to a silicon surface.[4] The approach has also been used to surface tether oligonucleotides, allowing automated surface synthesis of DNA. The semiconductor properties of silicon and absence of an intervening oxide layer allow the process to be monitored electrochemically.[5] These two very different examples show the diverse range of surface chemistry that can be achieved using SAMs based on simple surface reactions.

13.3 Liquid Crystals

Collings, P. J., *Liquid Crystals: Nature's Delicate Phase of Matter*, 2nd ed.; Princeton University Press: Princeton, NJ, USA, 2001.

13.3.1 Nature and Structure

True long-range order in liquids is referred to as *mesomorphic* or *liquid crystalline* behaviour. The term 'liquid crystal' is highly evocative of the true state of the substance that possesses some of the bulk order of the crystalline state and the facile deformability and dynamics of the liquid phase. In fact, liquid crystals represent an intermediate phase between liquid and solid (or, indeed, a series of liquid phases in some cases). The origin of this anisotropic behaviour is mainly a function of molecular shape. Liquid crystal-forming molecules, termed *mesogens*, are generally either long and cylindrical (rodlike), such as 4′-*n*-pentyl-4-cyanobiphenyl (**13.3**) and cholesteryl nonanoate (**13.4**), or flat and circular (disclike), as in *hexakis*((4-octylphenyl)ethynyl)benzene (**13.5**) and *bis*(3,4-nonyloxybenzoyl)methanato copper(II) (**13.6**). Mesogens can even be polymers or aggregates such as elongated micelles (Section 13.2.1). Even the alkyl-chain-substituted hydrogen-bonded 2,6-diaminopyridine-uracil (PU) system developed by Lehn (Section 10.8.8) shows mesogenic behaviour. The highly anisotropic shape of mesogens causes them to line up with one another in various ordered ways, partly as a result of intermolecular interactions, and partly because the molecules are bulky and the liquid phase is relatively viscous. However, tiny perturbations such as dust particles, or surface inhomogeneities, can cause differential orientation of one zone of mesogens with respect to its neighbours. The result is a fluid material with macroscopic domains of aligned molecules, usually visible to the naked eye as scattering light to give bright, iridescent colours. The liquid order is clearly apparent under a polarising microscope (Figure 13.10), in which each domain

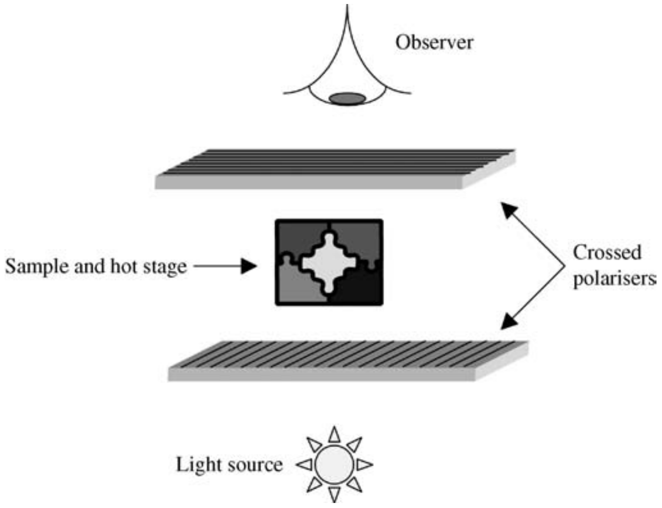


Figure 13.10 Operation of a polarising hot-stage microscope.

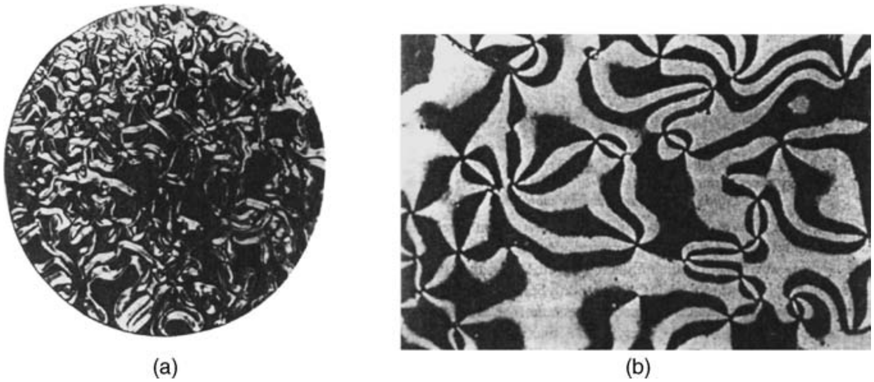
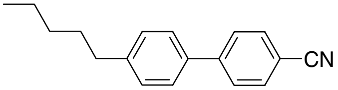
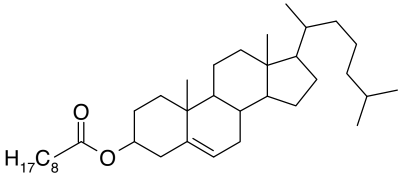


Figure 13.11 (a) Thread-like domains in a nematic liquid crystal of thickness 100 μm viewed under crossed polarisers. (b) Schlieren texture in a nematic film of thickness 10 μm (reproduced with permission from [6]).

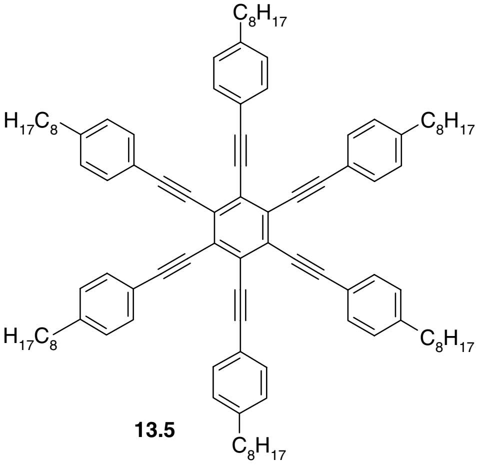
rotates plane-polarised light as in a solid-state crystal, giving light and dark patterns according to whether the polarised light is able to pass through the analyser (Figure 13.11).



