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Synthesis, Characterization and Thermal behaviour of Some new Azo-Polymers Containing trichloroethylene Derivatives

Saja Saeed Rajeh, Mohammed Ali Mutar

College of Sciences, University of AL-Qadisiyah, Iraq.

Department of Chemistry, College of Sciences, University of AL-Qadisiyah, Iraq.

sci.chem.mas.22.14@qu.edu.iq

mohammed.ali@qu.edu.iq

Abstract

The diazocoupling reaction of hexamethylenediamine, 5-amino-2-hydroxybenzoic acid, and ethylenediamine with benzoyl chloride and carbazole, respectively, in the presence of HCl, NaNO2, and 10% NaOH was used to create a series of azobenzene compounds. The reaction was stirred for an hour in an ice bath at 0–5°C.The resulting azobenzene compounds react with vinyl compounds, including trichloroethylene compounds. In the presence of nitrogen, 1-hydroxy cyclohexyl phenol ketone was used as the initiator in free-radical photopolymerization to polymerize azo benzene **trichloroethylene Derivatives** that included trichloroethylene molecules. FTIR, 1H, and 13CNMR have been used to characterise the spectroscopic properties of the small compounds and polymers of azobenzene.Azobenzene polymer thermal (DSC and TGA) methods were investigated.

Introduction

In 1964, azopolymer was synthesised by diazo coupling bis diazonium salts with phenols [1–4]. Azo polyamides and polyesters can also be synthesized through interfacial or solution polymerization of azo benzene monomers, in addition to the previously mentioned reactions [5–9]. The reaction between 4,4'-diamino azobenzene and terephthdaldehyde, along with the polymerization of 4,4'-azo dibenzaldehyde using a bifunctional Wittig salt, has resulted in the formation of highly conjugated polymers. Azo polymers are becoming more and more popular due to their unique qualities and their uses. The trans-cis isomerisation of the -N=N- groups has been the subject of numerous investigations, and Rau recently reviewed the literature on the isomerisation of azo aromatic compounds in solution or in the solid form. To create polymer composites and alter the characteristics of standard polymers, a variety of azobenzene derivatives have been used as dopants [11].In this instance, the effects are typically controlled by the mixture's compatibility and the azo dopants' concentration. A growing number of people are interested in azo polymers, which are polymers with azo groups covalently bonded inside them. Kinetic investigations on several azo polymers have shown how the features of the polymer affect both photochemical and thermal isomerisation, and the structural characteristics of the polymer matrix determine how quickly the azo groups covalently bonded to the polymers isomerise [12]. Azo polymers can exhibit light-induced dichroism and birefringence, be liquid crystalline, and have nonlinear optical characteristics. These unique characteristics of the azo polymers are the primary focus of this review. In 1989, Kumar and Neckers evaluated the conformational changes brought about by photochemical trans-cis isomerisation of the azo groups and their impact on the characteristics of the polymer or polymer solution [13].

Materials and Instruments

Materials

(Benzyl chloride , 5-amino-2-hydroxybenzoic acid, Ethylenediamine , Trichloroethylene ,HCl, $NaNO_2$, NaOH) from THMOS-BAKER India (Hexamethylenediamine , carbazole) from SIGMA , 1-hydroxy cyclohexyl phenol ketone as Photo initiator (B.D.H / USA).

Instruments

The Bruker company in Germany supplied the fourire transport infrared spectrophotometer of type FTIR -8400s, which was used in the Dept. of Chemical Engineering at the University of AL-Qadisiyah to characterize the recorder preparation compound by detecting the active group and determining the type of bounds that bind the mineral particles. The lattice Stuart smp30 melting point equipment and the penile were used to measure the degree of fusion (melting points). Model 81, Albinos, the Netherlands, is a hotplate stirrer. Korean manufacturer K&K Scientific Supply's K-VO27 vacuum drying oven. A 400 MHz ultra-shield Bruker spectrometer with DMSO d6 as a solvent was used to record 1HNMR spectroscopy at the University of Tehran in Iran.

Synthesis of AZO (1)

Focused on hydrochloric acid (10 mL), water (25 mL), and ice (25 g) were used to dissolve hexamethylenediamine (1.53 g, 10 mmol) in a 500 mL conical flask. A sodium nitrite solution (3.45 g, 50 mmol) in 7.5 mL of water was introduced gradually over a period of 10 minutes, following the swirling of the solution to achieve clarity while maintained in an ice bath at 0ºC. The reaction mixture was subsequently stirred for an additional 20 minutes at a temperature range of 0–5 ºC. A 10% sodium hydroxide solution (comprising 3 g of NaOH and 25 mL of distilled water) was then added dropwise to benzoyl chloride (1.38 g, equivalent to 10 mmol) while continuing to stir for an extra hour in an ice bath. The chemicals that were created precipitated. The product was filtered, cleaned with water, then vacuum-dried overnight at room temperature. **The others AZO compounds (2-3) were prepared by the same procedure as above using from Ethylenediamine with Benzyl chloride , 5-amino-2-hydroxybenzoic acid with carbazole .**

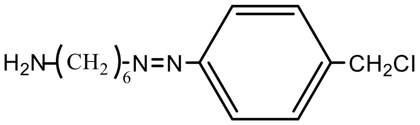
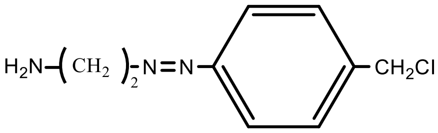


Figure (1) Structure of AZO(1)

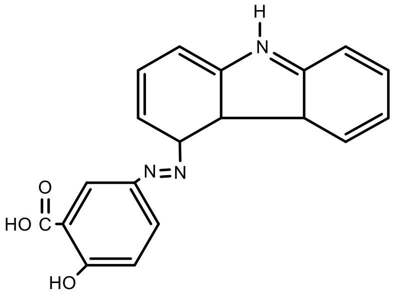
Table (1) The colour ,yield and melting point for synthesis of AZO (1) compounds

Compound	***Formula***	***Substances***	***Color***	***Weight (gm)***	***Yield (%)***
AZO(1)	$C_{24}H_{41}I_2N_6NaO_2$	Hexamethylenediamine / Benzyl chloride	Yellow	1.05	76

Synthesis of AZO (2-3)



AZO(2)



AZO(3)

Figure (2) Structure of AZO (2-3)

Table (2) The colour ,yield and melting point for synthesis of AZO (2-3)compound

compounds	*Formula*	*Substances*	*Color*	*m.p /C*	*Weight (gm)*	*Yield (%)*
AZO (2)	$C_{12}H_{19}IN_3$	Ethylenediamine, Benzyl chloride	White	286-288	1	74
AZO (3)	$C_{21}H_{22}N_3O_3$	5-amino-2-hydroxybenzoic acid, carbazole	green	176-178	2.61	89

Synthesis of trichloroethylene derivative monomers containing AZO group

Synthesis of monomer1 (M1)

0.8 mmol of trichloroethylene is maintained in an ice bath. Drop by drop, sodium hydroxide (0.2 mmol) is added to a solution of hexamethylenediamine and benzyl chloride (0.1 mmol) in water. The mixture was stirred, then kept at 0–5 temperature. For two hours, the solution was agitated at 0–5°C. The mix was then filtered, cleaned with acetone and methanol, and vacuum-dried: A solid with a white hue developed. **The others AZO monomers (2-3) were prepared by the same procedure as above using (Ethylenediamine with benzyl chloride with Trichloroethylene , 5-amino-2-hydroxybenzoic acid with carbazole with Trichloroethylene).**

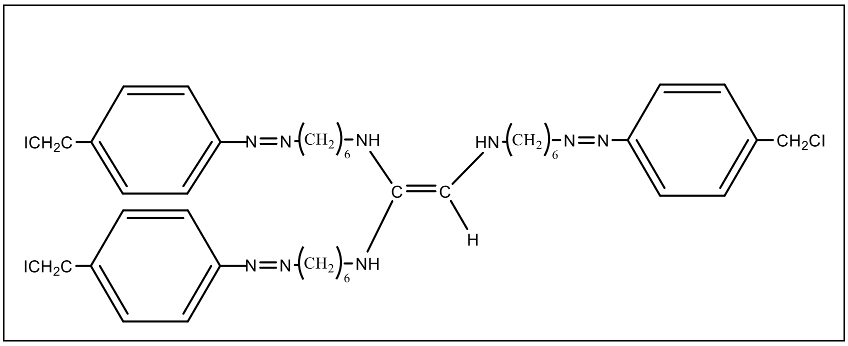
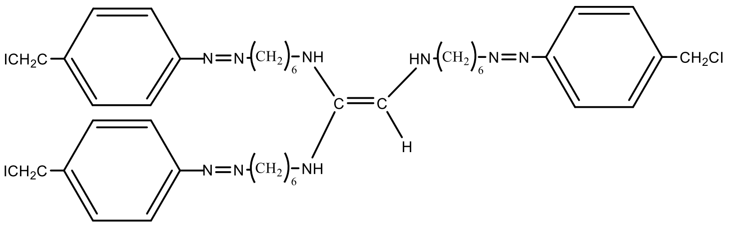


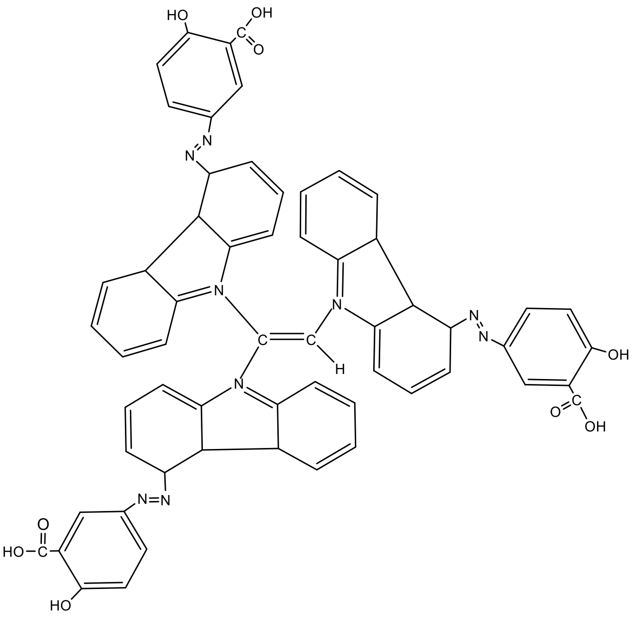
Figure (3) Structure of M(1)

Table (3) The colour ,yield and melting point for monomers (1)

Monomer	***Formula***	***Substances***	***Color***	***Weight (gm)***	***Yield (%)***
M(1)	$C_{42}H_{69}I_3N_9$	Hexamethylenediamine,benzylchloride, Trichloroethylene	colorless	0.32	65



AZO (2)



AZO (3)

Figure (4) Structures of monomers (2-3)

Table (4) The colour ,yield and melting point for monomers (2-3)

compounds	Formula	Substances	Color	m.p /C	Weight (gm)	Yield (%)
M (2)	$C_{42}H_{69}I_3N_9$	Ethylendiamine,benzylchloride with Trichloroethylene	White	288-291	0.30	68
M (3)	$C_{64}H_{61}N_9O_9$	5-amino-2-hydroxybenzoic acid,carbazole,Trichloroethylene	Brown	245-250	0.75	53

Synthesis of AZO polymer

Synthesis of AZO polymer (1)

(5) gm of AZO benzene monomers was dissolved in DMSO and stirred for 30 minute. The reaction are polymerized by free-radical photopolymerization in presence of nitrogen in the presence of1-hydroxy cyclohexyl phenol ketone as photo initiator (0.1 gm) and then the solvent was evaporated under vacuum to remove the DMSO completely. The other AZO polymers (2-3) were prepared by the same procedure as above .

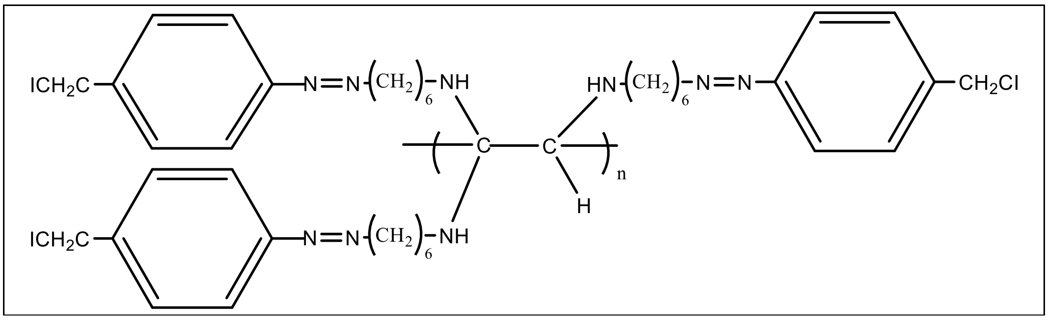
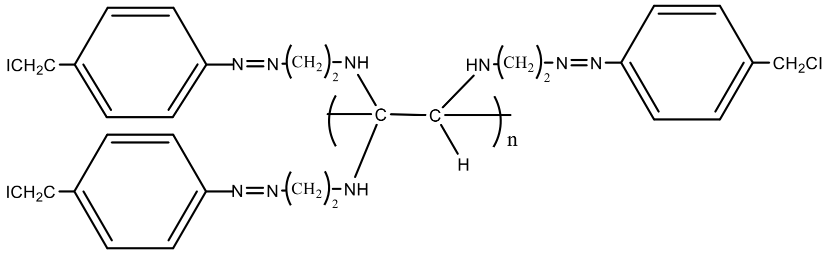


Figure (5) Structure of AZO polymer (1)

