

Synthesis of new mesogenic Schiff bases ether with polar halogen Substituent and study their liquid crystalline properties

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Abstract

A series of new mesogenic phenolic Schiff bases compounds was successfully synthesized. Schiff bases was prepared by condensation p-vanillin with a p-halo aniline in acidic medium, and the generated compound was reacted with alkyl bromide. The structures of such compounds were confirmed by FT-IR and ¹H-NMR spectrometer. The liquid crystal phases were studied by Differential Scanning Calorimeter (DSC) and polarizing optical microscope with heating. A thermal stability of liquid crystal phases was increased by increasing the length of aliphatic chain to smectic phases and decreasing in the thermal stability of nematic phase. Also, the thermal stability was increasing when the Cl was as terminal group more than Br and I

Keyword: polar group, thermal stability, mesogens, liquid crystal, terminal group .

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الخلاصة :

حضرت سلسلة جديدة من مركبات قواعد شف الفينولية عن طريق تكاثف بارا-فانيلين مع بارا-هالو-انيلين في وسط حامضي، تمت مفاعلة الناتج الرئيسي مع هاليد الكيل اليقاتي. شخضت المركبات المحضرة بجهاز FT.IR وجهاز ¹HNMR. درست الاطوار البلورية السائلة بجهاز مسعر المسح التفاضلي DSC ومجهر الضوء المستقطب المزود بمسخن POM، لوحظ ان الاستقرار الحراري للاطوار البلورية السائلة يزداد بزيادة طول السلسلة الاليفاتية للاطوار السمكتية ويقل الاستقرار الحراري للطور النيماتى وايضاً فان الاستقرار الحراري يزداد عندما يكون Cl كمجموعة طرفية اكثر من Br ، I .

1. Introduction

Organic compounds show thermotropic liquid crystalline properties when the molecules possess rod- or disc-like structure [1]. The stabilizability and polarizability of liquid crystal were two of the most important factors in liquid crystal devices [2]. Researchers have been discovered that small molecules were also capable of exerting a significant impact on the polarizability of the molecular as well as the stabilizability in the liquid crystal compounds [3, 4]. High thermal stability and good optoelectronic properties were also attributed to the resonance stabilization of the Schiff's base unit [5].

With development of liquid crystal science and technology, more mesogens have been prepared and studied. Thermotropic liquid crystal was extensively studied as a type mesogens. Also, it was known as imine (CH=N), which was used as linking group to connect between core groups. It provides a stepped core structure but it still maintains the molecular linearity in order to exhibit higher stability and form mesophases. Azomethine group (CH=N) linkages, which present in the backbone, provide an attractive class of high performance material [6].

One of the important typical terminal exhibiting liquid crystal properties was contained high electronegative, such as halogen groups. Terminal halogens (F, Cl, Br and I) are polar substituents possessing strong dipole moments which promote mesomorphic properties [7, 8]. The molecules

tend to orientate in parallel arrangement. The smectic polymorphism is not unusual for chloro terminal substituent, which has been frequently observed as the alkyl or alkoxy length increase [9].

2. Experimental

Materials:

p-Chloroaniline, p-Bromoaniline, p-Iodoaniline, propyl bromide, pentyl bromide, heptyl bromide, DMF, sodium hydrogen carbonate, glacial acetic acid, and Absolute ethanol were purchased from. All these components were in ACS grade or higher.

Characterization:

The melting point measurements were done using apparatus Griffin -Made in Britain-London - Serial NO. 90-01-154. IR spectra were obtained using Shimadzu Fourier transform infrared spectrometer FT-IR 8400S (KBr) scale (4000-400). CHN.O was acquired using Evrovector EA 3000A Italy. ¹HNMR spectrum was recorded Using Ultra shield 300 MHZ Bruker 2003. The liquid crystalline properties were measured using Differential Scanning Calorimeter (DSC-60) Shimadzu, polarizing optical microscope type (BEAM ENGINEERS (INDIA)).

Synthesis:

I. Preparation of n-alkyl bromide (RBr) [10].

2 mole of HBr hydrobromic acid 48% and 1mole of H₂SO₄ Sulphoric acid were placed in 500 ml round flask. As a result, some hydrogen bromide may be evolved. After that, 1mole of n-alkyl alcohols (alkyl = propyl, pentyl and heptyl) was added to the flux followed by 0.5 mole of H₂SO₄ under shaking.

