

# An assessment of carborane-containing liquid crystals for potential device application

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Two 4-alkoxyphenyl 12-pentylcarborane-1-carboxylate nematic liquid crystals have been synthesized. The materials are found to exhibit ideal mixing of nematic phases in their binary mixtures with analogous bicyclo[2.2.2]octane derivatives and with the polar nematogen 4-(4-isothiocyanatophenyl)-1-(*trans*-hexyl)cyclohexane. The smectic phases for the bicyclo[2.2.2]octanes are destabilized by addition of the carborane derivative. For carborane compound **5BC5** the extrapolated dielectric anisotropy and measured optical anisotropy are  $-1.3$  and  $0.057$  respectively at  $20^\circ\text{C}$ . The refractive indices have been correlated with the calculated electronic polarizabilities and the low birefringence measured for **5BC5** can, at least in part, be attributed to the carborane cylindrical symmetry.

## Introduction

Current liquid crystal display applications rely on nematic, smectic A or C materials.<sup>1,2</sup> Molecules forming such liquid crystalline phases typically comprise a rigid core with flexible substituents attached in such a way as to produce an extended rod-like shape.<sup>3,4</sup> While the chains reduce the melting point of a compound, the mesogenic rigid cores provide the anisotropic interactions necessary for the occurrence of the liquid crystal phase and, to a large extent, dictate the properties of the bulk materials. Our studies have focused on inorganic boron *closo*-clusters<sup>5</sup> as rigid core structural elements and their role in modifying thermal, dielectric and optical properties of liquid crystalline materials.<sup>6-11</sup>

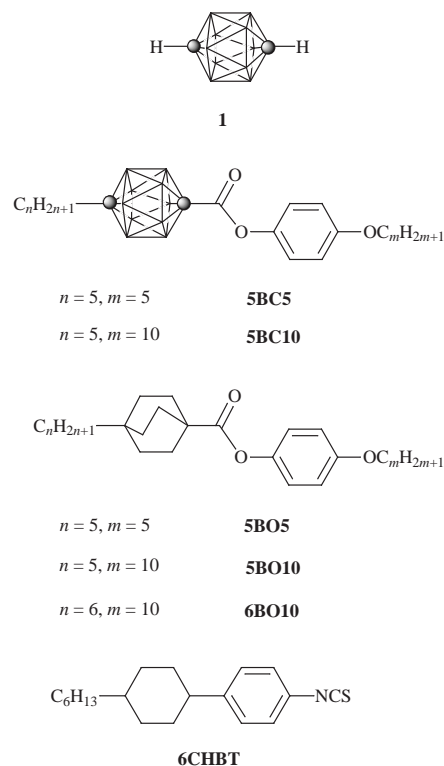
*p*-Carborane (**1**) shown in Fig. 1 appears to be an excellent candidate for use in the mesogenic core of a calamitic liquid crystal. It is a three-dimensional,  $\sigma$ -aromatic ring system<sup>12</sup> which readily undergoes C-substitution with a variety of organic groups<sup>13,14</sup> and hence can easily be incorporated into typical organic molecules. Previously, we demonstrated that mesogens containing **1** are good nematogens and have a tendency to destabilize smectic phases.<sup>6,9,11</sup> This desirable property prompted us to study in detail two-ring esters containing **1** since analogous hydrocarbons possess low negative dielectric anisotropies and are used as additives to improve the performance of nematic devices.<sup>1</sup>

Here we provide synthesis and miscibility studies and describe mesogenic, dielectric and optical properties of two carborane esters, **5BC5** and **5BC10**, and compare them with the analogous bicyclo[2.2.2]octane esters **5BO5**<sup>15</sup> and **5BO10** (Fig. 1). The esters have been studied in pure states and as binary mixtures with their analogs and also with the polar nematogen 4-(isothiocyanatophenyl)-1-(*trans*-4-hexyl)cyclohexane (**6CHBT**).<sup>16</sup> This provides an extensive assessment of the potential for these carborane-containing liquid crystalline esters for use in display devices.

## Results

### Synthesis

The carborane esters **5BC5** and **5BC10** were synthesized from carbonyl chloride **2** and the bicyclo[2.2.2]octane esters **5BO5** and **5BO10** from carbonyl chloride **3** using the appropriate 4-



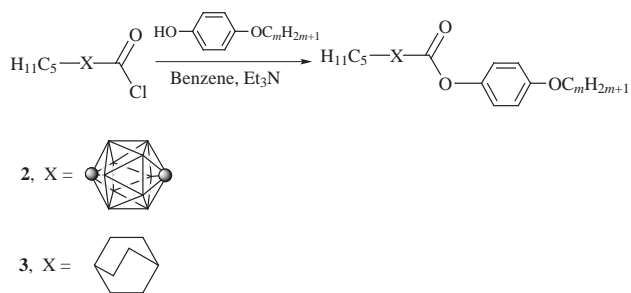
**Fig. 1** *p*-Carborane (**1**), liquid crystal compounds and designations. For carborane each vertex represents a B-H fragment and each filled circle a carbon atom.

alkoxyphenol (Scheme 1). The preferred reagent for the preparation of chloride **2** is  $\text{PCl}_5$ ,<sup>17</sup> while the 4-pentylbicyclo[2.2.2]octane-1-carbonyl chloride (**3**) was prepared using  $\text{SOCl}_2$ .<sup>18</sup> Formation of esters with **3** required 48 h reflux for complete reaction<sup>15</sup> whereas the apparently more reactive carborane carbonyl chloride (**2**) was reacted at room temperature overnight.

### Thermal analysis and miscibility studies

The transitional data for the five compounds **5BC5**, **5BC10**, **5BO5**, **5BO10** and **6BO10**<sup>19</sup> are presented in Table 1. Both carborane-containing materials, **5BC5** and **5BC10**, exhibit low clearing temperatures and their supercooled nematic phases

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Scheme 1

are stable at room temperature on the order of weeks. Increasing the terminal chain length from five to ten methylene units increases the nematic phase range for these materials from 2 °C for **5BC5** to 14 °C for **5BC10**. The nematic–isotropic transition temperatures for the bicyclo[2.2.2]octyl compounds, **5BO5** and **5BO10**, are significantly higher than those for the analogous carboranes. The enthalpies for the nematic–isotropic transitions for the carborane derivatives are equal whereas that for **5BO10** is larger than that for **5BO5**. Of the five compounds only **5BO10** and **6BO10** are smectogenic forming enantiotropic smectic A and either monotropic smectic C or hexatic B<sup>20</sup> phases.

