Liquid Crystalline Properties of 4,4'-methylenebis(N-(4-Alkanoxybenzylidene)aniline): Synthesis, Characterization, and Theoretical study

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Summary: The paper presents six homologues series of Schiff bases ether compounds distinguished by the length of terminal alkoxy groups which substituted on a side benzene nucleus. The above structures were demonstrated through the use of spectroscopic techniques, like FT- IR and ^{1}H-NMR. Polarized hot stage optical microscopy was used to study both mesomorphic properties and phase transitions. The results showed that out of the six compounds only three (B2, B3 and B4) were pure (marble) nematic mesophase, while no liquid crystal properties for (B5, B6 and B7) compounds. The theoretical study for the electronic structures was intended to study the effects of alkyl chain length on the electronic structure by using Gaussian program, DFT and 6-31G as basis set. The theoretical results indicate that there is no effect to the terminal substituted alkoxy groups on the HOMO energies but there is an effect on LUMO energies through decreasing energy for the prepared compounds.

Keywords: Schiff bases, Terminal alkoxy, Liquid crystal, Theoretical, DFT.

Introduction

Lately, there has been a considerable interest in the liquid crystalline properties of banana shaped molecules [1]. In general, these compounds are consist of two parts, 1st provides curvature angle, 2nd two rod-like units linked to 1st part [2-10]. Literature data reported several central core aromatic molecules which are able to ensure the necessary bending angle between (120-140)°C and containing two reactive groups as substituent: 1,3- disubstituted benzene, 2,7-disubstituted-naphtalene, etc. The bent-core systems in this paper are based on methylene group as central core obtained by direct condensation of 4,4′-diaminodiphenylmethane with 4-alkanoxy benzaldehyde to study the decrease of bending angle (109.5) between two rod-like units and the prevention of the conjugation between two rod-like units besides studying the alkoxy chain length on the liquid crystals properties.

Experimental

Materials and methods

Synthesis of 4-Alkoxy Benzaldehyde: **(A2–A7)**

In 250 ml round bottom flask containing 100 ml ethanolic NaOH (4%) was dissolve 0.9 mmole of 4-hydroxy Benzaldehyde after complete dissolving appropriate 0.9 mmole Alkyl Bromide was added, the mixture was refluxed for 24 hours, then extracted two times: 1st by (1/1v) of 1% NaOH solution/Chloroform, 2nd (1/1v) of water /Chloroform, then the Chloroform was evaporate and oily 4-Alkoxy Benzaldehyde was dried over anhydrous sodium sulfate overnight [11] .

Synthesis of Schiff bases: **(B2–B7)**

In a 100 ml round-bottom flask, 25 ml of absolute ethanol was stirred in (10 mmole) of appropriate 4-Alkoxy Benzaldehyde with 5 drops of glacial acetic acid for 15 min. 20 ml of ethanolic 4,4′-Diaminodiphenylmethane (5 mmole) was then added. The mixture was refluxed for 2 hr.. The micro-crystalline white colored precipitate filtered and washed with ethanol, recrystallized from ethanol [12]. Scheme (1) below shows the synthetic route to the series:

Characterization

Infrared spectra were used to characterize the series members. Bruker-Tensor 27 spectrometer recorded the infrared spectra as KBr pellets.. Bruker-500 MHz spectrometer was used to record ^{1}H-NMR spectra where $CDCl_3$ is used as a solvent. The phase transitions were observed with a NOVEL polarized optical microscope with hot stage equipped with a SONY camera DSC-W120.

FT-IR spectrophotometer was used to identify 4-Alkanoxy Benzaldehyde. All recorded spectra show that the stretching vibration of hydroxyl group disappears and the appearance of stretching vibration for ethers C-O-C group (1257-1259) for asymmetric and (1054-1057 cm^{-1}) for symmetric [13]. Table-1 shows the results.

