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Synthesis, Characterization and Computational Study of Discotic Liquid Crystal Compounds

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Abstract

Discotic liquid crystal compounds were synthesized and characterized. Liquid crystalline texture of these compounds was investigated by polarized optical microscopy (POM). The Hartree-Fock approximation (HF) was used to calculate theoretical molecular parameters for synthesized compounds such as optimization, hardness, E_{HOMO}, E_{LUMO}, and energy gap using the Gaussian 09W program.

Keywords: Liquid Crystals, Discotic Liquid Crystals, Computational Chemistry, Hartree-Fock.

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تحضير ,تشخيص ودراسة حاسوبية للمركبات القرصية البلورية السائلة

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الخلاصة

حضرت المركبات البلورية السائلة القرصية وتشخيصها .تم فحص النسيج البلوري السائل لهذه المركبات بواسطة الفحص مجهر الضوء المستقطب (POM). تم استخدام تقريب Hartree-Fock (HF) لحساب المعلمات الجزيئية النظرية للمركبات المحضرة مثل التحسين والصلابة و EHOMO و ELUMO وفجوة الطاقة باستخدام برنامج Gaussian 09

الكلمات المفتاحية : البلورات السائلة، بلورات سائلة قرصية، كيمياء حاسوبية، هارتري - فوك.

Introduction

The discovery of discotic liquid crystals is attributed to S. Chandrasekhar's 1977 regards benzene hexa esters. Discotic liquid crystals consist of two parts: a rigid core and flexible chains linked to it [1]. This arrangement makes it possible for disk-like molecules to self-assemble into columnar liquid crystalline phase. In the area of discotic liquid crystals, the introduction of chirality is an interesting and important subject. Columnar phases are characterized by rapid one-dimensional energy and charge carrier transfer, making them potential application materials [2-7]. Discotic Liquid Crystals materials have been extensively studied, especially in the last decade. Fuji's "Wide-View" (WV) optical compensation films have been effective in commercializing Discotic Liquid Crystals materials [8,9]. Quantum chemistry provides insights into the electronic structures of molecules, and it strongly propels the development of traditional experimental chemistry, appreciation to the development of computational chemistry [10]. The term ‘Hartree – Fock’ would be used only for sufficiently large and optimized basis sets to ensure insignificant deviation from an eventual numerical solution, Hartree – Fock's real limit

Many those scenarios will be referred to as SCF-MO. Today, widespread misuse of the term Hartree – Fock signifies a step backward, especially when using extremely truncated basis sets to magnify the superposition error and obtain 'apparently nice' binding energies [11].

Experimental

Trimesoyl chloride , p-amino benzoic acid , ethanol , butanol , pentanol , heptanol 2-octanol ,Sodium chloride , Sodium bicarbonate, Sulfuric acid , were of analytical grade and were used without further purification. FT-IR data were acquired with a Shimadzu8300 FT-IR spectrophotometer in the frequency range of 4000–400 cm^{-1}. ^{1}H.NMR spectra were recorded by using an Ultrashield FT-NMR (500 MHz) spectrometers in which the deuterated DMSO-d6 were used as the solvent, with tetramethylsilane as internal standard. Melting points were recorded by using melting point instrument BUCHI-EBA20. The texture of the compounds was observed using polarized light with crossed polarizers (Optika, Microscopies, Italia), the sample being prepared as a thin film sandwiched between a glass slide and a cover. A video camera (E_plan 10×0.25/ 160/0.17) was installed on the polarizing microscope and coupled to a video capture card allowing real-time video capture and image saving. The HOMO and LUMO energy eigenvalues were used to calculate the energy gab ΔE, chemical hardness and the optimized compounds were also examined using the Hartree Fock approximation.All calculations are performed using the Gaussian 09 suite of program.

Synthesis of Alkyl-4-amino benzoate [H_0-H_4]

In a conical flask, 30 grams of sodium chloride, and then add drops of concentrated sulfuric acid to it and release the hydrochloric gas that passes through a tube into a gas bubbler containing alcohol that is acidified with the liberated hydrochloric gas. Then the acidified alcohol is transferred to a round flask and then added p-amino benzoic acid (0.01 mol,1.99gm) and refluxed the mixture for 6 hours, the solution was cooled, filtered and washed with a sodium

bicarbonate solution, and then with distilled water, and the product was recrystallized with the ethanol absolute, some physical properties were summarized in table 1.

Table 1: Some of the Physical properties and percentage of the synthesized compounds (H_0-H_4)

COMP .NO	R	MOLECULAR FORMULA	M.P °C	COLOR	YIELD %
H_0	n.Ethyl	$C_9H_{11}NO_2$	90	White	67
H_1	n.Butyl	$C_{11}H_{15}NO_2$	60	White to Light yellow	40
H_2	n.Pentyl	$C_{12}H_{17}NO_2$	54	White-yellow	43
H_3	2-Octyl	$C_{16}H_{25}NO_2$	152	White-yellow	41
H_4	n.Heptyl	$C_{14}H_{21}NO_2$	108	Yellow	39

Synthesis of tri alkyl.4,4′,4″-((benzene-1,3,5-tri carbonyl) tris (azanediyl)) tri benzoate [A_0-A_4]

Alkyl 4-amino benzoate (0.003 mol) was dissolved in dry pyridine (15 ml) and to the solution was added trimosyl chloride (0.18ml, 0.001mol) in ice bath.The solution was stirred at room temperature for about 24 hours. After the end of the reaction, the reaction mixture Poured to acidic iced water in order to remove the pyridine residue and then filter the product and wash it with a solution of sodium bicarbonate and then wash it with distilled water, some physical properties were summarized in table 2.

