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

Structural effects in three-ring mesogenic derivatives of *p*-carborane and their hydrocarbon analogues

Kiminori Ohta[a]; Adam Januszko[b]; Piotr Kaszynski Corresponding author[b]; Takashi Nagamine[a]; Genadz Sasnouski[c]; Yasuyuki Endo[a]
[a] Tohoku Pharmaceutical University, Sendai 981-8558, Japan [b] Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA [c] Institute of Applied Physical Problems, Minsk 220064, Belarus

Online publication date: 25 May 2010

To cite this Article Ohta, Kiminori , Januszko, Adam , Kaszynski Corresponding author, Piotr , Nagamine, Takashi , Sasnouski, Genadz and Endo, Yasuyuki(2004) 'Structural effects in three-ring mesogenic derivatives of *p*-carborane and their hydrocarbon analogues', Liquid Crystals, 31: 5, 671 — 682
To link to this Article: DOI: 10.1080/02678290410001670584
URL: http://dx.doi.org/10.1080/02678290410001670584

LIQUID CRYSTALS, VOL. 31, NO. 5, MAY 2004, 671–682

Structural effects in three-ring mesogenic derivatives of *p*-carborane and their hydrocarbon analogues

KIMINORI OHTA, ADAM JANUSZKO†, PIOTR KASZYNSKI*†, TAKASHI NAGAMINE, GENADZ SASNOUSKI‡ and YASUYUKI ENDO

Tohoku Pharmaceutical University, 4-4-1 Komatsushima, Aoba-ku, Sendai 981-8558, Japan
†Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA
‡Institute of Applied Physical Problems, Minsk 220064, Belarus.

(*Received 3 November 2003; accepted 17 November 2003*)

Several series of structurally related three-ring esters containing benzene, cyclohexane, bicyclo[2.2.2]octane and *p*-carborane rings were synthesized and their mesogenic properties investigated using thermal analysis and optical microscopy. Carborane derivatives show only nematic phases, while the richest smectic polymorphism (up to three phases) was observed in the biphenyl series **D**. The structure–property relationships were studied by comparison of T_{NI} between series. The ring effectiveness in stabilization of nematic phases generally follows the order carborane < benzene ~ cyclohexane < bicyclo[2.2.2]octane. The results indicate that fill fraction plays a significant role in the stabilization of the mesophase. A notable positional effect of the carborane ring on T_{NI} was also observed.

1. Introduction

The geometrical, conformational and electronic features of 12-vertex *p*-carborane (**A**) make it an attractive structural element for liquid crystalline compounds. Our previous investigations [1] of the effect of carborane rings on mesogenic properties focused largely on comparative studies with typical carbocyclic rings among which the bicyclo[2.2.2]octane (**B**) is the closest topological analogue of **A**. Our data for isostructural compounds suggest that the effectiveness of *p*-carborane (**A**) in stabilization of mesophases is generally lower than that of bicyclo[2.2.2]octane (**B**), cyclohexane (**C**) and benzene (**D**) rings (figure 1). This order of ring effectiveness has been attributed to differences in size, conformational, and quadrupolar properties of the rings, which affect packing and lateral intermolecular interactions [2, 3].

In continuation of our structure–property relationship studies of *p*-carborane derivatives, we prepared series of compounds **1**–**8** and investigated their mesogenic behaviour. The effect of the *p*-carborane ring on mesogenic properties was compared with that of bicyclo[2.2.2]octane, cyclohexane, and benzene (series **1**–**4**), or to benzene only (series **5** and **6**). We were interested in the positional effect of the carborane ring, and briefly studied the effect of the chain length on stability of the nematic phase in two isomeric derivatives **8a** and **8b**.

*Author for correspondence;
e-mail: piotr@ctrvax.vanderbilt.edu

2. Results and discussion

2.1. *Synthesis*

Esters **1**–**8** were prepared from appropriate carboxylic acid chlorides and phenols **9** or alcohols in the presence of a base or by heating under reflux in CCl_4 as shown in schemes 1 and 2. The latter method of

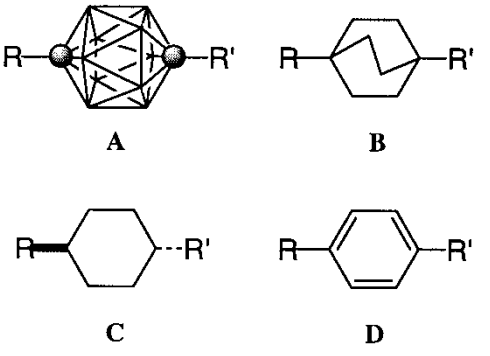
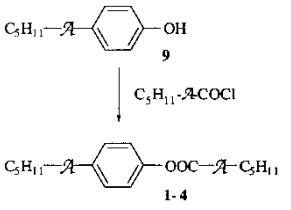


Figure 1. 1,12-Dicarba-*closo*-dodecaborane (*p*-carborane, **A**), bicyclo[2.2.2]octane (**B**), cyclohexane (**C**) and benzene (**D**). In **A** each vertex corresponds to a BH fragment and the sphere represents a carbon atom.

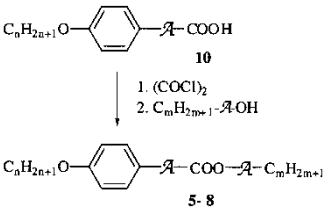
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001670584

esterification by alcoholysis of acid chlorides without base avoids the formation of a ketene intermediate and an isomeric mixture of products (cyclohexane-carbonyl chlorides), or decarbonylation, as observed for bicyclo [2.2.2]octane-1-carbonyl chlorides.

Crude acid chlorides were prepared from the corresponding carboxylic acids using $(COCl)_2$. All acid chlorides were used without further purification. Attempts to obtain ester **7A** were unsuccessful, presumably due to steric reasons.



