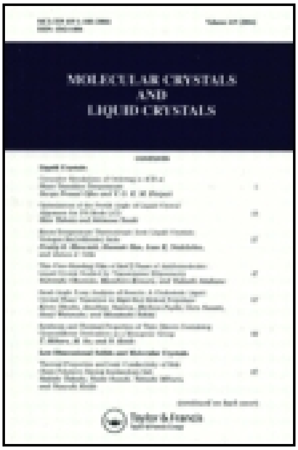

Molecular Crystals and Liquid Crystals

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Design and Constitutional Features of Mesophase-Forming Uni- or Supramolecular Discotic Materials [1,2]

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DESIGN AND CONSTITUTIONAL FEATURES OF MESOPHASE-FORMING UNI- OR SUPRAMOLECULAR DISCOTIC MATERIALS [1,2]

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After introductory comments on the situation of liquid crystal work and its importance in scientific, technological, and social respect before the discovery and start of systematic exploration of non-linear, flat, i.e., disc-shaped mesogens twenty-five years ago, illustrative thermotropic liquid crystalline uni- or supramolecular discotics are discussed in relation to geometric features of their constituent molecules or aggregates. These materials are divided into two main groups: radial-symmetric disc-like and unconventional non-linear mesogens. The first main group deals, first of all, with representative standard and thereafter with organometallic mesogens, whereas the second one is sub-divided into four parts: bulky unimolecular mesogens; hydrogen bonding and molecular recognition; polycatenar types of mesogens; inter- and intramolecular EDA/CT complexes. Clearly, the significance of micro-segregation for the mesophase formation in cases of unconventional molecular conditions is emphasized as well.

Keywords: discotics; LC chemistry; mesogens; micro-segregation; organometallics; overview; structure discussions

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1. INTRODUCTORY COMMENTS ON THE DEVELOPMENT OF THE ATTENTIVE INTEREST TOWARD NON-LINEAR, FLAT, AND CHIEFLY DISC-LIKE LIQUID CRYSTALS

One of the most important fields of natural sciences characteristic of the recent twentieth century was the systematic research on the chemistry, physics and technology of liquid crystals especially in its second half of the century where rapidly growing and extremely successful research took place. Looking back, one can certainly say that its outcome – in comparison with the standing of many another sciences – has clearly had and, hopefully, will further have, quick, immediate, and positive effects on daily life as well as on an almost unlimited number of activities, interests, and technological projects of human beings.

During the past hundred years not only the number of chemically pure mesomorphic compounds has increased by a factor of about 350 up to over 85000 [3]. In the course of this enormous synthetic effort in many research groups worldwide, various novel mesophases have been discovered. Very early, these results led to the realization that mesomorphism basically is a matter of the molecular shape, called ***Vorländer's Rule*** – for linear compounds [4]. Thus, seven decades later [5–8] it was found that the feasibility of occurrence of mesogenity is not restricted to rod-like molecules, but applies also to flat, discotic organic compounds. However, mesophases based on ***columnar*** ordering with molecular associations of ***rod***-like materials had already been observed in a greater number since about the middle of the last century; cf. a survey of the respective literature in a paper on amphiphilic character and liquid crystallinity [9].

Indeed, a great step toward the expansion of knowledge about liquid crystals was the discovery of the ***first*** mesogens based on ***non-linear***, ***flat***, i.e., ***disc***-shaped or ***discotic*** compounds about 25 years ago [5–8]; see further below. This important finding opened a door to another section of research on mesogens which, remarkably, was attempted to be accomplished already in the early twenties (!) but at that time without success yet [10,11]. Above all, from a contemporary point of view regarding today's knowledge on discotic liquid crystals, this failure did stem from substituents which either were totally lacking or much too short at cores of (aromatic) molecules available and studied in those days [10,11]. Unsubstituted compounds, the widest in molecular area, investigated at that time were, for instance, triphenylene, perylene, naphthodianthrone, and several other flat, aromatic multicycles [10].

Unfortunately, these forward-looking thoughts and efforts of brilliant scientists dealing with this matter already so early [10,11] remained for decades nearly unnoticed in the scientific community, most probably, due to the fact that their publication did occur in 1923 in German and, moreover, were not at all mentioned in Chemical Abstracts [10a]. However, the exception proves the rule: the very first reference to this work in contemporary scientific printing materials was given in 1980 [12]. At present, even an English version of that early, historical article in full does exist now but only since 1989 [10a].

According to experiences with mesogenity of discotics collected since their discovery in the late seventies [5–8], thread-like substituents are – apart from exceptions – necesarry indeed. Such chemical pendants must be flexible, long enough, and fastened onto the (flat) molecule cores. Mostly, this kind of side chains consists of linear alkyl or hetero-alkyl groups which may also be considered as "internal, substrate's-own solvent" [13,14]. Both their number (mostly six) and composition can differ with respect to the sequence of elements and the length of these chains.

In comparison with rod-like mesogens of which over 80000 are known today [3], the demands on syntheses of suitable materials with *flat* cores are somewhat higher; see also below. A big problem can sometimes be their purification due to a tendency of complex formation, e.g., with solvents or/and impurities. In the meantime, approximately 3300 flat, discotic samples (current growth rate: ~4%) have already been prepared [3] and, thereby, have strongly extended the research on liquid crystals in general. Two recent overviews [15,16] of synthetic details regarding also thermomesomorphic discotics are recommended for further study. They chiefly cover many of the facets of arene chemistry, dealing with the applications of a large number of common, basic, chemical transformation reactions, e.g., from all kinds of condensation and substitution reactions; Heck and other types of C-C coupling reactions/cyclizations; to cyclotrimerizations, orthocyclometallations, or metal complexing processes etc.

To avoid confusion, it should absolutely be borne in mind that the term ***discotic*** applies *only* to the ***molecules***, and *not* to the mesophases. The latter subject-matter observable in polarisation microscopes, may be columnar, nematic, lamellar, etc.

Finally, for further reading about the achievements in the interdisciplinary field of liquid crystal research in every sense since its beginning over hundred years ago it is recommended to browse through further extensive reviews currently published [2,6,7,17–21] and clearly laid out offering valuable information in a great number and detail on mesogens uni- to three-dimensional in their molecular shapes.

2. PRESENTATION OF ILLUSTRATIVE THERMO-MESOMORPHIC UNI- OR SUPRAMOLECULAR DISCOTICS DISCUSSED HERE IN RELATION TO GEOMETRIC FEATURES OF THEIR MOLECULES OR AGGREGATES

2.1. Radial-Symmetric Disc-like Mesogens

The part of disc-shaped materials, topic in the first of the following two sub-chapters, are examples of so-called classical discotic mesogens possessing a relatively flat, mostly multicyclic aromatic core, usually surrounded by six covalently bound, flexible chains; see above and Figure 1. The second group of disc-shaped organic materials presented here contain between one and four metal ions and are, therefore, called metallomesogens. Their molecular structures are either almost flat or have a slightly conical/bowl-like core geometry (cf. Fig. 2).

Systematic investigations on both discotic prototypes started in the later seventies and have quickly gained still-growing support in many research groups.

2.1.1. Representative Standard Mesogens

Most of the families of thermomesomorphic discotics selected here and compiled in Figure 1 have a more or less flat, multicyclic aromatic core. They shall demonstrate that cores of disc-like mesogens can be of manifold geometry and do not have to be ideally discotic in shape. The compounds can also be star- or cross-shaped, or of another pattern, and they may contain heteroatoms, e.g., chalcogens or nitrogen. There is also the possibility of a slightly bowl- or cone-like, or of another non-planar shape; see below.

Usually, the molecules carry six long alkyl chains covalently bound to their centre units each via a heteroatom (normally of the same kind) as, for instance, via oxygen or, occasionally, via sulphur, selenium or nitrogen.

The twenty-two standard structures **1** to **22** chosen as representative examples for discussion in this sub-chapter have been divided into the five divisions **I** to **V**, cf. Figure 1.

Division I

The simplest type of a *cyclic* core is a six-membered carbocycle either conjugated unsaturated, aromatic or even fully saturated, see the formulas **1** to **4** with their core diameters (space-filling models) of $\approx 15\,\text{Å}$ (**1** and **2**, cf. X-ray measurement of **2** below), $\approx 8\,\text{Å}$ (**3**), and $\approx 15\,\text{Å}$ (**4**). Four hexa-esters of type **1** (R = hexanoyl to nonanoyl) of hexahydroxybenzene, slightly uneven (see below), star-shaped, and as such known since the late thirties [22], have only forty years later been disclosed to be liquid crystals

