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Synthesis, Characterization and Biological Evaluation of Some Azo and Azo-Schiff Compounds

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Abstract

This work involves the preparation of some new azo and azo-Schiff compounds derived from benzothiophene, dibenzothiophene, and diamines (1, 5-diaminonaphthalene, and thiocarbohydrazide). Azo compounds of benzothiophene and dibenzothiophene have been prepared using different solvents to enhance the miscibility of the polar aqueous solution of the diazonium salt and the slightly polar benzothiophene and dibenzothiophene. The Schiff's bases have been synthesized by the condensation reaction of carbonyl compound with the diamines. FT-IR has been used to identify the prepared compounds, whereas ^{1}H-NMR and ^{13}C-NMR were used to identify some others.

Keywords: Benzothiophene; Dibenzothiophene; Azo-Schiff.

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تحضير و تشخيص وقياس الفعالية البايولوجية لبعض مركبات الآزو والآزو- شف

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الملخص

يتضمن هذا العمل تحضير بعض مركبات الآزو والآزو- شف مشتقة من البنزوثايوفين، ثنائي بنزوثايوفين والامينات الثنائية (1,5 – ثنائي امينو نفثالين والثايوكاربوهايدرازايد). تم تحضير مركبات الآزو للبنزوثايوفين وثنائي بنزوثايوفين في مذيبات مختلفة بغرض تحسين امتزاج المحلول المائي القطبي لملح الدايزونيوم مع البنزوثايوفين وثنائي بنزوثايوفين ذات القطبية القليلة. تم تحضير قواعد شف عن طريق تفاعل التكثيف بين مركبات الكاربونيل والامين الثنائي. استخدمت تقنية مطيافية الاشعة تحت الحمراء في تشخيص المركبات المحضرة ولبعض المركبات تم استخدام تقنية الرنين النووي المغناطيسي للبروتون والكربون.

الكلمات الدالة: بنزوثايوفين، ثنائي بنزوثايوفين، آزو- شف.

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1. Introduction:

Aromatic azo dyes, which are characterized by the functional group (-N=N-), are considered the largest group of organic dyes as they have widespread applications in many areas of textile and medicine [1,2]. The dyes are stabilized by incorporating the aromatic group through conjugation, which very often absorbs visible light frequencies yielding colored compounds [3]. Dyes are normally large aromatic molecules that are consisting of more than one linked ring [4]; the more stable derivatives are containing two aryl groups [5]. Prontosil is an azo dye that acts as an antibacterial drug, it is metabolized in vivo to produce the active amine part (sulfanilamide) [6]. Schiff bases resulted from salicylaldehyde condensation have arouse the researchers' interest because of their ability to act as bidentate ligands for transitional metal ions [7,11]. Studies concerning quantitative structure-antitumor activity relationship of a series of Schiff bases derived from variously substituted aromatic amines and aldehydes, it has been shown that azomethines from salicylaldehydes gave the best correlation [12,13]. The reported biological activity of azo dyes and the pharmacological activity of Schiff bases mentioned above were the motive to conduct this research.

2. Experimental:

The chemicals used in the synthesis of the studied molecules were of the brands (Aldrich, Alfa aesar, BDH, Merck and Sharlau) and they were used as they received from suppliers. Melting points have been determined by the use of open-ended capillary tube instrument and are uncorrected. Infrared spectra were recorded on Thermo Fischer Scientific Nicolet IR100 spectrometer, ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker 300 MHz ultra-shield with TMS as internal reference using $CDCl_3$, DMSO-d6 and D_2O as solvents

2.1 Preparation of 1-(4-substituted phenyl)-2-(dibenzothiophen-2-yl) diazenes (H_1 - H_6), and 1-(benzothiophen-3-yl)-2-(4-substituted phenyl) diazenes (H_7 - H_{11}):

Substituted anilines 0.002 mol were dissolved in 4 ml of 3M hydrochloric acid in a round bottom flask equipped with magnetic stirrer in an ice bath, then an icy solution of sodium nitrite (0.002 mol, 0.138 gm in 2 ml of water) was added dropwise keeping the temperature in the range of 0-5 ^{o}C. The resultant diazonium salt kept in ice bath. Then an icy solution of [(0.002 mol, 0.368 gm) of dibenzothiophene (for compounds **(**H_1 - H_6**)**) or (0.002 mol, 0.268 gm) of benzothiophene (for compounds **(**H_7 - H_{11}**)**] in 4 ml of acetic acid was added to the diazonium

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salt solution and the resultant mixture was vigorously stirred for 30 minutes. A solution of 2.5 M of sodium hydroxide was added slowly keeping the temperature under 5 ^{o}C until the pH level was above 7. The reaction mixture was kept under stirring in a cold medium for another 30 minutes. The resultant solid was filtered in a Buchner funnel and washed with water. Recrystallization of the products with a mixture of 90% Ethanol in water yielded the following derivatives and their data:

1-phenyl-2-(dibenzothiophen-2-yl)diazene (H_1): m.p. 123^{o}C-125^{o}C, 11%, Dark Brown; IR (KBr, cm^{-1}): 3050 (C-H Aromatic), 1595 (C=C), 1489 (N=N).

1-(4-nitrophenyl)-2-(dibenzothiophen-2-yl)diazene (H_2): m.p. 98^{o}C-100^{o}C, 40%, Olive; IR (KBr, cm^{-1}): 3000 (C-H Ar.), 1588 (C=C), 1504 (N=N). ^{13}C-NMR (DMSO-d6, ppm) δ= 25.3 (CH_3COOH), 118.1, 124.7, 141.1, 160.6 Fig.1

1-(4-acetylphenyl)-2-(dibenzothiophen-2-yl)diazene (H_3): m.p. 88^{o}C-90^{o}C, 68%, Brown; IR (KBr, cm^{-1}): 3000 (C-H Ar.), 1583 (C=C), 1423 (N=N). Fig.2

1-(4-chlorophenyl)-2-(dibenzothiophen-2-yl)diazene (H_4): m.p. 78^{o}C-80^{o}C, 83%, Dark Brown; IR (KBr, cm^{-1}): 3050 (C-H Ar.), 1605 (C=C), 1488 (N=N).

1-(4-bromophenyl)-2-(dibenzothiophen-2-yl)diazene (H_5): m.p. 96^{o}C-98^{o}C, 60%, Dark Brown; IR (KBr, cm^{-1}): 3050 (C-H Ar.), 1582 (C=C), 1423 (N=N).

Sodium 1-(4-benzenesulfonate)-2-(dibenzothiophen-2-yl)diazene (H_6): m.p. >300^{o}C, 25%, Light Brown; IR (KBr, cm^{-1}): 3010 (C-H Ar.), 1634 (C=C), 1438 (N=N). ^{1}H-NMR (D_2O, ppm): δ= 4.8 (D_2O), 7-8.14 (m, 11, Ar)

1-(benzothiophen-3-yl)-2-(4-nitrophenyl)diazene (H_7): m.p. 88^{o}C-90^{o}C, 17%, Brown; IR (KBr, cm^{-1}): 3100 (C-H Ar.), 1563 (C=C), 1521 (N=N).

1-(benzothiophen-3-yl)-2-(4-acetylphenyl)diazene (H_8): m.p. 163^{o}C-165^{o}C, 30%, Dark Brown; IR (KBr, cm^{-1}): 3600 – 3400 (H_2O), 3010 (C-H Ar.), 1597 (C=C), 1410 (N=N). Fig.3

1-(benzothiophen-3-yl)-2-(4-chlorophenyl)diazene (H_9): m.p. 118^{o}C-120^{o}C, 16%, Dark Brown; IR (KBr, cm^{-1}): 3030 (C-H Ar.), 1590 (C=C), 1488 (N=N).

1-(benzothiophen-3-yl)-2-(4-bromophenyl)diazene (H_{10}): m.p. 64^{o}C-66^{o}C, 36%, Dark Brown; IR (KBr, cm^{-1}): 3025 (C-H Ar.), 1583 (C=C), 1482 (N=N).

