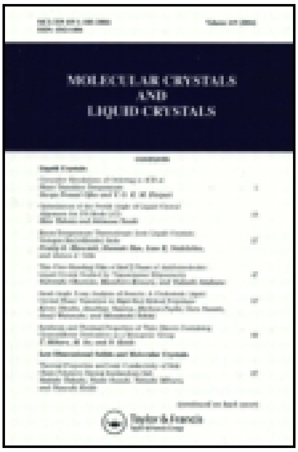

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electronic Transition Oscillator Strength and UV Stability of Nematogenic Cyanobiphenyls—Role of Alkyl Chains

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To cite this article: P. Lakshmi Praveen & Durga P. Ojha (2011): Electronic Transition Oscillator Strength and UV Stability of Nematogenic Cyanobiphenyls—Role of Alkyl Chains, Molecular Crystals and Liquid Crystals, 548:1, 209-219

To link to this article: http://dx.doi.org/10.1080/15421406.2011.591669

Mol. Cryst. Liq. Cryst., Vol. 548: pp. 209–219, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.591669

Electronic Transition Oscillator Strength and UV Stability of Nematogenic Cyanobiphenyls—Role of Alkyl Chains

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The electronic transitions in the ultraviolet (UV)/visible (VIS) range of nematogenic 4′-n-alkyl-4-cyanobiphenyl (nCB) with butyl (4CB) and hexyl (6CB) groups have been studied. The UV/VIS and circular dichroism (CD) spectra of nCB (n = 4, 6) molecules have been simulated using the TDDFT/B3LYP/6-31+G (d) method. Mulliken atomic charges for each molecule have been compared with Loewdin atomic charges to analyze the molecular charge distribution and phase stability. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies corresponding to the electronic transitions in the UV/VIS range have been reported. Excited states have been calculated via CI-singles (CIS) with semiempirical Hamiltonian ZINDO. Furthermore, two types of calculations have been performed for model systems containing single and double molecules of nCB. The dimer complexes during the different modes of molecular interactions have also been taken into consideration in order to investigate the most energetically stable configuration. These computations provide valuable information regarding the role and flexibility of end chains in a particular phase behavior and UV stability.

Keywords Charge distribution; oscillator strength; ultraviolet (UV) stability

Introduction

Liquid crystals (LCs) have the ability to self-organize into highly anisotropic and ordered structures. The mutual competition between this ability with suitable optical and electronic properties results in model building blocks for smart materials in optoelectronic devices. Apart from its mainstream applications, the unique properties of LCs also led to the advance of many other optical components such as light valves, tunable filters, and lenses [1,2]. However, the influential role played by the intermolecular interactions [3,4] is accountable for self-organization, which can also have a dramatic control on the electrical and photophysical properties of molecules. A systematic understanding of the types of intermolecular interactions and their physical effects is, therefore, looked-for in the rational design of novel materials for a range of applications. Understanding of the interaction of light with LC molecules [5] is of fundamental interest not only to gain insight into the electronic structure but also to help us in designing new optical devices. Hence, it is much

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*Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada 520 008, Andhra Pradesh, India. E-mail: durga_ojha@hotmail.com more interesting, if rather complicated, to model the optical properties. In comparison with the advances in experiments, theoretical developments have been relatively lagging behind in attaining this object.

Material/phase stability [6] is a primary concern for all devices desired to have a long operational lifetime. In direct-view displays, ultraviolet (UV) light is often used. The UV light causes a gradual degradation of the LC molecules so that the consequent electro-optic effects are altered. Therefore, it is critical to identify the ultimate LC material failure mechanism and search for molecular structures that can withstand a longer UV exposure. The most common nematic LC structure for displays consists of an alkyl chain, one or two cyclohexane rings, a phenyl ring, and a polar group. The aromatic ring system not only imparts structural anisotropy but also plays a central role in determining the electrical, magnetic, and optical properties of the bulk materials. For the active matrix LC display (LCD) applications, fluoro is the preferred polar group, as it exhibits a high resistivity, low viscosity, and low birefringence [7,8]. However, both cyano (CN) [9] and isothiocyanate (NCS) [10] are the popular preferences for use in most passive matrix LCD, as they exhibit a large dipole moment to the normally weakly polar or nonpolar core, and give excellent chemical stability, and contribute to the display and photonic applications.

