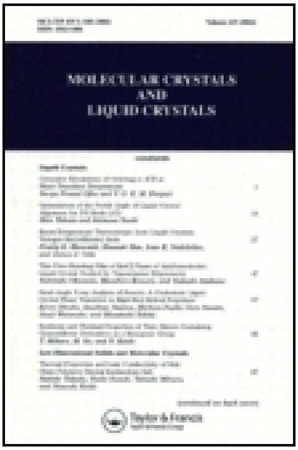

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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100 Years Liquid Crystal Chemistry

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100 Years Liquid Crystal Chemistry

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Keywords: Liquid crystals, chemistry, molecular structure, historical development, theory of the liquid crystalline state, non-conventional liquid crystals, applications, mixtures

This review article presents a short description of the historical development of the chemistry of thermotropic liquid crystals and the modern molecular-statistical interpretation of the liquid crystalline state. A short survey on the present state of the liquid crystal chemistry, divided in conventional (rod-like) and non-conventional (deviating more or less from the rod-like shape) molecular species is given. Liquid crystalline compounds for applications and their mixtures are treated from the chemical standpoint emphasizing the connections between molecular structure and properties.

1. INTRODUCTION

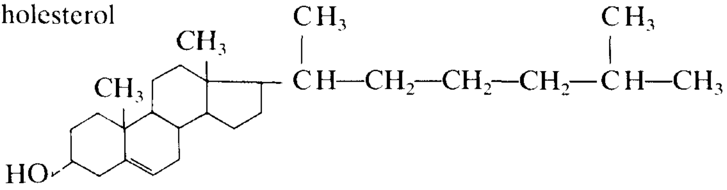
The aim of this paper is to show the development of the domain of the thermotropic liquid crystals from the chemical standpoint. Despite the fact that the liquid crystal research changed more and more to the side of the physics (see e.g. the topics of this volume, which may be considered as representative for the present state) it is clear that the success of the research in this field always was strongly dependent on the activities in the chemistry. Also the progress in the theoretical interpretation of the liquid crystalline state was going parallel to the advance in the chemical research or the latter was even in front. Several reviews[1–10] demonstrate the development of the liquid crystal chemistry.

The enormous development of the field of liquid crystals was started by the successful applications of liquid crystals, especially for optoelectronic displays. Modern displays demand highly developed materials with special properties. The liquid crystal material research—irrespective of the advance in the theoretical interpretation of this field—still mainly is based upon empirical rules used by experienced chemists.

2. THE DEVELOPMENT OF LIQUID CRYSTAL CHEMISTRY

The first liquid crystalline compounds have been some derivatives of cholesterol 1 in which Reinitzer[11] and Lehmann[12] detected the liquid crystalline state in 1888. It is interesting to note that in this time the chemical structure of cholesterol was not known,

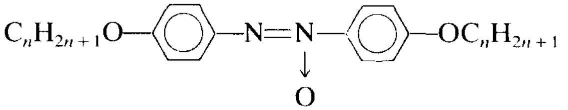
cholesterol



1

it has been completely elucidated not earlier than 1932.[14] Therefore the idea of the parallelity of the molecules in the liquid crystalline state published by Lehmann[12] was intuitive and could not be derived from the chemical background.

The first liquid crystalline compounds with completely known chemical structure have been the derivatives of azoxybenzene 2 synthesized by Gattermann in 1890.[13]

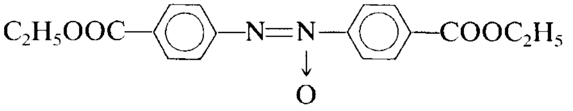


$C_nH_{2n+1}O-C_6H_4-N(\rightarrow O)=N-C_6H_4-OC_nH_{2n+1}$ 2

n = 1 p-azoxyanisole = PAA
n = 2 p-azoxyphenetole = PAP

Vorländer and his coworkers[1,15] have been the first to synthesize a smectic thermotropic compound 3:

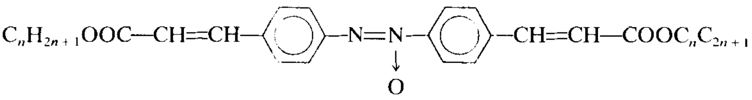
di-ethyl 4,4′-azoxybenzoate



$C_2H_5OOC-C_6H_4-N(\rightarrow O)=N-C_6H_4-COOC_2H_5$ 3

Starting from the synthesis of the first homologous series 4[16]

di-alkyl 4,4′-azoxycinnamates



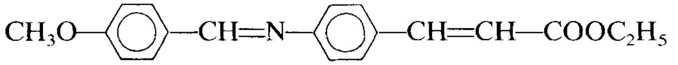
4

$n = 2$ to 16

Vorländer investigated systematically in a large number of compounds the relations among molecular structure and liquid crystalline properties. Up to 1908[1] he obtained about 170 liquid crystalline compounds from which he was able to derive his rule about the chemical structure of liquid crystals[1]: The liquid crystalline state is obtained by an utmost linear shape of the molecules. In principle his rule is valid up till now; it is not only the basis for the molecular-statistical theoretical description of the liquid crystalline state but also the main hypothesis of most concepts for the synthesis of liquid crystalline compounds.

Vorländer[1,2] also detected the polymorphism of the liquid crystalline state, he was the first to synthesize compounds with one nematic and one resp. two smectic phases:

ethyl 4-methoxybenzylideneamino-cinnamate[17]



5

K 107 (S_B)†S_A 117.6 N 138.5 is

The rule of the linear shape of the liquid crystalline molecules was based on comprehensive investigations concerning the *o*, *m* and *p*-substitution of aromatic compounds, the nature and length of chain like substituents, the role of polar and unsaturated groups and cis-trans-isomerism of compounds with double bonds. Vorländer[1,2] especially emphasized the increasing mesogenity by elongation of the aromatic core of the molecules. This may be demonstrated by the aid of the newer compounds compiled in Table I.

A striking example proving the rule of the linear shape was given by Vorländer 1927.[18] The plot of his results presented in Figure 1

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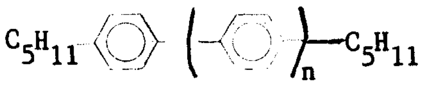
†This monotropic phase has been detected later.[2] Its phase classification is due to Arnold and Sackmann.[19]

TABLE I



n	K		S		is	ref.
1	•	12	•	52	•	20
2	•	192	•	213	•	21
3	•	297	•	352	•	22

demonstrates the extreme alternation of the clearing temperatures caused by the alternating linear and bent resp. molecular shape due to the carbon bond angle of about 109°. This example is looking quite modern with respect to the observed strong alternation of T_{NI} in *homologous series with an endstanding phenyl,*[23] *the discussion of* "linear twin" molecules[24,25] or the role of the spacer group in liquid crystalline polymers.[26-28]

Though Vorländer already synthesized single homologous series, Weygand[3] first started the investigation of the liquid crystalline be-

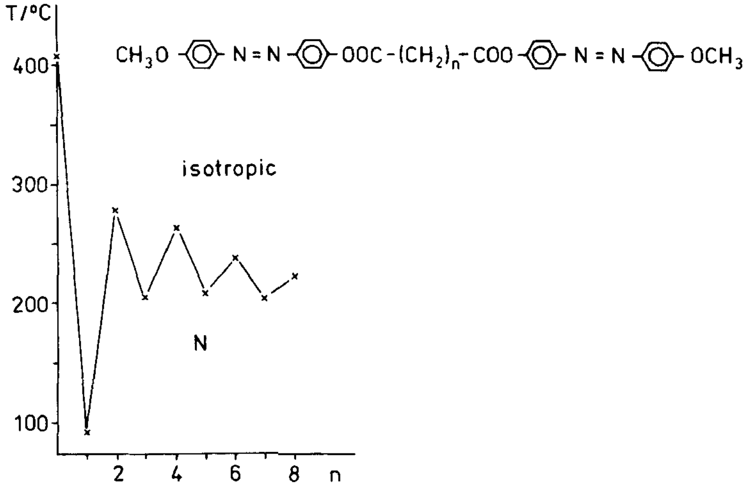


FIGURE 1 Clearing temperatures in the homologous series of the bis- 4-(4-methoxy-phenylazo)-phenyl *n*-alkane-dicarboxylates.[18]

haviour of homologous series systematically. The most famous example is given in Figure 2 which clearly shows the alternation of the T_{NI} and the appearance of smectic phases at middle members with the nonalternating transition curve. This series stands typically for many other series which have been synthesized later.[3,4,7,8,9] Weygand[3] already has pointed at the regularities of the transition temperatures in homologous series. These regularities later have been used as an important criterion for the classification of liquid crystalline phases in homologous series.[30–32] Figure 3[33] displays an example of a series with very high polymorphism which has been widely discussed in the literature. Since the elongation of alkyl chains in the most cases seems to be the simplest possibility of changing the molecular structure, the investigation of homologous series always has been widely used as a tool for the detection of the connection between molecular structure and the properties of liquid crystals.

3. THE THEORETICAL INTERPRETATION OF THE LIQUID CRYSTALLINE STATE

The idea of Lehmann[12,34] that the molecules in the liquid crystalline state should be parallel one to another and Vorländer's rule of the linear molecular structure of liquid crystals[1,2] delivered a basis for the molecular-statistical interpretation of the liquid crystalline state.

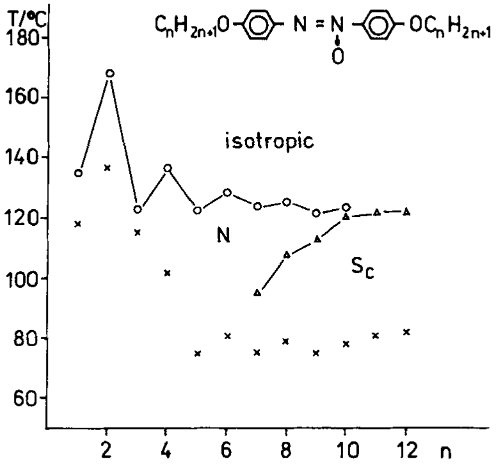


FIGURE 2 Transition temperatures of the homologous series of the 4,4′-di-*n*-alkyloxy-azoxybenzenes[29] + = melting temperatures.

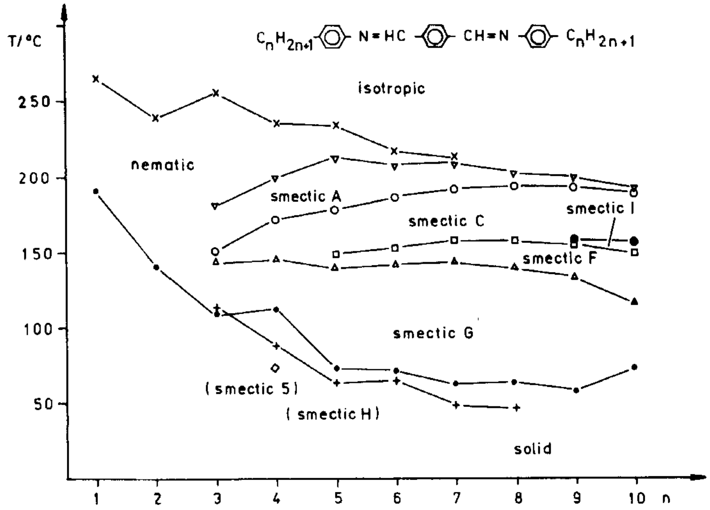


FIGURE 3 Transition temperatures of the homologous series of the terephthalylidene-bis-(4-*n*-alkylanilines).[33]

Molecular-statistical theories derive the macroscopic behaviour of the media from the properties of the molecules. Therefore they also deliver the key for the understanding of the existence of liquid crystalline states at chemical compounds of anisotropic shape. Since the nematic phase is the simplest liquid crystalline state, better known than the different types of smectic phases, the basic theoretical ideas concerning the existence of anisotropic liquids have been derived for nematic liquid crystals.

