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Journal of Organometallic Chemistry 581 (1999) 28–38

Journal of Organometallic Chemistry

Organic derivatives of *closo*-boranes: a new class of liquid crystal materials

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Received 2 October 1998; received in revised form 25 January 1999

Abstract

closo-Boranes and heteroboranes have been investigated as structural elements for liquid crystals. This paper reviews our progress to date in developing structure-property relationships for these boron cluster mesogens and assesses the effects of both steric and electronic influences on the liquid crystal behavior. The observation that nematic phases are favored over smectic phases is attributed principally to the steric effect of the clusters. Electronic and stereoelectronic effects can lead to materials exhibiting unusual properties. For example, compounds may exhibit high refractive indices yet low birefringence, they may be UV-transparent or, in some cases, exhibit strong charge transfer interactions with π-aromatic systems. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Liquid crystals; Boron deltahedra; Mesogens; Nematic phases

1. Introduction

Liquid crystals are organic or organometallic [1] compounds that exhibit a birefringent fluid phase between the crystal solid and ordinary (isotropic) liquid. The phenomenon, originally discovered by Reinitzer [2] in 1888 while studying the melting behavior of cholesteryl benzoate, has become a technologically important field of science at the boundaries of chemistry and physics. Certainly, the synthesis of stable, room temperature liquid crystal compounds suitable for use in electro-optic devices in the early 1970s revolutionized the display industry [3,4]. Continuing technological advances and new applications have kept up the demand for materials, and the liquid crystal field has burgeoned to the point that more than 70 000 thermotropic liquid crystals are known in the literature [5].

The principal structural requirement for any molecule to form a liquid crystal phase is that it must deviate from spherical symmetry [6]. In keeping with this prerequisite, liquid crystal phases have been observed for molecules shaped like disks, rods, pyramids, crosses and other even more exotic shapes [7–9]. Such shapes allow molecules to form partially ordered bulk materials characterized by long range orientational ordering but lacking the 3-dimensional long range positional order characteristic of typical solid crystals (Fig. 1(a) and (b)). As a consequence, the liquid crystalline phases [10] exhibit birefringence, a property dependent on long range angular correlations normally only associated with crystal phases, and flow, a property associated with the relaxation of positional correlations in liquids.

Rod-like (calamitic) molecules are typically composed of a rigid core comprising several rings (aromatic, aliphatic or heterocyclic) joined by linkages $\mathscr{L}$ (Fig. 1(c), [9,11–13]). It is the mesogenic core that provides the anisotropic interactions necessary for the formation of the liquid crystal phase and which has the dominating influence on bulk properties. Thus, the choice of ring system and linkage is critically important. Probably the most commonly studied core constituents are phenyl, cyclohexyl and bicyclo[2.2.2]octyl rings which can be joined directly or through linking groups, for example ester, azo, alkyl or alkenyl. To reveal the liquid crystal behavior, it is generally necessary to reduce the crystal melting point which is achieved by

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0022-328X/99/$ - see front matter
PII: S0022-328X(99)00088-1

attaching flexible substituents to the mesogenic core via connecting groups *C* (Fig. 1(c), [11,12]). By far the most commonly used flexible substituents are alkyl chains and these can be connected directly or through oxygen, sulfur or alkynyl groups, for example. Thus a chemist can actually take a modular approach to the synthesis of liquid crystalline molecules by selecting functional groups which will impart specific characteristics to the bulk properties and incorporating these in to the generic structure. It should be noted that while structure–property relationships are well developed and it is generally possible to predict whether or not a molecule will be a liquid crystal [5], prediction of the mesophase polymorphism remains a challenge.

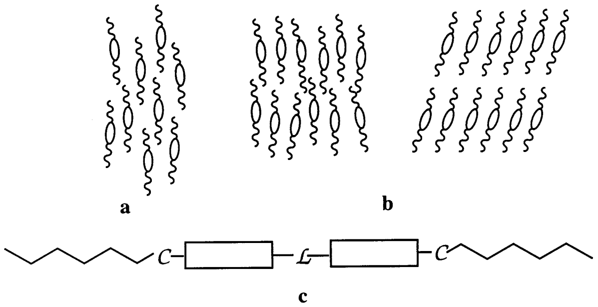


Fig. 1. Molecular arrangements in different calamitic liquid crystalline phases: nematic (a) and smectics (b), and a schematic representation of a rod-like liquid crystal molecule (c). The ovals in (a) and (b) represent the rigid cores and the lines are the flexible tails. The blocks in (c) represent the rigid units joined by linking group $\mathscr{L}$ and attached flexible chains through connectors *C*.

