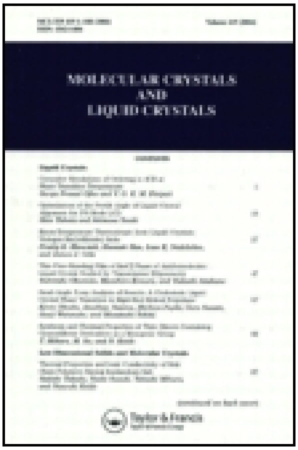

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One Century Liquid Crystal Chemistry: From Vorländer's Rods to Disks, Stars and Dendrites

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One Century Liquid Crystal Chemistry: from Vorländer's Rods to Disks, Stars and Dendrites

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The liquid crystals have been discovered in 1888. Until about 1900 only few mesogenic compounds were known. Daniel Vorländer started his work on liquid crystals about one century ago and he may be called "father of liquid crystal chemistry". By systematical syntheses of compounds with predetermined geometrical shape he was able to derive his rule of the most extended molecular shape. He initiated many special areas of LC chemistry, most of which are still topical. The historical development of the some topics of LC research will be sketched. Among the topics are: the role of impurities and polymorphism, inclusion of different chemical moieties (aromatic, cycloaliphatic and heterocyclic compounds, metallomesogens, supramolecular systems), compounds with unconventional molecular shape (twins, banana shaped compounds, lateral substituted compounds), glassy mesogens, oligomeric and polymeric compounds, discotic compounds, dendrimers, materials for applications.

Keywords: review; LC chemistry; polymorphism

INTRODUCTION

After the liquid crystalline state has been detected in 1888, for a period of about 15 years there existed no idea about a relation between

molecular structure and the occurrence of liquid crystalline phases. It has been D. Vorländer in the University of Halle, who founded the liquid crystal chemistry and established his rule of the most elongated molecular shape. This rule in principle is still valid, but in the nearly 100 years from his beginning the liquid crystal research a multitude of „unconventional" liquid crystals have been synthesized, and additional principles enabling the existence of liquid crystals have been found. It is the aim of this lecture to present a sketch of the development of the liquid crystal chemistry of the past 100 years, from the personal sight of the author who is aware of the fact that completeness in this exciting and fruitful field of research in a short sketch is not possible.

The author remembers well the time of around 1975, when quite a lot of liquid crystal researchers were of the opinion that all important facts about liquid crystals would be already known, and further research would only be useful to fill tables and handbooks, so that it should be better to switch to another topic, e. g. polymers. It will be shown that this opinion was not appropriate.

In order to support an overview at the hand of some numbers, Vill's database LiqCryst 3.4 (newest version) is very useful. The total number of registered compounds now is above 80000. The compilation Table 1 displays researchers who have synthesized more than 1000 liquid crystalline compounds. All insiders are aware of the dominating role of G. W. Gray in the second half of the 20th century. But surprisingly on the top of this list is H. Zaschke, former professor of the University of Halle, who is among the large number of East German scientists who lost their positions after Germany's unification and never had the chance to return to scientific work. Vorländer's work is impressive considering the fact that he contributed about 85% of the liquid crystals known until his retirement. Of course, the number of synthesized compounds alone is not an adequate measure for the quality of scientific work. There are enough scientists not included in this list, who opened new chapters in the book of the mesogens and who are well known in the scientific community.

THE PERIOD PRIOR TO VORLÄNDER

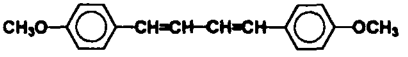
In 1888 Friedrich Reinitzer, a botanist at the German University in Prague, was performing investigations about cholesterol, which could be obtained from different sources (lanolin, brain, gallstones) and

TABLE 1: Authors with more than 1000 synthesized compounds, taken from LiqCryst 3.4 (May 2000)

	Author	Number of compounds		Author	Number of compounds
1	H. Zaschke	4311	10	C. Destrade	1323
2	G. W. Gray	4048	11	J. Goodby	1320
3	D. Vorländer	2760	12	D. Lacey	1282
4	H. Schubert	2609	13	C. Tschierske	1230
5	S. M. Kelly	2591	14	T. Inukai	1196
6	W. Weissflog	2267	15	J. Krause	1071
7	T. Nguyen	2013	16	R. Dabrowski	1082
8	Y. Matsunaga	1754	17	E. Poetsch	1012
9	H. J. Deutscher	1412	18	J. L. Serrano	1002

whose nature was „completely unclarified“[1,2]. In order to characterize cholesterol by derivatives, he synthesized the acetate and the benzoate and found the famous colour phenomena, two melting points and the cloudy liquid, which stimulated the investigations by Otto Lehmann[3] and lead to the detection of the liquid crystalline state. Reinitzer found two melting points and the colour phenomenon also in „hydrocarotin benzoate“, a compound which he erroneausly attached to the group of „cholesterins“. Probably he dealt with the benzoate of the dihydroxy derivative of one of the carotins, which is not related to cholesterol, but belongs to the group of tetraterpens and occurs in the dyestuffs of carrots. Summarizing we can say, that Reinitzer found the novel phenomena by chance in compounds of unknown chemical nature.

In 1889 Fittig and Politis[4] synthesized the compound

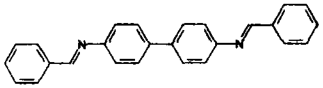


and between 225 and 235^{0} C they found the occurrence of a „turbid liquid“.

Gattermann and Ritschke in 1890[5] performed investigations about the isomers of „ of azoxy compounds“, because the chemical bonds in the azoxy group in this time were still unclear. They synthesized some hologues of the series of the 4,4'-di-n-alkyloxybenzenes, namely p-azoxyanisole and p-azoxyphentole, and „anisol-azoxy-phenetole". During the investigations, they „had to overcome another difficulty", because during heating the new compounds, they found in certain temperature intervals cloudy liquids. Knowing the work of Lehmann about the „cloudy liquids" of the cholesterol esters, they supposed the existence of liquid crystals in their compounds and they sent samples to Lehmann, who confirmed their suspicion. They present in their article a short description of Lehmann's results. Lehmann emphasizes the huge importance of the new cloudy liquids, because in contrast to the „weak crystals" of the cholesterol derivatives they are low viscous and do not belong to the solid crystals. And very important is the fact, that the new compounds have been chemically pure and of known chemical structure.

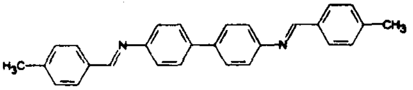
In 1900 Lehmann[6] published a comprehensive report about liquid crystals and their properties. Among the investigated compounds have been the following three, which according to Lehmann were „recently discovered by Prof. Gattermann". It seems that Gattermann did publish himself these compounds not earlier than 1906[7].

4,4'-Bis-(benzylideneamino)-biphenyl



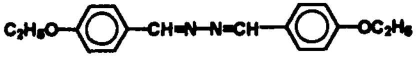
Cr 234 N 260 I

4,4'-Bis-(4-methylbenzylideneamino)-biphenyl



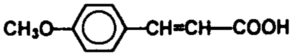
Cr 231.0 N >350.0 I

Bis-(ethoxybenzald)azin



Cr 175 kr fl. 201 I

In 1901 van Romburgh[8] found that 4-methoxy-cinnamic acid



at 169^0 C forms an opalizing liquid, which becomes clear at 185^0 C. This is the first example of a liquid crystalline compound forming hydrogen bonds, in modern nomenclature „supramolecular".

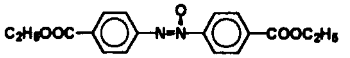
It should be mentioned that before 1888 several reports have been published about compounds (some cholesteryl derivatives, myelin, magnesium stearate), which later became known as liquid crystals[9]. In the very early period of liquid crystal research also compounds have been synthesized, without detection of their mesomorphic properties (e. g. 4-methoxycinnamic acid[4]).

VORLÄNDER's EARLY WORK

Vorländer has been the first chemist, who investigated the phenomenon of liquid crystals from the chemical standpoint, by systematic syntheses of compounds with predetermined molecular shapes.

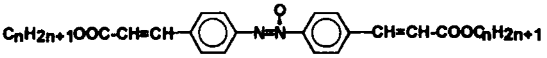
Daniel Vorländer (1867-1941) studied chemistry in several German universities and performed the experimental part of his PhD „About the amidines of oxalic acid" in 1888/89 in the University of Berlin under supervision of F. Tiemann. He obtained his PhD degree in the University of Halle in 1890. Here he became scientific assistant and finished his habilitation „The synthesis of hydroresorcin derivatives" in 1896. In 1897 he was appointed leader of the organic division of the chemical institute, in 1900 he obtained the title professor and in 1908 he followed Jacob Volhard as director of the chemical institute. This position he held until his retirement in 1935, interrupted by his service as artillery officer in the first World War from 1914-1917. More details about Vorländer and his life are available in papers by Weygand[10], Kelker[11,12], Bruce et al.[13], Vorländer[14].

Until 1903 Vorländer published about 90 papers about different themes of the organic chemistry, among them papers on synthetic dyestuffs like indigo, azo compounds and their intermediates. In detail Vorländer studied the formation of azo compounds from diazonium salts[15], in cooperation with Felix Meyer, who finished his PhD in 1900 under his supervision. Because some the azo compounds synthesized by their new method showed melting points different from those of the former literature, Meyer and Dahlem[16] synthesized derivatives of the azo- and azoxy-benzoic acids, using different procedures. It became clear that some of the discrepancies were based on the fact, that the products described in the former literature have been mixtures of azo and azoxy compounds. Among the newly synthesized materials has been the di-ethyl 4,4'-azoxybenzoate, which



surprisingly showed „two melting points": at 114.5^0 C it was melting , producing a cloudy liquid, which at 122.5^0 C gave a clear droplet. And they reported: „This compound is belonging to the curious materials investigated by O. Lehmann and R. Schenck, which during melting are forming an anisotropic crystalline liquid. Dr. Schenck in Marburg, to whom our materials were available, confirmed our observations". This has been the first liquid crystalline compound, synthesized in Vorländer's laboratory. And it seems that it has been the only liquid crystal in Vorländer's group, obtained by chance, because this was the starting point for systematic investigations of molecular structure and liquid crystalline behaviour.

Obviously Vorländer had observed the research on liquid crystals and he knew the respective literature. This may be due to the fact, that Rudolf Schenck from 1896-1897 made physical investigations with different methods about three liquid crystalline compounds, in the same institute in Halle[17]. In 1906 the first two publications about liquid crystals, authored by Vorländer himself, appeared. In order to find new liquid crystalline compounds,in his paper finished in February 1906 he drew conclusions from the chemical structures of the few already known liquid crystalline materials[18]. By comparison of azo and azoxy compounds he found, that the azoxy group favours liquid crystalline properties. And comparing ortho, meta and para substituted compounds, he recognized that the para substitution is favourable. In order to rationalize his working hypothesis, he intended to check the idea if the liquid crystalline state is caused or favoured by the same atomic moieties which influence also other physical properties like light refraction, colour, optical activity and so on. Already his first attempt to use the ethylene moiety containing the carbon-carbon double bond yielded a surprisingly encouraging result. Whilst in the homologous series of the azoxybenzoates only the ethyl derivative showed liquid crystallinity, all azoxycinnamates from the methyl to the hexadecyl derivative were proven to be liquid crystalline.



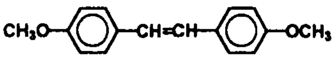
n = 1 - 16

At the same time this was the first liquid crystalline homologous series. Summarising Vorländer says, that clearly there is a relation between the existence of the anisotropic liquid phase and the chemical constitution, and except the salts of the oleic acid 35 liquid crystalline compounds are known.

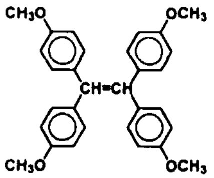
In the other paper also published in 1906 Vorländer[19] remarks that within one summer (obviously summer 1905) he was able to find 26 new liquid crystalline compounds, and „the detection of a much larger number is to be expected with respect to the relations between chemical structure and liquid crystalline behaviour“.

