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Low-Molar-Mass Thermotropic Liquid Crystals [and Discussion]

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Low-molar-mass thermotropic liquid crystals

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The impact of liquid crystals over the past 20 years in the area of electro-optical displays is generally acknowledged as stemming from a combination of chemistry (molecular engineering) and physics (development of practical display modes). Starting with the early experiments on dynamic scattering, a review is given of the developments in this field arising from the chemist's ability to respond to the requirements set first for reliable materials for twisted nematic displays, later for supertwist devices and electrically addressed smectic A displays, and most recently for ferroelectric displays and the electroclinic effect. Although the driving force for such research has been the demand for materials for ever faster switching devices able to portray more complex data, the benefits of this quest for new liquid-crystal materials on basic understanding of the properties of liquid crystals and their relation to molecular structure should not be forgotten, and this aspect is firmly emphasized.

Introduction

The organization of a Royal Society Discussion Meeting on molecular chemistry for electronics highlights a growing awareness of the importance of the role of synthetic chemistry in relation to materials applicable to electronics. It is an indicator of today's general concern to promote materials science as a whole by encouraging collaboration among synthetic chemists, physical scientists who evaluate the parameters of new materials and device engineers who seek technological applications for materials that are promising.

This broad new-found awareness of materials was evident in the establishment in September 1988 of the Materials Science and Engineering Commission of the Science and Engineering Research Council (SERC), which had its origins in the Materials Review Panel under the chairmanship of Dr Peter Day, F.R.S.

The new Commission has seven committees of which 1, 2 and 4 previously existed, 1 and 2 as SERC–DTI committees:

(1) molecular electronics;
(2) superconductivity;
(3) ceramics and inorganic materials;
(4) medical engineering and sensors;
(5) metals and magnetic materials;
(6) polymers and composites;
(7) semiconductors.

This certainly stresses the enhanced significance that materials are today seen to have in research and for the ultimate benefit of society, and emphasis of this point was also given by the recent launch of the new SERC initiative on the synthesis and evaluation of materials for the 21st century. This embraces both inorganic and organic materials, and it seeks (SERC Report 1988) to 'encourage both basic and strategic research into the synthesis and characterisation of new and improved materials having interesting and potentially valuable properties, but will stop short of being concerned with applied research'. The more applied aspects and the involvement of industry have in recent years been covered by collaborative university–industry programmes under the Joint Opto-Electronics Research Scheme (JOERS), and more recently under the new Link Scheme, both SERC–DTI funded.

From this it is clear that materials science – the synthesis, evaluation and ultimate exploitation of new materials in their widest sense, and including electronics – is to be strongly supported from different quarters and should become an area of active growth in the future.

These aims may be new, exciting, and challenging for some areas, but in the field of liquid crystals this kind of collaborative work has been going on for close on 20 years. In this field long-established programmes have cemented the closest collaboration between synthetic chemists (academic and industrial) and physicists involved with the creation of novel liquid-crystal materials with defined physical characteristics, and where promise exists, their commercial exploitation in a range of applications. Originally, these applications concerned display devices almost exclusively, together with a lesser activity in thermochromic liquid crystals, but today the applications extend into optics: spatial light modulation, signal processing, nonlinear optics, etc.

The origins of what became known as the U.K. Consortium on Liquid Crystals go back to 1970 when a team under Professor C. Hilsum, F.R.S., then at the Royal Signals and Radar Establishment (RSRE), Great Malvern, was addressing the problem of finding a thin, low-power, high-contrast, non-fatiguing display suitable for the concepts of office automation and information technology that were beginning to emerge. The conclusion reached was that a display based upon electro-optic effects in liquid crystals offered good prospects of success, despite the fact that prototype devices at that time were not impressive and the materials were unsatisfactory.

A collaborative materials programme funded by the Ministry of Defence (MOD) was therefore set up between the liquid crystal unit at the University of Hull (Chemistry) and the physics team at RSRE; their respective tasks were (i) the invention of stable, colourless, liquid-crystal materials with electro-optic properties tailored to fast response over a useful temperature range and (ii) mastery of the physics of liquid-crystal electro-optic effects, calculation of the properties of eutectic mixtures, and the harnessing of these properties for use in viable displays. Success in these programmes quickly necessitated an extension of the collaboration to include a team at BDH Ltd, led by Dr B. Sturgeon, to seize upon useful Hull materials and develop their preparation so that marketable quantities of the highest degree of purity would be available. Further developments required that teams from electronic companies joined the consortium, together with other university groups needed for their specialized input. Finally, in view of the affiliation between BDH Ltd and Merck at Darmstadt, a research agreement was signed between Merck, BDH Ltd, Hull University and RSRE.

Membership of the MOD consortium has changed with the effluxion of time, but the main collaborators have been the University of Hull, RSRE (Great Malvern), BDH Ltd (Poole), Merck (Darmstadt), STC Technology (Harlow), GEC Hirst Research Centre, and the Universities of Bristol and Exeter (X-ray input).

More recently, under a three-year JOERS–Alvey programme, five of these partners, together with Thorn EMI Central Research Laboratories at Hayes, have worked collaboratively on ferroelectric liquid-crystal displays.

These interactive partnerships go on today with continued MOD support, supplemented by SERC–DTI funding, first under JOERS and more recently under Link. The collaborations have had considerable successes, but it is stressed that such first-class collaborations do not develop simply by putting research groups together unless the leading personnel involved give much effort to make the interactions work and share a common strong motivation to achieve well-defined objects. The effective bringing together of disciplines as disparate as organic chemistry, pure physics, electronic engineering and device physics requires scientists who are adaptable: chemists prepared to learn the appropriate physics, physicists prepared to understand the chemistry of the materials, and engineers prepared to learn to communicate with both chemists and physicists. Success in a collaboration is not guaranteed; the right personalities are vital, as is timeliness, and we have all seen failures.

Academics can be reluctant to join such programmes, fearing that mission-oriented research will stultify their pursuit of basic fundamental science. It is essential indeed that such collaborations are not so dedicated to a final goal and so tight on time that freedom does not exist to pursue the 'blue sky' aspects when this is desirable. MOD-supported programmes are particularly enlightened in this respect.

Collaborative research programmes that are too short and have a concerted start date also make for difficulties. It takes time for materials to develop from the synthetic unit, during which time the physicists are impatient to start work, and then at the end of the programme, the chemists are generating a flow of products that cannot be physically assessed. A staggered start to three-year programmes is the obvious solution to both problems, but strangely this never seems to be accepted or administratively attainable.

Consequent upon the part that I have been privileged to play over the years in multidisciplinary research collaborations, there is set down in what follows a necessarily brief overview of the application-driven research in the field of low-molar-mass thermotropic liquid crystals since the late 1960s. Naturally, this has been an international scenario, but particular emphasis is given to the activities of British research consortia, which, by their successes and some failures, may provide the guidelines for the collaborative programmes now needed if the *new* impetus in materials science as a whole is to be fruitful. It is hoped too this will show that fundamental science does *not* die with materials-driven aims.

