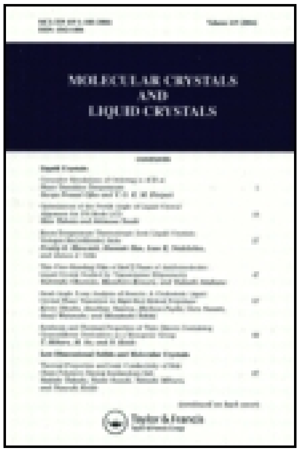

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Design of Low-molar Mass Thermomesogens in the Search for Biaxial Nematic Liquid Crystals

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Design of Low-molar Mass Thermomesogens in the Search for Biaxial Nematic Liquid Crystals

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In this article we describe research into the molecular design features for potential thermotropic biaxial nematogens of low-molar mass. We discuss how we can systematically change the shape of molecular structures in view of this aim of our work. The optical biaxialities of the materials prepared were tested through conoscopic and birefringence measurements. So far none of these materials synthesised and tested in this way have unequivocally exhibited the biaxial nematic phase. An overview of numerous further materials different in molecular shape and in part studied by others is also given.

Keywords: Biaxial nematics; liquid crystals; geometrical factors; metal complexes; metallomesogens; multifunctional compounds; radial multifaces; synthetic routes

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1. INTRODUCTION

Over the past few years, biaxiality in liquid crystal systems has been a topic of some importance to research in molecular materials. However, the term biaxiality has been used indiscriminately to describe a number of different physical phenomena at different length scales, thereby leading to a confusing situation.

Firstly, it should be recognised that the term biaxiality can be used in the description of various optical and electrical properties, for example, it can be shown that a strong dielectric biaxiality is important in ferroelectric liquid crystal devices (SSFLCDs) [3], whereas optical biaxiality is less relevant in such applications. Thus, the nature/type of the biaxiality is important in the description of the system [4].

Secondly, the length scale for which biaxiality is measured is critically important to the portrayal of a bulk system. For example, *locally* a system may be biaxial as described by X-ray diffraction, but for the bulk system the biaxiality, as determined by conoscopy, may be lost. This could be due to a loss in the long range order for the bulk system stemming from either a breakdown in translational order, or alternatively because of the presence of mosaic domains. Thus, as we examine a system more closely, as the magnification of our examination increases, so too does the likelihood of observing biaxial order.

Thirdly, biaxiality is a property which is expected to have a significant life time. Thus, the molecular dynamics of the system will play an important rôle in the stability of the biaxial order.

Fourthly, biaxiality can be conferred by the surrounding environment of a bulk system, *e.g.*, by any kind of surface and wall effects *etc.* These effects need to be screened out in order to make a correct evaluation of the biaxial order of a system!

In nematic phases all of the above concerns have to be taken into account when we describe the mesophase as being biaxial. Certainly surface and wall effects, molecular dynamics, and the scale of the measurements must be carefully considered when investigating nematic phases. The criteria, however, for determining the extent of the optical biaxiality of such a phase is usually related to birefringence or conoscopic measurements taken over sample areas of at least several microns (*i.e.*, rather than measurements made by X-ray diffraction in the Ångstrom regime).

2. DESIGN TEMPLATES FOR BIAXIAL NEMATOGENS

At present two forms of the nematic phase are known, one that is optically uniaxial with a positive birefringence and one that is optically uniaxial but with a negative birefringence.

These forms correspond to the nematic calamitic (positive) and nematic discotic (negative) phases. Essentially, these two types of nematic phase differ because the principal transition moment axes are at right angles to one another in respect of the structures of the materials that form the two types of phase. In the nematic phase of a calamitic system the molecules can be considered as having rod-like or cylindrical shapes with their breadths (a) being considerably shorter than their lengths (b), see Figure 1. The reverse is the case for the flat, disc-like variant. If we consider taking a calamitic molecule and converting it into a disc-like one, we would have to compress the length and stretch out the breadth. In doing so it is possible that we might pass through a situation where the molecular structure becomes somewhat *board*-like. In this case the thickness of the molecule will differ from the breadth, and the transition moments along the *a*, *b*, and *c* directions will have to be taken into account when considering the optical properties, *i.e.*, the material will become optically biaxial [5].

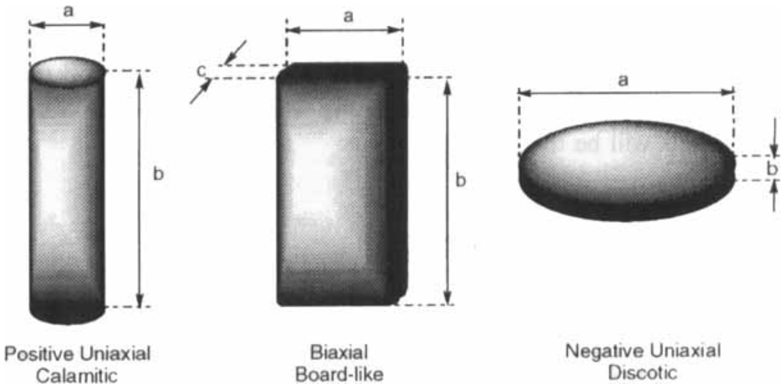


FIGURE 1 Shapes of molecular structures that might form either uniaxial or biaxial phases.

Thus the first criteria in designing materials that might exhibit optically biaxial nematic phases is to create molecules with structures that are *board*-like [6], and that have three principal transition moments. However, translating this design feature into real molecular templates is difficult for the following reasons.

1. Materials that have large board-like molecular structures are more likely to be crystalline and, therefore, melt at high temperatures thereby reducing the possibility of observing a biaxial phase.
2. Materials that have large board-like molecular structures are more likely to form mesophases that have a more ordered structure than a nematic phase.
3. For the materials to exhibit liquid crystal properties they typically must have flexible aliphatic tail units which will tend to weaken the board-like characteristics of the molecules.
4. In the final analysis the materials must not be able to exhibit conformational folding, bending or twisting which might change their molecular shapes.

Once a template structure has been developed, it is hoped that the structure will help to maintain the local biaxial packing over a long distance. Figure 2 shows a proposed structure for a biaxial nematic phase where the molecules have board-like template structures. For the biaxial order to be preserved, the molecules must not be allowed to flip easily about any of their three axes (in the *a*, *b*, and *c* directions shown in Fig. 1) so as to produce a disordered structure, rather it is hoped that they will at least have rotational energy minima that will stabilise the structure. However, given that the calamitic molecules in their conventional nematic phase rotate about their short axes on a time scale of 10^6 times per second, and about their long axes 10^{11} times per second, it is difficult to envisage how a local biaxial arrangement of molecules could persist for long periods. In actual fact, it is more likely that dynamically fluctuating clusters of biaxial molecular arrangements will be the norm.

3. β-DIKETONATE TEMPLATES

The first material that was thought to exhibit a biaxial nematic phase was a copper(II) complex of a β-diketone [7], the structure for which is shown in Figure 3(b). This material is a member of the general family of metal complexes which have the common structure shown in Figure 3(a), where

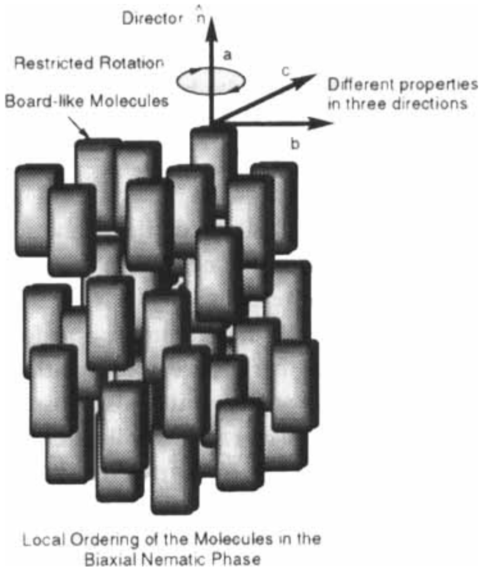


FIGURE 2 Cartoon of the proposed structure of the biaxial nematic phase.

