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Plenary Lecture. One hundred years of liquid-crystal chemistry: Thermotropic liquid crystals with conventional and unconventional molecular structure

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Plenary Lecture

One hundred years of liquid-crystal chemistry: thermotropic liquid crystals with conventional and unconventional molecular structure

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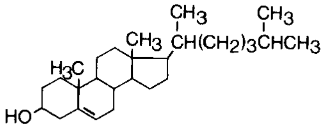
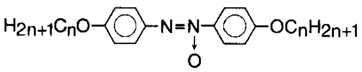
The roots of the chemistry of conventional rod-like liquid crystals are briefly considered. The low-molecular-weight liquid crystals are analysed in terms of rigid groups (rod-like and disc-like ring systems), flexible groups, polar groups and short, linking segments. On the basis of this analysis, the liquid-crystalline compounds actually existing can be classified into 48 types, which are illustrated with the aid of examples. The relationships of low-molecular-weight and polymeric liquid crystals are briefly indicated. Finally, from the presented material, some general conclusions are drawn.

1. Introduction

One hundred years ago Reinitzer [1] and Lehmann [2] detected the liquid-crystalline state in some esters of cholesterol **1**, a natural product occurring in animals. Since the detailed structure of cholesterol was not known before 1932 [3], no conclusion was possible concerning the relation between molecular structure and its liquid-crystalline properties. Gattermann [4] synthesized in 1890 some low homologues of the series of the 4,4′-di-*n*-alkyloxyazoxybenzenes **2**.



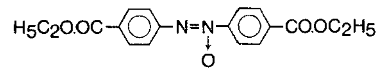
1



2

$n = 1$: *p*-azoxyanisole = PAA
$n = 2$: *p*-azoxyphenetole = PAP

The first smectic compound, diethyl-4,4′-azoxybenzoate **3**, was synthesized by Vorländer [5] and his pupils Meyer and Dahlem [6].



3

The detection of liquid-crystalline properties in these compounds was accidental, the small amount of data did not allow the derivation of rules on the necessary molecular structural requirements for the existence of liquid-crystalline phases.

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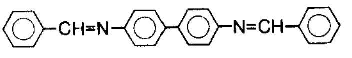
2. Rod-like thermotropic liquid-crystalline compounds

In about 1900 Vorländer in Halle started a systematic programme in order to synthesize new liquid-crystalline compounds and to discover general rules for the interconnection between molecular structure and liquid-crystalline properties. Already in 1908 Vorländer was able to present his rule about the chemical structure of liquid crystals, namely that the liquid-crystalline state is obtained for the most linear shape of the molecules. This rule has proved to be valid until now. Vorländer derived this rule on the basis of many examples [7], selected material is given in table 1.

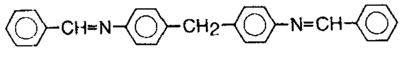
Table 1.

1.



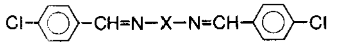
C 234°C N 260°C I

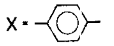
2.



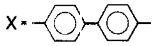
not liquid-crystalline

3.



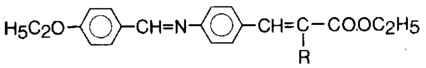


C 180°C N 288°C I



C 265°C N 318°C I

4.



R	C		S		N		I
H	●	81	●	157	●	160	I
CH_3	●	95	●	(77)	●	123	●
C_2H_5	●	73	–	–	●	(62)	●
C_6H_5	●	104	–	–	–	–	●

Example 1 is a typical liquid-crystalline compound with a nearly linear structure, whereas molecules of the second material are bent by about 109° because of the central CH_2 group. The increase in T_{NI} by the addition of aromatic groups in linear molecules is demonstrated by the third system. Example 4 proves the strong decrease of nematic and smectic properties by the influence of lateral substituents of increasing size.

The nematic state is characterized by the ordering of the long molecular axes parallel to the nematic director, which may be expressed by the nematic order parameter. Smectic phases may be considered as consisting of this basic nematic order to which one or several additional order parameters are added. Therefore the theoretical analysis of nematic order is a point of basic importance in understanding liquid-crystalline states. The nematic state may be treated by minimizing the free energy

$$A = -kT\ln Q_c. \qquad (1)$$

The configurational partition function may be given by an expression of the form

$$Q_C = \frac{1}{N!}\int_{\Omega_i} d\Omega_i \int_{R_i} dR_i \exp\left(\frac{-U_C}{kT}\right), \qquad (2)$$

where N is the number of particles. The configurational partition function Q_C is restricted to the configurational part of the potential energy U_C, which is dependent only on the orientation Ω_i and positions R_i of the molecules.

In the framework of van der Waals theories [8–10] the potential energy is dependent on the length-to-breadth ratio X of the molecules, and, considering only dispersive attraction forces, on the mean polarizability α (isotropic attraction) and on the anisotropy of the polarizability $\Delta\alpha$ (anisotropic attraction). This means that the nematic–isotropic or clearing temperature T_{NI} is determined by these molecular properties:

$$T_{NI} = T(X, \alpha, \Delta\alpha). \tag{3}$$

In order to find the relative importance of these various molecular properties, we may try to correlate T_{NI} with them. Generally, it is not possible to change only one physical property of a compound by changing the chemical structure of the molecule slightly. In conventional homologous series the determination of X is difficult because of the flexible nature of the terminal alkyl chains. We have therefore taken a basic molecule and changed it by adding lateral substituents (see figure 1) [11]. It can be clearly seen that there is only a good correlation of T_{NI} with X, but not with α and $\Delta\alpha$. Nevertheless, the isotropic attraction is important in producing a sufficiently high density, and by coupling with the geometrical anisotropy of the molecules it strongly influences T_{NI} [10]. The anisotropic attractive forces (reflected by $\Delta\alpha$) have for a long time been overestimated—they make only a minor contribution to T_{NI}. This will become clear on comparing the properties of aromatic molecules with those of the analogous alicyclic or heteroalicyclic compounds (e.g. table 2 [33]).

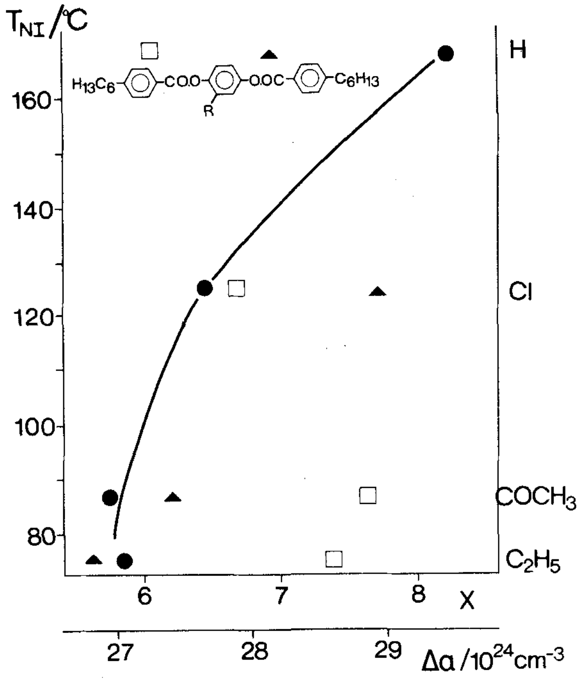
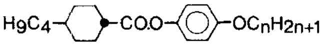
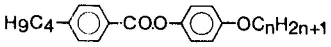


Figure 1. Nematic–isotropic transition temperatures T_{NI} of some liquid crystals plotted against the length-to-breadth ratio X (●), the mean polarizability α (□) and the anisotropy of the polarizability, $\Delta\alpha$ (▲) [14].

For a detailed discussion of the molecular statistical description of the nematic state [8–10] and comparison with experiments [13–17, 139] we refer to the literature cited. Here we mention that the molecular statistical theories can only give a semiquantitative description of the nematic state—the exact quantitative calculation

Table 2. [12, 23]

	n	$T_{NI}/°C$	X	$\bar{\alpha}/10^{-24} cm^3$	$\Delta\alpha/10^{-24} cm^3$
	2	75·7	4·05	34·6	11·6
	4	69·5	4·50	38·2	13·1
	5	66·0	4·67	40·1	12·6
	6	69·0	4·90	41·9	13·9
	2	49·5	3·88	36·4	22·2
	4	45·0	4·09	40·0	22·6
	5	39·0	4·24	41·9	21·8
	6	47·0	4·44	43·7	23·8

of its properties is not possible because of the many simplifications in the models and the mathematical treatment.

The theoretical understanding of the smectic states is still more complex. Many models have been proposed, but they are not without contradictions (see e.g. [18]) and so they will not be discussed here.

