ADVANCED
MATERIALS

Liquid Crystals—New Compounds, New Applications

By Rudolf Eidenschink *

Thermotropic Phases
Disk-Like Nematics
Electrooptical Devices
Laser Optics

1. Introduction

Fluidity and long range molecular orientational order are the common characteristics of liquid crystal phases. Depending on temperature and pressure, rod-like molecules can form the well known nematic and various smectic phases which have an additional positional order.[1] Optically active molecules form special helical phases, the cholesteric phase formed being closely related to the nematic phase and its helical structure gives rise to temperature dependent selective reflection. Quite recently a new helical smectic phase, named the S_A^* phase, with an unusual structure has been found.[2]

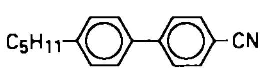
Fluidity and order can be realized with disk-like molecules in a similar way.[3] In the so-called phasmids, for example, the rod-like core and the half-disk ends of the molecules generate mesophases structurally different from known phases.[4a] Polarization microscopy aided by differential scanning calorimetry and X-ray diffraction have been the main tools used for structural classification. Now, scanning tunnelling microscopy of liquid crystal layers on graphite is offering some exciting details of molecular arrangement.[4b, 4c] The patterns of molecular order of the above mentioned phases can be transferred to polymers with a huge applicational potential.

Until now the technical application of low molecular weight thermotropic liquid crystals has been almost restricted to electrooptical displays using nematic and smectic phases although nematic phases are of scientific interest as anisotropic solvents in NMR spectroscopy and foils with encapsulated cholesteric liquid crystals have found a small field of application in thermometry.[5]

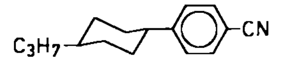
In the case of polymers, fibers with high tensile liquid strength have reached a state of industrial production and lyotropic phases, colloid disperse systems being formed by lamellae or nonspherical micelles, are of fundamental importance for biological processes. In some novel compounds and mixtures the characteristics of thermotropic and lyotropic phases overlap. In the following article some main points of this fast developing field shall be touched upon, the emphasis being on nonpolymer thermotropic materials with a potential for new technical application.

2. Nematogenic Compounds

Since their first application in displays some twenty years ago there has been an intensive search for new nematogenic compounds. Compounds **1** to **4** are examples of technologically important species (C = crystalline, S_A = smectic A, etc., N = nematic, I = isotropic, transition temperatures in °C.


1

C 23 N 35 I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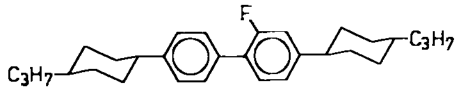
C 45 N 46 I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C 51 S_B 103 S_A 131 N 296 I


4

C 74 N 178 I

A nematic phase used for the twisted nematic cell[6] nowadays often contains 12 or more compounds in order to match the values of the parameters required: transition temperature from the nematic to the isotropic phase (T_{NI}), melting temperature, viscosity coefficients, elastic constants, optical and dielectric anisotropies and specific ohmic resistivity. A precondition for applicability is the long term stability of the compounds.

By now seemingly all simple molecular building elements permitting linear linking in order to obtain long shaped molecules have been applied.[7, 8, 9] An important task of research in this field is the fine tuning of special physical parameters of known classes of compounds. A good example is the systematic introduction of fluorine atoms.[8, 9, 10]

The newly introduced 1,3-bicyclo[1.1.1]pentylene moiety leads to a number of interesting compounds, exemplified by

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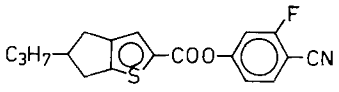
5. It was found, however, that the corresponding 1,4-bicyclo[2.2.2]octylene or 1,4-phenylene compounds generally have higher T_{NI} values.[12]

Replacing one 1,4-disubstituted six membered ring of a nematogenic molecule by a 1,3-disubstituted carbocyclic or heterocyclic five membered ring often yielded compounds with interesting physical properties. However, the decrease in the transition temperatures was prohibitive. To overcome this drawback, fused ring systems such as indanes[13] and s-hydrindacenes without a conventional ring system[14] have been synthesized. A particularly interesting example is the propanothiophen carboxylate **6**.[15]

New aspects of the field are opened up by some nematic transition metal complexes of Au, Ag, Pt, Pd and Ni[16], e.g. the platinum complex of 4'-pentylbiphenyl-4-carbonitrile **7**.