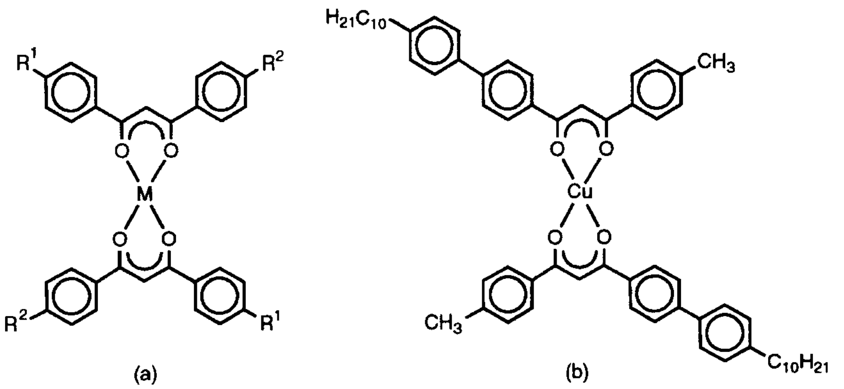


FIGURE 3 The first class of materials thought to exhibit biaxial nematic phases [7, 8], R^1 and R^2 substituents as described in the text of this paragraph.

the substituents R^1 and R^2 and the metal can be varied. The general β-diketonate template shown has a board-like structure, and when it is asymmetrically substituted as shown in (b) it will have three different transition moments, and hence will have the potential to exhibit a biaxial nematic phase. Chandrasekhar *et al.* [7] have extensively investigated the optical properties of this material in the presence and absence of electrical fields and in mixture studies, and they record that the material exhibits optical biaxiality. However, this material has been resynthesised in the Hull group [8], and unfortunately it was not possible to reproduce the results obtained previously [7].

Nevertheless, this template proved to be a useful starting point for investigating the effect of molecular shape on the formation of liquid crystal phases with particular emphasis on the nematic phase [8 – 11]. Symmetrical systems, where $R^1 = R^2$, can have either disc-like or X-shaped structures depending on the length of the R^1 and R^2 units, and for unsymmetrically substituted systems $R^1 \neq R^2$, the materials can have either cross- or zigzag-shaped structures. It should be noted that it is also possible to have *cis* and *trans* isomers for these materials. The *cis* isomer has never been found in the systems studied because all of the materials investigated recrystallise in their *trans* formats. Nevertheless, it is possible that the materials undergo *trans*/*cis* interconversions at high temperatures.

Figure 4 shows three variations in template structure for copper(II) complexes of β-diketones investigated during a programme of research at Hull university yielding results for such materials discussed in the following Sections 3.1 – 3.3 along with oxovanadium complexes in Section 3.4 being *bowl*-like in structure.

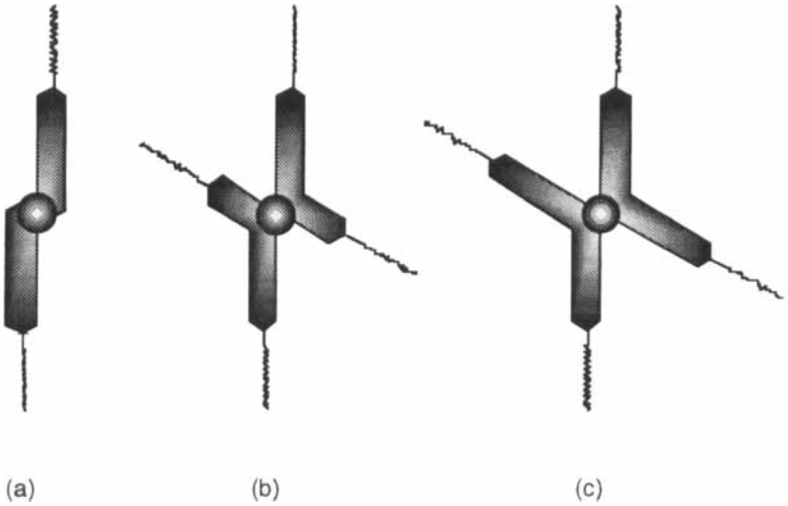


FIGURE 4 Three variations in template structure for copper(II) complexes of β-diketones, (a) *zigzag*-, (b) *cross*-, and (c) X-shaped materials.

3.1. β-Diketone Copper(II) Complexes with *Zigzag* Structures

Table I shows β-diketonates that were prepared where two of the arms of the basically X-shaped arrangement of substituents are relatively short, *i.e.*, they do not contain aromatic rings.

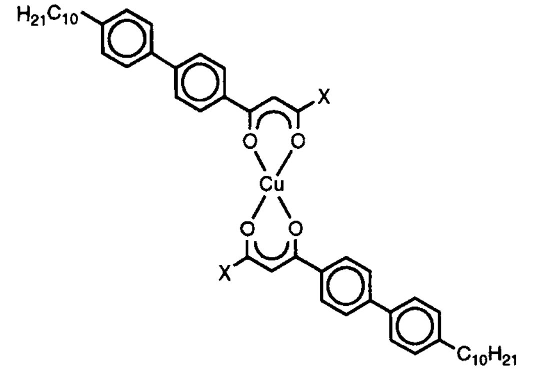
For short substituents such as methyl no liquid crystal phases were observed, however, decomposition of the materials was a problem. The melting points of these materials are relatively high, so in order to investigate the liquid crystal properties of this zigzag template further either the melting points had to be lowered or the clearing points needed to be raised.

Table II shows how this was achieved by either replacing one of the aromatic rings in the biphenyl unit with a cyclohexyl ring, or by introducing fluoro-substitution into the biphenyl unit. In both cases the symmetry of the template structure was further reduced, resulting in *monotropic* nematic phases being observed for all three materials shown in Table II. Conoscopic studies on these materials revealed that the nematic phases were uniaxial.

3.2. β-Diketone Copper(II) Complexes with *Cross*-shaped Structures

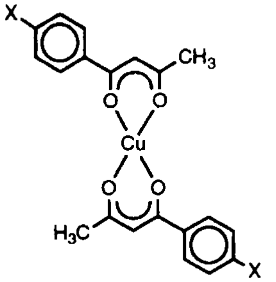
Materials with cross-shaped structures were prepared from β-diketones where one arm of the β-diketone carried a single phenyl unit and the other a

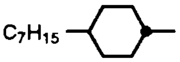
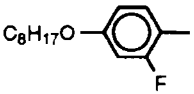
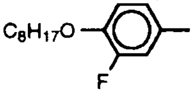
TABLE I Transition temperatures (°C) for some zigzag shaped copper(II) β-diketone complexes, Cr = crystalline, Iso = isotropic, dec. = decomposition



X	*Cr*		*Iso*
H	•	160 (dec.)	•
CH_3	•	192	•

TABLE II Transition temperatures (°C) for some substituted *zigzag*-shaped copper(II) β-diketone complexes, Cr^1, Cr^2 = two crystalline phases, N = nematic (here: monotropic), Iso = isotropic

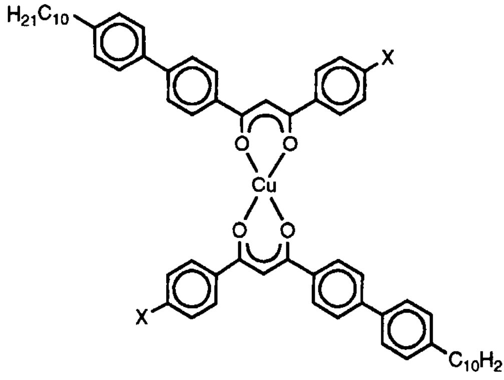


X	*Cr*^{1}		*Cr*^{2}		*N*		*Iso*
	•	140	•	193	(•	192)	•
	•	180	•	198	(•	191)	•
	•	225	•	231	(•	202)	•

biphenyl moiety. The effects of various substitutions and substitution patterns in the arms were investigated, again in relation to the formation, stability and biaxiality/uniaxiality of the liquid crystal phases produced. However, in order to make rigorous comparisons between the various complexes, we retained a decyl terminal chain in the 4-position of the biphenyl arm in all of the materials prepared, whereas the systematic changes were made to the phenyl arm.

