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Synthesis and Characterization of New Mesomorphic Azo Compounds and Study their Photoluminesecence Properties

Marwa S. Hatem* ***Nasreen R. Jber****

*Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

E-mail: nasreen301174@yahoo.com

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Abstract:

The preparation of a new Azo compounds of highly conjugated dimeric and polymeric liquid crystal to achieve the crystalline characteristics Which have structures assigned based on elemental analysis, IR 1HNMR and CHNS-O while mesogenic properties have been set for DSC and hot-stage polarizing optical microscopy. The compounds show enantiotropicnematic phase being displayed.

The compounds show photoluminescence properties in the organic solution at room temperature, with the fluorescence band centered around 400 nm.

Key words: Nematic liquid crystal,Azo compounds of highly conjugated dimeric and polymeric liquid crystal

Introduction:

Liquid crystal displays (LCDs) still occupy a dominant position in a display industry. LCDs take the advantages in low energy consumption and the flat panel fabrication compared with the cathode ray tube monitors. However, the LCD panels themselves cannot produce light. As such, they require an external light source for visualizing the images [1]. Therefore, the luminescent LCD is a favorable alternative. It is a type of emissive display, which can simplify the device design and substantially increase the device brightness, contrast, efficiency, and viewing angle. Their LC phase temperature range should be low enough for the LCD fabrication requirement [2]. Liquid crystals (LCs) with their numerous thermodynamically stable phases present a dramatic illustration of how a small alteration of the molecular structure can lead to profound changes in the long-range order. The simplest uniaxial nematic phase is typically formed by rod-like molecules with a straight central rigid core and two aliphatic chains. The rods prefer to align parallel to each other, along a single axis, called the director ˆn, setting anisotropic character of all physical properties of the material [3].In nematics the centers of mass of the molecules are unordered, as in isotropic fluids; but the relatively long molecules exhibit an orientational ordering and, locally, seek to remain parallel to one another. In an ideal sample of nematic there is uniform parallel alignment of the molecules, and short-range molecular forces resist any departures from this homogeneous state. Chiral molecules with a liquid crystalline phase exhibit avariation of the nematic ordering [4].It is well known that light-induced molecular reorientation processes may lead to photoinduced anisotropy in macroscopically isotropic media. The photoinduceddichroismandyorbirefringence were already observed in numerous systems containing photoisomerisable molecules. Among various types of chromophoresazobenzenes were intensively studied [5]. Azobenzenes when attached as side groups to main polymer chains show their photochromic properties though the host polymer can seriously modify their properties. It is well known and understood that the influence of polarized light, having a wavelength lying within an absorption band of the azo-benzene groups [6].

Materials and Methods:

Materials: All the chemicals (reagents and solvents) were supplied from Merck, BDH, Fluka and Alfa chemicals Co. and used as received.

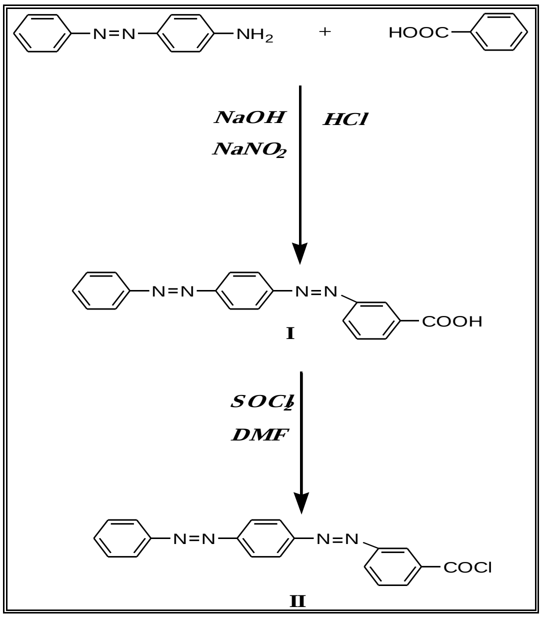
Techniques: The infrared spectra of the prepared compounds were recorded using FTIR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) cm^{-1}. Uncorrected melting points were recorded on hot stage Gallenkamp melting point apparatus. The ^1H NMR spectra were recorded on Brüker ACF 300spectrometer at 300 MHz, using DMSO as solvent with TMS as an internalstandard. Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. Transition temperatures and enthalpies were scanned in TA instruments LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0◦C/min in air and it was calibrated with indium (156.6◦C, 28.45 J/g). The temperatures were read as the maximum of the endothermic peaks. The optical behavior observations were made using MEIJI microscope equipped with INSTEC hot stage and central processor controller mK 1000 and connected with Lumenera color video camera.

Synthesis of phenylene (1-azobenzen)(4,3`-azobenzoic acid) I [7]:

Phenylene (1-azobenzen) (4,3`-azobenzoic acid) was prepared by dissolving 4-amino azo benzene (0.01mol, 1.97g) in acidified distilled water with 3 drops of conc. hydrochloric acid. The nitrous acid was prepared using sodium nitrite (0.7gm) in distilled water then added to the mixture drop by drop . After that diazonium salt was added to the solution of 10% sodium hydroxide and benzoic acid (1.22gm) drop wise, these reactions is done in ice bath (0 – 4)°C.

