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Molecular Electronic Structure and Structure–Property Relationships of 5cb: A Dispersion-Corrected Dft Study

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Abstract
This study examined 5CB (4-cyano-4′-pentylbiphenyl) using density functional theory (DFT) to investigate its geometry and electronic properties. The calculations were carried out with the ωB97XD functional and the 6-311G(d,p) basis set. The optimized molecule showed the elongated, rod-like shape expected for 5CB. Its terminal cyano group also produced a clear difference in the electrostatic character of the two ends of the molecule. The frequency calculation showed no imaginary frequencies, confirming that the optimized structure corresponds to a stable minimum. The HOMO was located mainly on the biphenyl part of the molecule, while the LUMO extended more toward the cyano containing end. The calculated HOMO and LUMO energies were −8.34 and 1.64 eV, respectively, giving a HOMO–LUMO gap of 9.98 eV. This value represents the separation between the calculated frontier orbitals at the selected level of theory and should not be treated as an experimental optical band gap. The dipole moment of 5CB was calculated as 6.52 D, confirming its appreciable molecular polarity. The MEP map identified the terminal cyano nitrogen as the most electron-rich site.
Because the present calculations describe a single isolated Submission ID trn:oid:::1:3690290120 molecule, they cannot directly represent collective nematic ordering or bulk liquid-crystalline behavior. Nevertheless, they provide a useful molecular-level description of the structural and electronic features of 5CB that may contribute to its intermolecular behavior.

Keywords
5CB;
Density Functional Theory;
Dipole Moment;
Frontier Molecular Orbitals;
Molecular Electrostatic Potential

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1. INTRODUCTION

Thermotropic liquid crystals (TLCs) show behavior that lies between crystalline solids and isotropic liquids. Depending on temperature, liquid-crystal molecules can adopt different mesophases, including nematic and smectic phases (Miskovic et al., 2022; Khatun et al., 2025). rigidity of a crystal. Such partial ordering is responsible for the anisotropic optical, dielectric, and electronic behavior exploited in displays and other optoelectronic systems (Guardià et al., 2024; Alipanah et al., 2022). Mesophase behavior is closely related to molecular geometry and intermolecular interactions. Molecular packing and orientation can therefore depend on shape anisotropy, charge distribution, dispersion forces, dipolar interactions, and the aromatic π system (Alamro et al., 2023; Merkel et al., 2022). 4 Cyano 4′-pentylbiphenyl (5CB) is an established model compound for studying nematic liquid-crystal behavior. Structurally, 5CB combines a rigid biphenyl unit with a flexible pentyl chain and a polar terminal cyano (–CN) group (Figure 1). Its elongated shape and terminal polarity make it particularly suitable for examining links between molecular geometry, electronic distribution, and liquid-crystalline behavior (Goodby et al., 2024; Pathak et al., 2025

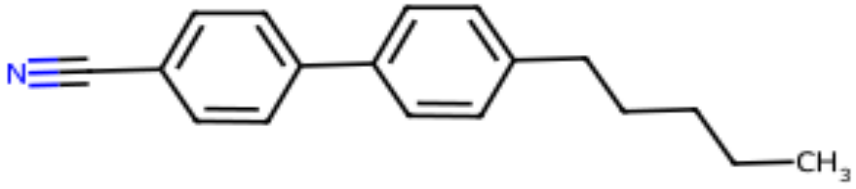


Figure 1. Chemical structure of 5CB.

Experimental and theoretical studies have reported structural, dielectric, optical, and mesomorphic properties of 5CB and related systems (Goodby, 2024; Pathak et al., 2025; Alamro et al., 2021), while DFT calculations have been used to investigate molecular geometry, frontier orbitals, charge distribution, and other electronic 16 1 3 2 descriptors (Alamro et al., 2021; Upadhyay et al., 2015; Garg et al., 2024). Since these calculated properties are influenced by the exchange-correlation functional, basis set, and molecular model, the present study uses the long range-corrected and dispersion inclusive ωB97XD functional with the 6-311G(d,p) basis set (Chai and Head-Gordon, 2008).