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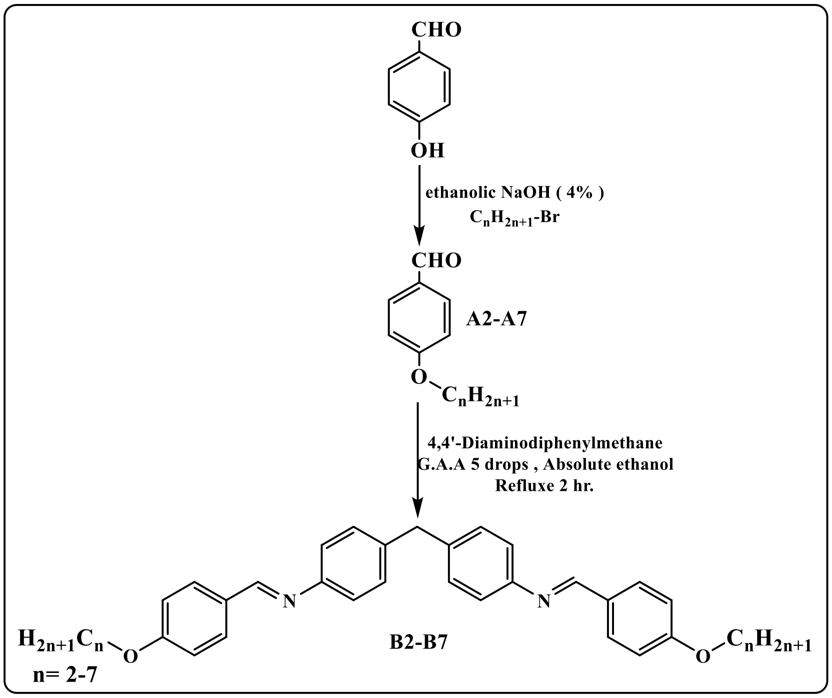


Scheme-1: Synthetic route to the Bn series.

Table-1: FT-IR absorption bands for prepared (A2–A7) Compounds (cm^{-1}).

N	Comp. Symbol	νC-H		CO-H Alde.		νC=O Aldeh	ν C═C		C-O-C		Para Subs.	γ CH_2
		Arom	Aliph	Str.	bend				As.	Sy.		
2	A2	3073	2936	2739	1395	1689	1599	1510	1258	1041	835	757
3	A3	3073	2968	2788	1392	1689	1597	1510	1259	1057	834	756
4	A4	3072	2956	2736	1392	1691	1600	1510	1259	1067	835	756
5	A5	3073	2935	2738	1389	1689	1601	1511	1257	1051	834	757
6	A6	3072	2933	2739	1388	1684	1596	1511	1259	1054	834	728
7	A7	3073	2930	2735	1391	1691	1600	1511	1258	1052	834	757

Table-2: FT-IR absorption bands for prepared Schiff bases (B2–B7) Compounds (cm^{-1}).

n	Comp. Symbol	νC-H		υC=N	ν C═C		C-O-C		Para Subs.	γ CH2
		Arom	Aliph				As.	Sy.		
2	B2	3029	2930	1604	1578	1509	1248	1041	834	721
3	B3	3029	2933	1604	1574	1510	1249	1057	838	721
4	B4	3030	2949	1604	1573	1510	1249	1061	840	725
5	B5	3032	2933	1605	1573	1510	1248	1054	842	725
6	B6	3028	2930	1603	1573	1510	1249	1054	839	724
7	B7	3032	2927	1608	1574	1511	1250	1047	844	723

Table-3: ^{1}H-NMR data for **(B2–B7)** compounds (ppm).

Comp.	ϕ-CH_2-ϕ	CH_3	α CH_2	β CH_2	$(CH_2)_n$	N=C-H	Ar-H
B2	1.80	1.47	4.11	-	-	8.41	6.98 + 7.86 / 7.17-7.25
	(2H, s)	(3H, t)	(2H, q)			(1H, s)	(2H, d) , (2H, d) / (4H, dd)
B3	1.83	1.09	4.01	1.87	-	8.41	6.99 + 7.86 / 7.17-7.28
	(2H, s)	(3H, t)	(2H, t)	(2H, m)		(1H, s)	(2H, d) , (2H, d) / (4H, dd)
B4	1.60	1.05	4.05	1.84	1.54	8.41	6.99 + 7.85 / 7.13-7.24
	(2H, s)	(3H, t)	(2H, t)	(2H, p)	(2H, h)	(1H, s)	(2H, d) , (2H, d) / (4H, dd)
B5	1.78	0.98	4.04	1.84	1.48	8.41	6.98 + 7.86 / 7.17-7.25
	(2H, s)	(3H, t)	(2H, t)	(2H, p)	(4H, m)	(1H, s)	(2H, d) , (2H, d) / (4H, dd)
B6	1.59	0.94	4.04	1.83	1.53	8.41	6.98 + 7.85 / 7.16-7.28
	(2H, s)	(3H, t)	(2H, t)	(2H, p)	(6H, m)	(1H, s)	(2H, d) , (2H, d) / (4H, dd)
B7	1.65	0.93	4.05	1.83	1.48	8.41	6.99 + 7.85 / 7.16-7.24
	(2H, s)	(3H, t)	(2H, t)	(2H, p)	(8H, m)	(1H, s)	(2H, d) , (2H, d) / (4H, dd)

According to the prepared Schiff bases that the FT-IR spectrophotometer identified, all the spectra show disappearance of the stretching (symmetric and asymmetric) vibrations of amino groups and aldehyde carbonyl groups, and appearance of stretching vibration for azomethine group (1603–1608 cm^{-1}) [13]. Table-2 shows the results.

