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Article

DFT-Based Study of Physical, Chemical and Electronic Behavior of Liquid Crystals of Azoxybenzene Group: *p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate

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Abstract: The present work describes the geometry and electronic structures of liquid crystals of azoxybenzene group and their reactivity with respect to molecular properties: total energy, ionization potential, electron affinity, HOMO energy, LUMO energy, electronegativity, hardness and dipole moment. Literature shows that mesomorphism depends particularly on the nature of terminal groups and their linkages with parent molecule. And thus, substitution of terminal groups can help to fine tune the liquid crystal behavior and also their applications. In this work the effect of four terminal groups of same and diverse nature has been studied. For the study, the molecular modeling and geometry optimization of the compounds have been performed on workspace program of CAChe Pro 5.04 software of Fujitsu using DFT method.

Keywords: Nematic liquid crystal, Azoxybenzene, DFT, Molecular properties

1. Introduction

All highly deformable materials (soft matter) including polymers, collides and surfactant solutions are studied in liquid-crystal physics and have novel technological applications [1, 2]. Liquid crystalline behaviors of materials depend on chemical structure and physical properties of structural unit [3]. At present theoretical conclusions are available, based on extensive experimental data regarding mesomorphism of low molecular weight mesophases, depending on the structure of molecules, particularly on the nature of terminal groups and linkages [4]. This enables to synthesize new compounds with desired liquid crystalline properties. *p*-Azoxyanisole (PAA) is an organic compound. In a solid state, it appears as a white powder, but when heated it forms a liquid crystal. As one of the first known and most readily prepared liquid crystals, PAA has been played an important role in the development of liquid crystal displays [5, 6]. Presently, a number of azoxy based liquid crystals are well known. Some of azoxybenzene-based liquid crystals, listed in Table-1, belonging to nematic class are *p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate. In our previous work, we have described some behavior of these liquid crystals based on (i) partial atomic charges [7], (ii) frontier orbital densities [8] and (iii) bond properties viz., bond length, bond order and bond angle [9]. In this work, we present geometry and electronic structure of above liquid crystals based on molecular properties: total energy, ionization potential, electron affinity, HOMO energy, LUMO energy, electronegativity, hardness and dipole moment.

2. Materials and Methods

The study materials of this work are listed in Table 1. For present study the three dimensional modeling and geometry optimization of all the compounds have been done in DGauss using the DFT B88-PW91 GGa functional with the DZVP basis sets [10, 11]. The application of DFT has given a new concept to chemical system [12]. The DFT based calculations of above parameters were performed with CAChe software and results are tabulated in Table 2 to Table 10.

Table 1. List of azoxy-based liquid crystal (LC)
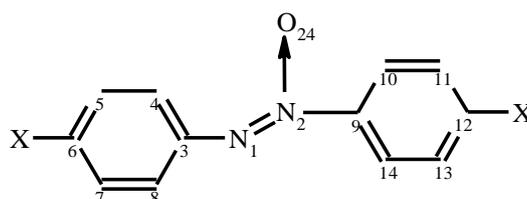
No.	X	Compd. Name
1	–OCH$_3$	*p*-azoxyanisole
2	–OC$_2$H$_5$	*p*-azoxyphenetole
3	–COOC$_2$H$_5$	ethyl-*p*-azoxybenzoate
4	–CH=CH-COOC$_2$H$_5$	ethyl-*p*-azoxycinnamate
5	–CH=CH-COOC$_8$H$_{17}$	*n*-octyl-*p*-azoxycinnamate

3. Results and Discussion

If *p*-azoxyanisole is treated as reference compound (RC) then the study shows that replacement of –OCH$_3$ group of RC by –OC$_2$H$_5$, –COOC$_2$H$_5$, –CH=CH–COOC$_2$H$_5$ and –CH=CH–COOC$_8$H$_{17}$ groups formed *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate, respectively. Molecular properties provide essential information of a molecule with respect to its physical, chemical and electronic performance. For sake of simplicity the study of above liquid crystals with respect each molecular property is described in different heads as given below.