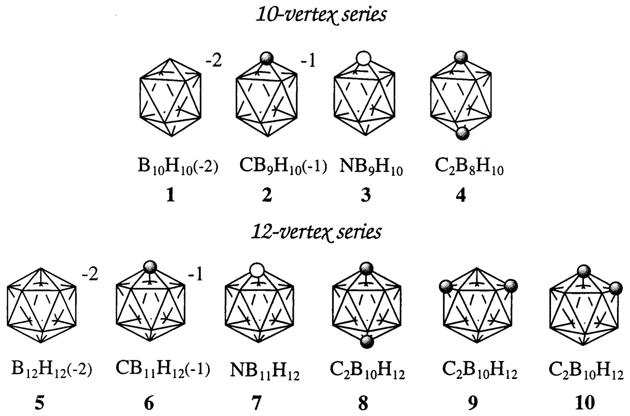


Fig. 2. Skeletal representations of the borates (**1**, **5**), monocarbaborates (**2**, **6**), azaboranes (**3**, **7**), *p*-carboranes (**4**, **8**), *m*-carborane (**9**) and *o*-carborane (**10**) with shown chemical formulas. In the structures each vertex corresponds to a BH fragment and the CH and NH groups are marked by filled and open circles, respectively.

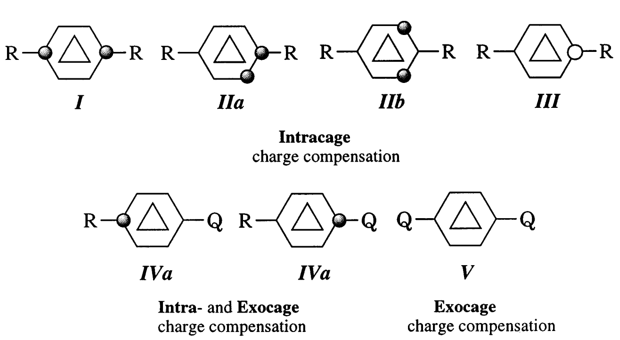


Fig. 3. Five types of neutral derivatives of *closo*-boranes represented by the hexagon. The full and open circles represent C and N atoms, respectively, and Q is an onium fragment such as ammonium, sulfonium, or pyridinium.

2. Boron *closo*-clusters: inorganic building blocks

The geometrical requirements for structural elements for liquid crystal rigid cores are satisfied by *closo*-boranes and heteroboranes especially the five-, six-, ten and twelve-vertex clusters [14–23], i.e. those characterized by high molecular symmetries. Here we will concentrate on the 10- and 12-vertex boranes **1–10** shown in Fig. 2, which are the most readily available and are currently being explored as building blocks for liquid crystals [24–34].

Most of the clusters exhibit high chemical, thermal and electrochemical stabilities with the 12-vertex clusters being generally more stable than their 10-vertex analogs [15–17,19–22]. The azaboranes **3** and **7** appear least stable in the considered series and show a significant reactivity towards nucleophiles [23] and inadequate solvolytic stability [33].

2.1. Polarity

Thermotropic liquid crystals are typically electrically neutral compounds. The negative charge compensation in the parent *closo*-borates, **1** and **5**, can be achieved by using heteroatoms (intra-cage) and/or positively charged onium substituents (*exo*-cage, Fig. 3, [24,26]). Intra-cage charge compensation results in the nonpolar *p*-carboranes **4** and **8** (Type I) or moderately polar *o*- and *m*-carboranes **9** and **10** (Type II) and azaboranes **3** and **7** (Type III) whose dipole moment is less than 5 D [35,36]. The double *exo*-cage charge compensation of **1** and **5** yields highly quadrupolar bisbetaines (Type V) whose dipole moment is predicted to be less than 6 D depending on the substituents [25,26]. The most interesting case, however, is the combination of intra- and *exo*-cage charge compensation characteristic for betaines Type IV because the dipole moments in these derivatives of monocarbaborates **2** and **6** are predicted to be between 10 and 16 D [24–26]. In all types of compounds except for those of Type II the dipole moment vector coincides with the cage-substituent bond direction, which typically lies along the long molecular axis of the mesogenic compound. High dipole moment compounds are critical components for