The simulation of UV-visible spectra by computational chemistry tools is particularly appealing since contemporary approaches are proficient to provide results with accuracy comparable to that obtained by experiments. Of particular importance in this sense, methods based on time-dependent density functional theory (TD-DFT) provide very accurate results [11,12]. Such approaches allow for the calculation of electronic transitions between the ground state and the different excited states, which gives the energies of the corresponding radiations. Each transition can be enlarged with a Gaussian shape due to several factors such as thermal excitement, natural line width, etc.

The objective of this theoretical evaluation is to provide an insight into the key electronic quantities and optical properties of nematogenic 4′-*n*-alkyl-4-cyanobiphenyl (*n*CB) molecules with butyl (4CB) and hexyl (6CB) groups. The variations in the spectral characteristics and other optical properties with respect to homolog number have been taken as a prime concern. The molecules show strong absorptions in the UV range only and that are very sensitive to the changes in the alkyl chain length. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies have also been reported for all single molecules and dimer complexes during the different modes of molecular interactions. An attempt has been made to find out the most energetically stable configuration in each mode of interaction. Furthermore, the role of alkyl chains has been analyzed in altering the electronic and optical properties of the systems. An examination of thermodynamic data has revealed that the 4CB molecule exhibits a nematic-isotropic transition temperature at 289.5K [13], and 6CB exhibits at 302.2K [14].

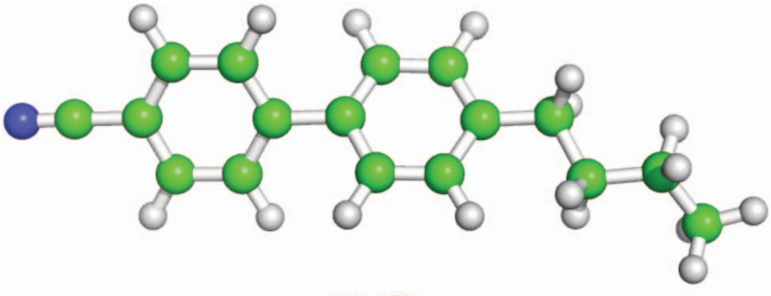
Methodology

The studied model comprised the monomer and dimer assemblies of 4′-*n*-alkyl-4-cyanobiphenyl (*n*CB, $n = 4, 6$). Geometry optimizations have been performed using DFT approach [11] using 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 [15] and Kohn and Sham [16,17] to provide an efficient method of handling many-electron systems. 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 and excited states have been calculated at a semiempirical Hartree–Fock level with the ZINDO/S method [18,19] (intermediate neglect of differential overlap method, as parameterized by Zerner and coworkers) coupled with the configuration interaction (CI) single level of approximation including all $\pi \rightarrow \pi^*$ single excitations. This has been found adequate to determine the UV-VIS absorption spectra and circular dichroism (CD) spectra.

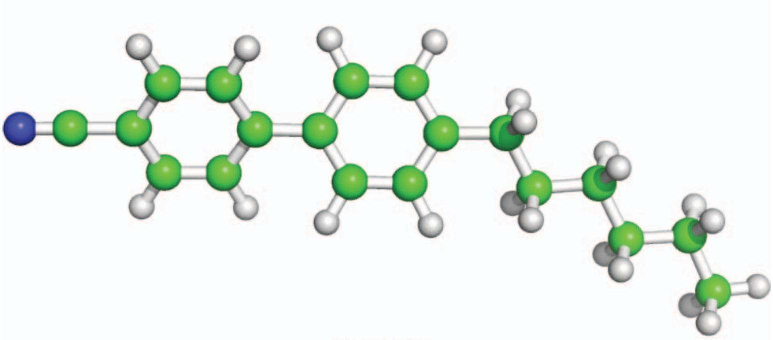
Common structural parameters of the systems such as bond lengths and bond angles have been taken from published crystallographic data [13,20]. Charge distributions of the molecules have been calculated by performing Mulliken population and Loewdin population analyses. The behavior and the nematic phase stability have been predicted through the calculated local charge distributions. On the basis of the optimal geometry obtained for each molecule, a systematic examination of interactions between a pair of isolated molecules has been carried out. The absorption maxima, HOMO, and LUMO orbitals have been analyzed to describe the electronic properties of the systems.