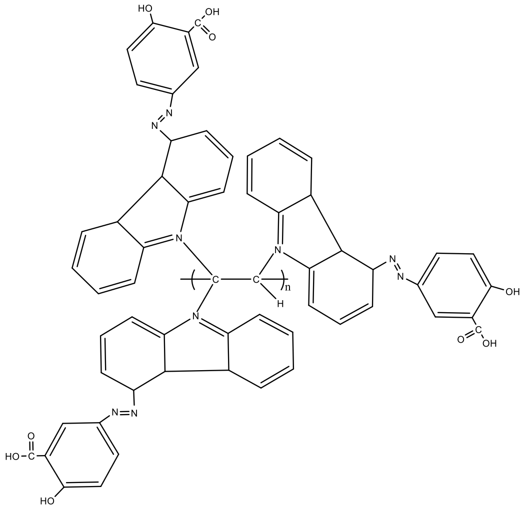
Table (5) The colour and yield for synthesis of AZO polymer (1)compound

Polymer	Formula	Substances	colors	Weight (gm)	Yield
AZO Polymer (1)	$C_{44}H_{74}I_3N_9$	Hexamethylenediamine with benzyl chloride,	white	0.32	76

Synthesis of AZO polymer (2-3)



AZO polymer (2)



AZO Pplymer (3)

Figure (6) Structure of AZO polymer (2-3)

Table (6) The colour and yield for synthesis of AZO polymer (2-3)compound

compounds	Formula	Substances	colors	Weight (gm)	Yield (%)

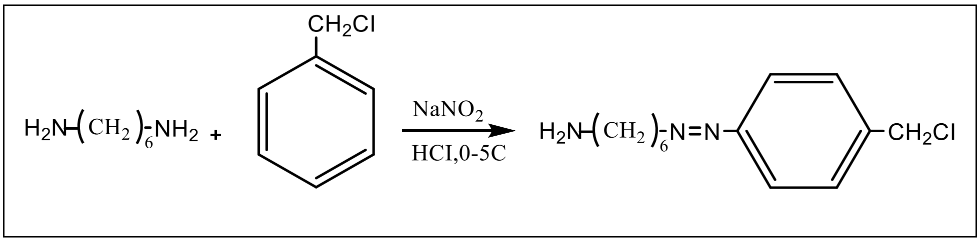
AZO Polymer (2)	$C_{44}H_{74}I_3N_9$	Ethylendiamin,benzylchloride,photoiniator,N2	white	0.35	74
AZO Polymer (3)	$C_{66}H_{67}N_9O_9$	5-amino-2-hydroxybenzoic acid, carbazole, photo initiator,N2	brown	0.67	73

Results and Discussion

Synthesis of AZO compounds

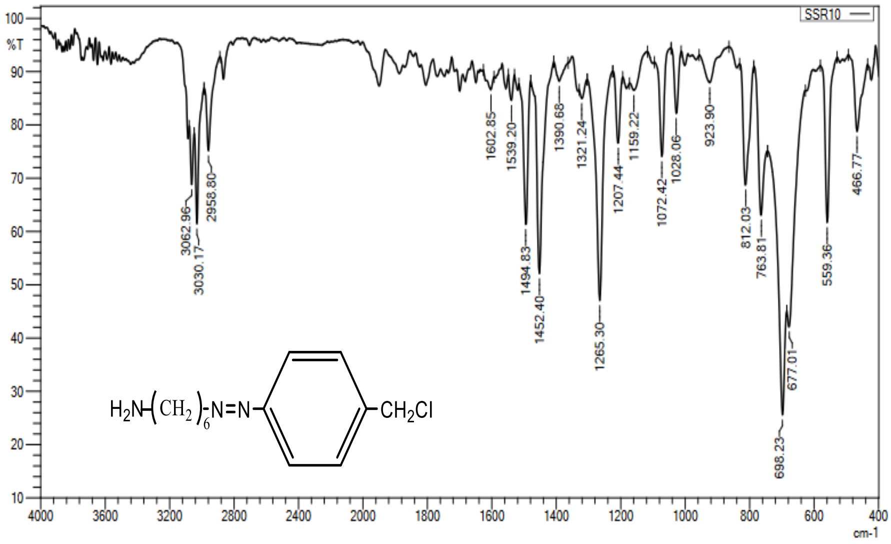
Synthesis of AZO (1)

The synthesis of AZO (1) is done through reaction of diazocoupling reaction of Hexamethylenediamine with benzoyl chloride as exposed in Scheme (1).



Scheme (1) Synthesis of AZO(1)

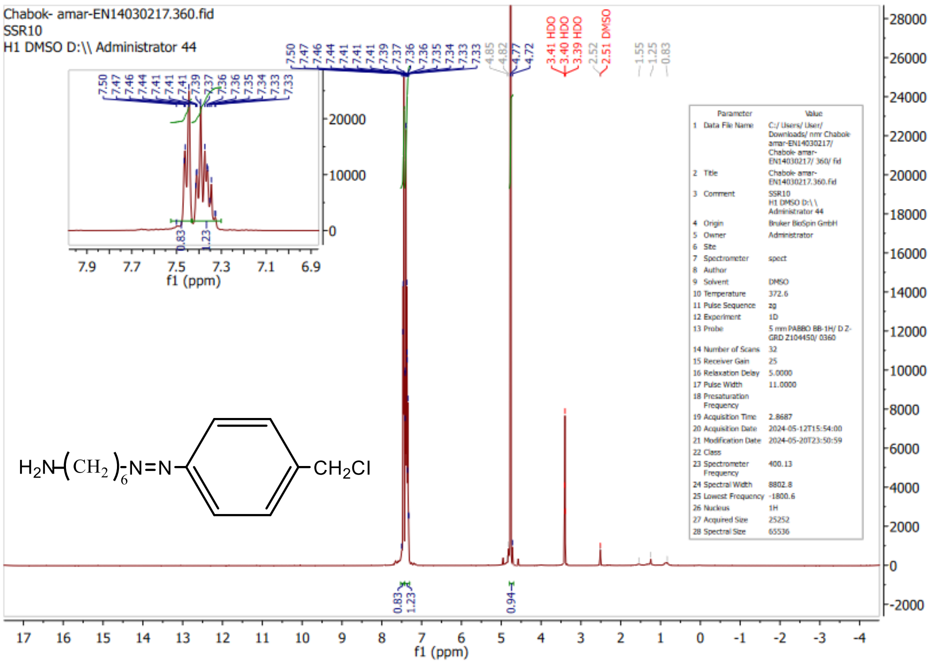
FTIR spectrum of AZO (1)



Figure(7) FTIR spectrum of AZO (1)

As illustrated in Figure (7), the FTIR spectrum of AZO (1) displays absorption bands at 3062 and 3030 cm^{-1} to –NH2 stretching, 2958 cm^{-1} to C-H, 1207 cm^{-1} to C-N, (1452) cm^{-1} to CH2, 559 cm-1 to C-Cl, 1492 cm^{-1} to N=N, and 1602 cm^{-1} to C=C (aromatic). [13–15]

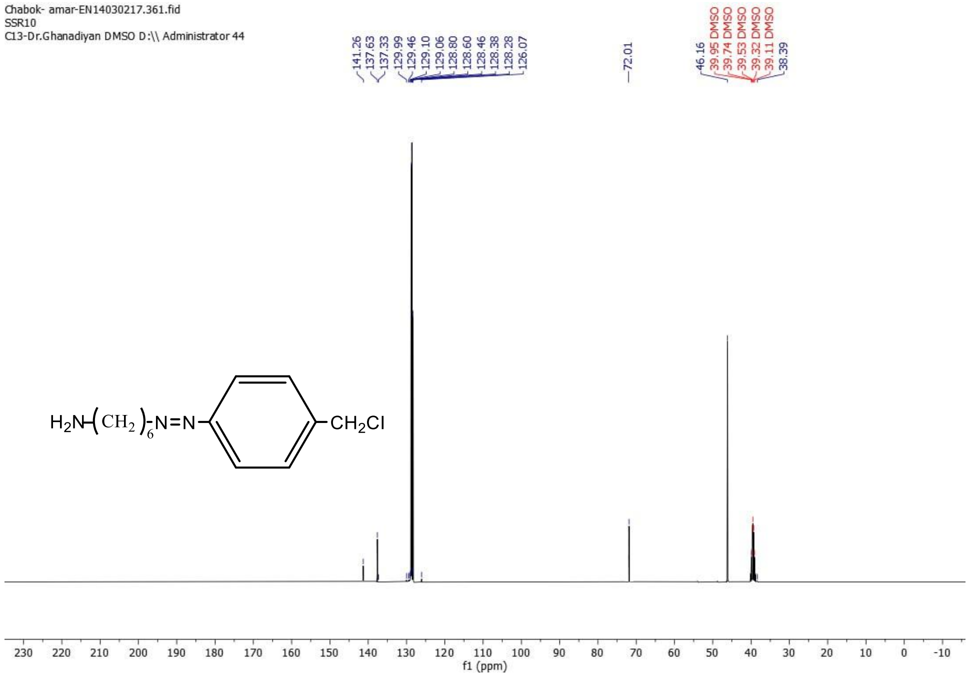
^{1}HNMR Spectrum of AZO (1)



Figure(8) ^{1}HNMR spectrum of AZO (1)

Figure (8) shows the ^{1}HNMR spectrum of AZO (1). The primary signal at δ 1.5-2.1 ppm is indicative of DMSO-d6 as the solvent; singlate to CH2 at ΄ 2.5 ppm, singlate to C-H at 1.4 ppm, multiplet singlate to (4H, phenyl ring) at 7.5 ppm, as well as a singlet to (2H, NH) at 3.5 ppm.[13-15]

^{13}C NMR Spectrum of AZO (1)

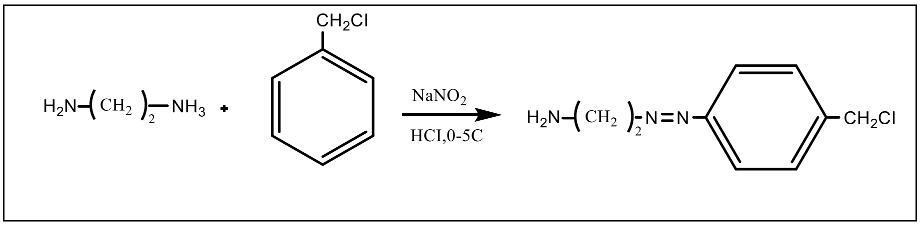


Figure(9) ^{13}C NMR spectrum of AZO (1)

Figure (9) ^{13}C-NMR of AZO (1) displays the third region contains the signals of aromatic as well as olefinic carbons, with one associated with C-N at 62 ppm and one associated with C-Cl at 47 ppm. [13-15]

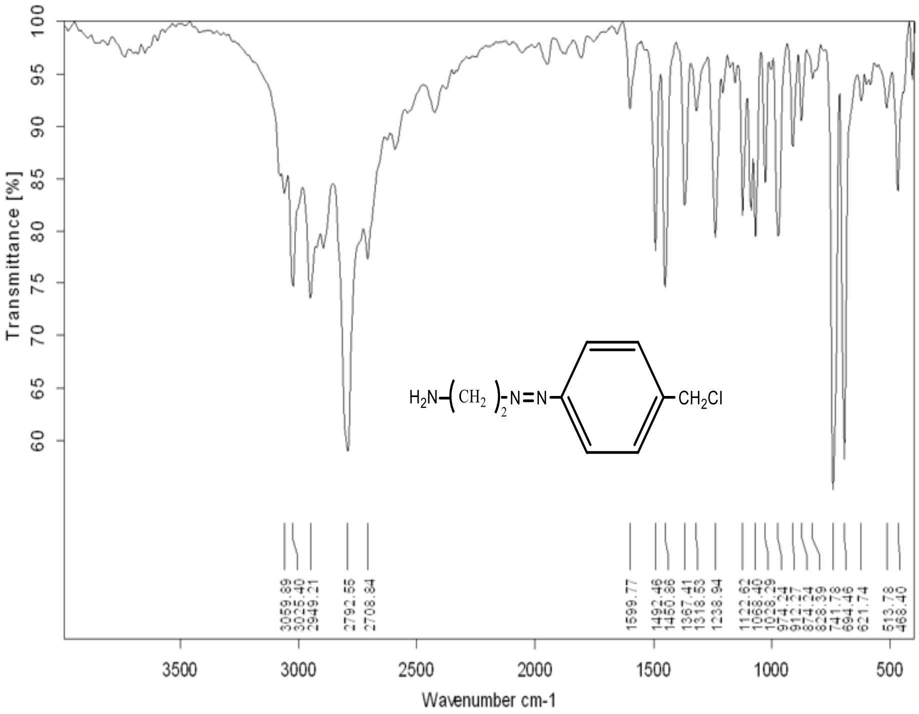
Synthesis of AZO (2)

The synthesis of AZO(2)is done through reaction of synthesized using diazocoupling reaction of Ethylendiamin with benzylchloride as shown in Scheme (2).