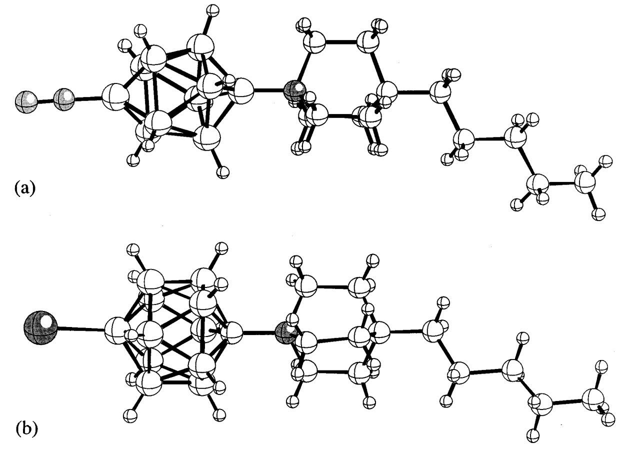


Fig. 4. Ball and stick representation of experimental molecular structures of (a) 1-dinitrogen-10-(4-pentyl-1-quinuclidine)-*closo*-decaborane (**11**) and (b) 12-iodo-1-(4-pentyl-1-quinuclidine)-1-carba-*closo*-dodecaborane (**12**).

electro-optic displays as the resultant high, bulk dielectric anisotropy in the liquid crystal phase ensures a large response to an applied electric field [37,38].

2.2. Molecular dimensions

The overall shapes of the clusters are probably most similar to bicyclo[2.2.2]octane, a well characterized structural element for liquid crystals [39]. The molecular dimensions of the clusters are generally greater than those for bicyclo[2.2.2]octane and its hetero-analogs. Single crystal X-ray analysis of the two quinuclidine derivatives **11** [40] and **12** [41], compounds of Type V and IVb respectively, provides an excellent means to compare the ring sizes for the three general classes of cages (Fig. 4). While the quinuclidine ring is relatively small with $L/D = 2.6$ Å/4.2 Å (where L is the inter-bridgehead intracage distance and D is the diameter of cylinder of rotation defined by the hydrogen atoms), the 10-vertex cluster in **11** (Fig. 4(a)) is larger ($L/D =$ 3.3 Å/4.7 Å) and the 12-vertex in **12** (Fig. 4(b)) is the largest in the series with an aspect ratio of $L/D = 3.1$ Å/5.0 Å.

Molecular symmetries of the clusters are also significantly different from those of typical organic rings (Fig. 5). The clusters have high order rotation axes and intra-cage twist (45 and 36° for 10- and 12-vertex, respectively) and thus their conformational space complements those provided by the organic rings such as bicyclo[2.2.2]octane, benzene and cubane (Fig. 5). Cubane is the only organic ring used in liquid crystals [42] which exhibits the intra-ring twist (60°).

The stereochemical properties of the core rings and the distribution and depth of conformational minima of their derivatives are believed to have an important effect on the dynamic molecular shape and hence on mesophase stability [27,34,43]. The symmetry of the 12-vertex carborane **8** and cubane allows for the terminal alkyl chains to adopt antiperiplanar conformational minima in the entire series of homostructural oligomers regardless of the number of the rings in the core (Fig. 5(a) and (e)). In contrast, the terminally disubstituted oligomers of bicyclo[2.2.2]octane and phenyl should exhibit an ‘odd–even’ effect where the antiperiplanar arrangement of the substituents is available only for the odd number of phenyl rings or even number of bicyclo[2.2.2]octane cages (Fig. 5(c) and (d)). In the series of oligomeric 10-vertex p-carborane derivatives the substituents are expected to be always offset from coplanarity by 45° forming chiral ground state conformers (Fig. 5(b)).