Using Vorländer's rule as well as theoretically or empirically founded additional rules, chemists have been able to synthesize about 20000 rod-like thermotropic liquid-crystalline compounds (in the table of Kast 1960 [19] about 1400 compounds are compiled, and in the book of Demus *et al.* 1974 [20] about 5000, with about additional 8000 in the second volume of this book 1984 [21]; according to our estimates about 1000 new liquid-crystalline compounds are synthesized in the world every year.) From a chemical stand-point these compounds cover a large field: aromatic, alicyclic and heterocyclic compounds; rings with four to eight atoms, different flexible chains including perfluorinated alkyl chains as well as unconventional atoms such as Si, Sn, Ge, Hg, Se, Te (see e.g. [15, 72]).

3. The anatomy of liquid crystals

In the last fifteen years several new principles associated with molecular structure have been introduced into liquid-crystal chemistry. Perhaps the most important of these are the discotic molecules [22].

Using a simplifying consideration, liquid-crystal chemistry may be reduced to the basic moieties shown in table 3. By combination of the first three basic moieties, most

Table 3.

Moiety	Symbol
Flexible chain	〰
Core (mainly ring systems)	⬬
Discotic skeleton without flexible chains	●
Short connectors with low flexibility	—
Polar groups	x

Table 4.

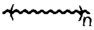
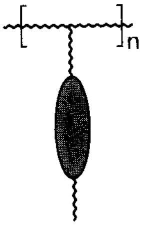
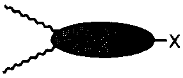
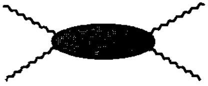
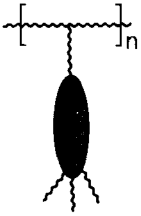
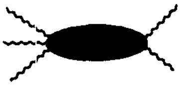
Low-molecular-weight	Polymeric [30, 73–75]
4.1.1. Acyclic 	Flexible main-chain long-chain polymers, e.g. polytetrafluorethylene, polypropylene, [28] 
4.1.2. Rigid molecules 	Stiff-main-chain liquid-crystalline polymers, lyotropic or thermotropic liquid crystals [30] 
4.1.3. One terminal substituent 	Main-chain polymers with flexible moieties [30, 75] 
4.1.4. Two terminal substituents 	Comb-like polymers, Shibaev and Plate [141] 
4.1.5. Flexible central spacer 	
4.2. Polycatenar compounds	
4.2.1. Flexible cyclic 	Mesomorphic polymeric cycloalkanes [28] 
4.2.2. Acyclic branched salts 	
4.2.3. Acyclic branched 	
4.2.4. Acyclic, three chains 	
4.2.5. Polar forked 	
4.2.6. Biforked 	

Table 4 (*continued*).

4.2. Polycatenar compounds	
4.2.7. Hemiphasmidic 	Polysiloxanes [126] 
4.2.8. Forked hemiphasmidic 	
4.2.9. Phasmidic 	
4.2.10. Polar swallow-tailed  	
4.2.11. Swallow-tailed 	
4.2.12. Bi-swallow-tailed 	

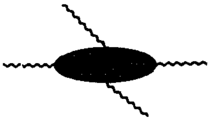
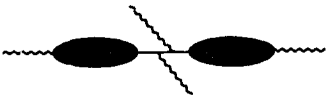
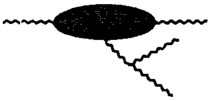
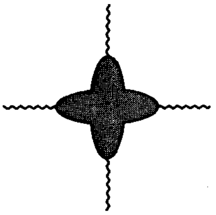
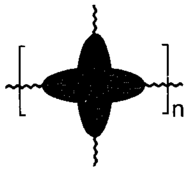
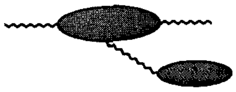
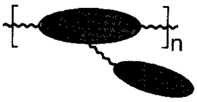
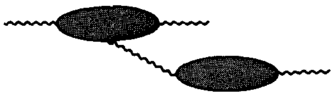
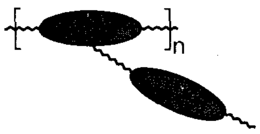
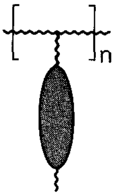
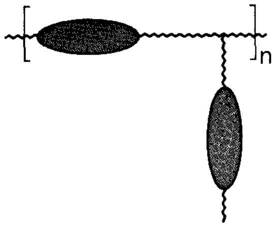
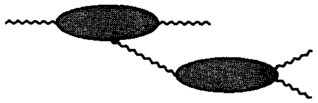
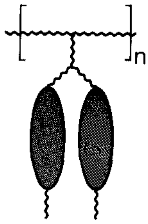
4.3. Compounds with large lateral acyclic substituents		
4.3.1. 	 	Ballauff and Schmidt [119] Stern *et al.* [68]
4.3.2. 		
4.3.3. 		
4.3.4. 		
4.3.5. 		
4.3.6. 		

Table 4 (*continued*).

4.4. Compounds with large lateral ring-containing substituents			
4.4.1.			
4.4.2. Cross-shaped			Sanidic, Berg *et al.* [70, 121]
4.4.3.			Ringsdorf *et al.* [30], Reck and Ringsdorf [122]
4.4.4.			Ringsdorf *et al.* [30], Reck and Ringsdorf [122]
			
			Ringsdorf *et al.* [30], Endres *et al.* [81], Reck and Ringsdorf [82]
4.4.5. Lateral forked			Diele *et al.* [80]

of the known liquid-crystalline compounds, low-molecular-weight species as well as polymers, may be constructed. The data in table 4 give an overview of those possible combinations that have actually been realized. It can be seen that the data are neither highly systematic nor complete.

The aim of this paper is to survey low-molecular-weight liquid-crystalline compounds. Since there are many relations to polymer liquid crystals, the latter are mentioned in table 4, but they are not discussed in any detail.

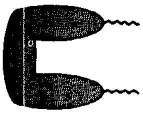
Table 4 (*continued*).

4.5. Twins

4.5.1. Fused twins

4.5.1. Terminal–terminal, antiparallel, rigid

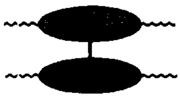
4.5.1.2. Terminal–terminal, parallel, rigid

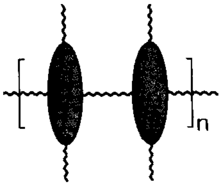


4.5.1.3. Lateral–lateral

4.5.2. Ligated twins

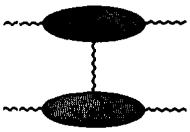
4.5.2.1. Lateral–lateral, rigid

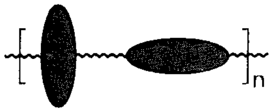




Berg *et al.* [121]

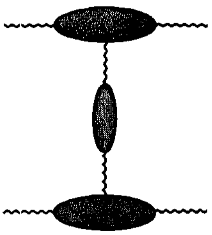
4.5.2.2. Lateral–lateral, flexible acyclic

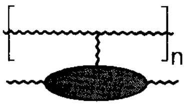




Ringsdorf *et al.* [30]
Finkelmann [75]

4.5.2.3. Lateral–lateral, ring-containing flexible



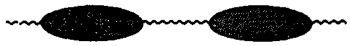


Hessel and Finkelmann [129]
biaxial nematic

4.5.3. Tail-to-tail twins

4.5.3.1. Acyclic 

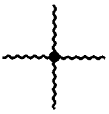
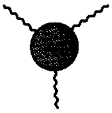
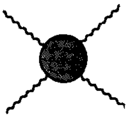
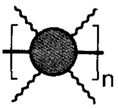
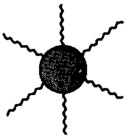
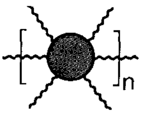
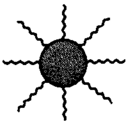
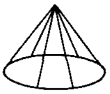
4.5.3.2. Terminal–terminal, flexible

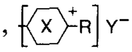


Ringsdorf *et al.* [30], Finkelmann [75]

4.5.3.3. Terminal–terminal, rigid

Table 4 (*continued*).

4.6. Discotic compound		
4.6.1. Acyclic 		
4.6.2. Without flexible substituents 		
4.6.3. Three flexible substituents 		
4.6.4. Four flexible substituents 		Sanidic, Ringsdorf *et al.* [114]
4.6.5. Six flexible substituent 		Kreuder *et al.* [115], Wenz [116]
4.6.6. Eight flexible substituents 		
4.6.7. Pyramidic (cone-shaped; bowlic) 		

Another remark that should be made concerns lyotropic liquid crystals, which are systems of amphiphilic compounds that interact strongly with solvents. Many amphiphilic compounds in their pure state are also thermotropic liquid crystals [20, 21] By addition of polar (–OH, –(CH$_2$O)$_n$–) or ionic (–COO$^-$X$^+$,  Y$^-$) groups, most of the substance types compiled in table 4 should be converted to amphiphiles.

