
**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# Comparative studies of three- and four-ring mesogenic esters containing *p*-carborane, bicyclo[2.2.2]octane, cyclohexane, and benzene

Bryan Ringstrand[a]; Jacob Vroman[a]; Dell Jensen[a]; Adam Januszko[a]; Piotr Kaszynski[a]; Jerzy Dziaduszek[a]; Witold Drzewinski[a]
[a] Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, USA

**To cite this Article** Ringstrand, Bryan , Vroman, Jacob , Jensen, Dell , Januszko, Adam , Kaszynski, Piotr , Dziaduszek, Jerzy and Drzewinski, Witold(2005) 'Comparative studies of three- and four-ring mesogenic esters containing *p*-carborane, bicyclo[2.2.2]octane, cyclohexane, and benzene', Liquid Crystals, 32: 8, 1061 — 1070
**To link to this Article: DOI:** 10.1080/02678290500291699
**URL:** http://dx.doi.org/10.1080/02678290500291699

*Liquid Crystals*, Vol. 32, No. 8, August 2005, 1061–1070



# Comparative studies of three- and four-ring mesogenic esters containing *p*-carborane, bicyclo[2.2.2]octane, cyclohexane, and benzene†

BRYAN RINGSTRAND‡, JACOB VROMAN‡, DELL JENSEN‡, ADAM JANUSZKO, PIOTR KASZYNSKI*, JERZY DZIADUSZEK§ and WITOLD DRZEWINSKI

Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

(*Received 25 February 2005; in final form27 June2005; accepted 2 July 2005*)

Twelve esters were prepared from pentyl-substituted *p*-carborane, bicyclo[2.2.2]octane, cyclohexane, and benzene carboxylic acids and three substituted phenols. The mesogenic properties of the series of esters were examined using thermal analysis and optical microscopy. The relationships between structure and mesogenic properties were analysed by comparison of the series of homostructural esters. Thus, the effects of variation of the carboxylic acid structure, introduction of fluorine into the phenol part, and replacement of the central phenyl ring with the $-CH_2CH_2-$ group on the stability of mesophases and their widths were investigated. In general, carborane derivatives exhibit broad nematic phases and narrow SmA phases, while other derivatives demonstrate rich smectic and soft crystal polymorphism.



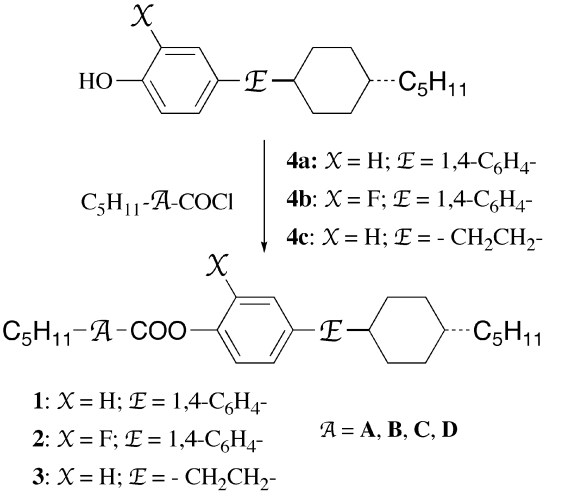
## 1. Introduction

In continuation of our studies on the effect of carborane on mesogenic properties [1–3], we have focused on esters **1**–**3** (see scheme 1). The esters are derived from phenols **4**, whose derivatives were previously investigated as components of nematic [4–6] and ferroelectric materials [7, 8]. Scant patent data [4–6] indicate that derivatives of the three-ring phenols **4a** and **4b** exhibit nematic and smectic phases, and cyclohexanecarboxylates of **4a** show high Sm–N and N–I transition temperatures [4, 5]. In contrast, benzoates of the two-ring phenol **4c**, in which the $-CH_2CH_2-$ linker replaces the central phenyl ring in **4a**, have generally lower clearing temperatures and increased nematogenic behavior [7–9]. There was, however, no systematic investigation of the effect of ring fluorination (**4a**→**4b**) or ring replacement (**4a**→**4c**) on liquid crystalline properties. The better to understand these structural effects on mesogenic behaviour, we now investigate esters of phenols **4** and carboxylic acids derived from *p*-carborane (**A**), bicyclo[2.2.2]octane (**B**), cyclohexane (**C**) and benzene (**D**) rings (figure 1). Here we report the synthesis of phenols **4a**–**4c** and their esters **1**–**3**, and detailed investigations of their mesogenic properties.

## 2. Results and discussion

### 2.1. *Synthesis*

Esters **1**–**3** were synthesized from carboxylic acid chlorides and phenols **4** in the presence of a base, or by refluxing in $CCl_4$ (scheme 1). Crude acid chlorides




Scheme 1.

*Corresponding author.
Email: piotr.kaszynski@vanderbilt.edu

† Presented in part at the 36th GLRM-ACS, Peoria, IL 17–20 Oct, 2004 (Abstract 221) and at the Argonne Undergraduate Symposium, Nov 5th, 2004.

‡Visiting VU from Augustana College, Chemistry Department Rock Island, IL 61201, USA.
§Military Technical University, Warsaw, Poland.

*Liquid Crystals*
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500291699

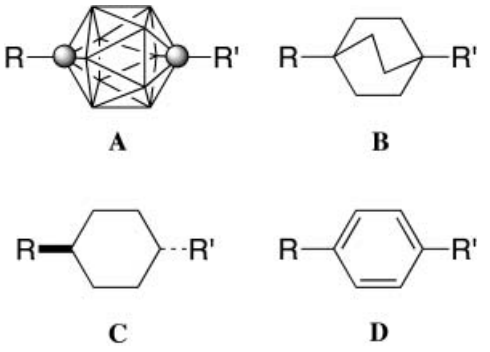



Figure 1. Four ring systems: 1,12-dicarba-*closo*-dodecaborane (*p*-carborane, **A**), bicyclo[2.2.2]octane (**B**), cyclohexane (**C**) and benzene (**D**). In **A** each vertex represents a BH fragment and each sphere is a carbon atom.

were prepared from corresponding carboxylic acids using $SOCl_2$ or $PCl_5$. All acid chlorides were used without further purification other than removing volatiles.

