

Influence of Electron Donating and Electron Withdrawing Substituents on the Structural Electronic Spectroscopic and Nonlinear Optical Properties of Liquid Crystalline Molecules: A DFT and TD DFT Investigation Based on Published Evidence Through 2025

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Abstract:

Substituent engineering connects the electronic structure of an organic chromophore with the collective ordering required for liquid-crystal applications. Electron donors and acceptors redistribute charge, modify conjugation and change the response to electric and optical fields. Their effects nevertheless depend on position, molecular conformation, linkage chemistry and condensed-phase organization. This article presents an original critical synthesis of density functional theory and time-dependent density functional theory concepts alongside published evidence available before 2026. It considers aromatic mesogens containing imine, ester and related conjugated units, while identifying nonmesogenic donor-acceptor compounds used only as mechanistic comparisons. Published numerical findings are replotted in original graphs, and qualitative tables distinguish established tendencies from conditional interpretations. The analysis emphasizes the difference between orbital gaps and optical excitations, between molecular hyperpolarizability and bulk nonlinear susceptibility, and between calculated molecular stability and experimentally established mesophase stability. Stronger electronic polarization can improve an individual molecule's optical response but can also increase absorption, aggregation or orientational cancellation. Useful liquid-crystalline optical materials therefore require coordinated control of electronic asymmetry, molecular shape, transparency and polar organization. No new molecular calculations or experimental measurements are represented as having been performed.

Keywords: liquid crystals; substituent effects; density functional theory; time-dependent density functional theory.

Introduction

Liquid-crystalline molecules provide an unusual combination of molecular mobility and directional organization. An aromatic core can establish an elongated or otherwise anisotropic shape, while flexible chains, polar terminals and lateral substituents control how neighboring molecules assemble. The resulting material can respond differently to light or electric fields parallel and perpendicular to its preferred orientation. This makes substitution a practical chemical route for connecting molecular electronic properties with tunable optical behavior. The relevant design question is broader than whether an electron donor or acceptor produces a large dipole: the same group also changes molecular width, flexibility and intermolecular contacts.

Density functional theory supplies a framework for examining the ground-state electron density and optimized molecular structure. Its foundations were established by Hohenberg and Kohn and by the effective single-particle formulation of Kohn and Sham [1,2]. Time-dependent density functional theory extends the density-based description to electronic response and excitation phenomena [3]. In molecular applications, these frameworks help interpret substituent-dependent geometries, orbital distributions, vibrational features and optical transitions. Their predictions are most useful when related to experimental evidence and when the observable being predicted is identified precisely.

The title's investigation is therefore developed here as a literature-based analysis rather than a report of an unperformed computational experiment. Numerical entries retain the meanings, units and computational conditions of their sources. Qualitative deductions are presented as physical interpretations, not as newly calculated measurements. The literature cutoff is 31 December 2025. This distinction is necessary because an apparently complete set of fabricated bond lengths, excitation energies and hyperpolarizabilities would create the impression of reproducible calculations without the molecular structures, coordinates and output files needed to support them.

Substitution can be considered at three connected levels. At the electronic level, a group changes local electron availability and charge-transfer pathways. At the molecular level, it alters geometry and the direction of response tensors. At the material level, it modifies packing and orientational order. The central argument of this article is that no one level is sufficient to explain all four property categories in the title. A persuasive interpretation must connect them without converting a plausible molecular tendency into an unsupported claim about a liquid-crystal device.

Substituent Chemistry and Molecular Architecture

Electron-donating substituents include alkoxy and amino groups when their lone pairs can interact with a suitable conjugated system. Alkyl groups generally exert weaker donating effects through induction and hyperconjugation. Electron-withdrawing groups include nitro, cyano and carbonyl-containing terminals, although the magnitude and direction of their influence depend on the attachment site and neighboring bonds. Fluorine requires particular care: its strong inductive withdrawal coexists with possible resonance donation in aromatic environments. Describing every fluorinated mesogen as a stronger push-pull chromophore therefore oversimplifies its chemistry.