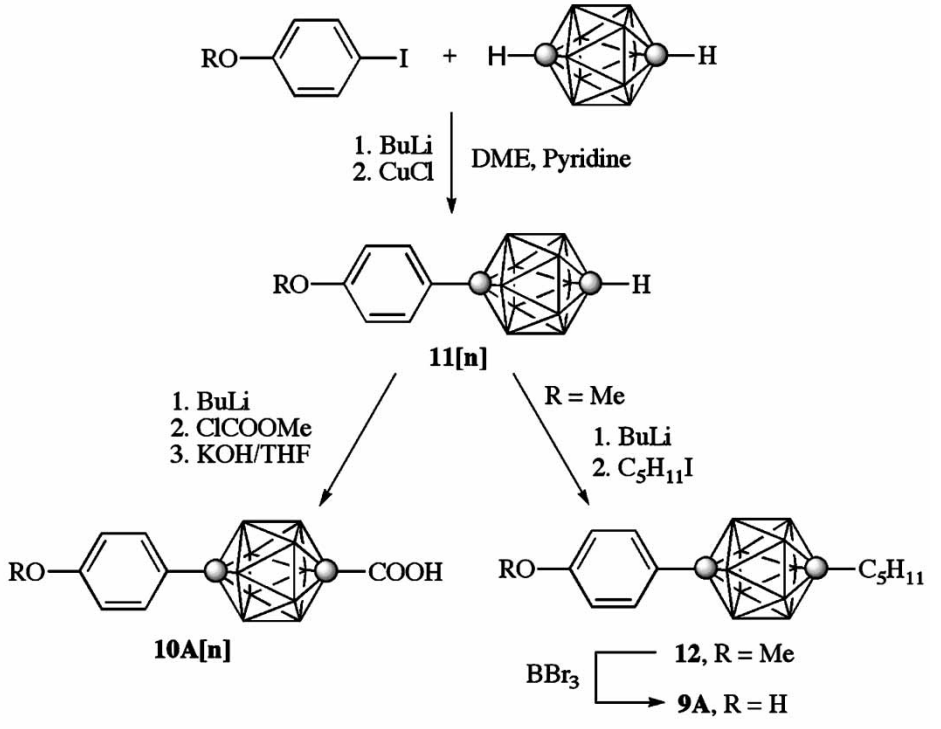
Scheme 1



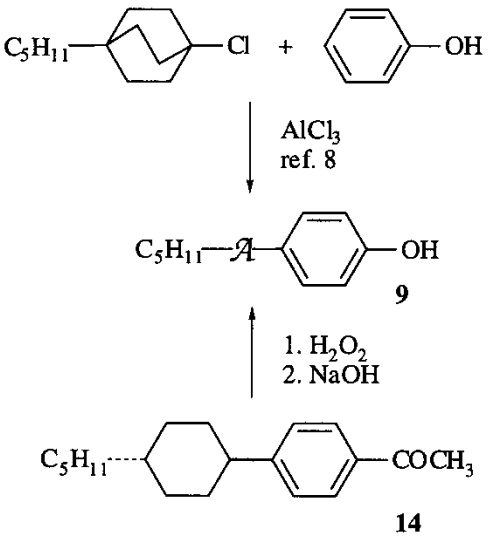
Scheme 2

The carboxylic acids **10A[5]** and **10A[7]**, used in the synthesis of esters **5A**, **6A** and **8**, were prepared by methoxycarbonylation of the corresponding 4-alkoxyphenyl-*p*-carboranes, **11[5]** and **11[7]** [4], respectively, followed by basic hydrolysis of the resulting methyl esters (scheme 3). The monoaryl-*p*-carboranes **11[*n*]** were obtained according to Wade's general procedure for arylation of *p*-carborane [5]. Alternatively, C-arylation of 1-triphenylsilyl-*p*-carborane with 1-heptyloxy-4-iodobenzene followed by removal of the silyl group simplifies the isolation of the pure monoaryl derivative **11[7]** [4].

4-(12-Pentyl-*p*-carboran-1-yl)phenol (**9A**), the precursor to esters **1A**–**4A**, was obtained by demethylation of the methoxy derivative **12** with BBr_3 according to a general method (scheme 3) [6]. The BBr_3 method was found to be significantly more efficient and convenient to use than the pyridine hydrochloride procedure previously reported for a similar reaction [7]. Derivative **12** was easily prepared by alkylation of 1-(4-methoxyphenyl)-*p*-carborane [6] (**11[1]**) but its purification was difficult due to similar polarities and volatilities of the starting material and the product. The pure methoxy derivative **12** was isolated in 75% yield using reverse phase column chromatography. Alternatively, the desired derivative **12** could be prepared by arylation of 1-pentyl-*p*-carborane [4] and conveniently separated from the starting material by distillation/sublimation, but this route was not investigated. The bicyclo[2.2.2]octyl analogue **9B** was obtained according to a literature method (scheme 4) [8]. The phenol **9C** was prepared by Baeyer–Villiger oxidation of 4-(*E*-4-pentylcyclohexyl)



Scheme 3



Scheme 4

acetophenone (**14**) followed by basic hydrolysis (scheme 4) [9].

2.2. *Mesogenic properties*

Transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC). The phase structures were assigned by comparison of microscopic textures observed in polarized light with those published for reference compounds [10, 11]. All results for mesogenic compounds are shown in tables 1–3.

Generally, all carborane derivatives exhibit only nematic phases with clearing temperatures (T_{NI}) above 90°C. The two carboxylic acids **10A**, intermediates for esters **5A**, **6A** and **8**, show no mesogenic behaviour. A monotropic nematic phase was found for the methoxyphenyl derivative **12** at 31°C using the microdroplet method. The observed N–I transition is about 40°C below that reported for the bicyclo[2.2.2] octane analogue (Cr 64 N 70 I) [12]. Several of the carborane derivatives exhibit solid phase polymorphism in virgin samples obtained from crystallization, and observable on first heating. Particularly noteworthy is ester **8b**, which has two crystal-to-crystal transitions before melting to a nematic phase at 60°C. Upon cooling, another crystalline polymorph is formed. This new crystalline modification melts into a nematic phase at 39°C, which is 13°C below the lowest Cr–Cr transition in the virgin sample. The enthalpy of this new transition is 15.4 kJ mol^{-1}, which represents approximately half of the combined enthalpies for all Cr–Cr and Cr–N transitions in the virgin sample.

The most stable nematic phase in the four series in table 1 is formed by **3B** (T_{NI} = 262°C), which has an isolated phenyl ring in the centre of the molecule. All-aromatic ester **1D** forms a nematic phase with a significantly lower clearing temperature by about 90°C, despite the presence of a seemingly more favourable 'continuous π system' [13]. This suggests that steric factors and molecular rigidity play an important role in stabilization of the mesophase.

In contrast to series **A** and **4**, a number of compounds in series **B**–**D** exhibit smectic phases in addition to relatively broad range nematic phases. All enantiotropic smectic phases displayed by mesogens in series **1**–**7** are orthogonal. Only two tilted phases were found in compound **1D**, which forms a monotropic smectic C followed by a G phase.

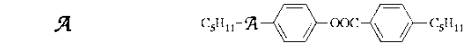
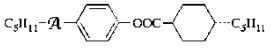
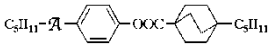
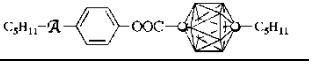
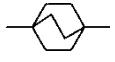
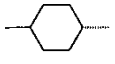
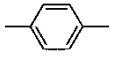
All 4′-pentyl-4-biphenyl esters **1D**–**3D** revealed a rich smectic polymorphism shown in figure 2 for **2D** and in figure 3 for **1D**. Two new derivatives **2D** and **3D** exhibit enantiotropic orthogonal phases SmA and SmB, in addition to a smectic E phase present in **2D**. Our results for **1D** confirm the earlier report of an enantiotropic nematic phase [14, 15], and revealed three narrow temperature range monotropic smectic phases below 84°C (figure 3). In the series **5D**–**7D**, smectogenic properties diminish from two smectic polymorphs formed by **5D** to only nematic behaviour observed for **7D**.

The smectic phases displayed by the bicyclo[2.2.2] octane and cyclohexane derivatives (series **B** and **C**) are highly ordered E phases with the exception of **1C**, which exhibits a monotropic B phase. The E phases exist in a broad temperature range of over 70°C, reaching the broadest range (140°C) for **2B**. DSC and microscopic studies of **2C** and **3C** revealed another highly ordered monotropic phase below the E phase, presumably K or H. In addition, the clearing temperature for **2C** was found to be higher than that in the literature [16], which suggests that the reported ester was contaminated with the *cis*-isomer.

Generally, the order of clearing temperatures within series **1**–**4** is bicyclo[2.2.2]octane > cyclohexane > benzene > carborane (**B** > **C** > **D** > **A**). The simplest illustration of this trend is a comparison of mesogens with two identical rings in table 1. The bicyclo[2.2.2]octane derivative **3B** has a clearing temperature of about 75°C higher than that of the cyclohexyl ester **2C**, which, in turn, has a higher T_{NI} than **1D** or **4A** by about 10°C.

Deeper insight into structure–property relationships is offered by analysis of series of mesogens. A graphical comparison of T_{NI} relative to the biphenyl series **D** in figure 4 shows that replacement of the benzene ring in biphenyl by a bicyclo[2.2.2]octane ring (**B**) increases the clearing temperature by over 40°C in each series **1**–**4**. The same substitution with carboranes (**A**) decreases

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for series **1**–**4**. Cr = crystal, S = smectic, N = nematic, I = isotropic.

		1	**2**	**3**	**4**
	$\mathcal{A}$				
A		Cr_1 79 Cr_2 88 N 158 I (0.1) (29.8) (1.3)	Cr 101 N 174 I (25.7) (1.2)	Cr_1 130 Cr_2 157 N 208 I (1.3) (16.7) (1.7)	Cr_1 177 (N 179) I (19.7) (1.0)
B		Cr 119 N 218 I (27.4) (1.5)	Cr 59 S_E 199 N 227 I (7.4) (9.5) (1.6)	Cr_1 97 Cr_2 159 S_E 231 N 262 I (9.1) (5.4) (8.5) (1.3)	Cr_1 144 Cr_2 161 N 211 I (11.7) (15.1) (1.1)
C		Cr_1 67 Cr_2 76 Cr_3 89 (S_B 73) N 174 I (5.6) (1.5) (3.6) (23.1) (1.6)	Cr 40 (S_X 30)[b] S_E 157 N 188 I[a] (6.6) (24.6) (8.7) (1.4)	Cr_1 43 Cr_2 72 (S_X 57)[b] S_E 176 N 219 I (15.2) (3.1) (10.4) (8.0) (1.9)	Cr_1 75 N 169 I (24.2) (1.2)
D		Cr 98 (S_G 81 S_C 82 S_A 84) N 175 I[c] (26.5) (0.3) (1.0) (1.8) (1.3)	Cr 44 S_E 61 S_B 138 S_A 153 N 188 I (31.7) (1.1) (4.4) (0.8) (1.6)	Cr 85 S_B 125 S_A 141 N 218 I (26.3) (2.8) (0.1) (1.1)	Cr_1 61 Cr_2 67 N 159 I (0.7) (21.2) (1.0)

[a]Reported Cr 112 N 179 I [16].
[b]The phase is either H or K.
[c]Reported Cr 97 N 172 I [14].

