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Liquid Crystals

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Germanium liquid crystals

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Liquid-crystalline compounds containing germanium atoms were synthesised and assessed for liquid-crystalline properties. These new compounds generally possess smectic C phases, and many also possess nematic, smectic A and higher order smectic phases. The germanium-containing liquid crystals were incorporated into smectic C mixtures. These mixtures tend to exhibit little change in smectic C* layer thickness over temperature. This characteristic is associated with de Vries smectic A materials, but measurements show that, although they have high smectic C stability, the materials' smectic cone angles are small. Measurement of smectic cone angle versus temperature of an exemplar material and its analogues containing carbon and silicon in place of the germanium, all show small cone angles which fall smoothly and extrapolate to zero as the smectic C* to smectic A transition is approached. These measurements largely explain the observed small layer changes and establish that the materials are not first-order de Vries materials. They must be located elsewhere along the de Vries-orthogonal continuum of smectic A phases.

Keywords: germanium; de Vries; conventional FLC; low tilt; high smectic C stability; phase map

1. Introduction

Germanium's properties make it unique as a substituent in organic compounds. In the same column as carbon, it generally has four attached atoms in a tetrahedral configuration, thus acting much like the lighter carbon and silicon atoms. However, being a true metal, the first in the group, germanium can be divalent or pentavalent in addition to its preferred tetravalent state. We were intrigued by the possibility that including germanium atoms in liquid-crystalline molecules might lead to materials with new and unexpected properties, while keeping in mind its metallic nature and possible instability to harsh conditions.

Monomeric thermotropic liquid crystals (LCs) predominantly consist of hydrogen and elements from the second row of the periodic table, although chlorides, bromides, iodides, sulphurs, and silicons are used in perhaps 10% of these LC compounds. LCs containing silicon, either as siloxanes or silanes, have been reported to exhibit special properties (*1*, *2*), including bistability (*3*) and de Vries phases (*4–9*). We wanted to know whether germanium-containing variants would retain these desirable properties. Bistability is especially valuable, but ferroelectric liquid crystals (FLCs) previously reported to have bistability have always had fatal practical drawbacks. For instance, Mochizuki's (*10*) materials had relatively high viscosity and a very low tilt angle. Radcliffe's (*11*) materials lacked a nematic phase, making their alignment problematical, since only FLCs which possess both a nematic and a smectic A phase can be easily aligned.

The first published germanium-containing liquid crystal (Ge-LC) was mentioned in a paper by Young and Haller (*12*) in 1971, contained a chemically unstable Schiff base, and possessed two high temperature unidentified smectic phases. Dulog and Gittinger (*13*) have studied germanium-containing phthalocyanines that form discotic phases, but that is the extent of Ge-LCs reported in the literature. Thus, the materials mentioned in this paper are the first examples of moderate temperature, chemically stable smectic LCs that incorporate germanium. Throughout this paper, the term Ge-LC will be used to designate either individual LC-type compounds incorporating germanium atoms, or mixtures containing these compounds.

2. Properties of Ge-LC compounds

2.1 *Chemical stability of Ge-LCs*

Since germanium is a metal, there was some question as to how chemically stable Ge-LCs would be. Accordingly, **DTC2366** (see Figure 3) was subjected to tests in acidic, basic and oxidising solutions. Samples of it were dissolved in solvent and treated, respectively, with sulphuric acid, sodium hydroxide and hydrogen peroxide for a day, then tested by high-performance liquid chromatography. They showed no breakdown. In another study, **DTC2183** (see Figure 4) was subjected to UV radiation for

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1700 hours, and showed no breakdown. These tests put to rest our worries that Ge-LCs would not be stable enough to be used for commercial purposes.

2.2 *Liquid-crystalline properties of Ge-LC compounds*

Our group has made 130 germanium-containing compounds with a wide variety of functionality that would potentially have liquid-crystalline phases. Of these, the majority possessed smectic C phases. The breakdown is as follows: of the 130 Ge-LCs, 13 were not assessed for phase map[1] and 19 had no LC phases. All but two of the remaining 98 possessed a smectic C phase, and of those two one had a smectic A phase, the other a smectic G (*14*) phase[2]; there were no mesomorphic Ge-LCs that did not exhibit a smectic phase. A nematic phase was also seen in 22 of these Ge-LCs, while a smectic A phase was seen in 17 of them; three compounds exhibited both a nematic and a smectic A phase, with all three also showing a smectic C phase. We are particularly interested in compounds with an I–N–SmA–SmC phase sequence because of their compatibility with conventional FLCs. A smectic G phase was identified in 12 of the Ge-LCs, a smectic H phase in one of them, a smectic B in one of them, and five had unidentified higher order tilted smectic phases, which were labelled SmX. The structural makeup of these compounds falls into several broad classes, where each class has one or two elements which seem to be the overriding influence on the classes' LC properties, and they are organised into tables by these classes. These classes, in Sections 2.2.1to 2.2.11, generally refer to the size of the germanium group, the type of core, the spacer between the two, and lastly, the other tail.

The unifying structural feature of Ge-LC compounds is, not surprisingly, the germanium-containing tail. The germanium was attached to the core by a spacer group, and due to synthetic considerations the other three attached groups were identical, generally either ethyl or methyl. The spacer portion of the tail usually was attached to the core by an ether linkage, and generally contained between 5 and 11 atoms along its chain, although there is one class of compounds that had only one or two atoms between the germanium atom and the core. Coming at the end of a long tail and surrounded by three alkyl groups, the germanium gives a bulbous[3] group taking up a lot of space. The larger the alkyl groups, the more space this group takes up. This is illustrated in the space-filling model of **DTC2096** (Figure 1), which contains a triethylgermane group.

Bulky terminal groups on alkyl tails, especially silanes and siloxanes, are reputed (*15*, *16*) to disturb the random placement of tails, instead preferentially segregating to form their own sub-layer between smectic layers. This nanophase separation is in turn deemed responsible for the reduced SmA–SmC layer shrinkage, known as de Vries behaviour, of many of these materials. Since germanium is just under silicon in the periodic table, there was a reasonable expectation that these Ge-LCs might have de Vries behaviour.

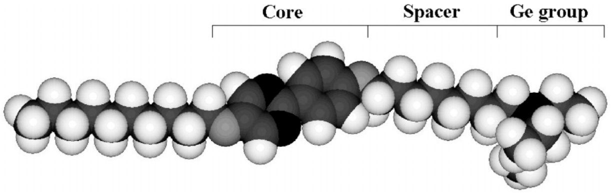


Figure 1. (Colour online). Ge-LC compounds have a bulbous end group at the end of a long tail.

2.2.1 *Triethylgermanes with two-ring cores*

This class, shown in Figure 2 with phase map data in Table 1, contains compounds which have three ethyl groups attached to the germanium atom, and two conjugated aromatic rings making up the core of the LC. Having only two linear conjugated rings in the core results in moderate birefringence materials with low transition temperatures. Most of these compounds had relatively low smectic C phase stability, with the highest I–SmC transition being that of **DTC2096** at 80.6°C. This class contains one of only two non-discotic Ge-LC compounds, which have an LC phase but do not possess a smectic C phase: **DTC2600** has a smectic A phase as its sole LC phase. Compound **DTC2332** appeared to show two different crystalline[4] phases.

2.2.2 *Triethylgermanes with three-ring cores*

This class, shown in Figure 3 with phase map data in Table 2, contains compounds which have three ethyl groups attached to the germanium atom, and three conjugated aromatic rings making up the core of the LC. Again, the triethylgermane group constitutes a large bulbous group at the end of the tail. The compounds in this class all had enantiotropic smectic C phases as their sole liquid-crystalline phase, supporting the general rule that terphenyl-like cores tend to sustain smectic C phases. Of the 62 Ge-LCs with ethyl groups attached, 47 (or about three-quarters) exhibited smectic C phases. The four Ge-LCs with even larger groups, butyl or isopropyl, attached to the germanium atom showed no liquid-crystalline phases. So, the size of the bulbous end group is quite important.