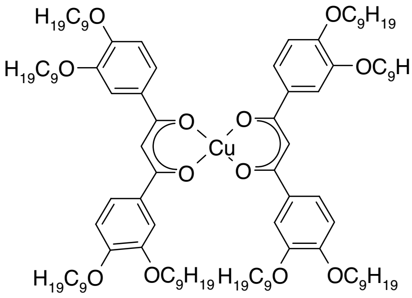
13.3



13.4



13.5



13.6

The fact that mesogens are highly fluid, and domains may be deformed very easily, suggests that liquid crystalline behaviour should be highly temperature-dependent, and this is indeed the case. Liquid crystalline behaviour occurs above the melting point of the pure solid material at temperatures low enough such the molecular motion is slow and the energies of intermolecular interactions are strong compared with thermal energies. As the temperature is increased, so molecular motion increases and the liquid crystal may undergo further phase changes, often to less ordered mesophases,

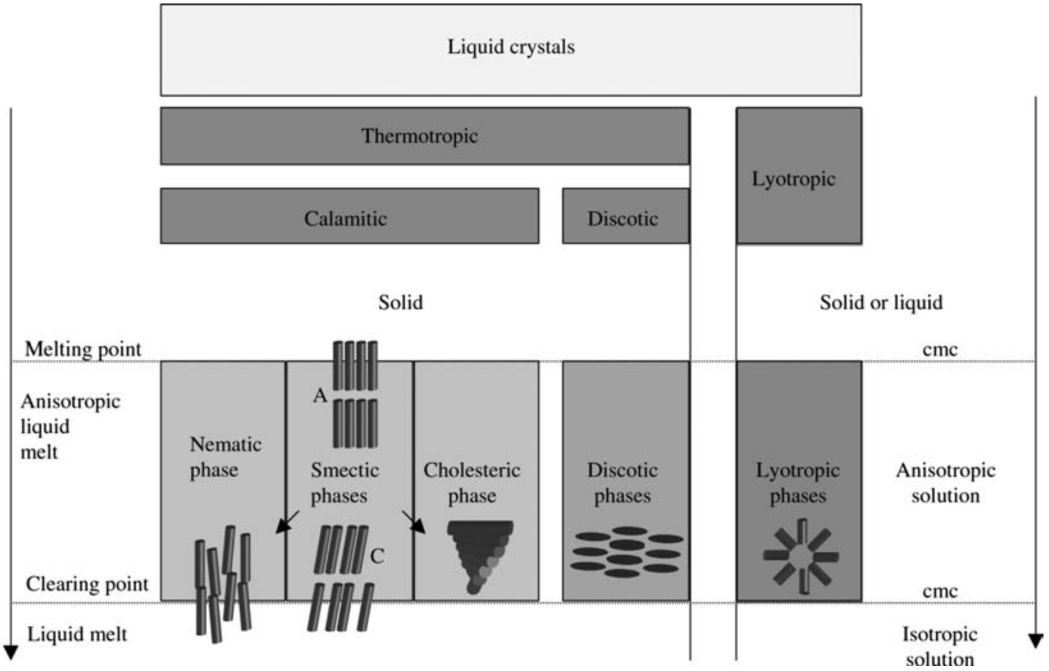


Figure 13.12 Fundamental classes of liquid crystalline behaviour (temperature increases downwards).

before finally melting into an isotropic liquid once thermal energy is sufficient to induce rapid motion of one molecule with respect to its neighbours. The thermal behaviour is the basis for the first fundamental distinction in liquid crystals. Substances that form mesophases as a function of temperature are termed *thermotropic*, whereas those that require the influence of a solvent or medium (*e.g.* micelles) are termed *lyotropic* (Figure 13.12). Thermotropic phases arise from the gradual melting of a crystalline solid. As the temperature increases, so the molecular vibrations increase until, at the melting point, intermolecular (supramolecular) bonds are broken and a liquid results. In about 5 % of organic molecules, not all intermolecular interactions are broken at once and a liquid crystalline phase results in which the solid order has broken down, but varying degrees of crystalline order are still apparent. As the temperature increases, the various intermolecular interactions are broken one by one, resulting in less and less ordered liquid crystalline phases, until an isotropic melt is finally achieved. In addition to melting, the other way to break down a solid lattice is to dissolve it in a solvent. As with melting, it is possible that, depending on concentration, not all of the crystal is broken up at once and degrees of solute order may exist within the solution. This is a lyotropic phase.

Thermotropic liquid crystals come in two types: *calamitic* and *discotic*. Calamitic phases (from the Greek for ‘tube’) are all those that are caused by rod-like mesogens. The more recently characterised discotic phases are caused by disc-like species. Calamitic phases may be either *nematic* (from the Greek for ‘thread’), *smectic* (from the Greek for ‘soap’) or *cholesteric* (named after the cholesterol derivatives such as **13.4**, which exhibit this behaviour).

The nematic phase (Figure 13.13a) is characterised by a high degree of long-range orientational order of the molecules but no long-range translational order. In other words, the mesogens all point in the same direction but are disordered with respect to slippage along the rod axis; it is this ready slippage that gives the nematic phase a high degree of fluidity. The nematic phase represents the least ordered of all calamitic phases and, in systems that possess more than one mesophase, the nematic

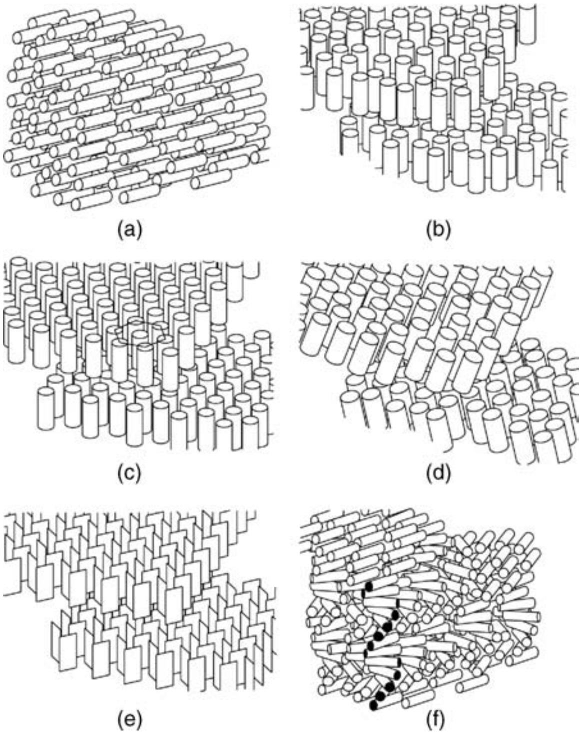


Figure 13.13 Schematic representation of calamitic liquid crystalline phases: (a) nematic, (b) smectic A, (c) smectic B, (d) smectic C, (e) smectic E and (f) cholesteric (reproduced with permission from [7]).

