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Comparative Study of Azoxy-Based Liquid Crystals (*p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate) Based on Partial Atomic Charges

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ABSTRACT

Computational study of electronic structure of some of azoxybenzene-based liquid crystals belonging to nematic class: *p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate have been studied. In order to obtain more information on the reactivity of above molecules towards nucleophile and electrophile, we performed semiempirical (AM1, PM3 and PM5) and density functional theory (DFT) based calculation to evaluate the negative and positive charge distribution in all the cases. *p*-Azoxyanisole is treated as reference compound (RC). The study shows that replacement of -OCH₃ group of RC by -OC₂H₅ group increase the Q_{MAX} , while successive addition of -CH=CH-COOC₈H₁₇, -CH=CH-COOC₂H₅ and -COOC₂H₅ groups decreases the Q_{MAX} , respectively. In all the compounds it is the carbon atom at site 12, C12, which has Q_{MAX} , except in ethyl-*p*-azoxybenzoate, where Q_{MAX} is at C9. In respect to Q_{MIN} , it is the azoxy oxygen, O24, which has Q_{MIN} and the only differences in the trend is due to the positions of ethyl-*p*-azoxybenzoate and *n*-octyl-*p*-azoxycinnamate, which are interchanged. The study also shows that DFT based calculations provide better result than the semiempirical based calculations.

Keywords: Azoxy-based liquid crystals, Partial atomic charges, Austin model 1, parametric model 3, parametric model 5 and density functional theory.

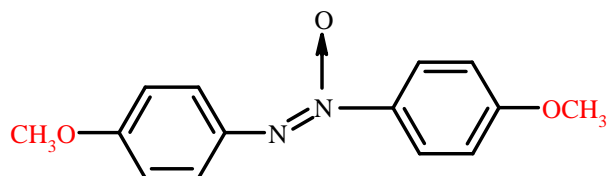
INTRODUCTION

Liquid crystal (LC) materials are unique in their properties and uses.¹ As research into this field continues and as new applications are developed, liquid crystals will play an important role in modern technology. Liquid-crystal physics, although a field in itself, is often included in the larger area called 'soft matter', including polymers, colloids, and surfactant solutions, all of which are highly deformable materials. This property leads to many unique and exciting phenomena not seen in ordinary condensed phases, and possibilities of novel technological applications.² The characteristic feature of macromolecules is known to be flexibility which depends on the chemical structure of units and governs the physical properties of polymers. It follows that liquid crystalline behaviour of polymers; in particular the polymers with mesogenic side groups would depend on chemical structure of monomers, and including the nature of the polymerizable group.³⁻⁵ We are interested in the matter as we dealt with the computational study of electronic structure of some of azoxybenzene-based liquid crystals belonging to nematic class: *p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate.⁶ The chemistry of azoxy-based liquid crystals is characterized by azoxy-group. This group has two nitrogen atom and an oxygen atom. One of them is doubly bonded with a lone pair of electrons, while the other is

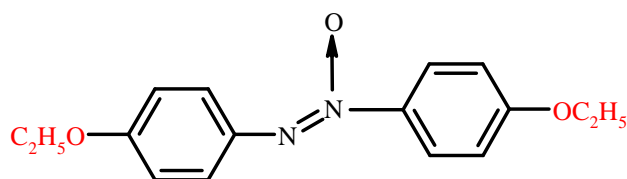
also doubly bonded but bears a positive charge. In this work, we describe the electronic structures of the above liquid crystals and their reactivity with respect to partial atomic charges.

MATERIALS AND METHODS

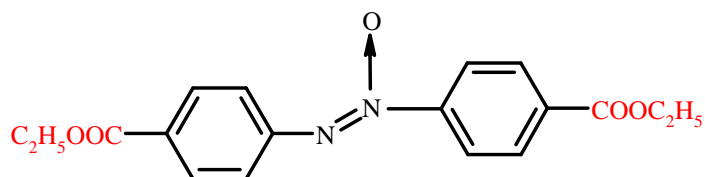
The study material of this work is five azoxybenzene-based liquid crystals of the nematic LC class. The 2D structures of these compounds as drawn by MDL ISIS Draw 2.5 software are presented as below.



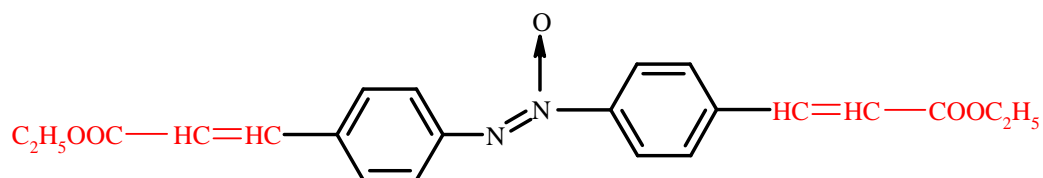
Compound-1. p-azoxyanisole



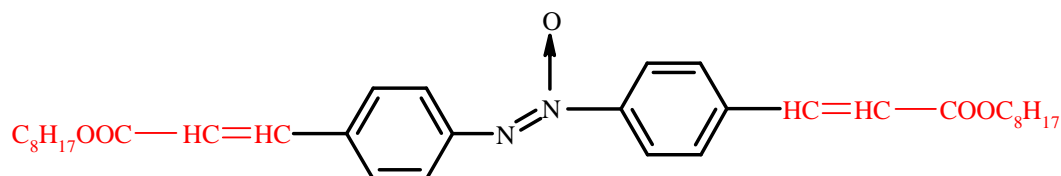
Compound-2. p-azoxyphenetole



Compound-3. ethyl-p-azoxybenzoate



Compound-4. ethyl-p-azoxycinnamate



Compound-5. n-octyl-p-azoxycinnamate

In order to obtain more information on the reactivity of above molecules towards nucleophile and electrophile, we performed semiempirical and density functional theory (DFT) based calculation to evaluate the negative and positive charge distribution in all the cases.

In principle, any semiempirical method can be used to calculate above properties. A number of semiempirical methods have been developed over the last several decades. To name but some of the most popular: extended Hückel theory (EHT),⁷ complete neglect of differential overlap (CNDO),^{8,9} intermediate neglect of differential overlap (INDO),¹⁰ modified INDO (MINDO),¹¹ modified neglect of diatomic overlap (MNDO),¹² Austin model 1 (AM1),¹³ parametric model 3 (PM3)¹⁴ and parametric model 5 (PM5).¹⁵ These methods have been developed within the mathematical framework of the molecular orbital theory (self-consistent field molecular orbital [SCFMO]), but

based on simplifications and approximations introduced into the computational procedure, which dramatically reduce the computational time.

DFT is based on two famous theorems of Hohenberg and Khon.¹⁶ According to DFT the electron density is the fundamental properties of molecular and electronic system, however electron density alone could not define the entire chemical phenomenon. Its sensitivity to structural perturbation and response to the changes in external condition are rather more important in reflecting the chemical reactivity of a system rather than the absolute value of electron density.

The 3D modeling and geometry optimization of all the compounds have been performed with the help of *CAChe Pro software of Fujitsu*. All the semiempirical calculations performed with the help of *MOPAC 2002 V2.20 software*¹⁷ associated with *CAChe*. And the DFT-based calculation performed with the *DGauss* also associated with *CAChe*.¹⁷

RESULTS AND DISCUSSION

According to classical chemical theory, all chemical interactions are by nature either electrostatic (polar) or orbital (covalent). Electrical charges in the molecule are obviously the driving force of electrostatic interactions. Indeed, it has been proven that local electron densities or charges are important in many chemical reactions and physico-chemical properties of compounds. Atomic partial charges have been used as static chemical reactivity indices.¹⁹ The calculated σ - and π -electron densities on a particular atom also characterize the possible orientation of the chemical interactions and, thus, are often considered to be directional reactivity indices. In order to obtain more information on the reactivity of above compounds towards nucleophile and electrophile, we performed AM1, PM3, PM5 and DFT-based calculations to evaluate the negative and positive charge distribution in all the cases.

3.1. p-Azoxyanisole: 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.²⁰ A molecule of PAA is composed of thirty three atoms, out of which there are fourteen carbon, fourteen hydrogen, three oxygen and two nitrogen atoms. In order to predict the nucleophilic and electrophilic sites of attack, the most positive and negative charged sites must be known.²¹ The charge distributions (Q) of each atom of this compound were calculated by using the AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ methods and the results are reported in Graph-1 and the arbitrary numbering scheme used in the above analysis is shown in Figure-1, which represents a perspective view of the molecule.

