



Comparative DFT Study of Parallel and Antiparallel Conformation of 5CB and 6CB Liquid Crystal Dimers

Research Article

Shivani Chaudhary^{id}, Narinder Kumar^{id} and Devesh Kumar*^{id}

Department of Physics, School of Physical and Decision Sciences,
Babasaheb Bhimrao Ambedkar University, Vidya Vihar, Raebareli Road,
Lucknow 226025, Uttar Pradesh, India

*Corresponding author: dkclcre@yahoo.com

Abstract. An investigation of the interaction of 5CB and 6CB liquid crystals along with their dimer configurations in different conformations. The total energy, thermal energy, HOMO-LUMO Gap, dipole moment, polarizability, constant volume heat capacity, entropy, zero-point energy (ZPE), and enthalpy of the different configurations of 5CB and 6CB liquid crystal dimers are affected during the molecular interaction. The different interaction properties of 5CB, 6CB, and 5CB-6CB dimers studied in parallel and antiparallel conformation with the help of density functional theory method lc-blyp by NWChem software package. The 5CB and 6CB liquid crystal dimers have the least dipole moment and negative entropy in the antiparallel conformation. The cross conformation of 5CB liquid crystal dimer (5CB-5CB) has the least isotropic polarizability; however, the parallel conformation of 5CB liquid crystal dimer has the highest isotropic polarizability. The isotropic polarizability is minimum in the antiparallel conformation of 6CB liquid crystal dimer (6CB-6CB), while isotropic polarizability is maximum in the parallel conformation of 6CB liquid crystal dimer. The 5CB liquid crystal dimer and 6CB liquid crystal dimer have minimum negative interaction energy in the antiparallel conformation, but 5CB-6CB liquid crystal dimer has positive interaction energy for all the possible conformations.

Keywords. 5CB-6CB; DFT (LC-BLYP); Molecular properties; Interaction energy

PACS. 78.20.Ci; 73.50.Rb; 78.67.-n; 68.55.-a; 78.66.Bz; 78.20.-e

Received: March 1, 2020

Accepted: April 3, 2020

Copyright © 2020 Shivani Chaudhary, Narinder Kumar and Devesh Kumar. *This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

1. Introduction

The liquid crystal [22, 32] dimer exhibits the broadest range of mesomorphic phase for the desired applications [4]. The 5CB and 6CB liquid crystal molecules have long-range conjugated rigid cores and active polar groups (cyano) that required for exhibits high-birefringence liquid crystals [9, 11, 12]. The 5CB liquid crystal has linear π -electron conjugation continual with the biphenyl rigid core and the polar terminal cyano group, so the optical and dielectric anisotropy is comparatively high in the 5CB liquid crystal [10, 38]. The 6CB liquid crystal has a more top dipole moment comparison of the 5CB liquid crystal molecule [17, 25]. The Cyano (CN) groups have an extreme polarization with the carbon-hydrogen triple bond, and the Huckel charges of the carbon and nitrogen atoms are very high. All cyanobiphenyl derivative dimers would be established by strong intermolecular interactions between the nitrile groups [5, 7, 8, 14, 27, 28, 30, 35]. The 5CB liquid crystal dimers (5CB-5CB) have excellent interaction energy at a distance of 4.2Å [2]. In the nematic phase, the enthalpy decreases as the pressure on molecules increases. The electrostatic repulsion between the dipole of the cyano groups diminishes in the anti-parallel conformation and also have a nematic phase of cyanobiphenyl dimer [36]. The potent polar cyanobiphenyl derivatives are the most important molecules for the applications of nematic liquid crystal in display applications. The antiparallel conformations of cyanobiphenyl liquid crystal dimers have reduced sufficient dipole moment. The liquid crystal packing plays a vital role in the creation of their mesophase and defines their optical properties for the display applications [26]. The cyano group terminal possesses a massive dipole moment along the long molecular axis. The cyanobiphenyl compounds are colorless, have a low melting point, chemically and photochemically stable [31]. The intermolecular forces are durable due to the polarity of the terminal groups of the 5CB and 6CB liquid crystal molecules [33]. The entire even member dimer of cyanobiphenyl liquid crystal has antiparallel conformation, and they also have CN-Phenyl strong interaction between the dimer [18]. The negative intermolecular energy of the dimer is responsible for the antiparallel structure which has negative entropy [13]. If the interaction energy is negative, then the entropy of the dimer is too negative that is responsible for the homogeneous phase [39]. The entropy is higher in 6CB liquid crystal as comparison of the 5CB liquid crystal during nematic to isotropic (N-I) phase transition [1]. It is important to note that only σ -electrons exist on cyclohexyl rings, whereas π -electrons live in phenyl rings. The presence of the rings in liquid crystal provides the short-range intermolecular forces needed to form the nematic phase, and they also affect the absorption, dielectric anisotropy, birefringence, elastic constant, and viscosity. Alkyl is the non-polar group that has a small effect on the dielectric anisotropy of liquid crystals. On the other hand, a polar terminal group such as a cyano group can contribute significantly to the dielectric anisotropy. The cyano group has the highest polarity leads to a high dielectric anisotropy and optical birefringence property. The liquid crystal compounds containing cyano group as terminal exhibit high viscosity, insufficient resistivity, and stability problems under UV illumination. Such liquid crystal compounds are not suitable for high-temperature operation as those used in a projection display application. Besides, liquid crystal molecules with the CN terminal group could be dissociated from the illumination of UV [6, 20, 23, 41–43]. In the antiparallel conformation of cyanobiphenyl liquid crystal dimer, the length of the pair is higher, so it minimizes the dipolar energy [40]. The even member dimer (6CB) mostly acquires antiparallel conformation because the length of the pair is higher, so it reduces the dipole moment of the dimer. In contrast, the odd member dimer (5CB)

mostly gets inclined or parallel mesogenic, so it increases the dipolar energy because the length of the dimer is small [24]. The 1CB to 3CB molecules have the rod-like structure that is useful to the formation of a crystalline structure. The active polarity of the cyano group increased the anisotropy of the molecule due to the reason the intermolecular forces increased. The triple bond of cyano group $-C\equiv N$ cannot rotate freely; that is the reason the molecular rigidity and melting temperature increased [16, 19, 29, 34, 44].

2. Computational Methodology

The 5CB and 6CB liquid crystal molecules optimized with the NWChem software package [37] with the help of DFT method LC-BLYP [3, 21] and 6-31G basis set [15]. After the optimization of liquid crystal molecules, we generated 360 conformations by python aggregation. Out of 360 conformations; we have considered four minimum energy conformations of the 5CB and 6CB dimers. Out of 360 conformations, we have found only four minimum energy conformations. All conformations are generated under free optimization (co-ordinates not fixed). Under free optimization, all monomers randomly interact with each other and generate minimum energy conformations. Firstly, we create 5CB, 6CB, and 5CB-6CB liquid crystal dimer molecules. All the liquid crystal dimers have the first monomer fixed, and the second monomer moves forward or backward at a distance of 0.5\AA . When the first monomer set and the other monomer moved forward or backward, then the interaction energy, polarizability, thermochemistry, and dipole moment will increase or decrease depending on the conformation of the liquid crystal dimer molecules.

3. Results and Discussion

Based on molecular interactions, we have studied different molecular properties of different conformations of 5CB, 6CB, and their dimers using the density functional theory method LC-BLYP with the help of NWChem software package in different sections.

3.1 5CB-5CB Parallel Conformation

In this section, we study the interaction properties of 5CB-5CB liquid crystal dimers in parallel conformation, as shown in Figure 1.

