **5** (0.51 g, 1.38 mmol) and 7-mercapto-4-methylcoumarin (**2d**) (0.265 g, 1.38 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

6d: Yield: 0.32 g (45 %); oil. R_f = 0.79 (hexane). IR (film): ν_{max} = 3490 (OH), 2854, 2956 (C-H), 1717 (C=O), 1537, 1590

(C=C). ^{1}H NMR ($CDCl_3$): δ = 5.90-7.01 (m, 5H, Ar-H), 3.21-4.20 (m, 8H, CH_2), 2.0 (s, 1H, OH), 1.72 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 20.8, 28.3, 32.6, 37.3, 60.9, 61.2, 112.5, 117.9, 120.1, 123.5, 125.0, 128.6, 136.0, 131.0, 139.1, 150.4, 152.8. $C_{18}H_{16}Cl_4S_3O_3$ (518.32): calcd. (%) C, 41.71; H, 3.11; S 18.56. Found (%) C, 41.34; H, 3.07; S 18.49. MS (*m/z*): 517.09 $[M]^+$.

Synthesis of 2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8a): Compound **8a** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.4 g, 1.24 mmol) and 2-mercaptobenzimidazole (**7a**) (0.189 g, 1.25 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8a: Yield: 0.348 g (64%); oil. R_f = 0.76 (Hexane). IR (film): ν_{max} = 3520 (NH), 2990 (C-H), 1550, 1590**,** 1620 (C=C). ^{1}H NMR ($CDCl_3$): δ = 7.22-7.59 (m, 4H, Ar-H), 5.04 (s, 1H, NH), 3.03-4.28 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 28.7, 36.5, 115.2, 120.1, 123.0, 124.2, 126.7, 136.0, 138.9, 147.1 $C_{13}H_9Cl_5S_2N_2$ (434.928): calcd. (%) C, 35.97; H, 2.09; N, 6.44; S 14.74. Found (%) C, 35.84 H, 2.78; N, 6.59; S 14.72.

Synthesis of 5-methyl-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8b): Compound **8b** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5-methylbenzimidazole (**7b***)* (0.26 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8b: Yield: 0.357 g (50 %); oil. R_f = 0.86 (hexane). IR (film): ν_{max} = 3520 (NH), 2958 (C-H), 1595, 1600 (C=C). ^{1}H NMR ($CDCl_3$): δ = 7.12-7.54 (m, 3H, Ar-H), 5.04 (s, 1H, NH), 3.27-4.06 (m, 4H, CH_2), 2.34 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 21.3, 28.2, 36.5, 115.1, 115.3, 120.1, 124.2, 125.8,126.7, 132.7, 135.9, 136.0, 138.8, 147.1. $C_{14}H_{11}Cl_5S_2N_2$ (448.65): calcd. C, 37.48; H, 2.47; N, 6.24; S 14.29. Found (%) C, 37.94 H, 2.46; N, 6.78; S 14.56. MS (*m/z*): 450.00 $[M + H]^+$.

Synthesis of 5-amino-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole 8c: Compound **8a** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5-aminobenzimidazole (**7c**) (0.26 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8c: Yield: 0.358 g (51 %); oil. R_f = 0.75 (Hexane). IR (film): ν_{max} = 3520 (NH), 2990, 3010 (C-H), 1545**,** 1595 (C=C). ^{1}H NMR ($CDCl_3$): δ = 6.46-7.34 (m, 3H, Ar-H), 6.27 (s, 2H, NH_2), 5.04 (s, 1H, NH), 3.27-4.06 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 28.2, 36.5, 97.3, 112.0, 116.0, 120.1, 124.2, 126.7, 128.9, 136.0, 139.7, 144.7, 147.1 $C_{13}H_{10}Cl_5S_2N_3$ (449.638): calcd. C, 34.73; H, 2.24; N, 9.35; S 14.26. Found (%) C, 34.78 H, 2.85; N, 9.56; S 14.47. MS(*m/z*): 449.9 $[M + H]^+$.