phase is usually the last to occur before isotropic melting. The degree of order in a nematic phase is quantified by a parameter, *S* (Figure 13.14), which represents the amount of rotational freedom the rod-like molecule has perpendicular to its rod axis. An *S* of 1 represents an ideally organised nematic phase, while an isotropic liquid has $S = 0$. Nematic phases are characterised by brightly coloured, rapidly moving spots, visible to the naked eye or under a microscope, and by the schlieren (centred) texture (Figure 13.11b). This property arises from line singularities perpendicular to the mesophase layer and are analogous to disolocations in crystals. They are termed *disclinations*, and are a form of defect where two regions of different order meet.

Smectic phases represent a higher degree of order then nematic. Smectic phases are based on two-dimensionally ordered layer arrangements in which the layer thickness is approximately equal to the length of the molecular rods. Interactions between layers are limited, allowing one layer to slip easily with respect to the others. Within a layer, less ordered smectic phases such as A and C (Figure 13.13b and Figure 13.13d) exhibit a liquid-like, statistical distribution of mesogens. Increasing order is observed with hexagonal arrangements between rods (smectic B) and a herringbone arrangement of flatter rods such as **13.8** allowing no rotation about the rod axis (smectic E). A total of at least 12 different smectic phases have been characterised (labelled S_A–S_L), with the most ordered exhibiting a high degree of viscosity. The smectic D phase has a rather unusual cubic structure, and is an exception to the layered rule. Generally, on warming, ordered phases shift to less ordered forms in an order such as $S_E/S_G \rightarrow S_B \rightarrow S_F \rightarrow S_C \rightarrow S_D \rightarrow S_A$. For example, the *n*-octyl derivative of compound **13.3** undergoes a total of three phase transitions. Initially, it melts as 24°C to give a smectic A phase (enthaply of fusion 25.5 kJ mol^{-1}). At 34 °C, this is transformed into a nematic

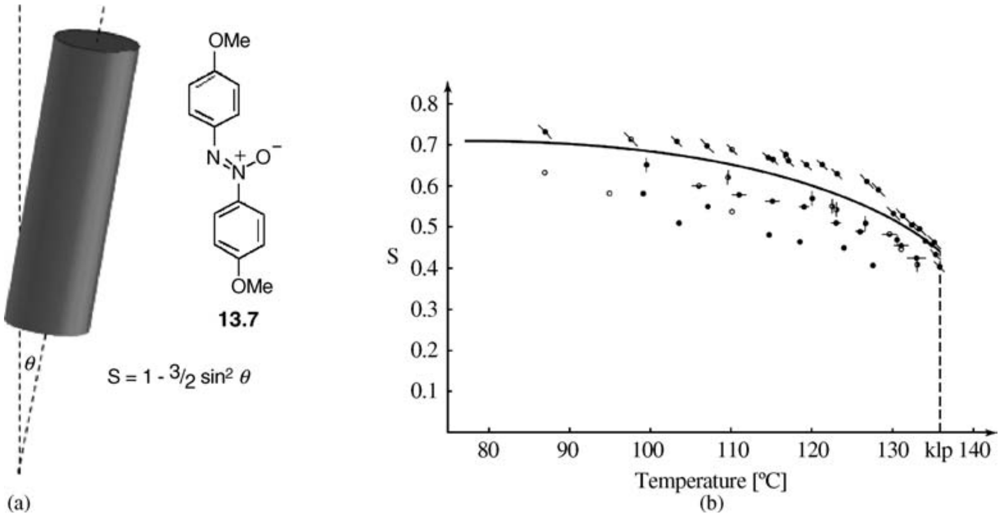
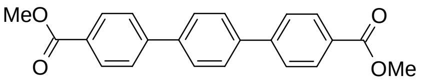


Figure 13.14 (a) Degree of order, *S*, in a nematic phase. (b) Variation of *S* with temperature for 4,4′-dimethoxyazoxybenzene (**13.7**) (reproduced with permission from [7]).

phase (0.13 kJ mol^{-1}), before decomposing finally to an isotropic melt at 42.6 °C (0.97 kJ mol^{-1}). This kind of phase behaviour of such systems is best studied by a polarised hot-stage microscope, in which the sample may be examined visually for characteristic optical patterns as a function of temperature (Box. 13.1).



13.8

Box 13.1 Characterisation of Mesophases

There are three main techniques used in characterisation of mesophases: polarised optical hot-stage microscopy, differential scanning calorimetry (*cf.* Box 9.1) and small-angle X-ray scattering.

Polarised Optical Hot-Stage Microscopy

This technique, shown diagrammatically in Figure 13.10, is the easiest way to characterise a mesophase, and is generally the first to be employed. The sample (typically < 1 mg) is sandwiched between two transparent microscope cover slips and placed on a hot stage that has a precise temperature control. The sample is examined visually through a microscope as it is heated in a slow and controlled manner. Incident light on the sample is first plane-polarised with a polariser between light source and sample. The observer looks through a second polariser at 90 degrees to the first. In the absence of sample, or in the case of an isotropic sample, no light passes and the microscope field is dark. Because of the birefringence of liquid crystals, however, the plane of the polarised light passing through the sample is altered (it becomes elliptically polarised), allowing it to pass through the second polariser to the observer. The textures observed are characteristic of a given mesophase and are best observed during sample cooling.

(*Continued*)

Box 13.1 (*Continued*)

Differential Scanning Calorimetry

The DSC experiment is described in Box 9.1. DSC is strictly complementary to optical microscopy in liquid crystal work. DSC gives information about the enthalpy change during a phase transition. Generally, this change is large during melting and much smaller during a transition between mesophases. DSC results are useful because they enable the operator to be sure that changes in optical appearance observed by microscopy correspond with a phase change, and to identify phase changes that do not give rise to very different appearances.

