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Sign Inversion of the Helical Pitch in Carbohydrate-based Liquid Crystals

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Abstract: A four-step synthesis starting from tri-O-acetyl-D-glucal leads to chiral trioxadecalin compounds containing a cyano group. The mesogenic properties of a homologous series of liquid crystals are reported; for two derivatives a helix inversion of the cholesteric phase is observed.

The cholesteric mesophase can only be formed by non-racemic chiral molecules; their stereogenic centres produce a twisting power and are responsible for the resulting helical structure of the mesophase. They also allow the induction of a helical twist in nematic phases formed by non-chiral molecules simply by mixing with them. Thus, the macroscopic properties of chiral liquid crystalline phases are a powerful tool for studying the microscopic chirality of molecular shapes[1].

The phenomenon of an inversion of the helical twist sense in a single compound was first reported in 1989[2]: a norcholesterol ester changed the sign of the helical pitch with temperature. The assumption of different chiral centres with different twisting power and twist sense that compete for the resulting helical twist sense explains this observation. In 1992, a propiolate ester with only a single stereogenic centre was presented showing the same effect[3] . The effect in this case was explained by assuming two sterically preferred conformations of the chiral side chain with different twisting sense abilities so that there is a temperature-dependent domination of either the left- or right-twisting conformation. Further investigations on helix inversions were reported in 1993[4].

We have now synthesized a homologous series of molecules with a trioxadecalin ring bearing four conformationally fixed stereogenic centres; two members of this series show a cholesteric helical pitch inversion. The synthesis is based on commercially available tri-O-acetyl-D-glucal which is derived easily from glucose. The advantage of this strategy is that it makes use of the already existing natural chirality.

The synthetic route[5] (fig. 1) starts with glucal **1**. A Lewis-acid catalyzed allylic rearrangement reaction[6] gives the unsaturated compound **2**. Hydrogenation with palladium on charcoal, separation of the anomers by silica gel column chromatography and deprotection leads to the chiral building block **3** which can be combined in an acid-catalyzed reaction with the dimethyl acetals of 4-cyanobenzaldehydes[7] to form (1S,3R,6R,8R)-3-(4''-cyanophenyl)-8-(4'-alkoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decanes **5** with a trans-decalin ring system in the core of the molecule.

We synthesized a homologous series of liquid crystals with aliphatic chain lengths of 1, 6, 8, 9, 10, 11, 12 and 14 carbon atoms. The mesomorphism is shown in table 1.