Indeed, single crystal X-ray analysis of bicarboranes **13a** and **13b** shows that while the heptyl chains in the former adopt the antiperiplanar orientation, the substituents in the crystal structure of **13b** are not coplanar, and one is severely disordered [44]. The difficulties with the close packing are also evident from the intermolecular separation in the crystal of **13b** (6.3 Å) which

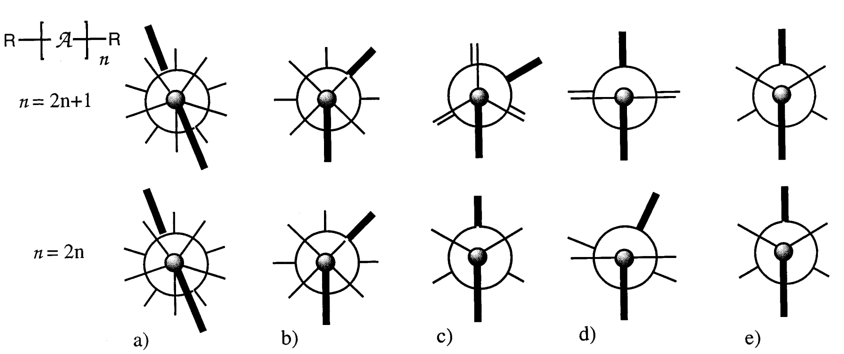
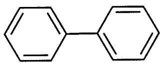
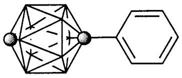
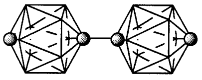


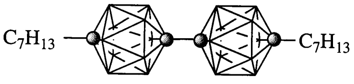
Fig. 5. Extended Newman projection along the long molecular axes of odd- (upper row) and even-membered (lower row) oligomers of (a) 12-vertex p-carborane **8**, (b) the 10-vertex p-carborane **4**, (c) bicyclo[2.2.2]octane, (d) p-phenylene, and (e) cubane. The bar represents the alkyl substituent plane.

Table 1
Calculated (MNDO) polarizabilities (Å^3) and polarizability anisotropies for benzene and carborane compounds [30]

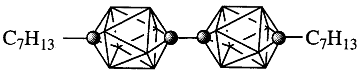
	α_{avg}	$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$[a]
	21.4	15.2
	30.2	10.7
	38.5	7.1

[a] $\alpha_{\parallel}$ is the polarizability tensor along the long molecular axis (α_{xx}) and $\alpha_{\perp}$ is the average of the two remaining diagonal tensor values (α_{yy} and α_{zz}).

is larger than that found in **13a** (6.1 Å) despite the smaller core width for the former.



13a



13b

Besides the distribution of the conformational minima, the heights of the rotational barriers also may affect the dynamic molecular shape and influence the mesogenic properties. Calculations show that conformational interconversion energies for boron *closo* cluster derivatives are generally lower than those for the organic analogs. For instance, ab initio results (HF/6–31G*) for a series of 1-methoxy derivatives show the following order of conformer interconversion energy in kcal/mol: bicyclo[2.2.2]octane (2.66) > phenyl (1.65) > carborane **4** (1.37) > carborane **8** (1.20). The combination of inorganic boron clusters and organic rings such as that in **11** and **12** certainly affects the relative ground state orientation of the terminal substituents, and the expected low interconversion barriers for the cluster-organic ring system may lead to increased conformational flexibility of the mesogens.

From a more fundamental point of view, it is expected that by providing alternative molecular symmetries and magnitudes for rotational barriers, boron clusters will contribute to a better understanding of the role of conformational effects on the bulk properties of liquid crystal materials.

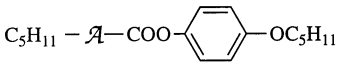
2.3. Electronic structure

The electronic structures of boron *closo* clusters are unique among the rings used in the synthesis of liquid crystals. The clusters are considered to be three dimensional σ-aromatic [45] with an estimated resonance energy of 1.145 β and 1.763 β for **1** and **5** [46], respectively. The high stabilization energy is revealed in their chemical [47,48], electrochemical [48–51], and thermal stability, as well as in their reactivity towards electrophiles, which is reminiscent of π-aromatic compounds. Borates **1** and **5** and their isoelectronic hetero-analogs **2–4** and **6–10** have only a marginal electronic absorption above 200 nm [52,53], but they show significant electronic polarizability [54,55].