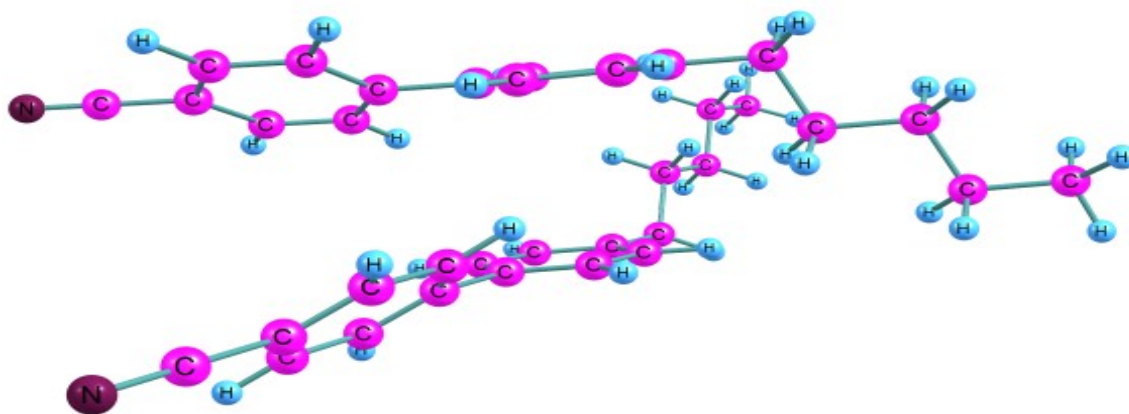


Figure 1. Parallel conformation of 5CB liquid crystal dimer

The polarizability of 5CB-5CB conformation decreases continually when the 5CB monomer moves in forwarding or backward direction (Figure 1). In this conformation, total energy increases continuously, and overall energy decreases. The cyano (CN) group of the first monomer interacts towards the benzene of the second monomer at a distance of 2.43Å. The tail of the first monomer interacts with the benzene of the second monomer at a range of 2.71Å. These conformations are generated under free optimization (co-ordinates not fixed) and have the minimum energy of the parallel conformation. Under free optimization, monomers (5CB) randomly interact with each other. When the first monomer (5CB) has fixed and the second monomer (5CB) moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 1, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap increases continually.
- (ii) Polarizability decreases continually.
- (iii) Total energy increases continually.
- (iv) Dipole moment decreases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume heat capacity first decreases and then increases continually.
- (vii) Entropy first decrease and then increases continually.
- (viii) Zero-point energy first decreases and then increases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 1. The Highest occupied molecular orbital(HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Parallel Conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.51	4.51	4.52	4.52
Dipole moment (Debye)	10.37	10.36	10.36	10.35	10.34
Thermal Energy (kcal/mol)	427.71	427.69	427.08	427.07	427.68
Polarizability (kcal/mol)	256867	256779	256691	256603	256522
Total Energy (kcal/mol)	-9440.86	-9440.91	-9440.95	-9440.99	-9441.02
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.13	0.13	0.14
Entropy (kcal/mol)	0.23	0.23	0.22	0.22	0.23
ZPE (kcal/mol)	404.53	404.50	404.44	404.43	404.46
Enthalpy (kcal/mol)	428.29	428.28	427.66	427.66	428.27
Gibbs Energy (kcal/mol)	358.39	357.92	360.19	360.06	358.19

When the first monomer (5CB) has fixed and the second monomer (5CB) moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 2, and we conclude the following statements:

- (i) The HOMO-LUMO gap decreases continually.
- (ii) Polarizability decreases continually.

- (iii) Total energy increases and then decreases continually.
- (iv) Dipole moment first decreases and then increases continually.
- (v) Internal thermal energy increases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy first increases and then decreases continually.
- (viii) Zero-point energy first increases and then decreases continually.
- (ix) Enthalpy increases continually.
- (x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 2. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-5CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.50	4.49	4.48
Dipole moment (Debye)	10.35	10.34	10.34	10.35	10.35
Thermal Energy (kcal/mol)	427.68	427.69	427.72	427.74	427.74
Polarizability (kcal/mol)	256377	256308	256239	256183	256120
Total Energy (kcal/mol)	-9440.06	-9440.07	-9440.07	-9440.07	-9440.06
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.24	0.23	0.23	0.22
ZPE (kcal/mol)	404.46	404.46	404.50	404.54	404.53
Enthalpy (kcal/mol)	428.27	428.28	428.30	428.33	428.33
Gibbs Energy (kcal/mol)	358.11	357.89	358.25	358.43	358.16

3.2 5CB-5CB Antiparallel Conformation

In this section, we study the interaction of 5CB-5CB liquid crystal dimers in the antiparallel configuration, as shown in Figure 2.