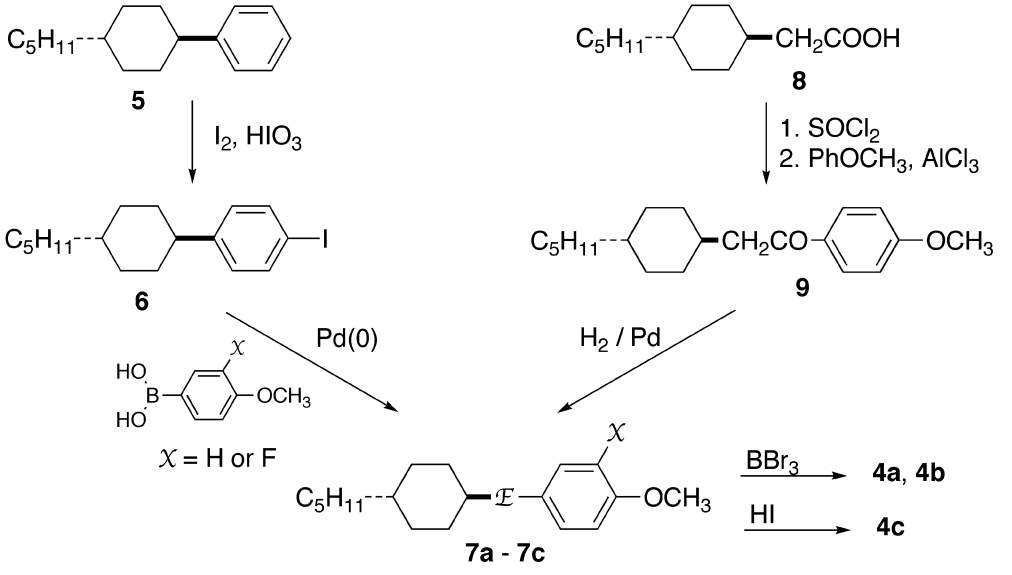
4-Hydroxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**4a**) and 3-fluoro-4-hydroxy-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (**4b**), used in the synthesis of esters **1** and **2**, were prepared from *trans*-4-pentylcyclohexylbenzene (**5**) [10, 11]. Thus, the hydrocarbon **5** was iodinated under general conditions [12] to form the iodo derivative **6**, which was used for a ligandless palladium-catalysed coupling [13] with 4-methoxyphenyl- or 3-fluoro-4-methoxyphenyl-boronic acid. The resulting 4-methoxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**7a**) and 3-fluoro-4-methoxy-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (**7b**) were demethylated with $BBr_3$ to give the corresponding phenols **4a** and **4b**. An alternative preparation of phenol **4a** involves direct coupling of arylboronic acid derived from **5** with *p*-iodophenol [13], or a Grignard reagent derived from **6** with *p*-bromophenol in the presence of a Pd catalyst [14] (scheme 2).

4-[(2-(*trans*-4-Pentylcyclohexyl)ethyl]phenol (**4c**) [7], used in the synthesis of esters **3**, was obtained from *trans*-4-pentylcyclohexanecarboxylic acid following a reported synthetic scheme [9]. Thus, (*trans*-4-pentylcyclohexane)acetic acid (**8**) was converted to the corresponding acid chloride which was used to acylate anisole under modified general Friedel–Crafts conditions [15]. The resulting ketone **9** was catalytically reduced to give 1-(4-methoxyphenyl)-2-(*trans*-4-pentylcyclohexyl)ethane (**7c**). Demethylation with HI (or $BBr_3$ [7]) produced the desired phenol **4c**.

### 2.2. *Mesogenic properties*

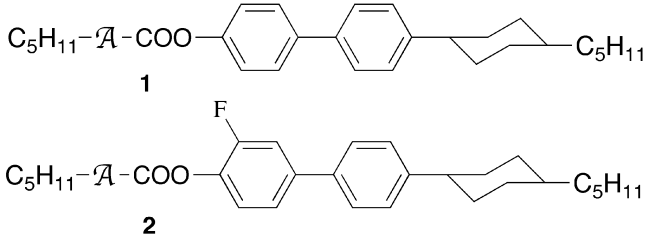
Phase transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC). The phase structures were assigned by analysing microscopic textures seen in polarized light and by comparing them with those reported for reference compounds [16–18]. Results are reported in tables 1 and 2.

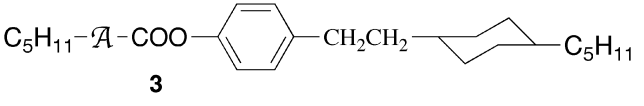
In general, the esters exhibit nematic and smectic polymorphism. The only exception is the carborane derivative **3A**, which has an exclusive nematic phase even when supercooled 50°C below melting. All four-ring esters **1** and **2** show high N–I transition temperatures above 290°C. Exceptionally high clearing temperatures of about 350°C are observed for the bicyclo[2.2.2]octane derivatives **1B** and **2B**. The three-ring esters **3** become isotropic liquids at significantly lower temperatures relative to **1** and **2**.

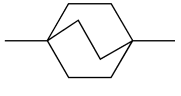
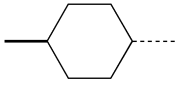
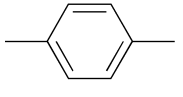



Scheme 2.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for **1**–**3**.[a]

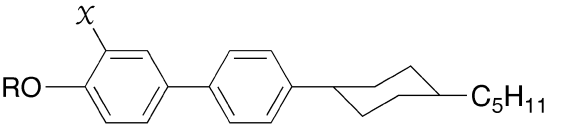



| | A | B | C | D |
|---|---|---|---|---|
| $\mathcal{A}$ |  |  |  |  |
| **1** | $Cr_1$ 111 $Cr_2$ 126 SmA 139 N 304 I<br>(15.6) (7.3) (0.14) ([c]) | $Cr_1$ 76 $Cr_2$ 102 E 142 E′ 228 SmA 256 N 352[b] I<br>(13.4) (16.3) (3.4) (5.6) (0.4) ([c]) | Cr 83 E 131 E′ 233 SmB 236 SmA 266 N 315 I<br>(10.5) (0.2) (~4.5)[d] (~2.1)[d] (0.43) ([c]) | Cr 116 (X 103) E 130 E′ 198 SmC 203 N 312 I<br>(20.2) (6.0) (0.2) (5.0) (0.2) ([c]) |
| **2** | $Cr_1$ 91 $Cr_2$ 114 SmA 122 N 306 I<br>(10.7) (7.1) (0) ([c]) | $Cr_1$ 65 $Cr_2$ 99 E 140 SmB 190 SmA 216 N 350 I[b]<br>(8.9) (15.8) (1.7) (4.5) (0.1) ([c]) | Cr 73 E 119 SmB 198 SmA 237 N 305 I<br>(22.0) (0.8) (5.7) (0.4) ([c]) | Cr 128 (G 101 SmA 108) N 291 I<br>(29.5) (0.1) (0.8) ([c]) |
| **3** | Cr 84 N[e] 139 I<br>(19.4) (1.7) | Cr 66 E 96 SmB 143 N 182 I<br>(5.1) (6.2) (6.9) (2.8) | $Cr_1$ 38 $Cr_2$ 47 (G 37) SmB 145 N 163 I<br>(5.2) (13.3) (7.5) (9.1) (2.5) | Cr 41 G 46 SmB 72 N 147 I<br>(13.3) (6.0) (3.4) (1.8) |

[a]Cr=crystal, X=soft crystal, SmX=smectic, N=nematic, I=isotropic.
[b]Heating rate of 15°C min$^{-1}$ and hermetically sealed pans were used.
[c]Unreliable enthalpy.
[d]Combined entalphy for E′–SmB and SmA–N transitions is 6.6 kJ mol$^{-1}$.
[e]The nematic phase supercools to 33°C before crystallization.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for methoxy and phenol precursors.[a]




| | R | a, $X$=H | b, $X$=F |
|---|---|---|---|
| **4** | H | Cr 206 (SmA 202 N 205) I[b]<br>(33.9) (2.0) (1.3) | Cr 147 N 162 I<br>(30.1) (1.1) |
| **7** | $CH_3$ | $Cr_1$ 66 $Cr_2$ 90 G 103 SmB 109 N 197 I[c]<br>(7.5) (16.1) (1.2) (0.6) (0.8) | Cr 108 SmB 110 SmA 112 N 175 I<br>(19.9) (1.0) (0.37) (0.64) |

[a]Cr=crystal, X=soft crystal, SmX=smectic, N=nematic, I=isotropic.
[b]M.p. 202°C [24]. M.p. 208–210°C [13].
[c]Cr 80 N 165 I [25].