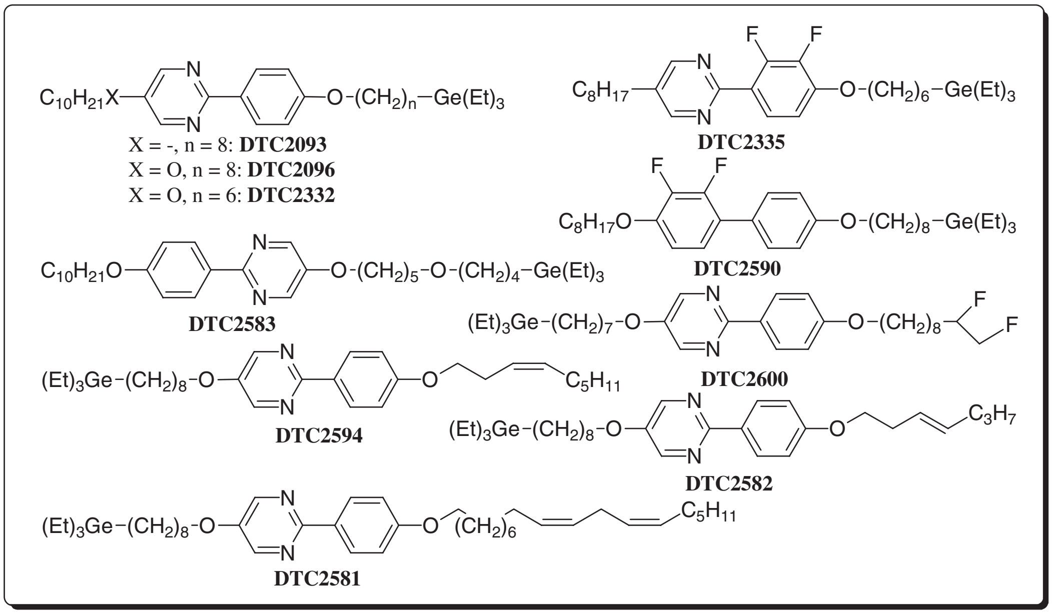


Figure 2. Triethylgermanes with two-ring cores.

Table 1. Phase map data for triethylgermanes with two-ring cores.

DTC#	Cr2		Cr1		SmC		SmA		I
2093			¤	25(20)	¤	49			¤
2096			¤	24.5	¤	80.6			¤
2332	¤	34.7	¤	42.4	¤	70.3			¤
2335				Oil at RT					¤
2590			¤	16.7(–7.8)	¤	29			¤
2583			¤	17.5	¤	52.2			¤
2581			¤	12.2(4.8)	¤				¤
2582			¤	14.9(13.5)	¤	20.1			¤
2594			¤	8.3(5.0)	¤	28.2			¤
2600			¤	13.7(41.9)			¤	55.1	¤

2.2.3 Trimethylgermanes with two-ring cores

This class, shown in Figure 4 with phase map data in Table 3, contains compounds which have three methyl groups attached to the germanium atom, and two conjugated aromatic rings making up the core of the LC. The trimethylgermane group is much smaller than the triethyl analogue, and thus has a less profound effect on the properties of compounds and mixtures made with them. Although most members of this class had smectic C phases, these were sometimes monotropic and occasionally no LC phases were present. A higher order tilted smectic phase was sometimes present. In comparison to their triethyl analogues (Section 2.2.1), these

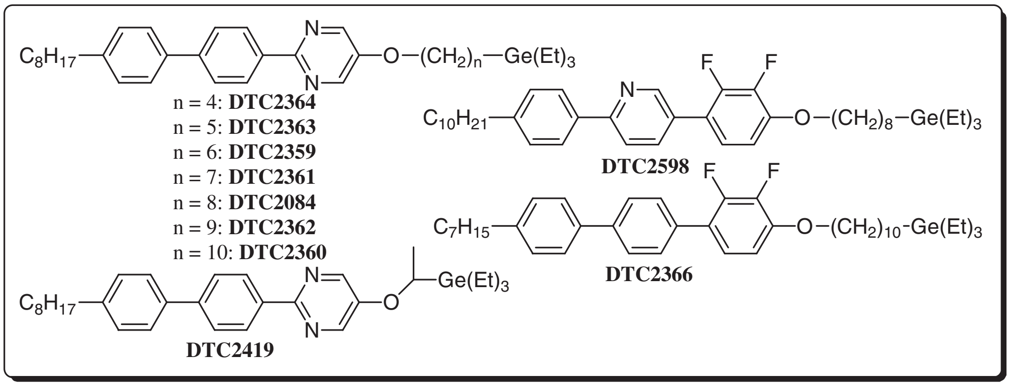


Figure 3. Triethylgermanes with three-ring cores.

Table 2. Phase map data for triethylgermanes with three-ring cores.

DTC#	Cr		SmC		I
2364	¤	59(<27)	¤	87.8	¤
2363	¤	42.0(24.4)	¤	111.6	¤
2359	¤	32(<25)	¤	108.2	¤
2361	¤	55.6	¤	120.3	¤
2084	¤	45(30)	¤	132	¤
2362	¤	61.5(40.4)	¤	128.9	¤
2360	¤	63.9(40.8)	¤	131.9	¤
2366	¤	65.2(62.7)	¤	123.2	¤
2598	¤	38.5	¤	110.5	¤
2419		Phase map not taken			

compounds tend to have higher smectic C stability. For instance, the compound **DTC2183** has a triethyl analogue in **DTC2096**, and its I–SmC transition is about 17°C higher than that of **DTC2096**. **DTC2513** and **DTC2590** are a similar pair, with the I–SmC transition of **DTC2513** about 130°C higher.

2.2.4 *Trimethylgermanes with three-ring cores*

This class, shown in Figure 5 with phase map data in Table 4, contains compounds which have three methyl groups attached to the germanium atom, and three conjugated aromatic rings making up the core of the LC. As was seen with the triethyl analogues (Section 2.2.2), these materials all possess enantiotropic smectic C phases, but unlike the triethyl compounds, some other liquid-crystalline phases occasionally occur. The trimethylgermane compounds tend to have higher smectic C stability, compared with their triethyl analogues. The first seven compounds listed in the two tables are analogues, with the smallest increase in smectic C stability being 15°C, and the average increase being about 27°C. Note that **DTC2427** possessed a nematic phase not seen in any of its longer-tailed trimethyl analogues. This nematic phase appears to be more common when the link between the core and the bulbous germane group is shorter; for additional examples, see the table of short-tail Ge-LCs (Section 2.2.7).

2.2.5 *Cyclohexyl ester and ether ge-LCs*

This class, shown in Figure 6 with phase map data in Table 5, contains compounds with cyclohexyl esters or ethers, and that portion of the core seems to dominate the behaviour of the material. For instance, the nematic phase is relatively rare in Ge-LC compounds, but occurs fairly frequently in materials with a cyclohexyl ester attached to a phenylpyrimidine core. This was first seen with **DTC2340**, but is also seen when the core is reversed, as in **DTC2404**, or when a trimethylgermane group is substituted for the triethyl analogue, as in **DTC2414**. In all, 14 members of the cyclohexyl ester class of materials had nematic phases, whereas

Table 3. Phase map data for trimethylgermanes with two-ring cores.

DTC#	Cr		SmF		SmC		I
2574	¤	39.0(7.8)			¤	(30.7)	¤
2183	¤	48.3(20.0)			¤	98	¤
2462					¤	71.8	¤
2520	¤	74.5(70.2)			¤	86.6	¤
2522	¤	53.0(42.7)			¤	48.6	¤
2513	¤	99.0(69.4)			¤	162.1	¤
2511	¤	43.2(<−32)	¤	(37.1)	¤	(38.5)	¤
2457	¤	47.6(24.9)			¤	52.9	¤
2518	¤	61.6(51.2)			¤	(61.2)	¤

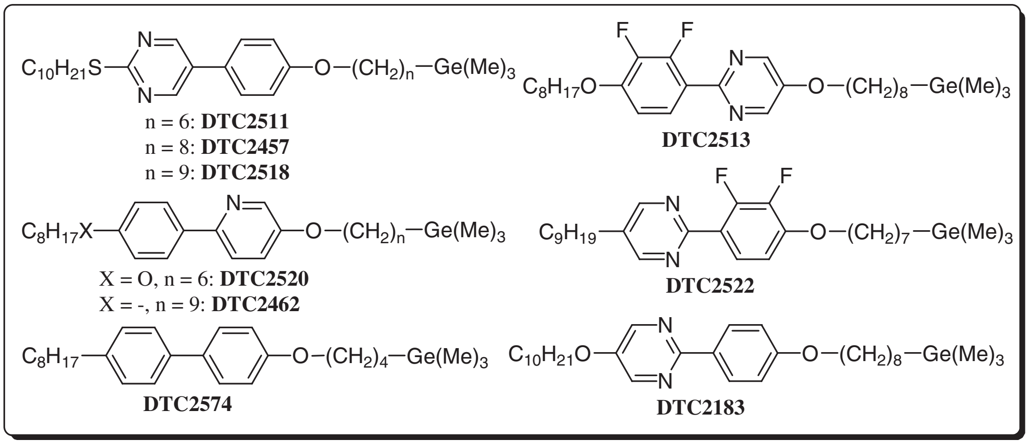


Figure 4. Trimethylgermanes with two-ring cores.