Table III shows the effect of varying the polarity of the substituent at the 4-position of the phenyl ring in cross-shaped copper(II) β-diketone complexes. All of the materials show *monotropic* nematic phases, with the trifluoromethyl- and bromo-substituted materials exhibiting additional smectic A phases. The melting points and clearing points for the series are high and are of a similar magnitude to the zigzag-shaped complexes. Thus, the addition of a phenyl unit (compare structures with the zigzag-series of materials shown in Tabs. I and II) has not made much difference to the melting and clearing transition temperatures. This outcome is surprising as the addition of phenyl units to conventional rod-like calamitic systems

TABLE III Transition temperatures (°C) for some substituted cross-shaped copper(II) complexes of the 1-(4′-decylbiphenyl-4-yl)-3-(4-substituted phenyl)propane-1,3-diones where the polarity of the substituent is varied, SmA = smectic A, *cf.*, the other notations in Table II



X	Cr^1		Cr^2		*SmA*		*N*		*Iso*
H	•	198	–		–		(•	156)	•
F	•	189	•	193	–		(•	175)	•
CF_3	•	188	–		(•	131	•	131)	•
Br	•	205	•	212	(•	182	•	183)	•
CN	•	230	–		–		(•	203)	•

generally results in large increases in transition temperatures; however, conversely the temperatures may not increase concomitantly with the number of phenyl groups, and hence molecular weight, because the molecules are becoming more disc-like.

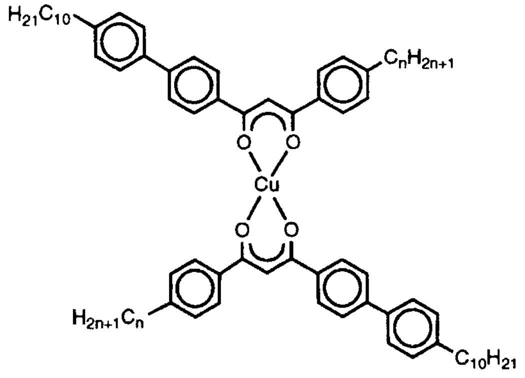
The smectic A and nematic phases of these materials (see Tab. III) were also found to be uniaxial by conoscopy. It is interesting that these materials exhibit smectic phases in addition to the nematic phase. This demonstrates that the materials must have structures that are calamitic rather than disc-like even though they are cross-shaped. Obviously this raises fundamental questions concerning how the molecules pack in the layered structure of the smectic A phase. Even though the molecules have cross-shaped structures they must have disordered packing arrangements in order to sustain the layered structure of the smectic phase, which in turn also suggests that the nematic phase is disordered and as a consequence not biaxial.

The 1-(4′-decylbiphenyl-4-yl)-3-(4-alkylphenyl)propane-1,3-diones, where the alkyl chain of the substituent on the shorter arm was varied in length, were also used in synthesising cross-shaped complexes. Like the polar substituted systems, these materials exhibit *monotropic* nematic phases for the shorter homologues (methyl to butyl), or else they were not mesogenic, see Table IV. The materials, like others studied, did not appear to exhibit biaxial nematic phases.

Various other substitution patterns were tried in order to stabilise the mesomorphic properties of the copper(II) complexes. For example, polar substituents were incorporated into the longer biphenyl arm of the complex, see Table V, and off-axis substituents were incorporated into the shorter arm *via meta*-substitution, Table VI.

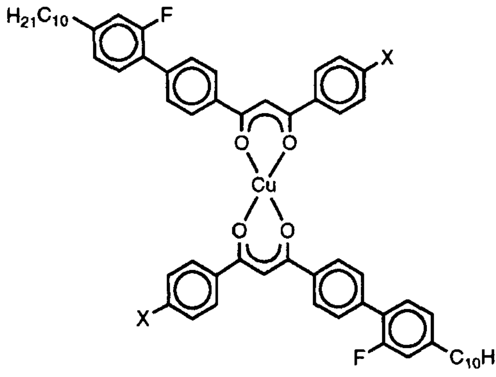
In both cases the only liquid crystal phase observed was the (*monotropic*) nematic phase. As with the other materials in this study, melting points remained stubbornly high and the liquid crystal phases were consequently monotropic. As with other series in this family of materials, polymorphism of the crystal state was observed for some compounds, with crystal to crystal transitions being detected by differential scanning calorimetry. The nematic phases investigated did not appear to be biaxial from conoscopic investigations.

TABLE IV Transition temperatures (°C) for some substituted cross-shaped copper(II) complexes of the 1-(4′-decylbiphenyl-4-yl)-3-(4-alkylphenyl)propane-1,3-diones where the aliphatic chain length of the substituent is varied, see the notation given in Table II



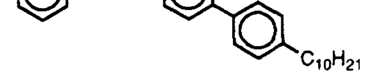
n	Cr^1		Cr^2		*N*		*Iso*
1	•	197	•	221	(•	167)	•
3	•	173	–		(•	153)	•
4	•	175	–		(•	150)	•
5	•	176	–		–		•
6	•	178	–		–		•
7	•	181	–		–		•
9	•	178	–		–		•
10	•	188	–		–		•

TABLE V Transition temperatures (°C) for some substituted cross-shaped copper(II) complexes of the 1-(4′-decyl-2′-fluorobiphenyl-4-yl)-3-(4-substituted phenyl)propane-1,3-diones, see the notations given Table II



X	*Cr*¹		*Cr*²		*N*	*Iso*
CH_3	•	157	•	192	(• 146)	•
OCH_3	•	174	•	178	(• 153)	•
F	•	153	–		(• 141)	•

TABLE VI Transition temperatures (°C) for some substituted cross-shaped copper(II) complexes of the 1-(4′-decylbiphenyl-4-yl)-3-(3-substituted phenyl)propane-1,3-diones, see the notations given in Table II



X	*Cr*		*N*	*Iso*
CH_3	•	165	(• 138)	•
OCH_3	•	195	(• 140)	•

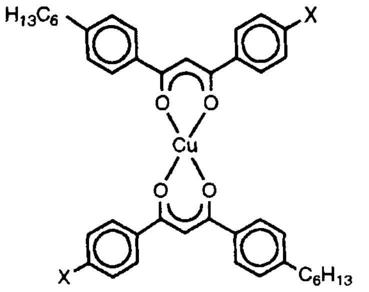
3.3. β-Diketone Copper(II) Complexes with X-shaped Structures

A wide variety of X-shaped systems were prepared in order to compare their physical properties with those of the cross-shaped compounds (see Section 3.2). Single phenyl units were used in the short arm systems, but, as with members of the other series, asymmetry was introduced *via* the use of different substituents placed usually at the 4-positions of the phenyl arms.

For the first series of X-shaped systems, shown in Table VII, two of the phenyl arms were designed to carry a hexyl chain, whereas the nature (polarity) of the substituent at the 4-position in the other two arms was varied (*i.e.*, from CH_3O to H, and H to F, Br, CF_3, CN). The melting points of these systems, like the others investigated, remained high, whereas the isotropic liquid to liquid crystal transition temperatures were considerably lower. Thus the mesophases observed for the fluoro- and methoxy-substituted systems are *monotropic*, however, all of the other materials were found to be non-mesogenic.

