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Chu Chuan Dong [a], Peter Styring [a], Lawrence K. M. Chan [a] [b] & John W. Goodby [a]

[a] School of Chemistry, University of Hull, Hull, HU6 7RX, UK

[b] Thorn EMI - CRL, Dawley Road, Hayes, Middlesex, UB3 1HH, UK

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DIFLUOROBIPHENYL DIOXABORINANES FOR FERROELECTRIC LIQUID CRYSTAL APPLICATIONS

CHU CHUAN DONG, PETER STYRING, LAWRENCE K. M. CHAN[§] AND JOHN W. GOODBY
School of Chemistry, University of Hull, Hull HU6 7RX, UK;
[§]Thorn EMI - CRL, Dawley Road, Hayes, Middlesex, UB3 1HH, UK

Abstract Six difluorobiphenyl dioxaborinanes, a new class of heterocyclic mesogen, have been synthesised. Compounds possessing lateral 2,3-difluorination of the end ring possess smectic C and nematic phases for the alkyl-alkoxy homologues. The smectic C phase is replaced by smectic A phase for the dialkyl homologues. While lateral 2,3-difluorination of the middle ring increase the nematic mesophase range, smectic phase stability is suppressed to such an extent that the smectic C phase appears only for longer chain length homologues. Compared to the analogous dioxanes, the transition temperatures of the dioxaborinanes are generally lower. Dioxaborinanes are more nematic in character with difluro substituents in the end phenyl ring, while they are more smectogenic when the difluorinated phenyl ring is in the middle of the core.

INTRODUCTION

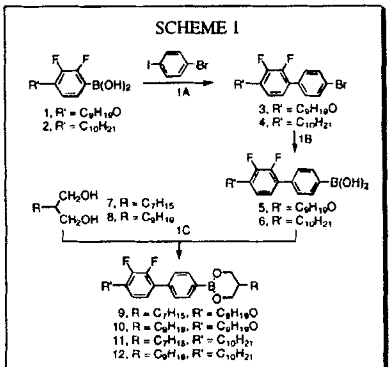
The excellent performance of surface stabilised ferroelectric liquid crystal (SSFLC) devices has attracted many scientists to seek new materials with low birefringences (Δn), low viscosities (η) and negative dielectric anisotropies for the preparation of suitable FLC mixtures. Some saturated alicyclic rings have been used, instead of aromatic rings, to link with a laterally difluorinated phenyl ring to form the mesogenic core structure and so reduce viscosity and birefringence. However, cyclohexane compounds are not conducive to the formation of the smectic C phase.[1] Dioxane compounds have wide smectic C ranges, but the melting points are somewhat high.[2-4] In 1985, Seto et al. reported the synthesis of the first examples of thermotropic liquid crystalline molecules containing a boron atom in the principal structure.[5] A number of different types of 1,3,2-dioxaborinanes have been prepared which are characterised by low nematic-isotropic transition temperatures in comparison with the analogous 1,3-dioxane derivatives.[6]

In order to obtain low temperature mesomorphic compounds, which would be of benefit in the preparation of room temperature FLC mixtures, we have synthesised some difluorobiphenyl dioxaborinanes materials and the results are presented in this paper. Because the boron atom is sp^2 hybridised, and therefore possesses a trigonal planar geometry, the problem of *cis-* and *trans-* isomerism encountered with the 1,3-dioxanes does not arise.

EXPERIMENTAL PROCEDURES

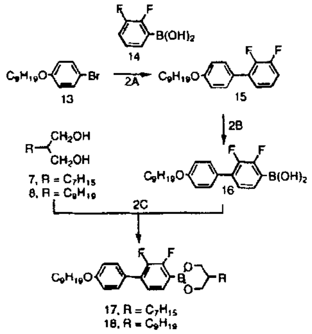
The basic synthetic procedures are illustrated in Schemes 1 and 2. The preparation of compounds 1, 2, 7, 8, 13 and 14 have been reported previously.[4,7] In contrast to the dioxane ring, the dioxaborinane ring structure shows no *cis-* and *trans-* isomerism because the boron atom is sp^2 hybridised. The dioxaborinane ring is a type of boronic ester and will hydrolyse and react with aryl bromide in the cross-coupling reaction with the boronic acid. Therefore, the biphenylboronic acid was prepared prior to dioxaborinane ring closure.