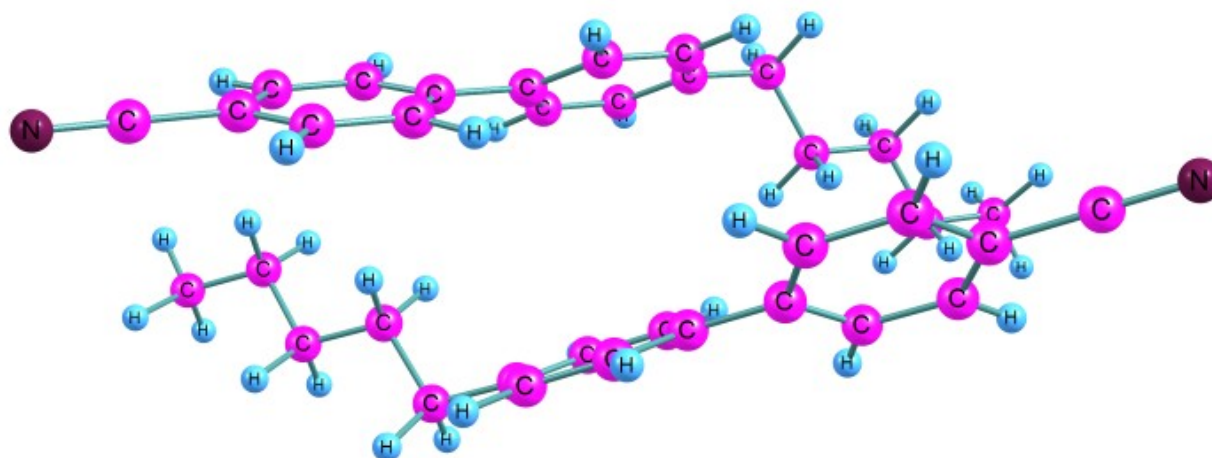


Figure 2. Antiparallel conformation of 5CB liquid crystal dimer

The polarizability of the 5CB-5CB dimer in antiparallel conformation decreases continually when the 5CB monomer moves in forwarding or backward direction in contrast to Figure 2. The dipole moment of this dimer in antiparallel conformation increases continuously when the monomer (5CB) moves in forward or backward direction. This conformation has the least dipole moment as a comparison to the four conformations of 5CB liquid crystal dimer. The cyano group of the first monomer (5CB) interacts with the tail of another monomer at a distance of 2.82Å. The benzene of the first monomer (5CB) interacts with the benzene another monomer (5CB) at a range of 2.60Å. The benzene of the first monomer interacts with the benzene of another monomer; they interact mutually at a distance of 2.39Å. The cyano group of the first monomer interacts with the tail of another monomer at a range of 2.80Å. This conformation has the least energy as a comparison to all the conformation of 5CB dimer the interaction energy of this conformation (antiparallel Figure 2) is higher as a comparison with all the conformations of the 5CB dimer. When the first monomer (5CB) has fixed and the second monomer (5CB) moves forward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 3, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap remains constant.
- (ii) Polarizability decreases continually.
- (iii) Total energy increases continually.
- (iv) Dipole moment increases continually.
- (v) Internal thermal energy decreases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy remains constant.
- (viii) Zero-point energy first decreases and then increases and again decreases continually.
- (ix) Enthalpy decreases continually.
- (x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 3. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.53	4.53	4.53	4.53	4.53
Dipole moment (Debye)	4.69	4.70	4.72	4.73	4.74
Thermal Energy (kcal/mol)	427.66	427.66	427.65	427.64	427.63
Polarizability (kcal/mol)	256478	256346	256227	256107	255994
Total Energy (kcal/mol)	-9440.10	-9440.20	-9440.30	-9440.30	-9440.40
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.23	0.23	0.23	0.23
ZPE (kcal/mol)	404.43	404.42	404.67	404.39	404.36
Enthalpy (kcal/mol)	428.25	428.24	428.24	428.23	428.21
Gibbs Energy (kcal/mol)	358.44	358.33	358.36	358.27	357.94

When the first monomer (5CB) has fixed and the second monomer (5CB) moves backward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 4, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap increases continually.
- (ii) Polarizability decreases continually.
- (iii) Total energy increases continually.
- (iv) Dipole moment increases continually.
- (v) Internal thermal energy increases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy first remains constant.
- (viii) Zero-point energy first decreases and then increases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first decreases and then increases continually.

Table 4. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-5CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.53	4.53	4.53	4.53	4.54
Dipole moment (Debye)	4.76	4.76	4.77	4.78	4.78
Thermal Energy (kcal/mol)	427.59	427.59	427.59	427.60	427.61
Polarizability (kcal/mol)	255794	255699	255612	255536	255474
Total Energy (kcal/mol)	-9440.30	-9440.40	-9440.50	-9440.60	-9440.70
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.23	0.23	0.23	0.23
ZPE (kcal/mol)	404.29	404.27	404.27	404.29	404.30
Enthalpy (kcal/mol)	428.18	428.17	428.18	428.19	428.19
Gibbs Energy (kcal/mol)	357.27	357.25	357.23	357.36	357.43

3.3 5CB-5CB Cross to Each other Conformation

Here, we study the interaction properties of the same dimer (5CB-5CB) but in the cross to each other conformation, as shown in Figure 3.

The polarizability, total energy, and Gibbs energy of this dimer conformation decrease continually when the monomer (5CB) moves in forward or backward direction. The dipole moment and entropy of this dimer increases continuously when the monomer (5CB) moves in forward or backward direction. The benzene of the first monomer (5CB) interacts with the tail of another monomer (5CB) at a distance of 2.96Å. The benzene of the second monomer interacts with the tail of the first monomer at a distance of 2.87Å. This cross conformation of 5CB-5CB represents better interaction energy as a comparison with the parallel conformation of 5CB dimer. Still, this conformation does not give the best interaction energy as a comparison with

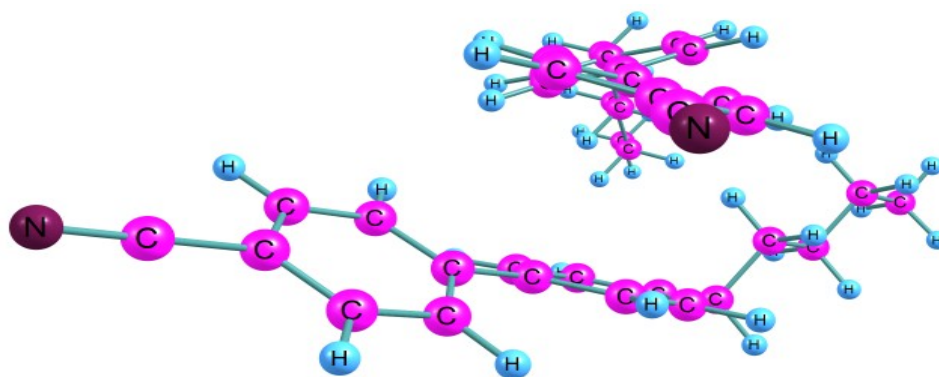


Figure 3. Cross conformation of 5CB liquid crystal dimer

antiparallel conformation because this conformation represents higher electronic energy. When the first monomer (5CB) has fixed and the second monomer (5CB) moves forward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 5, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap increases continually.
- (ii) Polarizability decreases continually.
- (iii) Total energy decreases continually.
- (iv) Dipole moment increases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume heat capacity first decreases and then increases continually.
- (vii) Entropy first decreases and then increases continually.
- (viii) Zero-point energy decreases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first increases and then decreases continually.

Table 5. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO(eV)	4.51	4.51	4.52	4.52	4.52
Dipole moment (Debye)	10.47	10.48	10.49	10.49	10.49
Thermal Energy (kcal/mol)	427.61	427.00	426.98	426.98	427.56
Polarizability (kcal/mol)	256089	255963	255844	255731	255630
Total Energy (kcal/mol)	-9440.40	-9440.30	-9440.20	-9440.10	-9440.00
Heat capacity (C_v) (kcal/mol)	0.14	0.13	0.13	0.13	0.14
Entropy (kcal/mol)	0.23	0.22	0.22	0.22	0.23
ZPE(kcal/mol)	404.38	404.34	404.33	404.32	404.31
Enthalpy (kcal/mol)	428.19	427.58	427.57	427.56	428.15
Gibbs Energy (kcal/mol)	358.09	360.02	359.93	359.87	357.49

When the first monomer (5CB) has fixed and the second monomer (5CB) moves backward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 6, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap remains constant.
- (ii) Polarizability decreases continually.
- (iii) Total energy decreases continually.
- (iv) Dipole moment increases constantly.
- (v) Internal thermal energy increases continually.
- (vi) Constant volume heat capacity increases continually.
- (vii) Entropy increases continually.
- (viii) Zero-point energy first decreases and then increases continually.
- (ix) Enthalpy increases continually.
- (x) Gibbs's energy decreases continually.

Table 6. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in backward direction

5CB-5CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.51	4.51	4.51
Dipole moment (Debye)	10.50	10.50	10.51	10.51	10.52
Thermal Energy (kcal/mol)	423.97	426.96	426.96	427.56	427.56
Polarizability (kcal/mol)	255436	255348	255267	255197	255122
Total Energy (kcal/mol)	-9440.10	-9440.08	-9440.06	-9440.05	-9440.03
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.14	0.14
Entropy (kcal/mol)	0.22	0.22	0.22	0.23	0.23
ZPE (kcal/mol)	404.29	404.27	404.27	404.28	404.28
Enthalpy (kcal/mol)	427.55	427.55	427.55	428.14	428.14
Gibbs Energy (kcal/mol)	359.67	359.56	359.48	353.21	357.10

3.4 6CB-6CB Parallel Conformation

Now, we study the interaction properties of another dimer 6CB-6CB in parallel conformation, as shown in Figure 4.