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for series **5**–**7**. Cr = crystal, N = nematic, I = isotropic.

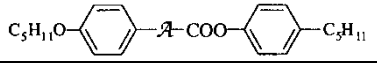
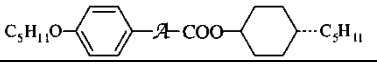
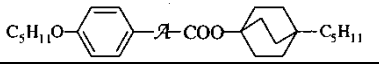
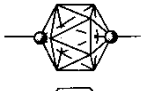
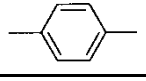
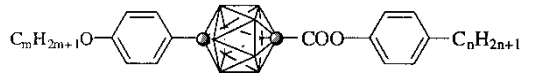
		5	**6**	**7**
	$\mathcal{A}$			
A		Cr 60 N 117 I (29.6) (1.7)	Cr 89 N 125 I (37.5) (1.4)	na
D		Cr_1 104 (S_B 98) S_A 188 N 203 I (2.1) (23.7) (2.2) (1.3)	Cr_1 48 Cr_2 89 S_A 123 N 174 I (10.1) (21.2) (0.3) (1.7)	Cr_1 74 Cr_2 115 N 225 I (13.2) (20.7) (1.5)

Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for esters **8**. Cr = crystal, N = nematic, I = isotropic.



Compound	*m*	*n*	Cr		N		I
8a	5	7	•	41 (31.7)	•	96 (1.7)	•
8b	7	5	•	60[a] (3.3)[a]	•	104 (1.7)	•

[a]Additional Cr-Cr transitions were observed at 52 (21.1 kJ/mol) and 55°C (4.7 kJ/mol). The combined enthalpy of melting is 29.1 kJ/mol.

the T_{NI} by about 15°C, while substitution with a cyclohexane ring (**C**) has practically no effect on the clearing temperature. These structural effects are very similar in series **1**–**3** but the nematic phase in series **4** gains additional stabilization of about +10°C in series **B** and **C** and a surprising +30°C in series **A** relative to the biphenyl series **D**.

The trends revealed in figure 4 suggest that the increasing volume of the rings increases the stability of the nematic phase. The most dramatic increase is observed when a benzene ring is replaced with a second carborane ring in **4A**; this is consistent with significant stabilization of the mesophase in bi-*p*-carborane derivatives relative to biphenyl analogs [3, 17]. This presumably results from a higher fill fraction, defined as the ratio of the van der Waals volume to the volume of a cylinder inscribed on the molecule, and hence higher stability of the nematic phase in accordance with the generalized Van der Waals theory of the nematic state [18].

Another presentation of the data in table 1, shown in figure 5, is consistent with the notion that a high fill fraction is important for stability of a nematic phase. Substitution of a cyclohexane ring for benzene in series **1** increases the stability of the nematic phase by an average of 13°C in series **2**, and in the bicyclo[2.2.2] octane derivatives **3** the T_{NI} is higher by about 45°C than that in **1** (figure 5). Series **4** shows a more complex relationship to the benzoate series **1**.

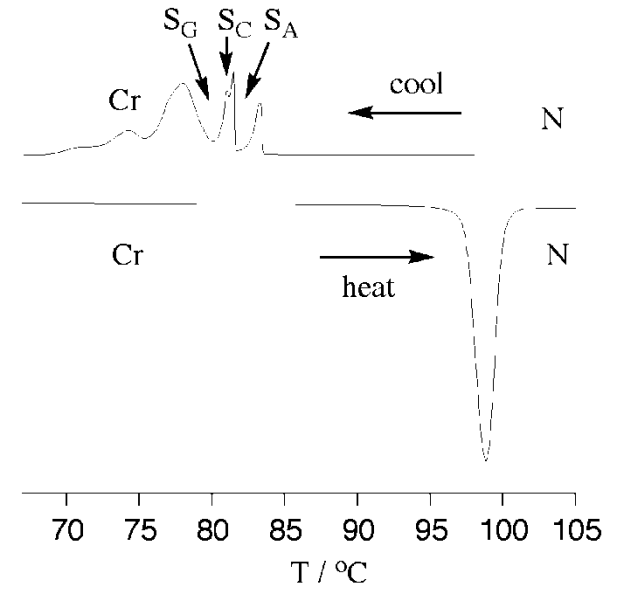


Figure 3. Partial heating and cooling DSC curves for **1D** recorded at a rate of 5°C min^{-1}.

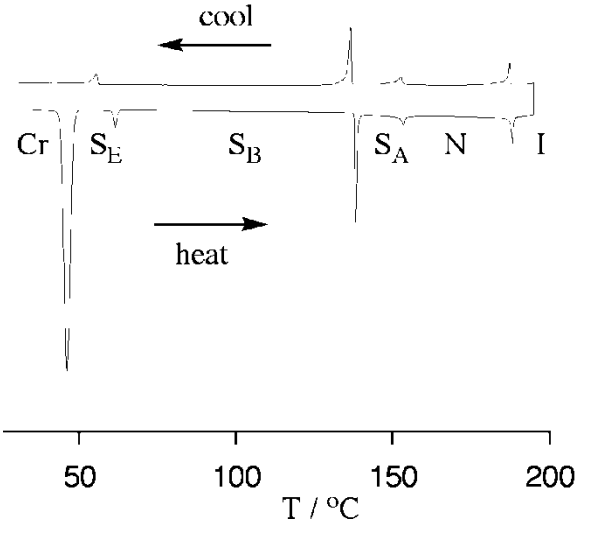


Figure 2. Heating and cooling DSC curves for **2D** recorded at a rate of 5°C min^{-1}.

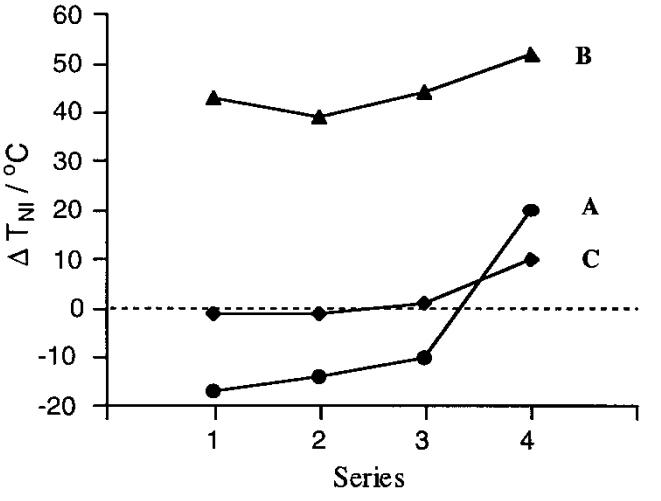


Figure 4. T_{NI} values for *p*-carborane (**A**, circles), bicyclo [2.2.2]octane (**B**, triangles), and cyclohexane (**C**, diamonds) derivatives relative to the T_{NI} for the benzene derivatives **D**. The lines are to guide the eye.

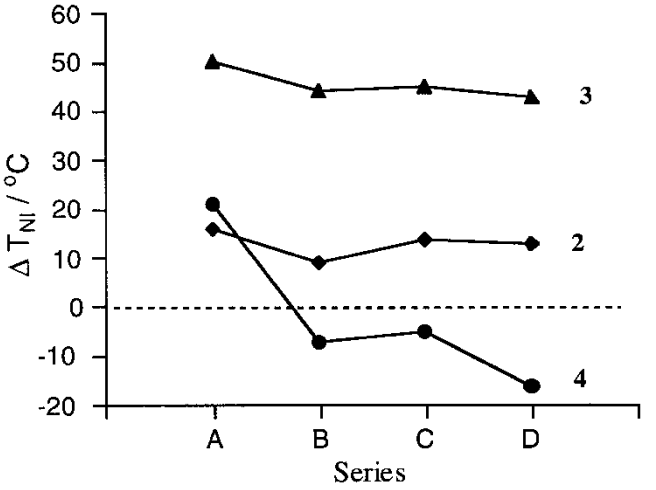


Figure 5. T_{NI} values for series **2** (diamonds), **3** (triangles) and **4** (circles) relative to the T_{NI} for series **1**. The lines are to guide the eye.