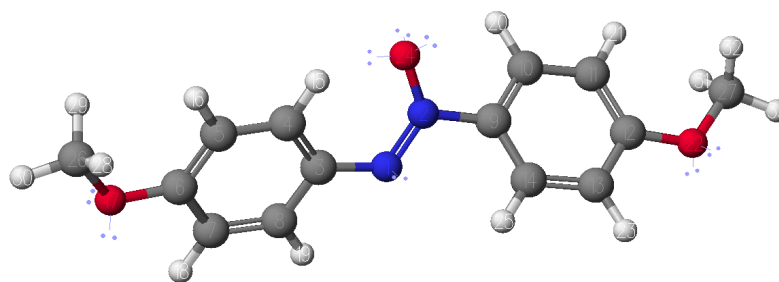
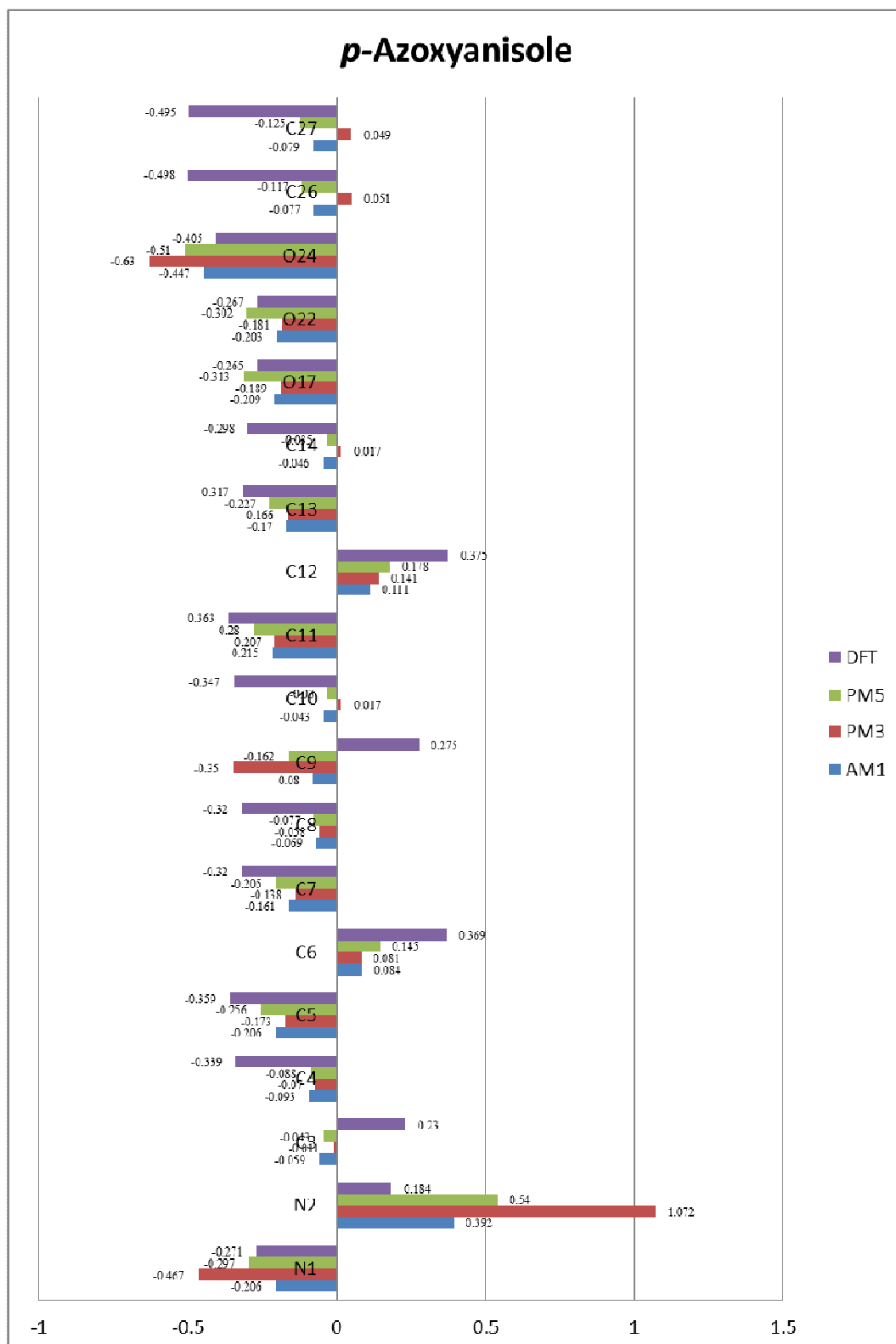


Figure 1. Perspective view of Compound-1, p-azoxyanisole

AM1 is a semiempirical method for the quantum calculation of molecular electronic structure in computational chemistry. It is based on the Neglect of Differential Diatomic Overlap integral approximation. Specifically, it is a generalization of the modified neglect of differential diatomic overlap approximation. AM1 was developed by Michael Dewar and co-workers and published in 1985.¹³ AM1 is an attempt to improve the MNDO model by reducing the repulsion of atoms at close separation distances. The atomic core-atomic core terms in the MNDO equations were modified through the addition of off-center attractive and repulsive Gaussian functions. The results of AM1 calculations are sometimes used as the starting points for parameterizations of force fields in molecular modelling. AM1 data show that, there are seventeen positive charge atoms in *p-azoxyanisole*, including two carbon atoms (C6 and C12), one nitrogen (N2) and all the fourteen H-atom. It is also shown by the Graph-1. Thus, there are three positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.392) > C12 (0.111) > C6 (0.084). The most positive position in *p-azoxyanisole* is the azoxy nitrogen, N2 ($Q_{MAX} = 0.392$) and the lowest positive position is carbon atom C6 ($Q = 0.084$). It is also shown by the Graph-1 that there are sixteen negative charge sites for electrophilic attack.



Graph 1. Graphical representation of magnitude of partial atomic charges of *p*-azoxyanisole

The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.447) > C11 (-0.215) > O17 (-0.209) > N1 (-0.206) > C5 (-0.206) > O22 (-0.203) > C13 (-0.170) > C7 (-0.161) > C4 (-0.093) > C9 (-0.080) > C27 (-0.079) > C26 (-0.077) > C8 (-0.069) > C3 (-0.059) > C14 (-0.046) > C10 (-0.043). The most negative position in *p*-azoxyanisole is the azoxy oxygen, O24 ($Q_{\text{MIN}} = -0.447$) and the lowest negative position is carbon atom C10 ($Q = -0.043$).

PM3 is a semi-empirical method for the quantum calculation of molecular electronic structure in computational chemistry. It is based on the Neglect of Differential Diatomic Overlap integral approximation.¹⁴ The PM3 method uses the same formalism and equations as the AM1 method. The only differences are: (1) PM3 uses two Gaussian functions for the core repulsion function, instead of the variable number used by AM1¹³ (which uses between one and four Gaussians per element); (2) the numerical values of the parameters are different. The other differences lie in the philosophy and methodology used during the parameterization: whereas AM1 takes some of the parameter values from spectroscopical measurements, PM3 treats them as optimizable values. The method was developed by J. J. P. Stewart and first published in 1989.¹⁴ PM3 data show that, there are twenty one positive charge atoms in *p-azoxyanisole*, including four carbon atoms (C6, C10, C12, C14, C26 and C27), one nitrogen (N2) and all the fourteen H-atom. It is also shown by the Graph-1. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (1.072) > C12 (0.141) > C-6 (0.081) > C26 (0.051) > C27 (0.049) > C10 = C14 (0.017). The most positive position in *p-azoxyanisole* is the azoxy nitrogen, N2 ($Q_{MAX} = 1.072$) and the lowest positive position is carbon atom C6 = C14 ($Q = 0.017$). It is also shown by the Graph-1 that there are twelve negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.630) > N1 (-0.467) > C9 (-0.350) > C11 (-0.207) > O17 (-0.189) > O22 (-0.181) > C5 (-0.173) > C13 (-0.166) > C7 (-0.138) > C4 (-0.070) > C8 (-0.058) > C3 (-0.011). The most negative position in *p-azoxyanisole* is the azoxy oxygen, O24 ($Q_{MIN} = -0.630$) and the lowest negative position is carbon atom C3 ($Q = (-0.011)$).