VORLÄNDER's RULE

Already in his very early papers about liquid crystals Vorländer was able to realize, „that the crystalline liquid state is caused by the most elongated structure of the molecule“[20]. He proved this statement by comparison of o-, m- and p-substituted benzene derivatives, only the latter showed liquid crystalline properties. And he studied the role of additional lateral substituents, e. g. :



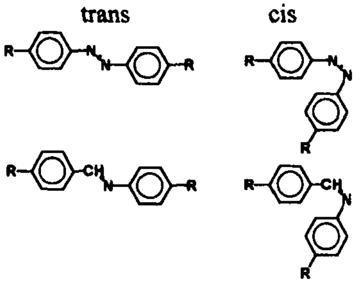
Cr 216 N 176 I



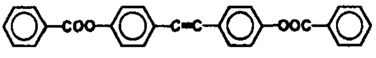
not liquid crystalline

In this and in other examples he found that bulky lateral substituents destroy the liquid crystallinity of the molecules. Further he was able to show that branched alkyl chains are less favourable for the existence of the liquid crystalline state than normal alkyl chains.

In the beginning of the liquid crystal science there was the idea, that the existence of the liquid and the liquid crystalline phases could be due to chemical isomers of the molecules. In this time liquid crystalline azo compounds and Schiff's bases have been known, which in principle can exist as cis and trans isomers:



In order to prove this hypothesis, Vorländer synthesized derivatives of tolane, in which this isomerism is not possible. He found several liquid crystalline tolane derivatives, e. g.[21]



Cr 214 N 254 I

Because in tolanes, and also other compounds checked by him cis-trans isomerism is impossible, he concluded that this cannot be the reason for the existence of liquid crystalline phases. A further argument for this opinion was delivered by dielectric investigations, which showed nearly the same value of the dielectric constants in the liquid crystalline and liquid isotropic state of ethyl 4-(4-methoxybenzylidene)-cinnamate[21] .

Mainly due to Vorländer's activities, in 1907 about 160 liquid crystalline p-substituted benzene derivatives have been known[21] . It is interesting to mention, that Vorländer used this knowledge for the clearification of some unknown chemical structures. When the compounds showed liquid crystallinity, he stated p-substitution. When liquid crystalline phases were lacking, o- or m-substitution was assumed[21,22] . Vorländer made similar conclusions later, when he tried to find out the still unknown bond angles of nitrogen, oxygen, sulphur and mercury[23] .

Vorländer summarised the knowledge about the liquid crstals, emphasizing the chemical standpoint, in his first book in 1908[22] . There he mentions , that 200 - 250 compounds are liquid crystalline.

Despite the fact that Vorländer in his main interest was experimental organic chemist, he published about aspects of the theoretical organic chemistry and organized physical investigations of his materials in his own laboratory as well as in cooperation with physicists. This concerted procedure was one of the reasons for his great success in liquid crystal science.

EMULSIONS, IMPURITIES, MIXTURES

Around 1900 the generally accepted teaching was, that there are three states of the matter: solid crystalline, isotropic liquid, gas . In this situation it was not surprising, that a liquid crystalline state could not be accepted by the specialists without contradiction and tough struggle. Among the people who denied the existence of the liquid crystalline state was specially Gustav Tammann, who was famous because of his fine experimental and theoretical work about phases and phase transitions. In 1901 he established the „emulsion hypothesis“[24], which says that the turbid liquids of the „so-called liquid crystals“ are emulsions of solids in ordinary liquids. In azoxyanisole and azoxyphenetole during extended heating he had observed brown solid reaction products, the amount of which increased with the heating time. Unfortunately his idea was supported by the situation in cholesteryl benzoate, because the chemical structure of cholesterol was not known in this time and which by some scientists was considered to be a mixture of several natural products. Curiously, after Tammann's attack Lehmann denied to have ever classified cholesteryl benzoate as liquid crystal[25a].

Lehmann was the toughest advocate of the new state of matter, which he always claimed to be his own discovery. He tried to overcome Tammann's standpoint using arguments like the existence of optically clear liquid crystals, optical extension of the birefringent liquids in defined directions and others. Specially he mentioned that the extended heating by Tammann produced new impurities, due to decomposition of the azoxy compounds[25]. Schenck[26] investigated the temperature dependence of several physical properties of liquid crystals and found physical proofs for phase transitions at the claring temperatures. Liquid crystals have been investigated by electrophoresis, and the results showed that they cannot be divided into different materials, like emulsions[27] . Especially the very careful chemical syntheses of Gattermann and Ritschke[5] as well as Meyer and Dahlem[16], using different methods for the preparation of the same compound, proved the purity of the materials from the chemical standpoint. In contrast to that, it is interesting to note that the proof of Tammann's original azoxyanisole yielded large amounts of impurities, specially considerable amounts of azoanisole[28].

Nevertheless, Tammann insisted in his „emulsion hypothesis“[29] , and still in his book „Aggregatzustände“ in 1923 he judges „summarising it is allowed to say, that the existence of liquid crystals or anisotropic liquids of chemically homogenous materials until now has not been proved“[30].

In contrast to this attitude W. Nernst, who initially has been very critical to the existence of liquid crystals[31], later contributed own experiments to the knowledge of liquid crystals and defended their existence against attacks by Tammann[32].

In the early times the chemical purity of liquid crystalline compounds was a question deciding their acceptance at all. But now in that extent in which the demands on the special properties of liquid crystals are increasing, the importance of their purity is growing. Most of the chemists are aware of this fact. Unfortunately, sometimes physicists using extremely sophisticated methods did not take enough care about the purity or chemical stability of their compounds. It is general standard to indicate the limits of error of physical methods, but the numerical indication of the purity of chemical compounds is rather seldom. An instructive example is the case of MBBA[33] , the first compound which is in the liquid crystalline state at room temperature and which therefore is one of the most investigated compounds. Unfortunately it belongs to the class of Schiff's bases, compounds which are long known for their weak chemical stability. Fig. 1 exhibits the melting and clearing temperatures of samples of different origin. The strong scattering of the data visible here, of course exists also in all other measured physical data of the compound. The most surprising fact is, that there seems to be no general progress in course of time, because the scattering of the data remains.

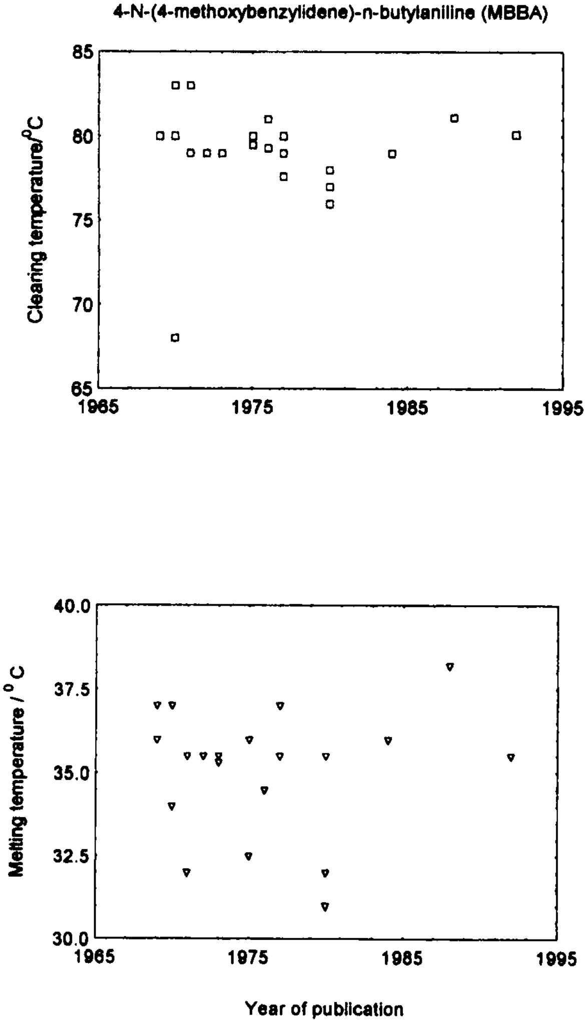


Figure 1 Clearing and melting temperatures of MBBA[33]

The author would like to make a remark about the long-term stability of chemical compounds.Using the heating stage microscopy, he has investigated at least 500 original compounds from Vorländer's group. The compounds have been still available in the stock of the old collection of the former Institute of Chemistry in the University of Halle, situated in Vorländer's original building, and have been stocked in small glass tubes closed with cork stops. In most cases the compounds were preserved for decades without decomposition. Only few of the old materials showed deterioration, but even most of the Schiff's bases, e. g. those from M. E. Huth 1909[34], were in good condition[35]. On the hand of the sharpness of the melting temperatures it was possible to evaluate the quality of the chemical work of Vorländer's doctorands, 30-50 years after synthesis of their compounds.

The purity and chemical stability of materials are now basic demands for compounds to be used in modern LCD's. We can see the development at the hand of the electrical resistivity of materials for practical applications (Table 2). Specially for use in AMLCD's the demands are very high.

TABLE 2 Electrical resistivity of mixtures for displays

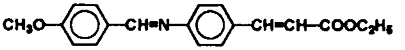
Mixture	Resistivity Ωcm	Application	Reference
Mixtures with conductivity dopants	10^6- 10^8	DSM,	[36]
Mixtures of phenyl benzoates Mi5	$5x10^9$	DSM	[36,37]
Licrystal 997	$1.3x10^9$	DSM	[38] 1977
Mixtures	10^8 - 10^9	DSM	[39]
E7	$>5x10^{10}$	TN	[40] 1978
Mixtures	$5x10^{11}$ - $5x10^{13}$	STN	[41] [42]
MNPO 4014	$5x10^{11}$	AM-LCD	[43] 1994
Mixtures	$>1x10^{11}$	AM-LCD	[41] 1992
4580	$2.5x10^{13}$	AM-LCD	[38] 1994
Advanced mixtures	$> 10^{14}$	AM-LCD	[41, 42, 44]

The small conductivity of highly purified materials is based on traces of weak electrolytes, which dissociate in accordance to the dielectric constant of their environment. The purification of the materials by routine methods therefore comes to critical values of the conductivity, depending on the dielectric constants[42].

POLYMORPHSIM AND CLASSIFICATION OF LIQUID CRYSTALS

During his very careful observation of the transition phenomena (he already used the polarising microscope with gas driven heating stage, later electrical heating as routine instrument) Vorländer found, that in many cases supercooling the isotropic liquid is important in order to find monotropic liquid crystalline phases[19].

During cooling the nematic phase (in Vorländer's nomenclature „schlieren phase“ derived from the texture; or „pl“ phase, derived from the azoxyphenyl ethers showing this phase type) of ethyl 4-(4-methoxybenzylideneamino)cinnamate[19,21]



Cr 108 „kr. fl. II“ (batonnets) 117 kr. fl. I (schlieren) 138 I

Cr 108 (Sm B 92) Sm A 118.5 N 139.5 I[45]

he found a second liquid crystalline phase („Stäbchenphase“, derived from the observation of batonnets = Stäbchen during formation from the nematic phase, sometimes called „Pockenphase“ from the observation of a pocken texture; also called „bz“ phase derived from ethyl azoxybenzoate showing this phase type), in modern nomenclature a smectic A phase. Vorländer[21] has included measurements of the dielectric constants made by Prof. E. Dorn (Physical Institute of Halle University), which showed changes at the same transition temperatures, which he had obtained by optical observations. This was the first clear proof of liquid crystalline dimorphism, which had been already claimed in 1906 by Lehmann[46] in cholesteryl caprinate, without indication of transition temperatures .

Cholesteryl caprinate Cr 82.2 (Sm A 77.4) N* 90.6 I

Because in this case the second liquid crystalline phase is monotropic with respect to the solid state, the proof of its existence seemed less convincing.

Vorländer in his early papers several times claimed three liquid crystalline phases in some compounds[21,22]. Later investigations, including DTA and DSC measurements, proved, that Vorländer had observed texture changes and misinterpreted them as phase transitions[47]. On the other hand, in some of his early compounds like ethyl 4(4-alkyloxy-benzylideneamino)cinnamates and the 4,4'-azoxycinnamates in fact several smectic phases existed (in modern nomenclature Sm A, B, C phases), but in this time he was not aware of this fact. However, he reported the full polymorphism of some of these and other smectic dimorphic compounds later[23].This points at the difficulties, to detect phase transitions on the basis of mere texture investigations .