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Sodium 1-(benzothiophen-3-yl)-2-(4-benzenesulfonate)diazene (H_{11}): m.p. >300^{o}C, 37%, Dark Orange; IR (KBr, cm^{-1}): 3010 (C-H Ar.), 1600 (C=C), 1447 (N=N). ^{1}H-NMR (D_2O, ppm): δ= 7.4-7.8 (m, 9, Ar). ^{13}C-NMR (D_2O, ppm) δ= 125.3, 126.1, 129, 131.6 Fig.4

2.2 Preparation of 5-((4-substituted phenyl)diazenyl)-2-hydroxybenzaldehydes (H_{12} - H_{14}):

The azo dyes of salicylaldehyde were synthesized according to the reported well-known literature procedure [14,16].

2.3 Preparation of 1-(4-((4-methylbenzylidene)amino)phenyl)ethan-1-ones (H_{15} - H_{19}):

These schiff bases have been synthesized according to the reported procedures and they are well-known [17,19].

2.4 Preparation of N,N'-naphthalene-1,5-diyl)bis(1-(4-((-4-substituted benzylidene)amino)phenyl)ethan-1-imines (H_{20} - H_{24}):

1,5-diaminonaphthalene (0.0005 mol, 0.079 gm) and 0.001 mol of various Schiff's bases of 4-aminoacetophenone were added to 20 ml of Ethanol in a 50 ml round bottom flask equipped with a magnetic stirrer and refluxed for 2 hours. After completing the reaction time, the solutions kept in a fridge overnight and filtered by gravity. The resultant solids were washed with petroleum ether of boiling range 60-80 ^{o}C and recrystallized with ethanol to yield the following derivatives and their data:

2,2'-((((naphthalene-1,5-diylbis(azaneylylidene))bis(ethan-1-yl-1-ylidene))bis(4,1-phenylene))bis(azaneylylidene))bis (methaneylylidene))diphenol (H_{20}): m.p. 223^{o}C-225^{o}C, 48%, Light Green; IR (KBr, cm^{-1}): 3000 (C-H Aromatic), 2920 (C-H Aliphatic), 1576 (C=C), 1614 (C=N). ^{1}H-NMR ($CDCl_3$, ppm): δ= 1.3 (s, Aliph), δ= 6.7 - 8.2 (m, Ar) δ= 8.8 (s, CH=N) δ= 13.4 (s, O-H) Fig.5 ^{13}C-NMR ($CDCl_3$, ppm) δ= 11.5, 19.5, 22.9, 31.7, 114.9, 117.3, 119.2, 119.4, 122.2, 126.5, 128.8, 132.4, 132.5, 133.5, 143.6, 146.2, 161.2, 163.8, 187.5, 195.1 Fig.6

4,4'-(((((naphthalene-1,5-diylbis(azaneylylidene))bis(ethan-1-yl-1-ylidene))bis(4,1-phenylene))bis(azaneylylidene))bis(methaneylylidene))diphenol (H_{21}): m.p. 294^{o}C-296^{o}C, 34%, Light Grey; IR (KBr, cm^{-1}): 3025 (C-H Aromatic), 2890 (C-H Aliphatic), 2363 – 2340 CO_2, 1577 (C=C), 1603 (C=N). Fig.7

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N,N'-(naphthalene-1,5-diyl)bis(1-(4-((-4-methoxybenzylidene) amino)phenyl)ethan-1-imine) (H_{22}): m.p. 198^{o}C-202^{o}C, 10%, Light Brown; IR (KBr, cm^{-1}): 3050 (C-H Aromatic), 2925 (C-H Aliphatic), 1602 (C=C), 1628 (C=N).

4,4'-(((((naphthalene-1,5-diylbis(azaneylylidene))bis(ethan-1-yl-1-ylidene))bis(4,1-phenylene))bis(azaneylylidene)) bis(methaneylylidene))bis(N,N-dimethylaniline) (H_{23}): m.p. >300^{o}C, 40%, Pale Green; IR (KBr, cm^{-1}): 3075 (C-H Aromatic), 2920 (C-H Aliphatic), 1527 (C=C), 1592 (C=N).

4,4'-(((((naphthalene-1,5-diylbis(azaneylylidene))bis(ethan-1-yl-1-ylidene))bis(4,1-phenylene))bis(azaneylylidene)) bis(methaneylylidene))bis(2-methoxyphenol) (H_{24}): m.p. 206^{o}C-208^{o}C, 25%, Light Olive; IR (KBr, cm^{-1}): 3120 (C-H Aromatic), 2925 (C-H Aliphatic), 1513 (C=C), 1594 (C=N).

2.5 Preparation of Thiocarbohydrazide N'-(-1-(4-((-4-chlorobenzylidene)amino) phenyl)ethylidene)-2-(1-(4-((-4-chlorobenzylidene)amino) phenyl)ethylidene)hydrazine-1-carbothiohydrazide (H_{25} - H_{28}):

Carbondisulfide (4 mL, 0.066 mol) was added slowly dropwise to hydrazine hydrate (14.6 mL, 0.232 mol) In a 50 mL round bottom flask with stirring, keeping the temperature of the solution under 15 ^{o}C. After completion of the addition of carbondisulfide, 12 mL of ethanol was added and the mixture was refluxed for 8 hours in a water bath at 85 ^{o}C. The slightly greenish-yellow suspension was kept overnight in a fridge then filtered in a Buchner funnel and washed with cold distilled water. The melting point of the white product was in the range 164-166 ^{o}C. Recrystallization with distilled water yielded white crystals melting and decomposing at 170 ^{o}C (lit. m.p. 168 ^{o}C) [20,21] weighing 4.8 gm (68% yield).

Thiocarbohydrazide (0.00025 mol, 0.026 gm) and 0.0005 of various Schiff's bases of 4-aminoacetophenone were added to 20 ml of ethanol in a 50 ml round bottom flask equipped with a magnetic stirrer, and refluxed for 2 hours. After completing the reaction time, the solutions kept in a fridge overnight and filtered by gravity, the resultant solids were washed with 60-40 ^{o}C grade petroleum ether and recrystallized with ethanol to yield the following derivatives and their data:

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N'-(1-(4-(((2-hydroxybenzylidene)amino)phenyl)ethylidene)-2-(1-(4-((2-hydroxybenzylidene)amino)phenyl)ethylidene)hydrazine-1-carbothiohydrazide (H_{25}): m.p. 223^{o}C-225^{o}C, 23%, Light Green; IR (KBr, cm^{-1}): 3410 (N-H), 3200 (C-H Ar.), 2910 (C-H Aliph.), 1560 (C=C), 1620 (C=N).

N'-(1-(4-((4-hydroxybenzylidene)amino)phenyl)ethylidene)-2-(1-(4-((4-hydroxybenzylidene)amino)phenyl)ethylidene)hydrazine-1-carbothiohydrazide (H_{26}): m.p. 293^{o}C-296^{o}C, 30%, Light Brown; IR (KBr, cm^{-1}): 3270 (N-H), 3000 (C-H Ar.), 2925 (C-H Aliph), 1544 (C=C), 1603 (C=N). ^{1}H-NMR ($CDCl_3$, ppm): δ= 1.28 (s, Aliph), δ= 2.2 (N-H), δ= 6.9 - 7.9 (m, Ar) δ= 7.25 (s, CH=N), δ= 9.75 (s, O-H). Fig.8 ^{13}C-NMR ($CDCl_3$, ppm) δ= 13.5, 47.9, 108.5, 112.2, 112.3, 116, 117.2, 119.8, 130.3, 168. Fig.9

N'-(1-(4-((4-methoxybenzylidene)amino)phenyl)ethylidene)-2-(1-(4-((4-methoxybenzylidene)amino)phenyl)ethylidene)hydrazine-1-carbothiohydrazide(H_{27}): m.p. 198 ^{o}C-202 ^{o}C, 36%, Reddish Brown; IR (KBr, cm^{-1}): 3425 (N-H), 3050 (C-H Ar.), 2918 (C-H Aliph.), 1524 (C=C), 1594 (C=N).

