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Review Article

Inclusions between Large Flat Organic Molecules; the Induction of Columns and Mesophases[1]

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Abstract. We describe here an overview on the formation of mesophases by the interaction between large flat aromatic cored molecules and relatively small organic electron acceptors which form stacked, sandwich-like columnar π–π electron donor–acceptor complexes. The inclusion of suitable donor and acceptor components may be used to induce columnar mesophases in mixtures of compounds which can be either mesomorphic or non-mesomorphic in the pure state. With judicious choice of donor and acceptor partners, induced mesophases of remarkable range and thermal stability can be prepared.

Key words. Arenes, electron donor–acceptor complexes, heterocycles, induction phenomena, liquid crystals, metallomesogens, radial multiynes.

1. Outline

Liquid crystals present a unique amalgamation of long-range orientational and translational order with an intrinsic fluidity which makes the liquid crystal phase essentially self-annealing and self-repairing. This combination of order and fluidity presents a fascinating opportunity for the design and utilisation of new self-organising and self-assembling supramolecular architectures.

An important recognition is that liquid crystal phases may be induced, or the phase type manipulated, by intramolecular interactions between components in mixtures of compounds. In particular, we have been interested in the formation of mesophases from intercalated columnar π–π stacks of flat electron donor and acceptor components. This offers much greater scope for control of phase properties than can be achieved with pure compounds and points a route to new discoveries and uses for liquid crystals. In this paper, we present an overview of an exciting area of liquid crystal research involving the inclusion of relatively small, organic

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electron acceptors in donor–acceptor complexes with electron rich, flat aromatic compounds. This is not intended as an exhaustive review. Instead, using examples from our own work and that of others we will illustrate the different aspects of this approach to the formation and manipulation of columnar liquid crystal phases.

2. Introduction

The field of liquid crystal research and application has grown considerably since the first observation of liquid crystalline behaviour, by the Austrian Botanist F. Reinitzer in 1888 [2]. Although the first observation of liquid crystallinity was almost 110 years ago, the subject remained of only academic interest for a long period of time. Indeed, less than 30 years ago, M. J. S. Dewar said that *"while liquid crystals are uncommon and of no practical importance, they are of interest for the light they throw on the conflict between order and disorder"* [3]. It was the pioneering work of G. W. Gray and coworkers on cyanobiphenyl liquid crystals [4, 5] which led to the development of liquid-crystal display technology and the rapid growth in research from 1970 to the present day. Presently over 65 000 mesogenic compounds have been characterised, almost 85% of these in the last 25 years.

Matter is often considered as being either highly ordered, crystalline or disordered liquids, glasses and gases. There are many intermediate states between these, and liquid crystals are of particular interest. Molecules, aggregates or macromolecules self-organise into phases which have orientational order and may in addition have translational order in one or two dimensions. The resulting properties depend on the architecture of the phase.

Thermotropic liquid crystals are obtained by melting solids or cooling liquids and may consist of mainly rod-shaped or, for instance, sheet-shaped molecules which, depending on the degree or orientational and translational order may be nematic, smectic (rods) or columnar (discs or more generally, sheets).

Lyotropic liquid crystals are formed by the organisation of molecules into supramolecular aggregates in a solvent; the aggregates then orientate into phases. The properties of lyotropic liquid crystals depend on the solvent concentration. The most common are formed from amphiphiles (which contain hydrophobic and hydrophilic groups), most familiarly surfactants in water. Other types of lyotropic liquid crystals are obtained from stacked arrays of non-amphiphilic compounds, notably certain aromatic dyes or drugs (in aqueous solution) or some flat metalorganyl complexes (in apolar, organic solvents).

Perhaps the most striking aspect of liquid crystal research, apart from the massive impact that liquid crystal display devices have on everyday life, is the interdisciplinary nature of the subject, drawing on chemistry, physics, materials technology and the life sciences.

Liquid crystals have found wide-ranging uses, from displays and storage devices to organised fibres such as Kevlar used in materials as diverse as reinforced tyres and bullet-proof vests. Liquid crystal properties are found in a diverse range of compounds including soaps, carbohydrates, dyes, drugs, transition metal complexes. The challenges now for liquid crystal research are in using supramolecular chemistry to engineer new liquid crystals for new applications.
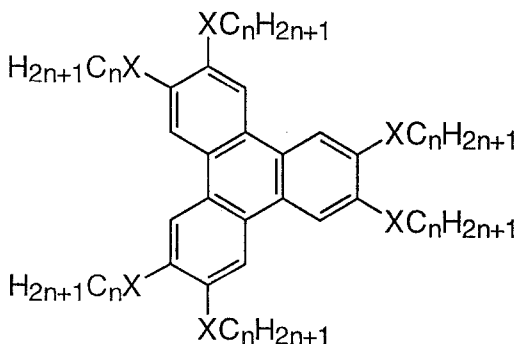
Notably for liquid crystal research, in 1995, G. W. Gray was awarded the prestigious Kyoto Prize for Advanced Technology for his work on the development of liquid crystal displays. This award is a culmination of over 40 years of research which has also yielded the Queen's Award for Technological Achievement in 1979 which was awarded to the Liquid Crystal Group at Hull University. In 1992, the Nobel prize for Physics was awarded to P.-G. de Gennes for his contribution to the theoretical understanding of soft matter (complex fluids) [6] and another Nobel prize winner in chemistry, J. M. Lehn [7], has made contributions to liquid crystal research, acknowledging the potential that mesogenic materials have for self-assembly and supramolecular organisation.

3. Basics of Liquid Crystals

We will use the term *mesogen* throughout this paper in its fullest form, that is, to describe a compound which appears to have a structure that should reveal liquid crystalline properties. This means that not all mesogens display mesomorphism (liquid crystal phases), however all have *liquid crystal-like* structure.

3.1. BASIC CORE GEOMETRIES/LIQUID CRYSTAL STRUCTURES

Thermotropic liquid crystals generally have a rigid central core, the structure of which in general defines the type of mesophases observed in each case; the two major structural motifs are rods and sheets. Rod-like mesogens are the most widely