3.1. Total Energy

The structure and stability of a molecule is determined by the total energy *E* of the molecule [13]. Total energy can be partitioned as follows.

$$E = T_n + T_e + V_{nm} + V_{ne} + V_{ee} \qquad (1)$$

where T_n is the kinetic energy of all nuclei, T_e is the kinetic energy of all electrons, V_{nn} the potential energy of all Coulomb interactions between the nuclei, V_{ne} the potential energy of Coulomb interactions between the nuclei and the electrons, and V_{ee} the potential energy of all Coulomb interactions between the electrons. The total energies of the above LCs were evaluated and are reported in Table 2. A reference to the table indicates that the total energy of RC is -877.067 hartree. On replacement of –OCH$_3$ group of RC by –OC$_2$H$_5$, there is an increase of 78.635 hartree energy of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of –OCH$_3$ group of RC by–COOC$_2$H$_5$, –CH=CH–COOC$_2$H$_5$ and –CH=CH–COOC$_8$H$_{17}$ groups increases the E of the resulting compounds. This is also demonstrated by Figure 1.

3.2. Frontier Orbital Energies

Energies of the highest occupied molecular orbital ($\varepsilon HOMO$) and lowest unoccupied molecular orbital ($\varepsilon LUMO$) are very popular quantum chemical descriptors. It has been

shown that these orbitals play a major role in governing many chemical reactions and determining electronic band gaps in solids; they are also responsible for the formation of many charge transfer complexes [14]. According to the frontier molecular orbital theory (*FMO*) of chemical reactivity, the formation of a transition state is due to an interaction between the frontier orbitals (*HOMO* and *LUMO*) of reacting species. Thus, the treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions. The *HOMO* energies of the above LCs were evaluated and are reported in Table 3. A reference to this table indicates that the *HOMO* energy of RC is -4.994. On replacement of –OCH$_3$ group of RC by –OC$_2$H$_5$, there is an increase of 0.053 eV value of *HOMO* energy of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of –OCH$_3$ group by –COOC$_2$H$_5$ (compd. no. 3) shows a decrease (0.969 eV) in the value of HOMO energy. Thus, ethyl-*p*-azoxybenzoate has lower value of HOMO energy of 1.022 eV than the former compounds. On further replacement of –OCH$_3$ group by –CH=CH–COOC$_2$H$_5$ (ethyl-*p*-azoxycinnamate) shows a decrease in the value of HOMO energy with respect to compd. no. 1 and 2 but an increment in respect to 3. Finally, replacement of –OCH$_3$ group by CH=CH–COOC$_8$H$_{17}$ (*n*-octyl-*p*-azoxycinnamate) shows an abnormal decrease in the HOMO energy. The decreasing order of HOMO energy of above LCs for electrophilic attack is *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate > *n*-octyl-*p*-azoxycinnamate (Figure 2).

Table 2. Total energy of azoxy-based LC

No.	Compd. Name	E (Hartree)
1	*p*-azoxyanisole	-877.067
2	*p*-azoxyphenetole	-955.702
3	ethyl-*p*-azoxybenzoate	-1182.402
4	ethyl-*p*-azoxycinnamate	-1337.230
5	*n*-octyl-*p*-azoxycinnamate	-1387.760
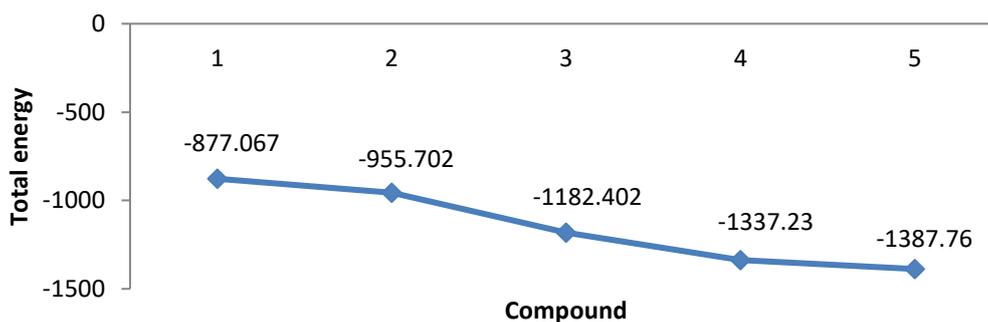
Figure 1. Graph showing effect of substitution on total energy of the compound

