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Liquid crystals for twisted nematic display devices[†]

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This article describes the use of nematic liquid crystals in the Twisted Nematic Liquid Crystal Display (TN-LCD) since the large majority of instruments manufactured currently incorporating a liquid crystal display (LCD) utilise this type of device. The correlation between the electro-optical performance of these devices and the invention and synthesis of nematic liquid crystals with a continually improved property spectrum in order to meet constantly changing specifications is illustrated using the TN-LCD as an example of general trends and relationships.

Introduction

Over the last 25–30 years liquid crystals have found wide commercial application as functional organic materials in electrooptical display devices for consumer audio-visual and office equipment such as watches, radio clocks, stereos, calculators, portable telephones, personal organisers, note books, laptop computers. Further applications include information displays in technical instruments and in vehicles initially as clocks, then speedometers to a limited extent and now increasingly as navigation aids. More specifically they have come to dominate the displays market in portable instruments. Liquid crystal displays (LCDs) are now starting to replace cathode ray tubes (CRTs) from a segment of the computer monitor market and the share of LCDs of the total market for displays is expected to increase, despite the invention and development of promising competing technologies, such as Light-Emitting Polymers (LEPs), Field Emission Displays (FEDs), Plasma Displays, Vacuum Fluorescence Displays (VFDs). The successful development of LCD technology was dependent on developments in a combination of scientific disciplines such as chemistry, physics, electronics and device engineering. These include improvements in batteries, polarisers, electrodes, CMOS drivers, spacers, alignment layers and nematic liquid crystals. These developments were made in response to a clear market requirement for a low-voltage, low-power-consuming display screen for portable, battery-operated instruments in order to display digital information of ever more increasing volume, speed and complexity. We will attempt to illustrate this development using the Twisted Nematic Liquid Crystal Display (TN-LCD)[1,2] as an example, although it was not the first LCD on the market (Dynamic Scattering Effect) and is not the only LCD in production, *e.g.*, STN-LCDs, or in development, *e.g.*, ferroelectric LCDs or polymer stabilised LCDs. It is, however, the most widely used LCD type by far and its historical development is illustrative of the general dependence of consistent improvement in the performance of LCDs as a consequence of the invention, laboratory preparation, evaluation, scale-up and then large-scale manufacture of liquid crystal components and mixtures.

Nematic liquid crystals

The liquid crystalline state represents an intermediate state of matter between that of a crystalline solid with three-dimensional order at one extreme and a completely disordered liquid at the other. A liquid crystal may exhibit order in one or two dimensions. From the turn of the century, many liquid crystals were synthesised[3,4] by academic research groups, especially in Germany, mostly at the Martin Luther University in Halle,[5–9] and from the late forties in the UK at the University of Hull.[10–13] Many systematic studies soon established the relationships between central linkages, terminal groups, lateral substituents, number of rings and the type of mesophase and transition temperatures, which are still valid today.[3–13] A typical liquid crystal of this time possessed a linear structure with a central core containing several collinear rings, a linear unsaturated linkage and two terminal chains, as exemplified by the chemical structures[14–19] for the compounds **1–9** collated in Table 1. It was known that short chains favoured nematic rather than smectic formation. The combination of one short alkyl chain on one ring and a polar substituent on the other was also known to be favourable for nematic phase formation and an order of efficiency for these terminal polar substituents had been reported.[10–13] This seemed to confirm the Maier–Saupe theory,[20] which suggested that the anisotropy of polarisability of the molecular electron density was responsible for the formation of the nematic phase. This is now known to be an oversimplification and a number of theories based on different approaches have been derived to describe various aspects of liquid crystal formation,[20–25] although none of them are completely satisfactory. However, at the time it led synthetic chemists to focus their research on conjugated aromatic molecules. Therefore, all of the compounds reported in Table 1 are aromatic with two phenyl rings joined by an unsaturated central linkage in order to maximise the degree of conjugation and anisotropic polarisability of electron density. The synthesis of these earlier materials and later of the more stable and highly pure materials synthesised for displays provided physicists with the liquid crystals required to investigate and to determine the anisotropic nature of their physical properties.[26,27] These physical properties determine the response of nematic liquid crystals to an electric field in LCDs.[28–36]

In the nematic state formed by calamitic organic compounds, with a rod-like or lathe-like molecular structure, where the length-to-breadth ratio is much greater than one, there is a parallel orientation of the molecular long axis of individual molecules. This results in a long-range orientational order, but no positional order. This is the prime factor, which differentiates the nematic state from an isotropic liquid. The average direction of these molecular long axes at any one point is defined as the director, *n*, whereby *n* is identical to $-n$, *i.e.*, there is an inversion symmetry axis at any one point along the director. The order parameter, *S*, is a scalar quantity and represents the average orientation of the molecules in the liquid crystal relative to the director and is a macroscopic

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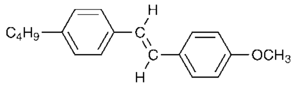
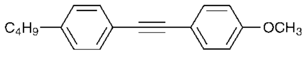
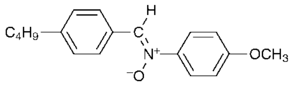
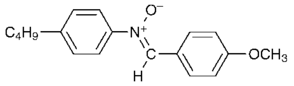
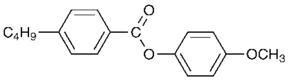
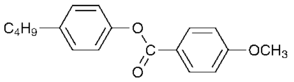
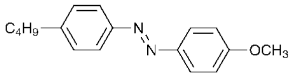
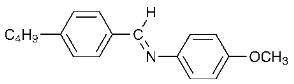
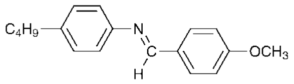
[†]

Table 1 Transition temperatures/°C for the compounds **1–9**

Compound	Molecular structure	Cr		N		I	Ref.
1		•	118	•	121	•	14, 15
2		•	49	•	$(37)^a$	•	14, 16
3		•	108	•	(70)	•	14
4		•	113	•	(53)	c	14
5		•	61	•	(25)	•	15
6		•	40	•	(25)	•	15
7		•	32	•	47	•	15, 17
8		•	46	•	49	•	18
9		•	20	•	47	•	19

[a]( ) Represents a monotropic transition temperature.

property, see eqn. (1)

$$S = \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle \quad (1)$$

where θ the angle between the long molecular axis of an individual molecule and the director. In a completely disordered liquid made up of rod-like molecules $\cos^2\theta = 1/3$ and S is 0. Conversely in an ideal macroscopically ordered nematic liquid crystalline state $\cos^2\theta = 1$ and $S = 1$. Usually S lies between 0.5 and 0.7 for a typical compound in the nematic state at a temperature relatively far away from the clearing point, *i.e.*, the temperature at which the compound ceases to exhibit the liquid crystalline state and forms the isotropic liquid.

The rod-like shape of liquid crystal molecules means that the physical properties of the liquid crystal states also possess a degree of anisotropy, *i.e.*, they exhibit different values when measured parallel or perpendicular to the director. Due to the axis of symmetry parallel to the director arising from free rotation around the molecular long axis, the values of the physical properties of nematic liquid crystals measured perpendicular to the director, *i.e.*, along the y- and z-axes are identical. However, they differ from those measured parallel to the director, *i.e.*, along the x-axis. It is the anisotropic nature of the physical properties of liquid crystals due to their shape anisotropy combined with the ability to influence the bulk spatial orientation of these molecules, *i.e.*, the director, by the interaction with external magnetic and electric fields as a result of their fluid nature, which renders them of such importance to electrooptic display devices. Like most physical properties of normal organic compounds they also depend on temperature, pressure and the type of liquid crystal state, *e.g.*, nematic, smectic, and the degree of ordering in the liquid crystalline state. It is the anisotropy of the physical properties of liquid crystals combined with their fast reorientation under the influence of a moderate electric field, which is responsible for their use as functional organic materials in LCD technology. The anisotropic properties of relevance to LCDs are defined below.

Optical anisotropy (birefringence)

Liquid crystals exhibit optical anisotropy, *i.e.*, birefringence, Δn, with two principal refractive indices n_e and n_o, where n_e is the refractive index of the extraordinary ray with the electric vector parallel to the optic axis and n_o is the index for the ordinary ray with the electric vector perpendicular to the optic axis, see eqn. (2). The refractive index, n, of a medium is defined by the ratio of the velocity of light in a vacuum and the velocity of light in the medium. These can be determined from refraction measurements by the application of Snell's law.

$$\Delta n = n_e - n_o \quad (2)$$

The optic axis of a nematic liquid crystal is defined as being parallel to the director for liquid crystals of positive birefringence and perpendicular to the director for liquid crystals with negative birefringence.