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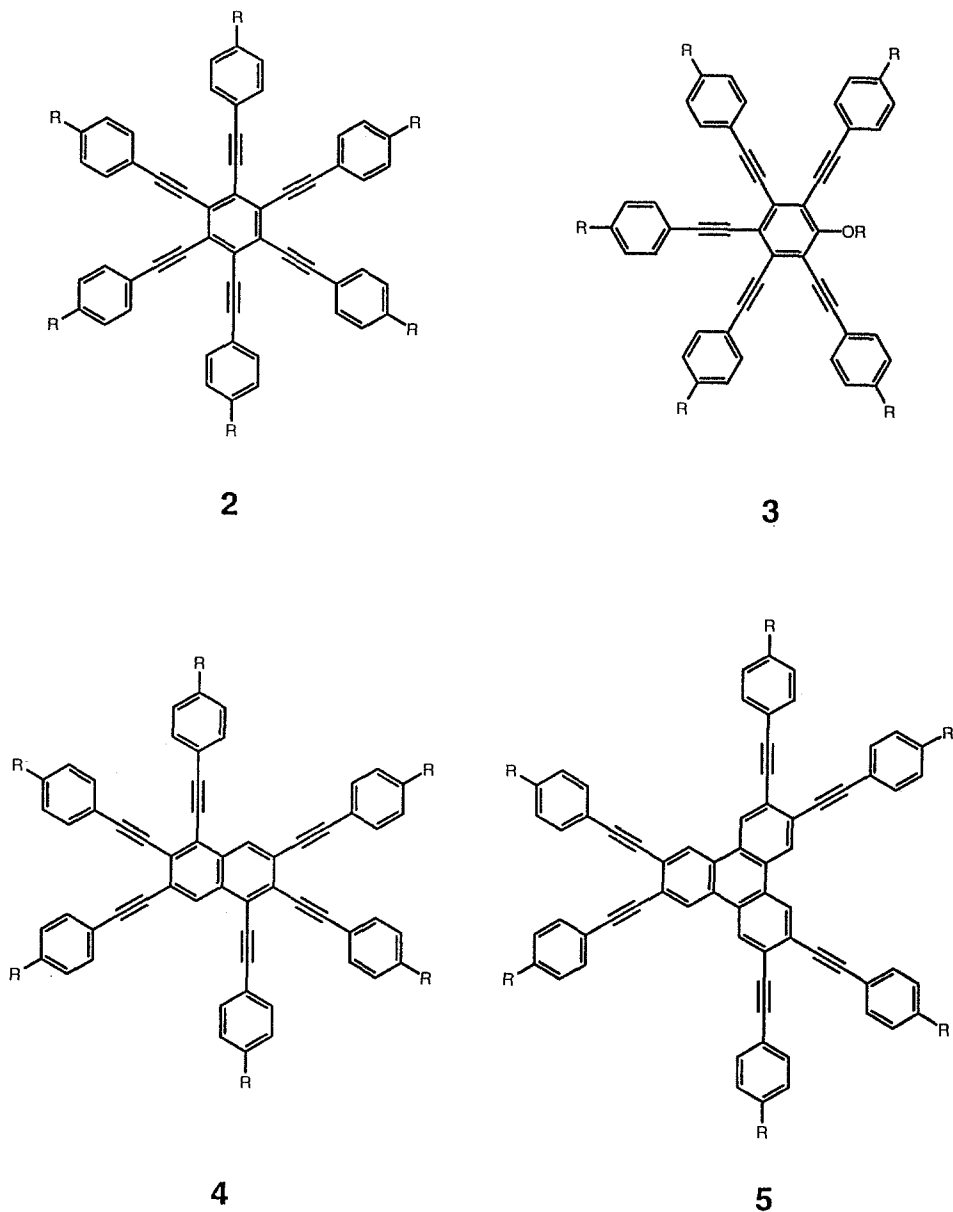*Figure 1.* The core in triphenylene mesogens (**1**, $n \geq 5$) with X=O [8–10], S [11] or Se [12].

Figure 2. The "super-disc"-cores of substituted radical multiyne mesogens with benzene (**2** and **3**), naphthalene (**4**) and triphenylene (**5**) central hubs (R: for example various alkyl [13–16] groups).

studied, while liquid crystals have recently been prepared with more elaborate core geometries and corresponding mesophase behaviour, often combining aspects of the prototype rods and sheets. It should be noted that in many of the latter cases liquid crystalline compounds possess a rigid, planar aromatic core, see for example
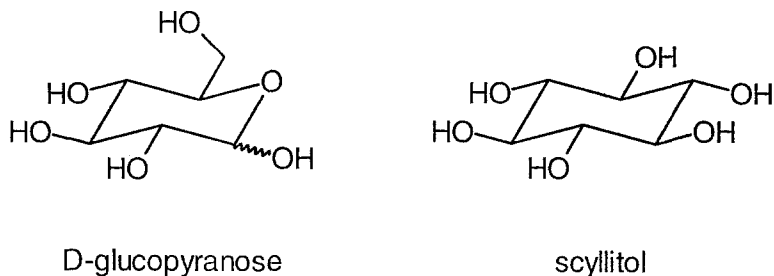
HO
HO O
HO
HO
HO OH

OH
HO OH
HO OH
HO

D-glucopyranose   scyllitol

Figure 3. D-Glucopyranose and scyllitol with their *saturated* cores are examples of carbohydrates and inositols which are valuable starting materials for liquid crystal syntheses [17–19].

the triphenylene (1) [8–12] and radial multiyne (2–5) [13–16] derivatives in Figures 1 and 2 although there are many, notable exceptions with saturated cores, e.g. carbohydrate/inositol liquid crystals [17–19] (Figure 3). The different mesophases are characterised by differing degrees of order, in each case by orientational order (with respect to some unique axis within the molecules) and by the absence of translational order about one, two or all three axes. Examples of the key liquid crystal states are shown in Figure 4.

The orientational order of a phase is an averaged order and the degree of correlation, known as the order parameter (S), between the average direction (defined by the director, N) and the actual orientation of all the molecules is given by:

$$S = \tfrac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

where θ is the angle between the molecular axis and the director. The nematic phase contains only orientational order and no translational order, other mesophases show increasing degrees of translational order.

3.2. FLAT MESOGENS; SHEETS/DISCS AND BOARDS

In this paper we concentrate on the mesophases formed by flat, or sheet-like highly unsaturated molecules, and in particular the induced phases formed from inclusion complexes having mostly small organic electron acceptor molecules intercalated between large electron donor molecules [20]. The structures of the sheet-like mesogens can vary widely from true circular discs through pronounced oval shapes to boards and sheets which have large, flat topologies but distinct length and width.

The simplest mesophase of sheet-like compounds, the nematic discotic (N_D) phase, has an orientational correlation of the short, unique molecular axis but no positional ordering. This can be considered as a heap of coins which lie on a table; all the coins have approximately the same orientation, but with no organisation in the arrangement between each other. There are also a wide range of columnar phases in which the molecules are stacked into columns which are arranged in some
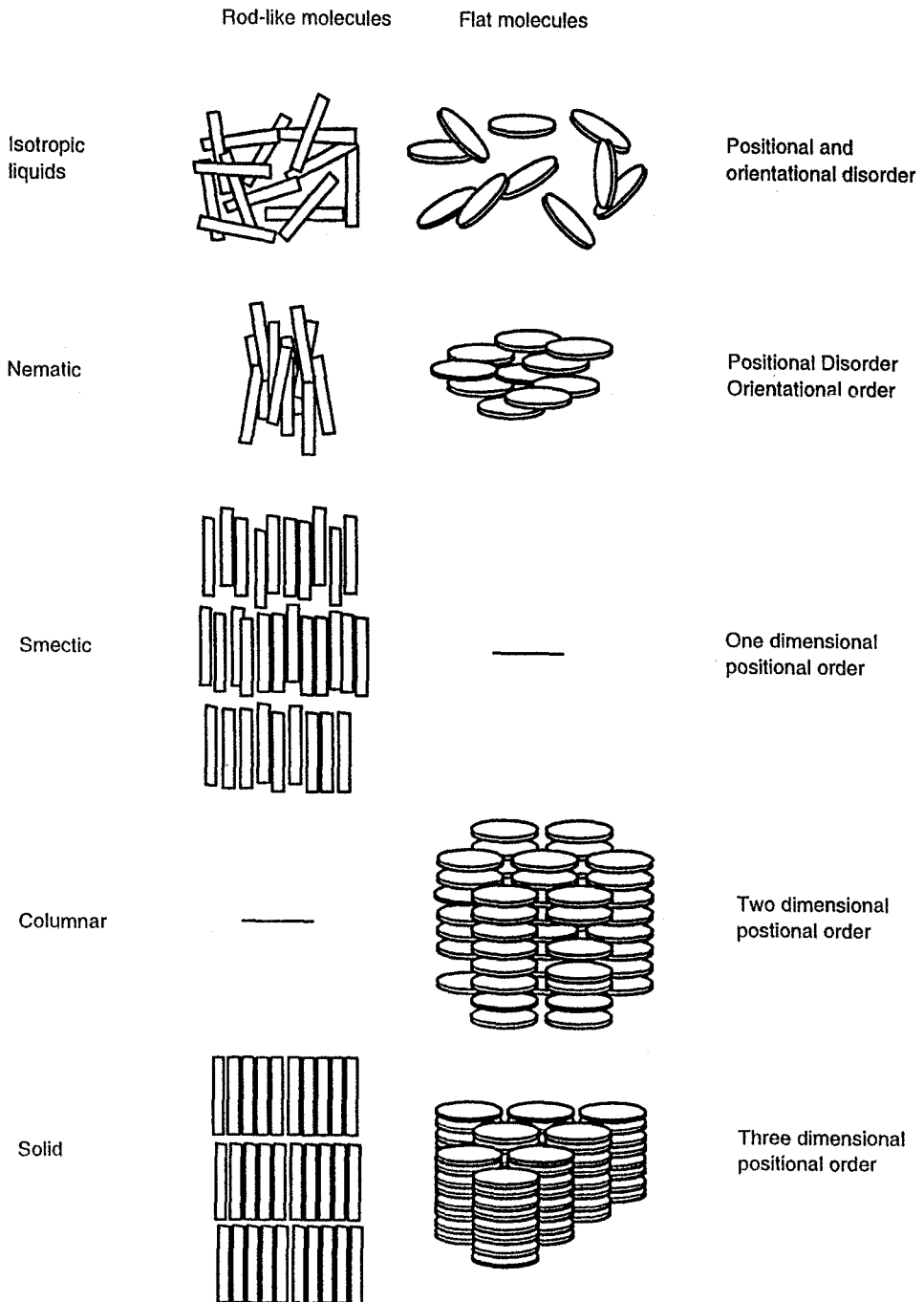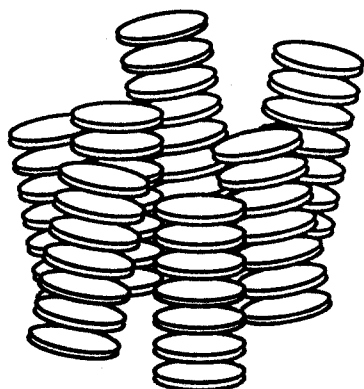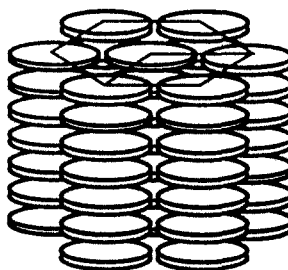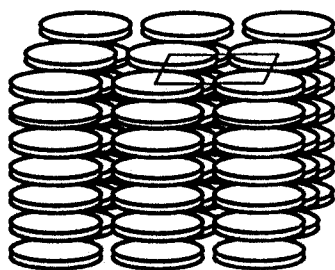
Rod-like molecules   Flat molecules