Results and Discussion

The geometric structures of *n*CB ($n = 4, 6$) have been shown in Fig. 1. The structures have been constructed based on the published crystallographic data with the standard values of bond lengths and bond angles [13,20]. Mulliken and Loewdin atomic net charges have been calculated and the group charges of the molecules using both methods have been reported



(a) 4CB



(b) 6CB

Figure 1. The geometric structures of (a) 4CB and (b) 6CB molecules.

Table 1. Mulliken (M) and Loewdin (L) group charges and nematic-isotropic transition temperatures for *n*CB ($n = 4, 6$) molecules

	Core		Cyano		Alkyl		
Molecule	M	L	M	L	M	L	T/K
4CB	0.341	0.112	−0.182	−0.171	−0.159	0.059	289.5 [13]
6CB	−0.237	0.046	−0.184	−0.172	0.421	0.126	302.2 [14]

in Table 1. The molecular charge distribution and phase stability of the molecules have been analyzed in the following sections.

Molecular Charge Distribution and Phase Stability

It is expected that the specific charge distributions and electrostatic interactions in mesomorphic molecules play an influential role in the configuration of various mesophases. An appropriate modeling of this fundamental molecular feature relies on the possibility of assigning a partial charge to all atomic centers [21]. The possibility to take a detailed look at the electronic structure of the molecules can be done by determining atom-based partial charges [22], which are not quantum mechanical observables. Since group charges are needed to explain the behavior of mesogens, Mulliken population analysis, which partitions the total charge among the atoms in the molecule, has been performed for each molecule and compared with those obtained from Loewdin population analysis. However, there is much agreement among the methods when it comes to the group charges of each molecule.

Mulliken and Loewdin group charges for *n*CB ($n = 4, 6$) molecules have been listed in Table 1. The results show that the alkyl chain plays a vital role in the formation of the charge distribution and phase stability. Evidently, the core in 4CB consists of a large positive charge. Hence, alkyl chains will be strongly attracted by the positively charged core and provide enough chemical stability. Furthermore, the positively charged alkyl chains in 6CB will be strongly attracted by the negatively charged core as well as the cyano group, causing the formation of longer units in the mesophase. Therefore, the phase stability is expected to be high for 6CB. The nematic-isotropic transition temperature ($T_{\text{N-I}}$) of *n*CB ($n = 4, 6$) molecules reported by the crystallographers (Table 1) supports this finding.

Electronic Absorption Spectrum

The possibility of using light instead of electricity to control the behavior of an LC material [23,24] enabled the exciting developments in LC science and technology. Altering the number of carbon atoms in the end chain is the widely used technique in order to change the physical properties of LC molecules. In the calculation of electronic spectra, the CI method is widely employed. By using a CI method in combination with a semiempirical model Hamiltonian, an evaluation of absorption spectra of large organic molecules and LCs becomes possible [25–27]. It is expected that the absorption spectrum of an LC molecule containing a single phenyl ring would exhibit similarities to that of an isolated 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 [28]. In general, these benzene-like transitions are roughly conserved in the model systems studied, but they are influenced by

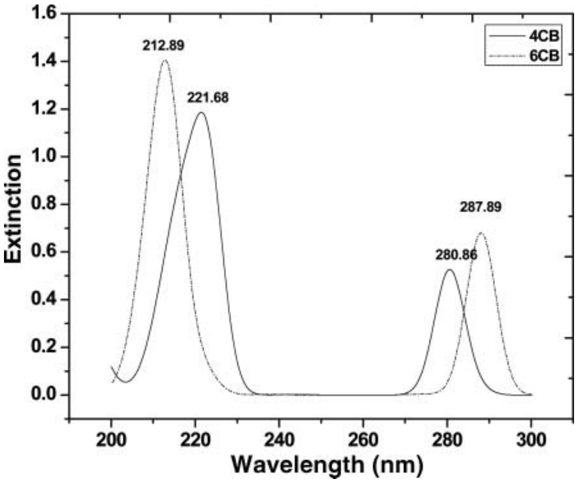


Figure 2. Electronic absorption spectra of (a) 4CB and (b) 6CB molecules. Extinction unit: 10^4 dm^3 mol^{-1} cm^{-1}.

