



Research Article

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Synthesis , Characterization and Theoretical Study For Azo mesogenic compounds

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ABSTRACT

Series of elongated azo esters containing three rings with methyl moiety as one of the terminal carbon chain and various substituents $R(R=H, CH_3, OCH_3, NO_2, Cl)$ at the other end of the molecule have been isolated , and their structure were characterized by 1H -NMR and IR as well as elemental analysis . The mesomorphic properties of these compounds were investigated via differential scanning calorimetry and polarizing microscopy . . The thermal data indicate that all of these compounds exhibit mesomorphic properties (Nematic phase).The group efficiency order for the Nematic phase thermal stability can be derived for the compounds as : $NO_2 > OCH_3 > CH_3 > Cl$, With Density Functional Theory (DFT), we have calculated the electronic the electronic structures for azo compounds and the effects of the terminal groups in the azo liquid crystalline compounds on the electronic structure have been discussed .Our results indicate that the energy differences between the lowest unoccupied molecular orbit and the highest occupied molecular orbit are predominantly affected by the terminal groups of the azo liquid crystalline compounds.

Keywords: Mesophase , Azo , Terminal polar groups, Density Functional Theory, electronic structure.

INTRODUCTION

The azo compounds are highly colored and have been used as dyes and pigments. In addition, they have been studied broadly because of their outstanding thermal and optical properties in purposes such as toner, ink-jet printing, and oil-soluble lightfast dyes optical recording medium. In recent times, azo metal chelates have also paying attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems^[1].

The development of liquid crystal science technology has led to the preparation and study of numerous mesogens in particular , thermotropic liquid crystals^[2,3]. Most thermotropic liquid crystals are rod-like molecules having a rigid core composed of two or more aromatic rings and one or more terminal chains. Azo , is a linking group used in connecting two core groups. Though it provides a stepped core structure , it maintains molecular linearity , hence providing higher stability and enabling mesophase formation^[4-6]. Several studies have been conducted on azoesters owing to their interesting properties and considerable temperature range^[7]. The different substituents residing at the other end along the long molecular axis of the mesomorphic compounds have been known to either promote or suppress the mesomorphic properties^[8,9].

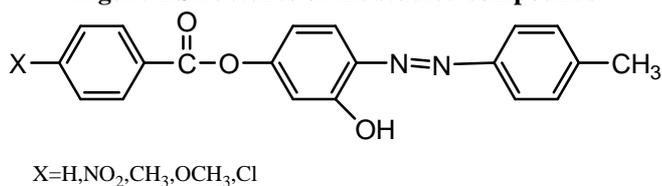
One of the typical terminal moiety exhibiting liquid crystal properties is those with terminal electronegative moiety, such as halogen groups . Terminal substituents as (Cl , NO_2 , OCH_3 , CH_3 , Br) are polar groups possess strong dipole moments which promote mesomorphic properties^[10], the increased dipole moment can enhance the stability of lattice and melting temperatures^[11].

In order to accomplish the investigation upon the mesomorphism of the series consisting three aromatic rings core system, we continued with the other substituent's (Cl , CH₃ , OCH₃ and NO₂) positioned along the molecular long axis .

The common structural features of the compounds are they consist of two phenyl rings linked through azo and ester central linkages with different terminal groups at one end (Fig. 1).

The aim of this study explain the effects of terminal polar groups which are different in the type of the dipol moments on the liquid crystalline phases and their thermal stability as well as atheoretical study was performed in order to evaluate some physical chemistry data related with mesomorphic properties .

