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Uncommon building blocks in liquid crystals

R. J. Mandle^{a,b}, C. J. Gibb^b and J. L. Hobbs^a

^aSchool of Physics and Astronomy, University of Leeds, Leeds, UK; ^bSchool of Chemistry, University of Leeds, Leeds, UK

ABSTRACT

Just as nematic liquid crystals are widespread in display technology, a small number of building blocks find widespread use in the design and synthesis of liquid crystalline materials. This review explores the intricate relationship between the molecular structure of thermotropic liquid crystals (LCs) and their phase behaviour, emphasising the role of specific structural fragments in determining LC properties. We also detail into the impact of non-conventional building blocks on LC properties by comparing families of materials differentiated by only a single structural variation, allowing us to probe the extent to which deviations from traditional structures can maintain liquid crystallinity. This comprehensive overview not only underscores the importance of specific molecular fragments in LC design but also opens avenues for the innovative use of non-traditional building blocks in the development of new LC materials. Just as the ubiquity of 1,4-disubstituted benzene rings has its genesis (partly) in the extremely robust and predictable synthesis of such systems through cross-coupling chemistry; we consider that, the rapid progress in coupling sp^3 fragments, coupled with the growing availability of suitable building blocks, makes the inclusion of said fragments ever more practical and attractive for use in liquid crystalline systems.



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Liquid Crystals; nematics; structure property relationship

Introduction

Thermotropic liquid crystalline phases are intimately related to molecular structure [1] Broadly speaking, the structure of thermotropic liquid crystals can be divided into four principal sub-groupings as shown in Figure 1(a): terminal chain(s) (i), rigid core unit (ii), linking units (iii), lateral groups (iv) and terminal groups (v). We briefly consider some elementary variations to the nematogen 5CB; increasing the terminal chain leads to an increase in melting and clearing points, as well as a smectic A rather than nematic mesophase. In this system, extending the core unit by addition of a single 1,4-disubstituted benzene leads to dramatic increases in both melt and isotropisation

temperatures (Figure 1(a), compound 1b). Inclusion of conjugated linking groups such as esters (compound 1c) increases the clearing point, while non-conjugated links typically lead to depression (compound 1d); this is a consequence of both electronic and steric effects, with non-conjugated links (such as methyleneoxy in Figure 1(a)) also endowing rather different conformational profiles than their conjugated equivalents. Replacement of 1,4-disubstituted benzene(s) with 1,4-disubstituted cyclohexane(s) gives increased clearing points along with higher melting points and reduced dielectric anisotropies. Although these behaviours for 5CB and its modifications can be applied broadly to thermotropic materials, any

CONTACT R. J. Mandle  r.mandle@leeds.ac.uk

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structural modification must be considered in the context of the entire molecular structure. While not shown in Figure 1(a), typically lateral fluorination leads to a depression of 30–40 K in T_{NI} [9]; it is therefore unsurprising that fluorinated 5CB variants are non-mesogenic [10–14]. The molecular structures of thermotropic liquid crystalline materials is typically constructed from a rather limited set of fragments, a point we will now illustrate. We constructed a database of materials which are reported as exhibiting one or more liquid-crystalline phases. Data were taken from two commercial databases (Reaxys, Scifinder). After removing duplicate entries, we obtained the most common core fragments (Figure 1(b)), lateral/terminal groups (Figure 1(c); excluding alkyl/alkoxy groups which are ubiquitous, being found in >98% of materials) and linking units (Figure 1(d)). The well-known material 5CB is constructed from some of the most common fragments; two directly bonded 1,4-disubstituted benzene rings, a terminal nitrile, and an alkyl chain.

Our primary aim with this database was to use the fragments for generative design of new liquid crystalline materials [15], but we realised that we could also examine this for to find which fragments occur most often, and which could be considered unappreciated. As shown in Figure 1(a), benzene rings are found in the vast majority of thermotropic liquid crystalline materials. The prevalence of substituted benzenes reflects their utility, and also the typically mild chemistry employed (and predictable reactivity) in the construction of complex molecular architectures. Other cyclic groups, such as those in Figure 1(a), are equally adept at generating mesomorphic states and ever-advancing progress in sp²-sp³ and sp³-sp³ cross couplings makes the synthesis of such systems increasingly routine [16–19]. We consider that the increasing ease of synthesis of such units, coupled with the rapidly growing commercial availability of suitable building blocks, makes these increasingly attractive for use in liquid crystalline materials. However, are these any good? What prior art exists for the use of non-conventional building blocks in liquid crystals? How far can we deviate from ‘conventional’ building blocks and still retain liquid crystallinity? These questions prompt us to review the use of non-conventional building blocks in thermotropic liquid crystals. Throughout this review, we introduce families of materials, typically grouped together from multiple sources; the grouping is based on materials being related by a single structural change (e.g. swapping 1,4-disubstituted benzene for a disubstituted acetylene) so as to enable us to make a meaningful comparison between materials.

Variations in terminal-chain length are commonplace and dictate, among other things, the melting point and tendency for nematic/smectic phase formation, as exemplified by the 4-alkyl-4'-cyanobiphenyl family shown in Figure 2.

The role of terminal groups is also typically well explored, as illustrated by the family of 4-pentylbiphenyl materials with various polar termini given in Table 1. The ability of the parent of this series (5CB, **1**) and other nitrile terminated materials to form transient antiparallel pairs is well established [35,36]; this affords a higher clearing point than would be anticipated based on molecular length alone, as the ‘effective’ molecular length is far larger – a point well illustrated by comparing other popular terminal groups (e.g. F, **3**; NO₂, **7**). Polar groups which further extend the molecular length give large increases in clearing point (e.g. cyanoacetylene **8**, cyanostilbene **9**), whereas the corresponding non-polar equivalents do not (acetylene **4**, stilbene **5**). Isothiocyanates are generally competent at generating mesophases (e.g. **10**), while the equivalent isocyanates (**11**) are not. Typically carboxylic acids spontaneously dimerise through hydrogen bonding, this effectively doubles the molecular length and hence compounds such as **12** can have seemingly extremely high melting/clearing points. Conversely, amides (such as **13**) typically do not show liquid crystallinity in calamitic systems owing to extensive hydrogen bonding between N-H and C=O groups on adjacent molecules; curiously, N-methylation offers a means to circumvent this [37]. Polar ring systems such as N-pyrrole (**15**) can also be utilised as a means to both extend the rigid core and introduce additional polarity, leading to impressive increases in clearing points. Compact fluorinated termini (**16–20**) do not lead to anti-parallel dimerisation in the same manner as nitriles and so they typically require a larger rigid core unit in order to exhibit liquid crystalline phases.