5

C 137 S_G 167 N 192 I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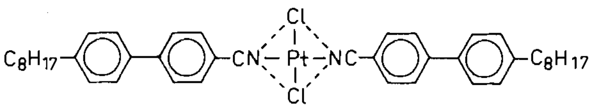
C 48 N 92 I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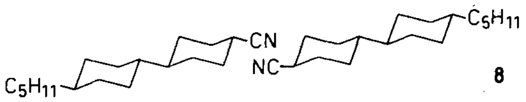
C 165 N 180 I

Some deviations from the usual building principle have become known. The fact that *trans,trans*-4'-alkylbicyclohexyl-4-carbonitriles like **8** are nematic has been explained in terms of association via the carbonitrile groups. It turns out, however, that bicyclohexyl compounds like **9** which do not undergo association because of steric deshielding are also nematic.[17]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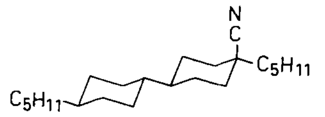
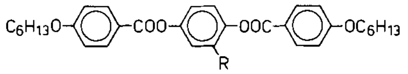

9

C 25 S_B 30 N 66 I

If in esters of type **10**, R = H is substituted by n-C_nH_{2n+1}, T_{NI} decreases.[18] The fact that the nematic state can be observed even with very long alkyl chains (up to n = 16!) has been explained in terms of an energetically preferred conformation permitting this chain to run parallel to the rigid core.[9]

The free rotation around the longest molecular axis of the biphenyldiol-dibenzoate **11** is obviously restricted. This compound is the first example of a biaxial thermotropic nematic phase found among nonpolymer compounds.[19]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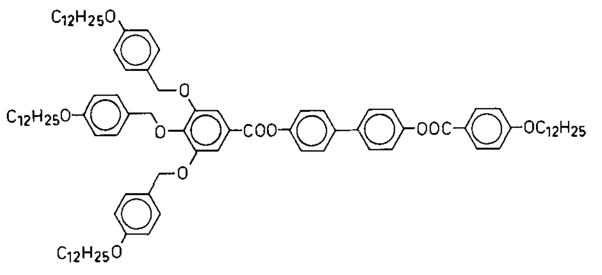
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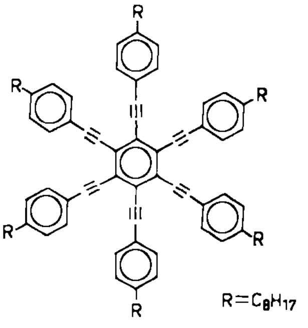
Today it is widely assumed that the occurrence of a thermotropic nematic phase is due to a combination of the at-

Rudolf Eidenschink worked as an engineer on selenium diodes and electroplating before moving to chemistry, completing a Doctoral Thesis in synthetic uses of anionic 1,3-cycloadditions at the University of Münster, FRG. After a postdoctoral fellowship at the University of Sussex, UK, he joined the company Merck in Darmstadt, FRG where he was responsible for the discovery and exploitation of a number of classes of liquid crystals, for example those known by the acronyms PCH, BCH, CCH, CBC, and CCN. In 1987 he left the group he had built up at Merck to found his own company, Nematel, which is situated in Mainz, FRG.

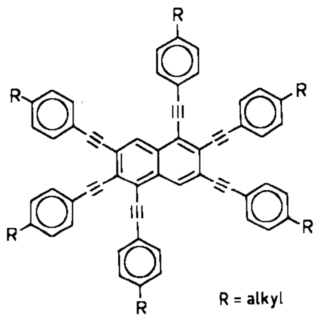
tracting dispersion forces and the hard core repulsion interactions, both of which are enhanced by the anisotropic shape. In the generalized van der Waals theory of *M. Cotter* and *W. M. Gelbart*[20] the first order phase transition from the isotropic to the nematic state at T_{NI} depends on the molecular package density and on a term for the attractive forces. The package density in a fluid can be assumed to depend on the ratio of molecular length over width.[9] Here—as with any molecular theory dealing with T_{NI}—the question of the conformation equilibrium is essential. In this context it was shown by ^{13}C-NMR of *trans*-1-alkoxy-4-alkoxy-carbonyl-cyclohexanes[21] that a distinct anomeric effect influences the concentration of the long shaped equatorial, equatorial-form in the conformational equilibrium. The hypothesis that the uncertainty of the local assignment of energy quanta passing between parallel molecules leads to an orientational effect was helpful in correlating chemical bonding parameters with T_{NI}.[22]

