

A Review of Liquid Crystal Dimers

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Abstract

Liquid crystal dimers are formed by linking two mesogenic groups by an alkyl chain spacer. They have been attracting a great deal of interest in recent years both in theoretical and experimental studies due to their quite unusual properties as compared to conventional low molar mass liquid crystals. Dimers can be divided in two classes viz symmetric and non-symmetric dimers. In symmetric dimers, both the mesogenic groups are identical whereas in non-symmetrical dimers, both are different. Dimeric structures depend upon the number of carbon atoms in the spacer. The nematic-isotropic transition temperature is found to alter as the number of carbon atoms in the alkyl spacer changes from odd to even. Liquid crystalline dimers are attracting much attention because they exhibit variety of phases and serve as useful models for the semi-flexible main chain liquid crystal polymers. This paper reviews the important properties, classification and application potential of the liquid crystalline dimers.

Key words : Liquid Crystal Dimer, Mesogen.

Introduction

Liquid crystals designates a state of matter that is intermediate between the solid crystalline and the ordinary liquid phases. It was first discovered by an Austrian Botanist Fridrich Reintzer in 1888. After the accidental discovery the term liquid crystal was first used by O. Lehmann in 1890. Liquid crystalline materials are unique in their properties and use. Liquid crystals flow like ordinary liquids. On the other hand they exhibit anisotropy. Liquid crystals are also called mesophases or mesomorphic phases because of their intermediate nature.

In general, liquid crystals are isotropic liquids at high temperatures and as the temperature is reduced they exhibit phase transition into anisotropic phases. Liquid crystalline materials generally have anisometric molecular structures that are either rod-like or disk-like in shape.

Distinguishing features of solid, liquid and liquid crystal

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules i.e. mesogens to point along a common axis, called

the director. This is in contrast to molecules in liquid phase which has no intrinsic order. In the solid state, molecules are highly ordered and have little transitional freedom. The characteristic orientational order of the liquid crystalline state is intermediate between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with the liquid crystal state. The average alignment of the molecules of the molecules for each phase are shown in the following diagrams.

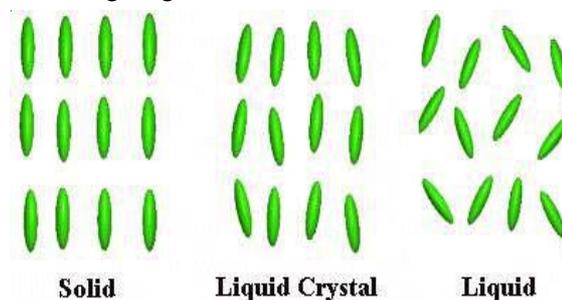


Fig. 1: Alignment of molecules in solid, liquid crystal and liquid

It is sometimes difficult to determine whether a material is in the crystal or liquid crystal state.

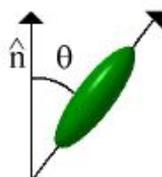
Crystalline materials demonstrate long range periodic order in three dimensions. By definition an isotropic liquid has no orientational order. Thus substances that are not as ordered as a solid, yet have some degree of alignment are properly called as liquid crystals.

Parameters determining liquid Crystalline structure

The following three parameters describe the liquid crystalline structure:

1. Positional order
2. Orientational order
3. Bond orientational order

Each of these parameters describes the extent to which the liquid crystal sample is ordered. Positional order refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows). Orientational order represents a measure of the tendency of the molecules to align along the director on a long-range basis. Bond orientational



$$S = (1/2) \langle 3 \cos^2 \theta - 1 \rangle$$

order describes a line joining the centres of the nearest- neighbor molecules without requiring a regular spacing along that line. To quantify how much order is present in a material an order parameter(s) is defined. Traditionally, the order parameter is expressed as

where *theta* is the angle between the director and the long axis of each molecule. In an isotropic liquid crystal, the average of the cosine terms is zero. For a perfect crystal, the order parameter evaluate to one. Typical values for order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result kinetic molecular motion.

Classification of liquid crystals

Liquid crystals can be broadly classified into two groups viz thermotropic and lyotropic, depending on the processes by which the intermediate phases occur. However, on the basis of their molecular

structures liquid crystals are divided into four comprehensive groups viz calamitic and discotic.