The mixture was refluxed for 2-3 hours and then the distillation product was moved to the separator funnel in order to remove the halide. Then, the product was washed successively with several solvents individually, such as (water, an equal volume of concen-

trated HCl, water, 5% NaHCO₃ and water. The water was removed completely as possible then dried with 2-3 gm of anhydrous calcium chloride (CaCl₂). The final product was collected as pure and colorless product as shown in Table 1.

Table 1: the properties of alkyl bromide

Compound	B.p	Color	Yield
propyl bromide	70-72	colorless	76%
pentyl bromide	128-130	colorless	81%
heptyl bromide	179-180	colorless	83%

II. Synthesis of Schiff base (IIa-IIc) [11]

0.01mole of 3-Methoxy-4-hydroxybenzaldehyde (p-vanillin) was dissolved in 50 ml of absolute ethanol. After that, some drops of glacial acetic acid and 0.02mole of p-x-aniline were added to the mixture with a refluxed for 6-7 hours. The product was cooled, filtrated, and recrystallized from the absolute ethanol.

III. Synthesis of ether (IIIa-IIIi) [12]

0.01 mole of the compound prepared previously was dissolved (1-3) in 30ml of DMF in a conical flask. Then, 0.02 mole of sodium hydrogen carbonate was added to the mixture. The mixture was reflux for 30 minute. After that, 0.025mole of alkyl halide, such as propyl bromide, pentyl bromide and heptyl bromide was added to the main mixture in order to prepare three different final products varied in the length of the alkyl halide. The reflux was continued on oil bath at 130°C for 10-12 hours. The mixture is cooled and added to ice water.

The products obtained was filtered, washed with water and diethyl ether then recrystallized from DMF.

1) Results and discussion

A new series of Schiff bases was prepared as showed fig. 1

3.1 The Phenolic Schiff bases (IIa-IIc)

The preparation of the phenol Schiff base compounds is described in the Experimental section. The infrared spectra, which displayed characteristic bands in the (1615-1644) cm⁻¹ region was attributed to the presence of the Schiff base group (-CH=N), hence it provides the completion of the reaction between the NH₂ and C=O groups.

IIa 4-(((4-chlorophenyl) imino) methyl)-2-methoxyphenol

Properties: Yield = 83 %, orange color
m.p = (163-166) °C

IR (KBr, cm⁻¹): 3056 cm⁻¹ (C - H Aromatic, 2876 cm⁻¹ (C - H Aliphatic 1493/1547 ,) cm⁻¹ (C = C Aromatic), 1627 cm⁻¹ (C=N), 3409 cm⁻¹ (OH), 1237 cm⁻¹ asym. 1091 sym cm⁻¹ (C-O-C).

I Ib 4-(((4-bromophenyl) imino) methyl)-2-methoxyphenol

Properties: Yield = 80 %, yellow color
m.p = (153-154) °C

IR (KBr, cm⁻¹): 3041 cm⁻¹ (C - H Aromatic, 2894 cm⁻¹ (C - H Aliphatic 1506/1581 ,) cm⁻¹ (C = C Aromatic), 1618 cm⁻¹ (C=N), 3438 cm⁻¹ (OH), 1271 cm⁻¹ asym. 1135 sym cm⁻¹ (C-O-C). 1622 cm⁻¹ (C=N).

¹H NMR (300 MHz, DMSO-d) δ /ppm: 3.68 (s, 3H, CH₃ Aliphatic proton), 6.74-7.90 (m, 7H, Aromatic benzene), 8.50 (m, 1H, CH=N), 9.76 (m, 1H, OH Phenol). As shown in fig. 16.

I Ic 4-(((4-iodophenyl) imino) methyl)-2-methoxyphenol

Properties: Yield = 75 %, lightly yellow color
m.p = (149-151) °C

IR (KBr, cm⁻¹): 3017 cm⁻¹ (C - H Aromatic, 2854 cm⁻¹ (C - H Aliphatic 1517/1572 ,) cm⁻¹ (C = C Aromatic), 1631 cm⁻¹ (C=N), 3448 cm⁻¹ (OH), 1255 cm⁻¹ asym. 1121 sym cm⁻¹ (C-O-C).

