Results and Discussion

Synthesis, Structure Elucidation, Dyeing Performance and Measuring Antibacterial Activities for Synthesized Dyes

Part I, Part II

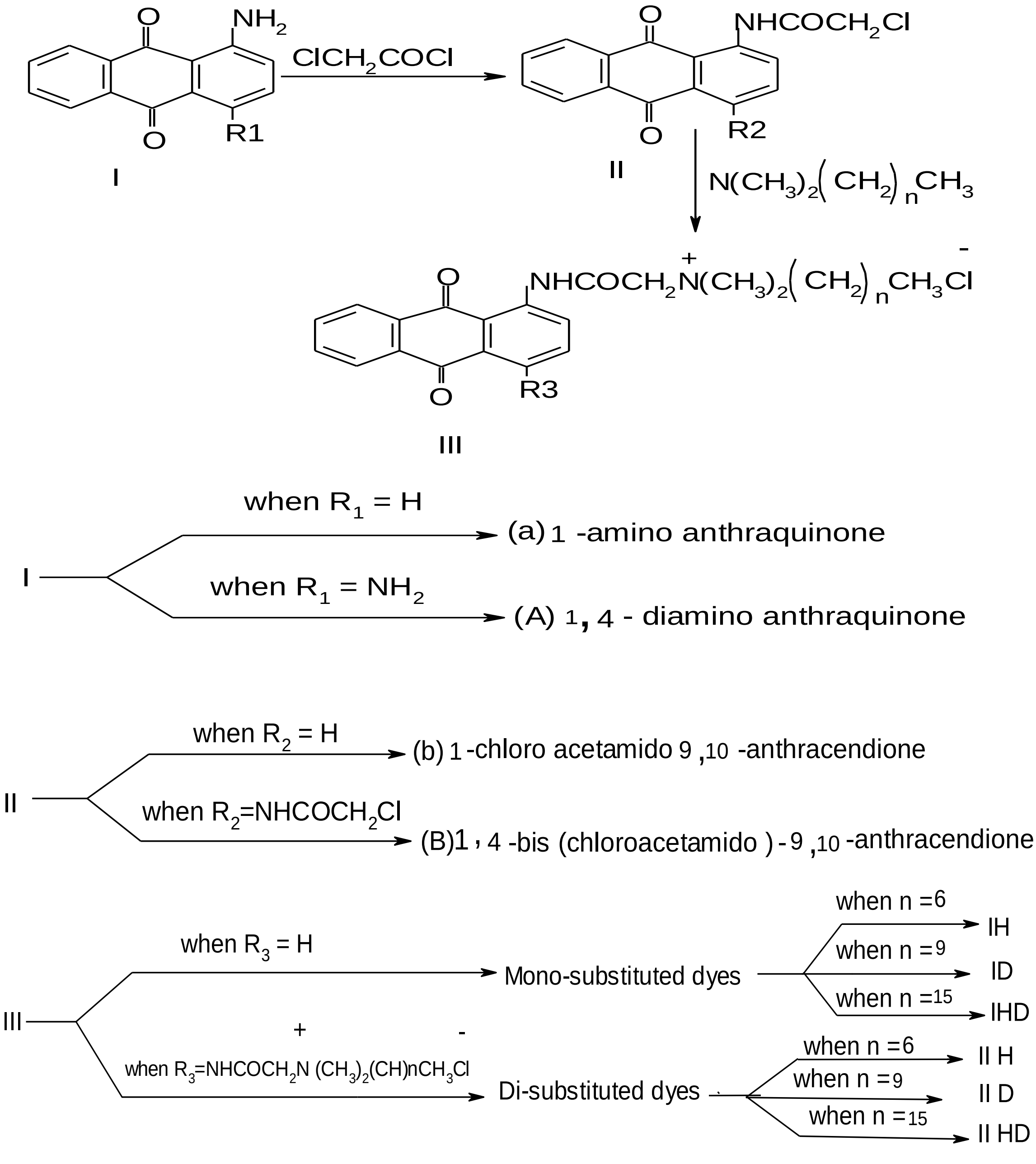
2.1 Introduction

For textile materials, dyeing and functional finishing are two important but traditional separated treatments. This separation results in several disadvantages, such as higher cost and increased waste water. As mentioned earlier, simultaneous dyeing and finishing offer economical and environmental advantages in real application. Recently, many researches have been carried out in this field.

In our study, antibacterial cationic dyes are proposed to combine dyeing and finishing together. We hope to chemically link dyes and finishes by simply following the treatment conditions of certain dyes.

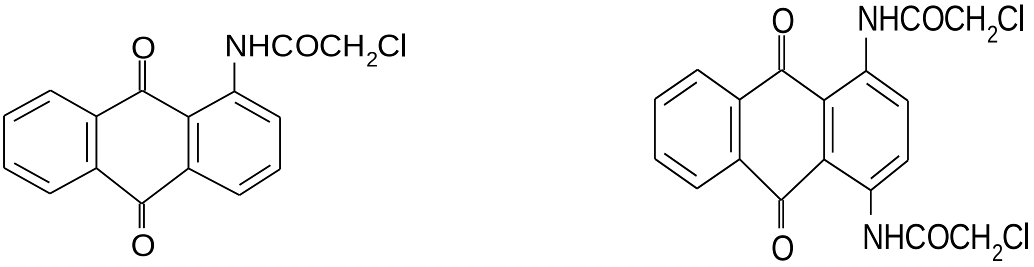
Acrylic fabrics are widely used synthetic fabrics, due to a combination of desirable properties, such as soft wool-like handle, good elasticity and mechanical properties, as well as the high resistance to outdoor exposure and many chemical compounds [94]. Extensive studies have been carried out in the cationic dyeing of acrylic fabrics .It has been well established [9,95] that three steps are involved in the acrylic dyeing : (1) the dye cations are adsorbed at the fabric surface, (2) the dye cations diffuse into the fiber, and (3) the cations occupy anionic dye sites within the fabrics . During dyeing, the major force for the fixation is the ionic interaction between the dye cations and anions present with the fabrics. In addition, the Van der Waals interactions between the dyes and the fabrics may also play an important role.

The synthesis of antibacterial cationic dyes was achieved following the routes depicted in scheme 12.



Scheme12. The synthetic procedures for cationic dyes

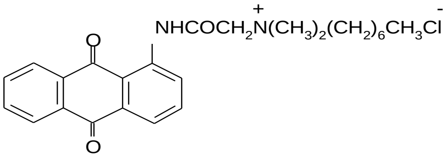
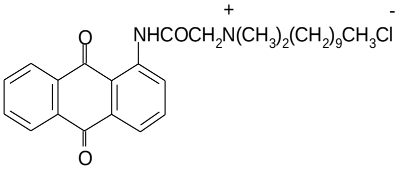
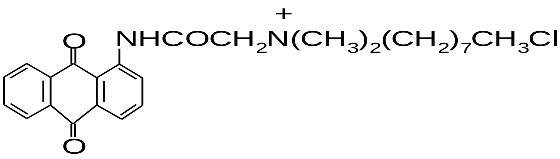
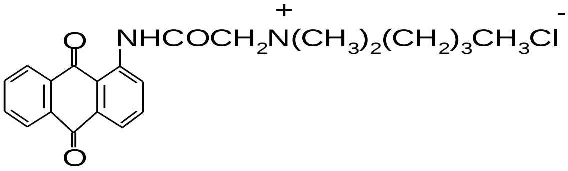
The chemical structure of 1-chloroacetamido -9,10-anthracenedione(b), 1,4-bis(chloroacetamido)-9,10-anthracenedione(B) intermediate and synthesized antibacterial cationic dyes (1-10) are given in figure (2.1) and in table (2.1).

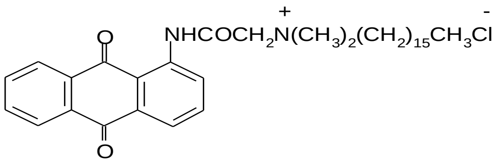
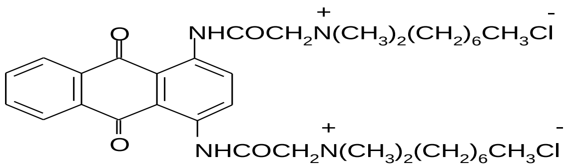
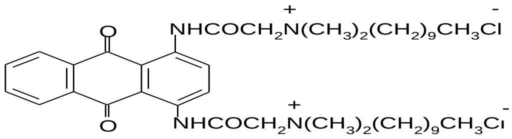
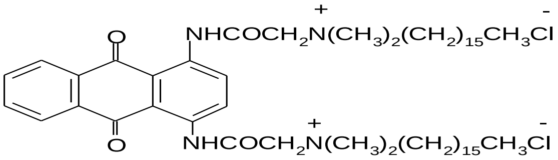
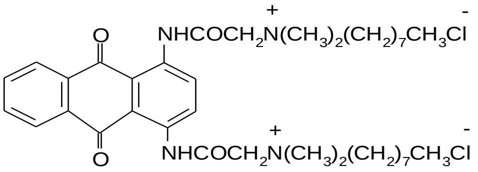
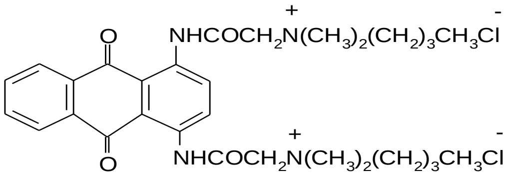


(b) **(B)**

Figure (2.1): The chemical structure of intermediate

Table (2.1): List of synthesized dyes

NO	compound	Dye structure	λmax
1	**IH**		357
2	**ID**		357
3	**IO**		353
4	**IB**		375

NO	compound	Dye structure	λmax
5	**IHD**		390
6	**IIH**		429
7	**IID**		433
8	**IIHD**		450
9	**IIO**		432
10	**IIB**		435

Part I

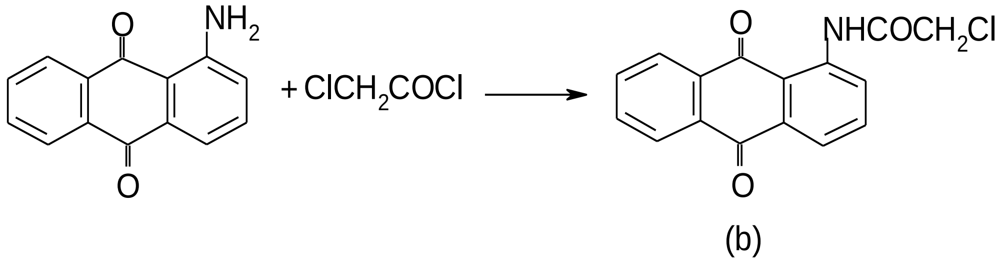
2.2. Synthesis of mono and di – substituted cationic dyes

All (antibacterial) cationic dyes (IH-IHD; (IIH-IIHD) were synthesized by reaction of anthraquinone derivatives (a) and (A) with chloroacetylchloride to give intermediate (b) and (B) with good yields. The resultant intermediate was reacted with N, N- dimethyl (butyl , heptyl , octyl, decyl, and hexadecyl) amine in DMF as solvent to give the final products with yield percentage ranging from 40 to 65 %. The purification of the prepared dyes was proceeding using ethyl ether as washing solvent. The synthetic procedures are outlined in scheme 1.