Figure 4. Parallel conformation of 6CB liquid crystal dimer

The polarizability, total energy, and internal thermal energy of this dimer increase continually when the monomer (6CB) moves in forward or backward direction. The dipole moment of this dimer decreases continuously when the monomer (6CB) moves in forwarding or backward direction. The benzene of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.43Å. The benzene-benzene interaction (2.43Å) of the 5CB dimer is equivalent to the benzene-benzene interaction (2.43Å) of the 6CB dimer in parallel conformations. The tail of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.80Å. The tail of the second monomer (6CB) interacts with the benzene of the first monomer (6CB) at a distance of 2.63Å. When the first monomer (6CB) has fixed and the second monomer (6CB) moves forward all possible interaction properties of the dimer in this conformation have been tabulated as Table 7, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap remains constant.
- (ii) Polarizability increases continually.
- (iii) Total energy increases continually.
- (iv) Dipole moment decreases continually.
- (v) Internal thermal energy increases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy remains constant.
- (viii) Zero-point energy first increases and then decreases and again increases continually.
- (ix) Enthalpy remains constant.
- (x) Gibbs's energy first increases and then suddenly it falls and again increases continually.

Table 7. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

6CB-6CBParallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.63	4.63	4.63	4.63	4.63
Dipole moment (Debye)	10.43	10.42	10.41	10.40	10.39
Thermal Energy (kcal/mol)	465.08	465.08	465.08	465.09	465.09
Polarizability (kcal/mol)	272065	272203	272341	272479	272623
Total Energy (kcal/mol)	-9933.32	-9933.38	-9933.43	-9933.48	-9933.54
Heat capacity (C_v) (kcal/mol)	0.15	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.25	0.25	0.25	0.25	0.25
ZPE (kcal/mol)	440.16	440.16	440.17	440.16	440.17
Enthalpy (kcal/mol)	465.67	465.67	465.67	465.67	465.67
Gibbs Energy (kcal/mol)	390.70	390.76	390.76	390.43	390.55

When the first monomer (6CB) has fixed and the second monomer (6CB) moves backward then the all possible interaction properties of the dimer in this conformation can be tabulated as Table 8, and hence then we conclude the following statements:

- (i) The HOMO-LUMO gap remains constant.
- (ii) Polarizability increases continually.
- (iii) Total energy increases continually.
- (iv) Dipole moment decreases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy remains constant.
- (viii) Zero-point energy first decreases and then increases continually.
- (ix) Enthalpy increases continually.
- (x) Gibbs's energy first decreases and then increases continually.

Table 8. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in backward direction

6CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.64	4.64	4.64	4.64	4.64
Dipole moment (Debye)	10.38	10.37	10.37	10.36	10.35
Thermal Energy (kcal/mol)	464.49	464.48	464.48	464.49	464.49
Polarizability (kcal/mol)	272912	273056	273207	273351	273495
Total Energy (kcal/mol)	-9933.60	-9933.70	-9933.70	-9933.80	-9933.90
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.24	0.24	0.24	0.24	0.24
ZPE (kcal/mol)	440.15	440.14	440.13	440.14	440.15
Enthalpy (kcal/mol)	465.07	465.07	465.07	465.07	465.08
Gibbs Energy (kcal/mol)	392.95	392.90	392.91	392.92	392.92

3.5 6CB-6CB Antiparallel Conformation

In this section, the interaction properties of antiparallel conformation of 6CB-6CB liquid crystal dimers (Figure 5) have studied.

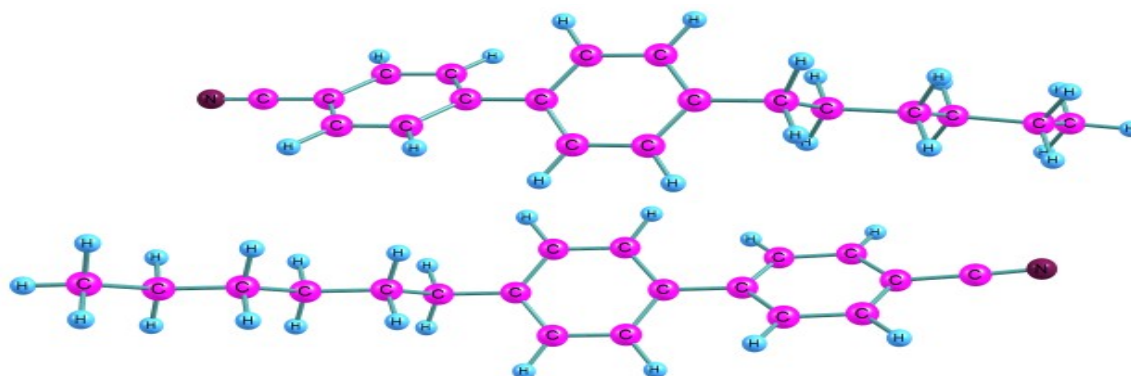


Figure 5. Antiparallel conformation of 6CB liquid crystal dimer

The dipole moment, total energy, and entropy of this dimer in antiparallel conformation increase continually when the monomer (6CB) moves in forward or backward direction. The polarizability of this dimer decreases continuously when the monomer (6CB) moves in forwarding or backward direction. The tail of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.91Å. The tail of the second monomer (6CB) interacts with the benzene of the first monomer (6CB) at a distance of 2.95Å. When the first monomer (6CB) has fixed, and the other monomer (6CB) moves forward all possible interaction properties of the dimer in this conformation can be tabulated as Table 9, and hence then we conclude the following statements:

- (i) The HOMO-LUMO gap decreases continually.
- (ii) Polarizability decreases continually.
- (iii) Total energy first decreases and then increases continually.
- (iv) Dipole moment increases continually.
- (v) Internal thermal energy increases continually.
- (vi) Constant volume of heat capacity increases continually.
- (vii) Entropy increases continually.
- (viii) Zero-point energy increases continually.
- (ix) Enthalpy increases continually.
- (x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 9. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

6CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.51	4.51	4.50
Dipole moment (Debye)	2.40	2.41	2.41	2.42	2.43
Thermal Energy (kcal/mol)	464.47	465.07	465.07	465.07	465.08
Polarizability (kcal/mol)	271406	271343	271274	271211	271155
Total Energy (kcal/mol)	-9933.96	-9933.07	-9933.17	-9933.26	-9933.34
Heat capacity (C_v) (kcal/mol)	0.14	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.23	0.24	0.24	0.25	0.25
ZPE (kcal/mol)	440.20	440.21	440.21	440.21	440.21
Enthalpy (kcal/mol)	465.06	465.65	465.66	465.66	465.66
Gibbs Energy (kcal/mol)	394.14	391.94	392.26	392.25	392.24

When the first monomer (6CB) has fixed and the second monomer (6CB) moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 10, and hence we concluded the following statements:

- (i) The HOMO-LUMO gap decreases continually.
- (ii) Polarizability decreases continually.
- (iii) Total energy increases continually.

- (iv) Dipole moment increases continually.
- (v) Internal thermal energy decreases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy increases continually.
- (viii) Zero-point energy decreases continually.
- (ix) Enthalpy decreases continually.
- (x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 10. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

6CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.49	4.49	4.49	4.48
Dipole moment (Debye)	2.44	2.45	2.46	2.46	2.47
Thermal Energy (kcal/mol)	465.07	465.06	465.05	465.04	465.04
Polarizability (kcal/mol)	271042	270992	270948	270910	270872
Total Energy (kcal/mol)	-9933.40	-9933.50	-9933.60	-9933.70	-9933.80
Heat capacity (C_v) (kcal/mol)	0.15	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.24	0.24	0.25	0.25	0.26
ZPE (kcal/mol)	440.18	440.14	440.12	440.11	440.09
Enthalpy (kcal/mol)	465.65	465.64	465.63	465.63	465.62
Gibbs Energy (kcal/mol)	392.05	391.80	391.69	392.04	391.50

3.6 5CB-6CB Antiparallel Conformation

Now, we study the interaction of 5CB with 6CB liquid crystal in antiparallel conformation, as shown in Figure 6.