LOW-MOLAR-MASS THERMOTROPIC LIQUID CRYSTALS

The systems now to be discussed exclude polymer liquid crystals, covered by Professor Ringsdorf (this Symposium), and focus on low-molar-mass materials. Further exclusions concern (i) lyotropic liquid-crystal systems and (ii) liquid crystals formed by disk-shaped molecules; to date, these have not found applications in electronic systems. Concern is therefore entirely with the liquid crystals (mesophases) formed by the effects of heating or cooling (figure 1) upon materials composed of rod- or lath-like molecules, i.e. with *calamitic mesophases*.

$$\text{crystal} \underset{<T_1}{\overset{T_1}{\rightleftarrows}} \text{mesophase} \underset{T_2}{\overset{T_2}{\rightleftarrows}} \text{isotropic}$$

FIGURE 1. Formation of a thermotropic mesophase or a sequence of thermotropic mesophases with temperature change; $T_2 > T_1$.

With reference to figure 1, T_1 and T_2 may both be above or below ambient temperature; if T_1 is below and T_2 is above ambient, the mesophase is thermodynamically stable at room temperature, which is the most interesting situation for applications.

Calamitic mesophases are conveniently divided into three main categories (see, for example, Leadbetter 1987).

1. *The nematic mesophase.* In this fluid, anisotropic phase (figure 2*a*) there is a statistically parallel long-range orientational ordering of the molecules. This is the least-ordered mesophase and it possesses no positional order. The molecules are free to rotate about their long axes, and a 180° rotation of any molecule about the short axis does not affect the energy of the system which is defined by a director, ***n***, running parallel to the preferred orientational direction and by an order parameter,

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

where Θ is the angle between each long axis and the director, and $\langle\,\rangle$ implies an average over many molecules. In a bulk nematic sample, the director may change direction dramatically between two separated volume elements, but always in a continuous manner.

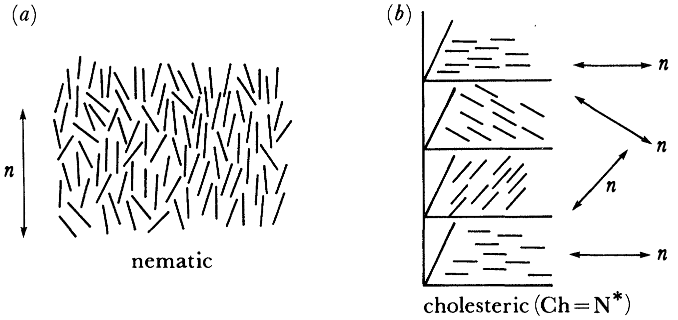


FIGURE 2. (*a*) Average parallel alignment of molecules in a nematic mesophase; (*b*) helical arrangement of chiral molecules in a cholesteric mesophase.

2. *The cholesteric mesophase.* If the molecules are chiral, then the nematic mesophase has a helical twist of the director (figure 2*b*). The associated pitch may be of the order of the wavelength of light; this results in Bragg scattering and characteristic colour effects that are temperature dependent. Cholesteric mesophases therefore find applications in surface thermography (see, for example, McDonnell 1987). Doping of a nematic liquid crystal with a chiral material also develops a helical twist, but with a long pitch, and a classical nematic may be regarded as a cholesteric with infinite pitch. Cholesteric phases, being simply spontaneously twisted nematics, are now denoted by N* rather than Ch, the asterisk denoting chirality.

3. *Smectic mesophases.* Additional to the long-range orientational ordering of the molecular long axes, smectic liquid crystals possess lamellar ordering. Different smectic polymorphic forms are possible and eleven have been characterized (Gray & Goodby 1984; Demus & Richter 1978). They differ from one another in the degree of ordering within a given lamellum, and in the tilt of the molecules with respect to the layer plane. The least-ordered smectic is the smectic A phase in which there is no positional ordering within or between the layers and the average orientation of the long axes is orthogonal to the layer planes. As shown in figure 3 the layers are not sharply defined and are best considered in terms of a density wave, usually

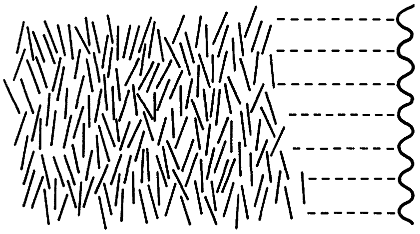


FIGURE 3. Arrangement of molecules in a smectic A mesophase.

sinusoidal. A tilted analogue of the S_A phase, the S_C phase, has a tilt of the long axes of the molecules in the layers, with correlation of the tilt direction from one layer to the next. Chirality affects only tilted smectic systems. There is therefore a chiral version of the S_C phase, denoted S_C^*. The pitch in this case is associated with a helical distribution of the tilt *directions* on passing up through a stack of layers.

LIQUID CRYSTALS AND ELECTRONIC DEVICES

Early work

Surprisingly, the first patent relating to an optoelectronic application of a nematic material came in 1936 from the Marconi Wireless Telegraph Company (Levin & Levin 1936). The patent describes how a film of an anisotropic fluid such as a nematic may be birefringent and under electrical strain produces varying light effects. No room-temperature nematics were then available and the patent sought to overcome the need to heat the Kerr cell by replacing the thermotropic nematic by aqueous lyotropic liquid-crystal systems.

Matters then lay dormant until the 1960s, when a group at the David Sarnoff Research Center of the RCA Corporation at Princeton, led by G. H. Heilmeier and involving L. Zanoni, J. Goldmacher, L. Barton and J. A. Castellano, undertook studies of electro-optical effects in liquid crystals, including displays using dynamic scattering, liquid crystals containing dichroic dyes and cholesteric–nematic phase-change displays (see, for example, Castellano 1988). Of these, the dynamic scattering cell probably made most impact and was exploited commercially.

The dynamic scattering effect

As in all liquid-crystal display devices, the dynamic scattering cell employed a thin film of liquid crystal sandwiched between two glass plates coated on their inner surfaces with a transparent electrode film of tin or indium oxide. The liquid crystal was a nematic of negative dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$), i.e. the component of the permittivity across the molecular long axis is greater than the parallel component, aligned *homogeneously* by appropriate treatment of the surfaces, i.e. with the long axes of the molecules aligned unidirectionally and on average parallel to the substrate electrodes (figure 4).

The liquid crystal was doped with an ionic dopant and as a consequence of the conductivity anisotropy, application of an electric field across the film produced an electrohydrodynamic turbulence converting the clear film into a cloudy opaque state. Addressing of selected regions of the cell therefore gave areas of written information (numbers, characters, etc.).

Materials giving room-temperature nematic phases of appropriate $\Delta\epsilon$ that were available

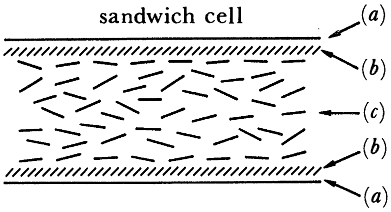
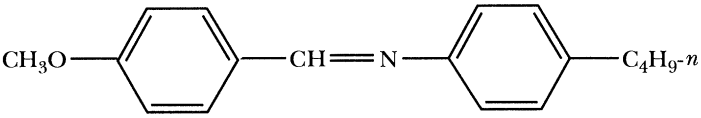


FIGURE 4. Average homogeneous alignment of rod-like molecules in a display cell: (*a*) glass plates; (*b*) transparent ITO electrodes; (*c*) nematic liquid crystal.

then were Schiff's bases, e.g. MBBA (**1**) and mixtures with its homologues (see, for example, Kelker & Scheurle 1969*a*, *b*), which were difficult to obtain and maintain pure because of hydrolytic and oxidative instability:



1

Cr 22 °C N 47 °C I

Unless devices were constructed with great care to exclude moisture, lifetimes were relatively poor. However, by their existence, these displays stimulated research activity in the field.