Table 3. Energy of highest occupied molecular orbital of azoxy-based LC

| No.	Compd. Name	εHOMO (eV)
1	*p*-azoxyanisole	-4.994
2	*p*-azoxyphenetole	-4.941
3	ethyl-*p*-azoxybenzoate	-5.963
4	ethyl-*p*-azoxycinnamate	-5.745
5	*n*-octyl-*p*-azoxycinnamate	-75.532
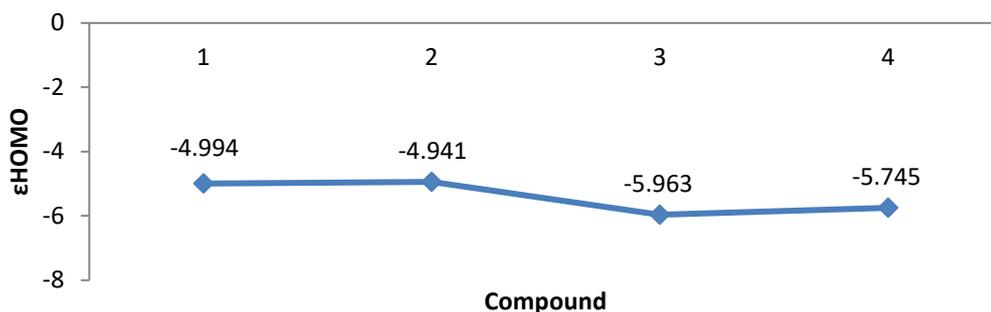
Figure 2. Graph showing effect of substitution on energy of HOMO of the compound

The LUMO energies of the above LCs were evaluated and are also reported in Table 4. A reference to this table indicates that the LUMO energy of RC is -2.718 eV. On replacement of –OCH$_3$ group of RC by –OC$_2$H$_5$, there is an increase of 0.05 eV value of LUMO energy of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of –OCH$_3$ group by –COOC$_2$H$_5$ (compd. no. 3) shows a decrease (0.922 eV) in the value of LUMO energy. Thus, ethyl-*p*-azoxybenzoate has lower value of LUMO energy than the former compounds. On further replacement of –OCH$_3$ group by –CH=CH–COOC$_2$H$_5$ (ethyl-*p*-azoxycinnamate) shows a decrease in the 2.058 eV and 2.108 eV value of LUMO energy with respect to compd. no. 1 and 2 but an increment of 0.026 in respect to 3. Finally, replacement of –OCH$_3$ group by –CH=CH–COOC$_8$H$_{17}$ (*n*-octyl-*p*-azoxycinnamate) shows an abnormal decrease of 73.121 eV in the LUMO energy. The decreasing order of LUMO energy of above LCs for nucleophilic interaction shows trend similar to the HOMO energy, *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate > *n*-octyl-*p*-azoxycinnamate (Figure 3).

Table 4. Energy of lowest unoccupied molecular orbital of azoxy-based LC

| Compd. Name	εLUMO (eV)
p-azoxyanisole	-2.718
p-azoxyphenetole	-2.668
ethyl-*p*-azoxybenzoate	-3.640
ethyl-*p*-azoxycinnamate	-3.806
n-octyl-*p*-azoxycinnamate	-78.115
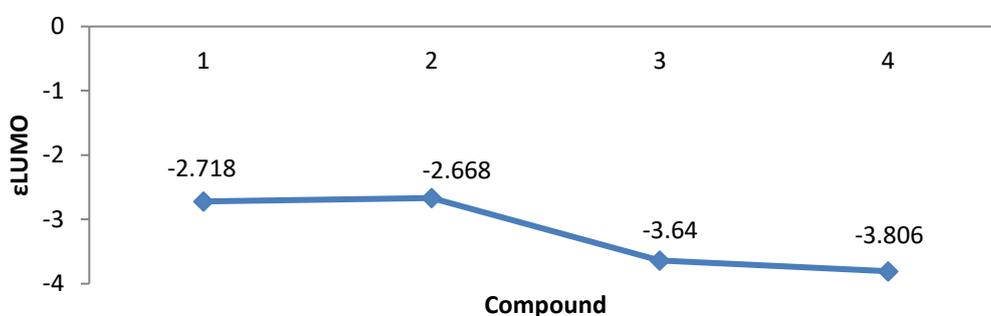
Figure 3. Graph showing effect of substitution on energy of LUMO of the compound

The HOMO-LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index [14]. A large HOMO-LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions. The HOMO-LUMO

gaps of the above LCs were calculated and are also reported in Table 5. A reference to the data shows the following sequence of above LCs with respect to their stability: Ethyl-*p*-azoxycinnamate > *p*-Azoxyphenetole > *p*-Azoxyanisole > Ethyl-*p*-azoxybenzoate > *n*-Octyl-*p*-azoxycinnamate. The trend of HOMO-LUMO gap is also demonstrated by Figure 4.