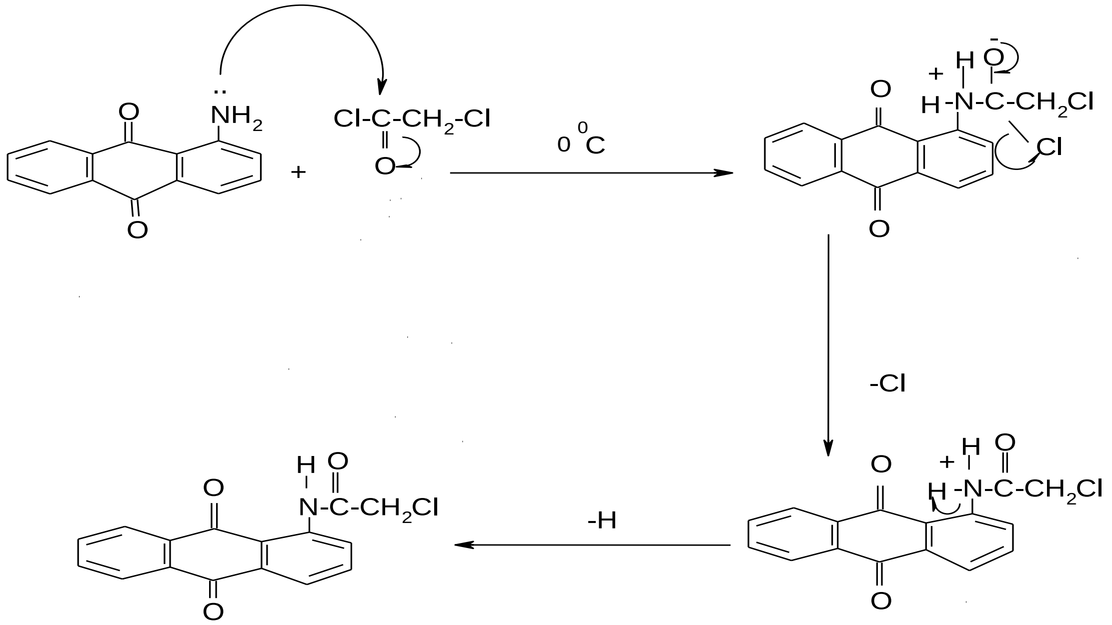
2.2.1. Synthesis of mono– substituted cationic dyes

2.2.1.1. Synthesis of 1-chloroacetamido 9, 10 –anthracenedione

When 1-aminoanthraquinone was allowed to react with chloroacetyl at 00c lead to formation of 1-chloroacetamido 9, 10 –anthracenedione (b): (Exp.section)



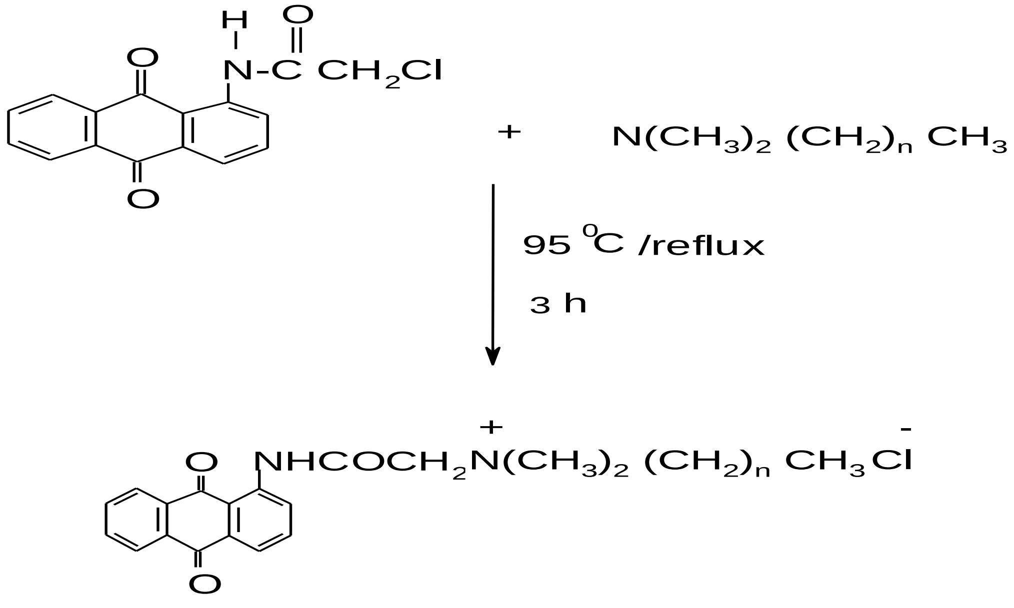
The reaction proceeds through the following mechanism:



(b)

2.2.1.2. Synthesis of mono– substituted cationic dyes

The synthesis of mono- substituted cationic dyes (IB-IHD)were completed by the reaction of (b) with N,N-dimethyl (butyl , heptyl , octyl, decyl, and hexadecyl) amine at 95 ^{0}c for 3h .(Exp.section)

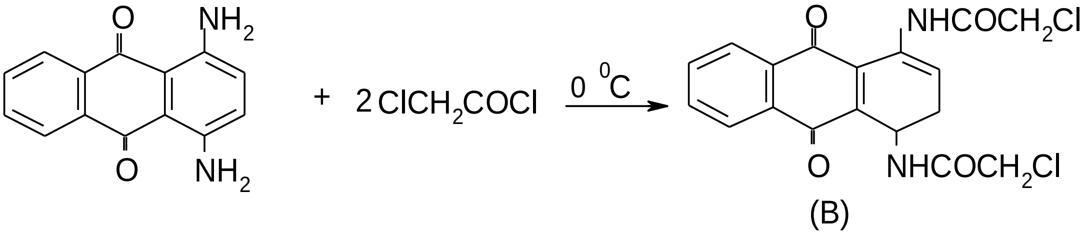


Where n = (3, 6, 7, 9, and 15)

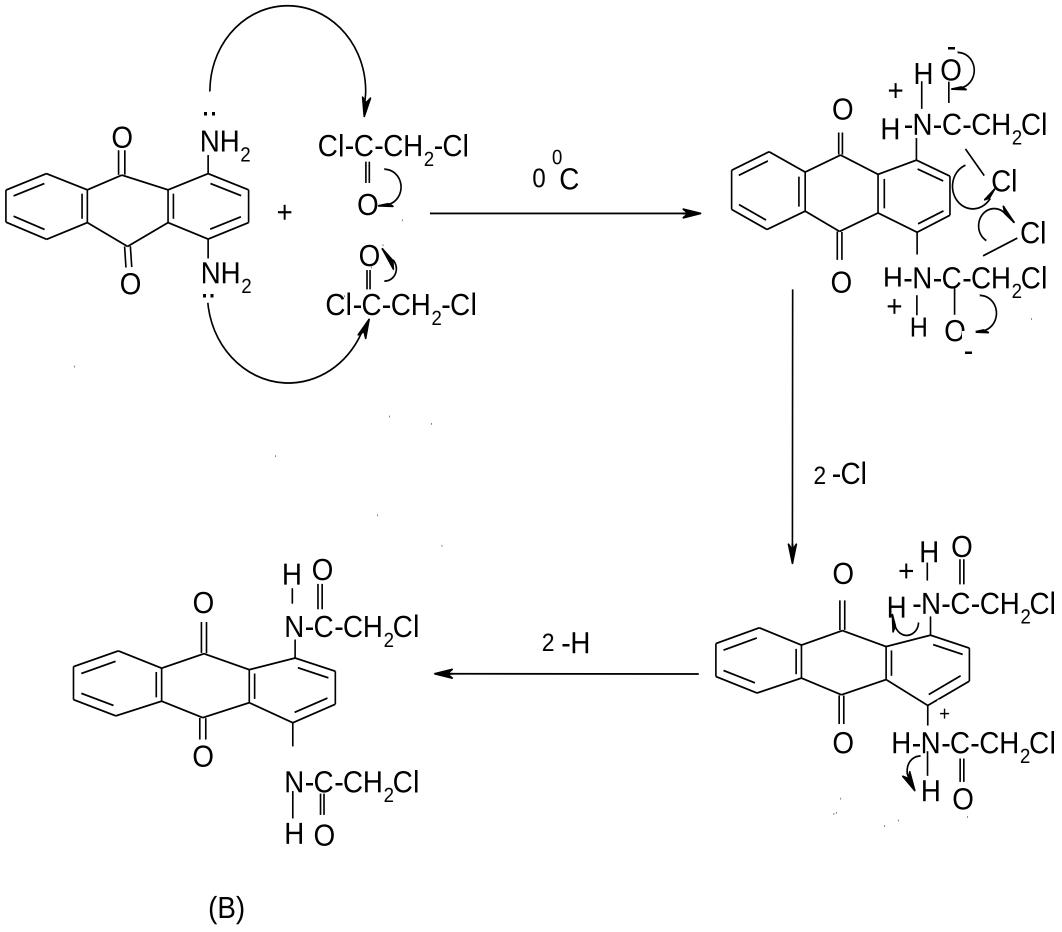
2.2.2. Synthesis of di– substituted cationic dyes

2.2.2.1. Synthesis of 1,4-bis (chloroacetamido)9, 10 –anthracenedione

When 1,4-diaminoanthraquinone was allowed to react with chloroacetyl at 0^{0}c lead to formation of 1,4-bis(chloroacetamido) 9, 10 – anthracenedione (B): (Exp.section)

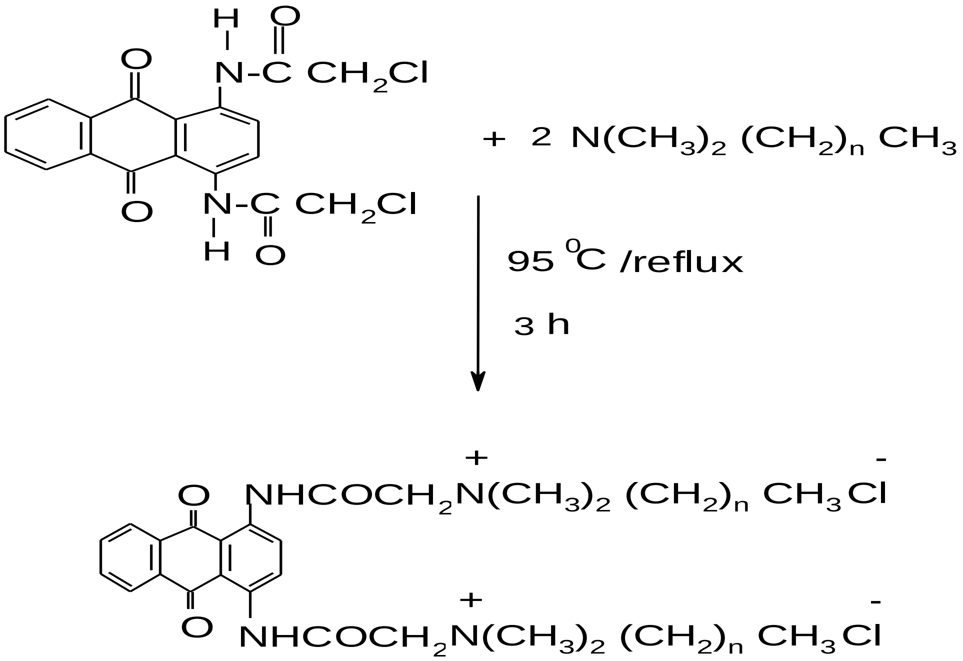


The reaction proceeds through the following mechanism:



2.2.2.2. Synthesis of di– substituted cationic dyes

The synthesis of di- substituted cationic dyes (IIB-IIHD) were completed by the reaction of (B) with N,N-dimethyl (butyl , heptyl , octyl , decyl , and hexadecyl) amin at 95 ^{0}c for 3h .(Exp.section)



Where n = (3, 6, 7, 9, and 15)

2.3. Structure Elucidation of the synthesized dyes

The structures of synthesized dyes were confirmed by IR, ^{1}HNMR, ^{13}CNMR, and Elemental analysis.

- **IR spectra** of the mono–substituted (IB-IHD) and di-substituted (IIB-IIHD) dyes: the most important absorption bands in the structure of the prepared cationic dyes was reavled by IR spectra are; $\nu_{C\,=\,O}$ at 1700-1710 cm^{-1} of anthraquinone structure; $\nu_{C=\,O}$ at 1600-1680 cm^{-1} of NHCO; νN-H 3390-3423 cm^{-1} of amid; $\nu_{C\text{-}H}$ aliphatic at 2800-3000 cm^{-1} and ν $_{C\text{-}H}$ aromatic at 3010-3017 cm^{-1} (c.f. Figs.2.2, 2.3).

- ^{1}**HNMR spectra** of synthesized dyes, in all these 1HNMR spectra, the must characteristic signals are: δ ppm at 12.552-12.159 corresponding to proton (NH-CO) of amid group; δ ppm at 8.657-7.643 are assigned to the aromatic protons of anthraquinone nucleolus; δ ppm at 3.646 - 0.844 are assigned to – (CH2) n aliphatic chain. (C.f. Figure 2.4 of comp. IH, Figure 2.5 of comp. ID, Figure2.6 of comp IHD, Figure 2.7of comp. IIH, Figure2.8of comp. IID, Figure 2.9 of comp. IIHD)
- ^{13}**CNMR spectra** of the mono and di–substituted (IB-IHD), (IIB-IIHD) prepared cationic dyes, the must signals are: δ ppm at 185.8274 and 181.9739 are assigned to the two carbonyl carbons in the anthraquinone structure, respectively; δ ppm at 163.241 is assigned to the amide carbon; δ ppm at 121.6249~ 135.5032 are caused by aromatic carbons of anthraquinone structure; and δ ppm within 10 ~ 70 are corresponding to the alkyl carbons chain, which locate in different chemical environments. However, the 13CNMR spectra of di–substituted (IIB-IIHD) of the prepared cationic dyes, the must signals are: δ ppm at 185.4745 is assigned to the two carbonyl carbons in the anthraquinone structure; δ ppm at 163.25502 is assigned to the amide carbon; δ ppm in the range of 121.5296 ~ 135.1884 are caused by aromatic carbons of anthraquinone structure, and δ ppm within 10 ~ 70 are corresponding to the alkyl carbons chain. Exactly the appearance of mono and di-substituted cationic dyes are at the same signals positions, the difference was relevance by appear of two 13C NMR signals of the two different environment carbonyl groups of mono- while in case of disubstituted cationic dyes only one types of signals appear at 185.4745 of these two carbonyl groups. (C.f. Figure 2.10 of comp. IH, Figure 2.11of comp. ID, Figure 2.12 of comp. IHD, Figure 2.13 of comp. IIH, Figure2.14 of comp. IID).