3.2 Series of ethers (IIIa-IIIi)

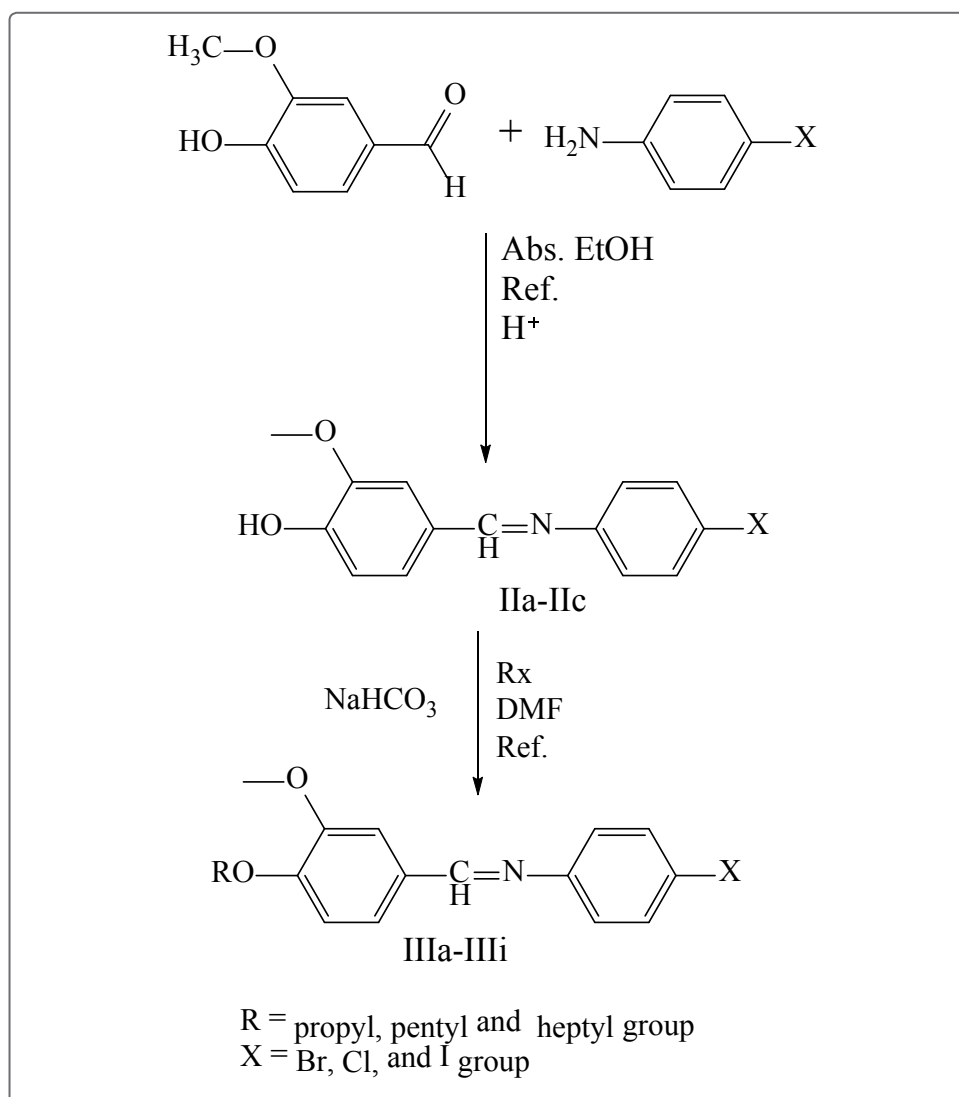
Some physical properties of the compounds in this series were showed in table 2

In the study of infrared spectra (IR), the absorption package of OH group at range (3409-3448) was disappeared and the absorption package of Ar-O-C group was appeared at range (symmetric 1012-1063 and asymmetric 1176-1227) as show in table: 3

The ¹HNMR spectra was studied using DMSO-d as a solvent and measured in standard units expressed by ppm to (a) compound. Multiple signals within the range (7.04-8.02) ppm was appeared belong to the aromatic ring protons, a single signal at (8.58) ppm was obtained for the proton of the azomethine group (N=CH). Also, a single signal at (3.89) ppm was belonged to the protons of (CH₃) group in ortho position. The alkyl group protons showed in the table 4:

Table 4: position of alkyl group protons

alkyl	Type of single	Position (ppm)
CH ₂	t	4.30
CH ₂	p	1.81
CH ₃	t	0.85

**Table2: physical properties of Schiff bases compounds**

Comp. No.	R	X	Yield %	m.p. °C	Colour
	Propyl	Cl	78	186-187	Orange
	Pentyl		74	174-176	Deep yellow
	heptyl		71	164-165	Yellow
	Propyl	Br	76	163-164	Yellow greenish
	Pentyl		69	151-153	Yellow
	heptyl		73	139-141	Lightly yellow
	Propyl	I	68	166-168	Yellow
	Pentyl		65	156-157	Orange
	heptyl		69	145-147	Orange