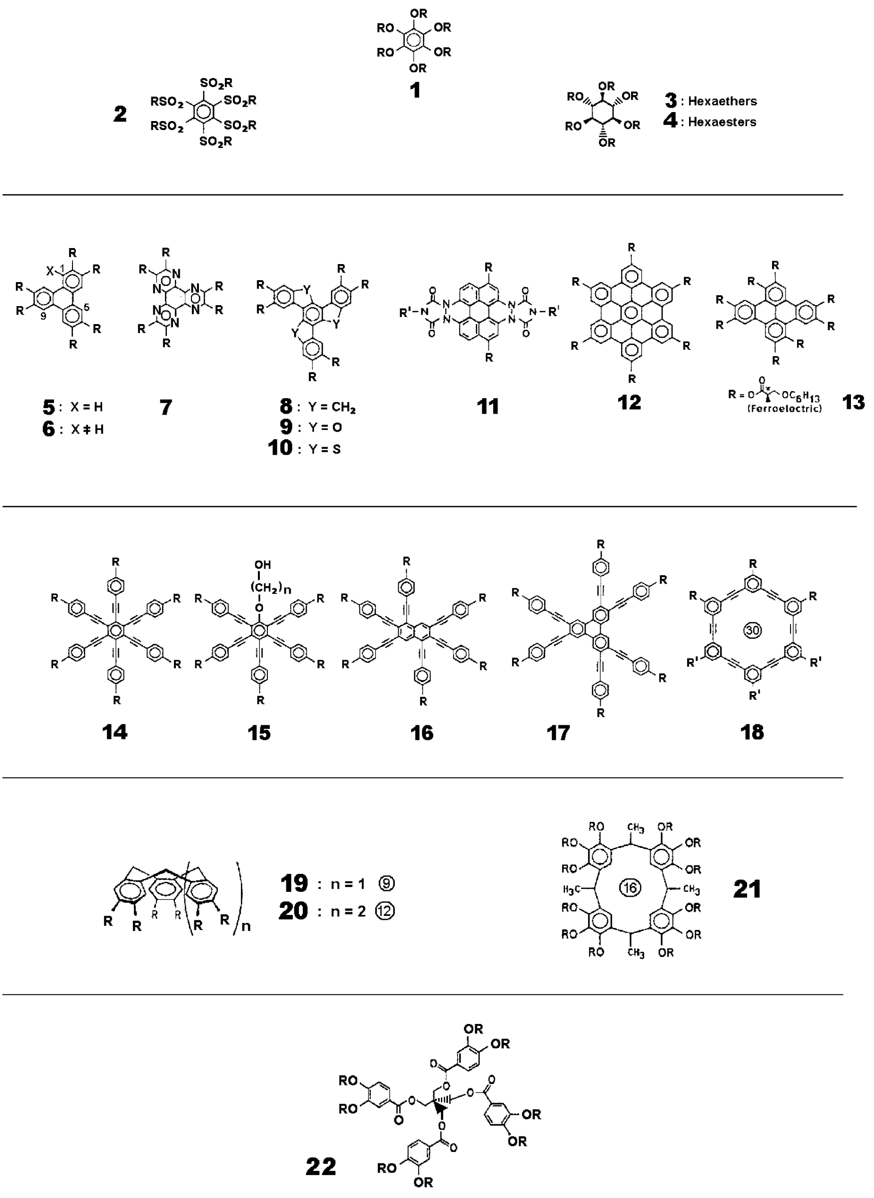

FIGURE 1 Presentation of twenty-two standard cores (**1** – **22**) of mesogens either disc-like or only slightly *non*-planar in structure divided in five divisions by horizontal lines. – Depending on their position at the different cores, the groups R and R' are alkyl, alkylchalcogeno, alkanoyl, or alkanoyloxy chains. The four encircled numbers 9, 12, 16, and 30 indicate the size of the respective macro-carbocycles.

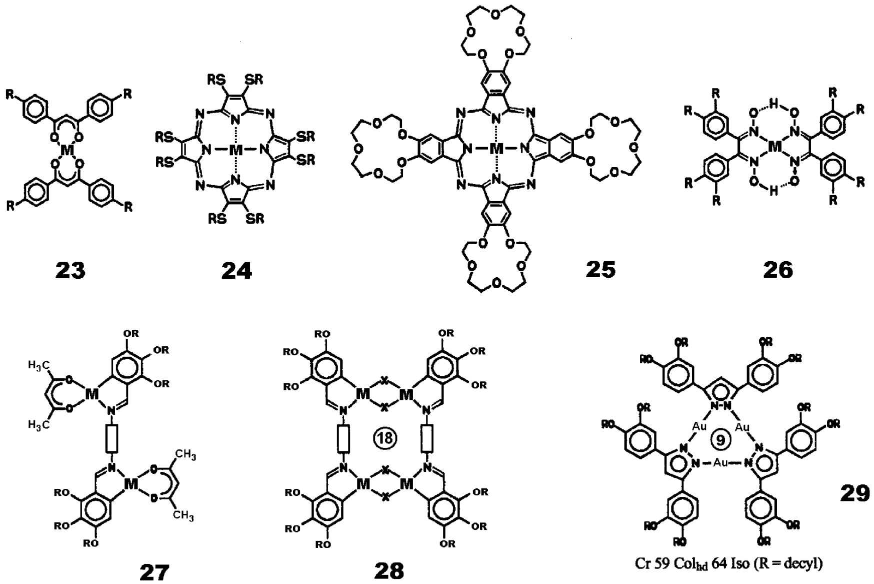

FIGURE 2. A selection of seven flat, disc-like organometallic core structures (**23**–**29**) as an illustration of the structural variety of mesogens in this relatively young and rapidly growing branch of liquid crystal research. - R = longer alkyl or in cases of **23** and **26** also alkyloxy or alkylthio chains; M = metal: copper, nickel, palladium, platinum; X = : chlorine; -▭- = 1,4-phenylene. - The two encircled numbers 9 and 18 indicate the size of the respective central heterocycles formed by complexation.

[5–7]. These compounds are the ***first*** disc-shaped examples of ***pure***, i.e., ***single***-component thermomesogens displaying a ***columnar*** phase (Col$_{hd}$, proved by X-ray [5]), really, a great highlight in liquid crystal research. The designation ***columnar*** for this new type of liquid crystal phases has been introduced in 1979 on the occasion of an International Liquid Crystal Conference in Bangalore, India [23].

In this connection it is right and proper to remind oneself of early imaginations from 1923 [10a]: "... One might well think that flat molecules via their broadsides stack up in a kind of ***Voltaic column***, so that anisotropic buildings do follow. However, our experiments are against this assumption."

Since the mid-nineties it is recommended to use the mesophase description quoted before [23] in the abbreviated way as "*Col*" [24].

Soon after the columnar phase of **1** was established, one of these mesomorphic hexaesters **1** helped to classify conclusively the mesophase of the bulky, structurally not related diisobutylsilanediol as a columnar one which stayed unsolved since the early fifties, in miscibility studies; see the second paragraph of the introductory comments of chapter 2.2 further below, including references given there.

It would surely be wrong to assume that luck was the main reason for the discovery of the columnar phase of discotic compounds. Rather would a famous saying of a great German (*H. Graf von Moltke*, 1800–1891) emphasize the requirements for such an important piece of work [5] which goes: "*Glück hat auf die Dauer nur der Tüchtige*"; a rough translation in English would be: *Fortune Favours the Dedicated*!

In contrast to these four hexaesters **1** [5–7] a homologous series of nine hexasulfones **2** (R = heptyl to pentadecyl), likewise of discotic shape, exhibits that particular type of mesophase without exception *enantiotropically* and with wide areas of their existence [25–27]. This is a surprise since the periphery of the sulpfur compounds **2** is massively overcrowed due to their six bulky sulfono groups having the oxygen atoms alternately oriented above and below the benzene core with the result of a rather uneven molecule. However, the benzene ring confined in that kind of tight, wavy-like girdle of sulfono groups remains flat. The proof for this remarkable stereochemical situation was given by a single crystal X-ray study of one (non-mesomorphic) homologue of series **2** which also allowed to calculate the diameter ($\emptyset = 15.8\,\text{Å}$) of the 'outer molecular ring' formed *non*-covalently by the sulfono groups [27]. The sulfono substituents are not only very strong electron acceptor groups but, moreover, each of them is *directly*, i.e., with its *sulphur atom as the acceptor centre* covalently bound to the benzene unit. In difference about this, the smaller, triangular-like carboxyl functions of the six alkanoyloxy chains of series **1** are clearly less electron attractive. Furthermore, each of them is *bridged* to the benzene core by an *oxygen* atom, an *electron donor* element. The fact that their carbonyl groups point alternately up- and downward let also the hexaesters **1** not be really flat. Regarding this particular steric situation, there is a certain relationship between the series **1** and **2**. Homologues of both (aromatic) series **1** and **2** with all their *substituents reduced*, formally hydrogenated, i.e., their hexaethers or hexathioethers respectively, do *not* show mesogenity any more [25–27].

Much to everyone's surprise, *both* ethers *and* esters (**3** and **4**, R = alkyl or alkanoyl, respectively) of the naturally occurring *scyllo*-inositol or scyllitol [1,2,3,4,5,6-hexa(eq)hydroxycyclohexane, **3** or **4**, R = hydrogen] having now a *fully saturated molecule core* which carries the six substituents - *either* alkoxy *or* alkanoyloxy chains – in *equatorial* order, i.e., all of them in *trans*-positions turned out to be superb thermo- and also (see below) lyotropic discotic liquid crystals. These interesting derivatives are now uniformly thick both along their side chains and across the *cyclohexanyl* core. This stereochemical situation can easily be proved with the aid of space-filling models. According to this it is clear that the cyclohexane derivatives **3** and **4** as a whole are flatter, more regularly even than the compounds of the series **1** and **2** possessing a phenylene centre less thick than the alkylchalcogeno chains. Consequently, the hexaethers **3** and -esters **4** behave completely different and display an unexpected rich mesomorphism [28,29] both on heating and cooling over an extremely wide temperature range: the occurrence of the ***disordered*** columnar hexagonal type of phase ($\mathrm{Col_{hd}}$) from the hexaacetate to the hexabutyrate, thereafter a ***cubic*** phase in one case, and the ***ordered*** columnar hexagonal phase ($\mathrm{Col_{ho}}$) for all of the higher homologues of the saturated hexaester series **4** have been observed [28–30]. A review offers additional information [31].