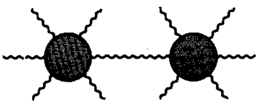
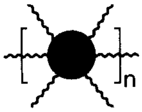
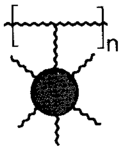
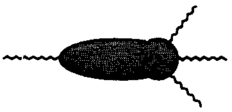
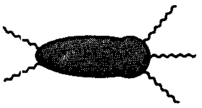
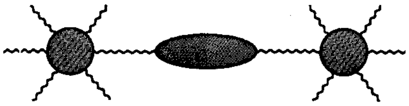
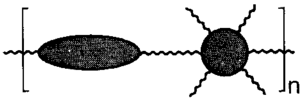
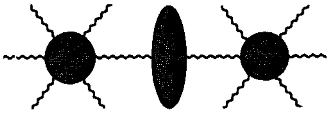
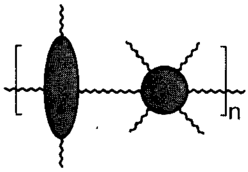
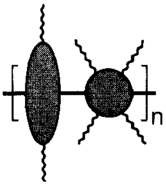
4. From conventional to unconventional liquid crystals

In this section the general types of low-molecular-weight species of table 4 are exemplified by referring to particular chemical compounds and their properties.

4.1. *Conventional rod-like compounds*

All conventional rod-like (also known as 'calamitic') liquid-crystalline compounds exhibit nematic and/or smectic and (in a few cases) cubic mesophases.

Table 4 (*continued*).

4.7. Combined rod-like/discotic compounds			
4.7.1. Discotic twins		 	Kreuder *et al.* [115] Kreuder and Ringsdorf [118]
4.7.2. Hemiphasmidic			
4.7.3. Hemiphasmidic forked			
4.7.4. Phasmidic			
4.7.5			Kreuder *et al.* [113]
4.7.6.		 	Ballauff [120] Sanidic, Ringsdorf *et al.* [114], Ballauff and Schmidt [119]

4.1.1. *Type* 〰 *(acyclic compounds)*

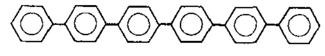
The liquid-crystalline properties of some unsaturated acids and derivatives of some acids and aldehydes have been described [20, 21]. In certain cases their identification as liquid-crystalline phases does not seem to be fully convincing. In addition, the liquid-crystalline nature of *n*-alkanes with chain lengths above 20 carbon atoms remains open [23] despite their strong similarities to smectic B phases. Recently, in perfluorodecyl-decane **4** the existence of a smectic B phase has been proved [24] by the use of optical microscopy, calorimetry and X-ray studies.

$F_3C(CF_2)_9-(CH_2)_9CH_3$ **4**

Many salts of alkane carboxylic acids exhibit mesomorphic phases, some of them with a high degree of polymorphism [20, 21]. There are many derivatives of acyclic sugars that exhibit liquid-crystalline properties (see [123] and references given there).

4.1.2. *Type*  *(rigid cyclic mesomorphic compounds)*

In this class the *p*-polyphenyls **5** (nos. 3699–3702 in [20]) should be mentioned. The first members of most homologous series belong to this class, as well as salts of aromatic acids or cyclohexane carboxylic acids [20].



5

p-sexiphenyl
C 435°C S 465°C N 565°C I [143]

4.1.3. *Type*  *(cyclic compound with one terminal flexible chain)*

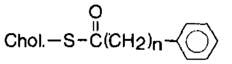
This type is widespread in the field of liquid crystals [20, 21] and does not need elaboration.

4.1.4. *Type*  *(cyclic compounds with terminal flexible chains at both ends)*

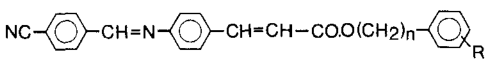
This type may be considered as the most common variant [20, 21].

4.1.5. *Type*  *(two ring-containing compounds linked by a flexible group)*

The series of the thiocholesterol ω-phenylalkanoates **6** [25] and substituted cinnamates of ω-phenylalkanols **7** [26] belong to this class.

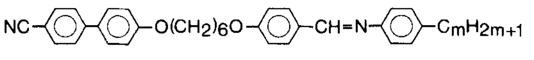


6



7

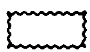
The compounds of this type are related to the tail-to-tail twins (see §5.3), in which both ring-containing moieties of the molecule are equivalent. Very recently, Hogan *et al.* [125] have reported polar compounds of this type **7a** with nematic properties.



7a

4.2. *Polycatenar compounds with terminal flexible chains*

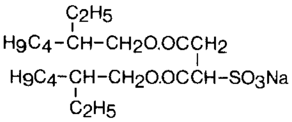
The term 'polycatenar' was introduced initially by Nguyen *et al.* [27] for the designation of some series terminally bisubstituted with long alkyloxy chains. Since there are many types of liquid-crystalline compounds possessing more than two flexible chains, we propose the term polycatenar as a general designation for all of these compounds.

4.2.1. *Type*  *(flexible cyclic compounds)*

According to Möller *et al.* [28, 29], the cycloalkanes with 12–96 methylene groups are able to form mesomorphic phases. The molecules form lamellar structures with hexagonal order in the lamellae, and the flexible rings are folded. The axial symmetry must be the result of complex segmental molecular motions with correlation times smaller than 10^{-8} s (dynamic conformational disorder).

4.2.2. *Type*  (*acyclic branched salts*)

Several salts of this type are known to exhibit mesomorphic phases, e.g. **8** [31].



$$\begin{array}{l} \quad C_2H_5 \\ H_9C_4-CH-CH_2O.OCCH_2 \\ H_9C_4-CH-CH_2O.OCCH-SO_3Na \\ \quad C_2H_5 \end{array}$$

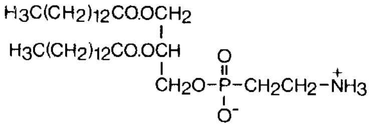
8

sodium di-2-ethylhexylsulphosuccinate; room temperature: middle modification

Compound **8** could be imaginated as having an elongated shape; however, since in mesophases of salts there is a separation of the polar and the non-polar groups, the molecule must be folded. The thallium α-substituted alkanoates do not exhibit mesophases [32]. In [30] several quaternary ammonium salts and dialkyl phosphates of these structures are mentioned that are able to form bilayer membranes. In many cases amphiphiles with such properties also exhibit thermotropic mesomorphism. According to Ringsdorf [30], these compounds should be called amphotropic, which means both lyotropic as well as thermotropic.

4.2.3. *Type*  (*acyclic branched compounds*)

Natural and synthetic lipids [20, 30] (e.g. kephalines **9**) belong to this type.

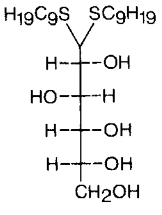


$$\begin{array}{l} H_3C(CH_2)_{12}CO.OCH_2 \\ H_3C(CH_2)_{12}CO.OCH \quad O \\ \qquad\qquad CH_2O-\overset{\|}{P}-CH_2CH_2-\overset{+}{N}H_3 \\ \qquad\qquad\qquad O^- \end{array}$$

9

C 120°C S 200°C I

Eckert *et al.* [124] have described several series of aldose dithioacetals with mesomorphic properties (e.g. **9a**). The compounds are identified as smectic, probably with a new phase type.

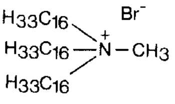


9a

C 101·6°C S 125·8°C I [124]

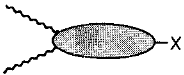
4.2.4. *Type*  (*acyclic compounds with three flexible chains*)

Kunitake *et al.* [34] have synthesized salt-like compounds of this type that in water-containing systems exist as a liquid-crystalline bilayer over certain temperature intervals (e.g. **10**).

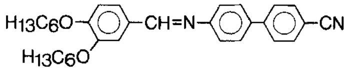


10

as bilayer: C 48·6°C mesophase 60·0°C I [34]

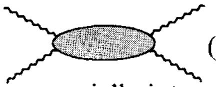
4.2.5. *Type* -x (*polar forked compounds*)

Compounds of this type have been synthesized by Nguyen *et al.* [35] and by us [36]. The compound **11** has been investigated by X-ray diffraction, the smectic A phase showed $d/L = 1{\cdot}25$. This means it is an S_{A_d} phase, the terminal branches in the 3-position at the opposite end with respect to the polar group do not prevent association as found for even small substituents such as F and Cl in the 3-position near the CN group [37–39].

