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Impact of Intermediate and Terminal Groups on the Thermal Stability of Bent-Core Liquid Crystals

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1) Introduction

Liquid crystals are intermediate states between crystals and isotropic liquids and thus having intermediate physical properties between them[1-3]. Actually, a variety of liquid crystalline phases consisting of a rod like and disc like molecules that have been discovered. Particularly, rod like molecules showing the nematic phase and have widely been studied because of their application to flat panel displays [4].

Liquid crystals have a long-range orientational order, molecular symmetry axes, and the long axes of rod like molecules and the disc like molecules align on average in a particular direction. This average molecular direction is called a director, and the orientational order parameter is defined by the molecular orientational distribution around the director. Since the rotation about the symmetry axis does not affect the order parameter, liquid crystal molecules normally rotates freely along this symmetry axis, unless there is no symmetry requirement. From this viewpoint, molecules with shapes deviating from a rod, such as board or bent shape, have been thought as bad molecules for forming liquid crystals. If such molecules, freely rotate about their long molecular axes, the excluded

Abstract

A series of new mesogenic chalcone, azomethine and azo compounds were successfully synthesized. A chalcone was prepared via condensation of isophthaldehyde with a p-hydroxyacetophenone in a basic medium, Schiff bases was prepared by condensation isophthaldehyde with a p-hydroxyaniline in acidic medium. While azo compound was obtained by a reaction of m-diaminobenzen with NaNO₂ and phenol, 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 were increased by increasing the length of aliphatic chain to smectic phases and decreasing in the thermal stability of nematic phase. It has been observed that the thermal stability of liquid crystal in chalcone compounds were higher than others, azo and azomethine compound.

> volume becomes large leading to violate the liquid crystalline. For these reasons, only a very few bentcore molecules have been synthesized before the discovery of their polar switching [5].

Bent-core (BC) mesogens represent a novel class of thermotropic liquid crystals (LCs) [6] First synthesis of bent-shaped liquid crystals has been reported previously (seventy years ago) by Vorlander [7]. However they have not attracted much interest until the synthetic work of Matsunaga [8] in the early of 1990, the discovery of the mesogenic properties of bent-core molecules has opened up a major new and exciting dimension in the science of thermotropic liquid crystals (LCS). There are a broad implications for the general field of soft condensed matter including the observation of Ferro electricity and spontaneous breaking of chiral symmetry in smectic phases composed of molecules that are not intrinsically [9]. An increase in the temperature, liquid crystal phases in bent-core mesogens appear different from what is commonly known. Banana mesogens take the form of a smectic C. As shown in Fig. 1 [10].



Fig. 1: Banana mesogens

Pure bent-core compounds are usually have a liquid crystalline phases above the room temperature which limits their usability for many applications [11].

2) Experimental work

The melting points were recorded by apparatus Griffin - Made in Britain-London - Serial NO. 90-01-154.IR spectra were recorded using Shimadzu Fourier transform infrared spectrophotometer FT-IR 8400S (4000-400)¹HNMR (KBr) scale spectrum was recorded Using Ultra shield 300 MHZ Bruker 2003. Studying of liquid crystalline properties was out by using Differential carried Scanning

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Calorimeter (DSC-60) Shimadzu, polarizing optical microscope type (BEAM ENGINEERS (INDIA)). **General Procedure**

I. Preparation of n-alkyl bromide (RBr) [12].

In 500ml round flask put 2 mole of HBr hydrobromic acid 48% and 1mole of H₂SO₄ Sulphoric acid and some hydrogen bromide may be evolved, 1mole was added of n-alkyl alcohols (alkyl = propyl, pentyl and heptyl), followed by 0.5 mole of H_2SO_4 with shaking. The mixture was refluxed to 2-3 hours and then the distillation product will be moved to the separator funnel to remove the halide. Then, wash it successively with water, an equal volume of concentrated HCl, water, 5% NaHCO3 and water. Separating the water as completely as possible and drying it with 2-3 gm. of anhydrous calcium chloride (CaCl₂). The product was collected the 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%	



Fig. 2: synthesis steps of prepared compounds

II. Synthesis of Chalcone (1) [13]

Chalcone was synthesized a basic catalyzed claisenschmidt condensation reaction of appropriately substituted acetophenone and aldehydes via a known literature method.

A mixture of isophthaldehyde 0.01mole and 10ml of 20% NaOH was dissolved in the ethanol and was IV. Synthesis of azo compounds (3) [15] added to the mixture 0.02mole of p-hydroxy acetophenone. After that, the mixture is put on the ice-water bath and stirrer for 5-6 hours. The reaction mixture was neutralized by (0.1- 0.2) N of HCl whereby the precipitation occurred, filter the crude chalcone and recrystallized from 95% ethanol.