The 5CB and 6CB monomer have π - π interactions in the antiparallel conformation that has shown in Figure 6. This antiparallel conformation has the least dipole moment as a comparison to the four conformations of 5CB-6CB liquid crystal dimer. The cyano group of 6CB monomer interacts with the tail 5CB monomer at a distance of 2.71Å. The benzene of 5CB monomer interacts with the benzene of 6CB monomer at a distance of 2.88Å. The cyano group of 5CB monomer interacts with the tail of 6CB monomer at a distance of 2.84Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward and all possible interaction properties of dimer shown in Table 11, and hence then we conclude the following statements:

- (i) The HOMO-LUMO gap first decreases and then increases continually.
- (ii) The polarizability first decreases and then increases continually.
- (iii) Total energy decreases continually.
- (iv) Dipole moment increases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume heat capacity remains constant.

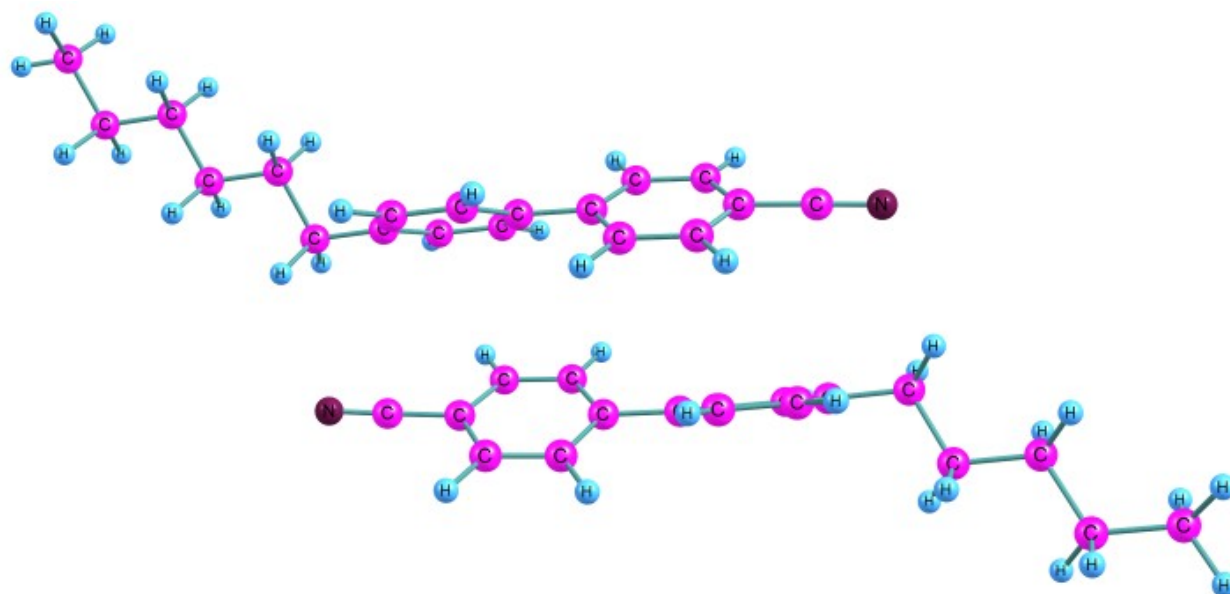


Figure 6. Antiparallel conformation of 5CB and 6CB liquid crystal dimer

- (vii) Entropy first decreases and then increases continually.
- (viii) Zero-point energy increases and then decreases and again increases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first increases then decreases and then again increases continually.

Table 11. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.42	4.28	4.28	4.44	4.57
Dipole moment (Debye)	0.54	0.55	0.56	0.57	0.58
Thermal Energy (kcal/mol)	444.78	444.30	444.35	444.93	445.04
Polarizability (kcal/mol)	259408	258705	258486	258875	259345
Total Energy (kcal/mol)	-9686.40	-9686.35	-9686.30	-9686.25	-9686.20
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.13	0.13
Entropy (kcal/mol)	0.21	0.20	0.20	0.21	0.21
ZPE (kcal/mol)	423.16	423.38	423.47	423.45	423.61
Enthalpy (kcal/mol)	445.37	444.89	444.93	445.52	445.62
Gibbs Energy (kcal/mol)	380.11	383.12	383.27	381.54	381.88

When the first 5CB monomer has fixed and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 12 and hence we conclude the following statements:

- (i) The HOMO-LUMO gap first decreases and then increases continually.

- (ii) The polarizability first decreases and then increases continually.
- (iii) Total energy first decreases and then increases continually.
- (iv) Dipole moment decreases continually.
- (v) Internal thermal energy first decreases and then increases and again decreases continually.
- (vi) Constant volume heat capacity remains constant.
- (vii) Entropy first increases and then decreases continually.
- (viii) Zero-point energy decreases continually.
- (ix) Enthalpy first decreases and then increases and then again decreases continually.
- (x) Gibbs's energy first increases and then decreases and again increases continually.

Table 12. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.42	4.46	4.56	4.62
Dipole moment (Debye)	0.54	0.53	0.52	0.52	0.51
Thermal Energy (kcal/mol)	444.69	444.04	443.95	444.52	443.32
Polarizability (kcal/mol)	262834	260625	261209	262050	263079
Total Energy (kcal/mol)	-9686.80	-9686.30	-9686.40	-9686.40	-9686.43
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.13	0.13
Entropy (kcal/mol)	0.21	0.21	0.21	0.22	0.21
ZPE (kcal/mol)	422.91	422.75	422.57	422.53	422.45
Enthalpy (kcal/mol)	445.27	444.62	444.54	445.11	443.90
Gibbs Energy (kcal/mol)	379.75	380.77	379.83	377.20	381.01

3.7 5CB-6CB Parallel Conformation

In this section, we study the interaction properties of the 5CB-6CB in parallel conformation, as shown in Figure 7.

The polarizability of this dimer in parallel conformation increases continually when the 5CB and 6CB monomer moves in forward or backward direction. The total energy of this dimer decreases continuously when the 5CB and 6CB monomer moves in forward or backward direction. This conformation has π - π interaction between 5CB and 6CB liquid crystal dimer, as shown in Figure 7. The tail of the 6CB monomer interacts with the tail of 5CB monomer at a distance of 2.19Å. The benzene of 6CB monomer interacts with the benzene of 5CB monomer at a distance of 2.47Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 13, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap decreases continually.
- (ii) Polarizability increases continually.
- (iii) Total energy decreases continually.