Isotropic
liquids   Positional and
                                                                           orientational disorder

Nematic   Positional Disorder
                                                                           Orientational order

Smectic   —————   One dimensional
                                                                           positional order

Columnar   —————   Two dimensional
                                                                           postional order

Solid   Three dimensional
                                                                           positional order

Figure 4. The basic organisation of rod- or sheet-like molecules in some of their principle liquid crystal phases.
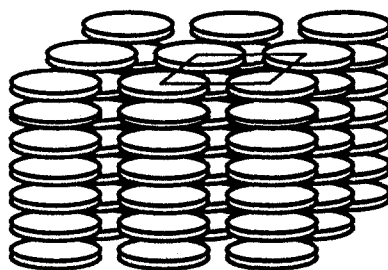
N$_{col}$
No translational order

Col$_h$
Hexagonal translational order

Col$_r$
Rectangular translational order

Col$_{ob}$
Oblique translational order

Figure 5. Examples of the intracolumnar packing in different mesophases of columnar order; N$_{col}$ = nematic columnar, Col$_h$ = columnar hexagonal, r = rectangular, ob = oblique.

relationship to each other. The columns may have no translational order between them, the nematic columnar phase (N$_{col}$) or the columns may be packed with some translational order. Examples are columnar hexagonal (Col$_h$), rectangular (Col$_r$) and oblique (Col$_{ob}$) phases, see Figure 5. Additionally, the phases may be ordered or disordered, depending on the absence or presence of liquid-like ordering within the columns or even tilted, where the orientation of the molecular unique axis is tilted with respect to the director (n) of the columns.

4. Examples of Mesophase Induction/Manipulation

4.1. BASIS OF INDUCTION IN LIQUID CRYSTALS

One result of the growing research in the field of liquid crystals is the realisation that this state of matter is not only formed by *pure* compounds with specific molecular structures, but also by *mixtures* of suitable compounds which may be mesogenic or even non-mesogenic in character.

Work on the thermotropic properties of mixtures of compounds was pioneered by Sackmann, Demus, Pelzl and their co-workers at Halle [21], who showed particularly that mixtures of calamitic liquid crystals containing electron donor and acceptor functions formed mesophases which displayed properties characteristic of a stoichiometric complex, rather than a simple mixture of compounds, and recognised the importance of charge transfer interactions [22] in the formation or stabilisation of smectic phases.

Later, using theoretical treatments, a model was postulated in which electron donor–acceptor complex formation was shown to be responsible for the formation of the majority of induced smectic phase behaviour [23] by enhancing lateral rigidity within the phase structure relative to the nematic phase. Since the molecular field treatment of *smectic* and *columnar* phases is similar [24], columnar mesophases should also be stabilised by the formation of electron donor–acceptor complexes which would enhance the tendency to columnar stacking of the molecules.

Mixtures of liquid crystals [25,26], however, usually display phase diagrams of a simple eutectic type (i.e. derived from simple mixtures) with a depression of transition temperatures. It follows that the usual behaviour on adding non-mesomorphic compounds to a liquid crystal is destabilisation of the mesophase, often with only very small doping levels. The donor–acceptor complexes are an exception, where mixing two components can lead to either stabilisation or manipulation of existing phases [27–30]. When the molecules are flat, sheet-like rather than calamitic, the formation of donor–acceptor complexes is associated with columnar stacking; not only may existing columnar phases be stabilised but also new columnar mesophases can be induced in materials displaying nematic discotic (N_D) phases or even in compounds which show no mesophases in the absence of electron donor–acceptor complexation.

Although the idea that induced columnar stacking interactions could be beneficial to the formation of liquid crystal mesophases is relatively recent, the existence of strong electron donor–acceptor charge transfer complexes between flat, aromatic ring systems was known many years earlier.

Probably one of the earliest observations of electron donor–acceptor or charge-transfer complexes between flat aromatic systems was noted by Patrick and Prosser in 1960 [31], who showed that mixtures of hexafluorobenzene and benzene formed solid complexes with relatively high melting points (24 °C compared to 5 °C for each of the two components). Similarly, complexes were formed between hexafluorobenzene and mesitylene or 2-methylnaphthalene which proved stable

enough to allow crystallisation from ether. Importantly, it was recognised that the charge transfer complexes formed resulted from the strong negative inductive effect of the fluorine atoms of the hexafluorobenzene and it was suggested that similar complexes should be obtained with other aromatic systems containing functions with strong negative induction effects such as nitro groups.

4.2. THE INTERACTION BETWEEN SMALL ELECTRON ACCEPTORS AND FLAT DONORS

The columnar mesophases formed by flat, sheet-like molecules comprise columnar stacks of molecules. Since the formation of donor–acceptor complexes may stabilise stacking interactions, as seen between hexafluorobenzene and benzene, then columnar mesophases should also be stabilised by interaction between electron acceptors and mesogenic electron donors. This is observed and it is also possible to induce mesophases in compounds which show no mesomorphism in the pure state. We can consider several situations for formation of mesophases in donor–acceptor complexes; mixing two mesogens; mixing a mesomorphic compound with a non-mesomorphic compound; and finally mixing two non-mesomorphic compounds. Similarly, there are three possible successful outcomes from these methods: stabilisation, manipulation or induction of mesophases where an existing mesophase may be stabilised over a larger temperature range, an existing mesophase may be manipulated – changing for instance a nematic discotic phase into the more ordered columnar hexagonal phase – or induction of totally new mesophases in non-mesomorphic compounds, or the induction of columnar phases in material which only displays a nematic discotic phase in the pure state.