Friedel in his pioneer work of 1922[48] divided the liquid crystals into nematic, cholesteric and smectic phases and coined these terms, which are used until now. He characterized these phases, based on optical observations, in great detail and predicted a layer structure for smectics, which has been confirmed later by x-ray investigations.
It is surprising, that Friedel had compounds with smectic A and B [ethyl 4(4- methoxy-benzylideneamino)cinnamate] and smectic A and C phases [di-n-octyl 4,4'-azoxycinnamate] in his hands, but he did not recognize the respective transitions. He was stick to his theory of the existence of only one smectic phase (in modern nomenclature smectic A) , and with respect to polymorphism of the liquid crystalline state he denied the existence of more than one smectic phase type [48].

After Vorländer's retirement in 1935, in the University of Leipzig Conrad Weygand performed systematic syntheses of liquid crystalline compounds. Until his death in 1945 he was able to produce quite a lot of materials with up to 3 smectic phases[49]. About 1950 G. W. Gray started his predominant work about liquid crystals. He synthesized many homologous series , among them compounds with up to 3 smectic phases.

Despite the fact, that quite a lot of polymorphic liquid crystalline compounds had been prepared, until about 1955 nobody knew, how many different types of smectic phases existed. The main tool of liquid crystal scientists was the texture observation, which lead to the already mentioned classification of Friedel, without any information about smectic polymorphism. The texture observations of Vorländer's and Weygand's school only proved the phase transitions, without nearer characterisation of the smectic phases. Few X-ray investigations showed for single cases the existence of low ordered smectic layer structures (in modern nomenclature Sm A) and layer structures with hexagonal order (now called Sm B)[50].

In this situation in 1957 Sackmann and Arnold began studies of miscibility of liquid crystalline phases of calamitic compounds. In a limited number of cases they found, that the miscibility of the phases is selective. When two phases showed complete miscibility, they were attached to the same phase type. The selectivity means, that never a phase of a certain phase type showed complete miscibility with a phase of another phase type. 4 groups of phases could be established: nematic, smectic A, B, C . Since 1960 Sackmann and Demus continued this work on a broader substance basis, including more detailed texture studies. The phases of one type could be characterized by typical textures, which in many cases can be used for the classification without the necessity of mixture investigations. In the following years additional phase types were established, compiled in Table 3 .

TABLE 3 Detection of phase types of calamitic compounds

Phase type	Reference
Sm A, B, C	1959 [45]
D (cubic)	1968 [51]
E	1973 [52]
Sm F, G	1971 [53]
H	1980 [54]
Sm I	1980 [55]
J, K	1983 [56]
L (crystal B)	1981 [57]
Sm M	1991 [58]
Sm O, Q	1983 [59]

Despite the fact, that the phases of the same phase type derived from chiral and non-chiral compounds can be completely miscible, they can show characteristic differences specially in structures and optical properties.

Because the phase transitions of liquid crystal phase types in homologous series show regular trends, often it is possible to classify the phases of the whole series, after classification of the phases of one typical member of the series. In addition to the classification according to miscibility and textures, structure investigations supported the classification. On the one hand the compounds belonging to the same phase type show common structural features, on the other hand the structure investigation proved the existence of subtypes. The evolution of the investigation of the structures of the phase types has been reviewed by Billard [60]. There are additional single cases of phases not included in the above classification scheme. This points at the fact that the scheme is not perfect, and new cases may be expected. In addition to the original phase types many subtypes (e. g. types with double layers, undulations, twisted structures, intercalation, interpenetration) are known. These subtypes cannot be differentiated by miscibility or simple texture studies and need more sophisticated investigations. The details of the structures can be found in ref.[61a,b,c].

The selective miscibility is a general phenomenon in liquid crystals and could be applied also to discotic materials as a valuable tool for classification[62].

CONVENTIONAL COMPOUNDS

Benzene derivatives

Vorländer already in his early papers pointed at the elongated shape of liquid crystalline molecules, and at the important role of benzene in constructing such molecules. In his book[22a] 1908 he wrote: „In contrast to the aliphatic compounds, the chain of aromatic substitution products on the basis of benzene as a regular hexagon ... is not only linear, but also relatively stiff. Another than the following linear structure is scarcely to be taken in consideration for the para substitution products.“ Fig. 2a,b,c shows his ideas about the para, meta and

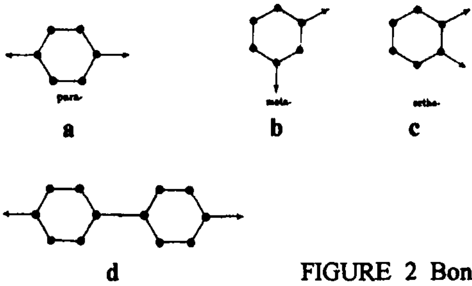
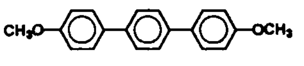
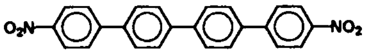
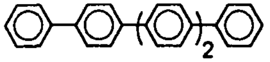
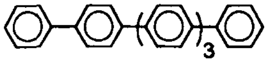
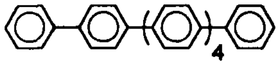


FIGURE 2 Bond directions in benzene and biphenyl after Vorländer[22]

ortho substitution products of benzene, which are still valid. He emphasized, that by bonding several benzene rings in p-position linear molecules are obtained, even when the rings show free rotation around the bond axis (Fig. 2d).

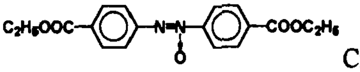
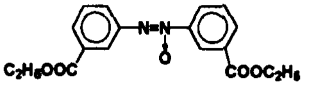
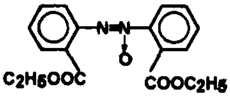
Vorländer proved his ideas by experiments. He was able to show that terphenyl and quaterphenyl still needs endstanding substituents in order to be mesomorphic, but quinquiphenyl is liquid crystalline as such (Table 4). In the meantime polyphenyls up to n = 7 have been synthesized, which are smectic and nematic and serve as ideal stiff rod-like model molecules for checking theoretical considerations [65,101-103].

TABLE 2 Transition temperatures of p-oligophenyls

	T_m	T_{AN}	T_{NI}	Ref.
	259	267	268	[63]
	260	-	290	[64]
	401	-	445	[64]
	440	475	565	[65]
	545	?	?	[66]

Vorländer investigated the 3 isomeric ethyl azoxybenzoates (Table 4) and many other examples. Only in the p-substituted compounds he found mesomorphic properties. However, it is interesting to note that in later experiments he attached larger moieties in m- or o-position , and he obtained compounds which actually are called

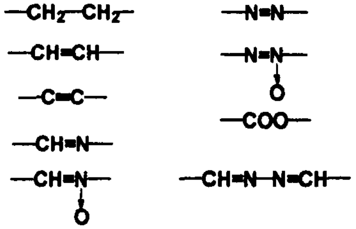
TABLE 5 The isomeric ethyl azoxybenzoates[16]

	Cr 114.5 SmA 122.5 I
	Cr 78 I
	Cr 77 I

„unconventional liquid crystals" (see section below).

Vorländer already in his book 1908 listed several bridge moieties, connecting benzene rings in mesomorphic compounds (Table 6). Later he enlarged the number of bridges step by step, and we can say that he already used the majority of bridges known until now.

TABLE 6 Bridge groups used by Vorländer[22]



In the database LiqCryst 3.4[49] about 59 000 benzene derivatives are compiled. This is about 74 % from about 80 000 compounds over all.

Vorländer synthesized a relatively small number of homologous series[23, 64]. He found the alternation of the clearing temperatures in dependence on the number of carbon atoms, and he explained this in terms of the zig-zag shape of the alkyl chains (tetraeder model of the carbon bonds). In the later works of Weygand[67] and Gray[68] his results have been confirmed and sophisticated on a broader basis.

Most dramatic effects he obtained in changing the length of the middle group in compounds, now called „twins“ or „dimers“ (see section below). From the mesogenic properties of a large variety of compounds Vorländer was able to conclude, that the bond directions in trivalent nitrogen and divalent oxygen and sulphur are not linear, but similar to those of tetravalent carbon, and these atoms can substitute carbon in liquid crystalline compounds without changing substantially the mesogenic properties. For divalent mercury he concluded linearity of the bond directions[23a]. Based on his work about liquid crystals, Vorländer suggested the angular shape of the molecules of H_2O and H_2S, long before this could be confirmed by X-ray analysis.

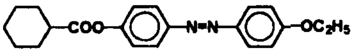
Cyclohexane derivatives

In his search for moieties, useful for liquid crystals synthesis, Vorländer in some cases introduced cyclohexane rings in the molecules, but only in few examples he found mesogenic properties (Table 7). He made several derivatives of cyclohexanone (example 2), among them also non-chiral and chiral derivatives of methyl-cyclohexanones. Also cyclohexane-di-one was a successful moiety (example 3). His attempts to use the cyclohexane carboxylic acid (examples 1 and 4) have been forgotten until 1967, when in the liquid crystal group in the University of Halle cyclohexane was introduced systematically in mesogenic molecules. In some examples Vorländer used cyclohexyl-cyclohexane as building unit, without obtaining mesogenic compounds. Probably he was not able to overcome the separation of the trans and cis isomers.

In 1967 Schubert et al. prepared several alkyl substituted cyclohexane carboxylic acids, which showed mesogenic properties (Table 8, example 1). Another important step was the synthesis of bis-(alkyl-phenyl)-cyclohexanes (example 2) and di-alkyl tercyclohexanes (example 3). These and some other series from Schubert's group proved the usefulness of cyclohexane as a valuable building unit for mesogenic molecules. After substituted cyclohexanoates by the Halle group have been used as valuable materials for practical applications, many research groups started syntheses using the cyclohexane moiety. Actually about 9000 mesogenic derivatives of cyclohexane are known, among them more than 800 subst. cyclohexanoates[49] A review is presented in ref. [109].

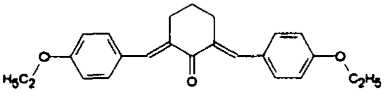
TABLE 7 Cyclohexane derivatives from Vorländer

1.

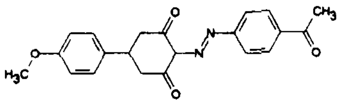


Cr 158 I monotropic l. c.[64]

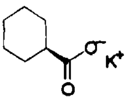
2.



Cr 146.0 N 176.0 I[34, 69]



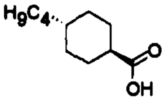
3.
Cr 208.0 (N 186.0) I[70]



4.
Cr 280.0 S >360.0 I[71]

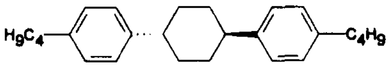
TABLE 8 Cyclohexane derivatives from Schubert's group

1.



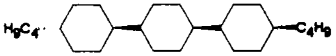
Cr 41.0 N 94.0 I[72, 73]

2.



Cr 89.0 So 107.0 I[74, 75, 76]

3.

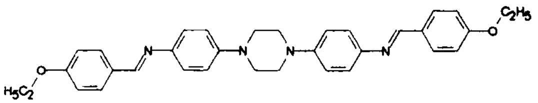


Cr 104.0 So 265.0 I[74, 76]

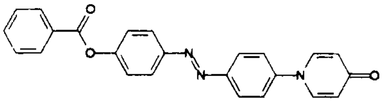
Heterocyclic compounds

Vorländer in single cases successfully used heterocyclic six and five membered rings for syntheses of liquid crystals (Table 9). In addition he applied several other heterocyclic rings, without obtaining liquid crystalline compounds [49].

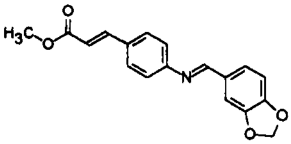
TABLE 9 Herocyclic compounds from Vorländer



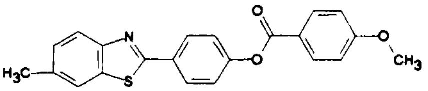
Cr 273.0 N 299.0 decomposition [77]



Cr 259.0 N 315.0 I [78]



Cr 161.0 (S 117.0) I [79, 80]

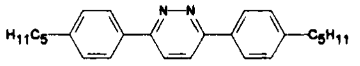


Cr 200.0 N 309.0 I [81]

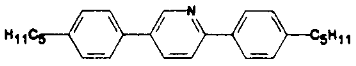
Weygand and Lanzendorf (Tab. 10) in 1938 prepared the homologous series of the di-alkylphenyl-pyridazines, showing nematic and smectic phases.