A combination of carborane (**A**) ring with two aliphatic rings in **4B** and **4C** shows a moderate decrease in the T_{NI} of about 5°C relative to the benzoate series **1**. In contrast, a combination of the bulky carborane with a benzene ring in **4D** has an unfavorable effect on T_{NI}, while the presence of two carborane rings provides significant additional stabilization of the nematic phase in **4A** by about +20°C relative to **1A**. This, again, can be related to the density of molecular packing in the nematic phase. The trends shown in figures 4 and 5 are similar to those recently found in another series of three-ring compounds [19].

The data in table 1 allow the analysis of ring position effect on mesogenic properties in isomeric pairs. For example, the interchange of the carborane and benzene rings in **1A** changes the clearing temperature for **4D** insignificantly, but markedly affects the melting point. Similarly small effects on T_{NI} are found for pairs with interchanged bicyclo[2.2.2]octane and benzene rings (**1B** and **3D**) or bicyclo[2.2.2]octane and carborane rings (**3A** and **4B**). In contrast, interchanging the cyclohexane ring with other rings has a significant effect on the T_{NI}, with the largest difference of 14°C found for the cyclohexane–benzene exchange in the **2D**–**1C** pair. Generally, the cyclohexanecarboxylate esters **2** appear to form more stable nematic phases than the analogous cyclohexylphenol esters in series **C**. These findings are contrary to expectations based on the difference in thermodynamic stability of the cyclohexane diaxial conformers in esters **2** and **C**† or the difference in barriers to the rotation around the (O=C)-ring bond.‡ Thus, it appears that more stable nematic phases are found in more conformationally flexible molecules.

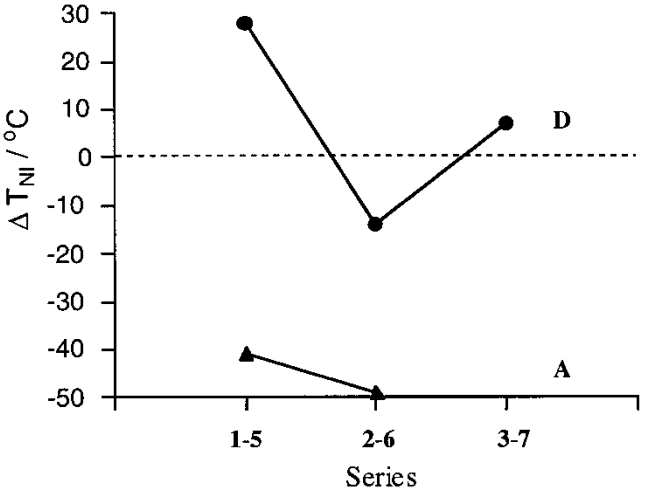


Figure 6. The difference between the T_{NI} for the esters **1**–**4** and **5**–**7** for *p*-carborane (**A**, triangles), and benzene (**D**, circles) derivatives. The lines are to guide the eye.

A comparison of two series of carborane derivatives in table 1 (**1A**–**3A**) and table 2 (**5A** and **6A**) provides an opportunity to analyse the effect of other structural changes on the stability of the nematic phase. Thus, moving the carborane ring from the terminal (**1A**–**4A**) to an internal (**5A** and **6A**) position in the rigid core, changing the orientation of the COO group and adding an oxygen linking group, results in lower clearing temperatures by over 40°C (figure 6). In contrast, the average change in the T_{NI} in the analogous pairs in the **D** series, which are different only by the orientation of the COO group and the presence of the oxygen atom, is +7°C. The result for series **D** is consistent with general trends observed among calamitic liquid crystals [15]. Analysis of literature data shows that there is little difference in clearing temperatures between **1D** and its isomer with different orientation of –COO– group [21]. The T_{NI} for the analogous isomer of **2D** is lowered by 36°C [22] and for **3D** by 16°C [12]. In contrast, the use of oxygen to connect the alkyl chain to the ring generally results in higher clearing temperatures, and for the series **5D**–**7D** the T_{NI} increases by about 25°C. Thus the observed significantly lower T_{NI} for **5A** and **6A** relative to **1A** and **2A**, suggests a rather dramatic

†The estimated free energy of the diaxial conformer of **1C** is about 1.5 kcal mol^{-1} higher than that for its isomer **2D**. Based on tabularized A values for monosubstituted cyclohexanes [20].

‡The difference in $\Delta G^{\ddagger}$ for rotation around the ring–(COOH) and ring–Ph bonds has negative correlation with the ΔT_{NI} for isomeric pairs (slope −0.30, $r=0.93$). The energies were obtained at the MP2/6-31G* level of theory with B3LYP/6-31G* thermodynamic corrections.

positional effect of the bulky carborane ring on the mesogenic properties.

Finally, the pair of isomeric compounds **8a** and **8b** in table 3 shows a chain length effect on the clearing temperature. The addition of two methylene units to one of the alkyl chains in **5A** results in the lowering of the clearing temperature by 13°C (**8a**) or 21°C (**8b**), a difference in the T_{NI} between the two isomers of 8°C. This is consistent with general trends in homologous series [15]. For example, the differences in T_{NI} between isomeric 4-alkyl and 4-alkoxyphenyl 4-alkylbicyclo [2.2.2]octane-1-carboxylates are within 10°C, and for the C_7–C_5 pairs the differences are about 3°C [23].

3. Conclusions

The general order of ring effect on the nematic phase stability is bicyclo[2.2.2]octane > cyclohexane > benzene > carborane, which is consistent with other studies. Fill fraction and hence density of packing in the nematic phase plays an important role and is presumably responsible for the significant stabilization in two-carborane ring mesogen **4A** relative to **1A**. As expected, a carborane ring performs significantly better as a terminal group than as an internal element of the molecular rigid core.

4. Experimental

4.1. *Materials and characterization*

^{1}H NMR spectra were obtained at either 300 or 270 MHz in $CDCl_3$ and referenced to TMS. Elemental analysis was provided by Atlantic Microlab, GA or Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. *p*-Carborane was purchased from Katchem (Prague, Czech Republic). 12-Pentyl-*p*-carborane-1-carboxylic acid was prepared as described earlier [24]. Other chemicals were purchased from Aldrich, Tokyo Kasei Ltd, or received as gifts.

Optical microscopy and phase identification were performed using a PZO 'Biolar' polarizing microscope equipped with an 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 N_2. For DSC and microscopic analyses, each compound was additionally purified by dissolving in CH_2Cl_2, filtering to remove particles, evaporating and recrystallizing from hexanes or a toluene/heptane mixture. The resulting crystals were dried in vacuum overnight at ambient temperature.

4.2. *Preparation of esters: general procedures*

Method A. A carboxylic acid (0.5 mmol) was dissolved in CH_2Cl_2 (2 ml) and treated with oxalyl chloride (5.0 mmol) and a catalytic amount of DMF at room temperature for 2 h. Solvents were removed under reduced pressure and the oily residue of crude acid chloride was dissolved in pyridine (2 ml). Phenol or alcohol (0.6 mmol, 1.2 equiv.) and a catalytic amount of DMAP were added to the acid chloride solution. The mixture was stirred for 12 h at r.t., 10% aq. HCl was added, and the mixture was extracted with AcOEt. The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The pure product was isolated by column chromatography (SiO_2, AcOEt/hexane). The product was recrystallized from hexane or *iso*-octane until a constant melting temperature was achieved.

Method B. Crude acid chloride, prepared from carboxylic acid and PCl_5, was dissolved in dry CCl_4 (2 ml), phenol (1.0 mmol) was added and the mixture was heated under reflux overnight. Upon cooling, the mixture was passed through a silica gel plug, washed with CH_2Cl_2, and the eluant evaporated. The resulting crude product was purified as described in method A.

4.3. *The individual esters*

4.3.1. *4-(12-Pentyl-p-carboran-1-yl)phenyl 4-pentylbenzoate (**1A**)*

Obtained as colourless leaflets (hexane) using method A: ^{1}H NMR δ 0.84 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H), 1.09–1.35 (m, 12H), 1.50–3.60 (brm, 10H), 1.64 (quint, J = 7.5 Hz, 2H), 2.68 (t, J = 7.7 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H). Anal: calcd. for $C_{25}H_{40}B_{10}O_2$, C 62.47, H 8.39; found C 62.23, H 8.77%.