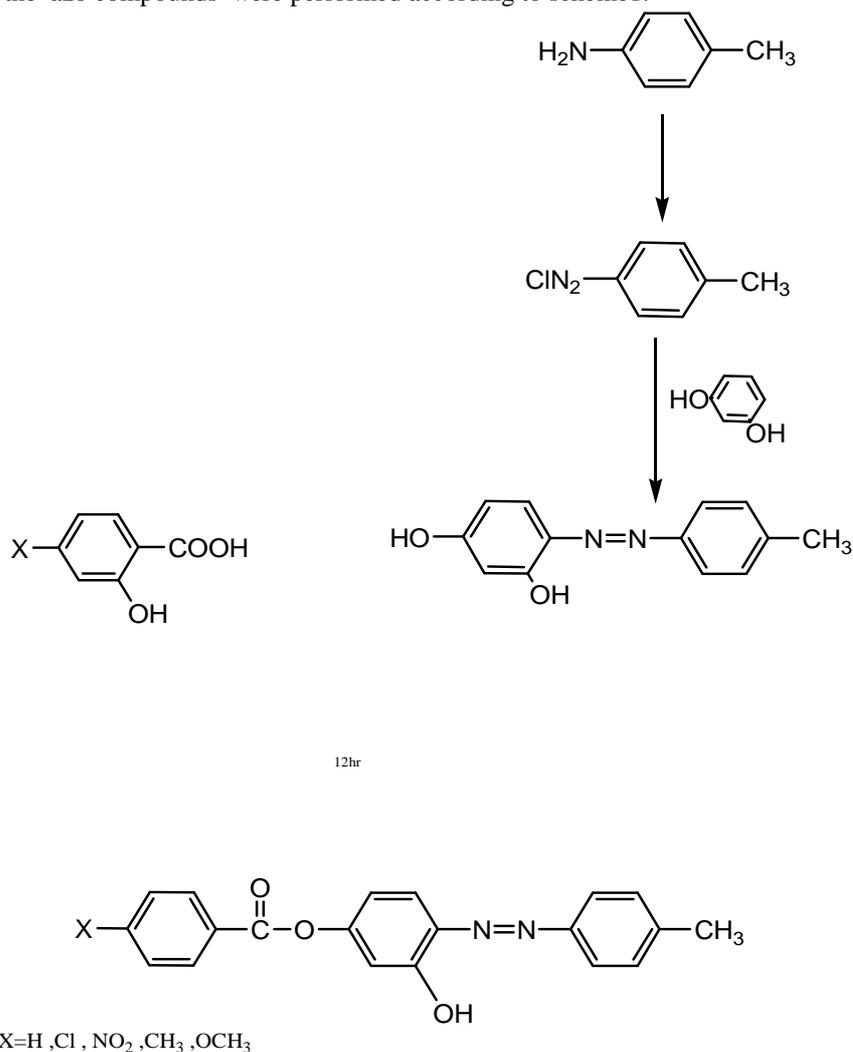
Figure 1. Structures of the studied compounds



EXPERIMENTAL SECTION

Synthesis

The preparation of the azo compounds were performed according to scheme1.



Scheme.1:Synthesis steps of the prepared compounds

Synthesis of 4(P-tolyldiazenyl)Benzen-1,3-diol

This compound was synthesized by using conventional method of diazotization and coupling^[12-13]. Orange solid, Yield :39%, m.p:150-154⁰C, IR(KBr disk)cm⁻¹:(abroad peak of intermolecular hydrogen – bonded phenolic -O-H between 3000-3400,(C =C) 1600,1508, 1458. C₁₃H₁₂O₂N₂:%C 68.42, %H 5.26, %N 12.28.Found: %C 68.73, %H 5.29, %N 12.39.

Synthesis of 3-hydroxy-4-(P-tolyldiazenyl)phenyl Benzoate and 3-hydroxy-4-(P-tolyldiazenyl)phenyl-4-Chloro(A-Cl),nitro(-NO₂),methyl(A-CH₃), Methoxy (A- OCH₃)Benzoate

Solutions of 4-Chloro,Nitro, Methyl ,Methoxy benzoic acid and Benzoic acid(50mmol),4-(p-tolyldiazenyl)Benzen-1,3-diol (50mmol), DCC (11.35g, 55mmol) in dry dichloromethane along with solid DMAP(0.3g,2.5mmol as catalyst)were magnetically stirred at room temperature for 12h^[14].The by product (dicyclohexyl urea) was filtered off under suction and the solvent was removed on rotavaporater .The crude product was recrystallized from hot solutions of ethanol and dried in vacuum .

Instruments

Infrared spectra were recorded as KBr pellets on a Buck – M500 spectrometer. ¹H-NMR spectra were recorded on Bruker – 300 MHz using CDCl₃ as a solvent and TMS as internal standard. Elemental analysis were done by elemental Micro - analysis. The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a leitz 350 hot stage equipped with a Vario – Orthomat camera of transition temperatures were made using a Netzsch DSC 200 F3 differential scanning calorimeter with a heating rate of 10 ⁰C min⁻¹.