It has been Schubert with his group, who systematically elaborated new families of mesogenic compounds, using different six- and five-membered heterocyclic rings (Table 10) . Among his several hundred heterocyclic compounds there are some substance classes of importance for practical applications (see section below). Besides the Halle groups, led by H. Schubert and H. Zaschke, specially the group of the NIOPIK Institute Moscow (V. V. Titov,) and the group of Yamanashi University , Japan (Y. Haramoto) have been successful in introducing new heterocyclic rings in the liquid crystal chemistry.

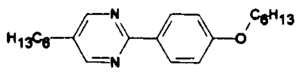
TABLE 10 Heterocyclic mesogens



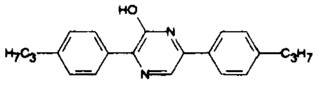
Cr 194.0 S 226.0 N 227.0 I [82]



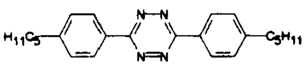
Cr 99 S 205 I [83]



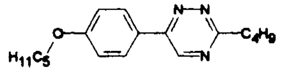
Cr 30.5 N 60.8 I [84]



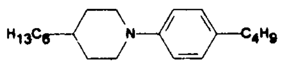
Cr 243 Sm 303 I [85, 86]



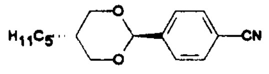
Cr 163.0 N 172.5 I [87, 88]



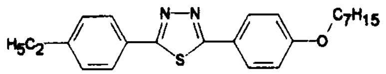
Cr 55.0 Sm A 101.0 I [89, 90]



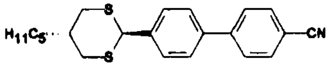
Cr 20.0 Sm B 44.0 I [91]



Cr 56.0 (N 49.0) I [92-97]



Cr 67.0 Sm A 142.0 N 178.0 I [98]



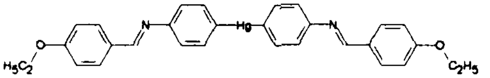
Cr 134.0 N 178.0 I [99, 100]

METALLOMESOGENS

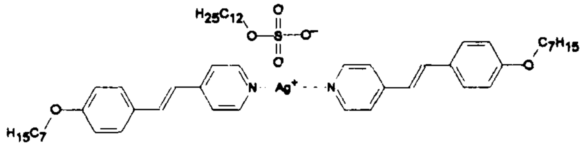
Metallomesogens are metal containing compounds. They can exhibit thermotropic calamitic, discotic and cubic phases as well as lyotropic phases of different structures.

Vorländer already in his early work prepared a lot of salts of aliphatic and aromatic acids, using Li, Na, K, Rb, Cs, NH_4, Tl, Cu, Pb and Al. In order to determine the bond directions of divalent mercury, Vorländer [23, 104] synthesized aromatic mercury compounds, e. g. example 1 in Table 11. From the strong mesogenic properties of the compounds he concluded, that the bond directions in mercury are different from those of non-metals like O and S, „possibly linearly directed".

TABLE 11 Metallomesogens



1 Cr 204.0 N 272.0 I [23, 104, 105]



2 Cr 132.0 S 135.0 C 139.0 cub 152.0 A 179.0 I [106]

The metallomesogens are an actual field of research. Besides the group I and group II metals, transition metals like Ag, Au, Ni, Cu, Co, V, Fe , Cr, W, Mo, Mn, Si, platinum group metals like Pt, Pd, Ir, Rh , Ru, rare earth elements like Lu have been used. The silver complex (Tab. 11 example 2) exhibits the unexpected polymorphism including a cubic phase.

Many of the metal complexes have a molecular shape similar to discotic compounds. Therefore they exhibit columnar phases. For details we refer to the reviews [61d, 107, 108].

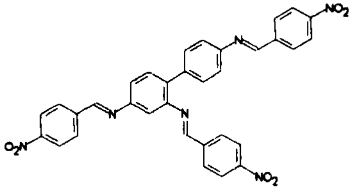
UNCONVENTIONAL COMPOUNDS

During his search for counterexamples of mesogens, Vorländer produced quite a lot of compounds, that in the actual nomenclature are called „unconventional“ liquid crystalline compounds.

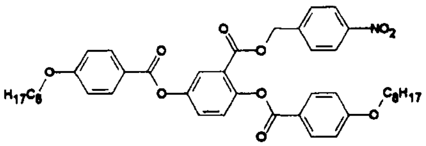
<u>Lateral substituted</u>

In several dissertations of Vorländer's group compounds with lateral large aromatic substituents have been described[110, 11, 121]. Table 12 presents one example. The high clearing temperatures are surprising and may have led to the opinion that the compounds did not seem reliable and have been forgotten for many decades. Not earlier than 1984 more mesogens with lateral aromatic branches have been published[114], and in several papers by Weissflog and Demus since 1986 many compounds with large lateral substituents (e. g. example 2 in Tab. 12) were synthesized. In the solid state example 2 was proved to have a non-planar, but optimally stretched structure[113]. There are laterally substituted compounds showing the bridge to twins (Table 13) [115].

TABLE 12 Lateral substituted compounds

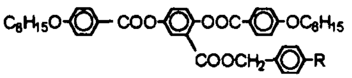


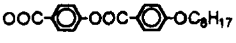
Cr 218.0 X 274.0 dec[110, 111]



Cr 95.9 Sm A 163.9 I[112, 113]

TABLE 13 From laterally substituted compounds to twins [115]



R	Cr		Sc		N		I
-H	•	98	-		•	98	•
$-OC_8H_{17}$	•	89	(•	67	•	104	•
	•	99	(•	88.5	•	151.5	•
	•	130	-	-	•	197	•

According to Vorländer's rule lateral substituents like methyl , ethyl etc. with increasing size suppress the mesogenic properties. This rule has been confirmed later in hundredth of compounds with small lateral substituents [49] . In the light of this knowledge in a paper of 1983 [116] it was highly surprising, that increasing the size of flexible lateral substituents did not completely suppress the mesogenic properties, but lead to a convergence clearing temperature. Fig. 3 shows an example. This effect has been explained in terms of the flexibility of the lateral substituents, that can take a conformation widely parallel to the molecular long axis [116]. This idea later has been confirmed by ^{13}C NMR investigations [117-119]. In the meantime there are many examples of such series [61e, 61f,120] .

From twins to dendrimers

Vorländer himself never used the term twin, but he was the first to synthesize series of compounds which in modern nomenclature are tail-to-tail twins (Fig. 4). From the „oscillation" of the clearing

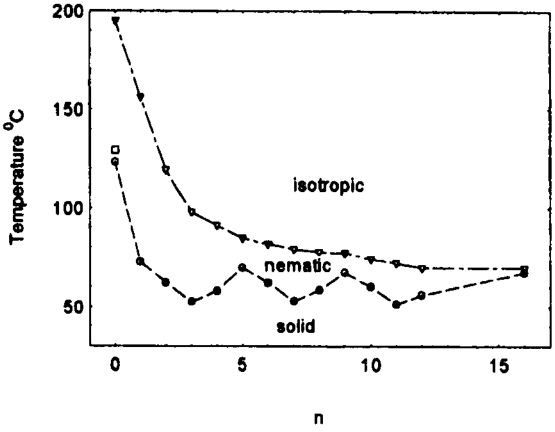
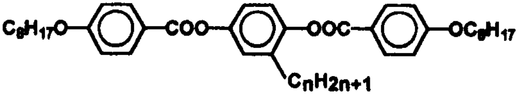


FIGURE 3 Transition temperatures of the homologous series[116]



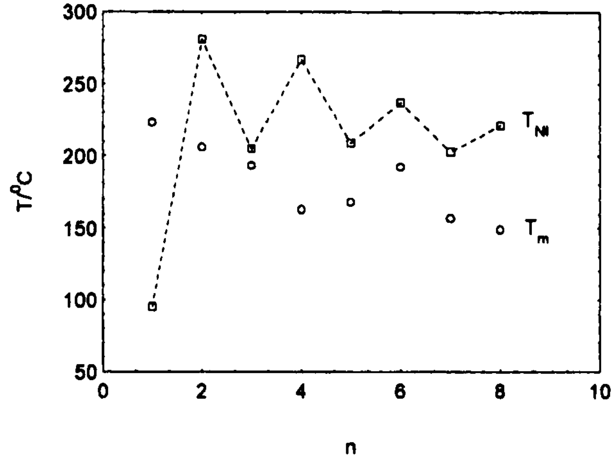
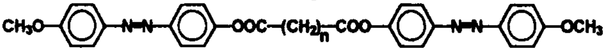


FIGURE 4 Transition temperatures in the series [64]



temperatures he concluded that the the carbon chains possess zig-zag shape, but not circular or spiral shape, which had been still under discussion in this time. He also points at the fact, that with increasing length of the chains their flexibility increases .

The investigation of tail-to-tail twins is an actual topic of LC research, since about 15 years ago Luckhurst in his group started syntheses and detailed physical investigations of these fascinating materials [61g]. There are tail-to-tail twins with intercalated SmA phases [122] , with Sm C_2 phases [124] and with high smectic polymorphism [123, 125] .

Twins can be formed also by lateral linking and by use of small stiff bridges or in form of fused twins. More details can be found in the reviews [61f, 61g] .

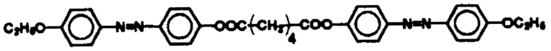
Since the development of the side group liquid crystalline polymers an important principle was used: stiff moieties are connected by flexible spacers. Since the stiff moieties are „decoupled“, they can switch in positions enabling them to form mesophases. Vorländer already mentioned that with increasing length the alkyl chains are becoming more and more flexible [23]. The principle of flexible spacers cannot be used only for the design of dimers, but also for trimers and oligomers of different shape. Tab. 14 shows typical examples of twins, trimers, tetramers and polymers. In all cases the flexible spacers are bond at the tails of the mesogenic moieties.

There are oligomers, that with respect to their „star-like“ molecular structure at a glance seem to be discotic. Tab. 15 presents a trifold substituted benzene derivative. However, due to the flexible spacers the compound exhibits smectic and nematic phases, and the molecular shape should be rather that of formula 2 . There is another striking example derived from tribenzo-cyclononene: Compound 3 due to the flexible spacers is smectic, compound 4 in which flexible spacers are lacking shows a columnar phase.

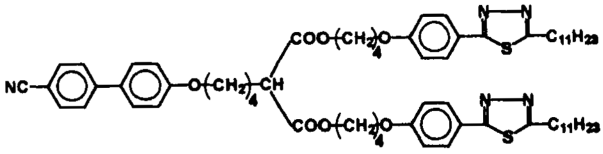
The so-called „H-shaped“ molecules in the liquid crystalline state in fact have a shape in which the stiff mesogenic units can be parallel, as it is necessary in nematic and smectic phases (Tab. 16). This shape also exists in trimers and polymers shown in Tab. 16.