PM5 represents an improvement of the widely used PM3 method.¹⁵ PM5 data show that, there are seventeen positive charge atoms in *p-azoxyanisole*, including two carbon atoms (C6 and C12), one nitrogen (N2) and all the fourteen H-atom. It is also shown by the Graph-1. Thus, there are three positive charge sites for nucleophilic attack.²¹ The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.540) > C12 (0.178) > C6 (0.145). The most positive position in *p-azoxyanisole* is the azoxy nitrogen, N2 ($Q_{MAX} = 0.540$) and the lowest positive position is carbon atom C-6 ($Q = 0.145$). It is also shown by the Graph-1 that there are sixteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.510) > O17 (-0.313) > O22 (-0.302) > N1 (-0.297) > C11 (-0.280) > C5 (-0.256) > C13 (-0.227) > C7 (-0.205) > C9 (-0.162) > C27 (-0.125) > C26 (-0.117) > C4 (-0.088) > C8 (-0.077) > C3 (-0.043) > C14 (-0.035) > C10 (-0.030). The most negative position in *p-azoxyanisole* is the azoxy oxygen, O24 ($Q_{MIN} = -0.510$) and the lowest negative position is carbon atom C3 ($Q = (-0.030)$).

DFT is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many body-systems, in particular atoms, molecules, and the condensed phases.¹⁶ With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. DFT data show that, there are nineteen positive charge atoms in *p-azoxyanisole*, including four carbon atoms (C3, C6, C9 and C12), one nitrogen (N2) and all the fourteen H-atom. It is also shown by the Graph-1. Thus, there are five positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is C12 (0.375) > C6 (0.369) > C9 (0.275) > C3 (0.230) > N2 (0.184). The most positive position in *p-azoxyanisole* is the carbon atom, C12 ($Q_{MAX} = 0.392$) and the lowest positive position is N2 ($Q = 0.184$). It is also shown by the Graph-1 that there are fourteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is C26 (-0.498) > C27 (-0.495) > O24 (-0.405) > C11 (-0.363) > C5 (-0.359) > C10 (-0.347) > C4 (-0.339) > C7 (-0.320) > C8 (-0.320) > C13 (-0.317) > C14 (-0.298) > N1 (-0.271) > O22 (-0.267) > O17 (-0.265). The most negative position in *p-azoxyanisole* is the carbon atom, C26 ($Q_{MIN} = -0.498$) and the lowest negative position is oxygen atom O17 ($Q = -0.265$).

3.2. *p*-Azoxyphenetole: A molecule of *p*-azoxyphenetole is composed of thirty nine atoms, out of which there are sixteen carbon, eighteen hydrogen, three oxygen and two nitrogen atoms. In order to predict the nucleophilic and electrophilic sites of attack, the most positive and negative charged sites must be known.²¹ The charge distributions (Q) of each atom of this compound were calculated by using the AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ methods and the results are reported in Graph-2 and the arbitrary numbering scheme used in the above analysis is shown in Figure-2, which represents a perspective view of the molecule.

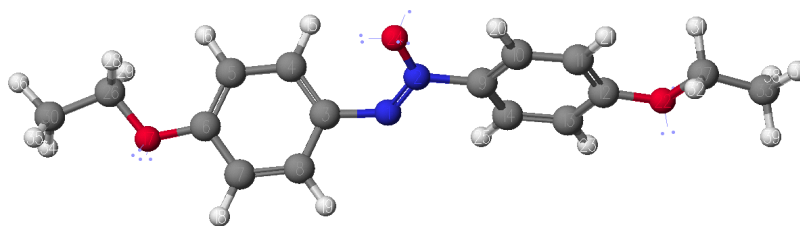
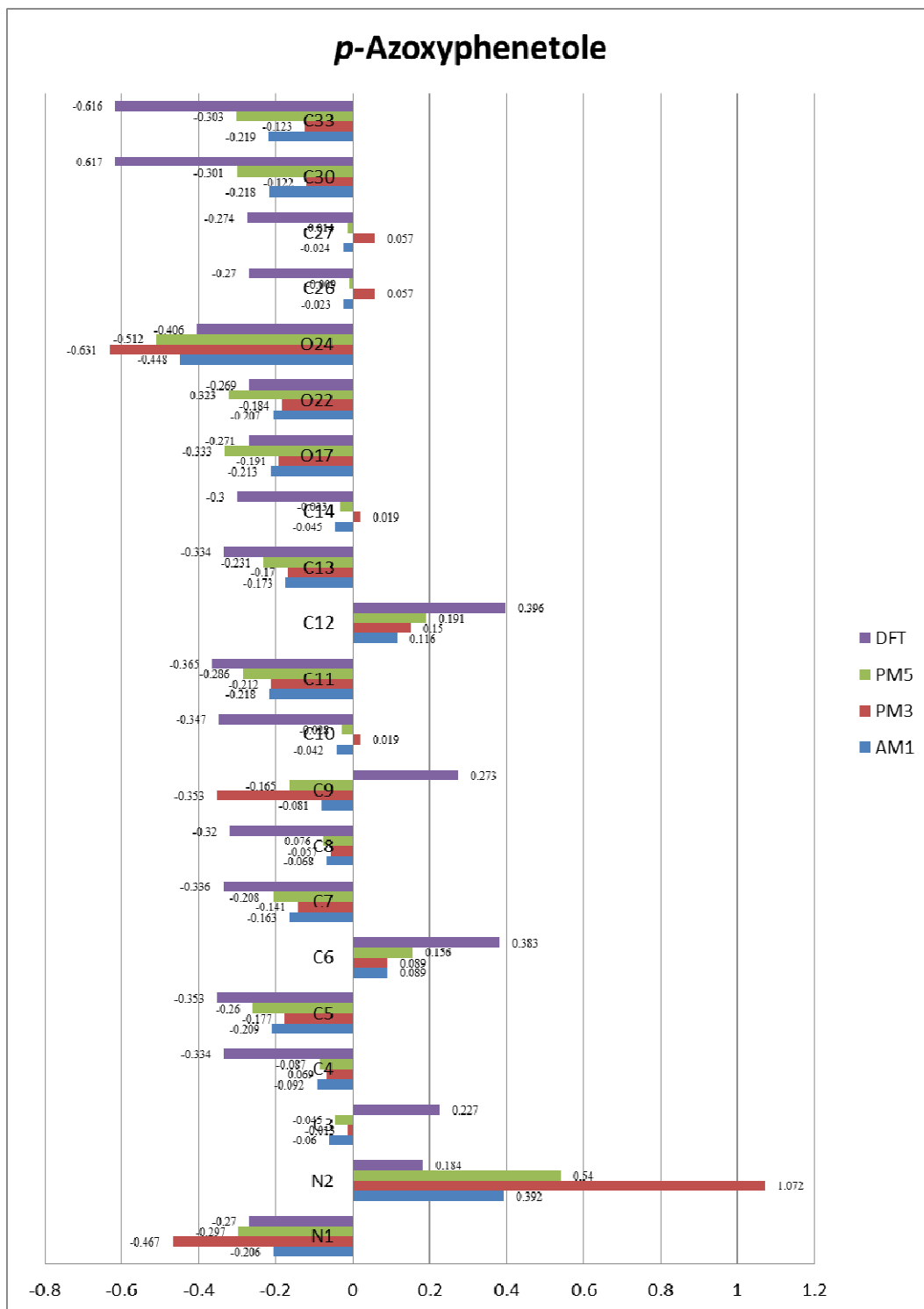


Figure 2. Perspective view of Compound-2, *p*-azoxyphenetole



Graph 2. Graphical representation of magnitude of partial atomic charges of *p*-azoxyphenetole

AM1¹³ data show that, there are twenty one positive charge atoms, including two carbon atoms (C6 and C12), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-2. Thus, there are three positive charge sites for nucleophilic attack.²¹ The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.392) > C12 (0.116) > C6 (0.089). The most positive position in *p*-azoxyphenetole is the azoxy nitrogen, N2 ($Q_{MAX} = 0.392$) and the lowest positive position is carbon atom C6 ($Q = 0.089$). It is also shown by the Graph-2 that there are eighteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.448) > C33 (-0.219) > C11 = C30 (-0.218) > O17 (-0.213) > C5 (-0.209) > O22 (-0.207) > N1 (-0.206) > C13 (-0.173) > C7 (-0.163) > C4 (-0.092) > C9 (-0.081) > C8 (-0.068) > C3 (-0.060) > C14 (-0.045) > C10 (-0.042) > C27 (-0.024) > C26 (-0.023). The most negative position in *p*-azoxyphenetole is the azoxy oxygen, O24 ($Q_{MIN} = -0.448$) and the lowest negative position is carbon atom C26 ($Q = -0.023$).