The model for π–π electron donor–acceptor-induced stacking of flat organic electron donors and acceptors is shown in Figure 6. Interaction between the electron donors and acceptors leads to columnar stacking in which the (relatively) small electron acceptors are sandwiched between the large, flat donor molecules. The intercalation of the acceptor molecules into columns *or* the induction of columns in non-mesomorphic sheets or discs is a function of the electron donor–acceptor interactions; the types of mesophases that may be formed (i.e. N_{col}, Col_h etc.) depends on specific features of the periphery of the columns, in particular the length and distribution of peripheral substituents.

However, in contrast to this example and first descriptions of lamello-columnar mesophases between donor and acceptor molecules which were analogues of solid state organic conductors based on substituted dithiapyranylidine complexes [32, 33], where the donor and acceptor components are of essentially equal size, the commonest motif for columnar electron donor–acceptor complexes comprises large, flat organic electron donors with the relatively small electron acceptor components intercalated in a 'sandwiched' multilayer structure.

Although many strong electron acceptors [34] may be used to form mesomorphic electron donor–acceptor complexes (see Figure 7), in our experience the best
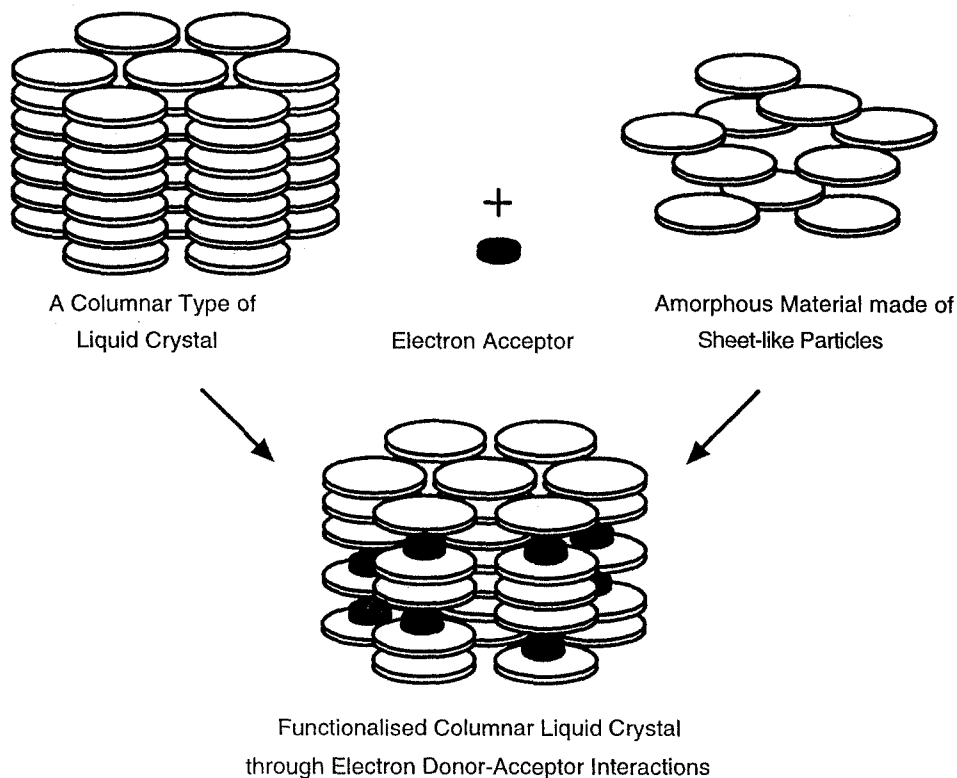
A Columnar Type of
Liquid Crystal   Electron Acceptor

Amorphous Material made of
Sheet-like Particles

Functionalised Columnar Liquid Crystal
through Electron Donor-Acceptor Interactions

Figure 6. Incorporation of electron acceptors into π–π electron donor–acceptor stabilised columnar mesophases, either from existing columnar phases (left), nematic discotic phases or even from amorphous sheet-like compounds (right).

results (for instance greatest mesophase range) are often obtained using TNF (6) as the electron acceptor component. The specific interactions between the donor and acceptor groups also play important roles; some complexes show startlingly different mesomorphism which is dependent on the nature of the electron acceptor component of the complex. The effects of particular aspects of the electron acceptors, i.e. the magnitude of the inductive effect, the structure of both the electron acceptor and the interplay between these factors is not yet clearly understood. The other electron acceptors shown in Figure 7 are an amphiphilic TNF derivative (7) and TAPA (8) which has been used to induce chiral mesophases. It should be emphasised that many other electron acceptors are equally applicable including, for example, TCNQ (tetracyanoquinodimethane), bromine and iodine.

We can see that at the molecular level, columnar stacked mesophases are analogous to layered solid-state inclusion lattices; the key difference is that liquid crystal phases form *dynamic* systems (remember, we still have liquid-like reduced translational order in at least one dimension) rather than solid, crystalline structures. In the case of induced mesophases in which electron donor–acceptor complex formation
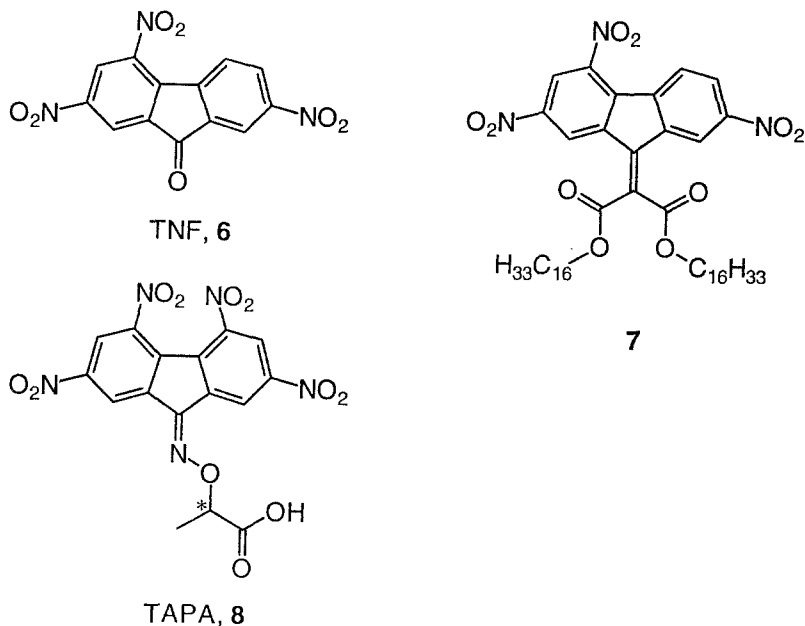
Figure 7. Some efficient electron acceptors used to form electron donor–acceptor complexes [20, 37]. TNF (2,4,7-trinitrofluorenone, **6**), an amphiphilic long chain TNF derivative (**7**) and (+)- or (−)-TAPA [(±)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy) propionic acid (**8**)].

stabilises the columnar structures, the *included* electron acceptor has a key role in assembly of the superstructure. We will consider this, and the potential and key possibilities for chemical/physical manipulation in the concluding section of this paper.