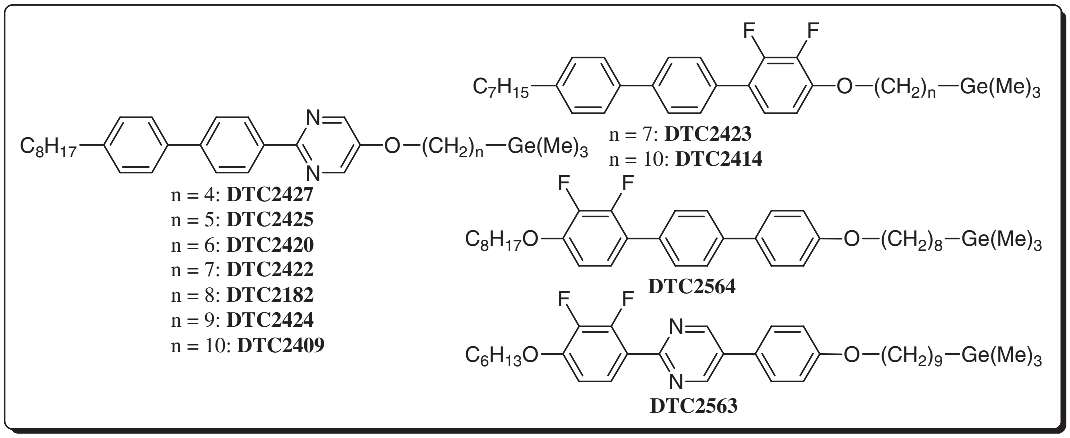


Figure 5. Trimethylgermanes with three-ring cores.

Table 4. Phase map data for trimethylgermanes with three-ring cores.

DTC#	Cr		SmX*		SmG		SmC		N		I
2427	¤	64.6(36.9)					¤	119.7	¤	123.6	¤
2425	¤	74.8(38.3)	¤	(69.5)			¤	144.9			¤
2420	¤	60(21.3)					¤	138.3			¤
2422	¤	95.4(77.0)					¤	153.2			¤
2182	¤	67.0(40.0)					¤	147.0			¤
2424	¤	78.3(56.2)					¤	156.0			¤
2409	¤	84.3(67.4)					¤	153.4			¤
2564	¤	88.0(85.5)					¤	160.0			¤
2423	¤	65.6(62.5)					¤	141.5			¤
2414	¤	54.6			¤	58.3	¤	137.5			¤
2563	¤	76.0(48.6)					¤	170.9			¤

*SmX indicates an unidentified smectic phase.

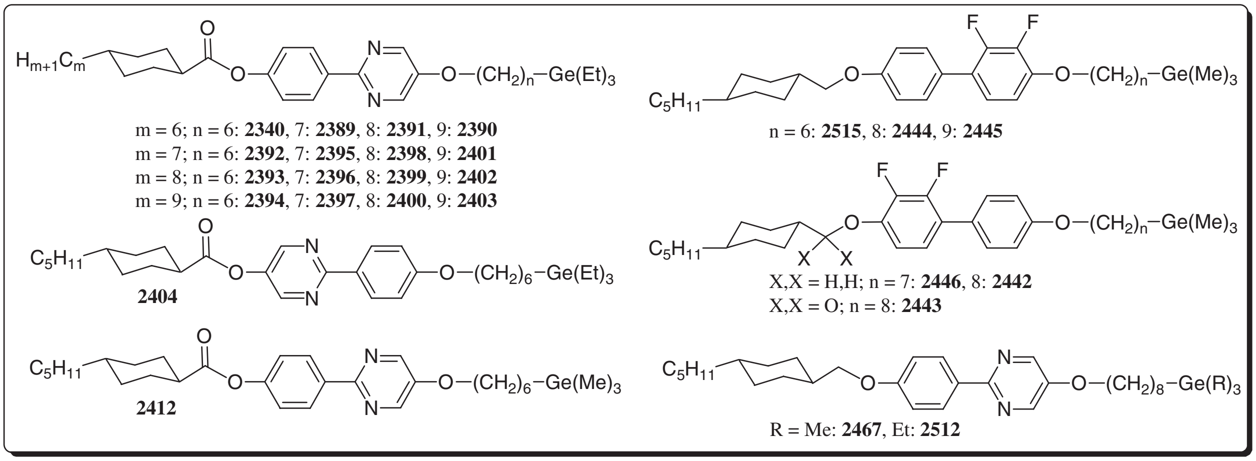


Figure 6. Cyclohexyl ester and ether Ge-LCs.

five did not. Nematic phases were rarer in the cyclohexyl ether class, with only two of the seven having a nematic phase. In places where there are ester/ether pairs, sometimes both compounds have a nematic phase (in the **DTC2391/DTC2512** pair) and sometimes only the ester has a nematic phase (in the **DTC2443/DTC2442** pair). Three of the seven cyclohexyl ethers have a smectic A phase instead of a nematic phase.

Table 5. Phase map data for cyclohexyl ester and ether Ge-LCs.

DTC#	Cr		HOS*		SmC		SmA		N		I
2340	¤	87(66.4)			¤	92			¤	114.4	¤
2389			SmB	112.8	¤	113.1			¤	117.9	¤
2391	¤	100.4	SmG	102.6	¤	112.7			¤	123.4	¤
2390	¤	102.3			¤	123.4			¤	124.9	¤
2392	¤	58	SmG	75.7	¤	96			¤	114.8	¤
2395	¤	69	SmG	83.3	¤	114.9			¤	116.8	¤
2398	¤	69.9			¤	114.7			¤	121.8	¤
2401	¤	82.9	SmG	93.5	¤	124.3					¤
2393	¤	52			¤	85.4	¤	95.8	¤	110.8	¤
2396	¤	52.2	SmG	72.1	¤	114.2					¤
2399	¤	38			¤	114.9			¤	119.4	¤
2402	¤	74.1			¤	123.5					¤
2394	¤	38	SmG	67.5	¤	95			¤	111.2	¤
2397	¤	47.9	SmG	67.6	¤	115.6					¤
2400	¤	46.7			¤	113.9			¤	119.4	¤
2403	¤	51	SmX	54	¤	124.5					¤
2404			SmG	65	¤	94.3			¤	117.2	¤
2412	¤	53.6	SmH	117.9	¤	132.7			¤	153.9	¤
2443	¤	62(20.3)			¤	101.5			¤	128.8	¤
2512	¤	111.2(100.2)			¤	(108.2)			¤	112	¤
2467			SmG	113.3	¤	130			¤	134.5	¤
2442	¤	41.9(20.9)			¤	89.1	¤	110.7			¤
2446	¤	51.7(7.4)			¤	102.7					¤
2444	¤	45.1(15.2)			¤	57	¤	115.2			¤
2445	¤	70.6(37.7)			¤	72.8	¤	117.3			¤
2515	¤	48.6(1.8)	SmX	(25.3)	¤	111.4					¤

*HOS = higher order smectic; SmX indicates an unidentified smectic phase.

One compound, **DTC2393**, even has an I–N–SmA–SmC phase sequence, much coveted due to its perceived compatibility with conventional FLCs.

2.2.6 Low birefringence Ge-LCs

In some cases, it is desirable to have LC components that can be used to lower a mixture's birefringence. The compounds in this class, shown in Figure 7 with phase map data in Table 6, all possess only a single aromatic ring, along with one non-aromatic ring, in their core. Three of these materials have no LC phases, and two have only a monotropic smectic C phase.

2.2.7 Short-tail Ge-LCs

Proximity of the bulbous germanium group to the LC core strongly influences the behaviour of the LC. Young's (*12*) original Ge-LC had its germanium atom directly connected to the aromatic core and had two unidentified smectic phases. The materials that we have put in this class, shown in Figure 8 with phase map data in Table 7, all have one or two atoms between the core and the germanium atom. Of the 13 compounds in this class, six were not mesomorphic. Of the remaining LCs, one was restricted to having only a smectic C phase; four of the others combined the smectic C phase with a nematic phase, and two had both a smectic A and smectic C

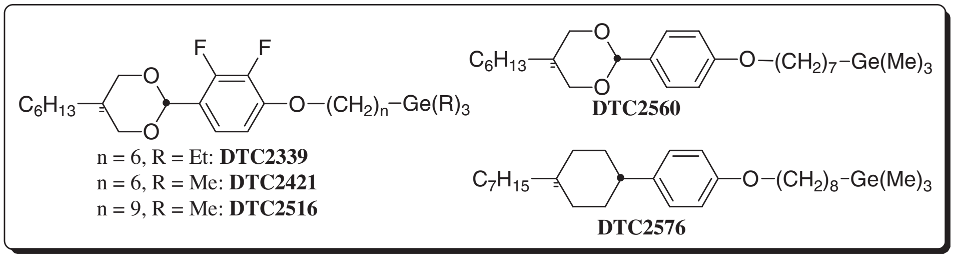


Figure 7. Low birefringence Ge-LCs.

Table 6. Phase map data for low birefringence Ge-LCs.

DTC#	Cr		SmC		I
2560	¤	61.1(13.9)	¤	(42.3)	¤
2421	¤	25.8			¤
2339		Oil at RT			¤
2516	¤	25.6(20.4)			¤
2576	¤	36.4(2.7)	¤	(35.6)	¤

phase. Two of the compounds, **DTC2365** and **DTC2415**, have an I–N–SmA–SmC phase sequence, strongly desired because of its compatibility with conventional FLCs.

