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

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Two 4-alkoxynaphthyl 1-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) bicyclo[2.2.2]octane. 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 °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.1,6 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.1,6 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 clusters as rigid core structural elements and their role in modifying thermal, dielectric and optical properties of liquid crystalline materials.1,6

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, σ-aromatic ring system2,12 which readily undergoes C-substitution with a variety of organic groups11,15 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.5,11 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.6

Here we provide synthesis and miscibility studies of two carborane esters, 5BC5 and 5BC10, and compare them with the analogous bicyclo[2.2.2]octane esters 5BO513 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-(4-isothiocyanatophenyl)-1-(trans-4-hexyl) bicyclo[2.2.2]octane (6CHBT).14 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-alkoxynaphthyl (Scheme 1). The preferred reagent for the preparation of chloride 2 is PCl3,17 while the 4-pentylbicyclo[2.2.2]octane-1-carbonyl chloride (3) was prepared using SOCl2.18 Formation of esters with 3 required 48 h reflux for complete reaction15 whereas the apparently more reactive 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 6BO1016 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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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 5BO5-6CHBT to 14°C for 5BO10-6BO10. 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° 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 Sb and Sa 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 Δε = −1.3 ± 0.1.

Table 1 Phase transition temperatures and transitional enthalpies for the BC and BO materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T° C</th>
<th>ΔH kcal mol⁻¹</th>
<th>Sb</th>
<th>Sa</th>
<th>S C</th>
<th>N</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>5BC5</td>
<td>7°</td>
<td>34.1</td>
<td>36.1</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.27</td>
<td>0.18</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5BC10</td>
<td>7°</td>
<td>22.2</td>
<td>42.9</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.90</td>
<td>0.18</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5BO5</td>
<td>7°</td>
<td>49.5</td>
<td>93.5</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.20</td>
<td>0.10</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5BO10</td>
<td>7°</td>
<td>55.5</td>
<td>98.4</td>
<td>30.5</td>
<td>71.0</td>
<td>92.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>5.30</td>
<td>-</td>
<td>0.03</td>
<td>0.33</td>
<td>0</td>
</tr>
<tr>
<td>6BO10</td>
<td>7°</td>
<td>55</td>
<td>80.5</td>
<td>-</td>
<td>77.5</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(35)</td>
<td>88.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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, $T - T_{NI}$.

*J. Mater. Chem.*, 1998, 8(11), 2391-2398 2393
The refractive indices and birefringence for 4-

The parameters \( n_o \) and \( n_e \) 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 5CH526 and 4PH627. These molar volumes and those for 5BC528 and 5BO529 have been estimated using group additivity to molar volume30 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 \( (\alpha_{avg}) \) is the 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 \( (\alpha_{calc}) \) 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 alkoxyl group was constrained to be coplanar with the benzene ring in all cases.28 The carbonyl group was set to be coplanar with the benzene ring of the benzoate,29 perpendicular to the cyclohexyl ring of 5CH530 and staggered for 5BO5. The alkyl chains were constrained to be staggered in all cases.29,30

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 benzoate31 (Fig. 9). The carbazole derivative 5BC5 shows a small hypochromic 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 3 Experimental refractive indices measured at \( T - T_{NI} = -12.5 \degree C \)

<table>
<thead>
<tr>
<th>( T/\degree C )</th>
<th>( n_o )</th>
<th>( n_e )</th>
<th>( n_{avg} )</th>
<th>( n_{e-o} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5BC5</td>
<td>22.5</td>
<td>1.571</td>
<td>1.514</td>
<td>0.037</td>
</tr>
<tr>
<td>5BO5</td>
<td>20.5</td>
<td>1.533</td>
<td>1.471</td>
<td>0.062</td>
</tr>
<tr>
<td>5CH5</td>
<td>63.6</td>
<td>1.527</td>
<td>1.466</td>
<td>0.081</td>
</tr>
<tr>
<td>4PH6</td>
<td>36.0</td>
<td>1.608</td>
<td>1.497</td>
<td>0.111</td>
</tr>
</tbody>
</table>

Table 4 Comparison of experimental \( (T - T_{NI} = -12.5 \degree C) \) and calculated (MNDO) molecular polarizabilities (\( \AA^2 \))

<table>
<thead>
<tr>
<th>( V_m' )</th>
<th>( n_{avg} )</th>
<th>( n_{avg} ) (calc.)</th>
<th>( n_o - n_e ) (calc.)</th>
<th>( \Delta ) (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5BC5</td>
<td>396 -</td>
<td>48.7 54.5</td>
<td>6.3</td>
<td>22.0</td>
</tr>
<tr>
<td>5BO5</td>
<td>382 -</td>
<td>43.9 48.6</td>
<td>6.7</td>
<td>18.6</td>
</tr>
<tr>
<td>5CH5</td>
<td>360 (382)</td>
<td>41.0 45.5</td>
<td>6.2</td>
<td>17.9</td>
</tr>
<tr>
<td>5PH5</td>
<td>325 (346)</td>
<td>40.1 46.0</td>
<td>10.2</td>
<td>26.0</td>
</tr>
</tbody>
</table>

*Estimated based on group additivity, see ref. 25-27. Experimental data are in parentheses. \( \Delta \) not available. Values are for analog 4PH6.
analogous bicyclo[2.2.2]octanes. In fact, the binary phase
a
anes are required to suppress smectic behavior than for
this observation as
or benzene.

greater breadth of the carborane cage
phases
a
for carborane-containing compounds to destabilize smectic
p
is smectogenic whilst
5BC10
is not. Further, the binary phase diagrams with
both
and
5BO5
are similar to that for the
5BO5-5BC10
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 carboranyl 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.