the conjugation length, degree of conjugation, and the different substituents. The analysis of electronic absorption spectra of isolated molecules has been given below:

4′-n-Butyl-4-Cyanobiphenyl (4CB). The electronic absorption spectrum of 4CB is shown in Fig. 2. In the UV region, two absorptions at 221.68 nm (λ_1) and 280.86 nm (λ_2) have been observed. However, no absorption has been observed in the visible region. The strongest band appears in a region of 203.52–233.98 nm, with absorption maxima (λ_{max}) at 221.68 nm. This band arises from the HOMO→LUMO transition and is assigned as $\pi \rightarrow \pi^*$ transition in the molecule. The other absorption band corresponding to λ_2 indicates $\pi \rightarrow \pi^*$ transition in the molecule at a greater wavelength. The oscillator strengths (*f*) corresponding to two absorptions corresponding to λ_1 and λ_2 are 0.68 and 0.51, respectively. Therefore, these transitions contribute higher oscillator strength corresponding to the strongest absorption band at λ_1.

4′-n-Hexyl-4-Cyanobiphenyl (6CB). The dotted line in Fig. 2 represents the electronic absorption spectrum of 6CB molecule. The two prominent bands have been identified in the UV region with absorption maxima at 212.89 nm (λ_1) and 280.86 nm (λ_2). The strongest band has been observed from 200 to 233.40 nm, with absorption maxima at 212.89 nm (λ_1). This band arises due to the HOMO→LUMO transition and is assigned as $\pi \rightarrow \pi^*$ transition in the molecule. The other band indicates the possibility of $\pi \rightarrow \pi^*$ transition in higher wavelength region. Furthermore, the oscillator strengths corresponding to λ_1 and λ_2 are 0.42 and 0.31, respectively. Hence, the molecule 6CB contributes higher *f* value corresponding to $\pi \rightarrow \pi^*$ transition at λ_1.

CD Spectrum

The CD spectra of *n*CB ($n = 4$, 6) molecules have been shown in Fig. 3. Evidently, the molecule 4CB exhibits two absorption bands in the UV region at 216.41 nm (λ_1) and 280.86 nm (λ_2). The strongest absorption band has been noted in a region from 204.69 to 233.40

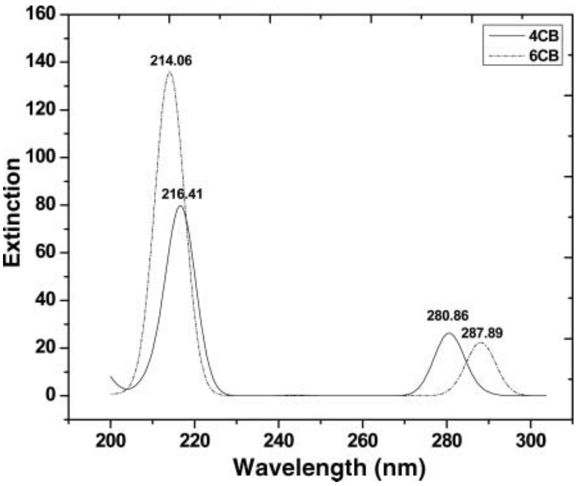


Figure 3. CD spectra of (a) 4CB and (b) 6CB molecules. Extinction unit: 10^4 dm^3 mol^{-1} cm^{-1}.

nm, with absorption maximum at λ_1. The rotatory strengths (R) corresponding to these two absorptions are 78.92 and 25.87, respectively.

Hence, the absorption maxima of 4CB in the CD spectrum have been noted in lower wavelength side than UV absorption spectrum.

Furthermore, two absorption bands have been noted for 6CB at 214.06 nm (λ_1) and 287.89 nm (λ_2), with rotatory strengths of 112.59 and 22.49, respectively. The strongest band has been observed from 200 to 232.10 nm, with absorption maxima (λ_{max}) at 214.06 nm. It has also been noted that the absorption maxima in the CD spectrum have been shifted to lower wavelength side than absorption spectrum.