Geometry optimization and frequency analysis are combined with frontier orbital analysis, global reactivity descriptors, dipole moment calculations, and molecular electrostatic potential mapping. The HOMO–LUMO separation is discussed as a method-dependent molecular quantity, and the results are interpreted only within the limits of the isolated-molecule model.

2. MATERIALS AND METHODS

2.1. Molecular Modeling and DFT Calculations

A molecular model of 4-cyano-4′-pentylbiphenyl (5CB) was built in GaussView and pre-optimized by molecular mechanics to remove unfavorable steric contacts (Goodby, 2024). Subsequent DFT 7 4 5 calculations were performed with Gaussian 16 (Frisch et al., 2016). Geometry optimization used the ωB97XD/6-311G(d,p) method, which includes long range exchange and empirical dispersion corrections (Chai and Head-Gordon, 2008). No symmetry constraints were applied, and a single gas-phase 5CB molecule was considered. Frequency analysis showed no imaginary frequencies, confirming a local minimum.

2.2. Frontier Molecular Orbitals and Global Reactivity Descriptors

The frontier-orbital energies and their spatial distributions were extracted from the optimized structure. The HOMO–LUMO separation and global reactivity descriptors were derived from the frontier orbital energies using Koopmans-type relationships. The following expressions were used:

$$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}};\ IP = -E_{\mathrm{HOMO}};\ EA = -E_{\mathrm{LUMO}} \quad (1)$$

$$\chi = \frac{IP + EA}{2};\ \mu = -\chi \quad (2)$$

$$\eta = \frac{IP - EA}{2};\ S = \frac{1}{2\eta} \quad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

where E_{HOMO} and E_{LUMO} are the HOMO and LUMO energies, respectively; $\Delta E$is the frontier-orbital separation; $IP$is the ionization potential; $EA$is the electron affinity; $\chi$is the electronegativity; $\mu$is the chemical potential; $\eta$is the chemical hardness; $S$is the chemical softness; and $\omega$is the electrophilicity index. These quantities were used to describe the electronic response of 5CB within the adopted approximation.

2.3. MEP, Dipole Moment, and Visualization

MEP and dipole-moment calculations were also carried out with ωB97XD/6-311G(d,p). We examined the MEP surface of 5CB to locate rich and poor electronic regions and assess how the electrostatic potential varied across the molecule (Al-Mutabagani et al., 2021; Hagar et al., 2021). The calculate of dipole moment provided a measure of molecular polarity (Thoms et al., 2022). The optimized structure, frontier molecular orbitals, and MEP surface were visualized using GaussView 6 (Dennington et al., 2016).

3. RESULTS AND DISCUSSION

3.1. Optimized Molecular Geometry

The structure of 5CB optimized at the ωB97XD/6-311G(d,p) level shows the elongated shape typical of calamitic liquid crystals (Figure 2). The molecule has a rigid biphenyl core attached to a flexible pentyl chain. Its terminal cyano group is oriented approximately along the molecule's long axis. A torsional angle between the phenyl rings prevents the biphenyl unit from being fully planar. Such twisting may alter πconjugation between the rings while retaining the extended aromatic framework.

Conformational flexibility is provided by the pentyl chain, while the aromatic core maintains the molecular anisotropy. The terminal –CN group forms a strongly polar region at one end of 5CB. These structural features give the molecule its characteristic combination of elongation, rigidity, flexibility, and terminal polarity. Because the calculation describes an isolated molecule, it does not directly represent mesophase organization; however, these structural features are among those known to influence intermolecular association and orientational thermotropic liquid crystals

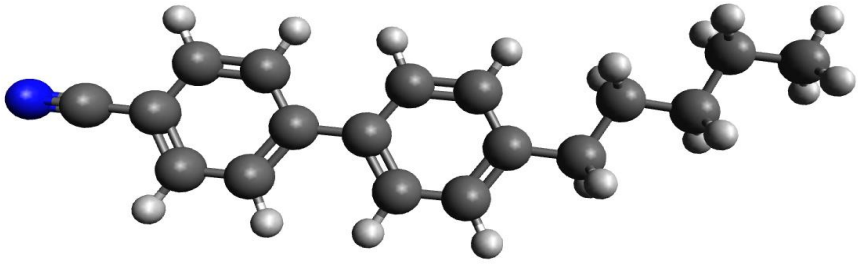


Figure 2. Optimized geometry of 5CB using the ωB97XD/6-311G(d,p) method.