Table 2: Some of the Physical properties and percentage of the synthesized compounds (A_0- A_4)

COMP	R	MOLECULAR FORMULA	M.P °C	COLOR	YIELD %
A_0	n.Ethyl	$C_{36}H_{33}N_3O_9$	295	White	74
A_1	n.Butyl	$C_{42}H_{45}N_3O_9$	268	White-yellow	68
A_2	n.Pentyl	$C_{45}H_{51}N_3O_9$	280	Brown	58
A_3	2-Octyl	$C_{57}H_{75}N_3O_9$	290	White-yellow	77
A_4	n.Heptyl	$C_{51}H_{63}N_3O_9$	305	White	67

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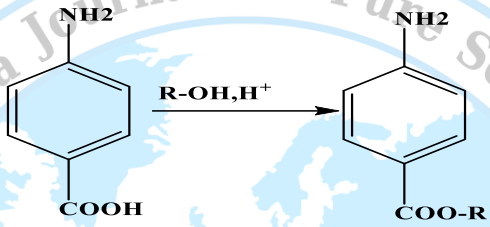
Results and Discussion

1. Synthesis of Alkyl-4-amino benzoate [H0-H4]

In this paper, a number of ester compounds were prepared and used as a starting material for the synthesis of various amides.



Scheme 1: Synthetic of Alkyl-4-amino benzoate

In the literature, the mechanism of ester formation has been thoroughly elucidated [12]. The structures of the synthesized ester were confirmed by their melting points and the FT-IR spectra, which showed the disappearance of the characteristic absorption frequencies of (OH) at (3300-3500) cm-1 and the appearance of the stretching absorption bands of carbonyl ester (C=O ester) at range (1660-1750) cm-1, tables 3 and 4 summarize the FT-IR and 1H.NMR spectrums data, respectively:

Table 3: IR characteristic bands of compound [H_0-H_4]

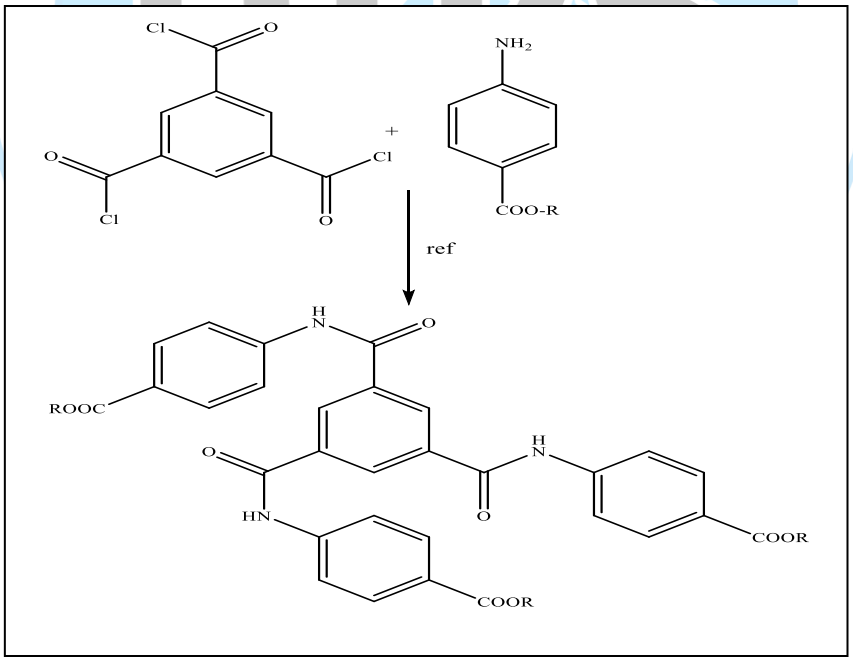
COMP	N C-H AR.	N C-H ALIPHATIC		NC=O	N NH_2		N C=C	
		asym.	Sym.	ESTER	asym.	Sym.		
H_0	3090	2950	2879	1756	3450	3279	1600	1541
H_1	3019	2905	2860	1728	3460	3363	1593	1490
H_2	3022	2900	2835	1734	3480	3320	1600	1508
H_3	3078	2890	2840	1723	3460	3366	1598	1528
H_4	3020	2900	2858	1701	3458	3360	1598	1500

Table 4: Chemical Shift δ ppm of [H_1 and H_2]

COMP	ALKYL GROUPS	NH_2	AR-H
H_1	CH_3,3H,t=0.78 $2CH_2$,4H,m =1.3-2.04 OCH_2,2H,t =4.3	2H,s=5.6	4H, dd =6.5-7.6
H_2	CH_3,3H,t =0.4 $5CH_2$,10H,m =0.9-1.89 OCH_2,2H,t =4.1	2H,s=5.6	4H, dd =6.5-7.6

2. Synthesis of tri alkyl.4, 4′,4″-((benzene-1,3,5-tri carbonyl) tris (azanediyl)) tri benzoate [A_0-A_4]

In this paper, a number of amide compounds were prepared and used as a starting material for the synthesis of various of amides derivatives (N-substituted amides) by the reaction of the [H_0-H_4] compounds with trimosyl chloride.