The binary phase diagrams for **5BC5-6BO10** and **5BO5-6BO10** (Fig. 2) demonstrate ideal mixing behavior for the nematic phases. The smectic phases for **6BO10** are, however, strongly destabilized upon addition of the carborane derivative [Fig. 2(a)]. Indeed, at 30 mol% of **5BC5** no smectic behavior could be observed to –20 °C. Similarly, the addition of **5BO5** destabilizes the smectic phases for **6BO10** although to a lesser

extent, and the smectic behavior is only extinguished above 55 mol% **5BO5** [Fig. 2(b)].

Fig. 3 presents the binary phase diagrams for **5BC10-6BO10** (a) and **5BO10-6BO10** (b). In common with data presented in Fig. 2 nematic phases are shown to exhibit perfect miscibility. Increasing the proportion of **5BC10** to **6BO10** depresses the smectic transition temperatures and S<sub>B</sub> and S<sub>A</sub> phases are not formed above 20 mol% and 60 mol% **5BC10**, respectively [Fig. 3(a)]. The phase diagram for **5BO10-6BO10** exhibits normal behavior [Fig. 3(b)] and as the concentration of **6BO10** is increased then the smectic B phase is stabilized in preference to the smectic C.

The phase diagrams for corresponding carborane and bicyclo[2.2.2]octane homologues **5BC5-5BO5** and **5BC10-5BO10** are presented in Fig. 4(a) and (b), respectively. For both diagrams nematic phases exhibit ideal mixing and for mixtures of **5BC10-5BO10** the smectic behavior is extinguished above 40 mol% of **5BC10**.

Binary mixtures **5BC5-6CHBT** and **5BO5-6CHBT** (Fig. 5) exhibit ideal mixing of the nematic phases. For mixtures of **5BO5-6CHBT** an induced smectic A phase is observed in addition to the nematic. This smectic induction is such that the nematic range is reduced to 25 °C for mixtures containing 50–80 mol% **5BO5**.

### Dielectric anisotropy

The dielectric anisotropies of solutions of **5BC5** in **6CHBT** were measured for four different concentrations and the results are plotted in Fig. 6. Extrapolation of the values obtained for the four solutions to pure **5BC5** gave a value of  $\Delta\epsilon = -1.3 \pm 0.1$ .

Table 1 Phase transition temperatures and transitional enthalpies for the BC and BO materials<sup>a</sup>.

Compound		C <sub>1</sub>	C <sub>2</sub>	S <sub>B</sub>	S <sub>C</sub>	S <sub>A</sub>	N	I
<b>5BC5</b>	T/°C		• 34.1				• 36.1	•
	ΔH/kcal mol <sup>-1</sup>		• 4.27				• 0.18	•
<b>5BC10</b>	T/°C		• 29.2				• 42.9	•
	ΔH/kcal mol <sup>-1</sup>		• 5.90				• 0.18	•
<b>5BO5<sup>b</sup></b>	T/°C		• 49.5				• 93.5	•
	ΔH/kcal mol <sup>-1</sup>		• 5.20				• 0.10	•
<b>5BO10</b>	T/°C	• 55.5	• 58.4		(• 30.5) <sup>c</sup>	• 71.0	• 92.5	<b>0</b>
	ΔH/kcal mol <sup>-1</sup>	• 0.94	• 5.30			• 0.03	• 0.33	<b>0</b>
<b>6BO10<sup>d</sup></b>	T/°C		• 55	(• 35)		• 77.8	• 89.5	<b>0</b>

<sup>a</sup>Observed phases are denoted by bullets and monotropic transitions in parentheses. <sup>b</sup>Lit. C-50.5 N-93.5-I, G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, 1981, **75**, 95. <sup>c</sup>Temperature recorded by optical microscopy. <sup>d</sup>R. Dabrowski, J. Szulc and B. Sosnowska, *Mol. Cryst. Liq. Cryst.*, 1992, **215**, 13.

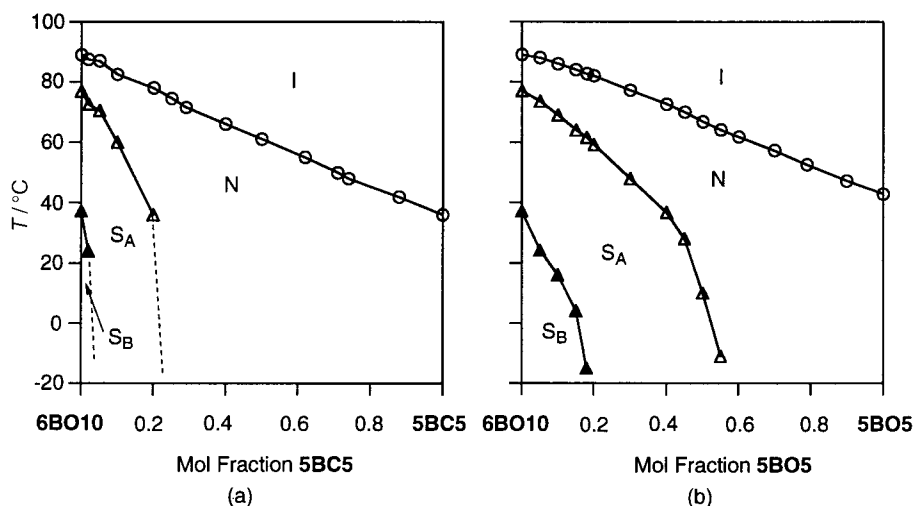


Fig. 2 Binary phase diagrams for (a) **5BC5-6BO10** and (b) **5BO5-6BO10**. The lines are guides to the eye.