III. Synthesis of Schiff base (2) [14]

Dissolving 0.01 mole of isophthaldehyde in 30 ml of absolute ethanol was added with some drop of glacial acetic acid and 0.02mole of p-hydroxyaniline with a refluxed for 6-7 hours. The product was cooling then filtration process and recrystallized from the absolute ethanol.

0.02 mol of phenol was weight and dissolved into 10% sodium hydroxide solution. The mixture was stirred until completing as the dissolution access than cooling the solution with an ice-water bath.

The benzenediazonium salt solution can be prepared by Dissolving 0.02 mol of NaNO2 in 5 ml of water. 0.001 mol of m-diaminobenzen was putting into 45 ml of water in a 100 ml conical flask after that 12 ml of concentrated hydrochloric acid was slowly added and stir the mixture until the m-diamino benzene is dissolved completely. Cooling the solution in an icebath. While keeping the solution at 0 °C added the sodium nitrate solution NaNO2 (eq) slowly with a dropper. The mixture should be well-stirred during addition. When the addition is completed, the mixture was stirred for another 2 - 3 minutes.

The alkaline phenol solution was added the benzenediazonium salt solution. The reaction mixture should efficiently be stirred and cooled on an ice-water bath during the addition. When the addition is completed, stir the mixture at 0 °C for 20 - 30 minutes. The mixture is filtered via suction filtration. Washing the solid product on the Buchner funnel with a small amount of cold water. Recrystallized from 85% ethanol.

V. Synthesis of ether (a-i) [16]

Dissolving 0.01 mole of one compounds were prepared (1, 2 and 3) in 30ml of DMF in a conical flask and added to the mixture with 0.02mole of sodium hydrogen carbonate. The mixture was reflux to 30 minute then was added 0.025mole of alkyl halides (propyl bromide, pentyl bromide and heptyl bromide). The reflux was continued on oil bath at 130°C with 10-12 hours. The mixture is cooled and added to ice water. The products obtained was filtered, washed with water, diethyl ether and recrystallized from DMF.

3) Results and discussion

Diagnosis of organic compounds

3:1 Diagnosis of Chalcone

Properties: Yield = 79%, yellow color m.p = (208-210) $^{\circ}$ C

IR (KBr, cm⁻¹) [17]: 3041 cm⁻¹ (C – H Aromatic), 1509/1583 cm⁻¹ (C = C Aromatic), 1702 cm⁻¹ (C=O), 1647 cm⁻¹ (C = C Aliphatic), 3319 cm⁻¹ (OH).

3:2 Diagnosis of Schiff base

Properties: Yield = 83%, yellow color m.p = (148-150) °C

IR (KBr, cm⁻¹): 3018 cm⁻¹ (C – H Aromatic, 1486/1579 cm⁻¹ (C = C Aromatic), 1616 cm⁻¹ (C=N), 3347 cm⁻¹ (OH).

3:3 Diagnosis of azo compound

Properties: Yield = 84%, deep yellow color m.p = (181-183) °C

IR (KBr, cm⁻¹): 3068 cm⁻¹ (C – H Aromatic), 1513/1601 cm⁻¹ (C = C Aromatic), 3301 cm⁻¹ (OH).

a- 3,3-(1,3-phenylene)bis(1-(4-(propoxy)phenyl) prop-2-en-1-one

Properties: Yield = 59%, yellow color m.p = (182-184) $^{\circ}$ C

IR (KBr, cm⁻¹): 1263 cm⁻¹ asym. 1016 sym cm⁻¹. (C– O–C), 3028 cm⁻¹ (C – H Aromatic), 2916 cm⁻¹ (C – H

Aliphatic) , $1566/1602 \text{ cm}^{-1}$ (C = C Aromatic), 1672

cm^{-1} (C=O), 1651 cm^{-1} (C = C Aliphatic.)

 ^1H NMR (300 MHz, DMSO-d) $\delta/\text{ppm:}$ 0.87 (s, 6H, CH_3 Aliphatic proton), 1.56 (m, 4H, CH_2 Aliphatic

proton), 3.79 (s, 4H, CH_2 Aliphatic proton), 6.68-8.24 (m, 12H, Aromatic benzene), 8.25 (m, 2H, C=C), 7.26 (m, 2H, C=C). As shown in fig. 15.

b- 3,3-(1,3-phenylene)*bis*(1-(4-(pentyloxy)*phenyl*) *prop-2-en-1-one*

Properties: Yield = 62%, orange color m.p = (171-173) °C

IR (KBr, cm⁻¹): 1242 cm⁻¹ asym. 1089 sym cm⁻¹ (C– O–C), 3047 cm⁻¹ (C – H Aromatic), 2908 cm⁻¹ (C – H Aliphatic), 1520/1576 cm⁻¹ (C = C Aromatic), 1696

 cm^{-1} (C=O), 1655 cm^{-1} (C = C Aliphatic.)