RESULTS AND DISCUSSION

Characterization

The compounds presented here were characterized by elemental analysis and various spectroscopic methods, ¹H-NMR and IR^[15]. The elemental analyses of the compounds are consistent with their proposed structures (Table.1)

Table 1:Elemental analytical data (calculated value in parentheses) and the most relevant IR data for azo compounds

Compound	Molecular Formula	%C	%H	%N	C=Ocm ⁻¹ Ester	C-H aliphatic cm ⁻¹
A-H	C ₂₀ H ₁₆ O ₃ N ₂	72.28	4.81	8.43	1724	2927
A-CH ₃	C ₂₁ H ₁₈ O ₃ N ₂	72.83	5.20	8.09.	1724	2927
A- OCH ₃	C ₂₁ H ₁₈ O ₄ N ₂	69.61	4.97	7.73	1724	2927
A-Cl	C ₂₀ H ₁₅ O ₃ N ₂	65.57	4.09	7.65	1724	2927
A-NO ₂	C ₂₀ H ₁₅ O ₅ N ₃	63.66	3.97	11.14	1739	2923

The ¹H-NMR data of the compounds in give definite evidence for the molecular structures (Table 3 and Figure 5).

Table 2 : ¹H-NMR data for compounds (ppm)

Compound	OH	Aromatic protons	Aliphatic protons
A-H	13.3(S,1H,OH)	7.00-8.30(m,11H)	2.54 (S, 3H,CH ₃), 2.34(S,3H,CH ₃),
A-CH ₃	13.3(S,1H,OH)	7.12-8.46 (m, .11H)	2.34 (S,3H,CH ₃),, 13.3(S,1H,OH).
A- OCH ₃	13.3(S,1H,OH)	6.50- 7.90(m,.11H)	2.34(S,3H,CH ₃) 3.91 (S,3H,OCH ₃)
A-Cl	13.4(S,1H,OH)	7.12- 8.46(m,11H)	2.34(S,3H,CH ₃)
A-NO ₂	13.3(S,1H,OH)	7.12- 8.48 (m,11H)	2.34(S,3H,CH ₃)

Table 3 : Phase transition temperatures (⁰C)

Compound	C-N	N-I	C-I	T _{NΔ}
A-H	-	-	165.4	-
A-OCH ₃	175	258	-	83
A- CH ₃	163.2	243	-	80
A-Cl	164	236	-	72
A-NO ₂	210	296.5	-	86.5

C:Crystal, N=Nematic phase, I = Isotropic ΔT_N:thermal range of Nematic phase

Mesogenic properties

The phase transition temperatures, values of all the compounds are summarized in table1.It should be mentioned that all of the phase transition temperatures evaluated on the basis of texture change in a good accord with those measured by DSC. From table 3, it is clearly shown that upon heating all compounds exhibit endotherms

characteristic of the crystal Mesophase(Nematic) and mesophase – isotropic transitions temperature (T_m) except compound A-H. For compound A-H, direct melting(fig.2) from crystal – to – isotropic phase was observed under crossed polarizer.