Dielectric anisotropy

The interaction between a liquid crystal and an electric field is dependent upon the magnitude of the relative permittivity measured parallel, $\varepsilon_{\parallel}$, and perpendicular, $\varepsilon_{\perp}$, to the director and to the difference between them, *i.e.*, the dielectric anisotropy, $\Delta\varepsilon$, see eqn. (3). The relative permittivity measured along the x-axis is unique, whereas the relative permittivity measured along the y- and z-axes are identical.

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \quad (3)$$

The relative permittivity, ε, of a material is defined as the ratio of the capacitance, C_{vac}, of a parallel plate capacitor containing a vacuum to that, C_{mat}, of the same capacitor containing the material, see eqn. (4).

$$\frac{C_{\mathrm{vac}}}{C_{\mathrm{mat}}} = \varepsilon \quad (4)$$

The relative permittivities are dependent upon temperature and the frequency of the applied field up to the transition to the isotropic liquid. Above the clearing point the relative permittivities are equal measured along all three axes due to the isotropic nature of a liquid and therefore the dielectric anisotropy decreases to zero. The resultant relative permittivity, ε_{l}, is the relative permittivity of the liquid. The sign and magnitude of the dielectric anisotropy are dependent upon the anisotropy of the induced polarisability, $\Delta\alpha$, and the anisotropy and direction of the permanent polarisation attributable to the resultant of permanent dipole moments.

Viscosity

The flow viscosity of the liquid crystalline state is also an anisotropic property, depending on the direction of flow of an individual molecule with respect to the director at any one point within the medium. The three so-called Miesowicz viscosities used to characterise nematic liquid crystals are η_1 perpendicular to the flow pattern but parallel to the velocity gradient, η_2 parallel to the flow pattern but perpendicular to the velocity gradient, and η_3 perpendicular to the flow pattern and to the velocity gradient. The bulk viscosity of an unaligned liquid crystal is an average of these three viscosity coefficients. However, in an electrooptic display device individual viscosity coefficients influence the optical response times due to the constrained anisotropic environment and the unidirectionality of any applied electric field. This is represented by the rotational viscosity, γ_1, which is associated with the movement of a molecule in a nematic phase from a homogeneous planar configuration parallel to the cell surfaces to a homeotropic configuration with the molecular long axis (director) perpendicular to the cell walls and parallel to the applied electric field.

Elastic constants

The elastic behaviour of a liquid crystal phase under a distorting force, such as an electric field or at an interface with a solid surface, is determined by the three elastic constants, k_{11}, k_{22} and k_{33}, associated with splay, twist and bend deformations, respectively. The elastic constants are molecular parameters and describe the restoring forces on a molecule within a liquid crystalline phase upon removal of an external force, which had distorted the medium from its lowest energy configuration. The elastic constants are obviously important for surface-stabilised electrooptic display devices based on dielectric interaction with an applied electric field. This distorts the elastic medium of the liquid crystalline phase from its equilibrium position, which is then restored by elastic forces originating at the surface between the liquid crystal and the orientation layers covering the device substrates upon removal of the field.

The light waveguiding action of a twisted nematic structure was first reported early in the twentieth century.[28–30] The twisted nematic structure was obtained either by rotating one of the substrates through 90° in its plane[28] or by the action of two rubbed surfaces placed at an angle of 90° to each other.[29] The interaction between a magnetic field parallel to the helix axis of a twisted nematic structure was described mathematically in 1970.[31] The effect of electric fields on various configurations of a thin film of nematic material sandwiched between two parallel planar substrates bearing electrodes had also been elucidated in the early 1930s.[31] Although the TN-LCD is a special case of the Fréederieks effect[31–33] and the electric field equivalent of the Maugin effect, it represented a genuine breakthrough for LCD technology.

Twisted nematic liquid crystal displays TN-LCDs

Since its invention, in the early 1970s,[1,2] the twisted nematic liquid crystal display (TN-LCD) has become the dominant display type in portable instruments. Directly addressed or multiplexed TN-LCDs are to be found in low-information-content electrooptic devices, such as watches and calculators. Actively addressed TN-LCDs, *e.g.*, with a silicon backplate, are the dominant technology in high-information-content displays such as notebooks or portable computers. This is due to characteristic properties of TN-LCDs such as low threshold voltage and operating voltage, low power consumption, good optical contrast for narrow viewing angles, relatively efficient multiplexing at low ratios (low-information-content matrix addressed displays), a long operating lifetime and, especially, low cost. A liquid crystal display device utilising nematic liquid crystals is essentially a parallel plate capacitor with the nematic liquid crystal as the non-conducting dielectric. However, the nematic liquid crystal exhibits two relative permittivities. If the nematic liquid crystal is constrained by an alignment layer to orient in such a way that the director makes an angle to the electrodes, then the application of an electric field across and perpendicular to the electrode plates causes the maximum value of the capacitance to be manifested by displacement of the nematic liquid crystal from its equilibrium position, defined by elastic forces exerted by the surface on the nematic liquid crystal. Removal of the electric field allows the elastic forces to reorient the nematic director to the equilibrium position of lowest energy. Light can pass through the cell (transmissive mode) or is reflected back through the cell (reflective mode), if a mirror is attached to the second substrate. Thus, the TN-LCD is a variable parallel plate capacitor, which uses the unique anisotropic dielectric and elastic constants and refractive indices of nematic liquid crystals to operate as a fast and efficient light shutter under the influence of a weak electric field. As with many types of LCDs, the main disadvantages of the TN device are its slow response at low temperatures, poor brightness and limited contrast and narrow viewing angle in passive matrix applications.

Mode of operation of TN-LCDs

A TN-LCD essentially consists of a very thin layer of a nematic liquid crystal mixture enclosed between two hermetically sealed parallel glass substrates, see Fig. 1. for an illustration of a single picture element (pixel) of a matrix TN-LCD.[34] The glass plates are held apart by solid spacers to form a uniform cell gap of 5–10 μm and are cemented together around the edges. Thicker cells can appear turbid due to light scattering and always exhibit much longer response times to the application of an electric field. The inner surfaces of the glass substrates are coated on the inside with a series of thin transparent layers. The first coating is often a barrier layer, *e.g.*, silica, in order to prevent leaching of ions from the glass substrates into the liquid crystal. Colour TN-LCDs also incorporate a regular pattern of red, green and blue colour filters corresponding to the pixel pattern. The next layer is a conducting material, most often indium-tin oxide (ITO), and between the upper and lower layers of which the electric field is applied. One electrode layer incorporates the desired pixel pattern, while the layer of conducting material on the second substrate provides the back electrode. On top of the electrode surface there may be another thin protective layer to prevent

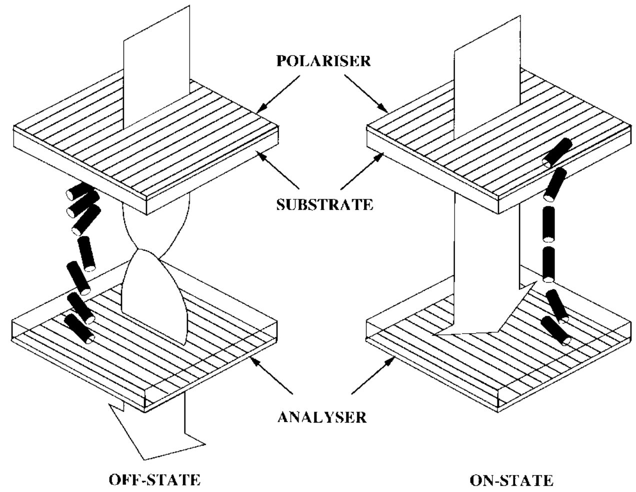


Fig. 1 Schematic representation of a Twisted Nematic Liquid Crystal Display TN-LCD.[34]

migration of ions into the nematic mixture. The last layer is an alignment layer in direct contact with the nematic liquid crystal mixture in order to induce a homogeneous, uniaxial orientation of the local optic axis (the director) in the azimuthal plane of the device. This is parallel to the direction of rubbing in the case of the polyimide alignment layers most often used for TN-LCDs. In some LCDs the layer of conducting material on the second substrate is not patterned and simply provides the back electrode. The two glass substrates are offset to some extent in order to allow contact with the drive electronics to be made. The contacts are usually plastic sheets with alternating strips of conducting and insulating polymers with dimensions which correspond to the width of the electrodes on the glass substrate. In high information displays contact is often achieved using patterns of conducting adhesives attached directly to the motherboard.

