Journal of the Chinese Chemical Society, 1989, *36*, 375–388

Invited Paper

MESOPHASES I.

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In this review of the properties and applications of mesophases, after a general description of the states of aggregation of matter, the types of liquid crystals are distinguished. The thermotropic liquid crystals are classified on the basis of their structural properties. A comparison of sets of chemically related molecules indicates how details of molecular structure (topology and conformation) affect the existence and sequence of mesophases for the lath–like thermotropic mesogens.

INTRODUCTION–STATES OF AGGREGATION OF MATTER

Ordinarily we consider that there exist four states of aggregation of matter: a solid body (whether crystalline or amorphous) that supports its own shape, and resists a shear stress; liquid matter that takes the shape of its container up to a certain level; gaseous matter that fills completely any available space (of finite volume), and plasma matter that consists of mixtures of atoms, ions and electrons, commonly existing under either rather extreme conditions of temperature and pressure or in the presence of electric and magnetic fields. That some chemical substances can exist in different crystalline structures–polymorphism–is well known; the different structures may reflect either allotropic forms with different structural units, as in the case of white and red elemental phosphorus, or a different packing of the same component units as in the case of $CaCO_3$, calcite and aragonite. Some amorphous, apparently solid materials, especially if pure substances, may be considered to be supercooled liquids, whereas others, such as various silicate glasses, are complicated mixtures of compounds for which no proper crystalline state exists at all. Only one substance helium exists in two liquid phases[1] both of which are isotropic, *i.e.* the physical properties have no dependence on direction within the liquid substance; in the superfluid phase at temperatures less than 2.2 K, liquid ^{4}He shows properties on a macroscopic scale that have been attributed to quantum–mechanical effects (it has been described as a degenerate boson gas). All pure, liquid substances, but not necessarily their mixtures, can be transformed to gases with a continuous change of properties by passage around the critical point. However, we generally expect abrupt changes of properties to occur during the transformation of pure substances from the solid to liquid phases. In fact for many pure substances, possibly five per cent of all organic compounds, as well as various mixtures, there are known mesophases: these are thermodynamically stable phases that have properties characteristic of both true (crystalline) solids and true (isotropic) liquids. Such mesophases exist within a range of temperature for each applicable pure substance between conditions in which properties characteristic of either true solids, at temperatures below the mesophase region, or true liquids, at temperatures above the mesophase region, are displayed. For certain kinds of mixtures, the mesophases exist within certain definite ranges of concentration at a particular temperature. Thus in both cases a mesomorphic state may be considered to be a true state of aggregation of matter, for those substances for which its properties have been identified, in addition to the other states of aggregation listed above.

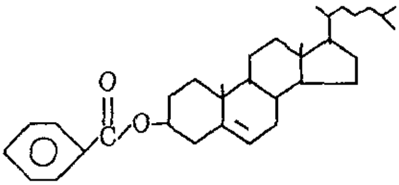
The prefix 'meso' means middle, and the two kinds of mesophases that have been found to exist between (or amid) the solid and liquid phases are commonly referred to as liquid crystals and plastic crystals. Liquid-crystalline substances may be considered to be solid–like liquids; the melting process appears to take place in stages such that the liquid–crystalline mesophase, or one such mesophase of several in a possible sequence, represents a condition of incomplete melting. In contrast, plastic crystals are liquid–like solids in which premelting phemomena occur; whereas plastic crystals have traditionally been treated in the literature of the solid state, they are among the most disordered of all mesophases and therefore may be considered the most liquid in character. In both cases, the macroscopic properties can be understood in terms of microscopic conditions, specifically, the structure, order and motion of molecules in these condensed phases. Both the absence of long–range order and the mysterious effects of intermolecular interactions have however prevented a quantitative characterization of these mesophases to the extent that has been achieved for either the regular crystalline or gaseous state. Not only are such liquid–crystalline mesophases known for compounds of relatively small molar mass, but also polymeric substances are known[2,3] that exhibit these properties as a result of the presence of certain kinds of groups in either a main chain of the polymer or the side chains. The investigation of such polymers has commenced more recently than for the compounds of smaller molar mass, but in due course perhaps the technological applications of the polymers will become the more important.

At present, not only has a century elapsed since the first clear recognition of liquid crystals, but also a half century since the characterization of plastic crystals. The technological applications of these liquid–crystalline compounds are already of great importance; although there is a rapidly growing specialised research literature on liquid crystals, their discussion, and even their existence, are commonly neglected in standard texbooks and general reviews for all branches of chemistry. Here we present a general survey of the properties and applications of mesphases, combining the traditional chemical aspects with the recent developments in relation to materials science so as to indicate fruitful directions of present and future research. There is great scope for research in this subject across most branches of chemistry and the related physics and materials science, and the stimulation of this research interest would be a worthy objective of this review. Any nation that seeks to maintain a strong effort in the research and development of electronics must also ensure that a meaningful research effort exists in the associated display technology, for which, among other applications, liquid–crystalline materials are already of immense importance. An improved awareness of this important state of matter by teachers of chemistry at all levels who can thus cinvey some of the recent exciting developments to their students would also be an appropriate objective, because all teachers and their students are aware of some common applications.