Many more multiethers of various multiols, carrying in addition free hydroxyl groups, do also exhibit columnar phases [32–36]. The same behaviour show similar derivatives of (so far) three of the nine naturally occurring stereoisomeric inositols [31–36]. Some of them will be discussed in sub-chapter 2.2.2 with regard to their mesophase behaviour as a function of the stereochemistry of their cyclic multiol skeletons. Due to the hydroxyl groups present in these molecules spontaneous multimerizations take place via intermolecular hydrogen-bridge formations with the possibility of the creation of columnar mesophases.

In general, these results seem to advise chemists and physicists to pay more attention to the ***degree of saturation*** also in case of other cores and/ or substituents as well as on the ***stereo-chemical positions*** of the latter attached to core systems relevant for studies of discotics instead of focussing interests almost only on highly unsaturated uni- or multicyclic/ aromatic ring moieties. Certainly, quite high demands (cf. above) are necessary to be met for solving manifold synthetic and stereochemical problems involved here in such kind of undertakings which, therefore, may act as a deterrent.

Compared with these ambitious suggestions or even intentions, the syntheses of members of both series – the hexaethers **3** and -esters **4** uniform or, occasionally, mixed in structure are relatively straightforward starting from commercially available *myo*-inositol which is first to be transformed into *scyllo*-inositol by two well described synthetic transformation steps [37,38]. The total chemical yields of all these syntheses are quite good [28,39].

Finally, it is worth mentioning that hexaesters of both series **1** and **4** (R = various homologous alkanoyl groups) in a comparative study [14] have also shown the development of mesophases in binary mixtures, e.g., with benzene and numerous other apolar organic solvents. With regard to derivatives of type **1** in the aromatic, disc-like solvent related to the core their lyomesophase behaviour was already described over two decades ago [40,41] and confirmed recently [14]. Above all, the latter ones are the first examples of lyotropic mesomorphism for disc-like mesogens [40,41].

Interestingly, as it appeared already from earlier preliminary work [42] on hexa-amides of benzenehexamine [43], i.e., on **1** carrying six alkanoyl-*amido* groups instead, our recent extensive study [14] clearly proves the conception that *saturated cyclic* hydrocarbons as solvents are *much more* (!) suitable for lyotropic purposes including those of the type **1** compounds. In other words, the suitability of solvents for lyotropy studies is rather determined by their molecular shape (*cyclic* or not), size/length, and steric/space-filling effects than by their degree of saturation. After all, the most efficient solvent in this connection is, therefore, *cyclo*-hexane, but homologues of it are also convenient. Thus, many homologous scyllitol hexaesters **4** display *two* lyomesophases: a hexagonal *and* a nematic chromonic-like one. Members of the aromatic hexaester series **1**, however, exhibit *only one* mesophase under equal conditions: the hexagonal chromonic-like type of phase [14].

Whereas hexaesters of structure **4** are also lyomesomorphic in mixtures with (fully saturated) *linear* alkanes, those of type **1** are not [14] which, in the latter case, is in agreement with results regarding a very first study [41] on a mixture of one representative of series **1** (R = heptanoyl) with undecane, a linear solvent comparable with the aliphatic side chains.

Consequently, this difference in behaviour between series **1** and **4** – both simple in their molecular structures can simply be caused only by their different cores which are unlike in space-filling, area, and in the number of mobile (π and lone pair) electrons etc. [14]. Analogous lyotropy investigations have not been started yet, neither of the hexasulfono derivatives type **2** [25–27] nor of the reduced forms of **1** and **2**, their respective hexaethers or hexathioethers [25,26] both with phenylene cores. The same is true for the cyclohexanyl centred hexaethers **3**. However, lyotropy investigations of these four series would also be interesting and promising results would be guaranteed.

Division II

The nine molecular structures **5** to **13** selected in this division and shown in Figure. 1 shall give a little view in the variability of multicyclic aromatic core systems interesting in research on discotic liquid crystals. Their core diameters are several times as much as that one of the little phenylene unit; cf. the formulas **1** and **2**. About fifty-five years after investigations of potentially thermomesomorphic triphenylene (**5**, R = X = H) and other large, multicyclic disc-like, aromatic ring systems, all unsubstituted, which ended negatively [10; cf. chapter 1], triphenylene in the shape of radially symmetric hexaethers returned into the focus of liquid crystal interests [8]. As a matter of fact, two of these pure, discotic hexaethers **5** (R = alkoxy, X = H) were really found at that time to display the expected novel type of thermotropic mesophase [8], a finding submitted for publication only five months and five days after the description of such a phase for the first time as exhibited by members of the benzene hexaether series **1** [5]. The hexagonal columnar phase structure of the studied hexaethers **5** (R = alkoxy, X = H) was somewhat later also proved by X-ray study. In contrast to the quite narrow columnar thermophase of the compounds of structure **1** [5] do member of series **5** [8] show that phase in rather wide temperature ranges. One is tempted to assume that the greater width of the columnar phase ranges of the hexaethers **5** could reflect their greater core diameter.

The studies on triphenylene derivatives (**5**, X = H) established this tetracyclic core system as the *second* flat type of carbocycle after benzene. Hitherto it plays by far the most important role in the research on discotic liquid crystals, see the overview [16].

Steadily, it gains growing importance for technological applications. However, as several contributions at the International Conference on Discotic Liquid Crystals, November 25–29, in Trieste, Italy (hereafter, abbreviated to ICDLC, Trieste), prove, it has already competitors as for instance derivatives of phthalocyanine, of the various so-called radial multiynes (cf. the next division of standrad mesogens), and seems now to get another one: derivatives of the hexaazatriphenylene **7**; see below.

Apart from the synthesis of the symmetric hexa(methoxy)triphenylene (**5**, R = CH_3O, X = H) in the mid-sixties [45], the first precursor for homologous hexa(alkyloxy)- or hexa(alkanoyloxy)triphenylene derivatives [8,16,46], substantially improved and expanded onto numerous homologous thermomesomorphic triphenylene hexaethers or esters in the nineties [16], the chemistry of triphenylene (**5**, R = X = H), i.e., its derivatization, originally at a very low level of knowledge, has only started to grow significantly in the last twenty years; see the overviews [2,16]. On this occasion it may be worth emphasizing that for instance the hexabromination [47], the hexathiolation [48] by (aromatic) S_N reactions in aprotic polar solvents analog [49a,50] or similarly [49b] the hexaselenization [51], the hexaethynylation [52,53], the selective chemical modification of aromatic methoxy groups [54] or the removal of phenolic hydroxy groups [55], and the creation of chirality by helical distortion of the tetracyclic aromatic nucleus of **6** [56,57] owing to a surprisingly uncomplicated, previously unknown *hepta* substitution which leads to atropisomeric compounds, all were pioneering, straightforward reactions either at the triphenylene ring system itself or mainly of its various types of derivatives nowadays easily accessible [47,48,51–58]. The *seventh* substituent X of the triphenylene derivatives of series **6** can, e.g., be halogen or nitro, whereas R equals here alkoxy.

Furthermore, it should be stressed here that (only) one member of the liquid crystalline hexaalkylthioether series (**5**: R = hexylthio) prepared almost two decades ago [48] was found to exhibit a unique helically ordered columnar phase at low temperatures [59,60]. Ten years after the synthesis [48] of that particular homologue it was discovered [61] that its highly ordered columnar (stacked) phase can exhibit high mobilities for photo-induced charge carriers, higher than for any organic materials other than single-crystal phases.

The driving force for this impressive development of synthetic work and studies on the tetracycle triphenylene with manifold alterations at its periphery, i.e., attaching, replacing, and removing of substituents, or even with the introduction of hetero atoms in its core centre as depicted by the formulas **5**, **6**, or **7**, respectively (cf. Fig. 1), was the strongly increasing interest in liquid crystalline discotics in general and, since the late seventies [2,6,7,16], especially in those with the triphenylene core and, currently, also with the (hexamercapto-substituted) 1,4,5,8,9,12-hexaazatetracyclic ring system **7** [62] as well as with condensed ones based on the latter [63]. The future of these discotic materials and further derivatives is expected to lie in their possible application as potential electron carriers [62,63].

With this promising perspective in view, it may be mentioned here that the first attempts to use the hexaazatetracycle **7** as core system for novel discotic liquid crystals stem from the time of the early eighties but failed [64]. The eight 2,3,6,7,10,11-hexasubstituted derivatives of **7** synthesized in that study lacked so-called bridging elements such as oxygen, sulfur, etc. between the tetracyclic heteroaromatic core and the various substituents such as long alkyl or other groups and did therefore, unfortunately, not show mesomorphism on heating [64].

The five discotic liquid crystal series **8**, truxene derivatives, **9** and **10**, derived from oxa- or thiatruxene, respectively [65], as well as the type of discotic pigment **11**, highly fluorescent perylene derivatives with only four flexible alkyl groups (R and R') [66], and derivatives **12** of the alkylated hexabenzocoronene [67] exhibiting remarkably stable columnar phases with very wide temperature ranges (especially the unsubstituted **12** with the largest phase width of 339 K among known columnar systems [67]) possess still larger aromatic cores than those present in series **5** and **6**, or in the hexaaza-family **7**.

Currently, many activities are concentrated around mesomorphic derivatives of hexabenzocoronene (**12**) because it is said that their charge-carrier mobilities shall be larger than any mobility value of previously investigated liquid-crystalline discotic materials, see for instance reference [68] and respective contributions at ICDLC, Trieste.