2.2.8 *Ge-LCs with semiperfluorinated tails*

It is well known that perfluoroalkanes tend to segregate from conventional hydrocarbon solvents (*17*) and there is some evidence (*18*) that suggests that such segregation also occurs in LCs. Thus, it is not surprising that the perfluoro portion of an LC's tail would dictate the liquid-crystalline behaviour of the LC. The compounds in this class, shown in Figure 9 with phase map data in Table 8, each possess a tail with both a hydrocarbon and a fluorocarbon portion, with the fluorocarbon portion being further from the core. The germanium-containing tail is attached to the other side of the core. We have found in the past that semifluorinated tails tend to induce smectic A phases, and Ge-LCs proved

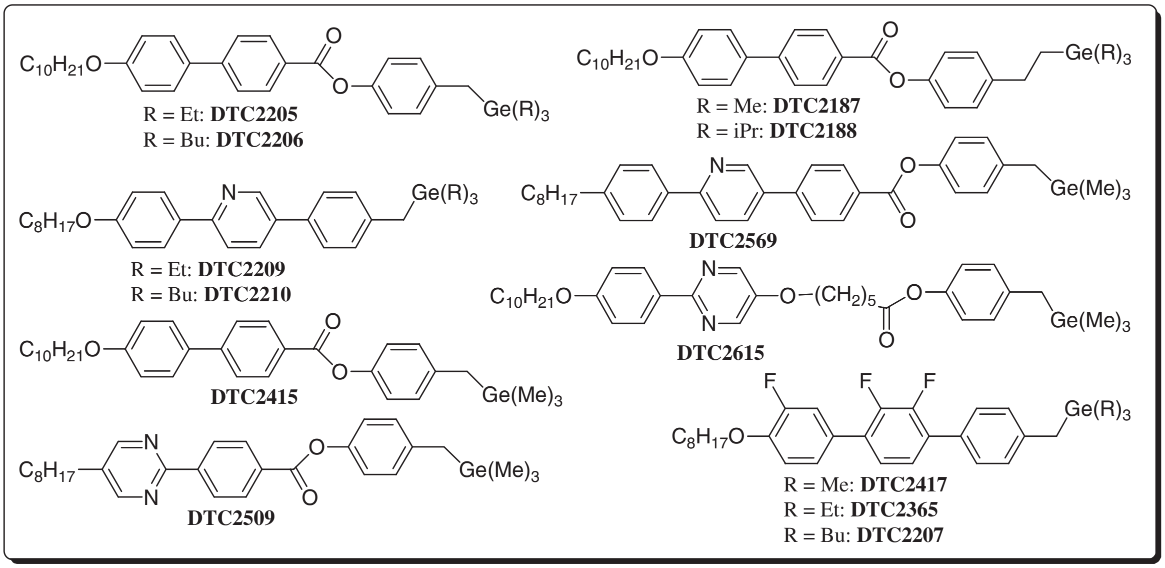


Figure 8. Short-tail Ge-LCs.

Table 7. Phase map data for short-tail Ge-LCs.

DTC#	Cr		SmX*		SmG		SmC		SmA		N		I
2417	¤	33.8					¤	38.9			¤	51.2	¤
2365	¤	32.0			¤	130.0	¤	182.5	¤	217.2	¤	218.9	¤
2207		Oil at RT											¤
2209	¤	45.0(35.0)											¤
2210	¤	40.0(30.0)											¤
2415	¤	14.4					¤	116.3	¤	126.4	¤	135.5	¤
2205	¤	70.0(50.0)											¤
2206		Oil at RT											¤
2509	¤	79.3					¤	94.3			¤	105.9	¤
2569							¤	227.3	¤	260.6			¤
2615	¤	92.5(78.6)					¤	101.6					¤
2187	¤	28.0(20.0)	¤	68.0			¤	145.0	¤	160.0			¤
2188	¤	70.0(50.0)											¤

*SmX indicates an unidentified smectic phase.

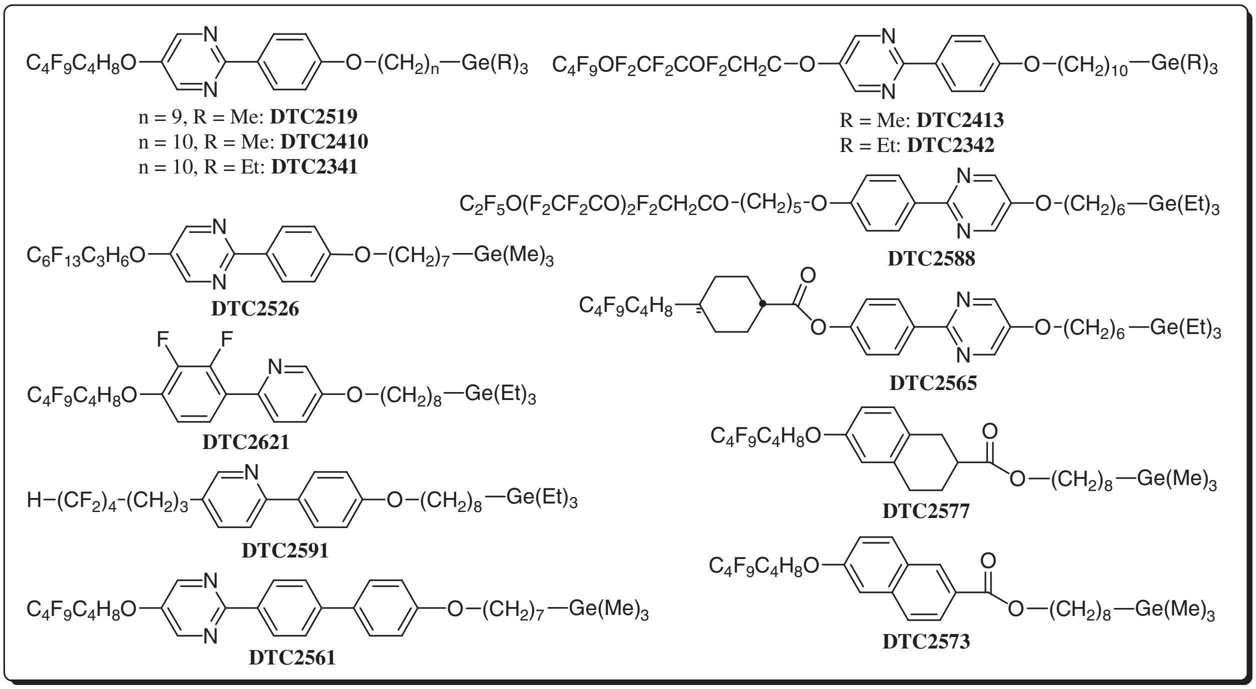


Figure 9. Ge-LCs with semiperfluorinated tails.

Table 8. Phase map data for Ge-LCs with semiperfluorinated tails.

DTC#	Cr		SmX*		SmG		SmC		SmA		I
2561	¤	141.9(126.2)					¤	203.9			¤
2519	¤	90.2(80.3)					¤	102.2	¤	103	¤
2410	¤	66.2					¤	100.9	¤	103	¤
2341	¤	60(42.5)					¤	83.2	¤	89.3	¤
2526	¤	113.6(91.9)			¤	(111.7)					¤
2591	¤	41.1	¤	(8.3)			¤	74.9			¤
2621	¤	(<–45)					¤	35.2	¤	40.8	¤
2413	¤	53.9					¤	59.5	¤	72.2	¤
2342	¤	42					¤	50	¤	74.7	¤
2588			Phase map not measured								¤
2565	¤	122.3									¤
2573	¤	50.8(8.3)									¤
2577			Phase map not measured								¤

*SmX indicates an unidentified smectic phase.

no exception: of the nine compounds of this class which proved to be mesomorphic, six had smectic A phases while eight had smectic C phases.

2.2.9 *Chiral Ge-LCs*

This class, shown in Figure 10 with phase map data in Table 9, includes all Ge-LCs with non-racemic chiral centres. Of the nine compounds for which phase maps were measured, three showed no mesomorphic phases, four exhibited only a smectic C phase, and two showed a smectic A phase in addition to the smectic C phase.

