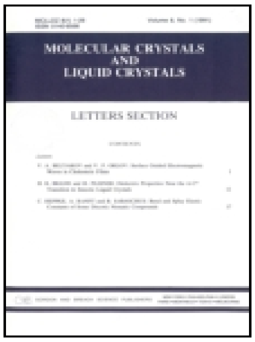

Molecular Crystals and Liquid Crystals

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Effect of Molecular Interactions and Homologue Number on UV Absorption Spectra of Liquid Crystalline Alkyl Cyanobiphenyl Dimers: DFT Calculations

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*The ultraviolet (UV) absorption spectra of the liquid crystalline dimer complexes of 4′-*n*-alkyl-4-cyanobiphenyls (*n*CB: *n = 3, 4, 5 *where* n *is the number of carbon atoms in the alkyl chain) have been presented. The* n*CB structures have been optimized using the density functional Becke3-Lee-Yang-Parr (B3LYP) hybrid functional with 6-31+G (d) basis set using the crystallographic geometry as input. The electronic structures of the dimer molecules have been computed using the optimized geometries. The spectra of the dimer molecules have been calculated by employing the density functional theory (DFT). The features of electronic transitions and excited states have been calculated via configuration interaction singles (CIS) with the semiempirical Hamiltonian Zerner intermediate neglect of differential overlap (ZINDO). The various modes of molecular interactions and the homologue number are found to be structural parameters affecting the formation of mesophases, UV absorption spectral characteristics, and photo stability of the compounds. These results offer a hint for the calculations involving the different modes of molecular interactions, and separations between dimers, to model photo stability or in tuning the absorbing chromophore to match the wavelength of desired application.*

Keywords Chromophore; computational techniques; dimers; liquid crystals

Introduction

Liquid crystals (LCs) are an enthralling set of soft condensed matter characterized by the counterintuitive combination of fluidity, and long-range order. They exhibit a plethora of unique and smart properties that offer tremendous potential for innovative applications well beyond the realm of displays [1]. The full breadth of the LCs is becoming increasingly recognized; numerous new, and exciting research problems are being opened up [2, 3].

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The interaction of light with different LC dimer complexes is of fundamental interest since their discovery in order to gain insight into its electronic structure, and to design new optical devices. LC dimers act as models for main group LC polymers that allow the study of flexibility, and properties of different mesogenic groups. Thus, LC dimers retain the crucial structural components of many thermotropic polymers. The physics in this area is quite rich, and it would be a very demanding chore to model the spectra of dimers. However, an indispensable prerequisite in order to describe absorption phenomena is the knowledge of electronic structure. Moreover, the use of nematic phases as model systems for the investigation of anisotropic intermolecular interactions is an important scientific application [4]. The molecular dimension (shape, and size) [5], conjugation length [6], separation between dimers [7], and packing density [8], make important contributions to the absorption spectral characteristics, and their interrelated parameters.

An understanding of the photophysics and chemistry of organic compounds requires the conception of molecular orbitals properties, spectra, and appropriate excited states. These spectroscopic and structural features are a big challenge to the interplay between theory, and experiment. Further, they have important implications for the substituent [9], molecular interactions effects [10], and spectroscopy of the materials. Moreover, their photochemistry and physics represent a challenge in understanding the excited states dynamics. The main difficulties against a reliable computational approach are related to the size of such systems, and the presence of strong electron correlation effects. Both properties are difficult to treat in the framework of the quantum mechanical methods rooted in the Hartree–Fock (HF) theory.

Many theoretical and experimental studies [11, 12] have demonstrated that in the solid state, intermolecular interactions can dramatically reduce the photo luminescence (PL) quantum yield. The PL intensity is directly proportional to their absorption. Further, the properties of molecular orbitals provide quantitative estimates of important parameters governing the transport properties. In view of this, it is in high demand to understand the UV absorption spectral characteristics, and the effects of intermolecular interactions. The absorption wavelength of a photoactive molecule is affected by the photon absorbing chromophore as well as interaction between the molecules, which cause red/blue-shifts. These spectral shifts are attributed to the different modes of molecular interactions, and substituent effects. Although, active-site models work reasonably well for many molecular systems [13, 14], their calculations overlook the interactions between the molecules that may be important for the exact estimation of absorption spectra of dimer models. Hence these interactions must be taken into consideration even, if chromophore and/or solvent are not involved in the system and/or calculation.

Therefore, the present study has been aimed to employ the density functional theory (DFT) method to calculate the optimal dimer geometries. Convolution of absorption spectra has been performed for dimer geometries using the time dependent DFT (TDDFT) theory [15] coupled with CIS method [16] based on the semiempirical ZINDO [17–19] Hamiltonian for excited states calculation. In the present work, an attempt has been made to investigate the effect of molecular interactions (stacking, in-plane, and terminal arrangements), and homologue number on the spectra. The UV absorption and photo stability of the dimer complexes have been explored based on these factors. The Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital energies (LUMO), vertical transition energy (E_V), and oscillator strength (f) have also been reported. An effort has been made to find out the most energetically favorable configuration in each mode of interaction.

Method and Calculations

In the present analysis, DFT calculations on UV absorption spectra of *n*CB ($n = 3$, 4, 5) dimer complexes during the stacking, in-plane, and terminal interactions have been reported. The DFT is successful to evaluate a variety of ground-state properties with accuracy close to the post-HF methods. An important factor that determines the accuracy of TDDFT excitation energies is the exchange correlation functional used in the calculation. The use of these hybrid functionals yields good accounts of the vertical excitation energies of the excited states with substantial charge transfer character. In this context, remarkable structural predictions have been obtained especially, using the "hybrid" density functionals [20] such as B3LYP [21] combining "exact exchange" with gradient-corrected density functionals. As a consequence, there is currently a great interest in extending DFT to excited electronic states. The TDDFT approach offers a rigorous route to the calculation of vertical electronic excitation energies, and other spectral characteristics.