The review is divided into two parts. In this part I we summarize the general classes of liquid crystals and illustrate by several instances how the effects of molecular structure affect the mesogenic properties. In part II to follow, we discuss the thermodynamic properties of both liquid crystals and plastic crystals, drawing comparisons between the structural forms and the nature of the mesomorphic properties, and we also indicate how some applications of these materials depend on the molecular structure. The selected references for both parts are numbered in one sequence and listed at the end of the part in which the first citation is made; the sections, figures and compounds of both parts likewise bear a common numbering sequence.

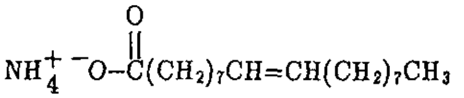
2. Types of liquid crystals

The phenomenon of liquid crystallinity was clearly described by the botanist Reinitzer in 1888, and during the following year the physicist Lehmann first described the optical properties of liquid crystals[4]. Reinitzer found that on heating cholesteryl benzoate (1),



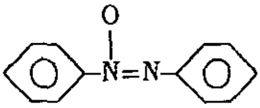
(1)

extracted from a plant, there formed first at 418 K a turbid (translucent or of milky appearance) system that although flowing as readily as a moderately viscous oil retained many characteristic optical properties of crystalline substances, before transforming at 452 K to a transparent liquid. Lehamann determined that ammonium (Z)-9-octadecenoate (or oleate) (2)



$$NH_4^+\ {}^-O{-}\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_7CH{=}CH(CH_2)_7CH_3$$

(2)



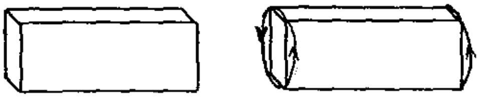
(3)

and derivatives of azoxybenzene (3) were also mesogens, *i.e.* pure substances capable of displaying the properties of mesophases each within a certain range of temperature. These simple visual observations of physical properties may still be used to distinguish the existence and transformations of mesophases, but naturally more quantitative measurements require sophisticated instruments. The latter commonly include a polarizing microscope (an optical microscope arranged to operate with polarized light, also equipped with a heating stage), a differential scanning calorimeter which permits the determination of the temperatures and enthalpy changes of the transitions between phases, and an xray diffractometer. Although few if any mesophases by their very nature provide by the latter means diffraction patterns that can characterize the intramolecular and supramolecular structure in the precisely quantitative manner now practised for regular crystalline phases that lack significant molecular motion or disorder, nevertheless these sparse patterns for mesophases do permit in successful cases the distinction of one mesophase from another, the classification of the mesophase, and some qualitative or even semiquantitative information about the supramolecular arrangements.

There are two main types of matter having these liquid-crystalline properties. Lyotropic liquid crystals are commonly formed as a result of the action of a limited proportion of solvent on the solid. Such a mixture could be stable as a liquid crystal within a limited range of concentration and temperature; with greater proportions of solvent or at greater temperatures an isotropic liquid solutin is formed. Generally, such amphiphiles as the synthetic substances used as detergents (for instance alkali salts of long-chain alkyl sulphonates), soaps (for instance potassium octadecanoate) and polypeptides are found to display liquid-crystalline properties with solvents such as water, methanol or dichloroethanoic acid. The technological applications of these lyotropic mesogens are so far little developed, but they serve as models of biochemical interest. Some more specific structural features of these lyotropic phases are discussed in part II, so as to benefit from the comparison with the other type, the thermotropic liquid crystal. Thermotropic mesogens are substances that become liquid crystals purely by thermal effects, *i.e.* heating a crystalline solid or cooling a true liquid, as a result of their intrinsic molecular structure and intermolecular interactions.

THERMOTROPIC LIQUID CRYSTALS

Distinguished by Friedel in 1922, two main classes of thermotropic liquid-crystalline mesophases are nematic (from Greek nema, meaning thread) and smectic (from Greek smectos, meaning grease or slime or soap-like). We consider these mesophases to be intermediate stages of relaxation of long-range order between the crystalline phase, having the order of a three-dimensional lattice, and the liquid phase, having only short-range order. The molecular shape common to most thermotropic mesogens other than polymeric compounds is either more or less elongated, so resembling a rod, or disk-like, termed discotic; the molecules of the former shape, at rest, have commonly more width than thickness, so they are conveniently described as haveing the shape of a lath. However in some phases in which rotation (really reorientation) about the long molecular axis can readily occur, such as the nematic and certain smectic phases, the volume swept out by the molecule is effectively cylindrical in nature. The smectic mesophases, of which at least twelve have been distinguished[5,6] by means of their optical and thermal properties, xray diffraction patterns and miscibility properties, have a two-dimensional order such that molecules align with their long axes parallel in layers; the molecules can migrate easily between layers, unlike in solid phases, and the layers move relatively freely over one another, in response to a shear stress for instance. The smectic mesophases can be further subdivided into th uncorrelated two-dimensional class, in which the structural arrangement in a given layer is not correlated with that in neighbouring smectic layers so that each layer resembles a two-dimensional liquid, and the class in which a long-range structural correlation (*i.e.* three-dimensional) exists over many layers and so each layer has some features of a two-dimensional solid. Mesophases of the latter class exhibit the more ordered structures, which are in fact particularly plastic three-dimensional crystals, but disordered.