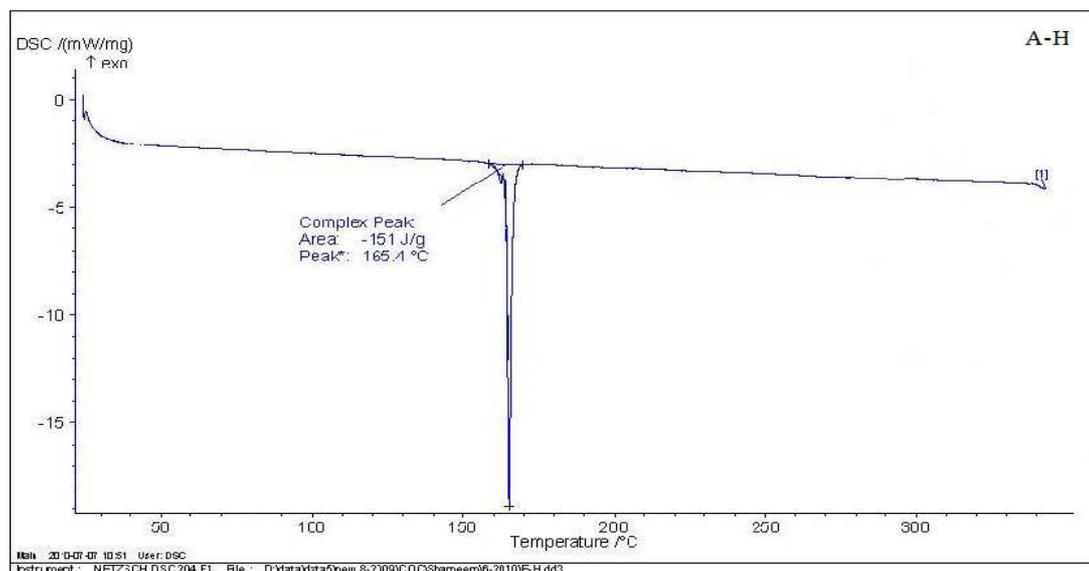


Fig.2: DSC thermogram for A –H

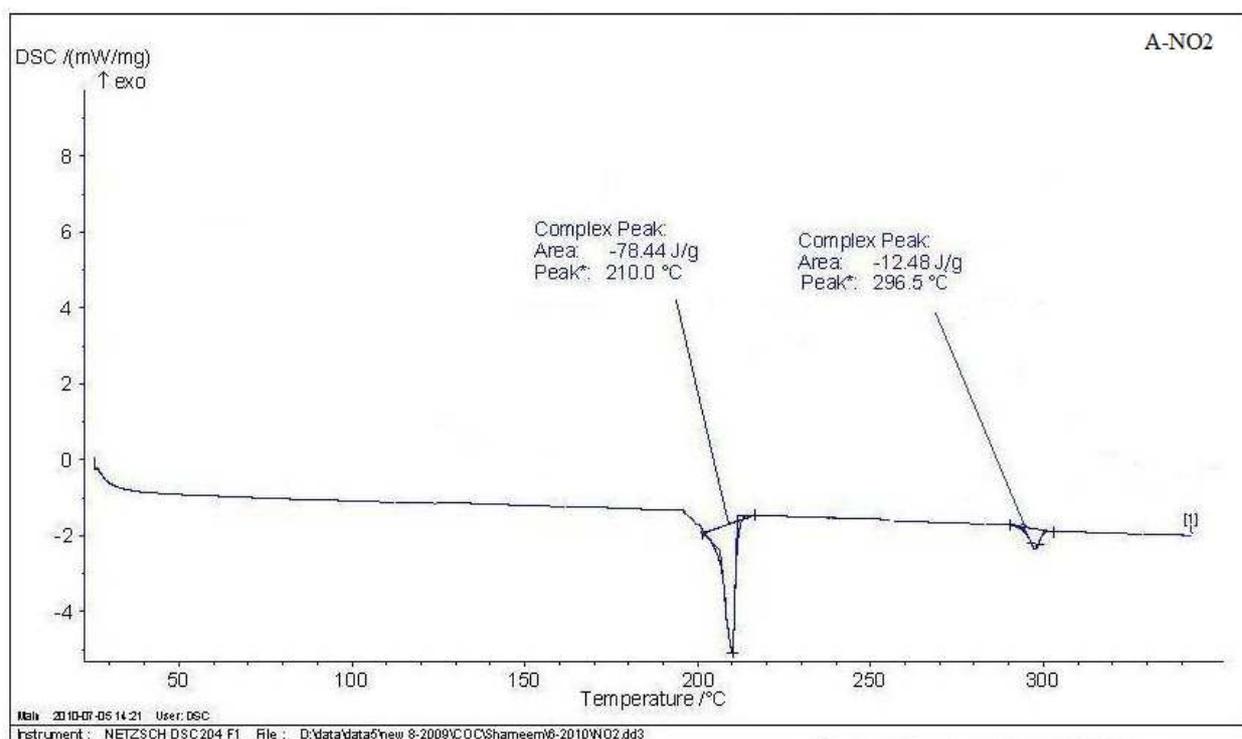


Fig.3: DSC thermogram for A-NO₂

The all compounds exhibit only Nematic phase, with the mesophase range being least for the compound having chlorine atom at the terminal position and the same being maximum when the hydrogen atom is replaced by NO₂ moiety. The substituted compound with dipole moment across the long axes of molecule as in the short alkyl chain CH₃ and OCH₃, this type of dipole moment enhance the terminal intermolecular attraction and exhibited Nematic phase^[11]. However we should note that the thermal stability of the Nematic phase of the CH₃ is considerably lower than that of the OCH₃ and this reminds us that the dipole of the ether group play some part in maintaining the parallel orientation in the Nematic melt^[16] but the substituted azo compound with dipole moment along the long axes of molecule were Cl and NO₂(fig.3), that's dipole moment would repel one another and reduce the lateral intermolecular attractions and enhance terminal intermolecular attractions which is enhanced Nematic phase as