The non-carborane esters **B**, **C**, and **D** exhibit rich polymorphism dominated by orthogonal smectic and soft crystal phases. In general, esters **1** and **2** exhibit smectic A phases, while a SmB phase is common for esters **3B**–**3D**. The exception is **1D**, which exhibits a narrow range SmC phase instead of the SmA phase.

Phase assignment for **1B**–**1D**, which exhibit the richest polymorphism in the series, was particularly difficult, since planar textures could not be obtained. Therefore, the observations were conducted at the edge of the material, and the assignment was based on the established order of phase stability [19], apparent viscosity, enthalpies of transition, and birefringent textures formed by mechanical distortion of the homeotropic textures. Thus, in all three cases the low temperature phases were assigned as E and its modification E′, based on the lack of noticeable changes in the optical texture at the phase transition and high viscosity. The assigned E–E′ phase transition is of low energy for **1C** and **1D** (figures 2 and 3), while for **1B** the enthalpy is significant (3.4 kJ). It is also possible that the very viscous monotropic X phase in **1D** (figure 3) is yet another modification of an E phase, rather than a crystalline polymorph, since the transition is hardly supercooled relative to the melting, and little change is observed in the optical texture. These results are consistent with reports of up to three modifications of the E phase ('E modulated') assigned for 4,4′-dialkylbiphenyls based on calorimetric and roentgenographic studies [20, 21]. Also, the previously reported enthalpies are similar to those observed in this work.

The observed polymorphism and transition temperatures of **1C** are consistent with those reported for its analogues with different terminal alkyl substituents [4]. Compounds with unlike alkyl chains exhibit Sm–N transitions in the range 190–240°C, while **1C** bearing

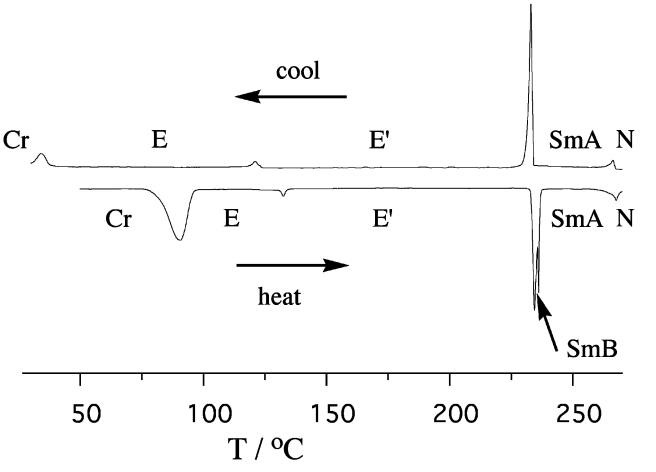



Figure 2. Partial heating and cooling DSC curves for **1C** recorded at a rate of 5°C min$^{-1}$.

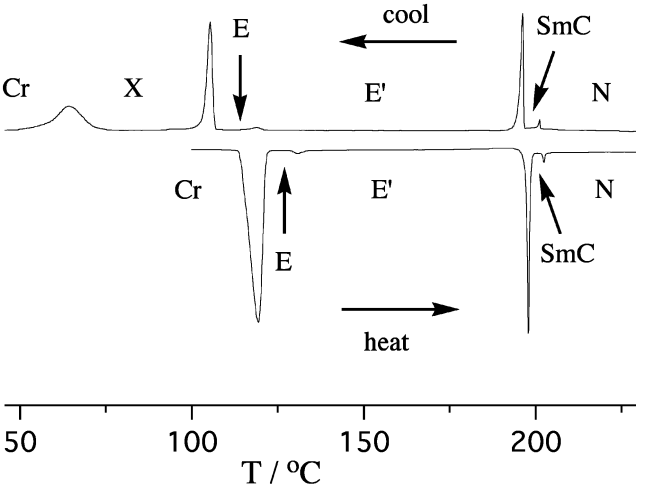



Figure 3. Partial heating and cooling DSC curves for **1D** recorded at a rate of 5°C min$^{-1}$.

two identical chains has the SmA–N transition at 266°C. The clearing temperatures for **1C** and its reported homologues [4] are typically about 310°C.

Detailed insight into the effect of structural changes on mesogenic behaviour is offered by a comparative analysis of the series of compounds shown in figures 4–7. A comparison of clearing temperatures in figure 4 shows that the bicyclo[2.2.2]octane derivatives **B** form significantly more stable nematic phases, by an average of about 45°C, than the benzene derivatives **D**. The nematic phases of cyclohexane esters **C** are moderately more stable than those of series **D** by an average of 11°C. Carborane esters **1A** and **3A** are the only two mesogens exhibiting lower clearing temperatures (by 8°C) than the benzene analogues. Considering the 15°C higher $T_{NI}$ for **2A** than for **2D**, the average stability of the nematic phases in carborane esters is about the same as in the benzene analogues. Interestingly, the plots for bicyclo[2.2.2]octane and carborane derivatives have similar profiles in figure 4, and the latter is shifted down by about 45°C relative to that for bicyclo[2.2.2]octanes **B**.

The fluorination of the phenol generally decreases the clearing temperatures in the carbocyclic esters **2B**–**2D** relative to the $T_{NI}$ for **1B**–**1D** analogues (figure 5). The largest destabilization of the nematic phase, by 21°C, is observed for the pair of benzene derivatives **1D**, **2D**. In contrast, fluorination of the carborane derivative **1A** results in a slight increase of the $T_{NI}$ by 2°C in **2A**. The observed change of $\Delta T_{NI}$ between the two series inversely correlates with the size of ring $\mathcal{A}$, as shown

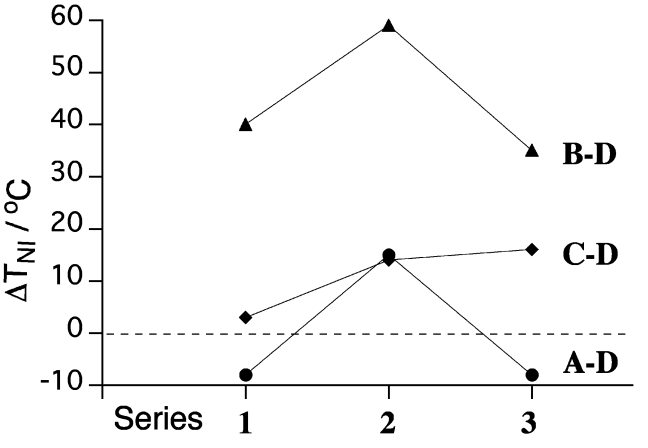



Figure 4. $T_{NI}$ for *p*-carborane (**A**, circles), bicyclo[2.2.2]octane (**B**, triangles) and cyclohexane (**C**, diamonds) derivatives relative to the $T_{NI}$ for the benzene derivatives **D**. The lines are guides for the eye.