Hexaalkynylbenzenes like **12**[23] being the first disk-like nematic (N_D) hydrocarbons have no permanent dipole moment. The dielectric anisotropy of **12** due to electronic polarizibility made possible the realization of an electrooptical cell.[24]

Despite the long term instability of **12** this result gives impetus towards the development of displays with discotic phases proposed earlier.[25] In this context it is worth noting also that the 1,2,3,5,6,7-hexakis[phenylethynyl]naphthalenes **13**[26] form discotic phases with sequences comprised of different columnar phases and the disk-like nematic phase in an order opposite to that usually observed.



12



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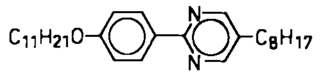
3. Compounds Forming Smectic C Phases

The invention of the surface stabilized ferroelectric liquid crystal displays (SSFLC)[27] in 1980 initiated the search for stable compounds with broad temperature ranges of S_C phases. Compounds forming this phase with a tilt of the molecules in the smectic layers have at least two aromatic rings,[28] with a few exceptions (see, for example, compound **16**). A perpendicular dipole, off center, combined with a polarizable center are the general features of such molecules and the phenylpyrimidines **14**[29] which have this feature are often used as basic components of S_C phases.

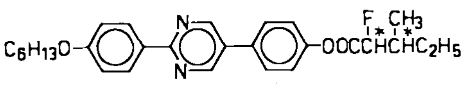


14

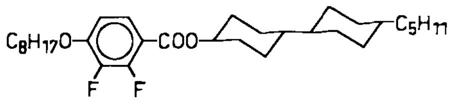
C 45 S_C 60 S_A 67 N 69 I

The environment of a molecule in an S_C phase can be described as monoclinic, with a 2-fold axis of symmetry and a mirror plane. To generate ferroelectricity, and to form a smectic S_C^* phase the mirror plane has to be removed. This is done by doping with an optically active compound, in most cases with an enantiotropic S_C^* phase. The spontaneous polarization *P* of thin layers (2 μm) can be expected to be high if high transverse dipole moments are connected as rigidly as possible to the chiral center and if intermolecular interactions impede the rotation around the long molecular axis. Compound **15**[30] synthesized from L(+)-isoleucine has a very high *P* of 400 nAs · cm^{-2}.

For low switching times in displays a small value of the coefficient of rotational viscosity[31] is advantageous. Here difluorobenzoates of the type **16**[32] are very useful.



15

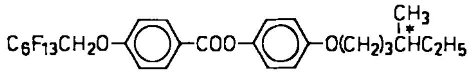


16

C 90 S_C 98 N 170 I

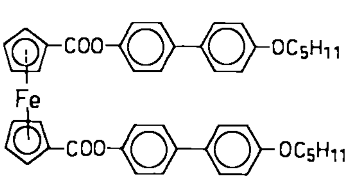
It has been long known that substitution in the alkyl chains of a mesogenic compound by several fluorine atoms leads to an enhancement of smectic phases (mostly S_A) over the nematic phase. In the case of simple phenyl benzoates[33] S_C phases could be induced by special substitution patterns, as shown in **17**.

The ferrocene derivative **18** is another example of the integration of a transition metal complex into a mesogenic struc-



17

C 52 S_C^* 78 S_A 89 I



18

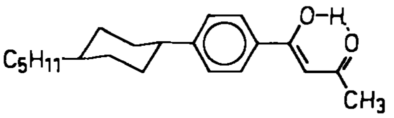
C 129 S_C 140 I

ture. Despite the participation of four 1,4-phenylene units the transition temperature to the isotropic state is relatively low. This is explained by the presence of different geometric isomers.[34]

4. Compounds with Hydrogen Bonds

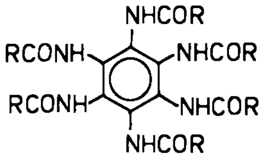
Compounds forming hydrogen bonds provide a variety of aspects not only for the well known aqueous lyotropics but more and more for thermotropic liquid crystals. *Trans*-4-alkylcyclohexane-carboxylic acids[35] and 1-(4-*trans*-4-alkylcyclohexyl-phenyl)-alkane-1,3-diones[36] being predominantly in their keto-enol form (**19**) have already been proposed for technical application in displays. Solutions of the high melting amide **20** in alkanes, chloroform or toluene are lyotropic nematic and can be oriented uniformly by a magnetic field.[37] This is probably due to the formation of intra and intermolecular hydrogen bonds.