2.2.10 *Ge-LCs with an additional silicon or germanium atom*

If one germanium atom in a molecule tends to induce a smectic C phase, as happened in about three-quarters of the Ge-LCs that we made, what would happen if two germaniums, or a germanium and a silicon, were introduced into a molecule? Several such compounds were synthesised and are shown in Figure 11, with the phase map data in Table 10. This class of Ge-LCs has, in addition to the first germanium atom, either a second germanium atom or one or two silicon atoms. Of the group IV atoms, silicon is larger than carbon, and germanium is larger than silicon, so we expected that a

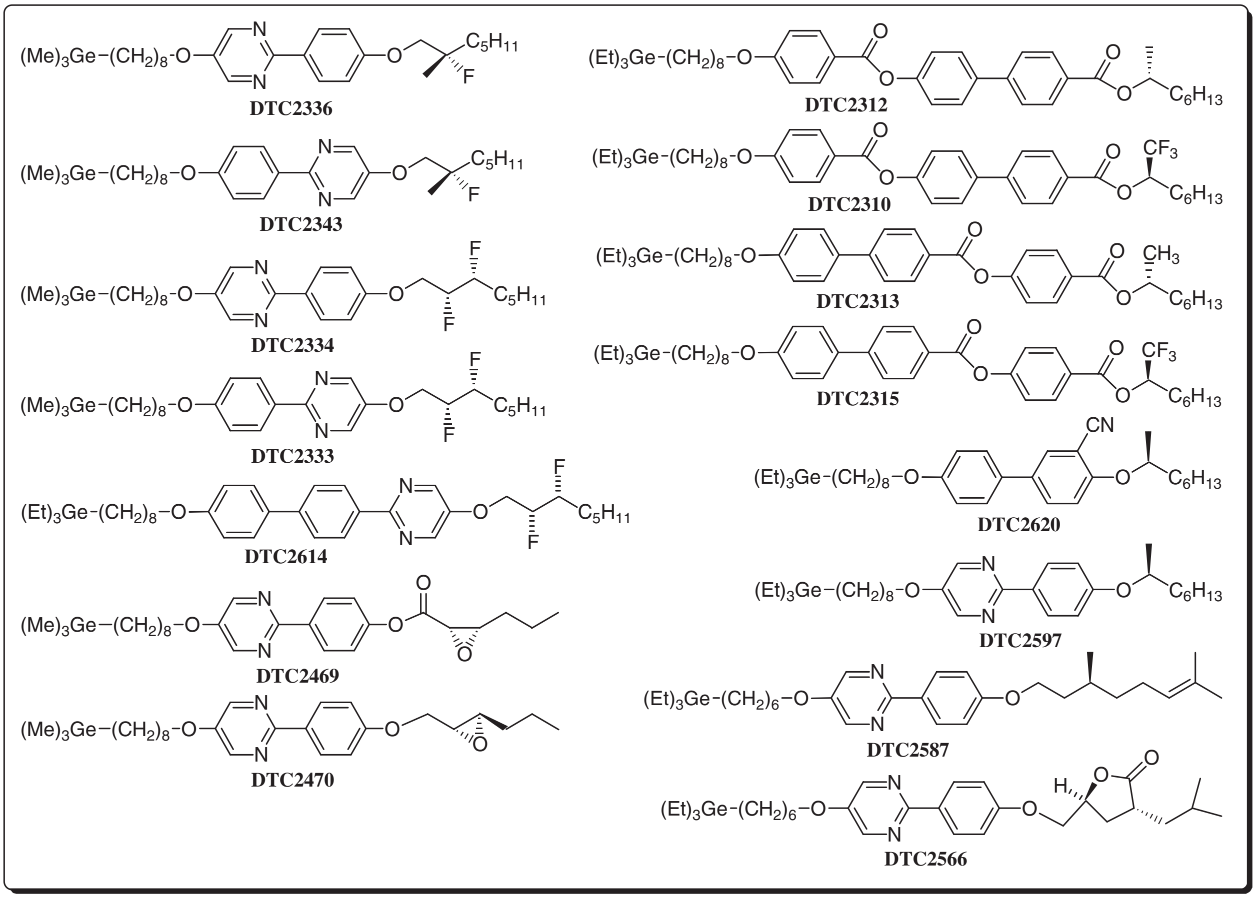


Figure 10. Chiral Ge-LCs.

Table 9. Phase map data for chiral Ge-LCs.

DTC#	Cr		SmX2*		SmX1*		SmC*		SmA*		I
2334	¤	97.0(84.0)									¤
2333	¤	84.0(77.0)	¤	(78.0)	¤	88	¤	94	¤	99.9	¤
2614	¤	140.7(134.7)					¤	171.5			¤
2336	¤	49.0(29.0)									¤
2343		Oil at RT									¤
2469	¤	50.7(29.5)									¤
2470	¤	84.8(54.3)					¤	88.3			¤
2597		Oil at RT									¤
2620			Phase map not measured								¤
2312	¤	41.3					¤	69.8			¤
2310	¤	(<−70)					¤	−19.1	¤	14.3	¤
2313	¤	38.0(12.9)					¤	72.9			¤
2315			Phase map not measured								¤
2587			Phase map not measured								¤
2566			Phase map not measured								¤

*SmX indicates an unidentified smectic phase.

second germanium would have a slightly larger effect on the system, but the size of the central atom in the bulbous group is dwarfed by the three groups attached to it. We expected compounds with two or more bulbous groups to show smectic C phases, much as compounds with only one germanium did, and about the same proportion of compounds (2:3) proved to show the smectic C phase. **DTC2149** is one of only

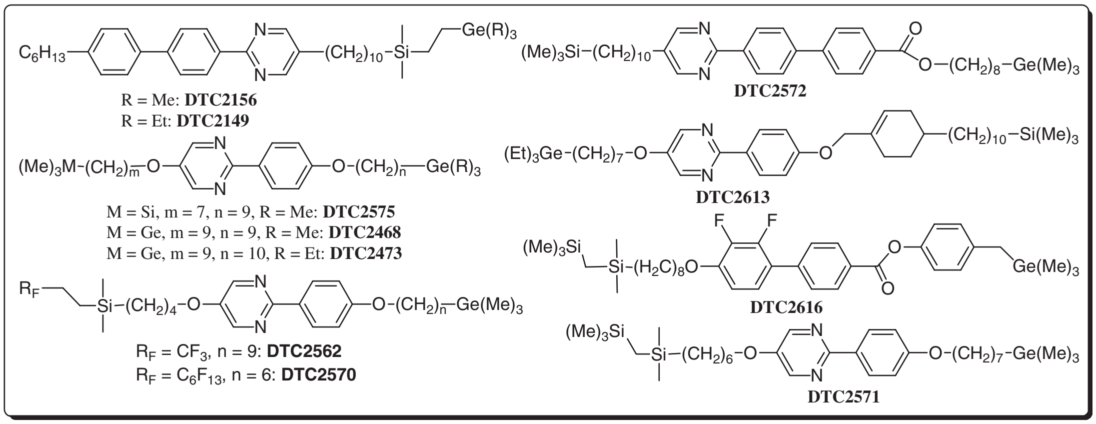


Figure 11. Ge-LCs with an additional silicon or germanium atom.

Table 10. Phase map data for Ge-LCs with an additional Si or Ge atom.

DTC#	Cr		SmC		I
2468	¤	65.5			¤
2473	¤	40.1(14.3)	¤	49.3	¤
2575	¤	78.5(74.1)			¤
2156		Phase map not measured			¤
2149	¤	−5.0(−10.0)	¤	100	¤
2562	¤	56.0(25.3)			¤
2570	¤	57.7(21.5)	¤	(55.1)	¤
2571		Phase map not measured			¤
2616	¤	68.3(18.1)	¤	(40.3)	¤
2613	¤	58.8(25.2)	¤	70.5	¤
2572	¤	82.6(62.1)	¤	141.5	¤

three Ge-LC compounds having smectic C widths of over 100°C. None of these compounds showed any other LC phases.

2.2.11 Miscellaneous Ge-LCs

The compounds in this class, shown in Figure 12 with phase map data in Table 11, do not quite fit into any of the previous classes established herein. **DTC2474**, for instance, has bulbous groups on both ends of the molecule, and has properties somewhat like those found in Ge-LCs with a second germanium atom, but it does not quite fit into the previous classes. Similarly, **DTC2525** is structurally similar to the cyclohexyl esters and has a nematic phase like the cyclohexyl esters. It has the widest smectic C phase of any of the Ge-LC compounds, with a range of over 120°C centred near room temperature! It is probably appropriate that this potpourri of compounds has the same rough proportion (2:3) of compounds exhibiting smectic C phases as are seen elsewhere in this work, while only one less ordered phase is seen.

3. Synthesis of Ge-LC compounds

Synthesis of the germanium compounds listed in this article was relatively straightforward, using standard techniques used for many LCs. In most cases, introduction of the germanium-containing functional group was done in one of three ways. First, germanium was introduced by hydrogermylation (*19*) of an alkene using either trimethyl- or triethylgermane. Second, a trialkylgermaniumchloromethane was treated with magnesium, and the resulting Grignard reagent was used to convert an alkyl halide tail into a germanium-bearing tail. Third, germanium dichloride could be inserted into a bond (*20*), giving an alkylgermanium with three reactive groups attached. In this last type of a reaction, germanium dichloride had previously been inserted only into a carbon-chlorine bond. We found that, in a system which contained a benzyl omega-chloro ether, the germanium actually inserted into the carbon-oxygen bond at the benzyl position, rather than inserting into the carbon-chlorine bond. This is a new reaction, never before reported in literature, and thus deserves a somewhat deeper explanation.