The fluoro- and methoxy-substituted materials were found to exhibit nematic phases, which is consistent with results obtained for the cross-shaped systems. As with the other systems, these materials did not show any tendency to form columnar structures or to be biaxial. It is interesting to

TABLE VII Transition temperatures (°C) for some substituted X-shaped copper(II) complexes of the 1-(4-hexylphenyl)-3-(4-substituted phenyl)propane-1,3-diones, see the notations in Table II

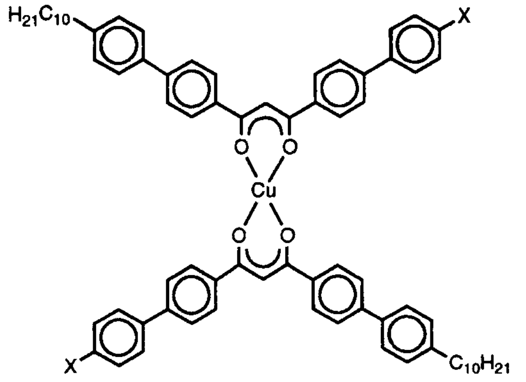


X	*Cr*^{1}		*Cr*^{2}		*N*		*Iso*
H	•	72	•	133	–		•
OCH_3	•	146	–		(•	83)	•
F	•	136	–		(•	78)	•
CF_3	•	139	–		–		•
Br	•	160	–		–		•
CN	•	195	–		–		•

compare these results with those obtained for the symmetrically substituted systems. The copper(II) complexes of the 1,3-bis-(4-alkylphenyl)propane-1,3-diones have been shown to exhibit columnar liquid crystal phases because they are disc-like. Thus, it is quite remarkable that just a small change, caused by altering the nature/type of substituents at the 4-position in the arms to give an asymmetrically substituted system, can change the mesophase from being columnar to a type characteristic for calamitic liquid crystals. These results show that we are in fact treading the fine line between negative and positive birefringence, and are located in the region where we might expect biaxial nematic phases to be found.

Table VIII shows results for a similar family of materials except in this case the phenyl units were replaced by biphenyl moieties. The inclusion of biphenyl units serves to emphasise the X-shaped structural template for this family. As with the materials shown in Table VII, the substituents attached to the 4′-position of two of the biphenyl arms were maintained as decyl

TABLE VIII Transition temperatures (°C) for some substituted X-shaped copper(II) complexes of the 1-(4′-decylbiphenyl-4-yl)-3-(4′-substituted biphenyl-4-yl)propane-1,3-diones, see the notations given in the Tables II and III



X	*Cr*^{1}		*Cr*^{2}		*SmC*		*SmA*		*N*		*Iso*
H	•	193	•	208	–		–		(•	195)	•
CH_3	•	195	–		–		–		•	206	•
F	•	155	–		(•	122)	•	250	–		•
CF_3	•	228	–		(•	203)	•	265	–		•
Br	•	150	–		(•	141)	•	260	–		•
CN	•	259	–		–		–		•	273	•
C_2H_5	•	226	–		–		–		•	228	•
$C_{10}H_{21}$	•	255	–		–		–	–	–		•

chains, whereas the substituents located on the other two arms were varied (*i.e.*, CH_3O, C_2H_5, $C_{10}H_{21}$, H, F, Br, CF_3, CN).

Interestingly, all but the symmetrical copper(II) complex of 1,3-bis-(4′-decylphenyl-4-yl)propane-1,3-dione were mesogenic. The halogeno-terminated biphenyl members of the series exhibited (in part *monotropic*) smectic A and C phases whereas the other complexes were nematogenic. Again, the slightest move away from a symmetrical template structure resulted in an increased probability of finding a liquid crystal phase, with the phase being typical of one exhibited by calamitic/rod-shaped chemical compounds.

As the halogeno-substituted compounds exhibited interesting smectic phase behaviour, the effect of positioning fluoro-substituents in different parts of the biphenyl arms (*i.e.*, at the 2, 2′, 3′ and 2′, 3′ positions) was investigated. Table IX shows the variation in transition temperatures and phase types as a function of position of the fluoro-substituents.

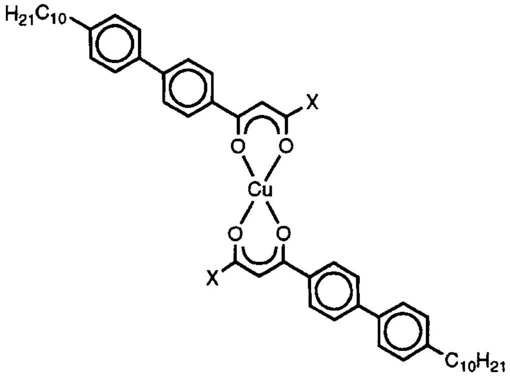
The results for the transition temperatures show no particular pattern in relation to the position of substitution. However, all but the di-fluoro-substituted system exhibited liquid crystal phases. In cases where the fluoro-substituent points away from the centre of the complex enantiotropic phases typical for calamitic/rod-shaped chemical compounds were found, but for the material where the fluoro-substituent points inwards the centre of the complex *monotropic* phases were found. As with the other asymmetric complexes studied, this series shows typical properties of compounds being calamitic in their molecular structures and no evidence of optical biaxiality.

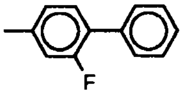
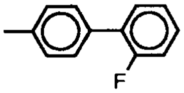
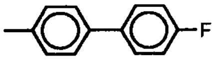
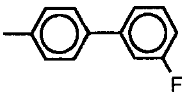
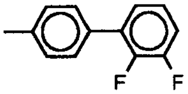
3.4. β-Diketone Oxovanadium Complexes, *Bowl*-like in Structure

The copper(II) complexes are essentially flat and, therefore, we are relying on the local packing of flat molecular boards having an appreciably long correlation length in order to generate a biaxial nematic phase. However, as we have seen, biaxiality in these systems is elusive, possibly because the local anisotropic packing arrangements of the molecules are randomised over relatively short distances. By altering the shape slightly and providing a site for lateral intermolecular interactions to be facilitated we hoped that the correlation length of the local packing could be extended. Thus, we selected to prepare oxovanadium complexes because they can have a bowlic shape. We expected bowl-like molecules to pack together in a preferred orientation (one dome inside another dome) which would lead either to a biaxial system or a columnar stack.

Initially we tested this idea in X-shaped systems with phenyl arms. Attached to the phenyl units were aliphatic chains, the chains attached to

TABLE IX Transition temperatures (°C) for some substituted X-shaped copper(II) complexes of the 1-(4′-decylbiphenyl-4-yl)-3-(fluoro-substituted biphenyl-4-yl)propane-1,3-diones, see the notations given in the Tables II and III

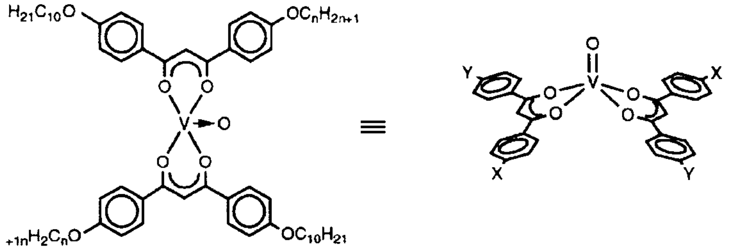


X	*Cr*		*SmC*		*SmA*		*N*		*Iso*
	•	170	(•	150)	•	179	•	188	•
	•	180	–		–		(•	165)	•
	•	155	•	(122	•)	250	–		•
	•	176	–		•	209	–		•
	•	171	–		–		–		•

two of the *trans* related phenyl groups were maintained the same throughout the study, whereas the other chains were varied in length [12]. Table X shows the results obtained for a family of seven complexes. For all of these materials *monotropic* columnar phases were found, *i.e.*, the materials acted as disc-like substances. Thus, the bowlic shape of the complexes provided for interactions that were too strong for the materials to exhibit nematic phases.