3.2. Frontier Molecular Orbitals and Global Reactivity Descriptors

Figure 3 shows the frontier molecular orbitals of 5CB. The HOMO is localized mainly over the π conjugated biphenyl core, whereas the LUMO is distributed across the aromatic framework and extends more strongly toward the cyano-substituted end of the molecule. The difference in orbital distribution reflects how the terminal –CN group influences the molecule's electronic structure.

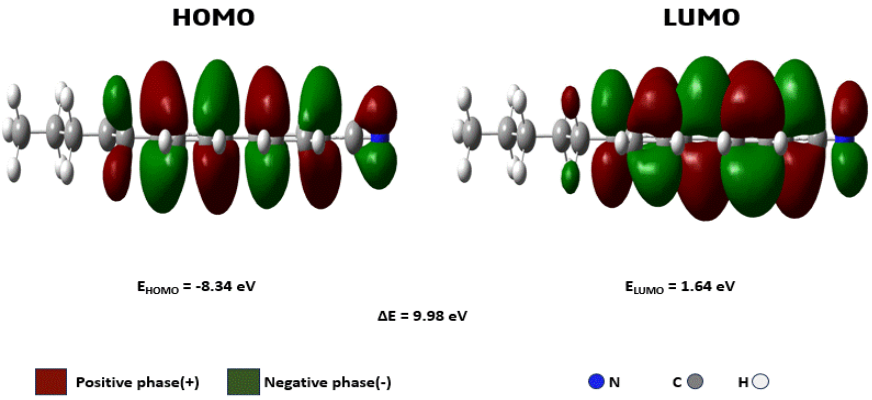


Figure 3. HOMO and LUMO distributions of 5CB at the ωB97XD/6-311G(d,p) level.

The calculated HOMO and LUMO energies were –8.34 and 1.64 eV, respectively, giving a HOMO LUMO separation of 9.98 eV. Within the present computational model, this relatively large value is consistent with limited electronic deformability. It should, however, be regarded as a Kohn–Sham orbital separation for an isolated molecule rather than as an experimental optical band gap. The global reactivity descriptors derived from these orbital energies are listed in Table 1. The calculated hardness (4.99 eV) and softness (0.100 eV^{-1}) reflect the large HOMO LUMO separation, while the electronegativity, chemical potential, and electrophilicity index provide additional descriptors of the electronic response of 5CB. The frontier-orbital distribution shows that the biphenyl framework makes the main contribution to the electronic structure, with the cyano substituted region contributing more clearly to the LUMO.

Table 1. Frontier orbital energies and Koopmans-based reactivity descriptors of 5CB.

Parameter	Symbol	Value	Parameter	Symbol	Value
HOMO energy	E_HOMO	–8.34 eV	LUMO energy	E_LUMO	1.64 eV
HOMO–LUMO gap	ΔE	9.98 eV	Ionization potential	IP	8.34 eV
Electron affinity	EA	–1.64 eV	Chemical hardness	η	4.99 eV
Chemical softness	S	0.100 eV^{-1}	Electronegativity	χ	3.35 eV
Chemical potential	μ	–3.35 eV	Electrophilicity index	ω	1.12 eV

To examine the method dependence of the frontier orbital energies, the present results were compared with selected computational data reported for 5CB and related liquid-crystalline systems. The ωB97XD/6-311G(d,p) calculation gave a HOMO LUMO separation of 9.98 eV, whereas a B3LYP/6 31++G(d,p) study of 5CB reported a value of about 4.65 eV (Yadav et al., 2023). A related liquid crystalline compound, 5O.14, showed a smaller separation of 4.18 eV at the B3LYP/6-31G(d,p) level (Garg et al., 2024). These differences confirm that the calculated frontier-orbital energies are strongly dependent on the computational method and should therefore be interpreted cautiously.

