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Spectroscopic and Electronic properties of PYP609 liquid crystal molecule: A DFT study

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Abstract
Structure and bonding in liquid crystals are important and diverse fields at the interface between modern physics and chemistry. The structure-property relationship is also a major issue for the study of liquid crystals. Most liquid crystals have a rod-like structure and contain one or more benzene rings at their core. Strong dipole–dipole interaction exhibits crystalline phase and has high thermal stability. To understand the liquid crystalline properties, the energy, dipole moment, molar mass, zero point vibrational energy, specific heat at constant volume, entropy, IR and Raman activity of PYP609 liquid crystal molecule were calculated using DFT method. The orbital information like HOMO and LUMO has been also computed.
Keywords: *Liquid Crystals, IR Spectra, Raman Activities, HOMO-LUMO*

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I. Introduction

The liquid crystalline state is characterized by a long-range orientational ordering of its constituent molecules. Different mesophases can exist and the transition between them is accompanied by changes in different tensor properties. They may also show changes in scalar quantities, such as enthalpy content or density, depending on the order of transition. The change in density and thermal expansion with the nematic to isotropic phase transition has been the subject of many investigations. The isotropic nematic phase transition reveals a discontinuous increase in density that is related to the increase of molecular packing in the orientally ordered mesophase. The liquid crystal (LC) phase represents a distinct state of matter characterized by the mobility and order of the molecule. All particles in the crystalline state have an orientational and three-dimensional position order. Liquid crystal phases have both orientational order and, in some cases, positional order in one or two dimensions. The liquid crystal behavior of molecules is attributed to a variety of intermolecular interactions acting between the sides, planes, and ends of a pair of molecules. Liquid crystal (LC) phases are formed by anisotropic molecules, in which one molecular axis is very different from the other two. The rod-like molecule is the most common type of LC molecular shape. The nematic phase exhibits long-range orientational order but no position order of the molecule [1-5].

The density functional calculations are one of the more interesting applied theoretical methods for liquid crystals and optical systems. Computation of the geometrical parameters for the molecular structure offers more interesting correlations between the obtained experimental results and the estimated theoretical simulations. This will offer the computation of the preferred molecular shape in the gas phase. In this article we calculated the energy, dipole moment, vibrational energy, entropy, molar mass etc. And all these results are in good agreements with experimental values.

Computational method

The geometry was optimized using DFT method B3LYP using 6-311G(d,p) which was found suitable for these type of systems with keeping all atoms free. The analytical frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit. The 6–311G(d,p) split valence-shell basis set has been used, augmented by the 'd' polarization function on heavy atoms and the 'p' polarization function on hydrogen atoms. [5-10].

II. Results And Discussion

The optimized geometry of PYP609 liquid crystal molecule is shown in the figure1. Bond lengths and bond angles of optimized geometry has been computed using density functional theory which are depicted in table1.