Once the cell has been constructed an appropriate liquid crystal mixture is introduced through a small hole in the cell, usually by capillary action under a vacuum, and then the hole sealed, *e.g.*, with epoxy resin. At the interface between the device substrate and the nematic liquid crystal there is also an inclination of the nematic director in the zenithal plane. This surface tilt angle is defined as the pretilt angle (θ) and is usually of the order of 1–3° for TN-LCDs. The major consequences of the presence of a pretilt angle are the suppression of areas of reverse tilt and lower threshold voltages. The direction of alignment at the upper glass substrate is perpendicular to that at the lower glass substrate. This results in an overall twist of 90° across the liquid crystal layer due to elastic forces, see Fig. 1, in the inactivated, or off-state. A film of plastic polariser is attached to the outer surface of each substrate with the polarisation direction parallel to the direction of rubbing and, therefore, the optic axis (director) of the nematic mixture. Therefore, when plane polarised light enters the cell after traversing the first polariser, the wave-guiding action of the twisted nematic medium rotates the plane of the light through 90°, since the wavelength of light (550 nm) is much smaller than the thickness (5–10 μm) of the nematic layer. This is the so-called Mauguin regime. This then allows it to pass through the second polariser (analyser) as the direction of plane polarised light is parallel to the transmission axis of the analyser. This represents the bright off-state or transmission-state, often referred to as the normally open-mode or white-mode, with no applied voltage. However, when a voltage above a certain threshold voltage, V_{th}, is applied across the cell the molecules and the molecules in the centre of the cell and therefore the director start to tilt in order to realign themselves in the direction of maximum polarisation, *i.e.*, parallel to the electric field. This requires the nematic phase to be of positive dielectric anisotropy. This results in a decrease in the effective average birefringence as well as the twist being concentrated in the centre of the cell. Increasing the voltage further leads to a tilt angle of 90° at the centre of the cell, where the twist is completely unwound; the effective birefringence is then zero and the plane of the polarised light is no longer rotated. However, there are residual transition regions of bend and splay at the cell boundaries, where the director is fixed rigidly. Therefore, the plane-polarised light strikes the analyser in the crossed polariser configuration and is absorbed by the analyser. This is the dark on-state. Alternatively, the polarisers can be parallel to one another leading to a dark off-state and a bright on-state. This is often the case for commercially available cells as this results in a wider viewing angle cone.

Off-state. In order to avoid the production of elliptically polarised light on traversing a TN-LCD it is necessary to fulfil certain conditions with respect to the cell thickness, *d*, the birefringence of the nematic medium, Δn, and the wavelength of light in a vacuum, λ, according to eqn. (5).

$$d\cdot\Delta n \ll \frac{\lambda}{2} \tag{5}$$

Since the response time of TN-LCDs is proportional to the square of the cell gap, *d*, modern TN-LCDs often operate with a uniformly small values of d ($\approx$5 μm) across the whole of the cell. The first commercial TN-LCDs operated at greater values of d ($\approx$8 μm) in order to compensate for an inability to control the cell gap accurately. However, the light becomes more elliptically polarised at thinner cell gaps due to the small pitch of the nematic medium and consequently the cells can appear coloured, *e.g.*, pink or green, due to interference between the extraordinary and ordinary rays. However, for certain wavelengths of light, interference at the analyser can minimise the production of elliptically polarised light, thus giving rise to linearly polarised light, according to the eqn. (6).

$$u = \frac{2d\Delta n}{\lambda} \tag{6}$$

where the coefficient u is much larger than unity, which is the Maugin limit. Thus, for the centre of the range (400–700 nm) of visible light, *e.g.*, at $\lambda_o \approx 550$ nm, the wavelength at which the eye is most sensitive, a series of minima are produced, where I is the transmission through a TN-LCD with ideal parallel polarisers and neglecting light absorbed by the first polariser [eqn. (7)].

$$I = \sin^2\left[\frac{\pi/2(1+u^2)^{1/2}}{1+u^2}\right] \tag{7}$$

A series of maxima and minima is produced for various values of I against u. These values are often referred to as the first, second, *etc.*, Gooch and Tarry[35] or Maugin minima for discrete values of the coefficient u (*i.e.*, $\surd 3$, $\surd 15$, $\surd 35$, $\surd 63$, *etc.*). Since the amplitude of transmission decreases with increasing value of u, it is advantageous to operate in the first minimum in order to obtain a bright TN-LCD with high contrast and a wide viewing angle. For crossed polarisers the curve is inverted and the minima become maxima and *vice versa*. A special combination of a nematic liquid crystal mixture with $\Delta n < 0.10$ allows operation in the first minimum for a cell gap of 6.55 μm.[36] This results in a very good optical performance, when combined with a nematic mixture of low viscosity in order to maintain fast response times. A certain amount of light still leaks through all TN-LCDs due to a variety of factors, such as non-perfect polarisers, non-uniform nematic alignment, cell thickness variation, temperature and wavelength dependence of Δn and the polychromaticity of visible light itself. This results in a lower contrast between the on-state and off-state.

On-state. The voltage at which the molecules reorientate themselves is called the threshold voltage (V_{th}). Near the threshold the deformation of the director gives rise to sinusoidal perturbations having the longest wavelength compatible with the boundary conditions. The elastic energy required and the dielectric energy released by this deformation vary as the square of the amplitude.[20] The instability threshold is attained when the two quadratic terms are equal. Thus, the threshold voltage for a twisted nematic cell can be defined[1] by the eqn. (8).

$$V_{\text{th}}=\pi\left[\frac{1}{\varepsilon_{\text{o}}\Delta\varepsilon}\left(k_{11}+\frac{k_{33}-2k_{22}}{4}\right)\right]^{1/2} \quad (8)$$

where k_{11}, k_{22} and k_{33} are the Frank elastic constants,[25] ε_{o} is the relative permittivity of a vacuum and $\Delta\varepsilon$ is the dielectric anisotropy of the nematic mixture. When the applied field is removed the surface and elastic forces restore the twist, allowing plane polarised light to be transmitted again. The time taken for the TN-LCD to be switched on (t_{on}) and switched off (t_{off}) is defined[36] in eqns. (9) and (10):

$$t_{\text{on}} \propto \frac{\gamma_1 d^2}{\Delta\varepsilon E-\kappa\pi^2} \quad (9)$$

$$t_{\text{on}} \propto \frac{\gamma_1 d^2}{\kappa\pi^2} \quad (10)$$

where

$$\kappa=\left[k_{11}+\left(\frac{k_{33}-2k_{22}}{4}\right)\right] \quad (11)$$

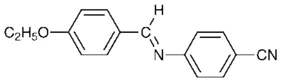
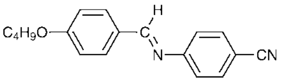
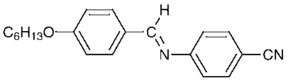
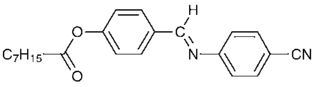
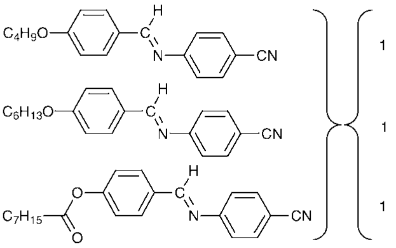
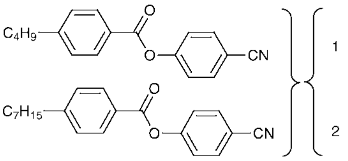
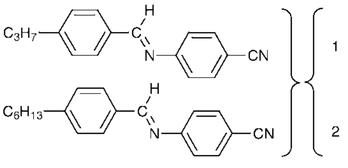
and γ_1 is the rotational viscosity, E is the applied field and d is the cell thickness. It is generally accepted[34] that the optical characteristics of the TN-LCD are optimised at low k_{33}/k_{11}, high k_{33}/k_{22} and low $\Delta\varepsilon/\varepsilon_{\perp}$. However, the response of the director is not identical throughout the cell due to strong anchoring at the substrate surfaces within the cell. The molecules of the nematic mixture closest to the inner surfaces probably do not move at all under an applied field. This anchoring of molecules near the surface is transmitted to neighbouring molecules in the nematic bulk and affects the director response to the applied voltage. It is the strong surface anchoring, which restores the twisted nematic structure through elastic forces after the applied field has been removed.