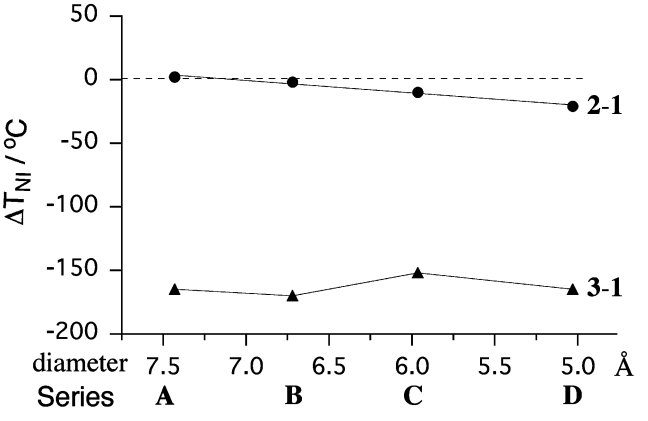



Figure 5. $T_{NI}$ for series **2** (circles) and series **3** (triangles) relative to the $T_{NI}$ for series **1**. The horizontal scale represents a diameter of the van der Waals cylinder formed by ring $\mathcal{A}$ rotating along the substitution axes. The best fit line for the **2**–**1** correlation: $y=9.8x-69$ ($r^2=0.98$). The lines in the **3**–**1** plot are guides for the eye.

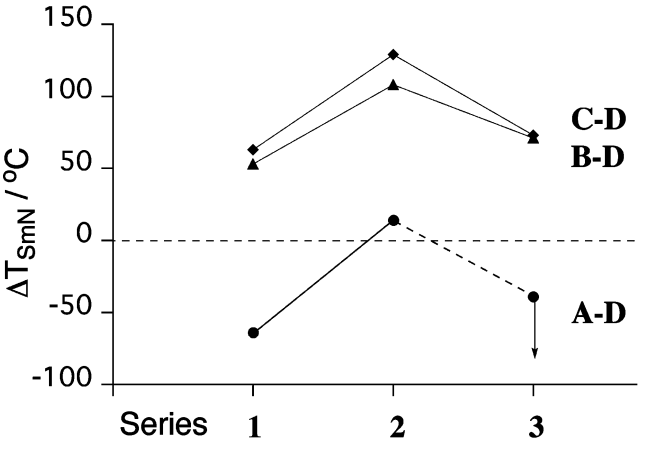



Figure 6. The Sm–N transition temperatures for *p*-carborane (**A**, circles), bicyclo[2.2.2]octane (**B**, triangles) and cyclohexane (**C**, diamonds) derivatives relative to the $T_{SmN}$ for the benzene derivatives **D**. The lines are guides for the eye.

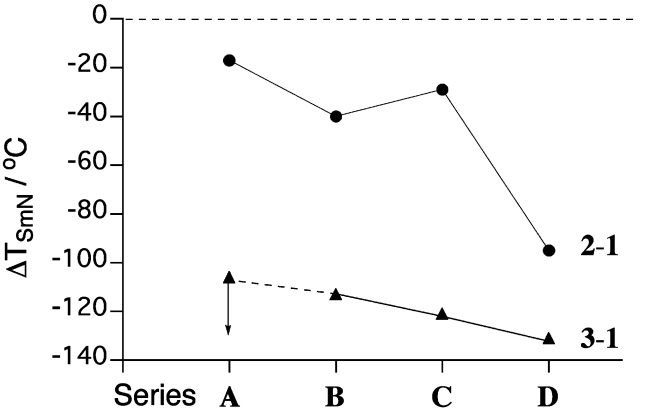



Figure 7. The Sm–N transition temperatures for series **2** (circles) and series **3** (triangles) relative to the $T_{SmN}$ for series **1**. The lines are guides for the eye.

in figure 5. The geometrical parameters for each ring were calculated (HF/6-31G(d)) and corrected for H and C (benzene) van der Waals radii (1.2 Å and 1.7 Å, respectively). Benzene and cyclohexane were treated as ellipsoids and the diameters $d$ represent averages of the two axes $a$ and $b$: **A**: $d$=7.43 Å; **B**: $d$=6.72 Å; **C**: $d$=5.97 Å ($a$=6.70 Å, $b$=5.23 Å); **D**: $d$=5.03 Å ($a$=6.66 Å, $b$=3.40 Å). This is consistent with our results for another series of compounds [22] and provides a quantitative analysis of steric shielding effect [23] of lateral substitution by the adjacent ring. Replacement of the central benzene ring in series **1** with the $-CH_2CH_2-$ link in series **3** results in a relatively uniform decrease in the nematic phase stability by about 160°C.

Trends in stability of the smectic phases in the series **A**–**C**, relative to series **D**, (figure 6) are similar to those observed for the corresponding $T_{NI}$ in figure 4. The smectic phases are significantly more stable in the cyclohexane and bicyclo[2.2.2]octane series, **C** and **B**, relative to the benzoates **D**, while the carborane generally destabilizes the smectic behaviour. Interestingly, the benzene derivative **2D** is the least smectogenic in the fluorinated series **2**, and even the carborane derivative **2A** exhibits a 14°C higher Sm–N transition than **2D**.

Another representation of data for the Sm–N transition shows relatively little impact of fluorination on the stability of the SmA phase in the carborane pair **1A**, **2A** (figure 7). In contrast, the introduction of a fluorine atom destabilizes the SmA phase in the bicyclo[2.2.2]octane and cyclohexane esters by 40°C and 29°C, respectively. The Sm–N transition is significantly suppressed in the benzene derivatives, and the SmA–N transition in **2D** is lower by about 95°C compared to the SmC–N transition in **1D**.

The SmB–N transition in esters **3** is lowered by an average of 120°C compared with the analogous Sm–N transition in series **1**. The datapoint for **3A** indicates the lowest temperature of the nematic supercooled by 50°C until it crystallized. A possible monotropic smectic phase could appear below this temperature. It is also possible that the crystallization at 33°C was induced by the N–Sm transition. However, for practical purposes the replacement of the central phenyl ring with the $-CH_2CH_2-$ link in **3** eliminated the smectic behaviour in the carborane derivatives.

The width of the nematic phase is largest for the carborane derivatives **A** in series **1** and **2** and follows the order **A**>**D**>**B**>**C**. Thus, for **1A** the nematic phase has a 165°C range and expands by 19°C upon introduction of the fluorine atom in **2A**. This expansion of the nematic phase in series **2** relative to **1** is a general phenomenon, and the largest such expansion of 54°C is observed for the **1D**, **2D** pair. The smectic phases are also broadened upon fluorination at the expense of the soft crystal phases in series **B** and **C**. In the pair of carborane derivatives **1A** and **2A** the SmA phase slightly contracts; however, the enantiotropic SmC in the benzene analogues becomes a monotropic SmA. The range of the soft crystal phases in series **1** is largest in **1C** reaching 153°C (figure 2) and smallest in **1D** of 82°C (figure 3). In the fluorinated series **2**, these phases are significantly destabilized by 85°C for **2B** and up to 107°C for **2C**.

On replacement of the central benzene ring in **1** with the $-CH_2CH_2-$ linking group in **3**, the width of the nematic phase is significantly reduced. The largest reduction of 110°C is observed for the carborane derivatives. In contrast, smectic phases are expanded for the non-carborane derivatives **B**, **D**.

Phenols **4** and their precursors, the methoxy derivatives **7**, are typically only mentioned in the literature, and their properties are poorly described. Our detailed investigations revealed rich polymorphism for all except for the two-ring phenol **4c**, and the results are shown in table 2. Thus, we found two monotropic short range phases in phenol **4a**, while only a melting point was previously reported [13, 24]. Upon substitution of **4a** with fluorine, the melting and clearing points of phenol **4b** are significantly lower and the monotropic SmA and N phases are replaced by a broad range enantiotropic nematic phase.

