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## BORON CLUSTERS IN LIQUID CRYSTALS

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**Abstract** 3-Dimensional aromatic moiety was used for the first time in the synthesis of liquid crystals. Several of the prepared compounds, based on  $\sigma$ -aromatic boron clusters **1** and **2**, show only nematic mesophases with relatively high  $T_i$ , good electrochemical but limited thermal stability. Absorption and emission spectra of pyridine derivative **15** are reported. Semiempirical methods were employed in evaluation of molecular properties and design of molecules with large coaxial dipole moments.

### INTRODUCTION

Almost all of the over 10,000 known calamitic liquid crystals<sup>1,2</sup> are built using only three general types of structural elements in the rigid core (Figure 1). Benzene is a prototype for a "flat" aromatic ring (e.g., naphthalene, pyridine, pyrimidine), one of the most often used moiety in the synthesis of liquid crystals. Its aliphatic counterpart is a "pseudo-flat" aliphatic ring (e.g., decalin, piperidine, piperazine) for which cyclohexane is a prototype. Three dimensional core elements are represented by polycyclic aliphatic structures (e.g., cubane, bicyclo[1.1.1]pentane, twistane), and bicyclo[2.2.2]octane can be a prototype of all these structures. Complementing the picture would be a three dimensional aromatic system such as, perhaps, C<sub>60</sub>.

Recently, we have focused our attention on boron clusters **1-6** as attractive candidates for the 3-D aromatic system for liquid crystals. In this paper we provide basic characteristics of the clusters, a description of synthetic methodology, and discuss initial measurements of physical properties of the new materials based on these clusters.

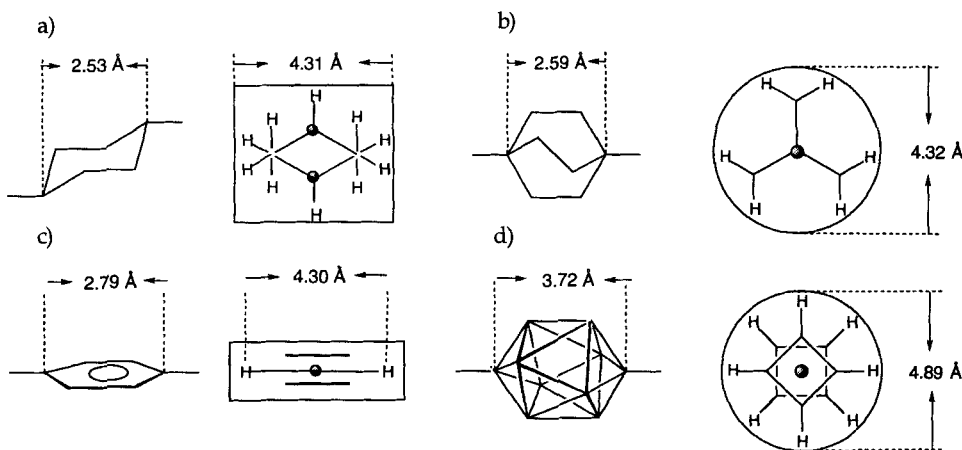
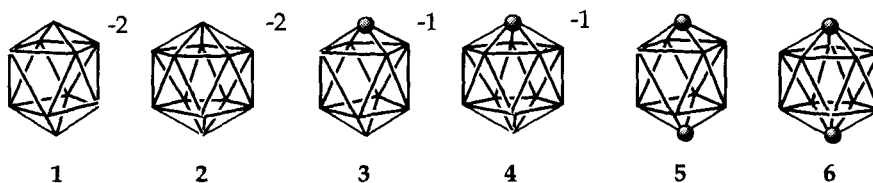


FIGURE 1 Four general types of rigid core elements represented by cyclohexane (a), bicyclo[2.2.2]octane (b), benzene (c), and decahydro-*closo*-decaborate(2-) (d). The distances and dimensions are derived from the literature experimental data.

### WHAT ARE CLOSO-BORON CLUSTERS?

Decahydro-*closo*-decaborate(2-) (**1**) and dodecahydro-*closo*-dodecaborate(2-) (**2**) belong to an extensive family of boron hydrides characterized by three-center two-electron bonds.<sup>3-6</sup> Consequently, the clusters are formally electron deficient, yet are negatively charged. The two additional electrons necessary to complement the closed-shell electronic structure are delocalized over the cage through the  $\sigma$ -framework. This delocalization in the clusters is accompanied by a significant resonance energy stabilization (1.145  $\beta$  and 1.763  $\beta$  for **1** and **2**,<sup>7</sup> respectively), which is revealed in their chemical,<sup>4,8</sup> electrochemical, and thermal stability, as well as in their reactivity towards electrophiles typical for  $\pi$ -aromatic compounds. There are some important differences between this type of aromaticity and that of benzenoid systems:

- *closo*-Boron clusters are  $\sigma$ -aromatic, while benzene is a  $\pi$ -aromatic system.



- The  $\pi$  orbitals characteristic for benzenoids, allowing for  $\pi$ - $\pi$  intermolecular interactions, are absent in the boron clusters, whose surface is covered with hydrogen atoms.

Another consequence of these peculiar electronic structures of clusters **1** and **2** and their carba- analogues **3-6** is a marginal electronic absorption above 200 nm.

The parent anions **1** and **2** show one electron oxidation wave at +0.8 V and >1.4 V, respectively.<sup>8</sup> Their electrochemical stability significantly increases with the number of electron withdrawing substituents and compensation of the negative charge.<sup>9</sup> Thus carboranes **3**, **4**, and **5** show much higher oxidation potential than the parent **1** and **2**, and they were measured to be 1.85 V,<sup>10</sup> >2.4 V,<sup>10</sup> and 2.39 V,<sup>11</sup> respectively.