Scheme (2) Synthesis of AZO(2)

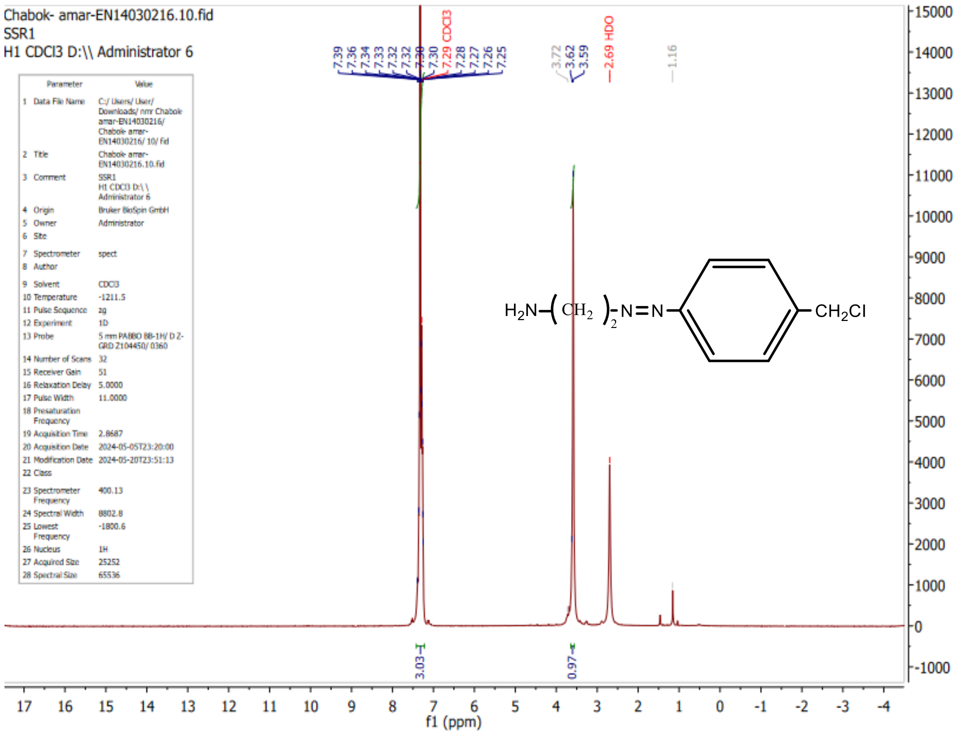
FTIR Spectrum of AZO(2)



Figure(10) FTIR spectrum of AZO (1)

The FTIR spectra of AZO (2) are displayed in Figure (10) and consist of absorption bands at 3059 cm^{-1} to –NH2 stretching, 2949 cm^{-1} to C-H, 1238 cm^{-1} to C-N, (1450) cm^{-1} to CH2, 513 cm-1 to C-Cl, 1492 cm-1 to N=N, and 1599 cm^{-1} to C=C (aromatic). At 3025 cm^{-1}, the C-H aromatic stretching occurrence was detected. At 3025 cm^{-1}, the C-H aromatic stretching frequency is detected. [13-15]

^{1}H NMR spectrum of AZO(2)



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27 Acquired Size	25252
28 Spectral Size	65536

Figure (11)^{1}H NMR of AZO (2)

Figure (11) shows the ^{1}HNMR spectrum of AZO (2). With a singlet at (2.5 δ ppm) to C-H, multiplet singlate at (7.5 δ ppm) to (4H, phenyl ring), singlet at (3.5 δ ppm) to (2H, NH2), as well as a singlet at (1.2 δ ppm) to CH2, the main signal at δ 1.5-2.1 ppm is typical of DMSO-d6 as solvent. [13-15]

^{13}C-NMR spectrum of AZO(2)

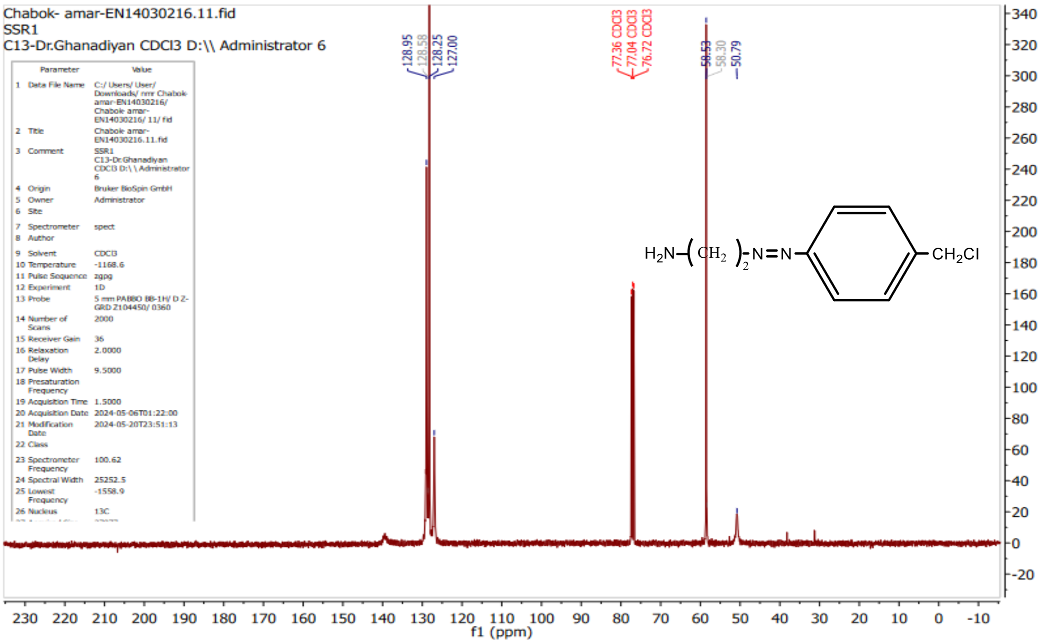

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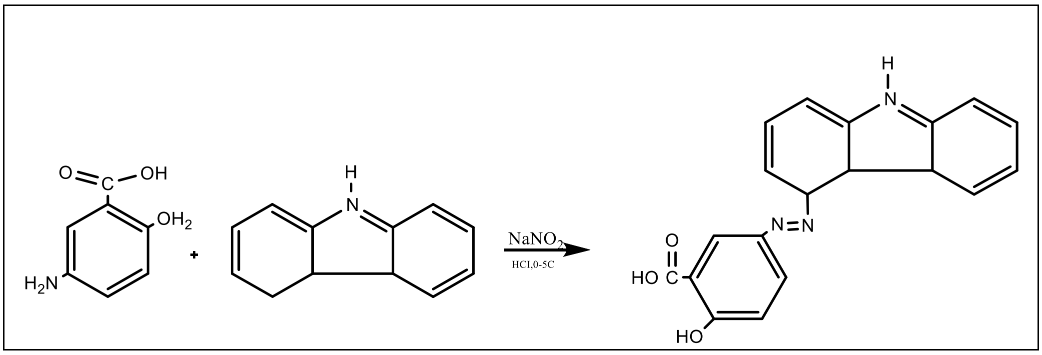
figure (12)^{13}C-NMR of AZO (2)

AZO (2) ^{13}C-NMR, Figure (12), displays the indications of aromatic and olefinic carbons are found. one associated with C-Cl at 50 ppm, one associated with CH2-C (C Secondary) at 38 ppm, and one associated with C-N at 76 ppm , single related to CH_2-N at 57 ppm. [13-15]

Synthesis of AZO (3)

The synthesis of AZO(3)is done through reaction of synthesized using diazocoupling reaction of 5-amino-2-hydroxybenzoic acid with carbazole as exposed in Scheme (3).



Scheme (3) Synthesis of AZO (3)

FTIR Spectrum of AZO(3)

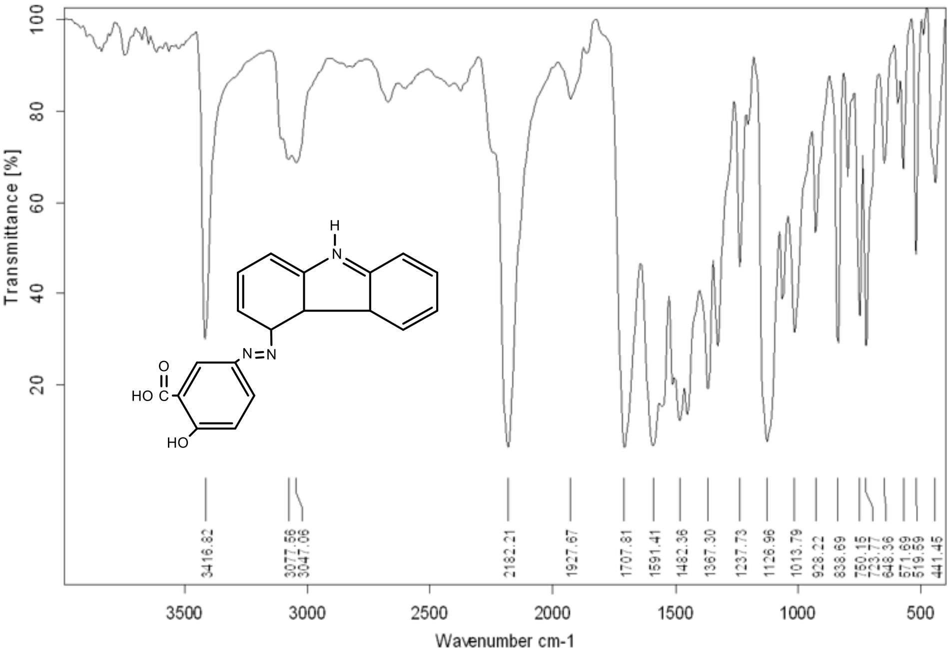


Figure (13) FTIR Spectrum of AZO(3)

Figure (13) displays the FTIR spectrum of 5 AZO (3).It shows a sharp absorption band at 3416 cm^{-1} to –OH stretching, a band at 1237 cm^{-1} to C-N, a band at 1482 cm^{-1} to N=N, a band at 1591 cm^{-1} to C=C (aromatic), as well as a band at 1707 cm^{-1} to C=O (carboxylic group). The FTIR spectra revealed the secondary amine N-H stretching occurrence for carbazole at 3077 cm^{-1}, while the C-H aromatic stretching frequency is recorded at 3047 cm^{-1}. [13-15]

^{1}HNMR Spectrum of AZO(3)

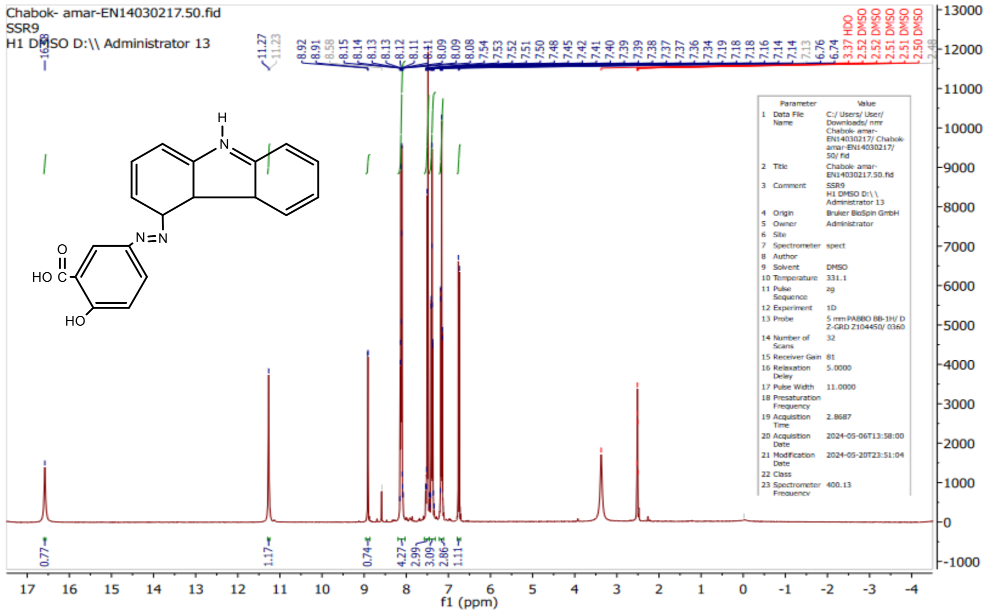


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figure (14) ^{1}HNMR Spectrum of AZO(3)

Figure (1) shows the AZO (3) ^{1}HNMR spectrum. A singlet at (3.5 δ ppm) to (1H, NH), a singlet at (9.0 δ ppm) to (1H, OH), a singlet at (11.2 δ ppm) to (1H, COOH), a multiplet singlate at (6.7-7.5 δ ppm) to (11H, phenyl rings), as well as a singlet at (8.2 δ ppm) to proton (Heteroaromatic) are the main signal at δ 1.5-2.1 ppm. [13-15].