N'-(1-(4-((4-(dimethylamino)benzylidene)amino)phenyl)ethylidene)-2-(1-(4-((4-(dimethylamino)benzylidene)amino)phenyl)ethylidene)hydrazine-1-carbothiohydrazide (H_{28}): m.p. >300^{o}C, 27%, Green; IR (KBr, cm^{-1}): 3475 (N-H), 3150 (C-H Ar.), 2920 (C-H Aliph.), 1545 (C=C), 1596 (C=N). Fig.10

2.6 Preparation of 6,6'-naphthalene-1,5-diylbis(azaneylylidene)) bis(methaneylylidene))bis(3-((4-chlorophenyl)diazenyl)phenols (H_{29} - H_{31}):

Solutions of 1,5-diaminonaphthalene 0.00025 mol and azo dyes of salicylaldehyde 0.0005 mol in 10 ml of ethanol in a round bottom flask were refluxed for 2 hours. After completion of reaction time, the suspensions were filtered with gravity giving after drying the following derivatives and their data:

6,6'-((naphthalene-1,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(3-(phenyldiazenyl)phenol) (H_{29}): m.p. >300^{o}C, 72%, Yellow; IR (KBr, cm^{-1}): 3200 (C-H Aromatic), 1590 (C=C), 1612 (C=N). ^{1}H-NMR ($CDCl_3$, ppm): δ= 1.5 (HOD), 6.9 - 8.6 (m, Ar) δ= 9.2 (s, CH=N), δ= 10.1 (O-H). Fig.11 ^{13}C-NMR ($CDCl_3$, ppm) δ= 29.6, 81.8, 108.7, 112.5,

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116.2, 118.8, 120.1, 122.7, 129.3, 130, 131.3, 131.6, 145.5, 150.3, 159.3, 159.9, 160.4, 161, 163.9, 197.3 Fig.12

6,6'-((naphthalene-1,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(3-((4-chlorophenyl)diazenyl)phenol)) (H_{30}): m.p. >300^{o}C, 71%, Light Orange; IR (KBr, cm^{-1}): 3000 (C-H Aromatic), 1580 (C=C), 1614 (C=N). Fig.13

6,6'-((naphthalene-1,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(3-((4-bromophenyl)diazenyl)phenol)) (H_{31}): m.p. >300^{o}C, 45%, Light Orange; IR (KBr, cm^{-1}): 3100 (C-H Aromatic), 1574 (C=C), 1616 (C=N).

2.7 Biological screening of some of the synthesized compounds:

The biological activities of the some of the synthesized compounds have been examined against *Staphylococcus aureus* and *E.coli* bacteria. Bacteria were cultured on an Agar plate and a solution of 1% (w/v) of each of the compounds in DMSO was used to prepare the sampling discs. The results were recorded depending on the diameter of inhibition of bacterial growth in mm as shown in Table 1.

Table 1: Anti-bacterial activities of some of the synthesized compounds against S.aureus and E.coli bacteria.

Compound no	Staphylococcus aureus (mm)	Escherichia coli (mm)
H_2	18	11
H_6	10	10
H_{11}	12	11
H_{20}	12	11
H_{23}	12	11
H_{28}	-ve	9
H_{29}	13	11
H_{30}	10	-ve
H_{31}	13	13

Highly reactive: (inhibition zone > 30mm), Active (inhibition zone 20mm - 30mm) Slightly active (inhibition zone 14mm – 20mm)[22].

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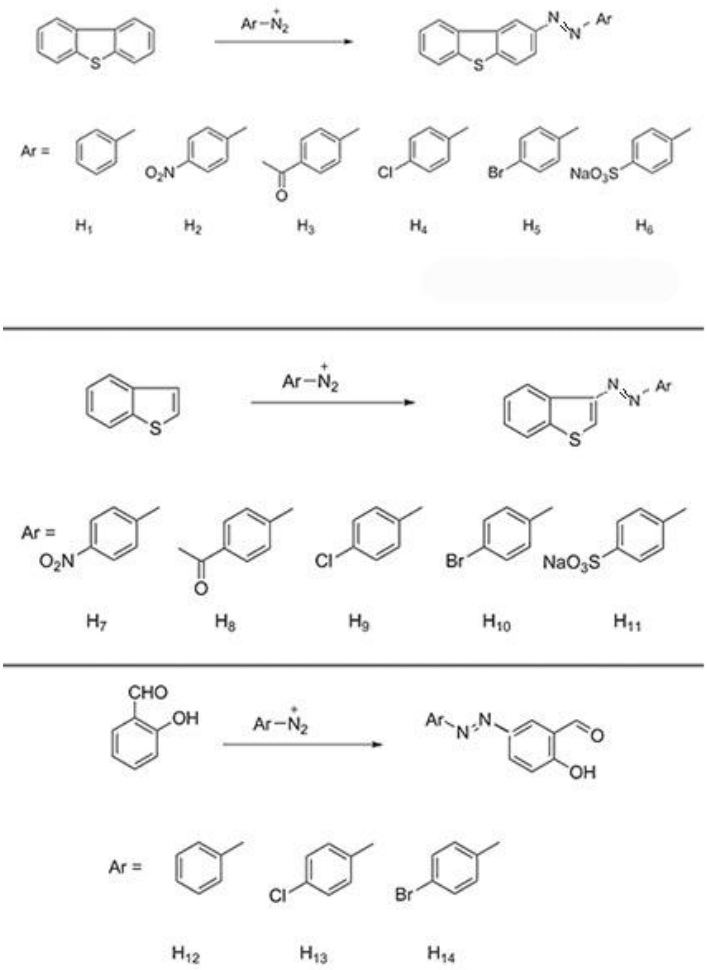
3. Results and Discussion:

3.1 General schemes:

The work in this research was according to the following schemes:

3.1.1 Scheme for the preparation of azo dyes of benzothiophene, dibenzothiophene and salicylaldehyde:



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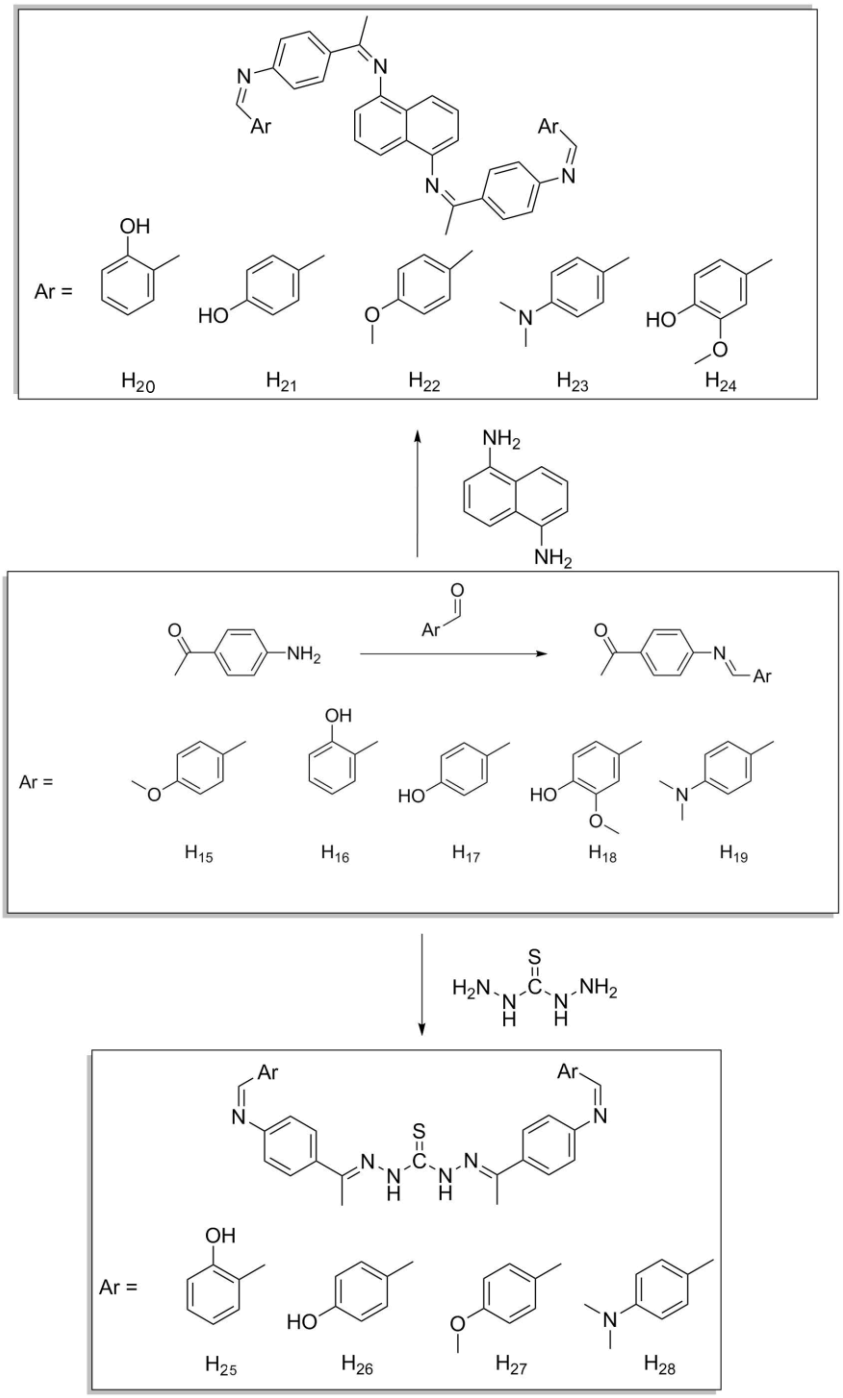
3.1.2 Scheme for the preparation of Schiff's bases of Thiocarbohydrazide and 1, 5-diaminonaphthalene:



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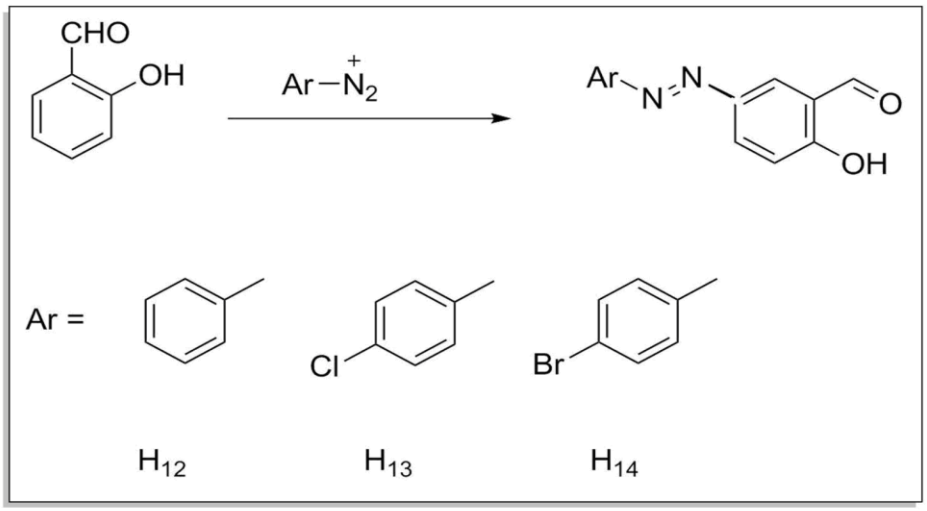
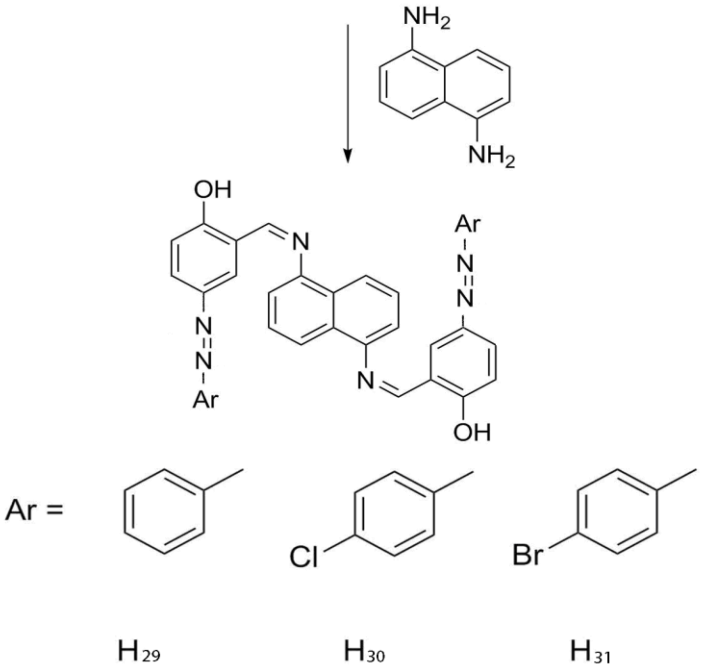
3.1.3 Scheme for the preparation of Schiff's bases of salicylaladehyde azo dyes with 1,5-diaminonaphthalene:





The two main reactions used in this research are diazo coupling and Schiff base formation, these two reactions were very important in that they can be exploited to link reactive aromatic molecules easily. The aromatic molecules containing more than one functional group could be used to synthesize multi-functional larger molecules which may tend to increase their biological activity [22].

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The new Azo dyes and Azo-Schiff compounds prepared were identified by FT-IR, and some of them by ^{1}H NMR. The synthesized compounds were screened against two types of bacteria for the evaluation of their biological activity.

The FT-IR of the compounds (H_1 – H_{11}), showed the disappearance of the NH_2 stretching band signifying the conversion of this group into (-N=N-) diazo group giving strong bands in the range (1410 – 1521) cm^{-1}. Aromatic (C-H) stretching bands showed absorption bands in the range (3000 – 3050) cm^{-1} [23]. ^{1}H NMR spectrum of compound H_{11} showed a multiplet for the aromatic protons in the range (7.4-7.8) ppm. No peak appeared in the area of the primary amine which signifies conversion into an azo group.

Compounds (H_{20} – H_{24}) showed the disappearance of the C=O stretching bands in FT-IR spectrum as an indicator for the conversion into an imine group. The latter group showed bands around (1592 – 1628) cm^{-1}. Some bands recorded around (3025 - 3120) cm^{-1} are belonging to the C-H aromatic stretching vibration, and other bands around (2890 – 2925) cm^{-1} are attributed to the aliphatic C-H stretching vibrations. The (C=C) Aromatic stretching vibrations were observed in the range (1513 - 1602) cm^{-1}. [23] ^{1}H NMR spectrum of compound H_{20} showed a single peak at 1.3 ppm assigned to the methyl group. The aromatic protons were recorded as multiplet peaks in the range (6.7 - 8.2) ppm. The imine group proton showed as single peak at 8.8 ppm. The O-H proton showed a single peak at 13.4 due to deshielding resulted from the internal hydrogen bonding with the imine group.

FT-IR for compounds (H_{25} – H_{28}) showed no bands in the C=O stretching region signifying its conversion into an imine group. O-H and N-H stretching vibration bands showed around (3270 – 3475) cm^{-1}, while the bands shown around (3000 – 3100) cm^{-1} were assigned to the (C-H) aromatic stretching vibrations. The C=C aromatic stretching vibrations were assigned the bands around (1524 – 1560) cm^{-1}. Absorption bands around (1594 – 1620) cm^{-1} were attributed to the stretching vibrations of the imine group C=N.

^{1}H NMR spectrum of compound H_{26} showed a single peak at 1.28 ppm which was assigned to the methyl groups, while the thiocarbohydrazide moiety N-H was recorded as singlet at 2.2 ppm. The multiplet peaks within the range (6.9 - 7.9) ppm were assigned to the aromatic protons. The protons of CH=N group were recorded as singlet at 7.25 ppm, while the protons of the two OH groups shown single peak at 9.74 ppm.

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For compounds (H_{29} – H_{31}), the FT-IR spectrum showed stretching bands around (3000 – 3100) cm^{-1} attributed to the aromatic C-H vibrations. No bands were observed in the region of the N-H group stretching indicating conversion into imine group. Aromatic C=C stretching vibrations were observed around (1574 – 1590) cm^{-1}. The imine groups were observed around (1612 - 1616) cm^{-1}.

For the compound H_{29}, the ^{1}H NMR spectrum showed a multiplet in the range (6.9 - 8.6) ppm that is attributed to the aromatic. A single peak showed at 9.2 ppm that is attributed to the imine group proton. And for the OH group it was assigned 10.1. Due to the deshielding effect of internal hydrogen bonding with the imine group, both the OH and the imine groups are shifted towards downfield.

4. Conclusion:

The aim of this work is to synthesize, study spectroscopically, and evaluate the Anti-bacteria activity of some new azo dyes containing benzothiophene and dibenzothiophene and Schiff's bases containing more than one functional group. These compounds are very stable which makes them suitable to be used in pharmacological and biological researches. Having more than one functional group makes them versatile molecules to be used in different reaction types and a good candidate for stable active photosensitizers[15].

