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Review

Azines as liquid crystalline materials: An up-to-date review

Shwetha Upadyaya, Poornima Bhagavath, Dhanya Sunil *

Department of Chemistry, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal 576104, Karnataka, India.

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ABSTRACT

There are exhaustive reports on the chemistry of organic compounds that exhibits liquid crystalline phases. The present review is first of its kind that emphasizes on an evidence based survey on the mesogenic properties of 2,3-diaza-1,3-butadienes or azines. The article opens with a brief introduction to liquid crystals, their types and commonly observed mesogenic phases in azines. An overview on the structural aspects of azines, their properties and relevant applications are also illustrated. A detailed discussion on the literature reports on the synthesis and application of azines as liquid crystalline materials is provided. Finally, the future prospects of azines as mesogenic materials are also presented.

Contents

1. Introduction

The ever-rising necessity for light-weight and power-efficient display systems triggered the exploration of new materials with electro-optical properties, which paved way to the innovation of substances with liquid crystal (LC) properties. LCs were considered as exotic materials for several years after its discovery as early as 1888 [1]. Currently, they find use in display systems that are based on optical properties of LC materials in response to the presence or absence of an electric field [2,3], thin film thermometers and semiconductors based on colour variation (dependent on pitch of the LC material) with temperature [4,5], LC lasers in the lasing medium as an alternative to external mirrors, switchable windows which can be electrically swapped between transparent and opaque and tunable filters in imaging [6,7].

Liquid crystals or mesomorphs are materials that exhibit an intermediate anisotropic phase of matter with properties between those of conventional liquids and that of crystalline solids. For instance, liquid crystalline mesophases demonstrate certain properties such as inability to sustain shear, fluidity, formation and subsequent coalescence of droplets which are characteristic of a liquid. In addition, they also possess typical features of crystalline solids such as regular molecular

* Corresponding author.
E-mail address: dhanya.s@manipal.edu (D. Sunil).

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organization in one or more spatial directions exhibiting electrical, optical and magnetic anisotropy [8]. Liquid crystals are classified into two types; i) the most common thermotropic, achieved by the action of temperature (either by heating a crystalline solid or cooling its melt) and ii) lyotropic found in certain colloidal solutions, based on the concentration of mesomorphic material or by the action of solvents [9,10].

Thermotropic nematic LCs represent the most technologically important mesogenic molecules, that are either rigid rod-like or disc-shaped [11]. They display either a single or a sequence of mesophases over a narrow to wide temperature range depending on the material. Thermotropics are widely used as operating fluid in LC displays (LCDs), in colour information technology-based applications [12] and organic electronic devices like light-emitting devices (OLEDs) and solar cells. Depending upon the molecular symmetry or arrangements in a mesophase, LCs are subdivided into four (Fig. 1) as;

i) Nematics (Fig. 1A): molecules possess a long-range orientational order with their long molecular axes aligned along a most favored direction called the director. The conformationally flexible backbones of the molecules enable them to rotate around their long axes, without any preferential arrangement of their end groups. The only restriction on the molecular arrangement is that they retain either a parallel or closely parallel orientation. Owing to the intrinsic microscopic order, their macroscopic arrangement is greatly facilitated by the application of mechanical, electrical or magnetic force/field.
ii) Cholesterics (Fig. 1B): retain long-range orientational order resembling nematics, but the director distribution is accomplished by twisting the nematic arranged alongside the y axis about the x axis. A phase transition between nematic and cholesteric phases do not happen since a nematic mesophase is a cholesteric one of infinite pitch (distance along the twist axis over which the director rotates through a full circle).
iii) Smectics (Fig. 1C): characterized by higher liquid crystalline order: both orientational and positional. They present a stratified, layered molecular arrangement with their long axes almost perpendicular to the planes of the layers, which are free to slide over one another. Based on the order of molecular arrangement in layers, various smectic forms have been identified and the most commonly witnessed are; smectic-A (S_A), in which molecules are aligned normal to the layers, lacking any long-range order within them (Fig. 1D), smectic-B (S_B), a hexagonal crystalline order is identified within the layers (Fig. 1E) and in smectic-C (S_C), the preferred molecular axis is not normal to the layers and has a biaxial symmetrical phase (Fig. 1F). Many LCs that are reported display both nematic/cholesteric and smectic mesophases. Generally, the smectic phases are observed at a lower temperature which have a higher crystalline order, whereas the nematic mesophase are always detected at a higher temperature. The smectic phases follow the order: $S_A \rightarrow S_C \rightarrow S_B$ with decrease in temperature.
iv) Columnars: are flat-shaped discotic molecules stacked into cylindrical structures (Fig. 1G).