The first prototype TN-LCDs[1] were constructed by the inventors at Hoffman-La Roche in Basle, Switzerland as part of a wider collaboration with Brown Boveri of Baden, Switzerland, who later constructed the first factory at Videlec in Lenzburg, Switzerland to manufacture TN-LCDs on a commercial scale. These prototypes used a single nematic material, *i.e.*, *N*-(4-ethoxybenzylidene)-4-aminobenzonitrile **10**, and then operated at elevated temperatures in the nematic phase found in between the melting point (Cr–N, 106 °C) and the clearing point (N–I, 128 °C), see Table 2. Compound **10** had been prepared in the first decade of the twentieth century.[37] Its dielectric anisotropy had been measured before the report of the invention of the TN-LCD and been found to be positive and of a large magnitude ($\approx +14$).[38] A tertiary mixture, M1, consisting of two *N*-(4-*n*-alkoxybenzylidene)-4-aminobenzonitriles[39] **11** and **12** and a 4-*n*-alkanoyloxybenzylidene-4-aminobenzonitrile[40] **13** was soon prepared,[41] which allowed operation at room temperature. This is illustrative of the fact that appropriately formulated nematic mixtures generally exhibit a melting point (eutectic) much lower than that of any of the individual components, whereas the clearing points are usually an average, although some deviation from ideal behaviour is often observed. Binary mixtures M2 and M3, see Table 2, were also prepared and found to be nematic at room temperature.[42] However, the threshold voltage for these mixtures is much lower than that found for M1. This must be due to an advantageous combination of elastic constants, see eqn. (8), since the dielectric anisotropy of all three mixtures is almost identical and the threshold voltage is independent of the cell gap. Moreover, since the value of κ for M2 and M3 is very similar, then the shorter switching times for M3 must be attributable to a lower rotational viscosity, γ_1, for the Schiff's bases compared to that of the esters, used in mixtures M2 and M3, see Table 2 and eqns. (9) and (10). The replacement of the alkoxy chains of the components of M1 by alkyl chains in the components of mixtures M2 and M3 also helped to lower the viscosity. These components were specifically made and patented for the TN-LCD by synthetic chemists at Hoffmann-La Roche. They are a very good example of the improvement in device operation achievable by the design and synthesis of new liquid crystal materials to a given specification.

The first commercially available TN-LCDs incorporated similar mixtures of Schiff's bases and phenyl benzoates supplied by Hoffmann-La Roche. However, the mixtures had to be handled with care due to hydrolysis by atmospheric moisture of the central linkage of the Schiff's bases. It was realised by G. W. Gray at the University of Hull that most of the instability problems found for standard liquid crystals at that time were caused by the unsaturated linking unit (Schiff's base, azo, azoxy, *etc.*) between the aromatic rings found in most of them. Therefore, about one year after the publication of the TN effect, they synthesised the cyanobiphenyls, *e.g.*, 4-cyano-4′-pentylbiphenyl **14**, see Table 3, which do not contain a central linkage between the two phenyl rings.[43] Therefore, they possess a much higher chemical, photochemical and electrochemical stability. Furthermore, the absence of the central linkage has the added advantage of lowering the viscosity and the melting point. Indeed, some homologues exhibit a nematic phase at room temperature. Mixtures of 4-*n*-alkyl-4′-cyanobiphenyls and the 4-*n*-alkoxy-4′-cyanobiphenyls also synthesised at Hull University were then evaluated at DERA, Malvern and then made commercially available by BDH Ltd (now Merck, UK) a subsiduary of E. Merck, Darmstadt, Germany. However, many LCD manufacturers considered the clearing point too low and initial sales were low. It was only with the synthesis, again by the Hull group, of the 4-*n*-alkyl-4″-cyano-*p*-terphenyls, with one more 1,4-disubstituted phenyl ring and exhibiting much higher clearing points, that this problem was solved. A consequence of their combination of advantageous properties, eutectic mixtures of 4-*n*-alkyl-4′-cyanobiphenyls, 4-*n*-alkoxy-4′-cyanobiphenyls and 4-*n*-alkyl-4″-cyano-*p*-terphenyls displaced the mixtures of Schiff's bases and phenyl benzoate esters from most commercially available TN-LCDs over a period of time. These new mixtures allowed the liquid crystal display industry for the first time to manufacture and commercialise reliable LCDs with long life times. They effectively provided the display industry with the secure basis, which has since led to its multibillion-dollar markets.

The success of the cyanobiphenyls naturally activated other chemists to look at structurally related materials, and, for comparison, the pentyl homologues of some nitriles **14–30**[43–56] are collated in Table 3. They are indicative of the substantial efforts carried out in order to improve on the cyanobiphenyls.[43] The 2-cyano-5-(4-pentylphenyl)pyridines **16**[45] and the 2-(4-cyanophenyl)-5-pentylpyrimidines **17**[46] both exhibit higher values of $\Delta\varepsilon$ (+21 and +9.4, respectively), than the 4-*n*-alkyl-4′-cyanobiphenyls **14** (+8.5). This is due to the contribution of the dipole moments attributable to the lone pair electrons on the nitrogen atoms along the molecular long axis. If the dipole moments are in the opposite direction, $\Delta\varepsilon$ is lower as seen for the 5-cyano-2-(4-pentylphenyl)pyrimidines **18** (+3.4).[46] The 2-(4-cyanophenyl)-5-pentylpyrimidines[46] and

Table 2 Transition temperatures/°C, dielectric anisotropy, threshold voltage/V and switching times/s for some nematic mixtures **M1**, **M2** and **M3** and their components **10–13**

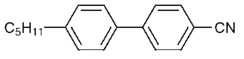
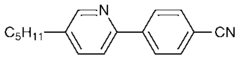
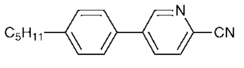
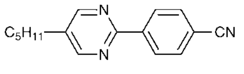
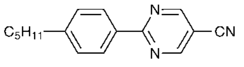
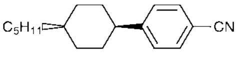
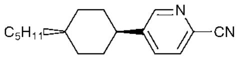
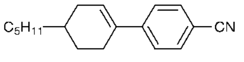
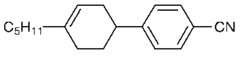
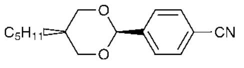
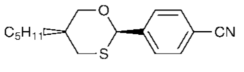
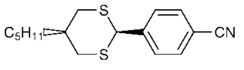
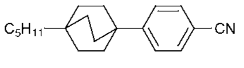
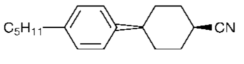
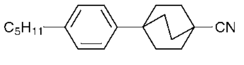
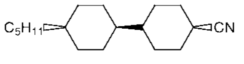
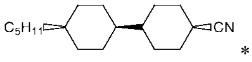
Compound	R	Cr		N		I	$\Delta\varepsilon$	V_{th}	t_{on}, t_{off}	Ref.
10		•	106		128		+14			37, 38
11		•	63	•	111	•				39
12		•	55	•	101	•				39
13		•	54	•	98	•				40
M1		•	20	•	94	•	+14	3.5		1, 41
M2		•	25	•	50	•	+14	0.9	0.2,0.15	42
M3		•	−30	•	62	•	+14	1.1	0.1,0.1	42

related derivatives from Hoffmann-La Roche represented replacement nematic liquid crystals for the Schiff's bases and phenyl benzoate esters. The replacement of the phenyl ring attached to the alkyl group of the 4-cyano-4′-pentylbiphenyl **14** by a *trans*-1,4-disubstituted cyclohexane ring to yield the *trans*-1-(4-cyanophenyl)-4-pentylcyclohexane **19** results in a lower Δn and a lower γ_1 without changing $\Delta\varepsilon$ very much.[47] The replacement of the second phenyl ring attached to the nitrile function to create the *trans*-1-(*trans*-4-cyanocyclohexyl)-4-pentylcyclohexane **29** lowers the polarisable electron density further and therefore, lowers $\Delta\varepsilon$ and γ even more.[56] Homologues of these compounds and related three-ring materials form the basis of very successful mixtures for TN-LCDs manufactured by E. Merck. Several types of nitrile reported in Table 3, such as the dioxanes **23**[51] are also manufactured for TN-LCDs.