PART II

2.4. Dyeing performance and fastness properties of the synthesized antibacterial cationic dyes

2.4.1. Factors affecting dyeing of acrylic fabrics

2.4.1.1. Effect of dyeing pH

Acrylic fabrics (0.5g) were dyed with antibacterial cationic dyes at pH (2-6) and L.R 1:50. Dyeing was continued for 45 mins at 100 °C. The color strength (K/S) values of dyed washed samples were cited in table (2.2) and Figure (2.15). It is evident that the dyeability of acrylic fabrics is a pH dependent. As can be seen from table (2.2), Figure (2.15), the maximum color strength value was obtained at pH 3 while the lowest value can be observed at pH 6. On increasing pH more than 6 there was no dye uptake occurs. This is true for all dyes used. This can be interpreted on the basis of that the ionization of the nitrile group (-CN) of the acrylic in high acidic medium lead to the formation of negatively centers capable of reacting with the cationic part of the dyes .Also, mono-substituted dyes gave higher color strength than di-substituted dyes. This may be due to that the di-substituted dyes contain two positively charged nitrogen atoms in each structure compared to the mono-substituted one they are more favorable to stay in the dye bath.

Table (2.2); Effect of dyeing pH on the color strength (K/S) value of acrylic fabric dyed with antibacterial dyes (2% (w.o.f.), L.R 1:50, dyeing temp 100 ^{0}C for 45 min.).

PH	K/S									
	IB	IH	IO	ID	IHD	IIB	IIH	IIO	IID	IIHD
2	13.66	14.66	12.32	13.81	10.55	4.34	3.57	3.78	4.13	1.15
3	14.56	15.39	14.23	14.14	12.34	5.38	3.73	4.09	4.42	1.34
4	14.23	15.02	13.63	13.72	11.98	4.73	3.49	3.78	4.23	1.29
5	13.83	14.84	13.24	13.34	11.56	4.34	3.31	3.57	4.11	1.27
6	13.52	14.41	12.66	13.11	11.31	4.13	3.2	3.49	4.07	1.16

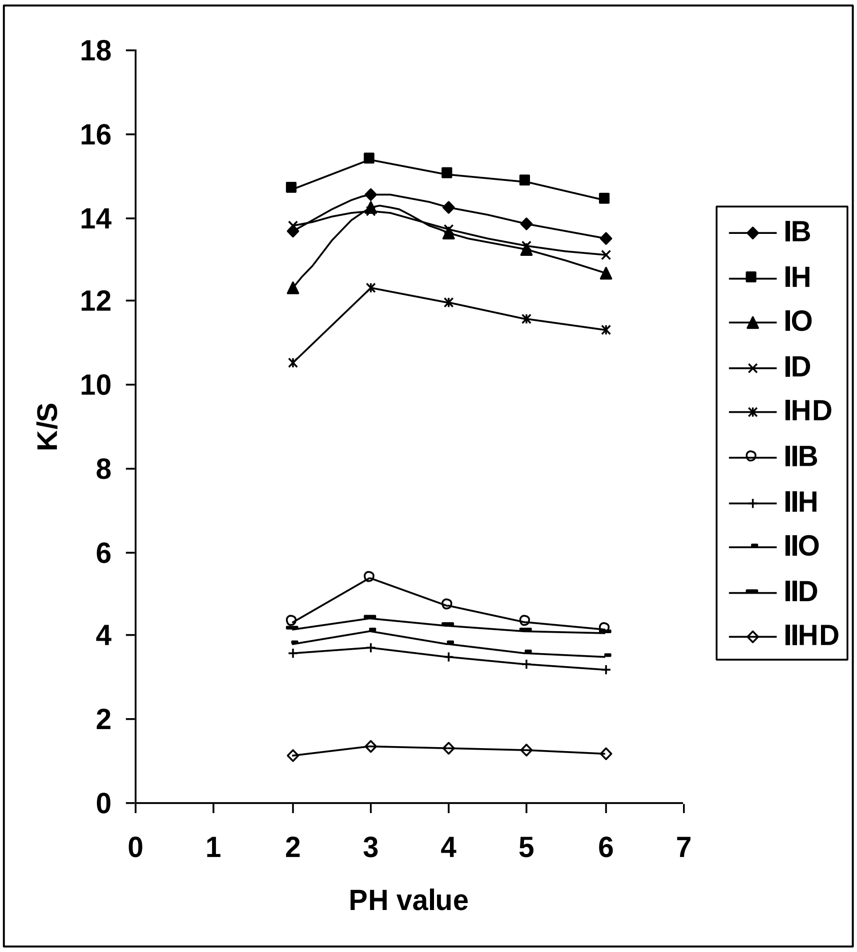


Figure (2.15): Effect of dyeing pH on the color strength (K/S) value (antibacterial dye 2% (w.o.f.), L.R 1:50, dyeing temp 100 ^{0}C for 45 min).

2.4.1.2. Effect of dyeing temperature

Acrylic fabrics (0.5g) were dyed with antibacterial cationic dyes(2% w.o.f.) at pH 3, L.R 1:50, temperature varied from (60-100ºC)and dyeing was continued for 45 mins . After that, the dyed samples were rinsed, washed and air dried. Data of color strength (K/S) for dyed washed samples were listed in table (2.3), Figure (2.16).

From table (2.3) and Figure (2.16) it can be observed that increasing temperature from 60 to 80 ^{o}c leads to a slight increment in color yield values (K/S). Increasing temperature more than 80^{o}c leads to an improvement in color yield value.

The maximum dyeability and color strength were obtained at 100^{o}c this holds true for all dyes used. These results are related to the glass transition temperature (Tg) of acrylic fabrics which might vary from 60^{o}c to 80^{o}c. Also, below Tg the acrylic fabric is a highly compact structure. Increasing the temperature more than Tg is accompanied by (a) increasing the rate of diffusion of the dye from the aqueous phase to the fiber macrostructure (b) enhancing the swellability of acrylic in the dye bath. Mono substituted dyes gave more color strength (K/S) than di-substituted dyes as mentioned before.

Table (2.3); Effect of dyeing temperature on the color strength (K/S) value of acrylic fabric dyed with antibacterial dyes (2% w.o.f.,) L.R 1:50, for 45 min.

Temp.	K/S									
	IB	IH	IO	ID	IHD	IIB	IIH	IIO	IID	IIHD
60	11.05	12.66	11.18	12.56	9.75	0.89	0.12	0.12	0.06	0.09
70	12.34	13.63	12.84	13.11	10.39	1.54	0.18	0.25	0.08	0.11
80	13.24	14.23	13.52	13.34	11.31	2.89	2.2	1.33	0.18	0.32
90	13.63	14.66	13.83	13.66	11.98	3.31	2.8	2.57	2.85	1.11
100	14.56	15.39	14.23	14.14	12.34	5.38	3.73	4.09	4.42	1.34

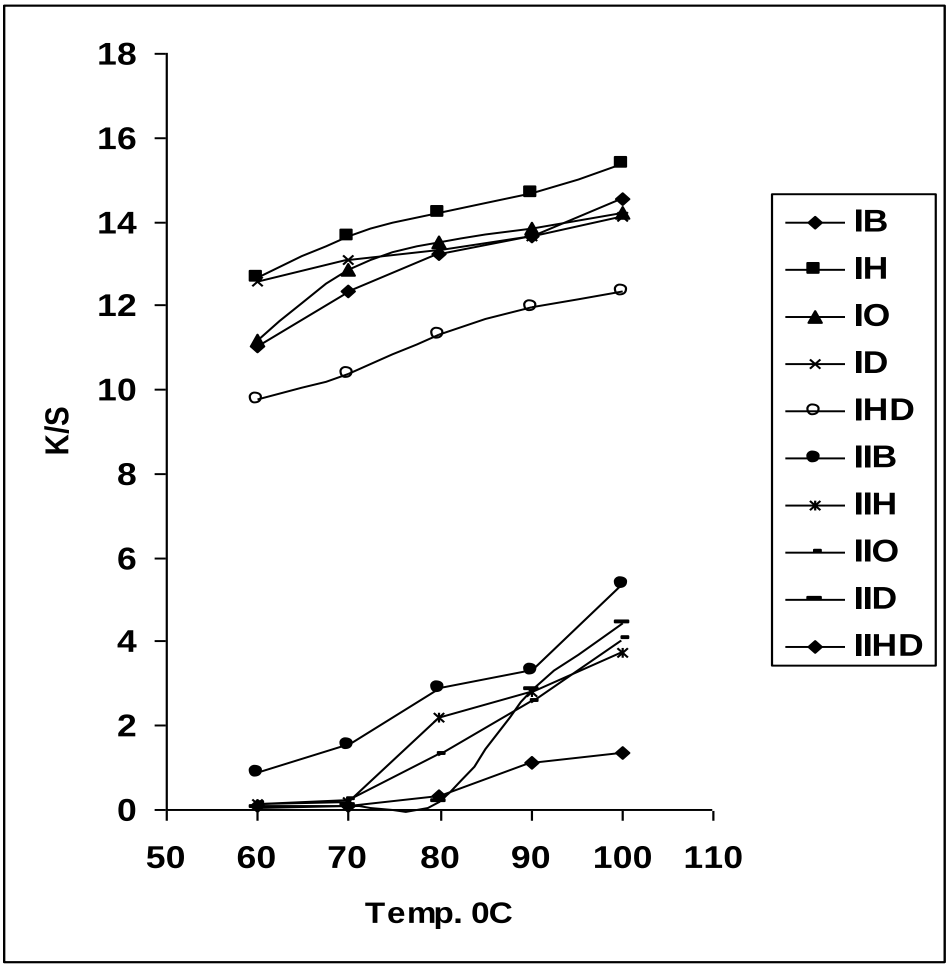


Figure (2.16): Effect of dyeing temperature on the color strength (K/S) value using antibacterial dye 2% (w.o.f.), L.R 1:50, for 45 min.

2.4. 1.3. Effect of dyeing time

Acrylic fabrics (0.5g) were dyed with antibacterial cationic dyes(2% w.o.f.) at pH 3, L.R 1:50, at 100ºC and time were varied from (15-105min). After that, the dyed samples were rinsed, washed and air dried .The color strength for the dyed washed samples were tabulated in table (2.4) and Figure (2.17).

From Table (2.4) and Figure (2.17) it can be seen that increasing dyeing time from 15 min to 60 min leads to increase in K/S for both mono and di –substituted dyes. After 60 min dyeing, no change in the color strength (K/S) will occur due to reaching complete exhaustion of the dyes. All the mono-substituted dyes show higher color strength (K/S) values than di-substituted ones .This may be due to dye sizes play an important role in the acrylic dyeing. Smaller dyes (mono-substituted) may diffuse faster into the fabric, while the larger ones (di-substituted) may diffuse slower and need more time. i.e dye IB has color strength value equal 14.86 at 60 min while II B at 105 min has 5.87 (K/S) value .

Table (2.4): Effect of dyeing time on the color strength (K/S) value of acrylic fabric dyed with antibacterial dyes 2% (w. o. f.), PH: 3, L. R 1:50, dyeing temperature: 100 ^{0}C.