3.1 Germanium dichloride insertion reaction

Germanium dichloride is known to insert into a carbon-chlorine bond (*20*), in the manner shown at the top of Scheme 1, usually with good success. This typically results in an alkylgermaniumtrichloride, such as compound **2**, which is immediately treated with refluxing Grignard reagent to give the tetraalkylgermane. The starting chlorooctyl hydroxybenzyl ether **1** was treated with germanium dichloride, with the expected result being the alkylgermaniumtrichloride **2**. Treatment with refluxing Grignard reagent gave, instead of the expected long-chain trialkylatedgermanium compound

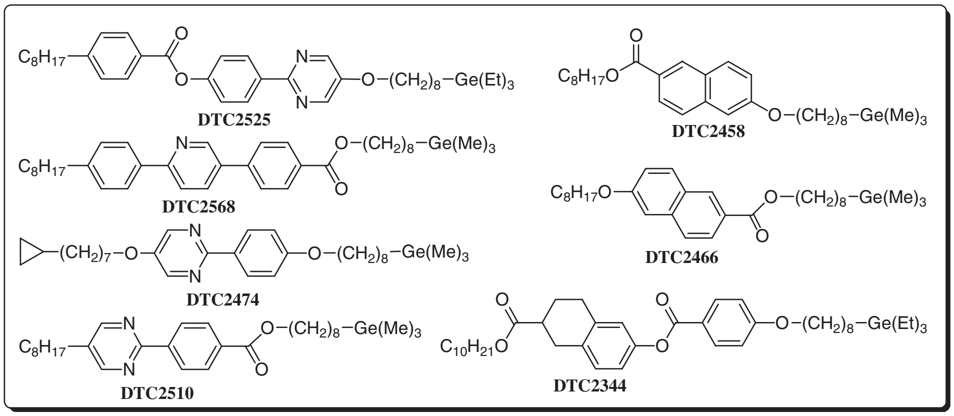


Figure 12. Miscellaneous Ge-LCs.

Table 11. Phase map data for miscellaneous Ge-LCs.

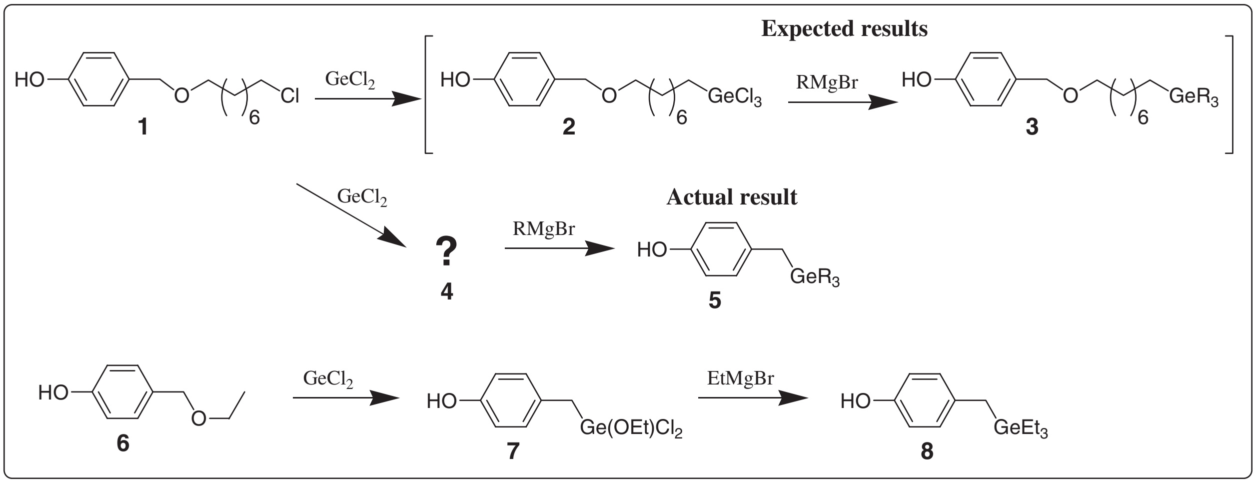
DTC#	Cr		SmC		N		I
2474	¤	53.8(16.3)	¤	69.7			¤
2510	¤	51.0(30.1)	¤	(42.7)			¤
2525	¤	–29.3	¤	94.7	¤	99.5	¤
2568	¤	79.5(60.5)	¤	164.4			¤
2466	¤	34.2(–1.4)					¤
2458		Phase map not measured					¤
2344	¤	7.9(6.1)					¤

3, the benzyltrialkylgermanium **5**. The germanium had clearly inserted into the carbon-oxygen bond at the benzyl position of the starting material, perhaps through some intermediate that involved the terminal carbon-chlorine bond. To ascertain that the actual intermediate **4** involved insertion straight into the carbon-oxygen bond, we re-ran the reaction, this time starting with the much simpler ethyl ether **6**. Again, consecutive treatments with germanium dichloride and ethyl Grignard gave the trialkylated germane **8**, this time with no possibility of an intermediate reaction involving a carbon-chlorine bond, so it presumably went through the ethoxydichlorogermane **7**. This suggests that unknown compound **4** was probably a dichloroalkoxy intermediate, similar to compound **7** but with a 6-chlorohexyloxy group instead of an ethoxy group.

4. The tilt angle and layer spacing of Ge-LC mixtures

4.1 Dependence of the tilt angle and layer spacing on temperature

X-ray analysis of smectic mixtures containing Ge-LCs, especially **GX2** (see Table 12), showed that their layer spacing does not vary much with changing temperature, especially in the area of the SmA–SmC transition. This led to speculation that perhaps the



Scheme 1. Insertion of germanium dichloride.

Table 12. Compositions, tilt angles and layer shrinkage of mixtures.

Mixture number*	Dopant	Central atom[a]	R on atom[b]	%[c]	Chiral %[d]	Max Tilt (°)[e]	Layer shrinkage[f] Theo.[g]	Layer shrinkage[f] Actual[h]
Base (MX10155)	none	–	–	–	–	26.6 est	10.6 %	9.0 %
GX1 (MX10569)	none	–	–	–	4[i]	26.6	10.6 %	
GX2 (MX10439)	2096	Ge	Et	50[i]	0	11.8 est	2.1 %	0.5 %
GX3 (MX10567)	2096	Ge	Et	48[i]	4[i]	13.2	2.6 %	1.2 %
GX4 (MX10596)	2096	Ge	Et	49.5[i]	1[i]	12.2	2.2 %	
GX5 (MX10637)	2348	Si	Et	47[i]	4[i]	12.6	2.4 %	1.1 %
GX6 (MX10568)	2096	Ge	Et	19[i]	4[i]	19.2	5.6 %	
GX7 (MX10638)	2348	Si	Et	19[i]	4[i]	20.0	6.0 %	
GX8 (MX10695)	2183	Ge	Me	40.3[j]	4.8[j]	18.2	5.0 %	3.0 %
GX9 (MX10696)	2408	Si	Me	40.3[j]	4.8[j]	18.0	4.9 %	2.9 %
GX10 (MX10697)	2407	C	Me	40.3[j]	4.8[j]	19.5	5.7 %	3.4 %

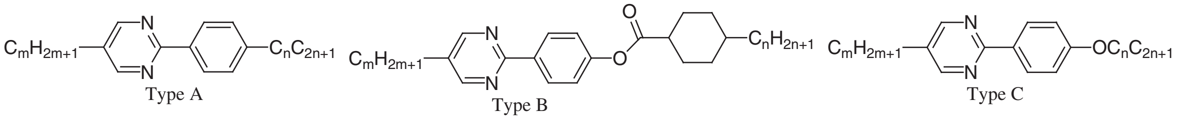
*The Displaytech mixture number is given in parentheses; the GX number is used only in this paper.
[a] Atom at centre of bulbous end group.
[b] Three of these groups on the central atom.
[c] Remainder of the mixture is the base (**Base**) and the chiral dopant.
[d] **DTC950**, a chiral dopant that allows the tilt angle to be measured.
[e] Maximum extinction angle, as measured in a 1.8-μm cell with a nylon alignment layer, at 25°C.
[f] Layer shrinkage from the SmA–SmC transition to 25°C.
[g] Based on $\cos(\theta c)$.
[h] Measured by X-ray scattering, measured from Tc to 25°C.
[i] Measured in weight percent.
[j] Measured in mole percent.

Ge-LCs would be classified as first-order de Vries materials (*21*) (namely materials with a first-order SmA–SmC phase transition). The initial layer spacing measurements were taken with achiral systems, preventing easy measurement of the smectic cone angle (tilt angle). When a chiral component was added to the mixture, the resulting cone angle measurements showed that Ge-LCs decreased the cone angle in smectic C LCs. Since for some applications, such as quarter-wave plates, mixtures with low tilt angles throughout the smectic C range are desirable, this makes Ge-LCs welcome additions to our formulation toolbox.