Furthermore the prepared Schiff bases identified (B2–B7) by Nuclear Magnetic Resonance for proton ^{1}H-NMR were $CDCl_3$ is used as a solvent while TMS is used as internal reference, all spectra show that all compounds have the correct structures. The results are given in Table-3. Figs (1), (2), and (3) show the ^{1}H-NMR spectra for some compounds.

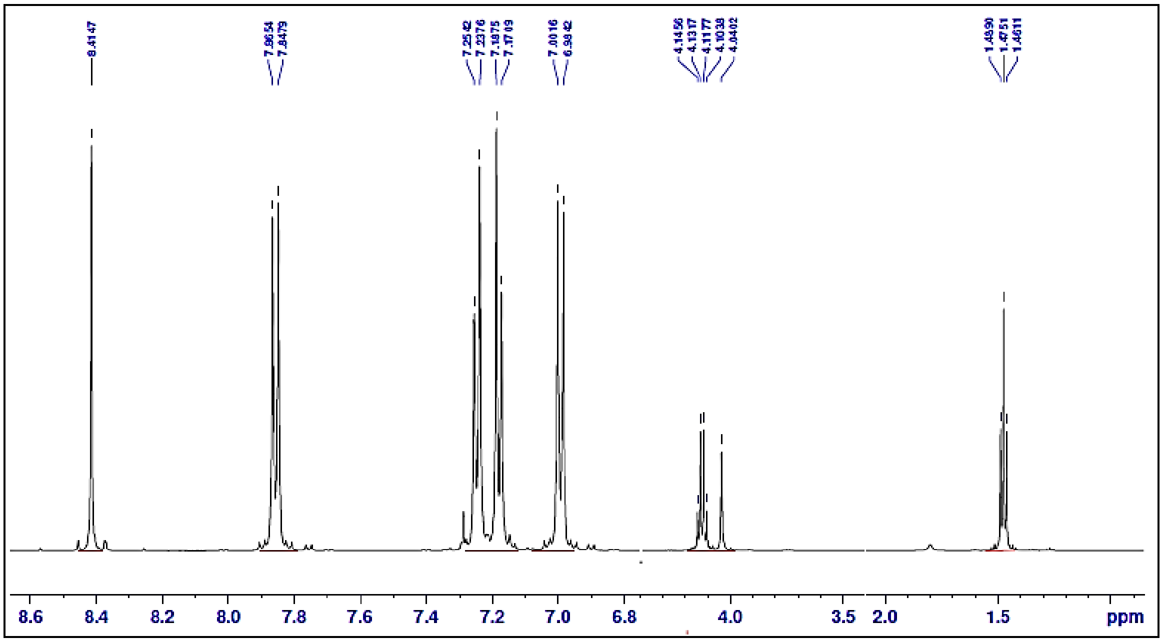


Fig. 1: ^{1}H-NMR Spectrum for B2 Compounds.