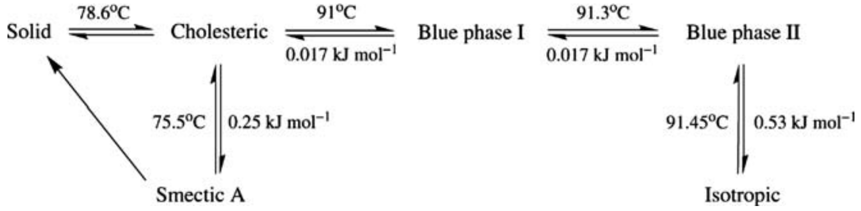
Small Angle X-ray Scattering

Mesomorphic phases are ordered and display a regular periodicity that results in diffraction. The diffraction drops off strongly with angle because the order is often not very long-range and hence measurements are carried out at small scattering angles. The X-ray diffraction pattern of a liquid crystal can give an enormous amount of information about the characteristics of the mesophase and may represent the only way to it definitively characterise. In a smectic phase, for example, diffraction lines that identify both the interlayer and intralayer periodicity can be observed. Correlation with calculated molecular lengths can give information on tilt angle. If the sample is aligned in a magnetic field, the technique gives further information about mesogen orientation.

Cholesteric phases are a kind of helical nematic phase with a helical pitch (length of a single helical turn; *cf.* helicates, Section 10.8) in the region of 200–2000 nm. Instead of lining up in parallel, the rod-like molecules change their orientation with respect to one another in an ordered fashion (Figure 13.13f). The cholesteric mesogens are optically active (indeed, cholesteric phases may be generated by adding nonmesogenic chiral molecules to an ordinary nematic phase, since the energy of twist forms only a very small part of the total energy associated with the molecular order). Cholesteric phases have very interesting optical properties, such as the selective reflection of circularly polarised light, circular dichroism and extremely high degrees of optical rotation in the region of 18 000° mm^{-1} compared to a few tens of degrees for molecular chirality, or some hundreds for chiral fullerenes such as C_{82}. As a result, cholesteric mesophases exhibit attractive, iridescent colours. These colours were first brought to the attention of Austrian botanist, Reinitzer, who discovered the liquid crystal phenomenon in 1888 while studying the acetate and benzoate derivatives of cholesterol. Helical cholesteric phases of pitch less than about 500 nm exhibit 'blue phases' (named because of their colour), which generally exist only over a very narrow temperature range (about 1 °C), just before the formation of the isotropic melt. This variable phase behaviour for cholesterol nonanoate (**10.4**) is illustrated in Scheme 13.2.

Blue phases have been known since the early days of liquid crystalline substances. Reinitzer, in a letter to his physicist collaborator, Lehmann, wrote of them in 1888:

> *On cooling [the liquid phase of cholesteryl benzoate] a violet and blue phenomenon appears, which then quickly disappears leaving the substance cloudy but still liquid.*



Scheme 13.2 Phase behaviour of cholesterol nonanoate showing the occurrence of 'blue phases'.

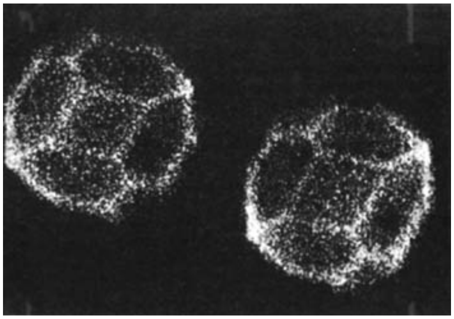
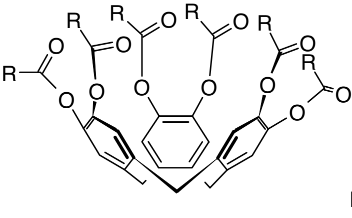


Figure 13.15 Single crystals of BP I in equilibrium with the isotropic melt (from 58 % weight mixture of cyano-4-methylbutylbiphenyl in Merck nematic ZLI 1840). (Reproduced with permission from [8]).

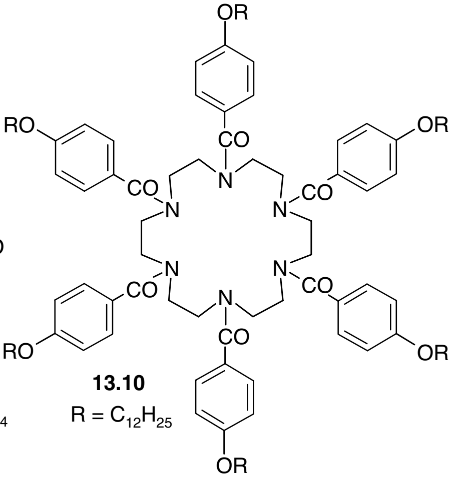
It was not until the 1970s that blue phases became accepted as thermodynamically distinct phases, but they have since become a main point of interest in condensed matter physics. Three distinct blue phases exist (which are not always blue), known as BP I, II and III, occurring in order of increasing temperature. The phases are due to the formation of tiny single crystals of cubic symmetry: body-centred for BP I and simple cubic for BP II; BP III is quasicrystalline. The crystals exhibit optical Bragg diffraction and small samples up to a few hundred microns in diameter have even been isolated (Figure 13.15). The colour arises from light scattering by the tiny crystallites. Interestingly, it is not possible to distort a helical structure continuously in order to fit a cubic structure, and as a result crystals of BP I and BP II contain defect lines, or disclinations, which contain isotropic liquid, running throughout the lattice.

Discotic phases have been characterised definitively only since 1977, although their existence was postulated by Vorländer in 1923. They fall into two distinct types: a nematic phase and a columnar phase (Figure 13.16). The columnar phase consists of discs stacked one on top of another aperiodically to form liquid-like columns. Order exists between the columns to give a two-dimensional lattice. The columns can form various arrangements such as hexagonal, rectangular, tilted *etc*. Columnar mesophases may also be formed by replacing the flat core of a discotic mesogen by a conical one, as in the cyclotricatechylene hexaester **13.9**. Columnar mesophases that are hollow in the middle are formed by corand derivatives such as hexa(*p*-*n*-dodecyloxybenzoyl)hexacyclen (**13.10**). These are referred to as *tubular mesophases* and are of potential interest as models for ion-channel proteins (*cf.* Section 12.9). The nematic phase is less ordered, with discs showing orientational order without any translational order.