This point is well illustrated by the extended core system in Table 2. Here, we see that the terminal fluoro substituent is competent at generating liquid crystalline phases and generates a modest positive dielectric anisotropy (**22**), in contrast to compound **3** encountered earlier. Increasing the polarity of the terminal group generally increases dielectric anisotropy, however as the physical dimensions of the unit increase and the molecular shape deviates from rod-like there is a tendency to depress clearing points significantly (e.g. **30**). Attention must be paid to the geometry of the polar unit, for example the N(CH₃)(CF₃) group (**31**) has a relatively low dielectric anisotropy as the dipole associated with the N-CF₃ group is far off axis. Further to this, the geometry of the *gem* difluorocyclopropylcarboxylate

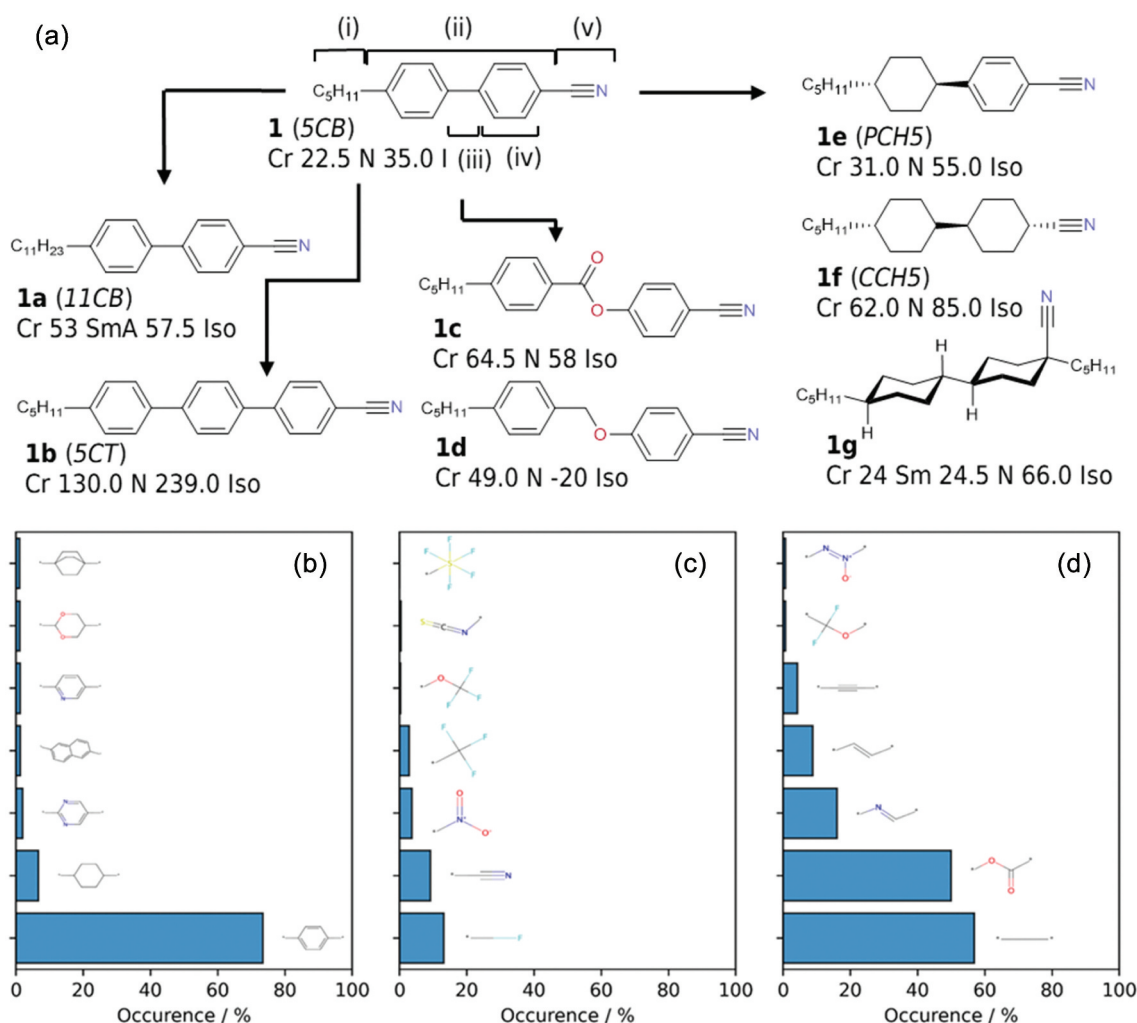


Figure 1. (Colour online) (a) subdivisions of liquid crystalline structure used in this work: (i) terminal chain; (ii) core-unit; (iii) linking unit; (iv) lateral group; (v) terminal group. Some more common structural variations of 5CB are given, along with their transition temperatures (°C): **1a** [2]; **1b** [3]; **1c** [4]; **1d** [5]; **1e** [6]; **1f** [7]; **1g** [8]. Common fragments used in the construction of thermotropic LCs: ring/cyclic fragments (b), lateral/terminal functionality (c) and linking units (d).

terminal group (**32**) is such that the resulting material yields a negative dielectric anisotropy [49].

Next, we consider a set of materials which derive from 8CB in which the alkyl-bearing benzene ring is replaced with various other ring systems (Table 3). Replacement of one benzene ring with pyridine (**34**) or pyrimidine (**35**) yields marginally higher clearing points, along with modest increases in dielectric anisotropy [50–52]. Conversely, replacement of the same benzene ring with thiophene (**36**) depresses the mesomorphic state(s) of 8CB due to its non-linear exit vectors. Similarly, fluorene (**37**) is somewhat non-linear, however the increased aspect ratio offsets the unfavourable geometric constraints of this unit and results in a large increase in the clearing point. The non-linearity of thiophene can be compensated for through use of

5,6-dihydro-4*H*-cyclopenta[*b*]thiophene [64–66] or thieno[3,2-*b*]thiophene [67].

The use of 1,3-dioxanes (**39**) is relatively commonplace in liquid crystals; the equivalent 1,2,3-dioxaborolanes (**38**), 1,3-thiopyrans (**40**), and 1,3-dithiane (**41**) are much less common and typically present with fairly significant depression of clearing points. The 1,2,3-dioxaborolanes are conveniently prepared from the corresponding boronic acid and diol and are generally competent at generating mesophases [55]. Liquid crystalline materials containing *trans* 1,4-cyclohexane (**42**) are commonplace, and when this unit is introduced in place of a 1,4-benzene ring typically there is a modest increase in melting and clearing point. This effect is even more pronounced with bicyclo[2.2.2]octane (**43**), itself relatively commonplace in liquid crystals. Other

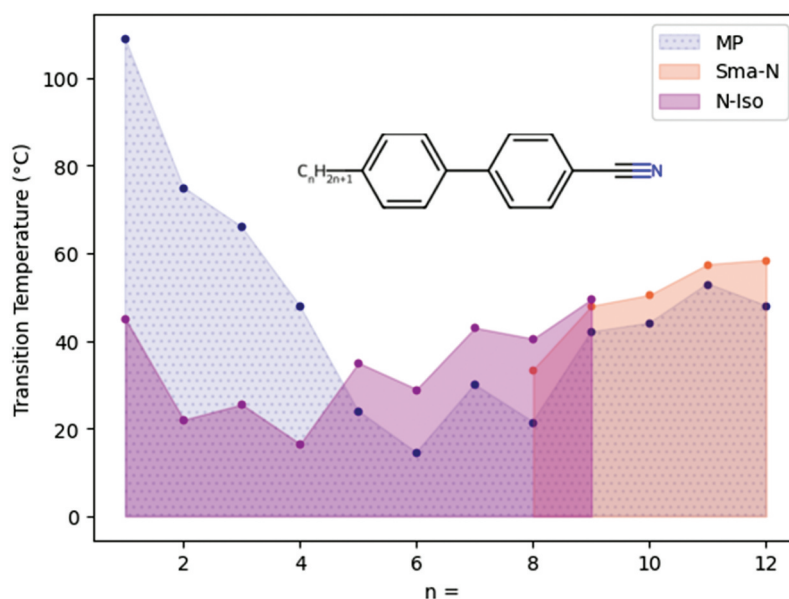


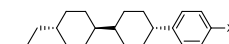
Figure 2. (Colour online) Transition temperatures (°C) of the first few members of the 4-alkyl-4'-cyanobiphenyl series. Hashed areas correspond to those below the melting point (monotropic regions).

Table 1. Transition temperatures (T , °C) of 4-pentylbiphenyl derivatives with various polar groups in the 4' position. #Compound is reported to be 'photochemical very unstable' [25]. ^Svirtual transition temperature extrapolated from mixtures. ##SmE.