A donor–bridge–acceptor arrangement can establish an asymmetric distribution of electron density along a rigid core. However, the bridge must actually transmit electronic coupling. An aromatic–imine segment, an ester-containing connection and a saturated spacer do not provide equivalent conjugation. A molecule may be geometrically long while its electronically communicating region is short. Conversely, a compact conjugated chromophore may have strong charge transfer but insufficient shape anisotropy or unsuitable intermolecular interactions to form a mesophase. Optical design and mesogenic design overlap without being interchangeable.

Position is as important as substituent identity. A para substituent can often interact with a longitudinal conjugated path, whereas a lateral group may create a transverse dipole or rotate neighboring rings. Ortho substitution can introduce steric crowding near an imine, ester or biaryl linkage. Such rotation changes orbital overlap and may oppose the electronic advantage of a nominally stronger donor. A meaningful comparison therefore holds the core and attachment site constant before assigning a difference to electron donation or withdrawal. Comparisons across unrelated scaffolds cannot establish a universal substituent ranking.

Table 1. Conditional substituent effects in aromatic mesogens

Substituent	Electronic influence	Structural or material qualification
Alkoxy or amino	Can donate through resonance	Requires lone-pair coupling; steric rotation may weaken it
Alkyl	Generally weak donation	Changes flexible volume and packing as well
Cyano or nitro	Can accept electron density	Position and dipole direction determine useful coupling
Fluorine	Inductive withdrawal with aromatic resonance effects	Small size, lateral placement and packing must be considered
Carbonyl-containing linkage	Polarizes neighboring fragments	An ester does not guarantee continuous core conjugation

Original qualitative synthesis. These tendencies are conditional, not calculated results for a new molecular series; contextual examples: [7,8,11].

The table is an interpretive map rather than a list of guaranteed outcomes. For example, adding an alkoxy chain simultaneously changes the donating group attached to an aromatic ring and the volume of the flexible region. Extending an already attached alkyl tail mainly alters flexibility and packing; it does not lengthen the aromatic π system. Likewise, a cyano group can increase a longitudinal dipole without necessarily producing a large first hyperpolarizability. The latter depends on how the whole electron distribution responds, including the symmetry and accessibility of excited states.

Structural Response and Mesomorphic Organization

Optimized bond lengths and torsional angles translate substituent chemistry into molecular structure. A donor–acceptor combination can increase quinoidal character within a conjugated segment, modifying the contrast between formally single and double bonds. Nevertheless, bond-

length alternation is a descriptor of a particular pathway, not a universal scalar for an entire mesogen. The choice of bonds matters, especially when aromatic rings and heteroatom linkages are present. Two molecules with similar average alternation can have different terminal polarization or markedly different inter-ring torsions.

A useful structural interpretation connects changes to specific chemical regions. Shortening near an imine bond may indicate altered conjugation, while rotation at an ester-linked ring can limit transmission between aromatic fragments. The electron donor itself can become less effective if its lone pair is geometrically decoupled from the ring. Reporting only a minimum energy and an image of an optimized structure leaves these possibilities unresolved. The important evidence is the relationship between geometry, electronic redistribution and a chemically identifiable change in the molecule.

Flexible tails complicate this relationship because several conformations may be accessible at experimental temperatures. A single optimized conformer represents one molecular arrangement. It does not establish the population of conformers in a liquid-crystalline material. The polarizability axis, total dipole direction and molecular aspect ratio may shift across those arrangements. Consequently, the most stable isolated conformer should not automatically be identified with the dominant structure in an aligned mesophase. Packing interactions and thermal motion can favor other conformations or mixtures of them.

Direct mesogenic evidence illustrates the importance of this distinction. Shirodkar and colleagues reported difluorinated Schiff-base esters with pentyloxy and dodecyloxy tails [7]. Their phase assignments were supported by polarized microscopy and calorimetry. On cooling, the shorter-tail compound 5OFB exhibited a nematic interval, whereas 12OFB exhibited smectic A ordering. Figure 1 replots their reported cooling endpoints. The electronic core and fluorine pattern are shared; the changed phase therefore highlights how flexible-chain architecture can redirect organization even when the polar substituents remain the same.