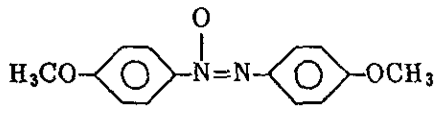
The nematic mesophase signifies a kind of molecular packing in which the molecules are spontaneously oriented in a parallel fashion, with the long axis of each molecule statistically parallel to an exis called the director, but there is no particular coherence of molecular positions (according to their centres of mass) in directions perpendicular to the director; thus only a one-dimensional order prevails. In the true crystalline phases of nematic mesogens, commonly the long axes of the molecules are approximately parallel, and for smectic mesogens the crystal structure is characterized by layers containing molecules similarly aligned in parallel; thus the transition to the mesophase involves mainly the lateral order between the molecules, and in some cases a lateral disorder persists even in the crystalline phase[5]. Under the polarization microscope, one may observe thread-like regions in thin films of these nematic substances; such a region in which a given orientation is preserved is called a domain. The nematic phase is both mobile and markedly affected by external fields and forces; therefore the molecules therein also possess considerable mobility and are capable of (somewhat hindered) rotational motion about the long axis. The fluidity of nematic mesophases is due to the ease with which molecules slide past one another although retaining a common alignment. In the bulk of a nematic mesophase the preferred direction of alignment may vary in different portions of the medium, corresponding to different domains, but a homogeneously aligned sample exhibits the optical properties of being uniaxial and strongly birefringent *i.e.* the refractive index takes two principal values in directions parallel and perpendicular to the aligned molecules. Nematic mesophases are optically inactive, *i.e.* they do not rotate the plane of polarization of linearly polarized light. If a nematic layer is however sandwiched between two glass plates, which are then rotated, optical activity may be induced as a result of the gradual twisting of the the direction of the long molecular axes which are aligned parallel to the glass surfaces.

An important subgroup of the nematic class, that might be considered almost a separate class, is the chiral nematic category of compounds; because of the existence of many derivatives of cholesterol (but not cholesterol itself) in this category, including one (1) of the first substances recognised to have liquid-crystalline properties, this subgroup is commonly also referred to as the cholesteric type. However, some derivatives of cholesterol have no cholesteric mesophase but pass directly from a smectic mesophase to the isotropic liquid. The cholesteric mesophase occurs only in optically active (chiral) substances, and corresponds to a twisted nematic layer that results in a helical structure. A nematic phase may be converted into a cholesteric phase by the addition of small proportions of an optically active compound, whether or not the latter exhibits any intrinsic mesomorphic properties; conversely, in a mixture at some finite molar fraction of one component, two cholesteric materials of opposite helical senses may produce a non-twisted nematic phase. Therefore a cholesteric phase may be regarded as a twisted nematic phase with a new director associated with the axis of the macromolecular cholesteric helix. For these cholesteric mesophases, the distance between the two nearest layers with parallel directors is called the pitch of the rotation of the helical structure; this pitch varies typically in the range 2×10^{-7} -- 2×10^{-5} m, and depends for a given substance on temperature, pressure, and the presence of electric and magnetic fields. The pitch generally decreases as temperature increases. The helical arrangement of the molecules in the cholesteric mesophase is responsible for the special optical properties: selective reflection of circularly polarized light, and an optical rotatory power thousands of times as great as that of ordinary chiral compounds.

Polymesomorphism is possible for mesogens, just as polymorphism exists for some crystalline compounds. The various mesophases are distinguished by their different optical, thermal and other physical properties and by their xray diffraction patterns; because of the relative lack of long-range order, the latter patterns are commonly sparse, leading to information about only the supramolecular structure not the intramolecular structure, but may nevertheless be useful for purposes of characterization. Typically only one nematic phase exists for a given compound, although in exceptional cases of either a pure substance or a mixture further nematic phases, caled re-entrant nematic, may be discerned at temperatures below the ranges of smectic phases. In contrast at least twelve possible smectic phases are known[5,6], although no single known compound displays them all. Both cholesteric and nematic mesophases cannot occur for the same pure substance. Some cholesteric mesogens also display further phases between the cholesteric mesophase and the isotropic liquid. There are also a few substances, for instance bis(2-methylpropyl)silandiol, that belong to no class of thermotropic mesogen specified above. Some liquid-crystalline mesophases are only metastable, being formed during cooling (supercooling) from the isotropic liquid phase but not during heating from the crystalline solid phase; this behaviour is called monotropism, just like the corresponding property for crystalline phases. In contrast, the truly stable liquid-crystalline phases of enantiotropic mesogens are formed reversibly during thermal treatment by means of both heating and cooling processes.

CLASSES OF THERMOTROPIC MESOGENS[5,6]

We may consider 4,4'-dimethoxyazoxybenzene (4) to have properties typical of a



(4)

lath-like liquid-crystalline mesogen; the length of the molecule between the terminal methyl groups is much greater than the width, and the structure of the molecule between the oxygen atomic centres may be considered fairly rigid. Thus a mesogen molecule consists characteristically of both a core structure characterized as having moderate rigidity and flexible appendages such as alkyl groups. (The quinquephenyl compound (5) is exceptional in having a nematic phase in the range of temperature 674–718 K between

(5)

crystalline and isotropic liquid phases despite the complete absence of alkyl appendages.) The direction approximately between the methyl groups in (4) is considered to be the long axis of the molecule, and the molecule may be represented by a line parallel to this long axis. Although the long axis might also be expected to have a *sense* of direction, as conventionally represented by an arrow head, in liquid-crystalline phases commonly no sense of direction is maintained in adjacent molecules; thus such liquid-crystalline phases display no ferroelectric properties. However, in certain smectic phases (*vide infra*) of chiral molecules, the presence of the asymmetric atomic centre in the molecules prevents the presence of planes of symmetry in the packing of the molecules together (loosely); in this case a weak ferroelectric effect may be observable in a direction within the layers of molecules, approximately perpendicular to the director. The nematic phase can then be depicted by a series of parallel lines, but the centres of molecular mass are disordered as in a liquid. In figure 1 we depict schematically the structures of several liquid-crystalline mesophases for comparison. In this diagram each line in a side view represents the long axis of a molecule, for instance the vector between the two methyl groups in (4); in the case of the cholesteric phase each line in the side view represents the projection of the long axis in the plane of the page.