Since the combination of a short alkyl chain, a *trans*-1,4-disubstituted cyclohexane ring and a cyanobenzene in the *trans*-1-*n*-alkyl-4-(4-cyanophenyl)cyclohexanes (PCHs)[47] appeared to be a good combination for TN-LCDs it seemed of interest to investigate the incorporation of a stable central linkage between the two rings to form the compounds[57–61] **31–40** collated in Table 4. The chemists at E. Merck had followed the example of G. W. Gray at Hull and removed the central linkage from the 4-cyanophenyl *trans*-4-*n*-alkylcyclohexanoates,[57] synthesised earlier at the Martin Luther University, Halle, Germany to yield the PCHs. These researchers were the first to investigate the effect of the *trans*-1,4-disubstituted cyclohexane ring on mesomorphic behaviour. However, only the *trans*-1-*n*-alkyl-4-[2-(4-cyanophenyl)ethyl]-cyclohexanes (PECHs) prepared by Carr, Gray and McDonnell at Hull University, *e.g.*, **33**, were almost equivalent from a display device viewpoint. These were developed under a DERA, Merck, Hull University research programme, and because of their similarity to the PCHs[47] and their greater synthetic complexity, it was not considered expedient to commercialise them. Indeed, none of these materials are currently being manufactured, apart from the original esters **31**.[57] It should be emphasised here that the mixtures used in today's liquid crystal display devices may contain well over twenty different components, which may be drawn from several classes of room temperature nematic liquid crystals in order to optimise the final mixture properties.

Changes in the terminal chains seemed to be one of the few remaining possibilities to modify the properties of these core systems, see Table 5, where a series of *trans*-4-substituted cyclohexylbenzonitriles **19** and **41–56** bearing a chain of fixed length (five units) is shown.[47,62–65] In the series[62] of ethers **41–44** which differ only in the position of the oxygen atom only the methoxypropyl-substituted benzonitrile **44** with an oxygen atom at some distance from the core exhibits a nematic phase. However, as the melting point is higher than that of the unsubstituted benzonitrile **19**, the nematic range is narrower. As the angle made by the carbon–oxygen–carbon bond (CH_2OCH_2) is very similar to that with a methylene unit instead of the oxygen atom ($CH_2CH_2CH_2$), it must be assumed

Table 3 Transition temperatures/°C, dielectric anisotropy and bulk viscosity/P for the compounds **14–30**

Compound	R	Cr		N		I	Δε	Δn	η	Ref.
14		•	22.5	•	35	•	$+8.5^{f}$	0.18	35	43
15		•	33.5	•	43.5	•				44
16		•	73	•	$[31]^{a}$	•	$+9.4^{f}$			45
17		•	71	•	$(52)^{b}$	•	$+21^{f}$	0.18	50	46
18		•	96	•	109^{c}	•	+3.4			46
19		•	31	•	55	•	$+9.9^{f}$	0.12	21	47
20		•	45.5	•	55.5	•				48
21		•	48	•	61	•				49
22		•	35	•	(5)	•				50
23		•	56	•	(52)	•	$+11^{a}$	0.8/9	46	51
24		•	74	•	(19)	•				52
25		•	98	•	$—^{d}$	•				52
26		•	62	•	100	•	$+10^{h}$	0.14	90	53
27		•	<25	•	−25	•				54
28		•	113	•	(50)	•				55
29		•	62	•	85^{e}	•	$+3\sim4^{f}$	0.04/5		56
30	 **F3Q	•	104	•	129	•				55

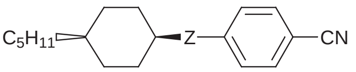
[a]Represents an extrapolated 'virtual' transition temperature. [b]( ) Represents a monotropic transition temperature. [c]SmA phase at 93.5 °C. [d]Supercoolable to 28 °C. [e]Unidentified smectic transitions at 43 °C and 52 °C. [f]Δε measured at 0.98 × T_{NI}. [g]Δε measured at 42 °C. [h]Δε measured at 25 °C.

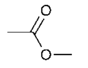
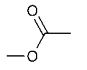
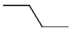
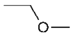
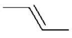
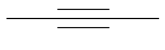
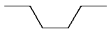
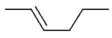
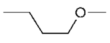
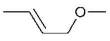
that the effects on the clearing point of the oxygen atom are primarily of a polar and not a steric nature. Substantial differences in the liquid crystal transition temperatures of the benzonitriles **45–51** with a carbon–carbon double bond (C=C) in the terminal chain are also observed.[63] The elastic constant and relative permittivity also differ greatly, which is of real commercial and technological relevance for LCDs, especially Super Twisted Nematic Liquid Crystal Displays (STN-LCDs).[34] Molecular modelling of ensembles of molecules indicates that steric effects due to different configurations of the terminal chain are primarily responsible for the very large differences in the transition temperatures. The corresponding acetylene derivative **52**[62] exhibits a virtual nematic clearing point just above 0 °C. This is probably due to the non-axial position of the acetylene group, which acts to increase the breadth of the molecule in this particular case. The effect of combining two functional groups, *i.e.*, one exerting polar, the other steric effects, on the mesogenic tendencies of compounds[64] is shown by reference to the ethers **53** and **54**. For one ether **53** no liquid crystal behaviour could be determined, while for the second ether **54** a monotropic nematic phase could be detected at a temperature slightly higher than that of the reference substance **19**. The compound **56** containing an ester group (COO) and a carbon–carbon double bond exhibits very high nematic transition temperatures for two-ring systems. This is probably attributable to an advantageous combination of molecular rigidity and extended conjugation, despite the presence of the flexible cyclohexane ring.

Reverse twist in TN-LCDs

The optical contrast for a TN-LCD is at a maximum along a direction parallel to the director in the middle of the cell and at a minimum at right angles to this direction. Therefore, the observed contrast for a TN-LCD is asymmetric and depends not only on the viewing angle, but also on the direction of view with respect to the director. Molecules in a twisted nematic structure can give rise to areas, or domains, of reverse

Table 4 Transition temperatures/°C for the compounds **19** and **31–40**



Compound	Z	Cr		N		I	Ref.
31		•	55	•	81	•	57
32		•	74	•	(67)[b]	•	58
19		•	30	•	59	•	47
33		•	45	•	55	•	59
34		•	74	•	(49)	•	59
35		•	54	•	107	•	60
36		•	41	•	73	•	60
37		•	51	•	(39)	•	61
38		•	40	•	(39)	•	61
39		•	63	•	(54)	•	61
40		•	64	•	(43)	•	61

[a]Monotropic SmX–SmB transition at 58 °C. [b]( ) Represents a monotropic transition temperature.

twist upon application of an electric field. These give rise to disclination lines between neighbouring domains and result in reduced optical contrast. This can be eliminated by the addition of a small amount of an optically active material (dopant).[66] This optically active dopant induces a uniform direction or handedness of twist in the nematic medium, which coincides with the twist in the cell. If p/d is too small then areas of reverse twist can form. Therefore, the pitch, p, induced in the nematic medium by the chiral dopant should be long and result in a ratio for p/d of about 7. Larger values for the pitch can result in areas of reverse twist.

The medium is also no longer a twisted nematic medium, but a chiral twisted nematic medium. This results in a higher threshold voltage according to the eqn. (12):

$$V_{\mathrm{th}}=\sqrt{\frac{k_{11}\pi^2+\left\{k_{33}-k_{22}\left(1-\frac{4d}{p}\right)\right\}\left(\frac{\pi}{2}\right)^2}{\varepsilon_0\Delta\varepsilon}}$$

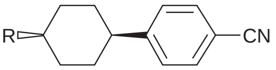
where the pitch of the chiral nematic mixture is also a term.

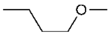
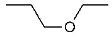
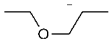
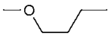
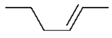
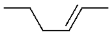
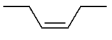
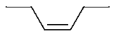
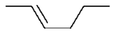
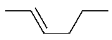
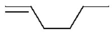
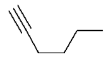
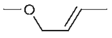
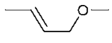
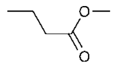
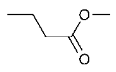
Initially derivatives of cholesterol, such as cholesteryl nonanoate[67] were added to induce the desired handedness of twist. However, such derivatives are hygroscopic to some extent and not particularly stable and so they were quickly supplanted by optically active derivatives of the cyanobiphenyls, such as 4-cyano-4′-[(*S*)-2-methylbutyl]biphenyl.[68]

Addressing methods for TN-LCDs

The addressing of any display device is the process whereby the image or information in digital form is converted into the appropriate voltage pulses in order to activate individual pixels and, thus, recreate the image or information on the display. In order for a liquid crystal display to be fully functional, then each individual pixel has to be switched on and off by applying and then removing an electric field. There are three main methods by which this can be achieved i) Direct Addressing, ii) Multiplex Addressing and iii) Active Matrix Addressing.