Also the cores of the three series **9** to **11** contain heteroatoms, i.e., chalcogens or nitrogen, respectively. Whereas columnar phases of disc- or star-shaped compounds are normal, the exhibition of a nematic one on heating is rare. Therefore, it is interesting to note that *all* of the known homologous hexaalkanoyloxy derivatives of **8**, **9**,and **10** display a thermotropic (inverse) nematic phase and some of them a columnar one in addition. The nematic type of phase appears enantiotropically in both series **8** and **10**, but only monotropically among analogous oxatruxene derivatives **9**; cf. a tabular survey of data compiled from French papers regarding this matter [53].

These five thermomesomorphic multicyclic series **8** to **12** increased by chiral derivatives of the also quite large dibenzopyrene **13**, showing for the first time ferroelectric electrooptical switching in tilted *columnar* mesogens [69], represent a great number of disc-like mesogens in the collection of this division having very different and large core geometries which do not have to be ideally discotic in structure, but can also be star- or cross-shaped or of another pattern. Most of the synthetic activities and details behind the materials depicted in this division as well as items of other discotics not pointed out here have been compiled in overviews published recently [6,7,16,53].

Division III

The group of the four series **14** to **17** of discotics selected here and shown in Figure. 1 are generally called ‘radial multiynes’ and have been introduced (**14**) into the liquid crystal research fifteen years ago [70]. This very symmetric type of discotics with an aesthetic touch looks like plane ‘wheels without rims’. The ethynylphenyl units in radial arrangements (cf. the structures of **14** to **17**) can be seen as their ‘spokes’ and the aromatic ring in the centre of the molecules as a kind of ‘axle bearing’. This latter piece is only a little part of the huge ‘wheel’ -/disc-like molecule core termed now ‘super-disc’ [28] moulded by the respective type and size of ‘wheel’. Such particular molecular cores are flat but not ideally even due to their peripheral phenyl rings rotated out of the ‘super-disc’ plane by about eleven degrees, a measure basing on a single crystal X-ray study [71]. The diameters of these ‘super-disc’ cores are, e.g., $\o \approx 19.5\,\text{Å}$ (**14** and **15**) or $\o \approx 24\,\text{Å}$ (**17**) and may even be still larger, e.g., $\o \approx 28.5\,\text{Å}$ [72] in cases of analogous discotics with (linear) ethynylbiphenyl segments as ‘spokes’ [72,73]. These (latter) measures according to Dreiding models are the distances between the centres of the first elements (carbon or oxygen) of pairs of mostly alkyl or alkoxy chains, respectively, diagonally located in the plane of the ‘super-discs’ (cf. the four formulas **14** to **17** of Fig. 1).

The chemical stability and excellent solubility of these molecules, their large core diameters in the nanometer range (cf. before), structural flatness, rigidity and unusual abundance of π-electrons due to the numerous phenylene units and triple bonds of their ‘super-disc’-like cores, their unique physical properties, as well as their really simple synthesis from easily accessible precursors in good chemical yields [52,70,74], let the radial multiynes increasingly become valuable liquid crystalline materials in many respects. In fact, this interesting situation of the radial multiynes was also discernible in so many contributions from various laboratories of universities, research institutes, and even of industry at ICDLC, Trieste. This class of highly unsaturated discotics was, presumably, one of the most mentioned materials during that meeting.

Interestingly, due to the very large sizes, such radial multiynes preferentially exhibit nematic (nematic discotic, N_D, or nematic columnar, N_{Col}) phases, a special and relatively rare behaviour among disc-shaped mesogens. The first disc-like mesogens showing this type of phase on heating are hexaesters of triphenylene-2,3,6,7,10,11-hexaol with 4-substituted benzoic acid synthesized already in the late seventies [46]; see also a tabular survey [53] regarding this matter and a study [75] on properties of the N_D, the cholesteric discotic, and of discotic blue phases as well as on special effects and potential applications.

The nematic discotic radial multiynes have also been brought in relation to a special physical property: biaxiality of thermotropic nematics currently a hot topic of interest [53,76,77]. Although such biaxial nematogens would indeed be of great importance for various principal reasons, there is still considerable doubt about its existence for low-molar mass thermomesogens [78,79] independent of shape and size of the molecules in question.

Another precious property of the radial multiynes follows from their highly unsaturated character, see above, which let them easily form inter- and intramolecular electron donor-acceptor (EDA or CT) complexes. This possibility allows either to stabilize, manipulate, or even to induce known or yet unknown (also chiral !) mesophases simply by mixing these radial multiynes (or other electron donor molecules disc-like in shape) with electron acceptor compounds of which both a priori not have to be thermomesomorphic by themselves, but may be chiral. Examples for electron acceptor molecules are multinitrofluorenone derivatives, for instance, 2,4,7-trinitrofluorenone or the commercially available chiral derivatives of this ketone: (−)- or (+)-TAPA. Specifications about such EDA or CT complexes regarding preparation, investigation, properties, and literature are fully detailed in three overviews published in 1998 and 2001 [2,53,80]; for further information about this latter topic see the sub-chapter 2.2.4.

The various attractive properties of the radial multiynes brought about a steadily growing interest in this type of large discotic material as demonstrated by the five papers selected here [52,72,74,81,82]. Since recently, the radial pentayne **13** gains even access to research on polymer chemistry [73,83]. Hopefully, this will also happen to other representatives of the class of radial multiynes which may further open fruitful ways for new applications of these emerging mesogens columnar and/or nematic in character.

Starting compounds for these and other radial multiynes are the respective arenes, e.g., benzene, naphthalene, triphenylene, phenol or (various) phenol ethers etc., almost all commercially available, furnishing the necesarry perbromo intermediates in high yields through well established perbrominations; cf. for instance [47]. Despite of the very poor solubility of the perbromo compounds in organic solvents, the following manifold ethynylation reactions (Heck reactions) smoothly transforms the perbromo compounds into the desired radial multiynes in chemical yields, e.g., up to about 40% for the triphenylene or up to about 60% for the benzene derivatives. Of course, also other aromatic hydrocarbons may be applied in analogous projects based on radial multiynes.

In contrast to the previous multiynes **14** to **17**, the last but one of this division, the hexaynes of type **18** have a distinctly different molecular geometry. Their *six* triple bonds are not in a radial but in a *cyclic* order, i.e., parts of a quite rigid, planar, and shape-persistent 30-membered gigantocycle which also can be considered as a hoop-like 'super-disc' *empty* in the centre of its nano-structure. The diameters of the 'super-disc' cores of the different multiynes **14**, **15**, and **18** are equal (ø ≈ 19.5 Å each); whereas the hydrogen to hydrogen distance across the macrocycle interior of **18** is ≈ 8.5 Å (Dreiding models). Derivatives of the unsaturated macrocycles of type **18** can easily be synthesized by a ringclosure reaction of monomeric, α,ω-unsymmetrically difunctionalized phenylacetylene precursors [84]. Similar to the radial multiynes, discussed above, do also the toroidal ones (type **18**) preferentially exhibit *nematic* (N_D/N_{Col}) phases on heating or cooling. In addition, at lower temperatures a *columnar* phase can occur as well of which X-ray studies obviously reveal a tubular structure [85].

Quite recently, a still very much larger, a 58-membered gigantocycle, likewise shape-persistent, was synthesized [86]. Similar to the former compound, this novel mesogen is also of a hoop-like nano-architecture, but being composed of *ten* phenylene units and *twelve* triple bonds in a *cyclic* order. This huge and yet fairly rigid macrocyclic core carries only *four* long aliphatic chains and has a somewhat elliptical shape with external diagonal diameters between ≈ 28 to 30 Å and internal ones, i.e., the hydrogen to hydrogen distances across the gigantocycle interior, between ≈ 18 to 20 Å (Dreiding models). However, this macrocyclic molecule is *non*-planar in the solid state but exhibits a *schlieren*-texture on heating which points in favour of the formation of a *nematic* type of phase [86].

It is noteworthy to stress that this unique liquid-crystalline compound, in comparison with other discotic mesogens, is the *first one* showing an *inverse topology*: a rigid, large hoop-shaped carbocycle carrying less flexible side chains which spontaneously point inwards filling the internal void of the gigantocycle. In other words, it is the *first discotic liquid crystal with a rigid periphery and a flexible core* [86].

Division IV

There are also possibilities for the existence of mesogen molecules with non-planar cores slightly bowl- or cone-shaped. Examples for such species are derivatives of 1) the tribenzocyclononatriene **19** (n = 1, cf. Fig. 1) with its invertible, cap-like, 9-membered cyclic core, three-fold symmetry, and a net dipole stemming from orderly piles of their 'dented' molecules one on top of the other [87], and 2) the tetrabenzocyclododecatetraene **20** (n = 2, cf. Fig. 1) also non-planar and rapidly interconverting between two 'couch'-like conformations [88] having 12-membered cyclic centres. Equally, the dodecaesters of the overcrowded, flexible 16-membered (in its centre empty, cf. formula **21**)metacyclophane system **21** are to be mentioned here which have a rigid cone-like conformation with four methyl groups at its macrocyclic centre arranged in *endo*-orientation [89]. The thermotropic mesophases observed in these three families of liquid crystals with their non-planar cores are of (different) columnar type which are potentially ferroelectric for members of the two series **19** and **21**. The transition temperatures found in the tetrabenzomacrocyclic series **20** are generally higher than those of the tribenzoderivatives of type **19**.

Reproducible syntheses for the compounds mentioned here examplarilly and their necesarry purifications, sometimes tedious procedures, are well described in the original papers cited here and also referred to in an overview [16].