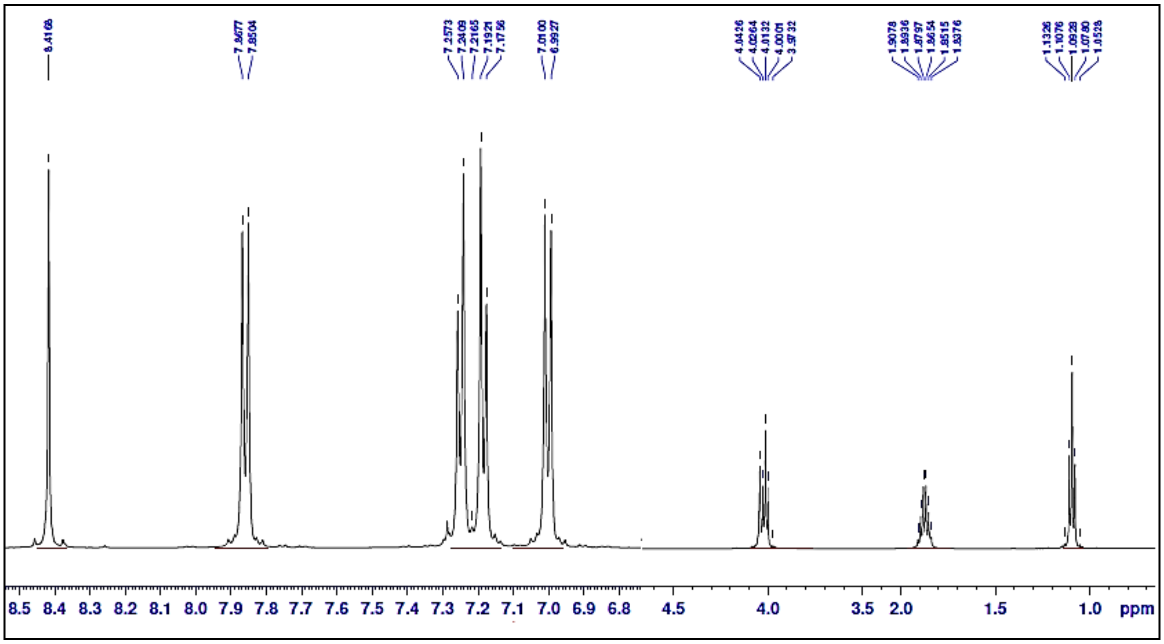


Fig. 2: ^{1}H-NMR Spectrum for B3 Compounds.

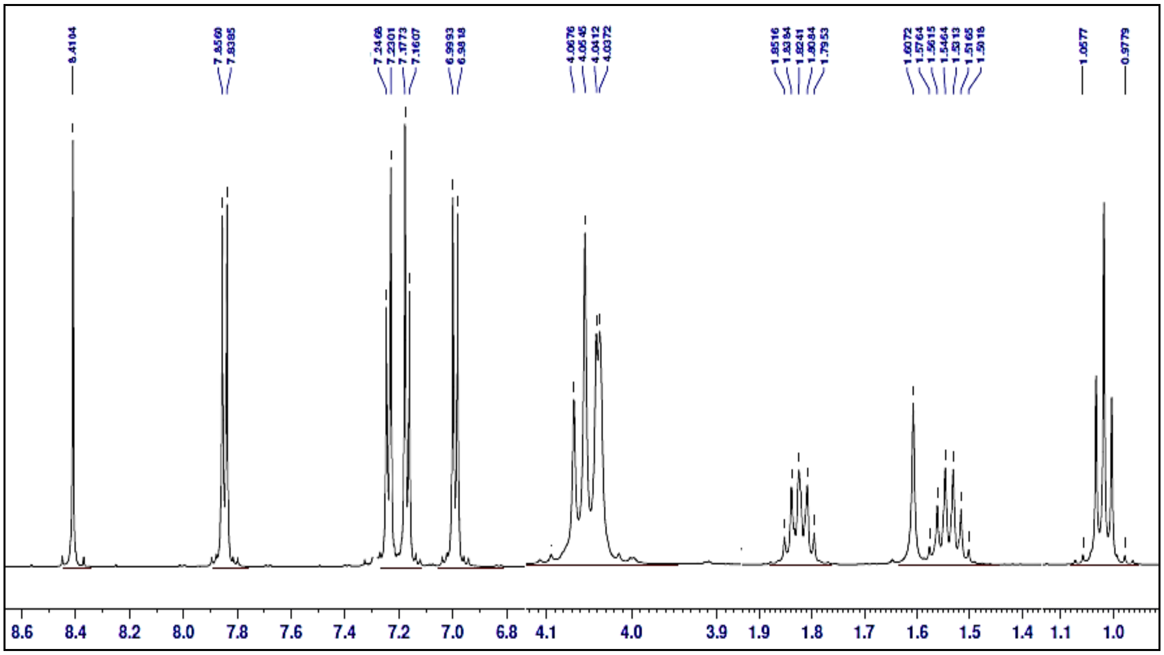


Fig. 3: ^{1}H-NMR Spectrum for B4 Compounds.

Table-4: Physical properties for prepared compounds.