4.3.2. *4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl 4-pentylbenzoate (**1B**)*

^{1}H NMR δ 0.89 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 6.9 Hz, 3H), 1.08–1.17 (m, 2H), 1.21–1.25 (m, 4H), 1.28–1.38 (m, 6H), 1.46–1.51 (m, 6H), 1.65 (quint, J = 7.5 Hz, 2H), 1.78–1.86 (m, 6H), 2.69 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H). Anal: calcd. for $C_{31}H_{42}O_2$, C 83.36, H, 9.48; found C 83.52, H 9.51%.

4.3.3. *4-(E-4-Pentylcyclohexyl)phenyl 4-pentylbenzoate (**1C**)*

Prepared using method B: ^{1}H NMR δ 0.90 (t, J = 6.8 Hz, 6H), 1.02–1.12 (m, 2H), 1.24–1.42 (m, 13H),

1.43–1.51 (m, 2H), 1.66 (quint, $J=7.5$ Hz, 2H), 1.85–1.93 (m, 4H), 2.49 (tt, $J_1=12.2$ Hz, $J_2=3.1$ Hz, 1H), 2.69 (t, $J=7.7$ Hz, 2H), 7.11 (d, $J=8.5$ Hz, 2H), 7.24 (d, $J=8.1$ Hz, 2H), 7.30 (d, $J=8.2$ Hz, 2H), 8.10 (d, $J=8.2$ Hz, 2H). Anal: calcd. for $C_{29}H_{40}O_2$, C 82.81, H 9.58; found C 82.73, H 9.57%.

4.3.4. *4′-Pentylbiphenyl-4-yl 4-pentylbenzoate (**1D**)*

Prepred from 4-pentylbenzoyl chloride using method B: ^{1}H NMR δ 0.91 (t, $J=6.5$ Hz, 6H), 1.33–1.38 (m, 8H), 1.62–1.72 (m, 4H), 2.65 (t, $J=8.0$ Hz, 2H), 2.71 (t, $J=7.5$ Hz, 2H), 7.25–7.29 (m, 4H), 7.32 (d, $J=8.2$ Hz, 2H), 7.51 (d, $J=8.2$ Hz, 2H), 7.62 (d, $J=8.6$ Hz, 2H), 8.13 (d, $J=8.3$ Hz, 2H). Anal: calcd. for $C_{29}H_{34}O_2$, C 84.02, H 8.27; found C 84.16, H 8.33%.

4.3.5. *4-(12-Pentyl-p-carboran-1-yl)phenyl E-4-pentylcyclohexane-1-carboxylate (**2A**)*

Obtained as colourless leaflets (CH_2Cl_2/EtOH) using method A: ^{1}H NMR δ 0.83 (t, $J=7.1$ Hz, 3H), 0.88 (t, $J=6.4$ Hz, 3H), 0.92 (dq, $J_1=12.9$ Hz, $J_2=3.1$ Hz, 2H), 1.09–1.27 (m, 15H), 1.50 (dq, $J_1=12.6$ Hz, $J_2=3.3$ Hz, 2H), 1.50–3.75 (brm, 10H), 1.64 (t, $J=6.8$ Hz, 2H), 1.85 (d, $J=11.4$ Hz, 2H), 2.07 (dd, $J_1=12.0$ Hz, $J_2=3.0$ Hz, 2H), 2.42 (tt, $J_1=12.2$ Hz, $J_2=3.5$ Hz, 1H), 6.85 (d, $J=8.7$ Hz, 2H), 7.18 (d, $J=8.9$ Hz, 2H). Anal: calcd. for $C_{25}H_{46}B_{10}O_2$, C 61.69, H 9.53; found C 61.40, H 9.69%.

4.3.6. *4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl E-4-pentylcyclohexane-1-carboxylate (**2B**)*

^{1}H NMR δ 0.88 (t, $J=7.0$ Hz, 6H), 0.94–1.04 (m, 2H), 1.10–1.13 (m, 2H), 1.18–1.38 (m, 15H), 1.41–1.50 (m, 6H), 1.52–1.61 (m, 2H), 1.75–1.88 (m, 8H), 2.08–2.14 (m, 2H), 2.45 (tt, $J_1=12.2$ Hz, $J_2=3.5$ Hz, 1H), 6.95 (d, $J=8.7$ Hz, 2H), 7.29 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{31}H_{48}O_2$, C 82.25, H 10.69; found C 82.33, H 10.81%.

4.3.7. *4-(E-4-Pentylcyclohexyl)phenyl E-4-pentylcyclohexane-1-carboxylate (**2C**)*

Prepared using method B: ^{1}H NMR δ 0.89 (t, $J=6.8$ Hz, 6H), 0.94–1.08 (m, 4H), 1.15–1.35 (m, 18H), 1.39–1.58 (m, 4H), 1.78–1.88 (m, 6H), 2.01–2.14 (m, 2H), 2.37–2.49 (m, 2H), 6.96 (d, $J=8.5$ Hz, 2H), 7.18 (d, $J=8.5$ Hz, 2H). Anal: calcd. for $C_{29}H_{46}O_2$, C 81.63, H 10.87; found C, 81.37, H, 10.89%.

4.3.8. *4′-Pentylbiphenyl-4-yl E-4-pentylcyclohexane-1-carboxylate (**2D**)*

Prepared using method B and crystallized from hexane: ^{1}H NMR δ 0.89 (t, $J=7.0$ Hz, 3H), 0.90 (t, $J=7.0$ Hz, 3H), 0.95–1.14 (m, 2H), 1.20–1.35 (m, 13H), 1.50–1.70 (m, 4H), 1.86–1.92 (m, 2H), 2.11–2.19 (m, 2H), 2.50 (tt, $J_1=12.2$ Hz, $J_2=3.1$ Hz, 1H), 2.64 (t, $J=7.7$ Hz, 2H), 7.11 (d, $J=8.6$ Hz, 2H), 7.24 (d, $J=8.1$ Hz, 2H), 7.47 (d, $J=8.1$ Hz, 2H), 7.56 (d, $J=8.6$ Hz, 2H). Anal: calcd. for $C_{29}H_{40}O_2$, C 82.81, H 9.58; found C 82.94, H 9.67%.

4.3.9. *4-(12-Pentyl-p-carboran-1-yl)phenyl 4-pentylbicyclo[2.2.2]octne-1-carboxylate (**3A**)*

Obtained as colourless leaflets (CH_2Cl_2/EtOH) using method A: ^{1}H NMR δ 0.83 (t, $J=7.1$ Hz, 3H), 0.88 (t, $J=6.9$ Hz, 3H), 1.11–1.31 (m, 14H), 1.39–1.45 (m, 6H), 1.50–3.60 (brm, 10H), 1.64 (quint, $J=6.7$ Hz, 2H), 1.83–1.89 (m, 6H), 6.81 (d, $J=9.1$ Hz, 2H), 7.17 (d, $J=8.9$ Hz, 2H). Anal: calcd. for $C_{27}H_{48}B_{10}O_2$, C 63.24, H 9.44; found C 62.87, H 9.53%.

4.3.10. *4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**3B**)*

Prepared using method B: ^{1}H NMR δ 0.88 (t, $J=7.0$ Hz, 6H), 1.08–1.35 (m, 16H), 1.40–1.49 (m, 12H), 1.75–1.80 (m, 6H), 1.87–1.93 (m, 6H), 6.92 (d, $J=8.7$ Hz, 2H), 7.28 (d, $J=8.8$ Hz, 2H). Anal: calcd. for $C_{33}H_{50}O_2$, C 82.79, H 10.53; found C 82.90, H 10.60%.

4.3.11. *4-(E-4-Pentylcyclohexyl)phenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**3C**)*

Prepared using method B: ^{1}H NMR δ 0.88 (t, $J=7.0$ Hz, 3H), 0.89 (t, $J=6.8$ Hz, 3H), 0.97–1.12 (m, 4H), 1.15–1.32 (m, 15H), 1.38–1.46 (m, 8H), 1.82–1.93 (m, 10H), 2.44 (tt, $J_1=12.1$ Hz, $J_2=2.9$ Hz, 1H), 6.92 (d, $J=8.5$ Hz, 2H), 7.17 (d, $J=8.5$ Hz, 2H). Anal: calcd. for $C_{31}H_{48}O_2$, C 82.25, H 10.69; found C 82.29, H 10.81%.