5. Mixtures of Different Compounds

We give here examples from three series of flat aromatic compounds studied as representative examples illustrating the principles of columnar mesophase stabilisation in mesomorphic and non-mesomorphic compounds. The first two sections describe derivatives of triphenylene or radial multiynes which were the first examples of flat organic mesogens which were investigated for induced mesomorphism in the presence of electron acceptors. The third group — flat metalorganyl compounds — show analogous mesomorphism and illustrate that these phenomena are not restricted to just purely organic metal-free compounds. Finally we will look briefly at the induction of mesophases by molecular recognition and consider the role that π–π electron donor–acceptor interactions have in mesophase formation by induction in *single* compounds.

5.1. TRIPHENYLENE ETHERS (LOW MOLECULAR WEIGHT DERIVATIVES AND
      POLYMERS)

Triphenylene derived liquid crystals (**1**, Figure 1) have been widely studied with
ether [8–10] and thio- [11] or seleno-ether [12] substituents and form the basis of
the first mesogenic flat donor molecules investigated for electron donor–acceptor
induced liquid crystal mesomorphism. Here, we present examples of mesophase
stabilisation, induction in non-mesomorphic compounds and mesophase manipu-
lation in both low molecular mass and polymeric triphenylene derivatives through
complexation with TNF.

   In simple (and representative) systems, using small organic electron acceptors
which on complexation are well hidden inside the width of the columns, forma-
tion of electron donor–acceptor complexes by addition of TNF causes an overall
stabilisation of the existing columnar structure and an extension of the mesophase
range. The pentyloxy-substituted triphenylene (**1d**, c.f. Figure 10) has a columnar
hexagonal mesophase (Col_{ho} from 69–122 °C) in the pure state [8]. The tempera-
ture range of this mesophase steadily increases (both the melting point drops and
the clearing temperature is raised) on addition of TNF as the columnar mesophase
is stabilised by π–π electron donor–acceptor complex formation. Maximum stabi-
lisation is obtained with a 1 : 1 donor–acceptor complex with the Col_{ho} mesophase
range extended from below room temperature to over 250 °C [24].

   Similarly, with amorphous, non-mesomorphic polymers based around the tri-
phenylene subunit, either as main-chain or side-chain polymers, addition of the
electron acceptor TNF induces columnar organisation of the triphenylene units
which stack into donor–acceptor complexes with the added TNF. The polymer–
TNF complexes show induced columnar mesophases which can be N_{col} (side-chain
polymers) or Col_{ho} (main-chain polymers) [24,35,36],

   When the size of the electron acceptor becomes large and starts to extend beyond
the periphery of the complex, then features of its structure start to have an influence
on the mesophase formation as well as on the column formation. Formation of an
electron donor–acceptor complex between the pentyloxy-substituted triphenylene
(**1d**) and a derivative of TNF containing long alkyl chains (**7**), stabilises the colum-
nar stacking of the triphenylene subunits [37] but unusually yields an apparently
destabilised mesophase, a monotropic N_{col} compared to the parent Col_{ho} phase.
In contrast, the non-mesomorphic longer chain substituted triphenylene (**1**, X=O,
$n = 16$) forms an electron donor–acceptor complex with the same electron accep-
tor (**7**) which has an induced Col_{ho} mesophase from 59–102 °C. This apparent
contradiction in behaviour between the two analogous complexes (electron donor–
acceptor complex stabilised and destabilised phases) can be understood since, in
both cases, the electron donor–accepter complex stabilises columnar stacking of
molecules, but the mesophase type depends on the periphery of the columns which
have two long and six short alkyl chains or eight long alkyl chains, respectively. The

differences in respective space filling then have the major influence on mesophase type.

5.2. RADIAL MULTIYNES

Functionalised multiynes (Figure 2) based around benzene (2 and 3), naphthalene (4) and triphenylene cores (5) [13–16] present particularly large, extended flat aromatic "super-disc"-cores. In the pure state, these large flat aromatic systems are usually either in a few cases non-mesomorphic, or exhibit nematic discotic (N_D) phases with orientational order, but lacking in translational order. On addition of electron acceptors, donor–acceptor complex formation leads to the stabilisation of columnar stacks and the formation of columnar mesophases [38,39].

For the two pentayne derivatives 3a and b [40,41] shown in Figure 8 which differ only by a methyl group (R=H or Me), we have a situation where mesophases can be either (i) induced or (ii) manipulated. When the peripheral aromatic rings are unsubstituted (3a, R=H [41]) this compound is non-mesomorphic in its pure state, but forms electron donor–acceptor complexes with TNF which show the induction of Col_{ho} and N_{col} phases. For the substituted example (3b, R=Me [41]) which displays a nematic discotic mesophase in the pure state, electron donor–acceptor complex formation with TNF initially destabilises the N_D phase, followed by the induction of stabilised and enhanced Col_{ho} and N_{col} phases. The greatest stabilisation of the induced or manipulated mesophases is obtained with 1 : 1 donor–TNF complexes, the phase diagrams of both the pure donors and the 1 : 1 complexes with TNF are shown in Figure 8. These are examples of mesophase manipulation, changing the phase type by addition of different amounts of the electron acceptor. It is possible in these systems to have all three phases, N_D, Col_{ho} and N_{col}, present at the same temperature as a function of the complex composition.

Similarly, other non-mesomorphic radial pentayne derivatives show nematic columnar (N_{col}) [42] or nematic columnar and columnar hexagonal (Col_{hd}) mesophases [40] as electron donor–acceptor complexes with TNF. Measurements of the dielectric and elastic properties of a nematic phase induced by electron donor–acceptor interaction have been made [42]. Amphiphilic examples (i.e. with an ether or a similar function at the end of the long OR group in the cleft of 3) of sheet-shaped mesogens based on pentakis(phenylethynyl)benzene [43] exhibit an N_D phase in their pure forms, but formation of electron donor–acceptor complexes with TNF induces the formation of a Col_{ho} phase. Analogous radial hexayne derivatives of naphthalene and triphenylene also show induced columnar mesophases in binary mixtures with a variety of dipolar aromatic compounds [44]. However, in this case, stabilisation of the columnar phases is probably a result of improved space filling between the compounds rather than a π–π stacking mechanism.