The twisted nematic effect

The most significant breakthrough occurred in late 1969 with the discovery of the twisted (TN) field effect, an ingenious and quite novel development of early observations by Fréedericksz concerning changes in orientation of the nematic director that can be achieved by an electric field (Fréedericksz & Zolina 1933).

As shown in figure 5, the unique aspect of the TN cell (Fergason 1973; Schadt & Helfrich 1971) is that the nematic director is rotated through 90° by having the director of the homogeneous alignment at the two supporting plates arranged at 90°. Plane-polarized light entering the cell (6–10 μm thick) with the electric vector parallel or perpendicular to the alignment direction is transmitted with rotation of the plane of polarization through 90° by the light-guiding property of the quarter helix. With crossed polarizers on either side of the cell, the cell transmits light. If the nematic material is of positive $\Delta\epsilon$, application of a field converts the twisted, homogeneously aligned liquid crystal into a homeotropically aligned stage, the 'on-state' in figure 5.

This occurs except in a very thin boundary layer at each substrate where strong surface alignment forces maintain the homogeneous condition. In the driven state, the cell no longer gives light guiding, and the light is cut off by the back polarizer. The cell then appears black, or if only selected areas have been electrically addressed, these appear black. The black numbers on a liquid-crystal display are just areas where the polarizers cause extinction of light. On switching off the field, the nematic relaxes to the homogeneously aligned quarter helix under the aligning influence of the boundary layers, and the addressed areas become bright again.

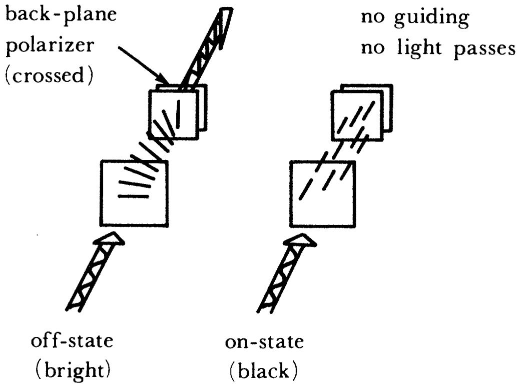
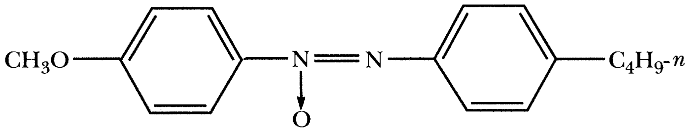


Figure 5. Off-state: plane-polarized light entering a display cell, containing a homogeneously aligned nematic liquid crystal with a surface induced twist of the director through 90°, and experiencing light guiding. On-state: no light guiding after the molecules have become aligned homeotropically by the applied electric field.

This has been an excellent display system and its commercial success has been great. This reflects the quality of the device engineering and the underlying physics of the invention, i.e. a passive field-effect display operating under ambient light with minimal power consumption and at voltages low enough to permit the use of battery operation and even solar-powered cells. But this success could not have been if quality liquid-crystal materials had not been made available by chemists.

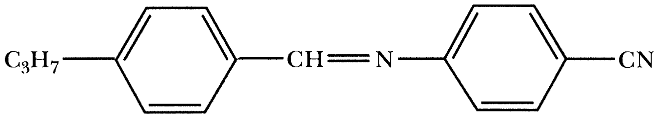
Around the time of the invention, few room-temperature liquid crystals existed. Schiff's bases have already been mentioned and mixtures of azoxy compounds such as the following,



2

Cr 43 °C N 76 °C I

gave commercial eutectic systems (E. Merck, Darmstadt) that were nematic at ambient temperatures. Like the Schiff's bases, these materials were coloured, and though more chemically stable, they were sensitive to ultraviolet (UV) light. Moreover, all were negative $\Delta\epsilon$, and this problem was first met by preparing $\Delta\epsilon$ positive cyano-substituted Schiff's bases such as

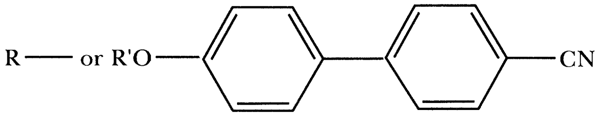


3

Cr 46 °C N 62 °C I

and using these to dope room-temperature Schiff's bases or azoxy mixtures. Such materials were adequate to demonstrate the viability of the TN display, but the undesirable colour remained, together with the problems of lifetime and handling of labile materials.

In the early 1970s, a solution was found by Gray *et al.* (1973), who reasoned that the colour and lability derived from the central linking group that was not, however, needed to maintain liquid-crystal properties with a terminal cyano-function, because it was known (Gray 1962) that this function stands high in the order of terminal groups promoting nematic properties and high T_{NI} transitions. This led to the now well-known class of cyanobiphenyl liquid crystals of general structure **4**, where R and R′ are alkyl:



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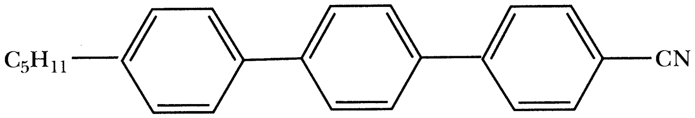
Single, pure homologues were room-temperature liquid crystals, e.g. $R = C_5H_{11}$ (Cr 22.5 °C N 35 °C I) and eutectic mixtures provided good-range nematic phases that were colourless, stable, free from hazard to health, of high resistivity (greater than 10^{10} Ω cm) and with $\Delta\epsilon = 11$. The upper limit of the nematic range was then extended by incorporating in mixtures the analogous terphenyls,



5

Cr 130 °C N 239 °C I

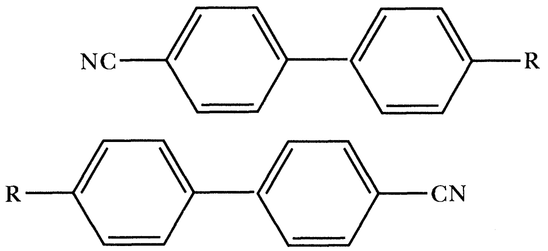
giving the first of many commercially successful systems (BDH Ltd) e.g. E7 (Cr −9 °C N 59 °C I), which enabled the manufacture of high-quality, long-life electro-optical displays. This created confidence in LC devices and provided the basis for the multimillion dollar LC display industry that was to follow and exists today.

This provides a good example of the results that can emerge from multidisciplinary, materials-oriented research under a well-managed collaborative programme. But some other consequences of this successful work should also be remembered.

1. For the first time, pure, single-component N, N* and S_A liquid crystals existing at ambient temperatures were available, enabling accurate physical studies to be made to substantiate and develop theories of the liquid-crystal state. The understanding of the fundamental science of liquid crystals was therefore strongly promoted and has led to hundreds of publications of a purely investigative kind.