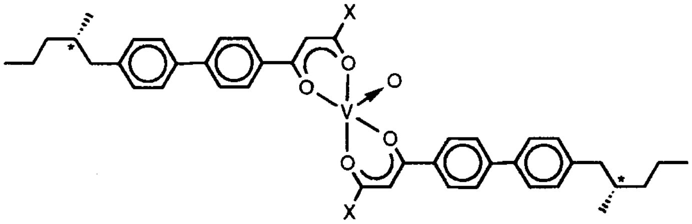
In an attempt to disrupt the columnar packing so as to generate nematic phases, the complexes were made asymmetric (*i.e.*, by having different arms) [13]. Complexes were prepared as shown in Table XI. Here it can be seen that the complexes are no longer X-shaped but zigzag/bent

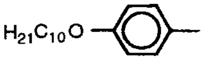
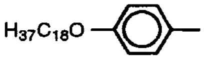
TABLE X Transition temperatures (°C) for some substituted bowl-shaped oxovanadium (IV) complexes of the 1-(4-decyloxyphenyl)-3-(4-alkyloxyphenyl)propane-1,3-diones, Cr = crystalline, Col = columnar, Iso = isotropic, $X = OC_nH_{2n+1}$, $Y = OC_{10}H_{21}$



n	*Cr*		*Col*		*Iso*
6	•	166	(•	131.0)	•
7	•	164	(•	128.2)	•
8	•	165	(•	134.0)	•
9	•	162	(•	134.2)	•
10	•	165	(•	142.7)	•
12	•	160	(•	126.3)	•
14	•	157	(•	124.7)	•

TABLE XI Transition temperatures (°C) for some asymmetrically substituted banana-shaped oxovanadium(IV) complexes, Cr = crystalline, SMC* = chiral smectic C (here: in two cases monotropic), N* = chiral nematic, Iso = isotropic



X	*Cr*		*SmC**		*N**	*Iso*
C_8H_{17}	•	109	–		• 115	•
	•	209	(•	171.8)	–	•
	•	178	(•	145.4)	–	•

(*i.e.*, banana-shaped). Remarkably, these systems were found to give chiral smectic and chiral nematic phases instead of columnar modifications.

The indication from these studies is that there is a fine line separating calamitic and disc-shaped variants in molecular structure, and the line could be so fine that there is no margin for error between the two!

4. SALICYLALDIMINE METAL COMPLEXES WITH *FLAT* OR *BOWLIC* STRUCTURES

In connection with the metal complexes discussed in the four previous sections some analogous derivatives of salicylaldimines containing copper, nickel, or oxovanadium, shown in Figure 5 and analysed by other workers [14], deserve to be mentioned here.

As in the case of the above β-diketone derivatives these metal complexes are in a way also flat and zigzag or bowl-like in structure, respectively. The biaxial order supposed here [14] in the nematic phase is claimed to be associated with the shape of the molecules which shall impose geometrical constraints on the supramolecular assembly.

5. MULTI-SUBSTITUTED MATERIALS WITH A *BENZENE* CORE

The flat cross-shaped nature of the β-diketone complexes, therefore, was found to be conducive to liquid crystal formation, however, many of the

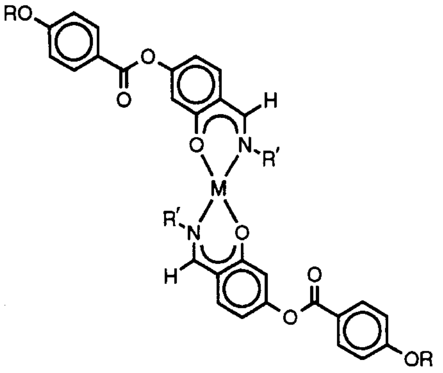


FIGURE 5 Basic structure of bis-[*N*-alkyl or *N*-(4-alkoxyphenyl)salicylaldimine]metal(II) complexes; [14, 15], *M* = Ni, Cu, VO, R = alkyl, *R'* = alkyl or 4-alkoxyphenyl, their phase transition data are given in the cited references and not repeated here.

substances prepared are high melting and thermally unstable at elevated temperatures. The high melting points in many instances did not allow us to investigate the incidence of monotropic or low temperature phases. Thus, it was decided in both our research groups to further investigate the cross-shaped template structure *via* removal of the complexed metal region as for most of the cases shown schematically in Figure 6. Removal of the metal was expected to yield lower melting and more thermally stable compounds. In addition to this, the nature, number and flexibility of the substituents (X and Y) attached to the central benzene ring *via* the linking group W were also varied.

The materials that were selected first for synthesis by the Hull group were the *tetra*-esters as represented by the general Structure II shown in Figure 7. This system seemed to be an obvious choice to investigate because it has a

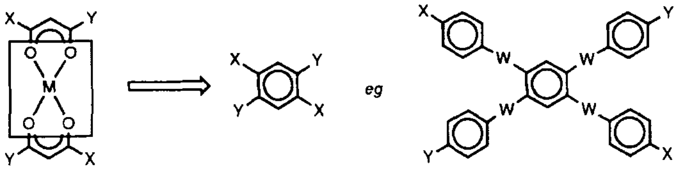
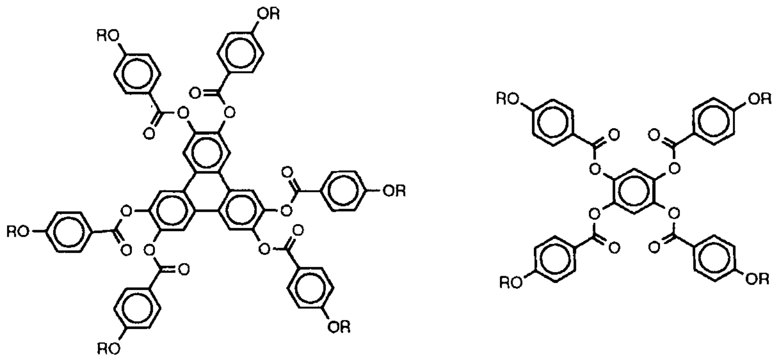


FIGURE 6 Removal of the metal complexed molecule region to give *tetra*-substituted benzene derivatives, M = metal, W = linking group, X and Y substituents as described in the text of this paragraph.



I

II

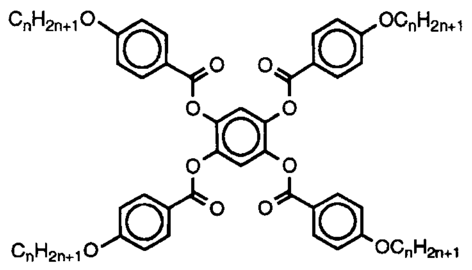
FIGURE 7 Examples of multi-esters I and II of 2,3,6,7,10,11-hexahydroxytriphenylene and of 1,2,4,5-tetrahydroxybenzene, respectively, $R = C_nH_{2n+1}$.

structural template that is similar to the *hexa*-esters of triphenylene, I. The triphenylene esters have been extensively investigated and shown to exhibit nematic discotic phases [16] that are uniaxial and negative. Extrapolation suggested that *tetra*-esters of benzene would also exhibit nematic phases, however, with their *board*-like shapes it was hoped that they might exhibit biaxial phases.

Table XII shows the variation in phase type and transition temperatures with respect to increasing aliphatic chain length for the 1,2,4,5-tetra-(4-alkoxybenzoyloxy)benzene derivatives, II. For the shorter homologues (up to the decyl member) nematic phases were observed, after this point smectic C phases were introduced for the higher homologues [17].

Detailed studies were made of the optical properties of these materials, both in the nematic and smectic C phases. It was conclusively found that the materials were uniaxial and not biaxial.

TABLE XII Transition temperatures (°C) for the 1,2,4,5-tetra-(4-alkoxybenzoyloxy)benzene derivatives, II, Cr = crystalline, SmC = smectic C, N = nematic (in brackets: monotropic), Iso = isotropic



n	*Cr*	*SmC*	*N*	*Iso*
3	• 160	–	(• 115)	•
4	• 123	–	• 125	•
5	• 122	–	(• 103)	•
6	• 133	–	(• 107.8)	•
7	• 118	–	(• 104.5)	•
8	• 109.9	–	(• 105.4)	•
9	• 103.4	–	(• 100.9)	•
10	• 93	–	• 102	•
11	• 100	(• 79.4	• 99.6)	•
12	• 102.5	(• 88.5	• 100.2)	•
13	• 97.8	(• 94.3)	• 100	•
14	• 97.2	• 98.9	• 100	•
15	• 95.1	• 100	–	•
16	• 96.5	• 101.5	–	•
18	• 98.5	• 101.6	–	•

The results suggest that the molecular structures of these materials are *not* in fact board-like in shape as expected, but that as the chain length is increased the molecules develop a more distinct anisotropic or calamitic shape which in turn favours the formation of smectic phases. This could be due to the peripheral arms on the same side of the molecule lying parallel to one another to give a rod-like structuring; increasing the chain length under these circumstances leads to increasing molecular anisotropy and thereby possibly to an increase in stability of calamitic phases. Thus at shorter chain length we might expect the molecules to have more of a disc-like shape, but upon chain extension they become rod-like. Figure 8 shows how the peripheral arms of the 1,2,4,5-tetra-(4-alkoxybenzyloxy)benzene derivatives could bend back over one another to give good overlap of the phenyl units. The molecular shape is then transformed from being postulated as board-like to being rod-like in reality, and as a consequence for this conformational structure as the terminal chains increase so too does the molecular anisotropy resulting in an increased stability for calamitic phases.