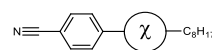
No.	R =	T_{Melt}	$T_{\text{SmA-N}}$	$T_{\text{N-Iso}}$
1 [5CB]		22.5	–	35.0
2 [20]		34	–	30
3 [11]		40.6	–	–
4 [21]		81.0	–	–
5 [21]		107	–	–
6 [21,22]		21.5	–	23.5
7 [23]		46	–	–
8 [24]		51	–	120.2
9 [24,25]		80	99.1	147.1 [#]
10 [21,26,27]		53	74.5 ^{##}	–
11 [21]		132	–	–
12 [28]		177	243	269
13 [29]		231	–	–
14 [30]		80	–	–
15 [31]		200	213	–
16 [32]		67	–	–
17 [33]		107	–	–30 ^S
18 [33]		31	–	–80 ^S
19 [33]		13	–	–40 ^S
20 [34]		25	–	–

polycyclic alkanes are essentially absent save for bicyclo[1.1.1]pentane (BCP, **45**), with a few bicyclo[3.1.0]hexanes (**44**) [62], bicyclo[3.3.0]octanes [68], bicyclo[2.2.1]

heptanes [69], tricyclo[4.4.0.0^{3,8}]decane [70]. The bicyclo[1.1.1]pentane unit is so compact that the direct benzene-for-BCP swap generally gives non-mesogenic

Table 2. Transition temperatures (°C) of *trans trans* 1-(4-propylcyclohexyl)cyclohexyl)benzenes with various polar groups in the 4-position. n/r not reported.



No.	X =	T _{Melt}	T _{SmB-N}	T _{N-Iso}	Δε	Δn
21 [38,39]	---CH ₃	62	108	177.1	n/r	n/r
22 [40,41]	---F	90	–	158.3	3.0	0.094
23 [40,42]		52	59	173.6	5.2	0.086
24 [40,43]		39	70	154.7	6.9	0.087
25 [44]		82	–	133	7.5	0.100
26 [33]		51	–	109.5	8.6	0.100
27 [40,45]		119	152	168.6	6.5	0.088
28 [40,46]		178	–	–	3.9	0.074
29 [38,40]		133	–	–	9.5	0.091
30 [40,47]		121	–	–	11.6	0.093
31 [48]		<20	173	–	5.9	0.091
32 [49]		68.2	176.6	–	–1.58	n/r

Table 3. Transition temperatures (T,°C) of analogues of 4-octyl-4'-cyanobiphenyl incorporating various 1,4-disubstituted benzene isosteres.


No.	X =	T _{Melt}	T _{SmA-N}	T _{N-Iso}
33 8CB		21.5	33.5	40.5
34 [50,51]		39.5	–	43.0
35 [50,52]		66	47	–
36 [53]		49.9	20.8	22.2
37 [54]		114.5	117.9	193.9
38 [55]		103	–	132.7
39 [56,57]		60	–	51
40 [56,58,59]		70	–	26
41 [56]		93	–	–
42 [60]		35	–	54.7
43 [61]		52	–	90
44 [62]		34.4	–	42.2
45 [63]		40	–	–
46 [63]		97.2	108.5	120.5

materials owing to the significant reduction in molecular length. However, BCP is useful for extending the rigid core unit resulting in a significant increase in transition temperatures, demonstrated by compound **46**.

In fact, materials whose rigid units are entirely of BCP units – so-called [n]staffanes – can exhibit liquid crystalline phases (Table 4) [71]. This is due to compact nature of the BCP unit, a minimum of three rings is required to exhibit liquid crystallinity,

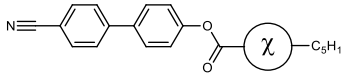
Table 4. Transition temperatures (°C) and phase assignments of [n]-staffanes [71]. [§]SmG phase. ^εSmB phase. [#]decomposes.















No.	R =	n =	T _{Melt}	T _{SmX-N}	T _{N-Iso}
47 [71]	SC(=O)CH ₃	2	99	–	–
48 [71]	SC(=O)CH ₃	3	137	167 [§]	198
49 [71]	SC(=O)CH ₃	4	107	277	>280 [#]
50 [71]	SC ₄ H ₉	2	8	–	–
51 [71]	SC ₄ H ₉	3	54.5	95 ^ε	–
52 [71]	SC ₄ H ₉	4	81	233	–

with the resulting materials various exhibiting nematic and highly ordered smectic phases. Further examples of BCP containing liquid crystals are known (for example see [63,72,73])

We now consider further ring variations in a series of 4'-cyanobiphenyl 4-pentylcarboxylates (53–66, Table 5). Again, compared to the parent compound the swap of the 1,4-disubstituted benzene ring for *trans* 1,4-cyclohexane or bicyclo[2.2.2]octane yields the expected changes in mesomorphism. The *trans* 1,3-dioxane gives a slight reduction in melting and clearing point relative to the parent system; when the dioxane is augmented with either a 5-methyl (59) or 5-cyano (60) group significant depressions in the melting and clear-

ing points are observed. The *trans* 1,3-cyclopentane (61) exhibits significantly lower transition temperatures than the equivalent cyclohexane due to its non-linearity and non-planarity. Contrast this with the aromatic thiophene derivative (62) which, although non-linear is planar, and while this has somewhat reduced transition temperatures than the parent. However, this change effect is less pronounced than seen earlier for compound 36 (Table 3) owing to the increased molecular length of the present compound. Although radically different in structure to the present thiophene materials, other liquid crystalline materials with chalcogenophenes bearing a chalcogen are known. For example, furans are ubiquitous and so are beyond the scope of this discourse

Table 5. Transition temperatures (T/°C) for 4'-cyano[1,1'-biphenyl]4-yl benzoates/carboxylates including various ring systems with a pentyl terminal chain; [#]chiral nematic phase.


No.	χ =	T _{Melt}	T _{SmA-N}	T _{N-Iso}
53 [74]		109.0	–	237.5
55 [75]		85.0	–	240.8
56 [76]		143.0	–	282.5
57 [77]		42.5	63.0	76.0
58 [78]		113	–	204
59 [79]		106	–	128
60 [80]		130	–	74
61 [81]		36.9	71.4	80.8
62 [82]		84	–	190
63 [83]		104	–	218
64 [83]		64	–	165
65 [84]		66.7	–	167.9 [#]
66 [85]		87	162	178

[86–88]. A handful of liquid crystalline 2,5-selenophenes are known [89,90], which is impressive as the olfactory challenges of working with low molecular weight organoselenium compounds are well appreciated [91]. Despite the relentlessly foul nature of organotellurium chemistry [92], the liquid-crystallinity of some 2,5-disubstituted tellurophene derivatives has been (very impressively) explored; they display modestly high birefringence which is comparable to the analogous selenophenes [93]. Examples of benzochalcogenophenes are also known within this context [94–100]. The spirobicyclo[5.5]undecane is one of the number of other materials which have been reported that include this functionality [101], as have additional related spiro-systems such as dispirotetradecanes [102], dispiro[5.1.5.2]pentadecan-7-ones [103], dispiro[5.2.5.2]hexadecanes [104], dispiro[3.2.5.2]tetradecanes [105], and dispiro[2.0.2.1]heptanes [106].

We now focus on a family of 4'-cyanobiphenyl esters containing various ring structures with a propyl terminal chain (Table 6). 2-Alkylcyclobutane carboxylic acids are readily synthetically accessible in both *cis* and *trans* configurations *via* alkylation/decarboxylation of diethylmalonate with 2-alkyl-1,3-dibromopropane [109], and these can be used as drop-in replacements for the benzene ring, albeit with reduced (significantly in the case of *cis*, 67) clearing points. *Trans* cyclopentane is a less effective isostere as it deviates significantly from linearity (70). Spiro[3.3]heptane (71) and dispiro[3.1.3.1]decane (72) preserve the linear exit vectors and are trivially prepared *via* the same alkylation/decarboxylation of malonate esters and make competent 1,4-benzene isosteres. Perhydroazulene has a more complex synthesis [108], yet offers a higher clearing point (and lower melting point) than the corresponding 1,4-benzene (73).