Role of Alkyl Chains

The extinction coefficients corresponding to absorption maxima, the HOMO, LUMO energies, and the energy gap (E_g) values of isolated *n*CB molecules have been reported in Table 2. In order to understand the role of alkyl chains, the spectral characteristics of isolated single molecules have been analyzed. It may, therefore, be concluded that the absorption maxima in both spectra show a clear preference for an increment in the homolog number. The absorption maxima have been shifted to lower wavelengths in both the spectra with an addition of alkyl groups. However, the substitution of two additional alkyl groups in 4CB (forming 6CB) causes an increment in the extinction coefficients. A drastic increment has been observed in extinction coefficients with respect to an increment in homolog number. Thus, the substitution of two alkyl groups in 4CB (forming 6CB) causes a hypsochromic (blue) shift (in terms of λ) and hyperchromic effect (in terms of absorbance).

It is clear from the above discussion that the molecules do not show a clear preference for increment in homolog number to exhibit HOMO/LUMO energies. However, a prominent decrement in the energy gap ($E_{LUMO} - E_{HOMO}$) has been noted with respect to an increment in homolog number (Table 2). Furthermore, the molecular charge distribution analysis suggests that the phase stability also increases with respect to the homolog number. However, the extension of alkyl chain length does not cause much effect on maximum oscillator strength (f) in the UV region. But the rotatory strength (R) has been drastically

Table 2. The extinction coefficients corresponding to absorption maxima (λ_{max}), HOMO, LUMO energies, and energy gap (E_g) of *n*CB ($n = 4, 6$) molecules

	λ_{max}/nm		Extinction*				
Molecule	UV-Vis	CD	UV-Vis	CD	HOMO/eV	LUMO/eV	E_g = (LUMO−HOMO)/eV
4CB	221.68	216.41	1.19	79.75	−8.40	−0.35	8.05
6CB	212.89	214.06	1.41	136.08	−8.37	−0.50	7.87
Dimer molecules							
4CB							
Stacking	223.44	221.09	1.87	0.12	−8.40	−0.47	7.93
In-plane	221.09	221.09	2.70	472.44	−8.49	−0.44	8.05
Terminal	223.44	216.99	2.09	851.18	−8.21	−0.19	8.02
6CB							
Stacking	212.89	212.30	2.38	34.88	−8.42	−0.64	7.78
In-plane	208.79	228.12	1.91	236.41	−8.27	−0.79	7.48
Terminal	212.89	214.65	2.82	399.83	−8.27	−0.57	7.70

*Extinction unit: 10^4 dm^3 mol^{-1} cm^{-1}.

increased with an extension in chain length (Table 3). The wavelength dependence of oscillator strength and rotatory strength corresponding to the UV absorption spectrum and the CD spectrum are shown in Figs. 4 and 5, respectively. The oscillator strength indicates the allowedness of electronic transitions in a molecule. Hence, the molecule 4CB is more flexible for electronic transitions as it is exhibiting higher oscillator strength. Since the maximum oscillator strength of 6CB in the UV region has been obtained at longer wavelength region, the UV stability of 6CB becomes higher than 4CB. It is evident from Table 3 that 6CB shows higher rotatory strength than 4CB at a lower wavelength. Furthermore, a

Table 3. The maximum transition oscillator strength (f), rotatory strength (R), and the corresponding wavelengths for isolated molecules and dimer complexes of *n*CB ($n = 4, 6$) molecules at the TDDFT/B3LYP/6-31+G (d) level of approximation

Molecule	λ (nm)	f	λ (nm)	R
4CB	222.3	0.69	216.7	78.92
6CB	288.1	0.68	214.2	112.59
Dimer molecules				
4CB				
Stacking	223.5	1.24	220.5	0.10
In-plane	218.9	1.28	218.9	211.14
Terminal	281.5	1.08	216.8	822.09
6CB				
Stacking	287.5	1.25	211.7	29.37
In-plane	209.1	1.12	228.1	236.35
Terminal	289.6	1.40	214.4	369.16