3.3. Dipole Moment, MEP, and Structure–Property Relationship

The optimized 5CB molecule had a dipole moment of 6.52 D, indicating pronounced molecular polarity associated mainly with the terminal cyano group. The MEP surface (Figure 4) showed the most negative potential around the cyano nitrogen, whereas more positive regions were located mainly over hydrogen containing parts of the aromatic and alkyl segments. This electrostatic asymmetry is consistent with the calculated dipole moment and highlights the strong contribution of the terminal –CN group to molecular polarity.

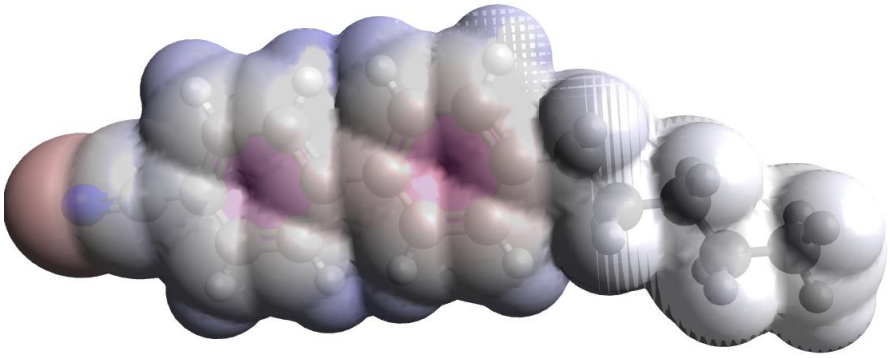


Figure 4. Molecular electrostatic potential surface of 4-cyano-4'-pentylbiphenyl (5CB) calculated at the ωB97XD/6-311G(d,p) level.

Together with the elongated molecular shape, rigid aromatic core, flexible pentyl chain, and frontier orbital distribution, these results show that 5CB combines geometric anisotropy, conformational flexibility, and pronounced electronic asymmetry within one characteristic molecular may framework. influence These intermolecular interactions and orientational behavior in the liquid. crystalline state. However, neither the dipole moment nor the isolated-molecule MEP can by themselves predict nematic stability or collective ordering, which require explicit intermolecular or condensed-phase models.

4. CONCLUSION AND RECOMMENDATION

A dispersion-corrected DFT study of 4-cyano-4' pentylbiphenyl (5CB) 8 6 15 1 was performed at the ωB97XD/6-311G(d,p) level. The optimized molecule retained its elongated geometry, with a relatively rigid biphenyl core, a flexible pentyl chain, and a polar terminal cyano group. corresponding chemical hardness and softness values of 4.99 eV and 0.100 eV^{-1}, respectively. Comparison with the B3LYP-based results showed that the orbital energies depended on the computational method.

The calculated gap should not be equated with an experimental optical band gap and the dipole moment of 6.52 D and the MEP map indicated a pronounced electrostatic asymmetry, largely associated with the terminal cyano group.

The electrostatic asymmetry of 5CB may affect how its molecules interact with one another and align. Further work could examine assemblies of several 5CB molecules and extend the calculations to condensed-phase systems. These models would allow a more direct assessment of molecular ordering and nematic behavior. It would also be useful to investigate how external electric fields and changes in the molecular environment affect the calculated properties.

REFERENCES

Alamro, F. S., Ahmed, H. A., Popoola, S. A., and Aboelnaga, A. (2021). "Synthesis, phase behavior and computational simulations of a pyridyl-based liquid crystal system." *Molecules*, 26(21): 6416. https://doi.org/10.3390/molecules26216416

Alamro, F. S., Ahmed, H. A., Khushaim, M. S., Bedowr, N. S., and Al-Kadhi, N. S. (2023). "Mesomorphic investigation of binary mixtures of liquid crystal molecules with different mesogenic architectonics." *Crystals*, 13(6): 899. https://doi.org/10.3390/cryst13060899

Al-Mutabagani, L. A., Alshabanah, L. A., Ahmed, H. A., and El-Atawy, M. A. (2021). "Synthesis, optical and DFT characterizations of laterally fluorinated phenyl cinnamate liquid crystal non-symmetric system." *Symmetry*, 13(7): 1145. https://doi.org/10.3390/sym13071145