4.1.1 X-ray layer spacing studies of Ge-LCs and analogues

The **Base** mixture used in these studies is a phenylpyrimidine-based mixture with a room-temperature smectic C phase and moderately wide nematic and smectic A phases. This mixture's composition and phase map are detailed in Table 13. To this **Base** mixture one could add combinations of a chiral component and Ge-LC components or analogues of Ge-LC components. The **Base** mixture showed 9% shrinkage from the SmA–SmC transition down to room temperature. **GX2** comprised 50 weight percent of the Ge-LC **DTC2096** in the **Base**, and showed only 0.5%

Table 13. **Base** composition; phase map = I–85–N– 1–SmA–65–SmC.



Structure type

DTC#	Type	m	n	Mole % in **Base**
005	A	8	12	23.1
004	A	9	8	26.1
003	A	7	8	27.0
337	B	10	5	12.9
374	C	8	6	10.9

shrinkage from its SmA–SmC transition down to room temperature. Results for this and other mixtures containing Ge-LCs are detailed in Table 12.

Since there were no chiral components in either the **Base** or **GX2**, the cone angle could not be measured. To remedy this situation, a high polarisation chiral dopant, **DTC950**, was added to **GX2** to give **GX3**. Similarly, **DTC950** was also added to the **Base** to give **GX1**. These two FLCs could be used to estimate the tilt angle of their achiral predecessors, with the result that the estimated cone angle of the **Base** was about 26.6°, and the estimated cone angle of **GX2** was about 13.2°. Although these mixtures both exhibit an I–SmC phase sequence, leading to poor alignment and to low-precision tilt angle measurements, the trend is clearly significant. The introduction of large amounts of Ge-LC components drastically decreased the tilt angle of the **Base** mixture, and other data included herein demonstrate that this is a general phenomenon; addition of Ge-LC components to a mixture tends to decrease the tilt angle of the mixture.

Since the chiral dopant itself might increase the tilt of a mixture, a new mixture (**GX4**) containing only 1% of the chiral dopant was formulated, and its cone angle was only 12.2°. Extrapolating from the cone angles of **GX3** and **GX4**, with their respective compositions of 4% and 1% **DTC950**, down to **GX2**'s 0% **DTC950**, we revised the estimated cone angle of **GX2** to 11.8°. So, the chiral dopant does slightly increase the tilt angle of mixtures. The extrapolation is shown in Figure 13.

One can attempt to understand the layer shrinkage results with simple model considerations. The predicted shrinkage of an ideal orthogonal smectic A phase, in which rigid-rod molecules tilt away from the layer normal in the smectic C phase, can be estimated by the cosine of the cone angle. For the **Base**, one predicts 10.6% shrinkage but one measures 9.0%, a lower value which indicates that the prediction is only approximate. Similarly, the predicted layer shrinkage of **GX2** is 2.1%, while the measured value is 0.5%. For the slightly higher tilt **GX3**, the expected and actual shrinkages are 2.6% and 1.2%, respectively.

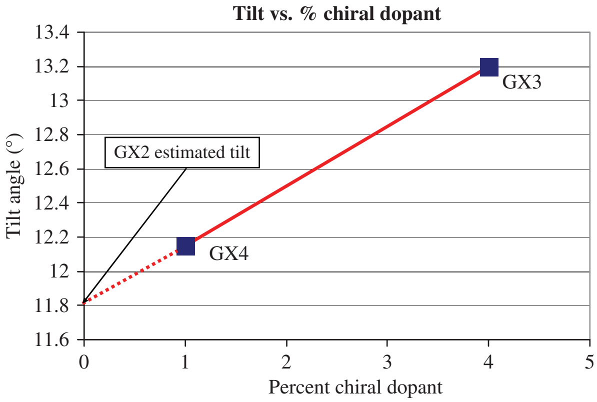


Figure 13. Estimation of tilt angle of **GX2**.

That the differences for these materials are about the same for each material can be interpreted as meaning that, whatever their ultimate cause, that cause is likely assignable to the **Base** alone and is largely unaltered by the dopants. Alternatively, one can postulate a 'partial de Vries-ness' (*22*) and analyse the differences by defining a de Vries quotient R_d via

$$R_d = \frac{(d_C/d_A) - \cos(\theta)}{1 - \cos(\theta)} \qquad (1)$$

where one assumes idealised FLC behaviour with no intermingling of layers. Then any reduction in layer shrinkage beyond that calculated from the cosine of the tilt angle is interpreted as partial de Vries character, which is quantified by the quotient. Subtracting the theoretical layer shrinkage in Table 12 from 1 gives the quantity d_C/d_A in this equation, and θ is the mixture's tilt angle at 25°C. Analysed in this way, the **Base** mixture is 15% de Vries, while **GX2** is 76%, **GX3** and **GX5** are 55%, and **GX8**, **GX9** and **GX10** are each about 40%.

While perhaps suggestive for those predisposed to one or another interpretation, all these analyses are based on overly simplistic model assumptions, and none is likely to reflect the real situation with any great accuracy. Real LC materials do not conform to such ideals. Looking at a large number of Displaytech's FLCs, one finds that the measured layer spacing change is always less than the simple stick model predicts, and that the difference is always about the same 1% to 3%. Quite likely, some systematic deficiency in the stick model is at the root. For example, it ignores the distinction between the rigid cores and floppy tails of LC molecules and the differing ways they respond in the smectic layers as temperature is changed. This is not to deny that real de Vries smectic A phases exist, as they are well documented, only that differences between measured layer spacing and simplistic calculations cannot alone establish the true situation.

Having looked at a mixture comprising about half Ge-LC components, we wished next to determine whether using smaller amounts of Ge-LCs would result in smaller changes in the tilt angle. To do this comparison, an additional mixture, **GX6**, was added to those already discussed. This allows a progression of mixtures containing various amounts of the triethylgermanium component **DTC2096**, where **GX3**, **GX6** and **GX1** contain 48, 19 and 0 weight percent **DTC2096**, respectively, with the remainder of the mixtures' composition comprising 4% **DTC950**

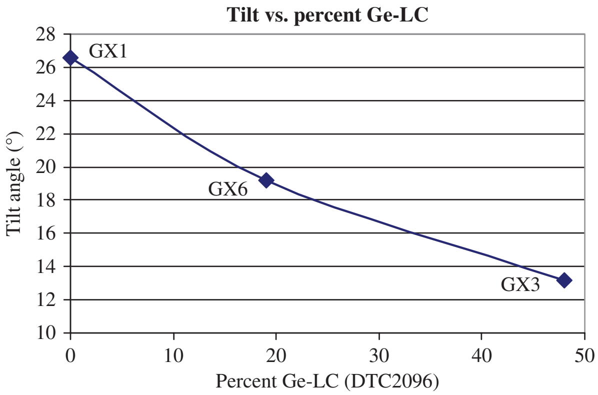


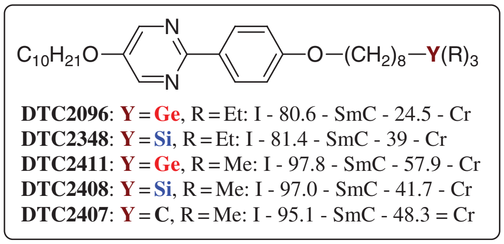
Figure 14. Progressive addition of Ge-LCs results in progressively smaller tilt angles.

and enough **Base** mixture to make up the balance. This study, shown in Figure 14, demonstrates that increasing the proportion of **DTC2096** in a mixture decreases its tilt angle. No colour change, evidence of a change in birefringence, was observed as mixtures **GX3**, **GX6**, **GX1** and **GX4** went through their SmA–SmC transitions. This indicates that the mixtures did not have first-order de Vries transitions.

4.1.2 Comparing Ge-LCs with their silicon and carbon counterparts

Since initial studies using Ge-LCs hinted that their properties might be similar to those of silane-containing LCs (Si-LCs), we decided to compare them by making **DTC2348**, a Si-LC identical to **DTC2096** but for the substitution of a silyl atom in place of **DTC2096**'s germanium atom. These two compounds were similar in phase map, with **DTC2096**'s I–SmC transition of 80.6°C being only 0.8°C less than that of **DTC2348**. **DTC2348** was used to make **GX5**, a direct analogue of **GX3**, with both mixtures containing about 50% of their respective dopant. The tilt angle and layer shrinkage of this mixture was remarkably similar to that of **GX3**, with the tilt angle being about 13° and the layer shrinkage being about 1.1%. Similarly, **GX7** was made as an analogue to **GX6**, with both containing 20% of the key dopant. These mixtures also had remarkably similar tilt angles and phase maps, with the Ge-LC mixture, **GX6**, having an I–80.7–N–78.8–SmA–60.7–SmC phase map, while the Si-LC mixture, **GX7**, had an I–80.8–N–79.3–SmA–61.2–SmC phase map. Both had tilt angles of about 19.5°.