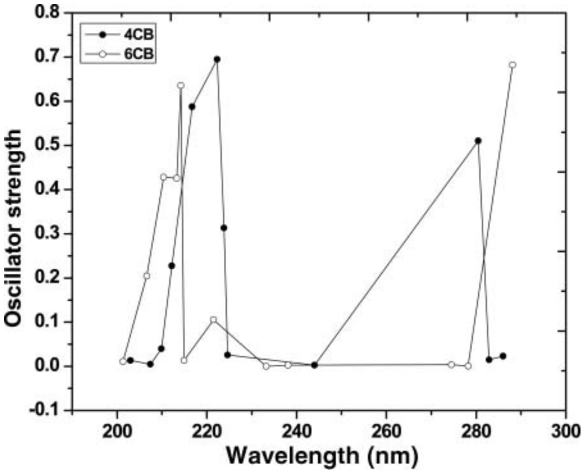


Figure 4. Wavelength dependence of oscillator strength of *n*CB ($n = 4, 6$) molecules.

particular UV wavelength range of 6CB is exhibiting a constant oscillator strength (Fig. 4) and rotatory strength (Fig. 5), which may be exploited for optoelectronic applications.

Intermolecular Interactions Between a Pair of Molecules

The results obtained for isolated molecules suggest that the optical properties are influenced by their electronic structures. Therefore, to understand the self-organizing ability of mesogens, the different modes of molecular interactions have been taken into consideration between a pair of *n*CB ($n = 4, 6$) molecules. The interaction energies of dimer complexes have been considered to investigate the most energetically stable configuration in each mode. Furthermore, the optical properties of dimer complexes are given in Table 2. LCs are not isotropic and clearly intermolecular interactions strongly influence their phase

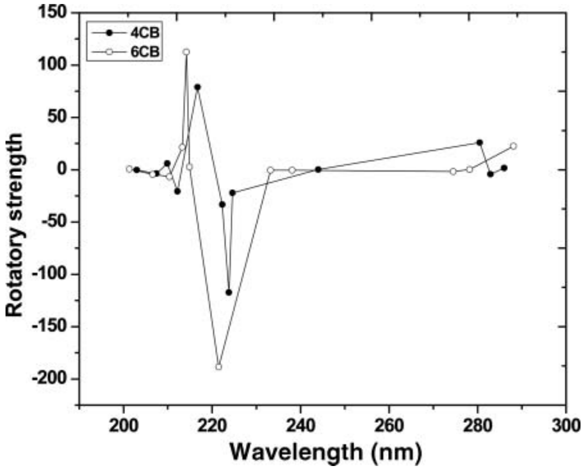


Figure 5. Wavelength dependence of rotatory strength of *n*CB ($n = 4, 6$) molecules.

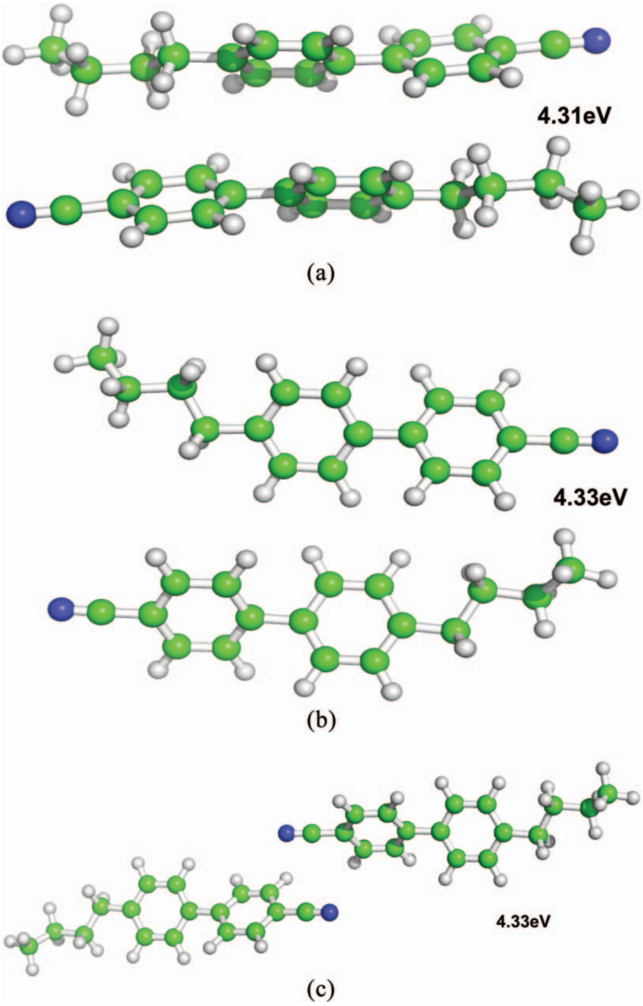


Figure 6. Energetically favorable structures of 4CB dimer in (a) stacking, (b) in-plane, and (c) terminal interactions.

behavior/stability and properties. The interpretation of physical measurements on LCs in terms of molecular properties is, therefore, a difficult problem.