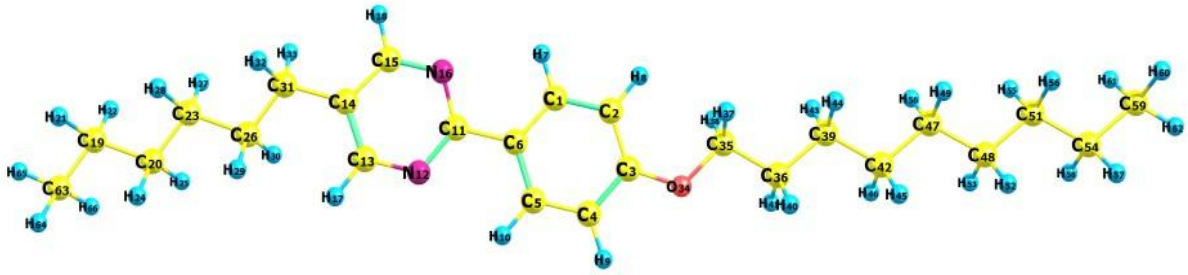


Figure1: Optimised geometry of PYP609 liquid crystal molecule

Table1: Optimized parameters of PYP609 liquid crystal

Bonds	Distance (ang.)	Angle's name	Angle's (deg.)	Angle's name	Angle's (deg.)
R(1,2)	1.3916	A(2,1,6)	121.3255	A(36,35,38)	110.7511
R(1,6)	1.3979	A(2,1,7)	120.0402	A(37,35,38)	108.0839
R(1,7)	1.0822	A(6,1,7)	118.6343	A(35,36,39)	112.5946
R(2,3)	1.3992	A(1,2,3)	119.7047	A(35,36,40)	108.474
R(2,8)	1.0815	A(1,2,8)	119.2973	A(35,36,41)	108.6064
R(3,4)	1.4024	A(3,2,8)	120.998	A(39,36,40)	110.0899
R(3,34)	1.3603	A(2,3,4)	119.4495	A(39,36,41)	110.1588
R(4,5)	1.3825	A(2,3,34)	124.7146	A(40,36,41)	106.7245
R(4,9)	1.0833	A(4,3,34)	115.836	A(36,39,42)	113.1629
R(5,6)	1.4052	A(3,4,5)	120.3195	A(36,39,43)	109.5515
R(5,10)	1.0821	A(3,4,9)	118.3133	A(36,39,44)	109.4612
R(6,11)	1.4783	A(5,4,9)	121.3672	A(42,39,43)	109.1463
R(11,12)	1.3414	A(4,5,6)	120.8807	A(42,39,44)	109.133
R(11,16)	1.3462	A(4,5,10)	120.4453	A(43,39,44)	106.1438
R(12,13)	1.3326	A(6,5,10)	118.6741	A(39,42,45)	109.1721
R(13,14)	1.395	A(1,6,5)	118.32	A(39,42,46)	109.2012
R(13,17)	1.0862	A(1,6,11)	120.8776	A(39,42,47)	113.5128
R(14,15)	1.3989	A(5,6,11)	120.8023	A(45,42,46)	106.0725
R(14,31)	1.513	A(6,11,12)	117.9571	A(45,42,47)	109.2791
R(15,16)	1.3269	A(6,11,16)	117.8197	A(46,42,47)	109.3346
R(15,18)	1.0894	A(12,11,16)	124.2231	A(42,47,48)	113.5725
R(19,20)	1.533	A(11,12,13)	117.3959	A(42,47,49)	109.2241
R(19,21)	1.0968	A(12,13,14)	123.412	A(42,47,50)	109.2716
R(19,22)	1.0967	A(12,13,17)	115.6146	A(48,47,49)	109.2216
R(19,63)	1.5312	A(14,13,17)	120.973	A(48,47,50)	109.2365
R(20,23)	1.5326	A(13,14,15)	114.0872	A(49,47,50)	106.0399
R(20,24)	1.0977	A(13,14,31)	124.7975	A(47,48,51)	113.6234
R(20,25)	1.0977	A(15,14,31)	121.1114	A(47,48,52)	109.2146
R(23,26)	1.533	A(14,15,16)	123.8424	A(47,48,53)	109.2337
R(23,27)	1.0975	A(14,15,18)	120.0542	A(51,48,52)	109.2167
R(23,28)	1.0976	A(16,15,18)	116.1032	A(51,48,53)	109.2497
R(26,29)	1.0961	A(11,16,15)	117.035	A(52,48,53)	106.0235
R(26,30)	1.0966	A(20,19,21)	109.1861	A(48,51,54)	113.6745
R(26,31)	1.5335	A(20,19,22)	109.1808	A(48,51,55)	109.2949
R(31,32)	1.0982	A(20,19,63)	113.2593	A(48,51,56)	109.2695
R(31,33)	1.0967	A(21,19,22)	106.0599	A(54,51,55)	109.1638

R(34,35)	1.4294	A(21,19,63)	109.4536	A(54,51,56)	109.1534
R(35,36)	1.5203	A(22,19,63)	109.4478	A(55,51,56)	106.0002
R(35,37)	1.0976	A(19,20,23)	113.6126	A(51,54,57)	109.1688
R(35,38)	1.0976	A(19,20,24)	109.1657	A(51,54,58)	109.1826
R(36,39)	1.5327	A(19,20,25)	109.1768	A(51,54,59)	113.2971
R(36,40)	1.0951	A(23,20,24)	109.2544	A(57,54,58)	106.0366
R(36,41)	1.095	A(23,20,25)	109.323	A(57,54,59)	109.4377
R(39,42)	1.5331	A(24,20,25)	106.0303	A(58,54,59)	109.4607
R(39,43)	1.0976	A(20,23,26)	113.4671	A(54,59,60)	111.1643
R(39,44)	1.0975	A(20,23,27)	109.2937	A(54,59,61)	111.1875
R(42,45)	1.0974	A(20,23,28)	109.2271	A(54,59,62)	111.4744
R(42,46)	1.0973	A(26,23,27)	109.2283	A(60,59,61)	107.5154
R(42,47)	1.5327	A(26,23,28)	109.2865	A(60,59,62)	107.6562
R(47,48)	1.5329	A(27,23,28)	106.0727	A(61,59,62)	107.6528
R(47,49)	1.0976	A(23,26,29)	108.8829	A(19,63,64)	111.1816
R(47,50)	1.0977	A(23,26,30)	109.4112	A(19,63,65)	111.4308
R(48,51)	1.5327	A(23,26,31)	112.6428	A(19,63,66)	111.1902
R(48,52)	1.0977	A(29,26,30)	106.35	A(64,63,65)	107.6534
R(48,53)	1.0976	A(29,26,31)	109.8424	A(64,63,66)	107.5373
R(51,54)	1.533	A(30,26,31)	109.5131	A(65,63,66)	107.659
R(51,55)	1.0979	A(14,31,26)	116.151		
R(51,56)	1.0978	A(14,31,32)	108.697		
R(54,57)	1.0968	A(14,31,33)	108.2966		
R(54,58)	1.0968	A(26,31,32)	108.7214		
R(54,59)	1.5313	A(26,31,33)	109.0126		
R(59,60)	1.0945	A(32,31,33)	105.4357		
R(59,61)	1.0946	A(3,34,35)	119.2275		
R(59,62)	1.0934	A(34,35,36)	107.6993		
R(63,64)	1.0945	A(34,35,37)	109.7681		
R(63,65)	1.0933	A(34,35,38)	109.8268		
R(63,66)	1.0945	A(36,35,37)	110.7122		