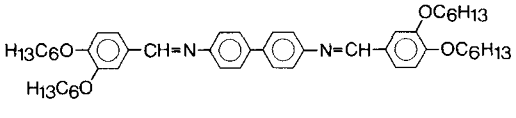


11

C 131°C S_{A_d} 141°C I [36]

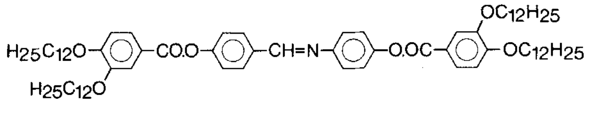
4.2.6. *Type*  (*biforked compounds*)

This is an especially interesting class of compounds, with a rich polymorphism. The four-ring compound **12** is not mesomorphic [36]; however, the four-ring compound **13** forms a smectic C phase [40].



12

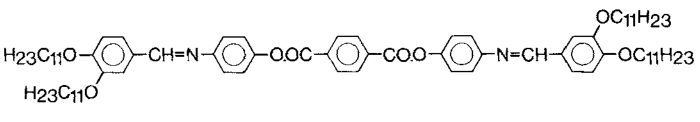
C 171°C I [36]



13

smectic C [40]

There is a remarkable number of biforked five-ring compounds, which may have an extremely unusual polymorphism, e.g. compound **14** [41].



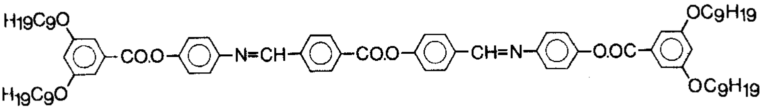
14

$$\begin{tikzcd}
\text{C} \arrow[r, "144^\circ\text{C}"] & S_C \arrow[r, "146^\circ\text{C}"] & \text{cubic} \arrow[r, "163^\circ\text{C}"] & \text{I} \arrow[dl, "158^\circ\text{C}"] \\
 & \text{cubic} \arrow[u, "140^\circ\text{C}"] & \text{hexagon. column} \arrow[l, "147^\circ\text{C}"] &
\end{tikzcd}$$

[41]

This forms the classical S_C phase, an optically isotropic cubic structure and a monotropic two-dimensional hexagonal columnar phase. A lower member (C_7) of the same series has only S_C, and a later member (C_{14}) the hexagonal columnar phase [41]. Compounds of this type are therefore the link between columnar and smectic phases.

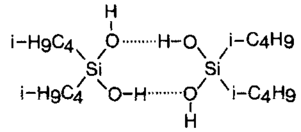
There are also biforked compounds with both lateral substituents in the *m*-position (e.g. **15**), which are also able to form columnar phases.



15

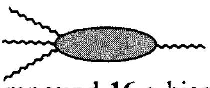
C 96°C hexagonal 112°C I [44]

The compound di-isobutylsilanediol **15a**, according to [130] forms dimers that are comparable in their shape to biforked compounds and exist in a columnar structure.

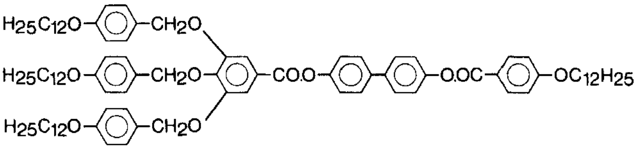


15a

C 89·5°C columnar 101·5°C I [131]

4.2.7. *Type*  (*hemiphasmidic compound*)

In the compound **16** a biaxial nematic phase (N_b), in addition to a uniaxial one (N_u), has been detected for the first time [42].

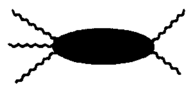


16

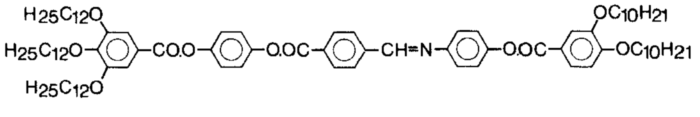
$$\begin{tikzcd}
C_2 \arrow[r] \arrow[drr, "82°C"] & C_1 \arrow[r, leftrightarrow, "86°C"] & I \\
N_u \arrow[u, "65°C"] \arrow[rr, leftrightarrow, "69°C"'] & & N_b \arrow[u, "86°C"']
\end{tikzcd}$$

[42]

In both phases cybotactic groups exist, in N_u of the type S_A, in N_b of the type S_C. The biaxial nematic phase probably exists because of a strong hindrance of rotation around the long molecular axis.

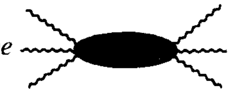
4.2.8. *Type* 

Compound **17** [40] exhibits a hexagonal columnar phase with a lattice spacing of 46·9 Å. The structure of the hexagonal phase is similar to that of lyotropic hexagonal structures. The paraffinic chains have a low order with a larger area than in thermotropic lamellar structures.

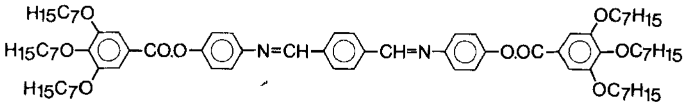


17

C 75°C hexagonal mesophase 132°C I [40]

4.2.9. *Type*  (*phasmidic compounds*)

The term 'phasmidic' (derived from the Greek *phasma*) was introduced by the Bordeaux group [45] for compounds with each three terminal flexible substituents at both ends, because of the similarity to certain insects called phasmids. Typically they form hexagonal columnar phases [40, 45, 46], e.g. **18**.



18

C 80°C hexagonal columnar 82°C I [45, 46]

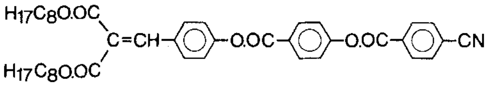
Phasmidic compounds consist of a rod-like nematogenic central part and half-discs at both extremities.

Swallow-tailed compounds

Liquid-crystalline compounds with ramifications outside the ring system have been termed 'swallow-tailed' by us [51]; there are several types of these.

4.2.10. *Type* x (*polar swallow-tailed compounds*)

We have synthesized swallow-tailed compounds with a terminal cyano substitutent, e.g. **19** [47].



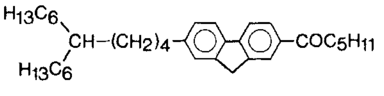
19

C 102°C N 115°C I [47]

All members of the homologous series are nematic with a small negative dielectric anisotropy, $\Delta\varepsilon$ of about $-0{\cdot}15$, which is caused by intramolecular compensation of the longitudinal components of the dipole moment. There is no indication of dimerization of these molecules. The compounds show an interesting electrooptic phenomenon. Above a threshold voltage of 5 V (cell thickness 10 μm) with tin oxide electrodes, there appear striped domains parallel to the initial director orientation (planar homogeneous) with a width of about three times the sample thickness. These domains show all the features of parallel surface-induced flexoelectric domains, which have been investigated in detail by Hinov and Vistin [48]. The asymmetrical shape of these swallow-tailed compounds should be conducive to the promotion of flexoelectric phenomena.

4.2.11. *Type*  (*swallow-tailed compounds*)

There is one series of these compounds made by Malthete *et al.* [49, 50] e.g. **20**.

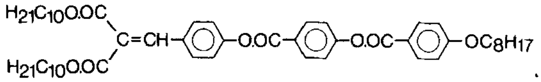


20

C 36°C S_A 52°C I [49]

These substances exhibit smectic A phases.

We have synthesized and investigated three-ring swallow-tailed compounds of the type **21**.

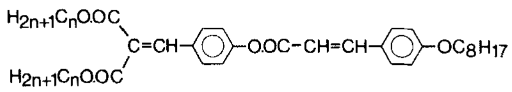


21

C 63°C (S_C 55°C) S_A 84°C N 91°C I [51]

All members of the series up to C_{16} exhibit the same polymorphism. From dielectric measurements, we have found evidence for strong antiparallel packing of the molecules in the liquid-crystalline state [52–54, 117], which should be caused mainly by the strong molecular-shape anisotropy. The antiparallel arrangement allows dense molecular packing, which is a general principle of condensed matter physics (see e.g. [55]). We have investigated the S_A phases of several members of this series using X-ray diffraction [56]. Obviously the two alkyl chains of the swallow tails tend strongly to a parallel orientation and, owing to the antiparallel packing, the conformations with the maximal molecule lengths are favoured; therefore the layer thicknesses in higher members of the series are in better agreement than usual [58] with the lengths of the molecules in their most-extended form. For the first time we have observed an additional incommensurate structural element (low-angle crescent-like reflections) in weakly polar compounds, which we interpret in terms of strings of interdigitated molecules.