The simple CIS approach is accurate in certain cases, in particular for so-called charge transfer transitions. In the CIS approach, orbitals of the Hartree-Fock solution have been used to generate all singly excited determinants of the configuration interaction (CI) expansion. This treatment can be thought as the Hartree-Fock method for excited states. It allows one to simultaneously solve for a large number of excited states, and to optimize the geometry of any desired state. The ground state of molecules near to their equilibrium geometry is well described by a single reference. However, some of the exited states in many important chromophores (such as benzene) have a significant multi-reference character. The CIS method, being an analog to the Hartree-Fock method for the excited states, does not include any electron correlation. This would not be a problem, if the ground and excited state were stabilized by electron correlation with the same degree. The obvious solution is to describe the electron correlation (both in the ground, and excited states) but a care must be taken to provide a balanced description for all the states.

The present molecular models comprise of *n*CB ($n = 3$, 4, 5) dimer complexes during the stacking, in-plane, and terminal interactions. The geometries optimizations have been performed using the DFT approach [15], in particular the Becke3-Lee-Yang-Parr hybrid functional (B3LYP) exchange-correlation functional, and the 6-31G+(d) basis set. The DFT approach was originally developed by Hohenberg and Kohn [22], Kohn and Sham [23, 24] to provide an efficient method of handling the many-electron system. The theory allows us to reduce the problem of an interacting many-electron system to an effective single-electron problem. On the basis of the DFT geometries, the electronic structures, excitation energies, and excited state wave functions have been calculated coupled with the CI single level of approximation including all $\pi \rightarrow \pi^*$ single excitations. This has been found adequate to determine the UV-Vis absorption spectra provided that the suitable parameterizations are used. The DFT calculations have been performed by a spectroscopy oriented configuration interaction procedure (SORCI) [25].

The general structural parameters of the systems such as bond lengths and bond angles have been taken from the published crystallographic data [26–28] to construct the electronic structures. Calculation of absorption spectra for pair of *n*CB molecules have been carried out during stacking, in-plane, and terminal interactions. An intermediate distance of 6 Å for stacking, 8 Å for in-plane, and 22 Å for terminal interactions have been maintained through out the calculation. The choice of distance has been made to eliminate the possibility of van der Waals contacts completely, and to keep the molecule within the short- and medium-range interactions. The most energetically favorable configuration in each mode of interaction has been reported.

Results and Discussion

The electronic structures of *n*CB ($n = 3$–5) dimers during stacking, in-plane and terminal interactions have been shown in Figs. 1–3. The detailed UV absorption spectra of *n*CB ($n = 3, 4, 5$) dimers during the three modes of interactions have been given later:

UV Absorption Spectrum

Since the most of LC compounds contain an extended conjugated aromatic moiety, UV-Vis absorption measurements, and calculation of absorption spectral shifts are considered to be crucial, which influences the desired electronic or optical properties in the bulk LC phases of materials. Usually, this is monitored by UV-Vis spectroscopy at the absorption maxima, which demand a destructive read-out of molecular systems. Hence, it is necessary to identify the molecular structures that can withstand a longer UV exposure. Further, it is expected that the absorption spectrum of a LC molecule containing a single phenyl ring would exhibit similarities to an isolate benzene molecule. The principal absorption bands in the molecules are due to the $\pi \rightarrow \pi^*$ transitions in the benzene analogous part of the molecule. In general, these benzene-like transitions are roughly conserved in the systems studied, but they are influenced by the conjugation length, degree of conjugation, and the different substituents. The present calculations have been carried out on dimer complexes of *n*CB ($n = 3, 4, 5$) molecules to study their ultraviolet absorption, photo stability in the light of the spectral shifts with respect to the homologue number, and different modes of molecular interactions. In view of these practical difficulties, and the increasing enforce to predict the properties of unsynthesised molecular materials; it is evidently of considerable importance to develop computational methods for the calculation of absorption spectral characteristics.

4′-n-Propyl-4-Cyanobiphenyl (3CB) Dimers

The ultraviolet absorption spectrum of 3CB stacked dimers has been shown in Fig. 4. In the UV region, stacked dimer exhibits four-peak absorption structure. The strong absorptions have been observed at 211.72 nm (λ_1), 227.54 nm (λ_2), 246.88 nm (λ_3), and 282.03 nm (λ_4). However, no absorption has been observed in the visible region. The strongest band appears in a region of 202.34 nm to 221.68 nm with absorption maximum ($\lambda_{\max}$) at 211.72 nm (λ_1). This band arises from the HOMO → LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the dimer molecule. The oscillator strength (f) values corresponding to four wavelengths are 0.34, 0.52, 0.33, and 0.29, respectively. The band situated at the higher wavelength is more intense than the lower wavelength. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak absorption bands at the remaining wavelengths (λ_2, λ_3, and λ_4).