The first attempt of a molecular-statistical interpretation of the nematic state was done by Born[35] in 1916. He assumed the permanent electric dipoles to be responsible for the stability of the nematic phase. Today it is well known that in most cases the dipole interactions play only a minor role and cannot explain anisotropic phases in general.

Maier and Saupe in their well known theory[36] pointed at the anisotropic dispersion forces (anisotropic attraction) as the predominant factor for the stabilisation of the nematic phases. At about the same time a completely different theoretical model was elaborated by Onsager[37] who assumed that in the case of very long molecules the steric interaction (hard core repulsion) is sufficient to produce the nematic state.

The most realistic approach now is the van der Waals theory of nematic liquid crystals which was proposed by Cotter[38] and Gelbart[39] and which is taking into account attractive as well as repulsive forces. There are brilliant reviews[6,40,41] from which details of the theory may be taken. Here we want to present only a short sketch of the physical basis of the theory and its conclusions concerning the chemical structure of the liquid crystalline molecules.

A minimum of the free energy F generally is the condition for the stability of a thermodynamic state. Within the frame of statistical theories for the nematic state F may be expressed in terms of the partition function Q_C:

$$F = -kT \ln Q_C \tag{1}$$

k = Boltzmann factor T = temperature (Kelvin)

$$Q_C = \frac{1}{N!} \int_{\Omega i} d\Omega i \int_{Ri} dR_i \exp(-U_C/kT) \tag{2}$$

Q_C is restricted here to that part of the inner energy U_C (configurational part) which is depending on the configuration (orientation Ω_i and distance R_i) of the molecules. The possible other parts of the inner energy (translation, rotation, vibration) are assumed to be equal in the nematic and the isotropic state.

U_C may be divided into a sum of pair potentials u_{ij}:

$$U_C = \sum u_{ij} \tag{3}$$

Pair potentials generally consist of an attractive (u_{ij}^{attr}) and a repulsive (u_{ij}^{rep}) part:

$$u_{ij} = u_{ij}^{\text{attr}} + u_{ij}^{\text{rep}} \tag{4}$$

The attractive term may be divided into two parts which consider an isotropic attraction which is also existing in isotropic liquids and an anisotropic attraction which only is effective in the nematic state. Cotter[38] within the mean field approximation derived an expression of the form:

$$V(\theta, \delta) = -L_o V_o \delta - L_2 V_o \delta \langle P_2 \rangle P_2(\cos\theta) \tag{5}$$

δ = number density of molecules

V_o = molecular volume

θ = angle of the molecular long axis with respect to the director

$\langle P_2 \rangle = \frac{1}{2} \langle 3 \cos^2 - 1 \rangle$ = order parameter

L_o = isotropic attraction parameter

L_2 = anisotropic attraction parameter

The molecules are represented by rigid hard cylinders which are coated at both ends by half-spheres. These cylinders are characterized by the length-to-breadth ratio X:

$$X = \frac{L}{2W} + 1 \tag{6}$$

These cylinders are not allowed to interpenetrate each other which is expressed in terms of the repulsive "hard rod potential":

$$u_{ij}^{\mathrm{rep}} = \begin{cases} \infty \text{ if the hard cores } i \text{ and } j \text{ would overlap} \\ 0 \text{ otherwise} \end{cases} \tag{7}$$

The packing fraction V_B/V (V_B = volume of the fictive densest packing obtained by an increment system of Bondi,[44] V = actual volume) is used as a measure for the density of the nematic system. On the basis of the theory of Cotter, using the procedures of Dunmur[42] and van Hecke,[43] we calculated some curves representing the influence of the different parts of the intermolecular potential (Figures 4, 5). Figure 4 proves that a critical packing fraction is needed to stabilize the nematic state. This critical packing fraction is strongly depending on the length-to-breadth ratio X: the longer the molecules, the lower is V_B/V_A. Since generally V_B/V is temperature dependent, this is strongly reflected in the clearing temperatures (Figure 5) which markedly increase with X. This behaviour qualitatively corresponds to the rule of Vorländer and has been proved in some detail (e.g., References 42, 43, 45, 62). In Figures 4 and 5 three curves are presented belonging to different values of the anisotropic attraction L_2. As the curves show, L_2 plays a minor role in determining the clearing temperatures. This finding also corresponds to the real behaviour of nematic liquid crystals. The most important contribution in determining T_{NI} is the anisotropy of the molecular shape, that means the repulsion potential. Therefore the use of Eq. (7) as the only potential in the "hard rod" theories (neglection of the attraction)[6,46,47] can be considered as a first approximation in describing the nematic state. The exclusive use of the attractive potential, and especially the anisotropic part of the attractive potential as it is used in the Maier–Saupe theory,[36] is not sufficient for a molecular-statistical realistic description of nematic liquid crystals.[6,45,62,95,97–99] The role of the attractive forces is mainly to maintain the required relatively high density.

It should be emphasized here that according to theoretical consid-

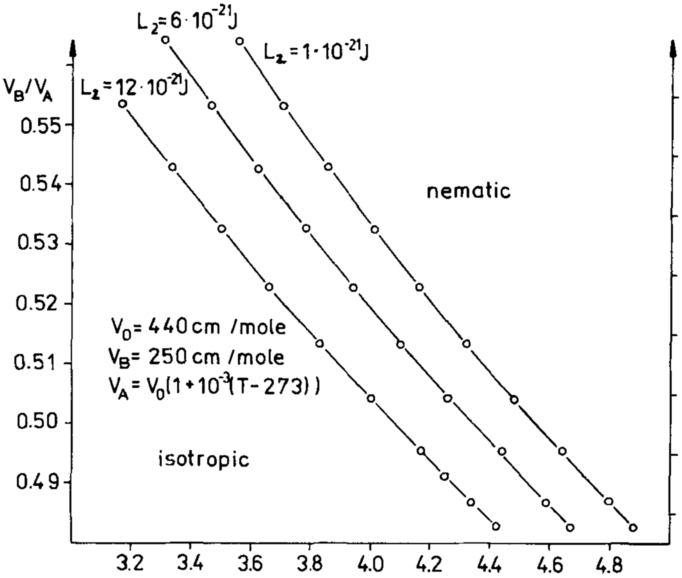


FIGURE 4 Packing fraction V_B/V_A at the clearing temperatures in dependence on the length-to-breadth ratio X, van der Waals theory of Cotter.[38]

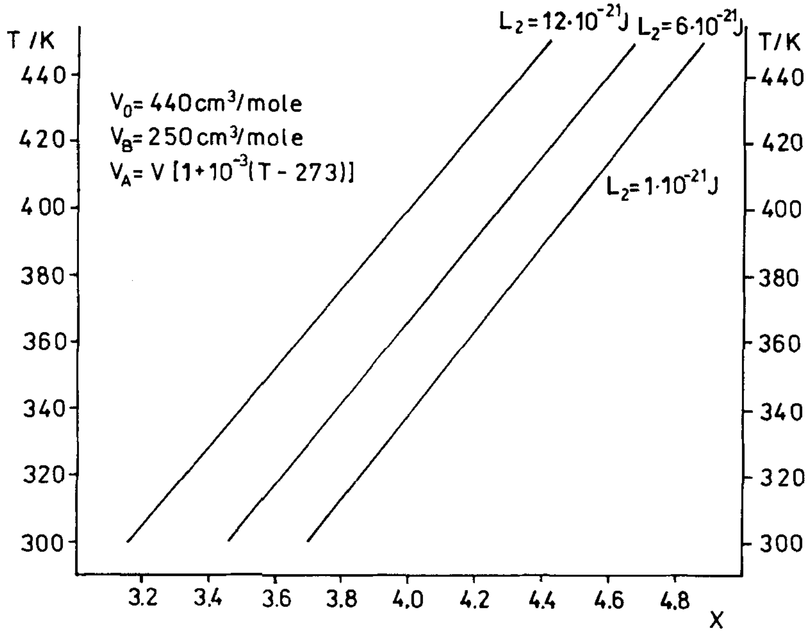


FIGURE 5 Clearing temperatures T_{NI} in dependence on the length-to-breadth ratio X, van der Waals theory of Cotter.[38]

erations of Gelbart[41,48,49] the isotropic attractive forces, which exceed by about one order of magnitude the anisotropic attractive part, couples with the anisotropic repulsion, yielding an important contribution to the stabilization of the nematic state. This coupling is reflected in several experimental facts[45] and delivers the main explanation for the influence of polar groups on the liquid crystalline properties.

The influence of the molecular structure on the existence of smectic phases is rather complex and confusing.[32,81,117] Therefore the theoretical attempts[80,83-85,113] in predicting smectic behaviour are not without contradictions. Even in the simplest case, the smectic A phase, the literature shows a contradictory picture concerning the importance of the roles of the attractive and repulsive forces[86,87] which is also reflected in the difficulties of generally explaining the reentrant nematic behaviour.[88-94,112]

4. THE PRESENT CHEMISTRY OF LIQUID CRYSTALS

With Vorländer's rule of the linear shape of the liquid crystal molecules and the theoretical confirmation of this concept, it is possible to construct liquid crystalline compounds as much as are wanted. The chemical moieties which are used for this purpose in principle are not limited—if Vorländer's rule is obeyed.

There are many reports concerning the general development of the chemistry of liquid crystals[1-6,51-54,59,62] or considering special aspects of the molecular structure of liquid cystals.[18,50,55-58,60,61,63,64,95,96,198,200] Also the existing table books[7,8,9] allow an overview on the liquid crystal chemistry.

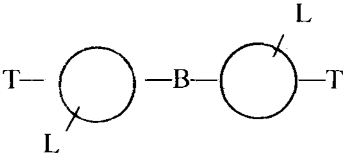
Therefore in the following we restrict to some summarizing remarks, completed by the concrete presentation of some newer developments. Since they are the contents of special papers in this issue, the discotic, ferroelectric and polymeric thermotropic liquid crystals are omitted here.

Acyclic Compounds

In this substance class there are liquid crystalline compounds derived from unsaturated acids and aldehydes, some esters of fatty acids and amino acids.[8,9] The liquid crystalline nature of the *n*-alkanes[5] remains questionable, however, there are strong similarities to the smectic B phases. In this context it is worth to be be mentioned that in perfluorodecyl-decane the existence of a smectic B phase was proved by optical microscopy, calorimetry and X-ray studies.[115]

Cyclic Compounds

Compounds with cyclic moieties may be schematically displayed by the general formula:



B = bridging group
T = terminal group
L = lateral substituent

The following Tables II–VII give examples for these different moieties of the molecules of liquid crystals.