Table 3: the absorption pack of (IR) spectrum to the prepared compounds

Comp. No.	R	X	C=C Ar	C-H Ar	C-H aliph.	C=N	C-O-C Sym-asy
	Propyl	Cl	1476-1548	3023	2889	1617	1048-1227
	Pentyl		1568-1596	3041	2873	1631	1089-1157
	heptyl		1516-1571	2997	2912	1626	1063-1214
	Propyl	Br	1469-1556	2971	2931	1615	1012-1197
	Pentyl		1506-1596	3046	2856	1621	1027-1201
	heptyl		1489-1591	3018	2871	1628	1018-1176
	Propyl	I	1444-1583	2948	2862	1644	1089-1157
	Pentyl		1499-1581	2986	2933	1619	1032-1187
	heptyl		1509-1577	2991	2891	1627	1013-1219

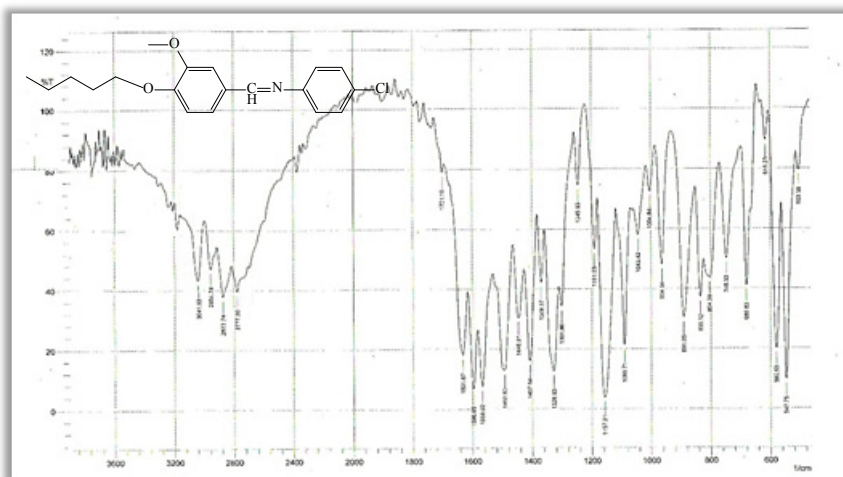


Fig. 2: IR spectrum of the compound IIb

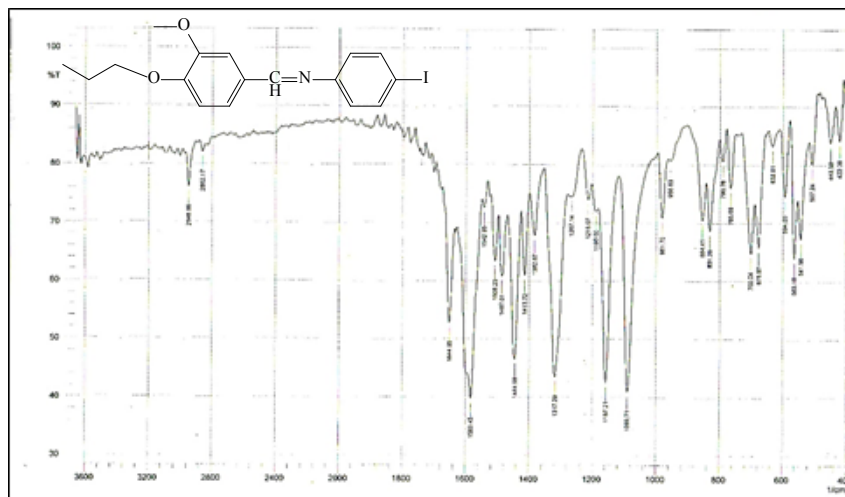


Fig. 3: IR spectrum of the compound IIg

the enthalpy (ΔH) because it involves the transition from a phase of three-dimensional to a phase of molecular regulation with a shorter duration. Whereas the phenol Schiff bases did not show any liquid crystalline behavior, but simply changed from a solid to an isotropic fluid. The phenol Schiff bases possess rigid cores and two aromatic rings in their structures, but the insufficient rigidity, which caused by the presence of a OH group will interrupt the conjugation (resonance). This leads to less delocalization and hence the failure to display liquid crystal behavior [13].