Another highly interesting result is the development of LC dendrimers (Fig. 5) by Percec[139] in 1992. According to the figures published by Percec the molecular conformation should be quite different in the isotropic and nematic state. However, this substantial conformation

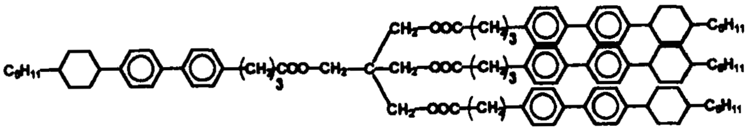
TABLE 14 From dimers to polymers



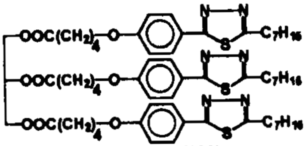
Cr 185.0 N 266.0 I[64]



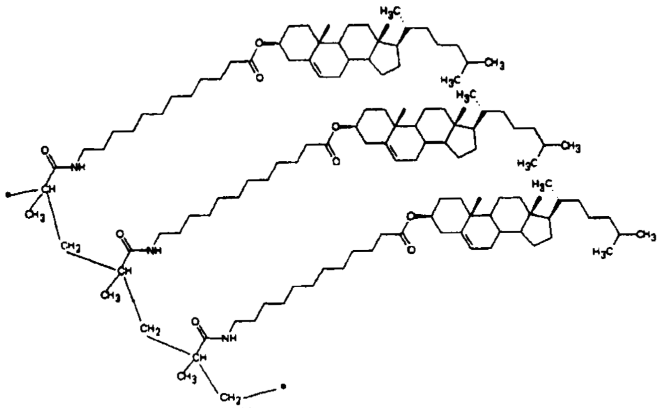
Cr 54 Sm A 103 I[126]



Sm X 152 Sm B 229 Sm A 275 I[127]

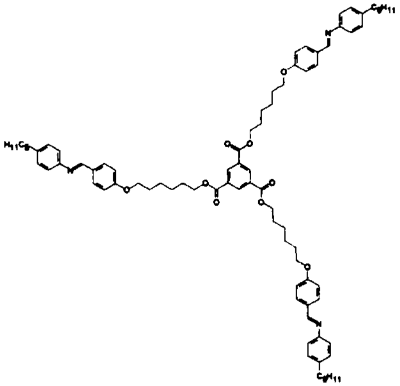


Cr 83 Sm C 98 I[128]

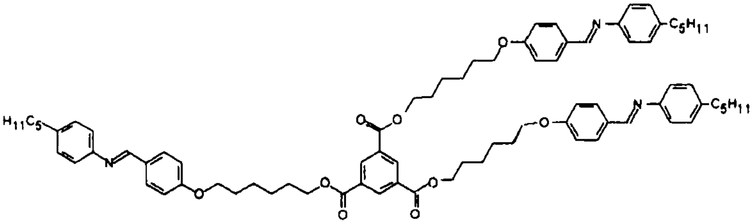


Tg 120 A 180 I[129-131]

TABLE 15 „Starlike“ compounds



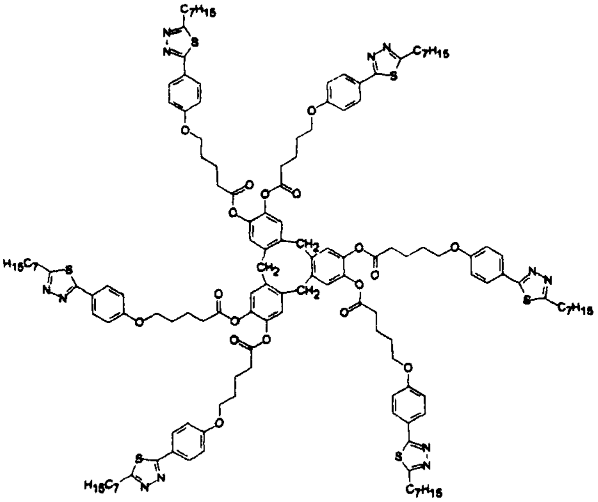
1



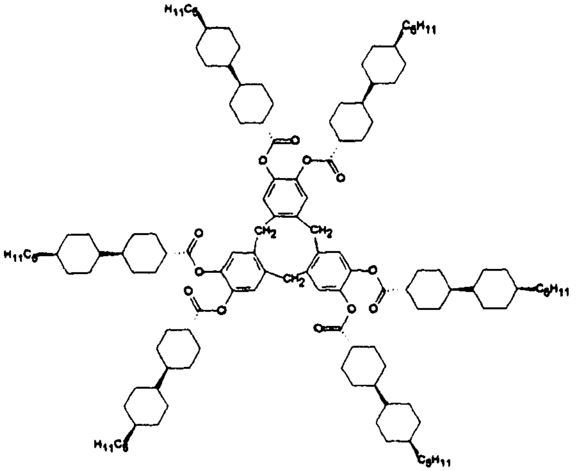
2

Cr ? B ? C ? A ? N ? is[132]

Tribenzocyclononene derivatives

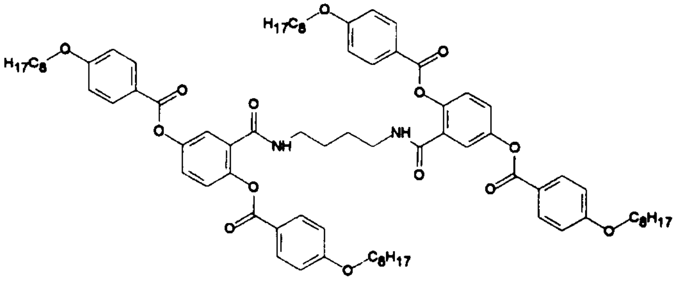


3 Cr 117.0 A 159.0 I[133]

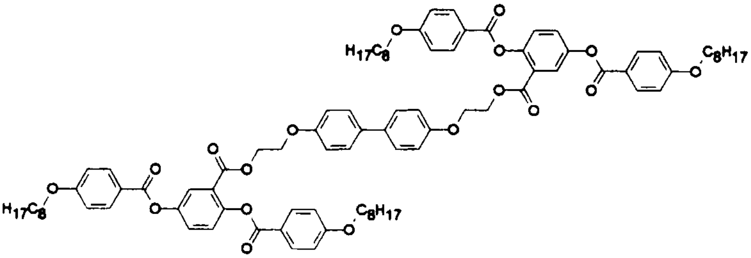


4 Cr 118.0 D 355 I[134]

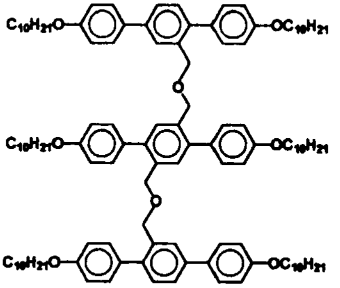
TABLE 16 „H-shaped“ compounds



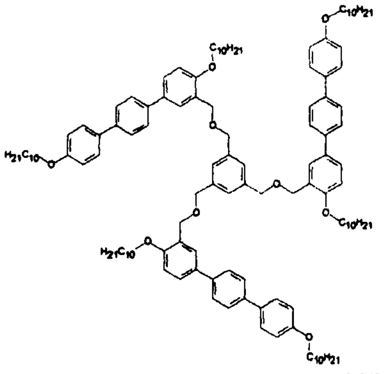
Cr 154.0 (C 115.0) N 172.5 I [135]



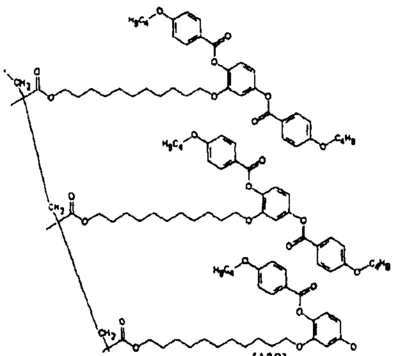
Tg 21.0 Cr 113.0 N 178.0 I [135]



Cr 117.0 A 162.0 I [136]



Cr 80.0 (C 67.0) A 156.0 I [137]



Tg 19.0 N 67.0 is [138]

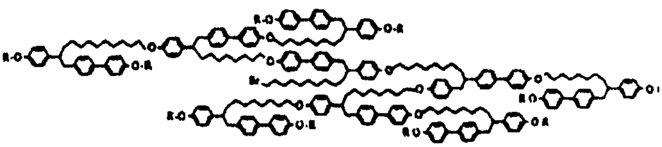


FIGURE 5 Nematic dendrimeric compound [139]

change seems doubtful with respect to the small volume differences of the isotropic and nematic phases. Recently metal containing dendromesogens [147] and dendrimers up to the fifth generation have been reported [140, 141].

The oligomers, consisting of typical mesogenic moieties connected with flexible spacers, can be cyclisized without loosing the mesogenic properties [142, 143] (Fig. 6).

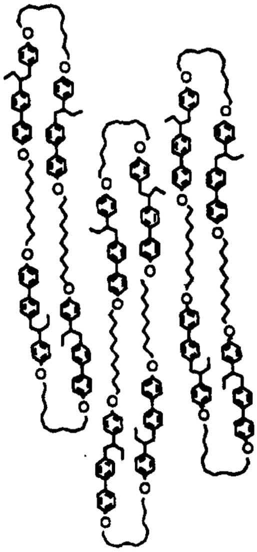


FIGURE 6 Cyclic oligomers [142]

The liquid crystalline elastomers, conceived by de Gennes in 1975 [144] and first synthesized by Finkelmann et al. in 1981 [145], are polymer networks, containing many cyclic units (Fig. 7). They exhibit unique physical properties, which make them promising for practical applications [61h, 61i, 146).

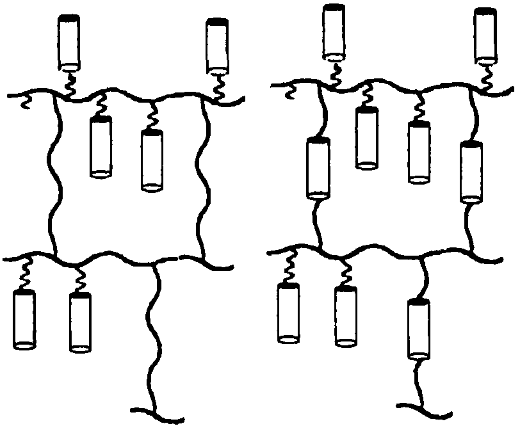


FIGURE 7 Elastomers

Glassy liquid crystals

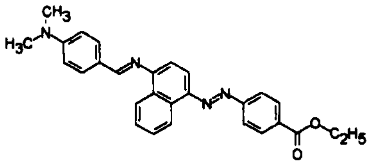
Among the unconventional liquid crystals, with molecular structures deviating substantially from the simple rod-like shape, are many which form glassy liquid crystalline phases at lower temperatures.

Already Vorländer was aware of glassy liquid crystals, which he called „resins" or „lacquers". In his book 1924 [23] he established some relations between molecular structure and the ability to form glassy states. Branched compounds, derivatives of condensed aromatic rings like naphthalene, phenanthrene, ortho- or meta-substituted benzene derivatives have a pronounced tendency to form glassy phases. Specially in the PhD dissertations of Kuhrmann 1926[121] and Baentsch 1931[149] many glass phases have been described. Tab. 17 presents one example, in which the glass transition occurs about room temperature. Vorländer was a very careful experimentalist. He was not fond of scientific speculations or unproven theories. In the famous discussion about liquid crystals in 1931 [150] he stated:

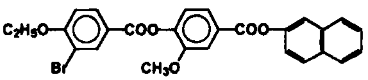
„Considering the partially very theoretically oriented discussion ... I became aware that sometimes the colleagues are lacking the perception of the things... Possibly it would have been better to start there where we stand now ...with a demonstration of the actual phenomena. I would have been able then to show that a schlieren liquid crystal (nematic in

the present nomenclature) *which in the schematic opinion of the colleagues should be always low viscous, in fact is so hard that therewith it would be possible to break anyone's skull".*

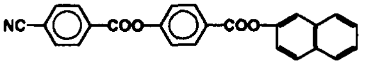
TABLE 17 Glassy liquid crystals



Tg 38.0 Cr 192.4 N 200.4 I[149, 153]



80 mole %



20 mole %

$$\begin{tikzcd}
\text{solid} \arrow[r, leftrightarrow, "136"] & \text{nematic uniaxial} \arrow[r, leftrightarrow, "139"] \arrow[d, leftrightarrow, "95-97"] & \text{isotropic} \\
\text{nematic glass} \arrow[u] \arrow[r, leftrightarrow, "39"] & \text{nematic biaxial} &
\end{tikzcd}$$

[152]

In the period after Vorländer by chance few glassy liquid crystals have been found. In 1990 we published results of comprehensive investigations about glass temperature and molecular structure [151]. Besides confirming Vorländer's perceptions, we were able to show that the stiffness, bulkiness and polarity of the molecules are important factors. Using unconventional low molecular LC molecules, we developed mixtures with glass temperatures above room temperature [152]. Some of them exhibit biaxial nematic phases, which undergo a transition to a uniaxial nematic phase at higher temperature (Tab. 17). When the nematic clearing temperature is lower than the glass temperature, the isotropic phase can be supercooled for a period of days. The run of the phase transition isotropic-nematic in the glassy state then needs several days [152].

Glassy nematic phases are useful materials for thermo-electrooptical storage displays and different optical components[154-159]. Of course, many polymeric liquid crystals also exhibit high glass temperatures. But they have the disadvantage, that the perfect orientation of the material is difficult or impossible. Actually, low molecular and polymeric liquid crystalline materials are known to exhibit glassy states of nematic, different smectic, cubic and columnar types [49, 160, 161].