In order to prevent bending of the side arms back above one another, the nature of linking group *W* was changed. Thus, a stiffer alkynic group was used to sequentially replace the more flexible ester units. This was done in two series: firstly, in a systematic fashion for seven tridecyloxy (C_{13}) homologues by the Hull group [18] and, secondly, in the Berlin group [19] where five more compounds were synthesised by varying the substitution pattern of the benzenetetrayne with respect to its four triple bonds, the flexible units (replacement of alkoxy by alkyl, namely by pentyl or heptyl), and the substituents at the ring positions 3 and 6. Figure 9 shows the structures of these materials prepared and their transition temperatures. The immediately striking feature of the results is that even with the flexible ester linkages being replaced by the stiffer alkynic groups, mesophases typical for calamitics still prevailed.

Most of the structures shown in Figure 9 were modelled using Cerius^2 (BIOSYM/Molecular Simulations) with tridecyloxy terminal groups (for a single molecule at 0 K in the gas phase) to give a constant basis for

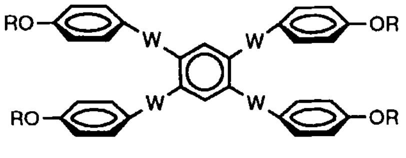


FIGURE 8 A sketch depicting the overlap of the phenyl units anticipated in 1,2,4,5-tetra-(4-alkoxybenzoyloxy)benzene derivatives, *W* = linking group: carbonyloxy.

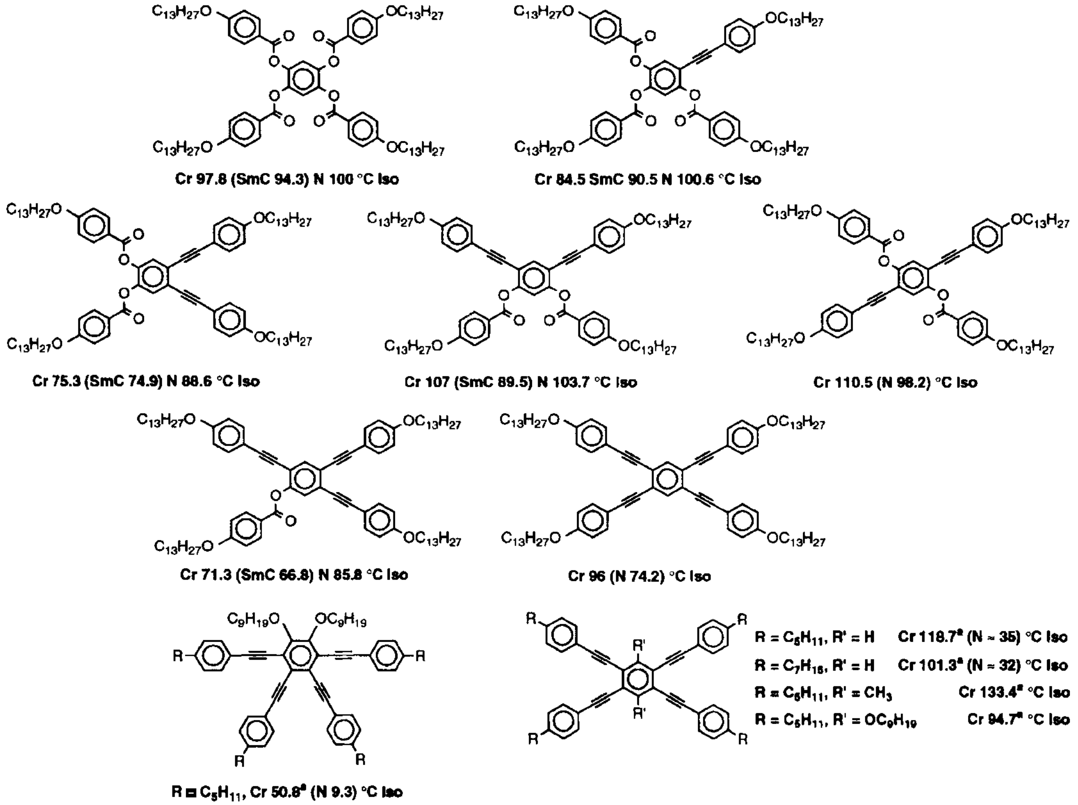


FIGURE 9 The twelve differently 1,2,4,5-*tetra*- or *hexa*-substituted benzene derivatives, including their phase transition data, synthesized [18, 19] as model compounds in the search for nematic biaxial liquid crystals; see the notation given in Table XII, [a]mean value of the measurements carried out by polarizing microscopy and differential scanning calorimetry.

comparison; the terminal groups were used in the fully-extended zigzag form in all cases, although it is acknowledged that crystal structure analysis, for example, sometimes shows that alkyl chains are distorted from the fully-extended form.

The minimum energy structure to emerge from modelling of the *tetra*-ester shows that the main feature is a face-to-face relationship of the 1,2- and 4,5-benzene rings. All the low energy structures which were generated show that the $\pi-\pi$-interactions of the peripheral benzene rings is the major feature and the orientation of the carbonyl oxygen atoms in the ester groups is less significant. This analysis shows that with flexible ester linking groups, $\pi-\pi$-interactions of the outer rings can create a structure with calamitic characteristics rather than one with a planar, disc-like appearance.

Similar modelling of the five compounds with combinations of ester and alkyne units was also carried out [18]. When an ester and an alkyne group are *ortho* to each other (in four cases), then the $\pi-\pi$-interaction of the benzene rings in the ester and alkyne arm is still possible. When two alkyne units are *ortho* to each other, the $\pi-\pi$-approach of the benzene rings in the *ortho*-dialkyne region is less feasible, but it appears to occur slightly at the expense of distortion from linearity of the alkyne region. The two bonds attached to the alkyne unit are bent approximately 9° and 7° with respect to the alkyne bond giving a total deviation from linearity of 16° in each case to allow interaction of the benzene rings, and giving a separation of 4.37 Å and 4.94 Å between the C_1 and C_4 atoms in the splayed benzene rings (see Fig. 10); the corresponding separations shown in Figure 10 for two 1,2-diesters are 3.42 Å and 3.75 Å respectively, and for the 1,2-ester/alkyne situations the separations are 3.67 Å and 3.85 Å respectively with angles around the alkyne bond of 176° in each case.

Several X-ray crystallographic studies [20] have shown that an alkyne bond can deviate appreciably from linearity both when the triple bond is part of a ring system (*e.g.*, the $C_{aryl}-C\equiv C$ angle in *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne is 156°) and when it is in an open-chain structure (*e.g.*, angles of 169/175° and 176° occur in 4-butyl-4′-methoxytolane for the $C_{aryl}-C\equiv C$ angle at the methoxyphenyl and butylphenyl ring respectively.