well as nitro group will endow the molecule with high polarity, greater terminal attractions and hence higher nematic^[17] mesophase range .

The order of decreasing Nematic thermal stability of the compounds – in terms of the substituent X is : NO₂ > OCH₃ > CH₃ > Cl.

It agrees well with the nematic group efficiency order obtained by Gray^[18] and another study^[19] for pure mesogenic systems.

The Nematic phase , exhibited by these compounds , show textures that was typical of this type of mesophase. The Nematic phase was reflected the marbled texture on heating and Schlieren texture on cooling (Fig.4).

Computational Details

All calculations were performed with GAUSSIAN 03 package ^[20]. The ground-state geometries were fully optimized at the DFT level with Becke's^[21] three parameters hybrid functional and Lee, Yang and Parr's correlation functional B3LYP ^[22] using a standard 6-31G(d,p) basis set ^[23,25]. The MOs calculation performed using DFT, B3LYP method and 6-31G basis set the values HOMO, LUMO and HOMO-LUMO gap of studied compounds are however consistent.

Table 4: The calculated amounts of HOMO and LUMO energies, dipole moment (μ), with the DFT/6-31G basis set, B3LYP method

Compounds	Dipole moment (Debye)	Total Energy (a.u.)	HOMO(a.u.)	LUMO(a.u.)	(HOMO-LUMO) Gap ΔE_L
A-H	1.840	-1106.750	-0.1260	-0.079	-0.047
A-OCH ₃	2.768	-1221.270	-0.125	-0.079	-0.046
A-CH ₃	2.345	-1146.076	-0.1256	-0.079	-0.0466
A-NO ₂	7.995	-1311.209	-0.1491	-0.107	-0.0421
A-Cl	2.300	-1566.351	-0.1299	-0.083	-0.0469

The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO and LUMO energy gaps for (A-H, A-CH₃, A-OCH₃, A-NO₂, A-Cl) calculated at DFT level in the 6-31G basis set. Results of DFT method are presented in table 4. The smaller the LUMO and HOMO energy gaps, the easier it is for the HOMO electrons to be excited; the higher the HOMO energies, the easier it is for HOMO to donate electrons; the lower the LUMO energies, the easier it is for LUMO to accept electrons. From the resulting data shown in table 4, it is obvious that the HOMO energies of A-NO₂ are higher than other compounds studied and the energy gap of A-NO₂ is smaller than other compounds studied. Consequently, the electrons transfer from HOMO to LUMO in A-NO₂ is relatively easier than that in other compounds studied. With the decrease of the LUMO energies, LUMO in A-Cl accepts electrons easily. The same methods were employed to study other compounds studied, also leading to the above stated conclusions and confirming the obtained results. Furthermore, dipole moment was according to DFT calculation frontier molecular orbital energy gap, namely the HOMO – LUMO gap,

Table5: Electronic properties of the studied molecules

Electronic properties	Molecules				
	A-H	A-OCH ₃	A-CH ₃	A-NO ₂	A-Cl
Electron affinity $A = (-E_{LUMO})$	0.079	0.079	0.079	0.107	0.083
Ionization potential $I = (-E_{HOMO})$	0.1260	0.125	0.1256	0.1491	0.1299
Absolute electronegativity	0.1025	0.102	0.1023	0.12805	0.10645
Absolute hardness	0.0235	0.023	0.0233	0.02105	0.02345
Electrophilicity $\omega = \frac{\eta^2}{2\eta}$	0.01175	0.0115	0.01165	0.010525	0.011725

Two important properties of any molecule (M) are its gas-phase ionization potential (I) and its electron affinity (A)^[26].



The determination of I and A allows the absolute electronegativity (χ) and absolute hardness (η) parameters for M to be calculated.