PM3¹⁴ data show that, there are twenty five positive charge atoms, including six carbon atoms (C6, C10, C12, C14, C26 and C27), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-2. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (1.072) > C12 (0.150) > C6 (0.089) > C26 = C27 (0.057) > C10 = C14 (0.019). The most positive position in *p*-azoxyphenetole is the azoxy nitrogen, N2 ($Q_{MAX} = 1.072$) and the lowest positive position is carbon atom C10 = C14 ($Q = 0.019$). It is also shown by the Graph-2 that there are fourteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.631) > N1 (-0.467) > C9 (-0.353) > C11 (-0.212) > O17 (-0.191) > O22 (-0.184) > C5 (-0.177) > C13 (-0.170) > C7 (-0.141) > C33 (-0.123) > C30 (-0.122) > C4 (-0.069) > C8 (-0.057) > C3 (-0.013). The most negative position in *p*-azoxyphenetole is the azoxy oxygen, O24 ($Q_{MIN} = -0.631$) and the lowest negative position is carbon atom C3 ($Q = -0.013$).

PM5¹⁵ data show that, there are twenty one positive charge atoms, including two carbon atoms (C6 and C12), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-2. Thus, there are three positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.540) > C12 (0.191) > C6 (0.156). The most positive position in *p*-azoxyphenetole is the azoxy nitrogen, N2 ($Q_{MAX} = 0.540$) and the lowest positive position is carbon atom C6 ($Q = 0.156$). It is also shown by the Graph-2 that there are eighteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.512) > O17 (-0.333) > O22 (-0.323) > C33 (-0.303) > C30 (-0.301) > N1 (-0.297) > C11 (-0.286) > C5 (-0.260) > C13 (-0.231) > C7 (-0.208) > C9 (-0.165) > C4 (-0.087) > C8 (-0.076) > C3 (-0.045) > C14 (-0.033) > C10 (-0.028) > C27 (-0.014) > C26 (-0.009). The most negative position in *p*-azoxyphenetole is the azoxy oxygen, O24 ($Q_{MIN} = -0.512$) and the lowest negative position is carbon atom, C26 ($Q = -0.009$).

DFT¹⁶ data show that, there are twenty three positive charge atoms, including four carbon atoms (C3, C6, C9 and C12), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-2. Thus, there are five positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is C12 (0.396) > C6 (0.383) > C9 (0.273) > C3 (0.227) > N2 (0.184). The most positive position in *p*-azoxyphenetole is the carbon atom, C12 ($Q_{MAX} = 0.396$) and the lowest positive position is azoxy nitrogen, N2 ($Q = 0.184$). It is also shown by the Graph-2 that there are fifteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is C30 (-0.617) > C33 (-0.616) > O24 (-0.406) > C11 (-0.365) > C5 (-0.353) > C10 (-0.347) > C7 (-0.336) > C4 = C13 (-0.334) > C8 (-0.320) > C14 (-0.300) > C27 (-0.274) > O17 (-0.271) > N1 = C26 (-0.270) > O22 (-0.269). The most negative position in *p*-azoxyphenetole is the carbon atom, C30 ($Q_{MIN} = -0.617$) and the lowest negative position is oxygen atom, O22 ($Q = -0.269$).

3.3. Ethyl-*p*-azoxybenzoate: A molecule of ethyl-*p*-azoxybenzoate is composed of forty three atoms, out of which there are eighteen carbon, eighteen hydrogen, five oxygen and two nitrogen atoms. In order to predict the nucleophilic and electrophilic sites of attack, the most positive and negative charged sites must be known.²¹ The charge distributions (Q) of each atom of this compound were calculated by using the AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ methods and the results are reported in Graph-3 and the arbitrary numbering scheme used in the above analysis is shown in Figure-3, which represents a perspective view of the molecule.

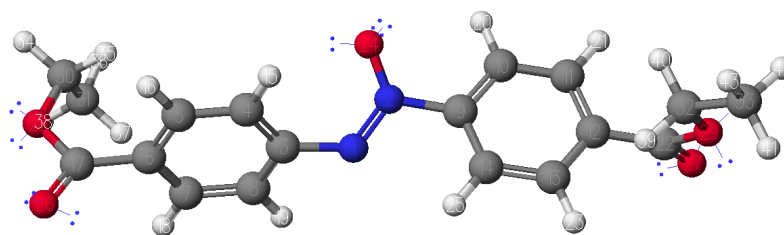
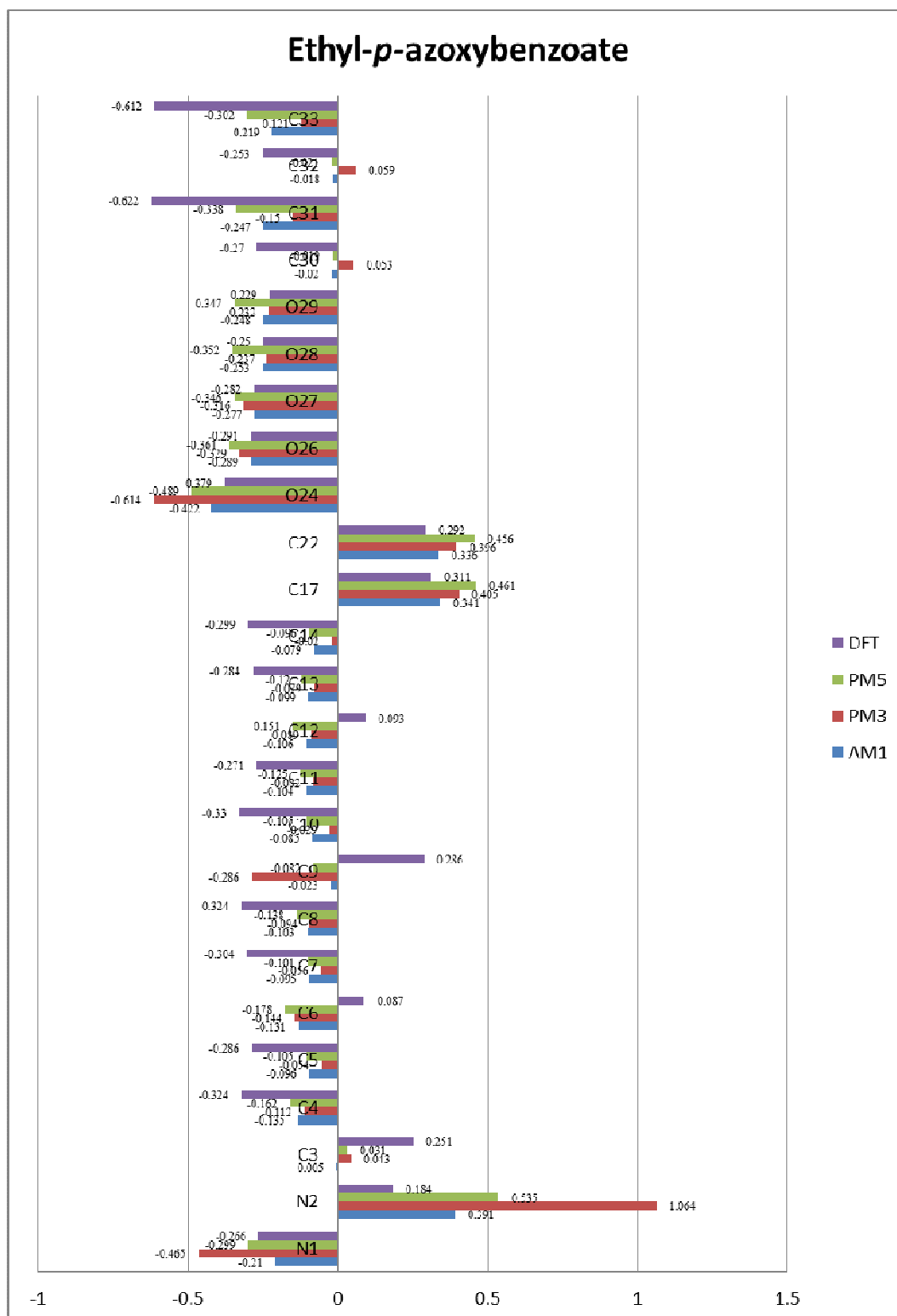