Steroids

In this substance class most of the chiral liquid crystalline compounds are derived from natural products as e.g. cholesterol, cholestanol, sitosterol, stigmasterol. In some classes, however, synthetic starting materials have been used leading to racemic nematic compounds.[65]

Metal Complexes

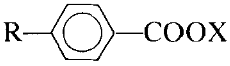
There are several series of compounds derived from central metal atoms as Fe, Ni, Pt, and classical complexing agents as ferrocene, dithioato-ethene.[9] But also "classical" liquid crystalline compounds like 4-*n*-penty-cyano-biphenyl have been found to be able forming liquid crystalline complexes with metal atoms of the platinum group.[116] Other complexes lead to discotic structures which are not dealt with in this paper.

Salts[8,9]

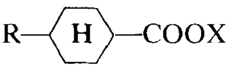
There are salts derived from

aliphatic C_nH_{2n+1}—COOX

aromatic



or cyclohexane



carboxylic acids

TABLE II

Ring systems with 6 atoms

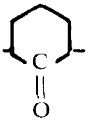
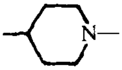
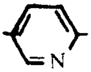
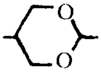
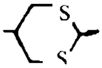
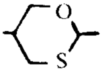
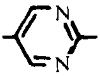
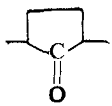
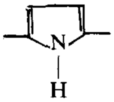
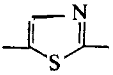
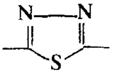
phenyl	
cyclohexane	
cyclohexanone	
piperidine	
pyridine	
piperazine	
dioxane	
dithiane	
oxathiane	
pyridazine	
pyrimidine	
pyrazine	
triazine	
tetrazine	

TABLE III

Ring systems with 5 atoms

cyclopentanone	
pyrrole	
furane	
thiophene	
thiazole	
thiadiazole	

using different cations like Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Tl^+.

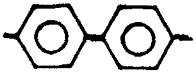
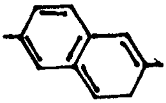
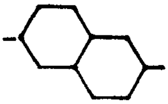
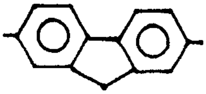
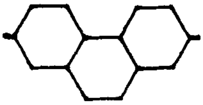
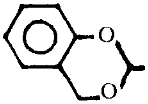
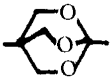
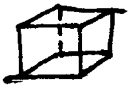
On the other hand liquid crystalline salts may consist of organic cations like 4-*n*-alkyloxy-anilinium, *N*-alkyl-pyridinium,[66] subst.-benzamidines and inorganic anions like Cl^-, Br^-, I^-. Of special interest are the liquid crystalline phases of the salt-like lecithines and kephalines.[9]

In principle, using the moieties given in Tables II–VII, by standard synthesis routes it is possible to synthesize as many liquid crystalline compounds as are desired. By use of the same building units differently linked, liquid crystalline polymers are obtainable which are the topic of special articles in this volume. On the other hand, by certain modifications of the ring systems, discotic liquid crystalline compounds are available which also are reviewed in a separate paper. By introducing chiral moieties usually derived from natural products (e.g. chiral amyl alcohol, amino acids, lactic acid) into conventional liquid crystalline molecules chiral (ferroelectric) smectic phases may be obtained which also are the topic of a paper in this volume.

The chemistry of the liquid crystals may be enriched by the use of elements which are not typical for organic compounds. Tables VIII

TABLE IV

Ring systems with more than 6 atoms

biphenyl	
naphthalene	
decaline	
fluorene	
perhydrophenanthrene	
dioxanaphthalene	
bicyclooctane	
bicyclotrioxane	
cubane	

and IX present some examples of liquid crystalline compounds containing "non-conventional" atoms.

Developing systematically new terminal groups with double bonds in different positions (alkenyl substituents) Petrzilka *et al.*[73–76] were able to modify the known substance classes essentially. In many cases

TABLE V

Bridging groups

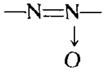
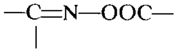
azomethine	$-CH{=}N-$
ester	$-COO-$
thioester	$-COS-$
ethyl	$-CH_2-CH_2-$
butyl	$-CH_2-CH_2-CH_2-CH_2-$
stilbene	$-C{=}C-$
tolanes	$-C{\equiv}C-$
azo	$-N{=}N-$
azoxy	 $-N{=}\underset{\substack{\downarrow\\ O}}{N}-$
oximbenzoate	 $-\underset{\vert}{C}{=}N-OOC-$
dicarboxylate	$-OOC-(CH_2)_n-COO-$
azine	$-CH{=}N-N{=}HC-$
mercury	$-Hg-$

TABLE VI

Terminal groups

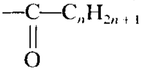
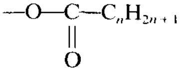
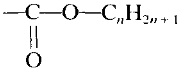
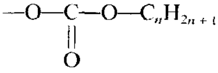
alkyl	$-C_nH_{2n+1}$
alkyloxy	$-OC_nH_{2n+1}$
alkylmercapto	$-S-C_nH_{2n+1}$
acyl	 $-\underset{\substack{\Vert\\ O}}{C}-C_nH_{2n+1}$
acyloxy	 $-O-\underset{\substack{\Vert\\ O}}{C}-C_nH_{2n+1}$
alkylester	 $-\underset{\substack{\Vert\\ O}}{C}-O-C_nH_{2n+1}$
alkylcarbonates	 $-O-\underset{\substack{\Vert\\ O}}{C}-O-C_nH_{2n+1}$
halogeno	$-F$, $-Cl$, $-Br$, $-I$
cyano	$-CN$
nitro	$-NO_2$
alkylamino	$-NH-C_nH_{2n+1}$
cyanoalkyl	$-(CH_2)_n-CN$
cyanoethenyl	$-CH{=}CH-CN$
dicyanoethenyl	$-CH{=}C(CN)_2$

TABLE VII

Lateral substituents

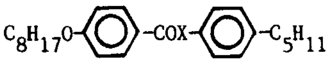
halogeno	—F, —Cl, —Br, —I
methyl	$—CH_3$
ethyl	$—C_2H_5$
nitro	$—NO_2$
cyano	—CN
aceto	$—CO—CH_3$

not only enhanced clearing temperatures (in comparison to alkyl substituted compounds) but also changed visco-elastic properties were obtained. Surprisingly despite of the isolated double bonds the compounds are claimed to be stable enough that they can be recommended for practical use in highly multiplexed as well as fast responding LCD's.

For practical applications nematic liquid crystals with high dielectric anisotropy are needed which may be obtained by introduction of strongly polar groups, especially the cyano group (see Section 5). These compounds tend to association and high viscosities. Dabrowski *et al.*[76-78] have been able to substitute this group in many already known substance classes by the iso-thiocyanato group -NCS, which gives compounds with moderate dielectric anisotropy, very low viscosity and good stability, which are well suited for the use in LCD's.

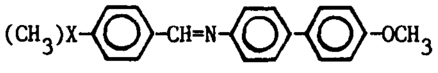
Another new element is the cyclobutane group applied by Gray[54,79] in several liquid crystal examples. In the case of the cyclobutane —◇— group he was able to separate the *cis* and *trans* isomers which have completely different liquid crystalline properties. *Cis–trans* isomers also exist in the dispiro (3.1.3.1) decanes —◇◇◇—, whereas the spiro (3.3) heptanes —◇◇— are simply racemic systems. These new moie-

TABLE VIII



X	K		S		S_C		S_A		N		is	ref.
O	.	56	–	–	–	–	.	57	.	66	.	69
S	.	58.6	(.	31.3	.	56.3)	.	63.5	.	86.5	.	70
Se	.	55	–	–	.	35	.	68	.	78	.	71
Te	.	42	–	–	–	–	.	47	.	50	.	71

TABLE IX



X	K		S_2		S_1		is	ref.
Si	.	180	-	-	.	183	.	72
Ge	.	176	(.	169	.	175)	.	72
Sn	.	165	.	171	.	173	.	72

ties which because of their high flexibility should be compared rather with *n*-propyl terminal chains than with other ring systems, allow the modification of known substance classes via nematic properties and therefore potentially may be interesting for practical applications.

5. THERMOTROPIC LIQUID CRYSTALS WITH NON-CONVENTIONAL MOLECULAR STRUCTURE

Compounds with Large Lateral Substituents

The rule of the linear shape of liquid crystalline molecules has been proved in more than 15000 examples. Further it has been founded by theoretical considerations (Section 2).

In the frame of this knowledge, the role of lateral substituents which has been extensively studied since Vorländer's times by several authors[1,2,3,4,51,53,95,97,98,119,120] seemed to be quite clear: only small lateral substituents should be allowed, since bulky or long chain lateral substituents should prevent the liquid crystalline state. Therefore it came quite unexpected that Weissflog and Demus[100] found new compounds with lateral alkyl chains with lengths up to C_{16} which are enantiotropic nematic. Figure 6 displays the series which has been investigated in some detail.[101,102] After a strong decrease of the clearing temperatures in early members of the series, the clearing temperatures in the later members obviously tend to a saturation value. There are some arguments[102] that this behaviour is due to a confor-

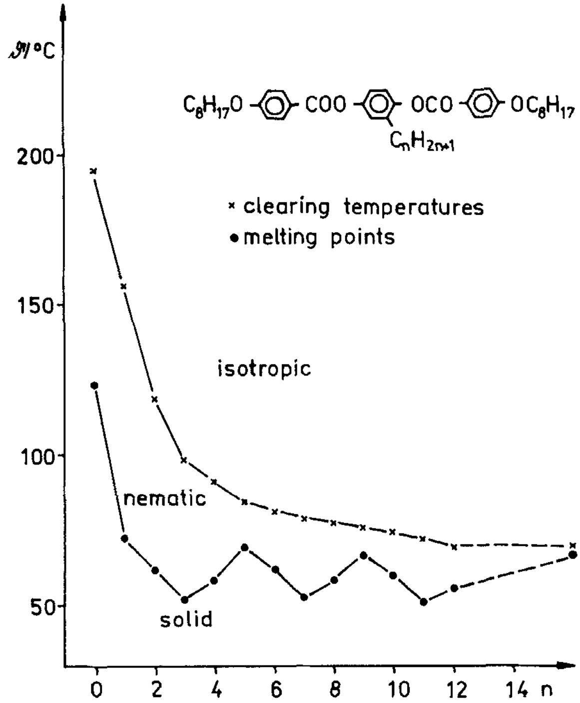


FIGURE 6 Transition temperatures of the homologous series of the 1,4-bis-(4-*n*-alkyloxybenzoyloxy)-2-*n*-alkylbenzenes.[100]

mation of the lateral alkyl chain which produces a more or less parallel orientation of the alkyl chain with the molecular long axis. That is, the molecules are not stiff species existing in the same conformation which corresponds to the minimum energy of the free molecules, but the environment of the molecules strongly influences the conformation so that deviations from the expected molecular shape are produced. There are some experimental and theoretical proofs of the fact that the nematic potential should shift the statistical weight of the gauche conformers to the more stretched conformations of alkyl chains[120–123] and also free alkanes solved in nematic media.[124,125] A comparable effect has been found in smectic A phases of nonsymmetric molecules, in which the layer thickness agrees unexpectedly well with the length of the most stretched form of the molecules.[126]

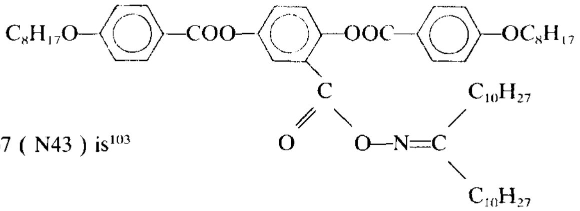
Ballauf[118] has published a molecular-statistical theory especially devoted to the molecules with large lateral substituents; since in this theory the side chains are assumed to be exempt of the ordering in the nematic field this theory seems to fail the description of the main feature of the series with lateral long chain substituents. Averyanov[130] has studied the steric influence of lateral substituents on the actual conformation of liquid crystalline compounds.