Division V

Even still simpler and smaller than a 6-membered core segment of the low molar mass columnar liquid crystals **1** or **4** shown in division **I** are, e.g., the tetravalent elements silicon, carbon, or a linear carbon chain instead. A molecule with such a tetrahedral situation in its centre, derived here from penta-erythritol, carrying a varying number of (mostly longer) alkyloxy groups by way of aromatic linking units is depicted in formula **22**, the last model compound of Fig. 1.

This kind of molecules and similar ones are of *non*-conventional shape and have centres in common in which the polar building blocks (carboxy-functions, ether oxygens, or arenylene groups etc.) are concentrated, thus, creating distinct polar regions away from *non*-polar ones at the molecular periphery. Their tetrahedral core units, which appear discoid in projection, can organize themselves under the formation of stakes founding by that *columnar* mesogenity. This process is mainly driven by the micro-segregation of the two well-defined, incompatible, covalently bonded, but sufficiently separated, and as such flexible molecular parts [9,32,90]: the polar centres surrounded by the liquid-like (lipophilic) aliphatic chains forming the 'hairy' periphery of the discs or the 'fur'-like surface of the columns.

Compounds with molecular shapes (**22**) and properties pointed out here belong to a novel family of thermotropic liquid crystals which are easily to be synthesized [90]. Their directed design without anisometric rigid units as known from classical disc-shaped mesogens and without a strong amphiphilicity as known from, e.g., polyhydroxy amphiphiles is a novel approach in the liquid crystal chemistry and may lead to valuable new materials in the near future [90].

2.1.2. Organometallic Mesogens

In the work on liquid crystals, as an art of balancing the various intermolecular interactions with the aim of achieving a desired mesomorphic behaviour, the incorporation of metal ions (the electron acceptors) into chemical compounds (the donor ligands) offers interesting additional possibilities for the design of liquid crystals because of different geometries about the metal centres. Besides dipole-dipole and dispersion forces holding molecules in anisotropic supramolecular arrangements, weak metal-metal and metal-ligand intermolecular interactions occur due to the metals that are part of them.

Several reviews on metallomesogens appeared in rapid succession in the nineties of which five representative examples are cited here [13,15,17–19] proving the wide-spread international interest in as well as the importance of this relevant topic of research on liquid crystals.

As can be learned from this and further literature, various classes of metal-containing liquid crystals large in number and very different in their molecular structures, have been designed and invented since the later seventies, of which, to begin with, seven disc-like, flat examples are selected here for a brief discussion and shown in Figure 2. These are certain cases of bis-(1,3-diketonato)-complexes, supposedly the very first disc-like type of organometallics (**23**), the related dipolar bis(salicylaldimato)oxovanadium(IV)-complexes, as well as lead and first dipolar vanadiumoxo or titaniumoxo complexes of phthalocyanine octaethers or -thioethers. Columnar mesomorphism is common in all these organometallic materials.

Many of the typical metal complexes belonging to this class are obtained by metallation of different macrocycles, e.g., saturated azacrowns, the porphyrin or tetraazaporphyrin system, tetraaza[14]annulenes, or the very large family of phtalocyanine derivatives [91], cf. the structures **24** and **25**, respectively. The same is true for 1,2- and 1,3-diketone or respective Schiff base heavy-metal complexes, e.g., bis(diphenylglyoximato) complexes **26** of nickel(II) and palladium(II) bearing alkoxy chains on the periphery of the molecules, as well as for similar ones of 1,3,5,-triketones or even 1,3,5,7-tetraketones.

Several novel di- or tetrapalladium(II) as well as di- or tetra-platinum(II), so-called orthometal-tallated complexes of multifunctionalized benzalimines or bis(benzal)diimines, cf. **27** and **28**, respectively, accessible from suitably alkylchalcogeno-substituted benzaldehyde and amino- or para-di(amino)arenes, have been synthesized [13,15]. The thermotropic as well as the lyotropic mesophase behaviour of **27** and **28** in apolar organic solvents, have been studied in greater detail. Not only thermotropic columnar ($\mathrm{Col_h}$) phases, but also the first cases of lyotropic nematic discotic ($\mathrm{N_D}$) and chiral nematic discotic ($\mathrm{N_D}$*) phases, have been observed [92]. The tetrametal examples **28** are among the heaviest low-molar mass discotic liquid crystalsand the largest flat metallomesogens ever prepared: their diagonal core-diameters (Dreiding models) from oxygen to oxygen are ≈ 21 Å ($X = \mathrm{Cl}$) or ≈ 24 Å ($X = \mathrm{SCN}$) [93]. For instance, depending on their two central arenylene segments (–▭–:1,4-phenylene in case of **28**, cf. Figure. 2, which from a synthetic viewpoint could easily be modified or extended [94]) the macro-heterocycle of the present tetrametallomesogens **26** is formed at least by eighteen elements: eight carbons, two halogens (e.g. chlorine), four nitrogens, and four metals (palladium or platinum).

Another novel class of metallomesogens displaying a columnar hexagonal phase on heating are the so-called metallocrowns **29** (two members known) which are trinuclear gold complexes with a 9-membered central heterocycle consisting of six nitrogen plus three gold atoms derived from pyrazole ligands [19,95].

The main mesomorphic behaviour of nearly all of these fairly flat metallomesogens is their thermotropic display of columnar types of phases.

Lamellar ($\mathrm{L_D}$) phases, i.e., phases showing the discotic molecules arranged in layers, may be exhibited instead if the number and length of the aliphatic substituents is reduced, see below. Several types of such lamellar phases have been discovered.

Significant examples for the exploration of the critical molecular structure responsible for the change between columnar and lamellar mesophases belong to ß-diketonate copper(II) complexes, to tetraphenylporphyrin copper(II), or to bis(diphenylglyoximato)-nickel(II) complexes. An example of a lamellar mesophase for a large, unique phthalocyanine derivative consisting of two phthalocyanine rings connected via a phenylene unit can also be mentioned [96]. Several other chemical compounds of different structure that also exhibit lamellar phases have been found and published, for instance, even derivatives of the 3-dimensional triptycene, epitaxygens, showing atropisomerism [97].

The chemistry of the respective species, in several cases macrocycles, and of all other possible ligands of interest is well documented in specialist books and/or review articles, see above, through which original papers can also easily be found. The incorporation of the metal ions is always the last step in the syntheses of the metal-containing liquid crystals. The variety of both metal ions and ligands is considerable, and it is surely not only a matter of knowledge but far more of imagination in the fields of synthetic, advanced organic, and physical chemistry to design and to realize new and promising metallomesogens.

2.2 Unconventional Non-linear Mesogens

It is now well established that certain molecules of ‘unconventional’ shapes can, due to specific association phenomena etc., constitute also supramolecular architectures well-suited to showing mesomorphism of a higher, for instance, a columnar order.

Examples of such intermolecular interactions are given in moities with π-π, electron donor-acceptor (EDA, & further below), or metal-metal interactions in case of metallomesogens, charge transfer interactions (cf. further below), large polarizability, strong dipoles due to polar groups, hydrogen bonding, or a possibility of molecular recognition (cf. Fig. 5 & further below), and last but not least by support of self-organization through micro-segregation effects.

Thus, the mesomorphism of diisobutylsilanediol which was initially impossible to classify in the early fifties as belonging to any of the then established mesogen types [98] could, only about twenty-five years later, on the basis of miscibility tests with one of the mesomorphic hexaesters **1** (cf. Fig. 1 and the first paragraph of division **I**, sub-chapter 2.1.1), *just* discovered as the *first discotic* compounds with a *columnar* phase [5], be proved conclusively to display the same mesophase on heating [99]. It was suggested that this silanediol forms a multimer [99,100]. The multimerisation of this small and *non*-discotic molecule with its short and *non*-linear substituents occurs decisively through hydrogen bonding furnishing an arrangement with a surface optimally shaped by the branched alkyl groups. Actually, it surprises that this supramolecular situation indicated by a great bulkiness, the possibility of spontaneous intermolecular hydrogen-bridge formations, by the shortness, as well as *non*-linearity/branching of substituents still allows the occurrence of a mesophase in general: a *columnar* phase.

However, this interesting historical and unconventional example demonstrates impressively that, indeed, many chemical compounds, either totally unsuspected in liquid crystalline regard or possessing a promising large discotic shape but without or only equipped with too short and/or unfavourable substituents, can still exhibit mesomorphic properties; in such cases, certainly, to a high degree because of influences of microphase segregation [9,90].

Materials of this kind are, therefore, of growing interest and will, consequently, in a relevant selection also be in the focus of attention in the following parts of this paper.

2.2.1 Bulky Unimolecular Mesogens

The examples of molecules beginning this sub-chapter are solely metallomesogens which not only show significantly extended physical properties, but also increase the range of geometrical shapes including, for instance, bulky octahedral, square-pyramidal or sandwich-like molecular structures.

Although very different in their mode of construction, each of these materials possess a spacious core region but, nevertheless, exhibits a columnar phase. This fact proves convincingly that a columnar ordering is not only caused by a flat, disc-like molecular shape, but rather

1) by micro-segregation of the rigid, bulky core section from the flexible chains,
2) by attractive core-core interactions, and
3) by the given geometrical situation between the apolar, lipophilic chains and the polar, sphere-like molecular centre.

Therefore, as the materials, selected here for a brief discussion, illustrated with four formulas in Figure. 3 will show, columnar mesomorphism is not restricted only to purely discotic compounds.