Further, the UV spectra of 3CB dimers during in-plane, and terminal interactions have also been shown in Fig. 4. The absorption maximum ($\lambda_{\max}$) has been observed at 212.30 nm during the both modes of interactions. The corresponding oscillator strength values are 0.24 (in-plane), and 0.17 (terminal), respectively. The band corresponding to absorption maximum arises from the HOMO → LUMO transition, and is assigned as

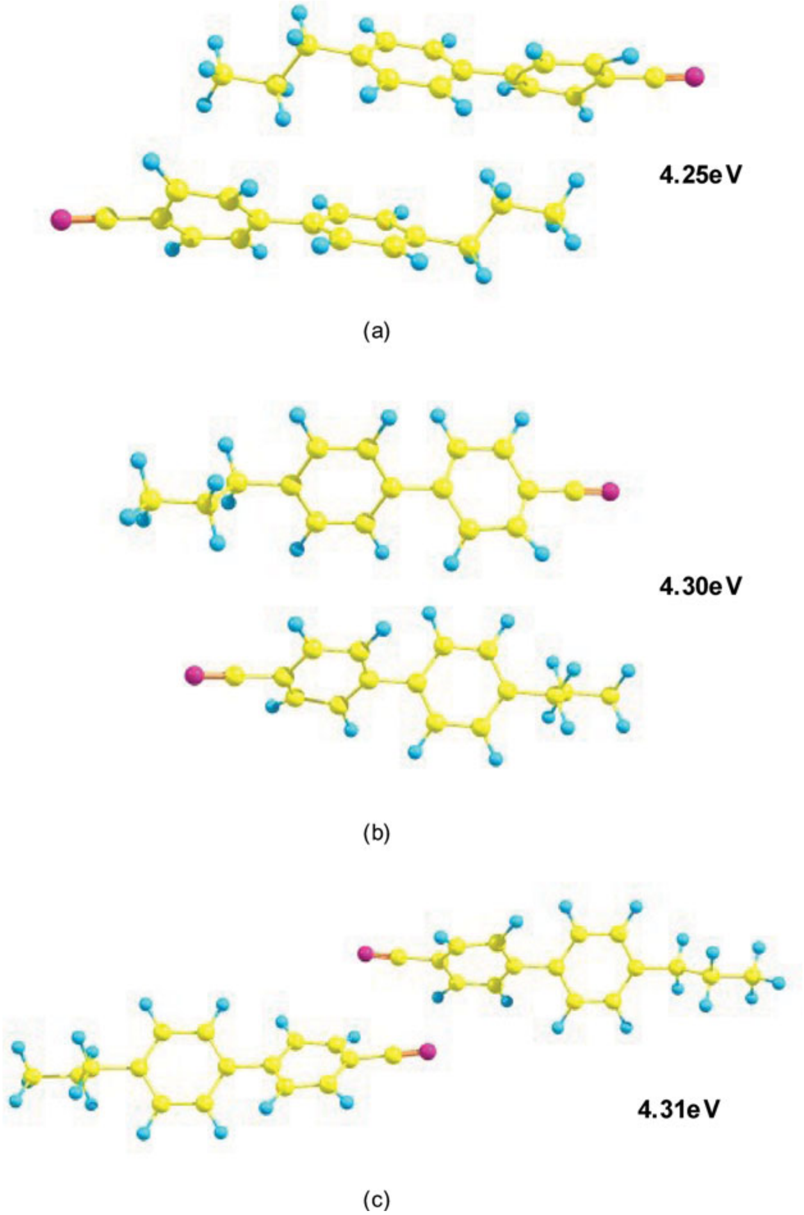

Figure 1. The electronic structures of 3CB dimer molecules during (a) stacking, (b) in-plane, and (c) terminal interactions.

$\pi \rightarrow \pi^*$ transition in the dimer molecule. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak absorption bands at the remaining wavelengths (λ_2, λ_3, and λ_4) during the both modes of interactions. The details of absorption bands, extinction coefficients, oscillator strength, vertical transition energy, HOMO, and LUMO energies during the stacking, in-plane, and terminal modes of interactions for 3CB dimers have been summarized in Table 1.