Even chiral mesophases can be obtained by phase manipulation [41]. Utilising the chiral electron acceptor (–)-TAPA (8) both chiral nematic discotic (N_D^*) and chiral nematic columnar (N_{col}^*) phases may be obtained in complexes with the radial
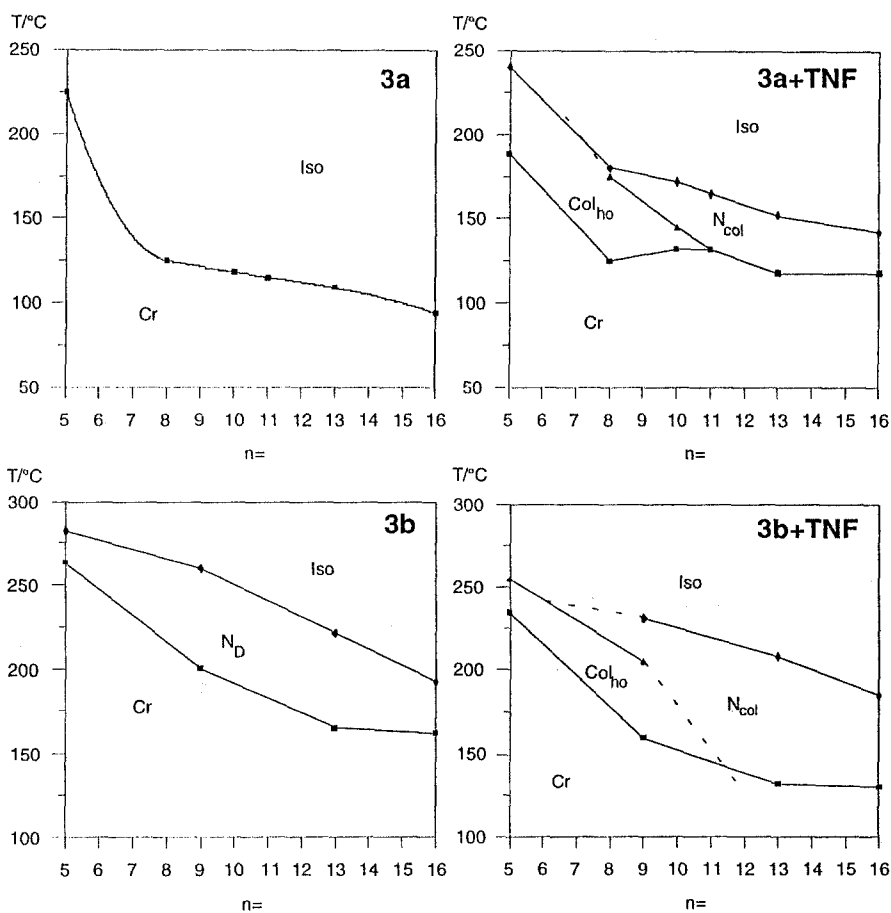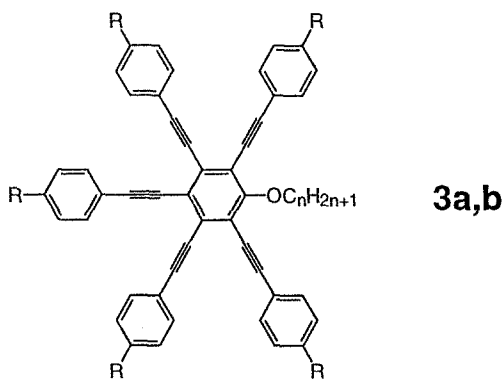
Figure 8. Induction and manipulation of mesophases from 1:1 complexes of two radial pentayne derivatives, e.g., **3a** or **3b** with TNF [40, 41]. When R=H (**3a**, top left), the compound is not mesomorphic in the pure state, however, when R=Me (**3b**, bottom left) a nematic type of phase is observed. Electron donor–acceptor complex formation with TNF (**6**, see Figure 7) stabilises columnar packing and either induces mesophase formation (top right) or manipulates existing mesophase structures (bottom right).

pentaynes (**3a** and **b**) by manipulation of the *natural* N_D phase of **3b** with addition of up to 30% (–)-TAPA, or for the N_{col}^* phase, by induction of the N_{col} and N_{col}^* phases in ternary mixtures of **3b** with TNF and (–)-TAPA. Chiral nematic discotic phases are at present rare, either in pure chiral materials [45] or in chirally induced systems [46].

The range of the chiral mesophases induced with TAPA are much smaller than the phases formed in electron donor–acceptor complexes with TNF. Despite this, the ability to manipulate mesophases and especially to induce chirality is important and very useful. The lower stability of the electron donor–acceptor induced mesophases when (+)- or (–)-TAPA is the electron acceptor compared to using TNF can be attributed to a lowering of the efficiency in assembling columnar electron donor–acceptor complexes compared to those with TNF [41].

5.3. METAL-ORGANYL MESOGENS

A further group of flat, sheet-shaped compounds which we have investigated extensively are cyclometallated organyl complexes containing either two or four metal centres [47–55] (Figure 9). It has been shown from single crystal X-ray structures [53, 54, 56] that each of these metalorganyls contain a large, flat central core defined by the metal centres and coordinated aromatic rings. In this way, the compounds are structurally analogous to the earlier examples of purely organic flat mesogens and display mesomorphic properties that are those of flat, sheet-like compounds. This is in contrast to other related metalorganyl mesogens [57] which have a different peripheral substitution pattern and an overall rod-like structure. In fact, the mesomorphism, especially of the tetrametallocompounds is particularly extensive forming, not only thermotropic, but also lyotropic mesophases [50–52, 55] in apolar organic solvents including the first examples of two lyotropic nematic columnar mesophases side by side in apolar, non-micellar systems.

In common with the earlier examples of π–π electron donor–acceptor-induced/ stabilised mesomorphism described here, the metalorganyl complexes display both induction and stabilisation of mesophases, including induction of chiral mesophases with the chiral electron acceptor, (+)- or (−)-TAPA (**7**). In addition, induced lyotropic mesophases are also observed in ternary mixtures of the donor and acceptors in apolar organic solvents.

The bis-metal complexes (**9**) with either palladium [47] or platinum [53] show a single monotropic N_D phase (that is, the mesophase is metastable and is only observed on cooling from an isotropic liquid and not on melting the crystalline solid) as pure compounds; the palladium examples were the first metallomesogens to display a nematic discotic phase. However, on doping with TNF, columnar stacking of the molecules in electron donor–acceptor arrays is induced and columnar mesophases (Col$_{ho}$ or Col$_{ho}$ and N$_{col}$) are stabilised [49].

The tetranuclearorganyls (**10**) with either palladium [47,48,54] or platinum [55] metals, show thermotropic, lyotropic and induced mesomorphism. In the
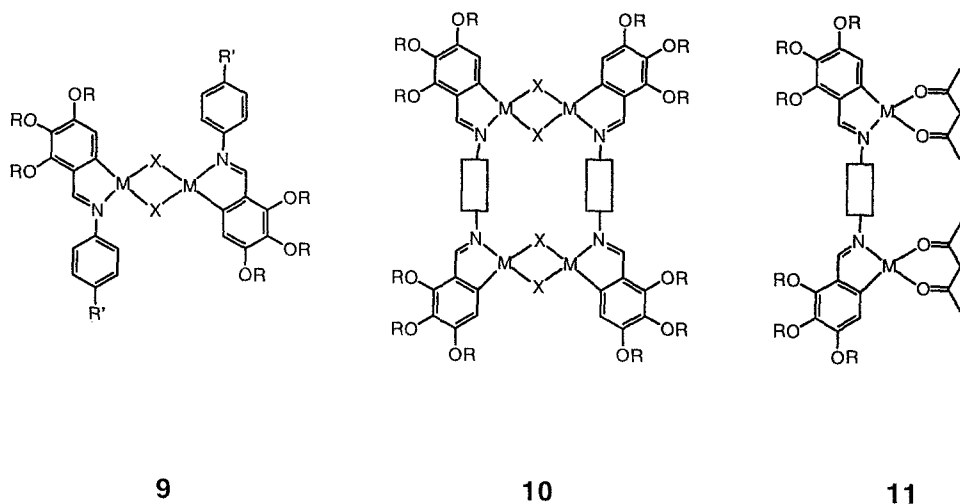
9   **10**   **11**

Figure 9. Bis- (**9**) and tetranuclear (**10**) metalorganyl mesogens (M=Pd or Pt; X=Cl, Br, I, SCN, N_3; R = alkyl, R' = alkyl or oxyalkyl chains) [47, 53–55] and the dipalladiumorganyl (**11**) derived from **10** by ligand exchange reaction [52]. The spacer unit (——□——) in the tetrametal complexes may be phenylene, stilbenylene or terphenylene).

pure state, a viscous columnar mesophase ($Col_{ob,d}$) is usually obtained which has oblique packing of the columns and liquid-like disorder of the molecules within the columns. The range of the mesophases for these compounds is particularly broad, typically over 200–250° [47, 54, 55] and is relatively insensitive to changes in the metal centre, bridging groups (X) or peripheral alkyl chain lengths (R). The mesophase persists until decomposition occurs around 300 °C. Formation of electron donor–acceptor complexes by addition of TNF again stabilises the columnar stacking yielding columnar mesophases with increased order, in this case, columnar hexagonal phases (Col_h).