13.9

R = C_9H_{19}, $C_{11}H_{23}$, $C_{12}H_{25}OC_6H_4$



13.10

R = $C_{12}H_{25}$

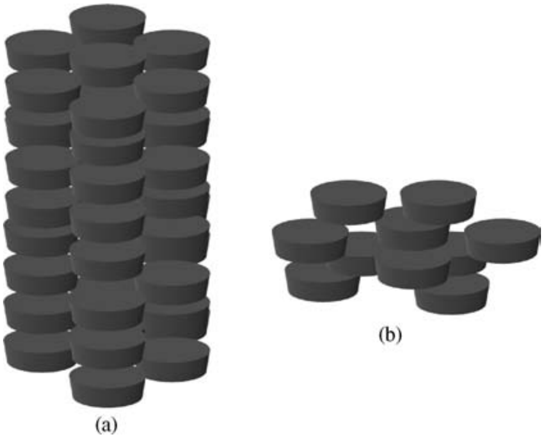


Figure 13.16 (a) Columnar and (b) nematic discotic phases.

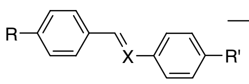
Lyotropic liquid crystal phases are made up of two or more components, one of which is generally an amphiphile (a molecule with hydrophilic and hydrophobic portions, Section 13.2) and the other water or, occasionally, another solvent. Various mesophases are obtained depending on amphiphile concentration. Mesophase formation requires reasonably high amphiphile concentrations in order to bring about interactions between amphiphile aggregates. These liquid crystalline aggregates may be of the lamellar bilayer, micelle or cylindrical type. Lamellar, or 'neat' phases consist of flat bilayers with water sandwiched in between in contact with their hydrophilic groups (*cf.* Figure 13.6). The order comes from the common orientation of the bilayers. These layers may also bend to form micellular or vesicle-based (*cf.* Figure 13.5) *cubic* or *viscous isotropic* phases in which spherical aggregates form a body-centred cubic arrangement. A *hexagonal* phase may also form in which rod-like micellular cylinders are organised parallel to one another in an array rather like the columnar discotic phase (Figure 13.6).

13.3.2 Design of Liquid Crystalline Materials

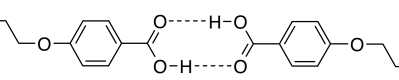
A great deal of work has gone into systematic studies designed to elucidate the molecular properties that give rise to liquid crystalline behaviour. An understanding of these principles has enabled the design of a large range of liquid crystalline materials with very interesting properties. The conventional wisdom may be summarised as follows:

- The molecular shape should be relatively thin or flat, especially within rigid molecular frameworks.
- The molecular length should be at least 1.3 nm (13 Å), consistent with the presence of long alkyl groups on many room-temperature liquid crystals.
- The structure should not be branched or angular (but see recent developments in supramolecular liquid crystals in the next section).
- A highly anisotropic polarisability is required in order to enhance intermolecular dispersive interactions. This is favoured by the presence of easily polarisable groups and permanent dipoles.
- A low melting point is preferable in order to avoid metastable, monotropic liquid crystalline phases. Low-temperature mesoporphic behaviour in general is technologically more useful, and alkyl terminal groups promote this.

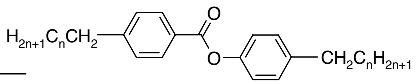
An extended, structurally rigid, highly anisotropic shape seems to be the main criterion for liquid crystalline behaviour, and, as a result, many liquid crystalline materials are based on substituted (particularly *p*-disubstituted) benzene rings. The *para* arrangement lends itself to a long, extended shape, as in stilbene and Schiff's base derivatives such as **13.11** and **13.12**. The *trans* conformation of the central double bond in these compounds is a much more efficient promoter of liquid crystalline behaviour than the analogous *cis* isomers because of the resultant elongated molecular shape. The Schiff's base motif can be problematic, however, as a result of hydrolytic cleavage. It is unnecessary, however, for the central unit to be an aromatic ring, and compounds based on saturated cyclohexyl derivatives also exhibit liquid crystallinity, supporting the notion that it is the structural rigidity (imparted by the ring system), rather than the dispersive, interactions with the aryl ring that are the most important. Polar groups to enhance the intermolecular interactions may be placed anywhere on the molecule. Traditionally they have been situated in the centre of the mesogen (as in **13.7**) with surrounding alkyl chains, but terminal functionalities such as CN, ester or carboxylic acid groups are equally effective, and are often used in modern technologically important liquid crystalline materials, *e.g.* **13.3**. The size and shape dependence is highlighted by non-molecular mesogens such as the hydrogen-bonded carboxylic acid dimer **13.13**. The hydrogen-bonding interactions allow the molecular pair to achieve the necessary length and are strong enough to give the dimer a long enough lifetime for mesophase formation.



13.11 X = CH
13.12 X = N



13.13



13.14

Alkyl chains lower the melting/clearing point (T_c – temperature of the isotropic phase transition) of the molecule and increase its molecular polarisability. Interesting variations in clearing-point temperature are observed with increasing alkyl chain length, with clearing point alternating with even and odd numbers of carbon atoms, as in **13.14** (Figure 13.17). This results from the effect of the substituent on the polarisation anisotropy of the molecule. The long molecular axis corresponds to the direction of highest polarisability. Addition of a carbon atom along this direction increases the polarisability along this axis more then at right angles to it. Conversely, adding another —CH_2—group at 109° to the previous one has the opposite effect, mostly increasing the polarisability perpendicular to the main axis. The liquid crystal clearing point is related closely to the difference between the longitudinal and

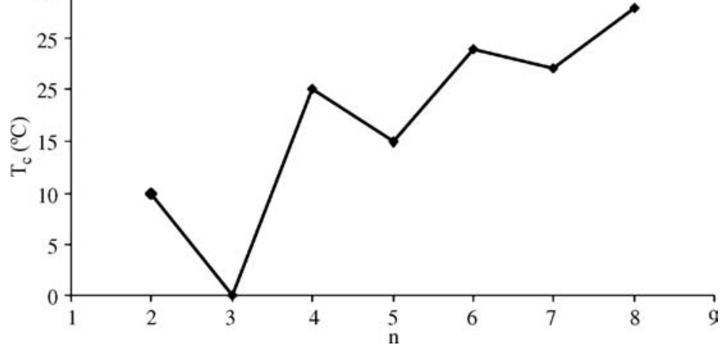


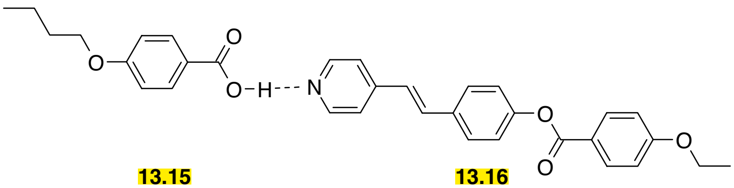
Figure 13.17 Alternation of clearing point temperature (°C) with alkyl chain length (*n*) for compounds of type **13.14**.

cross-polarisation, and hence the T_c alternates, with the effect gradually tailing off as chain length and flexibility increases.