Comp.	IUPAC name	Formula	M. Wt.
B2	4,4'-methylenebis(N-(4-ethoxybenzylidene)aniline)	$C_{31}H_{30}N_2O_2$	462.58
B3	4,4'-methylenebis(N-(4-propoxybenzylidene)aniline)	$C_{33}H_{34}N_2O_2$	490.64
B4	4,4'-methylenebis(N-(4-butoxybenzylidene)aniline)	$C_{35}H_{38}N_2O_2$	518.69
B5	4,4'-methylenebis(N-(4-pentoxybenzylidene)aniline)	$C_{37}H_{42}N_2O_2$	546.74
B6	4,4'-methylenebis(N-(4-hexyloxybenzylidene)aniline)	$C_{39}H_{46}N_2O_2$	574.79
B7	4,4'-methylenebis(N-(4-heptyloxybenzylidene)aniline)	$C_{41}H_{50}N_2O_2$	602.85

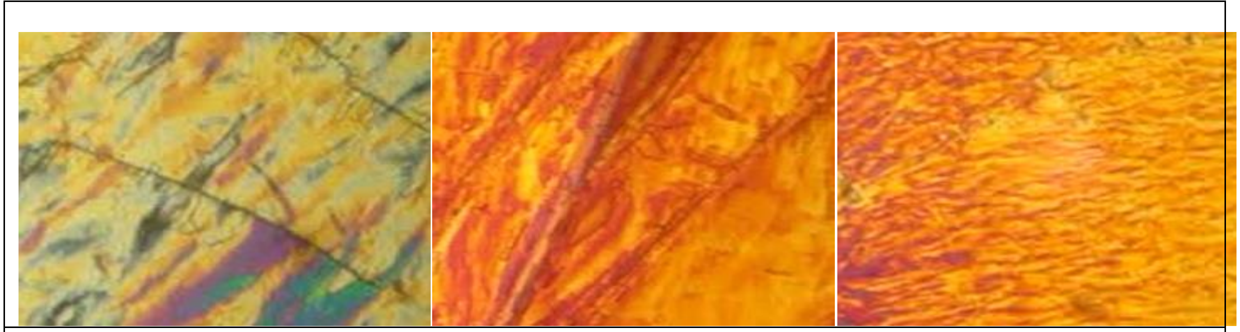
All the prepared compounds are solid and have white color. Table-4 lists compounds symbols, IUPAC name, formula and molecular weight.

Characterization of Mesophase

The POM (Polarized Optical Microscope) indicates that three compounds (B2,B3 and B4) have monotropic mesogenic behavior. They also show Nematic phase (N) only, with characteristic marble textures[14]. The phase transition temperature ranges ΔTN are between (12–28) °C of compounds Table-5. The marble texture is displayed in Fig (4).

Table-5: Phase transitions temperatures (°C).

Comp.	Cr-N	N-I	ΔTN
B2	132	160	28
B3	155	176	21
B4	170	182	12



B2 132 ⁰ C **B3 155 ⁰ C** **B4 170 ⁰ C**

Fig. 4: Nematic phase (marble) textures for B2, B3 and B4 compounds.

Cr-N transition temperature series Bn. Did not show any odd-even effect. There is a decrease in nematic phase range and an increase in aliphatic alkoxy terminal chain, while the transition temperature of nematic and isotropic phase increases with increase of carbon atoms (Fig 5).

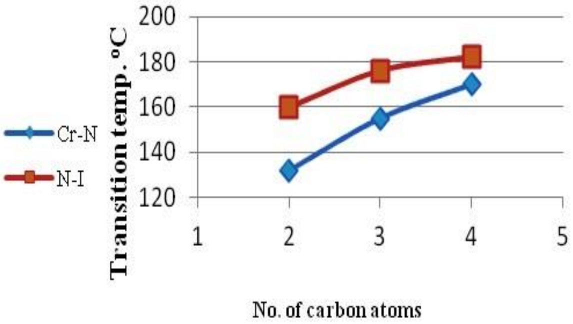


Fig. 5: Mesomorphic behavior as a function of the number of carbon atoms (n) in the terminal alkoxy chain.

The short alkoxy chain enhances nematic phase while long alkoxy chain enhances smectic phase; the expectation of the terminal attraction for nematic phase is illustrated in Fig (6).

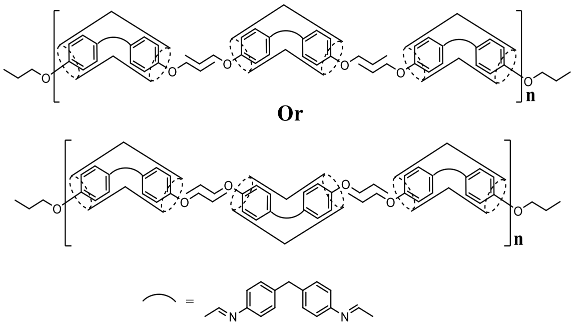


Fig. 6: Terminal attraction between Schiff bases ether molecules.

Computational study

DFT calculations

DFT was used to carry quantum mechanical calculations for molecular properties through employed of combination (B3LYP) and 6-31G as basis set, by using Gaussian 09 program in order to identify the data of prepared Schiff bases ethers compounds, like dipole moment, HOMO, LUMO, HOMO-LUMO gap and some other electronic properties, the results are listed in Table-6.