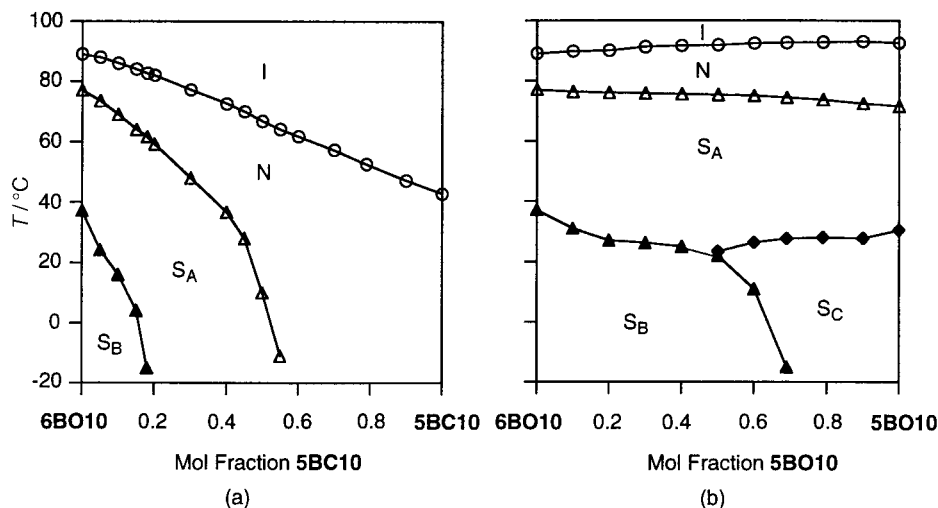


Fig. 3 Binary phase diagrams for (a) **5BC10-6BO10** and (b) **5BO10-6BO10**. The lines are guides to the eye.

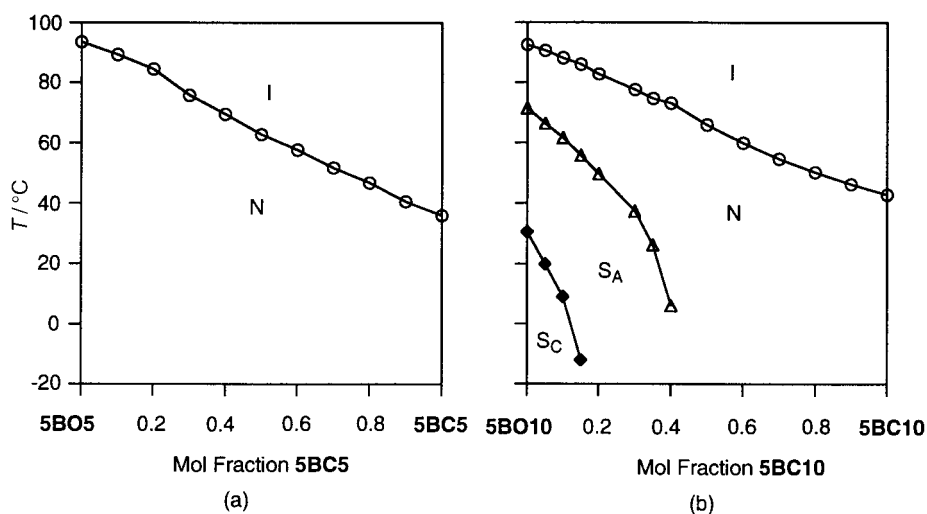


Fig. 4 Binary phase diagrams for (a) **5BC5-5BO5** and (b) **5BC10-5BO10**. The lines are guides to the eye.

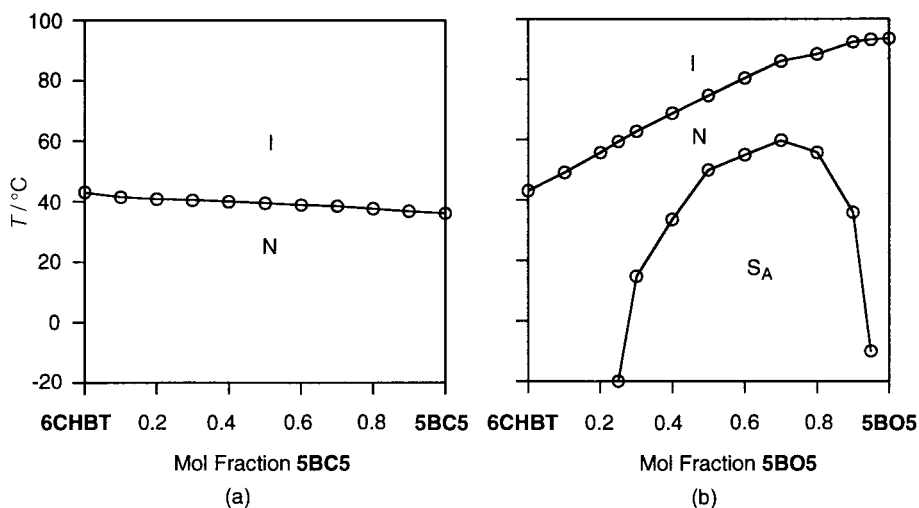


Fig. 5 Binary phase diagrams for (a) **5BC5-6CHBT** and (b) **5BO5-6CHBT**. The lines are guides to the eye.

### Optical anisotropy

The refractive indices for **5BC5** and **5BO5** have been measured for a range of temperatures (Table 2) and the data are plotted in Fig. 7 as a function of the shifted temperature  $T - T_{NI}$ . The isotropic refractive indices for **5BO5** were not measured due

to its high clearing point. The  $n_e$  and  $n_o$  values ( $n_e > n_o$ ) obtained for the carborane derivative **5BC5** are higher than those measured for the bicyclo[2.2.2]octane analog **5BO5** while the resulting birefringence is slightly lower for the former.