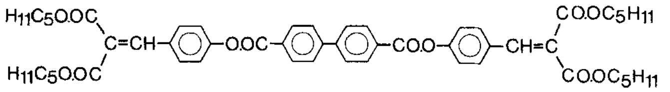
The idea of more or less parallel-oriented alkyl chains in the swallow tails is supported by the fact that in two-ring compounds of the type **22** the T_{NI} decrease to a minimum in the series at C_6 and again increase significantly for the later members [51]



22

4.2.12. *Type*  *(bi-swallow-tailed compounds)*

There is one homologous series of this type, e.g. **23**.



23

C 95°C (S_C 61°C) N 151°C I [51]

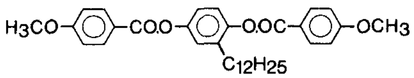
X-ray investigation [59] of the nematic phase of this compound showed the existence of skewed cybotactic groups [60]. Additionally, diffuse scattering on the meridian is incommensurate with the molecular length and indicates the existence of strings of molecules. Surprisingly we have found in binary systems of **23** with other non-polar compounds strongly induced S_A phases [57, 59]. Their existence may be explained by the steric effect of filling the gaps in the central part of the bi-swallow-tailed molecules by smaller species; therefore we propose the term 'filled smectic A phases' for these.

4.3. *Compounds with large lateral substituents (lateral long-chain substituents without ring systems)*

There are several kinds of this type, which in the general sense are also polycatenar; however, the additional flexible chains are not attached in terminal positions.

4.3.1. *Type*  *(lateral long-chain substituent attached to the basic ring system)*

There are several examples of this type, e.g. **24**.



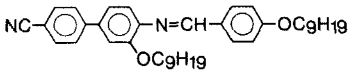
24

C 90°C (N 56°C) I [61]

All members of the series are nematic, with a trend of T_{NI} towards a limiting value [61]. This may be explained by an orientation of the lateral alkyl chains nearly parallel to the basic molecule.

4.3.2. *Type*  *(lateral long-chain substituents attached to the basic ring system, one terminal chain)*

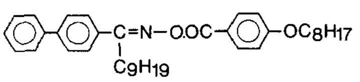
This type may be represented by the polar species **25**, an example of a nematic series.



25

C 95°C (N 65°C) I [36]

Compounds such as **26** are also of this type since the C = N group to which the lateral substituent is attached is in conjugation with the aromatic ring system and may therefore be considered as a part of it. The whole series is nematic.

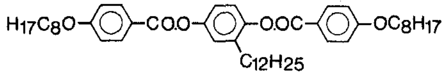


26

C 98·5°C (N 39°C) I [62]

4.3.3. *Type*  *(lateral long-chain substituent attached to the basic ring system, two terminal chains)*

We have dealt with several homologous series of this type [61], e.g. **27**.

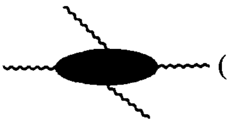


27

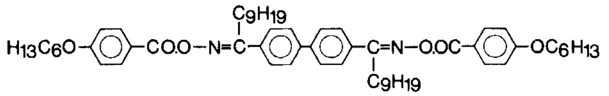
C 56·2°C N 69·2°C I [61]

The members of this series with variable lateral substituent have been investigated in detail using calorimetric, dilatometric, refractive-index, dielectric-constant, viscosity, order-parameter, miscibility and X-ray studies [63–65] and compared with the predictions of molecular statistical theories. The most important result is that the lateral alkyl chains are more or less parallel to the long axis of the basic molecule. So the converging trend of the transition temperatures T_{NI} and several other features can be explained. N.M.R. results [66] also support this idea.

The lateral long-chain substituents may also consist of other groups such as -S-alkyl, -COO-alkyl, -COO- (chiral alkyl) [67].

4.3.4. *Type*  *(two lateral long-chain substituents attached to the basic ring system)*

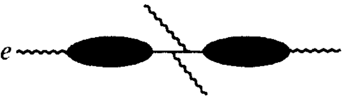
The liquid-crystalline state is not prevented even by two long lateral substituents, e.g. **28**.



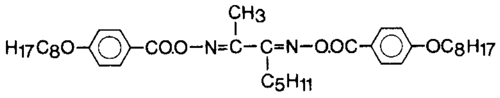
28

C 99°C N 151°C I [62]

The whole series with varying terminal alkyloxy chains or alkyl chains are nematic [62].

4.3.5. *Type*  *(two lateral long chains attached to the acyclic central part)*

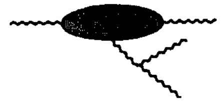
This type is represented by **29**.



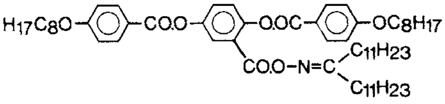
29

C 89°C (N 78·5°C) I [62]

The nematic series is found with only relatively small lateral alkyl chains, which strongly depress T_{NI} of the basic compound.

4.3.6. *Type*  *(lateral swallow-tailed substituent)*

There is one series of this type, e.g. **30**.



30

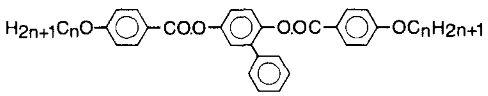
C 74°C (N 43°C) I [67]

The swallow-tailed substituent causes a strong suppression of the liquid-crystalline properties. The nematic behaviour may be explained by an antiparallel orientation of the two lateral alkyl chains in order for the molecules to have an optimal length-to-breadth ratio.

4.4. *Compounds with large-ring-containing substituents*

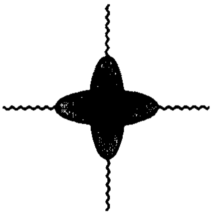
4.4.1. *Type*  (*lateral unsubstituted ring rigidly attached to the central core*)

Cox *et al.* [69] have synthesized the homologous series **31**, which exhibits liquid-crystalline properties.

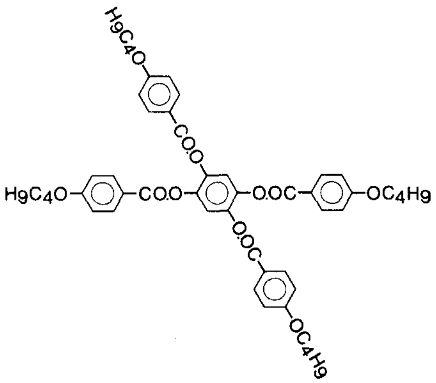


31

monotropic nematic [69]

4.4.2. *Type*  (*cross-shaped mesogens*)

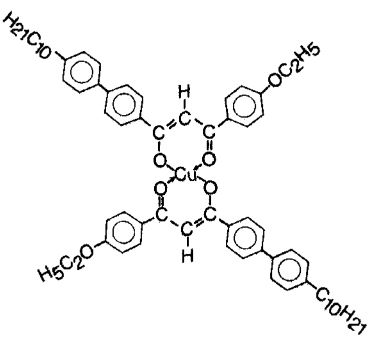
Berg *et al* [70] have reported about some liquid-crystalline cross-shaped compounds, e.g. **32**.



32

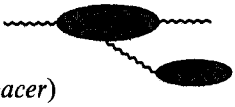
C 121°C (N 120·5°C) I [70]

The mesogenic behaviour of this compound is extremely surprising, since the COO-groups are not flexible enough to allow a more rod-like shape of the whole molecule. Another compound belonging to this class is **32a**. In this substances and also in some homologues Chandrasekhar *et al.* [131] have found biaxial nematic phases. This substance type may be considered as combining the features of rod-like and discotic compounds. It seems probable that there are also biaxial nematic phases in other compounds with bulky lateral substituents that have yet to be investigated in detail.



32a

C 186·6°C N_b 168·5°C I [131]

4.3.3. *Type*  *(lateral unsubstituted ring attached to the central core by a spacer)*

Recently we have described [71] several compounds of this type, among them the homologous series given in figure 2. The strong alternation of T_{NI} suggests the flexibility of the lateral spacers—a fact that is well known in polymer liquid-crystal chemistry [73, 74]. The bulky lateral substituent, similar to tertiary butyl groups [76], strongly suppresses the smectogenic properties.