FERRO- AND ANTIFERROELECTRIC LIQUID CRYSTALS

Ferroelectric liquid crystals

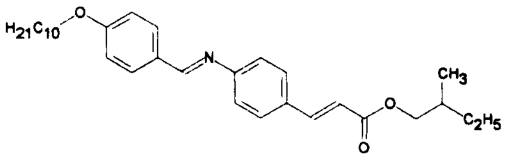
In 1974 R. B. Meyer, in that time at Harvard University, concluded by symmetry considerations, that smectic C liquid crystals composed of chiral molecules ought to be ferroelectric. In 1975 he proved by measurements in the famous „DOBAMC“ (Tab. 18 no. 1) the existence of his prediction [162]. This was the beginning of the fascinating story of FLC's, and later AFLC's as well as several types of ferrielectric liquid crystals, their scientific investigation and introduction in the display applications.

DOBAMBC is one of the best investigated LC compounds, however it was not the first FLC material. In fact Vorländer's pupil Huth [34] in 1909 prepared among other chiral materials two Schiff's bases, made from therephthalaldehyde by condensation with L-methylbutyl p-aminocinnamate and p-amino-α-methylcinnamate (Tab. 18 no. 2). Huth reported about nematic (pl-phase) and smectic (bz-Phase) behaviour of the compounds. After Meyer's publication from 1975 in both original compounds Sm C* phases have been confirmed. In our book „Textures of Liquid Crystals“ photographs of the C* phase of the latter original compound are contained, showing the striated broken fan shaped texture [163].

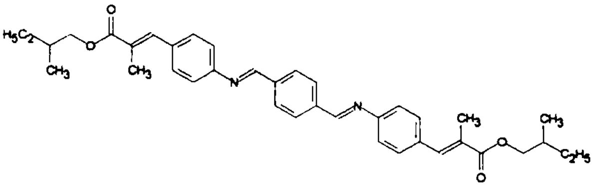
In 1968 Leclerc et al. [164] (Tab. 18 no. 3) reported several chiral substituted biphenyl carboxylic acids, in which due the observation of schlieren textures they concluded on the existence of two chiral nematic phases. In a later investigation, after the establishment of FLC's, the

„low temperature chiral nematic phases" were proved to be smectic C* phases [165].

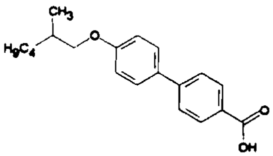
TABLE 18 Ferro- and antiferroelectric liquid crystals



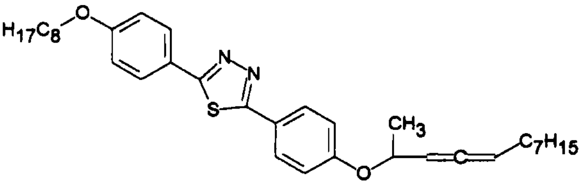
1 DOBAMBC Cr 74.6 (I* 62.0) C* 94.0 A 117.0 I [162]



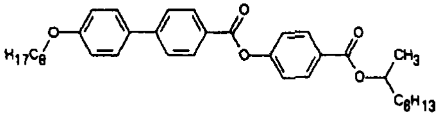
2 Cr 150.0 C* 166.0 A 226.0 N* 262.0 I [34, 163]



3 Cr 171.0 C* 215.0 N* 229.0 I [164, 165]



4 Cr 67.0 C* 99.0 N* 100.0 BP 101.0 I [166]



5 MHPOBC
Cr 84.0 CA* 118.4 C_γ 119.2 C* 120.9 C_α 122.0 A 148.0 I [169, 172, 173, 174]

In the meantime 12070 FLC's are known [49]. The majority of these compounds is derived from chiral alcohols, chiral aliphatic carboxylic acids or chiral ring systems like oxirane and thiirane, five and six membered lactone rings and some heterocyclic rings [61j]. There are few examples which do not contain a centre of chirality (asymmetric atom), e. g. the substituted allenes with axial chirality by Tschierske et al. [166] [Tab. 18 no. 4].

Antiferroelectric LC's

During their search for new ferroelectric materials, the chemists of Chisso Corporation synthesized MHPOBC (Tab. 18 no. 5) and made a joint patent application with Hitachi in 1982 [167]. In a report 1985 [168] the compound was designated as ferroelectric. In 1988 Inukai et al. [169] from Chisso Corporation published several derivatives of the 4-(1-methylheptyloxy-carbonylphenyl) 4'alkyloxy-biphenyl-4-carboxylates containing the famous MHPOBC. In 5 compounds of this type, exhibiting Sm C* phases, they found „a seemingly new phase" called S_γ* below the temperature region of the C* phases. The S_γ* phase showed electrooptical switching with a threshold voltage, a smaller dielectric constant than C* and continuous increase of P_s coming from the C* phase. Because they were unmiscible with the 5 smectic phases of TBBA, they concluded on „a seemingly new phase".

Chisso's samples of the D and L enantiomers of MHPOBC have been reinvestigated by the specialists for FLC's, Fukuda's group at the Tokyo Institute of Technology. In first investigations they found tristable switching, which has been interpreted as switching between chevron and bookshelf geometries in a C* phase [170, 171]. Further investigations let them conclude to antiferroelectric behaviour of the phase [172, 173]. It needed many further detailed investigations, until the complete polymorphism including the detection of ferrielectric phases was established [174].

The AFLC state is now well established [61k, 175, 176]. Actually 538 AFLC compounds are known [49]. On the basis of AFLC's fast switching displays have been constructed and introduced into production.

ASSOCIATED AND SUPRAMOLECULAR LIQUID CRYSTALS

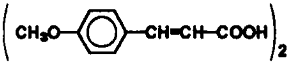
In 1901 van Romburgh [8] found that 4-methoxy-cinnamic acid (Tab. 19 no. 1) between 169^0 C and 185^0 C is in the liquid crystalline state. This was the first example of a liquid crystalline associated compound, which now are also called „supramolecular".

Vorländer already in 1906/1907 synthesized some mesogenic acids (Table 19 nos. 2 and 3) derived from cinnamic acid. He already observed that the esters of 4-methoxy-cinnamic acid are not mesogen in contrast to the free acid [18]. His experiments about mixtures of different acids, published in 1907 [181] are very interesting. He mentioned, that pure 4-methoxybenzoic acid is not liquid crystalline, but he found at least 8 carboxylic acids resulting in mesomorphic mixtures with it. Most of these acids are also not mesogenic in pure state. In total in Vorländer's school more than 200 hydrogen bonded liquid crystalline systems have been detected.

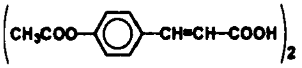
After the Second World War Gray synthesized several homologous series of carboxylic acids [68, 182]. Because at that time the existence of hydrogen bonds has been a well established fact, he was able to explain why the free acids are mesogenic, but their alkyl esters not. The influence of the hydrogen bonds on the stability of the mesophases was demonstrated by the comparison with compounds having deuterium bonds (Tab. 19 no. 4). Because the latter are weaker, the clearing temperatures of the corresponding compounds are lower by some degrees.

Associated systems have been a topic in liquid crystals research in the last 15 years. In addition to the hydrogen bonds in carboxylic acids, specially compounds containing nitrogen atoms were used in order to produce liquid crystalline phases in two component systems. Tab. 19 (nos. 5 and 6) presents examples by Kato et al. for low molecular and also polymeric systems. Kresse et al. [183] were able to

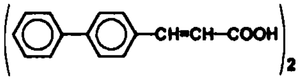
TABLE 19 Associated compounds



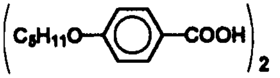
1 Cr 169 N 185 I[8]

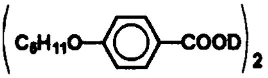


2 Cr 200-205 N ? I [18]

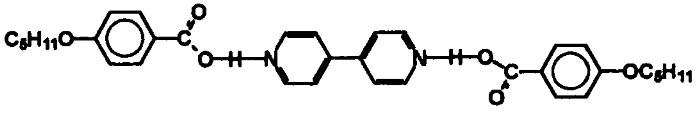


3 Cr 226 N 240 I [176]

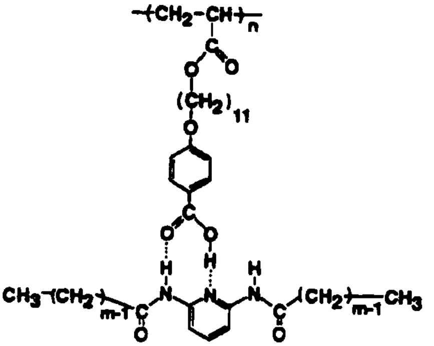




4 Cr 124.4 N 151.4 I Cr 123.4 N 148.4 I [178]



5 Cr 109 Cr 118 Sm A 155 I[179]



6 m = 4 Cr 111 (mesophase 98) I [180]

show that in hydrogen bonded systems rich polymorphism of smectic phases can occur (Fig. 8). More information is available in reviews [61], [188]

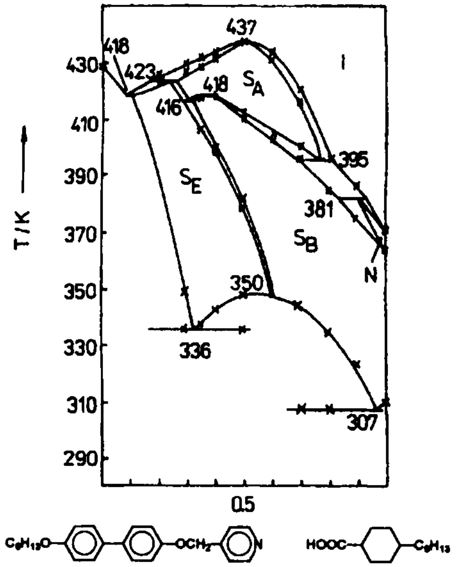
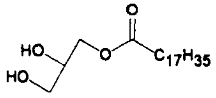


FIGURE 8 Polymorphism in associated compounds [183]

Polyoles

Compounds with several hydroxy groups (polyoles) can exhibit complicated associates, depending on the whole molecular structure. One glycerol derivative of this kind is contained in a dissertation of Vorländer's group:



Cr 81.5 (So 74.0) is [184, 185]

In the original paper [184] the birefringence of the compound was measured, the mesogenic properties have been established later [185].

The ability of scylloinositol ethers to form columnar phases is quite impressive. In a paper by Praefcke et al.[186] it is shown, that depending on the number of free OH groups, single molecules or associates of 2 or 5 molecules form the discs, a review presents more informations [189]. Tschierske et al. have investigated the influence of the molecular geometry on the mesomorphic behaviour in many examples of polyoles, results can be found in his review [187].

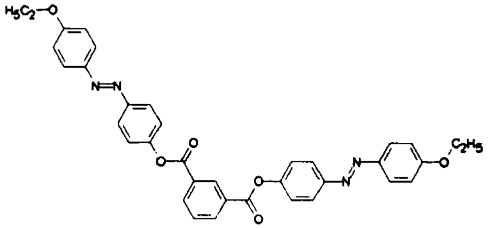
BANANA SHAPED COMPOUNDS

In Vorländer's group some liquid crystalline compounds with unconventional molecular structure have been synthesized , the molecules of which possess a bent structure (Tab. 20 nos 1, 2) . The second example exhibits a smectic phase. It cannot be excluded, that this is one of the actual „banana phases".

In 1994 Matsunaga and coworkers [192] published a homologous series with a molecular structure very similar to that of Vorländer's above examples (Tab. 20 no. 3). They found smectic C phases and phases of an unidentified type.

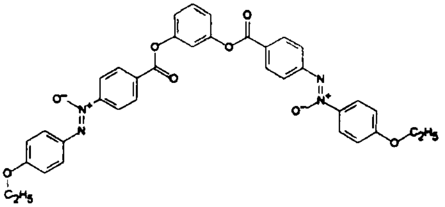
TABLE 20 **Banana shaped molecules**

1



Cr 252.0 X 256.0 [190]

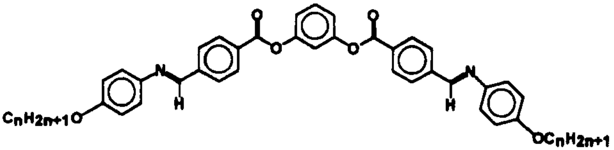
2



Cr 184.0 smectic 218.0 I [191]

The texture of the liquid crystalline phase shows batonnets („Stäbchen"). This points at a smectic phase, may be type A or C or one of the „banana phases".