Table 3 compares the refractive indices for four analogous phenyl esters at the same shifted temperature,  $T - T_{NI} =$

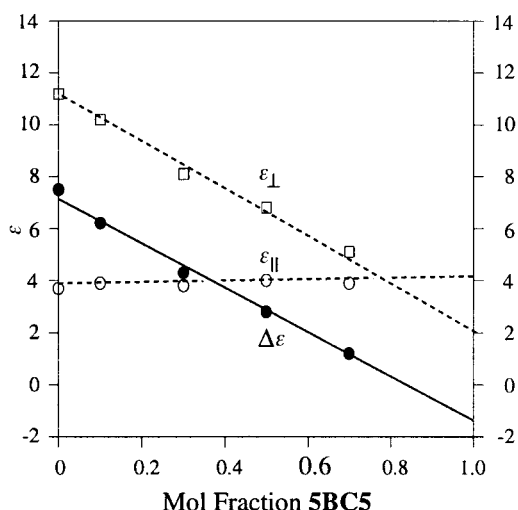


Fig. 6 Plots of  $\epsilon$ ,  $\epsilon_{||}$  and  $\epsilon_{\perp}$  vs. concentration for mixtures of **5BC5-6CHBT**. Line fit for  $\epsilon$  is  $R=0.999$ .

Table 2 Measured refractive indices for **5BC5** and **5BO5** as a function of temperature

5BC5			5BO5		
$T/^{\circ}\text{C}$	$n_e$	$n_o$	$T/^{\circ}\text{C}$	$n_e$	$n_o$
39.4		1.526	83.5	1.530	1.471
37.7		1.527	82.5	1.531	1.471
36.7		1.527	81.3	1.532	1.471
35.7	1.556	1.514	80.5	1.533	1.471
34.7	1.559	1.514	79.5	1.534	1.472
33.8	1.562	1.513	78.5	1.535	1.472
30.9	1.564	1.513	74.5	1.538	1.472
28.7	1.566	1.513	70.6	1.542	1.473
27.7	1.568	1.514	66.6	1.545	1.474
26.2	1.570	1.514	63.3	1.547	1.475
22.8	1.571	1.514	58.5	1.550	1.476

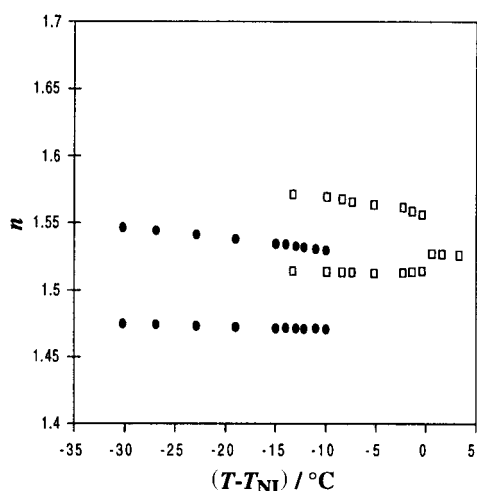


Fig. 7 Dependence of refractive indices ( $n_e$ ,  $n_o$  and  $n_{iso}$ ) on temperature for **5BC5** ( $\square$ ) and **5BO5** ( $\bullet$ ).

$-12.5^{\circ}$ .<sup>21</sup> The refractive indices and birefringence for 4-hexyloxyphenyl 4-butylbenzoate (**4PH6**)<sup>22</sup> are greatest whilst the values for 4-pentylcyclohexane-1-carboxylic acid 4-pentyl-oxyphenyl ester (**5CH5**)<sup>23</sup> are comparable with those for **5BO5**. Carborane **5BC5** has the lowest birefringence despite having an average refractive index [ $n_{\text{avg}}=(n_e+2n_o)/3$ ] equal to that of **4PH6**.

The molecular electronic polarizabilities  $\alpha_x$  have been calculated from the observed refractive indices  $n_x$  using Vuks

Table 3 Experimental refractive indices measured at  $T-T_{NI}=-12.5^{\circ}\text{C}$

	$T/^{\circ}\text{C}$	$n_e$	$n_o$	$n$	$n_{\text{avg}}^a$
<b>5BC5</b>	22.8	1.571	1.514	0.057	1.533
<b>5BO5</b>	80.5	1.533	1.471	0.062	1.492
<b>5CH5</b> <sup>b</sup>	63.6	1.527	1.466	0.061	1.486
<b>4PH6</b> <sup>c</sup>	36.0	1.608	1.497	0.111	1.534

<sup>a</sup> $n_{\text{avg}}=(n_e+2n_o)/3$ . <sup>b</sup>S. Takahashi, S. Mita and S. Kondo, *Mol. Cryst. Liq. Cryst.*, 1986, **132**, 53. <sup>c</sup>I. H. Ibrahim and W. Haase, *J. Phys. (Paris)*, 1979, **40**, 191.

model<sup>24</sup> [eqn. (1)] which assumes that the internal field is isotropic even in an anisotropic medium.

$$\frac{3 V_m}{4 \pi N_A} \frac{n_{e,o,\text{avg}}^2 - 1}{n_{\text{avg}}^2 + 2} = \alpha_{e,o,\text{avg}}$$

$$\text{where } n_{\text{avg}}^2 = (n_e^2 + 2n_o^2)/3 \quad (1)$$

The parameters  $\alpha_e$  and  $\alpha_o$  represent the electric vectors parallel and perpendicular to the optical axis. The molar volumes ( $V_m$ ) have been obtained from the experimental specific densities for **5CH5**<sup>23</sup> and **4PH6**.<sup>22</sup> These molar volumes and those for **5BC5**<sup>25</sup> and **5BO5**<sup>26</sup> have been estimated using group additivity to molar volume<sup>27</sup> and are provided in Table 4 for comparison. For self-consistency of the data the estimated molar volumes have been used in eqn. (1) to derive the experimental polarizability data collected in Table 4.