4.3.12. *4′-Pentylbiphenyl-4yl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**3D**)*

Prepared using method B and crystallized from hexane: ^{1}H NMR δ 0.89 (t, $J=7.1$ Hz, 3H), 0.88 (t, $J=6.9$ Hz, 3H), 1.10–1.39 (m, 12H), 1.42–1.49 (m, 6H), 1.60–1.70 (m, 2H), 1.90–1.97 (m, 6H), 2.63 (t, $J=7.7$ Hz, 2H), 7.08 (d, $J=8.7$ Hz, 2H), 7.24 (d, $J=8.2$ Hz, 2H), 7.47 (d, $J=8.2$ Hz, 2H), 7.55 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{31}H_{42}O_2$, C 83.36, H 9.48; found C 83.08, H 9.63%.

4.3.13. *4-(12-Pentyl-p-carboran-1-yl)phenyl 12-pentyl-p-carborane-1-carboxylate (**4A**)*

^{1}H NMR δ 0.83 (t, $J=7.1$ Hz, 6H), 1.05–1.28 (m, 12H), 1.50–3.60 (brm, 10H), 1.57–1.63 (m, 4H), 6.76 (d, $J=8.9$ Hz, 2H), 7.15 (d, $J=8.9$ Hz, 2H). Anal: calcd. for $C_{21}H_{46}B_{20}O_2$, C 46.13, H 8.48; found C 46.26, H 8.45%.

4.3.14. *4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl 12-pentyl-p-carborane-1-carboxylate (**4B**)*

Recrystallized from *iso*-octane: ^{1}H NMR δ 0.83 (t, $J=7.3$ Hz, 3H), 0.88 (t, $J=7.2$ Hz, 3H), 1.05–1.32 (m, 14H), 1.42–1.47 (m, 6H), 1.50–3.60 (brm, 10H), 1.59–1.64 (m, 2H), 1.72–1.77 (m, 6H), 6.86 (d, $J=8.8$ Hz, 2H), 7.25 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{27}H_{48}B_{10}O_2$, C 63.24, H 9.44; found C 63.41, H 9.49%.

4.3.15. *4-(E-4-Pentylcyclohexyl)phenyl 12-pentyl-p-carborane-1-carboxylate (**4C**)*

Recrystallized from MeOH: ^{1}H NMR δ 0.83 (t, $J=7.3$ Hz, 3H), 0.89 (t, $J=6.9$ Hz, 3H), 0.95–1.42 (m, 19H), 1.50–3.60 (brm, 10H), 1.57–1.64 (m, 2H), 1.81–1.86 (m, 4H), 2.43 (tt, $J_1=12.2$ Hz, $J_2=2.9$ Hz, 1H), 6.86 (d, $J=8.6$ Hz, 2H), 7.15 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{25}H_{46}B_{10}O_2$, C 61.69, H 9.53; found C 61.79, H 9.49%.

4.3.16. *4′-Pentylbiphenyl-4-yl 12-pentyl-p-carborane-1-carboxylate (**4D**)*

Recrystallized from EtOH: ^{1}H NMR δ 0.84 (t, $J=7.1$ Hz, 3H), 0.90 (t, $J=6.6$ Hz, 3H), 1.10–1.26 (m, 6H), 1.31–1.38 (m, 4H), 1.50–3.60 (brm, 10H), 1.60–1.68 (m, 4H), 2.63 (t, $J=7.8$ Hz, 2H), 7.02 (d, $J=8.7$ Hz, 2H), 7.23 (d, $J=8.4$ Hz, 2H), 7.44 (d, $J=8.1$ Hz, 2H), 7.52 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{25}H_{40}B_{10}O_2$, C 62.47, H 8.39; found C 62.47, H 8.28%.

4.3.17. *4-Pentylphenyl 12-(4-pentyloxyphenyl)-p-carborane-1-carboxylate (**5A**)*

Obtained as colourless prisms (hexane) using method A: ^{1}H NMR δ 0.87 (t, $J=6.9$ Hz, 3H), 0.91 (t, $J=7.1$ Hz, 3H), 1.25–1.43 (m, 8H), 1.50–4.00 (brm, 10H), 1.60 (quint, $J=7.3$ Hz, 2H), 1.74 (quint, $J=6.8$ Hz, 2H), 2.56 (t, $J=7.7$ Hz, 2H), 3.88 (t, $J=6.5$ Hz, 2H), 6.68 (d, $J=8.9$ Hz, 2H), 6.88 (d, $J=8.6$ Hz, 2H), 7.09 (d, $J=9.1$ Hz, 2H), 7.13 (d, $J=8.6$ Hz, 2H). Anal: calcd. for $C_{25}H_{40}B_{10}O_3$, C 60.46, H 8.12; found C 60.10, H 8.35%.

4.3.18. *4-Pentylphenyl 4′-pentyloxybiphenyl-4-carboxylate (**5D**)*

Obtained using method B: ^{1}H NMR δ 0.81 (t, $J=6.8$ Hz, 3H), 0.95 (t, $J=7.0$ Hz, 3H), 1.29–1.46 (m, 8H), 1.59–1.69 (m, 2H), 1.83 (quint, $J=7.0$ Hz, 2H), 2.63 (t, $J=7.5$ Hz, 2H), 4.02 (t, $J=6.5$ Hz, 2H), 7.00 (d, $J=8.7$ Hz, 2H), 7.13 (d, $J=8.5$ Hz, 2H), 7.23 (d, $J=8.7$ Hz, 2H), 7.59 (d, $J=8.6$ Hz, 2H), 7.68 (d, $J=8.5$ Hz, 2H), 8.23 (d, $J=8.4$ Hz, 2H). Anal: calcd. for $C_{29}H_{34}O_3$, C 80.89, H 7.96; found C 80.95, H 8.01%.

4.3.19. *E-4-Pentylcyclohexyl 12-(4-pentyloxyphenyl)-p-carborane-1-carboxylate (**6A**)*

Obtained as colourless needles (CH_2Cl_2/EtOH) using method A: ^{1}H NMR δ 0.87 (t, $J=6.9$ Hz, 3H), 0.91 (t, $J=7.1$ Hz, 3H), 1.15–1.44 (m, 17H), 1.50–4.00 (br m, 10H), 1.73 (quint, $J=7.2$ Hz, 2H), 1.78–1.86 (m, 4H), 3.87 (t, $J=6.6$ Hz, 2H), 4.51 (tt, $J_1=10.9$ Hz, $J_2=4.3$ Hz, 1H), 6.60 (d, $J=9.1$ Hz, 2H), 7.06 (d, $J=9.1$ Hz, 2H). Anal: calcd. for $C_{25}H_{46}B_{10}O_3$, C 59.73, H 9.22; found C 59.41, H 9.54%.

4.3.20. *E-4-Pentylcyclohexyl 4′-pentyloxybiphenyl-4-carboxylate (**6D**)*

Obtained using method B: ^{1}H NMR δ 0.89 (t, $J=7.1$ Hz, 3H), 0.94 (t, $J=7.0$ Hz, 3H), 1.00–1.14 (m, 2H), 1.20–1.36 (m, 10H), 1.40–1.51 (m, 5H), 1.77–1.88 (m, 4H), 2.08–2.15 (m, 2H), 4.01 (t, $J=6.6$ Hz, 2H), 4.93 (tt, $J_1=11.1$ Hz, $J_2=4.4$ Hz, 1H), 6.97 (d, $J=8.8$ Hz, 2H), 7.55 (d, $J=8.8$ Hz, 2H), 7.61 (d, $J=8.5$ Hz, 2H), 8.07 (d, $J=8.5$ Hz, 2H). Anal: calcd. for $C_{29}H_{40}O_3$, C 79.77, H 9.23; found C 79.75, H 9.24%.