The thermodynamical properties like zero point vibrational enrgy, thermal energy, specific heat and entropy of PYP609 molecule are shown in table2.

Table2: Thermodynamical properties of PYP609 liquid crystal molecule

Molecule	Zero-point vibrational energy (Kcal/Mol)	E (Thermal) KCal/Mol)	Specific heat at constant volume Cal/Mol-Kelvin	Entropy Cal/Mol-Kelvin
PYP609	367.49867	386.905	113.025	212.471

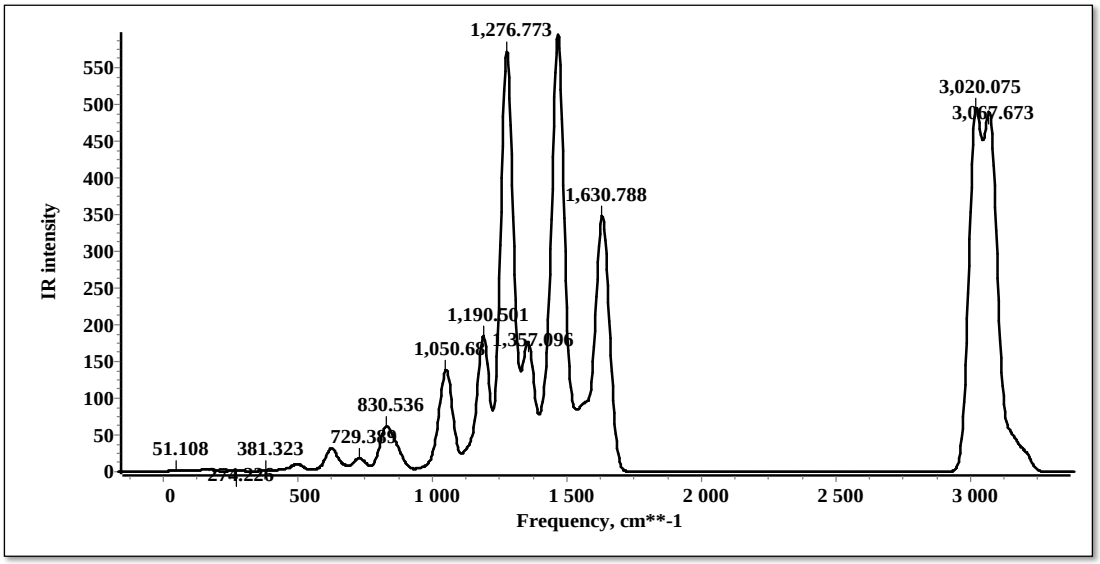
The energy, dipole moment, isotropic polarizability and molar mass of molecule are computed using B3LYP method with 3-111G(d,p) basis set which are in good agreements with the experimental values. All these value are depicted in table3.

Table3: Energy, dipole moment, isotropic polarizability and of PYP609 liquid crystal molecule