### Calculations

The average molecular polarizability ( $\alpha_{\text{avg}}$ ), polarizability anisotropy ( $\alpha$ ) and dipole moments for each of the four analogues **5BC5**, **5BO5**, **5CH5** and **5PH5** have been calculated using the MNDO method (Table 4). A plot of experimental versus calculated average polarizabilities ( $\alpha_{\text{avg}}$ ) is given in Fig. 8. The molecular coordinates used in the calculations have been chosen in such a way that the X-axis is defined by a line connecting the two terminal carbon atoms of the core and the phenyl ring lies in the XY plane. The molecular geometry of each compound was optimized with conformational constraints consistent with those found by X-ray analysis of analogous compounds. Thus the alkoxy group was constrained to be coplanar with the benzene ring in all cases.<sup>28</sup> The carbonyl group was set to be coplanar with the benzene ring of the benzoate,<sup>28</sup> perpendicular to the cyclohexyl ring of **5CH5**<sup>29</sup> and staggered for **5BO5**. The alkyl chains were constrained to be staggered in all cases.<sup>28,29</sup>

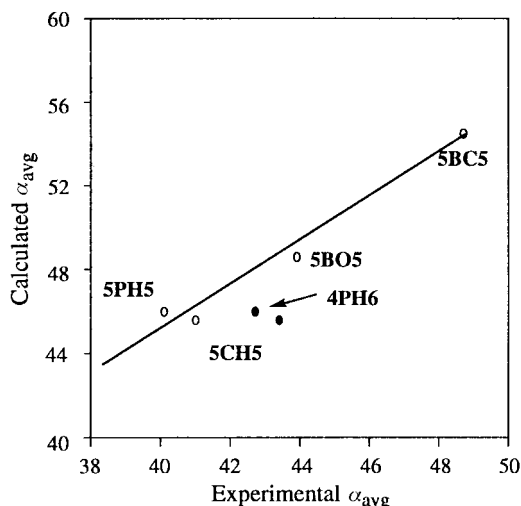
### Electronic absorption spectra

The UV absorption spectrum for **5BC5** in ethanol exhibits similar intensities in its absorption maxima to those for **5BO5** which are about half those reported for *p*-methoxyphenyl benzoate<sup>30</sup> (Fig. 9). The carborane derivative **5BC5** shows a small hypsochromic shift compared to the bicyclo[2.2.2]octane analog and exhibits a shoulder absorption at about 240 nm. Absorption spectra for both **5BC5** and **5BO5** are blue-shifted

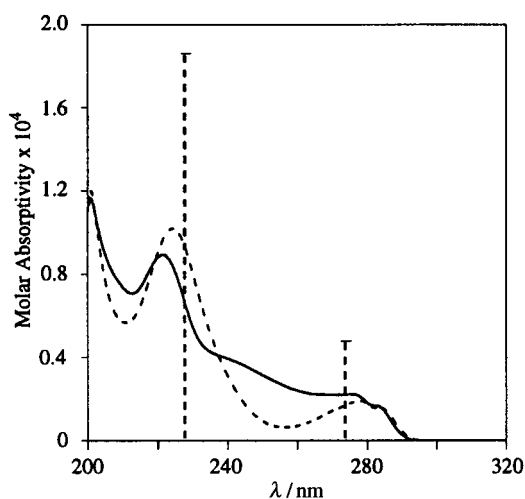
Table 4 Comparison of experimental ( $T-T_{NI}=-12.5^{\circ}\text{C}$ ) and calculated (MNDO) molecular polarizabilities ( $\text{\AA}^3$ )

	$V_m^a$	$\alpha_{\text{avg}}$	$\alpha_{\text{avg}}$ (calc.)	$\alpha_e - \alpha_o$	$\Delta\alpha$ (calc.)	$S$
<b>5BC5</b>	396 — <sup>b</sup>	48.7	54.5	6.3	22.0	0.29
<b>5BO5</b>	382 — <sup>b</sup>	43.9	48.6	6.7	18.6	0.36
<b>5CH5</b>	360 (382)	41.0	45.5	6.2	17.9	0.34
<b>5PH5</b>	325 (346) <sup>c</sup>	40.1 <sup>c</sup>	46.0	10.2 <sup>c</sup>	26.0	0.39

<sup>a</sup>Estimated based on group additivity, see ref. 25–27; experimental data are in parentheses. <sup>b</sup>Not available. <sup>c</sup>Values are for analog **4PH6**.



**Fig. 8** Plot of calculated (MNDO) vs. experimental average molecular polarizabilities. Open circles represent data obtained using estimated molar volumes and filled circles experimentally determined molar volumes. The slope and line fit (open circles only) are 0.93 and 0.986, respectively.



**Fig. 9** Plot of molar absorptivity against wavelength for **5BC5** (solid line) and **5BO5** (dashed line). The literature  $\lambda_{\max}$  values (228 nm,  $\log \epsilon=4.27$ ; 274 nm,  $\log \epsilon=3.67$ ) for *p*-methoxyphenyl benzoate are marked for comparison.

relative to that of *p*-methoxyphenyl benzoate<sup>30</sup> (vertical lines in Fig. 9).

## Discussion and conclusions

The carborane-containing compounds **5BC5** and **5BC10** both form nematic phases with lower clearing temperatures than those for the analogous bicyclo[2.2.2]octyl compounds. This is in accord with our general observation that clearing points are lowered when *p*-carborane is substituted into a mesogenic core.<sup>6,9–11</sup> Previous studies have also noted a tendency for carborane-containing compounds to destabilize smectic phases<sup>6,9,11</sup> which has been rationalized on the basis of the greater breadth of the carborane cage *cf.* bicyclo[2.2.2]octane or benzene.<sup>11</sup> The results from this study are consistent with this observation as **5BO10** is smectogenic whilst **5BC10** is not. Further, the binary phase diagrams with **6BO10** demonstrate that for equal homologues smaller percentages of the carboranes are required to suppress smectic behavior than for analogous bicyclo[2.2.2]octanes. In fact, the binary phase diagram for **5BC10-6BO10** [Fig. 3(a)] is similar to that for the **5BO5-6BO10** binary mixture [Fig. 2(b)]. It could be inferred

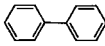


from this comparison that in order to have stabilization of smectic phases in mixtures comparable with that for bicyclo[2.2.2]octanes the carborane derivatives require a significant increase in terminal chain length. Further studies are necessary to test this hypothesis. The excellent miscibility demonstrated for the carboranyl compounds in the low polarity bicyclo[2.2.2]octyl hosts is also observed for mixtures in the polar nematogen **6CHBT**. It is interesting that **5BO5** actually induced smectic behavior in its mixtures with **6CHBT** as bicyclo[2.2.2]octane derivatives are generally regarded as being nematogenic rather than smectogenic compounds.<sup>15</sup> Obviously, the formation of smectic phases within the operating temperature range of a nematic device is undesirable although we note that certain devices have improved performance if there is a neighbouring smectic transition.<sup>1</sup>

The small, negative value of  $\Delta\epsilon$  for **5BC5** (–1.3) is consistent with a value of –1.1 reported for cyclohexane close analog **4CH6**.<sup>31</sup> It also consistent with expectation as the major contributors to the dielectric anisotropy are the outboard dipoles due to lone electron pairs on oxygen. Indeed, the MNDO calculations show that the transverse vector constitutes the major component of the molecular dipole moment which is about 1.8 D for **5BC5** and **5BO5**, 1.7 D for **5CH5** and 2.1 D for **5PH5** ( $D = \text{Debye}$ ,  $1 D \approx 3.33564 \times 10^{-30} \text{ C m}$ ).