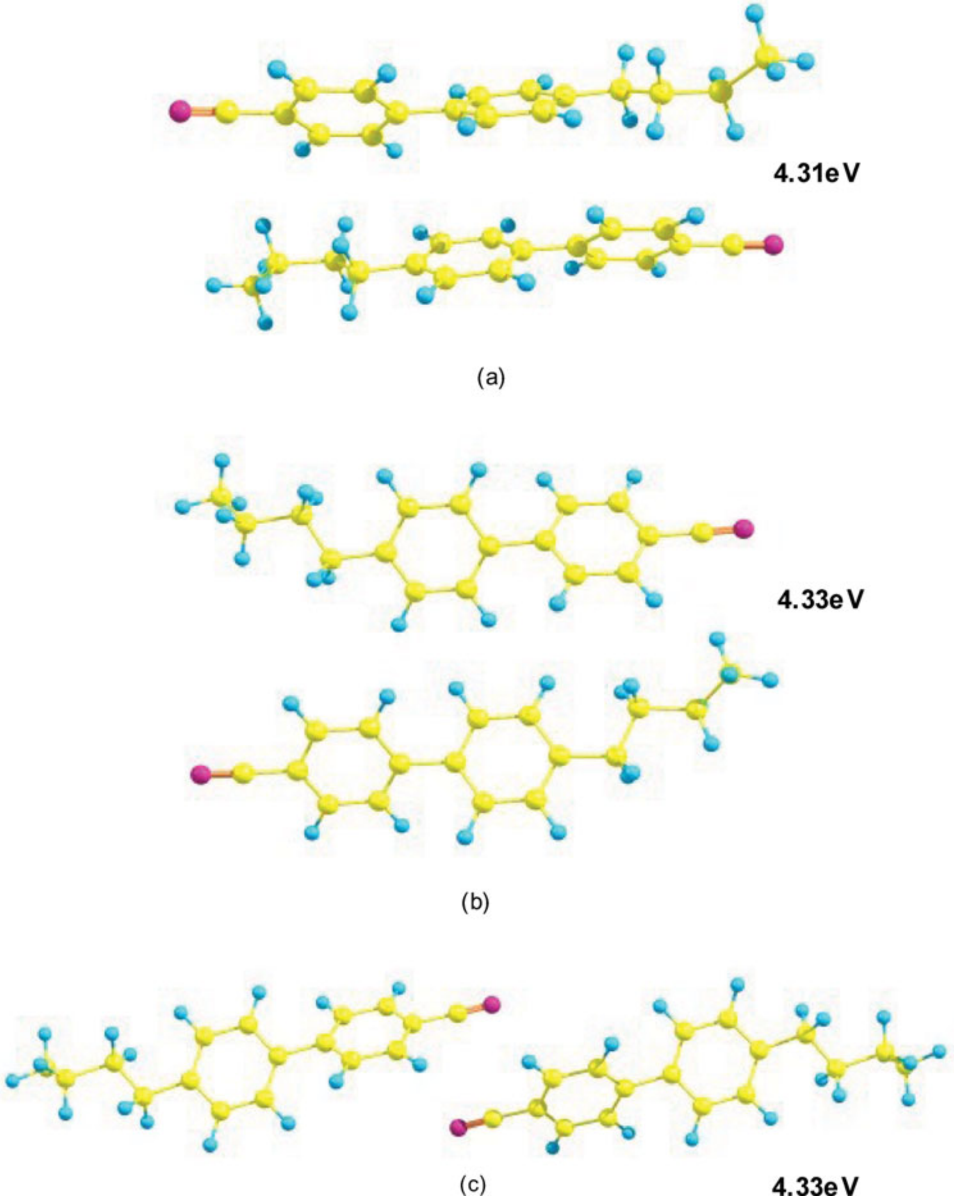

Figure 2. The electronic structures of 4CB dimer molecules during (a) stacking, (b) in-plane, and (c) terminal interactions.

4′-n-Butyl-4-Cyanobiphenyl (4CB) Dimers

The ultraviolet absorption spectrum of 4CB stacked dimers has been shown in Fig. 5. In the UV region, the stacked dimer exhibits two-peak absorption structure. The strong absorptions have been observed at 223.44 nm (λ_1) with a shoulder at 214.65 nm, and 279.69 nm (λ_2). However, no absorption has been observed in the visible region. The strongest band appears in a region of 217.58 nm to 236.33 nm with absorption maximum

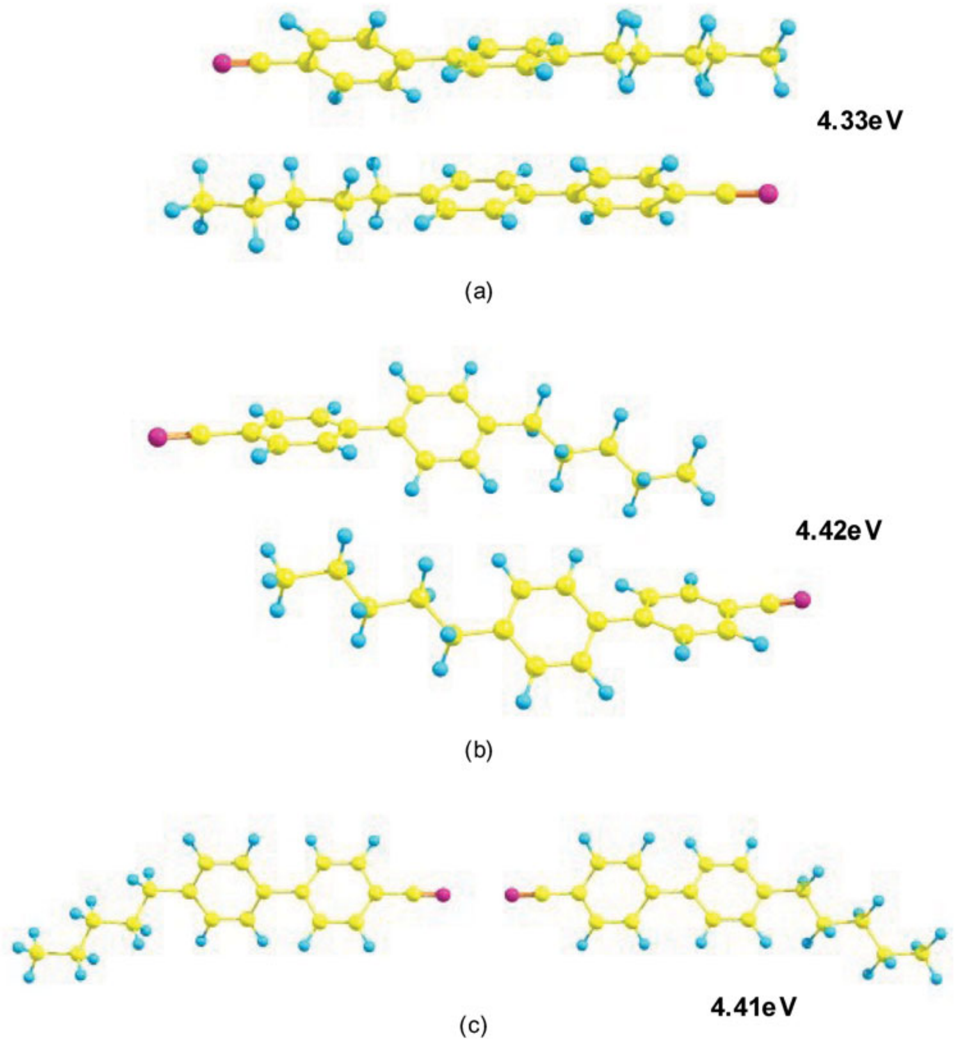

Figure 3. The electronic structures of 5CB dimer molecules during (a) stacking, (b) in-plane, and (c) terminal interactions.

($\lambda_{\max}$) at 223.44 nm (λ_1). This band arises from the HOMO → LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the dimer molecule. The oscillator strength (f) values corresponding to two wavelengths are 1.24, and 0.94, respectively. The band situated at the higher wavelength is more intense than the band situated at the lower wavelength. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak absorption bands at the other wavelength λ_2.