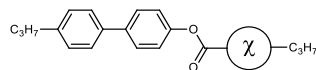
We shift focus now to a closely related set 4'-propylbiphenyl esters containing various ring structures with a second propyl terminal chain (Table 7). The behaviour of the *trans* 1,4-cyclohexane (75) and bicyclo[2.2.2]octane (76) derivatives mirrors that discussed elsewhere (e.g. compounds 55, 56). The cubane containing material 77 displays a markedly reduced melting point relative to the parent system. Whereas a modest number of cubane-containing liquid crystals are known [110–113], derivatives of cubane such as the tetracyclo[4.2.0.0^{2,4}.0^{3,7}.0^{6,8}]octane system (78, obtained by partial hydrogenolysis of the parent cubane) are extremely uncommon and appear to be limited to ref [107] only.

Regrettably, the parent material (compound 79) of the series presented in Table 8 has no reported clearing point but, given the high-reported melt, it may be non-mesogenic. The 2,6-disubstituted cunenane (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane (80) is readily prepared *via* isomerisation of the parent cubane over palladium or silver salts [118], and in this system it exhibits nematic and smectic A phase with significantly reduced melting points relative to the parent owing to its non-coplanar exit vectors. Recent improved synthetic routes promise to enable the synthesis of asymmetrically substituted 1,4-cunenanes which are of some relevance to liquid crystalline materials [119,120]. Further examples of liquid crystalline cubanes and cunenanes are known within the context of liquid crystalline dimers [113]. The analogous piperazine (81) exhibits a smectic B phase. The 1,*n*-diethenylcycloalkanones (83–85) variously exhibit nematic and SmA phases; as the cycloalkane unit increases in size the system becomes less linear, and so the melting and clearing points decrease.

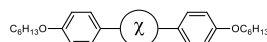
In the next family of materials (Table 9) we focus on heterocyclic rings within the same core structure introduced in Table 8. Incorporating pyrazole changes the

Table 6. Transition temperatures (°C) for 4'-cyano[1,1'-biphenyl]4-yl benzoates/carboxylates including various ring systems with a propyl terminal chain.

No.	χ =	T _{Melt}	T _{SmA-N}	T _{N-Iso}
67 [107]		126	–	245
68 [74]		55.5	–	63.0
69 [74]		47.5	–	141.5
70 [81]		52.2	–	66.5
71 [74]		82.0	–	154.7
72 [74]		74.0	–	161.1
73 [108]		95	–	267

Table 7. Transition temperatures (°C) for 4'-propyl[1,1'-biphenyl]4-yl benzoates/carboxylates including various ring systems with a propyl terminal chain.

No.	$\chi =$	T_{Melt}	$T_{\text{SmA-N}}$	$T_{\text{N-Iso}}$
74 [107]		109	–	195
75 [107]		108.5	–	199
76 [107]		131	–	232
77 [107,110]		110	–	118
78 [107]		84	–	142

Table 8. Transition temperatures (°C) for rod-like liquid crystals with various central units flanked by 4-hexyloxybenzene. n/r = not reported.


No.	$\chi =$	T_{Melt}	$T_{\text{SmB-SmA}}$	$T_{\text{SmA-N/Iso}}$	$T_{\text{N-Iso}}$
79 [102]		231	–	–	n/r
80 [114]		101.1	–	74.8	145.5
81 [115]		172	218	–	–
82 [116]		120	–	160	–
83 [117]		153	–	174	176
84 [117]		117	–	–	141
85 [117]		92	–	–	104

mesomorphic behaviour of the materials now exhibiting a smectic A rather than nematic phase and a significantly higher clearing point (**87**). Complexation of this compound with $\text{RhCl}(\text{CO})_2$ yields a non-mesogenic complex (**88**). Compared to pyrazole, the isoxazole (**89**) leads to generally lower transition temperatures. The analogous 1,3,4-oxadiazole (**90**) has rather non-linear exit vectors ($\sim 130^\circ$) and so is non-mesogenic, whereas the more linear 1,3,4-thiaziazole (**91**) exhibits the same phase sequence as the isoxazole. The thiazole **93** is non-mesogenic, and whilst the *bis* thiazole (**94**) behaves comparably to the *bis* oxadiazole (**92**), the *bis* thiadiazole (**95**) exhibits dramatically higher transition temperatures. While the majority of heterocyclic materials in Table 9 exhibits nematic phases, the N-amino 1,2,4-triazole (**96**) and pyrimidine (**97**) materials do not exhibit a nematic phase but rather smectic C and A phases. The closely related pyrazine compound exhibits a rather different phase sequence

(Cr 94 SmG 139 SmF 165 SmI 258 Iso) [130] and is left out of Table 9 for brevity.

Finally, remaining with the same core system, we now consider some examples of fused and non-conventional ring systems (Table 10). The diamantane (**98**, elsewhere referred to as [9]diamondoid and congressane) exhibits a dramatic increase in clearing point owing to the highly rigid structure of this elongated fused ring system. The $\alpha\alpha'$ -substituted succinic acid bis-(enol-lactone) **99** is non mesogenic. The 'trioxane' (**100**, 1,3,5-trioxadecalin) is chiral, and the resulting material exhibits cholesteric and smectic A phases. Conversely, the 'tetraoxane' (**101**, 1,3,5,7-tetraoxadecalin) unit exhibits only a SmA phase with a modest increase in clearing point. The *para* substituted [2.2]paracyclophane (**102**) was prepared in its (*R*) form *via* chiral resolution techniques of the (*S*)-phenylethylamine diastereomeric salt [135]; the material exhibits a wide temperature range chiral nematic phase; with

Table 9. Transition temperatures (°C) of . . . #identified as a B₂ phase. [§]Identified as a SmB phase. *Unidentified smectic phase (SmX) on cooling to 164.7°C.




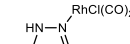



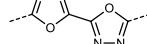

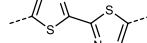
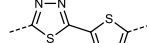









No.	χ =	T _{Melt}	T _{SmC-SmA}	T _{SmA-N/Iso}	T _{N-Iso}
86 [121]	---	124	–	–	130
87 [122,123]		158.5	–	198 SmC	–
88 [122]		68.3	–	–	–
89 [123]		110.8	–	134.6	161.0
90 [124]		121	–	–	–
91 [124]		109	–	184	204
92 [125]		181.2	177.7*	–	190.0
93 [126]		130	–	–	–
94 [126]		107	–	180	197
95 [124,127]		223.6 [127] 215 [124]	301.5 [127] 305 [124]	–	– [127] 350 [124]
96 [128]		147.0	203.4 [#]	261.0	–
97 [129]		120	189	215.5	–

Table 10. Transition temperatures (°C) of some uncommon ring systems. [#]chiral nematic phase.



No.	χ =	T _{Melt}	T _{SmC-SmA}	T _{SmA-N/Iso}	T _{N-Iso}
86 [121]	---	124	–	–	130
98 [131]		160.5	–	239.6	276.0
99 [132]		242	–	–	–
100 [133]		158	–	161	162 [#]
101 [134]	 (R, R, R, S)	158.5	–	189.4	–
102 [135]	 trans, trans  (R) (-)	159	–	–	229 [#]

other mesogenic units appended to the same planar chiral core variously exhibit chiral nematic and smectic A mesophases.

We now consider further non-conventional ring systems in a similar core system, this time with two ester linkages (Table 11). Compared to the parent system derived from hydroquinone (103), the 1,4-dioxane (104) and 1,4-dithiane (105) systems offer inferior

clearing points and comparable melting points. The tropolone (106) displays an impressively high clearing point considering its non-linearity which is possibly related to [1,9]-sigmatropic rearrangement of the ester and the oxygen atom bound to the C-2 carbon (*vide infra*). The isorbides (107 and 108) are both non mesogenic yet are often employed as chiral additives [146]. The biphenylene containing 109 exhibits an

Table 11. Transition temperatures (°C) of some uncommon ring systems.