Synthesis of phenylene (1-azobenzen) (4,3`-azobenzoyl chloride II:

Phenylene (1-azobenzen) (4,3`-azobenzoyl chloride A1 was prepared by reflux the corresponding Phenylene (1-azobenzen)(4,3`-azobenzoic acid) (0.01 mol) with freshly distilled thionylchlorid (10 ml). The excess of thionylchlorid was disstilled off and the acid chloride was directly used, the sequence of the steps shown in the scheme 1. Table 1 shows the melting points and % yield of the synthesized compounds, and Table 2 show the elemental analysis value for the synthesized compound.



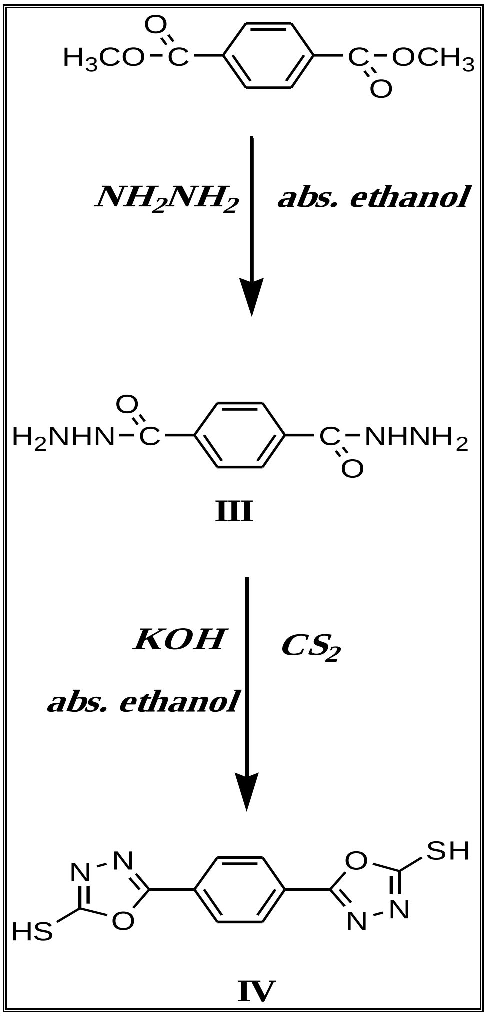
Scheme 1: The steps sequences of acid chloride synthesis

Preparation of terephthalicdihydrazide III:

Terephthalicdihydrazide was prepared by dissolving dimethyl terephthalate (1.94 gm,0.01 mol) in absolute ethanol 15ml in round bottom flask, then hydrazine hydrate (80%, 2ml) was added and reflexed for 4hrs .After that, hrs the solution was cooled to the room temperature and filtered ,the solid white crystals were obtained.

Preparation of 1,4-phenylene-5-bis-(1,3,4-oxadiazole-2-thiol) IV:

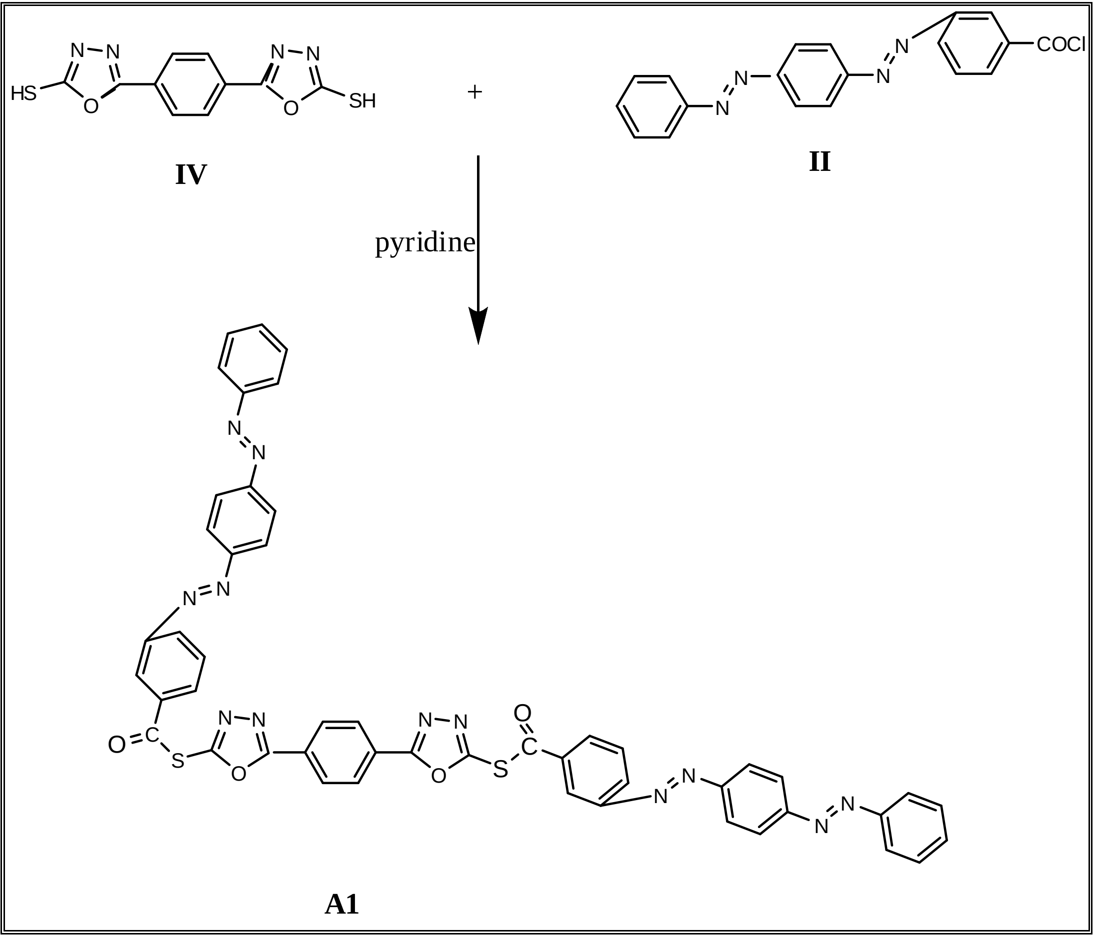
The IV was prepared by dissolving KOH (0.89 gm) in absolute ethanol (7.5 ml), dimethyl terephthalicdihydrazine (0.01mol , 1.5gm) and carbon disulfate (1.5 ml) added drop wise. The mixture, then, was stirred in ice bath till the yellow precipitate was obtained which was dissolved in absolute ethanol (10 ml), then refluxed about 7hrs. The steps of reaction shown in the scheme 2, Table 1 lists the melting points and % yield of the synthesized compounds, Table 2 lists the elemental analysis value for the synthesized compound.