From a chemical point of view, the collection of this four spacious liquid crystal systems discussed in the following, which is not completely exhaustive, consists of:

1) dinuclear heavy metal (e.g., copper, nickel, molybdenum, rhodium, ruthenium, tungsten, etc.) tetraalkanoates or tetrabenzoates of type **30**, as well as similar ones derived from alkanedithiocarbonic acids having cores with a ‘lantern’ shape,
2) heavy metal (e.g., iron, manganese, chromium) tris-1,3-diketonates **31** with an octahedral shape,
3) strongly bowl-shaped, non-centrosymmetric calix[4]arene derivatives **32**, or
4) double-decker-/sandwich-like phthalocyanine multiether rare-earth metal complexes of type **33**.

Concerning their relatively advanced chemistry and the huge number of original papers with valuable practical remarks, e.g. about interesting charge transport properties of sulphur-substituted phthalocyanine sandwich complexes of lanthanoids [101], and detailed synthetic descriptions,

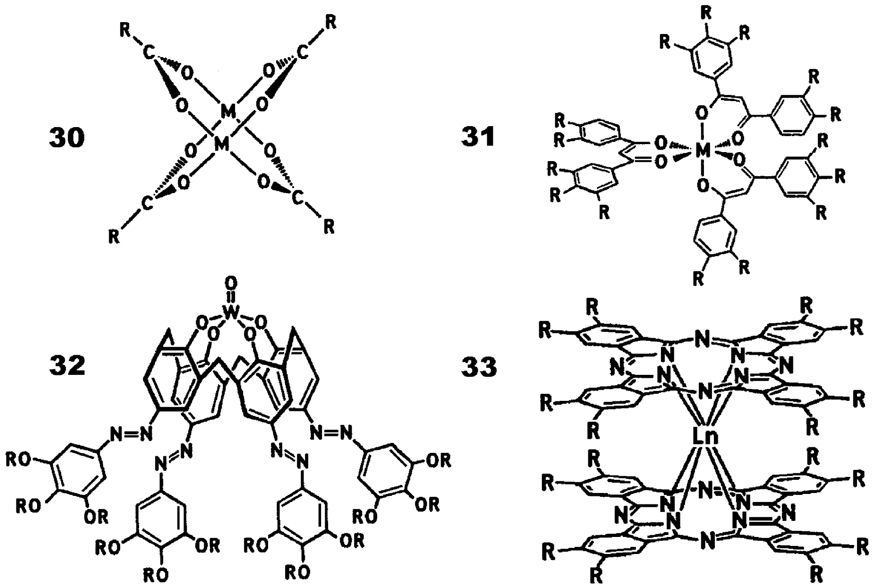

FIGURE 3 Four selected examples of *non*-disc-like, very bulky molecular structures (**30** – **33**) of unconventional but still liquid crystalline organometallics. – R = longer alkyl chains (for **30**, **32**, and **33**; for **30** also 4-substituted phenylene) or alkoxy (for **31** and **33**); Ln = some of the lanthanoids; M = various metals.

the reader is referred to three recent reviews [17–19] and to a book [15] in which the development of the metallomesogen research is critically reflected.

2.2.2 Hydrogen Bonding and Molecular Recognition

Hydrogen bonding between hydroxyl or amino groups and various hetero-functions of natural or synthetic chemical compounds gives rise to different and quite stable kinds of intra- as well as of intermolecular interactions.

In the mid-seventies, this elementary knowledge started only slowly to play a significant role also in liquid crystal research, for instance, on carbohydrate or on other naturally occurring or synthetic multiols, and chemically related materials [31,34–36,102,103]. This late exertion of influence is surprising, since the mainly *smectic* mesomorphism of carboxylic acids – by dimer formation due to hydrogen bonding between carboxylic groups of two such acids, leading to an 8-membered heterocycle – was already well established long before [21,104,105].

In the meantime it is fully accepted that also *columnar* phases can occur by way of hydrogen bonding between either identical or different individual

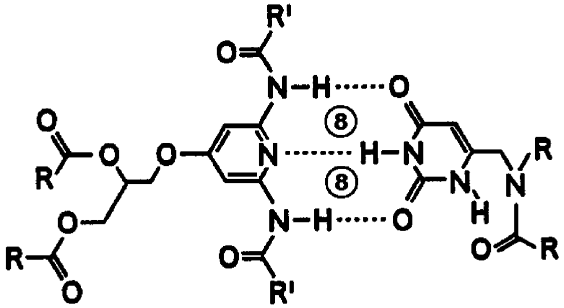

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FIGURE 4 A treply intermolecular hydrogen-bonded mesogenic, a $\mathrm{Col_{ho}}$ phase forming product (**34**) with two 8-membered heterocycles fused with one another, originated by molecular recognition of the two complementary components: the diacylaminopyridine (left) and uracil moieties [107]. R = longer alkyl chains; R′ = methyl.

molecules, each far from being discotic in shape [31,34–36,106]. In the latter case, such interactions symbolize molecular recognition processes becoming more and more important in basic research and natural sciences.

The *inter*-molecular, triply hydrogen-bonded mesomorphic complex **34** [107] consisting of the two complementary components uracil and diacylaminopyridine (cf. Fig. 4) giving rise to two condensed (fused) 8-membered heterocycles and to the display of a columnar hexagonal phase, may serve here as the leading example. See also the multicyclic, columnar mesogenic metal complex **26** [15,108] with its two *intra*-molecular hydrogen bridges in the vertical axis of the molecule (cf. Fig. 2) causing in this case the formation of two 6-membered, carbon-free, 'spiro'- like situated heterocyclic rings through which the molecular flatness is very well stabilized.

A recent example applying this experience on molecular recognition processes, e.g., as a strategy principle for the design or variation of columnar phases is depicted in Figure 5 [109]. The disc-like 2,4,6-tri(arylamino)-1,3,5-triazine, a melamine derivative with an own enantiotropic $\mathrm{Col_{hd}}$ phase between 70.4 and 154.6°C, suffers a variation of its mesophase in binary mixtures with *non*-liquid crystalline dialkoxybenzoic acids. The result is also an enantiotropic columnar phase either with a hexagonal or a rectangular lattice, however, at considerably lower temperatures [109], i.e., near room temperature. The two complimentary chemical units constitute the supramolecular adduct **35** with an 8-membered heterocycle due to the expected spontaneous intermolecular hydrogen-bond formations.

Besides these and many more such cases, studies on members of the large family of sugar derivatives [36] (open-chained [110,111] or cyclic

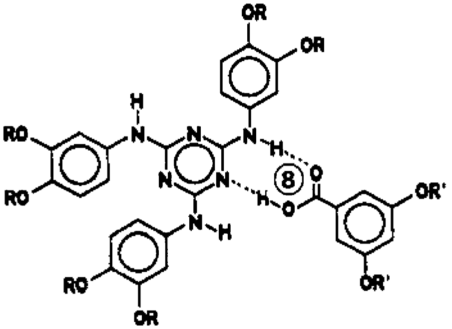

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FIGURE 5 A doubly intermolecular hydrogen-bonded mesogenic product (**35**) with an 8-membered heterocycle, fused with the 1,3,5-triazine ring, obtained in a molecular recognition process of a disc-like (by itself thermomesomorphic) N,N′,N″-triarylmelamine derivative with a *non*-mesomophic 3,5-dialkoxy-benzoic acid [109]. – R = R′ = decyl, or other long alkyl chains for R′.

ones [33,112]), mainly ethers of various isomeric but sterically stable, naturally occurring inositols [33–36,112], as well as of amino or amido compounds or of materials with mixed hydroxyl and amino functions, revealed important details about the formation of columnar phases under the delicate influence of stereochemical factors, as well as of the numbers and positions of the alkyloxy chains [33,112]. Figure 6, showing the columnar arrangements of the four inositol multiethers **3** and **36** to **38**, in part unlike in their numbers of ether groups or their stereochemistry, shall try to illustrate the structural details just mentioned before and also give an impression of these complicated and, at first glance, somewhat confusing interrelations. Whereas the scyllitol hexaether **3** is monomeric exhibiting a $\mathrm{Col_{ho}}$ phase, the two vicinal inositol tetraethers **36** and **37** form dimers displaying different columnar phases: a $\mathrm{Col_h}$ or a $\mathrm{Col_{sq,o}}$ phase, respectively. On the other hand, the scyllitol diether **38** forms a dynamic multimeric assembly of four to five molecules showing the same $\mathrm{Col_h}$ hase the dimer **36** does.

Parts of these results founded the following widely confirmed hypotheses [111,112]:

1) aliphatic chains of wedge-like amphiphiles, geminally branched spontaneously organize in micellar-like multimers by hydrogen bonding and contain on average per slice four to five of such molecules forming columns of a mesophase of hexagonal symmetry [110–114], or
2) cyclic vicinal *cis*- or *trans*-diols (**36** and **37**, cf. Fig. 6) each furnished with four chains give only hydrogen-bridged dimers, which also pile up

one on top of the other to form columns as parts of columnar phases [112]. These mesophases differ in their symmetry, as controlled by the configuration of the diols; see details in Fig. 6.

In general, the hydrogen bonds should be directed perpendicularly to the column axis, but simultaneously support the intracolumnar stability by a vertical hydrogen bonded network.