The refractive indices for **5BC5** are greater than those for **5BO5** and **5CH5** as a result of the highly polarizable electrons in the carborane cage.<sup>32</sup> However, because of the three-dimensional spherocylindrical symmetry of the carborane cage, *cf.* two-dimensional planar symmetry of a benzene ring, the resultant birefringence is expected to be lower in carborane-containing mesogens than in aromatic analogs. Indeed, calculations on biphenyl, 1,1'-bicarborane and 1-phenylcarborane clearly demonstrate that the carborane imparts a high average polarizability but low anisotropy of polarizability (Table 5). The same trend is observed in the data collected in Table 4; **5BC5** is predicted to have the highest average polarizability and a polarizability anisotropy intermediate between the phenyl and alicyclic analogues. Comparing the calculated and experimental values for  $\alpha_{\text{avg}}$  it can be seen that the experimental values tend to be 10–15% lower than the theoretical predictions (Table 4). Part of this overestimation by theory can be attributed to the use of estimated rather than experimental molar volumes which tend to be underestimated by about 5%. In view of the fact that we are comparing results from calculations on a single conformer in the gas phase to those obtained for conformationally mobile molecules in an anisotropic, condensed phase the correlation is reasonable ( $R = 0.986$  in Fig. 8).

The polarizability anisotropy values obtained for an idealized, gas phase molecule differ from those measured in the nematic phase due to intermolecular (orientational ordering) and intramolecular dynamics (conformational mobility) in the latter. The orientational ordering is generally approximated by the second rank orientational order parameter  $S$  where  $\beta$  is the angle between the long molecular axis and the director [eqn. (2)].<sup>33</sup> For an axially symmetric molecule the order

**Table 5** Calculated (MNDO) polarizabilities ( $\text{\AA}^3$ ) for benzene and carborane compounds

	$\alpha_{\text{avg}}$	$\Delta\alpha$
	21.4 <sup>a</sup>	15.2
	30.2	10.7
	38.5	7.1

<sup>a</sup>Experimental value obtained from molar refraction and density at 77 °C is 20.8  $\text{\AA}^3$ , A. L. von Steiger, *Chem. Ber.*, 1922, **55**, 1968.

parameter can be expressed as a ratio of experimental and theoretical birefringences or anisotropies of molecular polarizabilities [eqn. (3)].<sup>22</sup>

$$S = (3 < \cos^2 \beta > - 1) / 2 \quad (2)$$

$$S = (\alpha_e - \alpha_o) / \Delta \alpha \quad (3)$$

Thus, if the assumptions made in determining  $(\alpha_e - \alpha_o)$  are reasonable then the results suggest that **5BC5** has a lower degree of orientational ordering than its analogs (Table 4) at the same shifted temperature and that the lowered orientational ordering is contributing to lowering the observed birefringence. Unfortunately the assumptions made in obtaining order parameters (in particular estimation of the molar volume for **5BC5**) prevent these data from being considered fully reliable. Our intention was rather to assess whether semiempirical methods can reproduce the experimental data and consequently can be used for making predictions. Certainly the average polarizabilities are overestimated but reproduced reasonably consistently by calculations (Fig. 8). Calculations also suggest that the anisotropy of polarizability should be lower for mesogens containing carborane instead of phenyl. This is supported by experiment as the birefringence is low for **5BC5** cf. **4PH6**. At present it is not possible to assess the relative contributions of the orientational ordering and the molecular polarizability to this low birefringence for **5BC5**. Answering this question is important because low birefringence has been recognized as a desirable property for twisted nematic device applications.<sup>34</sup> In order to resolve this debate and to further investigate these carboranyl mesogens we hope to measure the temperature dependence of the density and the temperature dependent order parameters *via* deuterium NMR spectroscopy.

The contribution of the  $\sigma$ -aromatic carborane to the electronic absorption spectrum for **5BC5** is more comparable with that of an aliphatic ring than with that of a  $\pi$  chromophore. Molar absorptivities for the carborane and bicyclo[2.2.2]octane derivatives are very similar and they are essentially half of those for the compound with two phenyl rings (Fig. 9). As evident from Fig. 9, both **5BC5** and **5BO5** show the benzene E band at about 220 nm and the B band double absorption at about 280 nm. The E band for **5BC5** is blue-shifted by 3 nm with respect to that for **5BO5** and 6 nm with respect to *p*-methoxyphenyl benzoate.<sup>30</sup> The spectrum of **5BC5** exhibits a broad shoulder absorption at about 240 nm which is absent in the spectrum of the bicyclo[2.2.2]octane analog. Since UV spectra for the corresponding carboxylic acids are similar to each other the origin of this shoulder absorption is not clear.

In summary, the carborane-containing compounds are miscible with all-organic mesogens, have clearing points about 50 °C lower than analogous bicyclo[2.2.2]octane derivatives and appear to be strong suppressants of smectic phases. Substitution of carborane for bicyclo[2.2.2]octane into the mesogen does not appreciably increase the UV absorption or birefringence whilst refractive indices are increased markedly. This unique effect of the carborane cage on bulk properties can be rationalized on the basis of symmetry arguments and is supported by quantum mechanical calculations. The experimental birefringence for **5BC5** is excessively low compared to calculations suggesting a low order parameter. Dielectric properties are not significantly affected by substitution with carborane. The data collected thus far suggest that the carborane-containing compounds satisfy the criteria for nematic devices and that more detailed studies of this class of compounds are warranted.