Further, the UV spectra of 4CB dimers during in-plane, and terminal interactions have also been shown in Fig. 5. The absorption maxima ($\lambda_{\max}$) have been observed at 221.09 nm (in-plane), and 223.44 nm (terminal). The corresponding oscillator strength values are 1.05, and 0.95, respectively. The band corresponding to absorption maxima arises from the HOMO → LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the dimer molecule. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak

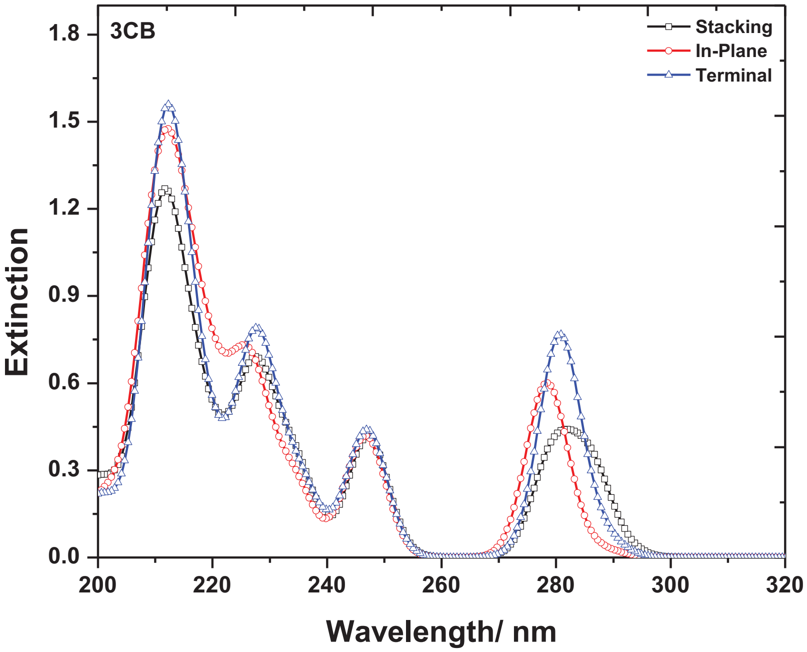

Figure 4. UV absorption spectra of 3CB molecule during stacking, in-plane, and terminal interactions.

Table 1. The absorption bands (AB), extinction coefficients (EC), Oscillator strength (f), Vertical transition energy (E_V), HOMO (H), LUMO (L) energies, and the band gap ($E_g = E_{LUMO} - E_{HOMO}$) of 3CB dimers during stacking, in-plane, and terminal interactions using DFT method

Molecule	Mode of interaction	AB (nm)	EC*	f	E_V (eV)
3CB	Stacking	**211.72**	1.27	0.34	5.86
		227.54	0.69	0.52	5.45
		246.88	0.41	0.33	5.02
		282.03	0.44	0.29	4.34
		$H = -8.40$	$L = -0.35$	$E_g = 8.05$	
	In-Plane	**212.30**	1.47	0.24	5.83
		225.78	0.73	0.60	5.48
		246.88	0.42	0.31	5.03
		278.52	0.60	0.53	4.46
		$H = -8.42$	$L = -0.28$	$E_g = 8.14$	
	Terminal	**212.30**	1.56	0.17	5.84
		227.54	0.79	0.73	5.45
		246.88	0.44	0.38	5.02
		280.86	0.77	0.70	4.41
		$H = -8.17$	$L = -0.04$	$E_g = 8.13$	

Bold value represents λ_{max} (nm).
*EC unit: 10^4 dm^{3}mol^{-1}cm^{-1}.

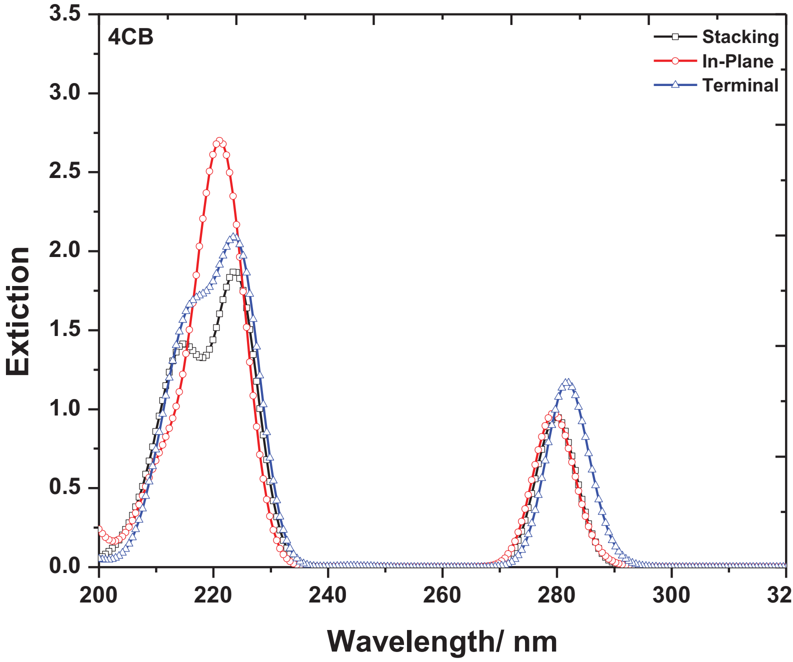

Figure 5. UV absorption spectra of 4CB molecule during stacking, in-plane, and terminal interactions.

absorption bands at the other wavelength λ_2 during the both modes of interactions. The details of absorption bands, extinction coefficients, oscillator strength, vertical transition energy, HOMO, and LUMO energies during the stacking, in-plane, and terminal modes of interactions for 4CB dimers have been summarized in Table 2.