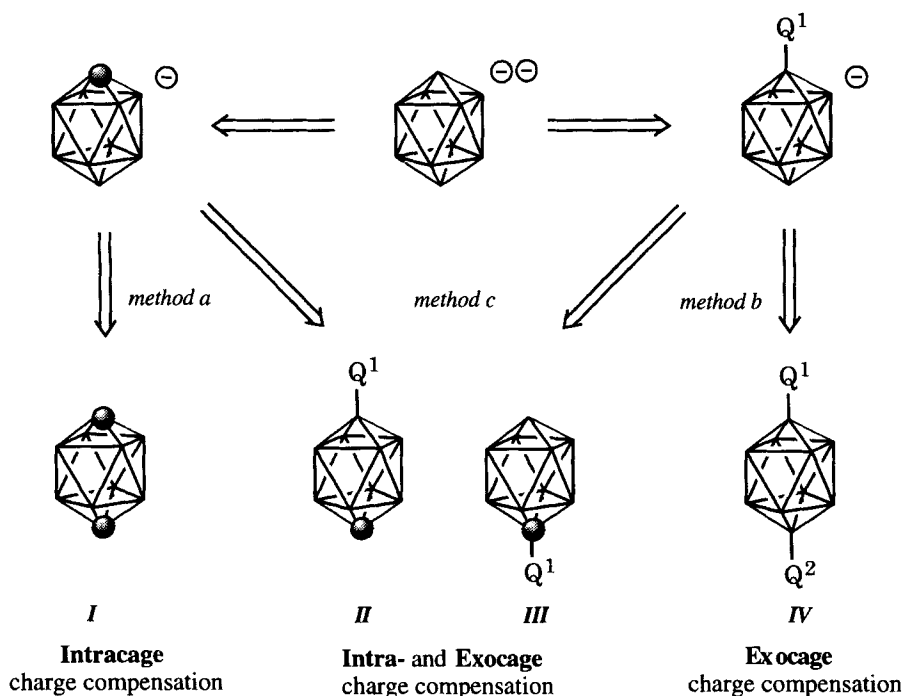


FIGURE 2 Different ways of negative charge compensation in  $B_{10}H_{10}^{2-}$  cluster. The sphere represents a CH fragment, and  $Q^1$  and  $Q^2$  are onium cations such as ammonium, sulfonium, or pyridinium.

It has been documented that boron clusters undergo thermal rearrangements at temperatures above 200 °C, i.e. 1,10- $B_{10}H_8(SMe_2)_2$  rearranges to the 2,7(8) isomer (isolated in 2.8% yield) at 230 °C.<sup>12</sup> Compound 1,10- $B_{10}H_8(NMe_3)_2$  heated at 230 °C for 30 min. undergoes no appreciable isomerization, but at 300 °C it rearranges to a

complex mixture of isomers.<sup>13</sup> Derivatives of **2** are much more resistant to thermolysis, and *p*-carboranes **5** and **6** are thermodynamically stable isomers. Inner salt  $B_{11}H_{11}CNMe_3$  decomposes above 340 °C.<sup>14</sup>

The negative charge of the boron clusters **1** and **2** can be changed from the dinegative to uninegative or neutral by intracage and exocage substitution (Figure 2), i.e., replacement of one boron atom by a carbon atom gives a uninegative isoelectronic monocarborane. The replacement of another BH fragment with a CH group leads to isoelectronic neutral compounds of type **I** (*method a*). The cage charge compensation can also be achieved by substitution of a positively charged group **Q** for a hydrogen atom and a formation of compounds of type **IV** (*method b*). In *method c*, neutral compounds of type **II** and **III** result from a combination of intra- and exocage substitution. In all three methods, charge compensation results in the formation of highly polarized bonds. This is shown in Figure 2 using the 10-vertex series as an example, and it is analogous for the 12-vertex system.

Comparison of extensive semiempirical calculations<sup>15</sup> with experimental data shows that the MNDO method<sup>16</sup> reproduces dipole moments of *closo*-borane derivatives well, and it can be useful in predicting dipolar properties of new compounds. Theoretical analysis of systems **II-IV** (system **I** has  $\mu=0$  D) suggests that while compounds of type **IV** may have maximum dipole moments  $\mu$  of 2 D, compounds of type **II** should have  $9 D < \mu < 11 D$  (Figure 3), and in series **III**, dipole moments should be even larger by 1-2 D.

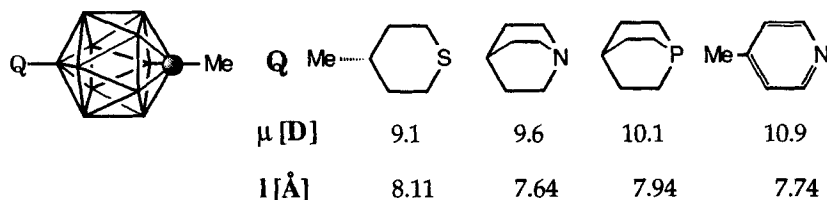


FIGURE 3 Calculated (MNDO) dipole moments ( $\mu$ ) and the length ( $l$ ) of the rigid cores for several derivatives of type **II**. The diameters of the H-H cylinders of rotation are about 5.22 Å.

The theoretical predictions indicate molecular targets for potentially mesogenic compounds with large coaxial dipole moments. While it is relatively simple to approximate molecular properties, it is much more difficult to predict bulk properties such as mesogeneity. Prediction of the latter usually relies on empirical data, but no such

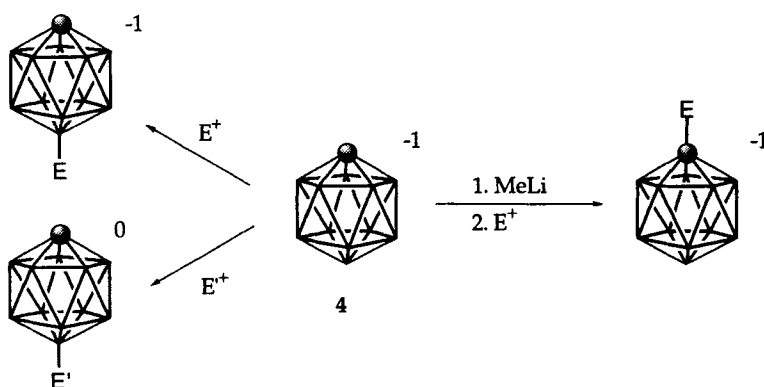
data exists yet for liquid crystals containing boron clusters. Thus, there are two major questions to be addressed:

- How do the boron clusters relate to the three other main classes of core elements with respect to the stability of mesophases ?
- Can the unusual properties of boron cages be utilized in the design and synthesis of new materials with high dielectric anisotropy ?

In this paper we provide initial characterization of mesogenic properties of several derivatives of **1**, **4**, and **6**.