Time	**K/S**									
	IB	**IH**	**IO**	**ID**	**IHD**	**IIB**	**IIH**	**IIO**	**IID**	**IIHD**
15	13.37	13.65	13.15	11.89	10.66	4.06	2.15	2.76	1.96	0.86
30	13.98	14.1	13.84	12.94	11.81	4.61	2.85	3.74	3.08	1.04
45	14.56	15.39	14.23	14.14	12.43	5.38	3.73	4.09	4.42	1.34
60	14.86	15.89	14.72	14.52	12.84	5.85	3.94	4.34	4.92	1.54
75	14.87	15.89	14.74	14.55	12.86	5.86	3.96	4.35	4.92	1.55
90	14.88	15.89	14.74	14.55	12.86	5.87	3.96	4.35	4.92	1.55
105	14.88	15.89	14.74	14.55	12.86	5.87	3.97	4.36	4.93	1.55

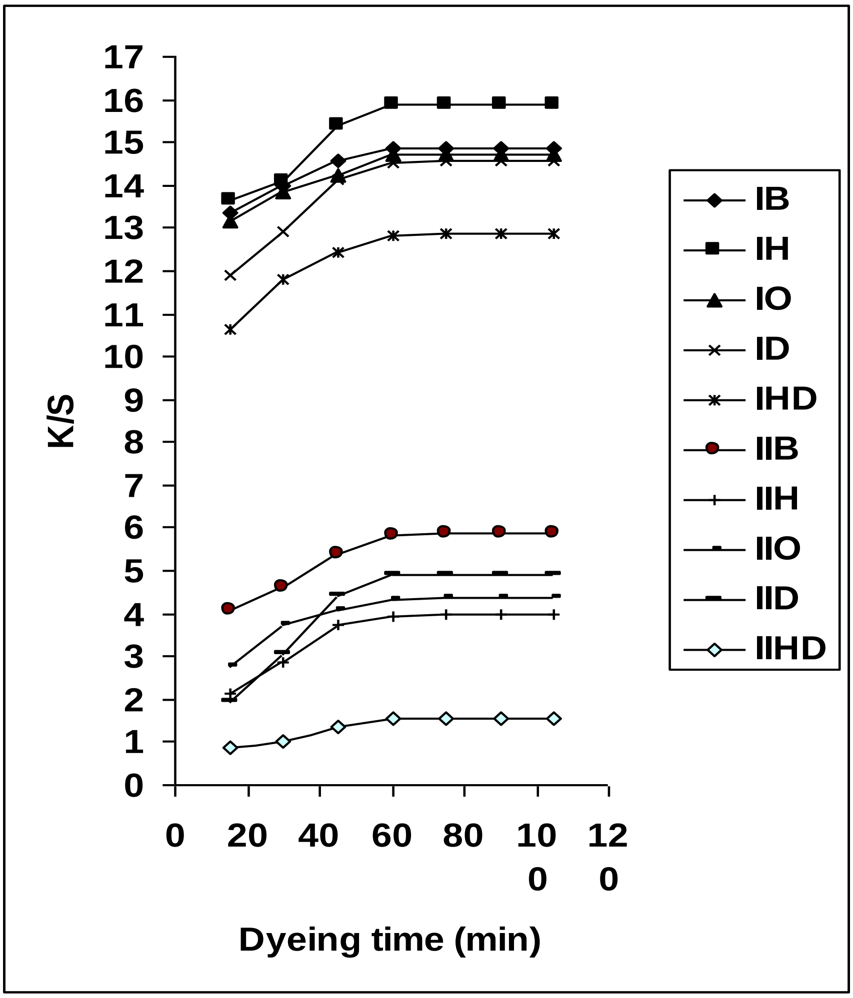


Figure (2.17): Effect of dyeing time on the color strength (K/S) value (antibacterial dye 2% (w.o.f.), pH: 3, L.R 1:50, dyeing Temperature: 100 ^{0}C).

2.4.1.4. Effect of dye concentrations

Acrylic fabrics were dyed with antibacterial cationic dyes at pH3 and L.R 1:50 at 100 ^{0}C for 60 min, then, the dyed samples were rinsed, washed and air dried. The colour strength (K/S) were measured and cited in Table (2.5) and Figure (2.18).

Table (2.5) and Figure (2.18) show that as the dye concentration increases from 1% to3%, the colour strength also increases with both mono and di- substituted dye. Above 3% dye concentration the colour strength values nearly levels off or a very slight improvement takes place.

It is possible that the adsorption of the dye molecules inside the acrylic fibres with –CN (nitrile) and COOH (carboxylic) will complete, this is true for all dyes used. Mono- substituted dyes gave higher colour strength values than the corresponding di-substituted dyes, this may be due to the di-substituted dyes may occupy twice the amount of dye sites within the fabrics compared to the mono- substituted dyes. Therefore theoretically one fixed di-substituted dyes should be only half the mono-substituted dyes if the dye sites are constant and full occupied.

Table (2.5): Effect of antibacterial dye concentration on the color strength(K/S) ,(pH :3 , L.R 1:50,dyeing temp 100 ^{0}C for 60 min) .

Conc.	**K/S**									
	IB	**IH**	**IO**	**ID**	**IHD**	**IIB**	**IIH**	**IIO**	**IID**	**IIHD**
1%	13.81	14.61	13.81	13.23	11.66	4.99	3.49	2.92	3.58	1.15
2%	14.86	15.89	14.72	14.52	12.84	5.85	3.94	4.34	4.92	1.54
3%	14.99	16.12	15.01	14.86	13.52	6.02	4.26	4.88	5.12	2.09
4%	15.13	16.15	15.11	14.99	13.66	6.11	4.34	4.93	5.22	2.18
5%	15.15	16.22	15.23	15.16	13.83	6.22	4.44	4.99	5.32	2.26

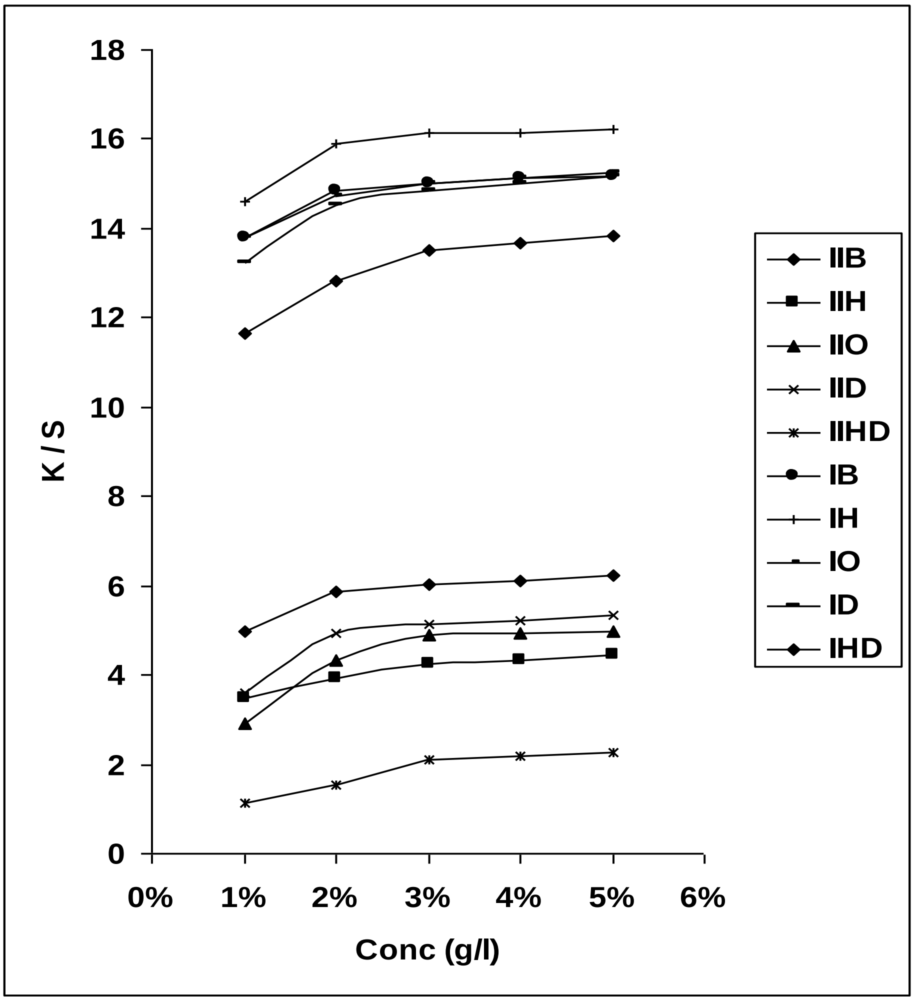


Figure (2.18): Effect of dye concentration on the color strength (K/S) (pH: 3, L.R 1:50, dyeing temp 100 ^{0}C for 60 min).

2.4.٢. Fastness Properties

Table (2.6) presents the fastness to washing, rubbing, perspiration and light of acrylic fabric dyed with mono and / or di substituted antibacterial cationic dyes. It can be seen that the washing fastness for dyed acrylic fabrics ranges from good to vary good (4-5) this can be attributed to the fact that washing procedures for acrylic fabrics take place below the glass transition temperature when the dye is trapped inside the hydrophobic fiber. Also, acidic and alkaline perspiration gave the same results and ranged from good to very good (4-5) while dry crocking gave better results (4-5) than wet crocking (3-4). On the other hand the light fastness properties ranges from vary good to excellent (5-7).It can be attributed to the hydrophobicity of the fibers, for it has been shown that the absence of water molecules materially reduces the rate of light fading.

Table (2.6): Fastness Properties of dyed acrylic fabrics with antimicrobial cationic dyes (2% o.w.f., L.R 1:50, pH: 3 and dyeing for 60 min. at 100 ^{0}C).

Dyes	Crocking		Acidic perspiration			Alkaline perspiration			Washing fastness			Light fastness
	Dry	Wet	St.*	St.**	Alt.	St.*	St.**	Alt.	St.*	St.**	Alt.	35hr
IB	4	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦ -٧
IH	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦
IO	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦ -٧
ID	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦
IHD	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٥ -٦
IIB	4-5	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦
IIH	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦ -٧
IIO	4	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦ -٧
IID	4	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٦ -٧
IIHD	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	٥ - ٦

St.* = Staining on cotton
St. **= Staining on wool
Alt. = Alteration in color

2.5. Antibacterial Activity of synthesized antibacterial cationic dyes

2.5.1. Effect of contact time on antibacterial efficacy

Antibacterial activity of the dyed acrylic fabric with mono- and di-substituted dyes (2%w.o.f.), PH3,L.R:1:50, temperature 100^0C for 60 min.was studied against gram positive (S.aureus) and gram negative (E.Coli) bacteria. As shown in table (2.7).

- All the dyed fabrics gave antibacterial activity against gram positive and gram negative bacteria with different degrees, depending on the dye used.
- Antibacterial activity of fabrics increase with increasing contact time till 6h of contact. With further increase of the contact time, the antibacterial activity decrease.
- In most cases antibacterial activity of dyed fabric against gram-negative bacteria was greater than the activity against gram-positive. It may be related to the fact that E-Coli shown less resistance to mechanical rupture compared to S.aureus[97] .
- Di-substituted dyes show higher antibacterial efficacy compared to mono-substituted dyes. Also, the alkyl chain of QAS containing less than eight carbons could only show weak antibacterial activities [98] .

Table (2.7): Effect of contact time on antibacterial efficacy.

Contact time (h)	Bacteria	Bacteria reduction (%) for fabric dyed by									
		IB	IH	IO	ID	IHD	IIB	IIH	IIO	IID	IIHD
2	E.Coli (-ve)	5	16	17	20	20	18	24	38	38	39
	S.aureus(+ve)	5	7	17	21	27	14	18	25	26	39
4	E.Coli (-ve)	33	45	45	58	61	40	47	49	65	67
	S.aureus(+ve)	19	43	46	60	62	30	44	54	64	66
6	E.Coli (-ve)	42	44	84	88	90	65	88	90	91	91
	S.aureus(+ve)	43	45	86	88	90	67	89	90	92	91
8	E.Coli (-ve)	0	0	55	67	70	0	57	58	62	66
	S.aureus(+ve)	0	0	58	67	71	0	57	57	62	63
10	E.Coli (-ve)	0	0	41	48	52	0	45	45	50	58
	S.aureus(+ve)	0	0	42	50	54	0	46	44	49	56

2.5.2. Effect of Number of washing Cycles on antibacterial efficacy and color strength.

From table (2.8) it can be seen that antibacterial activity of dyed fabrics decrease with increasing number of washing cycles. With increasing washing cycles from 3 to 9 washes, most of the sample lost their antibacterial activity (sample dyed with dyes IB,IH,IO,IIB and IIH) this may be due to the hydrophbic nature of acrylic fabrics, so there may not be sufficient contact between the fabric and the bacterial solution during bacterial test. In the antibacterial testing below the Tg temperature of the fabric the water accessible dye located on the surface of the fabric contributes the antibacterial efficacy of the treated fabric as they come into contact with the bacteria and thus kill it. During washing the accessible dyes washed away so, the antibacterial activities of dyed fabrics dropped significantly while the inaccessible dyes may not be affected.

Although the accessible dye washed away with every washing cycle, the K/S values shows only a slight decrease table (2.9), that is because the total visual effect may not be affected by the loss of water accessible dyes, since both the water accessible and water inaccessible dyes contribute to the shade depth colour strength. Also, for all the dyed fabrics did not change the λmax during washing, these indicate that the fixed dyes were stable, no decomposition and no structural change occurred.

Table (2.8): Effect of washing cycle on antibacterial efficacy of dyed acrylic fabrics against Gram-negative (E.Colie) bacteria. (antibacterial dye 2% w.o.f. ,L.R: 1:50, pH :3, at 100 ^{0}C for 60 min.)