These quantities are defined as:

$$X = \frac{I+A}{2} \quad (3)$$

$$\eta = \frac{I-A}{2} \quad (4)$$

In the most common case, I and A are related to the one-electron orbital energies of the HOMO and LUMO, respectively.

$$-I = E_{\text{HOMO}} \quad \text{and} \quad -A = E_{\text{LUMO}}$$

Then $(I-A)$ is simply the difference in energy between the HOMO and the LUMO. Soft molecules have a small energy gap. Low ' I ' creates a better electron donor and large ' A ' makes a better electron acceptor.

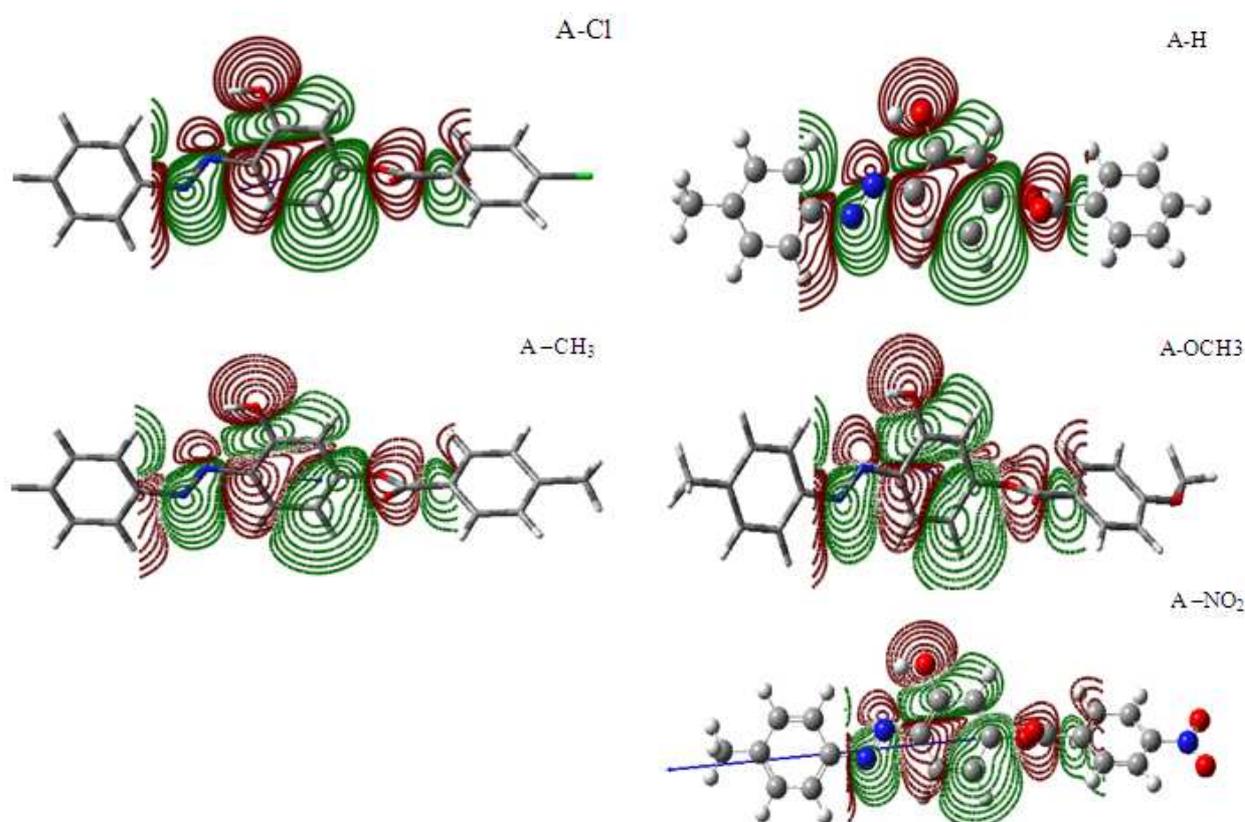


Fig.5: Electronic distribution in azo compounds

CONCLUSION

New azo mesogenic compounds with thioalkyl terminal group were synthesized. The study indicated that the molecular structural of mesogenic compound and the long of the thioalkyl chain effects on the mesomorphic properties of these compounds.

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