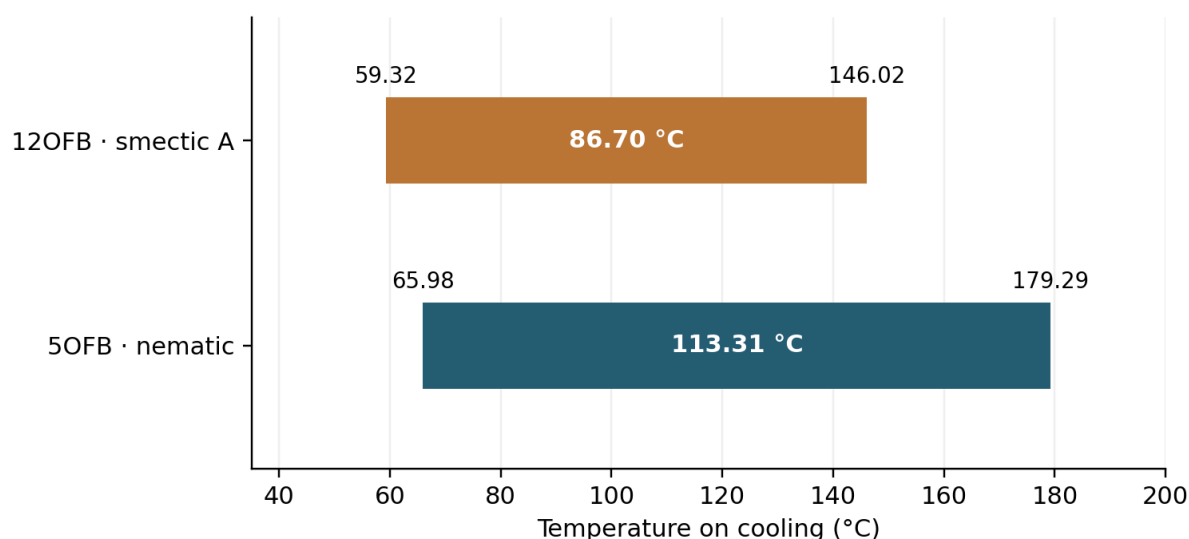


Figure 1. Cooling mesophase intervals of difluorinated Schiff-base esters. Source: Shirodkar et al. [7], reported DSC cooling temperatures. 5OFB: crystal–nematic endpoints 65.98 and 179.29 °C;

12OFB: crystal–smectic A endpoints 59.32 and 146.02 °C. Widths are derived by subtraction.

Original graph; no error bars were reported for these endpoints.

The plotted intervals are calculated differences between published transition temperatures, not uncertainty estimates or independent measurements. Heating and cooling results are not interchangeable because thermal history and hysteresis can matter. This example also does not isolate fluorine's effect: a matched nonfluorinated series under identical conditions would be needed for that attribution. More generally, differences between a nematic and a smectic material cannot be interpreted as proof that one has a larger molecular hyperpolarizability. Phase symmetry and electronic response are separate observables.

Hydrogen-bonded mesogens add another layer of structural control. Gomha and colleagues examined laterally chlorinated azo/ester components assembled with adipic acid [8]. Their study connects supramolecular association, terminal-chain variation and mesomorphic behavior. For such systems, a calculation on an isolated component describes only part of the relevant object. Hydrogen bonding can reshape charge distribution and geometry within the complex, while association equilibria affect the material actually present. Substituent effects should consequently be interpreted at the molecular or supramolecular level appropriate to the reported experiment.

Electronic Structure and Charge Redistribution

The highest occupied and lowest unoccupied molecular orbitals offer a useful first view of substituent-dependent electronic structure. A donor can influence occupied states near its attachment region, while an acceptor can stabilize accessible unoccupied states. In a conjugated asymmetric molecule, this may decrease the difference between their energies. The direction of change is conditional, however: a substituent can shift both levels, change their localization or alter the identity of the frontier orbitals. Simply stating that donors raise the HOMO and acceptors lower the LUMO misses these coupled possibilities.

The quantity $E(\text{LUMO}) - E(\text{HOMO})$ is an orbital energy difference for the specified calculation. It is not automatically the fundamental ionization–electron-affinity gap, a solid-state band gap or the energy of the lowest optically bright transition. Each involves a different physical definition. Using the word “gap” without identifying which one is intended can make a substituent comparison appear more experimentally direct than it is. In particular, converting a DFT orbital difference directly into an absorption wavelength generally bypasses the excited-state interactions addressed by TD-DFT.

