

ABSTRACT

Liquid crystals (LCs) are materials whose unique properties stem from both molecular and phase symmetry. A key feature of their behavior is the anisotropy of physical properties, particularly optical ones, which can be easily manipulated using external fields and surface effects. This has driven continued efforts to identify and design liquid crystalline phases with diverse symmetries, offering the potential for materials with innovative and valuable properties.

The twist-bend nematic (N_{TB}) phase represents a unique example of spontaneous mirror symmetry breaking in systems composed of achiral molecules lacking long-range positional order. In this phase, the average molecular orientation, referred to as the director, forms a conical helix with a nanometric pitch, with the long axis of the molecule tilted relative to the helix axis. Such a structure opens new electro-optical application possibilities, offering potentially much faster switching times than classical cholesteric materials.

Despite numerous studies, the relationship between molecular structure and the stability and physical properties of the N_{TB} phase remains not fully understood. Molecular bend, which arises from the geometry and flexibility of the spacer linking the two mesogenic arms, plays a particularly important role. The compounds studied in this work are liquid crystalline dimers in which two rigid mesogenic segments are connected by an odd-numbered flexible alkyl chain, often incorporating an additional chemical bridge containing a heteroatom (e.g., oxygen or sulfur). This architecture promotes the formation of bent molecular conformations, believed to be a key factor in the emergence of the N_{TB} phase.

This dissertation presents a comprehensive experimental and theoretical analysis of how the chemical structure of liquid crystalline dimers influences the formation of the N_{TB} phase and its macroscopic properties. For all studied systems, an attempt was made to correlate molecular structure and ordering with the macroscopic characteristics of the nematic and twist-bend phases. A combination of experimental techniques was employed, including polarized optical microscopy, infrared and Raman spectroscopy, as well as measurements of refractive index and dielectric permittivity. These methods enabled the determination of characteristic anisotropies – of refractive index, absorbance, and dielectric permittivity – in both nematic and twist-bend phases.

Special attention was given to the type of mesogenic unit (cyanobiphenyl, naphthalene, terphenyl), the length and parity of the flexible spacer, and the nature of the chemical bridge ($-CH_2-$, $-S-$, $-O-$, $-COO-$, $-OCO-$).

Experimental results were compared with quantum chemical (DFT) calculations, covering molecular conformations, vibrational modes, and intermolecular interactions. The calculated uniaxial and biaxial orientational order parameters were used to determine how the dimer opening angle varies with temperature and to estimate the helix cone angle. This approach enables the construction of a geometrical model that allows indirect estimation of the helix pitch without the need for advanced resonant X-ray scattering techniques (e.g., RSoXS).

The study encompassed both symmetric dimers (CB_nCB , CBS_nSCB , PNS_nSNP , $DTC5Cn$) and asymmetric ones (CBS_nOCB , $CBOCO_nSCB$, $CBCOO_nSCB$), featuring alkyl, ether, thioether, and ester bridges between the two mesogenic groups. Homologous series based on different mesogenic cores – cyanobiphenyl (CB_nCB , CBS_nSCB , CBS_nOCB , $CBOCO_nSCB$, $CBCOO_nSCB$), naphthalene (PNS_nPNS), and terphenyl ($DTC5Cn$) – were compared to assess the influence of core rigidity and dipole moment orientation. Selected asymmetric dimers and their binary mixtures were also analyzed to tune the N_{TB} phase temperature range.

The experimental findings, supported by quantum mechanical modeling, clearly indicate that the type of chemical bridge significantly influences both the conformational flexibility and biaxiality of the molecules, thereby affecting the formation and properties of the N_{TB} phase. The identified relationships provide a foundation for the rational design of new N_{TB} materials with controlled physical properties and stable temperature ranges, suitable for applications in fast-switching electro-optic devices and tunable photonic systems.

The materials studied were obtained in collaboration with Toyohashi University of Technology (Japan) and the University of Hull (UK). The dissertation is based on a series of four peer-reviewed scientific articles, supplemented with new results concerning terphenyl and ester-based dimers.