The series of Figure 6 is not a single case, there are many series derived from the same basic molecule differing in the lateral chains,[100,101] series with lateral swallow-tailed substituents[127] (e.g. no. 1 in Table X), compounds with very bulky substituents[127,129] (no. 2 in Table X) or compounds with even two lateral long chain alkyl substituents in the molecules[104] (no. 3 in Table X). Several compounds with lateral long chain substituents show pronounced evidence of skewed cybotactic groups in the nematic state,[106] however, they do not exist in the smectic state but in the contrary possess a strong ability to destroy

TABLE X

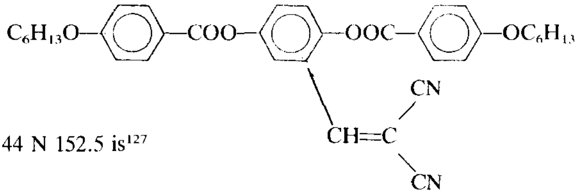
Compounds with large lateral substituents

1.



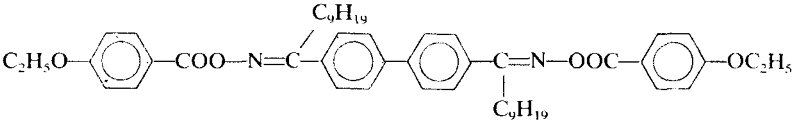
K 67 (N43) is[103]

2.



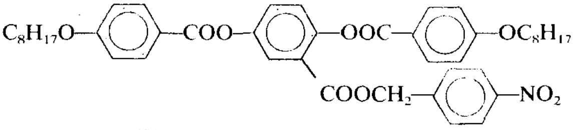
K 144 N 152.5 is[127]

3.



K 145 N 160 is[104]

4.



K 95.9 S_A 163.9 is[108]

$d = 34.2$ A $L = 42$ A

the smectic state.[114] Dielectric investigations point at a high mobility of the lateral chains which can change the conformations much faster than the basic molecule.[109]

In compounds with aromatic lateral substituents smectic *A* phases with $d/L < 1$ (see no. 4 in Table X) have been found, the structure of which is still under discussion.[108,110,128] In the light of these new data some liquid crystalline compounds with aromatic lateral substituents already synthesized by the school of Vorländer (see Reference 7, nos. 2522–2527, 2589, 2590, 3391, 3417, 3418, 3837 on p. 242) which former have been considered with certain doubt, gain in credibility (however, see the discussion in Reference 110).

Polycatenar compounds

Compounds with 2,4-di-substituted-endstanding benzenes (e.g. no. 1 in Table XI) are the bridge to substances with several endstanding chain like substituents, now called polycatenar compounds.[131a] Nos. 2 and 3 in Table XI are examples of a greater variety of series[107,132] which also are called "biforked" compounds.[133] Compounds with "biforks" at both ends of the molecule and a biphenyl central core are not mesomorphic,[107] however, by elongation of the central core extremely interesting new compounds have been produced by the Bordeaux group.[131b,133,134a] Actually, they seem to be the link between the rod-like and the disc-like liquid crystalline compounds, since there are several examples which show classical liquid crystal phases (smectic, nematic) and columnar phases in the same homologous series or even in the same compound. No. 4 in Table XI demonstrates this behavior; additionally the compound exhibits a cubic mesophase which up to now only has been observed in four homologous series.[32,54,135]

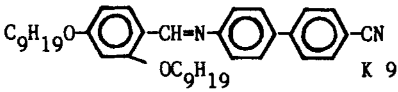
If there are three long chains at each end of the molecule ("phasmidic" compounds[136]), only columnar phases of different types have been found.[134b,136,137] Molecules with three long chains at one end, but only one chain at the other end exhibit uniaxial (N_u) nematic disk-like phases and biaxial (N_b) nematic phases at higher temperatures.[131c,137,139] No. 6 in Table XI presents one example. In the analogous octyloxy compound the N_u phase exists at higher temperatures than N_b.[131c] This is the first case of biaxial nematic phases in thermotropic liquid crystals, whereas this phase type is known in lyotropic systems already since 1980.[138]

It should be mentioned that compounds with three long chains at one end of the molecule and an OH-group at the other side exhibit columnar mesophases.[137]

TABLE XI

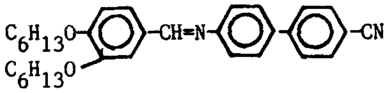
Polycatenar compounds

1.



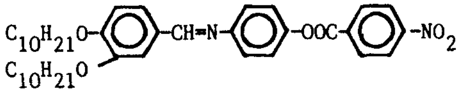
K 95 (N 65) is[107]

2.



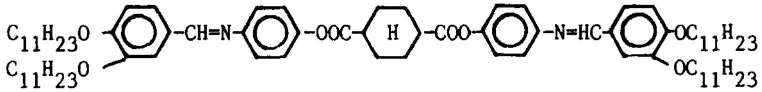
K 131 S_{A_d} 141 is[107]

3.



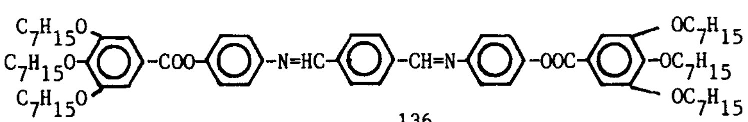
K 115.5 (S_C 101) S_{A_d} 139 is[132]

4.



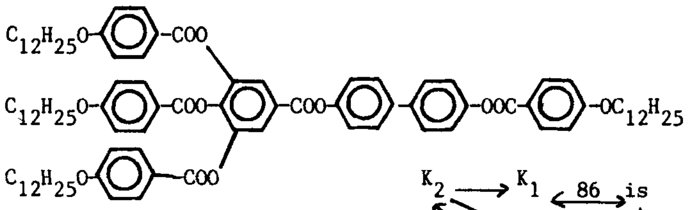
$$\begin{tikzcd}
K \arrow[r, "144"] & S_C \arrow[r, "146"] & \text{cubic} \arrow[r, "163"] & \text{is} \arrow[dl, "158"] \\
& \text{cubic} \arrow[u, "140"] & \text{hexagon. columnar} \arrow[l, "147"] &
\end{tikzcd}$$

5. Phasmid



K 80 oblique columnar 82 is[136]

6.



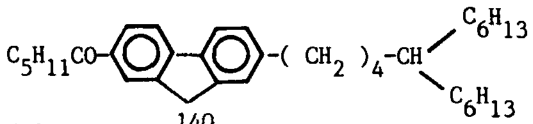
$$\begin{tikzcd}
K_2 \arrow[r] \arrow[dr, "82"] & K_1 \arrow[r, leftrightarrow, "86"] & \text{is} \arrow[d, "86"] \\
& N_u \arrow[ul, "65"] & N_b \arrow[l, "69"]
\end{tikzcd}$$

ref. 139

TABLE XII

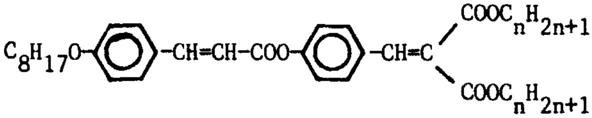
Swallow tailed compounds

1.



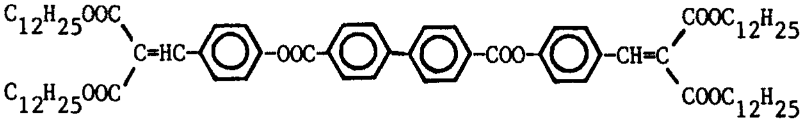
K 36 S_A 52 is[140]

2.



ref. 111

3.



K 94 (S_c 84) N 89 is[111]

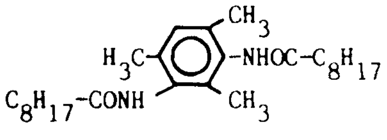
If the ramification of the molecule occurs outside the ring system, other types of biforked[140,141] or swallow tailed[111] compounds can be obtained which exhibit smectic and nematic phases (Table XII). It is of interest to note that the clearing temperatures T_{NI} of the homologous series no. 2 in Table XII show a decreasing trend to a minimum in C_6 and in the later members the T_{NI} distinctly increase. This should be taken as a hint to the effect of the liquid crystalline environment on the double alkyl chains to force the latter to a stretched conformation if the chains are long enough.

It may be mentioned that salt-like compounds with large lateral branches are known already for a long time; e.g. succinates (no. 4955 in Reference 8), salts with lateral phenyl substituents (no. 5015 and 5016 in Reference 8), kephalines (nos. 5052 and 5053 in Reference 8), lecithines (nos. 5054–5059 in Reference 8) and thallium salts.[203]

TABLE XIII

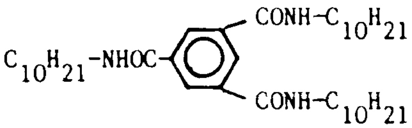
Amides with non linear molecular shape

1. N,N'-dialkanoyl-diamino-mesitylenes



K 136 S 188 N 217 is[142]

2. N,N',N''- trialkyl-1,3,5-benzene- tricarboxamides



K 49 S 208 is[143]

Non linear compounds

There are two further series which unexpectedly exhibit thermotropic liquid crystalline phases. The *N*,*N'*-di-alkanoyl-diamino-mesitylenes are *m*-substituted benzene derivatives, however, show pronounced smectic and nematic behaviour (e.g. no. 1[142] in Table XIII). It may be assumed that the formation of hydrogen bonds among the amide groups has a stabilizing influence on the liquid crystalline behaviour. Zuev et al.[151] synthesized esters of the 1,3-benzene-dicarboxylic acid with nematic properties (no. 8347 in Reference 9) which are non linear in shape.

Koden et al.[200] and Deutscher et al.[201] reported about the liquid crystalline properties of compounds with —O—, —S—, —CO—, and —CH_2— linkages, which according to the classical scheme should not be mesomorphic.

The *N*,*N'*,*N''*-trialkyl-1,3,5-benzene-tricarboxamides are mesomorphic with relatively low melting temperatures, but high clearing points (e.g. no. 2[143] in Table XIII). Since these compounds are trisubst.-benzenes, from the standpoint of the molecular structure one would expect rather columnar structures than classical smectics, and in fact the data given in Reference 143 do not exclude this interpretation.