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. 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. 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 contributes 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 = Debye, 1 D ≈ 3.3364 × 10⁻²² 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.64 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 \( \Delta \epsilon \) 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 intramolecular (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 \( S = \angle \) is the angle between the long molecular axis and the director [eqn. (2)].60 For an axially symmetric molecule the order

### Table 5. Calculated (MNDO) polarizabilities (Å³) for benzene and carborane compounds

<table>
<thead>
<tr>
<th>Calcd</th>
<th>Expd</th>
<th>( \Delta \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.40</td>
<td>21.40</td>
<td>15.2</td>
</tr>
<tr>
<td>30.2</td>
<td>30.2</td>
<td>10.7</td>
</tr>
<tr>
<td>38.1</td>
<td>38.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>

*Experimental value obtained from molar refraction and density at 77 °C in 208 Å³.* A. L. von Stengel, Chem. Ber., 1922, 55, 1922.

J. Mater. Chem., 1998, 8(11), 2391–2398

2395
polarizabilities \[ \text{eqn. (3)} \]. Thus, if the assumptions made in determining \( \sigma_{\pm} \) 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 carbaborane 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.\(^\text{44}\) In order to resolve this debate and to further investigate these carbaboranyl 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 \( n \)-aromatic carborane to the electronic absorption spectrum for 5BC5 is more comparable with that of an aliphatic ring than with that of a \( t \) chromophore. Molar absorptivities for the carbaborane 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 \( \rho \)-methoxyphenyl benzene.\(^\text{48}\) 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 carbaborane-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 carbaborane 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 carbaborane 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 carbaborane. The data collected thus far suggest that the carbaborane-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 Perkin-Elmer 221 birefringometer with a HCS250 Instec hot stage. Thermal analysis for pure materials were measured using small samples (1–2 mg) and a heating rate of 1 °C min\(^{-1}\), while for the transition enthalpies large samples (10–15 mg) and fast heating (10 °C min\(^{-1}\)) was used. The uncertainties in the transition temperatures and transitional enthalpies are estimated as ±0.1 °C and ±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\(_3\), and referenced to the solvent (\( \delta \)H and \( \delta \)C NMR).\(^\text{49}\) \( \delta \)H NMR spectra were obtained at 64.2 MHz using a Bruker 200 MHz spectrometer and referenced to \( \delta \)HOMe. 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 Textbox at room temperature and version 4.12b software (Displaytech, Inc.). The error in measurement of the dielectric constant is ±0.001 and ±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 \( T_m \) with a Litz 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 ±0.001 and ±0.002 for the extraordinary and ordinary rays respectively.

### Syntheses

12-Pentyl-1,12-dicarbododecaborane(10)-1-carboxylic acid. \( \rho \)-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 warmed to room temperature (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\(_2\) was bubbled through it for a further 1 h. The solvent was removed on a rotavapor and KOH added (2×3.0 ml). The mixture was extracted with hexanes (3×30 ml) which were discarded. The aqueous phase was acidified with conc. HCl (\( \phi \)H 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 (3×30 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-dicarbododecaborane(10)-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; \( \delta \)H NMR \( (\text{d}^{1} \text{H}, \text{acetone}) \), \# 0.81

\[ S = (3 \cos^2 \phi - 1)/2 \]

\[ S = (\sigma_{\text{E}} - \sigma_{\text{o}})/\Delta \]

\[ S = (\sigma_{\text{ex}} - \sigma_{\text{om}})/\Delta \]
12-Penty1-1,12-di-carbododecaborane(10)-1-carboxylic acid 4-decylphenyloxephen (SCB30). Prepared by the method used for SCB10 giving 472 mg (66% yield): mp 49.5 °C. 

1H NMR, δ 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), 1.89-1.91 (m, J = 7.2 Hz, 2H), 5.90-6.47 (2H), 6.83 (p, J = 9.1 Hz, 2H), 6.89 (d, J = 9.1 Hz, 2H), 14.6 (s, 1H). 13C NMR, δ 14.00, 14.07, 22.43, 22.66, 23.33, 23.85, 23.98, 28.30, 28.36, 32.57, 32.82, 32.88, 144.15, 156.57, 177.15. EIMS, m/z 386 (110), 180 (18), 179 (100), 125 (20), 109 (29%)3. 

IR (KBr, cm⁻¹): 2922, 2870, 2856, 1746, 1504, 1458, 1227, 1198 cm⁻¹. 

UV, λmax (log ε) 225 (4.01), 278 (3.30), 285 (3.21). Anal. Calc. for C₃₉H₄₅B₁₀O₁₁: C, 58.85; H, 9.44%. 

References
21. The more commonly used reduced temperature scale (77K in K) gives similar results. 
The molar volume contribution for the carborane cage was estimated to be $126.5\,\text{cm}^3\,\text{mol}^{-1}$ by statistical analysis of eight disubstituted $\alpha$- and $\omega$-carborane compounds. To our knowledge, no density data have been reported for disubstituted $p$-carboranes.

The temperature dependence of the calculated molar volume for $5\text{BO}_5$ was assumed to be equal to that measured experimentally for $5\text{CH}_5$.  

The experimental value for $B_{12}\text{H}_{122}^-$ has been measured as $22.0\,\text{Å}^3$.

A. Kaczmarczyk and G. B. Kolski, *Inorg. Chem.*, 1965, 4, 665; calculated (MNDO) value is $18.8\,\text{Å}^3$. Similarly for $p$-carborane disubstituted $o$- and $m$-carborane compounds. To our knowledge, the calculated value is $18.7\,\text{Å}^3$ and for benzene $10.2\,\text{Å}^3$ (exptl. $10.4\,\text{Å}^3$).

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