The use of 4-aminoacetophenone as a building block in the synthesis of macro molecular Schiff bases made it possible to attach additional phenyl groups to the diamines, i.e. 1,5-diaminonaphthalene and thiocarbohydrazide. Compound H_2 showed the highest value of biological activity among the other compounds studied. This anti-bacterial activity might be due to the effect of the azo group in the compound, although it has been reported that the activity of the azo compound prontosil against bacteria is due to its biodegradation product sulfanilamide which is liberated due to the action of the enzymes inside human body [24].

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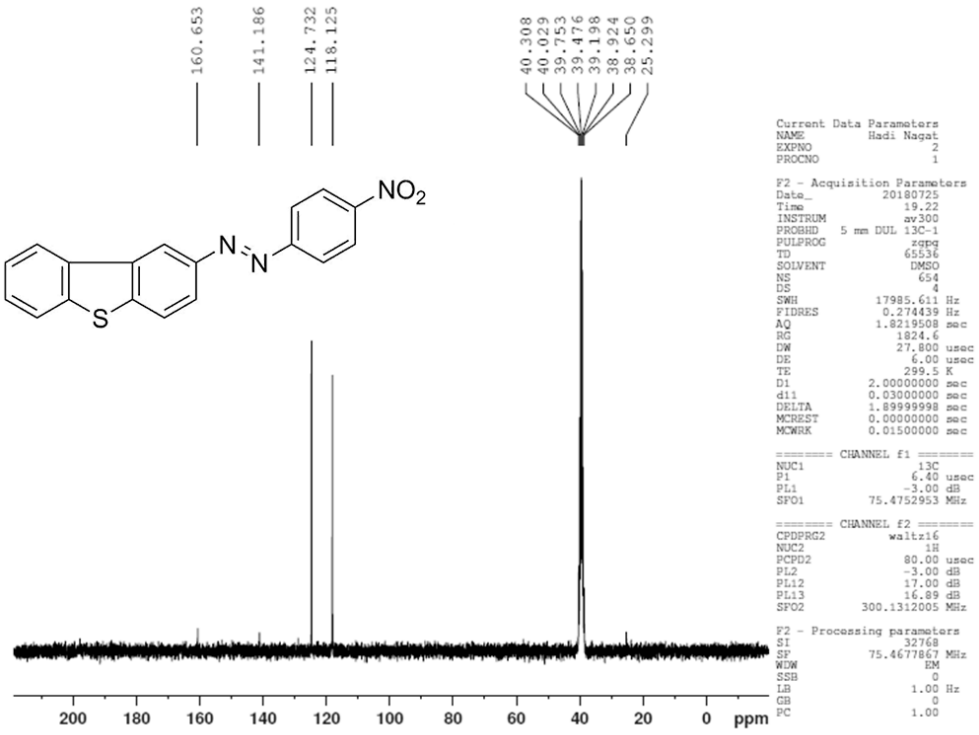

Fig. 1: 13C-NMR spectrum for compound H_2.

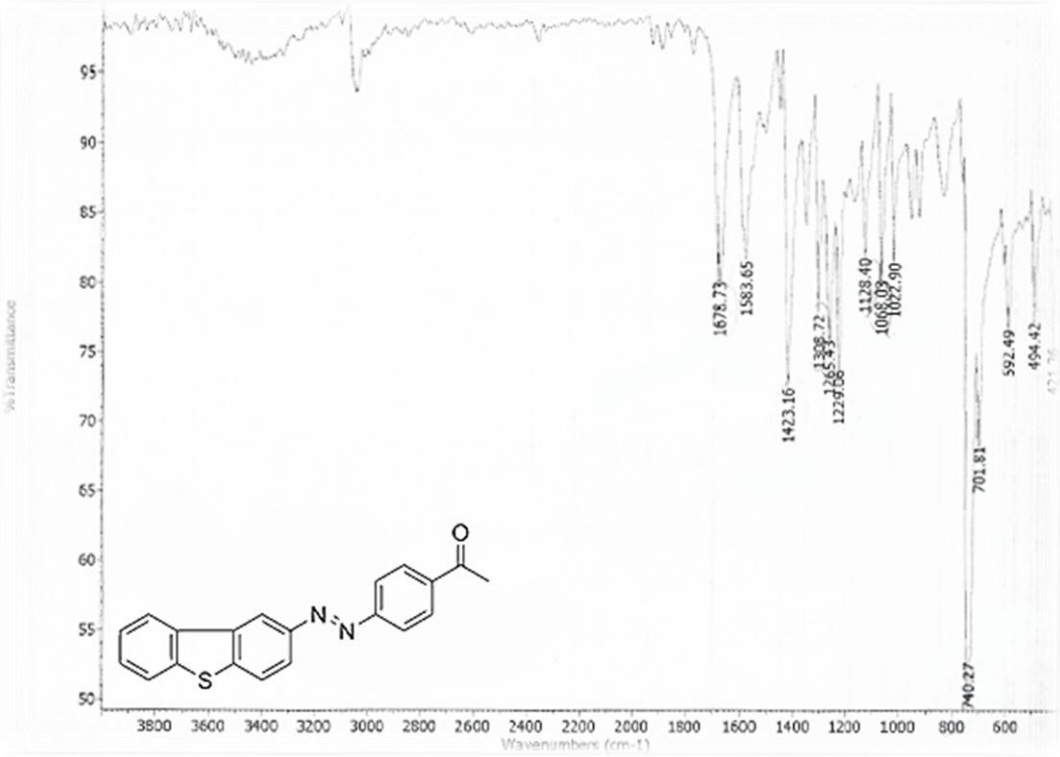

Fig. 2: FT-IR spectrum for compound H_3.

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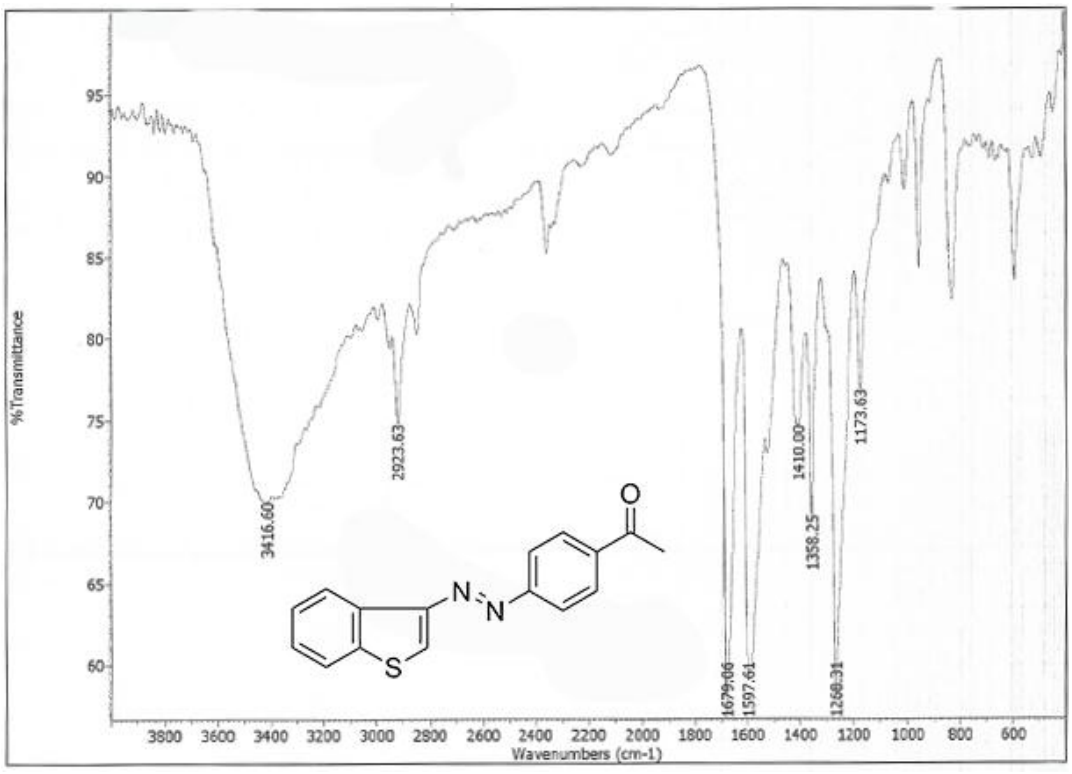