Compounds that exhibit liquid crystalline behavior were produced due to their high aspect ratio (length to breadth ratio). The polarized optical microscope (POM) images for all obtained compounds were done as shown in Figures (6-10). It is worth mentioning that similar studies had been done on liquid crystals with two aromatic rings in the rigid core. When a three, five and seven carbon alkyl chain was added to its terminal end, they did exhibit liquid crystal phases. The addition of the flexible chain length decreased the melting point of these compounds. This observation is supported by the previous research [14, 15]. The lateral substituents introduced into mesogen molecules depress the thermal stability of the mesophases. It is appeared due to the overall anisotropic broadening of the molecule, which influence cooperative packing needed in the structures that form mesophase [16,17].

It was observed that compound with X substituent attached to the ter-

minal aromatic ring system showed higher thermal properties. This observation was due to the presence of the halogen groups, which caused thermal suppression of the molecule [18], thus, it let to lower the melting temperature of the compounds. Moreover, these substituents are capable of reducing the planarity of adjacent mesogenic groups and increasing the diameter or decreasing the axial ratio of the mesogens.

The effect of a flexible substituent in depressing the mesophase stability is significant in more ordered phases such as smectics than nematics [19]. The alkylation of the flexible chain gives a larger smectic phase range when it was added at the terminal end (located as far as possible from the rigid part of the molecule) [20]. The effect of adding the length of flexible chain had limitation, so further addition of the carbon chain length can increase the transition temperatures.

The liquid crystal transition of the nematic to the isotropic involves the least transition. By observing the figures (11-13) of the DSC and the results of the tests of the microscope with heater as shown in tables 5 and figures (6-10), the above compounds showed a smectic and nematic phases with a high thermal range. This may be attributed to the presence of two aromatic rings in the molecular structure of these compounds giving the appropriate elongation molecule as well as the expansion of the electronic sequence along the axis of the molecule. Such increases in the variation of the molecular polarization result from

the peripheral gravitational forces of the dipole-dipole type, which include the attraction between the groups of the alkoxy and halogen, which confirmed helping the appearance of liquid crystals.

It was observed that the thermal range of the nematic phase decreased by increasing the length of the aliphatic chain attributed to the decrease of the peripheral gravitational forces with the stability of the particle width molecule. The appearance of the smectic phases of these compounds was observed due to the presence of lateral gravitational forces and increasing the ther-

mal range of the smectic phases by increasing the length of the aliphatic chain [21, 22]. Also, Schiff bases, which contain the Cl as terminal group, showed more thermal stability when compared with Br and I groups because of high polarity of Cl group. When comparing the results, it was observed that the thermal stability of the prepared compounds was increased in smectic phases by increasing length of aliphatic series. Also, the thermal stability of liquid crystal effected by increasing the polarity in the trend of $Cl > Br > I$, which consistent with the literature [23, 24].

Table 5: Liquid crystal phases transition of DSC and Microscope

Apparatus	NO.	R	X	Crystal	Smectic _A	S _B	S _C	Nematic	ΔT _{SA}	ΔT _{SB}	ΔT _{SC}	ΔT _N
DSC	a	Propyl	Cl									
Microscope				186			219	245			33	26
DSC	b	Pentyl										
Microscope				175	186	206		223	11	20		17
DSC	c	heptyl		164			222	233			58	11
Microscope				167			224	235				
Apparatus	NO.	R	X	Crystal	Smectic _A	S _B	S _C	Nematic	ΔT _{SA}	ΔT _{SB}	ΔT _{SC}	ΔT _N
DSC	d	Propyl	Br	164	173		218	257	9		45	39
Microscope				166	176		221	258				
DSC	e	Pentyl										
Microscope				152	179	193			27	14		
DSC	f	heptyl										
Microscope				140	163		178	194	23		15	16
Apparatus	NO.	R	X	Crystal	Smectic _A	S _B	S _C	Nematic	ΔT _{SA}	ΔT _{SB}	ΔT _{SC}	ΔT _N
DSC	g	Propyl	I									
Microscope				167				216				
DSC	h	Pentyl		157	173		198	241	16		25	43
Microscope				159	174		201	240				
DSC	i	Heptyl										
Microscope				146								

4. Conclusions

A series of Schiff bases compounds with various alkyl chain lengths (3, 5 and 7), was successfully synthesized. The prepared compounds were found to demonstrate enantiotropic nematic and smectic phase based on the POM and DSC observations. However, (IIa-IIc and IIIi) did not exhibit any liquid crystalline phase. DSC and POM

analyses showed that the increase in alkyl chain length in Schiff bases results due to the decrease in the transition temperature for nematic phases. It was also observed that the halogen as terminal group led to increase in thermal stability in liquid crystal compounds by increasing polarity of halogen. In addition, the thermal stability of smectic phases was increased by increasing the length of terminal groups.