Scheme 2: The steps sequence steps of synthesis 1,4-phenylene-bis-5-(1,3,4-oxadiazole-2-thiol) IV.

Synthesis of A1

Phenylene(1-azobenzen)(4,3`-azobenzoyl chloride II (0.02 mole) and (0.01 mole) of 1,4-phenyl-bis-(1,3,4-oxadiazole-2-thiol) IV with 10 ml pyridine. The mixture was stirred for 3hrs in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water. Table 1 lists the melting points and % yield of the synthesized compounds, Table 2 lists the elemental analysis value for the synthesized compound. These sequence steps are shown in the Scheme below:



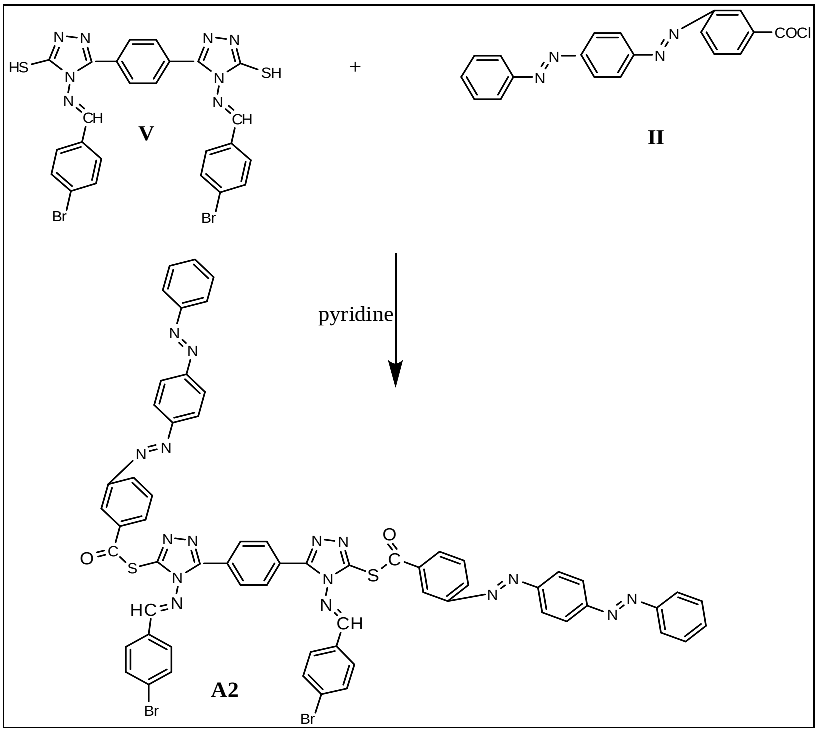
Scheme 3: The sequence steps of A1 synthesis

Synthesis of 4-3`-bromobenzylideneamino-1,2,4-tiazole-2-thiol V:

Compound V was synthesized according to literature [8], by the reaction of compound IV with excess of hydrazine hydrate (80%) which gave 4-amino-1,2,4-triazole-2-thiol, and the last prepared compound undergo condensation reaction with 4-bromobenzaldehyde to affored compound V. Table 1 lists the melting points and % yield of the synthesized compounds, and Table 2 liststhe elemental analysis value for the synthesized compound.