The *O*-methylation of phenol **4a** leads to a lower melting point and the appearance of enantiotropic ordered smectic and soft crystal phases, in addition to a nematic phase, in the methoxy derivative **7a**. This is in sharp contrast to the previous literature report in which no smectic behaviour was observed, and the N–I transition for **7a** was about 30°C lower than that found in this study [25]. This presumably was due to contamination of **7a** with the *cis*-isomer. Introduction of fluorine to the methoxy derivative **7a** lowers the N–I transition by 22°C and increases the melting point of **7b**. The G phase disappears, and a narrow SmA phase appears between the N and SmB phases. The methoxy derivative **7c** exhibits a narrow range enantiotropic nematic phase, which is consistent with previous literature reports [26].

## 3. Summary and conclusions

Our results show that all the esters, except for **3A**, exhibit a rich polymorphism which includes nematic, smectic, and soft crystals phases. Only one ester (**1D**) displays a narrow range tilted smectic phase (SmC), and three other esters (**2D**, **3D**, and **3C**) display the tilted

soft crystal phase G. The nematic phase stability ($T_{NI}$) follows the order: bicyclo[2.2.2]octane>cyclohexane> benzene>carborane (**B**>**C**>**D**>**A**) in series **1** and **3**, while in series **2** the order is **B**>**A**~**C**>**D**. The order for stability of the smectic phase ($T_{SmN}$) follows cyclohexane>bicyclo[2.2.2]octane>benzene>carborane (**C**>**B**>**D**>**A**) for series **1** and **3**.

Substitution of the phenol segment with a fluorine atom least impacted the carborane series; most affected were the benzoates, which experienced the highest reduction in the stability of smectic and nematic phases. The effect of fluorination on the $T_{NI}$ quantitatively correlates with the ring size and shows that the carborane ring acts as an effective shield against molecular broadening by lateral substitution.

Flexibility of the $-CH_2CH_2-$ linking group leads to a uniform and significant lowering of clearing temperatures $T_{NI}$ and reduction of smectic behaviour in series **3** relative to series **1**.

## 4. Experimental

### 4.1. *Materials and characterization*

$^1$H NMR spectra were obtained at 300 or 400 MHz in $CDCl_3$ and referenced to TMS. Elemental analyses were provided by Atlantic Microlab, GA. *p*-Carborane was purchased from Katchem (Czech Republic).

Optical microscopy and phase identification was performed using a PZO 'Biolar' polarizing microscope equipped with a HCS250 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (2–3 mg) and a heating rate of 5°C min$^{-1}$ under a flow of nitrogen gas. The N–I transitions for **1B** and **2B** were recorded in sealed pans using 15°C min$^{-1}$ heating rates.

### 4.2. *Preparation of esters: general procedure*

Method A: A mixture of 12-pentyl-*p*-carborane-1-carboxylic acid [27] (0.20 mmol, 52 mg) and $PCl_5$ (0.20 mmol, 41 mg) in dry benzene (2 ml) was stirred at 40–50°C until all was dissolved. Upon completion of the reaction, solvent and $POCl_3$ were removed under reduced pressure. The crude acid chloride was dissolved in dry $CH_2Cl_2$ (2 ml) and the appropriate phenol **4** (0.15 mmol) and anhydrous pyridine (0.1 ml) were added. The mixture was stirred at room temperature overnight (~18 h), passed through a short silica gel column, and the solvents removed. The solid was dissolved in $CH_2Cl_2$ and passed through a cotton plug to remove particulates. The product was recrystallized repeatedly from hexanes or an ethyl acetate/ethanol mixture until constant transition temperatures were recorded.

Method B: A suspension of 4-pentylbicyclo[2.2.2] octane-1-carboxylic acid (0.20 mmol, 45 mg) or *trans*-4-pentylcyclohexanecarboxylic acid (0.20 mmol, 23 mg) and $SOCl_2$ (2 ml) was stirred at 40–50°C until the acid was completely dissolved. Solvent was removed under reduced pressure. The resulting crude acid chloride (4-pentylbenzoyl chloride was commercially available) was dissolved in dry $CCl_4$ (2 ml) and reacted with phenol (0.15 mmol). The mixture was heated under reflux overnight (~18 h). Upon completion of reaction (monitored by TLC) the product was isolated as described in method A.

**4.2.1. 4′-(*trans*-4-Pentylcyclohexyl)-4-biphenylyl 12-pentyl-*p*-carborane-1-carboxylate (1A).** Microplates (EtOH). $^1$H NMR $\delta$ 0.82–3.25 (m, 10H) 0.82 (t, $J$=7.2 Hz, 3H), 0.87 (t, $J$=7.2 Hz, 3H), 1.00–1.36 (m, 17H), 1.39–1.51 (m, 2H) 1.61 (t, $J$=8.3 Hz, 2H), 1.88 (brt, $J$=12.0 Hz, 4H), 2.47 (tt, $J_1$=12.2 Hz, $J_2$=3.0 Hz, 1H), 7.00 (d, $J$=8.8 Hz, 2H), 7.24 (d, $J$=8.4 Hz, 2H), 7.43 (d, $J$=8.4 Hz, 2H), 7.50 (d, $J$=8.8 Hz, 2H). Anal: calcd for $C_{31}H_{50}B_{10}O_2$, C 66.15, H 8.95; found, C 66.62, H 8.91%.

**4.2.2. 4′-(*trans*-4-Pentylcyclohexyl)-4-biphenylyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (1B).** Plates (EtOH/EtOAc). $^1$H NMR $\delta$ 0.87 (t, $J$=7.2 Hz, 3H), 0.89 (t, $J$=7.2 Hz, 3H) 0.98–1.14 (m, 4H), 1.15–1.36 (m, 15H), 1.39–1.55 (m, 8H), 1.82–1.98 (m, 10H), 2.49 (tt, $J_1$=12.0 Hz, $J_2$=2.8 Hz, 1H), 7.06 (d, $J$=8.6 Hz, 2H), 7.25 (d, $J$=8.2 Hz, 2H), 7.46 (d, $J$=8.2 Hz, 2H), 7.53 (d, $J$=8.6 Hz, 2H). Anal: calcd for $C_{37}H_{52}O_2$, C 84.04, H 9.91; found, C 84.17, H 10.01%.

**4.2.3. 4′-(*trans*-4-Pentylcyclohexyl)-4-biphenylyl *trans*-4-pentylcyclohexanecarboxylate (1C).** Cotton-like crystals (EtOH/EtOAc). $^1$H NMR $\delta$ 0.87 (t, $J$=7.2 Hz, 3H), 0.88 (t, $J$=7.2 Hz, 3H), 0.92–1.12 (m, 4H), 1.15–1.36 (m, 18H), 1.39–1.62 (m, 4H) 1.82–1.95 (m, 6H) 2.13 (brd, $J$=13 Hz, 2H), 2.43–2.57 (m, 2H), 7.09 (d, $J$=8.7 Hz, 2H), 7.25 (d, $J$=8.4 Hz, 2H), 7.46 (d, $J$=8.4 Hz, 2H), 7.54 (d, $J$=8.7 Hz, 2H). Anal: calcd for $C_{35}H_{50}O_2$, C 83.61, H 10.02; found, C 83.29, H 10.11%.