## Experimental

The phase transition points of the compounds and their mixtures were determined using a PZO 'Biolar' polarized

microscope with a HCS250 Instec hot stage. Thermal analysis was obtained using a Mettler DSC 30 instrument. Transition temperatures for pure materials were measured using small samples (1–2 mg) and a heating rate of 1 °C min<sup>-1</sup>, while for the transition enthalpies large samples (10–15 mg) and fast heating (10 °C min<sup>-1</sup>) was used. The uncertainties in the transition temperatures and transitional enthalpies are estimated as  $\pm 0.1$  °C and  $\pm 5\%$  respectively. Mixtures were prepared by evaporation of dichloromethane solutions. For mixtures the transition temperature was taken as the upper limit of the biphasic region as observed by optical microscopy. The phase diagrams were determined by the single concentration method. NMR spectra were obtained on a Bruker 300 MHz instrument in CDCl<sub>3</sub> and referenced to the solvent (<sup>1</sup>H and <sup>13</sup>C NMR). <sup>11</sup>B NMR spectra were obtained at 64.2 MHz using a Bruker 200 MHz spectrometer and referenced to B(OMe)<sub>3</sub>. IR spectra were recorded using an ATI Mattson Genesis FTIR by deposition of a thin film from solution onto sodium chloride disks. Mass spectrometry was performed using a Hewlett-Packard 5890 instrument (GC-MS). Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia. Dielectric anisotropies were measured using an APT III Automated Polarization Testbed at room temperature and version 4.12b software (Displaytech, Inc). The error in measurement of the dielectric constant is estimated to be  $\pm 0.1$ . Refractive indices for 589 nm radiation were determined using a Leitz Abbe Mark II refractometer connected to a thermostated circulating-water bath. Samples were aligned by pretreatment of the prism surfaces with lecithin and rubbing unidirectionally. The errors in readings are  $\pm 0.001$  and  $\pm 0.002$  for the extraordinary and ordinary rays respectively. The temperatures recorded by the refractometer were scaled to those of the DSC by comparison of  $T_{NI}$ . UV-VIS spectra of solutions in absolute ethanol were recorded using a Hitachi U-3000 spectrophotometer. Benzene and dichloromethane was dried by distillation from calcium hydride and triethylamine by standing over potassium hydroxide. Quantum mechanical calculations were performed using AMPAC 6.0 package. Polarizabilities were obtained in the user-defined molecular coordinates by using BRUTEKPOLAR Keyword.

## Syntheses

**12-Pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic acid.** *p*-Carborane (2.0 g, 13.8 mmol) was placed in a dry 100 ml three-neck flask equipped with a condenser, stopper and sub-seal. After flushing with nitrogen, dry THF (50 ml) was added and the solution cooled to  $-78$  °C. *n*-Butyllithium (1.92 M in THF, 7.18 ml, 13.8 mmol) was added *via* syringe in a dropwise manner causing a white precipitate to form. The mixture was allowed to warm (redissolution occurs) and stir at room temperature for 20 min after which *n*-pentyl iodide (1.79 ml, 13.8 mmol) was added. After stirring a further 3 h the reaction was recooled to  $-78$  °C and *n*-butyllithium (1.92 M in THF, 7.18 ml, 13.8 mmol) was added dropwise *via* syringe. The reaction was allowed to stir at room temperature for 20 min and then CO<sub>2</sub> was bubbled through it for a further 1 h. The solvent was removed on a rotavapor and KOH added (2 M, 30 ml). The mixture was extracted with hexanes (3  $\times$  30 ml) which were discarded. The aqueous phase was acidified with conc. HCl (pH 1) causing a white precipitate to form. Diethyl ether (30 ml) was added effecting dissolution and the organic phase was separated. The aqueous phase was again extracted with ether (3  $\times$  30 ml) and the combined organics dried over sodium sulfate. The ether was removed and the white solid stirred in refluxing hexanes to extract the 12-pentyl-1,12-dicarbadodecaborane-1-carboxylic acid which was purified by sublimation (120–124 °C, 1 Torr) yielding a white solid (1.57 g, 44% yield): mp. 139–143 °C; <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]acetone),  $\delta$  0.81

(t,  $J=7.1$  Hz, 3H), 1.02–1.28 (m, 6H), 1.67 (t,  $J=7.8$  Hz, 2H), 10.06 (br s, 1H), 1.2–3.4 (br m);  $^{13}\text{C}$  NMR,  $\delta$  14.12, 22.80, 29.80, 31.74, 38.83, 76.31, 84.57, 163.40;  $^{11}\text{B}$  NMR,  $\delta$  –13.5 (d,  $J_{\text{BH}}=165$  Hz); IR 2952, 2929, 2606, 1716, 1415, 1282  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_8\text{H}_{22}\text{B}_{10}\text{O}_2$ : C, 37.19; H, 8.58. Found: C, 37.43; H, 8.47%.

**12-Pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic acid 4-pentyloxyphenyl ester (5BC5).** 12-Pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic acid (1.0 g, 3.87 mmol) and phosphorus pentachloride (841 mg, 4.04 mmol) were placed in a dry 25 ml flask and dry benzene (10 ml) added. The reaction was stirred under nitrogen for 20 min at 40 °C forming a clear solution. The solvent was removed yielding a colorless oil and after flushing with nitrogen dry benzene (10 ml) was added to dissolve acid chloride 2. This solution was added dropwise to a stirred solution of 4-pentyloxyphenol (729 mg, 4.04 mmol) and triethylamine (0.56 ml, 4.04 mmol) in dry benzene (10 ml) and the reaction stirred overnight at room temperature under nitrogen. The solution was then filtered through a silica gel plug eluted with benzene and the solvent removed. The product was purified by chromatography (dichloromethane–hexanes, 1:4) giving 1.3 g (80% yield) followed by repeated recrystallization from pentane, decolorization with charcoal in diethyl ether and finally distillation (194–196 °C, 0.3 Torr) to yield 847 mg colorless, opaque liquid (52% yield): mp 34.1 °C;  $^1\text{H}$  NMR,  $\delta$  1.0–3.4 (br m), 0.84 (t,  $J=7.1$  Hz, 3H), 0.92 (t,  $J=7.0$  Hz, 3H), 1.05–1.50 (m, 10H), 1.59–1.65 (m, 2H), 1.70–1.79 (m, 2H), 3.88 (t,  $J=6.5$  Hz, 2H), 6.80 and 6.84 (AB d,  $J=9.3$  Hz, 4H);  $^{13}\text{C}$  NMR,  $\delta$  13.83, 14.00, 22.18, 22.41, 28.11, 28.86, 28.98, 31.12, 38.36, 68.31, 74.19, 84.37, 114.89, 121.46, 143.73, 157.16, 161.56;  $^{11}\text{B}$  NMR,  $\delta$  –14.1 (d,  $J_{\text{BH}}=162$  Hz); EIMS,  $m/z$  423–417 (max. at 420, 58%, M), 244–237 (max. at 241, 100%); IR 2956, 2932, 2865, 2614, 1762, 1505, 1298, 1241  $\text{cm}^{-1}$ ; UV,  $\lambda_{\text{max}}/\text{nm}$  ( $\log \epsilon_{\text{max}}$ ) 222 (3.95), 277 (3.36), 283 (3.24). Anal. Calc. for  $\text{C}_{19}\text{H}_{36}\text{B}_{10}\text{O}_3$ : C, 54.26; H, 8.63. Found: C, 54.31; H, 8.71%.