Synthesis of 5-metoxy-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8d): Compound **8d** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5-metoxybenzimidazole (**7d**) (0.280 g, 1.55 mmol) according to the general procedure.The mixture was purified by column chromatography with hexane eluent.

8d: Yield: 0.355 g (50 %); oil. R_f = 0.76 (Hexane). IR (film): ν_{max} = 3579 (NH), 2990 (C-H), 1547, 1590 (C=C). ^{1}H NMR ($CDCl_3$): δ = 7.27-7.59 (m, 3H, Ar-H), 5.04 (s, 1H, NH), 3.72 (s, 3H, OCH_3), 3.03-4.28 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 28.7, 36.5, 55.9, 100.9, 109.8, 116.3, 120.1, 124.3, 126.7, 131.2, 136.0, 139.9, 141.7, 156.2 $C_{14}H_{11}Cl_5S_2N_2O$ (464.81): calcd. (%) C, 36.19; H, 2.39; N, 6.03; S 13.80. Found (%) C, 36.07; H, 2.52; N, 5.98; S 13.32. MS(*m/z*): 465.3 $[M]^+$.

Synthesis of 5-chloro-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8e): Compound **8e** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5-chlorobenzimidazole (**7e**) (0.2875 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8e: Yield: 0.315 g (43%); oil. R_f = 0.86 (Hexane). IR (film): ν_{max} = 3580 (NH), 2958 (C-H), 1547, 1590 (C=C). ^{1}H NMR ($CDCl_3$): δ = 7.12-7.54 (m, 3H, Ar-H), 5.04 (s, 1H, NH), 3.27-4.06 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$):δ = 28.3, 36.5, 115.8, 116.7,120.1, 124.1, 124.3, 126.7,129.2, 136.0,137.0, 140.3, 147.3. $C_{13}H_8Cl_6S_2N_2$ (469.021): calcd. (%) C, 33.29; H, 1.79; N, 5.97; S 13.67. Found (%) C, 33.11; H, 1.74; N, 5.91; S 13.56.

Synthesis of 5-nitro-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8f): Compound **8f** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5-nitrobenzimidazole (**7f**) (0.304 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8f: Yield: 0.350 g (47 %); oil. R_f = 0.75 (hexane). IR (film): ν_{max} = 3585 (NH), 2925, 2957(C-H), 1548, 1590, 1602 (C=C). ^{1}H NMR ($CDCl_3$): δ = 7.34-7.97 (m, 3H, Ar-H), 5.04 (s, 1H, NH), 3.27-4.06 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$):δ= 28.2, 36.5, 110.5, 116.2, 118.0, 120.1, 124.3, 126.7, 136.0, 139.8, 142.8, 145.0,147.1. $C_{13}H_8Cl_5S_2N_3O_2$ (479.581): calcd. C, 32.55; H, 1.68; N, 8.76; S 13.37. Found (%) C, 32.32; H, 1.63; N, 8.69; S 13.28.

Synthesis of 6-chloro-5-floro-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethylsulfanyl)benzimidazole (8g): Compound **8g** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-6-chloro-5-florobenzimidazole (**7g**) (0.315 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8g: Yield: 0.48 g (63 %); oil. R_f = 0.76 (Hexane). IR (film): ν_{max} = 3579 (NH), 2925, 2956, 3002 (C-H), 1547, 1590, 1602 (C=C). ^{1}H NMR ($CDCl_3$): δ= 7.35-7.59 (m, 2H, Ar-H), 5.04 (s, 1H, NH), 3.03-4.21 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$):δ = 28.3, 36.5, 103.8, 115.2, 117.2, 120.1, 124.3, 126.7, 135.9, 136.0, 138.9, 147.1, 156.9 . $C_{13}H_7Cl_6S_2N_2F$ (487.02): calcd. (%) C, 32.06; H, 1.45; N, 5.75; S 13.17. Found (%) C, 31.95; H, 1.42; N, 5.71; S 13.07.