Siamese twins

In siamese twins[25,144] two independently liquid crystalline "half" molecules are joined through a chemical bond. There are different types of twins (Table XIV):

i. Fused twins with lath-like shape which are nematic.[144,145]
ii. Ligated twins have been observed to exhibit nematic and smectic A and C phases. Of special interest are the two conformations of one compound given in Table XIV nos. 2a,b. The conformation is dependent on the thermal history of the sample and influences the structure of the S_C phase.[148] The sulfinyl and sulfonyl derivatives (Table XIV, 2c) are nematic; some compounds of this family show transitions to the nematic glassy state above room temperature and may be used for storage displays.[149]
iii. Tail-to-tail twins in principle are long known (see e.g. compounds nos. 929–948 k, 1171–1178, 1202–1205 in Reference 8) but they have not been designated as siamese twins in the former time[18] (see also remarks in section 1).

In this section of the paper we have given several examples of compounds, the molecular structure of which is not fully compatible with the existing theories of the liquid crystalline state. Obviously a further development of the theoretical concepts is needed. It is of interest to note that there are general theoretical speculations concerning the symmetry and structure of possible mesogenic molecules given by Petrov and Dershanski[131d] as well as by Lin Lei[152]; the question remains, however, which of the proposed structures will be confirmed by experiments.

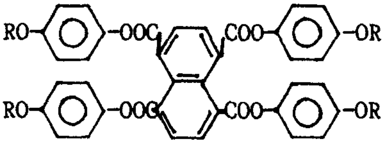
6. LIQUID CRYSTALS FOR APPLICATIONS

The great advances in liquid crystal research in the last 20 years clearly have been initiated by the possibilities of applying liquid crystals in different fields. Of course, the main application is the use of liquid crystals in electrooptic displays.[10,154,165,166] Since the display production is occurring in a large scale (the estimated world market output

TABLE XIV

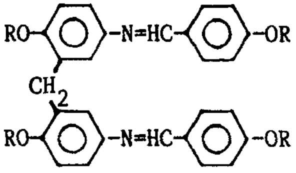
Siamese twin compounds

1. Fused twins[144,145]



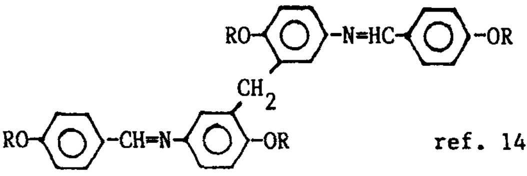
2. Ligated twins[146-149]

a)



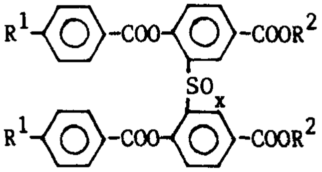
ref.148

b)



ref. 148

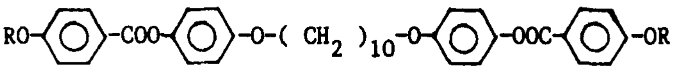
c)



$x = 1,2$

ref. 149

3. Tail-to-tail twins[18,24,25]



ref. 24,25

for 1985 was 790 Mio units, and the forecast for 1990 will exceed 1000 mio units[167]) there is a strong economic background from which not only the applied research and development profited very much but also the basic research. At the present much more than 15,000 thermotropic compounds are known.[7,8] Among this large number of substances there is no single compound, however which can approximately satisfy the practically needed demands. Therefore at the one hand, for electrooptic applications only mixtures of several compounds are used. At the other hand, there is still always the demand for compounds with improved properties.

This historical development as well as the state of the art today shall be sketched in the following section for liquid crystalline compounds useful for electrooptical applications. In the literature are several general surveys on liquid crystalline substances for applications[153,154a,155,157–159,163,168] and also survey papers restricted to certain substance classes.[74,75,78,156,160–162,163,164,193–195,199,202]

Single compounds

The basic properties of nematic substances are the melting and clearing temperatures (T_m and T_{NI}, resp.). Whereas T_{NI} may be predicted in the frame of the rules and theories presented in section 1 and 2, predictions of T_m are possible only very roughly within the general experience of the chemists and do not follow strict rules. Table XV presents a short survey on the development of low melting nematic liquid crystals. Compounds 1 and 2 reflect the situation till the first decade of this century up to which all liquid crystalline substances had melting temperatures above 100°C. No. 6 is an early example of a substance class which was developed in a broad scale about 1970 and is important for applications up till now. The very low melting alkyl-dien-carboxylic acids (e.g. no. 7), unfortunately, are chemically too unstable for any application. Examples 3–5 are some of the lowest melting nematic compounds elaborated by the Vorländer school.

With the famous MBBA (no. 8) the first compound has been synthesized which is nematic at room temperature. Before MBBA became known, the only possibility to have room temperature nematics was to use mixtures or supercooled substances. A mixture of examples 4 and 5 has been among the first nematic room temperature mixtures published in 1967.[174]

Since 1970 many low melting and even room temperature liquid crystals have been synthesized. Table XVI displays some examples belonging to substance classes of actual interest. This compilation proves that low melting temperatures per se are no longer a problem, however, there are many other properties which must be considered.

Table XVII presents selected compounds with different dielectric anisotropies. Before 1970 only compounds with medium values (say -0.5 to $+7$) have been available. Now the range is -22 to $+53$ or

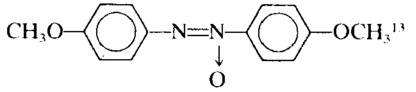
TABLE XV

Historical development of low melting liquid crystalline compounds

1. Cholesteryl benzoate[11]

K 145.5 N* 178.5 is 1888

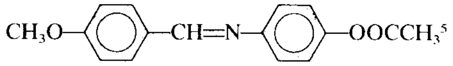
2.



(PAA)

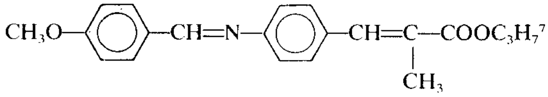
K 116 N 134 is 1890

3.



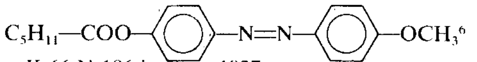
K 81.5 N 108 is 1907

4.



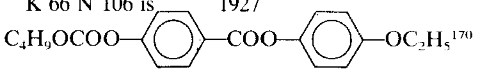
K 54.3 N 89.3 is 1909

5.



K 66 N 106 is 1927

6.

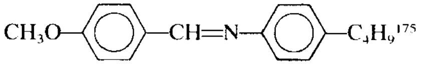


K 54 N 67 is 1927

7. $CH_3—(CH_2)_3—(CH{=}CH)_2—COOH$[169]

K 23 N 49 is 1941

8.



(MBBA)

K 21 N 46 is 1969

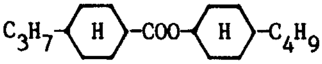
even higher. It is clear that by mixing the substances all intermediate values are obtainable.

Another very important property is the optical double refraction. Table XVIII gives some values ranging from about 0.04 to 0.24. Since the double refraction in mixtures exhibits linear dependence upon the composition, the mixtures may be adapted to the practical requirements.

The rotational viscosity is determining the dynamic behaviour (switching times) of liquid crystals in displays. Since there are only few data available, the connection with the molecular structure may be shown by use of the shear viscosities in Table XIX. There is no theory which would allow generally to predict the viscosities of liquid

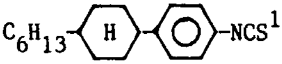
TABLE XVI

Actual low melting liquid crystalline compounds

1.


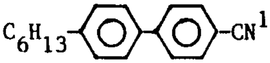
[181]

K 8 S 33.5 N 39 is

2.


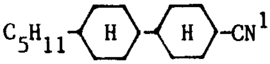
[176]

K 12.5 N 43 is

3.


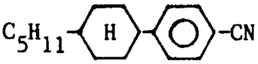
[177]

K 14.5 N 29 is

4.


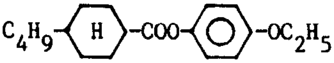
[179]

K 28 S 54 N 79 is

5.


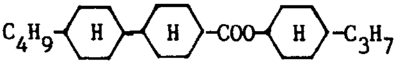
[179]

K 30 N 55 is

6.


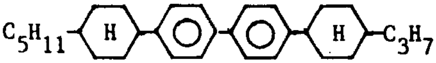
[179]

K 37 N 75 is

7.


[179]

K 43 S 169 N 184 is

8.


[179]

K 55 (S_3 50) S_2 228 S_A 251 N 311 is

TABLE XVII

Dielectric anisotropy of nematic compounds

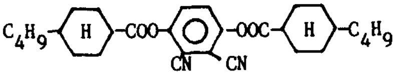
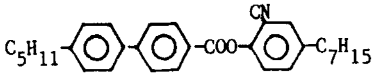
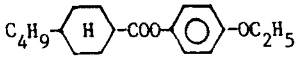
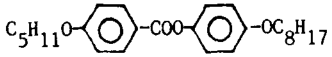
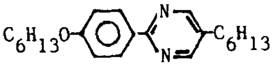
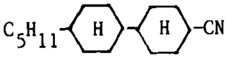
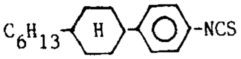
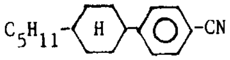
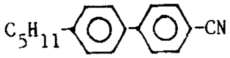
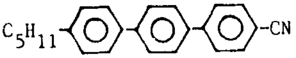
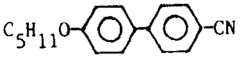
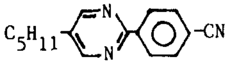
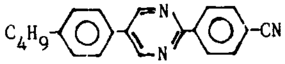
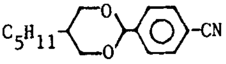
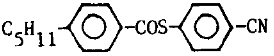
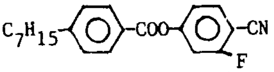
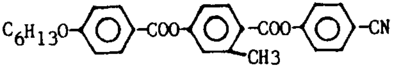
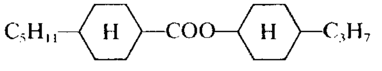
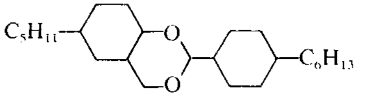
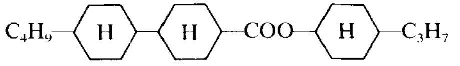
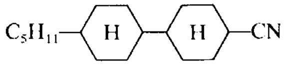
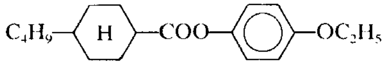
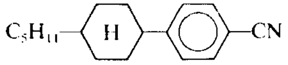
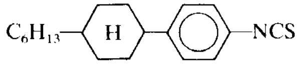
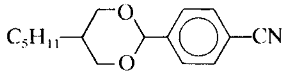
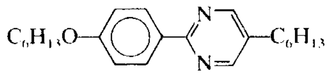
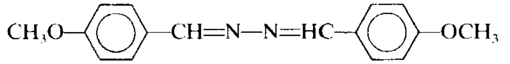
		Δε	ref.
1.		$-22^{1)}$	192
2.		-4	178
3.		-1.3	179
4.		-0.34	186
5.		+0.8	188
6.		+4.5	179
7.		+7	176
8.		+9.8	179
9.		+11	185
10.		+12.5 (130°C)	191
11.		13.7 (45° C)	191
12.		20.9 (45° C)	191
13.		22.1 (100° C)	191
14.		+32	179
15.		+33 (extrapolated)	178
16.		+48.9 (13° C)	184
17.		+53 (extrapolated)	180