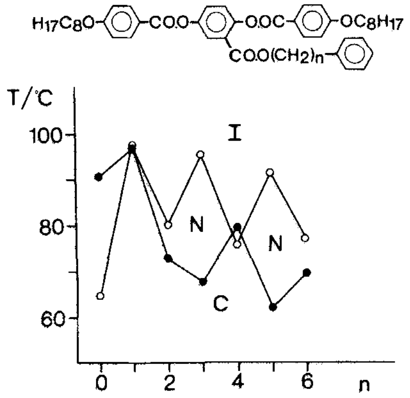
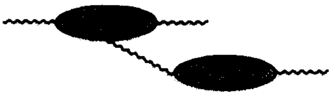
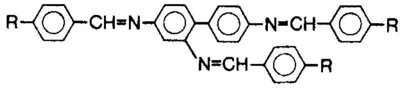


Figure 2. Transition temperatures T_{NI} (○) and T_{CH} (●) versus spacer length in a homologous series with ring-containing lateral substituents [71].

4.4.4. *Type*  *(lateral substituent containing substituted ring systems; later-terminal flexible bound twins, see §4)*

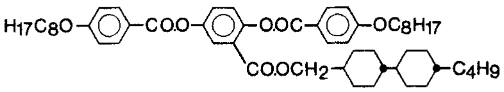
There are many examples of this type, among them the old results from the Vorländer school in Halle: Mauerhoff [77] synthesized three compounds of the type

33, which are nematic; Kuhrmann [78] also prepared compounds with aromatic substituents, with, however, some inconsistencies in the results reported [71].



33

R = $-NO_2$, $-OCH_3$, $-OC_2H_5$ [77]



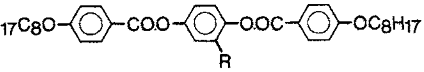
34

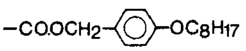
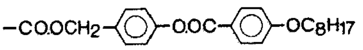
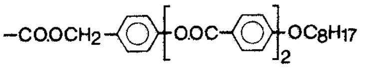
C 106°C (S_C 84°C) N 154°C I [71]

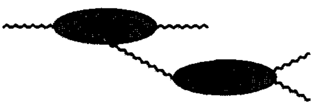
It may be mentioned here that compounds with lateral aromatic substituents are generally highly viscous. Some of them exhibit glass transitions above room temperature and so they are useful media for new thermoelectro-optic displays with storage properties [79].

There are compounds with large lateral ring-containing substituents in which the T_{NI} are higher than those of the basic compounds [96] (see table 5). Therefore the role of the lateral ring-containing substituents is not only to disturb the mesomorphic order, but also to act as mesogenic supporting moieties. From another standpoint these compounds can be considered as twins consisting of two different molecules that are attached by a flexible lateral–terminal link.

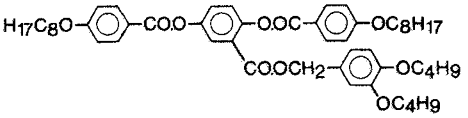
Table 5.



R	T_{NI}/°C
–H	194·9
	104
	151·5
	197

4.4.5. *Type*  *(flexible bound lateral ring-containing forked substituent)*

There are only a few examples of this kind, e.g. **35** [71].



35

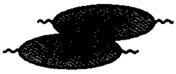
C 99°C (N 73°C) I [71]

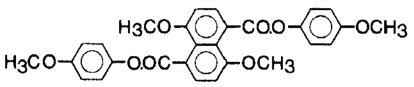
4.5. *Twin mesogens*

Twin mesogens, also called 'Siamese-twin mesogens' by Malthete *et al.* [83], consist of two mesogenic units, which may be linked in various ways. The twins may be considered as precursors of polymer liquid crystals.

4.5.1. *Fused twins*

In fused twins the mesogenic units are linked rigidly by a (mostly condensed) ring system.

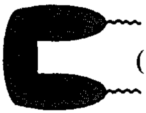
4.5.1.1. *Type*  (*terminal-terminal antiparallel rigid bound*) Kelker *et al.* [84] described the properties of **36**.

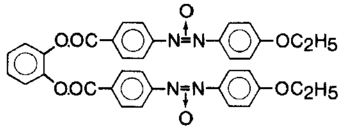


36

C 218·5°C N 287°C I [84]

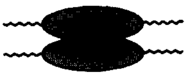
Some compounds synthesized in 1922 by the Vorländer school [85, 86] are of a similar shape.

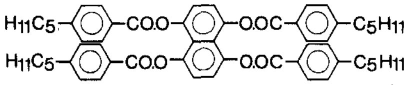
4.5.1.2. *Type*  (*terminal-terminal parallel rigid bound*) One compound of this type has been described by Vorländer and Apel [87], **37**.



37

C 184°C N 218°C I [87]

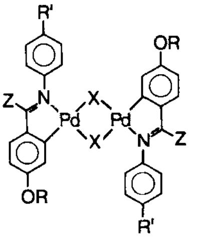
4.5.1.3. *Type*  (*lateral-lateral fused*) Some examples of this type have been described by Malthete *et al.* [83, 88], e.g. **37a**.



37a

C 220°C N 225·5°C I [83]

All fused twins deviate strongly from the classical rod-like shape. Metal complexes, which have been frequently synthesized in recent years (see [89] and references therein), e.g. **38**, and in a wider sense EDA complexes (see [90] and references therein) may also be considered as fused twins.



38

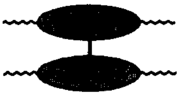
R, R' = $C_{10}H_{21}$, X = Cl, Z = H

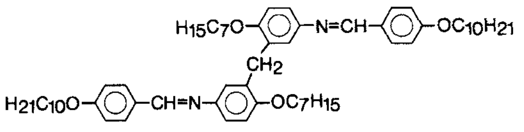
C 112·4°C S_C 135·0°C S_A 237·6°C I [89]

It should be mentioned that certain metal complexes of aromatic compounds are able to form discotic mesophases [91, 92]. EDA complexes typically induce strong smectic A behaviour in mixtures [90].

4.5.2. *Ligated twins*

In ligated twins the two molecules are connected by a spacer in a central position.

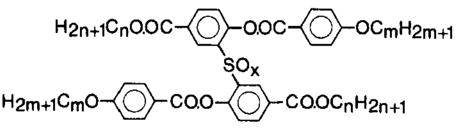
4.5.2.1. *Type*  (*lateral-lateral rigid*) The first example of this type have been presented by Griffin *et al.* [93, 94], e.g. **39**. There is some evidence [94] that the conformation of **39** given here can exist but the conformation with parallel oriented halves can also occur, depending on the thermal history of the sample.



39

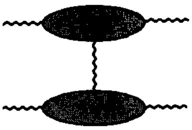
C 119·1°C (S_C 103°C N 112°C) I [93]

We have synthesized new sulphur-containing twins, e.g. **39a** [95]. The investigation of their physical properties has proved an antiparallel orientation of the halves. The compounds show a pronounced tendency to form mesomorphic glasses, remarkably the glass transitions may occur above room temperature.



39a

x = 1, 2, nematic [95]

4.5.2.2. *Type*  (*lateral-lateral flexible*) Very recently Weissflog [96] has synthesized the series **40**. X-ray investigations in the nematic phase suggest a

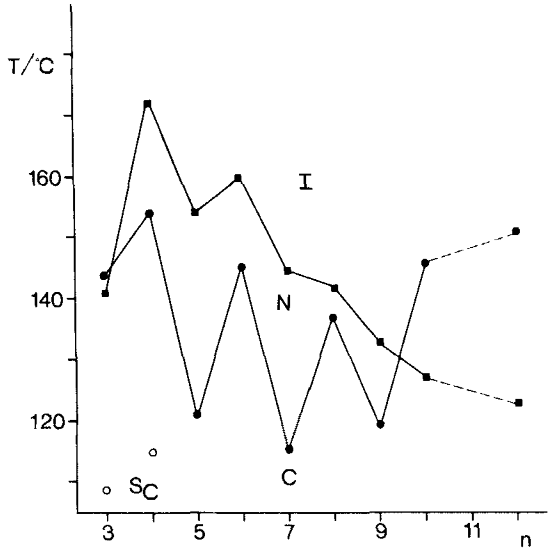
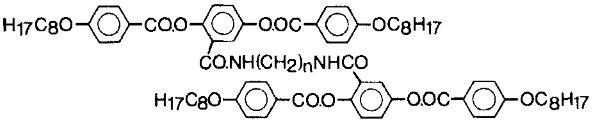


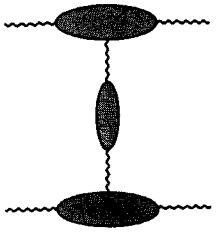
Figure 3. Transition temperatures of a series of liquid-crystalline twins with lateral–lateral flexible linking [96]: ■, T_{NI}; ●, $T_{CN(I)}$; ○, T_{S_CN}.

molecular conformation with the aromatic cores in close together, the spacer acting as a bulky lateral substituent. This conformation may be stabilized by hydrogen bridges. At about room temperature the compounds exhibit glass transitions.