c- 3,3-(1,3-phenylene)bis(1-(4-propoxyphenyl) prop-2-en-1-one

Properties: Yield = 65%, yellow color m.p = 164° C IR (KBr, cm⁻¹): 1265 cm⁻¹ asym. 1101 sym cm⁻¹ (C– O–C), 3028 cm⁻¹ (C – H Aromatic),2925 cm⁻¹ (C – H Aliphatic) , 1500/1580 cm⁻¹ (C= C Aromatic), 1705 cm⁻¹ (C=O), 1639 cm⁻¹ (C = C Aliphatic). as shown in fig 11.

d- 1,1-(1,3-phenylene)bis(N-(4-(propoxy) phenyl)methanimine

Properties: Yield = 68%, yellow color, m.p = (117-119) °C

IR (KBr, cm⁻¹): 1271 cm⁻¹ asym. 1088 sym cm⁻¹ (C– O–C), 3062 cm⁻¹ (C – H Aromatic),2895 cm⁻¹ (C – H Aliphatic) , 1591/1602 cm⁻¹ (C = C Aromatic), 1635 cm⁻¹ (C=N).

e- 1,1-(1,3-phenylene)bis(N-(4-(pentyloxy) phenyl)methanimine

Properties: Yield = 71%, Light yellow Color, m.p = (112-114) °C

IR (KBr, cm⁻¹): 1280 cm⁻¹ asym. 1073 sym cm⁻¹ (C– O–C), 3020 cm⁻¹ (C – H Aromatic),2908 cm⁻¹ (C – H Aliphatic) , 1595/1610 cm⁻¹ (C = C Aromatic), 1622 cm⁻¹ (C=N).

¹H NMR (300 MHz, DMSO-d) δ /ppm: 0.72 (m, 6H, CH₃ Aliphatic proton), 1.38 (m, 8H, CH₂-CH₂ Aliphatic proton), 1.82 (m, 4H, CH₂ Aliphatic proton), 3.83 (m, 4H, CH₂ Aliphatic proton), 6.53-8.43 (m, 12H, Aromatic benzene), 8.50 (m, 2H, CH=N). As shown in fig. 16.

f-1,1-(1,3-phenylene)bis(N-(4- heptyloxy phenyl) methanimine

Properties: Yield = 75%, Orange color m.p = (103-105) $^{\circ}$ C

IR (KBr, cm⁻¹): 1271 cm⁻¹ asym. 1048 sym cm⁻¹ (C– O–C), 3062 cm⁻¹ (C – H Aromatic),2895 cm⁻¹ (C – H Aliphatic) , 1591/1602 cm⁻¹ (C = C Aromatic), 1635 cm⁻¹ (C=N).

g- 1,3-bis((Z)-(4-propoxyphenyl)diazenyl)benzene

Properties: Yield = 62%, deep yellow color m.p = (166-168) °C

IR (KBr, cm⁻¹): 1240 cm⁻¹ asym. 1107 sym cm⁻¹ (C– O–C), 3074 cm⁻¹ (C – H Aromatic), 2951 cm⁻¹ (C – H Aliphatic) , 1586/1599 cm⁻¹ (C = C Aromatic), 1538 cm⁻¹ (N=N).

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¹H NMR (300 MHz, DMSO) δ /ppm: 0.65 (s, 6H, CH₃ Aliphatic proton), 1.66 (m, 4H, CH₂ Aliphatic proton), 3.88 (s, 4H, CH₂ Aliphatic proton), 6.93-8.48 (m, 12H, Aromatic benzene). As shown in fig. 17.

h- 1,3-bis((*Z*)-(4-(*pentyloxy*)*phenyl*)*diazenyl*) *benzene*

Properties: Yield = 63%, organic color, $m.p = (158-160) \degree C$

IR (KBr, cm⁻¹): 1247 cm⁻¹ asym. 1091 sym cm⁻¹ (C– O–C), 3010 cm⁻¹ (C – H Aromatic), 2849 cm⁻¹ (C – H Aliphatic), 1520/1582 cm⁻¹ (C = C Aromatic), 1499 cm⁻¹ (N=N).

i- 1,3-bis((Z)-(4-(heptyloxy)phenyl)diazenyl) benzene

Properties: Yield = 67%, brown color m.p = (147-149) $^{\circ}$ C

Discussion of liquid crystal phases General concepts

The values of the thermal transition rates of the liquid crystals and isotropic phases of the most compounds prepared using DSC were determined by taking about 2-3 mg of dry matter and heating them in an inert atmosphere of nitrogen gas. The liquid crystals were diagnosed using a polarized microscope with heating, it was observed that there is a correspondence between the temperature of the intermediate phases and isotropic transitions of the prepared compounds with the measured (DSC), as shown in Table 2.