No.	$\chi =$	T_{Melt}	$T_{\text{Sm-NTB}}$	$T_{\text{NTB-N}}$	$T_{\text{N-Iso}}$
103 [136,137]		121	–	–	215
104 [138]		112	–	–	83
105 [138]		129	–	–	122
106 [139]		125	–	–	188
107 [140,141]		104 [140] 89 [141]	–	–	–
108 [141]		69	–	–	–
109 [142]		154	–	–	272
110 [143,144]		100.8	–	–	142.5
111 [145]		78.2	78.4	85.2	97.1

impressively high clearing point, with a modest increase in melt compared to the parent system, with other examples of this system being known [147]. The 2,5-disubstituted-3,6-dichloroquinone (**110**) has a notably lower clearing point than the parent system. Lastly, the dimeric-type material **111** exhibits nematic, twist-bend nematic and smectic phases.

We conclude our focus on ring-systems by considering the same basic structure outlined in Table 12, but utilising alkynyl linking groups. Thiophene (**113**), thiazole (**114**) mirror behaviour seen elsewhere (e.g. compounds **36**, **62**, **93**) and are generally inferior to the parent 1,4-disubstituted benzene (**112**). The quinoxaline (**115**) retains the nematic phase of the parent, despite its protrusion away from the molecular long axis. A similar

effect is observed for the triptyceny compound **116** (albeit monotropically).

Linking groups

We now focus on various linking groups and their effects on transition temperatures (see Table 13). Arguably the most common linking unit is a direct bond, however esters and imines are commonplace due to their ease of synthesis and favourable interactions which support liquid crystalline order. Here, we define a linking group as a non-cyclic group which adjoins one or more ring systems. Mono-, di- and tri-acetylenes (**117–119**), extend the length of the rigid core unit and increase T_{NI} and give very large birefringence values,

Table 12. Transition temperatures (°C) of some uncommon ring systems.

No.	$\chi =$	T_{Melt}	$T_{\text{SmC-SmA}}$	$T_{\text{SmA-N/Iso}}$	$T_{\text{N-Iso}}$
112 [148]		179.5	–	–	239.4
113 [82]		81	–	–	137
114 [149]		85.5	–	–	141.5
115 [150]		154	–	–	172
116 [151]		181.8	–	–	158.5

Table 13. Transition temperatures ($T, ^\circ\text{C}$) of various linking groups employed between the two 1,4-benzene rings of the 4,4'-hexyloxybiphenyl system. [#]SmB phase. [§]SmC phase. *not reported.

No.	$\gamma =$	T_{Melt}	$T_{\text{SmA-N/Iso}}$	$T_{\text{N-Iso}}$
86 [121]	----	124	–	130
117 [152]	-----	94.8	–	98.8
118 [152]	=====	115.3	–	147.5
119 [152]	=====	133.1	–	174.0
120 [153]		36	71	–
121 [154]		104.4	–	113.0
122 [155]		86	98	110
123 [156]		48.5	44.5	79.8
124 [157]		90	–	80
125 [157]		67	–	–
126 [158]		187	–	194
127 [159]		128	157	–
128 [160]		150.8	–	–
129 [161]		112	122 [#] #SmB	–
130 [162]		72.8	–	–
131 [163]		70	66 [§] §SmC	120
132 [164]		80	–	124
133 [165]		n/r*	–	107.5
134 [166]		160	–	n/r*
135 [167]		118	105	113
136 [168]		109.8	–	–
137 [168]		149.7	–	128.5
138 [169]		159.3	–	–

albeit the chemo- and photo-stability of the materials is expected to be not that high. The cyanoethylene (**123**) exhibits nematic and smectic A phases, with the cyano moiety generating a large electric dipole moment. The analogous 1,2-substituted prop-1-ene linking unit (**124**) also sustains liquid crystalline order, whereas the 3,4-substituted hex-3-ene does not, on account of the large steric bulk of the two protruding $-\text{C}_2\text{H}_5$ groups. Azo-linkages are commonplace (e.g. **122**); and the less common but the closely related azine (**127**) and ethane-1,2-diimine (**129**) groups are also shown to be able to generate liquid crystalline phases. Longer homologues of the propan-1,3-dione linked material (**130**) show

various smectic mesophases [162]. The analogous (Z)-aminopropenone material is also known and displays a number of unidentified mesophases [170]. Oxime-esters (**131**, **132**) and hydrazides (**134**, **135**) are capable of generating liquid crystalline phases yet are not frequently encountered as linking groups. Homologues of the tetraketone (**138**) [169] with longer terminal-chain lengths exhibit columnar mesophases, however, the resultant complexes with boron trifluoride are non-mesogenic irrespective of terminal-chain length however. Other miscellaneous uncommon linking groups capable of supporting liquid crystalline order include selenoesters [171], and *trans* tetrafluorosulfanyl [172].

Terminal groups

We now focus on groups appended at the terminus of an alkyl chain in a 5-decyloxy-2-phenylpyrimidine liquid crystal (Table 14). Replacement of the terminal $-C_2H_5$ of the parent compound with ^tbutyl (**140**), trimethylsilyl (**141**) or trimethylgermyl (**142**) retains the smectic C phase with a slight reduction in clearing point accompanying a more pronounced drop in melting point. Using the bulkier triethylsilyl (**143**) or triethylgermyl (**144**) groups gives an even more pronounced depression. The heptamethyltrisiloxane terminated **145** experiences less of a depression in melting point and

clearing point, while the cyclopentyl terminated **146** actually has a higher melt than the parent. Other cyclic units employed in pyrimidine containing liquid crystals, such as dispiro[2.0.2.1]heptane derivatives [106], or various cyclic hydrocarbons in the 4-cyanobiphenyl system [177].

The nCB and nOCB liquid crystals remain arguably the most widely used core-type, and so unsurprisingly there are many known structures in which various terminal groups have been installed at the end of the alkoxy chain (Table 15). Generally, substituents which promote nanophase segregation (e.g. siloxanes, silanes etc., **154–160**) retain the SmA

Table 14. Transition temperatures ($T, ^\circ\text{C}$) of various groups appended at the terminus of one alkyl chain in a series of 5-decyloxy-2-phenylpyrimidine liquid crystals.

No.	X=	T_{Melt}	$T_{\text{SmC-Iso}}$
139 [173]	---Et	58	104
140 [174]	---C(Me) ₃	48.3	95.1
141 [174]	---Si(Me) ₃	41.7	97.0
142 [174]	---Ge(Me) ₃	57.1	97.8
143 [174]	---Si(Et) ₃	39.0	81.4
144 [174]	---Ge(Et) ₃	24.5	80.6
145 [175]	---(CH ₂) ₃ SiOSiOSi---	44.0	93.0
146 [176]	---Cyclopentyl	64.1	94.5

Table 15. Transition temperatures ($T, ^\circ\text{C}$) of various groups appended at the terminus of the alkyl chain in 4-cyano-4'-undecyloxybiphenyl.