2. The success and popularity of twisted nematic displays in which each active part of the displayed information is addressed separately, led to demands that ever more complex information should be presented in this manner in bigger and more sophisticated devices. The ability to make electrical connections to a very large number of picture elements (pixels) imposed real limitations, unless the device was engineered as a dot matrix and operated by multiplex addressing. Attempts to do this soon revealed that the threshold response curves of

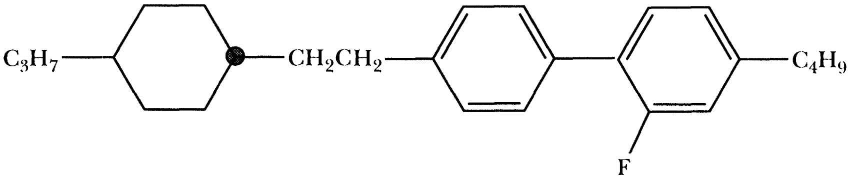
the materials were not sharp enough, and it was eventually realized that the tendency of cyano-terminated mesogens to be loosely involved in antiparallel pairwise correlations (Leadbetter *et al.* 1975) was an important factor (see **6**).



6

More basic science was therefore revealed, interdigitated and bilayer S_A phases were discovered and an explanation was made available for the effectiveness of the cyano-group in promoting liquid-crystal properties – the effective units have a length greater than the molecular length – and its relatively modest effect in promoting $\Delta\epsilon$.

These antiparallel correlations could be eliminated by adding to the systems mesogens containing no cyano-function, e.g. mesogenic esters with alkyl or alkoxy groups at each end. The quest for good systems of this type led to many new materials or mixtures, and eventually to a remarkable series of mesogens (Balkwill *et al.* 1985) many having very low melting points and very wide nematic ranges, e.g. **7**.



7

Cr 13 °C N 97 °C I

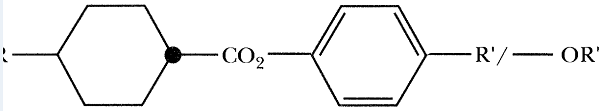
Mixtures of cyanobiphenyls with such non-cyano materials made available mixtures capable of high-level multiplex addressing and the display of much more complex data, e.g. 64-way multiplexed panels giving 1000 alpha-numeric characters (Waters *et al.* 1985).

Compounds such as **7** also made it possible to achieve wider-temperature-range mixtures, e.g. from −50 to +111 °C, which at 5 V have a response time of *ca.* 500 ms even at −20 °C.

The users' needs had therefore stimulated basic physical and synthetic research to supply the necessary materials.

3. The design of new materials was also driven forward commercially because of the growing market for these systems in displays, particularly twisted nematic displays, which are today still the dominant display type. Many of the new materials developed, in several cases by chemical companies (E. Merck, Darmstadt, F. Hoffmann–La Roche, Basle) were cyano-compounds,

modifications of the cyano-biphenyls and -terphenyls, while others were of the non-cyano type required for mixture formulation. Some examples are given below.



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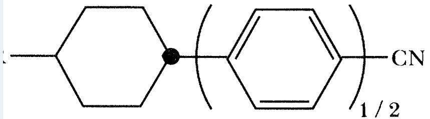

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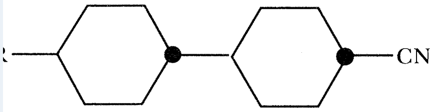

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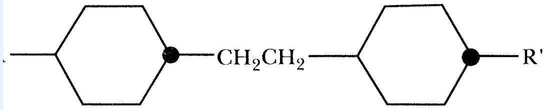

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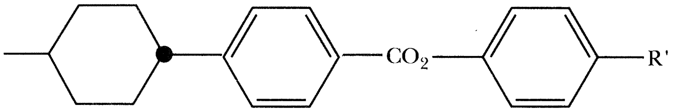

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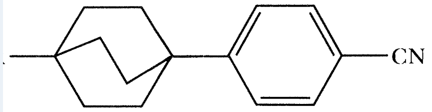

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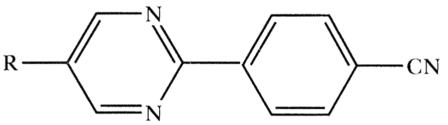
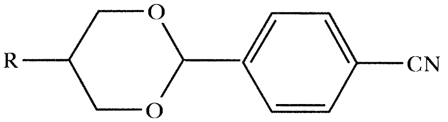


(Boller *et al.* 1977)



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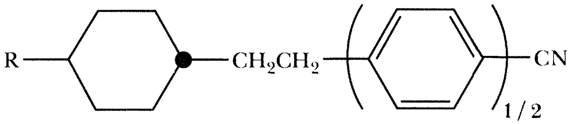
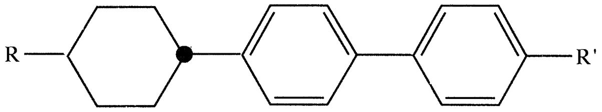
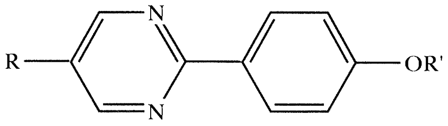


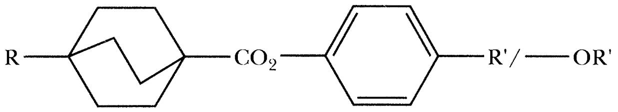
(Carr *et al.* 1983)



(Eidenschink 1985)



(Halle Group, unpublished data)



(Gray & Kelly 1980)

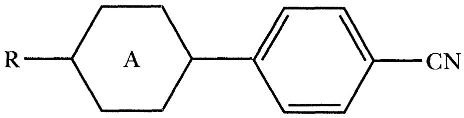
The recognition that alicyclic rings could be used beneficially in liquid-crystal materials, giving *higher* clearing temperatures and *lower* birefringence was structurally liberating. The success of flexible cyclohexane rings as core components led also to the use of hitherto shunned flexible linkages such as $—CH_2CH_2—$ (see also **7**) and $—CH_2O—$ (Carr *et al.* 1983, 1985); pyrimidine, 1,3-dioxan and pyridine rings also became widely used. Knowledge of structure property correlations was greatly promoted by these activities, and definitions of the molecular core as a rigid, rod-like unit were of necessity modified to incorporate a degree at least of flexibility.

Studies of so many cyano-compounds led too to the discovery of the reentrant phenomenon (Cladis 1975), the formation of a *less* ordered nematic (N_R) on cooling a smectic A phase, i.e.

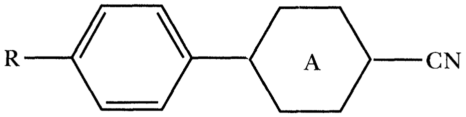
$$\mathrm{Cr} \rightleftharpoons N_R \rightleftharpoons S_A \rightleftharpoons N \rightleftharpoons I,$$

although this phenomenon is now known to occur also in mesogens that have no strongly polar terminal functions.

Structural permutations made in the quest for new room-temperature materials also revealed that whereas **8** (ring A is cyclohexane or bicyclo-octane) may be a good mesogen, the reverse structure (**9**) is not.

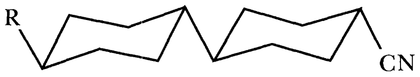


8



9

Because the materials **10** are very good mesogens, this taught (Eidenschink 1980; Gray 1983) that the sequence in which saturated and π-bonded units are linked together in a molecule is a critically important design factor.