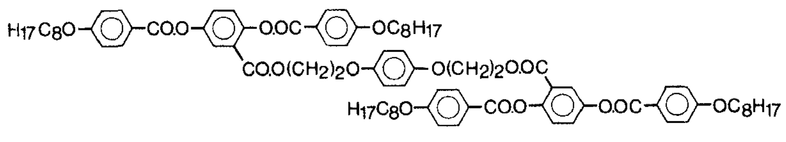


40

S_C, N [96]

4.5.2.3. *Type*  (*lateral–lateral flexible, ring-containing bridge*)

Weissflog has synthesized twin compounds with bridges containing aromatic ring systems, e.g. **41**,



41

C 135°C N 159°C I [96]

The benzene ring in the bridge may have one or two additional substituents, such as methyl or ethyl, without destroying the mesogenic properties. As X-ray investigations indicate, the conformation may be similar to that in compounds **40**. The effective molecular shape of the twins ligated by long spacers is more similar to those of twins ligated by short bridges than to the form of an H.

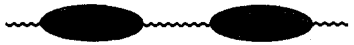
4.5.3. *Tail-to-tail twins*

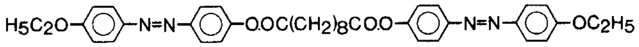
Tail-to-tail twins have a terminal–terminal bond between the single molecules. They belong to a long-known substance class despite the fact that this designation has been coined more recently (see [97] and references therein).

4.5.3.1. *Type*  (*terminal–terminal, acyclic*) There are many group II metal soaps with a high polymorphism [20], which from the chemical standpoint may be considered as acyclic tail-to-tail twins, e.g. **42**.

$H_{31}C_{15}CO.O-Ca-O.OCC_{15}H_{31}$ **42**

C 123°C S_2 195°C S_1 350°C I [127]

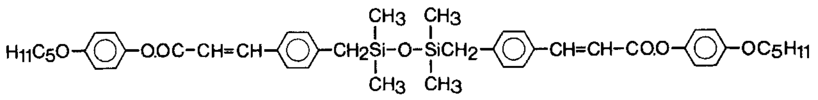
4.5.3.2. *Type*  (*terminal–terminal*) The Vorländer school has produced several series of such compounds, e.g. **42a**, which was made in 1927.



42a

C 155°C N 221°C I [98]

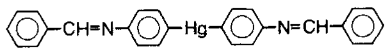
Compounds of this type are now of interest as precursors of polymers that allow the study of the flexibility of different groups, e.g. **43**.



43

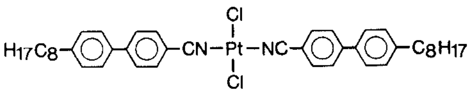
C 122·6°C (N 70°C) I [97]

4.5.3.3. *Type*  (*terminal–terminal rigid-bound ring systems*) There are metal complexes with a linear molecular shape that, in principle, are tail-to-tail twins, e.g. **44** and **45**.



44

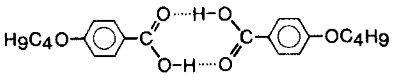
C 180°C N 184°C I [128]



45

C 166°C N 176°C I [99]

In addition, the well-known dimers (stabilized by hydrogen bonds) of all carboxylic acids [20] are of this type, e.g. **45a**.

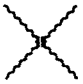


45a

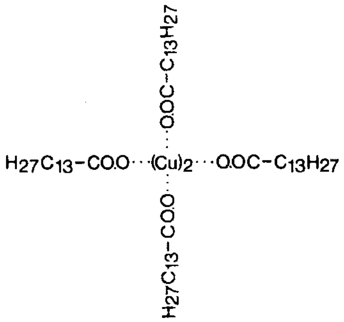
C 147°C N 160°C I [20]

4.6. *Discotic compounds*

The first discotic compounds were presented by Chandrasekhar *et al.* [22] as recently as 1977; however, since that time many molecular variants of this class has been developed. We do not present a complete survey of this field here, but only give one example for each of the different types.

4.6.1.  (*acyclic*)

Some soaps of group II metals form binuclear complexes that are able to exhibit columnar phases ([100] and references given there). A well-investigated example of this type is **46**.



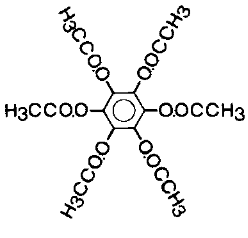
$$H_{27}C_{13}\text{-COO}\cdots(\text{Cu})_2\cdots\text{OOC-}C_{13}H_{27}$$

46

C 119°C columnar hexagonal 200°C I [100]

4.6.2. *Type* ● (*discotic compounds without long flexible substituents*)

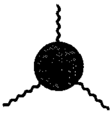
Kohne *et al.* [101] reported the series of the hexa-esters of *scyllo*-inosithe, the lowest member of which is by **47**. All substituents are in equatorial position. This result proves that in favourable cases long flexible chains are not necessary for the stabilisation of discotic mesophases.



47

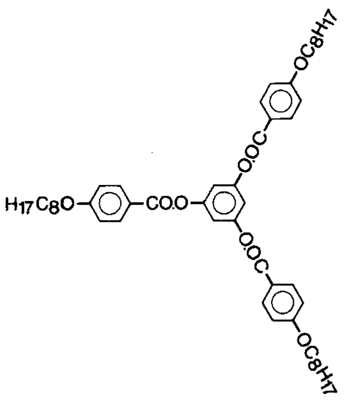
C 288·0°C discotic 292·8°C I [101]

The mesomorphic cycloalkanes in their effective molecular shape are not disc-like but rather rod-like [28, 29] and do not belong to this substance class (see §4.2.1). Also, octaphenylcyclotetrasiloxane, which in its simple chemical formula looks like a discotic molecule, has in fact a non-polar more-complicated shape and exhibits a structure similar to a smectic A [102].

4.6.3. *Type*  (*three flexible substituents*)

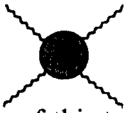
There is a series of trisubstituted benzenes with mesomorphic properties [103]; however, the mesophase type is somewhat unclear. The results do not exclude discotic mesophases.

Guillon *et al.* [104] have described a series of trisubstituted benzene derivatives with discotic nematic mesophases, e.g. **48**.

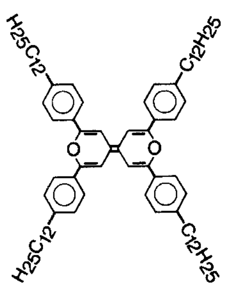


48

C 72·7°C (N_D 23·5°C) I [104]

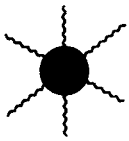
4.6.4. *Type*  (*four flexible substituents*)

Examples of this type are the discotic metal complexes (§4.5.1.3, [91, 92]). Further examples are the bipyrene compounds, e.g. **49**.

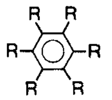


49

C 96°C discotic 147°C I [105]

4.6.5. *Type*  (*six flexible substituents*)

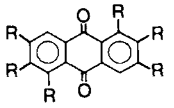
This is the most common type among the discotic compounds. Examples are the hexasubstituted benzenes, e.g. **50**, derivatives of triphenylene and truxene [106]. Of special interest are the hexasubstituted anthraquinones with a two-fold symmetry axis, e.g. **51**.



50

$R = C_7H_{15}\text{-}COO\text{-}$

C 79·8°C discotic 83·4°C I [106]

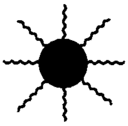


51

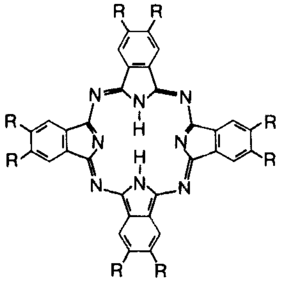
$R = C_7H_{15}\text{-}COO\text{-}$

C 107·5°C (D_2 95°C) D_1 127·5°C I [107]

Certain six-fold-substituted macrocyclic compounds exhibit hexagonal columnar structures, which are called 'tubular' because they form hollow columns (tubes) owing to the hollow space in the centre of the macrocycles [108].

4.6.6. *Type*  (*eight flexible substituents*)

There are some examples in the literature, e.g. **52** [104].



52

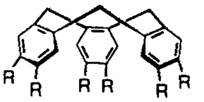
$R = -CH_2OC_{12}H_{25}$

C 78°C discotic 264°C I [104]

Piechocki *et al.* [109] presented Pb(II) and Sn(II) complexes of octasubstituted phthalocyanine derivatives possessing a large dipole moment perpendicular to the macrocycle plane. The lead complexes exhibit columnar phases with strong antiferroelectric coupling of the dipoles in pairs of molecules.