### SYNTHESIS

In general, introduction of a substituent into boron clusters can be achieved in two ways: a) electrophilic substitution at a boron atom, and b) formation of a carboanion and subsequent reaction with an electrophile (C-substitution in carboranes **3-5**). The former reaction usually gives the substituted anion but with some electrophiles neutral compounds are obtained. This is shown in Scheme 1, where monocarborane **4** is used as an example.<sup>17</sup>

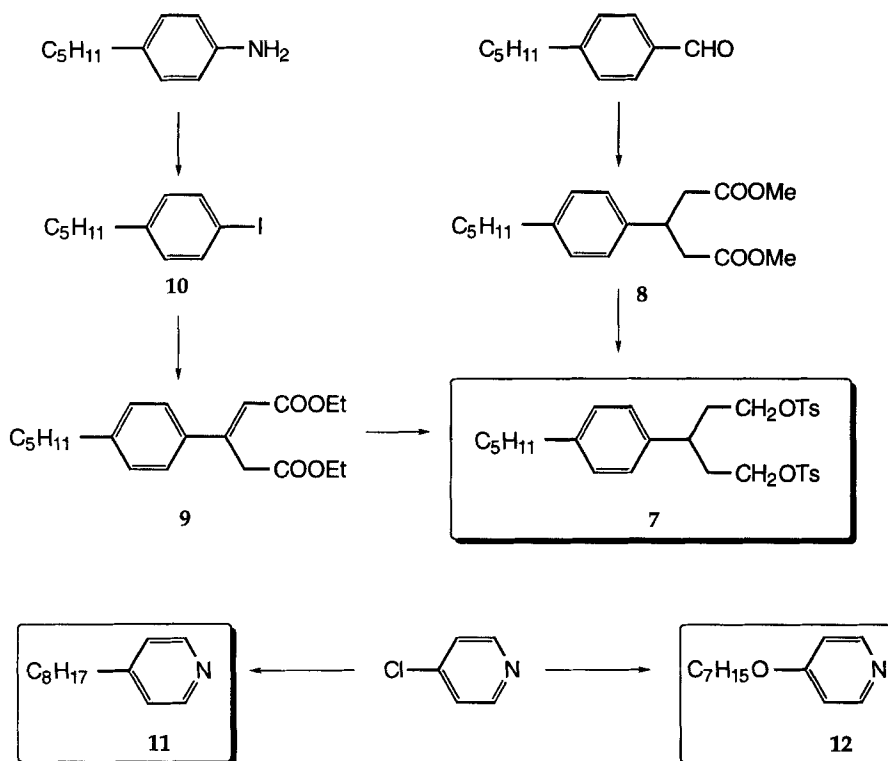


Scheme 1

### Synthesis of non-Boron Precursors

Ditosylate **7** was obtained in two ways (Scheme 2): by classical Knoevenagel's method using Meldrum's acid<sup>18</sup> *via* diester **8**, and by using palladium coupling techniques<sup>19</sup> *via* diester **9**. Experiments show that the latter method is much more efficient and it gives the tosylate in 26% unoptimized overall yield based on 4-iodopentylbenzene (**10**). Two

pyridine derivatives **11** and **12** were synthesized according to general literature procedures<sup>20,21</sup> from 4-chloropyridine (Scheme 2).

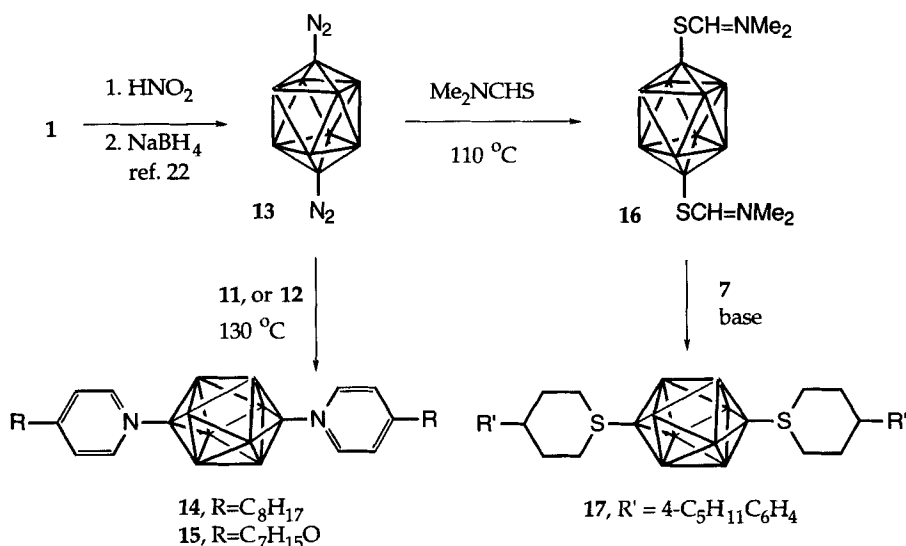


Scheme 2

#### Synthesis with Decahydro-*closo*-decaborate (2-)

Decaborate **1** easily undergoes electrophilic substitution with several reagents, but only reaction with nitrous acid followed by reduction gives exclusively 1,10-bis(dinitrogen)-*closo*-decaborane(8) (**13**).<sup>22</sup> It has been shown that **13** reacts thermally (above 100 °C) with several nucleophiles and radical traps that formally replace the dinitrogen, forming diapically substituted products in good yields.<sup>22</sup> The versatility of the dinitrogen derivative makes it a particularly useful synthetic precursor for the 1,10 derivatives, despite the low yield (25%) of its formation from **1**. Thus, reaction of **13** with pyridines **11** and **12** gave the corresponding 1,10-dipyridine derivatives **14** and **15**, respectively, in about 20% yield (Scheme 3). Adaptation of another literature procedure<sup>23</sup> allowed for conversion of **13** to inner salt **16** in 65% yield. Reaction of **16** with ditosylate **7**, in the presence of base, furnished a good yield of compound **17**,

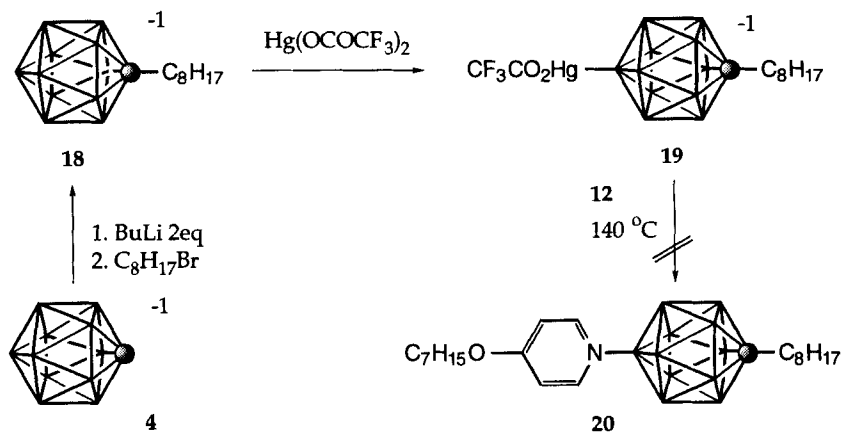
which demonstrates the usefulness of this method in the synthesis of such cyclic sulfides. NMR analysis suggests that the *trans,trans* isomer is accompanied by about 25% of the *cis,trans* isomer, but no further attempts were made to separate pure all-*trans* compound at this time.