Scheme 2: Synthetic of Compounds [A0-A4]

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FT-IR spectra also indicated the absorption bands of the compounds [B_1-B_4], the spectrum showed one band within the range (3279 – 3480 cm^{-1}) due to stretching of the bond for the -NH group, and disappearance of a band within the range (1800-1850cm^{-1}) due to removal of a CO-C-Cl bond in trimesoyl chloride , with the formation of a new bond of carbonyl amide (-C=O) this appear in the infrared spectrum within the range (3279 - 3480 cm^{-1}), tables 5 and 6 summarize the FT-IR and ^{1}H.NMR spectrums data, respectively.

Table 5: FT-IR characteristic bands of compound [A_0-A_4]

COMP	N C-H ALIPHATIC		NC=O ESTER	AMIDE		N C=C	
	asym.	Sym.		ν NH	νC=O		
A_0	3002	2970	1705	3340	1686	1597	1512
A_1	2950	2890	1701	3267	1686	1607	1500
A_2	2902	2893	1722	3449	1690	1589	1520
A_3	2970	2787	1725	3449	1660	1600	1532
A_4	2962	2911	1772	3529	1683	1593	1500

Table 6: Chemical Shift δ ppm of [A_0, A_1 and A_4]

COMP	ALKYL GROUPS	NH	AR-H
A_0	3CH_3,9H,t =1.3 3OCH_2,6H,q =4.3	3H,s =10.9	15H, m = 7.9-8.8
A_1	3CH_3,9H,t =0.72 3$(CH_2)_3$,18H,m =1.09-1.9 3OCH_2,6H,t =4.4	3H,s=10.5	15H, m =7.3-8.8
A_4	3CH_3,9H,t =0.82 3$(CH_2)_5$,30H,m =0.83-2.07 3OCH_2,6H,t =4.2	3H,s=10.5	15H, m =7.5-9.2

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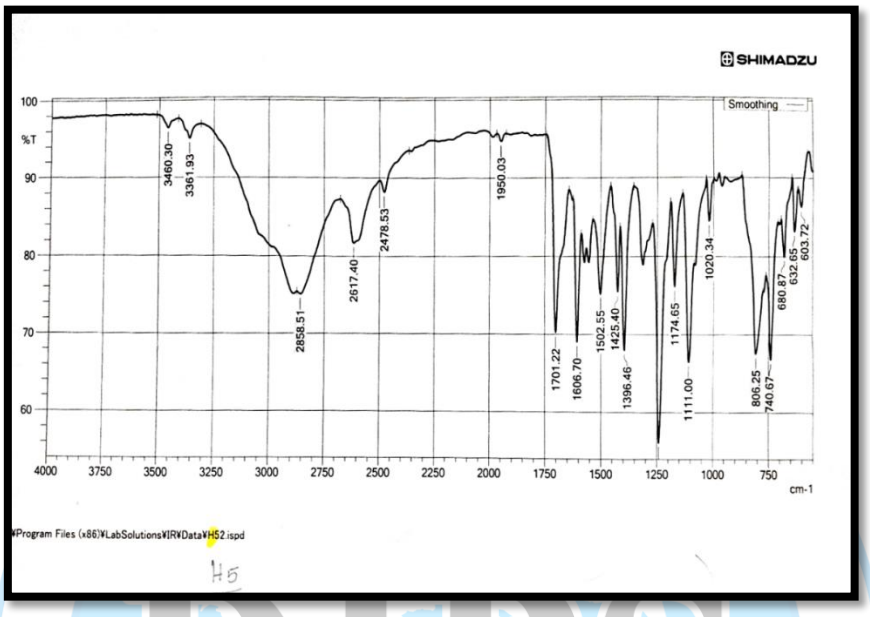