^{13}C-NMR spectrum of AZO (3)

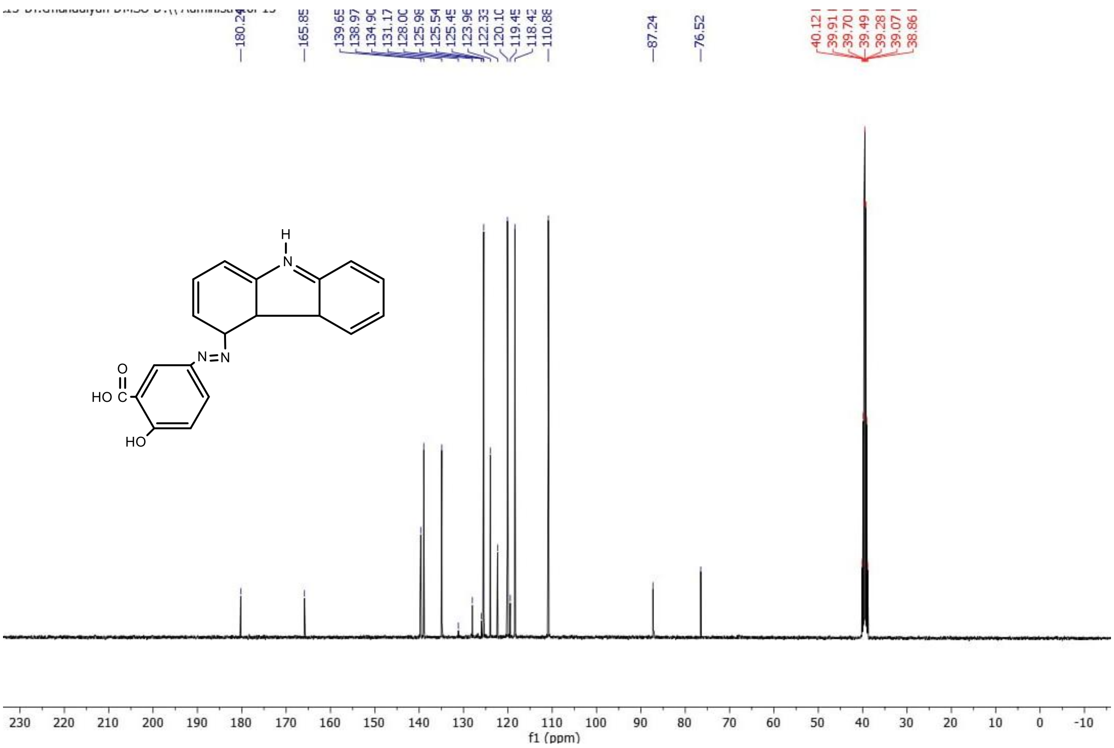


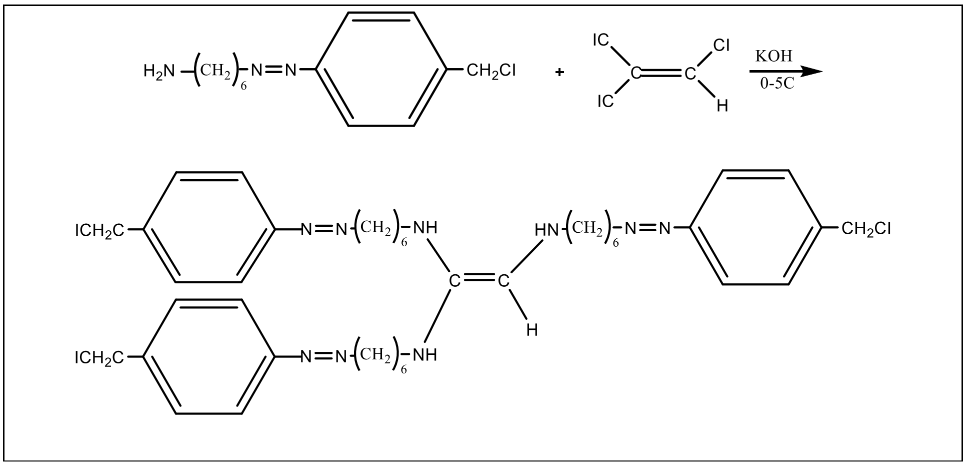
Figure (15) ^{13}C-NMR spectrum of AZO (3)

Figure (15) ^{13}C-NMR of AZO (3) reveals several signals dispersed across a broad spectrum of chemical shifts. Shows the signs of olefinic and aromatic carbons. One of these signals is associated with C-N at 62 ppm, one with C-O at 86 ppm, and one with C=O (carboxylic) at 175. [13-15]

Synthesis of trichloroethylene derivative monomers containing AZO group

Synthesis of monomer1 (M1)

The synthesis of M(1) is done through reaction of diazocoupling reaction of **Trichloroethylene with AZO (1**) as shown in Scheme (4).



Scheme (4) Synthesis of M(1)

FTIR Spectrum of Trichloroethylene with AZO (1)

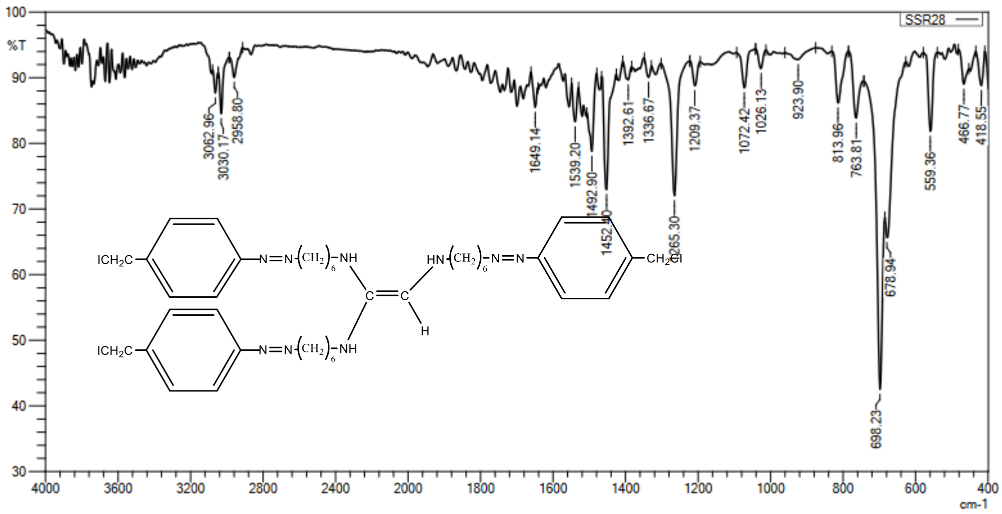
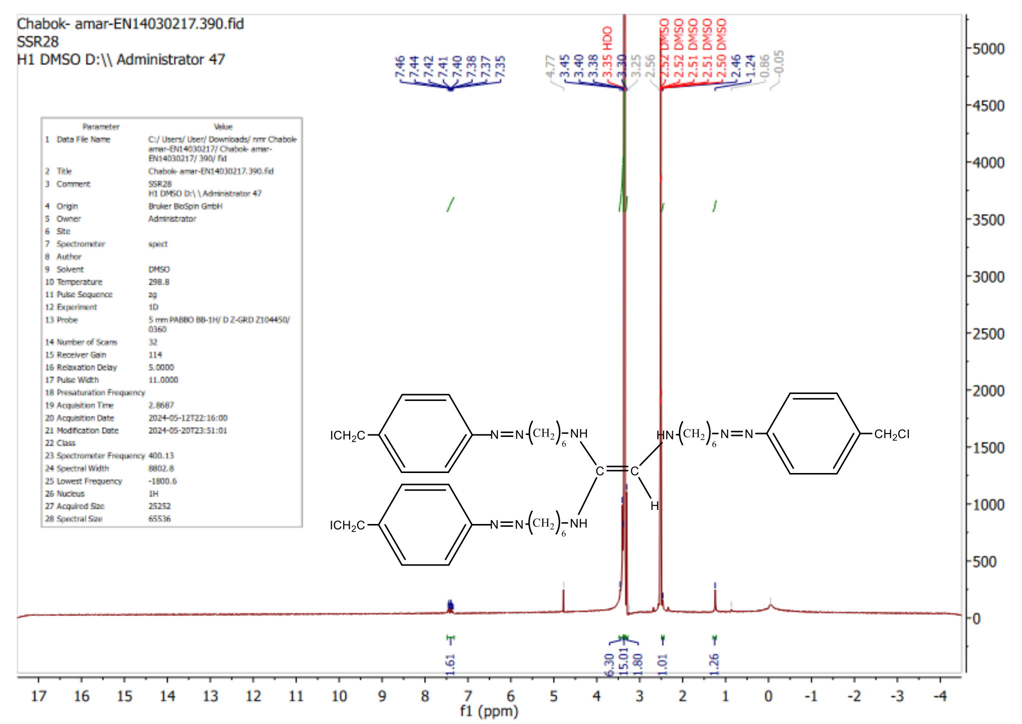


Figure (16) FTIR Spectrum of Trichloroethylene with AZO (1)

Figure (16) displays the FTIR spectrum of **M(1)**. It displays absorption bands at 3062 cm^{-1} to –NH stretching, 2958 cm^{-1} to C-H, 1265 cm^{-1} to C-N, 1452 cm^{-1} to CH2, 1492

cm^{-1} to N=N, 1539 cm^{-1} to C=C (aromatic), as well as 3030 cm^{-1} to C-H (aromatic). [13-15].

^{1}HNMR spectrum of Trichloroethylene with AZO(1)



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25	Lowest Frequency	-1800.6
26	Nucleus	1H
27	Acquired Size	25252
28	Spectral Size	65536

Figure (17)^{1}HNMR spectrum of Trichloroethylene with AZO(1)

Figure (17) shows the ^{1}HNMR spectrum of M (1). The primary signal at δ 1.5-2.1 ppm is indicative of DMSO-d6 as the solvent; singlate to CH2 at ˊ 2.5 ppm, singlate to C-H at 1.4 ppm, multiplet singlate to (4H, phenyl ring) at 7.4 ppm, as well as a singlet to (2H, NH) at 3.5 ppm. [13-15].

^{13}C-NMR spectrum of Trichloroethylene with AZO(1)

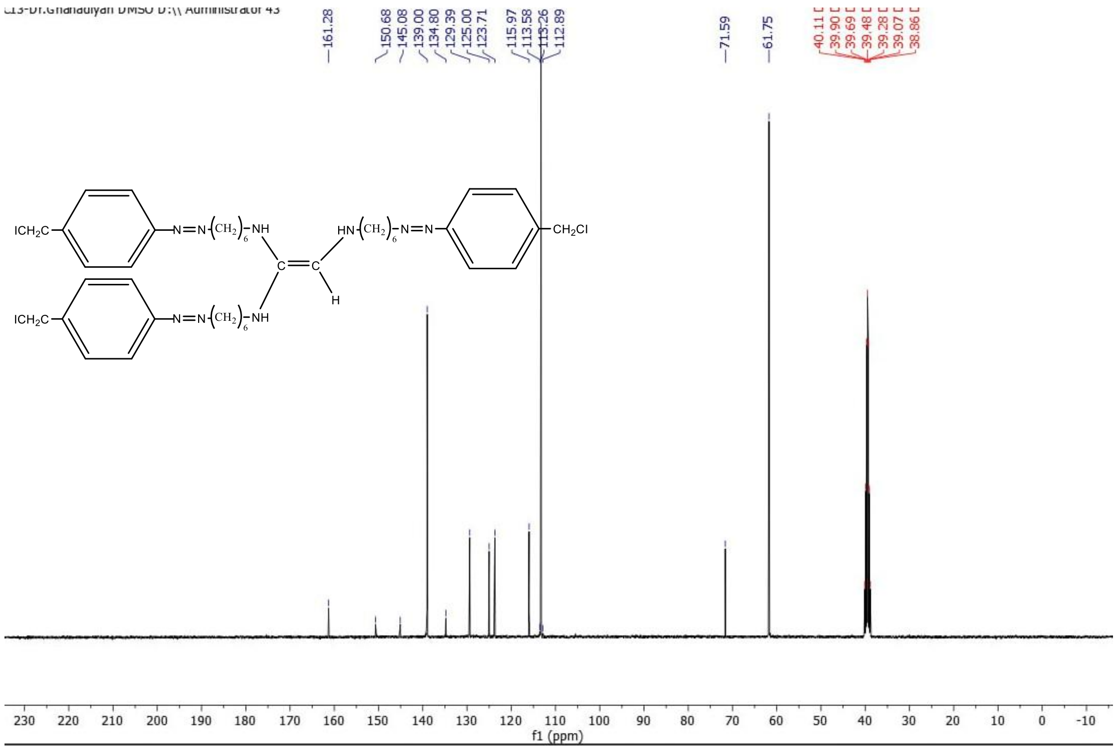
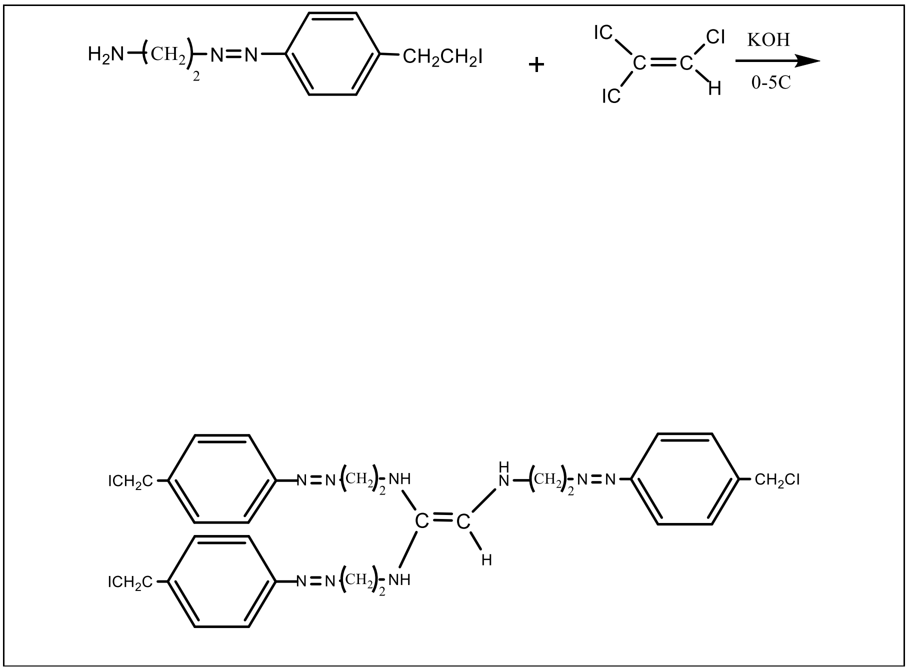


Figure (18) ^{13}C-NMR spectrum of Trichloroethylene with AZO(1)

M (1) 13C NMR of Figure (18) displays the third zone between 115 and 128 ppm shows the signals of olefinic and aromatic carbons, with one associated with C-N at 62 ppm and one associated with C=C at 133 ppm. [13-15].

Synthesis of monomer 2 M(2)

The synthesis of M(2) is done through reaction of diazocoupling reaction of **Trichloroethylene with AZO (2**) as shown in Scheme (5).