In the smectic A phase, the molecules are also aligned but within layers, with the directors parallel to the long axes and perpendicular to the planes of the layers. Within each layer of molecules, except for the parallel alignment of the long axes of the molecules there is no particular order, and no precise reproducibility of the distance between adjacent molecules. That there exist subclasses of the smectic A mesophase was first demonstrated by a phase transition that was detected calorimetrically but not observed optically. Xray studies have since revealed that the thickness of the layers of the phase A_1 at temperatures above this transition corresponds essentially to the length of one molecule, whereas below this transition temperature layer spacings in A_2 corresponding to both one and two lengths were observed. In the phase of the monolayer type A_1 the polar heads of the lath-like molecules are randomly oriented, whereas in the phase of the bilayer type A_2 the dipoles are all oriented parallel within one layer but all parallel in the opposite sense in each adjacent layer. A phase of the third type A_d with interdigitated layers has a layer thickness between one and two molecular lengths; the structure therein, having the polar heads at the boundary of a layer, is similar to the A_1 phase, but the molecules do not extend completely across the layer. If the polar molecules were all aligned parallel and in the same dipolar sense in every layer, then the entire liquid crystal would have a macroscopic dipole moment, the phenomenon called ferroelectricity. This behaviour is not so far observed for any smectic A phase but is known for a smectic C phase of chiral molecules.

The smectic B phases are two distinct subclasses. In the crystal B variant, there is hexagonal close packing within each layer, with the long axis of each

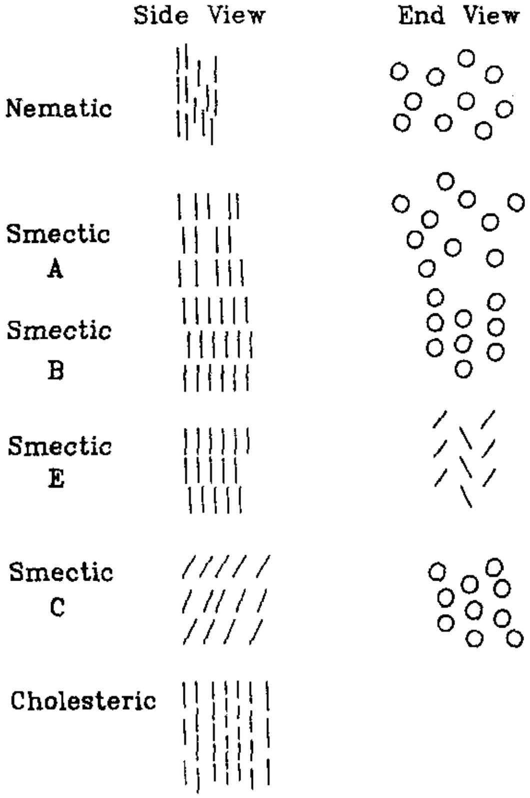
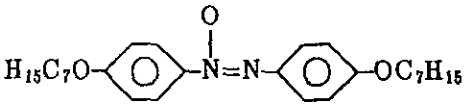


Fig. 1 Schematic representation of structures of thermotropic liquid-crystalline mesophases. In the side views, each line represents the long axis of a prototypical molecule, except that for the cholesteric mesophase each line represents the projection of the long axis in some plane containing the projector. For enhanced clarity, the scale of the end views (cross-sections) is larger than that of the side views.

molecule parallel to the director; rotation of a molecule about its long axis is possible, hindered rather than free and probably cooperative, and any orientation of the plane in the width of the molecule (across a phenyl ring in the azoxybenzene compound (4), for instance) is also possible, so the molecule effectively occupies a cylindrical volume. Commonly encountered in the sequence of mesophases

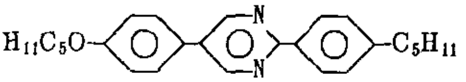
$$C \rightarrow S_E \rightarrow S_B \rightarrow S_A \rightarrow N \rightarrow I$$

the smectic E phase is related to the crystal B phase. Here C means the crystalline solid phase, and I means the amorphous isotropic liquid phase; the other symbols denote the nematic N and the various smectic S mesophases. In contrast, in the hexatic B phase, there exist stacks of interacting hexatic layers; within the planes of the layer there is short-range positional correlation, but negligible correlation between the layers, although there is a three-dimensional sixfold orientational order of the chemical bonds. This mesophase occurs between the smectic A (a fluid phase with negligible positional correlations both within the planes of the layers and between the layers) and three-dimensional mesophases with long-range translational order, such as the crystal B or E pahses. The smectic F and I phases correspond to tilted analogues of the hexatic B phase. In the case of the smectic E phase the plane defined by the width (of, for instance, a phenyl ring) of one molecule and its long axis is correlated with the cooresponding planes of adjacent molecules, still in approximately hexagonal close paking; reorientation of the molecule about the long axis in an orthorhombic array is still practicable, but the molecule has a large probability of adopting certain orientations in relation to the planes of the adjacent molecules. In the smectic C phase, the long axes of the molecules are inclined at some angle to the director and correspondingly to the normal of the planes containing the molecules, disordered like the A phase. The substance 4,4'-diheptoxyazoxybenzene (6) in