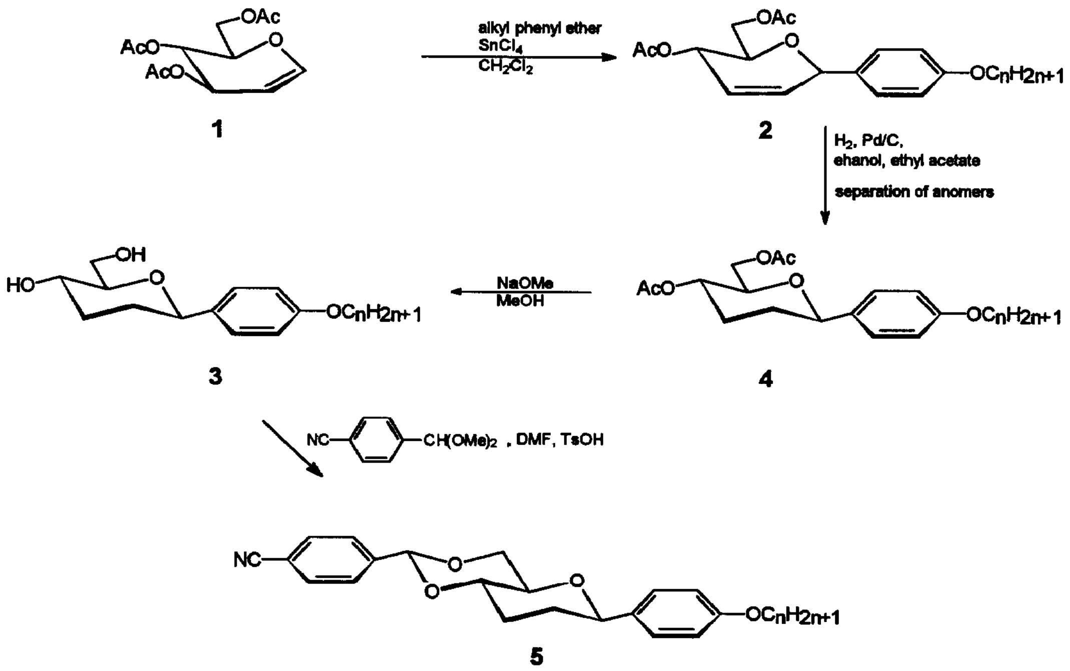


Figure 1: Synthetic Route to Compound **5**

Table 1 Mesomorphism of compounds **5a-5h**

Nr	n	Transition temperatures[8]						
5a	1	Cr	211.0			N*	215.0	I
5b	6	Cr	108.6			N*	174.0	I
5c[9]	8	Cr	107.9			N*	169.4	I
5d	9	Cr	107.0			N*	167.0	I
5e	10	Cr	106.5	S_A	137.4	N*	162.5	I
5f	11	Cr	106.4	S_A	152.0	N*	160.0	I
5g	12	Cr	105.9	S_A	152.7	N*	157.2	I
5h	14	Cr	95.4	S_A	154.2	N*	154.6	I

The compounds with shorter alkyl chains only form cholesteric phases. **5e** with n = 10 shows a smectic A and a cholesteric phase. **5b** (n = 6) exhibits a change of the pitch of the cholesteric helix: On cooling down, there is a continuous conversion of the cholesteric fan texture to fingerprint texture which is compatible with a decreasing helical pitch. Compunds **5c** and **5d** with n = 8 and 9 present the phenomenon of the inversion of the helical twist sense. On heating, the crystals melt showing a cholesteric oily-streak texture which changes to a typical nematic schlieren texture. This nematic texture changes again giving a cholesteric oily-streak texture. Further investigations on **5c** (for methods see ref. 2) show that it is a right-handed helix at lower temperature which changes to a left-handed one at higher temperatures. For **5c** an inversion temperature of approximately 116.5 °C is found (see fig. 2). This helical inversion may be caused by a temperature-dependent change of the degree of association of the cyano groups.

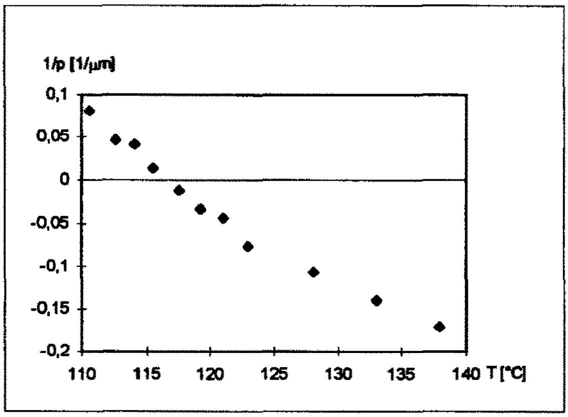
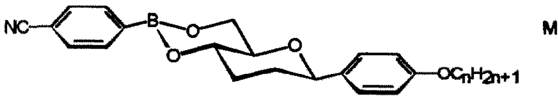


Figure 2: A plot of 1/Pitch Length against Temperature for the Cholesteric Phase of **5c**

The next member of the series, **5e** with n = 10, again exhibits a change in the helical twist, but no inversion is observable, probably because the S_A phase which now occurs diminishes the range of the cholesteric phase. For the long-chain members of the series with n > 9 a polymorphism in the solid state is observable.