The conformational behavior of LCs displays a large variation corresponding to 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 energy. The most energetically stable configurations of nCB ($n = 4, 6$) molecules during the different modes of interactions are shown in Figs. 6 and 7, respectively. The comparison of stacked dimers between both molecules suggests that the extension of the chain length causes a recognizable segregation of the dimers into a tilted layer structure. However, the comparison of planar dimers also indicates a highly tilted structure with respect to extension of chain length, which favors translational motion in a molecular pair along a planar axis. Mutual interaction between the dimers in these structures

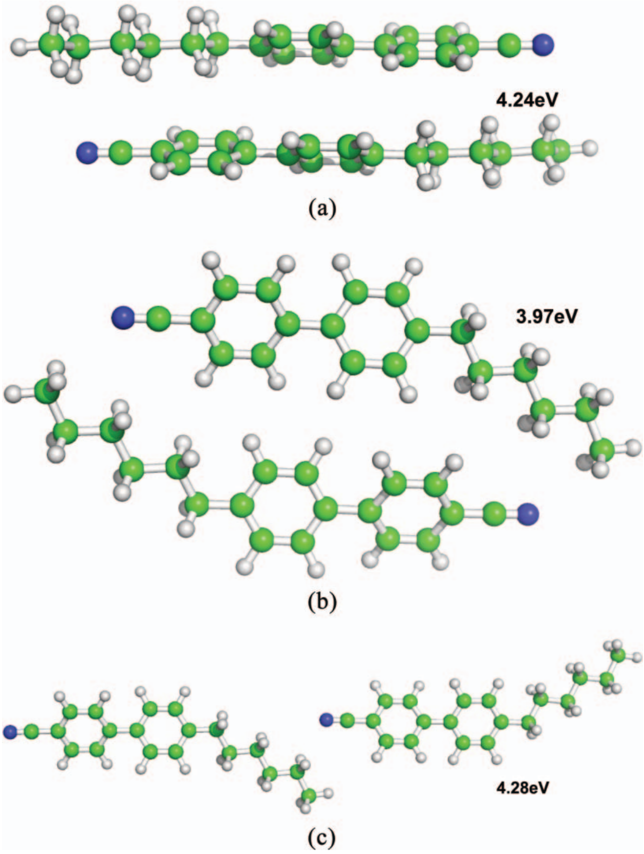


Figure 7. Energetically favorable structures of 6CB dimer in (a) stacking, (b) in-plane, and (c) terminal interactions.

is, however, quite weak, in particular to the chain atoms. Hence, the molecules do not show any preference in forming layer-like structures. Since the tilted nature of the dimers increases with the extension of chain length, molecules will attain sufficient flexibility to move along their planar axis. The end chains provide enough configurational entropy to the crystal structure to pass on to nematic phase. Hence, the phase stability is expected to be higher with extension of chain length. The interaction energies of dimers indicate that 6CB is more stable in nematic phase. This is in agreement with the molecular charge distribution analysis.

Conclusion

- The electronic absorption and CD spectra of butyl and hexyl cyanobiphenyls show strong absorption bands in the UV region.
- Alkyl chains have a dominant role in molecular properties and spectral characteristics. An increment has been noted in the absorption maxima and extinction coefficients with respect to extension of alkyl chain length, whereas a decrement has occurred in the energy gap values of isolated single molecules for an increment in alkyl chain length.

- Even though the allowedness of electronic transitions is maximum for 4CB (69%) (Table 2), the molecule 6CB exhibits high UV stability and the maximum oscillator strength occurs at longer wavelength region than 4CB.
- Since the tilted nature of the dimer complexes increases with the extension of chain length, molecules attain sufficient flexibility to move along their planar axis.
- The interaction energies suggest that the 6CB dimers are more stable than 4CB. Hence, the phase stability is expected to be higher for 6CB.