Table 5. HOMO-LUMO energy gap of azoxy-based LC

| Compd. Name	HOMO-LUMO gap
p-azoxyanisole	2.276
p-azoxyphenetole	2.273
ethyl-*p*-azoxybenzoate	2.323
ethyl-*p*-azoxycinnamate	1.939
n-octyl-*p*-azoxycinnamate	2.583
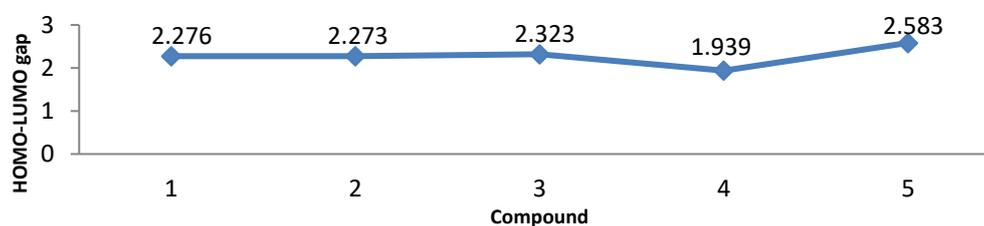
Figure 4. Graph showing effect of substitution on HOMO-LUMO energy gap of the compound

3.3. Ionization Energy (IE)

The minimal energy needed for the detachment of an electron for an atom or a molecule [15]. According to Koopman's theorem [16], the EA is simply the eigenvalue of HOMO with change in sign (IP = $-\varepsilon$HOMO) and characterizes the susceptibility of the molecule toward attack by electrophiles. The IP of the above LCs were calculated directly from the structure of the compound and are reported in Table 6. A reference to the table indicates that the IE of RC is 4.994. On replacement of $-OCH_3$ group of RC by $-OC_2H_5$, there is a decrease of 0.053 eV value of ionization energy of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of $-OCH_3$ group by $-COOC_2H_5$ (compd. no. 3) shows an increase (0.969 eV) in the value of ionization energy. Thus, ethyl-*p*-azoxybenzoate has larger value of ionization energy of 1.022 eV than the former compounds. On further replacement of $-OCH_3$ group by $-CH=CH-COOC_2H_5$ (ethyl-*p*-azoxycinnamate) shows an increase in the value of ionization energy with respect to compd. no. 1 and 2 and decrease in respect to 3. Finally, replacement of $-OCH_3$ group by $CH=CH-COOC_8H_{17}$ (*n*-octyl-*p*-azoxycinnamate) shows an abnormal increase in the ionization energy. The increasing order of IE of above LCs shows trend opposite to the HOMO energy (IE = $-\varepsilon$HOMO), *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate > *n*-octyl-*p*-azoxycinnamate and is good agreement to the Koopman's theorem (Figure 5).

Table 6. Ionisation energy of azoxy-based LC

| Compd. Name	IE (eV)
p-azoxyanisole	4.994
p-azoxyphenetole	4.941
ethyl-*p*-azoxybenzoate	5.963
ethyl-*p*-azoxycinnamate	5.745
n-octyl-*p*-azoxycinnamate	75.532
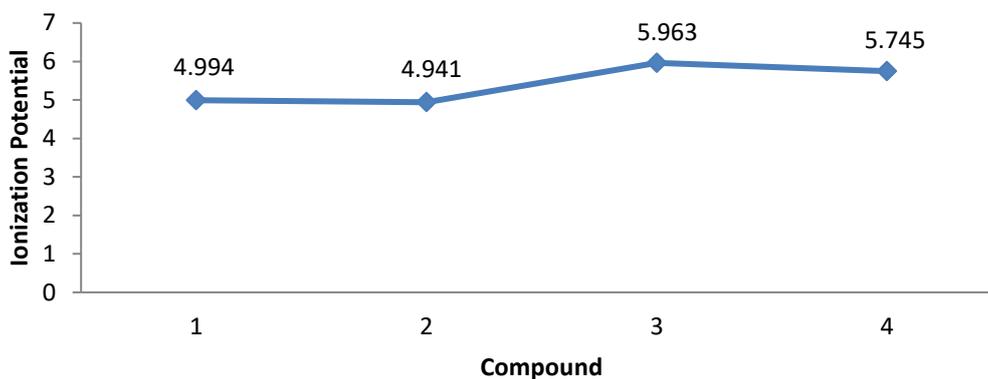
Figure 5. Graph showing effect of substitution on ionization potential of the compound