Frontier orbitals (HOMO),(LUMO) and HOMO-LUMO energy gaps were measured. It is found that the molecules with large LUMO-HOMO gaps are rather stable and unreactive, whereas those with small gaps are considerably reactive because it is easier for HOMO to donate electrons when HOMO energies are lower; whereas it is easier it is for LUMO to accept electrons when LUMO energies are lower [6-8]. The results indicate that no effect of the terminal substituted alkoxy groups has been observed on the HOMO energies but there is an effect on the LUMO energies through decreasing the energy for the prepared compounds compared with B0 Scheme (2). All previous results lead up to decreasing electron affinity (Fig. 7).

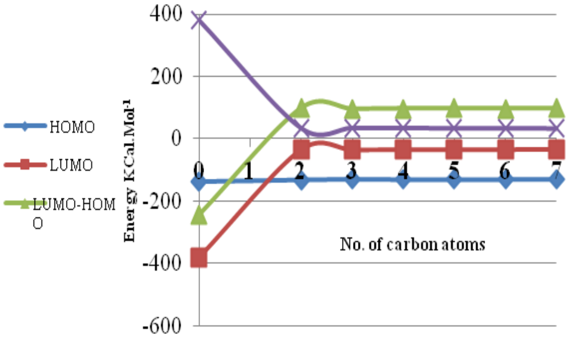


Fig. 7: HOMO, LUMO, LUMO-HOMO and A against no. of carbon atoms.

The following equations [15] were used to calculate the following electronic properties:

1. electron affinity A **2.** Ionization potential I **3.** absolute electronegativity μ 4. absolute hardness η, and elctrophilcity ω

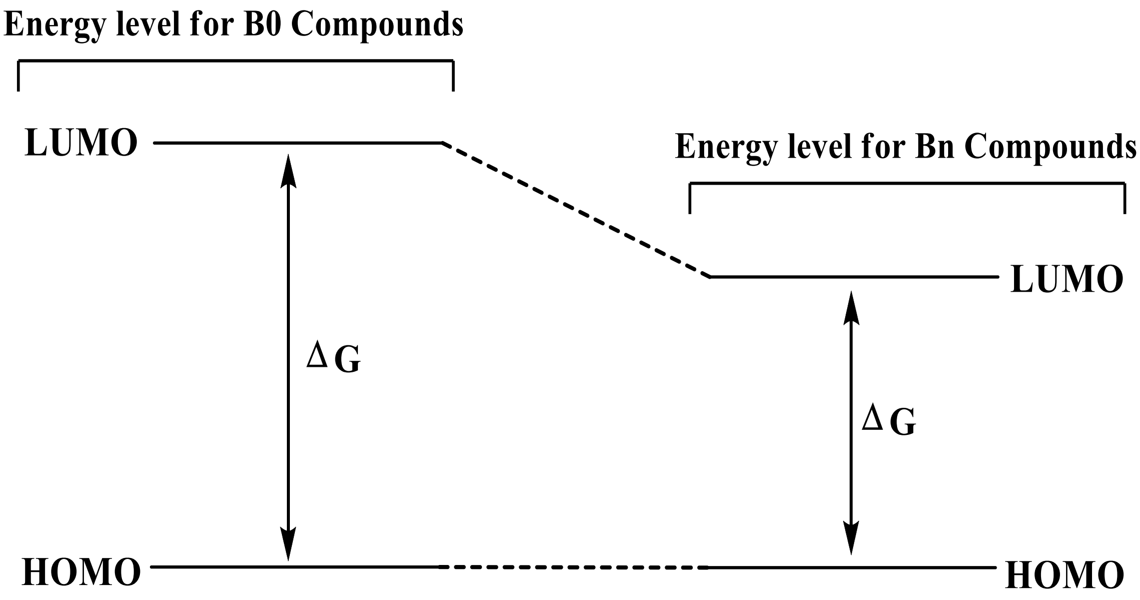
$$A = (-E_{LUMO}),\ I = (-E_{HUMO}), \qquad \mu = \frac{1}{2}(I + A),$$

$$\eta = \frac{1}{2}(I - A),\ \omega = \frac{\mu^2}{2\eta}$$

Table-6: HOMO, LUMO, LUMO–HOMO gap energies and some electronic properties for prepared compounds (Kcal.mol^{-1}).

