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Molecular Electronic Structure and Structure–Property Relationships of 5CB: A Dispersion-Corrected DFT Study

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Abstract

5CB (4-cyano-4′-pentylbiphenyl), a thermotropic liquid-crystal molecule, was investigated computationally to characterize its molecular geometry and electronic properties. Density functional theory (DFT) calculations were performed using the ωB97XD functional with the 6-311G(d,p) basis set. The elongated molecular architecture and terminal cyano group impart pronounced geometric and electrostatic anisotropy to the molecule. Geometry optimization followed by frequency analysis confirmed the stability of the optimized structure, with no imaginary frequencies observed. Frontier molecular orbital analysis showed that the highest occupied molecular orbital (HOMO) is concentrated predominantly over the biphenyl framework, whereas the lowest unoccupied molecular orbital (LUMO) extends further toward the cyano-substituted region. The calculated HOMO and LUMO energies were –8.34 and 1.64 eV, respectively, yielding a HOMO–LUMO energy separation of 9.98 eV. This separation is interpreted as a method-dependent frontier-orbital value and should not be regarded as an experimental optical band gap. The calculated molecular dipole moment was 6.52 D, indicating substantial molecular polarity. Molecular electrostatic potential (MEP) analysis further revealed that the most electron-rich region is localized around the nitrogen atom of the terminal cyano group. Collectively, the elongated molecular shape, aromatic electronic structure, and strong terminal polarity may influence intermolecular interactions and orientational organization in 5CB. These isolated-molecule calculations therefore provide molecular-level insight into structural and electronic features relevant to intermolecular organization. However, collective nematic behavior and associated bulk liquid-crystalline properties cannot be assessed directly from the present isolated-molecule model. The results establish a consistent quantum-chemical description of 5CB while defining the interpretive limits of single-molecule DFT calculations in practice.

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). These phases retain partial molecular order without the 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).

Connecting these molecular features with measurable properties helps explain the behavior of established liquid-crystal systems and supports the design of new materials (Yadav et al., 2023). 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)

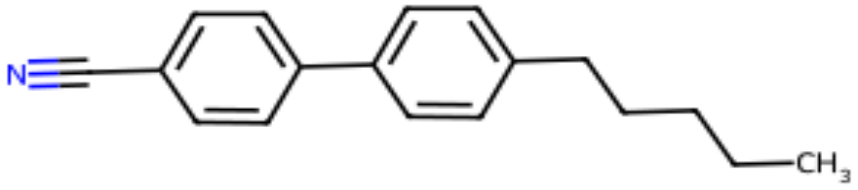

Figure 1. Chemical structure of 5CB.

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 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 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 $E_{\mathrm{HOMO}}$and $E_{\mathrm{LUMO}}$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). The MEP surface was examined to identify electron-rich and electron-poor regions and to characterize the electrostatic asymmetry of 5CB (Al-Mutabagani et al., 2021; Hagar et al., 2021). Molecular polarity was assessed from the calculated dipole moment, with particular attention to the effect of the terminal cyano group (Thoms et al., 2022). GaussView 6 was used to display the optimized structure, frontier orbitals, and MEP surface (Dennington et al., 2016).

3. RESULTS AND DISCUSSION

3.1. Optimized Molecular Geometry

Optimization with ωB97XD/6-311G(d,p) yielded an elongated 5CB geometry characteristic of calamitic liquid crystals (Figure 2). The structure combines a rigid biphenyl unit with a flexible pentyl chain, with the terminal cyano group oriented approximately along the molecular 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 ordering in thermotropic liquid crystals.

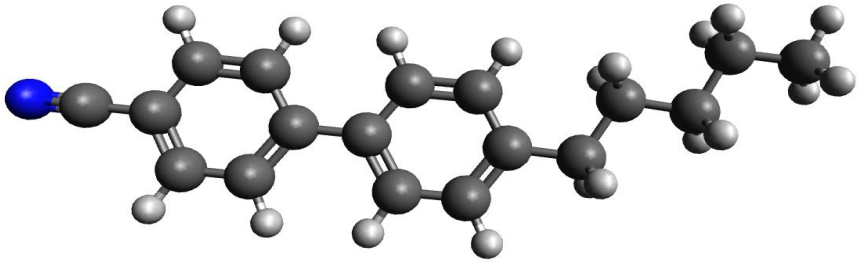

Figure 2. Optimized geometry of 5CB using the ωB97XD/6-311G(d,p) method.