Scheme (5) Synthesis of M(2)

FTIR Spectrum of Trichloroethylene with AZO (2)

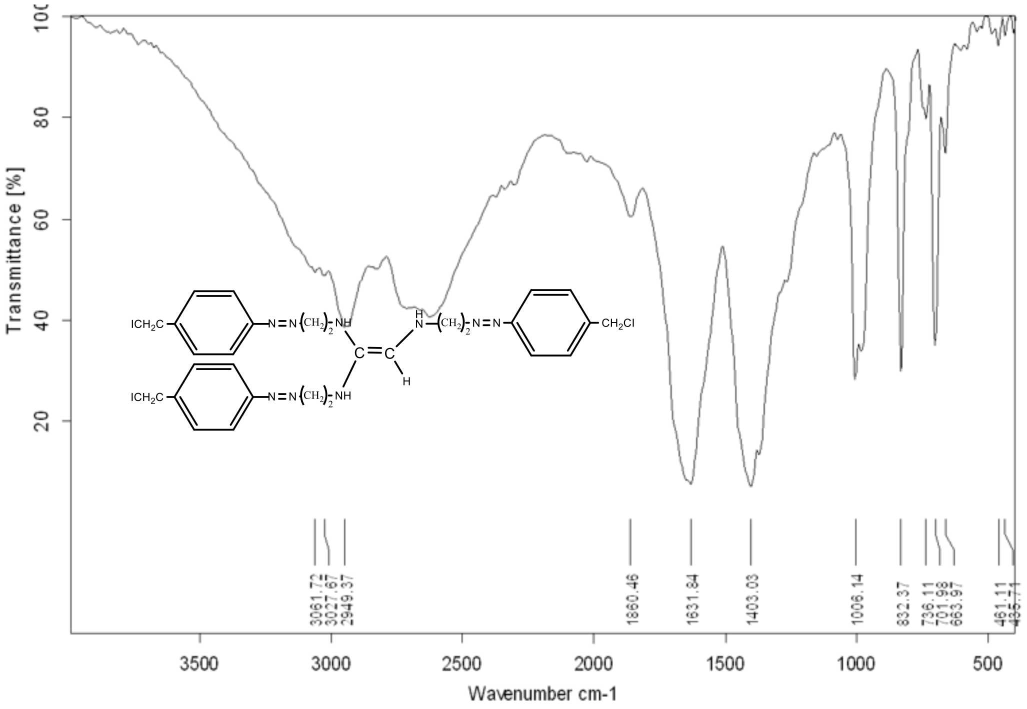
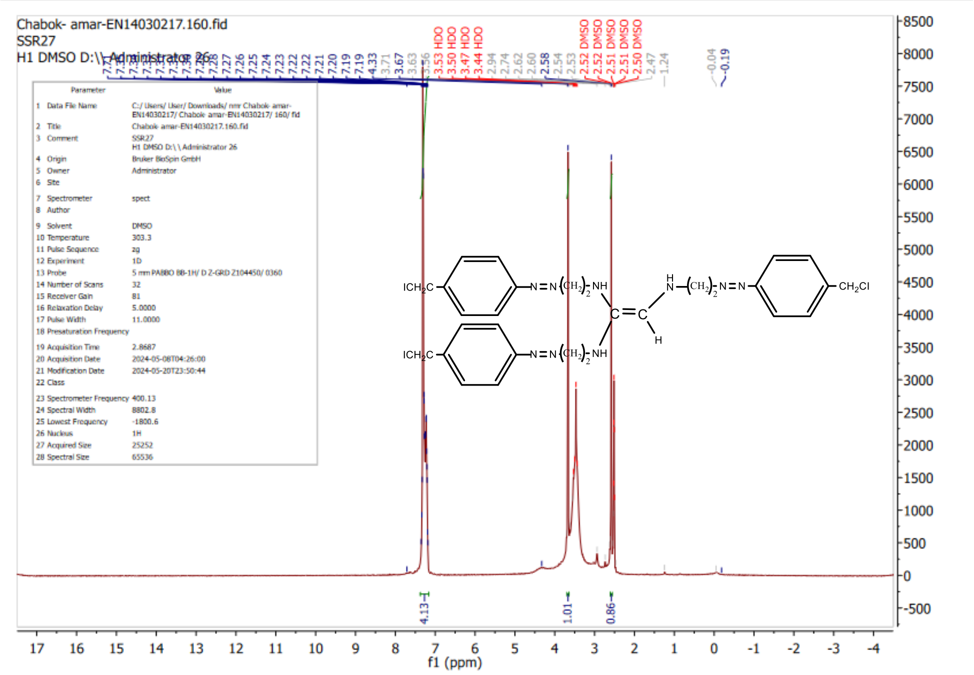


Figure (19) FTIR Spectrum of Trichloroethylene with AZO(2)

Figure (19) displays the FTIR spectrum of M (2). It displays absorption bands at 3283 cm^{-1} to –NH stretching, 2949 cm^{-1} to C-H, 1238 cm^{-1} to C-N, 1492 cm^{-1} to CH2, 1403 cm^{-1} to N=N, and 1631 cm^{-1} to C=C (aromatic). At 3027 cm^{-1}, the C-H aromatic stretching frequency was detected [13-15].

^{1}HNMR spectrum of Trichloroethylene with AZO (2)



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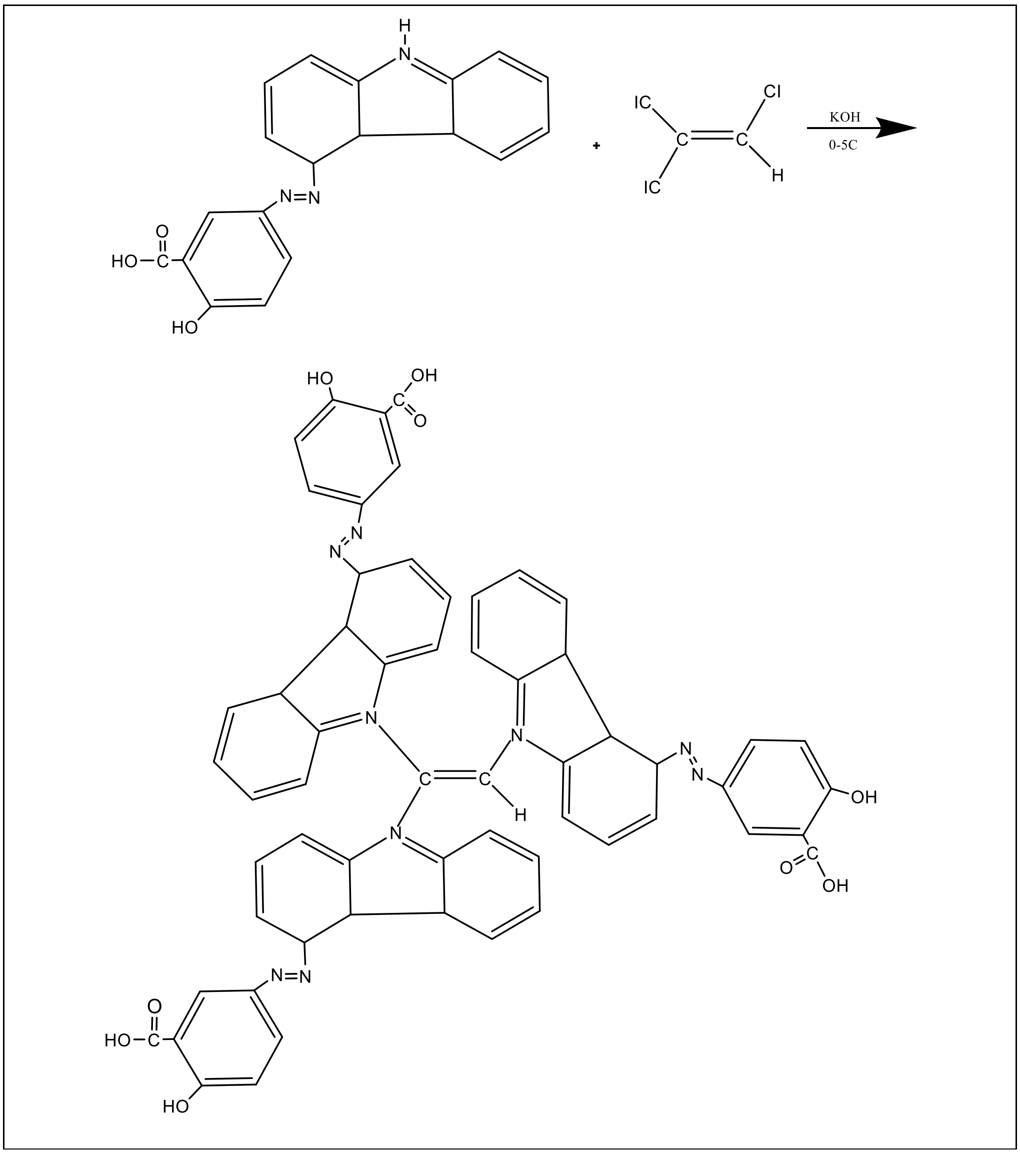
26	Nucleus	1H
27	Acquired Size	25252
28	Spectral Size	65536

Figure (20)^{1}HNMR spectrum of Trichloroethylene with AZO (2)

Figure (20) shows the ^{1}HNMR spectrum of M (2). With a singlet at (2.5 δ ppm) to C-H, multiplet singlate at (7.5 δ ppm) to (4H, phenyl ring), a singlet at (3.5 δ ppm) to (2H, NH2), and a singlet at (1.2 δ ppm) to CH2, the main signal at δ 1.5-2.1 ppm is typical of DMSO-d6 as solvent. [13-15]

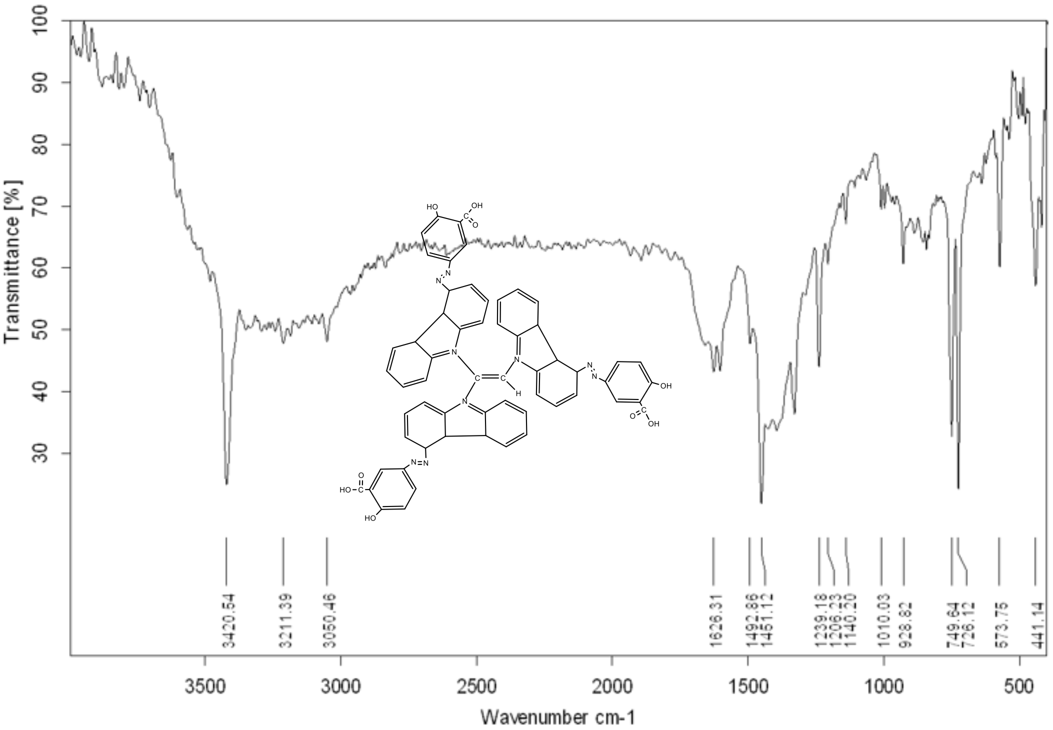
Synthesis of monomer 3 M(3)

The synthesis of M(3) is done through reaction of diazocoupling reaction of **Trichloroethylene with AZO (3)** as shown in Scheme (6).