TABLE XVIII

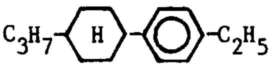
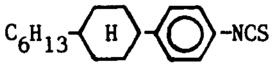
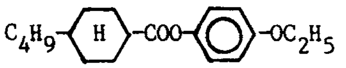
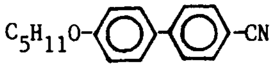
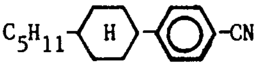
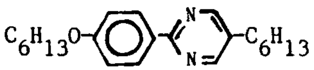
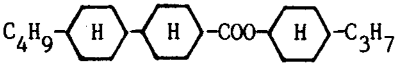
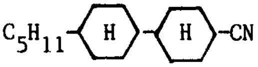
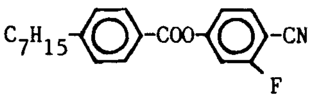
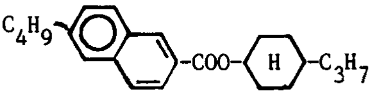
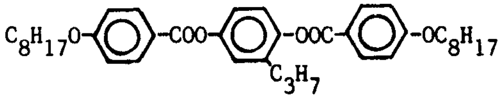
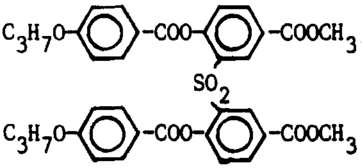
Double refraction of liquid crystalline compounds at 20°C

		Δn	ref.
1.	Cholesteryl ethyl carbonate	0.03	187
	calculated for the untwisted structure: 0.06		
2.		0.04 (extrapolated)	180
3.		0.04	180
4.		0.05	179
5.		0.06	179
6.		0.09	179
7.		0.13	179
8.		0.14	176
9.		0.14	179
10.		0.15	99
11.		0.24 ($T = T_{NI} - 5$)	189

crystals, therefore the behaviour can be considered only in terms of some empirical rules. The available range is extremely large: from very low values in compounds with small molecules the data increase with growing molecular weight and polarity. Extreme values are obtained in compounds with unsymmetric bulky molecular structure which even may be in the glassy state at room temperature, therefore they allow the construction of novel displays with storage properties.[180]

TABLE XIX

Shear viscosity of liquid crystalline compounds at 20°C

		η /mPas	ref.
1.		4	179
2.		12.5	176
3.		17	179
4.		18.5 (45° C)	191
5.		23	179
6.		42	180
7.		50	179
8.		65	179
9.		150	184
10.		160	190
11.		1100	101
12.		5000 (glassy state)	180

Mixtures

The impressive development of liquid crystalline substances demonstrated on the hand of Tables XV–XIX yields the basis for the development of mixtures for the different variants of displays which are important today. There are some reviews dealing with the properties of mixtures,[164,194] however, the best source of information are the leaflets of the leading companies producing liquid crystalline materials.

Table XX should give an idea of the development of technologically important mixtures. Merck IV is one of the early mixtures which despite its limited substance parameters was used in a broad scale. Merck V is chemically very similar but has remarkably improved properties. The following five mixtures are examples of the up-to-date possibilities of the substances adapted to the different types of applications. These mixtures offer impressive data, however, in no case one mixture does contain all positive properties in itself. In the contrary, what is to be considered as optimum properties is not unique but strongly depends on the intended application. As can be seen, in many mixtures the temperature region is a well solved problem. Also $\Delta\epsilon$ and Δn may be varied in relatively broad limits. The viscosity always should be as low as possible, and considering the modern types of displays[166] (highly multiplexed, supertwist variants, OMI) especially the elastic properties of the compounds have to be improved. Other demands relate to low melting enthalpies, high thermal and chemical stability, defined light absorption properties, low temperature dependence of the physical properties. Therefore also in future the research in nematic liquid crystals will be an actively elaborated field.

7. CONCLUDING REMARKS

This short survey should provide an impression of the development of the liquid crystal chemistry from a special sphere of some scientific outsiders working in a small number of centers to a comprehensive field of research and development in scientific institutions and the industry of all highly developed countries in the world. As this sketch already demonstrates, the chemist alone cannot be successful without the cooperation with physicists, theoreticians, technicians and other specialists. There are few scientific domains in which this cooperation is more urgently needed than in liquid crystal research.

TABLE XX

Technologically important mixtures

	Merck IV[1]	Merck V[1]	RO-TN-200[2]	ZLI-2851[3]	DI 6[7]	ZLI-2620[4]	ZLI-3281[5]	ZLI-3094[6]
m.p. (° C)	16	-5	~ -15	< -40	-55	< -20	< -30	< -30
T_{NI} (° C)	76	75	65	111	82	62	68	102
bulk viscosity	30	27.5	84	23	16	44	31	70
$\Delta\epsilon$	-0.2	-0.2	18.3	6.3	5.5	6.3	19.1	-4.8
t_{on} (ms)	15–20	8–12	500	—	4	—	—	—
t_{off} (ms)	130–180	80–130	290	—	12	—	—	—
Δn	—	—	0.276	0.13	0.125	0.12	0.11	0.04
k_{33}/k_{11}	—	—	—	1.38	—	0.73	—	—
U_o (V)	~ 7	~ 7	—	2.59	—	2.08	0.96	1.9

[1] Mixture of azoxy compounds for dynamic scattering mode; Merck leaflet 1972

[2] Mixture for TNP cells; Roche Liquid Crystals leaflet 1977

[3] Mixture for outdoor application, TNP; Merck leaflet 1987

[4] Mixture for dynamic drive, high level multiplexing (duty rate ≥ 1:64); Merck leaflet 1987

[5] Low voltage mixture, TNP; Merck leaflet 1987

[6] Black dichroic mixture for guest-host application; Merck leaflet 1987

[7] Low viscosity mixture, B. Bahadur, Data Images Inc., Ottawa; 10th Int. Liq. Cryst. Conference, York 1984

In this year we are commemorating the 100th anniversary of the discovery of the liquid crystals. In these 100 years a lot of knowledge about the liquid crystals has been obtained. Especially in the last 20 years the curve of the development did show a nearly exponential trend so that already at the end of the seventies some people believed that all important basic informations concerning thermotropic liquid crystals would be known and changed their interest to other fields. This, however, is not at all the case considering the so manifold surprising findings in this domain, e.g. reentrant behaviour, discotic and pyramidic mesophases, ferroelectric liquid crystals, associating systems, non-conventional liquid crystals and the first inclusion of many chemical groups (alicyclic and heterocyclic rings, non-conventional atoms, unsaturated substituents) into the liquid crystal chemistry.

Therefore we can trust that also in future the chemistry of thermotropic liquid crystals will keep its rank besides the development of the lyotropic and polymeric mesomorphic systems.

References

1. D. Vorländer, Kristallinisch-flüssige Substanzen, Enke Verlag, Stuttgart, 1908.
2. D. Vorländer, Chemische Kristallographie der Flüssigkeiten, Akadem. Verlagsgesellschaft, Leipzig, 1924.
3. C. Weygand: Chemische Morphologie der Flüssigkeiten und Kristalle. Hand- und Jahrbuch der chemischen Physik, Bd. 2, Abschn. 3c, Akadem. Verlagsgesell., Leipzig, 1941.
4. G. W. Gray: *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, 1962.
5. G. W. Gray and P. A. Winsor Eds.: Ellis Horwood series in physical chemistry: *Liquid Crystals and Plastic Crystals*, Halsted, New York, Vol 1 (1974), Vol 2 (1974).
6. G. R. Luckhurst and G. W. Gray, Eds.: *The Molecular Physics of Liquid Crystals*, Academic Press, London—New York—San Francisco, 1979.
7. W. Kast in Landolt—Börnstein: Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 6. Aufl., Bd. 2, Teil 2a, p. 266, Springer-Verlag, Berlin—Göttingen—Heidelberg, 1960.
8. D. Demus, H. Demus and H. Zaschke: Flüssige Kristalle in Tabellen, VEB Deutscher Verlag f. Grundstoffindustrie, Leipzig, 1974.
9. D. Demus and H. Zaschke: Flüssige Kristalle in Tabellen II, VEB Deutscher Verlag f. Grundstoffindustrie, Leipzig, 1984.
10. H. Kelker and R. Hatz: *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.
11. F. Reinitzer, *Monatsh. Chem.*, **9**, 421 (1888).
12. O. Lehmann, *Z. physikal. Chem.*, **4**, 462 (1889).
13. L. Gattermann and A. Ritschke: *Ber. Deut. Chem. Ges.*, **23**, 1738 (1890).
14. A. Windaus, Hoppe-Seylers *Z. physiol. Chem.*, **213**, 147 (1932), see also textbooks of organic chemistry.