Figure 3. Perspective view of Compound-3, ethyl-*p*-azoxybenzoate

AM1¹³ data show that, there are twenty one positive charge atoms, including two carbon atoms (C17 and C22), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-3. Thus, there are three positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.391) > C17 (0.341) > C22 (0.336). The most positive site in ethyl-*p*-azoxybenzoate is the azoxy nitrogen, N2 ($Q_{MAX} = 0.391$) and the lowest positive site is carbon atom C22 ($Q = 0.336$). It is also shown by the Graph-3 that there are twenty two negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.422) > O26 (-0.289) > O27 (-0.277) > O28 (-0.253) > O29 (-0.248) > C31 (-0.247) > C33 (-0.219) > N1 (-0.210) > C4 (-0.135) > C6 (-0.131) > C12 (-0.106) > C11 (-0.104) > C8 (-0.103) > C13 (-0.099) > C5 (-0.096) > C7 (-0.095) > C10 (-0.085) > C14 (-0.079) > C9 (-0.023) > C30 (-0.020) > C32 (-0.018) > C3 (-0.005). The most negative position in ethyl-*p*-azoxybenzoate is the azoxy oxygen, O24 ($Q_{MIN} = -0.422$) and the lowest negative position is carbon atom, C3 ($Q = -0.005$).



Graph 3. Graphical representation of magnitude of partial atomic charges of ethyl-*p*-azoxybenzoate

PM3¹⁴ data show that, there are twenty four positive charge atoms, including five carbon atoms (C3, C17, C22, C30 and C32), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-3. Thus, there are six positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (1.064) > C17 (0.405) > C22 (0.396) > C32 (0.059) > C30 (0.053) > C3 (0.043). The most positive position in ethyl-*p*-azoxybenzoate is the azoxy nitrogen, N2 ($Q_{MAX} = 1.064$) and the lowest positive position is carbon atom, C3 ($Q = 0.043$). It is also shown by the Graph-3 that there are nineteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.614) > N1 (-0.465) > O26 (-0.329) > O27 (-0.316) > C9 (-0.286) > O28 (-0.237) > O29 (-0.232) > C31 (-0.150) > C6 (-0.144) > C33 (-0.121) > C4 (-

0.112) > C8 (-0.094) > C12 (-0.089) > C11 (-0.082) > C13 (-0.079) > C7 (-0.056) > C5 (-0.054) > C10 (-0.029) > C14 (-0.020). The most negative position in ethyl-*p*-azoxybenzoate is the azoxy oxygen, O24 ($Q_{\text{MIN}} = -0.614$) and the lowest negative position is carbon atom, C14 ($Q = -0.020$).

PM5¹⁵ data show that, there are twenty two positive charge atoms, including three carbon atoms (C3, C17 and C22), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-3. Thus, there are four positive sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.535) > C17 (0.461) > C22 (0.456) > C3 (0.031). The most positive position in ethyl-*p*-azoxybenzoate is the azoxy nitrogen, N2 ($Q_{\text{MAX}} = 0.535$) and the lowest positive position is carbon atom, C3 ($Q = 0.031$). It is also shown by the Graph-3 that there are twenty one negative charge sites for electrophilic attack.

The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.489) > O26 (-0.361) > O28 (-0.352) > O29 (-0.347) > O27 (-0.346) > C31 (-0.338) > C33 (-0.302) > N1 (-0.299) > C6 (-0.178) > C4 (-0.162) > C12 (-0.151) > C8 (-0.138) > C11 (-0.125) > C13 (-0.120) > C5 = C10 (-0.105) > C7 (-0.101) > C14 (-0.096) > C9 (-0.082) > C32 (-0.021) > C30 (-0.019). The most negative position in ethyl-*p*-azoxybenzoate is the azoxy oxygen, O24 ($Q_{\text{MIN}} = -0.489$) and the lowest negative position is carbon atom, C30 ($Q = -0.019$).

DFT¹⁶ data show that, there are twenty five positive charge atoms, including six carbon atoms (C3, C6, C9, C12, C17 and C22), one nitrogen (N2) and all the eighteen H-atom. It is also shown by the Graph-3. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is C17 (0.311) > C22 (0.292) > C9 (0.286) > C3 (0.251) > N2 (0.184) > C12 (0.093) > C6 (0.087). The most positive position in ethyl-*p*-azoxybenzoate is the carbon atom, C17 ($Q_{\text{MAX}} = 0.311$) and the lowest positive position is C6 ($Q = 0.087$). It is also shown by the Graph-3 that there are eighteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is C31 (-0.622) > C33 (-0.612) > O24 (-0.379) > C10 (-0.330) > C4 (-0.324) > C8 (-0.324) > C7 (-0.304) > C14 (-0.299) > O26 (-0.291) > C5 (-0.286) > C13 (-0.284) > O27 (-0.282) > C11 (-0.271) > C30 (-0.270) > N1 (-0.266) > C32 (-0.253) > O28 (-0.250) > O29 (-0.229). The most negative position in ethyl-*p*-azoxybenzoate is the carbon atom, C31 ($Q_{\text{MIN}} = -0.622$) and the lowest negative position is oxygen atom, O29 ($Q = -0.229$).

3.4. Ethyl-*p*-azoxycinnamate: A molecule of ethyl-*p*-azoxycinnamate is composed of fifty one atoms, out of which there are twenty two carbon, twenty two hydrogen, five oxygen and two nitrogen atoms. In order to predict the nucleophilic and electrophilic sites of attack, the most positive and negative charged sites must be known.²¹ The charge distributions (Q) of each atom of this compound were calculated by using the AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ methods and the results are reported in Graph-4 and the arbitrary numbering scheme used in the above analysis is shown in Figure-4, which represents a perspective view of the molecule.

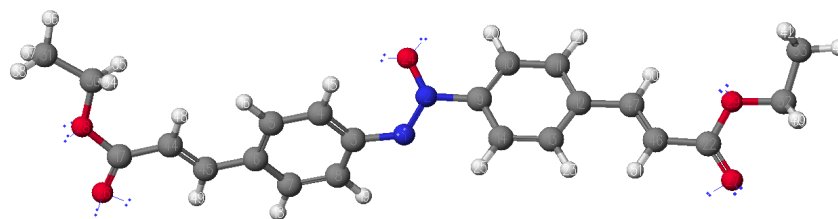
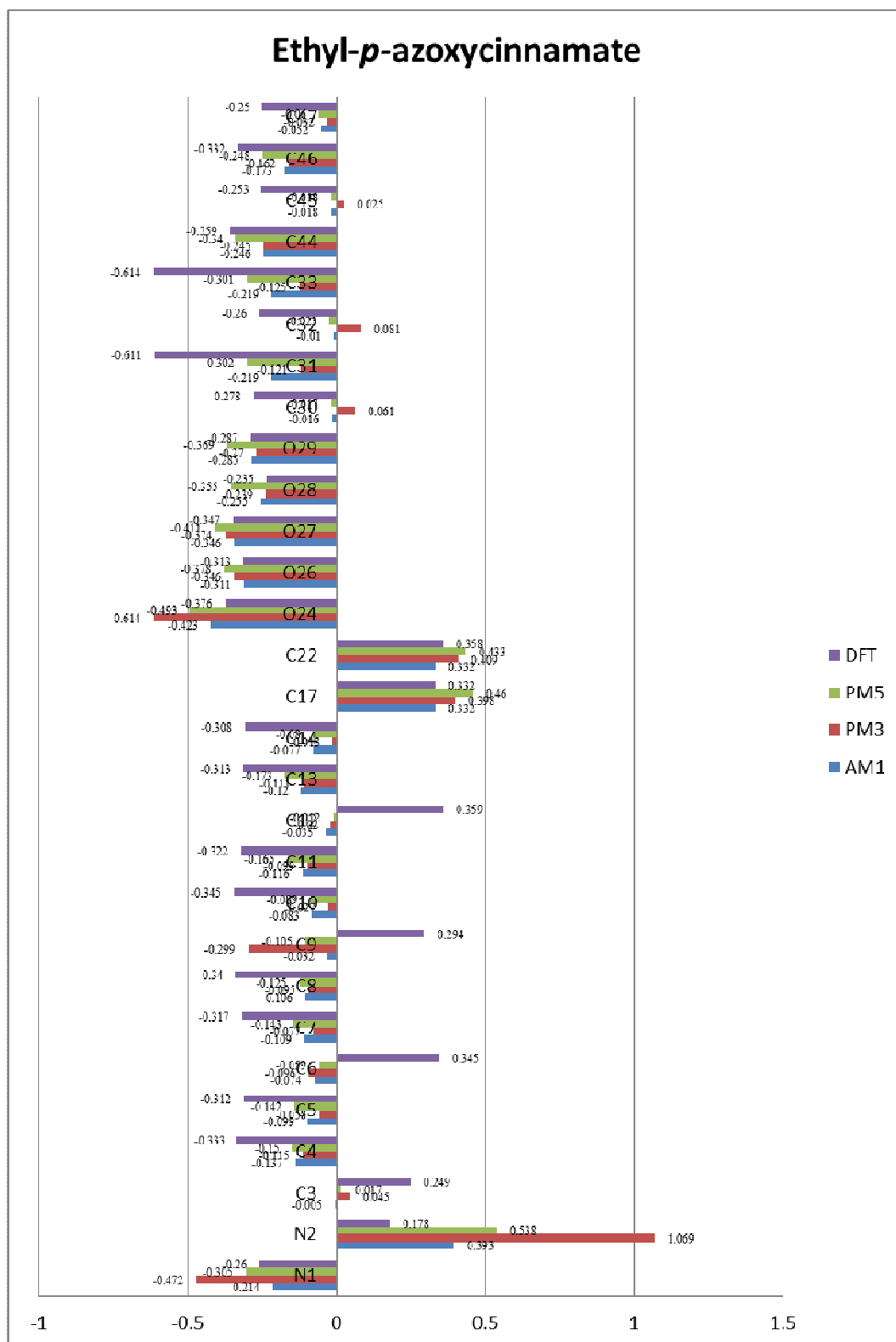