Synthesis of 5,6-dichloro-2-(2-pentachloro-buta-1,3-dienylsulfanyl-ethyl-sulfanyl)benzimidazole (8h): Compound **8h** was synthesized from 2-chloroethyl-penta-chlorobutadienyl-sulphide (0.5 g, 1.55 mmol) and 2-mercapto-5,6-dichlorobenzimidazole (**7h**) (0.34 g, 1.55 mmol) according to the general procedure. The mixture was purified by column chromatography with hexane eluent.

8h: Yield: 0.34 g (50 %); oil. R_f = 0.86 (hexane). IR (film): ν_{max} = 3585 (NH), 2925, 2957(C-H), 1548**,** 1590 (C=C). ^{1}H

NMR ($CDCl_3$): δ = 7.12-7.54 (m, 2H, Ar-H), 5.04 (s, 1H, NH), 3.27-4.06 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$):δ = 28.3, 36.5, 117.2, 120.1, 124.3,126.7, 128.6, 136.0, 138.4,147.1. $C_{13}H_7Cl_7S_2N_2$ (503.471): calcd. (%) C, 31.01; H, 1.40; N, 5.56; S 12.74. Found (%) C, 30.92; H, 1.78; N, 5.47; S 12.70.

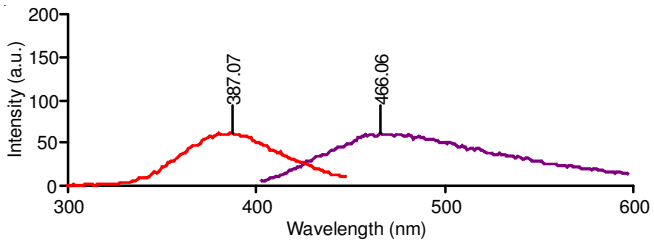
RESULTS AND DISCUSSION

The IR spectrum of compounds **3d** and **6d** showed sharp peak at 1717 cm^{-1} and compound **3c** showed sharp peak at 1730 cm^{-1}, indicative for the C=O stretching. The fluorescence properties of the two thiosubstituted butadienes **3d** and **6d** containing a coumarin group are presented in Table-1.

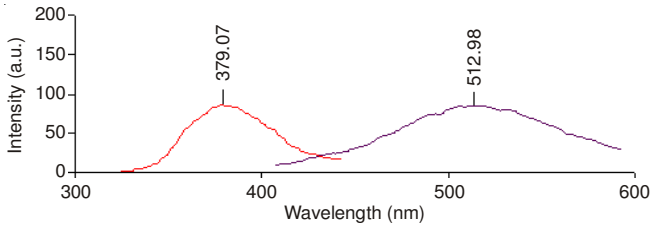
TABLE-1
EXCITATION AND EMISSION MAXIMUM WAVELENGTHS

Compound	Solvent	λ_{ex} (max)	λ_{em} (max)
3d	$CHCl_3$	387.07	466.06
6d	$CHCl_3$	379.07	512.98

The excitation and emission spectra for 4-methyl-7-(2-pentachlorobuta-1,3-dienylsulfanyl-ethylsulfanyl)coumarin (**3d**) and 5-(2-(4-(2-hidroxyethylthio)-1,2,3,4-tetrachlorobuta-1,3-dienyl)sulfanyl)ethylsulfanyl)-4-methyl-coumarin) (**6d**) in chloroform solution are shown in Fig. 1.