Scheme (6) Synthesis of M(3)

FTIR Spectrum of Trichloroethylene with AZO (3)



Figure(21)FTIR Spectrum of Trichloroethylene with AZO (3)

Figure (21) shows the FTIR spectrum of M (3) . It displays a sharp absorption band at 3420 cm^{-1} to –OH stretching, a band at 1239 cm^{-1} to C-N, a band at 1492 cm^{-1} to N=N, a band at 1591 cm^{-1} to C=C (aromatic), as well as a band at 1662 cm^{-1} to C=O (carboxylic group). The FTIR spectra revealed the secondary amine N-H stretching frequency for carbazole at 3211cm-1, while the C-H aromatic stretching occurrence is recorded at 3050cm^{-1}. [13-15]

^{1}HNMR spectrum of Trichloroethylene with AZO(3)

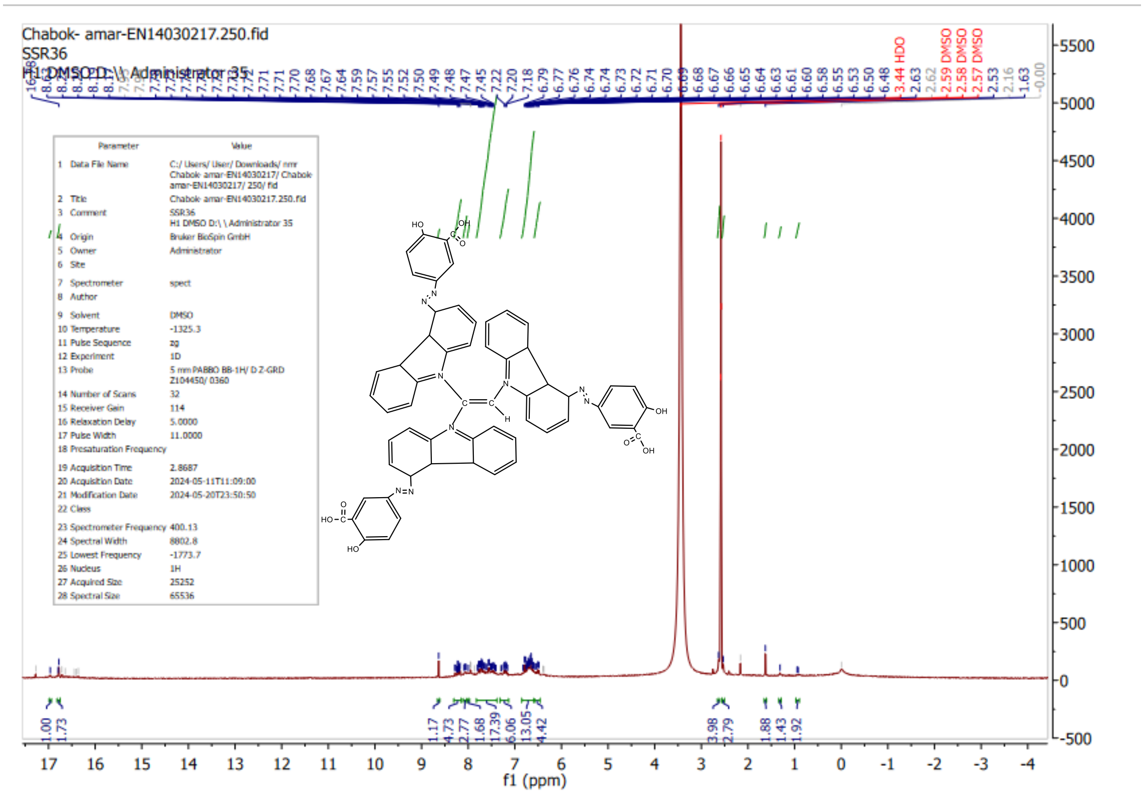


Figure (22) ^{1}HNMR spectrum of Trichloroethylene with AZO (3)

Figure (22) shows the ^{1}HNMR spectrum of M (3) . A singlet at 3.5 δ ppm to (1H, NH), a singlet at 6.2 δ ppm to (1H, OH), a singlet at 8.7 δ ppm to (1H, COOH), a multiplet singlate at 6.7-7.5 δ ppm to (11H, phenyl rings), as well as a singlet at 8.2 δ ppm to proton (Heteroaromatic) are the main signal at δ 1.5-2.1 ppm.[13-15]

^{13}C NMR spectrum of Trichloroethylene with AZO (3)

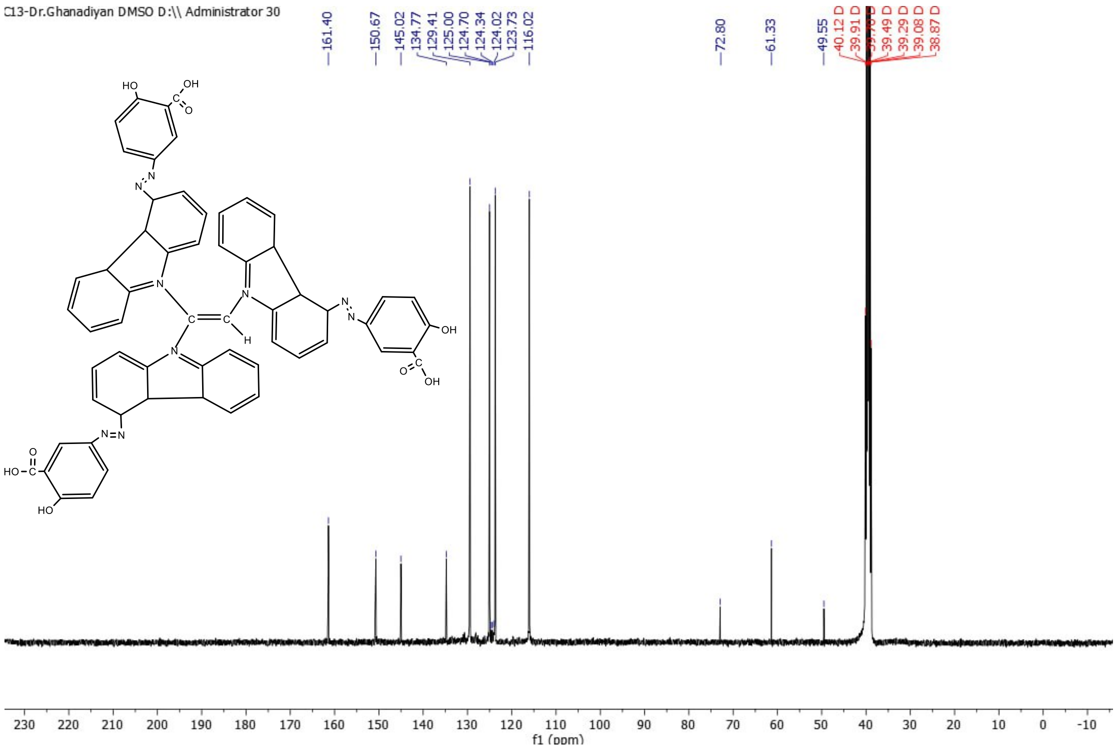
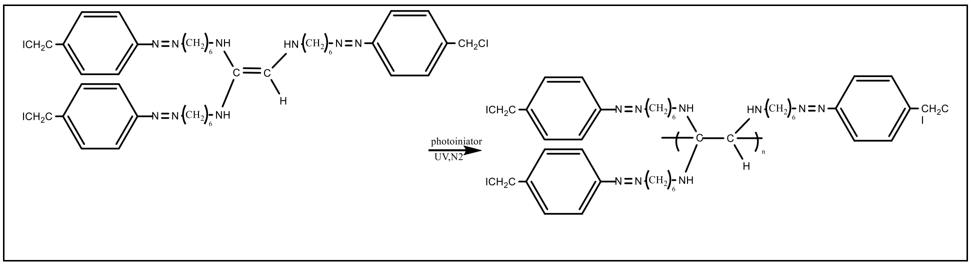


Figure (23) ^{13}C NMR spectrum of Trichloroethylene with AZO (3)

Figure 23's 13C NMR of M (3) . reveals several signals dispersed across a broad spectrum of chemical shifts. The olefinic and aromatic carbon signals are found in the third region between 120 and 129 ppm, with a solitary signal associated with C-N at 62 ppm, single associated with C=O (carboxylic) at 175, single associated with C=C (alkene) at 133 ppm, and single associated with C-O at 86 ppm. [13-15].

Synthesis of AZO polymer (1)

free-radical photopolymerization using 1-hydroxy cyclohexyl phenol ketone as the initiator in presence of nitrogen. Azo benzene monomer (M1) was polymerized as shown in Scheme (7)



Scheme (7) Synthesis of AZO Polymer (1)

FTIR Spectrum of AZO polymer (1)

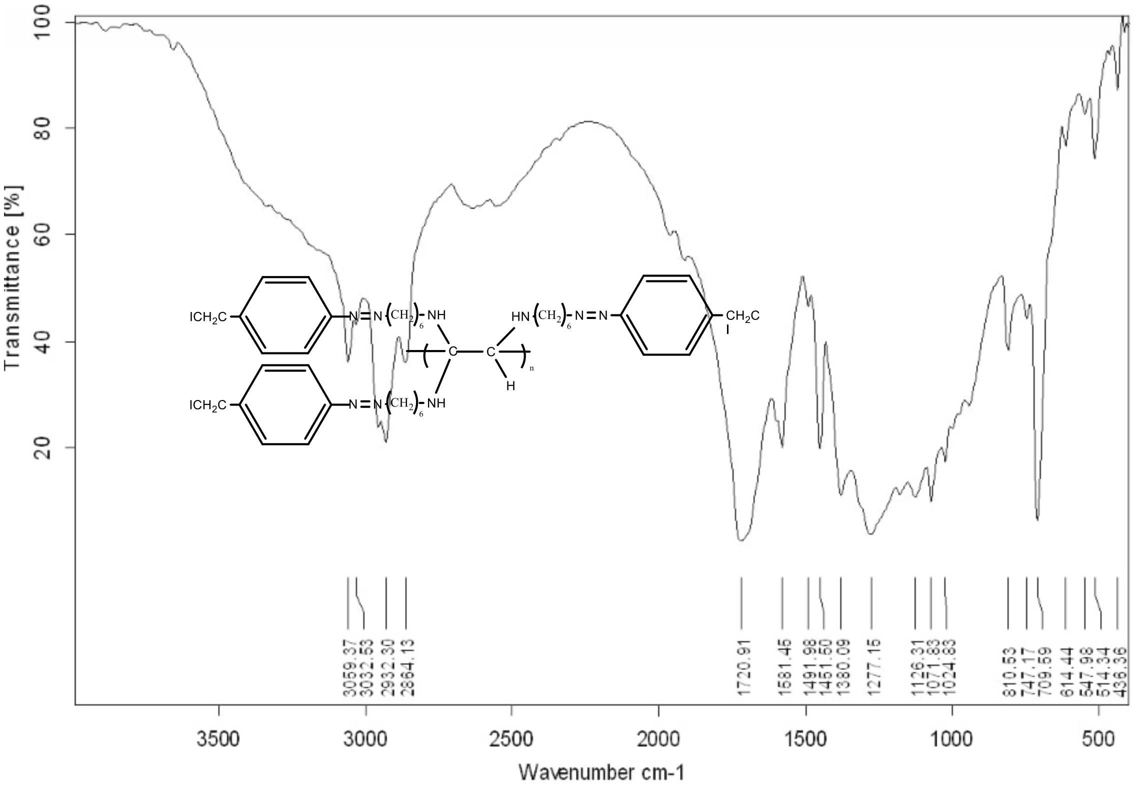


Figure (24) FTIR Spectrum of **AZO Polymer(1)**

Figure (24), which displays the FTIR spectrum of AZO Polymer (1), shows absorption bands at 3059 cm^{-1} to –NH stretching, 2932 cm^{-1} to C-H, 1277 cm^{-1} to C-

N, 1451 cm^{-1} to CH2, 1491 cm-1 to N=N, 1581 cm^{-1} to C=C (aromatic), as well as 3032 to C-H (aromatic). [13-15].

^{1}HNMR Spectrum of AZO polymer (1)

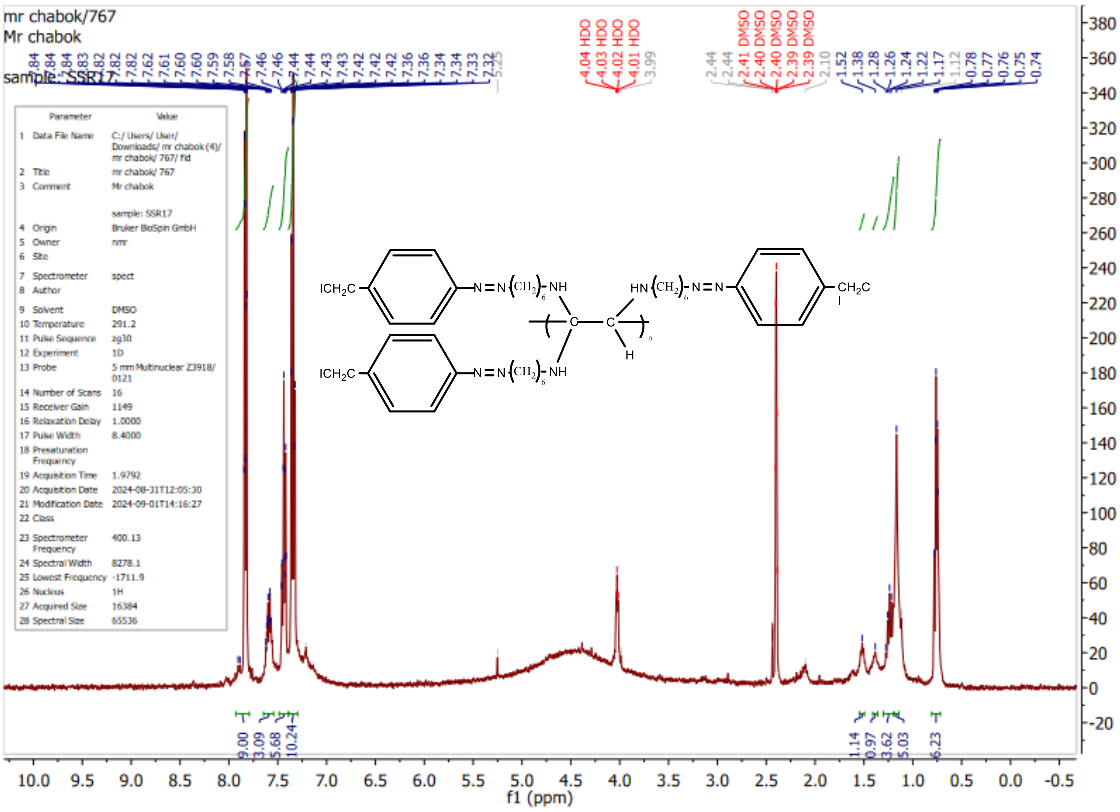
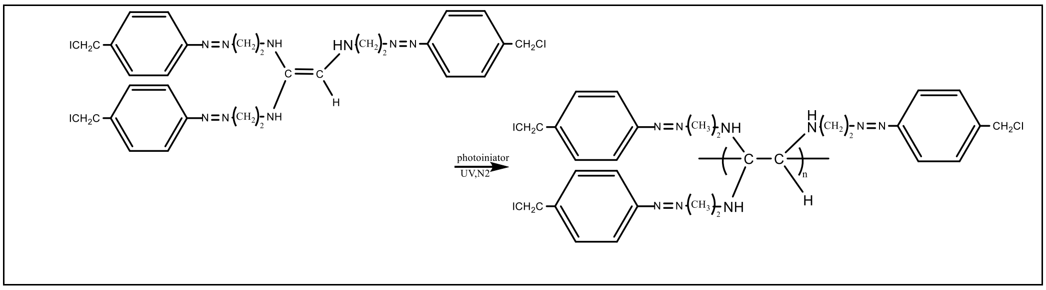


Figure (25) ^{1}HNMR spectrum of AZO Polymer (1)

AZO Polymer (1) ^{1}HNMR spectrum in Figure (25) DMSO-d6 is the solvent that exhibits the main signal at δ 1.5-2.1 ppm, singlet to CH2 at 2.4 δ ppm, singlet to C-H at 1.4 δ ppm, multiplet singlate to (4H, phenyl ring) at 7.5 δ ppm, and a singlet to (2H, NH) at 4.0 δ ppm. [13-15].