Molecular simulations coupled with results obtained *via* X-ray diffraction on model systems indicate that the peripheral arms of the tetra-substituted benzenes bend around so that the phenyl groups can lie on top of one other. This arrangement favours intramolecular interactions, but in turn it also ensures the presence of a *calamitic* structure. This study, therefore, provides an example of how internal conformational changes can lead to a change in

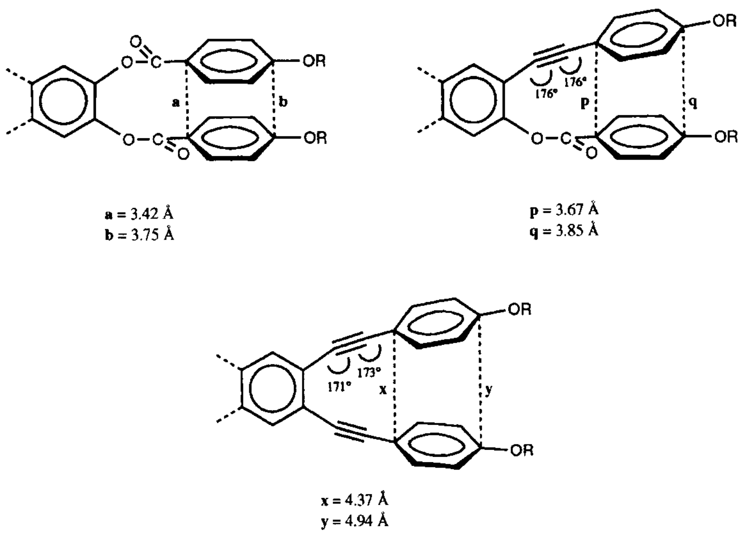


FIGURE 10 Diagram to show the distances separating the peripheral benzene rings in the 1,2-diesters, the 1,2-ester/alkyne and the 1,2-dialkynes, *cf.*, the corresponding formulas in the first three rows of Figure 9.

template structure. This highlights the difficulties faced by chemists in designing materials to exhibit biaxial nematic phases.

6. VARIOUS NEMATOGENS WITH ONE OR TWO TERMINAL HALF-*DISC*-UNITS

From the viewpoint of their molecular structures the six families of thermotropic mesogens, numbered here from **1** to **6**, depicted in Figure 11 with their transition data compiled in Table XIII, are non-classical in shape because they consist of a rod-like middle part ending in one or two trialkoxy-orthosubstituted benzene (half-*disc*-like) moieties. This constitutional situation confers on them a certain *board*-like character which from the 1980's has allowed these mesogens to move into the focus of physico-chemical interest for the possible detection of biaxial nematic properties [10, 21–23]. However, findings about this, published up to now, seem not to be accepted unanimously by the scientific community. For instance, the 4,4′-dihydroxybiphenyl derivative [21], **1**, *cf.*, Figure 11, introduced as a compound supposed to exhibit a thermotropic mesophase biaxial nematic

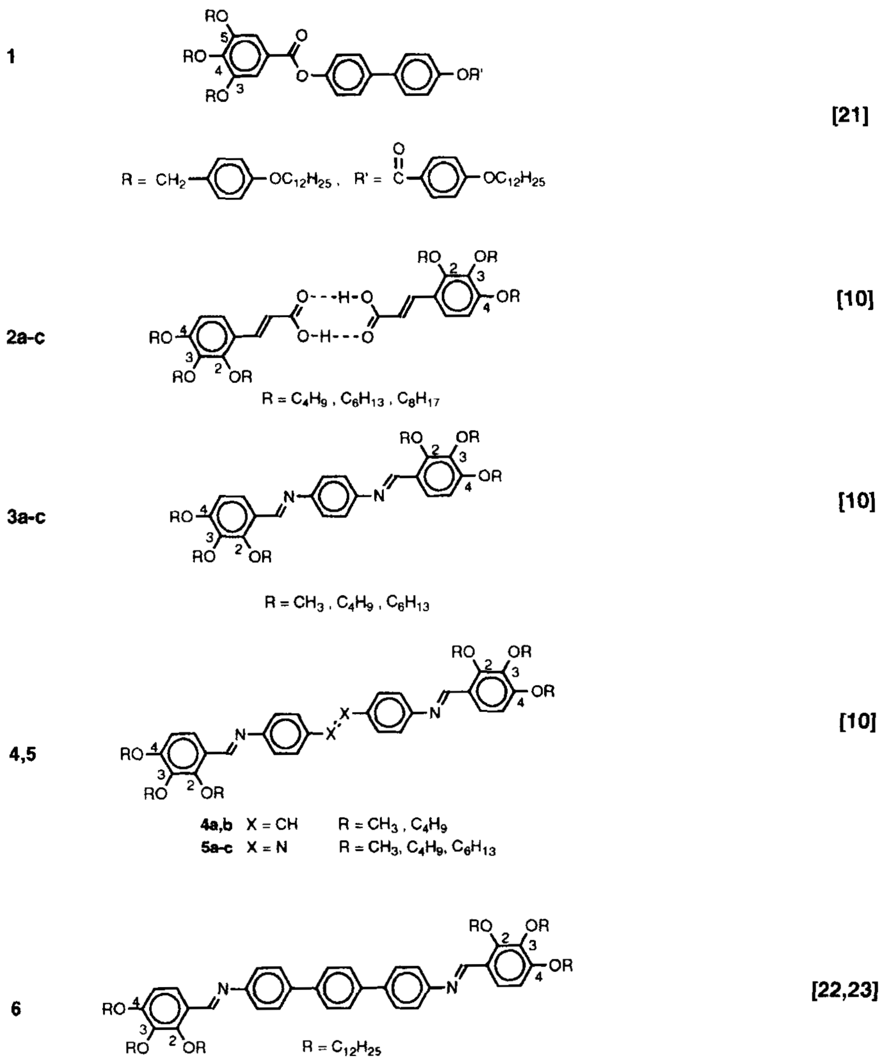


FIGURE 11 Overview of the families **1**–**6** of mesogens with unusual calamitic and half-*disc*-like molecular structures presented in this chapter and being subject of intensive search for nematic biaxial liquid crystals [10, 21–23]. Their phase transition data are taken from the respective references and are compiled in Table XIII in order to allow an easy comparison.

in character which, in the meantime, has been challenged and is now thought to be smectic [10]. On the other hand, the bisimine **6** looks promising and is currently under intensive study [23], however, final conclusions can, at present, not yet been drawn.

TABLE XIII Transition data for the unusual calamitic and half-*disc*-like shaped mesogens **1**–**6** shown in Figure 11, temperatures in °C, enthalpies (kJ/mol) in brackets, Cr = crystalline, M = type of mesophase, N = nematic (monotropic: in {}), Iso = isotropic

Mesogen	*Cr*		*M*		*Iso*
1	•	86 (95.5)[1]	{X[2]	86 (0.5)[1] }	•
2a	•	75.6 (18.6)	{N[3]	67.9 (0.8)}	•
2b	•	51.2 (14.1)	N[3]	59.6 (0.6)	•
2c	•	54.2 (48.7)	{N[3]	50.9 (0.5)}	•
3a	•	203.7 (52.2)	{N	103.4[4] (–)}	•
3b	•	95.8 (43.8)	{N	49.1[4] (–) }	•
3c	•	62.7 (39.2)	{N	33.6[4] (–) }	•
4a	•	232.0 (50.7)	N	292.1 (1.2)	•
4b	•	145.4 (39.3)	N	154.4 (1.3)	•
5a	•	225.2 (57.3)	N	268.1 (1.4)	•
5b	•	150.0 (41.1)	{N	144.2[4] (–)}	•
5c	•	123.8 (41.9)	{N	116.3[4] (–)}	•
6	•	82.7 (90.0)	N[5]	116.6 (0.8)	•

[1] Originally [21], this enthalpy is given in kcal/mol, furthermore, two different crystalline phases (m.p.:82 or 86°C) melting either into a mesophase, supposed to be of N_b type (*cf.*, comments at the beginning of this chapter), or the isotropic phase, respectively, were observed [21];

[2] this symbol represents a phase sequence described [21] as Iso 86 (0.13) N_b 69 (0,0) N_u 65 Cr;

[3] in Ref. [10] described to be N_b;

[4] clearing temperature determined by polarizing microscopy;

[5] on cooling, the phase sequence Iso 115.3 (0.464) N_u 114.5 (0.046) N_b was observed [23].

7. *FLAT/SHEET*-LIKE AND *MACROCYCLIC* NEMATOGENS

In this last section we want to refer to five more sophisticated, complex, inherently quite flat or macrocyclic nematogens, shown in Figure 12, on which investigations on nematic biaxial properties have been started, carried out or at least considered of interest, for instance, with respect to certain porphyrin derivatives.

