Carbohydrate-based Liquid Crystals: New Compounds showing Re-entrant TGB_A and Cholesteric Phases and Dopant-induced TGB_A, S_A and S_{C^*} Phases

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Re-entrant TGB_A and cholesteric phases are observed in a homologous series of pure chiral carbohydrate-based compounds, and contact preparation induces S_A phases between cholesteric and nematic compounds as well as re-entrant and S_{C^*} phases in two substances which in pure form only show cholesteric and S_A phases.

The discovery of the TGB_A (twist grain boundary) phase by Goodby *et al.* in 1989[1] initiated an increasing interest in chiral mesogens and twisted smectic mesophases. The TGB_A phase occurs in most cases at the transition of a cholesteric (Ch) to a smectic A (S_A) phase. At this point the molecules try to form a helical structure with the Ch helix axis perpendicular to the long axes of the molecules, and also try to form a lamellar S_A structure. These two structures are incompatible and cannot coexist, and this results in a lattice of screw dislocations, small blocks of molecules having the S_A structure rotated against each other forming a helical structure.

Ten years earlier, the phenomena of re-entrant nematic[2,3] and Ch[4] phases were published. Hence it should be possible to observe re-entrant TGB_A phases at the Ch–S_A and S_A–Ch phase transitions.

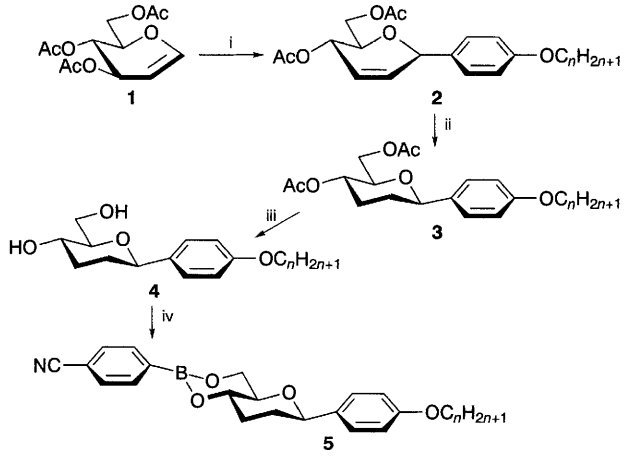
We report here the observation of re-entrant TGB_A and Ch mesophases of pure substances and the induction of smectic phases in a homologous series of carbohydrate-based compounds. To our knowledge, it is the first time that a re-entrant TGB_A phase has been found in a pure compound, and that a smectic C* (S_{C^*}) phase has been induced by mixing mesogens showing only S_A and Ch phases.

The (1*S*,6*R*,8*R*)-8-(4′-alkoxyphenyl)-3-(4″-cyanophenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decanes **5** are available from a four-step synthesis starting with tri-*O*-acetyl-D-glucal[5] (Scheme 1). We synthesized compounds **6–13** with different lateral chain lengths of 1, 6, 8, 9, 10, 11, 12 and 13 C atoms† (Table 1).

The cholesteric phase is observed for compounds **6–10**. Compounds **11–13** show Ch, TGB_A and S_A phases. The Ch phases are observed as a fan-shape texture, the TGB_A phase is represented by its typical filament texture. The S_A phase shows a homeotropic texture. Of special interest is compound **11**, the only one which forms in pure form a re-entrant TGB_A and Ch phase. Cooling down from the isotropic liquid, one observes the following phase order: isotropic, Ch, TGB_A, S_A, TGB_A, Ch, crystalline. Cooling down from the isotropic liquid, the Ch fan texture is formed. On further cooling, the filament texture of the TGB_A phase is formed which changes to the homeotropic S_A texture which looks black under crossed nicols. Cooling down below the melting point, a re-entrant TGB_A phase again forms filaments in the homeotropic S_A texture, changing at 152 °C to the fan texture of a re-entrant Ch mesophase; finally crystallisation occurs. This process is best observed in small drops of the sample owing to the fact that the described phenomenon of re-entrant phases occurs below the melting point of the compound and the observation of the monotropic mesophases is always accompanied by recrystallisation.

It is possible to induce and stabilize the re-entrant TGB_A phases by mixing the described compounds with other cyano derivatives, *e.g.* the contact preparation of **10** (which shows no S_A phase) with decyloxycyanobiphenyl. The mixture exhibits a S_A phase up to 106 °C, and on cooling down to 10 °C a re-entrant TGB_A phase and a re-entrant Ch phase occur.

Contact preparation of **10** also demonstrates the ability of these molecules to form dopant-induced smectic phases. A preparation of **10** (Ch only) and CCH7 [4-(4-heptylcyclohexyl)cyclohexylcyanide], nematic only, forms an S_A phase up to 104.8 °C. In Fig. 1 the CCH7 on the left shows a Ch mesophase because of the contact with the chiral compound **10**, on the right is the Ch phase of **10**. In the middle the homeotropic texture of the induced S_A phase is exhibited. The contact of **10** with (1*S*,3*R*,6*R*,8*R*)-3-(4″-cyanophenyl)-8-(4′-dodecoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane, a derivative of **8** in which the boron atom is replaced by a CH group (itself forming



Scheme 1 Synthetic route to **5**. *Reagents and conditions*: i, phenyl alkyl ether, $SnCl_4$, CH_2Cl_2; ii, H_2, ethanol, ethyl acetate, separation of anomers; iii, NaOMe, MeOH; iv, 4-cyanophenylboronic acid, toluene.

Table 1 Mesogenic properties of compounds **6–13**

Compound	*n*	(recryst.)	Transition temperatures		
6	1	(127) Cr 180.0			Ch 252.5 I
7	6	(84) Cr 143.7			Ch 198.5 I
8	8	(75) Cr 123.4			Ch 182.2 I
9	9	(59) Cr 104.3			Ch 172.5 I
10	10	(62) Cr 104.0			Ch 168.9 I
11	11	(51) Cr 106.0	Ch 52 TGB_A 57	S_A 137.7 TGB_A 138.9	Ch 164.2 I
12	12	(58) Cr 106.8		S_A 147.0 TGB_A 147.4	Ch 161.0 I
13	13	(49) Cr 103.5		S_A 146.3 TGB_A 146.7	Ch 158.6 I

Fig. 1 Contact preparation of CCH7 and **10**, 84 °C, crossed nicols. From left to right: cholesteric phase of CCH7, homeotropic S_A texture, Ch phase of **10**.

a Ch and S_A phase),[6] exhibits interesting behaviour: depending on the concentration of the compounds in the mixing zone, one observes induced re-entrant and S_{C*} phases which do not occur in the pure samples. The S_{C*} phase appears as a grey fan-like texture with lines of the helical pitch in the homeotropic parts of the phase. In parts containing more **10**, re-entrant Ch and TGB_A phases are observed up to 60 °C, represented by the typical filament texture developed from the homeotropic S_A texture, changing to the Ch fan-shape texture. In parts with less **10**, below 35 °C a S_{C*} phase exists.

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Footnote

† All compounds were characterized by ^1H and ^{13}C NMR data, melting behaviour, optical rotation and elemental analysis.

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