Scheme 3

#### Synthesis with 1-Carbadodecahydro-closo-dodecaborate(1-)

Alkylation of the carbon atom in **4** to form **18** was accomplished in 60% yield according to a general method.<sup>24</sup> It was not obvious how to introduce an onium substituent at the 12 position of **18**, since a dinitrogen derivative analogous to **13** is not known, and its

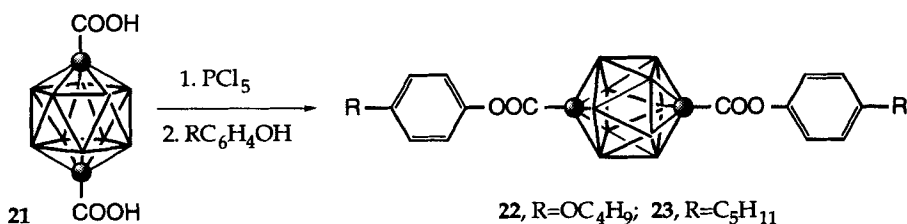




attempted preparation was unsuccessful. It has been mentioned in the literature<sup>24</sup> that a relatively easy to prepare 12-mercuro derivative reacts with nucleophiles (e.g., methoxide, disulfide), and other B-mercured *closo*-boranes react with radical traps, giving the corresponding B-substituted compounds.<sup>25</sup> Thus, mercuration of **18** gave crude compound **19**, which was thermally reacted with pyridine **12**. Spectroscopic analysis of product isolated in a small amount suggested structure **20**. However, elemental analysis indicated a presence of a mercury atom in the structure, perhaps between the N and B atoms.

#### Synthesis with 1,12-Dicarba-*closo*-dodecaborane(12)

Dicarboxylic acid **21**, obtained from commercially available *p*-carborane **6**, was converted into the corresponding phenol diesters **22** and **23** in about 50% yield using a general method.<sup>26</sup>



## RESULTS AND DISCUSSION

New compounds **14**, **15**, **17**, **22**, and **23** have been synthesized and fully characterized. They melt at relatively high temperatures and are easily soluble in aromatic and chlorinated hydrocarbons. They have limited solubility in ZLI-1132 mixture at room temperature.

#### Thermal Analysis

Compound **15** and the two esters **22** and **23** are the only enantiotropic liquid crystals displaying exclusively nematic phases. Enthalpies of transitions are typical for nematic systems and the isotropic transition temperatures compare favorably with those of similar structures (Table I and Table II). The isotropic transitions ( $T_i$ ) extrapolated from measurements in nematic solutions (ZLI-1132) are at surprisingly low temperatures, (in a range from -10 to 30 °C for **14** and **15**) much lower than those for pure substances.

The depression of  $T_i$  of **14** and **15** in ZLI-1132 solutions is largely due to the intermolecular interactions, which are influenced by differences in shape and electron density distribution within the boron clusters and other core ring systems. The MNDO calculations<sup>16</sup> show that while the hydrogen atoms in the parent cluster **1** have some hydride character [H(2):-0.04, B(2): -0.12], in the neutral compounds such as **15**, the equatorial hydrogen atoms are marginally positively charged [H(2):+0.008, B(2): -0.09]. This charge distribution is similar to that in benzene [H: +0.06, C: -0.06], yet very different from that in hexafluorobenzene [F: -0.134; C:+0.134]. These numbers should be considered with caution, and treated as a trend rather than absolute values.

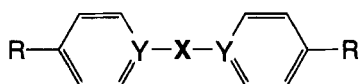
**TABLE I** Transition Temperatures of Esters **22** and **23** and Structurally Similar Compounds<sup>a</sup>

X	R=OC <sub>4</sub> H <sub>9</sub>				R=C <sub>5</sub> H <sub>11</sub>			
	K	S	N	I	K	S	N	I
	136 (7.0)	-	181 (0.4)		104 (5.0)	-	114 (0.3)	
	189	-	235 <sup>b,c</sup>		167	175	213 <sup>c</sup>	
	107	156	209 <sup>d</sup>		101.5	135	161 <sup>e</sup>	
	123	-	198 <sup>f</sup>			<sup>g</sup>		
	129	-	144 <sup>h</sup>			<sup>g</sup>		
	150	-	132.9 <sup>i</sup>			<sup>g</sup>		

<sup>a</sup>Temperatures in degrees C and enthalpy of transition in kcal/mol (in parenthesis). <sup>b</sup>Dewar, M. J. S.; Goldberg, R. S. *J. Org. Chem.* **1970**, *35*, 271. <sup>c</sup>Kelker, H.; Scheurle, B. *J. Physique*, **1969**, *30 C4*, 104. <sup>d</sup>Neubert, M. E.; Ferrato, J. P.; Carpenter, R. E. *Mol. Cryst. Liq. Cryst.* **1979**, *53*, 229. <sup>e</sup>Verbit, L.; Tuggey, R. L.; Pinhas, A. R. *Mol. Cryst. Liq. Cryst.* **1975**, *30*, 201. <sup>f</sup>Geyvandov, R. C. *Diss. Moscow 1979* (see ref. 2, compound 6313). <sup>g</sup>Not available. <sup>h</sup>Kaszynski, P.; Friedli, A. C.; McMurdie, N. D.; Michl, J. *Mol. Cryst. Liq. Cryst.* **1990**, *191*, 193. <sup>i</sup>Gray, G. W.; Langley, N. A.; Toyne, K. J. *Mol. Cryst. Liq. Cryst., Lett.* **1981**, *64*, 239.

Ester **22** shows very good thermal stability. The transition temperatures are identical after heating to 150 °C, but are lower by about 1 °C after exposing the sample to a temperature of 250 °C. In contrast, compounds based on pyridine (**14** and **15**) and **17** decompose above 200 °C, i.e., pure **15** slowly decomposes upon heating (5 °C/min.) to 240 °C, and no transitions are observed in the second DSC trace. The decomposition appears to be accelerated in solutions, and **15** starts to decompose at about 150 °C. All compounds are stable to multi-cycle heating to 120 °C.

**TABLE II Transition Temperatures of Compounds 14 and 15 and Structurally Similar Compounds<sup>a</sup>**



X	R=OC <sub>7</sub> H <sub>15</sub>				R=C <sub>8</sub> H <sub>17</sub>				
	Y=N	K	S	N	I	K	S	N	I
		205 (3.8)	-	225 (0.2)		211 (5.0)	-	-	
Y=C									
		126	211	212 <sup>b</sup>		104.6	178	187 <sup>b</sup>	
		146	183	197 <sup>c</sup>		145	-	151 <sup>c</sup>	
			<i>d</i>			176	191	- <sup>e</sup>	

<sup>a</sup>Temperatures in degrees C and enthalpy of transition in kcal/mol (in parenthesis). <sup>b</sup>Schubert, H.; Hacker, R.; Kindermann, K. *J. Prakt. Chem.* **1968**, *37*, 12. <sup>c</sup>Schubert, H.; Schliemann, W., *Diss. Halle* 1968 (see ref. 1, compounds 4310 and 4301). <sup>d</sup>Not available. <sup>e</sup>Schubert, H.; Schulze, W., *Diss. Halle* 1968 (see ref. 1, compound 3584).