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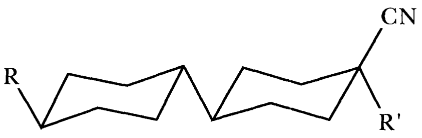


11

Research on such alicyclic materials also pointed the way to the achievement of strongly $\Delta\epsilon$ negative materials with good clearing temperatures, by the use of axial cyano-substitution (minimizing molecular broadening and adverse effects on T_{NI}) – see structure **11** – (Eidenschink *et al.* 1983) and also to many *hydrocarbon* liquid crystals, which were obviously highly stable materials.

New chiral materials were also extensively explored for use in twisted nematic mixture compositions to avoid reverse twist formation on switch off and also for thermochromic applications. In the latter case there was a need for aromatic cholesterogens, because cholesteryl esters have a low birefringence that results in a *narrow* selective reflection band and a *poor* brightness to the eye. Here once more, fundamental science was to benefit, as it became possible to correlate handedness of the cholesteric pitch with the position of, absolute configuration of (Gray & McDonnell 1977) and electron withdrawing or donating characteristics of the substituent (Goodby 1986) at the chiral centre in the molecule.

Other areas where basic knowledge of liquid crystals has been developed through materials-driven research relate to:

(i) *blue phases*, narrow range phases (less than 1–2 °C) occurring above cholesteric phases (Dubois-Violette & Pansu 1988), and now known for two of the three established types to involve cubic lattices of twist disclinations and to be capable of exhibiting electro-optic effects;

(ii) *discotic phases*, including those containing metal atoms and with particular reference to their phase classification;

(iii) *calamitic smectic phases*, their classification and in-depth studies of their structures;

(iv) *structural deviants from rod-like shape*, molecules with long alkyl chains attached laterally to the rods and acting as intermolecular lubricants, molecules that are rods with two or three flexible chains at each end, dimeric mesogens with two rod-like functions linked by a flexible chain, etc.

Later device development

The attractiveness of the multiplexed twisted nematic display soon generated pressures to develop displays capable of portraying information more complex than could be achieved (without unacceptable loss of contrast) because of limitations in multiplexing capability and viewing angle of twisted nematic devices.

This has had important consequences such as the discovery of the following displays.

(i) *The supertwisted nematic display* (Waters *et al.* 1985), where the twist of the TN display is increased to between π and $\frac{3}{2}\pi$ by attention to surface alignment and addition of a chiral dopant. This display has an *enhanced* multiplexing capability and can have bistability. The display may be operated in different modes making different demands on the materials in relation to birefringence.

(ii) *Thermally addressed smectic* A *displays* requiring a homeotropically aligned, $\Delta\epsilon$ positive smectic material with a narrow-range N phase. A matrix of heating strips or addressing with a laser heats desired areas of the clear smectic film into the isotropic phase, which upon cooling gives a scattering smectic texture (via the N phase). Erasure occurs by heating with a field on and dyes may be used to improve contrast. Longer-chain cyanobiphenyl mixtures have provided suitable materials (see, for example, Coates 1987).

(iii) *Electrically addressed smectic* A *displays*. This again uses a homeotropic smectic A phase of positive $\Delta\epsilon$ containing ionic dopant that, with field on, produces scattering and contrast (dye may be added) through hydrodynamic turbulence generated at 50–80 V and a high frequency. The device, first considered by Coates and his colleagues at STC Technology in 1978, has memory, erasure of written data being achieved at a low frequency (no dynamic scattering) that reinstates the homeotropic alignment (Coates 1987).

(iv) *Polymer dispersion devices* (Fergason 1985) in which nematic droplets are dispersed in a polymer matrix giving an unaligned scattering state. A voltage applied across the thickness of the polymer sheet, which may be very large in area, gives alignment of the nematic, and with matching of the refractive index of the polymer and n_0 of the nematic, gives a clear state. The device needs a high voltage and is not multiplexible, but large-area displays are feasible and are matched in size only by composites of many small display cells as used in the liquid-crystal indicator board in Paddington Station, London.

(v) *Active matrix displays* with a substrate carrying an array of active switching elements that selectively address individual pixels. The liquid-crystal colour televisions use this technology, using amorphous silicon TFTS and a twisted nematic film, and achieve colour by colour-filters on the pixels. At present, only *ca.* 10 cm diagonal screens are commercially practicable (see, for example, Kaneko 1987).

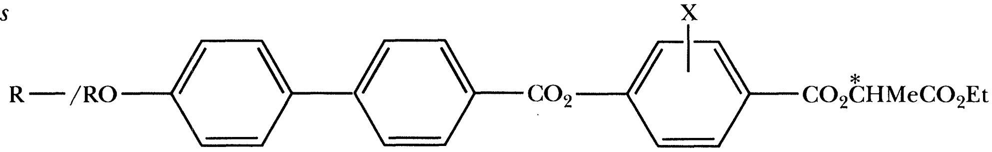
Ferroelectric liquid crystals

Smectic C liquid crystals involve a parallel distribution of rod-like molecules in layers, with a tilt of the molecular long axes away from the layer normal. In a chiral S_C phase (S_C^*), the tilt angle is the same in each layer, but the tilt direction precesses and traces a helical path through a stack of layers. Like Ch or N* phases, short-pitch S_C^* phases may exhibit thermochromism. Since 1975 the theoretical predictions of Meyer that for symmetry reasons an unwound S_C phase, composed of molecules with a transverse dipole, should exhibit a biaxial ordering of the molecules and a preferred macroscopic alignment of the transverse dipoles (parallel to the layer planes and perpendicular to the tilt direction) and hence be ferroelectric, interest has centred upon these materials for applications to electronic. This interest was stimulated by the observation that switching of the ferroelectric dipole could occur on the microsecond timescale (Meyer *et al.* 1975). The material used was an unsuitable Schiff's base ester, and progress faltered until more appropriate materials could be produced. Much synthetic effort has gone into this objective internationally, prompted by the possibility of a display mode capable of operation at video frame rates.

In the U.K. this drive has been led by a consortium operating with DTI–SERC funding under the Alvey Directorate, the chemistry being conducted at BDH Ltd and in the Liquid Crystal Group at Hull University and the device physics at RSRE, Thorn EMI, and STC Technology.

Initially, the three-year programme (ending in December 1988) aimed at very high P_s (spontaneous polarization) systems, either using chiral $\mathrm{S_C}$ materials or non-chiral $\mathrm{S_C}$ materials (hosts) that could be doped with a chiral additive. Early successes in producing high P_s materials soon taught us, however, that such $\mathrm{S_C^*}$ systems can suffer from a high viscosity that adversely affects switching responses. It also became clear that the pitch (P) of the $\mathrm{S_C^*}$ phase was important. This should be long ($P > 4d$), to facilitate formation of the unwound state in the cell (thickness of d), either through surface forces or partial compensation. The need for a 'bookshelf' arrangement of the $\mathrm{S_C^*}$ layers in the ferroelectric cell (layers 'orthogonal' to the electrode surfaces) also dictated that the $\mathrm{S_C^*}$ phase should be formed on cooling from an aligned N* phase via an aligned $\mathrm{S_A}$ phase. All these built-in requirements, including the guide-line that the transverse dipole should be locked or coupled to the chiral centre, did not make the materials quest easy for the chemist; additionally the materials should be stable and reasonably accessible if they were to be commercially viable. Big and complex is not beautiful in this field. Many materials (host and dopants) were therefore explored before real success was achieved, and some selected examples from the early work are given below.