Acknowledgments

The financial support rendered by the Council of Scientific & Industrial Research (CSIR), and University Grants Commission (UGC), New Delhi, India, is gratefully acknowledged.

References

[1] Yeh, P., & Gu, C. (2010). *Optics of Liquid Crystal Displays*, 2nd edition, John Wiley: New Jersey.
[2] McEwen, R. S. (1987). *J. Phys. E. Sci. Instrum.*, *20*, 364–377.
[3] Praveen, P. L., & Ojha, D. P. (2011). *Mat. Chem. Phys.*, *126*, 248–252.
[4] Haya, B. M., & Cuteos, A. (2007). *J. Phys. Chem. B*, *111*, 8150–8157.
[5] Lueder, E. (2010). *Liquid Crystal Dsipalys: Addressing Schemes and Electro-Optical Effects*, John Wiley: West Sussex, UK.
[6] Praveen, P. L., & Ojha, D. P. (2011). *J. Mol. Liq.*, *158*, 27–32.
[7] Geelhaar, T., Tarumi, K., & Hirschmann, H. (1996). *SID Tech. Dig.*, *27*, 167–172.
[8] Goto, Y., Ogawa, T., Sawada, S., & Sugimori, S. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 1–7.
[9] Gray, G. W., Harrison, K. J., & Nash, J. A. (1973). *Electron Lett.*, *9*, 130–131.
[10] Dabrowski, R. (1990). *Mol. Cryst. Liq. Cryst.*, *191*, 17–27.
[11] Koch, W., & Holthausen, M. C. (2000). *A Chemist's Guide to Density Functional Theory*, Wiley-VCH: Weinheim.
[12] Yuan, X. U., Duan, E., Zhang, Y., Hu, S., & Liu, Y. (2010). *Mol. Cryst. Liq. Cryst.*, *528*, 147–155.
[13] Vani, G. V. (1983). *Mol. Cryst. Liq. Cryst.*, *99*, 21–27.
[14] Tiberio, G., Mucciori, L., Berardi, R., & Zanoni, C. (2009). *Chem. Phys. Chem.*, *10*, 125–136.
[15] Hohenberg, P., & Kohn, W. (1965). *Phys. Rev.*, *136*, B864–B871.
[16] Kohn, W., & Sham, L. J. (1965). *Phys. Rev.*, *140*, A1133–A1188.
[17] Jones, R. O., & Gunnarsson, O. (1989). *Rev. Mod. Phys.*, *61*, 689–746.
[18] Zerner, M. C. (1991). *Rev. Comp. Chem.*, *2*, 313–365.
[19] Zerner, M. C. (2004). In: K. W. Lipkowitz, R. Larter, & T. R. Cunsari, (Eds.), (*Semiempirical Molecular Orbital Methods*, Wiley-VCH: New Jersey, p. 153.
[20] Kuribayashi, M., & Hori, K. (1999). *Liq. Cryst.*, *26*, 809–815.
[21] Praveen, P. L., & Ojha, D. P. (2010). *Mol. Cryst. Liq. Cryst.*, *533*, 92–101.
[22] Eikelschulte, F., Yakovenko, S. Y., Paschek, D., & Geiger, A. (2000). *Liq. Cryst.*, *27*, 1137–1146.
[23] Tamba, M. G., Weissflog, W., Eremin, A., Heuer, J., & Stannarius, R. (2007). *Eur. J. Phys. E.*, *22*, 85–95.
[24] Calucci, L., Geppi, M., Marini, A., & Veracini, C. A. (2010). *Phys. Rev., E82*, 041702-1-041702–8.
[25] Hanemann, T., Bohm, M. C., Haase, W., & Wu, S. T. (1992). *Liq. Cryst.*, *11*, 917–927.
[26] Markovic, Z., Manojlovic, N., & Zlatanovic, S. (2008). *J. Ser. Soc. Comp. Mech.*, *2*, 73–79.
[27] Quotschalla, U., Hanemann, T., Bohm, M. C., & Haase, W. (1991). *Mol. Cryst. Liq. Cryst.*, *207*, 103–116.
[28] Khoo, I. C., & Wu, S. T. (1993). *Optics and Non Linear Optics of Liquid Crystals*, World Scientific: Singapore.