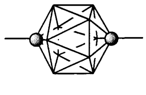
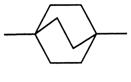
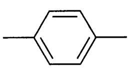
While the average electronic polarizability affects the refractive properties of a material, its anisotropy results in the birefringence of the liquid crystal. The birefringence, or the difference between the refractive indices measured for the two molecular orientations, dictates the magnitude of the electro-optic response of a liquid crystal and so is an important material parameter [37,38]. What is unique about the boron clusters is that while the electronic polarizability is large [54,55], the three-dimensional spherocylindrical symmetry of the cages ensures that the birefringence is low. Calculations on biphenyl, 1,1′-bicarborane and 1-phenylcarborane clearly demonstrate that the carborane imparts a high average polarizability α but low anisotropy of polarizability Δα (Table 1, [30]).

Optical measurements for a series of esters **14** confirmed the theoretical predictions (Table 2). The carborane derivative **14a** has a measured refractive index as

Table 2
Experimental refractive indices measured for **14** at $T - T_{NI} = -12.5$°C [30]



14

	a	c	d
$\mathscr{A}$			 a
Δn	0.057	0.062	0.111
n_{avg}[b]	1.533	1.492	1.534

[a] I.H. Ibrahim, W. Haase, J. Phys. (Paris) 40 (1979) 191.

[b] $n_{avg} = (n_e + 2n_o)/3$.

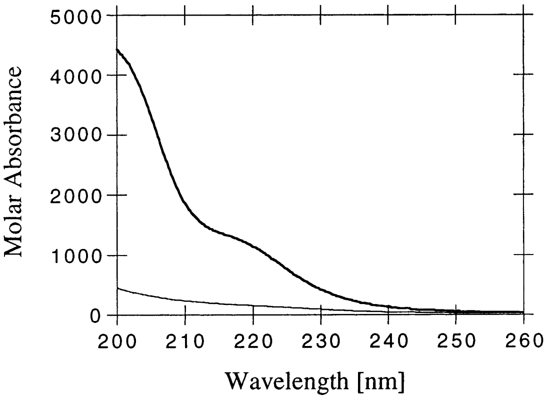


Fig. 6. Absorption spectra for 1-(4-pentyl-1-quinuclidine)-1-carba-*closo*-dodecaborane (**15**) and its 12-iodo derivative **12** (bold line) recorded in acetonitrile.

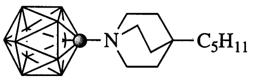
high as the phenyl derivative **14d** but its birefringence is comparable to that of the aliphatic bicyclo[2.2.2]octane derivative **14c** [30].

2.4. Electronic interactions with substituents

Large HOMO–LUMO gaps (> 13 eV) in the *closo* clusters [35] result in only marginal electronic absorptions above 200 nm [52,53]. Our recent studies of the 12-vertex derivative **15** shows absorption typical for saturated aliphatic systems with $\varepsilon = 450$ at $\lambda = 200$ nm (Fig. 6, [56]).

Electronic interactions of the 12-vertex clusters with n and π substituents is rather marginal, and they typically have only modest influence on the electronic spectra [52,57,58]. For instance, the absorption spectrum of iodide **12** [59] exhibits an n–σ* transition shifted by about 45 nm to higher energies relative to the analogous band in an alkyl iodide (Fig. 6). The spectrum of ester **14a** is almost identical to that of its bicyclo[2.2.2]octane analog **14c** [30]. The azaborane cage in 1-phenyl-1-aza-*closo*-dodecaborane (**16**) acts as an auxochrome, shifting the three benzene absorption bands to lower energies in accord with ZINDO calculations [33].

Such a small contribution of the 12-vertex boranes to the UV absorption spectra is desired for materials used in conventional display applications where the photochemical stability and optical dispersion are important issues. We have discovered, however, that symmetrical 1,12-diaryl derivatives of 12-vertex *p*-carborane **17a** and **18a** exhibit a strong new absorption band at about 245 nm and log $\varepsilon > 4$. According to ZINDO calculations, this new absorption is due to the B_u transition and its main component involves excitation from the HOMO localized on the aryls to the LUMO + 3 localized principally on the carborane cage [59].