(6)

its smectic C phase has a tilt angle 0.67 radians between the long axis and the director. The smectic H phase is related to the C phase by having the tilted molecules hexagonally close packed like the B phase; it can be described as a three-dimensional liquid crystal corresponding to the monoclinic system with the lengths of the axes a>b. Only a few substances adopt the smectic F phase, notably 2-(4-pentylphenyl)-5-(4-pentoxyphenyl)-1,3-diazine (7);

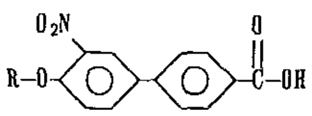


(7)

the molecular arrangement is tilted in layers and is relatively disordered within the layers, similar to the smectic C phase; this phase is described as a side-centred monoclinic structure (a>b) with short-range positional correlation within the planes but little or no positional correlation between the layers: thus it is a tilted hexatic phase. However this compound also shows a smectic C phase at greater temperatures, and the enthalpy and entropy changes at the $S_F \rightarrow S_C$ transition are relatively larger than at the following transition $S_C \rightarrow S_A$ in the following sequence, with the indicated temperatures of the phase transitions:

$$(7)\quad \overset{T/K}{}\; C \xrightarrow{352} S_G \xrightarrow{375.85} S_F \xrightarrow{386.95} S_C \xrightarrow{417.15} S_A \xrightarrow{483} I$$

The same substituted diazine (7) also has a smectic G phase, which in its highly structured layers has close similarities to the smectic E phase; thus the smectic G phase may be considered to be a tilted smectic E phase, having a three-dimensional crystalline order of the side-centred monoclinic system (a>b). A few other compounds are also known to have smectic G phases. Only a few compounds, including 4-(3-nitro-4-alkoxyphenyl)benzoic acid (8) with the alkyl (R) group being either hexadecyl or octadecyl or with the nitro



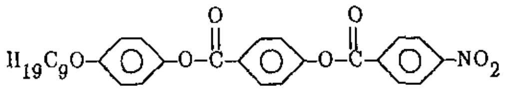
(8)

group replaced by a cyano group, are known[5,6] to display the smectic D phase, which is isotropic but ordered, thus of the cubic system; one possibility for the structure of this mesophase is that it consists of micelles, perhaps spherical in shape and containing many molecules, similar to the optically isotropic, micellar phases of amphiphiles in lyotropic liquid crystals. In contrast with the micelles in aqueous suspension in which in certain ranges of concentration the hydrocarbon tails of the polar groups tend to be located inside the micellar sphere, possibly in the smectic D phase the carboxylic acid groups are aggregated in hydrogen-bonded clusters at the centres of the purported spheres. In its smectic D phase, the compound (8) with the hexadecyl group in the alkoxy side chain is believed to have a unit cell of length 1.05×10^{-8} m containing 1150 molecules. For this compound, this isotropic smectic D mesophase occurs remarkably in the temperature range between the anisotropic smectic C and A phases.

Three other thermotropic mesophases having monoclinic structures may be classified. The structure of the smectic I phase consists of a side-centred unit cell with b>a; this tilted hexatic structure has slightly greater correlation within the planes than smectic F. The smectic J and K structures, both having b>a, are essentially three-dimensional crystals, but differ in that the unit cell of the former is side-centred whereas the latter has a primitive unit cell. Although some smectic phases, such as those above, are described in terms of crystal structures, it is important to recognize that the mobility of the molecules between the layers generally leads to a fluidity (despite a large viscosity) unshared by true crystals.

In summary then, the several smectic mesophases can be divided into three groups. In the group containing the A, B and E phases the molecules have their long axes parallel to the director, such that the thickness of the layer is essentially equal to the length of the molecules in the direction of that long axis. In the group containing (according to increasing order) the C, F, H, G, I, J and K phases the molecules have their long axes tilted with respect to the director; the director is perpendicular to the layers, so that the thickness of the layer is a much smaller distance than the length of the molecule in the direction of the long axis. Obviously the preceding classification based on the orientation of the directors with respect to the long molecular axes is an alternative to that based on the structural correlation between layers; according to the latter scheme, the contrast is made between the group containing the disordered arrangements in the layers A and C, the F and I phases, and the hexatic B phase, and the other group of three-dimensional correlations containing the crystal B, E, G, H, J and K phases. The remaining smectic D mesophase has optically isotropic properties. Polymeric substances with mesogenic groups along the main chain of the polymer generally tend to have nematic phases above the melting point, whereas the attachment of the mesogenic groups beside the main chain leads to a highly ordered smectic phase^3; the effects of asymmetric centres in the polymeric liquid crystals seem to be less important than for compounds of small molar mass, because the presence of the polymeric chain may interfere with the helical structure characteristic of the cholesteric mesophase. The formation of smectic layers implies that the side-wise interactions between the molecules are sufficiently strong; this condition may be assisted by the absence of projecting side groups which prevent close contacts. The mesogens of the optically isotropic smectic D category in fact contain the polar nitro or cyano side groups, in contradistinction to the preceding generalisation; this exceptional structural feature may be responsible for the existence of this D category, but the mesogens of tis D category also exhibit other smectic phases.