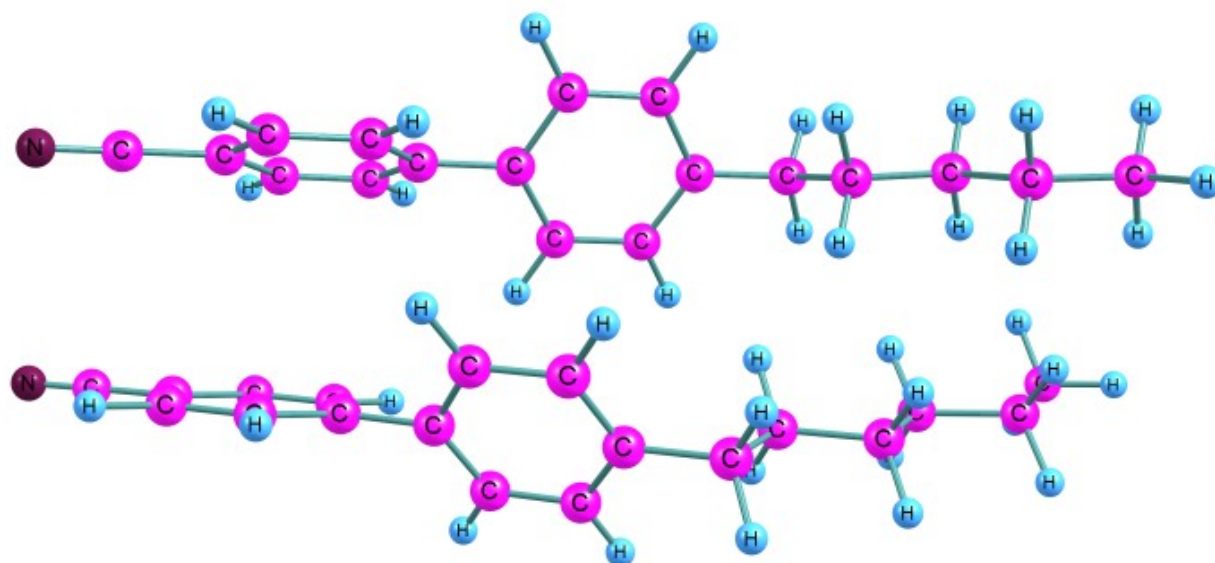


Figure 7. Parallel conformation of 5CB and 6CB liquid crystal dimer

- (iv) Dipole moment first decreases and then increases continually.
- (v) Internal thermal energy first increases and then decreases continually.
- (vi) Constant volume of heat capacity decreases continually.
- (vii) Entropy decreases continually.
- (viii) Zero-point energy first increases and then decreases continually.
- (ix) Enthalpy first increases and then decreases continually.
- (x) Gibbs's energy first increases and then decreases and again increases continually.

Table 13. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	5.02	4.98	4.71	3.72	2.81
Dipole moment (Debye)	4.10	4.03	4.09	4.55	5.42
Thermal Energy (kcal/mol)	446.00	446.16	445.89	445.58	444.31
Polarizability (kcal/mol)	248301	249638	251834	254714	257940
Total Energy (kcal/mol)	-9686.55	-9686.40	-9685.40	-9685.35	-9683.30
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.12
Entropy (kcal/mol)	0.21	0.20	0.19	0.19	0.18
ZPE (kcal/mol)	424.19	425.10	426.04	426.17	426.05
Enthalpy (kcal/mol)	446.59	446.74	446.47	446.17	444.89
Gibbs Energy (kcal/mol)	382.06	384.79	387.66	386.86	388.94

When the first 5CB monomer has fixed and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 14 and hence we conclude the following statements:

- (i) The HOMO-LUMO gap first increases and then decreases continually.
- (ii) Polarizability increases continually.
- (iii) Total energy decreases continually.
- (iv) Dipole moment first increases and then decreases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume of heat capacity decreases continually.
- (vii) Entropy decreases continually.
- (viii) Zero-point energy first decreases and then increases continually.
- (ix) Enthalpy first decreases and then increases and again decreases continually.
- (x) Gibbs's energy increases continually.

Table 14. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	5.05	5.06	5.03	4.98	4.92
Dipole moment (Debye)	4.26	4.33	4.36	4.32	4.25
Thermal Energy (kcal/mol)	445.03	444.46	443.93	443.56	443.76
Polarizability (kcal/mol)	247291	247373	247906	248910	250127
Total Energy (kcal/mol)	-9686.45	-9686.40	-9685.20	-9685.14	-9685.12
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.12	0.12
Entropy (kcal/mol)	0.21	0.20	0.20	0.19	0.19
ZPE (kcal/mol)	423.45	423.42	423.42	423.86	423.92
Enthalpy (kcal/mol)	445.61	444.45	444.52	444.15	444.34
Gibbs Energy (kcal/mol)	380.67	382.48	383.11	385.01	385.14

3.8 5CB-6CB Cross Conformation

Lastly, we study the interaction of 5CB and 6CB liquid crystal in cross conformation, as shown in Figure 8.

The total energy of this dimer decreases continually when the 5CB and 6CB monomer moves in forwarding or backward direction, as shown in Figure 8. The zero-point energy of this conformation increases continuously when the 5CB and 6CB monomer moves in forward or backward direction. The benzene of 5CB monomer interacts with the benzene of 6CB monomer at a distance of 2.94Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 15, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap decreases continually.
- (ii) Polarizability increases continually.

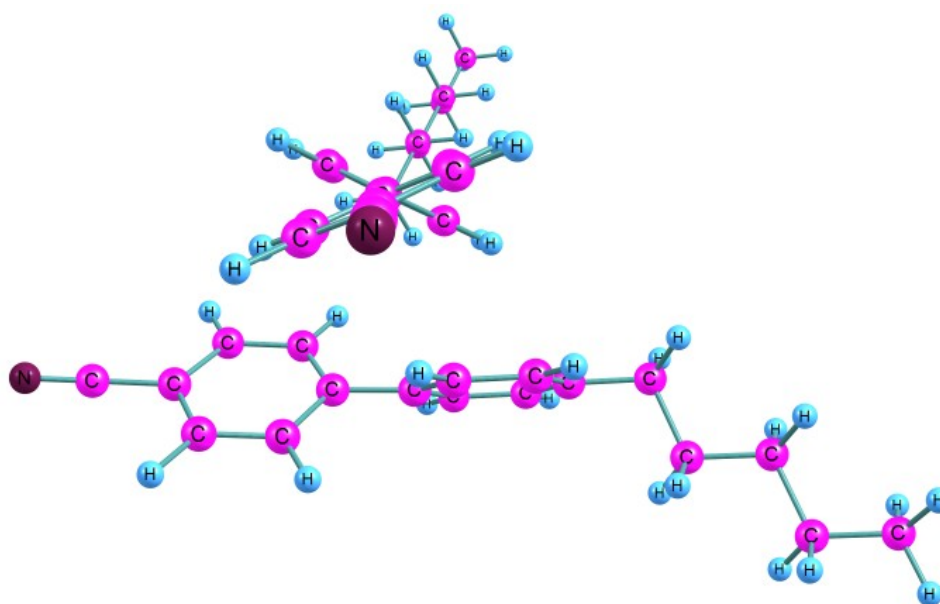


Figure 8. Cross conformation of 5CB and 6CB liquid crystal dimer

- (iii) Total energy decreases continually.
- (iv) Dipole moment first increases and then decreases continually.
- (v) Internal thermal energy first increases and then decreases and increases continually.
- (vi) Constant volume heat capacity first decreases and then increases continually.
- (vii) Entropy first decreases and then increases continually.
- (viii) Zero-point energy increases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first increases and then decreases continually.