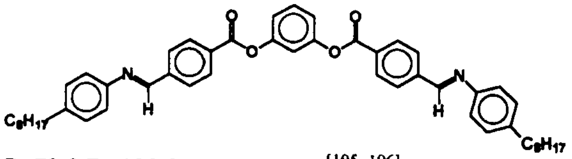
3



Smectic phases of type C and unidentified type [192]

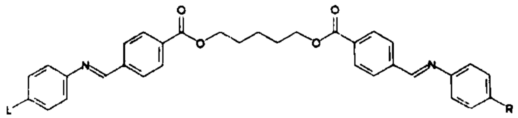
Banana phases were found by [193, 194]

4



Cr 72.2 B_3 139.9 B_2 158.1 I [195, 196]

5



R, L = $-OC_8H_{17}$, $-C_{12}H_{25}$ Banana phases[197]

In 1996 Takezoe and coworkers [195] investigated a compound with banana shape, very similar to Matsunaga's compounds (Tab. 20 no. 4). Despite the fact that the compound is not chiral they found ferroelectric switching on reversal of an applied electric field. This is due to the bent shape of the molecules, which in special packings can induce chirality in the smectic layers and can produce ferro- resp. antiferroelectric properties. These smectic phases are not miscible with the classical smectics and form a special group of phases, called „B" phases. Actually 7 different types of B phases are known [196]. In several compounds with bent molecular shape (among them series no. 3 in Tab. 20) published by Matsunaga et al. in 1994 [192], later up to 3 different banana phases, partly showing antiferroelectric switching, were found. [196]. At present about 20 different series of compounds with bent shape are known to exhibit banana phases [196]. This topic is under active research by several groups and many novel results are still to be expected.

The so-called „boomerang-shaped" liquid crystals, with bent molecules derived from 2,5-disubst.-1,3,4-oxadiazole [198, 199] show pecularities like biaxial orthogonal smectic phases and are suspicious having biaxial nematic phases.

In above sections the flexibility of alkyl chains and the decoupling of mesogenic moieties has been discussed. Contrary to this widespread phenomenon, recently bent-shaped (similar to banana shaped) molecules with central alkylene linking groups have been synthesized, showing antiferroelectric behaviour and double layer resp. frustated layer structures [197] (Tab. 20 no. 5). These properties point at the bent-shaped molecular structure and the quasi rigid character of the central pentylen group.

It is generally accepted, that the story of discotic compounds begins with the paper by Chandrasekhar et al. [200] published in 1977 and the independent publication by Billard et al. [201]. Chandrasekhar et al. [200] found mesophases in sixfold subst. benzene derivatives (Tab. 21 no. 1). It is interesting to note that some of Chandrasekhar's compounds have been synthesized already in 1937 by Backer et al. [202] and in 1943 by Neifert et al. [203], but the mesogenic properties of the compounds have not been detected. Billard et al. [201] found columnar mesophases in sixfold subst. triphenylene derivatives (Tab. 21 no. 2).

Vorländer expected liquid crystalline structures in non-rod-like molecules. In his book [23] on page 35 there is a chapter "Form star-like, cross-like and plate-like molecules liquid crystals?" The same title was given to the Ph. D. Thesis Voigt 1924 [204]. He considered derivatives of gallic acid and triphenyl-benzene, also triphenylene, perylene and others (Tab. 21 nos. 3-5). He explained his idea, that flat molecules could be packed in the manner of Volta's column in order to produce liquid crystalline structures. Volta's column[207] shows exactly the structure of columnar phases . But Vorländer was not successful in finding any LC example in these molecules, because he used too small substituents (methyl or ethyl) .

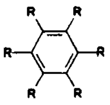
FIGURE 10 Volta's column [207]

It should be noted that de Gennes in 1975 in his book „Physics of Liquid Crystals“ discussed the existence of a nematic phase for thin hard discs in the Onsager approximation [208].

Vorländer investigated systematically salt-like materials. In sodium diphenylacetate (Tab. 21 no. 6) , sodium dibenzylacetate and copper hexanoate (Tab. 21 no. 7) he gave evidence of liquid crystalline phases, which later were shown to be columnar. In 1935 Schadendorff and Verdino [209] in tris(cholesteryloxycarbonyloxy)benzene found a

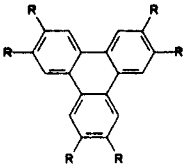
TABLE 21 Discotic liquid crystals

1



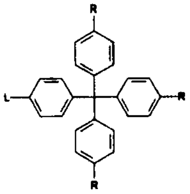
R = $OOCC_nH_{2n+1}$, n= 4 - 9
Chandrasekhar et al. 1977 [200]

2



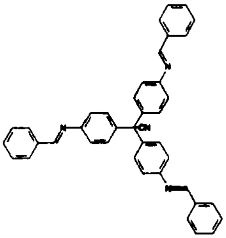
R = OC_nH_{2n+1} , n = 5, 7
Billard et al. 1978 [201]

3



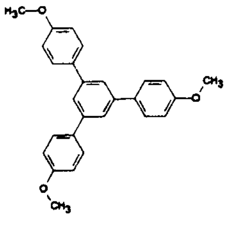
R = -H, -NO2

4



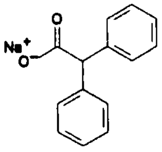
not liquid crystalline
Vorländer and Voigt 1924 [204]

5



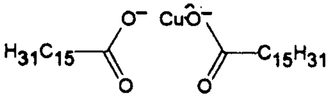
not liquid crystalline
Vorländer 1923 [104]

6



Cr 249.0 D 316.0 is [71, 205]

7



Cr 122.0 D 220.0 dec [71, 206]

mesophase, which according to the later investigation is columnar [210]. The mesophase of di-isobutyl-silane-diol, synthesized by Eaborn in 1952 [211], for long time could not be classified, until its columnar structure was proved in 1980 [212].

After 1960 the so-called „carbonaceous“ mesophases, showing nematic texture characteristics, have been found during the pyrolysis of graphitizable materials [213, 214a]. These mesophases consist of flat polyaromatic molecules, however, not by one defined kind of species. The phases are not homogenic and they could not be characterized in any detail.

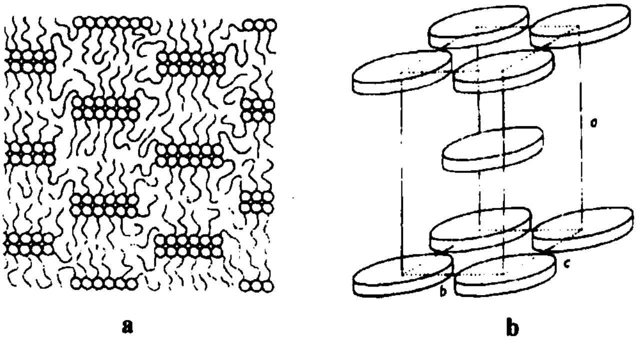


FIGURE 11 Structures in molten alkaline soaps, after Skoulios and Luzzati [217]. a ribbon-like structure, seen in the plane perpendicular to the direction of the elongation of the ribbons b three-dimensional structure with disks

Skoulios et al. [215, 216] investigated alkali and alkaline earth salts of long chain fatty acids. In salts of potassium and rubidium they found ribbon-like structures, that have some similarity to columnar structures. The centre of the ribbons consists of double sheets of molecules with limited breadth, but undefinite length (Fig. 11 a). The ribbons can be arranged in tetragonal or orthorhombic structures. On the other hand, in salts of the said kind three-dimensional structures with disks were identified (Fig. 11 b). The centre of the disks consist of associates of many molecules, whose molten alkyl groups fill the space between the disks.

In the database LiqCryst [49] now 2479 compounds with discotic properties are piled up. They can exhibit discotic nematic, columnar nematic and several different columnar phases. Of special interest are compounds (e. g. polycatenar compounds), which in different temperature regions can exhibit smectic, columnar as well as cubic phases. Details can be found in reviews [61m-p].

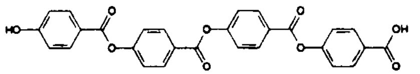
POLYMERIC LIQUID CRYSTALS

In his book [23b] Vorländer in 1924 included a section titled „The nature of the infinitely long molecules“. The section begins with :“*What happens with the molecules if they are further and further elongated? Will the liquid crystalline state finally disappear? According to my experience a limit for such a state by elongation of the chains does not exist, however it may happen that the compounds no longer melt without decomposition, or cannot longer be observed by miscroscopy.*“ Klepl [218] and Emil Fischer [219] already synthesized oligomers or polymers of the 4-hydroxybenzoic acid (Tab. 22 no. 1) without detecting their liquid crystalline properties. Vorländer [23] reported mesomorphic properties not in the polymer, but in the decomposition products after heating. In this and other materials (Table 22 nos. 2-4) he dealt with the first examples of oligomers or main chain polymers.
It was not by chance, that Vorländer looked for liquid crystalline polymers. He also was concerned with not liquid crystalline polymers and resins, which he called „supramolecular“. The most prominent pupil of Vorländer, the later Nobel Price Laureate H. Staudinger (PhD 1903 Halle, Nobel Price for Chemistry 1953), about the same time founded the basis of the polymer science.

Main chain polymers found important applications for the production of superstable fibers and tissues.

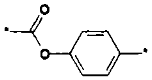
The liquid crystalline side group polymers have been developed after 1970 . They have been mentioned already above.

TABLE 22 Polymeric liquid crystals



1

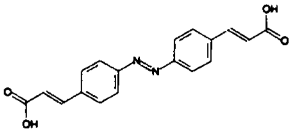
Cr 288.0 N ? decomposition [220, 221, 222]



2 Polymer

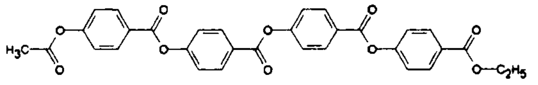
not mesogen, decomposition [221]

Cr 350.0 X 430.0 N ? I [223]



3

Cr 290.0 N ? dec [226]



4 Cr 187 X >296 dec [23, 224]

MATERIALS FOR APPLICATIONS

Vorländer in his book 1924 said [23c] : *„I have been casually asked if the liquid crystals can be used technically? I do not see any possibility for that.* „ This was the situation until the sixties, when the applications of liquid crystals for thermography became known, and when the applications of liquid crystals in optoelectronic displays caused a revolutionary progress in the whole LC research and development.

In fact, since 1941 there existed some patents from Dreyer about the use of liquid crystals for construction of dichroic polarizers [214b, 226]. It seems that these patents never have been used in commercial style.

It is generally accepted, that the starting point of the LCD development was the paper by Heilmeier et al. [227] about the dynamic scattering effect in nematic liquid crystals. This paper was based on former studies of the domain formation in nematics under the influence of electric fields, performed by Williams [228] and independently by Kapustin et al. [229]. It is interesting to note, that as early as 1918 Björnstahl [230] investigated the influence of electric fields on nematics and described the dynamic scattering in much detail. Due to the lack of electronic industry as background, in this time was no need and no chance to use the nematics in displays. Then his paper became forgotten for about 50 years.

In the first reports about the electrooptic effects in liquid crystals compounds with relatively high melting temperatures have been used. (Tab. 23, no. 1) . This is, the displays containing these materials had to be heated. It is worth mentioning, that the low homologues of these cyano substituted compounds have been synthesized in Vorländer's group [231] . The goal of the liquid crystal chemists then was, to synthesize compounds with low melting temperatures, if possible with the nematic state at ambient temperature. Before such compounds have been available, another possibility to obtain room temperature nematics became available. In 1967 Demus [233] published phase diagrams of 3 binary nematic mixtures with low eutectic temperatures. They could be supercooled below room temperature for periods of weeks or months. In patents applied about the same time, but published later, Goldmacher and Castellano described mixtures of Schiff's bases with eutectic temperatures about room temperature and strong supercooling properties [234] .The use of eutectic mixtures of multicomponent systems for applications in displays later became the general technique, applied by all companies of the LCD industry.

