

Synthesis and mesogenic properties of enantiopure trioxadecalin derivatives bearing an *n*-alkylphenyl substituent

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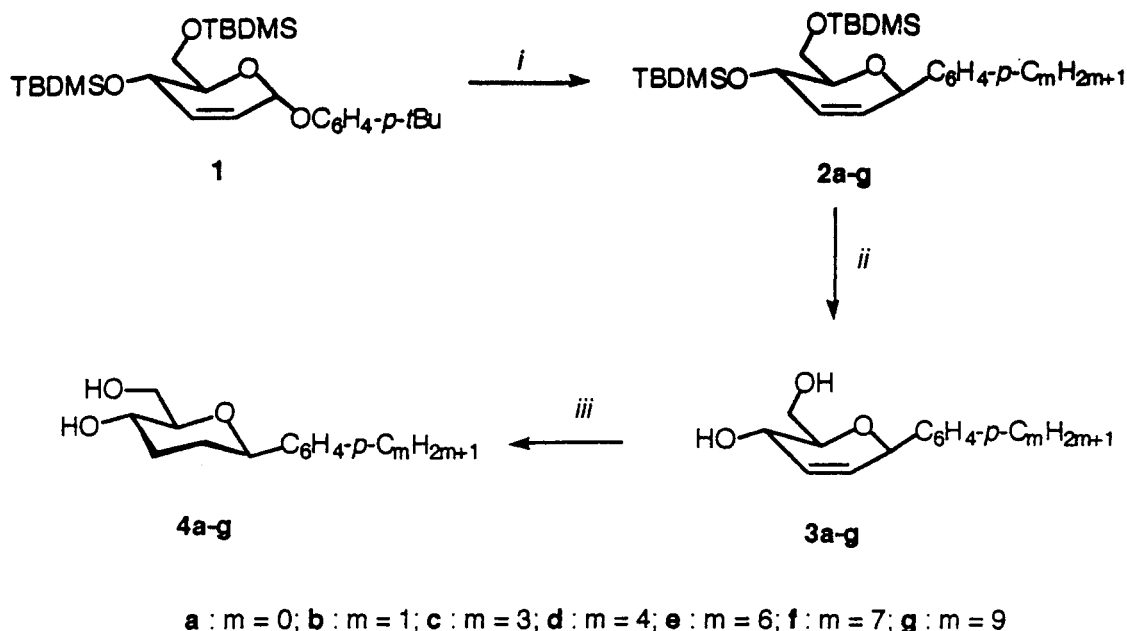
A number of chiral trioxabicyclo[4.4.0]decanes and boratrioxabicyclo[4.4.0]decanes have been prepared. The mesogenic properties of these compounds have been studied. They show short cholesteric pitch, blue phases and TGB_A phases depending on the chain length of the *n*-alkyl substituent, with quite large differences between the trioxa- and the boratrioxaderivatives.

Keywords: mesogenic properties, enantiopure trioxadecalin derivatives

In the course of our work aimed at the study of the mesogenic properties of chiral trioxabicyclo[4.4.0]decanes and boratrioxabicyclo[4.4.0]decanes,^{3,4} a large number of compounds **5–18** bearing a linear alkyl chain were prepared stereospecifically in quite good yields starting from the unsaturated carbohydrate **1** (Scheme 1) *via* the methodology previously described.⁵ The reaction of the Grignard reagents, prepared from various 4-*n*-alkyl-1-bromobenzene, with the unsaturated carbohydrate **1** in the presence of a catalytic amount of NiCl₂(dppe) in tetrahydrofuran at –40 °C gave the corresponding β-*C-n*-alkylphenylglycosides **2b–g** regio- and stereospecifically. The desilylation of compounds **2b–g** using hydrated tetrabutylammonium fluoride, followed by hydrogenation at atmospheric pressure in ethanol in the presence of the catalyst [Rh(COD)(dppb)]ClO₄, afforded the saturated diols **4b–g**.

An acid-catalysed transacetalization reaction of diols **4b–g** with the dimethyl acetal of the corresponding 4-alkoxybenzaldehyde afforded the trioxadecalines **5–11**, while the condensation with the appropriate arylboronic acid gave the boronic acid derivative **12–18** (Scheme 2).