**4.2.4. 4′-(*trans*-4-Pentylcyclohexyl)-4-biphenylyl 4-pentylbenzoate (1D).** Plates (hexane). $^1$H NMR $\delta$ 0.88 (t, $J$=6.8 Hz, 3H), 0.88 (t, $J$=6.8 Hz, 3H), 0.96–1.13 (m, 2H), 1.16–1.37 (m, 13H), 1.42–1.51 (m, 2H), 1.60–1.70 (m, 2H), 1.90 (brt, $J$=12 Hz, 4H), 2.50 (tt, $J_1$=12.3 Hz, $J_2$=2.6 Hz, 1H), 2.69 (t, $J$=7.7 Hz, 2H), 7.23 (d,

$J$=8.7 Hz, 2H), 7.27 (d, $J$=8.8 Hz, 2H), 7.30 (d, $J$=8.1 Hz, 2H), 7.50 (d, $J$=8.4 Hz, 2H), 7.60 (d, $J$=8.7 Hz, 2H), 8.11 (d, $J$=8.1 Hz, 2H). Anal: calcd for $C_{35}H_{44}O_2$, C 84.63, H 8.93; found, C 84.61, H 8.99%.

**4.2.5. 3-Fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-biphenylyl 12-pentyl-*p*-carborane-1-carboxylate (2A).** Microcrystals (EtOH). $^1$H NMR $\delta$ 0.86–3.50 (m, 10H) 0.86 (t, $J$=7.2 Hz, 3H), 0.88 (t, $J$=7.2 Hz, 3H), 0.93–1.36 (m, 16H), 1.37–1.72 (m, 5H), 1.79–1.98 (m, 4H), 2.48 (tt, $J_1$=12.2 Hz, $J_2$=3.2 Hz, 1H), 6.98–7.07 (m, 1H), 7.21–7.34 (m, 4H), 7.41 (d, $J$=8.1 Hz, 2H). Anal: calcd for $C_{31}H_{49}B_{10}FO_2$, C 64.11, H 8.50; found, C 64.40, H 8.54%.

**4.2.6. 3-Fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-biphenylyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (2B).** Needles (EtOH/EtOAc). $^1$H NMR $\delta$ 0.87 (t, $J$=7.1 Hz, 3H), 0.88 (t, $J$=7.1 Hz, 3H) 0.96–1.14 (m, 4H), 1.15–1.36 (m, 15H), 1.37–1.50 (m, 2H), 1.39–1.48 (m, 6H), 1.81–1.98 (m, 10H), 2.48 (tt, $J_1$=10.0 Hz, $J_2$=2.3 Hz, 1H), 7.05–7.12 (m, 1H), 7.23–7.35 (m, 4H), 7.44 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{37}H_{51}FO_2$, C 81.27, H 9.40; found, C 81.25, H 9.45%.

**4.2.7. 3-Fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-biphenylyl *trans*-4-pentylcyclohexanecarboxylate (2C).** Plates (hexane). $^1$H NMR $\delta$ 0.88 (t, $J$=6.8 Hz, 3H), 0.88 (t, $J$=6.8 Hz, 3H), 0.93–1.12 (m, 4H), 1.14–1.38 (m, 19H), 1.34–1.66 (m, 3H), 1.80–1.95 (m, 6H), 2.10–2.21 (m, 2H), 2.51 (tt, $J_1$=12.4 Hz, $J_2$=3.5 Hz, 2H), 7.08–7.16 (m, 1H), 7.26 (d, $J$=8.4 Hz, 2H), 7.27–7.37 (m, 2H), 7.45 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{35}H_{49}FO_2$, C 80.72, H 9.48; found, C 80.82, H 9.47%.

**4.2.8. 3-Fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-biphenylyl 4-pentylbenzoate (2D).** Needles (EtOH/EtOAc). $^1$H NMR $\delta$ 0.89–0.92 (m, 6H), 0.97–1.13 (m, 2H), 1.17–1.42 (m, 14H) 1.43–1.50 (m, 1H), 1.65 (quintet, $J$=7.4 Hz, 2H), 1.90 (brt, $J$=11 Hz, 4H), 2.50 (tt, $J_1$=12.0 Hz, $J_2$=3.0 Hz, 1H), 2.69 (t, $J$=7.7 Hz, 2H), 7.28 (d, $J$=8.1 Hz, 2H), 7.29 (d, $J$=8.1 Hz, 2H), 7.30–7.42 (m, 3H), 7.48 (d, $J$=8.1 Hz, 2H), 8.12 (d, $J$=8.1, 2H). Anal: calcd for $C_{35}H_{43}FO_2$, C 81.67, H 8.42; found, C 81.55, H 8.41%.

**4.2.9. 4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl 12-pentyl-*p*-carborane-1-carboxylate (3A).** Needles (EtOH/EtOAc). $^1$H NMR $\delta$ 0.81–3.22 (m, 10H) 0.81 (t, $J$=7.2 Hz, 3H), 0.85 (t, $J$=7.2 Hz, 3H) 0.74–0.96 (m, 4H), 1.05–1.30 (m, 16H), 1.36–1.48 (m, 2H), 1.55–1.63 (m, 2H), 1.66–1.76 (m, 4H), 2.55 (t, $J$=8.1 Hz, 2H), 6.83 (d, $J$=8.5 Hz, 2H), 7.09 (d, $J$=8.5 Hz, 2H). Anal: calcd for $C_{27}H_{50}B_{10}O_2$, C 63.00, H 9.79; found, C 63.14, H 9.69%.

**4.2.10. 4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (3B).** Plates (EtOH). $^1$H NMR $\delta$ 0.76–0.98 (m, 10H), 1.05–1.35 (m, 18H), 1.36–1.49 (m, 8H), 1.73 (brt, $J$=11 Hz, 4H), 1.87–1.95 (m, 6H), 2.57 (t, $J$=8.0 Hz, 2H), 6.90 (d, $J$=8.4 Hz, 2H), 7.13 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{33}H_{52}O_2$, C 82.44, H 10.90; found, C 82.17, H 10.86%.

**4.2.11. 4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl *trans*-4-pentylcyclohexanecarboxylate (3C).** Microcrystals (EtOH). $^1$H NMR $\delta$ 0.86 (t, $J$=7.2 Hz, 3H), 0.87 (t, $J$=7.2 Hz, 3H), 0.74–1.03 (m, 6H), 1.06–1.36 (m, 19H), 1.40–1.60 (m, 4H), 1.73 (brt, $J$=12 Hz, 2H), 1.85 (brd, $J$=11 Hz, 4H), 2.05–2.15 (m, 2H), 2.43 (tt, $J_1$=12.3 Hz, $J_2$=3.5 Hz, 1H), 2.58 (t, $J$=8.0 Hz, 2H), 6.93 (d, $J$=8.4 Hz, 2H), 7.13 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{31}H_{50}O_2$, C 81.88, H 11.08; found, C 81.82, H 11.07%.

**4.2.12. 4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenyl 4-pentylbenzoate (3D).** Microcrystals (EtOH/EtOAc). $^1$H NMR $\delta$ 0.87 (t, $J$=7.2 Hz, 3H), 0.88 (t, $J$=7.2 Hz, 3H), 0.77–0.99 (m, 4H), 1.08–1.41 (m, 14H), 1.45–1.53 (m, 2H), 1.60–1.83 (m, 6H), 2.62 (t, $J$=7.9 Hz, 2H), 2.68 (t, $J$=7.9 Hz, 2H), 7.07 (d, $J$=8.4 Hz, 2H), 7.20 (d, $J$=8.4 Hz, 2H), 7.29 (d, $J$=8.2 Hz, 2H), 8.09 (d, $J$=8.3 Hz, 2H). Anal: calcd for $C_{31}H_{44}O_2$, C 82.98, H 9.88; found, C 82.70, H 9.95%.