Synthesis A2

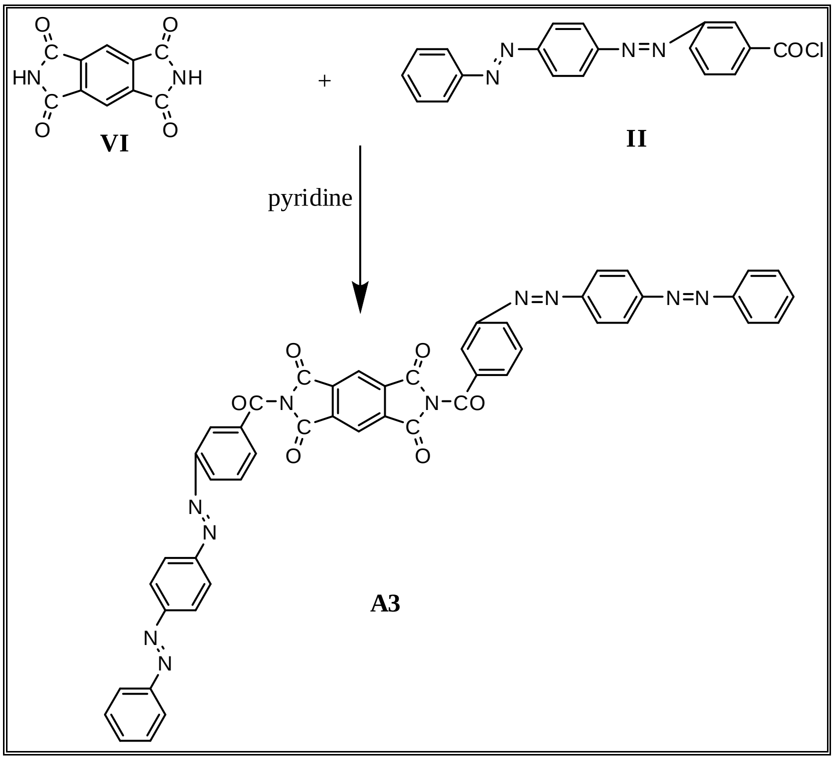
(0.02 mole) of phenylene (1-azobenzen)(4,3`-azobenzoyl chloride II and (0.01mol) of 4-3`-bromobenzylideneamino-1,2,4-tiazole-2-thiol V with 10 ml pyridine. The mixture was stirred for 3hrs in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water. Table 1 lists the melting points and % yield of the synthesized compounds, Table 2 lists the elemental analysis value for the synthesized compound. These sequence steps are shown in the Scheme below:



Scheme 4: The sequence steps of A2 synthesis

Synthesis A3

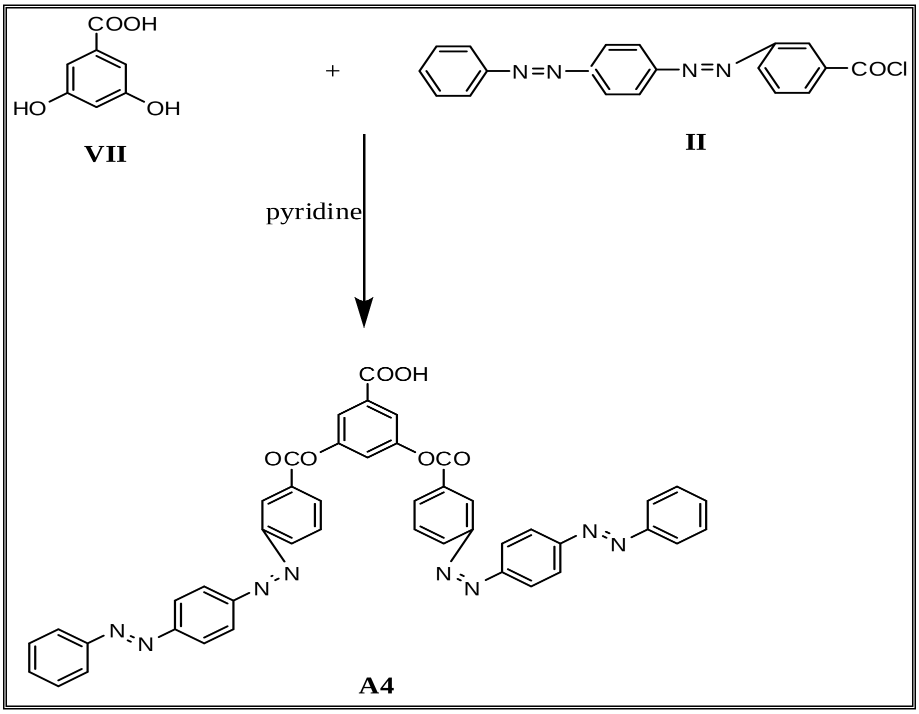
(0.02 mol) of phenylene (1-azobenzen)(4,3`-azobenzoyl chloride II and (0.01 mol) of pyromelitticdiimide with 10 ml pyridine. The mixture was stirred for 3hrs. in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water. Table 1 lists the melting points and % yield of the synthesized compounds, Table 2 lists the elemental analysis value for the synthesized compound. These sequence steps are shown in the Scheme below:



Scheme 5: The synthesis of A3

Synthesis A4

(0.02 mol) of phenylene (1-azobenzen) (4,3`-azobenzoyl chloride II and (0.01mol) of 3,5-di hydroxy benzoic acid with 10 ml pyridine. The mixture was stirred for 3hrs in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water. Table 1 lists the melting points and % yield of the synthesized compounds, Table 2 lists the elemental analysis value for the synthesized compound. These sequence steps are shown in the Scheme below:



Scheme 6: The synthesis of A4

Table (1): Melting points and % yield of synthesized compounds.

Comp.No.	Yield %	m.p (°C)
I	74	150-152
II	90	85-93
III	92	199-201
IV	70	182-183
V	82	174-176
A1	63	115-120
A2	58	200-210
A3	64	170 -180
A4	60	187-190

Table (2): Elemental Analysis (CHNS-O) for synthesized compounds.