Figure 4. Perspective view of Compound-4, ethyl-*p*-azoxycinnamate

AM1¹³ data show that, there are twenty five positive charge atoms, including two carbon atoms (C17 and C22), one nitrogen (N2) and all the twenty two H-atom. It is also shown by the Graph-4. Thus, there are three positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.393) > C17 = C22 (0.332). The most positive site in ethyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{\text{MAX}} = 0.393$) and the lowest positive site is carbon atom, C17 = C22 ($Q = 0.332$). It is also shown by the Graph-4 that there are twenty six negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.423) > O27 (-0.346) > O26 (-0.311) > O29 (-0.285) > O28 (-0.255) > C44 (-0.246) > C31 = C33 (-0.219) > N1 (-0.214) > C46 (-0.173) > C4 (-0.137) > C13 (-0.120) > C11 (-0.116) > C7 (-0.109) > C8 (-0.106) > C5 (-0.099) > C10 (-0.083) > C14 (-0.077) > C6 (-0.074) > C47 (-0.052) > C12 (-0.035) > C9 (-0.032) > C45 (-0.018) > C30 (-0.016) > C32 (-0.010) > C3 (-0.005).



Graph 4. Graphical representation of magnitude of partial atomic charges of ethyl-*p*-azoxycinnamate

The most negative position in ethyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{\text{MIN}} = -0.423$) and the lowest negative position is carbon atom C3 ($Q = -0.005$).

PM3¹⁴ data show that, there are twenty nine positive charge atoms, including six carbon atoms (C3, C17, C22, C30, C32 and C45), one nitrogen (N2) and all the twenty two H-atom. It is also shown by the Graph-4. Thus, there are six positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack

is N2 (1.069) > C22 (0.409) > C17 (0.398) > C32 (0.081) > C30 (0.061) > C3 (0.045) > C45 (0.025). The most positive position in ethyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{MAX} = 1.069$) and the lowest positive position is carbon atom, C45 ($Q = 0.025$). It is also shown by the Graph-4 that there are twenty two negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.614) > N1 (-0.472) > O27 (-0.374) > O26 (-0.346) > C9 (-0.299) > O29 (-0.270) > C44 (-0.245) > O28 (-0.239) > C46 (-0.162) > C33 (-0.125) > C31 (-0.121) > C4 (-0.115) > C13 (-0.111) > C11 (-0.099) > C6 (-0.096) > C8 (-0.095) > C7 (-0.077) > C5 (-0.058) > C47 (-0.032) > C10 (-0.027) > C12 (-0.020) > C14 (-0.013). The most negative position in ethyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{MIN} = -0.614$) and the lowest negative position is carbon atom, C14 ($Q = -0.013$).

PM5¹⁵ data show that, there are twenty six positive charge atoms, including three carbon atoms (C3, C17 and C22), one nitrogen (N2) and all the twenty two H-atom. It is also shown by the Graph-4. Thus, there are four positive sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.538) > C17 (0.460) > C22 (0.433) > C3 (0.017). The most positive position in ethyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{MAX} = 0.538$) and the lowest positive position is carbon atom, C3 ($Q = 0.017$). It is also shown by the Graph-4 that there are twenty five negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.493) > O27 (-0.411) > O26 (-0.378) > O29 (-0.369) > O28 (-0.355) > C44 (-0.340) > N1 (-0.305) > C31 (-0.302) > C33 (-0.301) > C46 (-0.248) > C13 (-0.173) > C11 (-0.165) > C4 (-0.150) > C7 (-0.143) > C5 (-0.142) > C8 (-0.125) > C9 (-0.105) > C10 (-0.089) > C14 (-0.080) > C47 (-0.060) > C6 (-0.059) > C32 (-0.023) > C45 (-0.018) > C30 (-0.017) > C12 (-0.012). The most negative position in ethyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{MIN} = -0.493$) and the lowest negative position is carbon atom C12 ($Q = -0.012$).

DFT¹⁶ data show that, there are twenty nine positive charge atoms, including six carbon atoms (C3, C6, C9, C12, C17 and C22), one nitrogen (N2) and all the twenty two H-atom. It is also shown by the Graph-4. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is C12 (0.359) > C22 (0.358) > C6 (0.345) > C17 (0.332) > C9 (0.294) > C3 (0.249) > N2 (0.178). The most positive position in ethyl-*p*-azoxycinnamate is the carbon atom, C12 ($Q_{MAX} = 0.359$) and the lowest positive position is N2 ($Q = 0.178$). It is also shown by the Graph-4 that there are eighteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is C33 (-0.614) > C31 (-0.611) > O24 (-0.376) > C44 (-0.359) > O27 (-0.347) > C10 (-0.345) > C8 (-0.340) > C4 (-0.333) > C46 = C11 (-0.322) > C7 (-0.317) > C13 = O26 (-0.313) > C5 (-0.312) > C14 (-0.308) > O29 (-0.287) > C30 (-0.278) > N1 = C32 (-0.260) > C45 (-0.253) > C47 (-0.250) > O28 (-0.235). The most negative position in ethyl-*p*-azoxycinnamate is the carbon atom, C33 ($Q_{MIN} = -0.614$) and the lowest negative position is oxygen atom, O28 ($Q = (-0.235)$).

3.5. *n*-Octyl-*p*-azoxycinnamate: A molecule of *n*-octyl-*p*-azoxycinnamate is composed of eighty seven atoms, out of which there are thirty four carbon, forty six hydrogen, five oxygen and two nitrogen atoms. In order to predict the nucleophilic and electrophilic sites of attack, the most positive and negative charged sites must be known.²¹ The charge distributions (Q) of each atom of this compound were calculated by using the AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ methods and the results are reported in Graph-5 and the arbitrary numbering scheme used in the above analysis is shown in Figure-5, which represents a perspective view of the molecule.