**4.2.13. 4-Hydroxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (4a) [13].** Neat $BBr_3$ (4.8 ml, 50 mmol) was added dropwise (0.5 h) to a stirred solution of the methoxy derivative **7a** (15.1 g, 44.5 mmol) in $CH_2Cl_2$ (150 ml) at −70°C. The mixture was stirred at ambient temperature overnight, poured into ice, and neutralized with $K_2CO_3$. The organic layer was separated and the aqueous layer extracted with $CH_2Cl_2$. The combined extracts were dried ($MgSO_4$), solvent removed, and the crude product crystallized (heptane/toluene or *iso*-octane/toluene) to give 6.9 g (63% yield) of the phenol as colourless needles. $^1$H NMR $\delta$ 0.88 (t, $J$=6.9 Hz, 3H), 0.97–1.14 (m, 2H), 1.18–1.38 (m, 9H), 1.48 (qd, $J_1$=12.7 Hz, $J_2$=3.2 Hz, 2H), 1.89 (brt, $J$=11.4 Hz, 4H), 2.48 (tt, $J_1$=12.1 Hz, $J_2$=3.2 Hz, 1H), 4.9 (brs, 1H), 6.87 (d, $J$=8.7 Hz, 2H), 7.24 (d, $J$=8.1 Hz, 2H), 7.44 (d, $J$=8.2 Hz, 4H). Anal: calcd for $C_{23}H_{30}O$, C 85.66, H 9.38; found, C 85.68, H 9.46%.

**4.2.14. 3-Fluoro-4-hydroxy-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (4b).** The phenol was obtained in 60% yield as described for **4a** in the form of colourless needles (*iso*-octane or EtOH/EtOAc). $^1$H NMR $\delta$ 0.90 (t, $J$=6.9 Hz,

3H), 0.98–1.14 (m, 2H), 1.16–1.37 (m, 9H), 1.47 (qd, $J_1$=12.3 Hz, $J_2$=3.2 Hz, 2H), 1.90 (brt, $J$=11 Hz, 4H), 2.50 (tt, $J_1$=12.0 Hz, $J_2$=3.2 Hz, 1H), 5.11 (d, $J$=3.9 Hz, 1H), 7.04 (t, $J$=8.7 Hz, 1H), 7.23–7.29 (m, 2H) 7.26 (d, $J$=8.4 Hz, 2H), 7.44 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{23}H_{29}FO$, C 81.14, H 8.58; found, C 80.70, H 8.59%.

**4.2.15. 4-[2-(*trans*-4-Pentylcyclohexyl)ethyl]phenol (4c) [7].** A 40% aqueous HI solution (260 g) was slowly added to well stirred and cooled acetic anhydride (850 ml). A solution of crude methoxy derivative **7c** (155 g, 0.399 mol) in acetic acid (250 ml) was then added and the resulting mixture gently refluxed at about 115°C. After about 16 h, the reaction was complete, and the mixture was cooled and poured into water. The product was extracted with $CHCl_3$, the extracts were washed with aqueous $Na_2SO_3$ and water, and dried ($MgSO_4$). The solvent was removed and the crude product crystallized from hexane (500 ml) at −20°C to give 82.0 g (75% yield) of colourless needles, m.p. 103°C (lit. [7] 101–102°C). $^1$H NMR $\delta$ 0.88 (t, $J$=7.2 Hz, 3H), 0.78–1.0 (m, 4H), 1.08–1.38 (m, 10H), 1.40–1.48 (m, 2H), 1.75 (brt, $J$=12 Hz, 4H), 2.54 (t, $J$=8.1 Hz, 2H), 4.7 (s, 1H), 6.74 (d, $J$=8.7 Hz, 2H), 7.04 (d, $J$=8.7 Hz, 2H). Anal: calcd for $C_{19}H_{30}O$, C 83.15, H 11.02; found, C 82.85, H 11.12%.

**4.2.16. 1-Iodo-4-(*trans*-4-pentylcyclohexyl)benzene (6).** A mixture of *trans*-(4-pentylcyclohexyl)benzene [11] (**5**, 229 g, 1.0 mol), iodine (101.6 g, 0.4 mol), iodic acid (35.2 g, 0.2 mol), concentrated sulphuric acid ($d$=1.98, 30 ml), acetic acid (700 ml), water (90 ml), and hexane (50 ml) was stirred under gentle reflux until complete dissolution of iodine crystals (about 2 days). The mixture was cooled and treated with solid sodium sulphite. Water (1 l) was added, and the organic products were extracted with a hexane/benzene mixture (1/l). The extract was washed with water and with sat. $NaHCO_3$, and dried ($MgSO_4$). Solvents were removed and the crude product purified by double recrystallization (acetone/ethanol) to give 227.2 g (64% yield) of **6** as colourless microcrystals, m.p. 47°C. $^1$H NMR $\delta$ 0.89 (t, $J$=6.9 Hz, 3H), 0.95–1.10 (m, 2H), 1.13–1.50 (m, 11H), 1.86 (brd, $J$=11 Hz, 4H), 2.41 (tt, $J_1$=12.3 Hz, $J_2$=3.0 Hz, 1H), 6.96 (d, $J$=8.4 Hz, 2H), 7.59 (d, $J$=8.4 Hz, 2H). Anal: calcd for $C_{17}H_{25}I$, C 57.31, H 7.07; found, C 57.45, H 7.02%.

**4.2.17. 4-Methoxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (7a).** A mixture of iodide **6** (12.8 g, 50 mmol), 4-methoxyphenylboronic acid (7.6 g, 50 mmol), $K_2CO_3$ (20.7 g, 150 mmol), water (80 ml), and acetone (150 ml) was gently refluxed and nitrogen was slowly passed for 20 min. The mixture was cooled, $Pd(AcO)_2$ (20 mg) was added, and the mixture again brought to reflux under an atmosphere of nitrogen. After 6 h, the mixture was cooled, poured into water (0.5 l), and the resulting precipitate filtered off. The crude product was recrystallized (260 ml of THF/EtOH mixture 4/9) to give 15.1 g (89% yield) of white crystals. An analytical sample was obtained as needles by recrystallization from *iso*-octane. $^1$H NMR $\delta$ 0.89 (t, $J$=6.9 Hz, 3H), 0.98–1.15 (m, 2H), 1.17–1.39 (m, 9H), 1.48 (qd, $J_1$=12.5 Hz, $J_2$=3.3 Hz, 2H), 1.90 (brt, $J$=12 Hz, 4H), 2.50 (tt, $J_1$=12.1 Hz, $J_2$=3.2 Hz, 1H), 3.85 (s, 3H), 6.96 (d, $J$=8.8 Hz, 2H), 7.26 (d, $J$=8.3 Hz, 2H), 7.48 (d, $J$=8.2 Hz, 2H), 7.51 (d, $J$=8.8 Hz, 2H). Anal: calcd for $C_{24}H_{32}O$, C 85.66, H 9.58; found, C 85.48, H 9.67%.