Comp. No.	Formula	%C		% H		%N		%S	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
I	$C_{19}H_{14}N_4O_2$	69.09	68.98	4.24	4.17	16.96	16.84	-	-
II	$C_{19}H_{13}ClN_4O$	65.43	65.41	3.73	3.65	16.07	16.11	-	-
IV	$C_{10}H_6N_4O_2S_2$	43.16	42.97	2.15	2.12	20.14	20.11	23.02	23.07
V	$C_{24}H_{16}Br_2N_8S_2$	45.00	45.02	2.50	2.49	17.50	17.54	10.00	9.88
A1	$C_{48}H_{30}N_{12}O_4S_2$	63.85	63.64	3.32	3.35	18.62	18.70	7.09	7.12
A2	$C_{62}H_{40}Br_2N_{16}O_2S_2$	58.86	59.03	3.16	3.11	17.72	17.65	5.06	5.09
A3	$C_{48}H_{28}N_{10}O_6$	68.57	68.87	3.33	3.36	16.66	16.71	-	-
A4	$C_{45}H_{30}N_8O_6$	69.40	69.29	3.85	3.81	14.39	14.18	-	-

Results and Discussion:

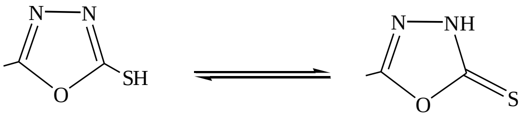
π-Conjugated luminance compounds containing azo group and heterocyclic ring were synthesized to study their photo luminescent properties due to wide range of applications like; information exchange, TV displays, and medical applications [9]. Compound I was synthesized through the azo coupling between 4-aminoazobenzene and benzoic acid in cold alkaline media, the structure of the product was confirmed by FTIR spectroscopy, which displays a broad (O – H) stretching absorption in the region of (3260 cm^{-1}) as well as the carboxylic acid (C = O) absorption at (1690 cm^{-1}).

Compound II was prepared by the internal nucleophilic substitution (SNi) reaction between the prepared phenylene (1-azobenzen)(4,3`-azobenzoic acid) I and thionyl chloride, the FTIR spectrum of this compound shows the disappearance of the broad absorption band in the range (3260 cm-1) together with the appearance of the stretching band around (1782 cm-1) assigned to the acid chloride υ (C = O), are good evidence for the structure given to this compound.

Terephthalicdihydrazide (III) was prepared by reaction of dimethyl terephthalate with hydrazine hydrate. This compound is identified by FTIR spectroscopy. The spectrum, (KBr disc cm-1), shows the appearance of the N - H group of hydrazide at 3459.4, 3272.9 and 3165.1 for asymmetrical and symmetrical stretching. The spectrum also shows bands at 1685.6, 1598.8 and 825.5 due to C=O (amide I), N - H bending (amide II), and out of plane bending of m- substituted respectively.

Compound (III) was converted into the oxadiazole by refluxing with the carbon disulphide in basic media. The mechanism involved oxidative cyclization reaction.

The structure of this compound was elucidated by FTIR spectroscopy. The FTIR spectrum of compound (IV) shows the disappearance of N – H stretching bands and appearance of bands at 1608.5 and 1251.7 due to C = N and C–O–C of (oxadiazole ring). The spectrum revealed a sulphohydryl absorption band S – H at 2740.2 cm-1 and an absorption N – H stretching band at 3201 cm-1 and a new band at 1350 cm-1 due to C = S was observe due to the tiol – thion equilibrium [10]:



(Thiol) I ***(Thion) II***

Fig.(1): thiolthionequlibrium

Reaction of compound (III), with phenylene (1-azobenzen)(4,3`-azobenzoyl chloride), led to prepare compound (A1). The structure of this compound was elucidated on the basis of elemental analysis, FTIR and 1HNMR spectral data. The FTIR spectrum of this compound shows the disappearance of S-H stretching band and detection of strong C=O stretching band at 1720.3 cm^{-1} are evidences for the carbonyl group. 1HNMR (DMSO, δ in ppm): 6.94 (d, 4H, arom. H) for the benzene ring fall between two oxadiazole ring, 8.14-8.17 (d, 8H, arom. H) for the two phenyl group attached to thio ester group, 8.11-8.13 (d, 8H, arom. H) for the two phenyl group fall between two azo group while the terminal two mono substituted benzene ring gave multiplate at 7.46-7.93 (10 H).

Reaction of compound II with 4-4`-bromobenzylideneamino-1,2,4-tiazole-2-thiol V led to the formation of the dimmer A2. The constitution of this product was supported by elemental analysis, FTIR and 1HNMR spectral data. The FTIR spectrum, showed the disappearance of S-H stretching band and detection of strong C=O stretching band at 1723.4 cm-1 are evidences for the carbonyl group. 1HNMR (DMSO, δ in ppm): 7.10-7.14 (two doublet, 4H, arom. H) for the benzene ring fall between two triazole ring, 8.22-8.28 (d, 8H, arom. H) for the two phenyl group attached to thio ester group, 8.18 (d, 8H, arom. H) for the two phenyl group fall between two azo group while the terminal two mono substituted benzene ring gave multiplate at 7.35-7.38 (10 H). The azo methane proton appears as singlet at 8.1 (2H), 7.5-7.9 (d, 8H, arom.) for the bromo m-benzene ring.

Combination between compound (II) and pyromelitticdiimide led to obtain dimmer A3, the structure of this compound was elucidated on the basis of elemental analysis, FTIR and 1HNMR spectral data. The FTIR spectrum of this compound revealed the disappearance of N – H amide stretching and the appearance of C = O stretching at 1686.3 cm-1. 1HNMR (DMSO, δ in ppm): 6.94 (s, 2H, arom. H) for the pyromelittic benzene ring, 8.10-8.16 (d-d, 8H, arom. H) for the two phenyl groups attached to amide group, 8.17-8.19 (d, 8H, arom. H) for the two phenyl groups fall between two azo groups while the terminal two mono substituted benzene ring gave multiplate at 7.39-7.52 (10 H).