As an instance of a compound that exhibits multiple nematic phases, we consider 4-nonoxyphenyl-4'-nitrobenzoyloxybenzoate (9) which has three nematic, four smectic A,

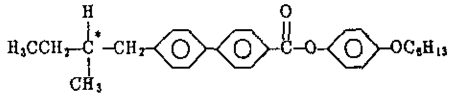

(9)

and two smectic C phases^6 in the following sequence from the isotropic liquid, all within a fairly narrow range of temperature:

$$(9)\ I \longrightarrow N \longrightarrow S_{A_d} \longrightarrow N_r \longrightarrow S_{A_d} \longrightarrow N_r \longrightarrow S_{A_1} \longrightarrow S_{C_1} \longrightarrow S_{A_2} \longrightarrow S_{C_2} \longrightarrow C$$

here N_r denotes a re-entrant nematic phase and S_{C_1} and S_{C_2} are two different forms of the smectic C phase.

The chirality of the mesogen molecules has no particular structural consequences in the smectic A, B and E mesophases in which the molecules tend to align with their long axes perpendicular to the layers of planes. However in the tilted smectic phases such as the C mesophase, the chirality of the molecules induces a helical distribution of the tilt directions about an axis drawn perpendicular to a stack of layers; the tilt angles are constant at a particular temperature. The possibility of ferroelectric properties of these compounds exists, as alluded to above. One instance of a compound that forms such a chiral C mesophase, and also a cholesteric phase (without being at all a derivative of cholesterol) at still greater temperatures, is (10)


(10)

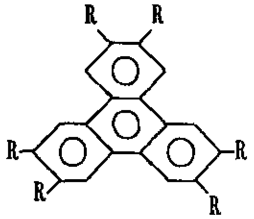
Because the pitches of the rotation of the tilt angle of this compound are in the range 200–500 nm, optical interference phenomena are possible, and selective reflection is observed at wavelengths corresponding to visible light. The pitch changes with temperature, but in opposite senses for the two mesophases. Specifically, during the cooling of compound (10) through the cholesteric mesophase, the colour of reflected light changes from blue to red and then into the infrared at the transition to the smectic C phase; as the temperature of the latter mesophase is further decreased, the colour of the reflected light changes back from the infrared to red and yellow. A mixture of compounds of this type exhibits changes of colour completely from red to blue within the thermal boundaries of the smectic C phase. The possibility of chiral smectic phases also exists for any other tilted smectic phase, and at least some chiral F, H and I mesophases are already known[5,6].

There are three further mesophases[6] of cholesteric mesogens; these are known as the blue phases and occur if the pitch of the cholesteric phase is less than about $5x10^{-7}$ m. First observed in cholesteryl benzoate by Reinitzer, these blue phases exist within a small range of temperature, typically ~1 K, between the cholesteric mesophase and the isotripic liquid phase. These phases are denoted BPI, BPII and BPIII, occurring in that order with increasing temperature. All are optically active but isotripic; although their colours, depending on pitch, may be other than blue, the name blue phase is still retained. The BPI phase has a body-centred cubic structure, whereas BPII is simple cubic; BPIII may be amorphous or quasicrystalline. For the compound (+)-(4-(2′-methylbutyl)phenyl-4′-octylbiphenyl-4-carboxylate), the phase sequence[7]

$$T/K \quad C \underset{315}{\overset{321}{\rightleftharpoons}} S_G \overset{335}{\longleftrightarrow} S_J \overset{338}{\longleftrightarrow} S_F \overset{340}{\longleftrightarrow} S_I \overset{344}{\longleftrightarrow} S_C \overset{354}{\longleftrightarrow} S_A \overset{409}{\longleftrightarrow} Ch \overset{412}{\longleftrightarrow} BP \overset{413}{\longleftrightarrow} I$$

includes cholesteric and blue phases as well as six different smectic phases, and shows supercooling of the smectic G phase.

Finally in this fairly comprehensive, if cursory and inevitably incomplete, survey of thermotropic mesophases, we consider discotic compounds, discovered[6] relatively recently (in 1977). These discotic phases may be considered to be alternative to smectic mesophases for lah-like molecules, because in a few cases a discotic mesogen has been observed to exhibit a nematic or cholesteric phase in the range of temperature between those of the discotic mesophase and of the isotropic liquid. In these discotic mesophases, the molecules may be stacked aperiodically in columns, but the different columns constitute a regular array, generally hexagonal or rectangular. Among derivatives (with varied alkyl or alkoxy groups, such as R= pentoxy or dodecacarboxy) of triphenylene (11) are some that exhibit such structures, but also other derivatives lead to tilted columnar structures. Even some compounds that lack an exactly planar central disk have been discovered to have discotic phases, and also other compounds having tubular phases in which the core is absent. In at least one case a discotic mesogen is known to exhibit two distinct discotic mesophases[8]; in this case the R group in (11) is hexylthio.

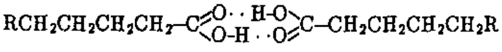


(11)

EFFECTS OF MOLECULAR STRUCTURE ON MESOGENIC PROPERTIES

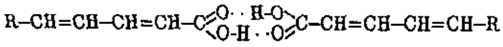
We consider several instances[5] of these effects by comparing related compounds or sets of compounds.