Table 2. The absorption bands (AB), extinction coefficients (EC), Oscillator strength (f), Vertical transition energy (E_V), HOMO (H), LUMO (L) energies, and the band gap ($E_g = E_{LUMO} - E_{HOMO}$) of 4CB dimers during stacking, in-plane, and terminal interactions using DFT method

Molecule	Mode of interaction	AB (nm)	EC*	F	E_V (eV)
4CB	Stacking	**223.44**	1.87	1.24	5.55
		279.69	0.95	0.94	4.43
		$H = -8.40$	$L = -0.47$	$E_g = 7.93$	
	In-Plane	**221.09**	2.70	1.05	5.59
		279.69	0.97	0.95	4.44
		$H = -8.49$	$L = -0.44$	$E_g = 8.05$	
	Terminal	**223.44**	2.09	0.34	5.56
		282.03	1.16	0.01	4.38
		$H = -8.21$	$L = -0.19$	$E_g = 8.02$	

Bold value represents λ_{max} (nm).
*EC unit: 10^4 dm^{3}mol^{-1}cm^{-1}.

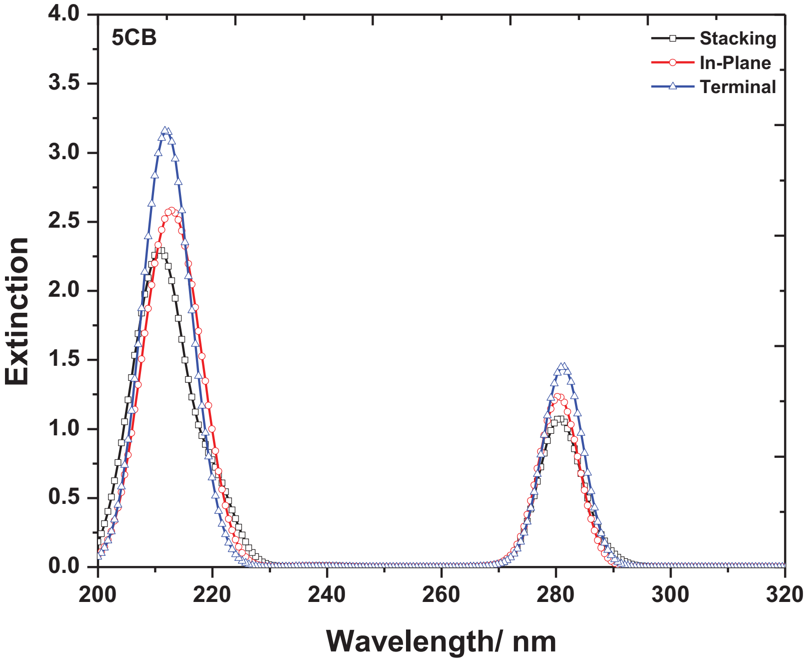

Figure 6. UV absorption spectra of 5CB molecule during stacking, in-plane, and terminal interactions.

4′-n-Pentyl-4-Cyanobiphenyl (5CB) Dimers

The ultraviolet absorption spectrum of 5CB stacked dimers has been shown in Fig. 6. In the UV region, stacked dimer exhibits two-peak absorption structure. The strong absorptions have been observed at 210.55 nm (λ_1), and 280.86 nm (λ_2). However, no absorption has been observed in the visible region. The strongest band appears in a region of 200 nm to 230.47 nm with absorption maximum (λ_{max}) at 210.55 nm (λ_1). This band arises from the HOMO → LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the dimer molecule. The oscillator strength (f) values corresponding to two wavelengths are 1.01, and 1.01, respectively. The band situated at the higher wavelength is more intense than the lower wavelength. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak absorption bands at the other wavelength λ_2.

Further, the UV spectra of 5CB dimers during the in-plane, and terminal interactions have also been shown in Fig. 6. The absorption maxima (λ_{max}) have been observed at 212.89 nm (in-plane), and 211.72 nm (terminal). The in-plane dimer does not exhibit any oscillator strength corresponding to λ_{max}, while terminal dimer exhibits a value of 0.02. The band corresponding to absorption maxima arises from the HOMO → LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the dimer molecule. Further, the calculation also predicts $\pi \rightarrow \pi^*$ transitions corresponding to weak absorption bands at the other wavelength λ_2 during the both modes of interactions. The details of absorption bands, extinction coefficients, oscillator strength, vertical transition energy, HOMO, and LUMO energies during stacking, in-plane, and terminal modes of interactions for 5CB dimers have been summarized in Table 3.

Table 3. The absorption bands (AB), extinction coefficients (EC), Oscillator strength (*f*), Vertical transition energy (E_V), HOMO (*H*), LUMO (*L*) energies, and the band gap ($E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) of 5CB dimers during stacking, in-plane, and terminal interactions using DFT method

Molecule	Mode of interaction	AB (nm)	EC*	*F*	E_V (eV)
5CB	Stacking	**210.55**	2.29	1.01	5.86
		280.86	1.07	1.01	4.42
		$H = -8.48$	$L = -0.58$	$E_g = 7.90$	
	In-Plane	**212.89**	2.58	0.00	5.82
		280.27	1.23	0.02	4.42
		$H = -8.53$	$L = -0.51$	$E_g = 8.02$	
	Terminal	**211.72**	3.16	1.27	5.87
		281.45	1.45	1.45	4.41
		$H = -8.29$	$L = -0.23$	$E_g = 8.06$	

Bold value represents $\lambda_{\max}$ (nm).
*EC unit: 10^4 dm^3 mol^{-1} cm^{-1}.