13.3.3 Supramolecular Liquid Crystals

Paleos, C. M., Tsiourvas, D., 'Supramolecular hydrogen-bonded liquid crystals', *Liquid Crystals* 2001, **28**, 1127–1161.

The carboxylic acid dimer **13.13** along with Lehn's 2,6-diaminopyridine-uracil system (Section 10.8.8) are examples of the use of supramolecular interactions to assemble mesogens. A similar system is the system formed by hydrogen-bonding interactions between 4-butoxybenzoic acid (**13.15**) and *trans*-[4-ethoxy(benzyol)oxyl]-4'-stilbazole (**13.16**) which gives mesogenic rod like structures.[9] Neither molecule is mesogenic by itself, however the heteromolecular hydrogen bonding interaction between the carboxylic acid and the pyridine groups results in a thermally stable rigid rod-like assembly which displays nematic phases up to 214°C.



13.15

13.16

Since this 1989 report there have been numerous examples of complex supramolecular liquid crystal systems. Supramolecular chemistry has played a significant role in the move away from traditional disc or rodlike molecules and the past 25 years has seen a whole raft of new liquid crystals based on dendrimers (Section 14.1), bent or bowl-shaped cores, non-covalent bonding, metal coordination or that rely on microphase separation to drive mesophase formation. For example, Figure 13.18 shows a liquid crystal system based on the common guanosine quartet assembly that changes from a smectic (rod-shaped) to hexagonal columnar (disc-shaped) phase on the addition of sodium ions, which template the quartet formation. The oxygen atoms chelate to the metal ions and the liquid crystal reorganises into a circular geometry.[10]

Metal ion coordination in general is an excellent way to generate large, rigid mesogens. Figure 13.19 shows the X-ray structure of a palladium(II) linked metallomesogen in which the palladium coordination links the two pyridyl ligands into an extended dumbbell like structure[11] Depending on the length of the alkyl chains this kind of mesogen forms a number of columnar liquid crystalline phases. These columnar phases were studied by X-ray diffraction of single, ordered liquid crystalline domains. The sample is prepared using uncovered droplets of the mesophase. The compound is deposited onto a glass surface and heated into the isotropic phase. The melt is the slow-cooled, favouring the nucleation of liquid crystal domains with specific orientations at the interfaces with both the glass and the air. In the case of these columnar phases the columns lie horizontally to the glass slide. The X-ray diffraction patterns for the decyloxy analogue of the compound shown in Figure 13.19 are shown in Figure 13.20 at temperature of 104 °C and 82 °C. The lower symmetry evident in the second image corresponds to transition from a columnar hexagonal phase to a columnar rectangular phase on cooling.

Supramolecular liquid crystals have also been reported based on more unusual supramolecular interactions such as halogen bonding (Section 1.8.9).[12] Neither of the components in **13.17** are mesomorphic by themselves but the presence of the highly activated iodine atom in pentafluoroiodobenzene results in a strong N···I interaction (N···I distance 2.81 Å by X-ray crystallography). These