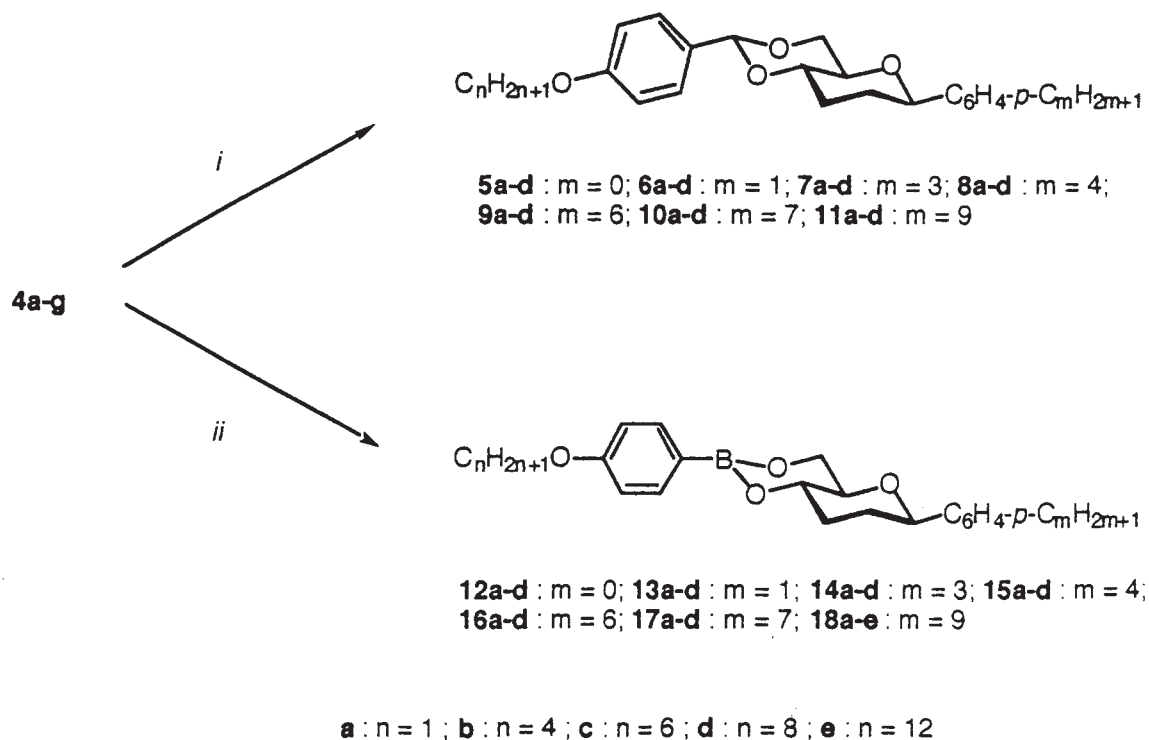
Chiral trioxabicyclo[4.4.0]decanes **5–8** showed only a cholesteric phase, whose pitch length decreased with increasing lateral chain length, however, compound **7d** (*m* = 3, *n* = 8) also exhibited an additional smectic A phase and a TGB_A phase. Compounds **9–11** showed a quite different behaviour, with a cholesteric phase for **9a–b**, **10a–b**, and **11a**, and a smectic A phase for **9c–d**, **10b–d**, and **11b–d**. By comparison with the results reported by Vill *et al.*,³ we noticed that the substitution of an oxygen by a methylene unit decreased notably the clearing temperature of the corresponding compound.



Reagents and conditions: *i* BrMgC₆H₄-*p*-C_{*m*}H_{2*m*+1}, NiCl₂(dppe), THF; *ii* Bu₄NF, THF, 25 °C; *iii* H₂, [Rh(COD)(dppb)]ClO₄, EtOH

Scheme 1

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Scheme 2

Table Mesomorphism of compounds **7a-d** and **14a-d** ($m = 3$)^a

Compound	n	Transition temperatures/°C			
7a	1	C ₁ 162.0	C ₂ 163.0		I
7b	4		C 147.0	N* 151.4	I
7c	6		C 146.8	N* 147.7	I
7d	8		C 135.2 S _A 127.2 TGB _A 128.4	N* 137.6	I
14a	1	C ₁ 117.0	C ₂ 134.0	N* 176.3	BP _{UV}
14b	4		C 114.1 S _A 131.5 TGB _A 133.0	N* 174.8	BP _{UV}
14c	6		C 103.2 S _A 151.5 TGB _A 152.6	N* 163.8	BP _{UV}
14d	8		C 98.3 S _A 154.7	N* 156.1	I

^aC: crystalline phase; S_A: smectic A phase; N*: cholesteric phase; TGB_A: twist grain boundary phase; BP: blue phase; I: isotropic phase.

Chiral boratrioxabicyclo[4.4.0]decane exhibited lower melting temperatures than those of the corresponding trioxadecalin derivatives. Cholesteric phases were generally observed for compounds **12–14**, as well as a blue phase, with an additional smectic phase for **12b–d**, **13d**, and **14b–d**, and a TGB_A phase for compounds **13d** and **14b–c**. Most of the compounds **16–18** showed only a smectic phase, with an additional cholesteric phase and a blue phase for compounds **16a**, **17a** and **18a**.

Techniques used: ¹H and ¹³C NMR (data on all new compounds), optical polarizing microscope

References: 10

Schemes: 2

Table 1: Mesomorphism of compounds **5–11**

Table 2: Mesomorphism of compounds **12–18**

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