4.6.7. *Type*  (*pyramidic, cone-shaped or bowlic molecules*)

Very recently some compounds have been synthesized [108, 110] that are similar to discotic substances; however, in the molecules the flat core is replaced by a rigid conical unit such as tribenzocyclononene, e.g. **53**.



53

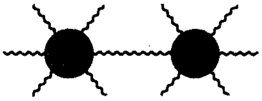
R = $C_9H_{19}COO-$

C 23·9°C columnar 152·6°C I [108]

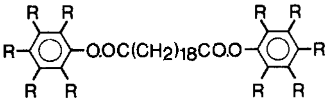
In this and some related compounds columnar phases with relatively high order have been found [111].

4.7. *Combined rod-like/discotic compounds*

Many combinations of rod-like moieties with disc-like units are possible, and several have actually been synthesized.

4.7.1. *Type*  (*discotic twins*)

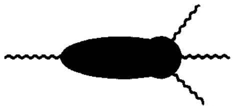
According to the results of Lillya and Murthy [112], twins of this type are only discotic when the bridging spacer is longer than that of substituents, e.g. **54**.



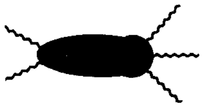
54

R = C_6H_{13}-COO-

C 112°C discotic 121°C I [112]

4.7.2. *Type*  (*hemiphasmidic compounds*)

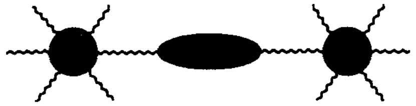
Hemiphasmidic compounds may be considered as combinations of a half-disc with a rod-like moiety. This substance class is treated in §4.2.7.

4.7.3. *Type* 

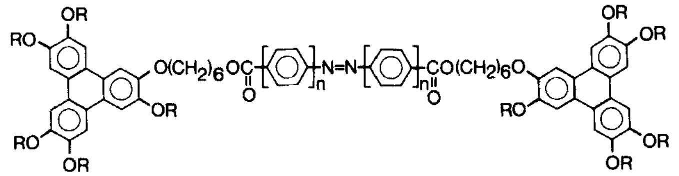
Formally, this substance type is a combination of a half-disc with a forked moiety and is treated in §4.2.8.

4.7.4. *Type*  (*phasmidic compounds*)

In this substance type two half-discs are combined with a rod-like centre; see §4.2.9.

4.7.5. *Type*  (*discotic twin with a terminal–terminal bound rod-like bridge*)

Kreuder *et al.* [113] recently reported the synthesis of a compound of this type, **55**, a typical precursor for polymer liquid crystals.

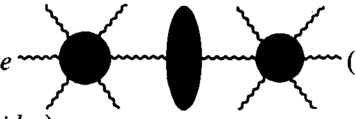


55

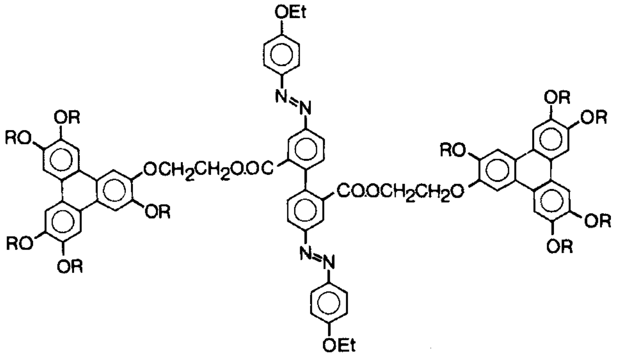
R = $-C_5H_{11}$, $n = 2$

C 72°C mesophase 120°C I [113]

The structure of the mesophase seems to be similar to that of **54**, the discotic parts forming columns in a hexagonal array and the rod-like moieties in a layered arrangement typical of smectic phases.

4.7.6. *Type*  (*discotic twin with a lateral–lateral bound rod-like bridge*)

A compound of this type resembling the 'Wheel of Mainz' has been synthesized by Kreuder *et al.* [113]; however, in contrast with the analogous polymers, which are sanidic, it does not exhibit mesomorphic properties.



56

R = $-C_5H_{11}$

C 167°C I [113]

5. Concluding remarks

In §4 we have dealt with 48 types of low-molecular-weight liquid crystals, which have been differentiated by the criteria given in §3. It should be mentioned that about 95 per cent of liquid-crystalline compounds belong to the conventional rod-like types described in §§4.1.1–4.1.4. Until now, only liquid-crystalline compounds of the conventional types have been used for practical applications; therefore the synthetic efforts of most research groups are concentrated on the development of new substances of these types.

In addition to their potential applications, unconventional liquid crystals are especially important for the theoretical understanding of the liquid-crystalline phenomenon. The classical molecular statistical theories [8–10] of the nematic state have been restricted to rod-like molecules, which are approximated by the model of an elongated rotational cylinder with the long axis *c* exceeding the short axes *a* and *b* by a factor of between 2 and 10 (case A in figure 4). Recently, molecular statistical theories have been extended to discotic molecules [132, 133] using the model of the rotational cylinder with a short *c* axis and longer *a* and *b* axes (case B in figure 4). Qualitatively in both extreme cases A and B the nematic phase can be predicted by the theories using similar arguments. Ballauff [134] has tried to improve the classical molecular statistical theory for molecules with large lateral substituents; however, the theory seems to be limited to very special cases. Tumanyan and Sokolova [142] have developed a molecular statistical theory including the general case of board-like (i.e. sanidic) molecules with three unequal axes (see figure 4), however, the theory fails to explain the properties of several types of unconventional liquid crystals. It seems that a new theoretical concept is needed for the general understanding of thermotropic liquid crystals.

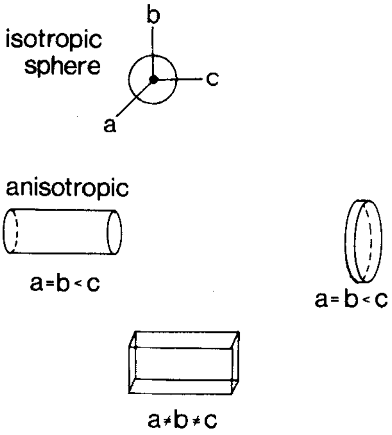


Figure 4. Molecular models in molecular statistical theories.

On comparing the molecular structures of low-molecular-weight and polymeric liquid crystals, it is clear that in the case of the latter there are many more possibilities for the manipulation of the molecules without the destruction of their mesomorphic properties. The low-molecular-weight liquid crystals are much more sensitive with respect to deviations from the basic rod-like or discotic shapes—the examples given are the successful trials and do not reflect fully the large number of unsuccessful efforts in order to obtain unconventional liquid crystals.

By comparing the proposed phase structures of liquid crystals (i.e. the arrangement of the molecules), it becomes clear that the basic principle valid in all structures is the necessity of filling space (similarly to the solid and isotropic liquid state [55]). This statement is strongly supported by a comparison of the packing fractions at the clearing temperatures of liquid crystals; these have values from about 0·5 in compounds with weak attractive forces up to about 0·62 in substances with strong attractions [13, 14]. Compounds with lateral substituents of different size also fit into this picture. The occurrence of the so-called filled smectic A phases [59], which is obviously due to steric interaction of different molecules, also supports this principle.

Probably owing to the requirement to fill space, the molecular conformation in the liquid-crystalline state can be influenced remarkably by the environment. This means that the conformation may deviate significantly from a shape that can be calculated from the condition of minimum free energy for the free molecule. This induced conformation exists in liquid-crystalline compounds with large flexible lateral substituents [64], in compounds with terminal substituents of strongly different length [135] and in swallow-tailed compounds [56]. In all of these cases the cavity that controls the conformation of the aliphatic chains consists at least partly of aromatic groups. That means that the concept of a separation of aromatic and aliphatic parts of the molecules, which is often used to explain the smectogenity of substances [136], needs a restricting modification.

There have been several attempts to classify the molecules of liquid crystals. Lin Lei [137] chose the dimensionality of the molecules as the differentiating criterion; this, however, only allows a rough classification into four groups. Petrov and Derzhanski [138] developed a generalized multipole model of molecular asymmetry, including the electrical, sterical, biphilic and flexibility asymmetry. This model allows the systematic development of different molecule types and therefore the prediction of novel variants.

The classification system presented here has already been applied in a very similar form to polymeric liquid crystals [30, 140, 144]. It has been developed in order to give a schematic overview of the different chemical species that are mesomorphic in character. Though it is not theroetically founded, it allows the development of new variants that until now are still lacking.

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