### Electronic Absorption Spectra

Free 4-heptyloxypyridine (**12**) solutions in acetonitrile display a typical UV absorption<sup>27</sup> pattern consisting of a  $\pi$ - $\pi^*$  transition at 218 nm and a weak broad shoulder of  $n$ - $\pi^*$  transition at 246 nm. In compound **15**, the  $\pi$ - $\pi^*$  transition is red-shifted by 14 nm and a new broad intense band, presumably due to a cage-to-ligand charge transfer, appears at 319 nm (Figure 4). The appearance of a similar low energy band at 318 nm was also observed<sup>12</sup> for 1-Me<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>-10-NC<sub>5</sub>H<sub>5</sub>. Compounds **14** and

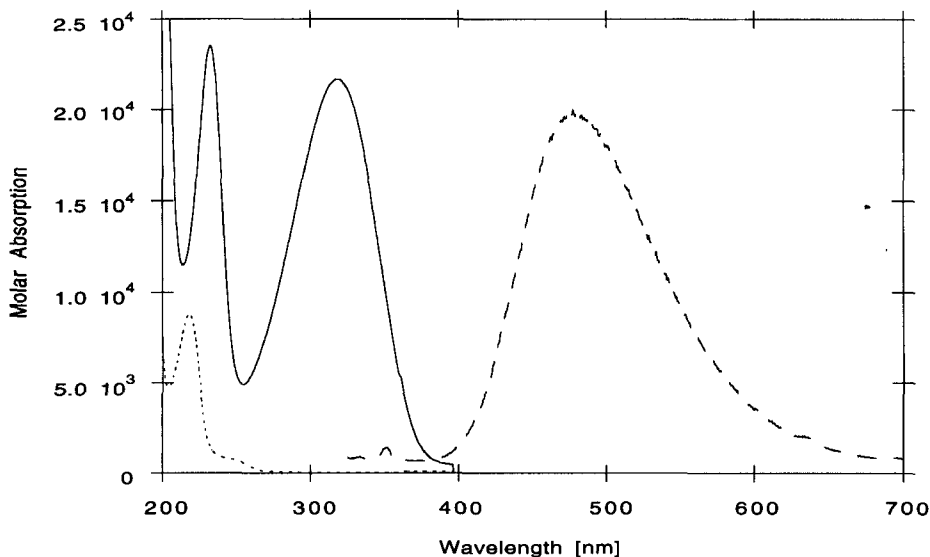


FIGURE 4 Electronic absorption spectra of **12** (····) and its derivative **15** (—), and emission spectrum (---) of **15** excited at 319 nm, in acetonitrile.

**15** both fluoresce, and the maximum of emission is at 480 nm for compound **15** (Figure 4). It should be noted that the photochemical behavior of compounds **14** and **15** is similar to that of pyridine complexes with copper halide clusters whose luminescence phenomena are reasonably well understood.<sup>28,29</sup>

Semiempirical calculations (MNDO) show that the HOMO is largely localized on the boron cluster, while the LUMO is mostly concentrated on the pyridine fragments.

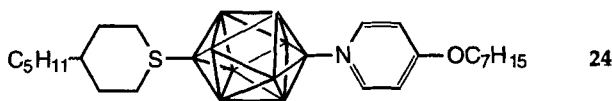
#### Electrochemical Analysis

Cyclic voltametry shows that pyridine derivative **15** undergoes a reversible redox process at  $E_{1/2}$  of 1.30 V. Compound **17** shows higher oxidation potential at 1.76 V, and the process is quasi-reversible.

#### CONCLUSIONS

We have demonstrated that aromatic *closo*-boron clusters can be used for the preparation of mesogenic compounds. Literature synthetic tools and those we have developed open access to a broad class of potential mesogens, some with expected large

dipole moments. Unsymmetrically substituted compounds are particularly attractive, i.e. compound **24** (type IV) displays a good range of nematic phase with  $T_i$  about 130 °C, despite a 20% contamination with the *cis* isomer.



The thermal behavior of derivatives of **1** and a possible thermal *cis/trans* isomerization of compounds of type **17** will require more detailed study. The results presented here are only the tip of the iceberg, and more effort is clearly needed for full evaluation of the usefulness of the clusters in the preparation of mesogens. Synthesis of other compounds based on clusters **1-6** and their physical characterization (e.g., dielectric anisotropy, birefringence, and miscibility) is currently in progress in our laboratory.

### EXPERIMENTAL PART

MOPAC 6.0 package was used in molecular modeling and computational analysis. No symmetry constraints were applied, and full geometry optimizations were obtained. Melting points and optical identification of mesophases were performed on Boetius PHMK 05 polarizing microscope with a hot stage. NMR spectra were obtained on Bruker 300 MHz instrument ( $^{13}\text{C}$  and  $^1\text{H}$  spectra), and Bruker 200 MHz ( $^{11}\text{B}$ ) in  $\text{CDCl}_3$  and referenced to TMS ( $^1\text{H}$  NMR),  $\text{CDCl}_3$  ( $^{13}\text{C}$  NMR), or  $\text{B}(\text{OMe})_3$  ( $^{11}\text{B}$  NMR), unless specified otherwise. IR spectra were recorded using Nicolet Magna 500 instrument in KBr unless specified otherwise. UV spectra were obtained on Shimadzu 2101PC instrument and emission spectra on Spex 1681 instrument in acetonitrile. Mass spectroscopy was performed using Hewlett-Packard 5890 instrument (GCMS). Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia. Thermal analysis was obtained using Mettler DSC 30 instrument. Electrochemical analysis were performed on PAR 273 instrument in acetonitrile with  $\text{Bu}_4\text{NBF}_4$  (0.1 M) as the electrolyte and referenced to SCE.