Fig. 3: FT-IR spectrum for compound $H_{8.}$

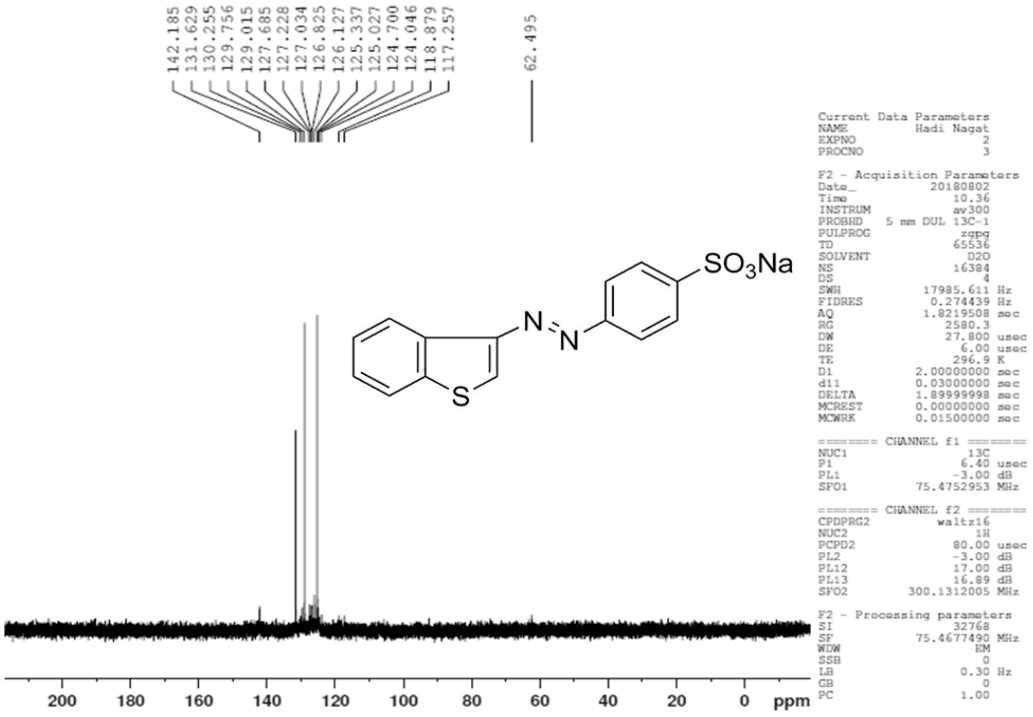

Fig. 4: ^{13}C-NMR spectrum for compound $H_{11.}$

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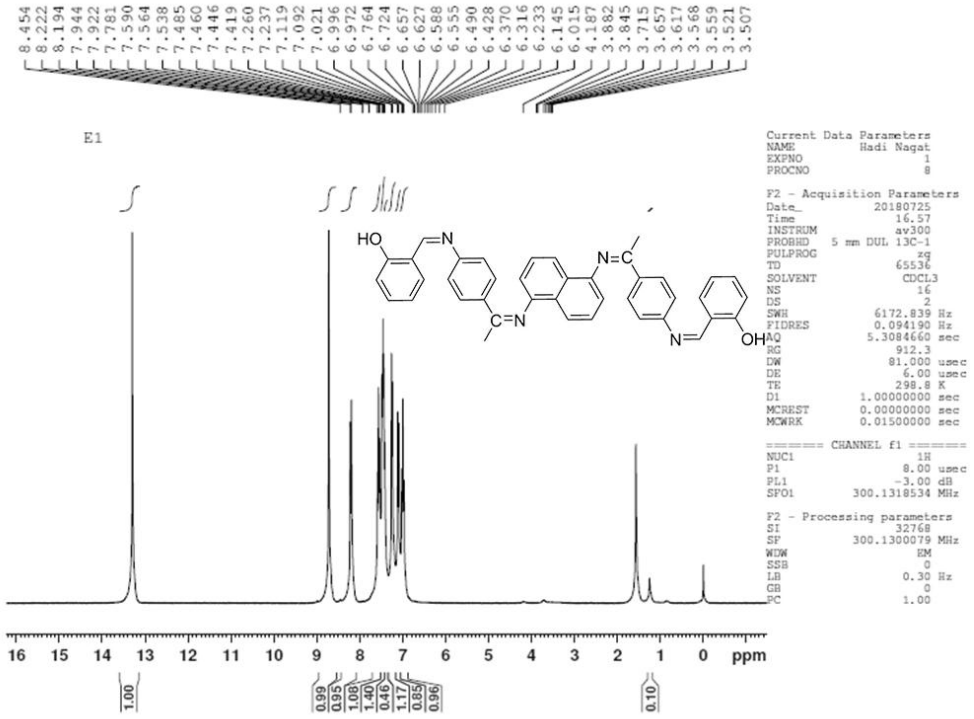

Fig. 5: ^{1}H-NMR spectrum for compound H_{20}.

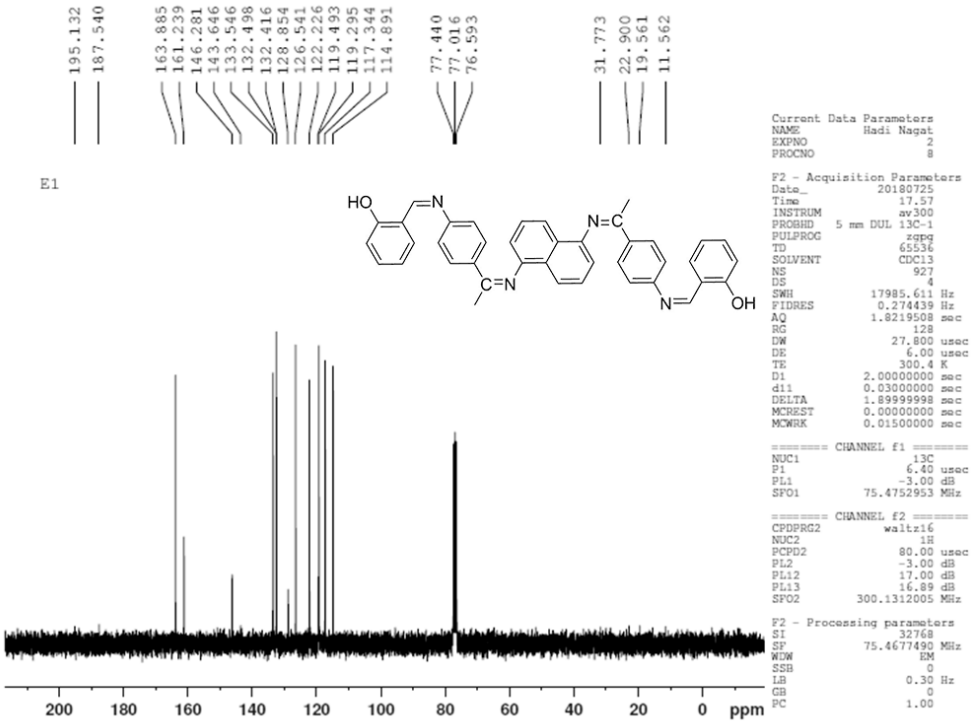

Fig. 6: ^{13}C-NMR Spectrum for compound H_{20}.