Figure 1: FT- IR spectrum of H_4 compound

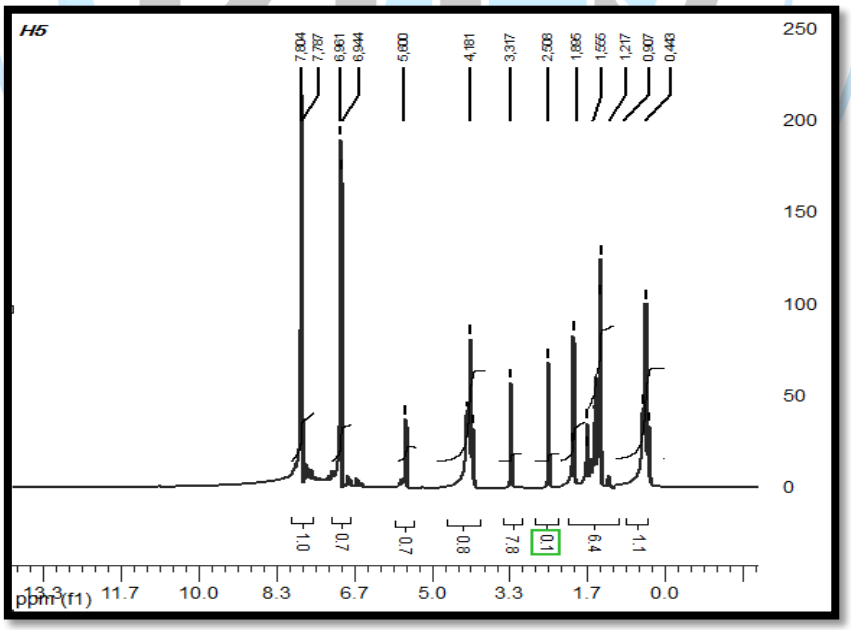

Figure 2: ^{1}H.NMR spectrum of H_4 compound

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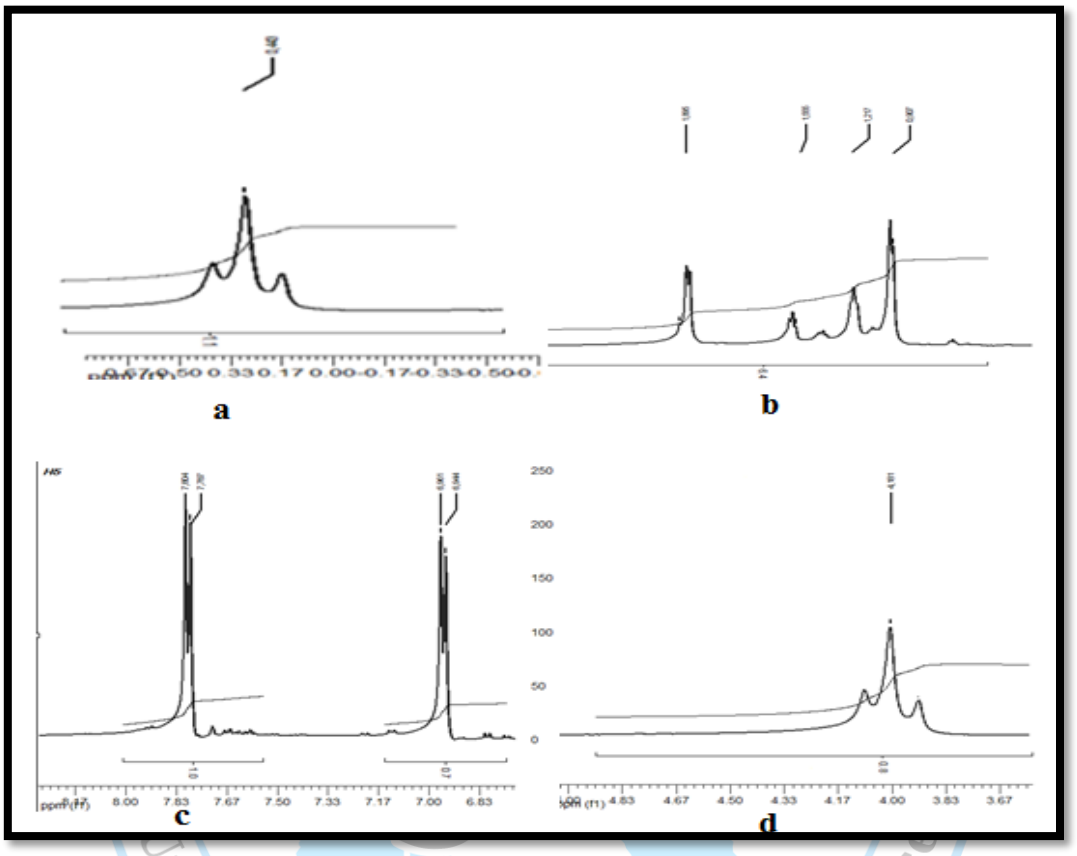

Figure 3: Expansion ^{1}H.NMR spectrum of $\mathbf{H_1}$ compound **a)**[-CH_3] **b)** [-CH_2-] **c)** [-C-H $_{Aromatic}$] **d)** [-OCH_2-]

Mesomorphic properties

Mesomorphic properties of synthesized title compounds were determined by polarizing optical microscope (POM). The representative polarized optical micrograph of series of prepared compounds ($\mathbf{A_0}$, $\mathbf{A_3}$ and $\mathbf{A_4}$) observed in the liquid crystalline phase for the second heating and cooling cycle, is shown in Figures [2],[3] and [4] for compounds $\mathbf{A_0}$, $\mathbf{A_3}$ and $\mathbf{A_4}$ respectively.