Table 2.	Liquid	crystal nh	ases tra	nsition o	f DSC	and Mi	croscone	
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Apparatus	NO.	Crystal	Smectic A	Smectic _B	Smectic _C	Nematic	ΔT_{SA}	ΔT_{SB}	ΔT_{SC}	ΔT_N
DSC	a	183								
Microscope		181				213				32
DSC	L	172	207		249	282	35		42	33
Microscope	D	173	208		248	282	35		40	34
DSC	с	164								
Microscope		166	223				57			
Apparatus	NO.	Crystal	Smectic A	Smectic _B	Smectic _C	Nematic	ΔT_{SA}	ΔT_{SB}	ΔT_{SC}	ΔT_N
DSC	d	167								
Microscope		165	181			216	16			35
DSC	e	159								
Microscope		160			181	225			21	44
DSC	f	148	187		240		39		53	
Microscope		148	186		241		38		55	
Apparatus	NO.	Crystal	Smectic A	Smectic _B	Smectic _C	Nematic	ΔT_{SA}	ΔT_{SB}	ΔT_{SC}	ΔT_{N}
DSC		118	128		146	242	10		18	96
Microscope	g	120	131		146	240	11		15	94
DSC	h	113								
Microscope	n	112	141	196			29	37		
DSC		104								
Microscope	l	105	143				38			

In proceeding with any form of DSC measurements (figure 12-14), the nature of the transition can largely be deduced. The transition from the crystalline phase to the liquid crystal (melting point) involves the highest change in the enthalpy (ΔH) because it involves the transition from a phase of threedimensional to a phase of molecular regulation with a shorter duration. The liquid crystal transition of the nematic to the isotropic involves the least transition. By observing the figures (12-14) of the DSC and the results of the tests of the microscope with heater, which are shown in tables 2 and the figures (3-10), the above compounds showed that a smectic and nematic phases with a high thermal range. This may be attributed to the presence of three 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 resulting from the peripheral gravitational forces of the dipole-dipole type, which include the attraction between the groups of the aloxy, as well as the presence of the forces of lateral attraction is the polarization of the group of chalcone group, azo group (N=N) and azomethine (C = N). This is showed with the literature [18-19], which confirmed that the presence of more than three rings of aromatics in the molecule increases its polarization and thus 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 [20]. The appearance of the

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smectic phases of these compounds was observed due to the presence of lateral gravitational forces and increasing the thermal range of the smectic phases by increasing the length of the aliphatic chain [21-23].

When comparing the results, it was observed that the thermal stability of the prepared compounds is higher in the corresponding chalcone compounds, the azo compounds than the azomethine compounds.

This is attributed to the increase of the lateral gravitational force in the chalcone compounds compared with the other compounds, which is consistent with the literature [24].



Fig. 3: SA for comp. b



Fig. 4: S_A for comp. i



Fig. 5: S_C for comp. e b



Fig. 6: S_C for comp. f

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Fig. 7: N for comp. g



Fig. 8: N for comp. a



Fig. 9: S_A for comp. h



Fig. 10: N for comp. d



Fig. 11: IR spectrum of the compound c



Fig. 12: DSC of the compound *b*



Fig. 13: DSC of the compound f



Fig. 14: DSC of the compound *g*







Fig. 16: ¹HNMR spectrum of the compound e



Fig. 17: ¹HNMR spectrum of the compound g

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تأثير المجاميع الوسطية والطرفية على الاستقرار الحراري للبلورات السائلة المنحنية

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الملخص

حضرت سلسلة ميزوجينية جديدة لمركبات الجالكون وقواعد شف ومركبات الازو، تم تحضير الجالكونات بتكاثف امول من ايزوفثالديهايد مع مولين من بارا-هيدروكسي اسيتوفينون بوسط قاعدي، حضرت قواعد شف بتفاعل امول من ايزوفثالديهايد مع مولين من بارا-هايدروكسي انلين بوسط حامضي، تم الحصول على مركبات الازو بتفاعل ميتا ثنائي-امينوبنزين مع NaNO والفينول، واخيراً فوعلت المركبات المحضرة مع بروميد الالكيل. شخصت المركبات المحضرة بجهاز طيف الاشعة تحت الحمراء IR وطيف الرنين النووي المغناطيسي المعالما. تمت دراسة الاطوار البلورية السائلة بجهاز مسعر المسح التفاضلي DSC ومجهر الضوء المستقطب. اظهرت الاطوار البلورية السائلة استقراراً حرارياً يزداد بزيادة طول السلسلة الاليفاتية للاطوار السمكتية يصاحبه انخفاض بالاستقرار الحراري للطور النيماتي. لوحظ ان الاستقرار الحراري للطوار البلورية السائلة المركبات المركبات المورية السائلة لمركبات المركبات المركبات الموريات الموري الطوار المورية المائلة استقراراً حرارياً يزداد بزيادة طول