4.3.21. *4-Pentylbicyclo[2.2.2]oct-1yl 4′-pentyloxybiphenyl-4-carboxylate (**7D**)*

Obtained using method B: ^{1}H NMR δ 0.88 (t, $J=7.0$ Hz, 3H), 0.94 (t, $J=7.1$ Hz, 3H), 1.05–1.31 (m, 8H), 1.35–1.48 (m, 4H), 1.54–1.60 (m, 6H), 1.82 (quint, $J=7.3$ Hz, 2H), 2.10–2.16 (m, 6H), 4.00 (t, $J=6.6$ Hz, 2H), 6.98 (d, $J=8.8$ Hz, 2H), 7.54 (d, $J=8.8$ Hz, 2H), 7.57 (d, $J=8.5$ Hz, 2H), 8.00 (d, $J=8.4$ Hz, 2H). Anal: calcd. for $C_{31}H_{42}O_3$, C 80.48, H 9.15; found C 80.42, H 9.10%.

4.3.22. *4-Heptylphenyl 12-(4-pentyloxyphenyl)-p-carborane-1-carboxylate (**8a**)*

Prepared using method A: ^{1}H NMR δ 0.87 (t, $J=6.8$ Hz, 3 H), 0.88 (t, $J=6.8$ Hz, 3H), 1.26–1.40 (m, 12H), 1.50–4.00 (brm, 10H), 1.57 (quint, $J=7.3$ Hz,

2H), 1.73 (quint, $J=6.5$ Hz, 2H), 2.56 (t, $J=7.7$ Hz, 2H), 3.88 (t, $J=6.5$ Hz, 2H), 6.68 (d, $J=8.9$ Hz, 2H), 6.88 (d, $J=8.6$ Hz, 2H), 7.09 (d, $J=8.9$ Hz, 2H), 7.13 (d, $J=8.7$ Hz, 2H). Anal: calcd. for $C_{27}H_{44}B_{10}O_3$, C 61.80, H 8.45; found C 62.08, H 8.55%.

4.3.23. *4-Pentylphenyl 12-(4-heptyloxyphenyl)-p-carborane-1-carboxylate (**8b**)*

Prepared using method A: ^{1}H NMR δ 0.87 (t, $J=6.9$ Hz, 3H), 0.88 (t, $J=6.7$ Hz, 3H), 1.29–1.43 (m, 12H), 1.50–4.00 (brm, 10H), 1.57 (quint, $J=7.3$ Hz, 2H), 1.73 (quint, $J=6.5$ Hz, 2H), 2.56 (t, $J=7.7$ Hz, 2H), 3.88 (t, $J=6.5$ Hz, 2H), 6.68 (d, $J=8.9$ Hz, 2H), 6.88 (d, $J=8.6$ Hz, 2H), 7.09 (d, $J=8.9$ Hz, 2H), 7.13 (d, $J=8.9$ Hz, 2H). Anal: calcd. for $C_{27}H_{44}B_{10}O_3$, C 61.80, H 8.45; found C 61.94, H 8.58%.

4.3.24. *4-(12-Pentyl-p-carboran-1-yl)phenol (**9A**)*

A solution of 1M BBr_3 (7.9 ml, 7.9 mmol) in CH_2Cl_2 was added dropwise to a solution of 1-(4-methoxyphenyl)-12-pentyl-*p*-carborane (**12**, 1.26 g, 3.94 mmol) in dry CH_2Cl_2 (12 ml) at 0°C under argon. After stirring for 2 h at r.t., the mixture was poured into ice, and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, AcOEt/hexane, 1/5) to give phenol **9A** (1.30 g, quant.) as a pale yellow solid. A colourless analytical sample of **9A** was obtained by recrystallization from hexane at −78°C: m.p. 105°C; ^{1}H NMR δ 0.83 (t, $J=6.9$ Hz, 3H), 1.11–1.29 (m, 6H), 1.50–4.00 (brm, 10H), 1.64 (t, $J=6.6$ Hz, 2H), 4.87 (s, 1H), 6.59 (d, $J=8.9$ Hz, 2H), 7.06 (d, $J=8.9$ Hz, 2H). Anal: calcd. for $C_{13}H_{26}B_{10}O$, C 50.95, H 8.55; found C 50.90, H 8.64%.

4.3.25. *4-(4-Pentylbicyclo[2.2.2]oct-1yl)phenol (**9B**)*

The phenol was prepared in 80% yield by Friedel–Crafts alkylation of phenol (1.9 g, 20 mmol) with 1-chloro-4-pentylbicyclo[2.2.2]octane (3.2 g, 16.3 mmol) according to a literature procedure [8]: m.p. 117–118°C (lit [8] 124°C); ^{1}H NMR δ 0.88 (t, $J=7.0$ Hz, 3H), 1.05–1.33 (m, 8H), 1.44–1.49 (m, 6H), 1.73–1.73 (m, 6H), 4.50 (s, 1H), 6.75 (d, $J=8.8$ Hz, 2H), 7.18 (d, $J=8.8$ Hz, 2H).

4.3.26. *4-(E-4-Pentylcyclohexyl)phenol (**9C**)*

A solution of 30% hydrogen peroxide (10 ml) in formic acid (25 ml) was slowly added to 4-(E-4-pentylcyclohexyl)acetophenone [9] (**14**, 8.5 g, 0.03 mol) in formic acid (65 ml) and stirred for 6–7 h at r.t. The reaction mixture was poured into water and the product extracted twice with ether. The organic layer was washed with water and dried (Na_2SO_4). Ether was removed and the residue treated with a mixture of water (100 ml), ethanol (35 ml) and sodium hydroxide (7.5 g). The mixture was heated under gentle reflux for 3 h, poured into water, acidified with hydrochloric acid and the resulting phenol was extracted with ether. After usual treatment the residue was crystallized from hexane to give the phenol **12C** in 56% yield: m.p. 133–135°C; ^{1}H NMR δ 0.89 (t, $J=6.9$ Hz, 3H), 0.95–1.09 (m, 2H), 1.18–1.44 (m, 11H), 1.82–1.89 (m, 4H), 2.40 (tt, $J_1=11.9$ Hz, $J_2=2.6$ Hz, 1H), 4.5 (s, 1H), 6.75 (d, $J=8.6$ Hz, 2H), 7.08 (d, $J=8.5$ Hz, 2H). Anal: calcd. for $C_{17}H_{26}O$, C 82.87, H 10.64; found C 82.93, H 10.71%.

4.3.27. *12-(4-Pentyloxyphenyl)-p-carborane-1-carboxylic acid (**10A[5]**)*

A 1.57 M solution of *n*-BuLi (4.25 ml, 6.67 mmol) in hexane was added dropwise to a solution of 1-(4-pentyloxyphenyl)-*p*-carborane (**11[5]**, 1.7 g, 5.56 mmol) in a mixture of benzene (24 ml) and ether (12 ml) at 0°C under argon. After stirring at room temperature for 30 min, the mixture was cooled to 0°C. Methyl chloroformate (0.52 ml, 6.67 mmol) was added, and the resulting mixture stirred for 3 h at r.t. The reaction mixture was poured into water and extracted with AcOEt. The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt, 50/1) to give 1.69 g (84% yield) of methyl 12-(4-pentyloxyphenyl)-*p*-carborane-1-carboxylate as a colourless solid: ^{1}H NMR δ 0.91 (t, $J=7.1$ Hz, 3H), 1.37–1.42 (m, 4H), 1.50–4.00 (brm, 10H), 1.73 (quint, $J=7.0$ Hz, 2H), 3.65 (s, 3H), 3.87 (t, $J=6.5$ Hz, 2H), 6.66 (d, $J=8.9$ Hz, 2H), 7.06 (d, $J=9.1$ Hz, 2H)). The methyl ester was dissolved in THF (23 ml); 1N KOH aqueous solution (23 ml) was added, and the mixture stirred for 6 h at r.t. The reaction mixture was poured into aq. 2 N HCl, and organic products were extracted with AcOEt. The extracts were washed with brine, dried ($MgSO_4$), and concentrated to give acid **10A[5]** (1.62 g, quant.) as a colourless solid. Recrystallization from an AcOEt/hexane mixture gave colourless cubes: m.p. 199°C (DSC: 197°C, 39.0 kJ mol^{-1}); ^{1}H NMR δ 0.91 (t, $J=7.1$ Hz, 3H), 1.31–1.43 (m, 4H), 1.50–4.00 (br m, 10H), 1.73 (quint, $J=7.0$ Hz, 2H), 3.87 (t, $J=6.5$ Hz, 2H), 6.66 (d, $J=8.9$ Hz, 2H), 7.06 (d, $J=9.1$ Hz, 2H). Anal: calcd. for $C_{14}H_{26}B_{10}O_3$, C 47.98, H 7.48; found C 48.04, H 7.55%.