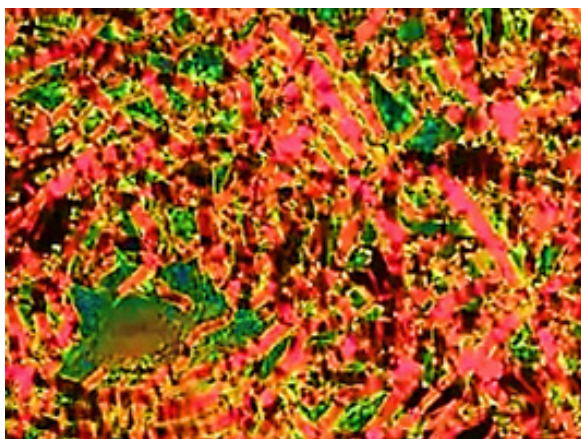


Fig. 7: SC for comp. IIIc

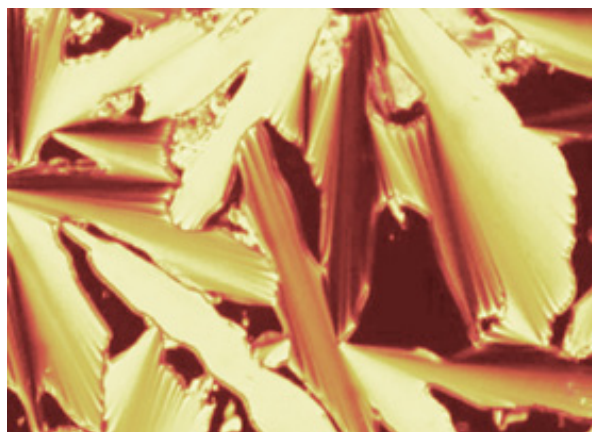


Fig. 6: SA for comp. IIIb

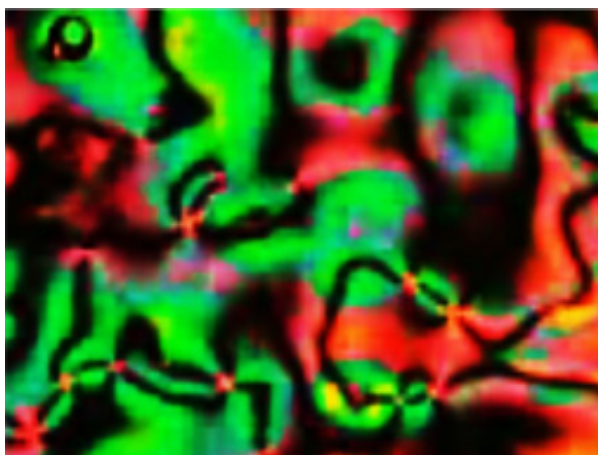


Fig. 9: N for comp. IIIf