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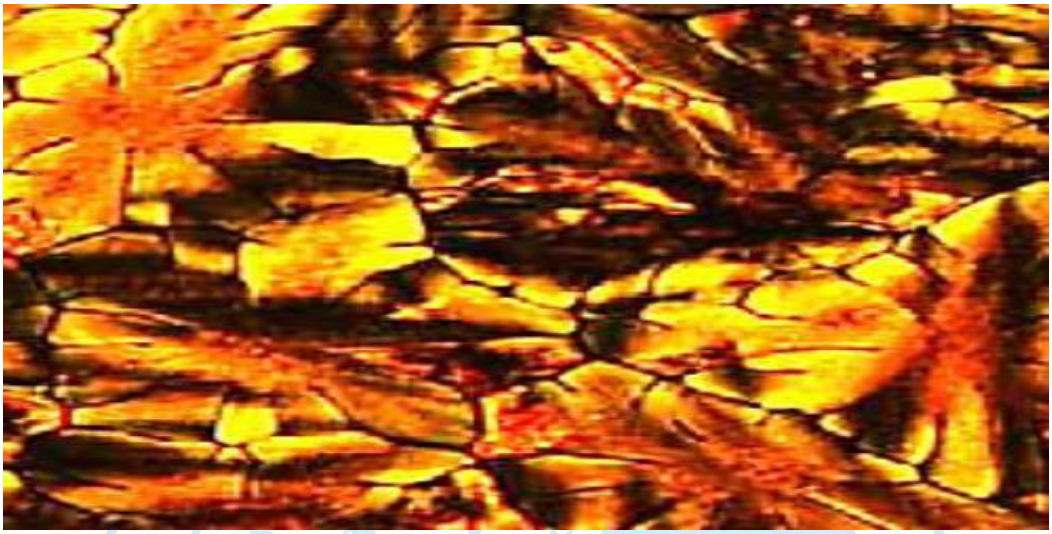
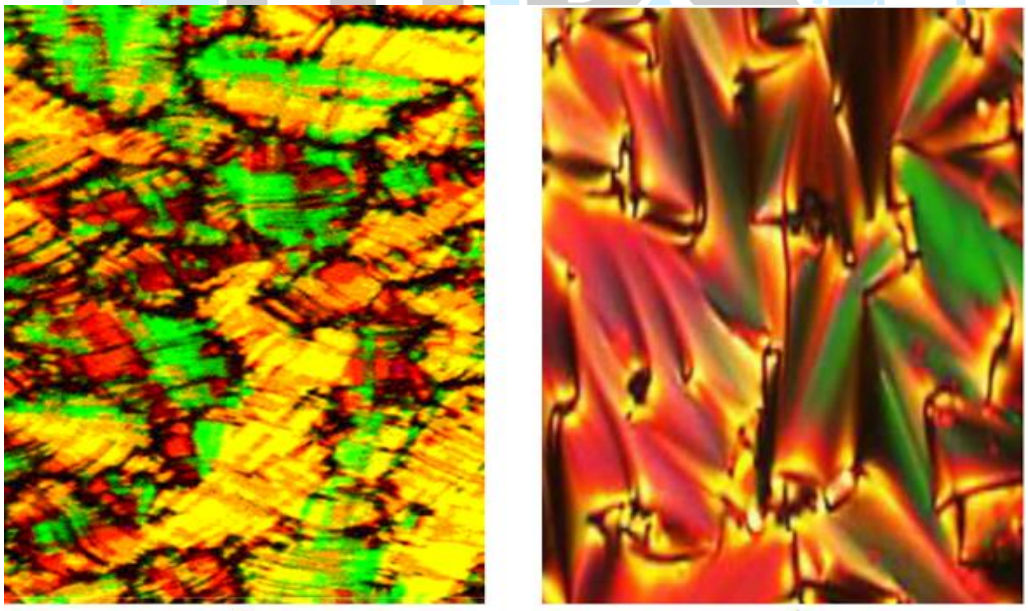


Figure 4: POM textures observed of S_A phase during heating to 309 °C of discotic liquid crystal target [A_0]



a b

Figure 4: POM textures of discotic liquid crystal target [A_3 Compound]

2(a): S_A phase during heating at 305 °C, 2(b): N phase during heating from 317 °C to isotropic.

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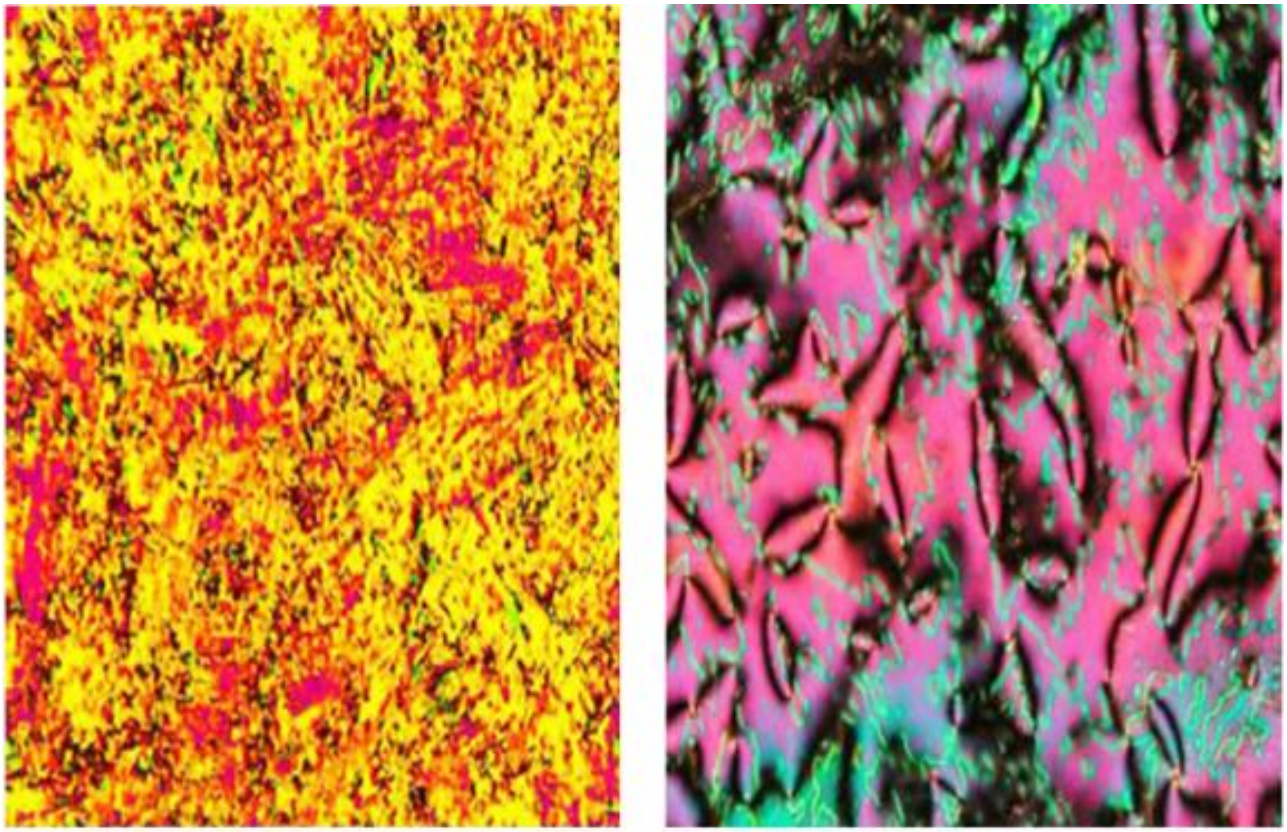