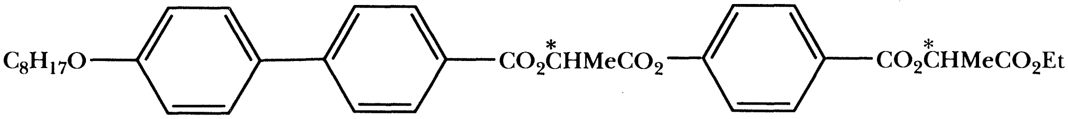
Lactates



(Bone *et al.* 1988)

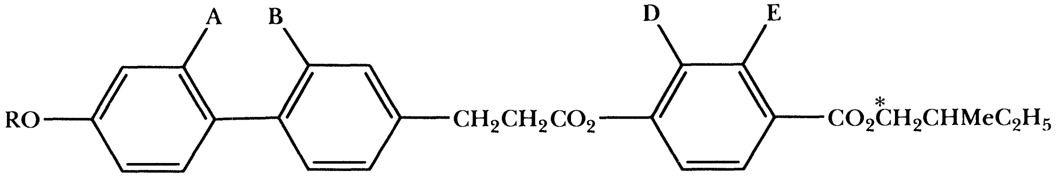
X = H, Me, Cl

Dilactates



(Bone *et al.* 1988)

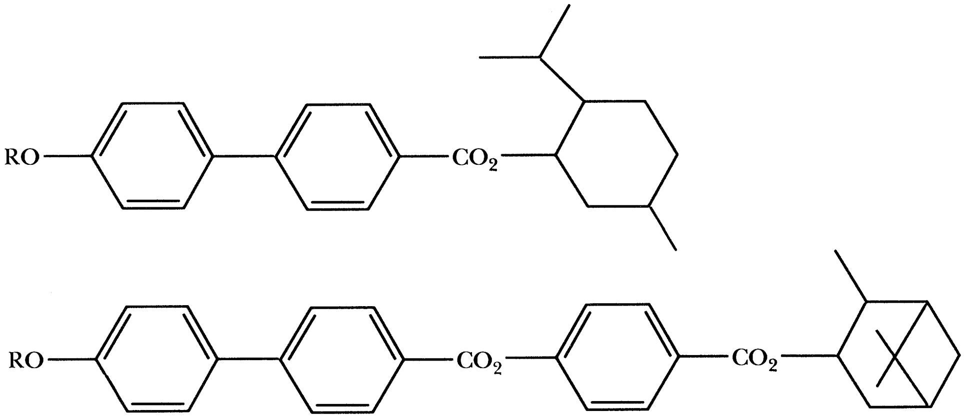
Biphenylpropanoic esters



(Gray *et al.* 1988*a*)

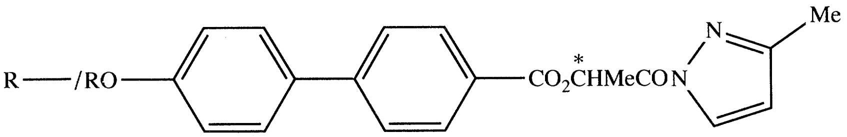
A, B, D, E, chosen from H and F

Terpenoid esters

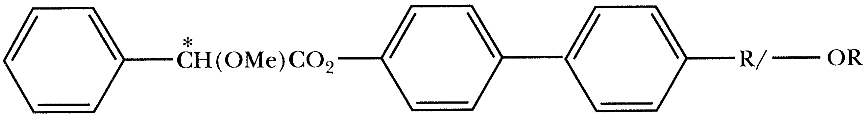


(Bone *et al.* 1986)

Cyclic Amides

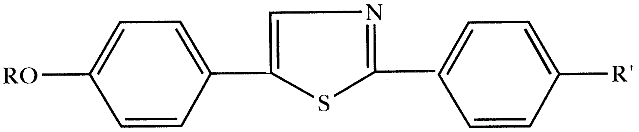


Mandelates



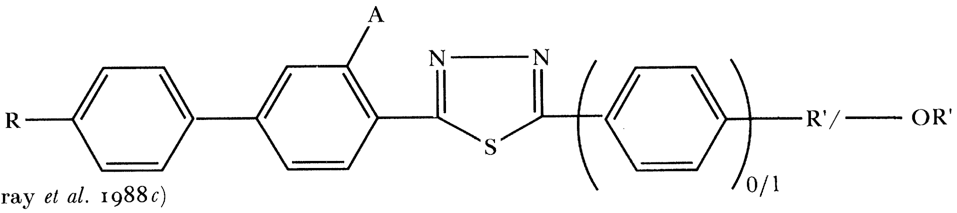
(Gray *et al.* 1988*b*)

Thiazoles



(Gray *et al.* 1988*c*)

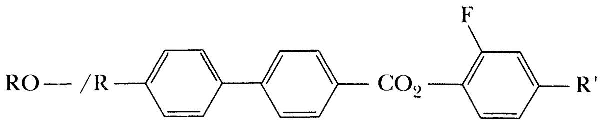
Thiadiazoles



(Gray *et al.* 1988*c*)

A = H or F

Successful host materials came eventually from the MBF esters (**12**) of BDH Ltd (Bishop *et al.* 1986) and later from fluorinated terphenyl systems (**15** and **16**) of Hull. The best chiral dopants were 2-octyl esters such as **13** (Bradshaw *et al.* 1988), followed by superior cyanohydrin esters (**17**) developed at Hull and first reported by Gray in 1987 at the Rank Prize Funds Symposium, Ledbury, U.K. (Gray 1987; Bradshaw *et al.* 1988).



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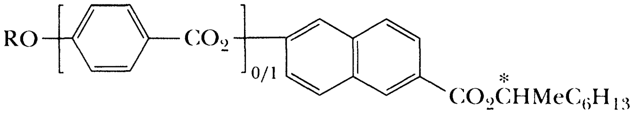

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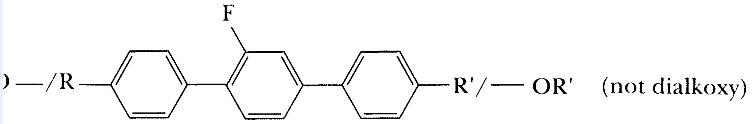

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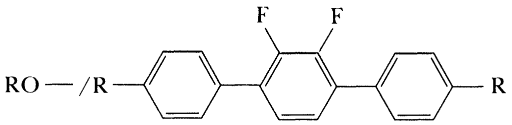

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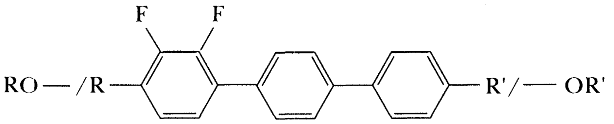

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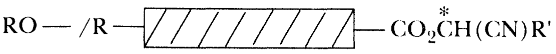