Wash Time	Bacteria reduction (%) for fabric dyed by									
	IB	IH	IO	ID	IHD	IIB	IIH	IIO	IID	IIHD
0 Wash	42	44	84	88	90	65	88	90	91	91
3 Wash	11.8	21.2	33.6	34.5	69.1	19.6	25.8	33.8	61.4	75
6 Wash	3.1	9.3	14.3	17.4	60	8.3	11.2	29	31.7	36.1
9 Wash	0	0	0	9.4	38.3	0	0	14.1	17.7	29

Table (2.9): Effect of washing cycle on color strength (K/S) andλmax of dyed fabric. .(antibacterial dye 2% w.o.f. ,L.R: 1:50, pH :3, at 100 ^{0}C for 60 min.)

Wash cycle	**K/S, λmax**	**Acrylic fabric treated by antibacterial dyes**									
		IB	**IH**	**IO**	**ID**	**IHD**	**IIB**	**IIH**	**IIO**	**IID**	**IIHD**
0 Wash	K/S	14.86	15.89	14.72	14.59	12.84	5.85	3.94	4.34	4.92	1.45
	λmax	٣٧٥	٣٨٠	٣٧٥	٣٨٠	٣٩٥	٤50	٤40	٤48	450	450
3 Wash	K/S	14.64	15.57	14.52	14.24	12.68	5.41	3.58	3.96	4.43	1.29
	λmax	٣٧٥	٣٨٠	٣٧٥	٣٨٠	٣٩٥	٤50	٤40	٤48	450	450
6 Wash	K/S	14.32	15.11	14.24	14.07	12.32	5.2	3.49	3.88	4.26	1.27
	λmax	٣٧٥	٣٨٠	٣٧٥	٣٨٠	٣٩٥	٤50	٤40	٤48	450	450
9 Wash	K/S	14	14.98	14	13.82	12.01	4.99	3.2	3.87	4.15	1.15
	λmax	٣٧٥	٣٨٠	٣٧٥	٣٨٠	٣٩٥	٤50	٤40	٤48	450	450

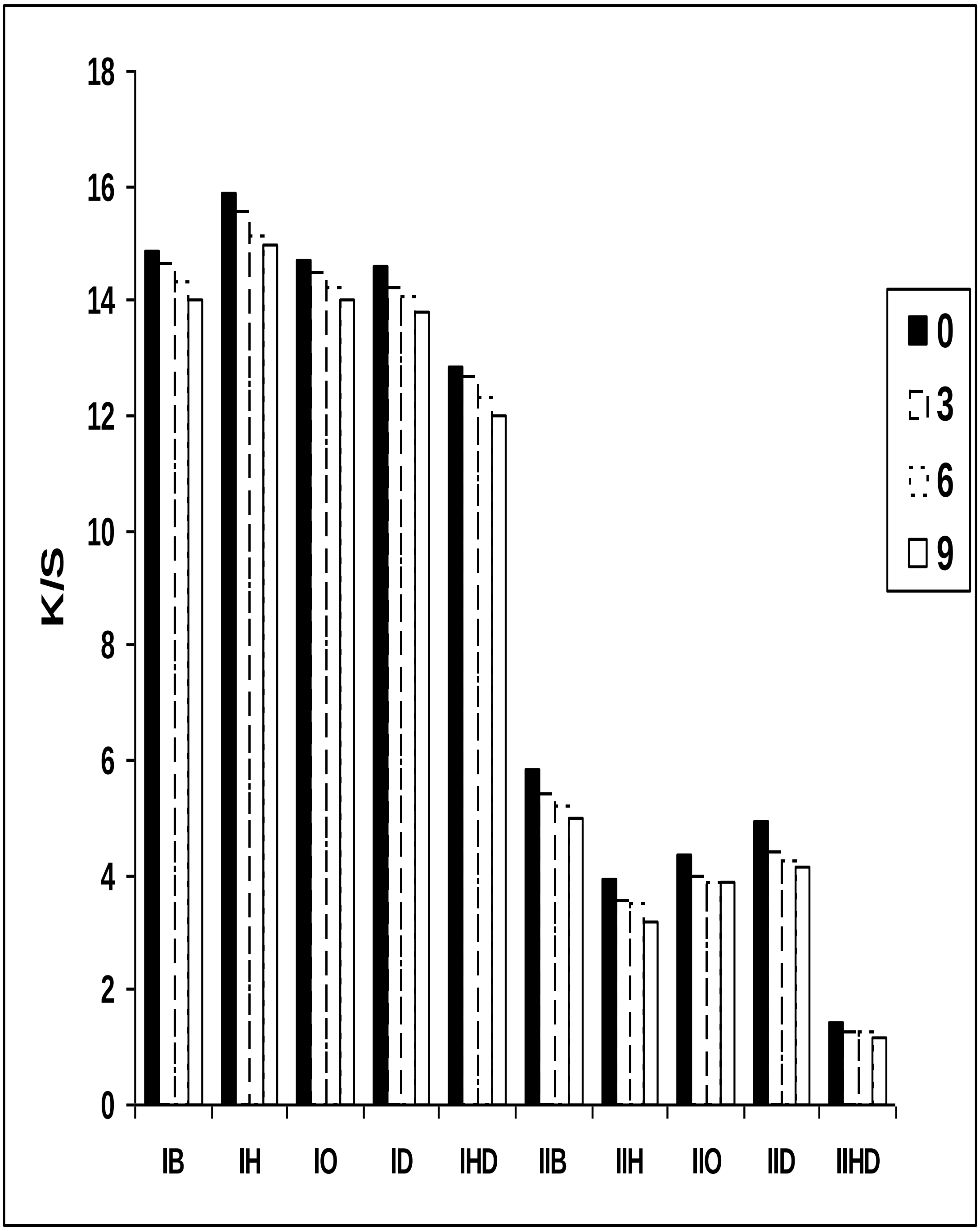


Figure (2.19): Effect of washing cycle on color strength (K/S) andλmax of dyed fabric. . (Antibacterial dye 2% W.o.f., L.R: 1:50, PH: 3, at 100 ^{0}C for 60 min.)