SCHEME 1



1A...... $Pd(PPh_3)_4$, 2M-Na_2CO_3, $CH_3OCH_2CH_2OCH_3$
1B..... (i) n-BuLi, THF; (ii) $B(OPr^i)_3$, THF; (iii) 10% HCl
1C...... Toluene, 4-Me-$C_6H_4SO_3H{\bullet}H_2O$

SCHEME 2



2A.....$Pd(PPh_3)_4$, 2M-Na_2CO_3, $CH_3OCH_2CH_2OCH_3$
2B.... (i) n-BuLi, THF; (ii) $B(OMe)_3$, THF;
(iii) 10% HCl
2C....Toluene, 4-Me-$C_6H_4SO_3H{\bullet}H_2O$

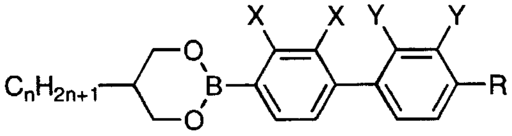
Step 1A was performed by the selective coupling reaction of appropriate 2,3-difluorophenylboronic acids with 4-bromoiodobenzene in the presence of tetrakis (triphenylphosphine)palladium(0)[8] to give the 4'-bromo-2,3-difluorobiphenyls (3 and 4). The iodine site is more reactive than the bromine site and so the reaction can be carried out in a shorter period (*ca.* 5 hr)[9] than step 2A, which needs to be refluxed overnight.[7] The preparation of 2,3-difluorobiphenyl-4'-ylboronic acids (5 and 6) from compounds 3 and 4 (1B) was performed by metallation of the bromine atom to give the lithium salt which is easier than direct lithiation of the 2,3-difluorophenyl ring (2B) and is complete in only half an hour.[10] These salts were then reacted in situ with triisopropyl or trimethyl borate and the resulting boronic esters were hydrolysed with 10% hydrochloric acid to give the desired boronic acids.[11] The final steps (1C and 2D) were the ring closure; a condensation reaction between the aryl boronic acids and appropriate 2-alkylpropane-1,3-diols in the presence of toluene-4-sulfonic acid fitted with a Dean and Stark trap to aid in the azeotropic removal of water.

RESULTS AND DISCUSSION

Table 1 shows the transition temperatures of the mesomorphic 2-difluorophenyl-1,3,2-dioxaborinanes. The alkyl-alkoxy homologues (9 and 10), with the ortho-difluoro unit at the end of the core, i.e., Y = F; X = H, possess smectic C and nematic phases. The nematic phase range is wide for the short chain homologue (9), whereas for a longer terminal chain on the dioxaborinane ring (10) it is the smectic C range which is reasonably wide (ca. 50 °C) The melting point of compound 9 is high which explains the shorter smectic C range in this homologue. The smectic C phase is replaced with a smectic A phase for the dialkyl homologues (11 and 12). The lateral dipole associated with the oxygen in the terminal alkoxy chain reinforces the lateral dipole from the ortho-difluorinated phenyl unit, and this combined with the dipole from dioxaborinane ring supports molecular tilt and is conducive to smectic C phase formation. As with the alkyl-alkoxy analogues, the smectic character is increased in the longer chain homologue (12).

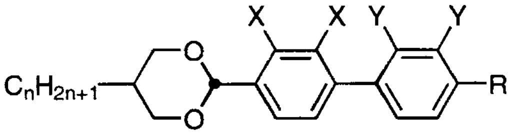
Lateral 2,3-difluorination of the middle ring (17 and 18), i.e. X = F; Y = H, increases the nematic mesophase range and suppresses smectic phases to such an extent that the smectic C phase only appears for the longer chain length homologue.