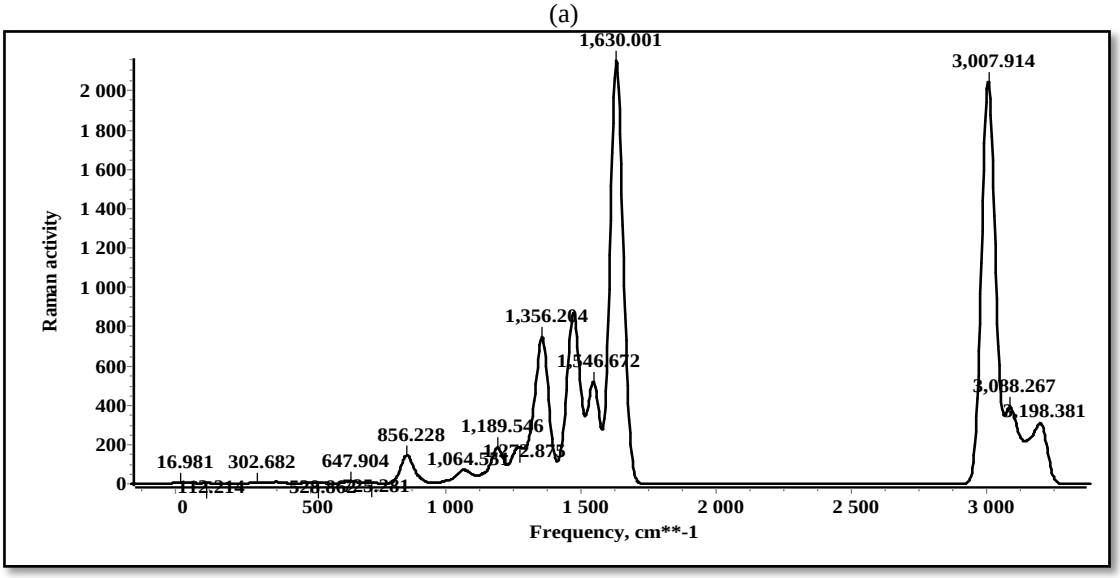
Molecule	Energy (a.u.)	Dipole moment (Debye)	Isotropic polarizability ($Bohr^3$)	Molecular mass (amu)
PYP609	-1160.608	1.485	330.260	382.298

The IR spectra of PYP609 molecule is shown in figure 2(a). From figure 2(a) visualized that there are several peak and the highest peak (in IR intensity) is at 1467.17 cm^{-1}. This frequency is associated with

vibration of C-N bond in the ring. Second highest peak is associated with the vibration of C-C bond in the benzene ring. In the raman spectra highest peak is associated with the symmetric stretching in the ring which is shown in the figure 2(b).



(a)



(b)

Figure2: IR and Raman activity of PYP609 liquid crystal molecule

The investigations of frontier molecular orbital HOMO (highest occupied) and LUMO (lowest unoccupied) distributions for present molecule is represented in figure3. The values of HOMO and LUMO are -5.796eV & -1.209eV. The value of energy gap is high which shows that the molecule is less reactive.

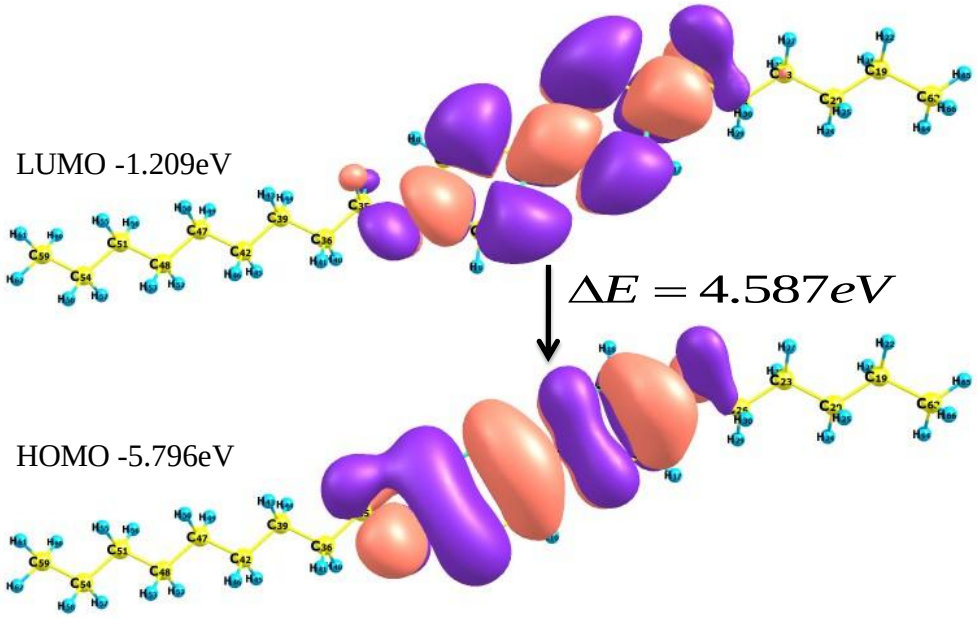


Figure3: HOMO-LUMO of PYP609 liquid crystal molecule

III. Conclusion

PYP609 liquid crystal molecule is optimized using Gaussian 09 and obtained stable geometry. Optimized geometries used for the calculation of molecular structure and thermodynamic and electronic properties. We have observed that thermal energy, vibrational energy, specific heat, dipole moment, molar mass, IR and Raman spectra, HOMO-LUMO and energy band gap which are in good with the experimental values.

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