Table 15. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.76	4.72	4.63	4.49	4.41
Dipole moment (Debye)	8.17	8.17	8.19	8.17	8.12
Thermal Energy (kcal/mol)	444.26	444.72	443.24	443.45	444.88
Polarizability (kcal/mol)	257369	258404	259904	261265	262351
Total Energy (kcal/mol)	-9686.89	-9686.84	-9686.77	-9686.70	-9686.65
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.13
Entropy (kcal/mol)	0.21	0.20	0.19	0.19	0.21
ZPE (kcal/mol)	423.10	423.15	423.34	423.64	424.00
Enthalpy (kcal/mol)	444.85	444.30	443.83	444.04	445.47
Gibbs Energy (kcal/mol)	381.03	382.50	384.67	385.13	381.26

When the first 5CB monomer can be fixed and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 16, and hence we conclude the following statements:

- (i) The HOMO-LUMO gap first increases and then decreases continually.
- (ii) Polarizability increases continually.
- (iii) Total energy decreases continually.
- (iv) Dipole moment decreases continually.
- (v) Internal thermal energy first decreases and then increases continually.
- (vi) Constant volume heat capacity first decreases and then increases continually.
- (vii) Entropy decreases continually.
- (viii) Zero-point energy increases continually.
- (ix) Enthalpy first decreases and then increases continually.
- (x) Gibbs's energy first increases and then decreases continually.

Table 16. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-6CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.80	4.81	4.76	4.71	4.70
Dipole moment (Debye)	8.19	8.16	8.12	8.09	8.05
Thermal Energy (kcal/mol)	444.21	443.65	443.16	443.28	443.99
Polarizability (kcal/mol)	256980	257356	258046	259057	260111
Total Energy (kcal/mol)	-9686.90	-9686.88	-9686.85	-9686.81	-9686.79
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.13
Entropy (kcal/mol)	0.21	0.20	0.20	0.20	0.20
ZPE (kcal/mol)	422.98	422.98	423.12	423.24	423.43
Enthalpy (kcal/mol)	444.79	444.24	443.75	443.86	444.58
Gibbs Energy (kcal/mol)	380.60	381.76	383.94	383.86	382.44

Table 17. The Interaction energy of all the Dimers in parallel and antiparallel configurations

Conformations	Dimer E_1 (kcal/mol)	Monomer \times Monomer E_0 (kcal/mol)	Interaction energy ($E_1 - E_0$) (kcal/mol)
5CB-5CB-Parallel	-943931.96	-943923.76	-8.20
5CB-5CB-Antiparallel	-943931.34	-943923.76	-7.58
5CB-5CB-Cross	-943929.54	-943923.76	-5.78
6CB-6CB-Parallel	-993269.59	-993264.40	-5.19
6CB-6CB-Antiparallel	-993269.41	-993264.40	-5.01
5CB-6CB-Antiparallel	-968591.63	-968594.08	2.44
5CB-6CB-Parallel	-968585.59	-968594.08	8.48
5CB-6CB-Cross	-968591.46	-968594.08	2.62

The interaction energies of the stable geometries of dimers have been tabulating as in Table 17, which reflects the interaction and dimers energies of 5CB and 6CB and their dimers in different configurations.

4. Conclusions

In this work, it has found that the antiparallel conformation of 5CB and 6CB liquid crystal dimers have minimum negative interaction energy and also have the least dipole moment as a comparison to all conformations of the dimers. The antiparallel conformations of 5CB and 6CB liquid crystal dimer have the least negative entropy. The parallel conformations of 5CB liquid crystal dimer have higher polarizability as a comparison to all the conformations of the 5CB dimer. The cross conformation of the 5CB dimer has the least polarizability and Gibbs energy. The antiparallel conformations of 6CB dimer have minimum negative polarizability and also have higher Gibbs energy as comparison to all the conformations of the 6CB dimer. But all the conformations of 5CB-6CB dimer have positive interaction energy, so we can conclude that the 5CB and 6CB liquid crystals weakly interact with each other. The antiparallel conformations of the 5CB-6CB dimer have minimum negative polarizability and also have the least dipole moment. On the basis of molecular interaction of 5CB and 6CB, we study the 5CB, and 6CB liquid crystal dimers have minimum negative interaction energy in the antiparallel conformation, but 5CB-6CB liquid crystal dimer has positive interaction energy for all the possible conformations. The isotropic polarizability is minimum in the antiparallel conformation of 6CB liquid crystal dimer (6CB-6CB), but isotropic polarizability is maximum in the parallel conformation of 6CB liquid crystal dimer. The cross conformation of 5CB liquid crystal dimer (5CB-5CB) has the least isotropic polarizability, but the parallel conformation of 5CB liquid crystal dimer has the highest isotropic polarizability.

Acknowledgments

The authors are very thankful to the University Grants Commission (UGC) New Delhi for providing NFSC fellowship for this work. The authors are also very grateful to Dr. Anoop Ayyappan (IIT KGP, WB) for providing computational help. Shivani Chaudhary is thankful to UGC for providing a non-net fellowship. We are grateful to Dr. Khem B. Thapa and Pawan Singh for scientific discussion.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

- [1] W. E. Acree and J. C. Chickos, Phase change enthalpies and entropies of liquid crystals, *Journal of Physical and Chemical Reference Data* **34** (2006), 1051, DOI: 10.1063/1.1901689.

- [2] C. Amovilli, I. Cacelli, G. Cinacchi, L.D. Gaetani, G. Prampolini and A. Tani, Structure and dynamics of mesogens using intermolecular potentials derived from *ab initio* calculations, *Theoretical Chemistry Accounts* **117** (2007), 885, DOI: 10.1007/s00214-006-0209-y.
- [3] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *The Journal of Chemical Physics* **98** (1993), 5648, DOI: 10.1063/1.464913.
- [4] L. M. Blinov and V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials*, Springer, Berlin (1994), DOI: 10.1007/978-1-4612-2692-5.
- [5] G. J. Brownsey and A.J. Leadbetter, Novel liquid crystal structures in cyano bi-cyclohexanes, *Journal de Physique Letters* **42** (1985), L135, DOI: 10.1051/jphyslet:01981004206013500.
- [6] I. G. Chistyakov, Ordering and structure of liquid crystals, *Advances in Liquid Crystals* **1** (1975), 143, DOI: 10.1016/B978-0-12-025001-1.50008-1.
- [7] Y. C. Chu, T. Tsang and L. Yin, Structures of cyano-biphenyl liquid crystals, *Physica Status Solidi (a)* **114** (1989), K1, DOI: 10.1002/pssa.2211140146.
- [8] S. Gauza, A. Parigh, S.-T. Wu, A. Spadlo and R. Dabrowski, Physical properties of laterally fluorinated isothiocyanato phenyl-tolane liquid crystals, *Liquid Crystals* **35** (2008), 711, DOI: 10.1080/02678290801956321.
- [9] P. G. de Gennes, *The Physics of Liquid Crystal*, Clarendon Press, Oxford, pp. xi + 333 (1974).
- [10] A. G. Gilani, *Dielectric and electro-optical properties of some cyanobiphenyl liquid-crystals*, Ph.D Thesis, Kent State University, Kent (1995), https://research.aston.ac.uk/files/13504563/Ghana1995_AURA.pdf.
- [11] G. W. Gray and A. Mosley, Trends in the nematic–isotropic liquid transition temperatures for the homologous series of 4-n-alkoxy- and 4-n-alkyl-4'-cyanobiphenyls, *Journal of the Chemical Society, Perkin Transactions 2* **1** (1976), 97, DOI: 10.1039/P29760000097.
- [12] G. W. Gray, K. I. Harrison and J. A. Nash, New family of nematic liquid crystals for displays, *Electronics Letters* **9**(6) (1973), 130 – 131, DOI: 10.1049/el:19730096.
- [13] A. Grzybowski, S. Urban, S. Mroz and M. Paluch, Activation volume of selected liquid crystals in the density scaling regime, *Scientific Reports* **7** (2017), 42174, DOI: 10.1038/srep42174.
- [14] W. Haase and H. Paulus, The Crystal and Molecular Structures of Three Homologous, Mesogenic Trans, Trans-4'-Alkylbicyclohexyl-4-carbonitriles (Cyclohexylcyclohexanes, CCHs), *Molecular Crystals and Liquid Crystals* **100** (1983), 111, DOI: 10.1080/00268948308073725.
- [15] P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *The Journal of Chemical Physics* **82** (1985), 299, DOI: 10.1063/1.448975.
- [16] I. H. Ibrahim and W. Haase, On the molecular polarizability of nematic liquid crystals, *Molecular Crystals and Liquid Crystals* **66** (1) (1981), 189, DOI: 10.1080/00268948108072672.
- [17] W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, New York (1980), <https://trove.nla.gov.au/version/46292297>.
- [18] M. Kuribayashi and K. Hori, Crystal structures of 4-cyano-4-hexylbiphenyl (6CB) and 4-cyano-4-heptylbiphenyl (7CB) in relation to odd-even effects, *Liquid Crystals* **26** (1999), 809, DOI: 10.1080/026782999204499.
- [19] R. J. W. Le Fèvre and B. P. Rao, Molecular polarisability. The anisotropies of seven monosubstituted benzenes and of nitromethane as solutes in carbon tetrachloride, *Journal of the Chemical Society* (1958), 1465, DOI: 10.1039/JR9580001465.