Charge redistribution can also be examined through electrostatic potential and population analyses. Electrostatic potential maps identify regions where the potential experienced by a test charge is relatively positive or negative. They are useful for discussing possible intermolecular contacts, but a color map is not a measurement of electron flow. Atomic charges are additionally dependent on the partitioning convention. Agreement between several descriptors is more convincing than a single especially large atomic-charge change, particularly when substituents introduce chemically dissimilar atoms into the comparison.

Natural bond orbital analysis gives another language for donor–acceptor interactions within a molecule. A stabilizing interaction between an occupied localized orbital and an unoccupied orbital

can indicate conjugative communication. Its perturbative energy nevertheless belongs to that analysis and should not be equated with a directly measured charge-transfer energy. A strong localized interaction can coexist with weak long-range transfer if a distant torsion interrupts the bridge. Interpreting local and global electronic descriptors together helps avoid treating any one diagnostic as conclusive evidence of enhanced optical performance.

An external electric field can redistribute density in directions that differ from the permanent dipole. For an elongated mesogen, a large longitudinal response is often desirable, but lateral substituents can increase transverse components. The total dipole magnitude then hides a potentially important change in orientation. Two compounds with similar dipole magnitudes may align differently or couple differently to an applied field. Tensor directions, rather than magnitudes alone, are therefore necessary for connecting electronic calculations with anisotropic liquid-crystal behavior.

Electronic “softness” inferred from a small orbital gap should also be separated from durability. Resistance to hydrolysis, oxidation, photochemical decomposition or thermal rearrangement depends on reaction pathways and environmental conditions. Neither a smaller nor a larger frontier-orbital gap proves a longer device lifetime. Likewise, a calculated molecular energy does not establish a clearing temperature. These distinctions are especially important when substituent engineering is proposed for practical optical switching, where repeated illumination and temperature cycling can change the material over time.

Spectroscopic Interpretation Using DFT and TD DFT

Infrared spectroscopy probes molecular vibrations and provides an experimental check on the proposed functional groups. Imine, carbonyl, aromatic and substituent-specific vibrations can help identify where substitution affects bonding. A frequency shift is meaningful only when the compared bands represent similar normal modes. In a complex mesogen, a band described casually as a “C=N stretch” may include ring motion and other coupled displacements. Substitution can alter that mixing, so the assignment should follow the displacement pattern rather than proximity to an expected wavenumber alone.

Harmonic frequencies describe vibrations near a selected equilibrium geometry. Experimental spectra additionally reflect anharmonicity, temperature, intermolecular interactions and instrumental conditions. Scaling a computed frequency can improve an empirical comparison, but it does not remove all of these differences. For hydrogen-bonded liquid crystals, the surrounding association network may strongly modify bands involving participating groups. A calculated isolated molecule and an experimental condensed-phase sample consequently need not exhibit identical frequencies even when the electronic structure model is chemically reasonable.

Nuclear magnetic resonance chemical shifts provide complementary structural evidence. Donors and acceptors can change shielding through both local electronic effects and altered conformation. However, assigning a shift solely to a substituent’s electron-withdrawing strength can be misleading when solvent, hydrogen bonding or proximity to aromatic anisotropy also changes. The useful interpretation follows a consistent set of chemically equivalent positions. Agreement among NMR,

infrared evidence and the proposed geometry is more informative than selecting one peak as a stand-alone confirmation of charge transfer.

TD-DFT treats electronic excitations through the response of the density. An excitation can combine several occupied-to-unoccupied orbital contributions, and its oscillator strength measures the allowedness and intensity within the relevant description. The lowest-energy state may be weak or optically dark, whereas a higher state can dominate the absorption spectrum. Thus, a red shift of a prominent band need not track the smallest orbital gap exactly. Substituents can change the energy, intensity and character of transitions independently, all of which matter for optical applications [3]. Charge-transfer excitations deserve special scrutiny because an approximate functional may describe spatially separated electron and hole distributions poorly. Dreuw and Head-Gordon demonstrated serious failures of conventional TD-DFT descriptions for long-range charge-transfer states [5]. Coulomb attenuation in CAM-B3LYP was introduced to improve the treatment of exchange across different distance scales [4]. These foundations justify comparing predictions across suitable functionals rather than accepting a single attractive low excitation energy. They do not imply that a range-separated functional guarantees accurate spectra for every liquid-crystalline molecule.