15. F. Meyer and K. Dahlem Liebigs, *Ann. Chem.*, **326**, 331 (1903).
16. D. Vorländer: *Ber. Deut. Chem. Ges.*, **39**, 803 (1906).
17. D. Vorländer and R. Wilke, *Z. physik. Chem.*, **57**, 361 (1906).
18. D. Vorländer, *Z. physik. Chem.*, A**126**, 449 (1927).
19. H. Arnold and H. Sackmann: *Z. Elektrochem. angew. physikal. Chem.*, **63**, 1171 (1959).
20. E. Zytinski and R. Dabrowski, Materialy II Szkoly Fizyki Cieklich Krysztalow, 1980, p. 64.
21. H. Schubert, H. J. Lorenz, R. Hoffmann and F. Franke, *Z. Chem.*, **6**, 337 (1966).
22. H. Schubert and G. Hänse, not published, see G. Hänse, Diplomarbeit Halle, 1967.
23. G. W. Gray, *J. Physique* (Paris) **36**, C1 337 (1975).
24. A. C. Griffin and T. R. Britt, *J. Am Chem. Soc.*, **103**, 4957 (1981).
25. A. C. Griffin, G. A. Campbell and W. E. Hughes, *Liquid Crystals and Ordered Fluids*, Vol. 4 (A. C. Griffin and J. F. Johnson, editors) Plenum Publ. Corp. 1984, p. 1077.
26. Liquid Crystal Polymers I-III in Adv. Polym. Sci., 59–61, ed. by M. Gordon and N. A. Plate, Springer, Berlin, 1984.
27. "Polymer Liquid Crystals" ed. by A. Ciferri, W. R. Krigbaum and R. B. Meyer, Academic Press, New York, 1982.
28. E. T. Samulski, Faraday, *Discuss. Chem. Soc.*, **79**, 7 (1985).
29. C. Weygand and R. Gabler, *Ber. dtsch. chem. Ges.*, **71**, 2399 (1938).
30. H. Sackmann and D. Demus: *Mol. Cryst.*, **2**, 81 (1966).
31. H. Sackmann and D. Demus: *Mol. Cryst. Liq. Cryst.*, **21**, 239 (1973).
32. D. Demus, S. Diele, S. Grande and H. Sackmann, *Advances in Liquid Crystals*, Vol. 6 (ed. by G. H. Brown), Academic Press, 1983, p. 1.
33. L. Richter, D. Demus and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **71**, 269 (1981).
34. O. Lehmann, Flüssige Kristalle sowie Plastizität von Kristallen im Allgemeinen, molekulare Umlagerungen und Aggregatzustandsänderungen, W. Engelmann, Leipzig, 1904.
35. M. Born, Sitzungsber. königl. preuß. Akad. Wiss. 1916, 614; *Ann. Phys.* (Leipzig) **55**, 221 (1918).
36. W. Maier and A. Saupe, *Z. Naturforsch.*, **13a**, 564 (1958); **14a**, 882 (1959); **15a**, 287 (1960).
37. L. Onsager, *Ann. N. Y. Acad. Sci.*, **51**, 627 (1949).
38. M. A. Cotter, *J. Chem. Phys.*, **67**, 1098 (1977).
39. W. M. Gelbart and B. A. Baron, *J. Chem. Phys.*, **66**, 207 (1977).
40. M. A. Cotter, *Phil. Trans. R. Soc. Lond.*, A**309**, 127 (1983).
41. W. M. Gelbart, *J. Phys. Chem.*, **86**, 4298 (1982).
42. D. A. Dunmur and W. H. Miller, *J. Phys. Colloque*, C3 **40**, C3-141 (1979).
43. A. C. Pineda, T. J. Jones and G. R. van Hecke: *Liquid Crystals and Ordered Fluids* 4, p. 265 (eds. A. C. Griffin and J. F. Johnson), Plenum Press, London—New York, 1984.
44. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
45. D. Demus and A. Hauser in: Selected Topics in LC Research, Akademie Verl., Berlin, 1988.
46. P. J. Flory in: *Liquid Crystal Polymers* (eds. M. Gordon, N. A. Plate) Vol. 1, p. 2, Springer, Berlin, 1984.
47. M. A. Cotter and D. E. Martire, *J. Chem. Phys.*, **52**, 1902; 1909 (1970); **53**, 4500 (1970).
48. B. A. Baron and W. M. Gelbart, *J. Chem. Phys.*, **67**, 5795 (1977).
49. W. M. Gelbart and A. Gelbart, *Mol. Phys.*, **33**, 1387 (1977).
50. D. Vorländer, *Ber. dtsch. chem. Ges.*, **70**, 1202 (1937).
51. G. W. Gray, *Phil. Trans. Roy. Soc. London*, A**309**, 77 (1983).
52. G. W. Gray, *Proceed. Roy. Soc. London*, A**402**, 1 (1985).
53. G. W. Gray, in *Advances in Liquid Crystals* (ed. G. H. Brown) Vol. 2, p. 1–

72, Academic Press, New York, San Francisco, London, 1976.
54. G. W. Gray in "Zehn Arbeiten über Flüssige Kristalle" (*Proceed. 6. LC Conf. Soc. Countries* 1985 ed by H. Sackmann) Martin-Luther-Univ., Halle Wiss. Beiträge 1986/52 (N17), p. 22.
55. H. Schubert, Wiss. Z. Univ., Halle XIX' 70, H. 5, p. 1.
56. H. Schubert and H. Dehne, *Z. Chem.*, **12**, 241 (1972).
57. H. Zaschke, Wiss. Z. Univ., Halle XXIX' 80 M, H. 3, p. 35.
58. H. J. Deutscher, H. M. Vorbrodt and H. Zaschke, *Z. Chem.*, **21**, 9 (1981).
59. E. I. Kovshev, L. M. Blinov and V. V. Titov, *Usp. Khim.*, **46**, 754 (1977).
60. C. Wiegand, Z. Naturforsch. 3b, 313 (1948); 4b, 249 (1949) 12b, 512 (1957).
61. C. Wiegand, *Angew. Chem.*, **63**, 127 (1951).
62. D. Demus, *Z. Chem.*, **26**, 6 (1986).
63. W. H. de Jeu and J. van der Veen, *Mol. Cryst. Liq. Cryst.*, **40**, 1 (1977).
64. J. P. van Meter, *Org. Chem. Bull*, **45**, 1 (1973).
65. S. Hoffmann, W. Weissflog, W. Kumpf, W. Brandt, W. Witkowski, H. Schubert, G. Brezesinski and H.-D. Dörfler: *Z. Chem.*, **19**, 62 (1979).
66. C. G. Bazuin, D. Guillon, A. Skoulios and J. F. Nicoud, *Liq. Cryst.*, **1**, 181 (1986).
67. M. A. Osman, *Z. Naturforsch*, **38a**, 693 (1983).
68. M. A. Osman, *Z. Naturforsch.*, **38a**, 779 (1983).
69. W. Weissflog, Dissertation Halle 1972.
70. R. M. Reynolds, C. Maze and E. Oppenheim, *Mol. Cryst. Liq. Cryst.*, **36**, 41 (1976).
71. B. Kohne, K. Praefcke, G. Heppke and E. J. Richter; *Isr. J. Chem.*, **18**, 199 (1979).
72. W. R. Young, J. Haller and A. Aviram, *Mol. Cryst. Liq. Cryst.*, **13**, 357 (1971).
73. M. Schadt, M. Petrzilka, P. R. Geber and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **122**, 241 (1985).
74. M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **131**, 109 (1985).
75. M. Petrzilka, R. Buchecker, S. Lee-Schmiederer, M. Schadt and A. Germann, *Mol. Cryst. Liq. Cryst.*, **148**, 123 (1987).
76. R. Dabrowski, J. Diaduszek and T. Szczucinski, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 155 (1984).
77. R. Dabrowski, J. Diaduszek and T. Szczucinski, *Mol. Cryst. Liq. Cryst.*, **124**, 241 (1985).
78. A. Boller, M. Cereghetti, M. Schadt and H. Scherrer, *Mol. Cryst. Liq. Cryst.*, **42**, 215 (1977).
79. L. K. M. Chan, P. A. Gemmell, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **147**, 113 (1987).
80. G. W. Smith in: *Advances in Liquid Crystals*, Vol. 1, p. 189 (ed. G. H. Brown), Academic Press, New York, 1975.
81. G. W. Gray, chapter 12 in ref. 6.
82. W. L. McMillan, *Phys. Rev.*, A**4**, 1238 (1971); **6**, 936 (1972); **8**, 1921 (1972).
83. R. J. Meyer and W. L. McMillan, *Phys. Rev.*, A**9**, 899 (1974).
84. A. Wulf, *Phys. Rev.*, A**11**, 365 (1975).
85. W. J. A. Goossens, *J. Physique*, **46**, 1411 (1985); *Phys. Rev.*, A**35**, 1843 (1987); *Europhys. Lett.*, **3**, 341 (1987).
86. W. H. de Jeu, L. Longa and D. Demus, *J. Chem. Phys.*, **84**, 6410 (1986).
87. S. Diele, G. Pelzl, W. Weissflog and D. Demus, *Liq. Cryst.* in the press.
88. L. Longa and W. H. de Jeu, *Physic. Rev.*, A**26**, 1632 (1982).
89. F. Dowell, *Physic. Rev.*, A**28**, 3520 (1983); 28, 3526 (1983); 31, 2464 (1985); 31, 3214 (1985).
90. G. R. Luckhurst and B. A. Timimi, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 253 (1981).
91. G. F. Kventsel and G. R. Luckhurst, H. B. Zewdie, *Mol. Phys.*, **56**, 589 (1985).
92. G. Pelzl, S. Diele, I. Latif, W. Weissflog, D. Demus, *Cryst. Res. Technol.*, **17**, K 78 (1982).

93. S. Diele, G. Pelzl, I. Latif and D. Demus, *Mol. Cryst. Liq. Cryst. Lett.*, **92**, 27 (1983).
94. G. Pelzl, S. Diele, I. Latif, D. Demus, W. Schäfer and H. Zaschke, *Mol. Cryst. Liq. Cryst. Lett.*, **1**, 39 (1985).
95. M. A. Osman, *Mol. Cryst. Liq. Cryst.*, **128**, 45 (1985).
96. M. A. Osman, *Mol. Cryst. Liq. Cryst.*, **131**, 353 (1985).
97. D. Demus, A. Hauser, C. Selbmann and W. Weissflog, *Cryst. Res. Technol.*, **19**, 271 (1984).
98. A. Hauser, R. Rettig, C. Selbmann, W. Weissflog, J. Wulf and D. Demus, *Cryst. Res. Technol.*, **19**, 261 (1984).
99. A. Hauser, C. Selbmann, R. Rettig and D. Demus, *Cryst. Res. Technol.*, **21**, 685 (1986).
100. W. Weissflog and D. Demus, *Cryst. Res. Technol.*, **18**, K21 (1983); **19**, 55 (1984).
101. D. Demus, A. Hauser, A. Isenberg, M. Pohl, C. Selbmann, W. Weissflog and S. Wieczorek, *Cryst. Res. Technol.*, **20**, 1413 (1985).
102. D. Demus, S. Diele, A. Hauser, I. Latif, C. Selbmann and W. Weissflog, *Cryst. Res. Technol.*, **20**, 1547 (1985).
103. W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.*, **129**, 235 (1985).
104. W. Weissflog, A. Wiegeleben and D. Demus, *Mater. Chem. Phys.*, **12**, 461 (1985).
105. W. Weissflog, A. Wiegeleben, S. Diele and D. Demus, *Cryst. Res. Technol.*, **19**, 583 (1984).
106. S. Diele, K. Roth and D. Demus, *Cryst. Res. Technol.*, **21**, 97 (1986).
107. W. Weissflog, S. Diele and D. Demus, *Mater. Chem. Phys.*, **15**, 475 (1986).
108. S. Diele, W. Weissflog, G. Pelzl, H. Manke and D. Demus, *Liq. Cryst.*, **1**, 101 (1986).
109. H. Kresse, M. Keil and W. Weissflog, *Cryst. Res. Technol.*, **18**, 563 (1983).
110. W. Weissflog and D. Demus, *Liq. Cryst.*, **3**, 275 (1988).
111. W. Weissflog, A. Wiegeleben, S. Diele and D. Demus, *Cryst. Res. Technol.*, **19**, 583 (1984).
112. G. Pelzl, I. Latif, S. Diele, M. Novak, D. Demus and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **139**, 333 (1986).
113. M. Nakagawa and T. Akahane, *J. Phys. Soc. Jap.*, **53**, 1951 (1984).
114. H. Kresse and P. Rabenstein, *Phys. stat. sol.*, (a) **100**, K 83 (1987).
115. W. Mahler, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst. Lett.*, **2**, 111 (1985).
116. H. Adams, N. A. Bailey, D. W. Bruce, D. A. Dunmur, E. Lalinde, M. Marcos, C. Ridgeway, A. J. Smith, P. Styring and P. M. Maitlis, *Liq. Cryst.*, **2**, 381 (1987).
117. J. W. Goodby in: *Liquid Crystals and Ordered Fluids* Vol. 4, p. 175 (eds. A. C. Griffin, J. J. Johnson) Plenum Publ. 1984.
118. M. Ballauf, *Liq. Cryst.*, **2**, 519 (1987).
119. G. W. Gray in ref. (6) p. 14.
120. J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Proc. Roy. Soc. London Ser.*, A. **381**, 117 (1982).
121. S. Kobinata, T. Kobayashi, H. Yoshida, A. D. L. Chandani and S. Maeda, *J. Molec. Struct.*, **146**, 373 (1986).
122. T. Kobayashi, H. Yoshida, A. D. L. Chandani, S. Kobinata and S. Maeda, *Mol. Cryst. Liq. Cryst.*, **136**, 267 (1986).
123. H. Toriumi and E. T. Samulski in *Liquid Crystals and Ordered Fluids*, Vol. 4, p. 597 (eds. A. C. Griffin, J. F. Johnson) Plenum Press, New York, 1984.
124. A. Ben-Shaul, Y. Rabin and W. M. Gelbart, *J. Chem. Phys.*, **78**, 4303 (1983).
125. B. Janik, E. T. Samulski and H. Toriumi, to be published.
126. S. Diele and D. Demus, Abstract no A 9, 7th Liq. Cryst. Conf. Soc., Countries Pardubice August, 1987.
127. W. Weissflog, G. Pelzl and D. Demus, *Cryst. Res. Technol.*, **21**, 117 (1986).
128. S. Diele, H. Kresse, W. Weissflog and D. Demus, Abstract no A 8, 7th Liq.