The lyomesomorphic properties of the tetrametalorganyls are particularly interesting. With apolar organic solvents (for example long-chain alkanes), the molecules also aggregate, forming either one or two nematic columnar mesophases (N_{chr}) which comprise of columnar stacks of molecules with nematic orientation in solution [1,50,52]. At high concentrations a viscous two dimensionally ordered columnar mesophase continuous with the thermotropic Col_{ob} is also observed. The behaviour of the phases depends strongly on the nature of the bridge (X) and spacer units [50, 52].

Importantly, the lyotropic nematic phase range can be extended by charge transfer induced stabilisation of the columnar stacking by addition of TNF. Additionally, chiral mesophases [51] can be induced by electron donor–acceptor complex formation between the tetrametallomesogens as electron donors and either (+)- or (−)-TAPA (**8**) as a chiral electron acceptor. The complexes display an induced

Table I. Mesophase induction in the three types of flat palladiumorganyl mesogens, **9** (X=Cl) [47, 49], **10** (X=Cl) [50–52] and **11** [52] in Figure 9.

–	9	10	11
Pure mesogen	N_D (monotropic)	$Col_{ob,d}$	Not mesomorphic
+ TNF	Col_{ho}	Col_h	Col
+ TNF + $C_{15}H_{32}$	N_{chr} (monotropic)	N_{chr}	

N_{chr}: lyotropic nematic chromonic mesophase [58], containing columnar mesogenic units.

lyotropic chiral nematic (N^*_{chr}) phase of chromonic [58] type which has greatest stability as a 1 : 1 complex of the donor and acceptor components.

To complete the picture of mesophase manipulation in this series of metallome-sogens; the di-palladium compound (**11**) is prepared by cleaving the parent tetrapal-ladium species (**10**), replacing the bridging groups with bidentate acetylacetonate ligands [52]. This compound is non-mesomorphic in the pure state, but induced columnar mesophases can be obtained on forming π–π electron donor–acceptor complexes with TNF, either a thermotropic columnar phase in binary mixtures or a nematic columnar phase of chromonic type (N_{chr}) in ternary mixtures with apolar organic solvents.

The generalised mesomorphic behaviour of these three types of metalorganyl mesogens (**9–11**) is shown in Table I. These metal complexes also display the different modes of mesophase manipulation discussed previously. Addition of an electron acceptor in all cases causes stabilisation of columnar stacks of intercalated donors and acceptors. This results in the stabilisation of mesophases based on columnar mesogenic units either from mesogens with existing columnar phases (**10**), a nematic discotic phase (**9**) or the induction of columnar phases in non-mesomorphic compounds (**11**).

5.4. HOST–GUEST COMPLEXES; MESOPHASES BY MOLECULAR RECOGNITION

A fascinating area of mesophase induction is the interface to molecular recognition. An interesting example are functionalised macrocyclic amine (18N6) complexes with Ni^{2+} or Co^{3+} [59, 60] which display columnar mesophases. The uncomplexed ligands are conformationally flexible and show no mesophase behaviour; here mesophase formation is a function of the conformational rigidity imposed by metal complexation.

5.5. MESOPHASE STABILISATION IN SINGLE COMPOUNDS

In the binary (and ternary lyotropic) electron donor–acceptor complex stabilised columnar mesophases described, stabilisation arises from π–π interactions between electron rich aromatic rings and electron deficient acceptor functions in the donor

and acceptor molecules respectively. These components need not necessarily be derived from separate molecules. It is possible to design mesogens which incorporate both donor and acceptor functions into a single molecule.

Ringsdorf, Wendorff and coworkers [61] were the first who prepared mesogens containing both electron acceptor and flat, aromatic electron donor units linked with a flexible spacer (**1a** and **b**, in Figure 10). These mesogens exhibit electron donor–acceptor stabilised columnar mesophases with transition temperatures comparable to those of the 1 : 1 binary mixture of the two components, hexa(pentyloxy)triphenylene (**1d**, N = 5) and TNF (**6**).

In addition to combining donor and acceptor functions by a relatively long flexible spacer as in **1a, b**, and other examples [61], it is also possible to introduce both functions separated by much shorter, rigid links, even by a single covalent bond. Figure 10 shows such examples of three different types of flat, sheet-like mesogens — to our knowledge known up to now — derived from triphenylene, a radial multiyne, and phthalocyanine incorporating highly polar substituents with negative inductive effects: 1a) substituted triphenylene *penta*ethers containing bromo (**1e**) [62] or triflicoxy (**1f**) [62] functions, 1b) *hexa*(alkyloxy)triphenylene mesogens containing nitro (**1h**) [63, 64], amido (**1i** as one example of a homologous acylamido series) [65], azido (**1j**) [65], chloro (**1k**) [64], or bromo (**1l**) [64], groups, 2) the nitrile substituted radial multiyne (**12b**) [66], and 3) the phthalocyanine derivative **13b** with even two nitrile groups directly attached to the macroheterocyclic mesogen core causing a permanent electric dipole moment which, in this particular case, has been estimated to be 7 Debye [67].

Interestingly, the latter one is the longest known (since 1985 [67]) disc-like thermomesogen with each a single covalent bond between their electron donor and acceptor part, but was — like the others mentioned — not discussed under the aspect of "intramolecular mesophase induction or stabilisation".

In comparison with their parent triphenylene multiethers and the radial multiyne or phthalocyanine without an electron acceptor function (i.e. **1c, d, g** and **12a**, or **13a** in Figure 10), the other mesogens show a drastic widening of their respective mesophases with *both* a decrease in melting point and an increase in the clearing temperature. Other nitrosubstituted triphenylene hexaethers with a different substitution pattern on one aromatic ring [65] also display the same effects on their columnar mesophases with respect to their unfunctionalised analogues. Although not initially recognised, it is tempting to consider that the enhancement of the columnar mesophase range for these functionalised mesogens is a result of π–π electron donor–acceptor interactions between adjacent molecules which stabilises columnar stacking relative to the unfunctionalised analogues. Certainly, both electron rich donor and electron deficient acceptor functions are present in the compounds, however, it is also equally possible that the stabilisation is caused by induced dipole–dipole interactions.