3.4. Electron Affinity (EA)

The energy difference between an uncharged species and its negative ion, referred to as an electron affinity, is an important property of atoms and molecules [15]. A survey of examples illustrates the diversity of areas in which electron affinities play a role: silicon and quantum dot (nanocrystal) semiconductor chemistry, Schottky diodes, molecular clusters, fullerene chemistry, interstellar chemistry, polymer photoluminescence, microelectronics, flat panel displays, and even hypotheses regarding the shuttle glow phenomenon. The EA of the above LCs were calculated directly from the structure of the compound and are reported in Table 7. A reference to this table indicates that the EA of RC is 2.718 eV. On replacement of $-OCH_3$ group of RC by $-OC_2H_5$, there is a decrease of 0.05 eV value of EA of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of $-OCH_3$ group by $-COOC_2H_5$ (compd. no. 3) shows an increase (0.922 eV) in the value of EA. Thus, ethyl-*p*-azoxybenzoate has larger value of EA than the former compounds. On further replacement of $-OCH_3$ group by $-CH=CH-COOC_2H_5$ (ethyl-*p*-azoxycinnamate) shows an increase in the 2.058 eV and 2.108 eV value of LUMO energy with respect to compd. no. 1 and 2 but a decrement of 0.026 in respect to 3. Finally, replacement of $-OCH_3$ group by $-CH=CH-COOC_8H_{17}$ (*n*-octyl-*p*-azoxycinnamate) shows an abnormal increase of 73.121 eV in the EA. The increasing order of EA of above LCs shows trend opposite to the LUMO energy ($EA = -\varepsilon LUMO$), *n*-octyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate > ethyl-*p*-azoxycinnamate > *p*-azoxyanisole > *p*-azoxyphenetole (Figure 6). It is good agreement of the Koopman's theorem, according to which the EA is simply the eigenvalue of LUMO with change in sign and characterizes the susceptibility of the molecule toward nucleophilic interaction.

Table 7. Electron affinity of azoxy-based LC

Compd. Name	EA (eV)
p-azoxyanisole	2.718
p-azoxyphenetole	2.668
ethyl-*p*-azoxybenzoate	3.640
ethyl-*p*-azoxycinnamate	3.806
n-octyl-*p*-azoxycinnamate	78.115
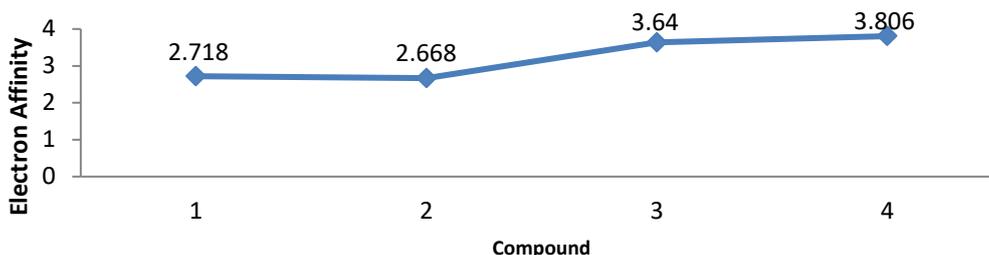
Figure 6. Graph showing effect of substitution on electron affinity of the compound

3.5. Electronegativity (χ)

In DFT, the electronegativity, commonly known to a chemist, is defined as the negative of a partial derivative of energy E of an atomic or molecular system with respect to the number of electrons N with a constant external potential $v(r)$ [15].

$$\mu = -\chi = -(E/N)_{v(r)} \tag{2}$$

When assuming a quadratic relationship between E and N a finite difference approximation Eq. 2 may be rewritten as

$$\chi = -\mu = -(IP + EA)/2 \tag{3}$$

where IP and EA are the vertical ionization energy and electron affinity, respectively, thereby recovering the electronegativity definition of Mulliken [17]. Moreover, a theoretical justification was provided for Sanderson's principle of electronegativity equalization, which states that when two or more atoms come together to form a molecule, their electronegativities become adjusted to the same intermediate value. According to Koopman's theorem [16], the IP or IE is simply the eigenvalue of HOMO with change in sign and EA is the eigenvalue of LUMO with change of sign; hence Eq. 3 may be written as