(a)



(b)

Fig. 1. Excitation and emission spectra measured for 10^{-4} M solutions for (a) compound **3d** and (b) compound **6d** in $CHCl_3$. Excitation and emission slit widths were set at 5 nm

The mass spectra of the compound **6d** in the positive ion mode for ESI confirmed the proposed structure; the molecular peak was identified at *m/z*: 517.09 $[M]^+$. The IR spectrum of compounds **3c**, **5** and **6d** showed a band characteristic at 3490 cm^{-1} for the -OH groups. The ^{13}C NMR spectrum of compound **3c** showed signals for the carbon of the carboxylic acid group at δ = 169.3 ppm and compound **3d** showed signals for the carbon of the carboxyl group at δ = 160.8 ppm. The ^{13}C NMR spectrum of compound **5** showed signals for the CH_2-Cl, CH_2-OH, -S-CH_2-CH_2-OH and –S-CH_2-CH_2-Cl at δ = 42.6, 61.2, 32.6 and 30.4 ppm, respectively. The ^{13}C NMR spectrum of compound **6d** showed signal for the S-CH_2-CH_2-S- and S-CH_2-CH_2-S- at δ = 28.3 and 37.3 ppm, respectively.The ^{13}C NMR spectrum of all compounds showed signal for diene compounds carbon atoms at δ = 136.0 ppm (C-1 and C-4) and 120.1 ppm (C-2 and C-3).

We synthesized compounds **8a-h** from the reaction of compound **1** with thiols **7a-h** in water-ethanol mixture in the presence of sodium hydroxide, respectively (**Scheme-I**).

The IR spectrum of **8a-h,** showed a band characteristic for the -NH groups The ^1H NMR spectra of compounds **8a-h** showed signals at δ = 5.04 ppm characteristic for the protons of the amine group. The mass spectrum of the compound **8b** and **8d** in the positive ion mode for ESI confirmed the proposed structure; the molecular peak was identified at *m/z*: 450.00 $[M + H]^+$, at *m/z*: 465.3 $[M]^+$, respectively.The mass spectra of the compound **8c** in the positive ion mode for ESI confirmed the proposed structure; the molecular peak was identified at *m/z*: 449.9 $[M+H]^+$. The molecular peak of **8c** was given in Fig. 2.

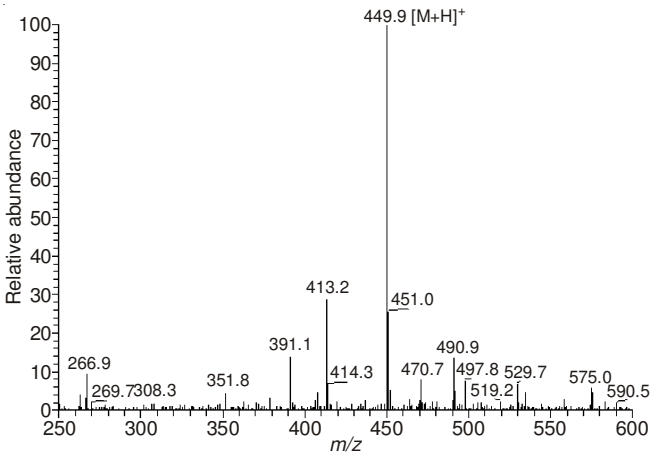


Fig. 2. Full-MS spectrum of compound **8c** in the positive mode of ESI

Compounds **3a-g**, **6d** are new heterocyclic perchlorobuta-1,3-dienylsulfanes. They are stable colourless oils. Compounds **8a-h** are new unsatured sulfanes containing a benzimidazole component. The new benzimidazole derivatives are stable brown oils. These novel compounds were formed by addition-elimination reaction sequence. All compounds were isolated in good yield and fully characterized. Their structures result from the spectroscopic data and are supported by microanalysis. The structure of the novel compounds are in accordance with the analytical and spectroscopic data as give in the experimental part.

Conclusion

The present work deals with the preparation of some novel unsatured sulfanes containing a heterocyclic component by treating unsatured polyhalogenated compounds and thiols in EtOH/H_2O solution of NaOH and their structures were characterized by spectroscopic methods.

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