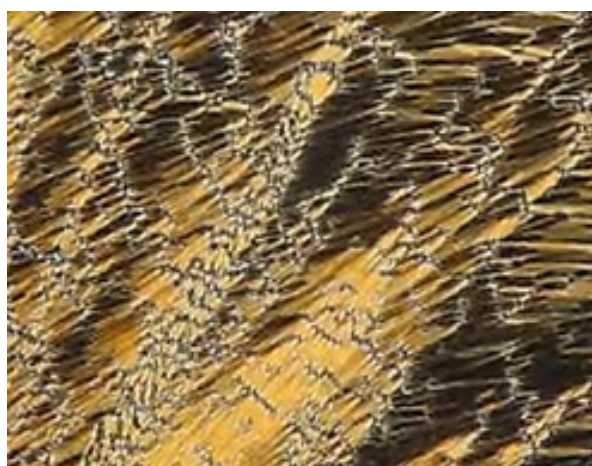


Fig. 8: SC for comp. IIIId

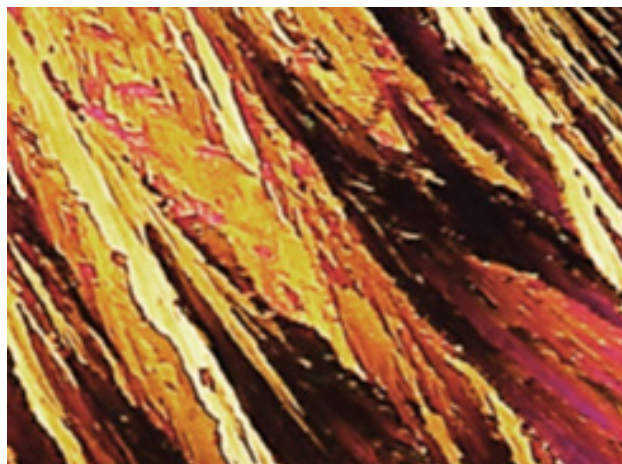


Fig. 10: SA for comp. IIIh

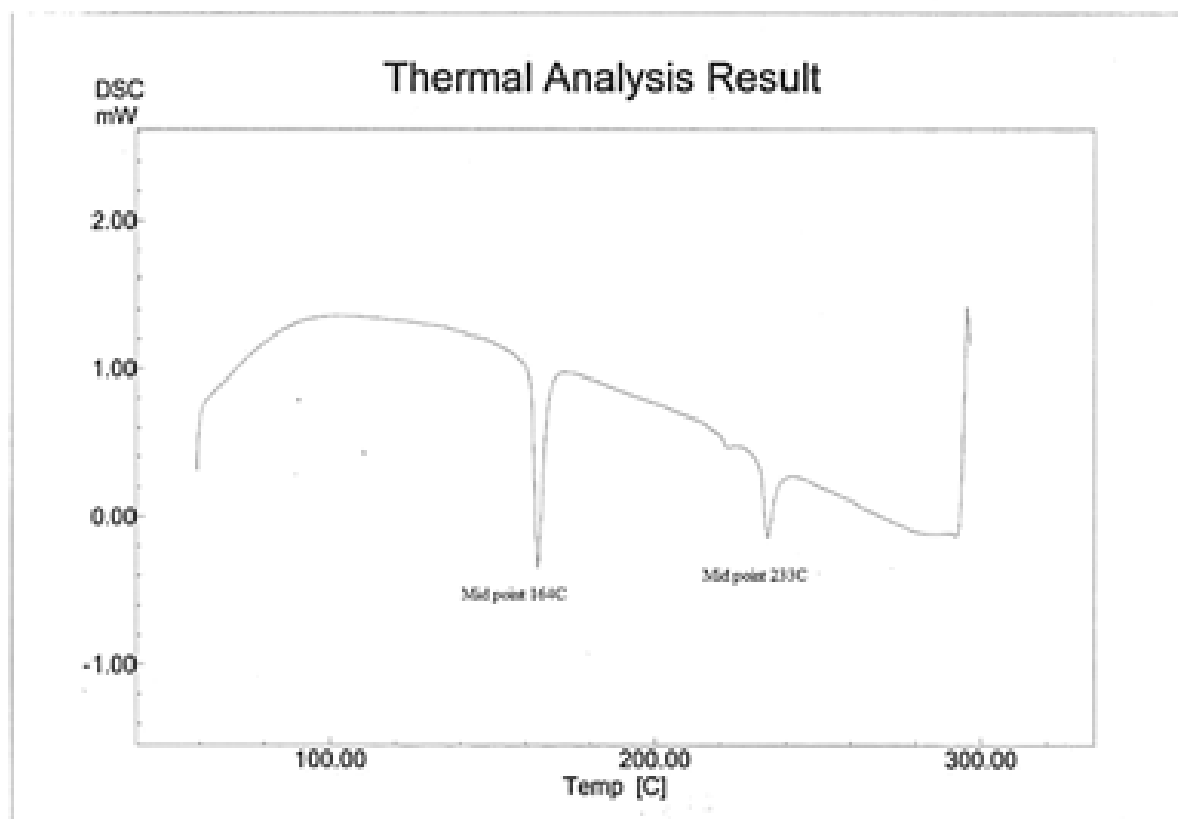


Fig. 11: DSC of the compound IIIc