$$\chi = -\mu = \tfrac{1}{2}(\varepsilon LUMO + \varepsilon HOMO) \tag{4}$$

The χ of the above LCs were calculated by solving the Eq. 4 and are reported in Table 8. A reference to this table indicates that the χ of RC is -3.856 eV. On replacement of –OCH$_3$ group of RC by –OC$_2$H$_5$, there is an increase of 0.051 eV value of χ of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of –OCH$_3$ group by –COOC$_2$H$_5$ (compd. no. 3) shows a decrease (0.946 eV) in the value of χ. Thus, ethyl-*p*-azoxybenzoate has lower value of χ than the former compounds. On further replacement of –OCH$_3$ group by –CH=CH–COOC$_2$H$_5$ (ethyl-*p*-azoxycinnamate) shows a decrease in the 0.092 eV and 0.0971 eV value of χ with respect to compd. no. 1 and 2 but an increment of 0.026 in respect to 3. Finally, replacement of –OCH$_3$ group by –CH=CH–COOC$_8$H$_{17}$ (*n*-octyl-*p*-azoxycinnamate) shows an abnormal decrease of 72.968 eV in the χ. The decreasing order of χ of above LCs is: *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxybenzoate > ethyl-*p*-azoxycinnamate > *n*-octyl-*p*-azoxycinnamate (Figure 7).

Table 8. Electronegativity of azoxy-based LC

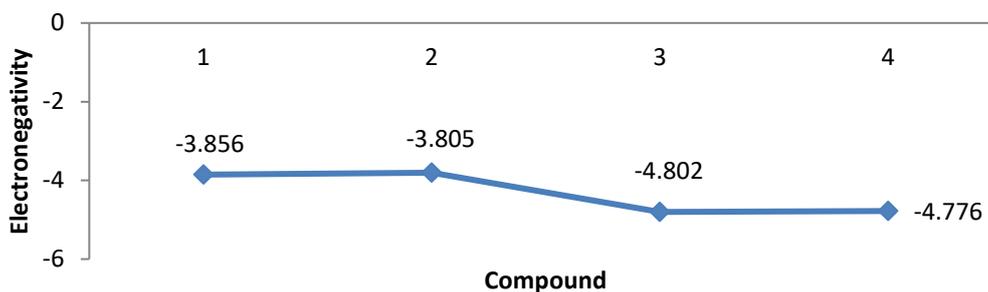| Compd. Name	χ (eV)
p-azoxyanisole	-3.856
p-azoxyphenetole	-3.805
ethyl-*p*-azoxybenzoate	-4.802
ethyl-*p*-azoxycinnamate	-4.776
n-octyl-*p*-azoxycinnamate	-76.824

Figure 7. Graph showing effect of substitution on electronegativity of the compound

3.6. Absolute hardness (η)

The absolute hardness η is defined as

$$\eta = \tfrac{1}{2}(\delta\mu/\delta N)v(r) = \tfrac{1}{2}(\delta^2 E/\delta N^2)v(r) \tag{5}$$

where *E* is the total energy, *N* is the number of electrons of the chemical species, and *v(r)* is the external potential [15]. The operational definition of absolute hardness is given as

$$\eta = \tfrac{1}{2}(IP + EA) \tag{6}$$

where IP and EA are the vertical ionization energy and electron affinity, respectively, of the chemical species. According to Koopman's theorem [16], the IP or IE is simply the eigenvalue of HOMO with change in sign and EA is the eigenvalue of LUMO with change of sign; hence Eq. 6 may be written as

$$\eta = \tfrac{1}{2}(\,\varepsilon LUMO - \varepsilon HOMO) \tag{7}$$

The η of the above LCs were calculated by solving the Eq. 7 and are reported in Table 9. A reference to this table indicates that the η of RC is 1.138 eV. On replacement of $-OCH_3$ group of RC by $-OC_2H_5$, there is a decrease of 0.001 eV value of η of the resulted compound, *p*-azoxyphenetole. Similarly, replacement of $-OCH_3$ group by $-COOC_2H_5$ (compd. no. 3) shows an increase of 0.024 eV in the value of η. Thus, ethyl-*p*-azoxybenzoate has higher value of η than the former compounds. On further replacement of $-OCH_3$ group by $-CH=CH-COOC_2H_5$ (ethyl-*p*-azoxycinnamate) shows an increase of   0.168 eV, 0.167 eV and 0.192 eV in the value of η with respect to compd. no. 1, 2 and 3. Finally, replacement of $-OCH_3$ group by $-CH=CH-COOC_8H_{17}$ shows a negative value of η, -1.292 eV. The decreasing order of η of above LCs is: ethyl-*p*-azoxybenzoate > *p*-azoxyanisole > *p*-azoxyphenetole > ethyl-*p*-azoxycinnamate > *n*-octyl-*p*-azoxycinnamate (Figure 8).