TABLE 1 Transition temperatures (°C) of the 2-difluorobiphenyl-5-alkyl-1,3,2-dioxaborinanes.



No	n	R	X	Y	K		S_C		S_A		N		Iso
9	7	$C_9H_{19}O$	H	F	•	73	•	81.5	-		•	109.5	•
10	9	$C_9H_{19}O$	H	F	•	56	•	103.5	-		•	111.3	•
11	7	$C_{10}H_{21}$	H	F	•	51	-		•	85.1	•	87.9	•
12	9	$C_{10}H_{21}$	H	F	•	36	-		•		-	88.6	•
17	7	$C_9H_{19}O$	F	H	•	49	-		-		•	113.7	•
18	9	$C_9H_{19}O$	F	H	•	63	•	84.5	-		•	114.3	•

TABLE 2 Transition temperatures (°C) of the 2-difluorobiphenyl-5-alkyl-1,3-dioxanes.



No	n	R	X	Y	Cryst		S_C		S_A		N		Iso
7O9	7	$C_9H_{19}O$	H	F	•	57	•	110.7	-		•	130.5	•
9O9	9	$C_9H_{19}O$	H	F	•	61	•	122.3	-		•	129.7	•
7,10	7	$C_{10}H_{21}$	H	F	•	66	•	69.4	•	105.3	•	109.0	•
9,10	9	$C_{10}H_{21}$	H	F	•	68	•	95.1	•		-	111.1	•
M7O9	7	$C_9H_{19}O$	F	H	•	86	-		-		•	120.4	•
M9O9	9	$C_9H_{19}O$	F	H	•	81	(•	67.1)	-		•	120.7	•

Compared to the analogous dioxane compounds with the same aliphatic chain lengths (Table 2), the transition temperatures of dioxaborinanes are generally lower, with the exception of the melting point of compound 9. It is interesting to note that the smectic C phase stability of compound 18 is higher than that of the analogous dioxane (M9O9) which only shows a monotropic smectic C phase. The smectic C mesomorphic ranges of the dioxaborinanes with the 2,3-difluorophenyl ring in the end of the core are smaller than those of the analogous dioxane materials, however the nematic mesomorphic ranges are generally larger.

It would appear therefore that the dioxaborinanes with the 2,3-difluoropenyl as a terminal ring are more nematogenic in character and less smectogenic, while the homologues with the 2,3-difluoropenyl as a middle ring are more smectogenic in character. Boron, which possesses three electrons in the outer orbitals, is usually sp^2 hybridised with a trigonal planar geometry. When bonded to an aromatic ring, the p-orbital, which is perpendicular to the plane of sp^2 hybrid orbitals, can take part in the p-π conjugated system with the aromatic ring. However, the p-orbital is empty and can accept the π electrons from the aromatic ring and therefore the electron density of the aromatic system is reduced. This leads to a reduction in the electron density of the whole rigid mesogenic core. Consequently, the van der Waal's force or intermolecular attraction is reduced. The lateral cohesive force may also be reduced more than the terminal force, so that a lamellar structure is more difficult to form. On the other hand, the boron extends the ring system, through the p-π conjugation, and therefore enlarges the rigid core. When the difluoro substituents are moved to the middle ring, this increases the width of the core. The length to the width ratio is reduced more for dioxane compounds than those of the analogous dioxaborinanes. Compared to other three-ring core system, the behaviour of difluorobiphenyl dioxanes more closely resembles that of difluorobiphenyl cyclohexanes,[1] while the properties of the difluorobiphenyl dioxaborianes are closer to those of the difluoroterphenyls.[7] This is further proof that the boron joins the conjugated core system and enlarges it. Introduction of a boron atom into the dioxane ring enlarges the conjugated core system and reduces the overall electron density of the conjugated core. This results in a general loss of mesophase stability in the dioxaborinanes, although an enantiotropic smectic C phase is stabilised for the long chain homologue with a fluorinated middle ring.

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