(i) **The carboxylic acids tend to form dimers with strong hydrogen bonds between the oxygen atomic centres of a pair of molecules:**



$$RCH_2CH_2CH_2CH_2{-}C\begin{matrix}\nearrow O\cdot\cdot H{-}O\searrow\\ \searrow O{-}H\cdot\cdot O\nearrow\end{matrix}C{-}CH_2CH_2CH_2CH_2R$$

(12)

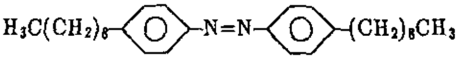


$$R{-}CH{=}CH{-}CH{=}CH{-}C\begin{matrix}\nearrow O\cdot\cdot H{-}O\searrow\\ \searrow O{-}H\cdot\cdot O\nearrow\end{matrix}C{-}CH{=}CH{-}CH{=}CH{-}R$$

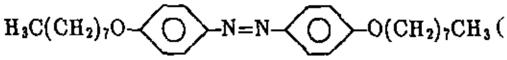
(13)

If the hydrocarbon tail of each acid is only alkyl (12), then the compounds are not mesogens. If however there is a dienyl group adjacent to the carboxylic group with a further alkyl group then these compounds (13) can form nematic mesophases. On the other hand, with only the purely conjugated (*i.e.* R=H) systems attached to the carboxylic groups, apparently no mesogenic properties of the pure compounds are observed. Thus in order for thermotropic liquid-crystalline mesophases to exist, it seems that some central portion of the molecule (or, in the case of these *dimers*, the two carboxylic groups together) must have some *structural rigidity*, that this rigidity must extend further in space such as by means of additional "conjugated" systems, but that some flexibility or ability to adopt various conformations at least one terminus of the molecule is also essential. (Note that the representation of these molecular topologies in such linear fashion as, for instance, $-CH_2CH_2CH_2CH_2-$ or $-CH=CH-CH=CH=CH-$ masks the real steric consequences of the molecular topology.)

(ii) In the case of the following two compounds, merely chaning one methylene group adjacent to the phenyl rings to an oxygen atomic centre is *sufficient* to alter the type of mesophase from smectic to *nematic*:



(14)

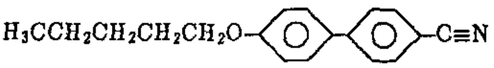


(15)

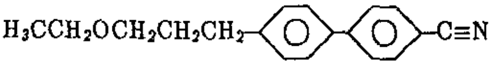
(14) T/K $C \xrightarrow{310} S_B \xrightarrow{313.65} S_A \xrightarrow{326} I$

(15) $C \xrightarrow{375} N \xrightarrow{382} I$

(iii) If the oxygen atomic centre is separated from the phenyl ring, then the mesogenic properties are lost:



(16)

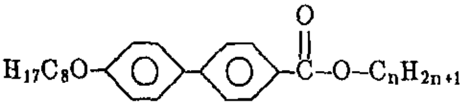


(17)

(16) T/K $C \xrightarrow{326} N \xrightarrow{340.65} I$

(17) $C \xrightarrow{309} I$

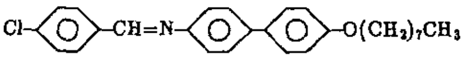
(iv) The remarkable effect of changing the length of terminal alkyl groups is shown in the following series of compounds, for the cooling operation from the isotropic liquid phase:



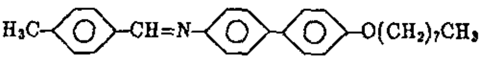
(18)

n=2 $I \rightarrow S_A \rightarrow S_B \rightarrow S_E \rightarrow C$
n=3 $I \rightarrow S_A \rightarrow S_B \rightarrow C$
n=4 $I \rightarrow S_A \rightarrow S_C \rightarrow C$
n=5 $I \rightarrow S_A \rightarrow C$

(v) Because of the similarity in the size of the unit cells of crystals containing one of two compounds differing by only the replacement of a chloro by a methyl substituent, organic chemists consider that these two substituents have similar sizes; their effects on the mesogenic properties are compared in the following compounds:



(19)

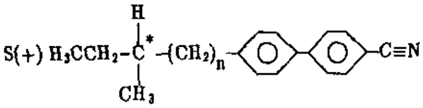


(20)

(19) T/K $C \xrightarrow{466} N \xrightarrow{534.65} I$

(20) $C \xrightarrow{428} S_A \xrightarrow{451} N \xrightarrow{495} I$

(vi) In this case we consider a series of chiral compounds, all having the same absolute configuration (S) at the single asymmetric carbon centre; with the number n of methylene groups in the range 1–3, all these compounds have cholesteric mesophases:



(21) $1 \leq n \leq 3$

However, if one mixes in appropriate proportions the compounds (21) with n=1 and 2, or 2 and 3, then one obtains a nontwisted nematic phase. When the asymmetric centre is moved from an even to an odd then to another even point in the chain, the sense of the cholesteric helix changes from right-handed to left-handed then reverts to right-handed again.