Thermotropic liquid crystals are the types of liquid crystals which are formed when the temperature is varied. These crystals are formed while heating a solid or cooling an isotropic liquid. Thus they are temperature dependant.

Lyotropic liquid crystals are those in which the intermediate phases are inhibited under the influence of the solvents on solids or liquids. A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases. They play an important role in biological systems but no technical applications are known yet. Soap is an everyday example of a lyotropic liquid crystal.

Calamitic liquid crystals are composed of rod-like molecules with one molecular axis much longer than the other two. A typical calamitic mesogen consists of rigid core unit, ensuring the anisotropic character together with flexible side chains, which provides stability effects within the liquid crystal phases.

Discotic liquid crystals are formed on heating compounds that are composed of relatively flat, disc shaped molecules. These have been recognized as a distinct class of liquid crystalline compounds where the short axis of the molecules maintains a preferred orientation.

Different phases of liquid crystal

Typically there are three anisotropic phases. They are called nematic, smectic and cholesteric phase. In the nematic phase, these molecules have an orientational order but there is no positional order. In fig. 2(a) we notice that the molecules point vertically but are arranged with no particular order. In the cholesteric phase shown in fig.2(b) the molecular orientation in a plane rotates spirally in direction perpendicular to the plane. If a nematic

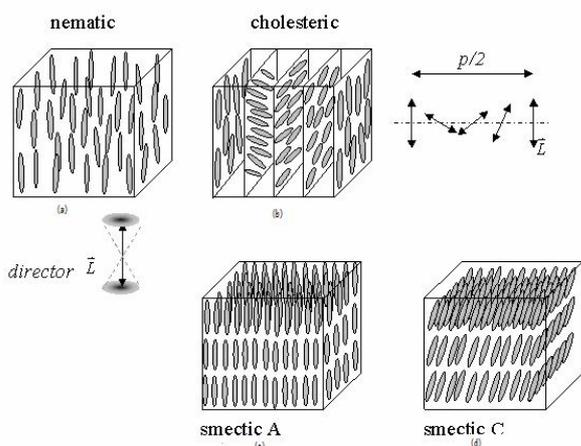


Fig. 2 : Liquid crystalline mesophases

liquid crystal is made of chiral molecules, i.e. the molecules differ from their mirror image; a cholesteric liquid crystal is obtained. Locally, cholesterics can be practically not distinguished from nematics but the preferred orientation forms a helical structure, with the helical axis perpendicular to the director

In the smectic phase, an additional spatial order appears. The smectic phases are characterized by additional degrees of positional order. Generally, the molecules are arranged in layers in these mesophases, which can be considered as one-dimensional density waves. There are various kinds of smectic phases but the most important are smectic A and smectic C. In smectic A (SmA) shown in fig.2(c), liquid crystals the molecular orientation is perpendicular to the layers, whereas the director is tilted in the SmC phase shown in fig.2(d). Both show no positional order within the layers and therefore are often considered as two-dimensional liquids.

Introduction to liquid crystal dimers

The orientational and translational ordering of the molecules in liquid crystals gives rise to a rich variety of mesophases. One of the most interesting groups of liquid crystalline compounds is that of the liquid crystal dimers. Normally, calamitic liquid crystals have a mesogenic region with terminal alkyl chains at the two ends. Liquid crystal dimers are formed by linking two mesogenic groups by an alkyl chain (spacer). Liquid crystal dimers have been attracting a great deal of interest in recent

years both in theoretical and experimental studies due to their quite unusual properties as compared to conventional low molar mass liquid crystals. They serve also as model compounds for semi flexible main chain liquid crystal polymers.

Types of dimers

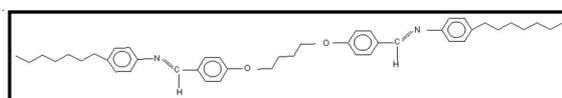
These dimers are divided into two categories

1. Symmetric dimers and
2. Non-symmetric dimers

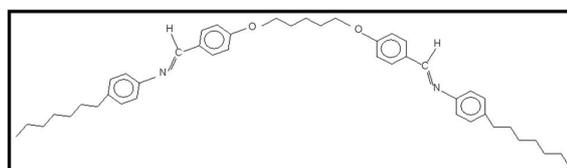
In the symmetric dimers, both the mesogenic groups are identical whereas in the non-symmetric dimers the two mesogenic groups are different.