Figure 5: POM textures of discotic liquid crystal target [A_4 Compound]

2(a): S_C phase during heating at 309 °C, 2(b): N phase during heating from 323°C to isotropic.
*S_A: Smectic A, *S_C: Smectic C, N: Nematic

Table 7: Liquid Crystal phase transition in polarized optical microscope

COMP	CRY	S_A	S_C	N	ΔTS_A	ΔTS_C	ΔTN
A_0	293	309	-----	------	16	-----	-----
A_3	292	305	-----	317	13	-----	12
A_4	301	-----	309	323	-----	8	14

Theoretical Calculations

Geometric Optimization of the Prepare Compounds

Theoretical calculations of the prepared Ester compounds have been accomplished utilizing the Gaussian 09W program package and using the Hartree- Fock (HF) and Basis set STO-3G* approximation method. The 3D geometric structure in the gas-phase for prepare compounds are shown below:

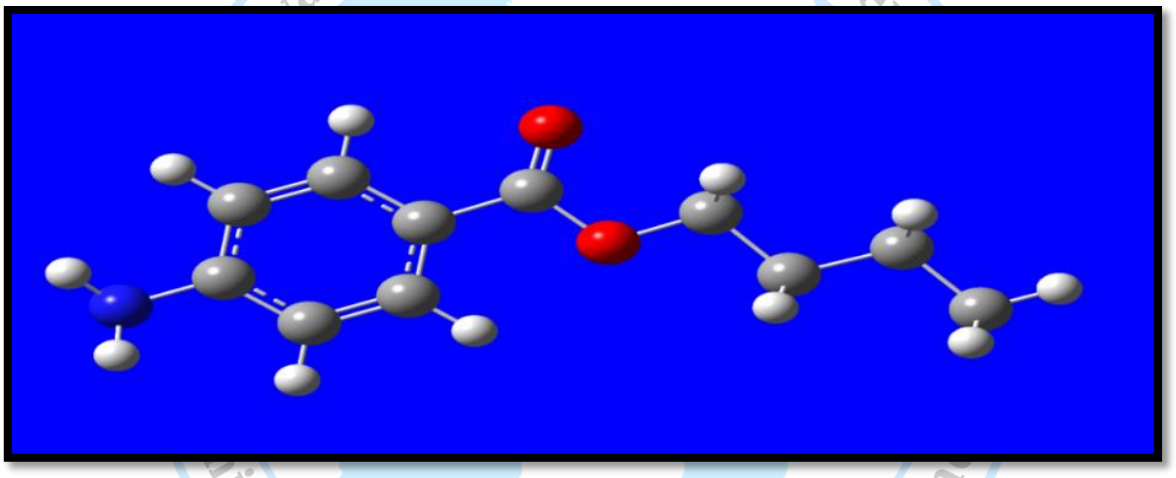

Figure 6: The optimized structure of compound H_1

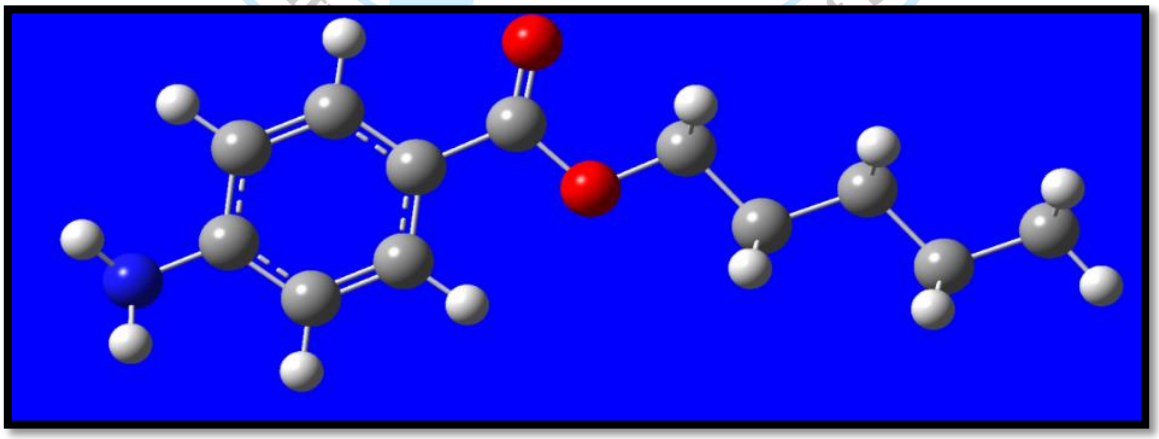

Figure 7: The optimized structure of compound H_2

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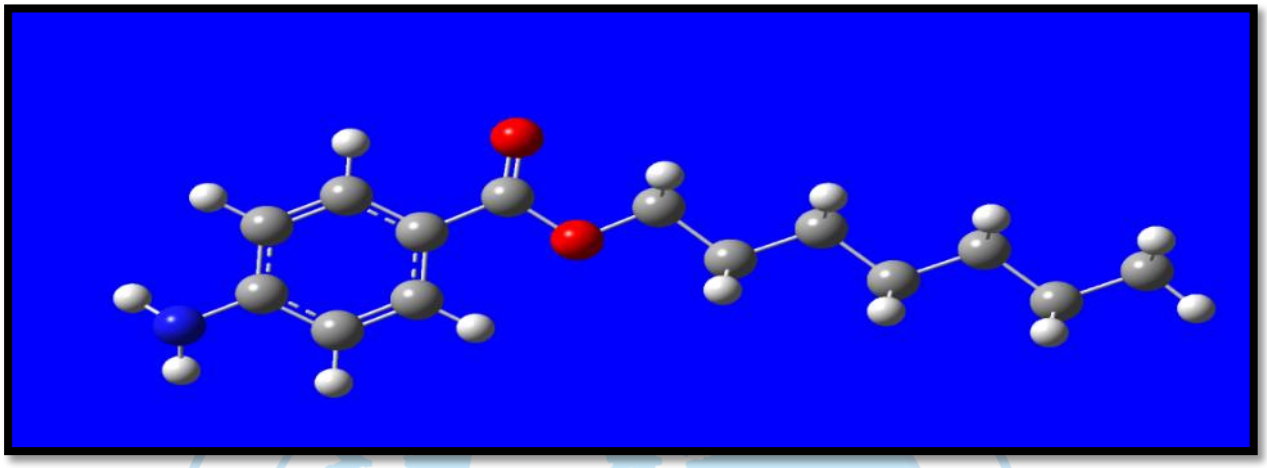