The synthesis of MBBA in 1969 as the first compound with a room temperature nematic phase (Tab. 23 no. 2) was a spectacular event. Because of its low chemical stability, MBBA soon has been substituted by more stable materials. Among these was the class of substituted phenyl benzoates (Tab. 23 no. 3), developed in 1970 in the University of Halle and still used in certain mixtures. In the same group in 1971 the first subst. phenylpyrimidines (Tab. 23 no. 4) have been synthesized. Their value for applications became obvious only about 10 years later, when nematic materials with low ratios of the elastic constants K_{33}/K_{11}, and smectic C basic mixtures for ferroelectric materials were needed.

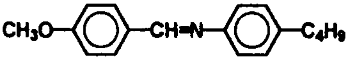
In 1972 the story of the the famous subst. cyano-biphenyls and - terphenyls began with the first publications by the group of the University Hull, headed by G. W. Gray (Tab. 28 no. 5). These compounds are still produced in amounts ot tons per year and provided the breakthrough over the substance problem for TN displays.

TABLE 23 Materials for applications

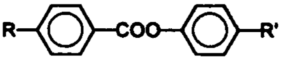
1

R = C_nH_{2n+1}-

n = 1 Cr 128.0 (N ?) I [231, 232]
n > 1 : [235]
R= $C_nH_{2n+1}O$-
n = 1,2 : [231]
n > 1 : [236]

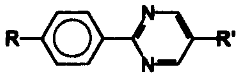


2 Cr 20 N 41 I [237]

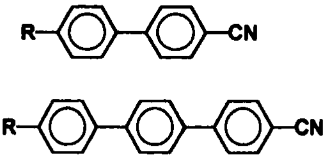


3

R, R' = $C_n H_{2n+1}$-, $C_n H_{2n+1}O$- [238]



4 [239]



5

R = $C_n H_{2n+1}$, $C_n H_{2n+1}O$ [240-242]

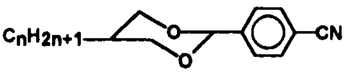
6

R = alkyl, alkyloxy, -CN and others [243-245]

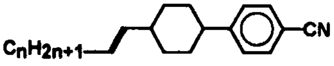
7 PCH's[246]

8 CCH's [247]

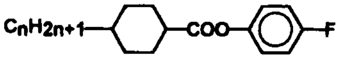
9 [248]



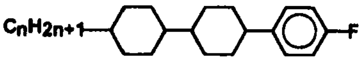
10 [249-253]



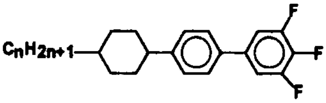
11 [254, 255]



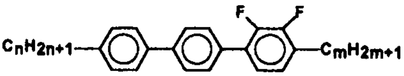
12 [256]



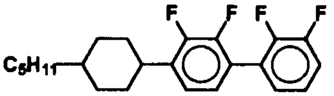
13 [267, 258]



14 [259, 260]



15 [261]



16 Cr <20.0 is [262]

In 1973 by the University of Halle the subst. phenyl cyclohexanoates (Tab. 28 no. 6) have been patented. In addition to the fact, that these materials became one of the most used substance class and are still produced in large amounts, they induced the synthesis of many series containing the cyclohexane moiety. Well known examples of this kind are the PCH and CCH compounds from Merck (Table 28 nos. 7,8), containing structural characteristics of the cyanobiphenyls as well as of the cyclohexanoates. The structural combination of the cyanobiphenyls and the older pyrimidines led to several series of cyano-substituted pyrimidine series, developed by Hoffmann-La Roche (Tab. 28 no.9). The synthesis of the subst. cyano-phenyldioxanes (Tab. 23 no. 10) by the Halle group in 1978 and some months later by Sorkin (USA) as well as by Hoffmann-La Roche proves, that the same ideas arise in about the same time in different places, when the time is ripe.

In all of the already mentioned substance classes as low-polar substituents alkyl or alkyloxy groups have been used. The introduction of alkylen groups, with double bonds possible in different positions, by Hoffmann-La Roche in 1984, was an important step towards the synthesis of „made-to-measure" compounds (Tab. 23 no. 11). The double bonds allow the control of elastic and optic properties, without changing much the dielectric constants.

In mixtures for TN and STN displays in relatively high amounts cyano-subst. materials have been used, in order to obtain the necessary large positive dielectric anisotropy. It turned out, however, that these materials possess a too high electric conductivity as an intrinsic property. In this situation the introduction of fluorine substituents instead of cyano groups brought the solution. In 1981 Chisso applied patents for esters with endstanding fluorine (Table 23 nos. 12 and 13), and then Merck and Chisso simultaneously developed compounds with two or three fluorines in the endstanding benzene ring (Table 28 no. 14). These compounds possess high dielectric anisotropy and low conductivity, as it is necessary for AMLCD's.

When in the eighties the in-plane-switching nematic displays have been constructed, materials with large negative dielectric anisotropy became necessary. For these purposes the Hull group (Table 23 no. 15) as well as Merck (Table 23 no. 16) developed compounds with two, three and four lateral fluorine substituents.

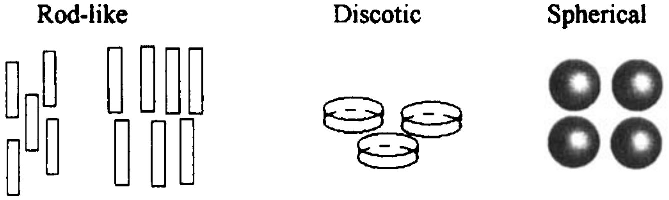
Despite the fact, that now thousands of nematic compounds are available, there is no single compound available with the properties needed for any special purpose. Therefore exclusively mixtures containing up to 15 or 20 compounds for displays are used.

FINAL REMARKS

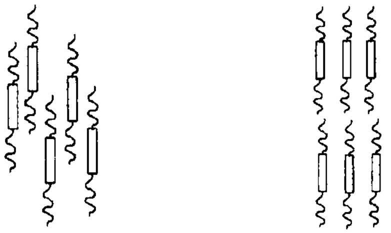
The vigorous development of the chemistry of LC's started with Vorländer's work, about 1902. The development was not continuous, because during both world wars the work nearly disappeared. After World War II it needed about 10 years, until LC research was reestablished in several countries. In 1960 in the tables by Kast [263] 1412 mesogenic compounds were listed. There was a revolutionary progress after the introduction of applications of LC's in displays. This led to the situation, that in 1974 in the table book [264] 5059 compounds were compiled, until 1984 the number increased to 12876 [265] and the actual number is 80080 [49]. In fact, after 1975 the extremely fruitful development of this area continued , and specially in chemistry many spectacular novel results were achieved. There are many types of compounds, different in their geometrical or chemical characteristics, with mesogenic properties. Now it is not the aim to list up these different types, but to try a brief discussion using very general principles, sketched in Fig. 12.

FIGURE 12 Mesogenic molecules

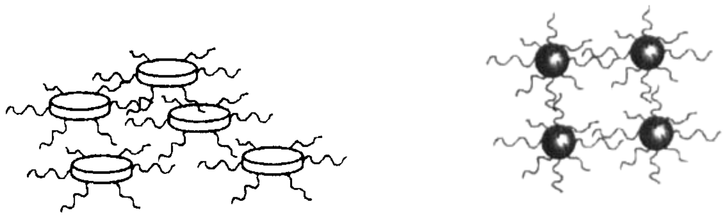
Simple molecules



Intermolecular decoupling by flexible moieties

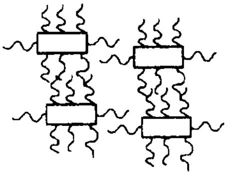


Rod-like molecules



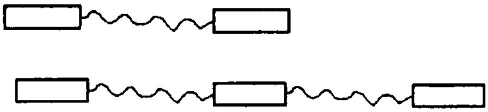
Discotic molecules

Spherical molecules

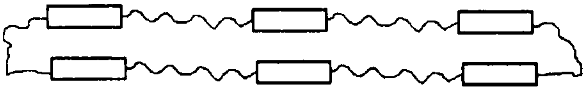


Board-like molecules

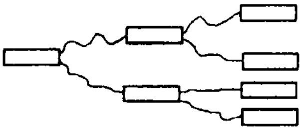
Intramolecular decoupling by flexible moieties



Rod-like twins, oligomers and polymers

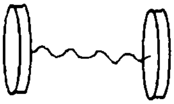


Cyclic oligomers



Dendrimers

Dimers, oligomers and polymers
with discotic moieties



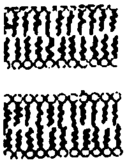
Diabolo-like twins

Supramolecular liquid crystalline structures

Rod-like associates (H-bridges, metal atoms)

disk-like: columnar phases, cubic networks

nematic columnar phases



lyotropic and thermotropic
layer structures

lyotropic supramolecular rods:
hexagonal and rectangular structures,
cubic networks

Spherical supramolecular
associates in lyotropic and
thermotropic liquid crystals

Vorländer has shown, that molecules very similar to rod-like shape exhibit nematic and smectic phases. The best examples are the

Vorländer has shown, that molecules very similar to rod-like shape exhibit nematic and smectic phases. The best examples are the polyphenyls (Tab. 4). Later simple disk-like molecules were proved to show columnar phases [266]. Simple spherical molecules can form plastic phases [267]. But simple molecules form the respective phases rather in exceptional cases, because the intermolecular interaction in most cases is so strong, that rather solid crystalline phases are stabilized. Since long time it is known that intermolecular decoupling of the stiff cores, using e. g. flexible alkyl chains, is a very effective means in order to achieve mesogenic properties. This can be found with rod-like and discotic molecules. Bent molecules (crooked [269], banana-shaped [196], boomerang-shaped [189, 199]) more recently were found to be mesogen. It is very surprising, that there are banana phases in compounds with a central alkylen moiety [197], because in most cases such materials behave as dimers with classical nematic or smectic phases. It would be a small step to test Z-shaped compounds in respect of this property. Molecules with globular cores (e. g. cubane, fullerene) and many flexible substituents could be able to form mesophases, may be of cubic character. Also board-like compounds with many substituents could form mesogenic, may be ribbon or columnar, structures. In general the decoupling by flexible chains is connected with the effect of microphase separation. This effect supports e. g. the formation of smectic phases, and is even more dramatic in fluorinated or silicon containing moieties.

The decoupling is important not only with respect to different molecules, but also as means to adapt the molecular shape to the demands of mesogenity by intramolecular decoupling, as it happens in twins, trimers, oligomers, main chain and side group polymers and dendrimers with rod-like or disk-like moieties. Also in some of these cases microphase separation is playing a role.

And there is another general principle for adapting the effective particle shape to the demands of mesogenity, namely the formation of supramolecular units. The stabilization of supramolecular units is possible by hydrogen bonds, by formation of charge-transfer or metallomesogen complexes and by geometrical reasons. The associates or micelles can be rod-like, disk-like [186, 268], column-like, layered, ribbon-like or spherical [268].

I would like to make a remark about a phenomenon which may be called „molecular electropolymorphism“. It is well known that mesogenic side group polymers show electrooptic effects. There is no doubt, that these effects require the change of the conformations of the molecules via flexible spacers. In the literature few reports exist about the change of the conformation in low molecular compounds, during the change from the antiferroelectric to the ferroelectric state under the influence of electric fields [270, 271]. Calculation of the energy of the interaction of molecular dipoles with electric fields yields small values of few Joule/mole. Since the different conformations of a molecule exist in a temperature dependent equilibrium according to a Boltzmann distribution, in most cases these small interaction energies will not change markedly the equilibrium. According to preliminary experiments of the author, it seems that the best chance to find electropolymorphism exists in systems with microphase separation. The energy situation may be different, when the effect of the electric field is supported by a cooperative effect or steric interaction (entropy effect) in the liquid crystalline phases.

In most projects for applications the molecular structure is modified in order to obtain „to-measure“ properties. This often can be achieved by use of functional groups. For applications the dielectric properties are steered by use of polar groups, introducing dipoles either in longitudinal or lateral directions. Sets of substituents can produce materials with non-linear properties and second harmonic generation. Specific cores introduce electroluminescent properties in the liquid crystals. The insert of chromophoric groups delivers liquid crystalline dyestuffs. The formation of metal complexes can produce liquid crystals with paramagnetic properties, high electrical conductivity or special colour. There are several possibilities to produce mesogenic sensors (mechanical, electrical, chemical, thermal, magnetic, pressure, optical). Complexation in large rings may be used for selection of ions or the formation of selective membrans. Glassy polymers and glassy low molecular LC's provide information storage properties.

Acknowledgement

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