The relatively low melting amides **21**[38] and **22**[39] have broad temperature ranges of thermotropic mesophases.



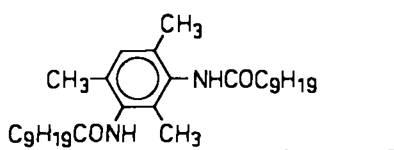
19

C 83 N 97 I



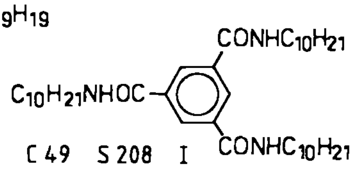
20

R = C_6H_{13}



C 126 S 168 N 211 I

21

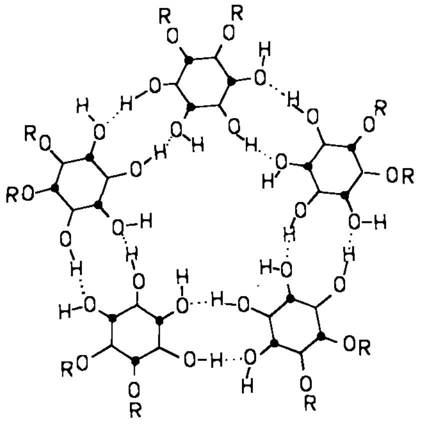


C 49 S 208 I

22

Although it was only 23 years after the synthesis of the liquid crystalline cholesteryl benzoate by *Reinitzer* in 1888 that the first 1-alkyl-o-glucosides with liquid crystal properties were synthesized,[40] the systematic search for liquid crystal derivatives of natural products in general and carbohydrates in particular is beginning[41,42,43] only now.

Interesting examples that exploit H-bonding are the columnar discotic phases formed by ionosite derivatives possibly having the supramolecular structure of **23** (R = alkyl).[44]



23

Also of interest are the 2-(*trans*-4-alkylcyclohexyl)-1,3-propandiols that form intermolecular hydrogen bonds in their S_A phases.[45] This molecular arrangement suggests the equivalent conductivity for $H^{\oplus}$ ions to be anisotropic. It was shown that diols are able to incorporate water that in certain concentrations enhances the thermodynamic stability of the S_A phase.[46] Generally speaking, with compounds forming intermolecular H-bonds, the characteristics of thermotropic and lyotropic liquid crystals begin to overlap.

5. Applications

5.1. New Electrooptical Devices

Today most of the liquid crystal displays are still twisted nematic cells. Recently major improvements have been made in the multiplexibility by using various techniques[6] which have a higher twist angle of the nematic layer (up to 270°) in common. The ratio of the elastic constants is regarded more and more as an important parameter for phases used in data screens. For pocket television screens the technique of an active matrix is favored, where one thin film transistor for every pixel switches a simple twisted nematic layer. The materials must be of very low viscosity and must have a high value for the product of dielectric constant and specific ohmic resistivity in order to limit the decrease of voltage at the pixels during the addressing cycle.[47] The above mentioned SSFL holds promise for a more economic realization.

A new and elegant technique to switch light using an electric field are the polymer dispersed liquid crystals (PDLC).[48,49] Droplets (2 to 5 µm in diameter) of a low molecular weight nematic phase are dispersed in an isotropic polymer (e.g. epoxy resin). Without an electric field the preferred direction of the nematic molecules is a statistical one

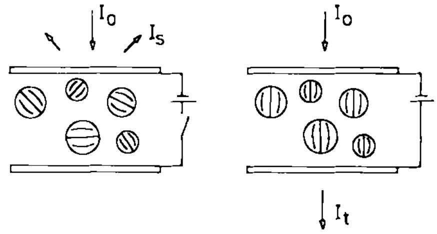


Fig. 1. Principle of PDLC films. I_0 = incident light, I_s = scattered light, I_t = transmitted light.