Comp.	HOMO	LUMO	LUMO – HOMO	μ	ω	H	*I*	A
B0	-136.891	-381.401	-244.51	259.146	-61.1275	-122.255	136.891	381.401
B2	-132.241	-34.7076	97.5334	83.4743	24.38335	48.7667	132.241	34.7076
B3	-130.673	-35.7116	94.9614	83.1923	23.74035	47.4807	130.673	35.7116
B4	-131.539	-35.0088	96.5302	83.2739	24.13255	48.2651	131.539	35.0088
B5	-131.608	-34.5382	97.0698	83.0731	24.26745	48.5349	131.608	34.5382
B6	-131.338	-34.8017	96.5363	83.06985	24.13408	48.26815	131.338	34.8017
B7	-130.735	-33.4839	97.2511	82.10945	24.31278	48.62555	130.735	33.4839

[μ= Electronegativity, ω= Elctrophilcity, η= Hardness, *I*= Ionization potential, A= Electron affinity]



Scheme-2: Orbitals energy diagram.

The study of hardness for the prepared compounds showed that the alkoxy groups increase the hardness of molecules, which means the resistance of molecules to change the electronic configuration. The same behavior can be observed on electrophilicity, while the electronegativity decreases with alkoxy groups. All electronic properties changed with alkoxy groups but no remarkable effect has been observed on number of carbon atoms in alkoxy groups, no effect for alkoxy groups on ionization potential because it correlated with HOMO energy for the prepared compounds (Fig 8).

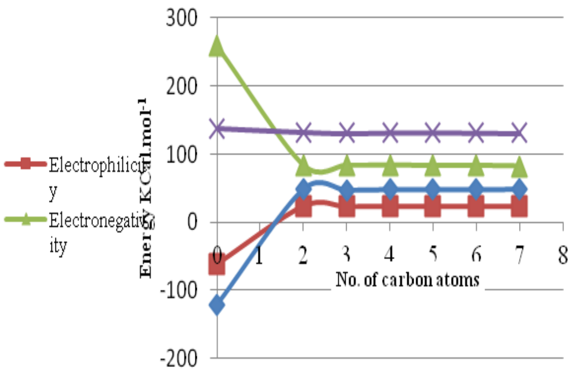


Fig. 8: Hardness, elctrophilcity and electronegativity against no of carbon atoms.

The study of theoretical Dipole Moment indicated that the alkoxy chain groups exhibit odd-even effect of carbon atoms (Table-7). Generally, it is found that all compounds with even number of carbon atoms increase value of dipole moment in accordance with previous value for odd number (Fig 9), this behavior can explains by inductive effect of alkoxy groups with even number which have axis parallel to the molecule axis (see Figs 10 and 11).

Table-7: Calculated Dipole moment, total energies for prepared compounds.

Comp.	Dipole moment Debye	Total E.Kcal.mol^{-1}
B0	2.604	-1144.81
B2	3.889	-1450.83
B3	3.792	-1529.28
B4	4.392	-1607.34
B5	4.018	-1685.71
B6	4.275	-1763.73
B7	1.714	-1481.9

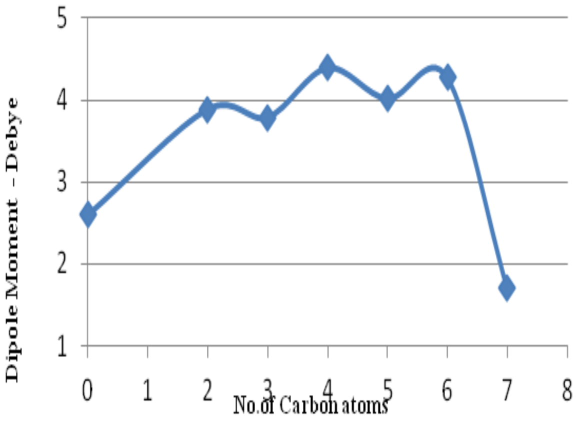


Fig. 9: Dipole moment against no. of carbon atoms.

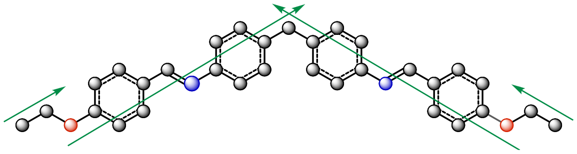


Fig. 10: Optimized geometry for B2 compounds.