Table 9. Absolute hardness of azoxy-based LC

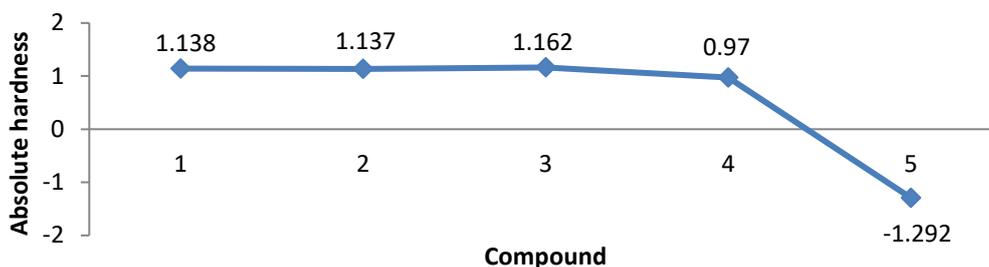| Compd. Name	η (eV)
p-azoxyanisole	1.138
p-azoxyphenetole	1.137
ethyl-*p*-azoxybenzoate	1.162
ethyl-*p*-azoxycinnamate	0.970
n-octyl-*p*-azoxycinnamate	-1.292

Figure 8. Graph showing effect of substitution on absolute hardness of the compound

3.7. Dipole moment (μ)

The dipole moments of polyatomic molecules depend on the nature of the atoms and on their arrangement. The dipole moment of a molecule is the vector sum of the dipole moments of the bonds and is calculated according to the rule of vector addition [18]. If two bonds with the dipole moments P and Q are at an angle θ the total dipole moment is given by

$$\mu^2 = P^2 + Q^2 + 2PQ \cos \theta \qquad (8)$$

For instance two identical bonds with the opposite directions ($\theta = 180°$) have $\mu = 0$. For identical bonds ($P = Q$) Eq. 8 yields

$$\mu^2 = 2P^2 (1 + \cos \theta) \qquad (9)$$

The dipole moments of the above LCs were computed directly from the optimized structure and are reported in Table 10. A reference to the data shows that the dipole moment of RC is 1.343 D. On replacement of $-OCH_3$ group of RC by $-OC_2H_5$, there is a decrease of 0.146 D of the resulted compound, *p*-azoxyphenetole. Further, replacement of $-OCH_3$ group of RC by $-COOC_2H_5$, $-CH=CH-COOC_2H_5$ and $-CH=CH-COOC_8H_{17}$ groups increases the dipole moments of the resulting compounds. This is also demonstrated by Figure 9.

Table 10. Dipole moment of azoxy-based LC

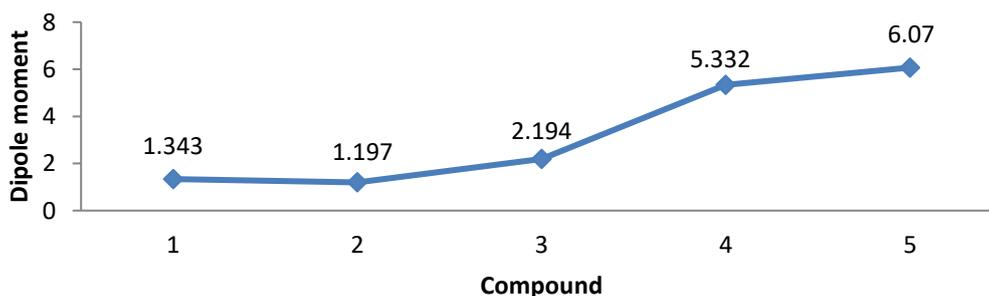| No.	Compd. Name	μ (D)
1	*p*-azoxyanisole	1.343
2	*p*-azoxyphenetole	1.197
3	ethyl-*p*-azoxybenzoate	2.194
4	ethyl-*p*-azoxycinnamate	5.332
5	*n*-octyl-*p*-azoxycinnamate	6.070

Figure 9. Graph showing effect of substitution on dipole moment of the compound

4. Conclusions

Above study concluded that

1. Total energy increases in sequence $-OCH_3 < -OC_2H_5 < -COOC_2H_5 < -CH=CH-COOC_2H_5 < -CH=CH-COOC_8H_{17}$ showing the stability of LCs.
2. The decreasing order of HOMO energy of above LCs for electrophilic interaction is *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate > *n*-octyl-*p*-azoxycinnamate.
3. The decreasing order of LUMO energy of above LCs for nucleophilic interaction shows trend similar to the HOMO energy.
4. The increasing order of IE of above LCs show trend opposite to the HOMO energy and the increasing order of EA of above LCs shows trend opposite to the LUMO energy that are good agreement to the Koopman's theorem.
5. The decreasing order of χ of above LCs is: *p*-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxybenzoate > ethyl-*p*-azoxycinnamate > *n*-octyl-*p*-azoxycinnamate,
6. The decreasing order of η of above LCs show trend similar to the χ.
7. The dipole moment increases in sequence $-OCH_3 < -OC_2H_5 < -COOC_2H_5 < -CH=CH-COOC_2H_5 < -CH=CH-COOC_8H_{17}$ showing polar interaction behaviour.