(Fig. 1). Incident light is scattered in all directions because of the mismatch of the refractive indices at the phase barriers. In an electric field the molecules have a preferred orientation because of their dielectric anisotropy. If the refractive index of the polymer is equal to the ordinary refractive index of the nematic phase the foil appears transparent. The PDLC is of interest for displays as well as solar control windows.

5.2. Laser Optics

The molecular order provided by the liquid crystal state makes possible some new applications of laser optics. Grids and other optical elements produced by a laser in a nematic phase can be used to switch another laser.[50] It has been claimed that switching times of fractions of nanoseconds can be achieved,[51] the molecular orientational movement in the laser field being the limiting factor.

To obtain materials with nonlinear optical properties, i.e. high values for the macroscopic hyperpolarizabilities ($X^{(1)}$) the integration of moieties with strong molecular hyperpolarizabilities (X) as side-chains of a liquid crystal polymer has been considered.[47] This might be exploited to build e.g. frequency doublers (high $X^{(2)}$) or to switch light by an electric field (high $X^{(3)}$, Pockels-effect). For high values of $X^{(2)}$ the moieties have to be ordered in an antiparallel way. To create a material with this feature, thin film techniques seem particularly suitable. Thin films being deposited as monomolecular layers of lyotropic lamellae onto a substrate[53] also have a good future in lithographics and antifriction layers. The molecular self organization in such layers is of fundamental significance in material science as well as in biology.[54]

5.3. Reaction Media

Influencing the kinetics of a chemical reaction by using anisotropic reaction media has in the past inspired many chemists. In recent times the possibilities have been substantiated. In the case of thermotropic liquid crystals[55] improvement of enantioselectivity in cholesteric phases and photochemical reactions are preferred topics. For technical application, lyotropic aqueous phases generally have a better perspective. A dramatic change of the rates of the acid-catalyzed hydrolysis of phosphinate esters in surfactant solutions has been observed going from a disk-like to a rod-like nematic phase.[58]

5.4. Engineering

The change of viscosity – a tensor quantity in mesomorphic phases – during phase transitions has some interesting aspects in engineering.[57, 58] The fast and reversible transitions accomplished by a change of temperature or pressure make possible a new method of construction of mechanical elements such as clutches, brakes, slide bearings and hydraulic devices.

6. Summary and Outlook

The growing interest in nonpolymer liquid crystal compounds in the past 20 years is attributed to the upswing in uses of liquid crystal displays. Synthetic chemistry and applied physics have promoted each other in a fruitful way. Besides some technologically important phases formed by rod-like molecules it has also become apparent that disk-like and so called phasmidic molecules exhibit fluidity and order. The building elements of molecular architecture are being extended to transition metal chemistry and hydrogen bonding, the latter with the potential to bridge the gap between thermotropic phases and the lyotropic liquid crystals which are of fundamental importance to biology. The technical exploitation of the special physical and physicochemical properties of the liquid crystal state can be regarded as being still in its initial state.

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Research News

High Resolution Solid State NMR of Quadrupolar Nuclei

By Bernhard Blümich [*]

Nuclear magnetic resonance spectroscopy is a standard technique used for the structural analysis of liquid and dissolved samples. The information about the molecular structure is contained in narrow resonance lines at various isotropic chemical shift values, which can be assigned to different segments of a molecule. In solids, however, the chemical shift information is hidden under overlapping wide lineshapes. As a result of the reduced molecular mobility in the solid state, a number of orientation dependent spin interactions such as the quadrupolar and the dipolar couplings and the anisotropy of the chemical shielding (chemical shift) dominate the resonance. For spin 1/2 nuclei, for instance ^{13}C, ^{29}Si and ^{31}P, there is no quadrupolar interaction, but even under dipolar decoupling from the protons, the NMR spectrum typically shows many overlapping chemical shielding powder patterns, each of which can be a few kilohertz wide. The standard approach to high resolution solid state spectra for spin 1/2 nuclei then is magic angle spinning (MAS). The sample is packed into a gas-driven turbine which is spun at a rotation frequency of 3 to 10 kHz with the rotation axis inclined against the magnetic field by the magic angle of $\Phi_m = 54.7°$. In this case liquid-like high resolution spectra are obtained, which at slow spinning rates exhibit side bands at integer multiples of the rotation frequency away from the isotropic chemical shifts.[1]

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