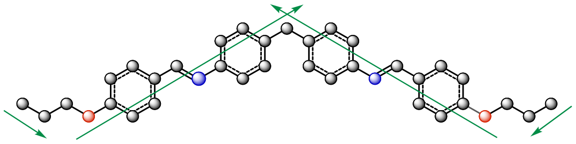
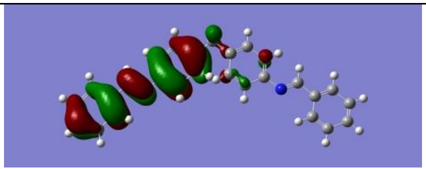
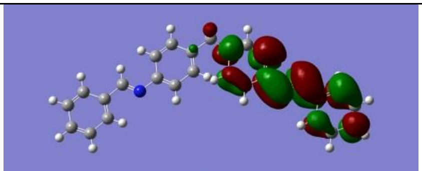
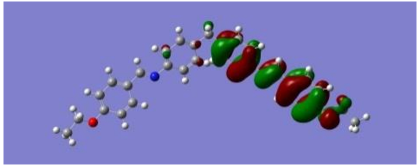
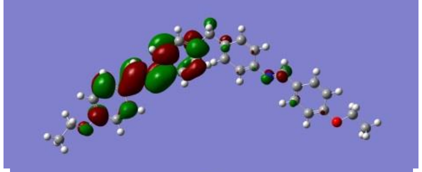
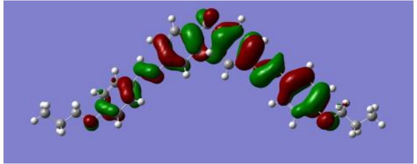
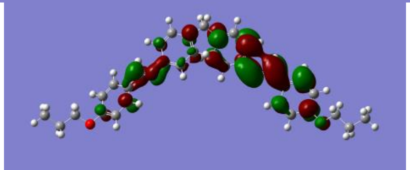
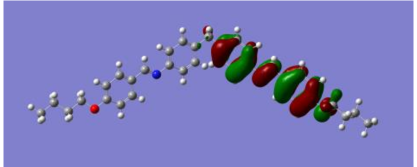
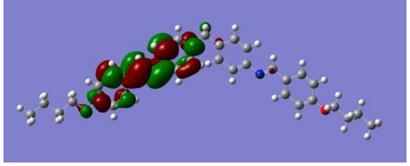
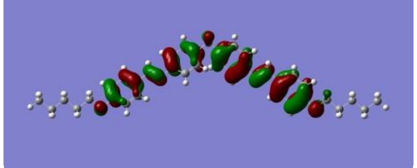
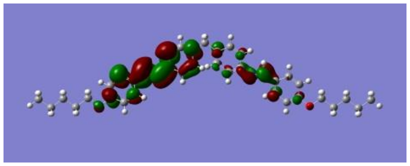
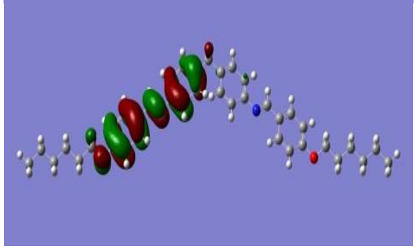
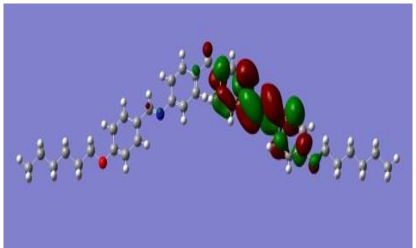
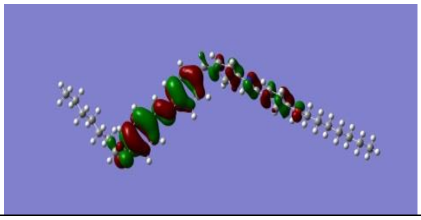
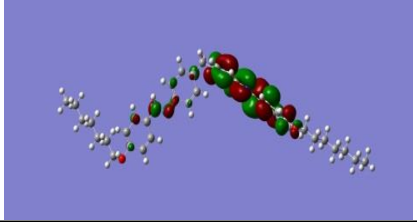


Fig. 11: Optimized geometry for B3 compounds.

The electronic distribution HOMO and LUMO for the prepared compounds listed in Table-8.

Table-8: Electronic distribution HOMO and LUMO.

Comp.	HOMO	LUMO
B0		
B2		
B3		
B4		
B5		
B6		
B7		

Conclusion

New Schiff base ethers were synthesized, purified and characterized. It is found that all the three compounds in the studied series are pure (marble) nematic mesophase; the theoretical study indicates that the prepared compounds decrease the LUMO energy as compared with B0 compound but no effect on HOMO energy has been observed, dipole moment study show the odd and even effect of carbon atoms in alkoxy chain groups.

Acknowledgments

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