Alipanah, Z., Zakerhamidi, M. S., and Ranjkesh, A. (2022). "Temperature-dependent optical properties of some mixtures nematic liquid crystal." *Scientific Reports*, 12: 12676. https://doi.org/10.1038/s41598-022-16750-x

Chai, J.-D., and Head-Gordon, M. (2008). "Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections." *Physical Chemistry Chemical Physics*, 10: 6615–6620. https://doi.org/10.1039/B810189B

Dennington, R., Keith, T. A., and Millam, J. M. (2016). *GaussView, Version 6*. Semichem Inc., Shawnee Mission, KS, USA.

Frisch, M. J., et al. (2016). *Gaussian 16, Revision C.01*. Gaussian, Inc., Wallingford, CT, USA.

Garg, K., Chakraborty, A., Bhattacharjee, A., Choudhury, S. P., Kumari, S., and Bhattacharjee, D. (2024). "A DFT analysis of thermodynamical, structural and non-linear optical properties of liquid crystalline compounds (5O.m, m = 14, 16)." *Journal of Molecular Liquids*, 414: 126124. https://doi.org/10.1016/j.molliq.2024.126124

Goodby, J. W. (2024). "4′-Pentyl-4-cyanobiphenyl – 5CB." *Liquid Crystals*, 51(8–9): 1272–1295. https://doi.org/10.1080/02678292.2023.2299277

Guardià, J., Reina, J. A., Giamberini, M., and Montané, X. (2024). "An Up-to-Date Overview of Liquid Crystals and Liquid Crystal Polymers for Different Applications: A Review." *Polymers*, 16(16): 2293. https://doi.org/10.3390/polym16162293

Hagar, M., Ahmed, H. A., Alnoman, R. B., Jaremko, M., Emwas, A.-H., Sioud, S., and Abu Al-Ola, K. A. (2021). "New liquid crystal assemblies based on cyano-hydrogen bonding interactions." *Frontiers in Chemistry*, 9: 679885. https://doi.org/10.3389/fchem.2021.679885

Khatun, N., Nkele, A. C., and Bagchi, K. (2025). "Liquid crystals as solid-state templates." *Physical Chemistry Chemical Physics*, 27(13): 6408–6424. https://doi.org/10.1039/D4CP04526B

Merkel, K., Loska, B., Arakawa, Y., Mehl, G. H., Karcz, J., and Kocot, A. (2022). "How do intermolecular interactions evolve at the nematic to twist-bent phase transition?" *International Journal of Molecular Sciences*, 23(19): 11018. https://doi.org/10.3390/ijms231911018

Miskovic, V., Malafronte, E., Minetti, C., Machrafi, H., Varon, C., and Iorio, C. S. (2022). "Thermotropic liquid crystals for temperature mapping." *Frontiers in Bioengineering and Biotechnology*, 10: 806362. https://doi.org/10.3389/fbioe.2022.806362

Pathak, G., Phettong, B., and Chattham, N. (2025). "Optimization of 4-Cyano-4'-pentylbiphenyl Liquid Crystal Dispersed with Photopolymer: Application Towards Smart Windows and Aerospace Technology." *Polymers*, 17(16): 2232. https://doi.org/10.3390/polym17162232

Thoms, E., Yu, L., and Richert, R. (2022). "From very low to high fields: The dielectric behavior of the liquid crystal 5CB." *Journal of Molecular Liquids*, 368: 120664. https://doi.org/10.1016/j.molliq.2022.120664

Upadhyay, P., Rastogi, M. K., and Kumar, D. (2015). "Polarizability study of nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) and its nitrogen derivatives." *Chemical Physics*, 456: 41–46. https://doi.org/10.1016/j.chemphys.2015.03.011

Yadav, N. P., Vishwkarma, A. K., Maddheshiya, A. K., Yadav, T., Moharana, S., Kumar, R., Pathak, A., and Tripathi, P. K. (2023). "Molecular geometries, vibrational spectra and electronic properties of biphenyl nematic liquid crystals: a quantum chemical analysis." *Molecular Physics*, 121: e2210957. https://doi.org/10.1080/00268976.2023.2210957