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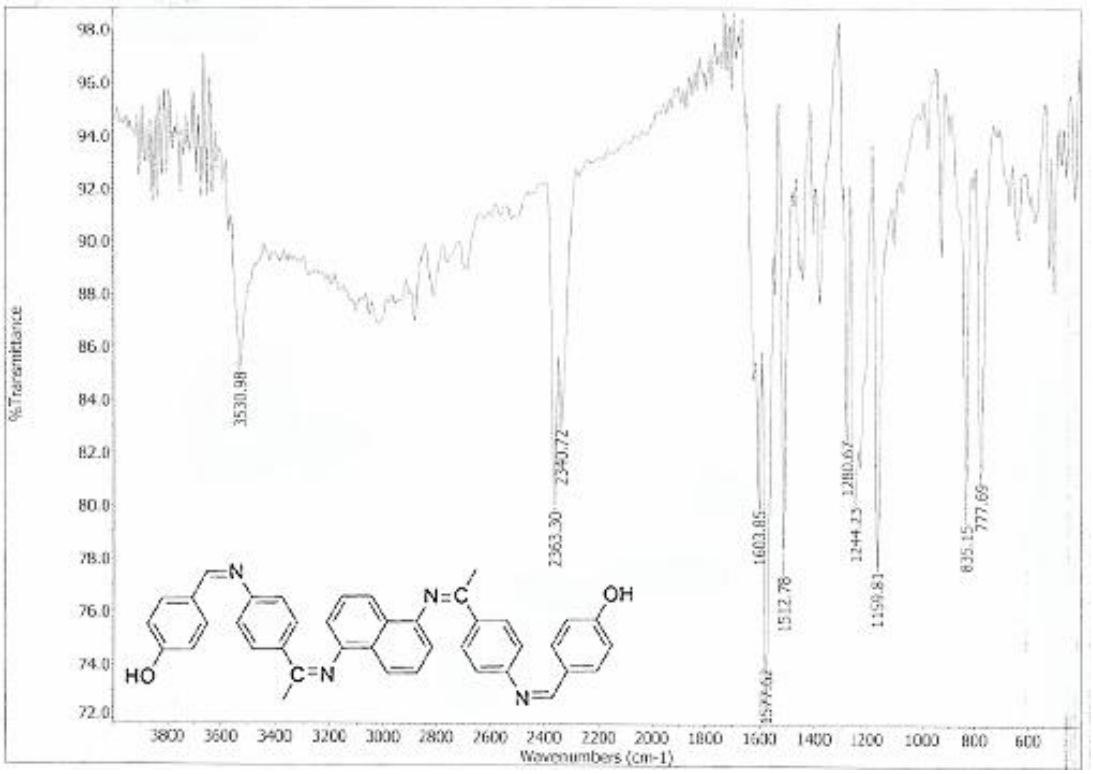

Fig. 7: FT-IR spectrum for compound $H_{21.}$

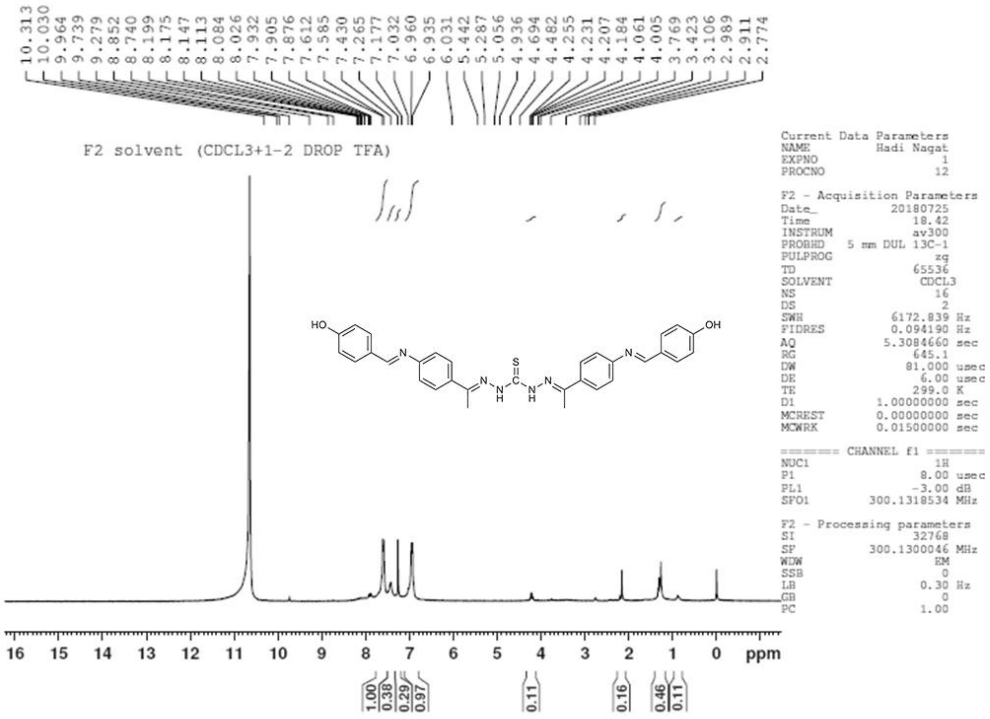

Fig. 8: ^{1}H-NMR spectrum for compound $H_{26.}$

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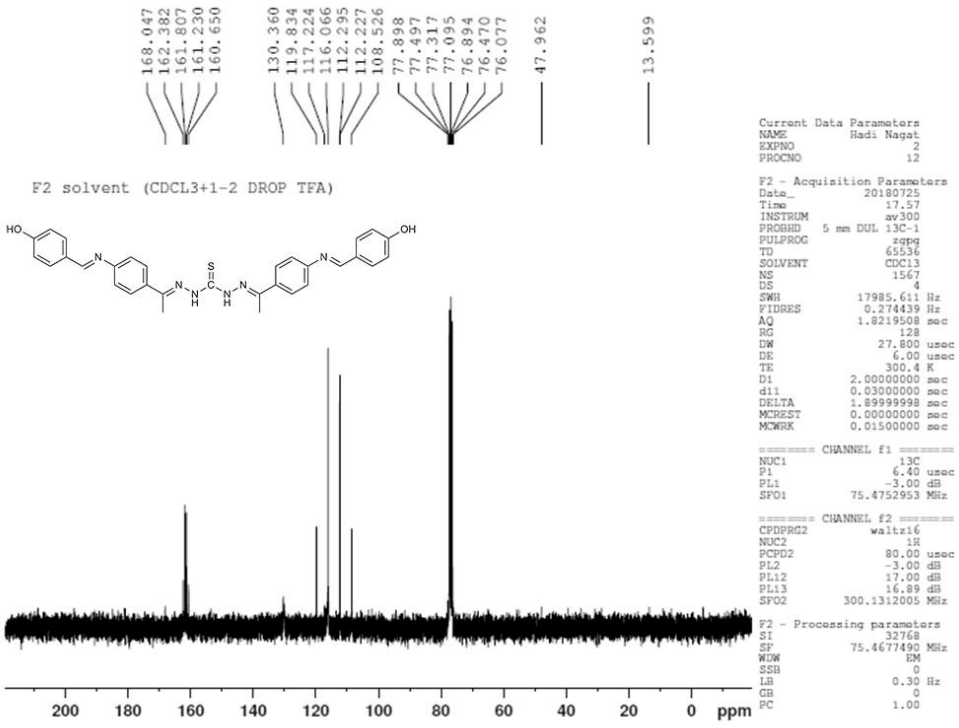