Interestingly, these sheet-like compounds are examples of mesogens where the addition of relatively strong polar functions (featuring a negative inductive effect)
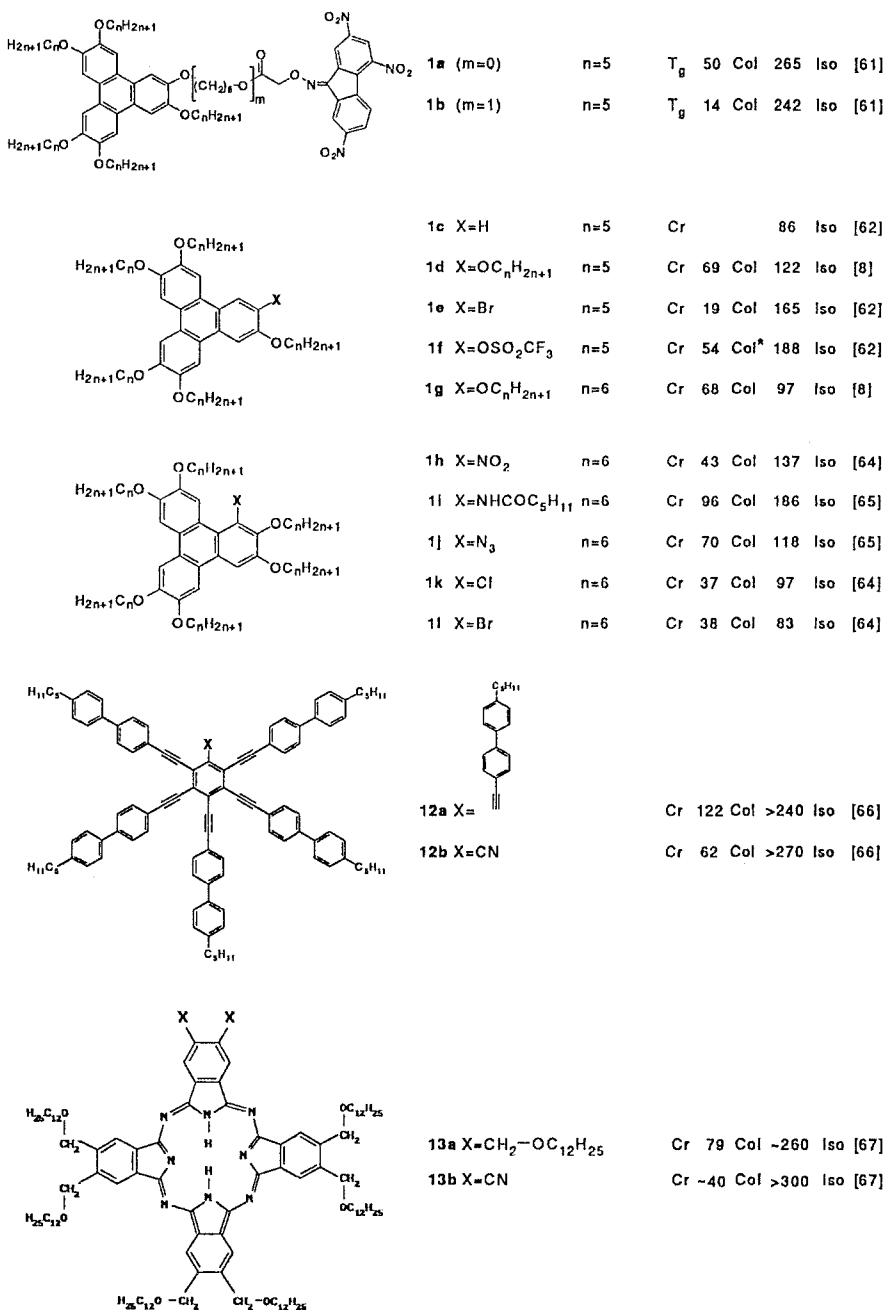
1a	(m=0)	n=5	T_g	50	Col	265	Iso	[61]
1b	(m=1)	n=5	T_g	14	Col	242	Iso	[61]

1c	X=H	n=5	Cr			86	Iso	[62]
1d	X=OC$_n$H$_{2n+1}$	n=5	Cr	69	Col	122	Iso	[8]
1e	X=Br	n=5	Cr	19	Col	165	Iso	[62]
1f	X=OSO$_2$CF$_3$	n=5	Cr	54	Col*	188	Iso	[62]
1g	X=OC$_n$H$_{2n+1}$	n=6	Cr	68	Col	97	Iso	[8]

1h	X=NO$_2$	n=6	Cr	43	Col	137	Iso	[64]
1i	X=NHCOC$_5$H$_{11}$	n=6	Cr	96	Col	186	Iso	[65]
1j	X=N$_3$	n=6	Cr	70	Col	118	Iso	[65]
1k	X=Cl	n=6	Cr	37	Col	97	Iso	[64]
1l	X=Br	n=6	Cr	38	Col	83	Iso	[64]

12a	X=		Cr	122	Col	>240	Iso	[66]
12b	X=CN		Cr	62	Col	>270	Iso	[66]

13a	X=CH$_2$—OC$_{12}$H$_{25}$		Cr	79	Col	~260	Iso	[67]
13b	X=CN		Cr	~40	Col	>300	Iso	[67]

Figure 10. Mesophase stabilisation in single component mesophases by inductive charge transfer interactions; Cr: Crystalline state, T_g: glass transition temperature, Col: Columnar mesophase, Iso: Isotropic liquid; the numbers between the assigned states of matter are the respective transition temperature in °C. * Two columnar mesophases are observed, here only the transitions Cr → Col′ and Col″ → Iso are shown.

to the molecules *enhances* mesophase formation. Also, with regard to our radial multiyne and to the phthalocyanine examples **12** [66], or **13** [67], respectively, nitrile groups are very common in many calamitic liquid crystals (for example the original cyanobiphenyl derivatives [4, 5]) and it has been shown that the formation of smectic phases are primarily due to the charge-transfer interactions. In our columnar mesophase examples, we have an indication of the magnitude of stabilisation afforded by such interactions. It also might be anticipated that (the synthetically challenging) incorporation of a nitro function, e.g., into the multiyne mesogen (**12**, $X = NO_2$) would further enhance columnar stacking, either by charge-transfer or dipole–dipole interactions.

6. Discussion and Concluding Remarks

The induction of columnar mesophases from the interaction between flat, sheet-shaped electron rich donor molecules and electron deficient partners provides great scope for the expansion of liquid crystal research and the development of new materials. Using this concept, it is possible to envisage the formation of a wide range of new liquid crystals tailored to meet specific needs by selecting a particular combination of electron donor and acceptor components. The mesomorphic properties (temperature range, clearing point and indeed the nature of the phase type) can be controlled by varying the ratio and nature of these two types of reaction partners in such mixtures.

The organisation of these liquid crystals with relatively small electron acceptors intercalated between larger, flat donor molecules in columnar stacks is similar to that found in solid-state layered inclusion compounds where small molecules are intercalated between layered sheets of the host matrix. However, in contrast to solid-state inclusion lattices, in the electron donor–acceptor induced liquid crystals there is, in general, a high correlation along the columns between the *included* component (the electron acceptor). With the electron acceptor present as only a small percentage of the composition, distribution within the columns is random. As the composition reaches that for optimum stabilisation, typically as the 1 : 1 complex, distribution of the components becomes more organised, tending towards a continuous donor–acceptor–donor sandwich. This correlation can be important for example in sensing of one-dimensional electrical conduction along the columnar axis.

Other important properties for consideration are the self-organisation and self-assembling features of liquid crystals which, coupled with ease of processing could probably make these highly appealing materials for applications. Materials may be incorporated into a cell in the liquid or liquid crystal state and then self-organise and orientate into the desired configuration. The fluidity of liquid crystals also helps to overcome many of the problems associated with crystal defects and grain boundaries in solid state devices. Liquid crystal devices are essentially self-annealing and self-repairing, dynamically reforming to maintain phase integrity.

These properties are highlighted in the charge conducting properties [68] along the columnar stacks of alkylthio-substituted triphenylene [11] liquid crystals and in alkyloxy-substituted ones doped with *inorganic* electron acceptors ($AlCl_3$ and $NOBF_4$) [69]. These materials have charge carrier mobilities much higher than any other organic materials, other than single crystals, resulting from the favorable combination of relatively high order with some flexibility in the liquid crystal phase.

The properties of electron donor–acceptor complex induced or stabilised liquid crystals can be controlled by both the choice of donor and acceptor components and by the ratio between them. Induced mesophases can be prepared with particularly wide ranges of thermal stability and also with stability in the presence of additives. Liquid crystals are generally very sensitive to doping; usually the result is destabilisation or complete loss of mesomorphism. The tolerance of these π–π interaction stabilised mesophases to changes in composition has important implications if liquid crystals are to be considered as media for catalytic or synthetic reactions.

Liquid crystal technology has moved quickly from being "*of no practical importance*" [3] to the widespread use of liquid crystal displays, but this is not the end of the story. Research ranging from new electro-optical devices through to the liquid crystal properties of DNA and cell membranes point to future design of new 'smart' fluids with self-organising and assembling properties. Using intermolecular electron donor–acceptor interactions in binary and higher mixtures as a method of inducing phase formation and including specific components within an organised mesophase offers an exciting route to these new materials.

Acknowledgments

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