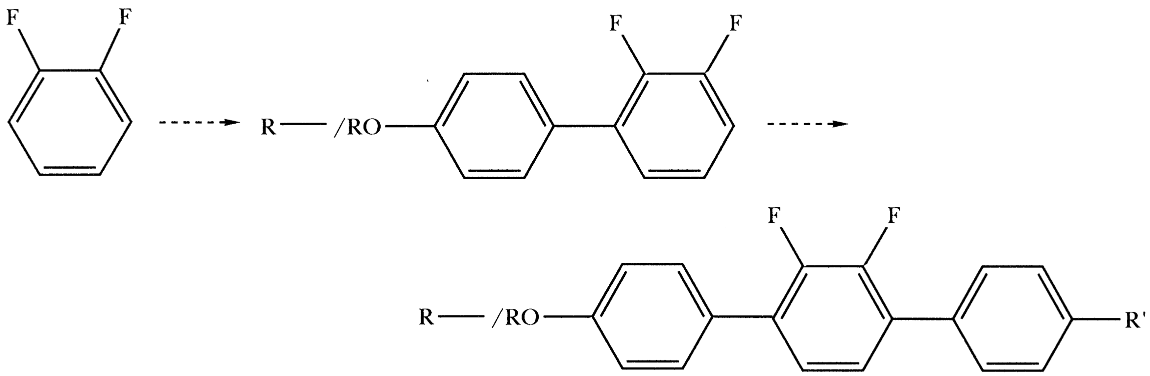
17

Dopants such as **13** gave reasonable extrapolated P_s values up to 100 nC cm^{-2}, but short N* pitches of about 0.1–0.2 μm. Esters **12** with dopants **13** gave S_C^* mixtures with P_s up to 10 nC cm^{-2}, but pitch compensation was needed. Response times (T_R) of 30–40 μs were achieved. This was an important step forward, but higher P_s values were not achievable until the cyanohydrin esters **17** were produced. These materials are particularly good, having extrapolated P_s values up to 400 nC nm^{-2}, long N* pitch values up to 1.0 μm, and good compatibility with S_C hosts, such that usefully large P_s values can be achieved with not more than 5% of the additive. The dopants **17** are readily prepared from commercially available amino acids (e.g. *L*-leucine, *L*-valine), of which both enantiomers can be obtained. Generally speaking, however, the dopants prepared from the naturally available amino acids give long enough pitch lengths in hosts not to require compensation of the pitch. Typical values for MBF ester (**12**) mixtures doped with cyanohydrin esters (**17**) are P_s ranging from 10 to 29 nC cm^{-2} and response times of 30 down to 7 μs.

It is noted next that spin-off between fundamental science and materials-driven research can work both ways. During a basic study (Chan *et al.* 1987) of the effect of lateral fluoro-substitution on the properties of dialkylterphenyls (**14**; R and R′ are alkyl) and reentrant phase behaviour in non-terminally polar mixtures, homologous series of these materials were made, and while maintaining R′ constant at say $\mathrm{C_3H_7}$, R was varied from 1 to 11. It was noted that a weak, parabolic injection of S_C phases occurred for medium length R groups. Knowing that alkoxy end groups favour S_C properties, the natural step was to examine the alkyl–alkoxy systems (Chan *et al.* 1988), whereupon a new series of very useful S_C materials and mixtures was made accessible. Mixtures giving wide-range S_C phases could be produced that had promising ferroelectric properties when doped with the materials **17**; their dielectric anisotropy was not, however, strongly enough negative, as was desirable to achieve $P_s > 10$ nC cm^{-2} and $T_R < 15$ µs. Interestingly, the dialkoxy systems (**14**) are not S_C in behaviour.

The way around this problem was to obtain difluoroterphenyls such as **15** and **16** in which the fluorines are on the *same* side of a ring so that reinforcement of $\epsilon_\perp$ will occur.

It is stressed that the availability of these dialkyl and alkyl–alkoxy terphenyls has only been possible through the development at Hull, notably by K. J. Toyne and M. Hird, of elegant aryl–aryl coupling methods by using boronic acids (Gray *et al.* 1989). Ten years ago, these materials could have been made only by long and laborious low-yield routes that would not have been practicable on any commercial basis. The procedure depends critically on the ability to lithiate *ortho*- to a fluorine in 1,2-difluorobenzene, followed by formation of the boronic acid, which is then coupled with an aryl bromide or iodide by using tetrakis(triphenylphosphine)palladium(0). The resulting biphenyl is then *ortho*-lithiated next to the other fluorine and the process repeated to yield the appropriate terphenyl, e.g.



An example is the dialkyl compound **15**, with R = C_7H_{15}, R′ = C_9H_{19}, which gives Cr 49 °C S_C 77 °C S_A 93 °C N 108.5 °C I. Mixtures of these materials, using if need be analogous difluorobiphenyls prepared by the same methods, can be obtained with wide-range S_C phases and the correct phase sequence for good alignment. Such mixtures are still under assessment at RSRE (Constant *et al.* 1989). However, it can be said that the negative dielectric anisotropy is nicely enhanced, particularly in the alkyl–alkoxy systems, and the viscosities are low. Doping with the cyanohydrin ester dopants (**17**) has generated good P_s values and faster switching speeds than any other systems we have studied, as quick as 1 µs at room temperature in 2 µm devices.

This provides another excellent example of chemistry–physics collaboration in the materials science field, and the way is now open to exploitation of such materials in a range of ferroelectric applications in optics and in displays in which multiplex drive is readily achieved at video frame rates around room temperature.

The electroclinic effect

As a consequence of the research activity involving chiral S_C phases, it has been observed (Anderson *et al.* 1987) that a chiral, laterally dipolar S_A phase can give rise to induced ferroelectric properties. When an electric field is applied to a homogenously aligned S_A phase that is chiral, an induced ordering of the lateral dipoles occurs, coupled with induction of a tilt of the director relative to the layer planes. The tilt angle is proportional to the applied field and switching akin to that in an S_C^* phase can be obtained. The tilt angle is greatest fairly close to an S_C^*–S_A transition, and switching on a timescale of a few hundred nanoseconds has been achieved. This electroclinic effect is of most interest for fast switching shutters and modulators, but having no threshold behaviour or bistability, cannot be multiplexed. As a consequence the effect does not seem relevant to display applications. Materials research in this area is an ongoing activity.

Conclusions

It is hoped that these examples of past and current collaborative interactions involving physics, chemistry and engineering in the area of materials science relevant to molecular electronics will provide both models and incentives for similar multidisciplinary research programmes in materials science in its widest sense, and that the enablement and success of these programmes will be more firmly assured in view of the more clearly defined support available for such initiatives today under SERC–DTI funding schemes.

I acknowledge that this article could not have been written without the research and collaboration of many colleagues past and present within the Liquid Crystal Group at Hull University, at RSRE, Great Malvern, U.K., at BDH Ltd, Poole, U.K., at E. Merck, Darmstadt, F.R.G., at STC Technology, Harlow, U.K., at GEC Hirst Research Centre, Wembley, U.K., and at Thorn–EMI, Central Research Laboratories, Hayes, U.K. I am grateful to all those concerned.

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Discussion

D. A. DUNMUR (*Department of Chemistry, University of Sheffield, U.K.*). Professor Gray has drawn attention to the importance of dipole–dipole association in liquid crystals. There is considerable experimental evidence for antiparallel dipole–dipole correlation or local antiferroelectric order in liquid crystals composed of rod-like molecules with dipole moments parallel to the long molecular axis. This evidence comes from dielectric and X-ray measurements, and antiparallel dipole–dipole ordering has been invoked (Prost & Barois 1983) to explain the variety of smectic A (A_1, A_2, A_d, A and A_{cren}) and smectic C phases. Reentrant phase behaviour with increase or decrease of temperature of the type, nematic → smectic → nematic, has been observed for some strongly dipolar compounds, and has been attributed (Indekeu & Berker 1986) to dipole–dipole association. However, there is no evidence that nematic phase stability is significantly influenced by dipole–dipole interactions, and so the intermolecular forces that cause nematic order must be apolar in nature. We have proposed (Toriyama & Dunmur 1985) that orientational correlation of molecules in liquid-crystal phases should result in both parallel and antiparallel dipole association, the predominance of one or the other being determined by the dipole moments and molecular geometry. Dielectric properties of liquid crystals can be interpreted in terms of a balance of parallel and antiparallel dipole association, and there is experimental evidence for parallel dipole association in some materials (Gray *et al.* 1988).