**4.2.18. 3-Fluoro-4-methoxy-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (7b).** This was obtained in 88% yield as described for **7a** using iodide **6** and 3-fluoro-4-methoxyphenylboronic acid [28]. $^1$H NMR $\delta$ 0.90 (t, $J$=6.9 Hz, 3H), 0.98–1.15 (m, 2H), 1.17–1.39 (m, 9H), 1.48 (qd, $J_1$=12.5 Hz, $J_2$=3.3 Hz, 2H), 1.90 (brt, $J$=11 Hz, 4H), 2.50 (tt, $J_1$=12.1 Hz, $J_2$=3.2 Hz, 1H), 3.92 (s, 3H), 7.00 (t, $J$=8.8 Hz, 1H), 7.23–7.32 (m, 2H), 7.26 (d, $J$=8.3 Hz, 2H), 7.45 (d, $J$=8.3 Hz, 2H). Anal: calcd for $C_{24}H_{31}FO$, C 81.31, H 8.81; found, C 81.08, H 8.76%.

**4.2.19. 1-(4-Methoxyphenyl)-2-(*trans*-4-pentylcyclohexyl)-ethane (7c).** Ketone **9** (145 g, 0.48 mol) was dissolved in acetic acid (500 ml) and hydrogenated over 10% Pd/C (3 g). After 21.5 l of $H_2$ was consumed and the reaction was complete, the catalyst was filtered off, and the solution poured into water. The crude product was filtered off and without further purification used for demethylation. A small sample was dissolved in hexanes and passed through a silica gel plug. The resulting product was recrystallized from an EtOH/hexane 9/1 mixture at −20°C and subsequently from hexane to give pure product as colourless needles, Cr 31 N 32 I (lit. [26] Cr 31 N 33 I). $^1$H NMR $\delta$ 0.88 (t, $J$=6.8 Hz, 3H), 0.80–1.00 (m, 4H), 1.10–1.36 (m, 10H), 1.42–1.52 (m, 2H), 1.77 (brt, $J$=12 Hz, 4H), 2.56 (t, $J$=8.1 Hz, 2H), 3.79 (s, 3H), 6.82 (d, $J$=8.6 Hz, 2H), 7.10 (d, $J$=8.6 Hz, 2H). Anal: calcd for $C_{20}H_{32}O$, C 83.27, H 11.18; found, C 83.57, H 11.39%.

**4.2.20. 1-(4-Methoxyphenyl)-2-(*trans*-4-pentylcyclohexyl)-ethanone (9).** 4-*trans*-Pentylcyclohexylacetyl chloride

[29] (129 g, 0.56 mol) was added dropwise to a suspension of anhydrous $AlCl_3$ (94 g, 0.7 mol) in $CH_2Cl_2$ (800 ml) at 10–15°C. After 0.5 h, a solution of anisole (60.4 g, 0.56 mol) in $CH_2Cl_2$ (200 ml) was added at 0° over a period of 2 h. The stirring was continued for an additional 2 h and the reaction mixture poured into ice (1 kg). After decomposition of the complex, the organic layer was separated, washed with water, and dried ($MgSO_4$). The solvent was removed and the crude product crystallized (MeOH) to give 148 g (87% yield) of colourless crystals of the ketone (m.p. 58.5–59°C), which was used for the reduction without further purification.

**Acknowledgement**

This project was supported by NSF grant DMR-0111657. Funds for the summer research program for Prof. Jensen and two undergraduate students (B.R. and J.V.) were generously provided by a supplement to the DMR grant.



**References**

[1] A. Januszko, P. Kaszynski, M.D. Wand, K.M. More, S. Pakhomov, M. O'Neill. *J. Mater. Chem.*, **14**, 1544 (2004).
[2] K. Ohta, A. Januszko, P. Kaszynski, T. Nagamine, G. Sasnouski, Y. Endo. *Liq. Cryst.*, **31**, 671 (2004).
[3] W. Piecek, J.M. Kaufman, P. Kaszynski. *Liq. Cryst.*, **30**, 39 (2003).
[4] H. Takatsu, H. Sato. US 4 472 592, Dainippon Ink and Chemical, Inc. (1984).
[5] R. Eidenschink, D. Erdmann, J. Krause, L. Pohl. US 4 330 426, Merck (1981).
[6] E. Poetsch, R. Hittich, E. Bartmann, H. Plach. DE 41 42 519, Merck (1992).
[7] S.M. Kelly, R. Buchecker. *Helv. Chim. Acta*, **71**, 451 (1988).
[8] S.M. Kelly, R. Buchecker. *Helv. Chim. Acta*, **71**, 461 (1988).
[9] N. Carr, G.W. Gray, D.G. McDonnell. *Mol. Cryst. liq. Cryst.*, **97**, 13 (1983).
[10] V.S. Bezborodov, O.N. Bubel, V.A. Konovalov, Y.L. Ptashnikov. *J. org. Chem. USSR*, **19**, 1479 (1983).
[11] T. Szczucinski, R. Dabrowski. *Mol. Cryst. liq. Cryst.*, **88**, 55 (1982).
[12] H.O. Wirth, O. Königstein, W. Kern. *Liebigs Ann. Chem.*, **634**, 84 (1960).
[13] N.A. Bumagin, V.V. Bykov. *Tetrahedron*, **53**, 14437 (1997).
[14] N.A. Bumagin, E.V. Luzikova. *J. organometal. Chem.*, **532**, 271 (1997).
[15] S.M. Kelly, H. Schad. *Mol. Cryst. liq. Cryst.*, **110**, 239 (1984).
[16] I. Dierking. *Textures of Liquid Crystals*. Wiley-VCH, Weinheim (2003).
[17] D. Demus, L. Richter. *Textures of Liquid Crystals,* 2nd Edn, VEB, Leipzig (1980).
[18] G.W. Gray, J.W.G. Goodby. *Smectic Liquid Crystals-Textures and Structures*. Leonard Hill, Philadelphia (1984).
[19] J.W. Goodby. In *Handbook of Liquid Crystals,* Vol. 2A, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 3–22. Wiley-VCH, New York (1998).
[20] K. Czuprynski. *Liq. Cryst.*, **16**, 399 (1994).
[21] K. Czuprynski, J. Przedmojski, J.W. Baran. *Mol. Cryst. liq. Cryst.*, **260**, 435 (1995).
[22] K.L. Glab, A. Januszko, P. Kaszynski, K. Patel, P.-C. Chen, G. Mehl. (In preparation).
[23] K.J. Toyne. In *Thermotropic Liquid Crystals*, G.W. Gray (Ed.), pp. 28–63, Wiley, New York (1987).
[24] See [5]; Also compound # 23599 in LiqCryst 4.3 databse.
[25] R. Eidenschink. *Mol. Cryst. liq. Cryst.*, **94**, 119 (1983).
[26] N. Carr, G.W. Gray. *Mol. Cryst. liq. Cryst.*, **124**, 27 (1985).
[27] A.G. Douglass, K. Czuprynski, M. Mierzwa, P. Kaszynski. *J. mater. Chem.*, **8**, 2391 (1998).
[28] R.J. Jr. Edsall, H.A. Harris, E.S. Manas, R.E. Mewshaw. *Bioorg. Med. Chem.*, **11**, 3457 (2003).
[29] C.A.S. Hill, A. Charlton, A.E. Underhill, K.M.A. Malik, M.B. Hursthouse, A.I. Karaulov, S.N. Oliver, S.V. Kershaw. *J. chem. Soc. Dalton Trans.*, 587 (1995).