Table 5 Transition temperatures/°C for the compounds **19** and **41–56**



Compound	R	Cr		N		I	Ref.
19		•	30	•	55	•	47
41		•	60		—	•	62
42		•	23		—	•	62
43		•	42		—	•	62
44		•	52	•	55	•	62
45	(*E*) 	•	16	•	59	•	63
46	(*Z*) 	•	—	•	[−144][a]	•	63
47	(*E*) 	•	16	•	[−67]	•	63
48	(*Z*) 	•	−8	•	[−54]	•	63
49	(*E*) 	•	60	•	74	•	63
50	(*Z*) 	•	33	•	(−14)[b]	•	63
51		•	30	•	(10)	•	63
52		•	86	•	[1.5]	•	62
53	(*E*) 	•	84		—	•	64
54	(*E*) 	•	66	•	(59)	•	64
55		•	56		—	•	65
56	 **F7Q	•	128	•	(119)	•	65

[a][ ] Represents a virtual (extrapolated) transition temperature. [b]( ) Represents a monotropic transition temperature.

Direct addressing. In simple displays, *i.e.*, clocks, calculators, *etc.*, if the information content is limited then each pixel is driven directly with a dedicated electrode contact and driver, see Fig. 2. With this type of addressing the off-voltage can be zero and the on-voltage can be several times the threshold voltage. Therefore, in a TN-LCD, where the electro-optical characteristic is relatively flat, a good contrast can be attained as well as low power consumption. However, the need for displays with a higher information content, *e.g.*, in portable notebooks, personal organisers, computers, *etc.*, requires more

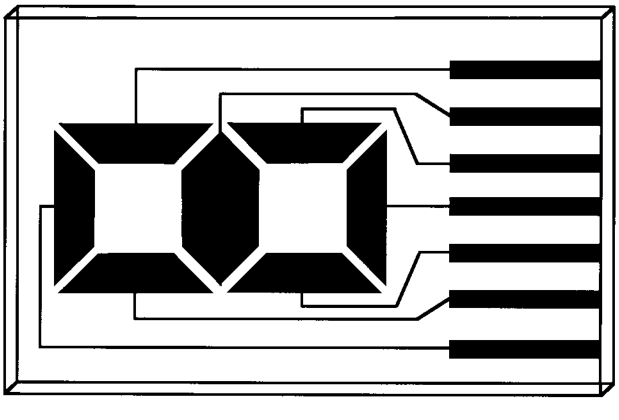


Fig. 2 Schematic representation of a low-information-content TN-LCD with direct addressing of segmented electrodes.

complex addressing schemes due to the increasing cost of drivers and an absence of space for individual contacts.

Multiplex addressing. A high-information-content display requires a large number of pixels, each having to be addressed.[34] Individual connections to each element will give $M \times N$ connections. There is obviously a limit over which it is impossible physically to connect all the pixels. Multiplex addressing, however, with M electrode columns and N electrode rows allows $M \times N$ pixels to be driven by $M+N$ connections, thereby significantly reducing the number of electrode connections, see Fig. 3. This renders it possible to address more lines, thereby allowing larger flat panel displays with good optical properties to be produced.

In a TN-LCD with multiplex addressing, parallel lines of electrodes are etched on to both glass substrates and then positioned so that they are perpendicular to one another, resulting in a matrix of rows and columns. Each row is sequentially scanned by a scan or select pulse (V_s) while the columns are addressed by data pulses (V_d), which contain the information to be displayed. As each row receives a voltage, each column receives a positive or negative voltage. The combination of a row voltage and positive column voltage in phase with each other generates a voltage above the threshold voltage, therefore, turning the pixel on. An appropriate negative voltage from the column electrode turns the pixel off and elastic relaxation due to surface forces can take place. Ideally, assuming the response of the liquid crystal is caused solely by an induced polarisation of the nematic medium in response to the applied electric field, then the optical response is proportional to the square of the electric field and, therefore, to the square of the combined applied voltage, *i.e.*, the rms voltage. Unfortunately, the number of addressable lines in a multiplexed TN-LCD with good legibility is limited, although to a much lesser extent than direct addressing. Alt and Pleshko showed[69] that the maximum number of addressable lines (N) is given by eqn. (13).

$$\frac{V_{ns}}{V_s} = \sqrt{\frac{\sqrt{N-1}}{\sqrt{N+1}}} \qquad (13)$$

V_S and V_{NS} are the select and non-select voltages respectively, see Fig. 4. For 64 addressable lines, there is only a difference of about 11% between the select and non-select voltages. Therefore, the more lines there are to be addressed, the smaller the permissible voltage change becomes. This results in lower contrast due to the inadvertent activation of neighbouring pixels, *i.e.*, cross-talk. In order to increase the number of addressable lines without reducing the contrast, it is essential that the electro-optical response curve should have a very steep, or indeed, an infinite slope. However, a steep electro-optic characteristic reduces the capacity for grey-scale and, therefore, full colour. Grey-scale allows the brightness of a pixel to be controlled almost linearly by varying the applied voltage, see Fig. 4. Therefore, multiplexed TN-LCDs are only capable of displaying a limited amount of information with good contrast and legibility. In practice a duty cycle of 1 : 64 is the upper limit, *i.e.*, 64 rows can be addressed in one frame.

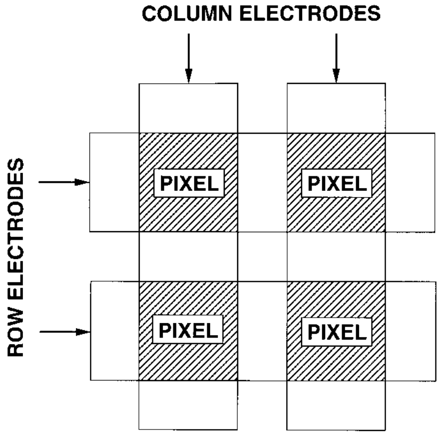


Fig. 3 Schematic representaion of a high-information-content TN-LCD with multiplex addressing using electrode rows and columns to generate pixels.[34]

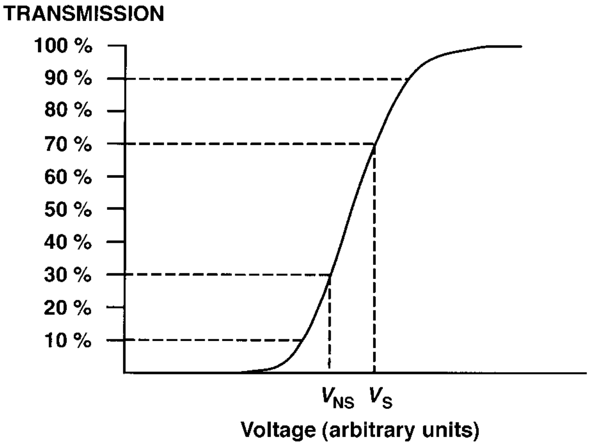
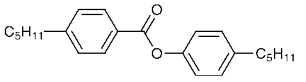
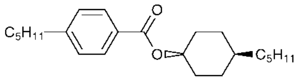
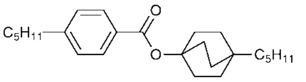
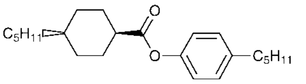
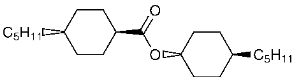
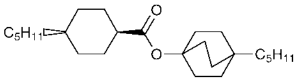
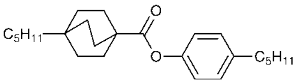
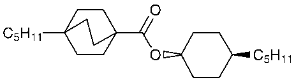
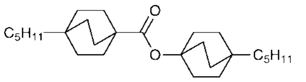


Fig. 4 Schematic representation of the electrooptic response curve of a TN-LCD with multiplex addressing using electrode rows and columns to generate pixels.[34]

The large dipole moment (≈4.0 D) of the cyano-group bonded covalently to a phenyl ring of the nematic liquid crystals used in early TN-LCDs such as the cyanobiphenyls generally results in strong antiparallel molecular correlation.[70,71] This can be represented in a simple fashion as a binary mixture of virtually uncorrelated molecules (monomers) and pairs of associated molecules (dimers).[72] These are envisaged to be in a dynamic, temperature dependent equilibrium. The dipole moment of the dimer will be almost zero due to the antiparallel configuration of the terminal dipoles. The effective relative permittivities will also be smaller. However, the effective molecular length is greater, *i.e.*, 1.4 times the molecular length for cyanobiphenyls.[70] This contributes to the formation of a nematic phase at or just above room temperature for these short molecules. The degree and nature of the molecular association of polar nematic liquid crystals is described by the Kirkwood Froehlich factor g which can be calculated from physical data, such as the refractive index, relative permittivities, molecular dipole moments, obtained for the bulk nematic material.[73,74] When $g=1$ there is no correlation and when $g=0$ there is complete correlation of the molecular dipoles. Thus, the Kirkwood Froehlich factor indirectly influences the bulk physical properties, such as dielectric constants, clearing point, elastic constants, viscosity.