If travelling up within group IV of the periodic table from germanium to silicon made little difference, will taking the next step up to carbon make any difference? It proved very difficult to synthesise a triethyl-substituted carbon analogue of **DTC2096**, so we decided to make the three trimethyl-substituted analogues **DTC2183**, **DTC2408** and **DTC2407**, which had, respectively, a germanium, silicon and carbon as the central atom to which the three methyls were attached. See Figure 15 for the structures and phase maps of these compounds, and Table 12 for information about mixtures containing them. These three compounds had similar phase maps, and when doped at a 40 mole percent level into a combination of the **Base** and **DTC950**, they gave mixtures that had almost identical phase maps. Since the tail-terminating bulbous group containing the group IV atom contained methyls instead of the bulkier ethyls, the bulbs were smaller and the compounds' effect on the mixtures' tilt angles were smaller, leading to tilts of about 18° rather than the tilts of about 12° seen with the triethyl moieties. The mixtures containing the germanium, silicon and carbon analogues are, respectively, **GX8**, **GX9** and **GX10**, and their tilt angles are 18.2°, 18.0° and 19.5°. Based on the cosine of those tilt angles, their expected layer shrinkage is about 5%, and the actual layer shrinkage is about 2% less than that, with measured values of 3.0%, 2.9% and 3.4%, respectively. These values are in the expected range for low-tilt conventional materials.



DTC2096: **Y** = **Ge**, R = Et: I - 80.6 - SmC - 24.5 - Cr
DTC2348: **Y** = **Si**, R = Et: I - 81.4 - SmC - 39 - Cr
DTC2411: **Y** = **Ge**, R = Me: I - 97.8 - SmC - 57.9 - Cr
DTC2408: **Y** = **Si**, R = Me: I - 97.0 - SmC - 41.7 - Cr
DTC2407: **Y** = C, R = Me: I - 95.1 - SmC - 48.3 = Cr

Figure 15. Ge-LC components and analogs used in mixtures.

Another class of compounds with a bulbous tail group, the siloxane class of materials, has been extensively studied elsewhere (*4–9*), and has been found to show de Vries behaviour. For instance, the siloxane TSiKN65, which has a second-order SmA–SmC transition (*23*), is reputed to show de Vries behaviour. There are several other reports of second-order (*24–27*) de Vries materials, which could be argued to fall somewhere between purely de Vries FLCs and conventional FLCs on a de Vriesness scale. In any event, given their similarity to siloxanes, if Ge-LCs showed de Vries behaviour, it would likely be second order rather than first order. However, we wished to verify that this transition was not first order in Ge-LCs.

4.1.3 Dependence of the tilt angle of Ge-LCs on temperature

When Ge-LCs were first synthesised, their small amount of layer shrinkage was interpreted as a sign of de Vries behaviour. In most de Vries LCs, the SmA*–SmC* transition is first order, while this transition is second order in conventional FLCs. With first-order transitions, one expects small layer shrinkage and a correspondingly small change in the tilt angle throughout the smectic C* phase, whereas for second-order behaviour, the tilt angle changes continuously and vanishes at the SmA–SmC transition.

As a means of probing the nature of the SmA–SmC* transition in Ge-LCs, we measured the tilt angle behaviour of the three mixtures **GX8-10**, which contain the trimethylgermanium compound **DTC2183** and its silicon and carbon analogues, **DTC2408** and **DTC2407**. Since these mixtures lack a nematic phase, they are difficult to align, but we were able to align them between glass plates carrying parallel-rubbed polymer alignment layers and shearing those plates in the smectic A* and/or smectic C* phases while observing them through a polarising microscope. This procedure produced broad regions of bookshelf alignment within which subsequent measurements could be made. The cells were next cooled to room temperature after which their temperatures were slowly raised. At each of several successively higher fixed temperatures, the cells were allowed to come to thermal equilibrium and were then driven by external fields to enable determination of their tilt angle. This angle was taken to be half the difference between extinction orientations for the two drive polarities, with the cells placed between crossed polariser and analyser. Since the director in the bookshelf regions was always anchored by polar surface interactions, the extinction orientation depended on the magnitude of the driving signal. At each of the fixed temperatures T, the field was raised from a low value to the smallest value beyond which the extinction orientations saturated, never more than several volts per micron. The extinction angles measured at this voltage then yielded the tilt.

Owing to the need to access the plates at high temperature for shearing, the thermal equilibration times were rather long, and the temperature sensor inside the hot stage indicated a value higher than that of the uncovered FLC cells whose top surfaces were in contact with the surrounding air. For each of the mixtures, the tilt angle was found to vanish at some temperature. For purposes of illustration, we have taken this temperature to be T_{AC}, the SmA*–SmC* transition. In Figure 16, we have plotted the tilt angle measured for each material against its temperature difference $T\text{-}T_{AC}$. The data exhibit no signs of any electroclinic effect, so there is no misidentification of T_{AC} on this account.

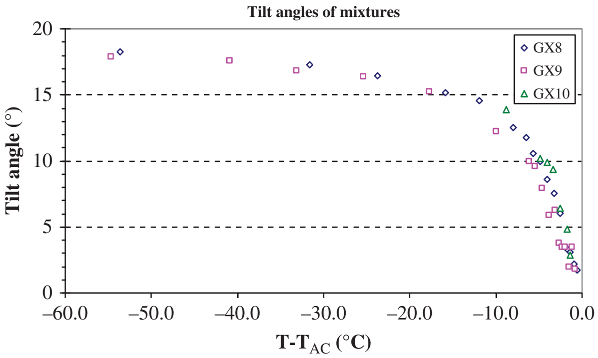


Figure 16. The tilt angle versus temperature of mixtures **GX8-10**.

The character of the phase transitions are all similar. All fall smoothly as the SmC*–SmA phase transition is approached, and all extrapolate to zero. Thus all are at least approximately second order. The Ge-LC is undistinguished from the analogues in this regard. The optic axis was saturated at each temperature and no significant electroclinic effects, which often accompany de Vries behaviour, were evident. It is also worth noting that measurements made on the Ge-FLC at higher applied fields did not show any evidence of field-induced critical behaviour. Such behaviour is expected in some first-order transitions, and has been employed to study materials which are in fact first-order de Vries materials (*21*). Taken together, all our observations strongly imply that the mixtures are conventional FLCs whose tilt angles are lower than normal.

A consensus is emerging that regards any particular smectic A* as existing on a continuum between a purely orthogonal smectic A and a purely de Vries smectic A (*28–30*). Precisely locating arbitrary materials on this continuum also seems to locate its proximity to an N–SmA–SmC* tricritical point and thus to a particular mixture of pure first-order and pure second-order phase transition characteristics. The tilt angle measurements we have made are sufficient to locate our germanium materials much nearer the pure orthogonal end than to the pure de Vries end of the continuum. While this is more than adequate to resolve our original questions regarding these germanium materials, more precise location would require different measurements.

5. Summary

We have shown in this work that including a germanium atom, particularly as a trialkylated group at the end of a moderately long tail, into an LC induces the LC to form a tilted smectic C phase, often to the exclusion of any other liquid-crystalline phases. Only two individual Ge-LC compounds in this study showed liquid crystallinity without having a smectic C phase, but about 20% showed nematic or smectic A phases, with about the same amount showing higher order smectics such as smectic G or smectic H. The liquid-crystalline phases exhibited depended in part on the size of the alkyl groups attached to the germanium atom, with smaller groups exhibiting a higher percentage of phases other than the smectic C.

It is somewhat ironic that the trialkylgermanium group, while inducing a tilted smectic phase, also tends to reduce the tilt angle of tilted smectic mixtures. Again, the alkyl groups' size has an impact, with larger groups decreasing the tilt angle more. Substituting a carbon or silicon for the germanium atom had only a small impact on the properties of the LC compounds formed, or the mixtures made with them. Ge-LC mixtures were expected to have de Vries behaviour, although most of the diminished layer shrinkage through the SmA–SmC transition of the mixtures studied in this paper was assigned to lowered tilt angles. Their SmA–SmC transitions were shown to be second order, but could still be considered to be partially de Vries in nature. Ge-LC mixtures were shown to have low, relatively invariant tilt over wide temperature ranges.

Acknowledgements

This work was supported by the National Science Foundation under grant OII-0522304. We wish to acknowledge Christopher Jones, who took the X-ray scattering layer spacing measurements at the University of Colorado.

Notes

1. Although the term 'phase diagram; is often used to describe the phase sequence and transition temperatures of thermotropic LC, the term properly describes a situation where there are two variables, one generally being temperature, and the other sometimes being pressure or mole percent. The term 'phase map' adequately describes an LC's phase behaviour with varying temperature, without the accompanying alternative definition, and we have thus used this term for several years.
2. Liquid-crystalline phases, especially higher order phases, were identified on an optical microscope equipped with a temperature stage, by considering whether the overlying lower-order phase was tilted or not, and by comparison with pictures in Gray, G.G.; Goodby, J.W. *Smectic Liquid Crystals – Textures and Structures*; Leonard Hill: London, 1984.
3. Much like a *Euoplocephalus* tail, or a ball-and-chain flail medieval weapon.
4. The transition from the smectic C phase to the underlying phase started from seed locations, and thus was clearly to a crystalline phase, but another transition was observed at a lower temperature. The types of crystalline phases were not identified.

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