The reaction of two equivalents of compound (II) with 3,5-dihydroxy benzoic acid gave compound A4, the structure of this compound was elucidated on the basis of elemental analysis, FTIR and 1HNMR spectral data. The FTIR spectrum of this compound revealed the disappearance of phenolic hydroxyl group and the appearance of carbonyl ester group at 1742.5 cm-1. 1HNMR (DMSO, δ in ppm): 7.20-7.24 (s, 3H, arom. H) for the benzene ring fall between two ester group, 8.05-8.08 (d, 8H, arom. H) for the two phenyl group fall between ester group and azo group, 8.12-8.18 (d, 8H, arom. H) for the two phenyl groups fall between two azo groups while the terminal two mono substituted benzene ring gave multiplate at 7.38-7.42 (10 H). The proton of carboxylic acid group occured as singlet at 12.11.

Table (3): Characteristic FTIR absorption bands of synthesizes compounds(A1-A4).

Comp.No	υ C-H aro.	υN = N	υ C=O	υ C=C	υ C - O	other
A1	3062.1	1421.7	1720.1	1600.2	1241.3	
A2	3065.7	1430.0	1723.4	1598.0	1252.1	1618.8 (CH=N)
A3	3071.3	1428.7	1686.3	1587.6	1242.7	
A4	3067.4	1424.9	1742.5	1600.1	1215.8	3312.5 (COOH)

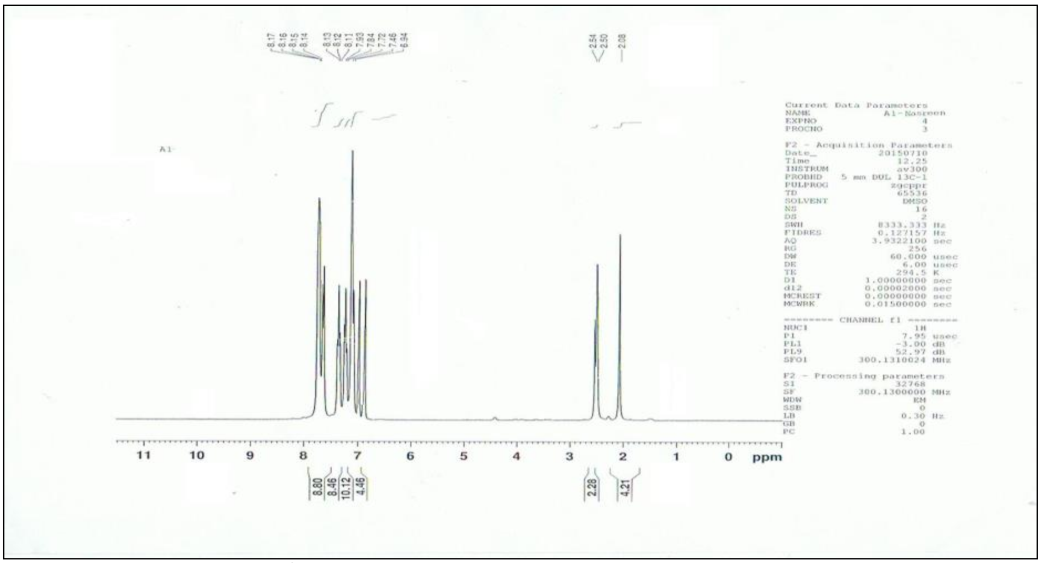


Fig. (2): ^{1}HNMR spectrum of compound A1.

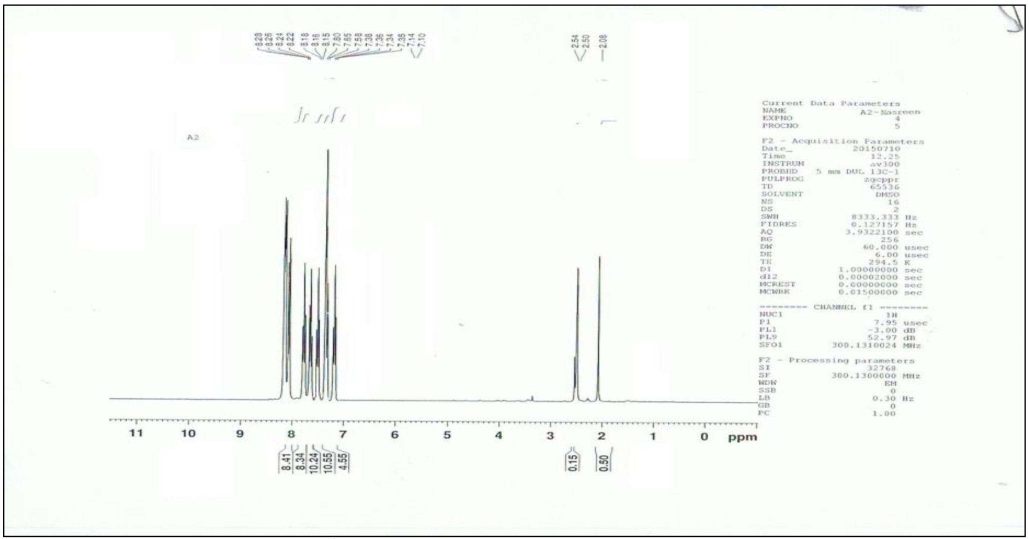


Fig. (3): ^{1}HNMR spectrum of compound A2.