Natural transition orbitals offer a compact representation of an electronic transition [6]. Their value for substituted mesogens is conceptual clarity: the dominant hole-like and electron-like distributions can show whether a transition is localized on one ring, distributed across the core or displaced between donor and acceptor regions. This representation avoids assigning a complex excited state to one frontier-orbital pair without checking its composition. For a torsionally flexible system, transition character can also help explain why changing geometry alters the band intensity as well as its energy. A material's measured absorption is influenced by more than vertical molecular excitations. Orientational distribution affects how transition dipoles couple to polarized light, while aggregation and local environments can shift or broaden spectral features. A change in a liquid-crystal spectrum near a phase transition therefore cannot automatically be assigned to a changed donor strength. When an electronic transition calculation and a measured film absorption edge differ, the discrepancy may reflect their different physical settings rather than a simple arithmetic error. Spectral interpretation should preserve that distinction.

Molecular Nonlinear Optical Response

Nonlinear optical response occurs when induced polarization contains contributions beyond the term linear in the applied field. At the molecular level, the polarizability α describes the linear electronic response, the first hyperpolarizability β contributes to the second-order response, and the second hyperpolarizability γ contributes at third order. These are tensors. A scalar contraction can facilitate comparison, but the chosen convention must remain consistent. Otherwise, apparent substituent improvements can result from combining different definitions rather than from a genuine change in molecular behavior.

For an ideal molecule possessing inversion symmetry, the electric-dipole first hyperpolarizability vanishes by symmetry. A donor-acceptor arrangement can remove that constraint and permit a substantial β . This does not mean that adding more donors and acceptors always produces a larger

response. Their spatial arrangement can preserve or restore cancellation, and a transverse response may not contribute usefully to a desired longitudinal component. A permanent dipole also does not determine β uniquely: the relevant quantity is the nonlinear field-induced redistribution of electron density.

A simplified two-state interpretation links enhanced first hyperpolarizability with transition strength, the difference between excited- and ground-state dipoles, and excitation energy. It offers an explanation for why some push-pull chromophores respond strongly. It is not a general replacement for the full response calculation. Several excited states can contribute with different signs, and stronger ground-state polarization can alter both geometry and transition moments. A narrow gap can therefore support a plausible enhancement while remaining insufficient to rank every member of a substituted mesogen series.

Figure 2 uses selected numerical entries from Khalid and colleagues' diacetylene study [9] to demonstrate this computational sensitivity. These compounds are mechanistic comparisons; the cited paper does not establish liquid-crystalline phases for them. The figure retains the source's labels and compares gas-phase calculations with the same stated basis set. Its purpose is to show how an apparent substituent benefit depends on the electronic-structure description, rather than to present these numbers as predictions for the liquid crystals discussed elsewhere.