(vii) The effect of increasing the number of phenyl rings in the chain within a particular compound is shown in this instance:

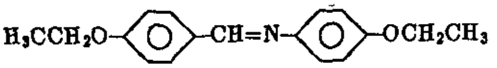
(22)

(23)

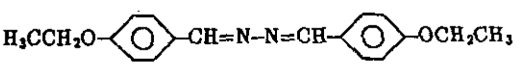
$$(22)\quad T/K\quad C \xrightarrow{295.6} N \xrightarrow{308} I$$

$$(23)\quad C \xleftrightarrow{403} N \xleftrightarrow{512} I$$

(viii) The effect of increasing the number of HC=N groups at the centre of the molecule is shown in this comparison:



(24)



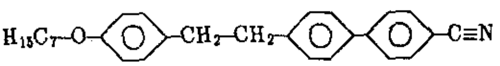
(25)

$$(24)\quad T/K\quad C \xrightarrow{421} I \xrightarrow{416} N$$

$$(25)\quad C \xrightarrow{445} N \xrightarrow{472} I$$

In the case of the compound (24), the nematic phase is formed only monotropically on cooling from the isotropic liquid, in fact after some supercooling, not reversibly in the warming operation, whereas for the compound (25) the nematic mesophase is formed enantiotropically.

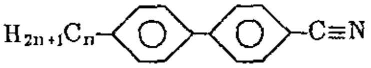
(ix) In the next case, the substance (26) has two mesophases despite the CH_2CH_2 flexible linking unit between two phenyl rings, presumably because the biphenyl moiety with its polar terminal substituent C≡N is sufficient to bestow these properties.



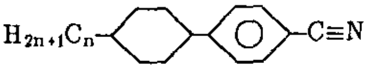
(26)

$$(26)\quad T/K\quad C \xrightarrow{334.45} S_A \xrightarrow{408.95} N \xrightarrow{430.95} I$$

(x) Here we compare th effect of replacing one phenyl ring by a cyclohexyl ring:



(27)



(28)

(27)

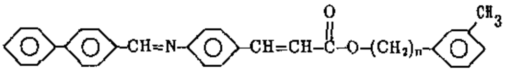
		$C \longrightarrow$	$N \longrightarrow I$
n=5	T/K	295.65	308
n=6	T/K	286.65	300
n=7	T/K	301.65	315

(28)

		$C \longrightarrow$	$N \longrightarrow I$
n=5	T/K	304	328
n=6	T/K	315	320
n=7	T/K	303	332

In fact the presence of two cyclohexane rings, with no phenyl rings, and with or without any intervening groups such as –C≡C–, –HC=CH–, –HC=N–, –N=N–, $-\overset{\overset{O}{|}}{N}=N-$, $-\overset{\overset{O}{\|}}{C}-O-$ etc., may still lead to liquid-crystalline properties.

(xi) We consider next the series of compounds having different numbers n of methylene groups between the carboxyl and 3-methylphenyl groups:


(29)

n=0 T/K $I \xrightarrow{521} N \xrightarrow{464} S_A \xrightarrow{419} S_B \rightarrow C$

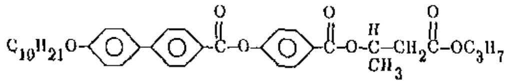
n=1 T/K $I \xrightarrow{441} S_B \xrightarrow{403} S_E \rightarrow C$

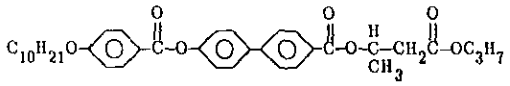
n=2 T/K $I \xrightarrow{465} N \xrightarrow{451} S_A \xrightarrow{422} S_B \xrightarrow{365} S_E \rightarrow C$

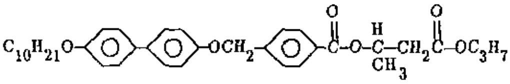
n=3 T/K $I \xrightarrow{432} S_A \xrightarrow{428} S_B \xrightarrow{381} S_E \rightarrow C$

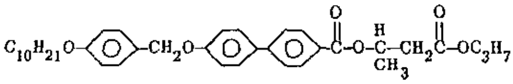
The approximate *transition temperatures* are given only for the cooling direction from the isotropic liquid phase, and not for the final crystallization process. In this series the nematic mesophases are observed for only the even values of n; although the smectic A phase is observed for the case that n=3 the temperature range for the existence of this phase is quite small.

(xii) As the final comparison in this series we consider the following four compounds:

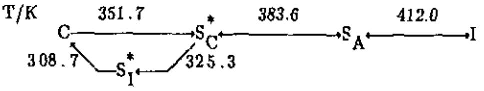

(30)

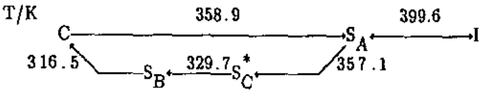

(31)

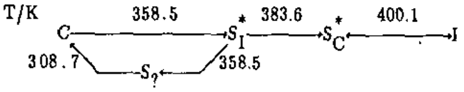

(32)

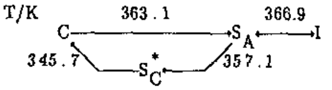

(33)

The sequences of these mesophases are:

(30)


(31)


(32)


(33)


All these compounds exhibit chiral smectic C phases, denoted S_C^*; these are stable phases for compounds (30) and (32) but metastable for the other two. The phases denoted S_I^* and S_B are only tentatively assigned, and a further smectic phase of (32) also awaits assignment[9]. For these compounds, the effect of length of alkyl chain on the mesomorphic properties have also been investigated[9].

Naturally there have been investigated the effects of placing polar and nonpolar substituents on the various rings in various positions. Some essentially qualitative hypotheses and models have been proposed[5] to account for the various effects, but at present the relationship of the *structural* influences to the *mesomorphic properties* of mesogens still seems essentially empirical.

Received June 30, 1989

Key Wrod Index– liquid crystal; thermotropic; lyotropic; mesophase; mesogen; states of aggregation.

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