**3-(4-Pentylphenyl)pentanediol Bistoluenesulfonate (7).** Ester **8** (0.43 g) was reduced with  $\text{LiAlH}_4$  (70 mg) and the crude diol (0.41 g) was reacted with tosyl chloride in pyridine at 0 °C. The oily crude product was purified on Chromatotron ( $\text{CH}_2\text{Cl}_2$ ) to give 0.38 g (50% overall yield) of colorless oil **7**. Reduction of **9** in boiling THF gave 35% yield of pure **7**:  $^1\text{H}$  NMR  $\delta$  0.91 (t,  $J=6.8$  Hz, 3H), 1.27-1.38 (m, 4H), 1.51-1.61

(m, 2H), 1.73-1.83 (m, 2H), 1.86-1.96 (m, 2H), 2.45 (s, 6H), 2.52 (t,  $J=7.8$  Hz, 2H), 2.64-2.72 (m, 1H), 3.62-3.73 (m, 2H), 3.82-3.92 (m, 2H), 6.76 (d,  $J=8.0$  Hz, 2H), 6.95 (d,  $J=8.0$  Hz, 2H), 7.31 (d,  $J=8.1$  Hz, 4H), 7.71 (d,  $J=8.1$  Hz, 4H);  $^{13}\text{C}$  NMR  $\delta$  14.0, 21.6, 22.5, 31.6, 35.5, 37.4, 68.2, 127.2, 127.9, 129.8, 133.0, 138.2, 141.6, 144.7; IR 2929, 1362, 1197, 664  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{38}\text{O}_6\text{S}_2$ : C, 64.49; H, 6.85; S, 11.48. Found: C, 64.67; H, 6.91; S, 11.37.

**Dimethyl 3-(4-Pentylphenyl)pentanedioate (8).** Obtained in a low yield from 4-pentylbenzaldehyde using Meldrum's acid according to a general procedure:<sup>18</sup> mp 37 °C;  $^1\text{H}$  NMR  $\delta$  0.88 (t,  $J=6.3$  Hz, 3H), 1.28-1.35 (m, 4H), 1.55-1.65 (m, 2H), 2.55 (t,  $J=7.8$  Hz, 2H), 2.59-2.76 (m, 5H), 3.59 (s, 6H), 7.11 (s, 4H);  $^{13}\text{C}$  NMR  $\delta$  14.0, 22.5, 31.0, 31.5, 35.5, 37.9, 40.5, 51.5, 126.9, 128.6, 139.7, 141.5, 172.1; IR 1737  $\text{cm}^{-1}$ ; EI MS,  $m/e$  306(M, 9), 275(9), 247(17), 246(100), 189(41), 117(24). Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_4$ : C, 70.56; H 8.55. Found: C, 70.44; H, 8.45.

**Diethyl 3-(4-Pentylphenyl)-2-pentenedioate (9).** 4-Iodopentylbenzene (4.22 g, 15.4 mmol) and diethyl glutaconate (2.87 g, 15.4 mmol) in triethylamine (2.5 mL) were stirred at 100 °C for 1 h under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.116 g, 0.10 mmol) was added and stirring continued for an additional 20 h. The reaction mixture was diluted with 10% aq HCl (*ca.* 30 mL), the mixture was filtered, and the product was extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL). The combined organic layers were washed with saturated aq  $\text{NaHCO}_3$ , dried over  $\text{Na}_2\text{SO}_4$ , the solvent removed, and the crude product was short path distilled (Kugelrohr; 75 °C/ 0.1 T) to give 3.77 g (74% yield) of yellowish oil. Analytical sample was obtained by purification on Chromatotron (ethyl acetate-hexanes, 1:20):  $^1\text{H}$  NMR  $\delta$  0.89 (t,  $J=6.8$  Hz, 3H), 1.19 (t,  $J=7.1$  Hz, 3H), 1.21-1.35 (m with t at 1.30,  $J=7.1$  Hz, 5H), 1.55-1.64 (m, 2H), 2.60 (t,  $J=7.7$  Hz, 2H), 4.12 (q,  $J=7.1$  Hz, 2H), 4.17 (s, 2H), 4.20 (q,  $J=7.1$  Hz, 2H), 6.28 (s, 1H), 7.18 (d,  $J=8.2$  Hz, 2H), 7.37 (d,  $J=8.2$  Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  13.9, 14.0, 14.2, 22.5, 30.9, 31.4, 35.6, 36.9, 60.0, 60.8, 119.0, 126.3, 128.6, 137.9, 144.4, 150.8, 166.4, 170.3; IR 2933, 1742, 1716, 1173  $\text{cm}^{-1}$ ; EI MS,  $m/e$  332 (M, 13), 287(30), 286(37), 258(94), 230(100), 173(30). Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{O}_4$ : C, 72.26; H, 8.49. Found: C, 72.35; H, 8.48.

**4-Iodopentylbenzene (10).** Obtained in 78% yield from 4-pentylaniline in a standard way: bp 76-78 °C/ 0.1 T;  $^1\text{H}$  NMR  $\delta$  0.88 (t,  $J=6.8$  Hz, 3H), 1.27-1.35 (m, 4H), 1.53-1.58 (m, 2H), 2.54 (t,  $J=7.8$  Hz, 2H), 6.93 (d,  $J=8.2$  Hz, 2H), 7.58 (d,  $J=8.2$  Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  14.0, 23.0, 30.9, 31.3, 35.4, 90.5, 130.5, 137.2, 142.5; IR 2956, 2929, 2857, 1485, 1007  $\text{cm}^{-1}$ ; EI MS,  $m/e$  274(M, 45), 217(100). Anal. Calcd for  $\text{C}_{11}\text{H}_{15}\text{I}$ : C, 48.19; H, 5.51. Found: C, 48.42; H, 5.54.

**4-Octylpyridine<sup>30</sup> (11).** Synthesized in 47% yield from 4-chloropyridine<sup>20</sup> and octylmagnesium bromide according to a general procedure<sup>31</sup> using Ni(dppp)Cl<sub>2</sub> as a catalyst<sup>21</sup>: bp 100 °C/0.3 T (lit.<sup>30</sup> 91 °C/0.1 T); <sup>1</sup>H NMR δ 0.88 (t, *J*=6.6 Hz, 3H), 1.22-1.35 (m, 10H), 1.55-1.70 (m, 2H), 2.59 (t, *J*=7.6 Hz, 2H), 7.09 (d, *J*=6.0, 2H), 8.47 (d, *J*=6.0, 2H); <sup>13</sup>C NMR δ 14.0, 22.6, 29.2 (2C), 29.3, 30.3, 31.8, 35.2, 123.9, 149.6, 151.7; EI MS, *m/e* 191(M, 4), 106(83), 93(100).