Mixtures consisting solely of components with a terminal cyano group are very difficult to multiplex to any significant degree. However, it was found[75,76] that adding nematic compounds of low dielectric anisotropy, such as the esters **57–65**[19,77–80] shown in Table 6, breaks up a significant number of these molecular dimers to generate a higher number of polar monomers. This not only results in a higher effective dielectric anisotropy, but also lowers the observed value of k_{33}/k_{11}. Thus, judicious mixing of apolar materials of low viscosity, weak positive or negative dielectric anisotropy and a low k_{33}/k_{11} elastic constant ratio with polar nematic liquid crystals of high positive dielectric anisotropy produces nematic mixtures more suited to multiplexed addressing of TN-LCDs than simple mixtures solely containing of polar liquid crystals. However, esters generally exhibit high viscosity values and a series of compounds **66–74**[81–86] incorporating one *trans*-1,4-disubstituted cyclohexane ring, see Table 7 or compounds

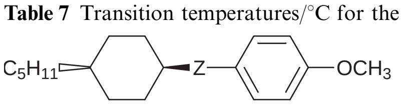
Table 6 Transition temperatures/°C for the compounds **57–65**

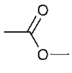
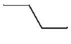
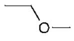
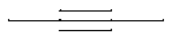
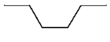
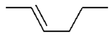
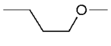
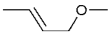
Compound	R	Cr		SmB		N		I	Ref.
57		•	36		—	•	(26)[a]	•	15, 79
58		•	28		—	•	(22)	•	77, 79
59		•	68		—	•	(59)	•	79
60		•	36	•	(29)	•	48	•	77, 79
61		•	51	•	71	•	—	•	78
62		•	−3	•	107	•	[100][b]	•	79
63		•	31		—	•	64.5	•	80
64		•	17	•	96	•	[92]	•	79
65		•	40	•	192	•	[130]	•	79

[a]( ) Represents a monotropic transition temperature. [b][ ] Represents a virtual extrapolated transition temperature.

75–83[87–93] with two *trans*-1,4-disubstituted cyclohexane rings, see Table 8, were explored in order to produce apolar nematogens of low viscosity. However, only the compounds linked directly, *e.g.*, **67**,[82] or by the ethane linkage, *e.g.*, **68**,[83] were found to exhibit an acceptable viscosity value. The birefringence and viscosity values for compounds containing two cyclohexane rings are very low. However, they have a tendency for smectic B formation. Although the ethers **77**[90] and the esters **78**[78] also exhibit a nematic phase, they possess high viscosity values. However, the esters **78** have been manufactured for certain applications where the viscosity is not absolutely critical. Only the ethers **76**[88] combine low viscosity with nematic phase formation.

Table 7 Transition temperatures/°C for the compounds **66–74**



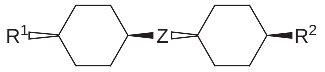
Compound	Z	Cr		SmB		N		I	Ref.
66		•	36		—	•	64	•	81
67	—	•	45		—	•	(15)[a]	•	82
68		•	30		—	•	34	•	83, 84
69		•	46		—	•	(38)	•	84
70		•	31		—	•	46	•	85
71		•	27	•	(16)		—	•	86
72		•	25		—	•	34	•	86
73		•	47		—	•	(46)	•	86
74		•	44		—	•	46	•	86

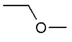
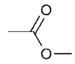
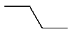
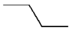
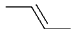
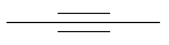
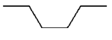
[a]( ) Represents a monotropic transition temperature.

Attempts were also made to produce single components combining a high positive dielectric anisotropy with low k_{33}/k_{11} and $\Delta\varepsilon/\varepsilon_\perp$ ratios by the incorporation of lateral substituents in polar molecules, such as those **84–86**[94] shown Table 9. This was only moderately successful, but yielded new nematic materials with unexpected advantages. The presence of a lateral fluorine atom results in lower absolute values for the elastic constants compared with those of the non-laterally substituted ester. However, the relatively high value for the k_{33}/k_{11} elastic constant ratio does not improve the multiplexability of mixtures containing such components. The degree of molecular association of the 4-cyano-2-fluorophenyl 4-heptylbenzoate **85** and 4-cyano-3-fluorophenyl 4-heptylbenzoate **86**, which possess a fluorine atom in a lateral position, is much lower than that of 4-cyanophenyl 4-heptylbenzoate **84**. Indeed **86** exhibits no association at all ($g=1$). This results in a much lower clearing point for this ester compared to that of the non-laterally substituted ester. However, the clearing point of the 4-cyano-2-fluorophenyl 4-heptylbenzoate is comparable. The absence of association and the large dipole moment of 6.1 D of **86** results in the largest value for the dielectric anisotropy found for a liquid crystal (≈ 50). Since these esters also possess low values for the elastic constants, they are manufactured on a large scale by E. Merck and Dai Nippon Ink and added to nematic mixtures for TN-LCDs in order to lower the threshold and operating voltages.

The transmission curves, *e.g.*, see Fig. 4 for a schematic

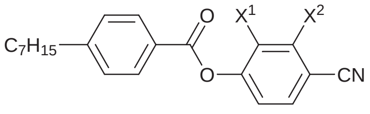
Table 8 Transition temperatures/°C for the compounds **75–83**



Compound	R^1	R^2	Z	Cr		SmB		N		I	Ref.
75	C_3H_7	C_3H_7	—	•	64	•	82^a		—	•	87
76	C_3H_7	OC_2H_5	—	•	49		—	•	50	•	88, 89
77	C_3H_7	C_3H_7		•	7	•	8	•	17.5	•	90
78	C_3H_7	C_3H_7		•	23		—	•	37	•	78
79	C_3H_7	C_3H_7		•	35	•	73		—	•	91
80	C_5H_{11}	C_5H_{11}		•	46	•	109		—	•	92
81	C_5H_{11}	C_5H_{11}		•	53	•	95		—	•	92
82	C_5H_{11}	C_5H_{11}		•	52	•	$(50)^b$		—	•	92
83	C_4H_9	C_4H_9		•	40	•	68			•	93

^{a}Monotropic SmX–SmB transition at 58 °C. ^{b}( ) Represents a monotropic transition temperature.

Table 9 Transition temperatures/°C, elastic constant ratio^a (k_{33}/k_{11}), birefringence^a (Δn), dipole moment (μ/D), Kirkwood Froehlich factor (g) and dielectric anisotropy^a ($\Delta\varepsilon$) for the compounds **84–86**



Compound	X^1	X^2	Cr		N		I	k_{33}/k_{11}	Δn	μ	g	$\Delta\varepsilon$	Ref.
84	H	H	•	44	•	57	•	1.52	0.15	5.6	0.7	19.9	72, 94
85	F	H	•	47	•	54	•	1.41		4.8	0.8	9.8	72, 94
86	H	F	•	28	•	28.5	•	1.71	0.14	6.1	1.0	48.9	72, 94

^{a}Measured at $0.95 \times T_{N\text{–}I}$.

representation, also depend on temperature, *e.g.*, 1% K^{-1}. This parameter is also dependent on molecular structure and the temperature dependence of the threshold values of mixtures containing different components is determined by it. This variation with temperature is usually compensated for externally or by using optically active components.[34]

Active matrix addressing. A large number of pixels for high-information-content displays is presently achieved in commercial displays by using versions of STN-LCDs[34] or an active matrix TN-LCD.[95–98] In the latter case, the most common commercial TN-LCD with active matrix addressing involves a discrete thin film transistor[96] or diode[97] at each individual pixel driving that pixel on an amorphous silicon backplate,[98] see Fig. 5. This does away with the requirement for rows and columns and removes the stringent size constraints imposed by active or multiplexed addressing. Thin film transistors using CdSe had been developed in the early nineteen sixties to address several kinds of display devices[99] and there are very many variants and combinations of TN-LCDs with active matrix addressing on the market.[95] This is attributable to the significant advantages of this technology, which include high contrast ratio, almost complete absence of cross-talk, grey-scale, fast response times, high-information-content and large-area. Major disadvantages are low luminescence or high power consumption, but more importantly, the high production cost associated with the silicon substrate and low production yield due to pixel damage and subsequent repair.