The change of the lateral substituents or the change of an atom in the decalin ring leads to completely different properties. If the carbon atom C-3 is replaced by a boron atom (**6**), no change in the cholesteric helix occurs, but a TGB_A phase at the transition of cholesteric and S_A phase exists. In one case with n = 11, a re-entrant cholesteric and a re-entrant TGB_A phase are observable[10], probably caused by temperature-depending association of cyano groups. The substitution of a methoxy group for a cyano group in **5** leads to molecules only exhibiting a cholesteric phase; additional introduction of a boron atom gives structure **7** showing TGB_A, S_A and blue phases for longer chain lengths[11].



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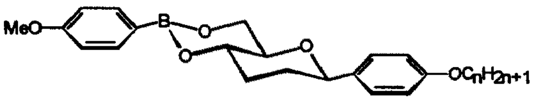

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The observation of TGB and blue phases for these related molecules shows the enormous twisting power of this class of carbohydrate-based compound. Small changes in the structure of this new class of liquid crystals result in a drastic change of physical properties; further investigations are in progress.

Acknowledgement

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8. Temperatures in [°C]; Cr = crystalline, S_A = smectic A phase, N* = cholesteric phase, I = isotropic.
9. Analytical data for 5c: ^{1}H-NMR (400 MHz, CDCl$_3$, TMS): δ = 3.65 (ddd, 1 H, 1-H), 5.60 (s, 1 H, 3-H), 4.33 (dd, 1 H, 5-Heq), 3.79 (dd, 1 H, 5-Hax), 3.58 (ddd, 1 H, 6-H), 4.48 (dd, 1 H, 8-H), 1.85 (m$_c$, 2 H, 9-Hax, 10-Hax), 2.04 (m$_c$, 1 H, 9-Heq), 2.22 (m$_c$, 1 H, 10-Heq), 7.63, 7.68 (d, d, 4 H, 2’-H, 6’-H, 3”-H, 5”-H), 7.40 (d, 2 H, 2”-H, 6”-H), 6.85 (d, 2 H, 3’-H, 5’-H), 3.94 (t, 2 H, α-CH$_2$), 1.75 (m$_c$, 2 H, β-CH$_2$), 1.40 (m$_c$, 2 H, γ-CH$_2$), 1.30 (br. s, 8 H, -CH$_2$-), 0.90 (t, 6 H, CH$_3$); $^3J_{1,6}$ = 8.5, $^3J_{1,10ax}$ = 10.3, $^3J_{5a,5e}$ = 10.2, $^3J_{5a,6}$ = 10.2, $^3J_{5e,6}$ = 5.1, $^3J_{8,9ax}$ = 10.8, $^3J_{8,9eq}$ = 2.0, $^3J_{Aryl}$ = 8.3 Hz; ^{13}C-NMR (100 Mhz, CDCl$_3$, TMS): δ = 73.8 (C-1), 100.2 (C-3), 69.6 (C-5), 78.5 (C-6), 79.8 (C-8), 31.9 (C-9), 33.0 (C-10), 133.6 (C-1’), 142.5 (C-1”), 127.4, 127.2 (C-2’, C-6’, C-2”, C-6”), 114.5 (C-3’, C-5’), 132.2 (C-3”, C-5”), 158.8 (C-4’), 125.2 (C-4”), 112.5 (CN), 68.1 (α-CH$_2$), 29.6, 29.4, 29.3, 29.2, 26.0, 22.7 (-CH$_2$-), 14.1 (CH$_3$); $[\alpha]_D^{20}$ = +33 (c = 0.1, CHCl$_3$); elemental analysis: calcd. for $C_{28}H_{35}O_4N$ (449.6): C 74.79, H 7.86, N 3.12, found C 74.89, H 7.79, N 3.13.
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11. Vill, V.; Tunger, H.-W., unpublished results.

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