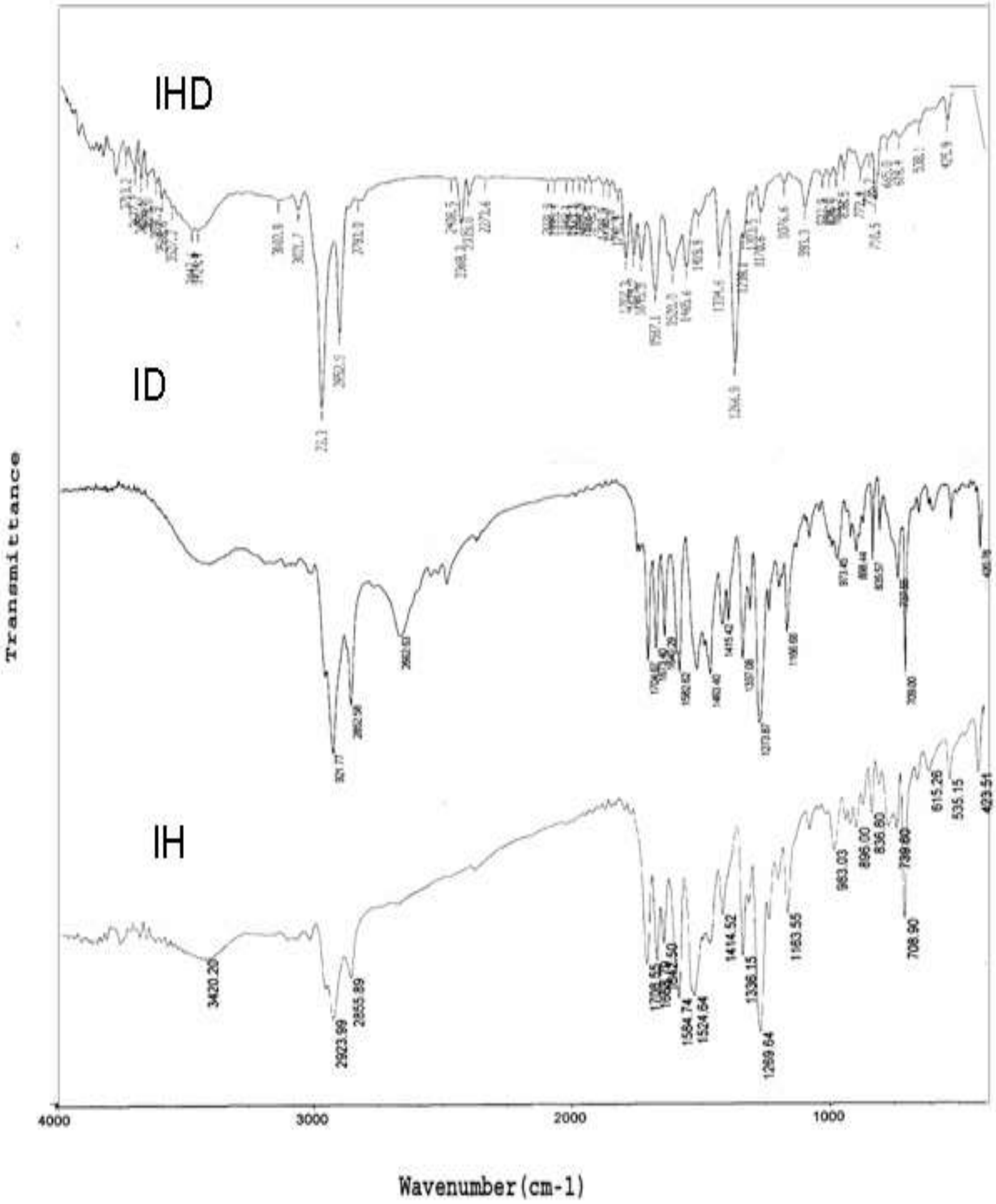


Figure (2.2): IR of spectra of mono– substituted dyes

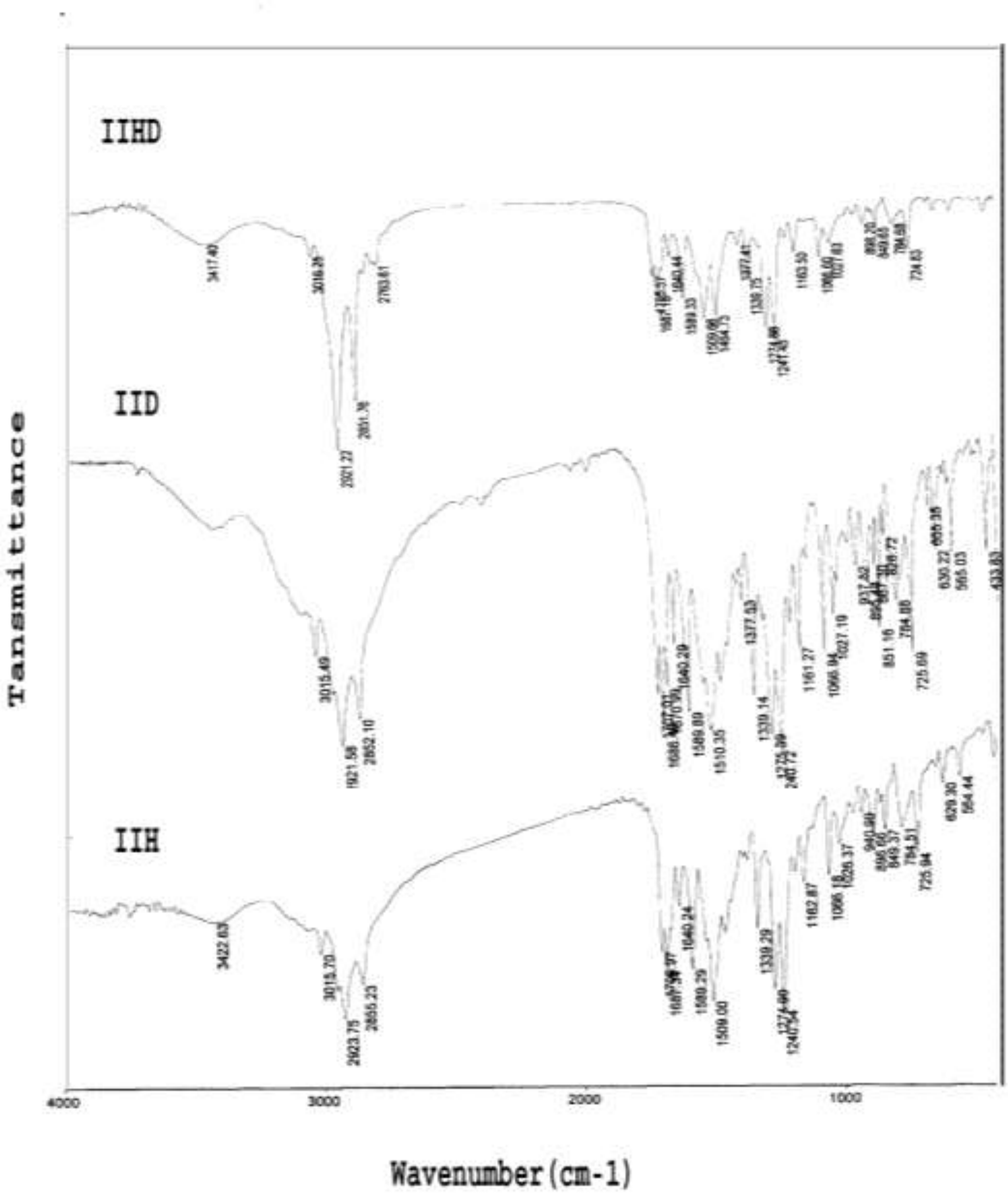


Figure (2.3): IR of spectra of di – substituted dyes

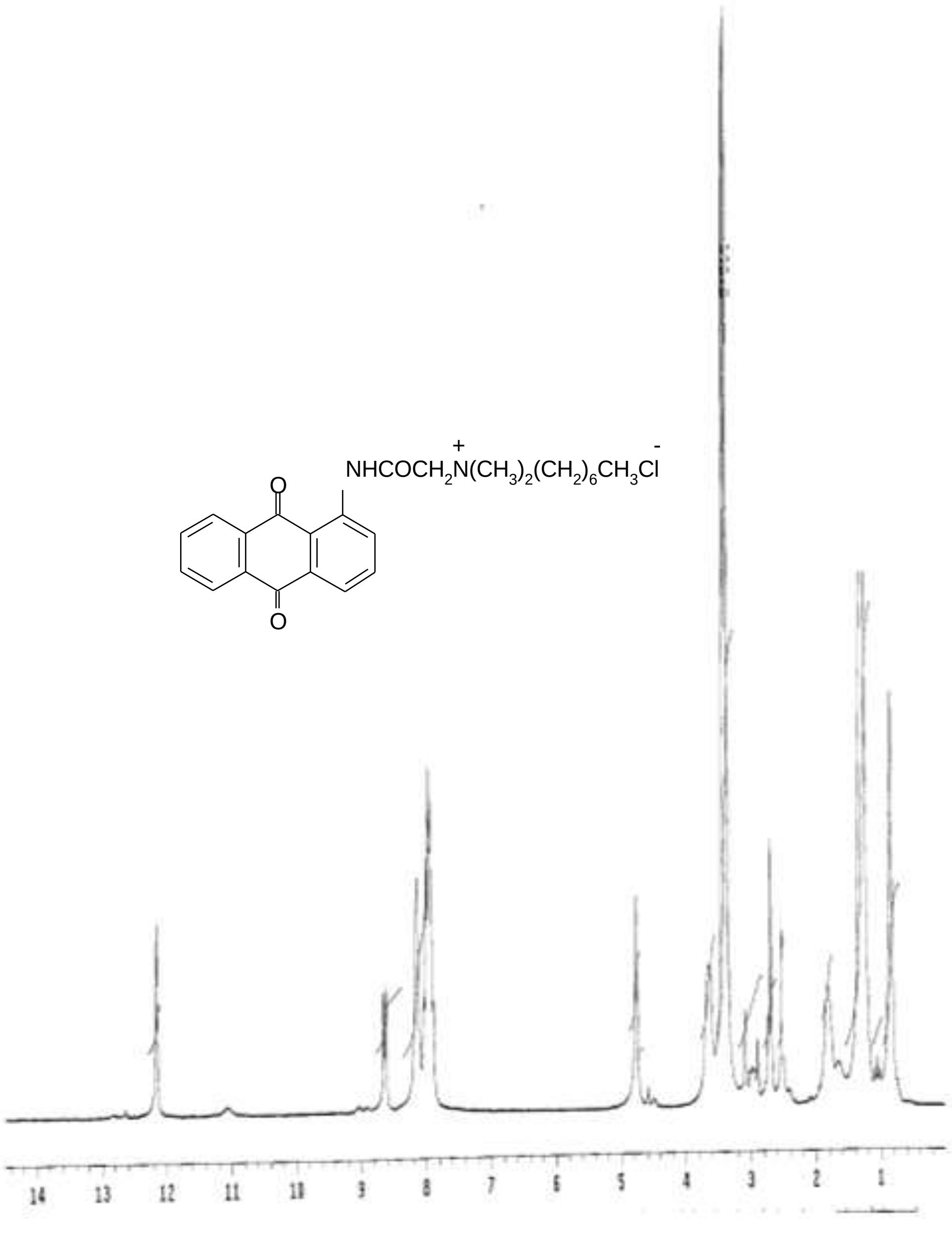


Figure (2.4): ^{1}H-NMR of spectra of IH

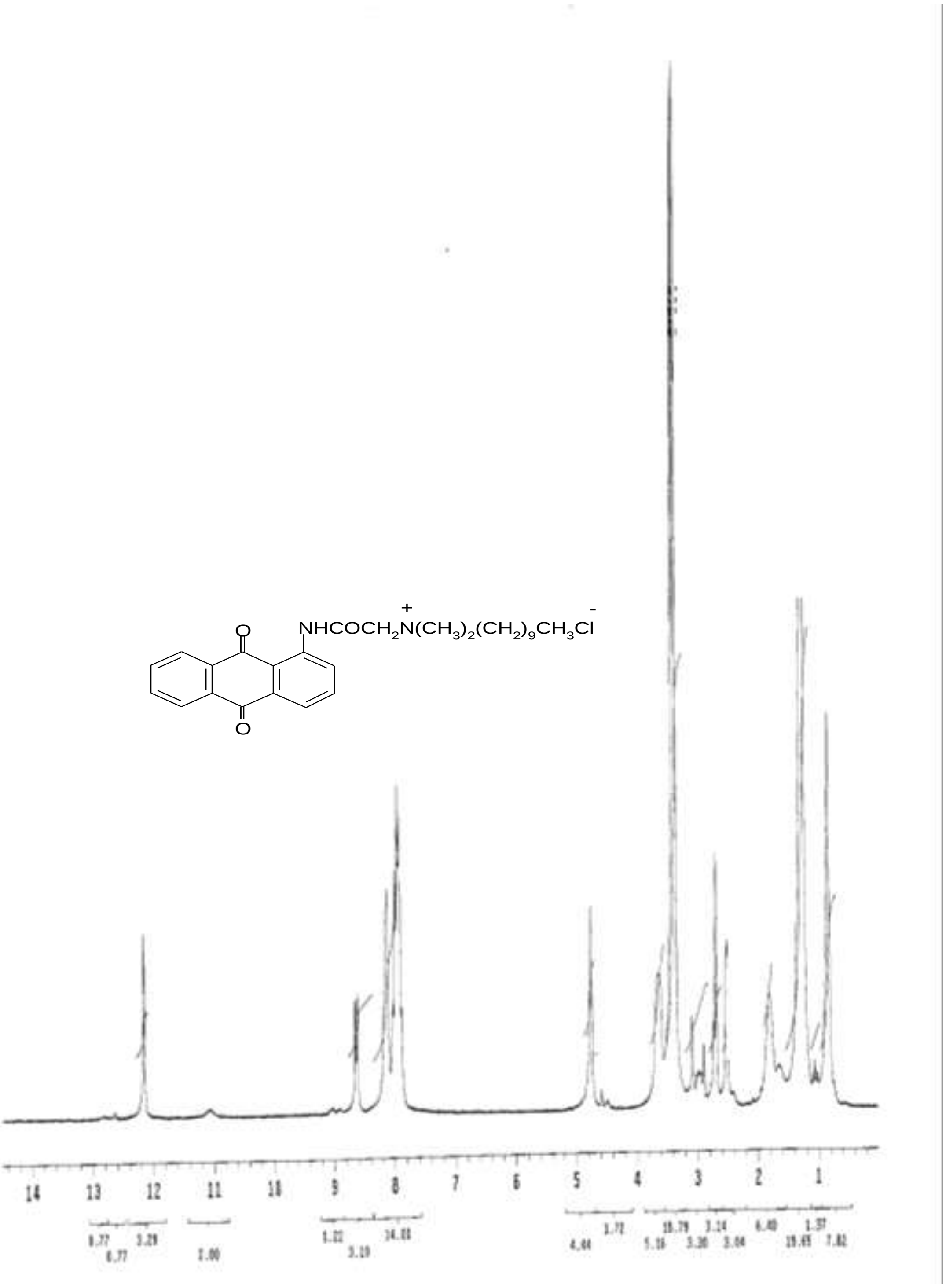


Figure (2.5):^{1}**H-NMR of Spectra of ID**