4.3.28. *12-(4-Heptyloxyphenyl)-p-carborane-1-carboxylic acid (**10A[7]**)*

The acid was obtained as described above for **10A[5]** as colourless cotton-like crystals (AcOEt/hexane): m.p. 175°C (DSC: 175°C, 30.7 kJ mol^{-1}); ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3H), 1.28–1.43 (m, 8H), 1.50–4.00 (brm, 10H), 1.73 (quint, J = 6.6 Hz, 2H), 3.87 (t, J = 6.5 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 9.1 Hz, 2H). Anal: calcd. for $C_{16}H_{30}B_{10}O_3$, C 50.77, H 7.99; found C 50.92, H 8.00%.

4.3.29. *1-(4-Pentyloxyphenyl)-p-carborane (**11[5]**)*

A 1.58 M solution of *n*-BuLi (6.8 ml, 10.7 mmol) in hexane was added dropwise to a solution of *p*-carborane (1.47 g, 10.2 mmol) in dry DME (40 ml) at 0°C under argon. After stirring for 30 min at room temperature, dry CuCl (1.31 g, 13.26 mmol) was added in one portion and the mixture stirred for 1 h. Pyridine (6 ml, 76.8 mmol) was added followed by 1-iodo-4-pentyloxybenzene [25] (2.98 g, 10.2 mmol) and the resulting mixture was stirred for 48 h at 100°C. After cooling to r.t. the reaction mixture was diluted with ether and stirred for 3 h; insoluble materials were filtered off through Celite. The filtrate was washed with 10% aqueous HCl, 10% aqueous $Na_2S_2O_3$, brine, and dried ($MgSO_4$). Solvents were removed, and the residue was purified by column chromatography (SiO_2, AcOEt/hexane, 1/10) to give **11[5]** (1.60 g, 51% yield) as a colourless solid which was recrystallized from hexane: m.p. 52–54°C; ^{1}H NMR δ 0.91 (t, J = 7.1 Hz, 3H), 1.37–1.42 (m, 4H), 1.50–3.75 (brm, 10H), 1.73 (quint, J = 7.0 Hz, 2H), 2.74 (brs, 1H), 3.87 (t, J = 6.5 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 7.09 (d, J = 9.1 Hz, 2H). Anal: calcd. for $C_{13}H_{26}B_{10}O$, C 50.95, H 8.55; found C 51.12, H 8.61%.

4.3.30. *1-(4-Methoxyphenyl)-12-pentyl-p-carborane (**12**)*

A 1.57 M solution of *n*-BuLi (10 ml, 15.7 mmol) in hexane was added dropwise to a solution of 1-(4-methoxyphenyl)-*p*-carborane [6] (**11[1]**, 3.2 g, 12.8 mmol) in dry THF (40 ml) at −78°C. The mixture was warmed to r.t. and after 30 min was cooled to −78°C and 1-iodopentane (2.0 ml, 15.3 mmol) was added. The resulting mixture was warmed to r.t., stirred for 1.5 h and poured into water. Organic products were extracted with AcOEt, and the combined organic fractions were washed with brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by column chromatography (ODS, MeOH) to give **12** (3.09 g, 75% yield). An analytical sample of **12** was obtained by recrystallization from MeOH: m.p. 59–60°C (DSC: 59°C, 18.3 kJ mol^{-1}); ^{1}H NMR δ 0.84 (t, J = 7.1 Hz, 3H), 1.06–1.26 (m, 6H), 1.50–4.00 (br m, 10H), 1.64 (t, J = 6.1 Hz, 2H), 3.73 (s, 3H), 6.67 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.9 Hz, 2H). Anal: calcd. for $C_{14}H_{28}B_{10}O$, C 52.47, H 8.81; found C 52.73, H 8.70%.

This project was supported in part by the NSF grant (DMR-0111657) and by Grant-in-Aid for Scientific Research (B) No. 13470468, of the Ministry of Education, Culture, Sports, Science and Technology, Japan. We are grateful to Dr Eike Poetsch (Merck, Darmstadt) for gifts of 4-pentylcyclohexane-1-carboxylic acid and 4′-pentyl-4-biphenol (**9D**), and to Prof. Roman Dabrowski (Poland) for 4-pentylcyclohexan-1-ol and 4′-pentyloxybiphenyl-4-carboxylic acid.

References

[1] Kaszynski, P., and Douglass, A. G., 1999, *J. Organomet. Chem.*, **581,** 28.
[2] Kaszynski, P., Pakhomov, S., Tesh, K. F., and Young, V. G. Jr., 2001, *Inorg. Chem.*, **40,** 6622.
[3] Piecek, W., Kaufman, J. M., and Kaszynski, P., 2003, *Liq. Cryst.*, **30,** 39.
[4] Douglass, A. G., Pakhomov, S., Janoušek, Z., Reeves, B., and Kaszynski, P., 2000, *J. Org. Chem.*, **65,** 1434.
[5] Coult, R., Fox, M. A., Gill, W. R., Herbertson, P. L., McBride, J. A. H., and Wade, K., 1993, *J. Organomet. Chem.*, **462,** 19.
[6] Endo, Y., Iijima, T., Yamakoshi, Y., Fukasawa, H., Miyaura, C., Inada, M., Kubo, A., and Itai, A., 2001, *Chem. Biol.*, **8,** 341.
[7] Fox, M. A., MacBride, J. A. H., Peace, R. J., and Wade, K., 1998, *J. Chem. Soc., Dalton Trans.*, 401.
[8] Adomenas, P. V., Girdzhyunaite, D. K., and Mazhunaitis, G. V., 1983, *J. Org. Chem. USSR*, **19,** 2069.
[9] Bezborodov, V. S., Bubel, O. N., Konovalov, V. A., and Ptashnikov, Y. L., 1983, *J. Org. Chem. USSR*, **19,** 1479.
[10] Demus, D., and Richter, L., 1980, *Textures of Liquid Crystals*; 2nd Edn. (Leipzig VEB).
[11] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals-Textures and Structures* (Philadelphia: Leonard Hill).
[12] Carr, N., Gray, G. W., and Kelly, S. M., 1985, *Mol. Cryst. Liq. Cryst.*, **129,** 301.
[13] Toyne, K. J., 1987, in *Thermotropic Liquid Crystals*, edited by G. W. Gray (New York: Wiley), pp. 28–63 and references therein.
[14] Krause, J., 1976, in *Freiburger Arbeitstagung Flussigkristalle VI*, Vol. 4; LiqCryst 4.3 database; ID # 26492.
[15] Vill, V. in *Landolt-Bornstein*, edited by J. Thiem, Group IV, Vol. 7; Vill, V. LiqCryst. 4.3 database.
[16] Yang, X., Hua, X., and Li, G., 1991, *Huadong Huagong Hueyuan Xuebao*, **17,** 730; LiqCryst 4.3 database; ID # 31807.
[17] Czuprynski, K., and Kaszynski, P., 1999, *Liq. Cryst.*, **26,** 775.

[18] DEMUS, D., and HAUSER, A., 1990, in *Selected Topics in Liquid Crystal Research*, edited by H.-D. Koswig (Berlin: Akademie – Verlag), pp. 19–44 and references therein.
[19] JANUSZKO, A., MORE, K. M., PAKHOMOV, S., KASZYNSKI, P., O'NEILL, M., and WAND, M. D., 2004, *J. Mater. Chem.*, in press.
[20] ELIEL, E. L., WILEN, S. H., and MANDER, L. N., 1994, *Stereochemistry of Organic Compunds* (New York: Wiley), p. 696.
[21] KUHNERT-BRANDSTAETTER, M., and SEIDEL, D., 1982, *Microchim. Acta*, **1,** 243.
[22] LIANG, J. C., and HUBBARD, R., 1985, *Mol. Cryst. liq. Cryst.*, **128,** 89.
[23] GRAY, G. W., and KELLY, S. M., 1981, *Mol. Cryst. liq. Cryst.*, **75,** 95.
[24] DOUGLASS, A. G., CZUPRYNSKI, K., MIERZWA, M., and KASZYNSKI, P., 1998, *J. mater. Chem.*, **8,** 2391.
[25] YANG, Y. G., CHEN, H., TANG, G., and WEN, J. X., 2002, *Mol. Cryst. liq. Cryst. Sci. Technol. Sect. A*, **373,** 1.