No.	R=	T_{melt}	$T_{\text{Sm-N/Iso}}$	$T_{\text{N-Iso}}$
147 11OCB	H	71.5	87.5	–
148 [178–180]	-OH	89.8	–	92
149 [181]	---O---CH=CH ₂	68	–	56
150 [180,182]	-Cl	78.7	–	96.4
151 [180,182,183]	-Br	77.4	–	69.1
152 [180]	-I	87.5	–	67.2
153 [184]	---C(=O)OH	121.4	–	104.0
154 [180]	---C---	54.9	83.3	–
155 [180]	---Si---	55.1	81.7	–
156 [180]	---Si-O-Si---	37.7	73.7	–
157 [180]	---Si-CH ₂ -Si---	31.7	70.1	–
158 [180]	---Si-C ₆ H ₅	22.4	73.1	–
159 [185]	---Si-O-Si-C ₂ H ₄ -Si---	27.3	50.6	–
160 [186]	---(CF ₂) ₃ -C(=O)O ⁻ K ⁺	135	190	–
161 [178]	---C ₆ H ₄ -CH=CH ₂	75.8	95.7	–
162 [187]	---C ₆ H ₄ -CHO	94.5	–	87.2
163 [187]	---C ₆ H ₄ -COOH	141.8	–	192.9
164 [188]	---C ₆ H ₄ -COOH	47.7	31.2	36.9
165 [180]	---Cyclopentyl	57.1	–	32.9

phase of the parent system while other groups instead form a nematic phase (148-153). Generally, the larger the bulk of the terminal group the bigger the depression in clearing point (e.g. the halogen series, 150 – 152). Groups capable of hydrogen bonding typically display higher clearing points than the parent (148, 153, 163). The effect of hydrogen bonding is well demonstrated by comparing the aldehyde 162 to the equivalent carboxylic acid 163. Lastly, the 2,5-dimethylbenzene terminal group (164) can be considered to be ‘half’ of the [2.2]paracyclophanyl group (in 164); both exhibit comparable clearing points, but the steric bulk of the cyclophane prevents the formation of smectic phases in the latter.

Fluorination

Fluorination of the rigid core aromatic unit is commonplace in liquid crystals with ~17% of materials bearing at least one fluoro substituent on an aromatic ring, and so falls outside our focus of ‘uncommon’ structural motifs and the reader is referred elsewhere [189]. Likewise, a significant number of materials with perfluorinated (or semi-fluorinated) alkyl chains are relatively

commonplace [190]. Fluorination of the non-aromatic portions of the core is far less common, and this is our initial focus here (Table 16).

While the cyclohexan-2-one motif is non mesogenic (166), replacement with *gem* difluorocyclohexane (167) or 2-fluorocyclohex-2-ene (168) afforded relatively wide temperature nematic phases [191]. The 5,5,6,6-tetrafluorocyclohexa-1,3-diene derived 169 has an impressively large negative dielectric anisotropy of -7.3 (extrapolated from mixtures with MLC-6608) [192]. Further examples of liquid crystalline *gem* difluorocyclohexanes are known, both with the fluorines acting as a lateral group (as above) [193,194] or as a terminal group [195]. In a similar vein, liquid crystalline *gem* difluorobicyclo[2.2.2]octanes are known [196], while the monofluoro bicyclo[2.2.2]octanes are known outside of the context of liquid crystals [197].

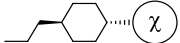
Axial fluorination on cyclohexanes is generally detrimental to the liquid crystalline phase, although it can be used to generate impressively large values of dielectric anisotropy (e.g. 171 and 173 in Table 17). Facially fluorinated cyclohexane derivatives such as 174-177 were found to be non-mesogenic, with fairly small values of dielectric anisotropy (Table 18). Other axially fluorinated cyclohexanes, such as 178, while attractive

Table 16. Transition temperatures (°C) of various polar non-aromatic ring systems.

No.	$\chi =$	R =	T_{Melt}	$T_{\text{N-Iso}}$
166 [191]		F	105	–
167 [191]		F	98	110
168 [191]		F	32	122
169 [192]		C ₂ H ₅	65	77

Table 17. Transition temperatures (°C) and extrapolated dielectric anisotropies of CG-3-N and CU-3-N, with and without axial fluorination.

No.	X =	Y =	T_{Melt}	$T_{\text{N-Iso}}$	$\Delta\epsilon$
170 [198]	H	H	39	–11	26.0
171 [198]	H	F	57	–	32.6
172 [198]	F	H	50	–	27.1
173 [198]	F	F	64	–	34.7

Table 18. Melting points (°C) of facially fluorinated cyclohexane (**174-177**), axially monofluorinated cyclohexane (**178**), and difluoroindane (**178-179**) derivatives. * has the phase sequence cr 75 SmB 94 iso, Δn of 0.054.


No.	$\chi =$	T_{Melt}	$\Delta\epsilon$
174 [199]		214	n/r
175 [199]		175	n/r
176 [199]		128	n/r
177 [199]		95	-1.19
178 [40,198]		75*	-2.2
179 [200]		99	-7.1
180 [200]		85	-8.6

in terms of wide nematic-phase range and low rotational viscosity [198], have the unfortunate propensity to spontaneously and autocatalytically eliminate HF. The tri- and tetrafluoroindanes (**178**, **179**) have impressive negative dielectric anisotropies, but also suffer the same issue of HF elimination [198,200]. The propensity for elimination is not seen in the analogous cyclohexanes bearing an axial cyano group [8].

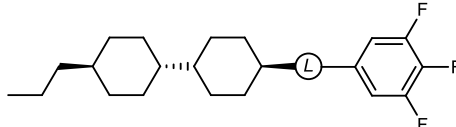
Fluorinated links

Turning now to explore the role that the linking group has not only on transition temperatures but also dielectric anisotropy (Table 19). The parent material **181** has a direct link between the 'central' *trans* 1,4-cyclohexane and the 3,4,5-trifluorobenzene motif. A dimethylene space (CH_2CH_2 , **182**) reduces transition temperatures and also dielectric anisotropy relative to the parent

owing to the increased conformational freedom. The carboxylate ester **183** has a comparable clearing point to the methyleneoxy **184**, and a notably larger dielectric anisotropy. The monofluoromethyleneoxy bridged **185** suffers a modest reduction in clearing point, whereas the difluoromethyleneoxy bridge (**186**) has a beneficial effect on transition temperatures as well as making a significant contribution to dielectric anisotropy which is of a similar magnitude to that of the ester bridged **183**.

Unconventional chiral systems

Further to the chiral systems already discussed, we now focus on more 'exotic' chiral moieties which have been shown to promote, or at least tolerate liquid crystallinity (Figure 3). The C_3 -symmetric (*S,S,S*) tricyclo[2.2.1.0^{2,6}]heptane-3,5,7-triol, functionalised with *trans*

Table 19. Transition temperatures (T , °C) of *trans trans* 4-(4-propylcyclohexyl)cyclohexyl liquid crystals with various (fluorinated) linking groups.


No.	$L =$	T_{Melt}	$T_{\text{SmB-N}}$	$T_{\text{N-Iso}}$	$\Delta\epsilon$
181 [40,199,201,202]		64.7	–	93.7	8.3
182 [40,201,202]		49.5	–	83.4	7.3
183 [9,203]		56	–	117.2	11.1
184 [40,204]		74	102	114.9	8.1
185 [40]		43	–	88.0	8.0
186 [40,205,205]		44	–	105.3	10.5