Synthesis of AZO polymer (2)

free-radical photopolymerization using 1-hydroxy cyclohexyl phenol ketone as the initiator in presence of nitrogen. Azo benzene monomer (M2) was polymerized as shown in Scheme (8)



Scheme (8) Synthesis of AZO Polymer (2)

FTIR Spectrum of AZO Polymer (2)

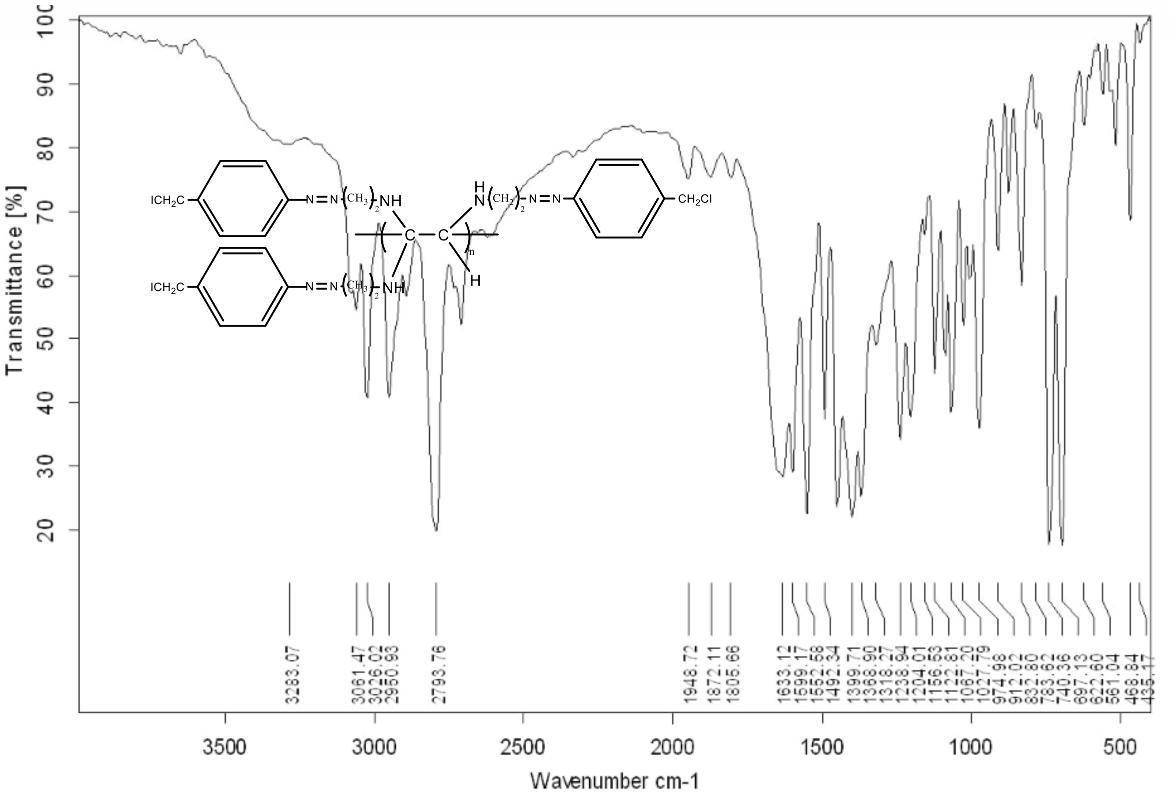
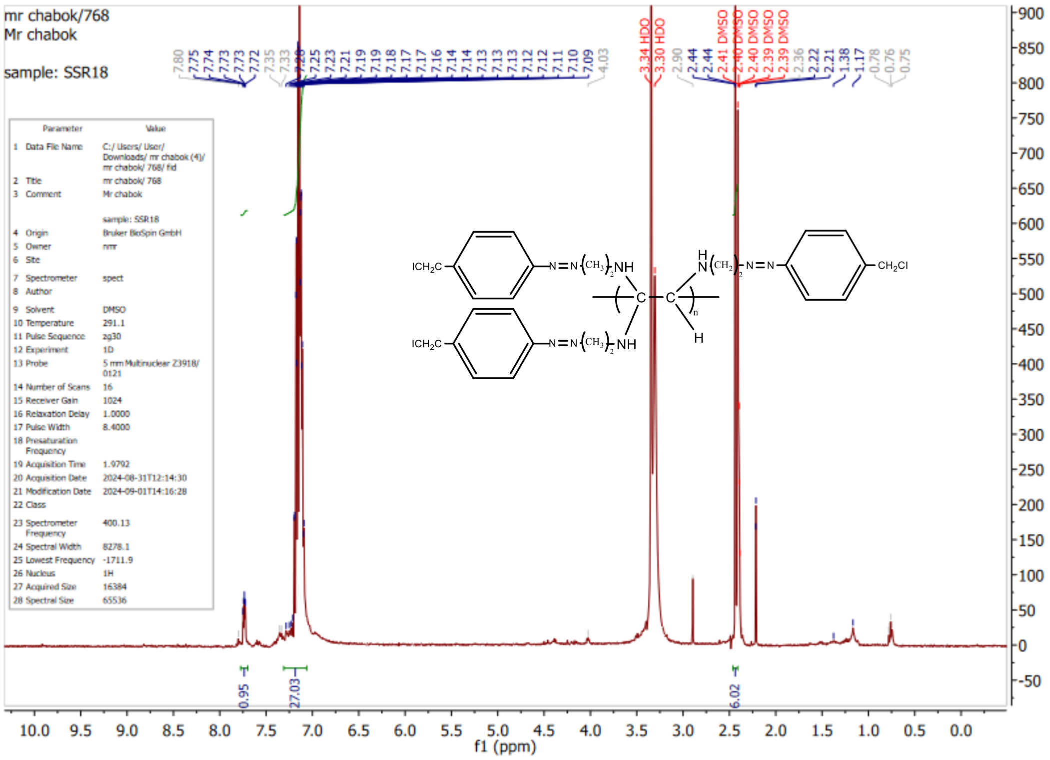


Figure (26) FTIR Spectrum of AZO polymer (2)

Figure (26), which displays the FTIR spectrum of **AZO Polymer (2)**, displays absorption bands at 3283 cm^{-1} to –NH stretching, 2950 cm^{-1} to C-H, 1238 cm^{-1} to C-

N, 1492 cm^{-1} to CH2, 1552 cm^{-1} to N=N, as well as 1599 cm^{-1} to C=C (aromatic). At 3026 cm^{-1}, the C-H aromatic stretching occurrence was detected. [13-15].

^{1}HNMR spectrum of AZO Polymer (2)



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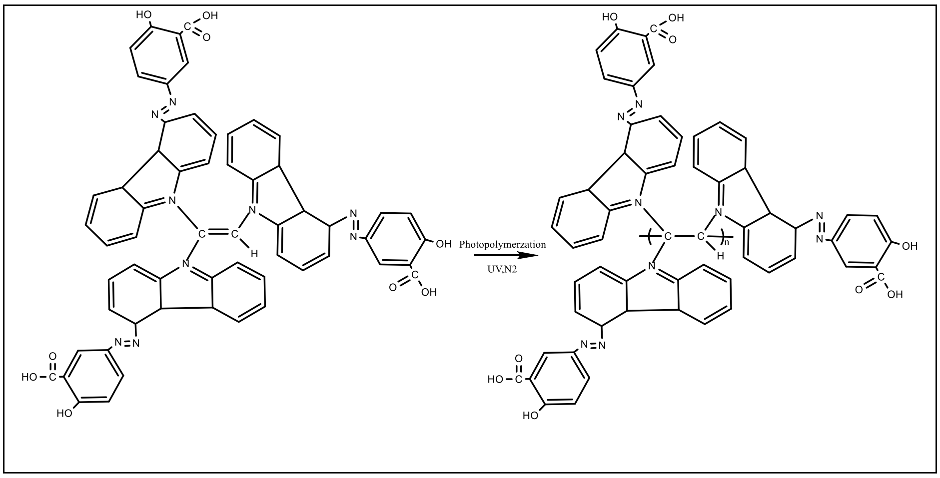
25	Lowest Frequency	-1711.9
26	Nucleus	1H
27	Acquired Size	16384
28	Spectral Size	65536

Figure (27) ^{1}HNMR spectrum of AZO Polymer (2)

Figure (27) shows the 1HNMR spectra of **AZO Polymer (2)**. A singlet at 2.4 δ ppm to CH2, a multiplet singlate at 7.5 δ ppm to (4H, phenyl ring), a singlet at 4.0 δ ppm to (2H, NH2), and a singlet at 1.2 δ ppm to C-H are the main signals at δ 1.5-2.1 ppm that are typical of DMSO-d6 as the solvent. [13-15]

Synthesis of AZO polymer (3)

free-radical photopolymerization using 1-hydroxy cyclohexyl phenol ketone as the initiator in presence of nitrogen. Azo benzene monomer (M2) was polymerized as shown in Scheme (9)



Scheme (9) Synthesis of AZO (3)

FTIR Spectrum of AZO polymer (3)

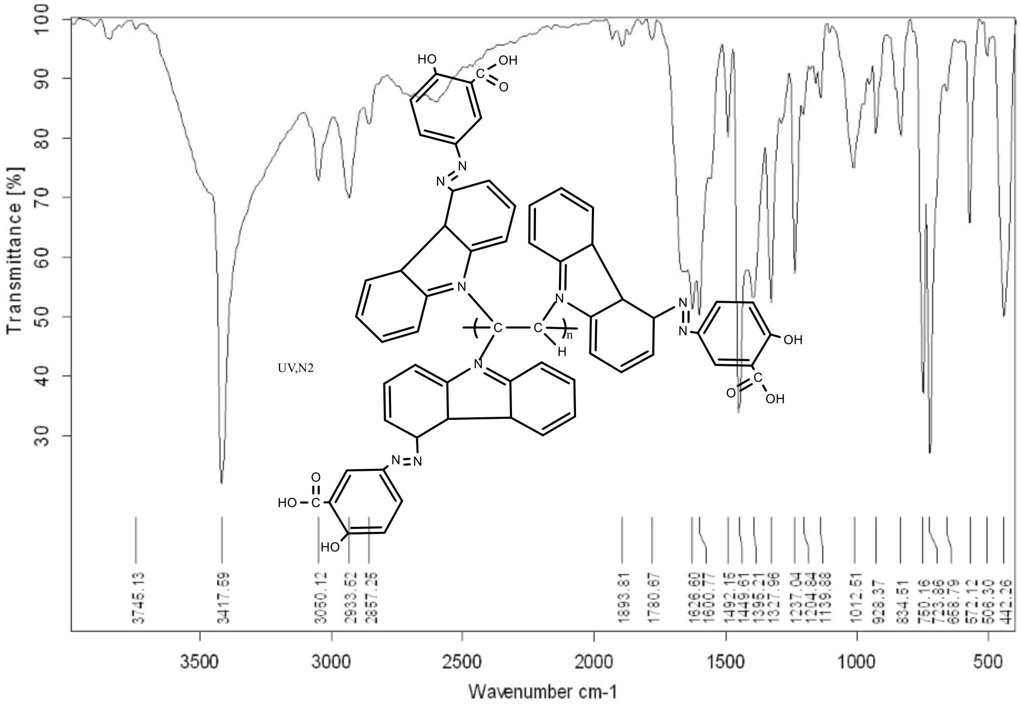
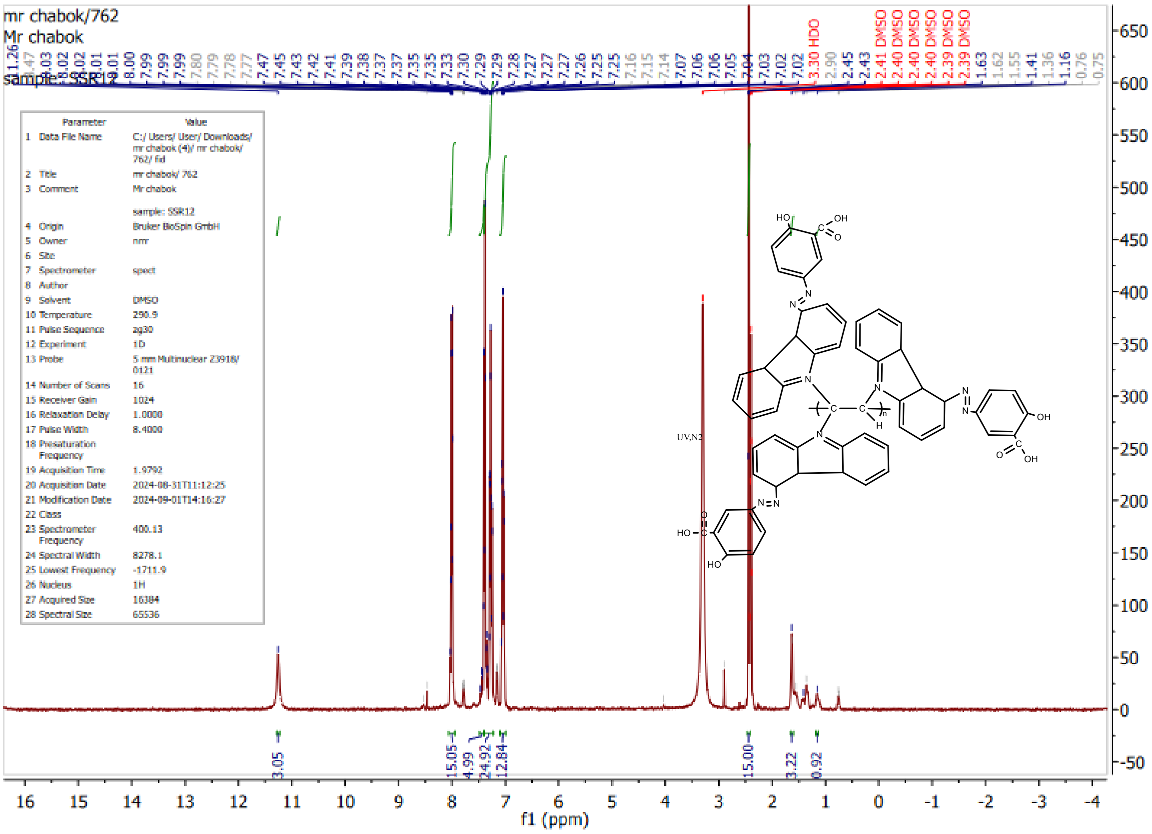


Figure (28) FTIR Spectrum of AZO polymer (3)

Figure (28) displays the FTIR spectrum of the **AZO Polymer (3)**, which displays a severe absorption band at 3416 cm^{-1} to –OH stretching, a band at 1367 cm^{-1} to C-N, a band at 1482 cm^{-1} to N=N, a band at 1591 cm^{-1} to C=C (aromatic), as well as a band at 1707 cm^{-1} to C=O (carboxylic group). The FTIR spectra revealed the secondary amine N-H stretching frequency for carbazole at 3077 cm^{-1}, while the C-H aromatic stretching occurrence was recorded at 3047 cm^{-1}.[13-15].