Properties of dimers

The liquid crystalline properties as well as the classes of compounds in this type are found to be dependent on the number of carbon atoms in the spacer. The nematic-isotropic transition temperatures are found to exhibit a dramatic alternation as the number of carbon atoms in the alkyl spacer changes from odd to even. However, the alternation is attenuated as the spacer grows in length. In contrast the alternation in the entropy of transition is essentially unattenuated, at least for spacers containing upto twelve carbon atoms. In addition the entropy change at the nematic-isotropic transition for dimers with odd spacers is comparable to that of monomer while for even spacers the transitional entropy is typically three times larger. The behaviors of the transitional entropy suggest that the orientation order for even



LIQUID CRYSTAL DIMERS FOR EVEN SPACERS



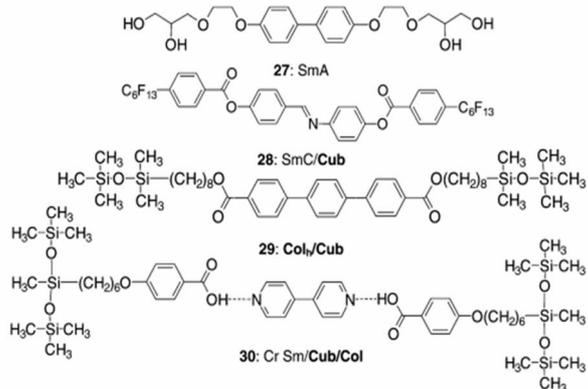
LIQUID CRYSTAL DIMERS FOR ODD SPACERS

Fig. 3 : The different shapes of the molecules forming liquid crystal dimers (even and odd) with chain linking the two mesogenic groups in its all-trans conformation.

spacers should be significantly greater than that of odd. Further, the order parameter for the odd dimers is observed to be comparable to those for the analogous monomers and significantly smaller than those for even dimers. This dramatic and unusual behavior of the transitional properties of the liquid crystal dimers has been attributed to the pronounced difference in their molecular topologies. These are sketched in Fig. 3.

For the even spacer, the mesogenic groups are parallel although the molecule has a zigzag appearance. In contrast, the odd dimers are bent with the mesogenic tilted with respect to each other. It is clear that the zigzag shape of the even dimers is more compatible with the molecular organization of a mesophases than the bent form of the odd dimers, apparently in accord with the behavior of liquid crystal dimers. The following structure shows some of the liquid crystal dimers.

STRUCTURE OF A DIMERIC LIQUID CRYSTAL



References

Date, R.W.; Imrie, C.T.; Lukhurst, G.R.; Sneddon, J.M. (1992). Smectogenic dimeric liquid crystals. The preparation and properties of the α , ω -bis(4-*n*-kylanilinebenzylidene-4'-oxy)alkanes. *Liquid Crystals*. 12(2):203-238

Date, R.W.; Lukhurst, G.R.; Shuman, M.; Sneddon, J.M. (1995). Novel modulated Hexatic Phases in Symmetric Liquid Crystal Dimers. *Journal de Physique II*. 5(4):587-606

Ferrarini, A.; Lukhurst, G.R.; Nordio, P.L.; Roskilly, S.J. (1993). Understanding the unusual transitional

Applications of dimers

The applications of dimers are as follows

- Properties of the dimers are yet to be completely explored
- Initial investigations reveal that they may potentially be used as high capacity storage devices
- These dimers are the precursors to liquid crystalline polymers and hence the properties of these dimers prove useful in understanding the behavior of polymeric liquid crystals

behaviour of liquid crystal dimers. *Chem. Phys. Lett.* 214(3-4):409-417

Gogoi, B.; Bhattacharjee, P.R.A.; Verma, A.L.(2003). Laser Raman studies on compounds 7.O4O.7 and 7.O5O.7 *Liquid Crystals*. 30(8): 931 – 938

Heeks, S.K.; Lukhurst, G.R. (1993). Deuterium nuclear magnetic resonance study of the orientational order in the nematic phase of 4-*n*-pentyloxy-4-cyanobiphenyl. Tests of the Emsley–Lukhurst–Stockley theory and of the Haller extrapolation. *J. Chem. Soc., Faraday Trans.*89:3783-3790