**4-Heptyloxy pyridine (12).** Synthesized in 76% yield from 4-chloropyridine and sodium heptyloxide according to a general procedure<sup>20</sup>: bp 96-98 °C/ 0.2 T; <sup>1</sup>H NMR δ 0.90 (t, *J*=6.6 Hz, 3H), 1.29-1.42 (m, 6H), 1.42-1.50 (m, 2H), 1.75-1.83 (m, 2H), 3.99 (t, *J*=6.6 Hz, 2H), 6.78 (d, *J*=6.1, 2H), 8.41 (d, *J*=6.1, 2H); <sup>13</sup>C NMR δ 14.0, 22.5, 25.9, 28.8, 28.9, 31.7, 67.8, 110.2, 151.0, 165.0; UV, λ<sub>max</sub> nm (log ε<sub>max</sub>) 218 (3.92), 246 (s, 2.90); IR (neat) 2930, 2858, 1594, 1571, 1503, 1286, 1212, 1017, 818 cm<sup>-1</sup>; EI MS, *m/e* 193(M, 8), 96(100), 95(42), 57(41). Anal. Calcd for C<sub>12</sub>H<sub>19</sub>NO: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.32; H, 10.03; N, 7.13.

**1,10-Bis(4-octylpyridine)-closo-decaborane(8) (14).** 1,10-Bisdinitrogen-closo-decaborane(8)<sup>22</sup> (13, 144 mg) and pyridine 11 (1 mL) were stirred at 120 °C under an atmosphere of nitrogen for 5 h. Excess pyridine was removed under reduced pressure and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and passed through a silica gel plug and washed with more CH<sub>2</sub>Cl<sub>2</sub>. The eluent was evaporated and the resulting semicrystalline product was purified on Chromatotron (CH<sub>2</sub>Cl<sub>2</sub>-hexanes, 5:2) and recrystallized from hexanes to give 85 mg (20% yield) of white crystals: <sup>1</sup>H NMR δ 0.90 (t, *J*=6.6 Hz, 3H), 1.24-1.44 (m, 8H), 1.73-1.79 (m, 2H), 2.86 (t, *J*=7.6 Hz, 2H), 7.53 (d, *J*=6.7, 2H), 9.43 (d, *J*=6.7, 2H); IR 2930, 2489 cm<sup>-1</sup>; EI MS, *m/e* 500(53), 499(99), 498(100), 497(63), 496(29). Anal. Calcd for C<sub>26</sub>H<sub>50</sub>B<sub>10</sub>N<sub>2</sub>: C, 62.61; H, 10.10; N, 5.62. Found: C, 62.53; H, 10.02; N, 5.61.

**1,10-Bis(4-heptyloxy pyridine)-closo-decaborane(8) (15).** It was synthesized in 18% yield as described for 14: <sup>1</sup>H NMR δ 0.92 (t, *J*=6.6 Hz, 3H), 1.30-1.44 (m, 6H), 1.44-1.56 (m, 2H), 1.85-1.95 (m, 2H), 4.22 (t, *J*=6.5 Hz, 2H), 7.12 (d, *J*=7.3, 2H), 9.34 (d, *J*=7.3, 2H); <sup>13</sup>C NMR δ 14.0, 22.6, 25.7, 28.6, 28.9, 31.7, 70.0, 111.5, 149.6, 168.6; <sup>11</sup>B NMR δ -27.1 (d, *J*<sub>BH</sub>=145 Hz, 4 B), 15.7 (br s, 1B); UV, λ<sub>max</sub> nm (log ε<sub>max</sub>) 232 (4.37), 319 (4.34); IR 2925, 2849, 2490, 1633, 1512, 1459, 1309, 1201 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>46</sub>B<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 57.34; H, 9.22; N, 5.57. Found: C, 57.50; H, 9.25; N, 5.66.

**1,10-Bis(N,N-Dimethylthioformamide-S)-closo-decaborane(8) (16).** A mixture of 1,10-bisdinitrogen-closo-decaborane(8)<sup>22</sup> (13, 172 mg) and dimethylthioformamide (5 mL) was stirred at 120 °C under an atmosphere of nitrogen overnight. Excess formamide was removed under reduced pressure, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>

(1 mL) and passed through a silica gel plug. Purification on Chromatotron (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, 1:4) yielded 190 mg (65%) of yellow crystals: mp 270 °C dec.; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ -0.2-1.6 (br, 4H), 3.37 (s, 3H), 3.53 (s, 3H), 9.72 (s, 1H); <sup>13</sup>C NMR (CD<sub>3</sub>CN) δ 42.0, 48.9, 188.1; <sup>11</sup>B NMR (CD<sub>3</sub>CN) δ -24.7 (d, *J*<sub>BH</sub>=143 Hz, 4B), 7.5 (br s, 1B); IR 2486, 1592, 1415, 1136 cm<sup>-1</sup>. Anal. Calcd for C<sub>6</sub>H<sub>22</sub>B<sub>10</sub>N<sub>2</sub>S<sub>2</sub>: C, 24.47; H, 7.73; N, 9.51; S, 21.77. Found: C, 24.74; H, 7.60; N, 9.60; S, 21.59.

**1,10-Bis[4-(4-pentylphenyl)thiacyclohexane]-closo-decaborane(8) (17).** A mixture of **16** (37 mg), ditosylate **7** (140 mg), and tetramethylammonium hydroxide pentahydrate (100 mg) in acetonitrile (5 mL) was stirred at ambient temperature under an nitrogen atmosphere overnight. The resulting suspension was poured into water, white precipitate was filtered off, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and filtered through a silica gel plug. The filtrate was evaporated and the resulting white solid (70 mg) was recrystallized from toluene-hexanes mixture to give 40 mg of white crystalline product: mp 269 °C dec.; <sup>1</sup>H NMR δ 0.90 (t, *J*=6.7 Hz, 3H), 1.25-1.47 (m, 4H), 1.53-1.67 (m, 2H), 2.13-2.29 (m, 2H), 2.42-2.53 (m, 2H), 2.60 (t, *J*=7.7 Hz, 2H), 2.81-2.89 (m, 1H), 3.58-3.66 (m, 2H), 3.77-3.82 (m, 2H), 7.17 (s, 4H). Anal. Calcd for C<sub>32</sub>H<sub>56</sub>B<sub>10</sub>S<sub>2</sub>: C, 62.70; H, 9.21; S, 10.46. Found: C, 62.59; H, 9.26; S, 10.59.