2.2.3 Polycatenar Types of Mesogens

Subject of this part is a brief discussion of chemical compounds imaginable as ‘extensively stretched’ discotic liquid crystals or as being composed of two properly substituted half-discs with a (widely unsaturated) rod in between. They are termed polycatenar mesogens (**39**–**44**) with four or up

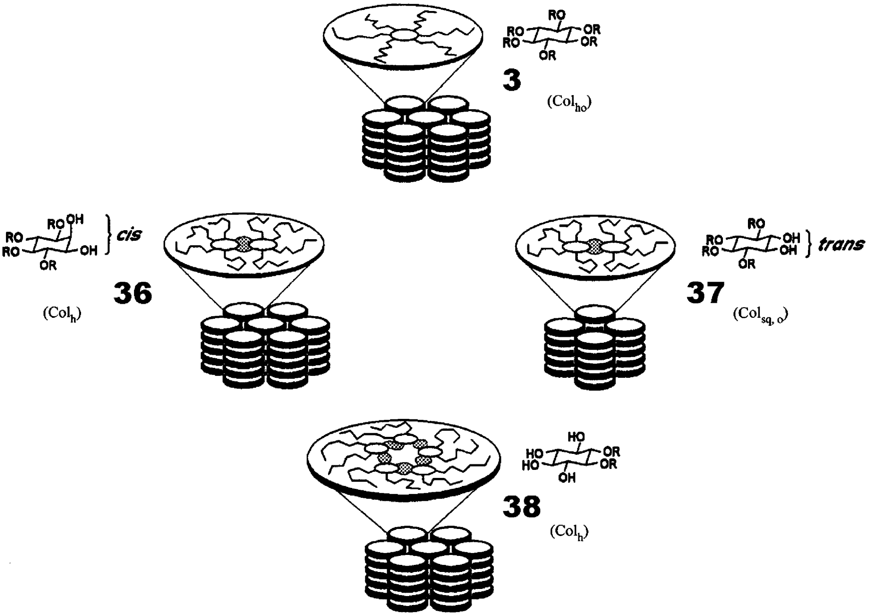


FIGURE 6 The mesophase formations of the four inositol multiethers **3** and **36** – **38** differing in numbers and positions of their ether groups and in the stereochemical situations of their free hydroxyl functions [33–36,112]. The blown-up slices of the columns depict their inner arrays with the different inositol multiethers in the numbers one (**3**), two (**36**, **37**) or five (**38**). The hydrogen-bonded regions of the hydroxyl functions of the three multiethers **36** – **38** in be-tween the cyclohexyl rings, shown as small ellipses, are hatched. The zigzags symbolize hexyloxy chains (R).

to six saturated linear chains in total at both ends of the molecules and a similar molecular architecture [20,115]; cf. the collection of selected model compounds shown in Fig. 7 which also shows a so-called ‘double-swallow’-tailed mesogen (**45**).

Shape and mesophase behaviour of phasmides, e.g., of **39**–**41**, and in particular of the so-called biforked compounds of type **44** which carry only *two vicinal* aliphatic chains instead in the 3,4-positions at both terminal phenylene rings, contribute to bridge the gap between rod- and disc-like liquid crystals. A similar role as the mesogens **44** [20,115] play those of series **45** [116] of which the latter are regarded to be special cases of the ‘bifork’-like *tetra*-catenar species.

The length of the inner (mostly linear) segment of polycatenars can be shortened if further potent interactions are present and the intramolecular contrast is thereby increased; see for instance the deep red bislactam **40** [117].

Lately, metallomesogens contribute more and more to this section of liquid crystal research, as it may be demonstrated by the three novel columnar phase-forming examples **41**–**43**:

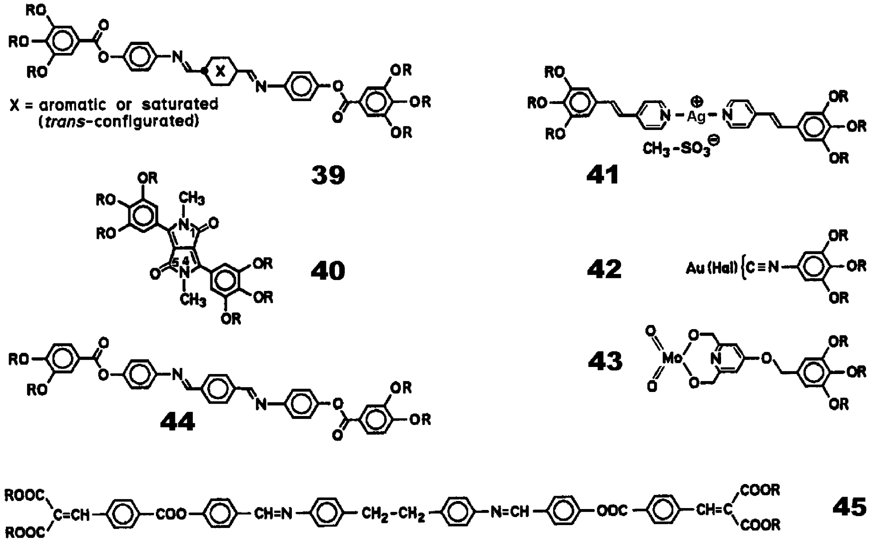


FIGURE 7. Thermomesomorphic ‘multicatenar’ phasmidic compounds **39** – **41** as well as **42** and **43**, examples of so-called ‘half-phasmidic’ materials [20,115,119]. The Compounds **44** and **45** represent the liquid crystal families of the so-called ‘biforked’ or ‘double-swallow-tailed’ substances, respectively [115,116], both showing similarity in mesomorphic behaviour.

1) the ionic, ideally phasmidic silver complex **41** [19,118,119] formed from two smaller 'half-phasmidic' building units of a trialkoxy-azastilbene linked together linearly by metallation with silver salts,
2) the copper(II) complexes of masked 1,3-dicarbonyl or 1,3,5-tricarbonyl precursors [120] with two shorter 'half-phasmidic' building units, in part, more broadly spaced core segments,
3) a helically twin-like ionic bis-copper(I) complex, i.e., a copperhelicate of a unique 'bis-phasmidic' structure [121], or
4) two similar 'half-phasmidic', 'racket'-like gold [122] or molybdenum [123] complexes: **42** or **43**, respectively.

Probably, the latter two mesogenic complexes stack in such a way that the metal head groups constitute the 'spinal centres' of the columns, from which the bodies of the molecules with their three chains point outwards. Thus, what might be termed as 'stepped phasmidic dimers' of infinite number (being then hexacatenar-like), assembled in a screw-like manner, might set up those columns responsible for the columnar mesomorphism of the two *non*-disc-like mesogens.

The hexacatenar phasmidic bislactams of series **40** and similar neutral or ionic liquid crystals with shorter core sections nearly always display *only* columnar phases [117].

In contrast, biforked mesogens, i.e., tetracatenars of type **44** as well as double swallow-tailed compounds of type **45**, give rise to a very interesting polymorphism which may include ***nematic***, ***smectic***, ***lamellar***, ***cubic***, and ***columnar*** phases [115,116]. The latter materials (**45**) may be considered as special cases of tetracatenar mesogens, of which the aliphatic chains are not directly attached to the terminal rings but via a C=C double bond.

At this point, it is important to take note of the results of dilatometry and X-ray diffraction experiments with such biforked materials regarding the change from a lamellar to a columnar phase [20]. Above the smectic to columnar phase transition, the rigid cores' sub-layers break into columns due to strong undulations, separated by the section of the aliphatic chains forming a continuous 'fur'-like medium. Furthermore, most X-ray diffraction patterns obtained of this columnar phase are characteristic of a hexagonal symmetry [20,115]. Obviously, π-π interactions and those caused by polar groups result in spontaneously assembled aggregates of two to four of the rod-like molecules, packed side by side to form the lattic units [20,115], becoming so more or less disc-like in shape. These 'slices' accumulate one on top of the other, forming a rope-like trunk with the aliphatic chains at its outside as a kind of 'fur' or soft matrix (in the latter picture a kind of 'internal, covalently bound solvent' [13,14]). The columnar core of this pattern has a diameter corresponding to the length of the linear, quite rigid core of the individual molecules.

It appears to the author that this particular kind of gradual ordering: single rod-like molecules ➲ supra-molecular 'slices' ➲ their columnar stacking can be compared with a picture put forward already years ago [9] explaining columnar phase formations through molecular associations of rod-like polymers of biological interest.

The synthesis of the long, calamitic representatives occurs in simple steps of condensation between differently functionalized, mostly aromatic carbocycles, as well as by esterifications of phenolic hydroxyl groups of commercially available precursors. Necessary amino groups are introduced by nitration of the selected arene derivatives and subsequent reduction of this nitro function.

The long core segments can also be formed from other smaller building units connected by hydrogen bonds or, as referred to above, by metallation. The chemistry of the metal-containing materials of this section mainly deals with synthetic efforts for the various ligands, which are based on standard reactions following literature procedures. The metals are always incorporated in the last step by well-known means. Usually, the overall chemical yields are quite good, as the purification of the target compounds is without difficulties.

Preparations of polycatenar compounds with shorter and other polar molecular backbones, e.g., of the bislactam series **40**, are more costly in money and time and give considerably lower chemical yields. This type of pigment material (cf. the other one: type **11**, chapter 2.1.1, division II [66]) is an extremely colourfast, diphenyl-substituted series of derivatives of the so called pyrrolopyrrol ring system, i.e., they are fluorescent, deep red dyestuffs of high thermostability which exhibit a columnar type of phase in temperature ranges between about 30 to 50 K around 100°C. These pigment mesogens belong to the industrially important family of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dions, the so-called DPPD-pigments [124].

Their preparation starts from suitably substituted benzonitriles which can be obtained from corresponding amides, for their part accessible in several steps by dehydration. Under basic conditions, these nitriles react with alkyl succinate under cyclization, furnishing the bihetero-cyclic ring system in **40** which after N-methylation yields the target compounds in low-to-moderate chemical yields [117].