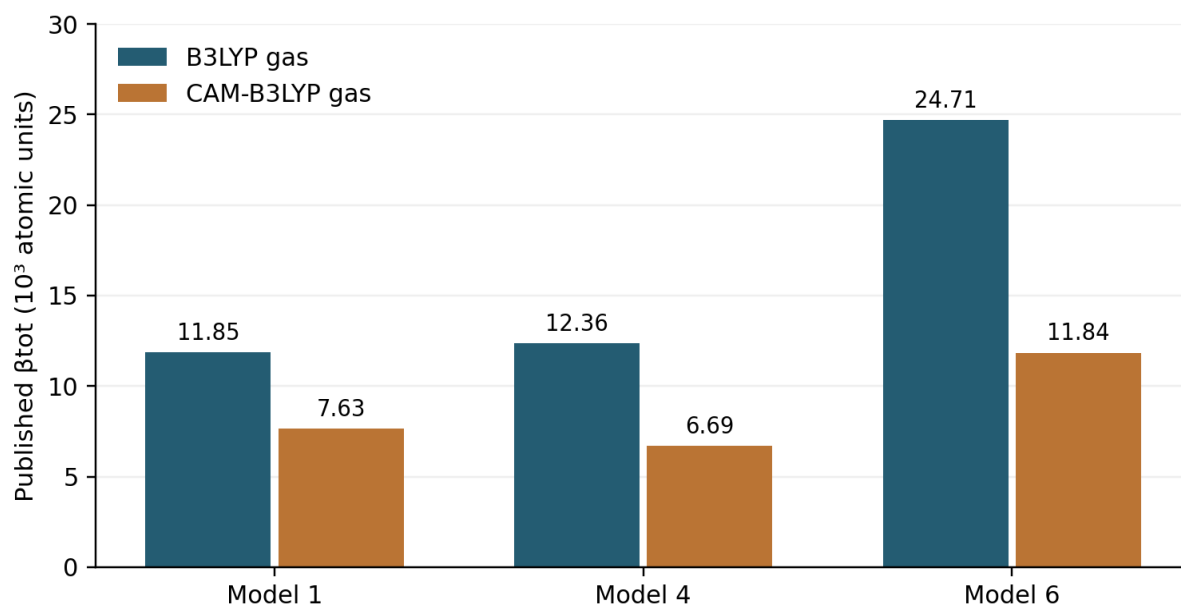


Figure 2. Functional dependence of selected calculated molecular first hyperpolarizabilities. Source: Khalid et al. [9], Tables 5 and 6; gas phase, 6-31G(d,p). Source labels 1, 4 and 6 are retained. These diacetylene models are not established liquid crystals. Original graph; values are computational predictions, not measured bulk response.

The comparison is particularly relevant when a molecular screening study advertises a very large enhancement relative to a weakly responding reference. Ratios become unstable when the denominator is close to zero, and small residual values can be sensitive to geometry or numerical details. Reporting absolute responses and symmetry together is more informative than an enhancement factor alone. Moreover, a basis set appropriate for a geometry calculation may not yet

provide converged response properties. Large numerical precision in a published output should not be confused with demonstrated predictive accuracy.

Static and optical-frequency responses also represent different conditions. A static β corresponds to the zero-frequency electronic response, whereas second-harmonic generation involves a frequency-dependent quantity. Close to resonance, response can increase alongside absorption and heating. An excellent static molecular value is therefore not a sufficient selection criterion for a transparent optical material at a specified wavelength. Vibrational contributions and local environmental effects may additionally influence measured response. The required comparison identifies frequency, tensor convention, units and the physical measurement being interpreted.

Connecting Molecular Response with Liquid Crystal Performance

A material's nonlinear susceptibility depends on molecular response, number density, local fields and orientational statistics. The orientational average is decisive. In a conventional apolar nematic phase, molecular axes can align while opposite head-to-tail orientations remain equally probable. An odd-rank electric-dipole contribution can then cancel in the bulk even when individual molecules are polar and have nonzero β . Birefringence or strong dielectric anisotropy alone therefore does not establish a bulk second-order nonlinear response.

Polar organization supplies a route beyond that cancellation. Chen and colleagues experimentally demonstrated ferroelectricity in a thermotropic nematic material in 2020 [10]. Their work established a macroscopically polar fluid rather than merely a large isolated-molecule dipole. This development is important for substituent design because electronic asymmetry must be accompanied by compatible collective ordering. It should nevertheless not be read as evidence that every nitro- or cyano-terminated mesogen forms a ferroelectric nematic, or that polarization measurements automatically determine its optical susceptibility.

Mandle and colleagues connected differences between closely related molecules with packing and polar organization through experiments and simulation [11]. Their findings support the view that steric architecture can determine whether strong molecular polarity becomes collective order. A donor or acceptor that improves electronic response may simultaneously disrupt favorable packing. Conversely, a comparatively modest electronic change can produce a substantial material-level difference by altering molecular shape. Substituent design is consequently a coupled packing-and-response problem, with no universal rule that maximizes both independently.