**Trimethylammonium 1-Octyl-1-carbaundecahydro-closo-dodecaborate(1-) (18).** Vacuum dried monocarborane **4** trimethylammonium salt<sup>32</sup> (1.05 g, 5 mmol) was dissolved in dry THF (25 mL) and under an atmosphere of nitrogen, butyllithium in hexanes (1.6 M, 8 mL) was slowly added at 20 °C. The mixture was stirred for 30 min. allowing the liberated NMe<sub>3</sub> to escape, and octyl bromide (1.5 mL) was added at once. The mixture was stirred overnight, water was added, and evaporated to dryness. Water was added, the solution was filtered and washed with hexanes. The clear yellowish aqueous layer was treated with excess NMe<sub>3</sub>·HCl, and the resulting precipitation was filtered off, and washed with water. The crude product (1.4 g) was recrystallized from aqueous ethanol, dissolved in toluene, filtered, and the product was precipitated out with hexanes to give 0.95 g (60% yield) of a creamy solid: mp 136.5 °C; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 0.86 (t, *J*=6.9 Hz, 3H), 1.13-1.36 (m, 12H), 1.73-1.79 (m, 2H), 2.79 (s, 9H); <sup>13</sup>C NMR δ 14.1, 22.6, 29.2, 29.4, 29.5, 30.2, 31.9, 39.3, 46.6; <sup>11</sup>B NMR δ -14.8 (d, *J*<sub>BH</sub>=135 Hz, 10B), -13.6 (d, *J*<sub>BH</sub>=121 Hz, 1B); IR 3412, 3160, 2953, 2929, 2848, 2553, 2532, 1471 cm<sup>-1</sup>. Anal. Calcd for C<sub>12</sub>H<sub>38</sub>B<sub>11</sub>N: C, 45.71; H, 12.15; N, 4.44. Found: C, 45.92; H, 12.02; N, 4.50.

**Trimethylammonium 1-Octyl-12-(trifluoroacetoxymercury)-1-carbadecahydro-closo-dodecaborate(-1) (19).** A solution of 1-octylmonocarborane salt **18** (0.60 g, 1.9 mmol) and anhydrous mercury trifluoroacetate (0.85 g, 2.0 mmol) in dry acetone (5 mL) was stirred and refluxed for 4 days under an atmosphere of nitrogen. Solvent



was removed and the viscous residue was vacuum dried to give a crude viscous product.  $^{11}\text{B}$  NMR spectrum showed a new peak at  $\delta$  -7.2 which appeared to be singlet. The main peak at  $\delta$  -14.8 (d,  $J_{\text{BH}}=142$  Hz) was broader on one side, suggesting peaks belonging to **18**. The crude material was used in the subsequent transformation without further purification.

**Thermal Reaction of 19 with 4-Heptyloxypyridine.** Crude mercurio compound **19** (600 mg) and 4-heptyloxypyridine (**12**, 2 mL) were heated at 130 °C for 5 h under nitrogen atmosphere. Excess pyridine was removed under reduced pressure, the resulting glassy residue was purified on Chromatotron ( $\text{CH}_2\text{Cl}_2$ ), and recrystallized from toluene/hexanes mixture to give white crystals: mp 225 °C dec.;  $^1\text{H}$  NMR (400 MHz)  $\delta$  0.87 (t,  $J=6.9$  Hz, 3H), 0.90 (t,  $J=6.7$  Hz, 3H), 1.10-1.48 (m, 20H), 1.75-1.87 (m, 4H), 4.14 (t,  $J=6.5$  Hz, 2H), 7.19 (dd,  $J_1=5.6$ ,  $J_2=1.3$  Hz, 2H), 8.26 (dd,  $J_1=5.8$  Hz,  $J_2=1.3$  Hz, 2H);<sup>33</sup>  $^{13}\text{C}$  NMR  $\delta$  14.0, 14.1, 22.5, 22.6, 25.7, 28.5, 28.9, 29.2, 29.4, 29.5, 30.2, 31.6, 31.9, 39.0, 69.8, 113.0, 149.2, 168.5;  $^{11}\text{B}$  NMR  $\delta$  -13.9 (d,  $J_{\text{BH}}=147$  Hz, 10B), -6.9 (br s, 1B); IR 2925, 2554, 2490, 1617, 1513, 1306, 1213, 1029  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{48}\text{B}_{11}\text{HgNO}$ : C, 38.80; H, 7.44; N, 2.15. Found: C, 38.80; H, 7.10; N, 2.21.

**1,12-Dicarba-closo-dodecaborane(10)-1,12-dicarboxylic Acid Esters.** Dicarboxylic acid **21** (prepared according to the literature<sup>34</sup> procedure in 87% yield; 120 mg, 0.5 mmol) was suspended in dry benzene (2 mL),  $\text{PCl}_5$  (210 mg, 1 mmol) was added in one portion, and the mixture was gently warmed up. After 40 min. the resulting yellowish homogenous solution was evaporated, and the residual white solid was dissolved in dry THF (2 mL), phenol was added (1.1 mmol), followed by triethylamine (0.15 mL). The mixture was stirred for 1 h at room temperature and evaporated. The resulting solid was dissolved in benzene (1 mL), passed through a silica gel plug and the eluate was evaporated. The crystalline residue was purified on Chromatotron ( $\text{CH}_2\text{Cl}_2$ -hexanes 1:1), and finally the product was recrystallized from hexanes (for **22**) or pentane (for **23**) at -80 °C to give about 50% of total yield.

**1,12-Bis(4-butoxyphenoxycarbonyl)-1,12-dicarba-closo-dodecaborane(10) (22).**  $^1\text{H}$  NMR  $\delta$  0.96 (t,  $J=7.3$  Hz, 6H), 1.421-1.53 (m, 4H), 1.71-1.77 (m, 4H), 3.91 (t,  $J=6.50$  Hz, 4H), 6.80-6.89 (m, 8H);  $^{13}\text{C}$  NMR  $\delta$  13.8, 19.2, 31.2, 68.1, 115.0, 121.4, 143.7, 157.3, 161.0; IR 2941, 2636, 2365, 1761, 1508, 1238, 1185, 981  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{36}\text{B}_{10}\text{O}_6$ : C, 54.53; H, 6.86. Found: C, 54.41; H, 6.94.

**1,12-Bis(4-pentylphenoxycarbonyl)-1,12-dicarba-closo-dodecaborane(10) (23).**  $^1\text{H}$  NMR  $\delta$  0.87 (t,  $J=6.6$  Hz, 6H), 1.24-1.35 (m, 4H), 1.52-1.64 (m, 4H), 2.56 (t,  $J=7.7$  Hz, 4H), 8.86 (d,  $J=8.3$  Hz, 4H), 7.13 (d,  $J=8.3$  Hz, 4H);  $^{13}\text{C}$  NMR  $\delta$  14.0, 22.5, 31.1, 31.3, 35.2, 120.3, 129.3, 141.4, 148.2, 160.8;  $^{11}\text{B}$  NMR  $\delta$  -14.7; IR 2929, 2626, 1759,

1247, 1189  $\text{cm}^{-1}$ . EI MS,  $m/e$  525(35), 524(36), 393(46), 392(48), 391(31), 363(32), 362(64), 361(68), 360(45), 231(39), 230(89), 229(100), 228(67), 227(29), 107(43). Anal. Calcd for  $\text{C}_{26}\text{H}_{40}\text{B}_{10}\text{O}_4$ : C, 59.52; H, 7.68. Found: C, 59.58; H, 7.63.

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