- [20] A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray and A. Mosley, The structure of smectic A phases of compounds with cyano end groups, *Journal de Physique* **40** (1979), 375, DOI: 10.1051/jphys:01979004004037500.
- [21] C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Physical Review B* **37** (1988), 785, DOI: 10.1103/PhysRevB.37.785.
- [22] O. Lehmann, Über fließende krystalle, *Zeitschrift für Physikalische Chemie* **4U** (1889), 462, DOI: 10.1515/zpch-1889-0434.
- [23] G. R. Luckhurst and G. W. Gray, *The Molecular Physics of Liquid Crystals*, Academic Press, Academic Press, London — New York, xiii, p. 494, <https://catalogue.nla.gov.au/Record/2946484>.
- [24] D. M. P. Mingos, *Liquid Crystals I*, Springer-Verlag, Berlin — Heidelberg (1999), DOI: 10.1007/3-540-68305-4.
- [25] S. Pestov, *Landolt-Börnstein - Group VIII Advanced Materials and Technologies 5A*, Springer-Verlag, Berlin — Heidelberg (2003), DOI: 10.1007/b71736.
- [26] V. F. Petrov and Y. Shimizu, (Iso)Thiocyanato substitution in calamitic liquid crystals, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals* **363** (2001), 107, DOI: 10.1080/10587250108025262.
- [27] L. Pohl, R. Eidenschink, G. Krause and D. Erdmann, Physical properties of nematic phenylcyclohexanes, a new class of low melting liquid crystals with positive dielectric anisotropy, *Physics Letters A* **60** (1977), 421, DOI: 10.1016/0375-9601(77)90040-8.
- [28] L. Pohl, R. Eidenschink, J. Krause and G. Weber, Nematic liquid crystals with positive dielectric and negative diamagnetic anisotropy, *Physics Letters A* **65** (1978), 169, DOI: 10.1016/0375-9601(78)90608-4.
- [29] R. Prabh and C. V. Yelamaggad, Structure-property correlations in cyanobiphenyl-based dimer-like mesogens, *The Journal of Physical Chemistry B* **119** (2015), 11935, DOI: 10.1021/acs.jpcc.5b06073.
- [30] E. Rahimzadeh, T. Tsang and L. Yin, Smectic phase structures of CVyano-Dicyclohexyl liquid crystals, *Molecular Crystals and Liquid Crystals* **139** (1986), 291, DOI: 10.1080/00268948608080134.
- [31] B. R. Ratna and R. Shashidhar, Dielectric properties of 4'-n-alkyl-4-cyanobiphenyls in their nematic phases, *Pramana* **6** (1975), 278, DOI: <https://www.ias.ac.in/article/fulltext/pram/006/05/0278-0283>.
- [32] F. Reinitzer, Beiträge zur kenntniss des cholesterins, *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften* **9** (1888), 421, DOI: 10.1007/BF01516710 (translation to English: Contributions to the knowledge of cholesterol, *Liquid Crystals* **5** (1989), 7 – 18, DOI: 10.1080/02678298908026349).
- [33] R. A. Shanks and D. Staszczyk, Thermal and optical characterization of polymer-dispersed liquid crystals, *International Journal of Polymer Science* **2012** (2012), 13, DOI: 10.1155/2012/767581.
- [34] A. Sikorska, B. J. Linde and J. I. Kukielski, The effect of solvent polarity on photo-acoustic spectra of alkyl-cyanobiphenyl derivatives, *Journal of Optics A: Pure and Applied Optics* **3** (2001), S71, DOI: 10.1088/1464-4258/3/4/362.
- [35] K. Skarp, S. T. Lagerwall, B. Stebler and D. McQueen, Flow alignment in cyanobiphenyl liquid crystals, *Physica Scripta* **19** (1979), 339, DOI: 10.1088/0031-8949/19/4/008.
- [36] S. Urban, T. Brückert and A. Würflinger, Dielectric studies on liquid crystals under high pressure: VI. Low frequency relaxation process in the nematic and smectic A phase of 4-n-Octyl-4'-Cyanobiphenyl (8 CB), *Zeitschrift für Naturforschung A*, **49** (1994), 552, DOI: 10.1515/zna-1994-4-506.

- [37] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus and W. A. de Jong, NWChem: A comprehensive and scalable open-source solution for large scale molecular simulations, *Computer Physics Communications* **181** (2010), 1477, DOI: 10.1016/j.cpc.2010.04.018.
- [38] L. Vicari, *Optical Applications of Liquid Crystals*, 1st edition, CRC Press — Taylor & Francis, Boca Raton — London (2003), DOI: 10.1201/9781420033748.
- [39] D. K. Yang and S. T. Wu, *Fundamentals of Liquid Crystal Devices*, 2nd edition, Wiley-SID, New Jersey, p. 591 (2014), <http://cds.cern.ch/record/1953379?ln=en>.
- [40] C. V. Yelamaggad, G. Shanker, U. S. Hiremath and S. K. Prasad, Cholesterol-based nonsymmetric liquid crystal dimers: an overview, *Journal of Materials Chemistry* **18** (2008), 2927, DOI: 10.1039/B804579H.
- [41] P. Yen and C. Gu, *Optics of Liquid Crystal Displays*, 2nd edition, John Wiley & Sons, Canada, <https://www.wiley.com/en-us/Optics+of+Liquid+Crystal+Displays%2C+2nd+Edition-p-9780470181768>.
- [42] L. I. Yin, J. I. Trombka and S. M. Seltzer, A portable X-ray imaging system for small-format applications, *Nuclear Instruments and Methods* **158** (1979), 175, DOI: 10.1016/S0029-554X(79)91615-X.
- [43] L. I. Yin, J. I. Trombka and S. M. Seltzer, A small rugged imaging X-ray spectrometer: a lixiscope with good energy resolution, *Nuclear Instruments and Methods* **172** (1980), 471, DOI: 10.1016/0029-554X(80)90337-7.
- [44] A. Yoshizawa, Y. Takahashi, R. Terasawa, A. Nishizawa, K. Takeuchi, M. Sagisaaka, K. Takahashi, M. Hazawa and I. Kashiwakura, Biological activity of some cyanobiphenyl derivatives, *Chemistry Letters* **38** (2009), 530, DOI: 10.1246/cl.2009.530.