Surfaces introduce further control. Experiments on ferroelectric nematic alignment show that surface interactions can organize the polarization field and produce polar monodomains [12]. A bulk molecular calculation contains no representation of that anchoring environment. Device behavior can therefore change even when chemical composition is held constant. The implications for optical design are practical: reproducible alignment, domain structure and temperature control must accompany molecular selection. They cannot be replaced by a favorable gas-phase hyperpolarizability, however carefully that number is computed.

Table 2. Property claims and the evidence needed to support them

Property	Relevant evidence	Inference to avoid
Structure	Bond lengths, torsions and conformer identity	One optimized geometry proves a mesophase
Electronic response	Orbital localization and defined energy differences	Orbital gap equals measured optical gap
Spectroscopy	Assigned modes or excitations and sample conditions	Every band shift proves stronger charge transfer
Molecular NLO	Tensor definition, frequency, units and functional	A static β guarantees optical device efficiency
Bulk liquid-crystal NLO	Polar symmetry, alignment and susceptibility measurement	Nematic alignment guarantees nonzero bulk $\chi^{(2)}$

Original analytical synthesis based on the distinctions developed in the text; theoretical and material context: [1–6,10–12].

Integrated Interpretation and Design Implications

A coherent substituted-mesogen comparison begins conceptually with a chemically matched family. Changes in donor or acceptor identity should be separated from changes in ring count, conjugated length and flexible-chain volume. This is an interpretive requirement, not a claim that such a family has been calculated here. Holding those features comparable makes it possible to distinguish electronic effects from steric ones. If a stronger donor also introduces greater torsion, both changes should enter the explanation rather than assigning the final trend to substituent strength alone. For structural properties, the most useful emphasis is the region that links the donor and acceptor. For electronic properties, it is the localization and direction of redistribution rather than a gap alone. For spectroscopy, it is the connection between transition character and measured band assignment. For nonlinear optics, it is the tensor response under defined frequency conditions. These perspectives form a connected interpretation: geometry controls coupling, coupling controls accessible electronic response, and the material's organization controls how that response survives orientational averaging.

The examples presented here also establish boundaries around numerical claims. The cooling intervals in Figure 1 describe experimentally assigned phases in a real mesogenic series. The values in Figure 2 describe calculated molecular responses in a separate chromophore series. They cannot be merged into a regression suggesting that mesophase width predicts β . Likewise, the data do not support a statistical ranking of all donor and acceptor groups. Their value lies in illustrating two different constraints that a credible liquid-crystalline nonlinear optical material must satisfy.

Transparency and operating temperature create additional tradeoffs. Moving absorption toward longer wavelengths may increase the strength of near-resonant response but reduce the transparent window. Increasing a dipole may promote association while also raising melting behavior or favoring unfavorable aggregates. Introducing a flexible tail may broaden useful phase behavior while lowering chromophore density. These are physically motivated design considerations rather than numerical outcomes established for the title's unspecified molecules. They explain why optimization should remain tied to the intended wavelength, temperature and form of material.

The evidence available before 2026 supports substituent engineering as a powerful but conditional tool. A defensible article can identify mechanisms, compare published numbers and outline consequences without manufacturing a complete new dataset. A future primary investigation would need defined molecular identities and accessible calculation outputs, followed by experimental confirmation of phase and optical behavior. Until then, conclusions should remain at the level supported here: connected molecular mechanisms and published examples, with clear separation between calculated molecular response and demonstrated liquid-crystal performance.

Conclusion

Electron donors and acceptors influence liquid-crystalline molecules through interacting electronic, geometric and intermolecular effects. Conjugated asymmetric substitution can redistribute density and enhance molecular nonlinear response, while torsion, linkage chemistry and substituent position can weaken or redirect that benefit. DFT supports ground-state interpretation; TD-DFT addresses excitation energies and transition character, with particular caution required for charge-transfer states. Spectroscopic comparisons must distinguish molecular calculations from condensed-phase measurements. Published examples show that tail architecture changes mesophase organization and that computed hyperpolarizability can depend strongly on the chosen functional. Neither effect alone establishes device performance. The most useful design strategy combines an electronically responsive core with suitable transparency, anisotropic shape and stable polar organization. The article's graphs and tables are original presentations of attributed evidence and analytical synthesis; they do not represent new experimental or computational results.

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