**12-Pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic acid 4-decyloxyphenyl ester (5BC10).** Prepared by the method used for 5BC5 and purified by distillation (220 °C, 0.1 Torr, 93 mg, 52% yield) followed by recrystallization from ethanol: mp 29.2 °C;  $^1\text{H}$  NMR,  $\delta$  1.0–3.5 (br m), 0.82 (t,  $J=7.2$  Hz, 3H), 0.86 (3H,  $J=6.6$  Hz, 3H), 1.05–1.40 (m, 20H), 1.57–1.68 (m, 2H), 1.70–1.77 (m, 2H), 3.88 (t,  $J=6.6$  Hz, 2H), 6.79 and 6.85 (AB d,  $J=9.1$  Hz, 4H);  $^{13}\text{C}$  NMR,  $\delta$  13.83, 14.10, 22.18, 22.66, 25.97, 28.98, 29.17, 29.30, 29.34, 29.53 (2C), 31.13, 31.87, 38.36, 68.37, 74.21, 84.36, 114.91, 121.48, 143.73, 157.16, 161.62;  $^{11}\text{B}$  NMR,  $\delta$  –14.2 (d,  $J_{\text{BH}}=166$  Hz); EIMS,  $m/z$  493–487 (max. at 490, 33, M), 244–237 (max. at 241, 100%); IR 2954, 2926, 2855, 2614, 1761, 1504, 1242, 1188  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{24}\text{H}_{46}\text{B}_{10}\text{O}_3$ : C, 58.74; H, 9.45. Found: C, 58.85; H, 9.44%.

**4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid 4-pentyloxyphenyl ester (5BO5).**<sup>15</sup> Prepared and purified by the method used for 5BO10 giving 472 mg (66% yield): mp 49.5 °C;  $^1\text{H}$  NMR,  $\delta$  0.87 (t,  $J=7.2$  Hz, 3H), 0.91 (t,  $J=7.1$  Hz, 3H), 1.09–1.44 (m, 18H), 1.70–1.77 (m, 2H), 1.86–1.91 (m,  $J=7.8$  Hz, 6H), 3.90 (t,  $J=6.4$  Hz, 2H), 6.83 (d,  $J=9.1$  Hz, 2H), 6.89 (d,  $J=9.1$  Hz, 2H);  $^{13}\text{C}$  NMR,  $\delta$  14.00, 14.07, 22.43, 22.66, 23.33, 28.15, 28.59, 28.93, 30.36, 30.46, 32.78, 39.21, 41.31, 68.32, 114.90, 122.15, 144.31, 156.57, 177.11; EIMS,  $m/z$  386 (13), 180 (18), 179 (100), 123 (20), 109 (29%); IR 2954, 2922, 2870, 2856, 1746, 1504, 1458, 1227, 1198  $\text{cm}^{-1}$ ; UV,  $\lambda_{\text{max}}/\text{nm}$  ( $\log \epsilon_{\text{max}}$ ) 225 (4.01), 278 (3.30), 285 (3.21). Anal. Calc. for  $\text{C}_{25}\text{H}_{38}\text{O}_3$ : C, 77.68; H, 9.91. Found: C, 77.76; H, 9.84%.

**4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid 4-decyloxyphenyl ester (5BO10).** 4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid and thionyl chloride (bp 150 °C/ 1 Torr, 76% yield) and 4-decyloxyphenol (210 mg, 0.91 mmol) were dissolved in dry benzene (5 ml) and dry pyridine (2.5 ml) was added dropwise. The reaction was stirred and refluxed for 48 h and the volatiles removed by rotary evaporation. The crude product was then passed through a 3 cm layer of silica eluted with 100 ml of dichloromethane–hexanes (1/4 v/v). Chromatographic separation (same eluant) and recrystallization from ethanol yielded 322 mg (70%): mp 58.4 °C;  $^1\text{H}$  NMR (400 MHz),  $\delta$  0.86 (t,  $J=7.1$  Hz, 6H), 1.08–1.50 (m, 28H), 1.72–1.77 (m, 2H), 1.88 (t,  $J=7.9$  Hz, 6H), 3.90 (t,  $J=6.5$  Hz, 2H), 6.82 and 6.89 (AB d,  $J=9.0$  Hz, 4H);  $^{13}\text{C}$  NMR,  $\delta$  14.07, 14.09, 22.66, 23.34, 26.00, 28.57, 29.24, 29.30, 29.37, 29.54, 30.36, 30.44, 31.88, 32.78, 39.19, 41.31, 68.31, 114.87, 122.14, 144.31, 156.56, 177.05; EIMS,  $m/z$  456 (10), 180 (14), 179 (100%); IR 2957, 2921, 2854, 1747, 1506, 1457, 1227, 1197  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{30}\text{H}_{48}\text{O}_3$ : C, 78.90; H, 10.59. Found: C, 79.19; H, 10.79%.

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