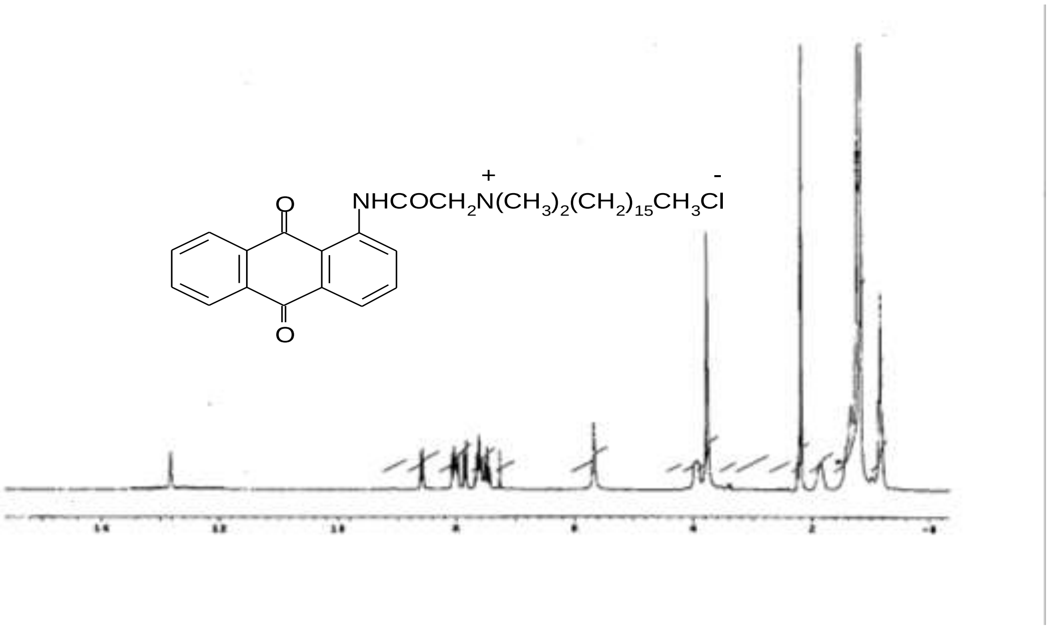


Figure (2.6): ^{1}H-NMR of Spectra of IHD

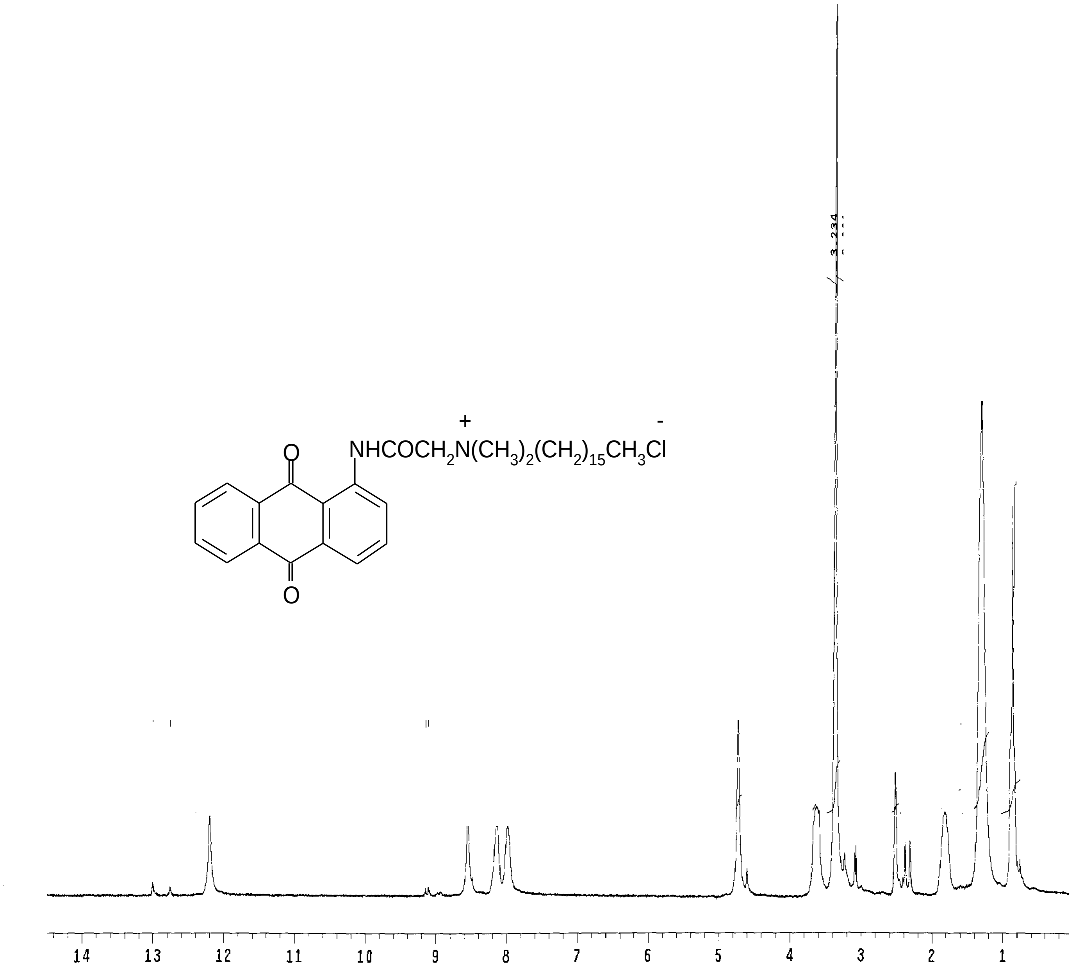


Figure (2.7): ^{1}H-NMR of Spectra of IIH

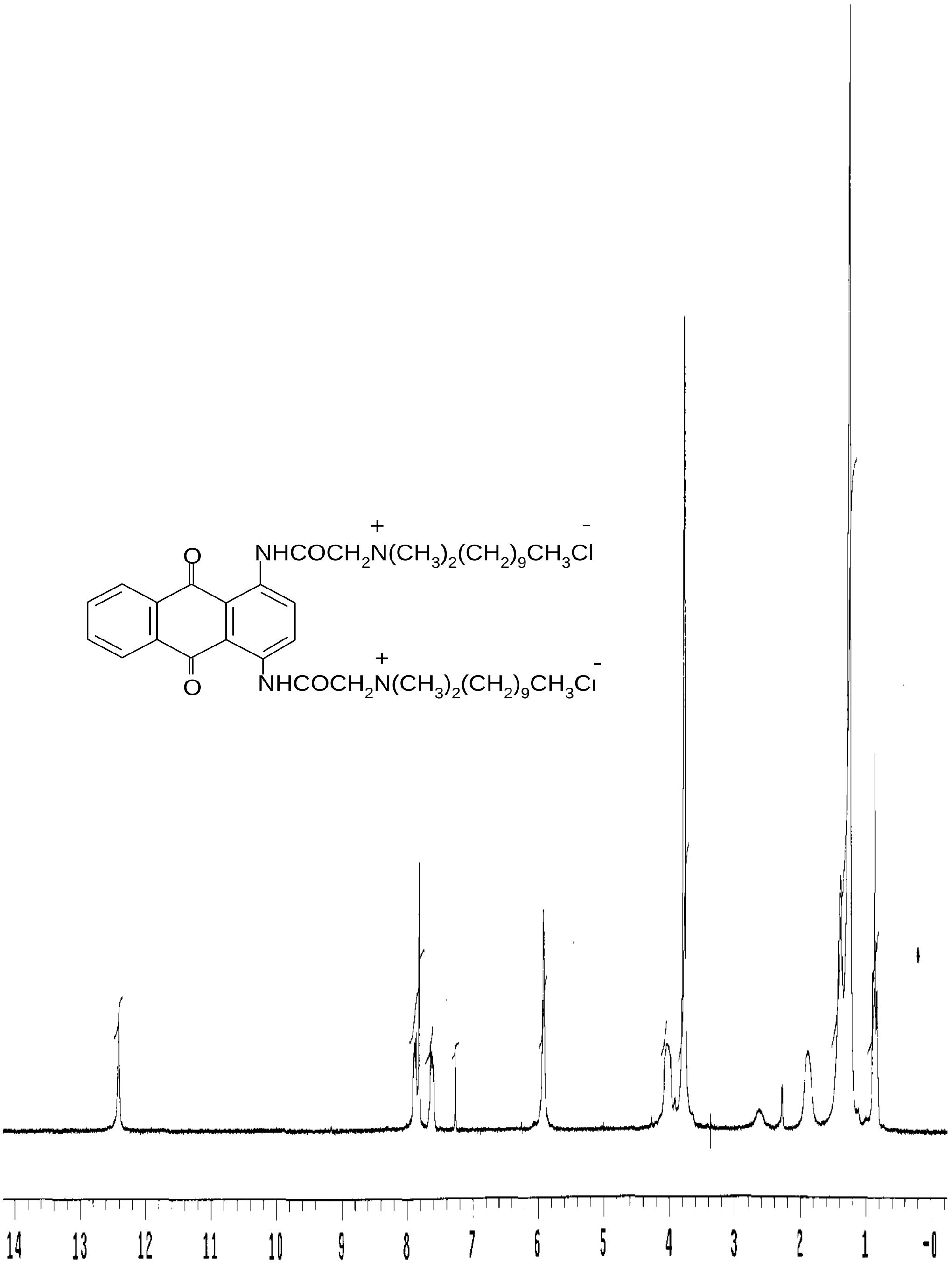


Figure (2.8):^{1}**H-NMR of Spectra of IID**

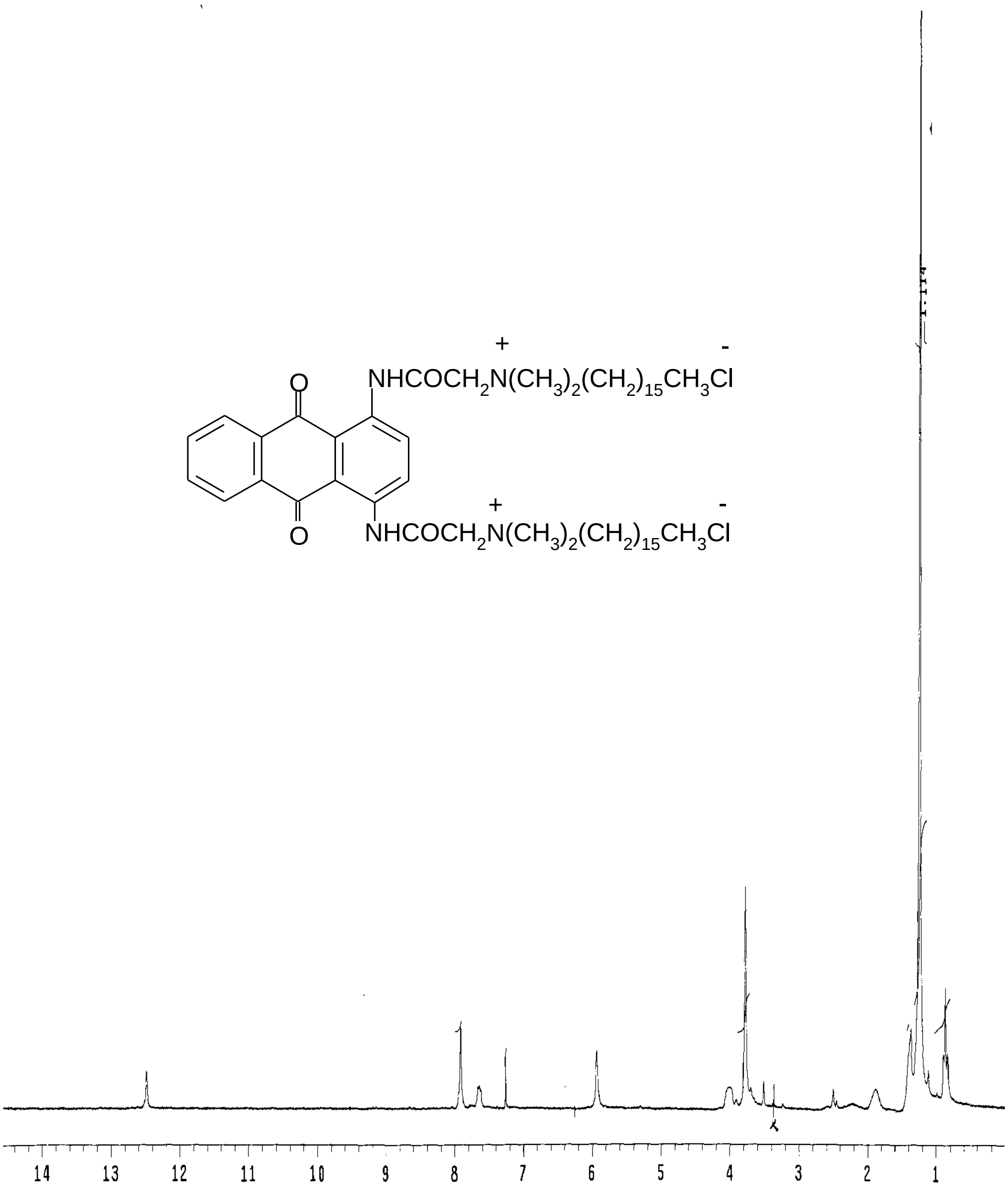


Figure (2.9): ^{1}H-NMR of Spectra of IIHD

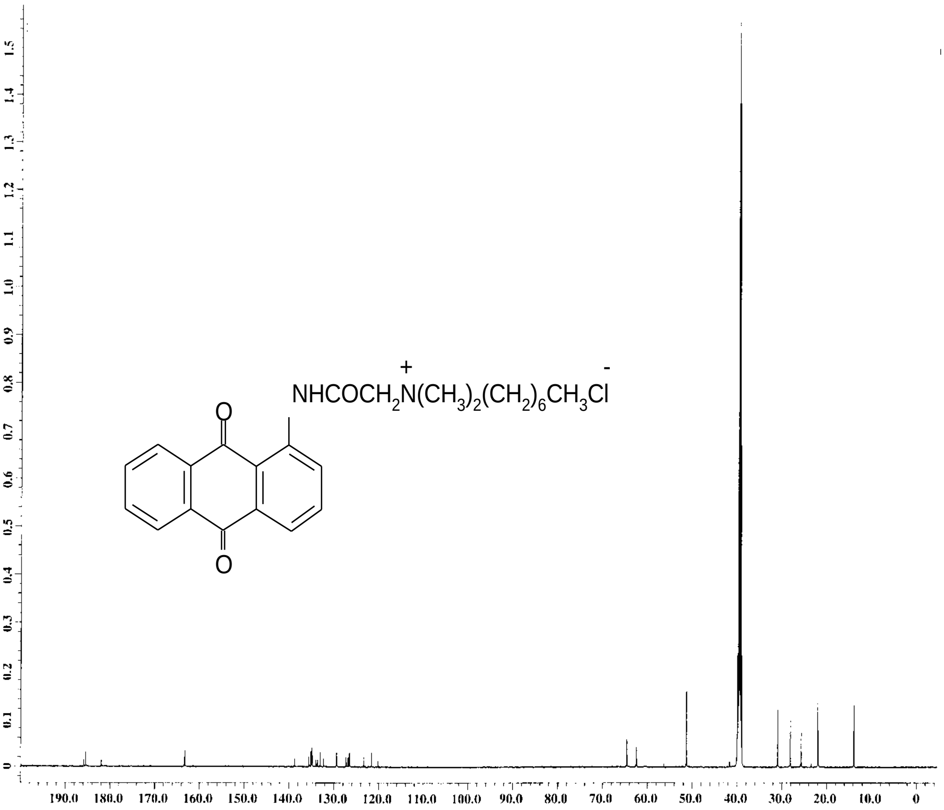