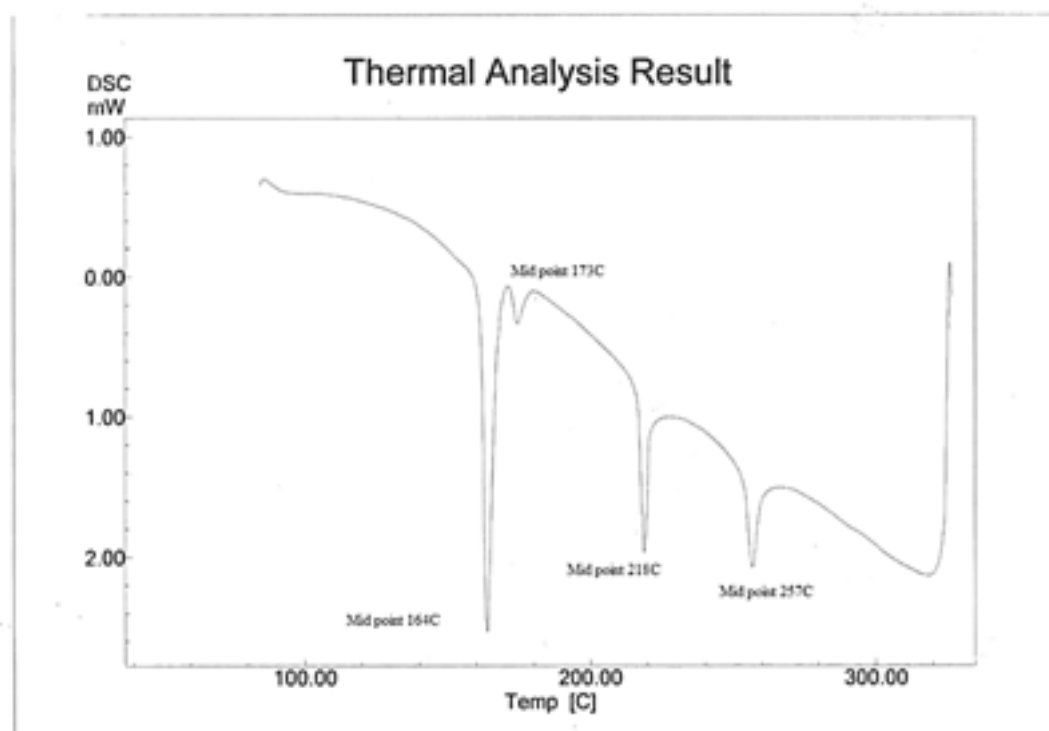


Fig. 12: DSC of the compound IIIId

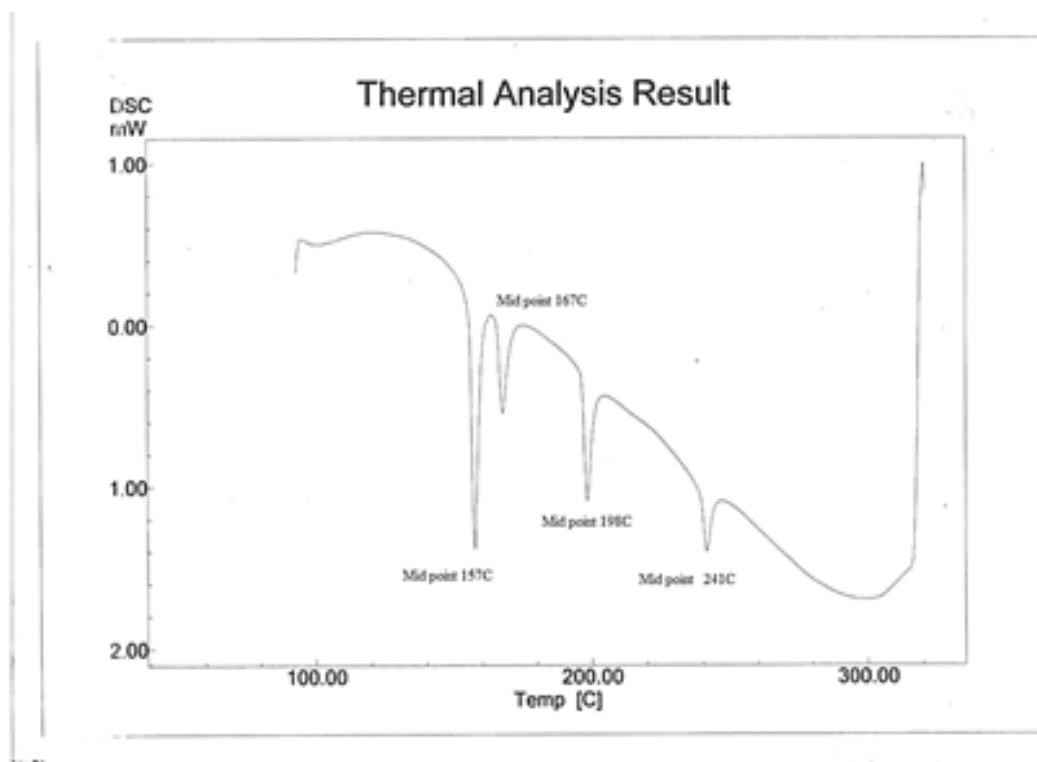


Fig. 13: DSC of the compound IIIh

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