^{1}HNMR spectrum of AZO Polymer (3)



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8	Author	
9	Solvent	DMSO
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11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm Multinuclear Z3918/ 0121
14	Number of Scans	16
15	Receiver Gain	1024
16	Relaxation Delay	1.0000
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24	Spectral Width	8278.1
25	Lowest Frequency	-1711.9
26	Nucleus	1H
27	Acquired Size	16384
28	Spectral Size	65536

Figure (29) ^{1}HNMR spectrum of AZO Polymer (3)

The **AZO Polymer (3)** ^{1}HNMR spectrum is shown in Figure (29) A singlet at 3.4 δ ppm to (1H, NH), a singlet at 4.0 δ ppm to (1H, OH), a singlet at 8.7 δ ppm to (1H, COOH), a multiplet singlate at (6.7-7.4 δ ppm) to (11H, phenyl rings), as well as a singlet at (8.2 δ ppm) to proton (Heteroaromatic) are the main signal at δ 1.5-2.1 ppm.[13-15].

Thermo gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted in a nitrogen environment at a heating rate of 10ºC/min to investigate the thermal properties of the AZO polymers. At T = (80 °C), tiny volatile molecules lead the first peak, followed by unreacted monomers. At T = 300 °C, the azo polymers rapidly degrade due to the second peak. Certain azopolymers with at least one β-hydrogen have been demonstrated to undergo a cyclic intermolecular transition state, which results in the breakdown of both acid and olefin end groups. This TGA figure illustrates how azopolymers break down in nitrogen at a rate of 10ºC per minute. The breakdown releases carbon dioxide, carbon monoxide, and water in three mass-loss phases. In addition to providing the decomposition rate, the TGA curve aids in the precise evaluation of the mass-loss processes. The creation of char at 400ºC and the outcomes like Ti, Top, Tf, T50%, and T Residue at 600ºC are exemplified in Table (7). A typical index for the thermal stabilization of azopolymers is 600ºC, at which a 50% loss in weight (azopolymers) occurs. A classic indicator of azopolymer thermal stability, the 50% weight loss temperature, was all above 600°C, indicating excellent azopolymer thermal stability. The more aromatic rings there were in the azopolymers, the more stable they became For dendrimers, the char yields of these azopolymers at 400°C ranged from % to % in nitrogen. All of the azopolymers produced greater than a percentage of char yields at 600°C in a nitrogen atmosphere, suggesting that they could be used as special materials for curing agents, fire retardants, and fiber reinforcements that require high temperature resistance. At 600°C, however, azopolymer 1 and azopolymer 6 had the largest weight residues of any azopolymers in this sequence, at 75% and 79%, respectively. The first weight monomer was determined to have both rates through TGA testing. At high temperatures, an exothermic behaviour was then noted. Table (7) summarizes the findings. These findings showed that the dendrimers with the highest thermal stability were those that included a phenyl group as a substituent in the pyridine ring. It appears that adding a larger substituent to the diamine monomers' pyridine ring at position 4 improves the resulting azopolymers' solubility and heat stability. The disintegration of dendrimers enables us to comprehend the material's thermal stability and guides the development of improved, new structures with higher thermal resistance. It was suggested that azopolymer heat breakdown happens in stages. Benzene, phenol derivatives, and aniline are examples of aromatic chemicals that are created during the initial stage of degradation. Carbonization comes after the second stage, which involves low-molecular molecules such aliphatic amines, carbon dioxide, and hydrocarbons. Additionally, its spontaneous splitting with chain end split in thermal degeneration for azopolymers and its immediate one-step radical transition raised by temperature indicate that β splitting occurs on a chain end prior to radical transition because the β split rate increases with temperature. The aliphatic chain in this azopolymer scenario, where at least two carbon atoms are nearest, indicates that the chance of spontaneous scission is extremely low. The hydroxyl and carboxylic end groups of azopolymers began to disintegrate first, followed by a dramatic drop in molecular weight due to water, was also observed in the comparable aliphatic polymer as azopolymers at these temperatures.

Table (7) Certain Thermal Stability Characteristics Curves Thermal Gravimetric Analysis (TGA) of azopolymers signifies the temperature of decomposition.

Azo polymers	T_i C°	T_{op1} C°	T_f C°	$T_{50\%}$ C°	Residue at °C600	Char % At 400°C
Azopolymer 1	110	230	500	290	85	75
Azopolymer 2	90	300	500	360	80	79
Azopolymer 3	120	220	490	240	84	79

This is the major disintegration.

DT: disintegration temperature.

Ti: Initial disintegration temperature.

Top: Optimum disintegration temperature.

Tf: Final disintegration temperature. The final degree of dissociation temperature.

T50%: Temperature of 50% weight loss, acquired by TGA .

Char% at 400 ° C.

T Residual weight ratio at 600 ° C in Argon from TGA.

Differential Scanning calorimeter analysis (DSC) study

The glass transition (Tg) value of the mix (190°C) according to the results of **azopolymer 1** showed a sharp exothermic peak curve in figure (30). This means that the temperature flowed and that the level of absorption of the sample increased till it reached the melting point (Tm) at 530°C. The sample was then completely dissolved, and the level of absorption to the heat was then set through the curve to determine the degree of crystallization (Tc) of the mixture (405°C).

The outcomes of **azopolymer 1** The curve in the figure illustrates the value of the glass transition temperature (Tg) of the mixture, which is 205°C, indicated by a pronounced exothermic peak. (31). This indicates an increase in the temperature flow, followed by the rate of sample absorption to temperature until it reaches the melting point (Tm) at (529°C), then finally the rate of sample absorption to heat according to the curve of the mixture's formation of (Tc) (260°C).

The outcomes of **azopolymer 3** showed A sharp exothermic peak curve in figure (32) represents the glass transition (Tg) value of the mix (230°C), which indicates a rise in temperature flow. After that, the sample's level of absorption to temperature increases till it reaches the melting point (Tm) at 510°C, followed by the sample's rate of absorption to heat and the mixture's formation curve (Tc) at 260°C.

Table (8): Shows the Thermal parameter obtained from DSc.

Azo polymers	Tc (c°)	Tm (c°)	Tg(c°)
Azo polymers 1	405	530	190
Azo polymers 2	240	529	205
Azo polymers 3	260	510	230

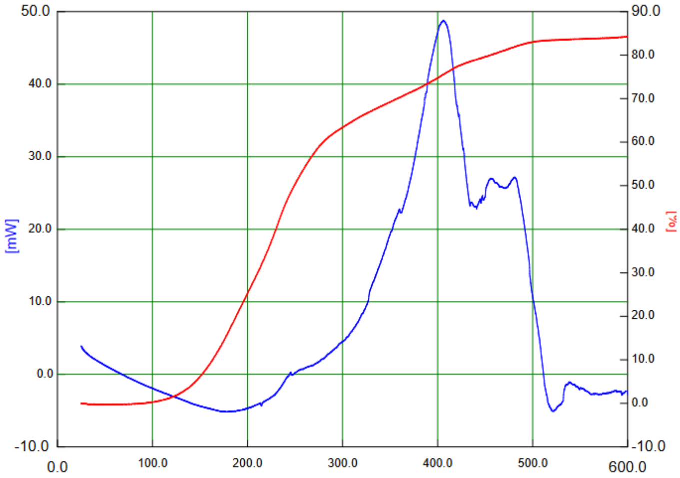

Figure (30) TGA and DSC curve of AZO polymer (1)

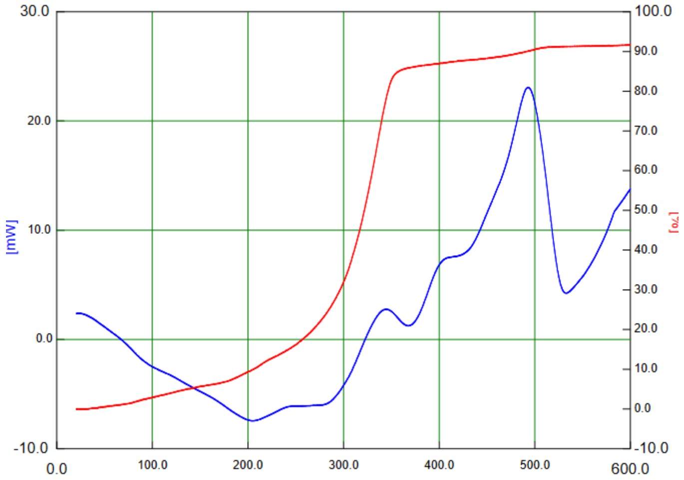

Figure (31) TGA and DSC curve of AZO polymer (2)

Figure (32) TGA and DSC curve of AZO polymer (3)

Conclusions

The compounds' thermal behaviours were investigated using thermal analysis (TGA and DSC). The polymer thermal analysis investigations showed a three-stage mass loss that was generally comparable to the margins for all polymers. It was confirmed that a polymerization reaction occurred when the double bond peak in the FTIR spectrum vanished and the carbonyl group shifted to longer wavelengths of absorption due to the removal conjugation caused by the opening of the double bond on the trichloroethylene group. Moreover, ^{1}HNMR and ^{13}CNMR investigations corroborated this. The peaks in these spectrums do not correspond to C=C groups. Thus, in terms of producing greater molecular mass polymers, polymerization occurring faster, and synthesizing a smaller range of molecular weights, the photopolymerization process can be considered more efficient than the thermal polymerization mechanism. In this investigation, FTIR, ^{1}HNMR, and ^{13}CNMR spectroscopies were used to determine the structures of synthetic polymers made by free-radical photopolymerization, as well as some azobenzene-polymers containing trichloroethylene and their derivatives. Due to their strong aromatic structure, these samples cannot be isotropized because the degradation processes begin beforehand. Because these polymers have two azo groups in each mesogen unit, strong conformational changes are anticipated when exposed to UV light.

References

[1].*k* ABerlin, B.I.Liogonsl$, and V.P.Perini, *Vysokornol. Soedin,* 2 *(1* 96 1) 689.

[2] A,Ravee *and* C.Fitko, *J.Polym.Sci.,* (.A), *2* (1964) *1925.*

[3] V.P.Perini and I. V.Gudvilovich, *I n . Acad. Nauk SSSR, Ser. khim.,* 370 (1965) *1965.*

[4] A. A.Berlin, *G. G.* Belova and 1. V. Gudvilovich, *Vysokurnol. Soedin, Ser. A 9*(1967) 2214.

[5] F. Agolini and *F.P. Gay, Mucrornolecules, 3 (1 970)* 349.

[6]G. S.Kumar, P.Depra and D, C.Neckers, Macromolecules, 17 (1 984) 2463.

[7] M. Balasubramanian, M J.Nanjan and M. Santappa *Mukromol. Chrn.,* 180 *(1979) 25* 17; 182 (1981) 853; 183 (1 982) 347.

[8] G.SXumar, P.Depra, K.Zhang and D.C.Neckers, *Macromoleclrles,* 17 (1984) 1912.

[9] G.Kossmehl and R Wallis, *Makromol. Chem.,* 183 (1 982) 347.

[10] N.Blake and H. W.HiI1, Jr. (to DuPont), U. S. Pat. 2,994,693 (1961).

[11] Uznanski, P.; Kryszewski, M.; Thulstrup, E. W. Eur. Polym. J.,

1991, 27, 41.

[12] A. A.Berlin, B.I.Liogonsl$, and V.P.Perini, Vysokornol. Soedin, 2 (1961)689.

[13] Dwivedi R, Maurya A, Verma A, Prasad R and BartwalKS .2011 J. Alloys and Comps. 509 684

[14] Silverstien, R.M., Webster, F.X and Kiemle, D.J.(2005). Spectrometric identification of Organic compound 7th ed .Joun Wiley and Sons.

[15] Pretsch, E., Buhlmann, P., Baderscher, M.(2009). Structure determine of Organic compound 4th ed .springer-Verlag Berlin Heidelberg .