References

[1] Gray, G. W. (1962) Molecular Structure and the Properties of Liquid Crystals, New York, Academic Press, London.

[2] Chandrasekhar, S. (1970) Liquid Crystals (2nd ed.). Cambridge: Cambridge University Press, 1992.Krigbaum, W. R.; Chatani, Y.; Barber, P. G. Acta Cryst., B26, 97.

[3] Sharma, D. and Tiwari, S.N. (2016) Comparative computational analysis of electronic structure, MEP surface and vibrational assignments of a nematic crystal: 4-n-methyl-4`-cyanobiphenyl. Journal of Molecular liquids, **214**, 128-135.

[4] Tiwari, S.N. (2006) Theoretical study of molecular ordering in a nematic liquid crystal. Progress in crystal growth and characterization of materials, **52**, 150-158.

[5] Carlisle, C.H. and Smith, C.H. (1971) The structure of p-azoxyanisole. Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, **27**, 1068-1069.

[6] Ogorodnik, K.Z. (2002) Four solid-crystal forms of parazoxyanisole and thermodynamic relationships between them. Crystallography Reports, **47**, 966-969.

[7] Tewari, R.P., Khan, G., Shukla, A. and Shukla, K.D.P. (2012) Comparative study of azoxy-based liquid crystals (p-azoxyanisole, p-azoxyphenolate, ethyl-p-azoxybenzoate, ethyl-p-azoxycinnamate and n-octyl-p-azoxycinnamate) Based on Partial Atomic Charges. Archives of Physics Research, **3**, 175-191.

[8] Tewari, R.P., Khan, G., Shukla, A. and Shukla, K.D.P. (2012) Study of azoxy-based liquid crystals (p-azoxyanisole, p-azoxyphenolate, ethyl-p-azoxybenzoate, ethyl-p-azoxycinnamate and n-octyl-p-azoxycinnamate) Based on Frontier Orbital Densities. Journal of Chemical, Biological and Physical Sciences, **3**, 534-546.

[9] Khan, G., Tewari, R.P. and Shukla, A. (2014) Study of azoxy-based liquid crystals (p-Azoxyanisole, p-Azoxyphenolate, Ethyl-p-Azoxybenzoate, ethyl-p-Azoxycinnamate and n-octyl-p-Azoxycinnamate) based on bond properties. Archives of Physics Research, **5**, 25-30.

[10] Parr, R.G. and Yang, W. (1989) Density functional theory of atoms and molecules, Oxford University Press, New York.

[11] Geerlings, P., Proft, F.D. and Martin, J.M.L. (1996) In Recent Developments in Density Functional Theory (Theoretical and Computational Chemistry) Seminario, S., Ed.; Elsevier: Amsterdam, **5**, 773-809.

[12] Chandrakumar, R.S. and Pal, S. (2002) The Concept of Density Functional Theory Based Descriptors and its Relation with the Reactivity of Molecular Systems: A Semi-Quantitative Study, International Journal of Molecular Science, **3**, 324-337.

[13] Clark, S.J., Adam, C.J., Cleaver, D.J. and Crain, J. (1997) Conformational energy landscapes of liquid crystal molecules. Liquid Crystals, **22**, 477-482.

[14] Sahu, V.K., Soni, A.K. and Singh, P.P. (2010) Stability Index Based Quantitative Structure-Activity Relationship Study of β-Carbolines. Asian Journal of Chemistry, 22, 3025-3035.

[15] DeProft, F. and Geerlings, P. (1997) Calculation of ionization energies, electron affinities, electronegativity and hardness using Density Functional Methods. Journal of Chemical Physics, **106**, 3270-3279.

[16] Koopmans, T. (1934) Ordering of Wave Functions and Eigenenergies to the Individual Electrons of an Atom. Physica, **1**, 104–113.

[17] Mulliken, R.S. (1934) A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities. Journal of Chemical Physics, **2**, 782-793.

[18] Soni, A.K., Singh, P. and Sahu, V.K. (2020) DFT-Based Prediction of Biocentration Factor of Polychlorinated Biphenyls in Fish Species Using Molecular Descriptors. Advances in Biological Chemistry, **10**, 1-5.