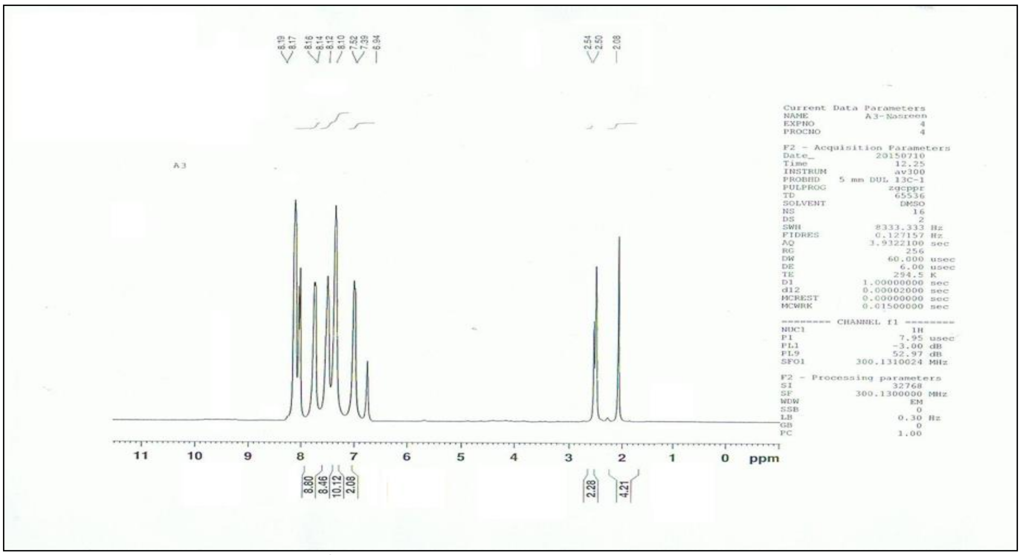


Fig. (4): ^{1}HNMR spectrum of compound A3.

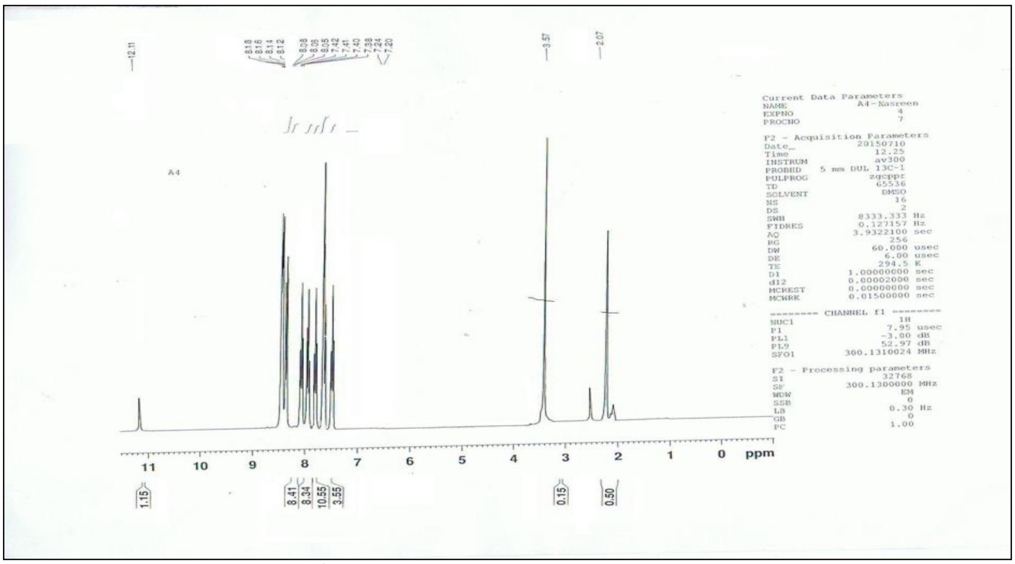


Fig.(5): ^{1}HNMR spectrum of compound A4.

Thermotropic Liquid Crystalline Properties of Synthesized Compounds

It is well known that the type of mesophase (smectic or nematis) is determined mainly by the intermolecular attractions which operate between the slides and planes of the molecules, i.e., the strength of the lateral and terminal attraction forces [11]. The synthesized compound showsSchlieren and thread-like nematic texture, as shown in Figures 6.

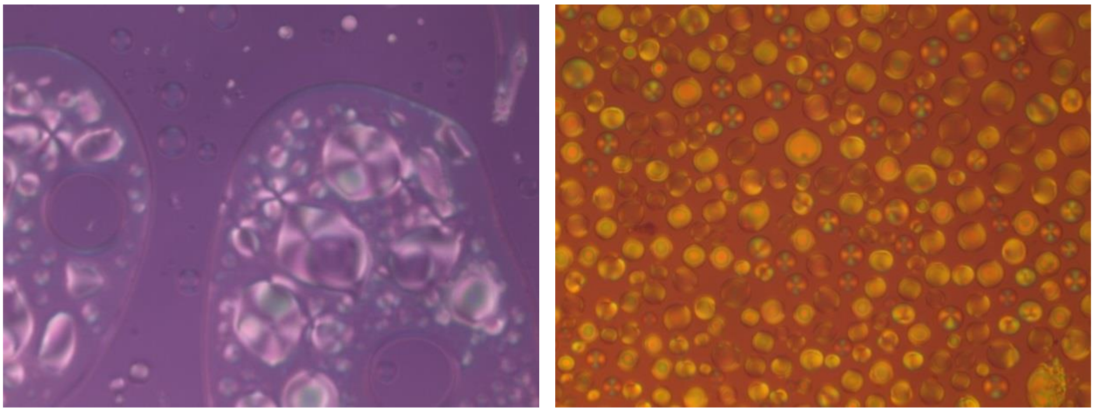


Fig. (6): Nematic texture of A1 and A3.