Other representatives of these pigment mesogens, with differently functionalized polar core sections, are only of scientific interest; their syntheses are similarly complex and tiresome.

2.2.4 Electron Donor-Acceptor/Charge-Transfer Complexes

In this last sub-chapter, another principle of preparing liquid crystals consisting of a disc-like electron donor-molecule and a non-discotic electron acceptor-material is discussed briefly, the study of which was started independently by two research groups nearly fifteen years ago; cf. also one paragraph of division III of sub-chapter 2.1.1 of this paper and review [80]. The first one [125] dealt mainly with derivatives of triphenylene (**5**, cf. Fig. 1) as donor and the trinitro-fluorenone **46** (TNF, cf. Fig. 8) as acceptor compounds, whereas the interests in the other laboratory [53,126] were focused on radial multiynes (**14–17**, cf. Fig. 1) also in combination with **46**.

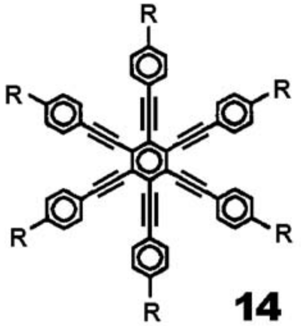
In mixtures of both components either in their pure states or advantageously in a suitable organic solvent, such donor and acceptor molecules pile up spontaneously in a regularly alternating way to form columns as sketched in the lower part of Fig. 8 and represented there by means of a radial hexayne (**14**) and the trinitro-fluorenone **46** as examples for such starting materials shown in the upper part of that Figure.

The products are completely different types of mesogenic species than known before but display columnar phase behaviour sometimes topped off with a nematic kind of appearance [80].

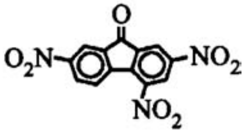
Interestingly, at least one of the components needs *not* to be of discotic shape, as also *non*-mesomorphic (e.g., the donor) compounds of various molecular structures, disc-like in shape, can develop columnar mesomorphism when doped with an acceptor compound, e.g., with the *non*-mesomorphic trinitrofluorenone **46** or with suitable derivatives of nitrated fluorenone [80]. Valuable examples for the latter derivatives are: the 2,4,7-trinitro-fluorenylidene-9-malonic acid di(hexadecyl)ester [127] and the commercially available (+)- or (−)-TAPA [128], both very effective and, therefore, commonly applied kinds of dopants; the last one induces even chiral mesophases.

As the last cases have clearly illustrated, these kinds of intermolecular interactions with their beautiful results are so-called mesophase inductions. Columnar phases can also be induced by mixing nematic discotic (N_D) materials (which are only poorly ordered) with TNF (**46**); cf. the arbitrarily chosen example shown in Fig. 8. Either new or other (e.g. ordered columnar) mesophases may occur, i.e., may be induced, or existing ones may (only) be stabilized by addition of the right dopant. For instance, compare the mesophase change from nematic (N_D) to columnar (Col_{ho}) and see how the transition temperatures change between the pure radial hexayne **14** (R = heptyl) and its charge-transfer complex with TNF (**46**); cf. the data given in the caption of Fig. 8.

Along with these *inter*molecular donor-acceptor mesogens also *intra*-molecular ones, so-called donor-acceptor twin mesogens, with long and flexible bridging chains between their electronically different moieties synthesis was started about ten years ago [129] with focus on hexaalkoxy-triphenylene **5** (Fig. 1; *columnar* liquid crystals) and suitable derivatives of



14



46

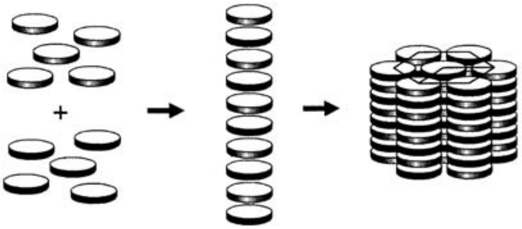


FIGURE 8. The chemical structures of the radial hexayne **14** (cf. Fig. 1; R = heptyl: Cr 99.0 (44.4) N_D 132.6 (0.4) Iso) [52] and the *non*-mesomorphic electron acceptor molecule 2,4,7-trinitrofluorenone (TNF, **46**, m.p.: Cr 176 Iso) [80]. An equimolar mixture of these two compounds **14** and **46**, an electron donor or acceptor molecule, respectively, leads to a conversion of the original nematic discotic phase of **14**, i.e. to the induction of a columnar phase with the transition data: Cr 67.9 (62.0)Col_{ho} 154.9 (8.3) Iso [80]. Cr: crystalline, N_D: nematic discotic, Col_{ho}: ordered columnar hexagonal, Iso: isotropic liquid; temperatures: °C; enthalpies: kilojoule, given in round brackets. ***Lower part***: A sketch depicting the spontaneously, in a regularly alternating way occurring pile up of donor (blank) and acceptor (shaded) molecules in columns and the subsequent induction of a Col_{ho} phase as a result of charge-transfer interactions.

multinitro-fluorenone. These first novel twin materials were described to display only columnar phases on heating.

A couple of years later, analogous covalently linked donor-acceptor complexes based on radial pentaynes of type **15** (Fig. 1; *nematic discotic* liquid crystals) and properly functionalized trinitrofluorenone (**43**) were found to exhibit (strongly depending on the substituents of the radial pentayne unit) a higher ordered columnar phase or with a nematic columnar, N_{Col}, phase in addition [130; cf. also a tabular survey of further twins with transition data in ref. 53]. There are also twin compounds known which exhibit an induced chiral nematic columnar type of phase due to the chiral TAPA as part of the starting material. It is presumed that the chemical linkage of the molecular donor and acceptor ends by the bridging section leads to an alternating arrangement of the molecules in neighbouring columns [129,130]. At the same time, the columns are laterally held together because of countless chain-like links between them, thus, forming a network of vertical columns more or less in a parallel array.

This very interesting electron donor-acceptor or charge-transfer concept of variation or induction of mesomorphic self-organization of proper compounds in mixtures or twins could be valuable in material science, for the design of columnar or nematic columnar mesomorphic systems and to tune their properties for different applications and syntheses of organic semiconductors, molecular electronics, or *non*-linear optics, etc.

3. CONCLUDING REMARKS

The wide variety of materials with regard to their chemical construction as well as to their molecular or supramolecular shape, selected and discussed in the preceding chapters, proves that discotic or rather *non*-linear mesogens have become a very strong, fascinating, and still growing field of liquid crystal research.

Curiosity and fantasy for innovative design of novel mesogenic molecule structures as well as for the elucidation of occasionally surprising behaviour of new materials are the main requirements for further progress in this area opened twenty-five years ago [5].

In this connection and in particular due to the spacious conditions of discotics in comparison with calamitics regarding their molecular dimension and space-filling (cf. Fig. 3), the recognition and/or prediction of the kind and degree of influences of the various intermolecular interactions on the type and strength of mesogenity plays here also a significant role. For the understanding of such phenomena does the attention of effects of microphase segregation gain more and more importance [9,90], although brought into notice, also for columnar orderings, already fifteen years ago [90].

The numerous classical synthetic routes to uni- or supramolecular discotic liquid-crystalline systems have been enriched by those leading, for instance, to polycatenar or swallow-tailed compounds, as well as to stereochemically controlled hydrogen bonding arrangements including cases of molecular recognition or to charge-transfer complexes displaying either varied or induced mesophases. Furthermore, the possibilities for the design of discotics have considerably expanded by the incorporation of metals into organic molecules through which a great variation of their shapes and the access to many novel classes of mesophases with exciting properties became possible due to the different geometries of the metal centres.

From an optimistic viewpoint it seems possible to foresee that tailor-made mesophases of disc-like materials and technological applications are more and more feasible. Already some time ago, a first glimmer of hope was one of the many thermomesomorphic triphenylene (**5**) derivatives [48] found to be an excellent photoconductor [61]. Recently, even a first commercial application of discotic liquid crystals with the same core system **5** by the Fuji Photo Film Company became known. More chances could probably be found in the field of polymer chemistry. This current promising development should strongly motivate people's work on self-organized materials following the motto: "Mesophases Made to Measure" .

A driving force behind the progress in this and every other area of synthetic work could be seen in the popular rhyme coined by the famous German writer ***Erich Kästner*** (1899–1974): "Es gibt nichts Gutes, außer man tut es", probably, similar to the English saying: "Actions Speak Louder Than Words".

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[10] a) Vorländer, D. (1923). ***Z Phys. Chem.***, ***105***, 211. A quotation of the first ten lines of a paragraph starting on page 241 of this German paper relevant to this matter: ***English version*** (by K. Praefcke): "**Do star-, cross-, and leaf-like molecules form liquid crystals?** The weakening of liquid crystalline properties, frequently proved in cases of slightly branched or angled molecules, allows it to foresee that molecules, chiefly leaf-, cross-, or star-like in shape, don't form liquid crystals at all. One might well think that flat

molecules via their broadsides stack up in a kind of Voltaic column, so that anisotropic buildings do follow. However, our experiments are against this assumption. . . . ”
b) See also in Vorländer, D. (1924). Leipzig: Akademische Verlagsgesellschaft m.b.H. 35 and 39. (1925). *Chem Abstr. 19*, 954.

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c) Cf. similar instructions in that *Handbook of Liquid Crystals*, Vol. 2B, concerning the *columnar* type of phases also given in chap VII, 693; chap VIII, 750; chap XVI, 954.

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