TFT-TN-LCDs are essentially based on a memory effect, *i.e.*, the charge on the pixel capacitor is maintained until the pixel is addressed again in the subsequent frame. Leakage of charge away from the pixel, *e.g.*, into the nematic liquid crystal, decreases the effective voltage across the pixel, which leads to lower contrast. Therefore, the resistivity of the nematic liquid crystal mixture must be especially high. The resistivity over time of the liquid crystal is defined by the holding ratio, HR [eqn. (14)].

$$\mathrm{HR} = \left[\left(1 - e^{\frac{-2T}{\tau}}\right)\left(\frac{\tau}{2T}\right)\right]^{1/2} \qquad (14)$$

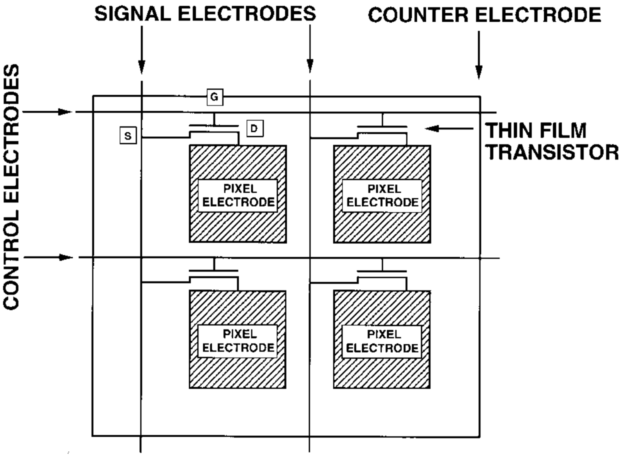
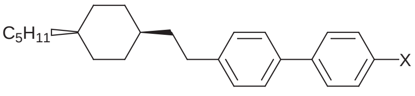


Fig. 5 Schematic representation of a high-information-content TN-LCD with active matrix addressing using thin film transistors at each pixel.[34]

Table 10 Transition temperatures/°C, C–X bond length/Å, dipole moment of C–X bond/D, birefringence (20 °C), dielectric anisotropy (20 °), and viscosity (η/cP at 20 °C) for the compounds **87–90**[100,101]



Compound	X	CR		N		I	C–X	μ	Δn	Δε	η
87	H	•	67	•	82	•	1.10	≈0	0.15	≈0	22.7
88	F	•	76	•	125	•	1.39	1.47	0.17	4.9	25.1
89	Cl	•	100	•	158	•	1.78	1.57	0.22	7.5	46.6
90	Br	•	125	•	163	•	1.93	1.59	0.24	7.6	63.0

Table 11 Transition temperatures/°C and dielectric anisotropy (Δε measured at 20 °C;[a] at $T_{\text{N–I}}-$ 10 °C) for the compounds **91–104**

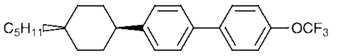
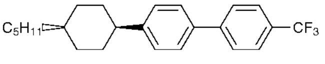
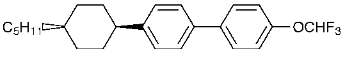
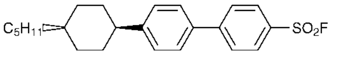
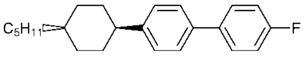
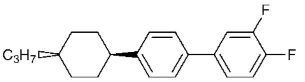
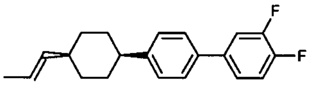
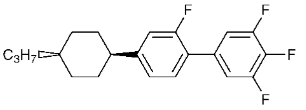
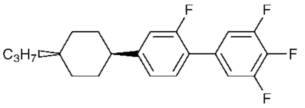
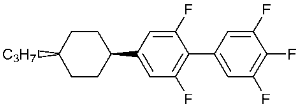
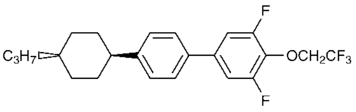
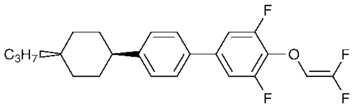
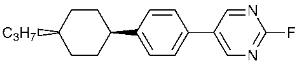
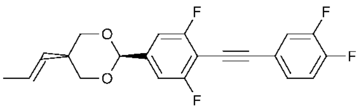
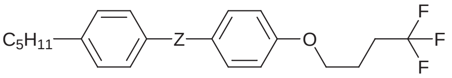
Compound	R	Cr		SmB		N		I	Δε	Ref.
91		•	43	•	128	•	147	•	+9	102
92		•	123		—	•	124	•	+13	103
93		•	67	•	120	•	162	•	+9	103
94		•	156		—		[60]	•	+27.1	104
95		•	90		—	•	158	•	+7.3	105
96		•	46		—	•	124	•	+9.3	102
97		•	48	•	85	•	159	•	+3.2[a]	41
98		•	42		—	•	(33)	•	+12.6	106
99		•	64		—		—	•	+15.2	107
100		•	123		—		—	•	+20.5	107
101		•	84		—	•	105	•	+12.2	108
102		•	52		—	•	104	•	+12.5	108
103		•	124		—	•	156	•	+17.7	109
104		•	99		—	•	157	•	+20.8[a]	110

Table 12 Transition temperatures/°C for the compounds **105** and **106**[112]



Compound	Z	Cr	SmX	SmB	SmA	N	I
105	—	• 63	—	• 99	• 103	• [63]^b	•
106	≡	• 98	• (86)^a	—	—	• [85]	•

^{a}( ) Represents a monotropic transition. ^{b}[ ] Represents an extrapolated value.

where T is the time frame, t is the RC time constant for the pixel and storage capacitor. A high value of the holding ratio requires a resistivity of over $10^{12}\ \Omega$ cm. This is a very high value for a nematic liquid crystal mixture and imposes very stringent specifications on the purity, chemical, photochemical and electrochemical stability and the resistivity over time of each of the individual mixture components and the mixture itself.

Nitriles are not suitable for LCDs with active matrix addressing as the high polarity of the cyano group tends to lead to dissolution of ions out of the layers on the LCD substrate. This leads to a low threshold voltage holding ratio. Therefore, liquid crystals containing a number of halogen atoms with a smaller dipole moment and especially fluorine atoms were synthesised and introduced commercially, see Table 10 and Table 11, for some three-ring derivatives **87–90**[100,101] and **91–104**.[102–110] The corresponding two-ring compounds are also used in admixture with some of the materials shown in Tables 10 and 11 for TN-LCDs with active matrix addressing, although many of them are not themselves liquid crystalline. The data collated in Table 10 for the compounds **87–90** show that the birefringence, dielectric anisotropy and the viscosity increase with the van der Waals radius of the terminal halogen atom.[100,111] However, the viscosity increases more than linearly with increasing size of the terminal substituent.[100] Therefore, compounds were synthesised with several fluorine atoms incorporated in a terminal group, *e.g.*, OCF_3, CF_3, OCF_2H, and in lateral positions on 1,4-disubstituted aromatic rings in order to produce a large positive value for the dielectric anisotropy with as low a viscosity value as possible, see Table 11. It can be seen that a high value of $\Delta\varepsilon$, comparable with that observed for analogous nitriles, can be obtained by using compounds incorporating trifluoromethoxy, difluoromethoxy or trifluoromethyl groups or a minimum of two fluorine atoms in a terminal position. Polyfluorinated compounds such as **98–100** exhibit especially high $\Delta\varepsilon$ values, although the nematic clearing point decreases with increasing degree of fluorine substitution. Heteroatoms, such as nitrogen and oxygen were also incorporated in the molecular structure in order to increase the permitivity value parallel to the long molecular axis, *e.g.*, compounds **103** and **104**. An additional carbon–carbon triple bond increases the birefringence, *e.g.*, compound **104**, for use in thinner cells with shorter response times. An interesting development[112] is the use of the 4,4,4-trifluorobutyloxy group in compounds **105** and **106** in order to maintain the resultant dipole moment along the molecular long axis, see Table 12. The extrapolated nematic clearing points are high for trifluoro-substituted two-ring compounds. This confirms the unique position of fluorine as a useful lateral and terminal substituent in liquid crystal chemistry.

Conclusions

It is evident that the design, synthesis, evaluation and subsequent manufacture of nematic liquid crystal materials as functional organic materials for use as thin films in electro-optic display device technology have made a significant contribution, amongst others, to the creation of the current multi billion dollar LCD industry. This has been facilitated by close interdisciplinary collaboration between chemists, physicists and technologists. It is also emphasised that many decisive discoveries were made and essential know-how generated in academic institutions as a consequence of fundamental, curiosity-driven research before LCDs had even been conceived.

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