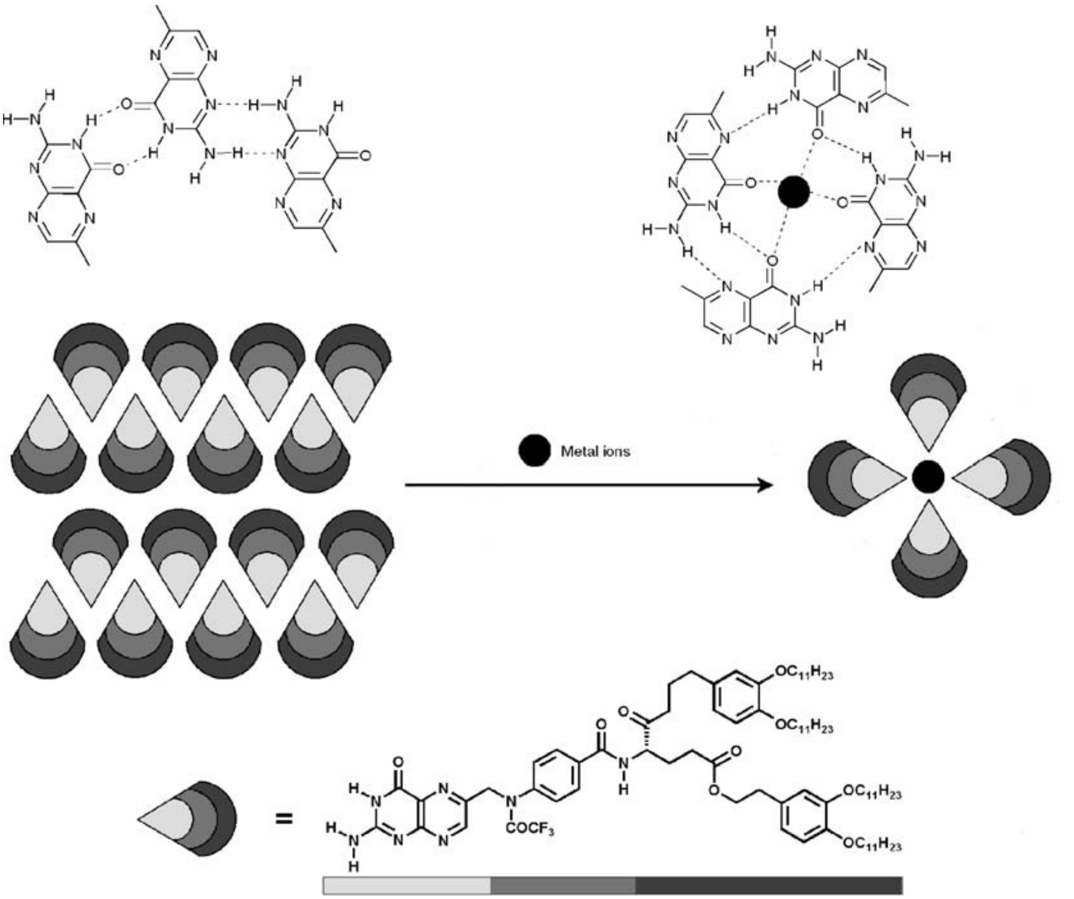


Figure 13.18 A ribbon structure of a folic acid derivative self-assembles into a disc-like tetramer based on a G-quartet motif showing liquid crystalline behaviour on the addition of a metal ion such as Na^+.

interactions are of comparable strength to hydrogen bonds and result in the formation of a smectic A liquid crystalline phase upon cooling the melt to 84 °C. The transition temperature is something of a measure of the strength of the interactions holding the supramolecular mesogen together and this transition temperature compares well with related hydrogen bonded systems.

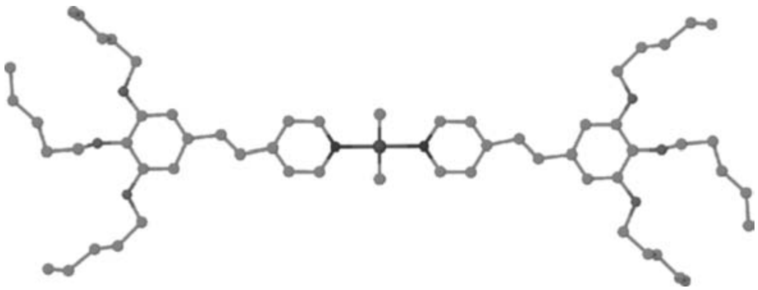


Figure 13.19 X-ray molecular structure of a metallomesogen based on square planar *trans*-$PdCl_2$ linkers.[11]

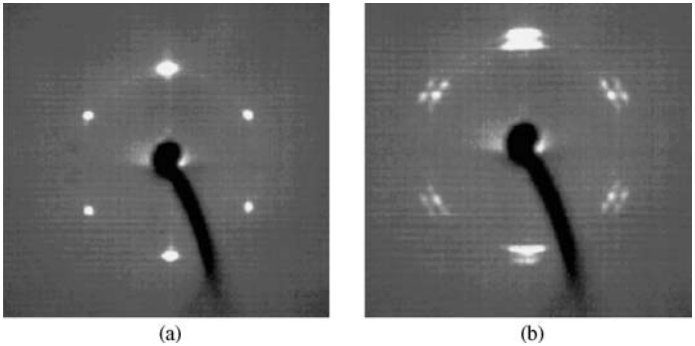
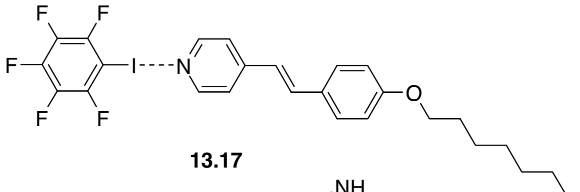
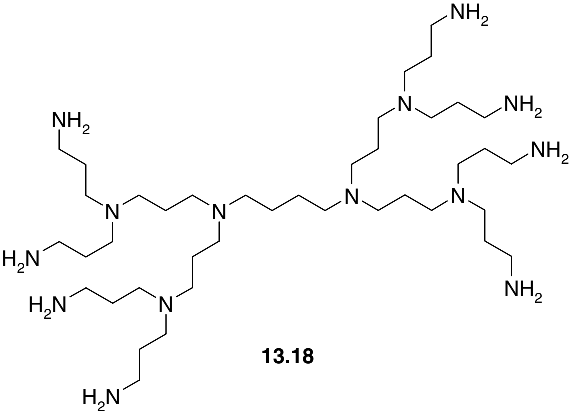
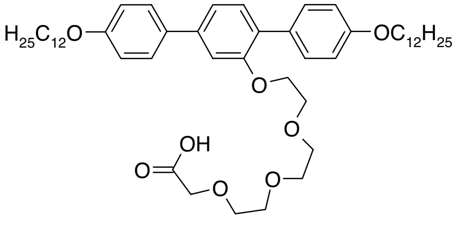

(a) (b)

Figure 13.20 Orientated monodomain X-ray diffraction images from the dodecyloxy analogue of the compound shown in Figure 13.19 at (a) 104 °C and (b) 82 °C corresponding to hexagonal and rectangular columnar phases respectively (reprinted with permission from [11] © 2004 American Chemical Society).


13.17


13.18


13.19

Two component hydrogen bonded mixtures of dendrimers and T-shaped branched amphiphiles are also a rich source of mesophases. Figure 13.21 shows a polarised optical microscope image of the contact region between the dendrimer **13.18** and the T-shaped amphiphile **13.19**. A wide variety of mesophases co-exist as one component diffuses into another. The majority of these have been identified and studied.[13]

Finally an interesting new class of liquid crystals has recently been reported based on the surfactant templating of low-melting *inorganic* salts like $ZnCl_2$. The inorganic component easily forms glasses with strands comprising linked tetrahedra. Addition of amphiphiles gives new hybrid liquid crystalline phases depending on the inorganic-organic composition ratio and the temperature. This class of materials has been named *metallotropic*.[14]

Liquid crystals remain an active and vigorous research area with many technological applications. We will look at one of these applications in the next section. We also return to liquid crystals made up of polymers in chapter 14.