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. This difference in orbital distribution reflects the electronic effect of the terminal –CN group.

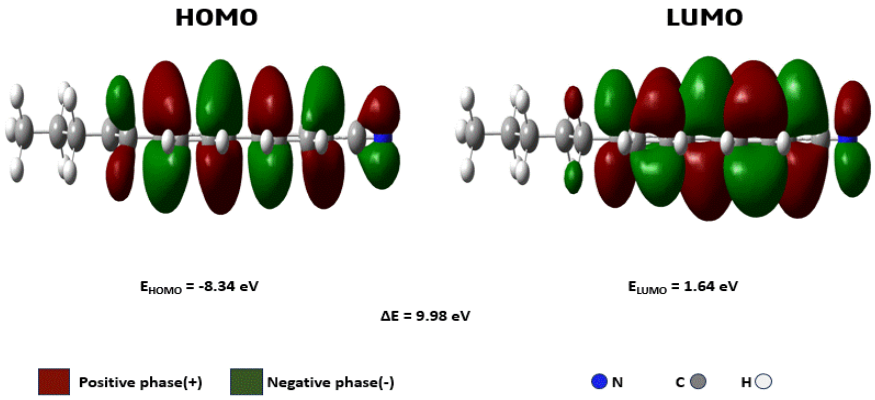

Figure 3. HOMO and LUMO distributions of 5CB at the ωB97XD/6-311G(d,p) level.

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.

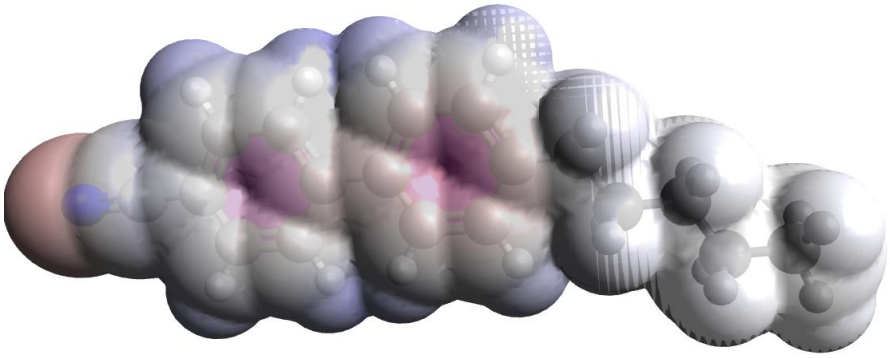

Figure 4. Molecular electrostatic potential surface of 4-cyano-4'-pentylbiphenyl (5CB) calculated at the ωB97XD/6-311G(d,p) level.

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 molecular framework. These characteristics may influence 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) 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. Frontier-orbital analysis showed that the HOMO is mainly associated with the biphenyl framework, whereas the LUMO extends more clearly toward the cyano-substituted region. The calculated HOMO–LUMO separation was 9.98 eV, with a chemical hardness of 4.99 eV and softness of 0.100 eV^{-1}. Comparison with B3LYP-based results confirmed that these orbital energies are strongly method dependent and should not be interpreted as an experimental optical band gap.

The calculated dipole moment of 6.52 D and the MEP distribution both showed pronounced electrostatic asymmetry associated mainly with the terminal cyano group. Together with the elongated molecular framework and aromatic π-system, these features may affect intermolecular interactions and the orientational behavior of 5CB.

Future studies could extend the present model by examining explicit intermolecular assemblies of 5CB and condensed-phase systems. Such approaches would permit a more direct assessment of molecular ordering and nematic behavior. The effects of external electric fields and different molecular environments on the calculated properties could also be explored.

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