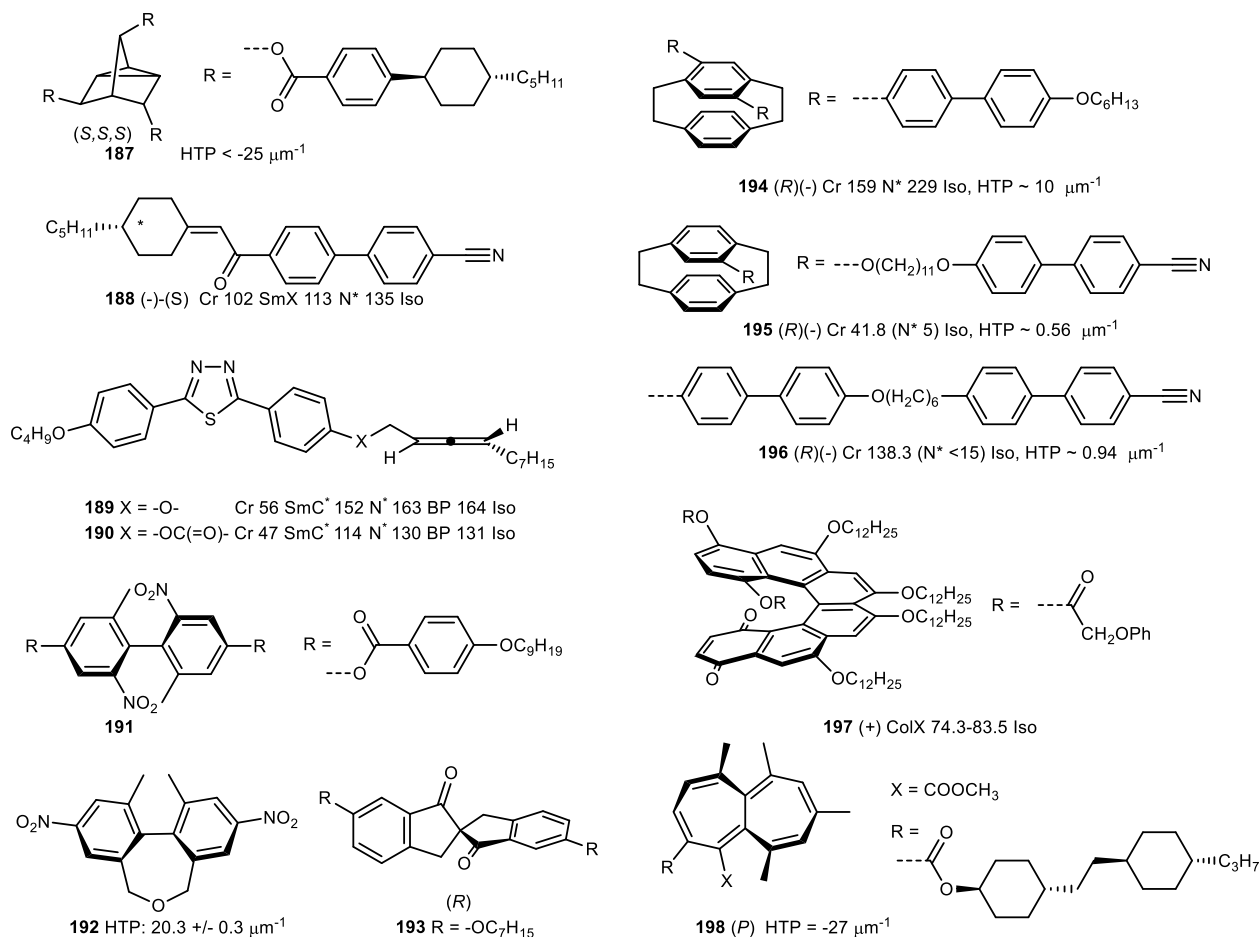


Figure 3. (Colour online) Transition temperatures ($^{\circ}\text{C}$, where available) and helical twisting powers (HTP, where available) for a selection of point, axial, planar, and helically chiral liquid crystalline materials.

4-(4-pentylcyclohexyl)benzoic acid (**187**), showed a helical twisting power of up to $25 \mu\text{m}^{-1}$ [206]. Chiral cyclohexylideneethanones (**188**) were prepared *via* asymmetric coupling *via* a chiral sulphoxide and are one of the earliest examples of axial chirality in an optically active liquid crystal [207]. Axially chiral allenes, appended to a thiadiazole bent-core system (**189**, **190**), were shown to generate SmC*, N* and blue phases [208].

Biphenyls substituted with bulky nitro/methyl groups to block rotation about the central bond and are atropisomeric [209,210], such as **191** in Figure 3. Related axially chiral biphenyls with a $-\text{CH}_2\text{OCH}_2-$ bridge have been reported and exhibit a cholesteric phase [211]; the helical twisting power of such compounds depends strongly upon substituents present, but values as high as $20.3 \mu\text{m}^{-1}$ were reported for **192** shown in Figure 3 [212]. A variety of alternate bridging groups have been reported, including amides, fused ring systems, 2,3-diaminobutyl [213,214]. Another notable demonstration of axially chirality is the 2,2'-spirobiindan-1,1'-dione [215,216]. These materials show large

ferroelectric polarisations in the SmC* phase, for example **193** displays a P_S of circa $1 \mu\text{C cm}^{-2}$ in NCB76 [216]. As mentioned briefly in the discussion around the paracyclophanyl compound in Table 10, systems with dissymmetrically substituted rings which are non-coplanar can exhibit so-called planar chirality. One prominent example is [2.2]paracyclophane; however, other systems have been shown within the context of liquid crystals (e.g. ferrocenes [217] and azobenzenophanes [218]). When the paracyclophane unit is in the centre of the rigid portion of the mesogen then the HTP values are modest (**194**) [135], however when relegated to the periphery *via* flexible chains or *via* appending to one side of a dimer the resulting HTP values are rather low (**195**, **196**) [219]. Helicenes are polycyclic aromatic compounds in which the regular annulation of aromatic rings gives rise to a helical structure. Beyond molecular aesthetics, the helicene derivative **197** has been shown to exhibit a columnar phase at ambient temperature [220–222]. Heptalenes are dissymmetric molecules with highly twisted symmetric C_2 structure and lack a stereogenic centre. It was shown that for a series of

chiral heptalene derivatives the position of the substituent groups on the heptalene core dictates the chiral sense of the helical twist (e.g. **198**) [223].

One (or less) ring systems

The vast majority of thermotropic liquid crystalline materials have two or more rigid cyclic groups. Typically, multiple cyclic groups (either directly bonded, fused, or with linking groups) are required to retain the requisite molecular shape for liquid crystallinity. As such, it is very uncommon to find mesogenic material with one, or even no, rings. That is not to say that there are no reported examples (Figure 4). Perhaps the most well-known examples of 'single ring' mesogens are the alkylbenzoic acids [224,225]. Of course, these benzoic acid derivatives readily dimerise through hydrogen bonding can we consider them true single-ring systems? Typically multiple cyclic groups (either directly bonded, fused, or with linking groups) are required to retain the requisite molecular shape for liquid crystallinity.

Despite having only a single ring, nitrobenzoates with fluorocarbon tails exhibit smectic phases (**199**, **200**), as the steric clash between fluorine atoms doubles the energy difference between *trans* and *gauche* conformers relative to the parent hydrocarbon system [226–229]. 2,5-Disubstituted tropones were shown to be able to generate smectic A mesophases (**201**, **202**) [230–232], a perfluorocarbon chain gives higher transition

temperatures than the analogous hydrocarbon in this system. The liquid crystallinity of the 2,5-disubstituted tropone results from a [1,3]-sigmatropic rearrangement of the acyl group and the oxygen atom bound to the C-2 carbon gives a transient ring system which gives a time-averaged linear molecular structure. Synthesis of non-[1,3]sigmatropic systems supports this conclusion [233]. Poly dialkylstannanes (e.g. **204**) were shown to be liquid crystalline, variously exhibiting nematic, lamellar and rectangular columnar phases depending on the length of the pendant alkyl chains [234]. Diisobutylsilane-diol [235] forms a columnar structure through hydrogen bonding between adjacent silanol groups (**206**). A family of 1-alkyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes were found to exhibit columnar mesophases despite having only a single rigid unit (**207–209**) [236], with the steric bulk of the (many) dimethylsilyl motifs driving the formation of a hexagonal columnar structure *via* shape segregation. Fluorocarbons can also confer 'rigidity' and generate liquid crystalline mesophases in systems that lack any ring systems, for example **210** in Figure 4 [40,237–240].