Figure (2.10):^{13}C-NMR spectra of IH

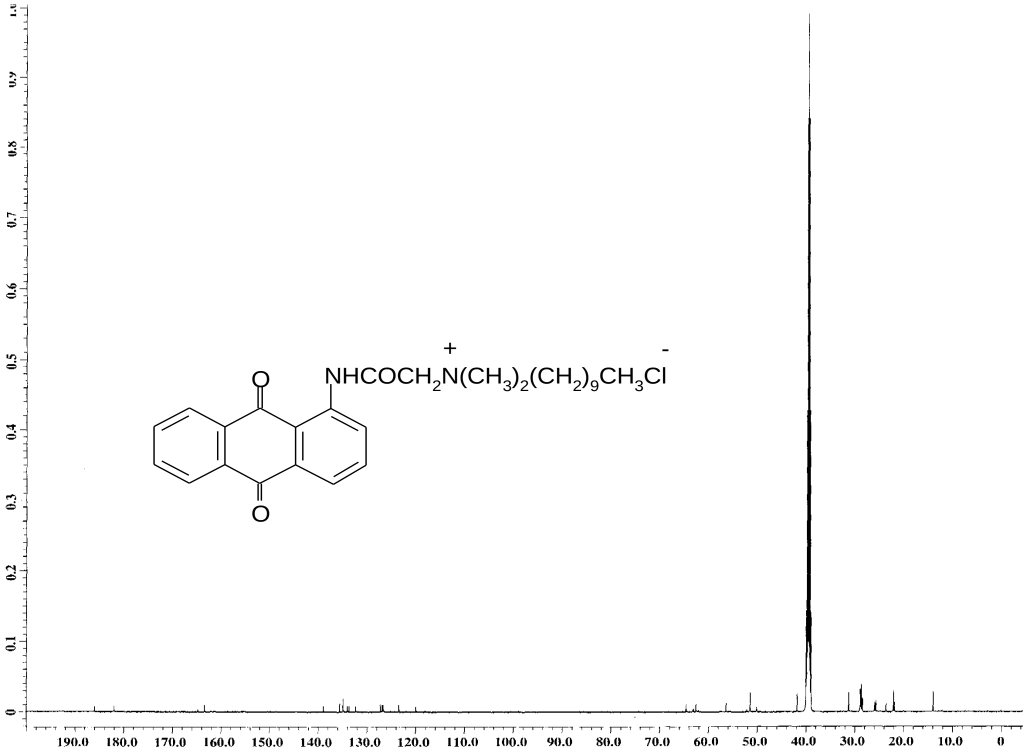


Figure (2.11): ^{13}C-NMR of spectra of ID

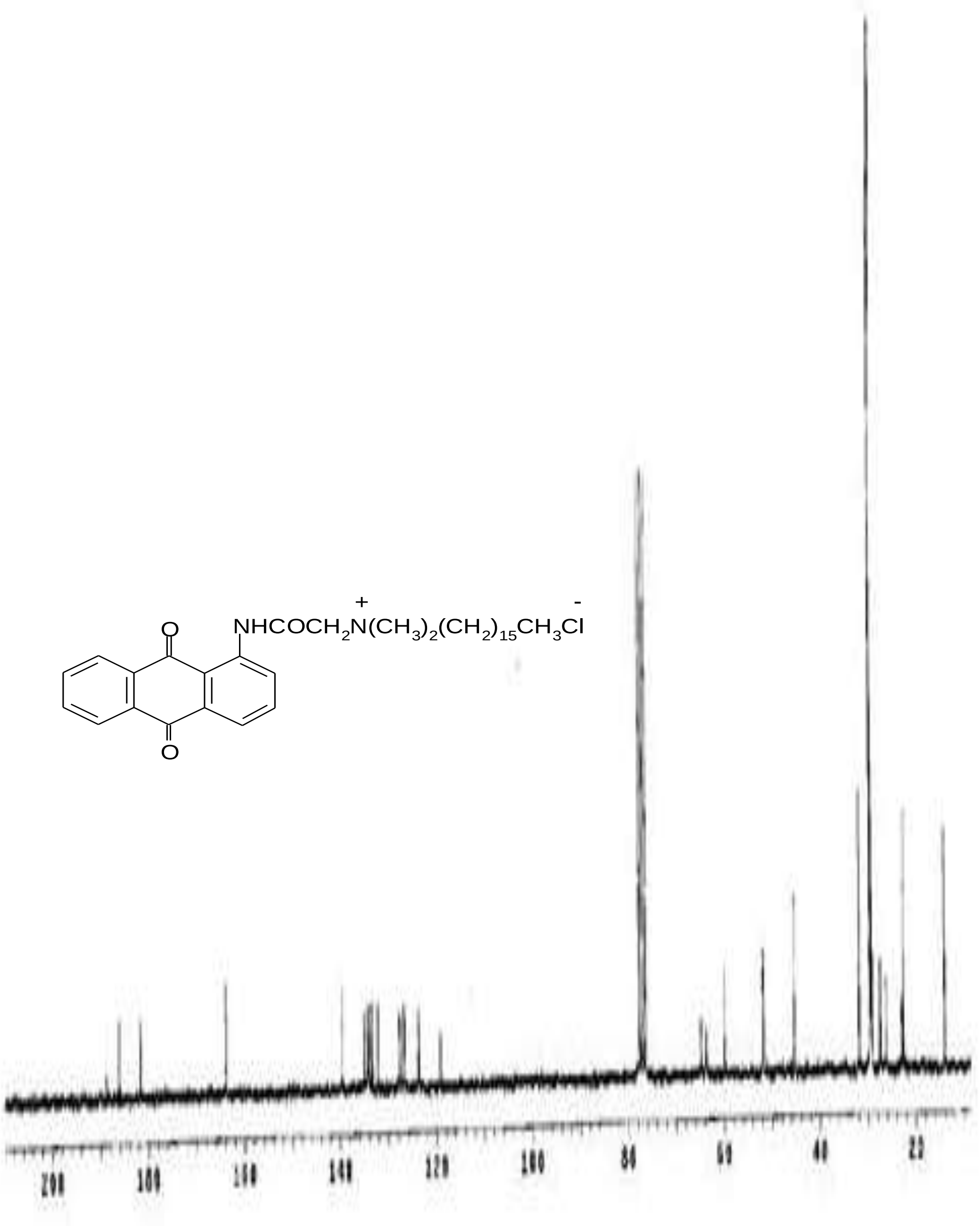


Figure (2.12): ^{13}C-NMR of spectra of IHD

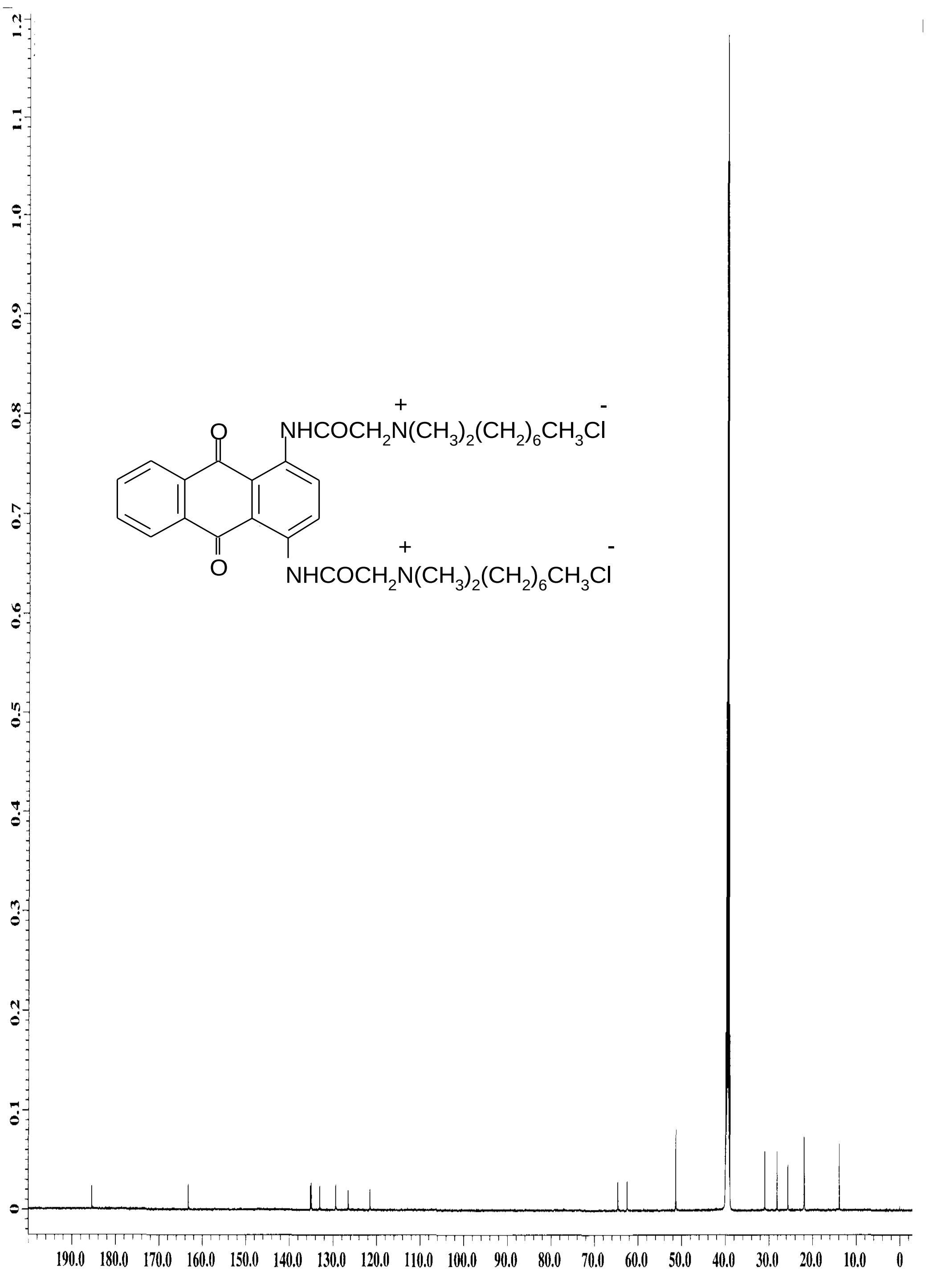


Figure (2.13): ^{13}C –NMR of spectra of IIH

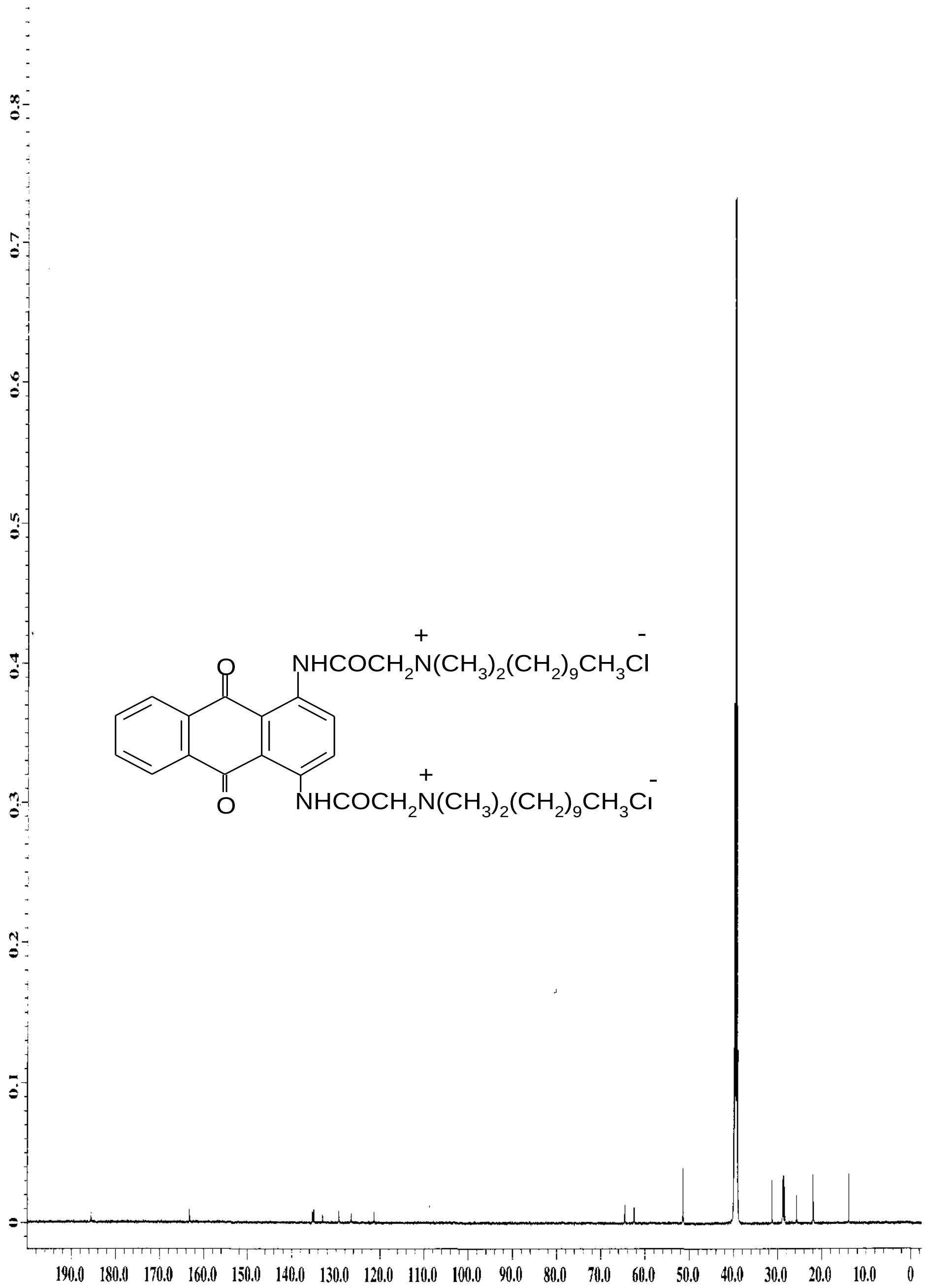


Figure (2.14): ^{13}C-NMR of spectra of IID