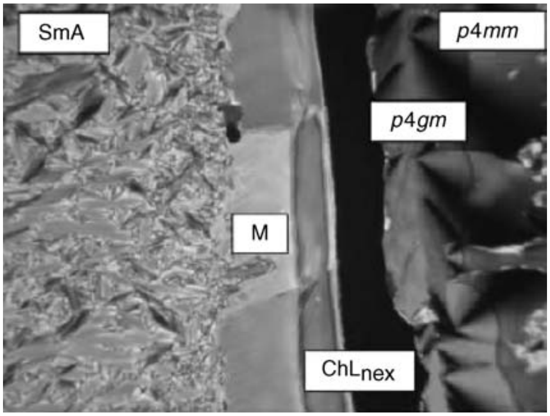


Figure 13.21 Contact region at 78 °C showing the phase sequence smectic-A (fan texture), M (unidentified mesophase), hexagonal channelled layer phase (ChLhex), square columnar phases p4gm and p4mm (from left to right) upon increasing concentration of **13.18** (reproduced by permission of The Royal Society of Chemistry). See plate section for colour version of this image.

13.3.4 Liquid Crystal Displays

Liquid crystals have a number of technologically important applications. They are used in precise temperature measurement, where the liquid crystalline phase changes can give temperature resolution of up to 0.007 K in a 1 K range. On a less precise level, temperatures of between –20 °C and +250 °C can be measured on liquid crystalline thermometers. They are cheap and toxicologically harmless and, as a result, are found in areas as diverse as medicine and even as wall thermometers in 'give away' advertising gimmicks. Liquid crystals are also found in various areas of analytical chemistry, and in any situation where it is important to measure direction- or orientation-dependent properties. Dissolution of the sample in a liquid crystalline nematic phase results in the orientation of the sample molecules in a precise and regular manner, facilitating measurement of anisotropic properties, such as circular dichroism phenomena, by IR and UV–visible spectroscopy. Liquid crystals are also used as stationary phases in the chromatographic separation of closely related isomers (*e.g.* dihaloarenes), which may often have very different solubilities in liquid crystalline phases. A range of NMR applications also exist.

By far the most important application of liquid crystals is in liquid crystal displays (LCD). These made their first appearances in wristwatches and pocket calculators, with the familiar seven-segment display (resembling a number '8' with square edges). Modern LCDs are now used in full-colour computer monitor displays (with the aid of dyes) based on twisted nematic cells (TNC), first outlined by Schadt and Helfrich in 1971. LCDs work on the principle that an applied electric field will alter the molecular orientations and result in changes in the optical behaviour. In a TNC, a thin layer (10–15 μm) of nematic liquid crystal is sandwiched between two transparent glass plates. The glass plates are pretreated with a director that has an orientating effect on the liquid crystalline phase, much like the mesogen orientates itself by interactions with its neighbours. If the two plates are rotated at 90 degrees to each another, a helical twist in the nematic phase is produced, with twist angle of 90° from one side to the other (Figure 13.22). The polarisation of plane-polarised light passing through the layer follows this 90-degree twist. The orientated liquid crystalline layer is placed between crossed polarisers, resulting in a display that is transparent to light at rest in the absence of an electric field. Application of a voltage produces a homeotropic rearrangement of the nematic phase and the twist is lost, resulting in no rotation of the plane-polarised light, no light transmission, and hence a darkened

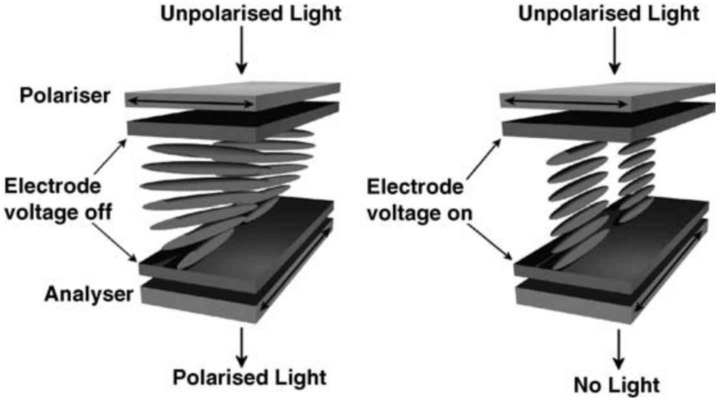


Figure 13.22 Operation of a twisted nematic cell. In the absence of an applied electric field, the twisted nematic rotates the plane of polarised light from one side of the cell to the other allowing light to pass through. An applied potential renders it opaque.

display. Because a voltage is required only to darken portions of the display when in use, the power consumption is extremely small, making the TNC ideal for use in portable applications such as watches, portable computers *etc*. The displays are also flat and compact, and their readability increases with ambient luminosity. Disadvantages are that the displays cannot be read in the dark (unless backlit), nor at an extreme viewing angle and their response time is slow (about 50 µs) compared with cathode ray tubes (10 µs), limiting their application in television sets, for example. The latest generation of flat panel displays get round some of these problems by using a patterned vertical alignment (PVA) method. In a conventional PVA a vertically aligned liquid crystal (LC) director tilts down in four directions making 45° with respect to crossed polarisers to give a wide viewing angle. The parallel geometry reduces the lag time while molecules reorientate when the voltage is turned off because the twisting occurs when the voltage is switched on.

More modern, much faster responding liquid crystalline displays use ferroelectric liquid crystals such as *p*-decyloxybenzylidine-*p′*-amine-2-methylbutylcinnamate, which can be switched between two stable states by application of an external field. Such properties may also be useful in optical data storage.

13.4 Ionic Liquids

🗝 Rogers, R. D., Seddon, K. R., 'Ionic liquids – solvents of the future?', *Science* 2003, **302**, 792–793.

An ionic liquid (IL) is literally an ionic compound (a salt) that is a liquid. Of most current interest are salts that are liquids at room temperature (RTILs), or at least below 100 °C. There is a range of compounds that form room temperature ionic liquids dating back to ethanolammonium nitrate, $(EtNH_3)^+(NO_3)^-$ (m.p. 14 °C), synthesised by Walden in 1914. Perhaps the most popular and well-studied are those based on the 1-butyl-3-methylimidazolium (bmim) cation, such as $bmim^+ PF_6^-$ (**13.20**) and $bmim^+BF_4^-$ which melts at *ca.* –80 °C. The imidazolium ionic liquids were initially used as their halogenoaluminate salts but they have a major drawback in that they are highly moisture sensitive.

In 1992, Zaworotko used weakly coordinating anions such as hexafluorophosphate and tetrafluoroborate, greatly expanded the range of ionic liquids available.[15] Modern ionic liquids that are air- and moisture stable based on non-coordinating anions has meant that the field has attracted tremendous