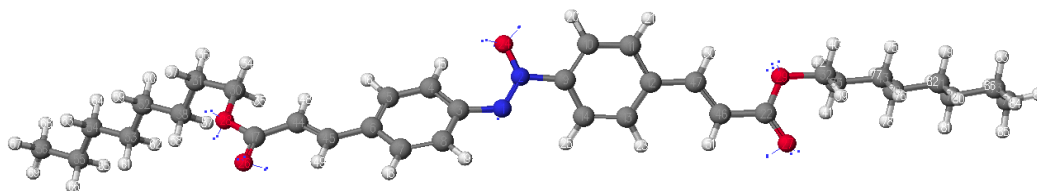
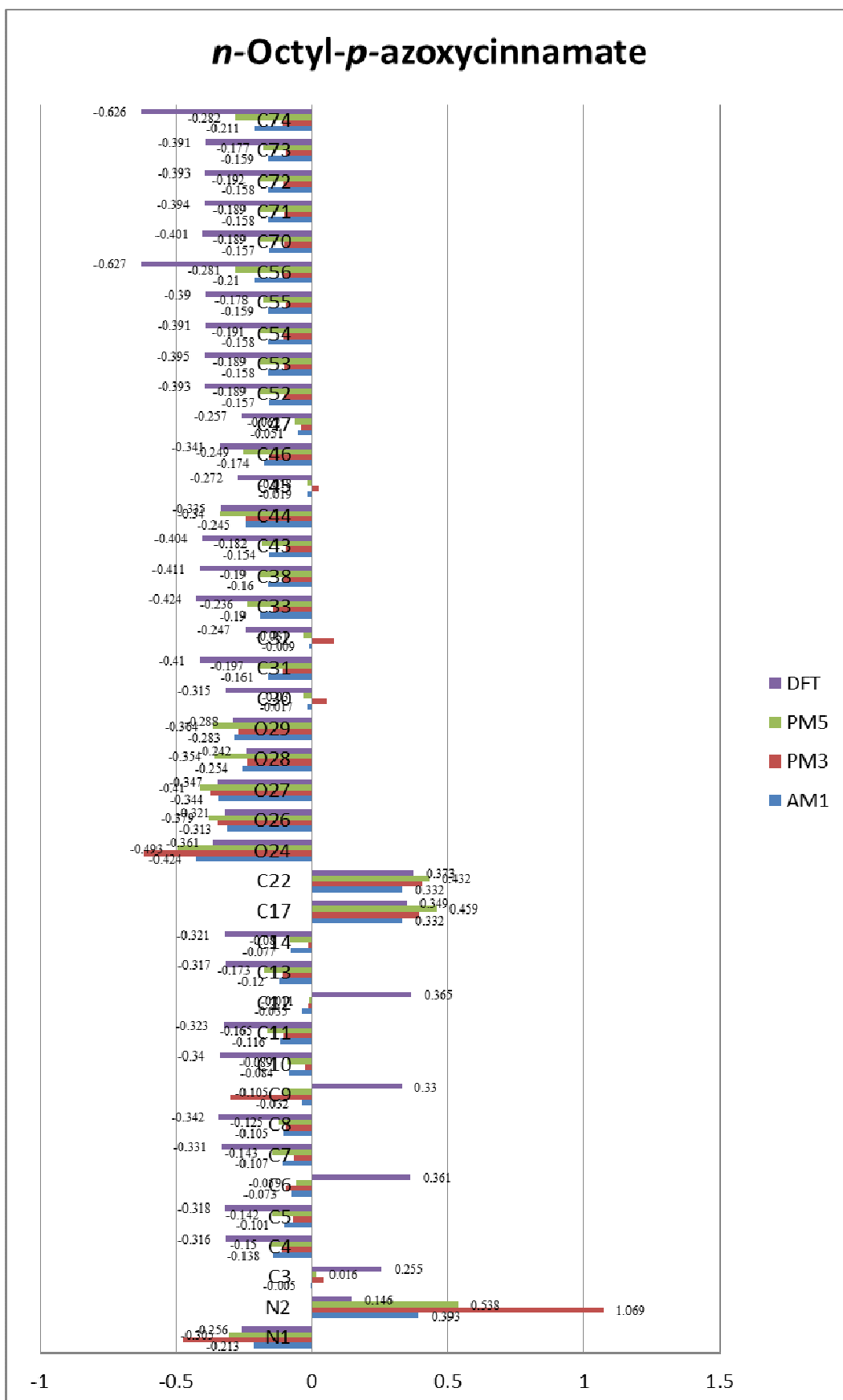


Figure 5. Perspective view of Compound-5, *n*-octyl-*p*-azoxycinnamate

AM1¹³ data show that, there are twenty five positive charge atoms, including two carbon atoms (C17 and C22), one nitrogen (N2) and all the forty six hydrogen two H-atom. It is also shown by the Graph-5. Thus, there are three positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.393) > C17 = C22 (0.332). The most positive site in *n*-octyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{MAX} = 0.393$) and the lowest positive site is carbon atom, C17 = C22 ($Q = 0.332$). It is also shown by the Graph-5 that there are twenty six negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.424) > O27 (-0.344) > O26 (-0.313) > O29 (-0.283) > O28 (-0.254) > C44 (-0.245) > N1 (-0.213) > C74 (-0.211) > C56 (-0.210) > C33 (-0.190) > C46 (-0.174) > C31 (-0.161) > C38 (-0.160) > C55 = C73 (-0.159) > C53 = C54 = C71 = C72 (-0.158) > C52 = C70 (-0.157) > C43 (-0.154) > C4 (-0.138) > C13

(-0.120) > C11 (-0.116) > C7 (-0.107) > C8 (-0.105) > C5 (-0.101) > C10 (-0.084) > C14 (-0.077) > C6 (-0.073) > C47 (-0.051) > C12 (-0.035) > C9 (-0.032) > C45 (-0.019) > C30 (-0.017) > C32 (-0.009) > C3 (-0.005). The most negative position in *n*-octyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{\text{MIN}} = -0.424$) and the lowest negative position is carbon atom, C3 ($Q = -0.005$).



Graph 5. Graphical representation of magnitude of partial atomic charges of n-octyl-p-azoxycinnamate

PM3¹⁴ data show that, there are fifty three positive charge atoms, including six carbon atoms (C3, C17, C22, C30, C32 and C45), one nitrogen (N2) and all the forty six hydrogen H-atom. It is also shown by the Graph-5. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (1.069) > C22 (0.404) > C17 (0.398) > C32 (0.078) > C30 (0.057) > C3 (0.045) > C45 (0.025). The most positive position in *n*-octyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{MAX} = 1.069$) and the lowest positive position is carbon atom, C45 ($Q = 0.025$). It is also shown by the Graph-5 that there are thirty four negative charge sites for electrophilic attack.

The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.616) > N1 (-0.471) > O27 (-0.369) > O26 (-0.347) > C9 (-0.301) > O29 (-0.267) > C44 (-0.245) > O28 (-0.237) > C46 (-0.154) > C33 (-0.139) > C4 (-0.113) > C56 = C74 (-0.109) > C13 = C31 (-0.108) > C38 (-0.104) > C11 = C54 = C72 (-0.103) > C53 = C70 = C71 (-0.102) > C52 (-0.101) > C55 = C73 > C8 (-0.097) > C6 (-0.096) > C43 (-0.095) > C5 (-0.071) > C7 (-0.065) > C47 (-0.038) > C10 (-0.026) > C12 = C14 (-0.015). The most negative position in *n*-octyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{MIN} = -0.616$) and the lowest negative position is carbon atom, C12 = 14 ($Q = -0.015$).

PM5¹⁵ data show that, there are fifty positive charge atoms, including three carbon atoms (C3, C17 and C22), one nitrogen (N2) and all the forty six hydrogen H-atom. It is also shown by the Graph-5. Thus, there are four positive sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is N2 (0.538) > C17 (0.459) > C22 (0.432) > C3 (0.016). The most positive position in *n*-octyl-*p*-azoxycinnamate is the azoxy nitrogen, N2 ($Q_{MAX} = 0.538$) and the lowest positive position is carbon atom, C3 ($Q = 0.016$). It is also shown by the Graph-5 that there are thirty seven negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is O24 (-0.493) > O27 (-0.410) > O26 (-0.379) > O29 (-0.364) > O28 (-0.354) > C44 (-0.340) > N1 (-0.305) > C74 (-0.282) > C56 (-0.281) > C46 (-0.249) > C33 (-0.236) > C31 (-0.197) > C72 (-0.192) > C54 (-0.191) > C38 (-0.190) > C52 = C53 = C70 = C71 (-0.189) > C43 (-0.182) > C55 (-0.178) > C73 (-0.177) > C13 (-0.173) > C11 (-0.165) > C4 (-0.150) > C7 (-0.143) > C5 (-0.142) > C8 (-0.125) > C9 (-0.105) > C10 (-0.089) > C14 (-0.080) > C47 (-0.062) > C6 (-0.059) > C32 (-0.031) > C30 (-0.030) > C45 (-0.018) > C12 (-0.011). The most negative position in *n*-octyl-*p*-azoxycinnamate is the azoxy oxygen, O24 ($Q_{MIN} = -0.493$) and the lowest negative position is carbon atom, C12 ($Q = -0.011$).