Effect of Molecular Interactions

Although many works on LC absorption spectroscopy (AS) have been documented [29,30], little is known about their self-aggregation, and effect of molecular interactions. The forces lead to molecular aggregation is known as non-covalent, which consist of the dipole orientation force, the induction force, and the dispersion force. Non-covalent interactions play a special role in photo-physics, and chemistry. The AS of dimer complexes (two identical molecules in non-covalent interaction) addresses the effect of molecular interactions, and to understand the self-aggregation/phase behavior based on the dimer structures. The system implemented has been mainly developed to address the different modes of molecular interactions in aromatic chromophores, and the dimer complexes in a detailed way. The most energetically stable configurations of *n*CB ($n = 3, 4, 5$) molecules during the different modes of interactions have been reported in Figs. 1–3, respectively. The spectral data of 3CB, dimers shows that the stacked dimer exhibits absorption maximum ($\lambda_{\max}$) at 211.72 nm (Table 1), whereas, in-plane, and terminal dimers exhibits $\lambda_{\max}$ at 212.30 nm (Table 1). In this way, a red-shift (the shift of $\lambda_{\max}$ to a longer wavelength, i.e. bathochromic) has been observed. This is due to the decrement in transition energies (Table 1), on excitation of the electron, which makes the band to interact more electrostatically, leads to a change in charge distribution, and an increased delocalization of electrons. This indicates a weak exciton coupling of chromophores. Thus, both the ground, and excited $n \rightarrow \pi^*$ transition does not occur due to the lack of rigidity in the ring system of the molecules. This ultimately, affects the other spectral data. Further, a hyperchromic effect (increment in absorbance) has been observed during in-plane, and terminal interactions. Further, a comparison of 5CB stacked, and in-plane dimers also show a red-shift, with the hyperchromic effect (Table 3).

The comparison of $\lambda_{\max}$ for 4CB stacked and in-plane dimers indicates the blue-shift (Table 2). The face-to-face orientation of molecular rings during the stacking interactions produces larger attractive dispersion energy [31]. This is considered to be a prime factor responsible in getting the absorption maxima at longer wavelength region for stacked dimers.

Further, due to the larger attractive dispersion energy, the electron requires larger vertical transition energy in the excitation process. This causes high transition energies for 3CB, and 5CB stacked dimers (Tables 1 and 3). This causes an increment in extinction coefficient of dimers during the in-plane interactions. It is evident from the comparison of transition energies, and extinction coefficients (except for 4CB stacked dimers) corresponding to $\lambda_{\max}$ during the both modes of interactions for all the dimer molecules (Tables 1–3). The same trend of increment in the oscillator strength has been observed for all the in-plane dimer molecules (except for 4CB stacked dimers). Thus, in-plane, and terminal dimers exhibit high extinction coefficients compared to stacked dimers. In view of this, their electronic absorption only may slightly increase (Figs. 4–6 and Tables 1–3).

The mutual orientation of aromatic rings represents the key factor, which modifies the electron π-conjugation. This evaluation represents a critical test, since the correct description of molecular interactions is essential for the subsequent analysis of spectral shifts/characteristics. In case of 3CB dimers, the in-plane, and terminal dimers exhibit absorption maxima at the longer wavelength region compared to stacked dimers. Hence the photo stability is high for the in-plane, and terminal dimers. Further, the extinction coefficients are also high for in-plane, and terminal dimers. Hence they are much flexible for absorption phenomena. The comparison of 4CB dimers reveals that the photo stability is high for stacked and terminal dimers. In the same way, 5CB in-plane dimers exhibits high photo stability as they exhibits absorption maximum at longer wavelength. These results may be exploited for the possible applications.

The conformational behavior of LCs displays a large variation in intermolecular effects, and depends on the nature and magnitude of interactions. Each conformation may have distinct energy, and lower energy conformations will be populated in preference to those of higher. The comparison of stacked dimers between the molecules suggests that the extension of the chain length causes a recognizable segregation of the dimers into a perfect layer structure with strong parallel orientation. Mutual interaction between the dimers in this structure is, however, quite strong, in particular to chain atoms. Moreover, the comparison of planar dimers indicates highly tilted structures with respect to extension of chain length, which favors translational motion in a molecular pair along planar axis. Further, the mutual interactions in these structures are quite weak. Hence, the end chains provide enough disorder in the crystal structure to pass on to nematic phase. Since, the tiltedness of the planar dimers increases with the extension of chain length, molecules will attain sufficient flexibility to move along their planar axis. Hence, the phase stability is expected to be high with extension of chain length.

Effect of Homologue Number

In 3CB molecule, the substitution of additional alkyl group (forming 4CB) leads to a bathochromic shift. Further, increment in the alkyl chain length causes a hyperchromic effect (increment in absorbance). However, a comparison of 3CB, 5CB, and 4CB, 5CB molecules reveals a blue-shift. The 5CB dimers exhibits a more planar structure compared to lower homologue dimers. Since, the dimer molecules are exhibiting a planar structure (Figs. 1–3) owing to the extensive conjugation throughout the molecules; it is possible to stack them on top of each other [32]. Hence the tendency for the planarization of molecule is responsible for the conformational stiffness (rigidity), and hence the 5CB dimers exhibit a larger vertical transition energy compared to 4CB dimers (Tables 2 and 3). The strongest absorption band for all the dimer molecules during the three modes of interactions have been found almost in the same range of wavelength (Stacking: 3CB:

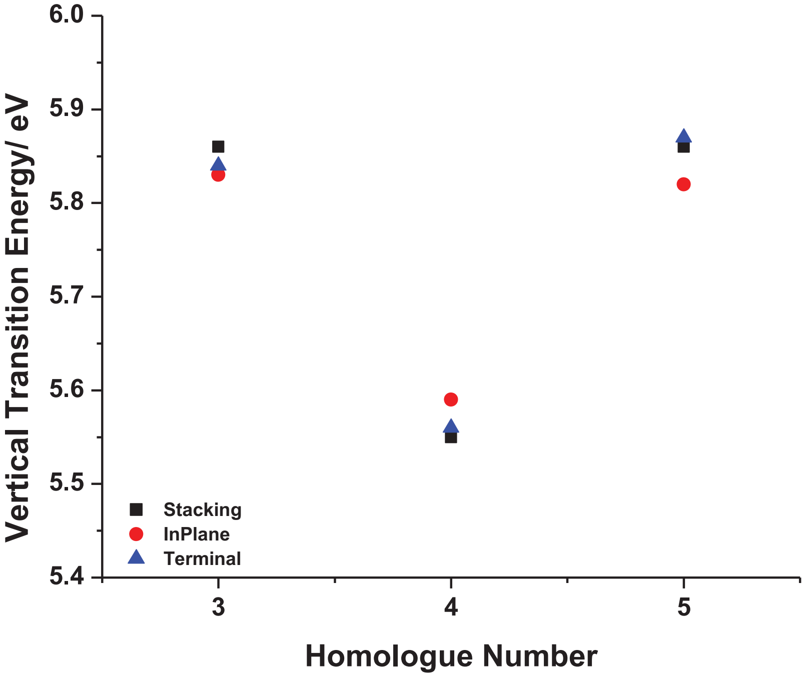

Figure 7. Transition energy of *n*CB ($n = 3, 4, 5$) dimers as a function of homologue number during stacking, in-plane, and terminal interactions.

202.34 nm–221.68 nm; 4CB: 217.58 nm–236.33 nm; 5CB: 200 nm–230.47 nm and In-Plane: 3CB: 200 nm–222.27 nm; 4CB: 202.93 nm–235.16 nm; 5CB: 200 nm–228.12 nm and Terminal: 3CB: 202.34 nm–221.68 nm; 4CB: 202.14 nm–236.35 nm; 5CB: 200 nm–226.37 nm). This indicates the identical absorption spectrum for all the molecules in UV region due to the similar π-electron structure [33].

In order to understand the effect of end chain length more closely, a graphical representation of homologue number with transition energy of *n*CB dimers during the stacking, in-plane, terminal modes of interactions has been shown in Fig. 7. Evidently, all three modes of interactions show a good agreement in exhibiting the transition energy values with increment of homologue number. It may be understood from the above graph that calculated vertical excitation energies are relatively sensitive to the mode of interaction, and the homologue number. Further, each mode of interaction also shows good agreement in exhibiting the shift of absorption wavelength, and oscillator strength values with increment in homologue number (Tables 1–3). The tendency of increment/decrement of these parameters with respect to homologue number is the same during the three modes of interactions. It may be concluded from the above discussion that all the dimer molecules exhibits excitation energies in a same range, and the increment in homologue number does not affect the range of the energy values. Further, it is important to note here that in spite of the spread of transition energies, the relative energies between lowest to highest transitions show more consistency among the individual methods. A comparison of individual dimers during the stacking, in-plane, and terminal dimers suggests an absorption maximum at longer wavelength for 4CB, indicating its high photo stability.

HOMO-LUMO Analysis

The HOMO, LUMO energies, energy gap, and excitation energies have an effect on the stability of a molecule. The energy gap between the HOMO, and LUMO is an important parameter in determining the molecular electrical transport proprieties, and photo stability. It is also a critical parameter in determining the molecular electrical transport proprieties as it is a measure of electron conductivity. The HOMO, LUMO energy, and the energy gap (E_g) values of nCB ($n = 3, 4, 5$) molecules during the three modes of interactions have been reported in Tables 1–3, respectively. The comparative results of individual stacked dimers reveal that the 5CB dimers exhibit a lower band gap; hence its conductivity is high in comparison with the 3CB, and 4CB dimers. Further, the same result has been noticed from the comparison of in-plane, and terminal dimers. The increment in homologue number suggests a decrement in energy gap values. Lower value of the energy gap determines the eventual charge transfer interactions taking place within the dimer molecule.

Conclusions

The salient features of the present work are:

1. The ultraviolet absorption spectra of dimer molecules of 4′-n-alkyl-4-cyanobiphenyls (nCB: $n = 3, 4, 5$) during the stacking, in-plane, and terminal modes have been studied. All the dimer molecules exhibits $\pi \rightarrow \pi^*$ transitions in the UV region.
2. The molecular interactions have a dominant role on spectral shifts/characteristics of all the molecules. In case of 3CB dimers, the in-plane, and terminal dimers exhibit absorption maxima at the longer wavelength region compared to stacked dimers. Hence the photo stability is high for the in-plane, and terminal dimers. Further, the extinction coefficients are also high for in-plane, and terminal dimers. Hence they are much flexible for absorption phenomena. The comparison of 4CB dimers reveals that the photo stability is high for stacked and terminal dimers. In the same way, 5CB in-plane dimers exhibits high photo stability as they exhibits absorption maximum at longer wavelength.
3. The comparison of stacked dimers between the molecules suggests that the extension of the chain length causes a recognizable segregation of the dimers into a perfect layer structure with strong parallel orientation. Moreover, the comparison of planar dimers indicates highly tilted structures with respect to extension of chain length, which favors translational motion in a molecular pair along planar axis. Further, the mutual interactions in these structures are quite weak. Hence, the end chains provide enough disorder in the crystal structure to pass on to nematic phase.
4. The strongest absorption band for all the dimer molecules during the three modes of interactions have been found almost in the same range of wavelength. This indicates the identical absorption spectrum for all the molecules in UV region due to the similar π-electron structure.
5. The spontaneous interaction of UV light with LC molecules, molecular interactions, and effect of homologue number are reasonably useful to predict their response on the material system for nonlinear optical property. The present article provides a new and interesting way to address this problem.

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