If the transition from one mesomorphic phase to another is reversible, it is termed as enantiotropic polymorphism. However, if it is an irreversible transition, then the polymorphism is classified as monotropic. Generally molecules that exhibit mesomorphism are either elongated or in some cases flattened with one or more polar groups, which facilitates a parallel positioning with each another. In the crystalline state, the molecules of a mesomorphic material have both long range orientational and positional order, and are held together by strong electrostatic forces between the polar groups and also by van der Waals interaction. On heating the solid LC material, the weaker bonds break initially, permitting some amount of relative movement. Further, on acquiring sufficient thermal energy, the molecules align themselves parallel to one another. Though the system finally turns into fluid in due course of heating, it remains birefringent due to the preferred orientation of few molecules. Most of the mesomorphic materials form smectic or nematic structure.

1.1. Textures formed by mesogenic materials

The first stage in the examination of the liquid crystalline nature of materials relies on thermal approaches of analysis. A mesomorphic substance in its crystalline state on heating, absorbs the supplied energy and transforms itself into an LC state and with further increase in temperature, absorbs more energy and converts to an isotropic liquid (I). Thermal analysis using a polarized optical microscope (POM) and differential scanning calorimeter (DSC) thereby permits to detect this sequence of phase transitions.

The identification of a certain texture is the preliminary step to distinguish the mesophase structure. POM is employed to perceive the textures of mesophases, by taking advantage of their anisotropic property, specifically birefringence, when it interacts with the polarized light. The appearance of nematic schlieren (Fig. 2A) or droplets texture (Fig. 2B) through POM of LC materials confirms a nematic (N) phase, whereas presence of focal conic fans endorse the S_A phase (Fig. 2C). Besides, other smectic textures like S_B focal conic fans (Fig. 2D), S_C schlieren (Fig. 2E) and S_G mosaic (Fig. 2F) are also observed. In S_G phase, the molecules are having a pseudo-hexagonal close packing; in the plane at right angles to the tilt direction. The appearance of transition bars ratifies S_A to S_B phase transformation. The characteristic textures pertaining to these mesophases are depicted in Fig. 2.

1.2. Characterization of liquid crystal materials

Physical anisotropy, fluidity and response to an applied electric field, are features typical of LCs. Various experimental techniques like thermal, spectral, electrical and optical can be used to characterize mesomorphic materials. Thermal characterization comprises of the POM equipped with a precision temperature controller and DSC that inspects

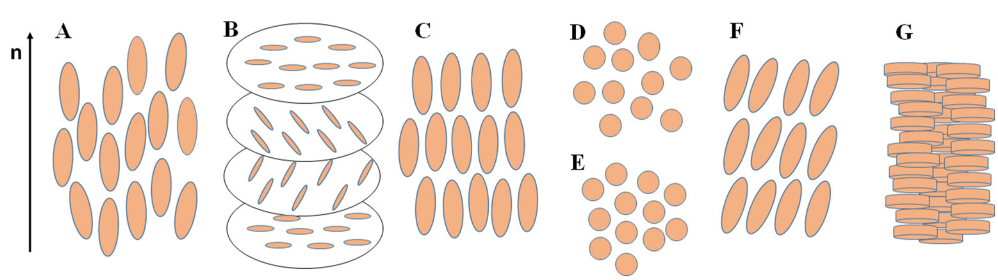

Fig. 1. Representation of molecular alignments in LC mesophases: A) nematic with molecular orientational order, while there is no positional order, B) cholesteric in which the average molecular orientation twists with a certain periodicity through the medium, without any positional order, C) smectic, D) S_A where molecules align in planes, with their axes at right angles to the planes, but devoid of any order within the planes, E) S_B with hexagonal molecular packing, F) S_C where the molecules are tilted within the planes and G) disc shaped columnar mesophases.