Conclusions and outlook

In this review, we have explored the use of non-traditional building blocks in liquid crystals and although these units are rarely encountered (and sometimes entirely novel), in many cases these follow expected patterns of behaviour. However, the context of the

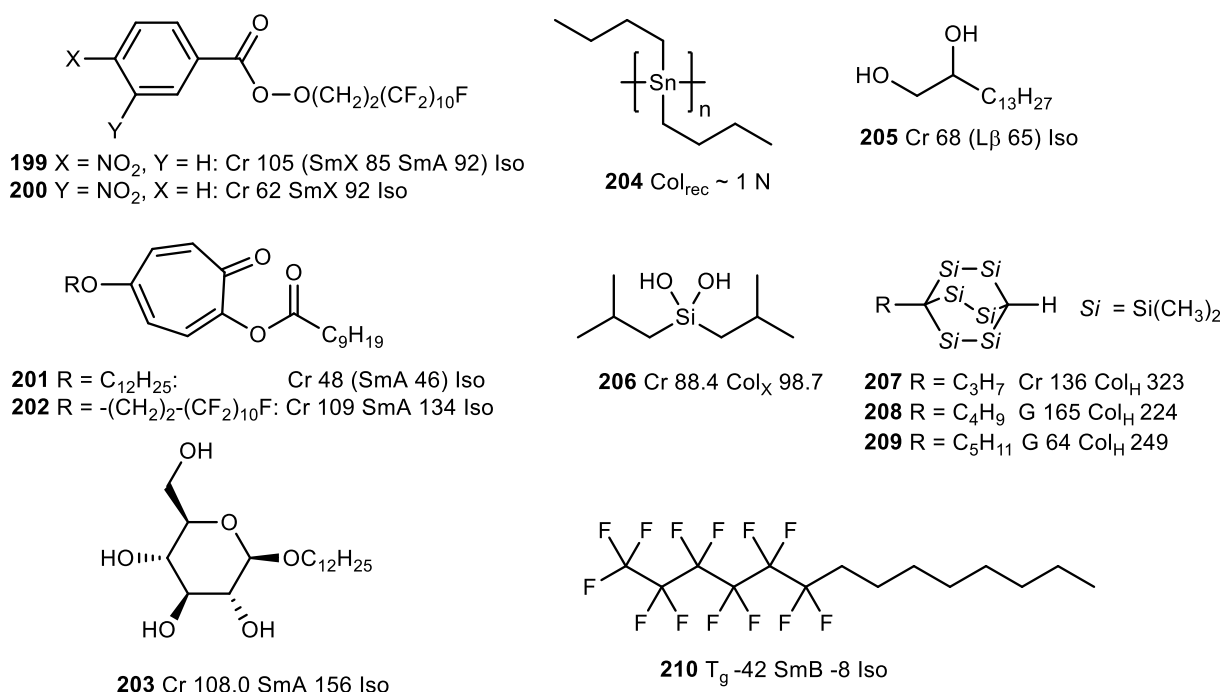


Figure 4. (Colour online) Further examples of non-conventional structures exhibiting liquid crystalline behaviour.

entire molecule is important when considering the impact of such changes. In the most general terms, the more anisotropic (i.e. longer) the rigid core unit the more forgiving it tends to be in terms of generating liquid crystalline phases with ‘unfavourable’ groups. We suspect that any ring system (or even relatively rigid group of bonded atoms) that reasonably approximates the linear exit vectors of 1,4-disubstituted benzene will probably have some capacity for generating liquid crystalline order, and this is supported by examples herein.

When encountering bulky groups appended at the end of a terminal chain (Table 15) it is tempting to conclude that it is simply the size of the group that dictates the mesogenic behaviour (e.g. compounds 147–159), however this overlooks subtle effects that can result from hydrogen bonding (e.g. 147, 160, 163), to give one example. Ultimately, these subtle interactions between many molecules are responsible for the genesis of liquid crystalline order; to consider only shape or polarity in isolation is not typically sufficient (e.g. Table 1; various entries). Again, the context of the entire molecule is again relevant – several of the polar terminal units in Table 1 that yield non-mesogenic materials are shown to be competent at generating nematic phases in Table 2 (e.g. SCF₃) when utilising a different core system.

Metal catalysed cross-coupling reactions are as essential to the synthetic chemist as a hammer and nails and a saw are to a carpenter. With the advent of new synthetic methodology that greatly simplifies sp³-sp³

couplings, these reactions can reliably be used in the design of liquid crystalline materials; specifically, complex ring systems can be installed as entire fragments rather than assembled step-by-step as in the past. For example, a large number of bicyclo[x.y.z]alkanes are available as the mono methyl esters of their dicarboxylic acids; through decarboxylative couplings these could be expanded into fully fledged rod-like liquid crystals. We performed basic geometric analysis on a selection of bicyclo[x.y.z]alkanes (Figure 5). This demonstrates that some (e.g. bicyclo[3.3.2]nonane) are probably sufficiently close to linear that they would suffice as a drop-in replacement for 1,4-benzene.

Just as sp²-sp³ and sp³-sp³ couplings are becoming routine, mild fluorination of sp³ carbon is a rapidly growing area. We suspect that direct and targeted fluorination of such 3D benzene isosteres is not only possible, but may be advantageous over ‘2D’ isosteres such as axially fluorinated cyclohexanes. Several examples of cubane-based liquid crystal have been discussed here, with more examples in the literature. Cubane is one of the platonic hydrocarbons, and of the other possible platonic hydrocarbons it seems probable dodecahedrane could be incorporated into a linear motif and coaxed into exhibiting liquid crystalline phases, although the 23-step synthesis presents a rather high barrier to this undertaking [241]

Lastly, so far we have largely restricted ourselves to discussion of materials evaluated experimentally after synthesis. Separate to this, computer hardware and software offer ever increasing performance, which allows us

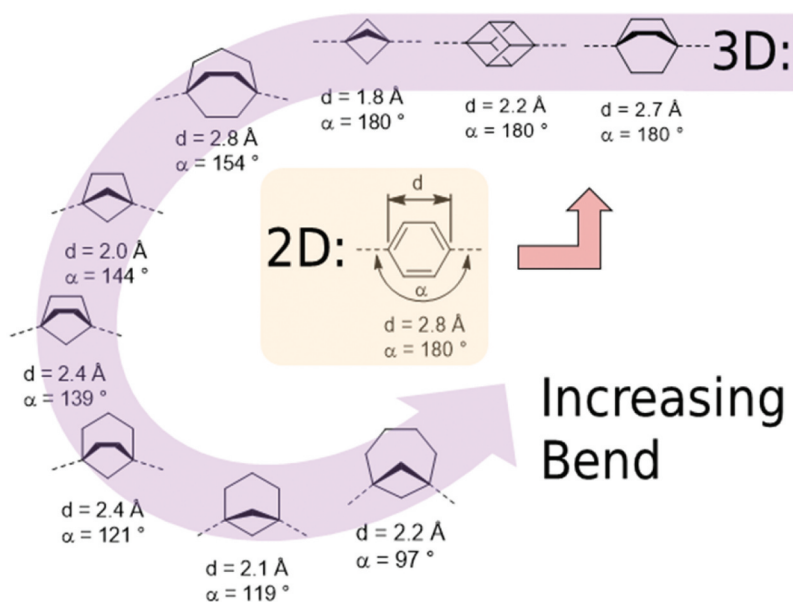


Figure 5. (Colour online) Geometrical properties of some 1,4-benzene isosteres, computed for geometry optimised at the B3LYP/6-31G(d) level of DFT shown in order of decreasing linearity.

the luxury of probing molecular interactions in atomistic detail through a computational lens. One especially attractive area for the future is in building molecules not by targeting properties by study of prior art, but through *specific design of intermolecular molecular interactions*. For example, four-centre heteroleptic dipole–dipole interactions between nitriles and sulphoxides [242].

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