Cryst. Conf. Soc. Countries Pardubice, August, 1987.
129. R. J. Cox, W. Volksen and B. L. Dawson, in: *Liquid Crystals and Ordered Fluids*, Vol. 4, p. 33 (ed. A. C. Griffin and J. F. Johnson) Plenum Press, New York, 1984.
130. E. M. Averyanov, *Liq. Cryst.*, **2**, 491 (1987).
131. 5th European Winter Liquid Crystal Conference on Layered and Columnar mesomorphic systems Borovets (Bulgaria), 1987, C. Destrade, N. H. Tinh, et al., (a) abstract no A11; (b) abstract no A 12; (c) Y. Galerne and N. Isaert, et al. abstract no A 16; (d) A. G. Petrov and A. Dershanski, abstract no A 39 and references given therein.
132. N. H. Tinh, J. Malthete and C. Destrade, *Mol. Cryst. Liq. Cryst. Lett.*, **2**, 133 (1985).
133. N. H. Tinh, C. Destrade, A. M. Levelut and J. Malthete, *J. Physique*, **47**, 553 (1986).
134. 7th Liquid Crystal Confer. Soc. Countries, Pardubice, Czechoslovakia, August 1987; (a) C. Destrade, H. T. Nguyen, A. M. Levelut and J. Malthete, abstract no G1; (b) R. Cayuela, C. Destrade, H. Gasparoux, A. M. Levelut, J. Malthete and H. T. Nguyen, abstract no G4.
135. G. Etherington, A. J. Leadbetter, X. J. Wang, G. W. Gray and A. Tajbakhsh, *Liq. Cryst.*, **1**, 209 (1986).
136. J. Malthete, A. M. Levelut and N. H. Tinh, *J. Physique Lett.*, **46**, L 875 (1985).
137. J. Malthete, N. H. Tinh and A. M. Levelut, *J. Chem. Soc., Chem. Commun.*, 1549 (1986).
138. L. J. Yu and A. Saupe, *Phys. Rev. Lett.*, **45**, 1000 (1980).
139. J. Malthete, L. Liebert, A. M. Levelut and Y. Galerne, *Compt. Rend. Acad. Sc.* Paris 303, Ser II, 1073 (1986).
140. J. Malthete, J. Canceill, J. Gabard and J. Jacques, *Tetrahedron*, **37**, 2823 (1981).
141. J. Malthete, J. Billard, J. Canceill, J. Gabard and J. Jacques, *J. Physique Colleque*, **37**, C3-1 (1976).
142. Y. Matsunaga and M. Terada, *Mol. Cryst. Liq. Cryst.*, **141**, 321 (1986).
143. Y. Matsunaga, Y. Nakayasu, S. Sakai and M. Yonenaga, *Mol. Cryst. Liq. Cryst.*, **141**, 327 (1986).
144. J. Malthete, J. Billard and J. Jacques, *Compt. Rend. Acad. Sci.* Paris, C**281**, 333 (1975).
145. J. Malthete, *Compt. Rend. Acad. Sci.*, Paris Ser. II **296**, 435 (1983).
146. A. C. Griffin, S. F. Thames and M. S. Bonner, *Mol. Cryst. Liq. Cryst. Lett.*, **43**, 135 (1977).
147. A. C. Griffin, M. L. Steele, J. F. Johnson and G. J. Bertolini, *Nouveau Journ. de Chimie*, **3**, 697 (1979).
148. A. C. Griffin, N. W. Buckley, W. E. Hughes and D. L. Wertz, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 139 (1981).
149. D. Demus, H. Dehne, A. Roger, W. Weissflog, A. Wiegeleben and G. Pelzl, patent DD 242 627 A1 (1987), see also *Proceed. Eurodisplay*, **87**, London, Sept. 1987.
150. A. C. Griffin and N. W. Buckley, *Mol. Cryst. Liq. Cryst.*, **41**, 141 (1978).
151. B. M. Zuev, A. P. Filippova and N. A. Palikhov, Isv. Akad. Nauk SSSR, Ser. Khim. 1975, 1884.
152. Lin Lei, abstract G2 7th Liquid Crystal Conference of Soc. Countries, Pardubice, August 1987.
153. D. Demus in: *Nonemissive Electrooptic Displays*, p. 83, ed. A. R. Kmetz and F. K. von Willisen, Plenum Press, New York/London, 1976.
154. *Physics and Chemistry of Liquid Crystal Devices*, ed. G. J. Sprokel, Plenum Press, New York/London, 1980; (a) J. Castellano and K. J. Harrison, p. 263.
155. G. W. Gray: *Advances in Liquid Crystal Materials for Applications*, BDH Chemicals, Ltd. Poole, 1978.
156. V. V. Titov and A. I. Pavluchenko, Khim. Geterotsikl. Soed. 1980, 3.

157. W. H. de Jeu, *Mol. Cryst. Liq. Cryst.*, **63**, 83 (1981).
158. W. H. de Jeu, *Phil. Trans. Roy. Soc.*, London A **309**, 217 (1983).
159. B. Sturgeon, *Phil. Trans. Roy. Soc.*, London A **309**, 231 (1983).
160. D. Demus and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **63**, 129 (1981).
161. M. A. Osman and T. Huynh-Ba, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 331 (1983) **82**, 339 (1983).
162. R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **123**, 57 (1985).
163. R. Eidenschink, *Kontakte*, **1**, 15 (1979).
164. M. Schadt, Lecture at the Meeting of the Japan Soc. for the Promotion of Sci. Tokyo, Nov. 1984.
165. W. E. Haas, *Mol. Cryst. Liq. Cryst.*, **94**, 1 (1983).
166. E. Kaneko: Liquid Crystal TV Displays: Principles and Applications of Liquid Crystal Displays, KTK Scientif. Publ., Tokyo, 1987.
167. Roche Liquid Crystals, Green Book no. 8, Sept. 1986.
168. D. Demus in: *Electrooptical Crystals and Liquid Crystals in Science and Industry*, Vol. II, Publ. Techn. Univ., Lodz (Poland), 1976, p. 30–58.
169. C. Weygand, R. Gabler and J. Zimmermann, *Z. physik. Chem.*, **B50**, 124 (1941).
170. E. Schroeter, Diss. Halle, 1927.
171. P. Hansen, Diss. Halle, 1907.
172. F. Bättenhausen, Diss. Halle, 1927.
173. W. Kasten, Diss. Halle, 1909.
174. D. Demus, *Z. Naturforsch.*, **22a**, 285 (1967).
175. H. Kelker and B. Scheurle, *Angew. Chem.*, **81**, 903 (1969).
176. Leaflet POCH, Gliwice, Poland.
177. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973).
178. Leaflet E. Merck, Darmstadt, 1977.
179. Leaflet E. Merck, Darmstadt, 1983.
180. Halle Group, not published.
181. M. Körber, H. J. Deutscher, D. Demus, H. Schubert and H. Altmann, DDR WP CO9K/215 743.
182. H. J. Deutscher, M. Körber and H. Schubert, *Adv. in Liquid Crystal Research and Applications*, Vol. 2, p. 1075, Ed. L. Bata, Pergamon Press, Oxford, 1980.
183. H. Zaschke, H. Schubert, F. Kuschel, F. Dinger and D. Demus, DD WP 95 892 (1971).
184. Hp. Schad and S. M. Kelly, *J. Chem. Phys.*, **81**, 1514 (1984).
185. A. Ashford, J. Constant, J. Kirton and E. P. Raynes, *Electron. Lett.*, **9**, 118 (1973).
186. H. Kresse, D. Demus and J. Krinzner, *Z. phys. Chem.* (Leipzig), **256**, 7 (1975).
187. R. Rettig, G. Pelzl and D. Demus, *J. prakt. Chem.*, **318**, 450 (1976).
188. H. Kresse, P. Schmidt and D. Demus, *phys. stat. sol.* (a) **32**, 315 (1975).
189. W. Maier in Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik-Chemie-Astronomie-Geophysik-Technik, Vol. 2, Springer, Berlin (1960), p. 533.
190. H. J. Deutscher, W. Schäfer, M. Keil, E. Pönicke and D. Demus, *Z. Chem.*, **24**, 406 (1984).
191. Roche Liquid Crystals, leaflet, 1984.
192. T. Inukai, K. Furukawa, M. Inoue and K. Terashima, *Mol. Cryst. Liq. Cryst.*, **94**, 109 (1983).
193. M. A. Osman, *Mol. Cryst. Liq. Cryst.*, **82**, Lett, 295 (1982), **92**, Lett., 57 (1983).
194. A. K. Garg, V. K. Agarwal and B. Bahadur, *Mol. Cryst. Liq. Cryst.*, **130**, 11 (1985).
195. A. Villiger, A. Boller and M. Schadt, *Z. Naturforsch.*, **34b**, 1535 (1979).
196. H. Takatsu, K. Takeuchi, Y. Tanaka and M. Sasaki, *Mol. Cryst. Liq. Cryst.*, **141**, 279 (1986).
197. W. H. de Jeu, *Physical properties of liquid crystalline materials*, Gordon and Breach, New York–London–Paris, 1980.
198. G. S. Chilaya and L. N. Lisetski, *Mol. Cryst. Liq. Cryst.*, **140**, 243 (1986).

199. B. Bahadur, Acta Ciencia Indica Vol. 7 (P) Special Number (1981).
200. M. Koden, S. Hayashi, K. Nishimura, S. Kusabayashi and S. Takenaka, *Mol. Cryst. Liq. Cryst.*, **106**, 31 (1984).
201. R. Frach, H.-J. Deutscher, H. Zaschke and D. Demus, patent DD 245 869 A1 (1987).
202. R. Klug, E. Poetsch, V. Reiffenrath and G. Weber, Vortrag No. 6, 17. Freiburger Arbeitstagung Flüssigkristalle 1987.
203. J. Lindau, W. Hillmann, H.-D. Dörfler and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **133**, 259 (1986).