The first case is a mixture of two *twin*-like (H-shaped) palladomesogens [24], followed by two so-called *disc*-like, radial pentaynes [10] **2** and **3** of which one is a twin of the other. Whereas potential biaxial nematic properties may be expected for cleverly substituted 5,15-diphenyl porphyrin derivatives [25], see **4**, results on this matter about the first *macrocyclic* trimeric nematic liquid crystal, see **5** in the bottom-part of Figure 12, have recently already been published [26].

For a suitable overview the transition data of the compounds **1** to **5** of this chapter are also compiled, see Table XIV.

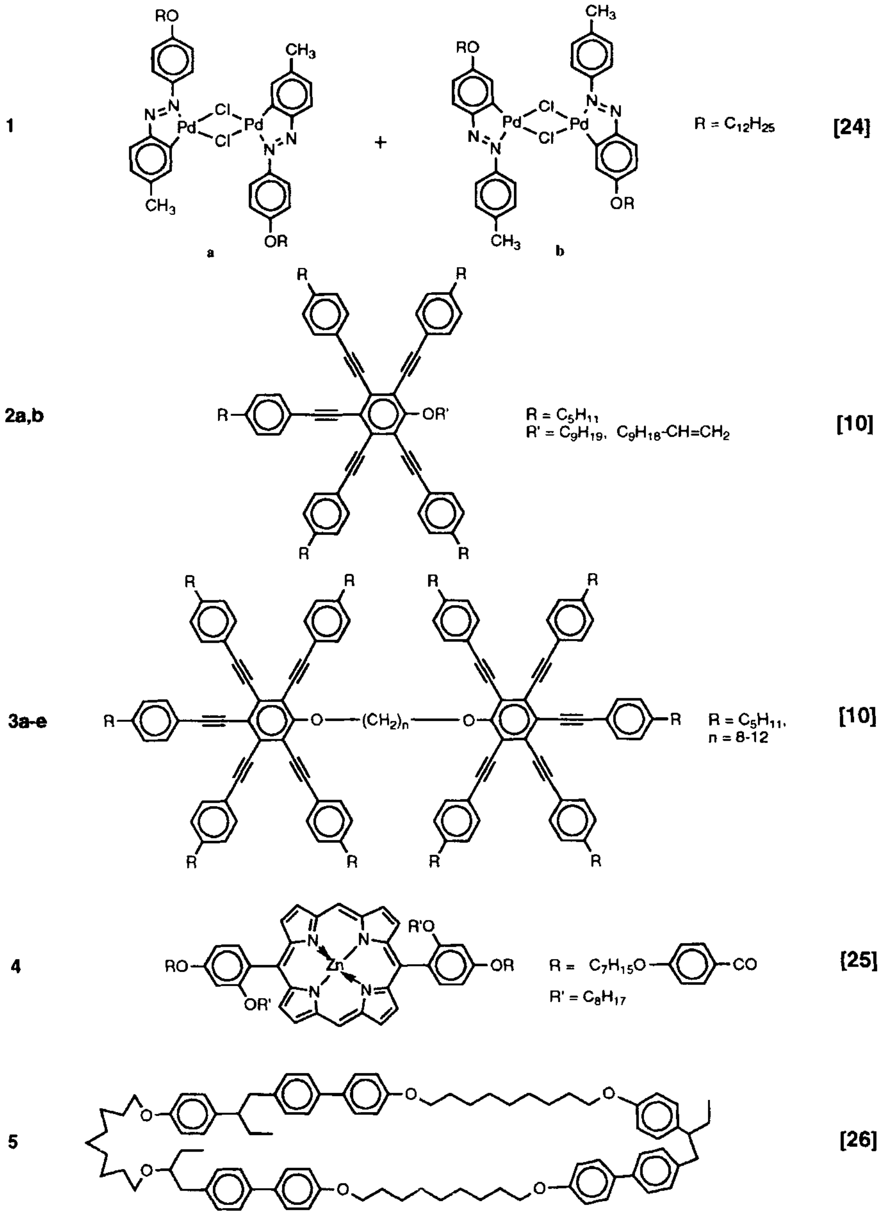


FIGURE 12 Overview of the five basic formulas **1**–**5** of flat/sheet-like and macrocyclic nematogens from literature [10, 24–26] forwarded in this chapter with regard to the topic of nematic biaxiality. Their transition data are taken from the respective references and are compiled in Table XIV.

TABLE XIV Transition data for the mesogens **1**–**5** shown in Figure 14, temperatures in °C, enthalpies (kJ/mol) in brackets, Cr = crystalline, g = glass state, M = type of mesophase, quoted from the respective references given in Figure 12, N = nematic, N_D = nematic discotic (monotropic: in {}), Iso = isotropic

Mesogen	*Cr*		*M*		*Iso*
1[1]	•	150.4 (25.4)[2]	$N_{D,b}$	174 (1.1)[2]	•
2a	•	86.4 (42.9)	$N_{D,b}$	109.9 (0.3)	•
2b	•	76.7 (36.2)	$N_{D,b}$	101.4 (0.2)	•
3a (n = 8)	•	127.0 (61.8)	$N_{D,b}$	127.8 (–)[3]	•
3b (n = 9)	•	131.0 (67.5)	{$N_{D,b}$	112.5[4] (–)}	•
3c (n = 10)	•	129.1 (57.0)	$N_{D,b}$	153.5 (0.3)	•
3d (n = 11)	•	118.2 (62.2)	$N_{D,b}$	140.8 (0.3)	•
3e (n = 12)	•	121.4 (67.9)	$N_{D,b}$	155.0 (0.4)	•
4 (n = 7)	•	141	N	177	•
5	g	43	N[5]	96	•

[1] Transition data given for a 1:1 mixture of *a* and *b* (*cf.*, Fig. 14); on cooling, the phase sequence Iso 174 N 165 (1.2) SmA 141 (13.5) SmC 108 (11.9) Cr was observed.

[2] Most probably kJ/mol; no unit is given for this value in Ref. [24].

[3] The enthalpy could not be extracted from the melting peak.

[4] Clearing temperature determined by polarizing microscopy.

[5] $T_{\mathrm{Nu-Nb}} \approx 62°\mathrm{C}$ [26].

8. CONCLUSION AND OUTLOOK

It appears that no matter how we design molecular structures in order to generate biaxial nematic phases of pure materials, molecules will find a way to minimize the effect of board-like molecular shapes. Either the molecules will internally compensate by undergoing conformational changes to give rod- or disc-like structures on heating or cooling of pure materials, or else the local biaxial orientational order cannot be sustained over an appreciable distance. Although our studies and those of other workers have so far not yet been able to deliver a biaxial nematic phase of a pure material without doubt, it is clear that we are very close to defining the limits between phases of calamitic and disc-like compounds where we might encounter such a phase, *i.e.*, the discussion of this phenomenon and the synthetic work to get it realized should go on [27].

For this still troublesome topic regarding pure, *thermotropic* nematogens, an interesting guide for it may be seen in recent results [27, 28] of "computer simulations showing that a relatively rigid type of molecule must possess an anisotropy of about 3:1 to form the nematic phase. In case of possible *thermotropic* biaxial nematics one needs this anisotropy in the transverse direction to promote the ordering of one short axis; thus, intuitively, the relation 5:3:1 between molecular dimensions along three axes seems to be reasonable here".

In the section of *lyotropic* materials of which the first case of a nematic biaxial phase is well established already since almost two decades [29], typical dimensions of intrinsically biaxial micelles have only been published in the later eighties [30]. Their average values based on X-ray diffraction studies [30], allowing here also the assumption of a board-like kind of shape (in these cases of assemblies), are each about 85, 55, and 26 Å resulting in a shape anisotropy of approximately 3.3:2:1.

Last but not least it should not be overlooked that in our opinion an important requirement of success in this matter is a much improved collaboration between chemists and physicists currently still missing [31].

Acknowledgement

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