Absorption and Photoluminescence study:

Absorption and photoluminescence spectrum were studied for the synthesized material to determine the interesting spectral range of operation of these materials to select them for the specific optoelectronic devices.

At the beginning, it was important to determine the absorption spectrum for the selected material. Then, the fluorescence spectra were measured using fluorescence spectrometer. The spectra were recorded by measuring the emissions from the molecule which have been excited either by the whole range radiation directly from the lamp or using different filters. Finally, it was necessary to analyze these spectra to decide the important range for further examinations and future applications.

Absorption Spectra

The absorption spectra for A1, A2 and A3 were recorded by using photospectrometer in the range (190-1200 nm) as shown in Figures (5, 6 and 7) respectively. It can be seen that the absorption spectra of the studied samples are mainly in the ultraviolet range and short wavelengths from the visible range. It is difficult to decide that the three species which appear at the spectra of the first sample are vibronic peaks. The vibronic peaks normally appear when the sample cool down to lower temperatures till 5 K and here, it is necessary to mention that the laboratory temperature were higher than 300K.

Obviously, that the second molecule has wider absorption range than the others. All the molecules are solved in the ethanol. The reason of the broadening spectra in the all studied samples come from the fact the molecules have high molecule weight because the molecules consists of large numbers of carbon and hydrogen atom. The interaction between the ethanol and the molecules could also cause a broadening spectrum.

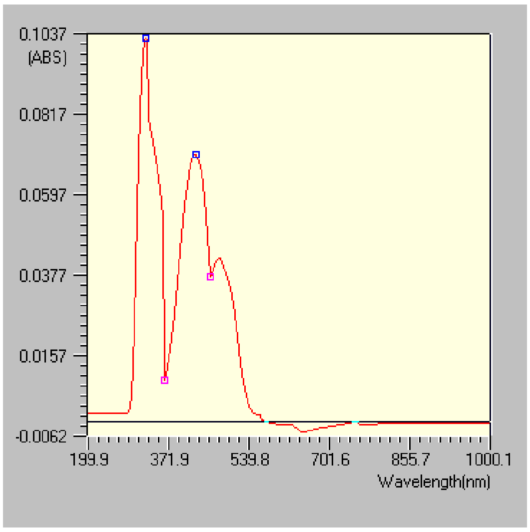


Fig. (7): The absorption spectrum for compound A1

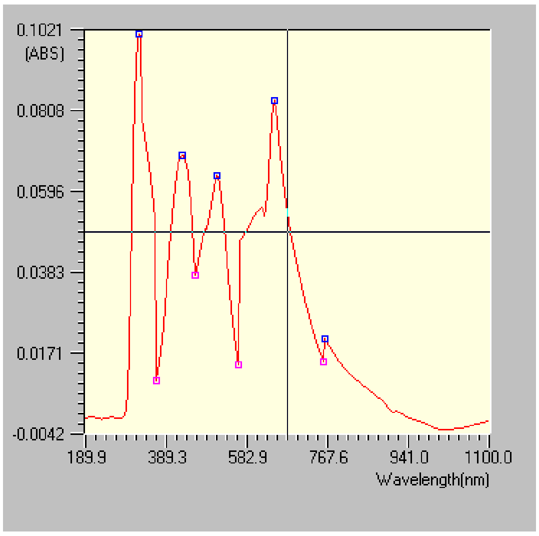


Fig. (8): The absorption spectrum for compound A2

Photoluminesce Spectra

The photoluminesce spectra or the fluorescence measurements have been studied using the fluorescence spectrometer in the range (200-900 nm). Figure (7) shows the emission spectrum for the Xe lamp used to excite the studied samples. If we compared this spectrum by the spectra emitted from compound A1 as shown in figure (7), we observe that the first sample highly absorb at the UV and blue range. There is high emission spectrum at the visible range between (480-800 nm). While the absorption edge for the same sample end at 570 nm. That is fit to the publication [11] where the overlap between the absorption spectrum and the emission spectrum is corresponding to the decay within the higher energy band.

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تحضير وتشخيص مركبات بلورية سائلة عالية التبادل

مروة سهيل حاتم **نسرين رحيم جبر**

قسم الكيمياء ، كلية العلوم ،جامعة النهرين ،بغداد ،العراق

الخلاصة :

تم إعداد مركبات نيتروجينية جديدة عالية الاقتران الثنائيه و البوليمر من السائل البلوري لتحقيق خصائصها البلورية. التي يكون هياكلها على أساس تحليل العناصر، IR 1HNMR وCHNS-O بينما تم تعيين خصائص mesogenic عن طريق DSC والمرحلة الساخنة للمجهر الضوئي المستقطب .تظهر مركبات التي تم تحضيرها الطور الخيطي enantiotropic.

كما تظهر خصائص تلألئ فوتوني عند اذابتها بواسطة المذيبات العضويه في درجة حرارة الغرفة، مع حزمة فلوره تتمحور حول 400 نانومتر.

الكلمات المفتاحية : السائل البلوري الخيطي ، المركبات النيتروجينية عالية الاقتران الثنائية والبوليمر من السائل البلوري.