Simple electrostatic considerations show that rod-like molecules with dipole moments parallel to their symmetry axes should prefer antiparallel association; similar considerations suggest that rod-like molecules with large transverse dipole moments should prefer parallel dipole association resulting in local ferroelectric order, and recent experiments (Toriyama & Dunmur 1990) have confirmed this. The same argument predicts that disk-like molecules with dipole moments perpendicular to the plane of the disk should show a preference for parallel dipole–dipole association. It is interesting to speculate on the possibility that local ferroelectric order could become long range to give macroscopically ferroelectric liquid-crystal phases. Such phases are already known for the tilted chiral smectic phases S_C^*, S_I^* and S_F^* in which the spontaneous polarization results from symmetry-driven ferroelectric order of transverse dipole components of constituent molecules. It may be possible for ferroelectric phases of higher symmetry to be formed, and a recent paper (Palffy-Muhoray *et al.* 1988) has considered the realizability of a ferroelectric nematic phase formed from disk-like molecules. The scope for partly ordered liquid-crystal phases does not seem to have been exhausted, and the discovery of new ferroelectric liquid-crystal phases, perhaps based on the considerations outlined here, could lead to many new and improved materials for application.

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G. W. GRAY, F.R.S. The points made by Dr Dunmur about both antiparallel and parallel dipole–dipole correlations in liquid crystals composed of rod-like molecules with strong dipole moments parallel to the molecular long axis are valuable, and I would have liked to have dwelt upon them in my own lecture had time permitted.

Dr Dunmur mentioned that reentrant phase behaviour has been observed for some such strongly polar systems and has been attributed to dipole–dipole association. I would not like the reader to presume from this that reentrant behaviour is confined to such strongly polar materials. As found by Chan *et al.* (1987), reentrant behaviour occurs with simple 4,4″-dialkyl-2′-fluoro-*p*-terphenyls confirming earlier results by Diele *et al.* (1983) that terminally non-polar systems also exhibit this behaviour. An explanation other than that involving dipole–dipole association has therefore to be found for reentrant behaviour in such terminally non-polar materials.

Dr Dunmur stated that no evidence exists to show that nematic phase stability is significantly influenced by dipole–dipole interactions. Strong evidence to this effect does in fact exist in a publication by Schad & Osman (1983). The evidence relates to studies of binary mixtures, of which one component has a strong dipole directed along the molecular axis, stemming from a terminal cyano-group, and the other component is only weakly polar. In other *single*-component systems where much weaker dipoles are involved and do not develop loose couplings between pairs of molecules, I would agree wholly with him that the intermolecular forces governing nematic order are apolar in nature. Indeed, in earlier publications (e.g. Gray 1979) I have argued as much. However, in the Schad–Osman systems where a terminal cyano-substituted mesogen is mixed with a non-cyano-substituted component, there are strong negative deviations of the T_{NI} against mixture composition transition lines. The extrapolated transition temperatures (T_{NI}) for the free, unassociated polar components are often significantly lower (up to 30 °C) than those observed experimentally for the single-component polar component where pairwise correlations are unperturbed by the presence of a non-polar or weakly polar additive.

Admittedly, such negative deviations from ideal behaviour have not been observed for all such binary mixtures. However, it must be remembered that there is a strong tendency for smectic phases to be injected in the middle composition range of such binary systems. This behaviour is very marked in mixtures of terminal cyano compounds and esters. The injected smectic behaviour can often cause the T_{NI} transition line to rise in the middle composition range (and this effect can be seen even when the injected T_{S_AN} maximum is *well below* the T_{NI} line), and this would mask any tendency of the T_{NI} line to be seen to deviate negatively with increasing content of the weakly or non-polar component of the binary system. The situation with respect to the influences of strong terminal dipoles causing pairwise correlations of molecules on nematic order is therefore not quite as clear as he would make out.

Another point to note is the very marked effect of a fluoro-substituent *ortho* to a terminal cyano-group on nematic–isotropic transition temperatures. Decreases in T_{NI} of 35–45 °C have been recorded, far in excess of those found for lateral fluoro-substituents in other positions and environments. Dielectric studies show that in 3-fluoro-4-cyanophenyl systems, antiparallel correlations are destroyed, a fact which may be linked with the large decreases in T_{NI} mentioned above.

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H. J. Coles (*Liquid Crystals Group, Physics Department, The University, Manchester, U.K.*). Professor Gray has given a beautiful account of the evolution and properties of low-molar-mass liquid crystals suitable for use in electro-optic or thermochromic displays. How will these materials evolve in the future and what will be the exciting areas of applications?

G. W. Gray, F.R.S. It would surely not be wise of me to answer this general question by divulging all the plans that my group and its research collaborators have for future applications of low-molar-mass thermotropic liquid crystals, and I am equally sure that Dr Coles would not expect me so to do. In very general terms, however, one could make the following remarks. Towards the end of my paper I indicated that ferroelectric smectic C* materials capable of switching at 1 μs in 2 μm cells had been developed in the Hull Group. The door is now open, with these stable and reliable materials, to produce ferroelectric liquid-crystal displays switching at better than video frame rate and, as the ability to introduce grey scale and full colour into these displays is developed, to make full colour, flat-screen ferroelectric liquid-crystal television monitors. Perhaps even faster switching materials will be required as the multiplexing capabilities of these devices are explored. If so, more organic synthesis will need to be done. The electroclinic effect in smectic A phases above chiral C phases is, again as mentioned at the end of my paper also a means of achieving liquid-crystal switching speeds of less than 1 μs (down to say 500 ns), and this is an area demanding more synthetic exploration so that the effect can be optimized, not for display purposes, but for very fast switching shutters, light modulators, etc. There is also, incidentally, a wealth of non-display applications of ferroelectric liquid crystals awaiting study.

Finally, the potential of discotic liquid crystals, particularly those containing metal atoms and also of metal-containing calamitic materials awaits development. In the latter context, fluid systems that are optically biaxial and/or exhibit interesting magnetic properties can be envisaged. The role of liquid crystals in the field of nonlinear optics and of organic superconductors is also under study.

I feel that in the competitive circumstances that operate in this general area of self-organizing systems giving anisotropic fluid states, I would be advised to confine myself to these general remarks.

S. Chandrasekhar, F.R.S. (*Raman Research Institute, Bangalore, India*). We have recently prepared some copper complexes that form paramagnetic nematic liquid crystals (Chandrasekhar *et al.* 1986, 1988 and references therein). From ESR studies on a similar copper complex that exhibits a discotic phase, Eastman *et al.* (1987) have concluded that single crystals at room temperature have the properties of a one-dimensional spin $-\frac{1}{2}$ Heisenberg antiferromagnet, and that in the columnar phase exchange interactions are still significant and a degree of long-range order persists. It is therefore not unreasonable to expect a certain measure of antiferromagnetic short-range order in the paramagnetic nematic phase as well, though this has yet to be established conclusively.

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