Figure 8: The optimized structure of compound H_4

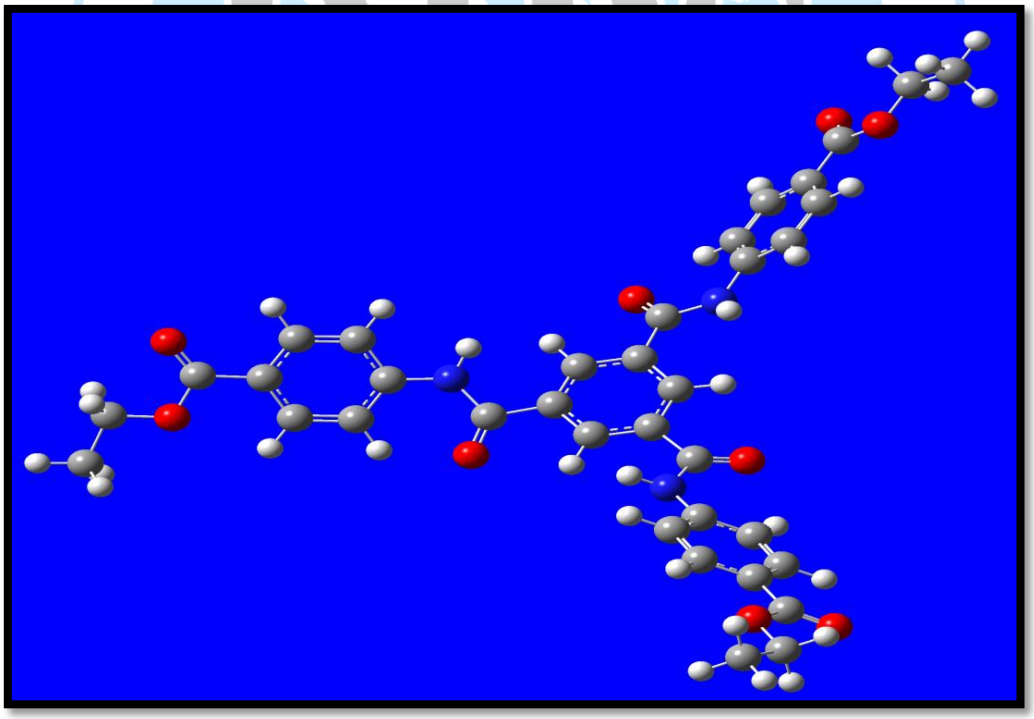

Figure 9: The optimized structure of compound A_0

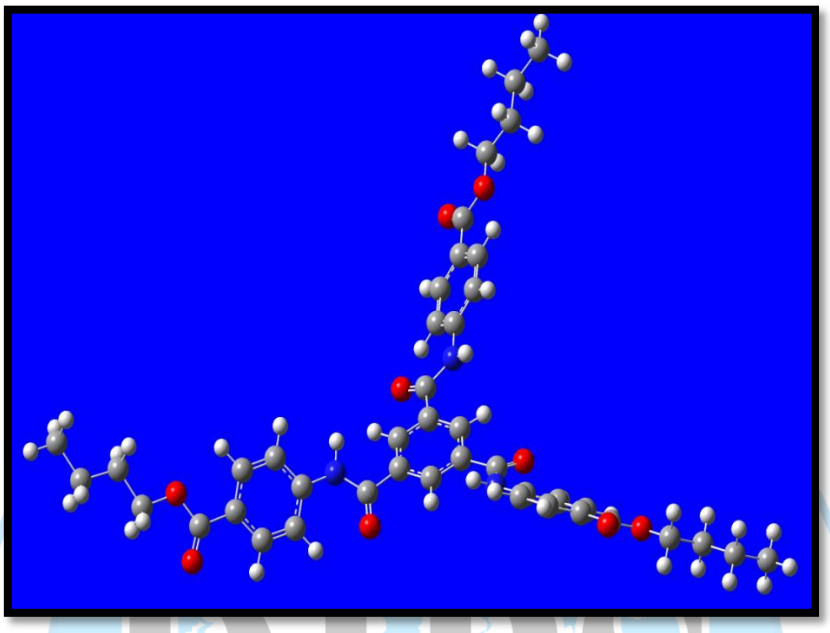

Figure 10: The optimized structure of compound A_1

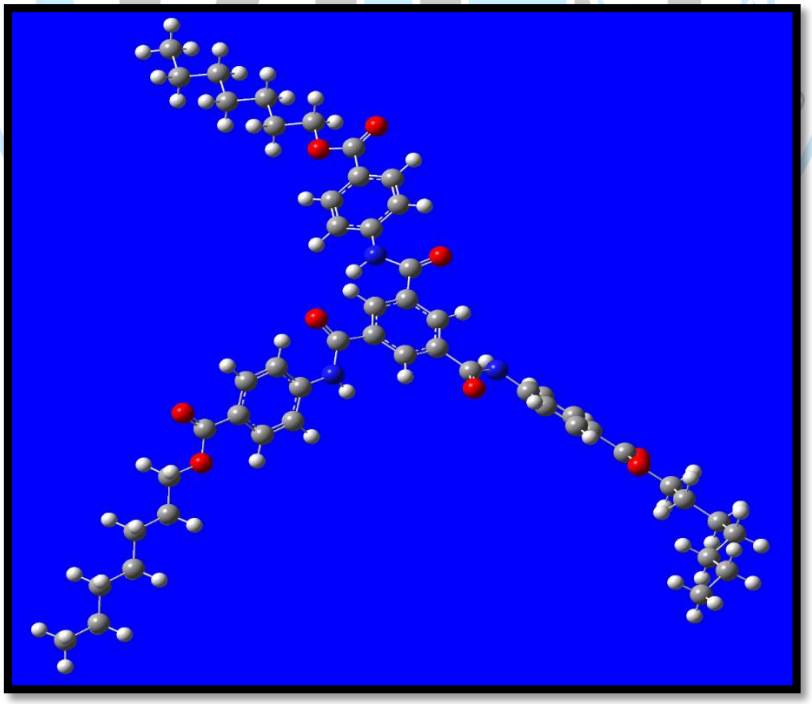

Figure 11: The optimized structure of A_4

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Table 8: Show some Theoretical Calculation properties

COMP COD	ENERGY KJ/MOLE		DIPOLE MOMENT (DEBEY)	HARDNESS (H). KJ/MOLE
H_1	-2.71		2.07	5.44+
	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap)}$ kJ/mole	Electron affinity
	1.06-	9.81+	10.88+	9.81-
Comp cod	Energy kJ/mole		Dipole moment (debey)	Hardness (η). kJ/mole
H_2	2.87-		2.08	+5.44
	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap}$	Electron affinity
	1.06-	+9.82	10.88+	-9.82
Comp cod	Energy kJ/mole		Dipole moment (debey)	Hardness (η). kJ/mole
H_4	-3.21		2.08	5.44+
	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap}$	Electron affinity
	1.06-	9.82+	10.89+	9.82 -

Table 9: Show some Theoretical Calculation properties

COMP COD	ENERGY KJ/MOLE		DIPOLE MOMENT (DEBEY)	HARDNESS (H).KJ/MOLE
A_0	-9.55		4.22	4.50239+
	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap)}$ kJ/mole	Electron affinity
	1.0783-	7.9264+	9.0047+	7.9264-
Comp cod	Energy/ Hartree		Dipole moment (debey)	Hardness (η). kJ/mole
A_1	- 2423.09		4.31	4.5085+
	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap)}$ kJ/mole	Electron affinity