Fig. 9: ^{13}C-NMR spectrum for compound $H_{26.}$

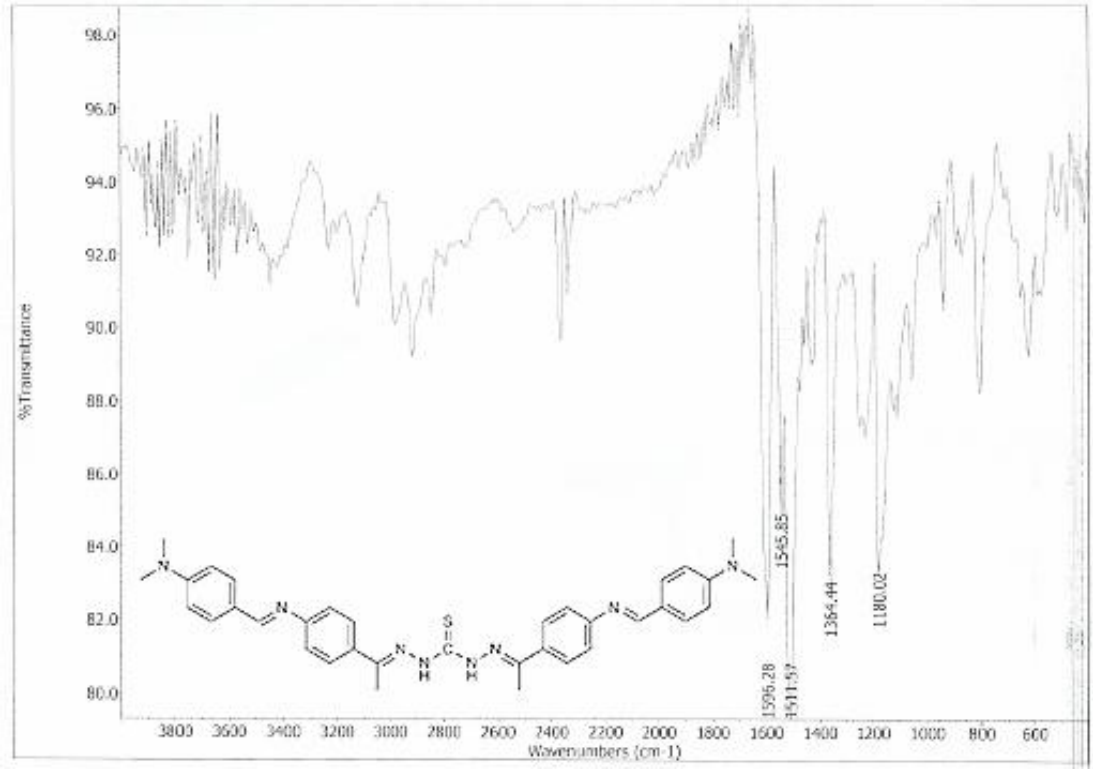

Fig. 10: FT-IR spectrum for compound $H_{28.}$

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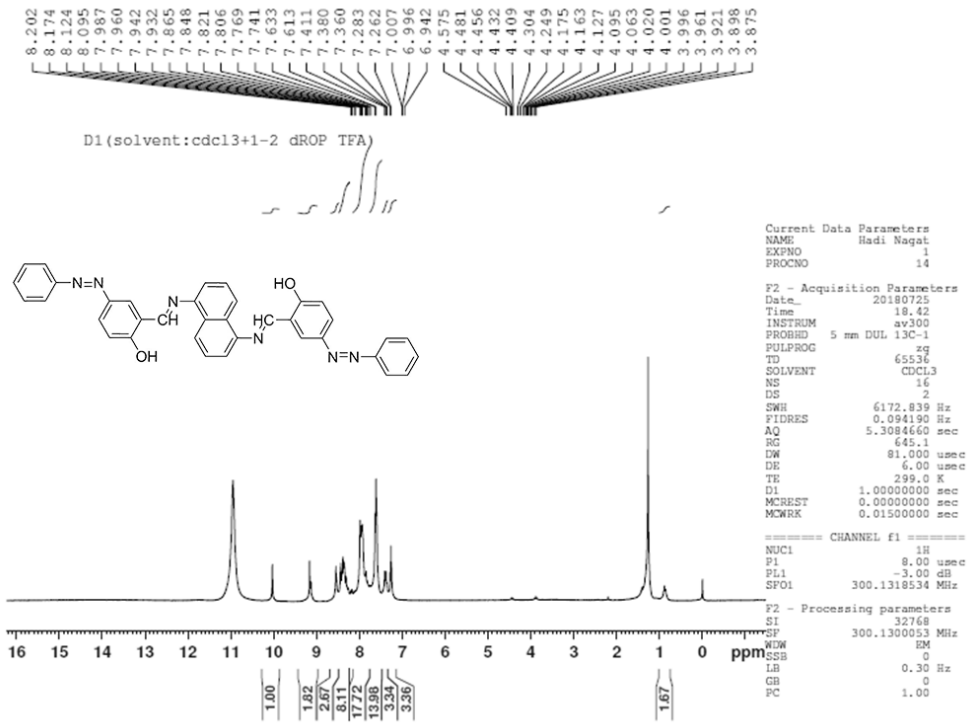

Fig. 11: ^{1}H-NMR spectrum for compound H_{29}.

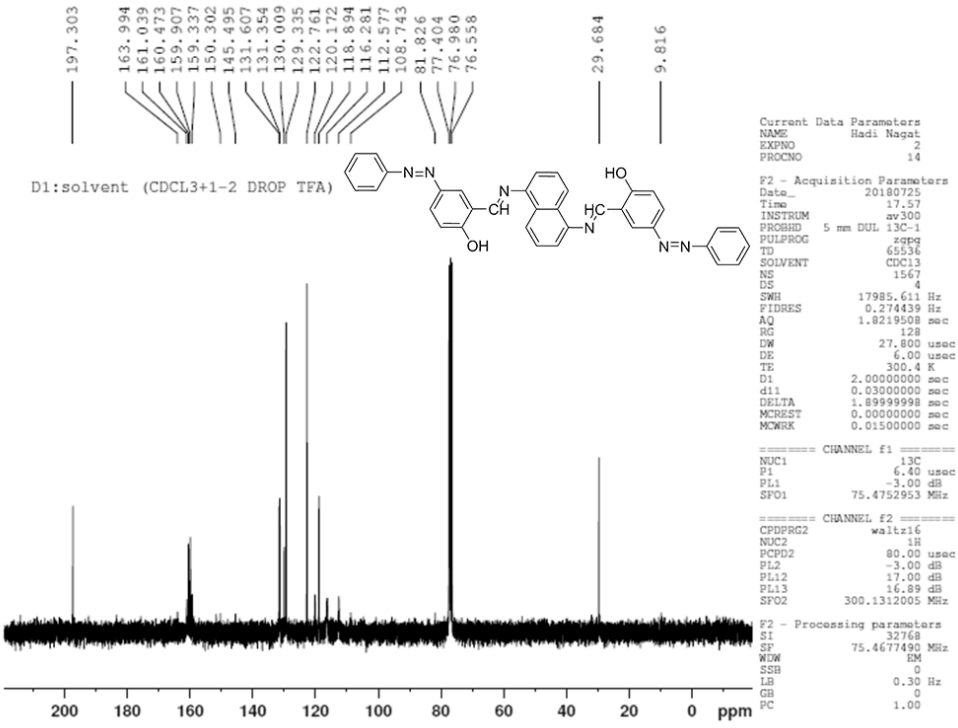

Fig. 12: ^{13}C-NMR spectrum for compound H_{29}.

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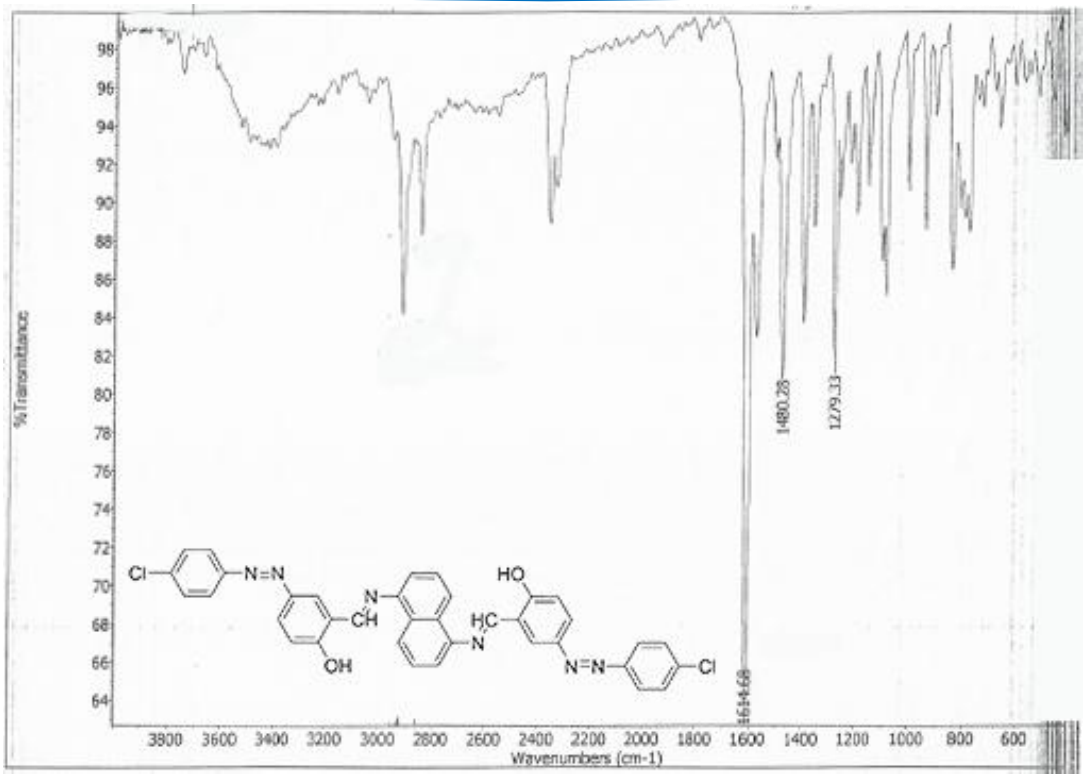

Fig. 13: FT-IR spectrum for compound $H_{30.}$

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