DFT¹⁶ data show that, there are fifty three positive charge atoms, including six carbon atoms (C3, C6, C9, C12, C17 and C22), one nitrogen (N2) and all the forty six H-atom. It is also shown by the Graph-5. Thus, there are seven positive charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is C22 (0.373) > C12 (0.365) > C6 (0.361) > C17 (0.349) > C9 (0.330) > C3 (0.255) > N2 (0.146). The most positive position in *n*-octyl-*p*-azoxycinnamate is the carbon atom, C12 ($Q_{MAX} = 0.373$) and the lowest positive position is N2 ($Q = 0.146$). It is also shown by the Graph-5 that there are eighteen negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack is C56 (-0.627) > C74 (-0.626) > C33 (-0.424) > C38 (-0.411) > C31 (-0.410) > C43 (-0.404) > C70 (-0.401) > C53 (-0.395) > C71 (-0.394) > C52 = C72 (-0.393) > C54 = C73 (-0.391) > C55 (-0.390) > O24 (-0.361) > O27 (-0.347) > C8 (-0.342) > C46 (-0.341) > C10 (-0.340) > C44 (-0.335) > C7 (-0.331) > C11 (-0.323) > C14 = O26 (-0.321) > C5 (-0.318) > C13 (-0.317) > C4 (-0.316) > C30 (-0.315) > O29 (-0.288) > C45 (-0.2720) > C47 (-0.257) > N1 (-0.256) > C32 (-0.247) > O28 (-0.242). The most negative position in *n*-octyl-*p*-azoxycinnamate is the carbon, C56 ($Q_{MIN} = -0.627$) and the lowest negative position is oxygen atom, O28 ($Q = -0.242$).

3.6. Comparative Study: The structure of above azoxybenzene based liquid crystals is based on the following parent skeleton (Figure-6), which has 15 sites.

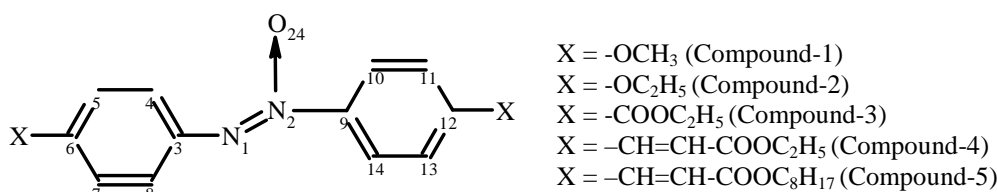


Figure 6. Parent skeleton of azoxybenzene based liquid crystal

Azoxy-Based Liquid Crystals	AM1				PM3				PM5				DFT			
	Site	Q_{MAX}	Site	Q_{MIN}	Site	Q_{MAX}	Site	Q_{MIN}	Site	Q_{MAX}	Site	Q_{MIN}	Site	Q_{MAX}	Site	Q_{MIN}
<i>p</i> -azoxyanisole	N2	0.392	O24	-0.447	N2	1.072	O24	-0.630	N2	0.540	O24	-0.510	C12	0.375	O24	-0.405
<i>p</i> -azoxyphenetole	N2	0.392	O24	-0.448	N2	1.072	O24	-0.631	N2	0.540	O24	-0.512	C12	0.396	O24	-0.406
ethyl- <i>p</i> -azoxybenzoate	N2	0.391	O24	-0.422	N2	1.064	O24	-0.614	N2	0.535	O24	-0.489	C9	0.286	O24	-0.379
ethyl- <i>p</i> -azoxycinnamate	N2	0.393	O24	-0.423	N2	1.069	O24	-0.614	N2	0.538	O24	-0.493	C12	0.359	O24	-0.376
<i>n</i> -octyl- <i>p</i> -azoxycinnamate	N2	0.393	O24	-0.424	N2	1.069	O24	-0.616	N2	0.538	O24	-0.493	C12	0.365	O24	-0.361

The Q values at all the 15 sites of all the above compounds have also been reported in Graph-1 to 5. For comparative study of the values of Q_{MAX} and Q_{MIN} as obtained by AM1,¹³ PM3,¹⁴ PM5¹⁵ and DFT-based¹⁶ calculations are summarized in Table 1. A reference to this table indicates that the above compounds have the following order for nucleophilic and electrophilic sites.

Summary of reactivity order of azoxy based liquid crystals for nucleophilic site

AM1- Q_{MAX}	ethyl- <i>p</i> -azoxycinnamate = <i>n</i> -octyl- <i>p</i> -azoxycinnamate > <i>p</i> -azoxyanisole = <i>p</i> -azoxyphenetole > ethyl- <i>p</i> -azoxybenzoate
PM3- Q_{MAX}	<i>p</i> -azoxyanisole = <i>p</i> -azoxyphenetole > ethyl- <i>p</i> -azoxycinnamate = <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate
PM5- Q_{MAX}	<i>p</i> -azoxyanisole = <i>p</i> -azoxyphenetole > ethyl- <i>p</i> -azoxycinnamate = <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate
DFT- Q_{MAX}	<i>p</i> -azoxyphenetole > <i>p</i> -azoxyanisole > <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate

Summary of reactivity order of azoxy based liquid crystals for electrophilic site

AM1- Q_{MIN}	<i>p</i> -azoxyphenetole > <i>p</i> -azoxyanisole > <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate
PM3- Q_{MIN}	<i>p</i> -azoxyphenetole > <i>p</i> -azoxyanisole > <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate = ethyl- <i>p</i> -azoxycinnamate
PM5- Q_{MIN}	<i>p</i> -azoxyphenetole > <i>p</i> -azoxyanisole > ethyl- <i>p</i> -azoxycinnamate = <i>n</i> -octyl- <i>p</i> -azoxycinnamate > ethyl- <i>p</i> -azoxybenzoate
DFT- Q_{MIN}	<i>p</i> -azoxyphenetole > <i>p</i> -azoxyanisole > ethyl- <i>p</i> -azoxybenzoate > ethyl- <i>p</i> -azoxycinnamate > <i>n</i> -octyl- <i>p</i> -azoxycinnamate

CONCLUSION

We have concluded following points from the above study:

1. It has already been mentioned that while the results produced by different semiempirical methods are not generally comparable, they do often reproduce similar trends. It is also clear from the reactivity order for nucleophilic site as obtained by PM3 and PM5 have similar trend.

p-azoxyanisole = *p*-azoxyphenetole > ethyl-*p*-azoxycinnamate = *n*-octyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate (PM3- Q_{MAX})

p-azoxyanisole = *p*-azoxyphenetole > ethyl-*p*-azoxycinnamate = *n*-octyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate (PM5- Q_{MAX})

2. DFT-based calculations indicate that the above compounds have the following order for nucleophilic and electrophilic sites.

p-azoxyphenetole > *p*-azoxyanisole > *n*-octyl-*p*-azoxycinnamate > ethyl-*p*-azoxycinnamate > ethyl-*p*-azoxybenzoate (DFT- Q_{MAX})

p-azoxyphenetole > *p*-azoxyanisole > ethyl-*p*-azoxybenzoate > ethyl-*p*-azoxycinnamate > *n*-octyl-*p*-azoxycinnamate (DFT- Q_{MIN})

If *p*-azoxyanisole is treated as reference compound (RC) then the study shows that replacement of -OCH₃ group of RC by -OC₂H₅ group increase the Q_{MAX} , while successive addition of -CH=CH-COOC₈H₁₇, -CH=CH-COOC₂H₅ and -COOC₂H₅ groups decreases the Q_{MAX} , respectively. In all the compounds it is the carbon atom at site 12, C12, which has Q_{MAX} , except in ethyl-*p*-azoxybenzoate, where Q_{MAX} is at C9. In respect to Q_{MIN} , it is the azoxy oxygen, O24, which has Q_{MIN} and the only differences in the trend is due to the positions of ethyl-*p*-azoxybenzoate and *n*-octyl-*p*-azoxycinnamate, which are interchanged.

3. The study shows that DFT based calculations provide better result than the semiempirical based calculations.

Acknowledgement

This paper is dedicated to the mother of Alok Shukla.

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