	1.0766-	7.9404+	9.0170+	-7.94

Table 10: Show some Theoretical Calculation properties

COMP COD	ENERGY KJ/MOLE		DIPOLE MOMENT (DEBEY)	HARDNESS (H). KJ/MOLE
	1.106-		5.39	4.54+
A_2	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap)}$ kJ/mole	Electron affinity
	1.06-	8.02+	+ 9.08	-8.02
Comp cod	Energy kJ/mole		Dipole moment (debey)	Hardness (η). kJ/mole
	1.207-		4.35	+ 4.51
A_4	E_{HOMO} kJ/mole	E_{LUMO} kJ/mole	$\Delta E_{(Egap)}$ kJ/mole	Electron affinity
	1.07-	7.94+	+ 9.02	-7.94

Conclusion

In this paper, disc-like compounds with even-odd terminal chains were prepared, and crystalline behaviour were investigated. Computational studies revealed a minimum energy, optimized capture of a prepared compound, and the calculation of High occupied Molecular Orbitals Energy (E-HOMO) and Low occupied Molecular Orbitals Energy (E-LUMO). Molecules hardness is calculated using the Hartree-Fock approximation, and the relationship between aromaticty and stability is determined. Molecules with a high hardness value have more stability and aromatcity, respectively. It was concluded that compounds with a rigid center and groups with flexible terminal ends give liquid crystalline properties to the molecule. The odd –even effect not observed on liquid crystal properties in this work. Also, the effect of the terminal collectors on the electronic properties appears to have a limited effect.

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