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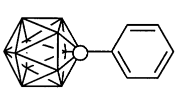

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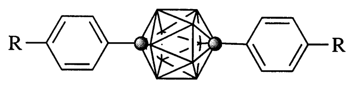
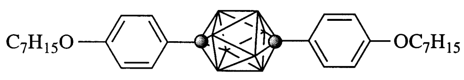
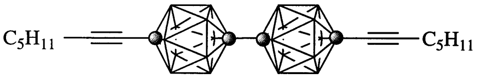


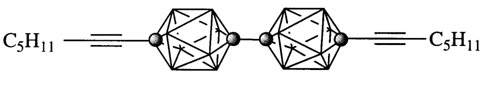
17a, R = OC_7H_{15}
18a, R = $COOC_6H_{13}$



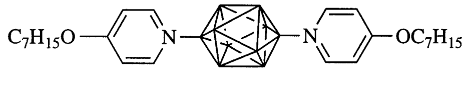
17b



19a



19b



20

The symmetry and energy levels of the MOs in the 10-vertex *closo* clusters are much more suited for electronic interactions with π substituents. Such interactions have been observed spectroscopically for derivatives of $B_{10}H_{10}^{2-}$ [60–62] but reports for other 10-vertex *closo* species are rare. For instance, bisacetylene derivative **19b** exhibits a distinct absorption band at 232 nm while its 12-vertex analog **19a** is virtually transparent above 210 nm [44]. Further evidence for electronic interaction is provided by X-ray analysis. A comparison of X-ray single crystal analyses for the two derivatives revealed a small shortening of the C_{cage}–C_{acet} single bond with simultaneous lengthening of the $C_{acet}{\equiv}C_{acet}$ triple bond in the 10-vertex compound relative to the 12-vertex analog. While the results are crystallographically insignificant, they are consistent with the results of ab initio calculations [44].

The dipyridine derivative **20** and the diphenyl derivative **17b** show strong absorption bands at 319 and 279 nm, respectively (Fig. 7). Analysis of the theoretical models reveals that there are symmetry-allowed cage-to-ring (**20**) or ring-to-cage (**17b**) transitions that involve the HOMO and the LUMO shown in Fig. 8.

In bisbetaines of Type V in which only one of the onium substituents is aryl (pyridine) the electronic excitation should significantly lower the local aryl-cage dipole and result in a substantial increase of the total dipole moment. Calculations suggest that the difference between the ground and excited state dipole moments can be as large as 6 D, and a solvatochromic effect [63] should be observed. Indeed, studies of **11**, **21** and **22** show moderate negative solvatochromic effects (Fig. 9), indicating the dominant role of the

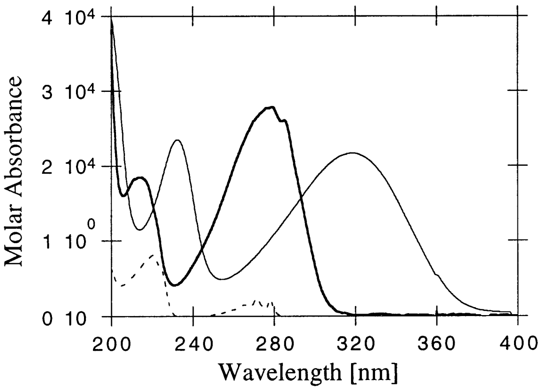
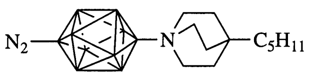


Fig. 7. Absorption spectra for 1,10-bis(4-heptyloxyphenyl)-*p*-carborane (**17b**, bold line), 1,10-bis(4-heptyloxy-1-pyridine)-*closo*-decaborane (**20**) and anisole (dashed line) recorded in hexane.

local rather than overall molecular polarity in the effect [40]. Such materials are of interest as potential liquid crystalline non-linear optical (NLO) chromophores [25,26].



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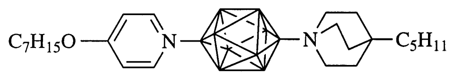

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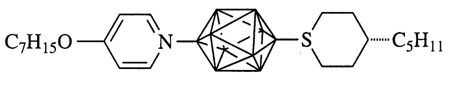

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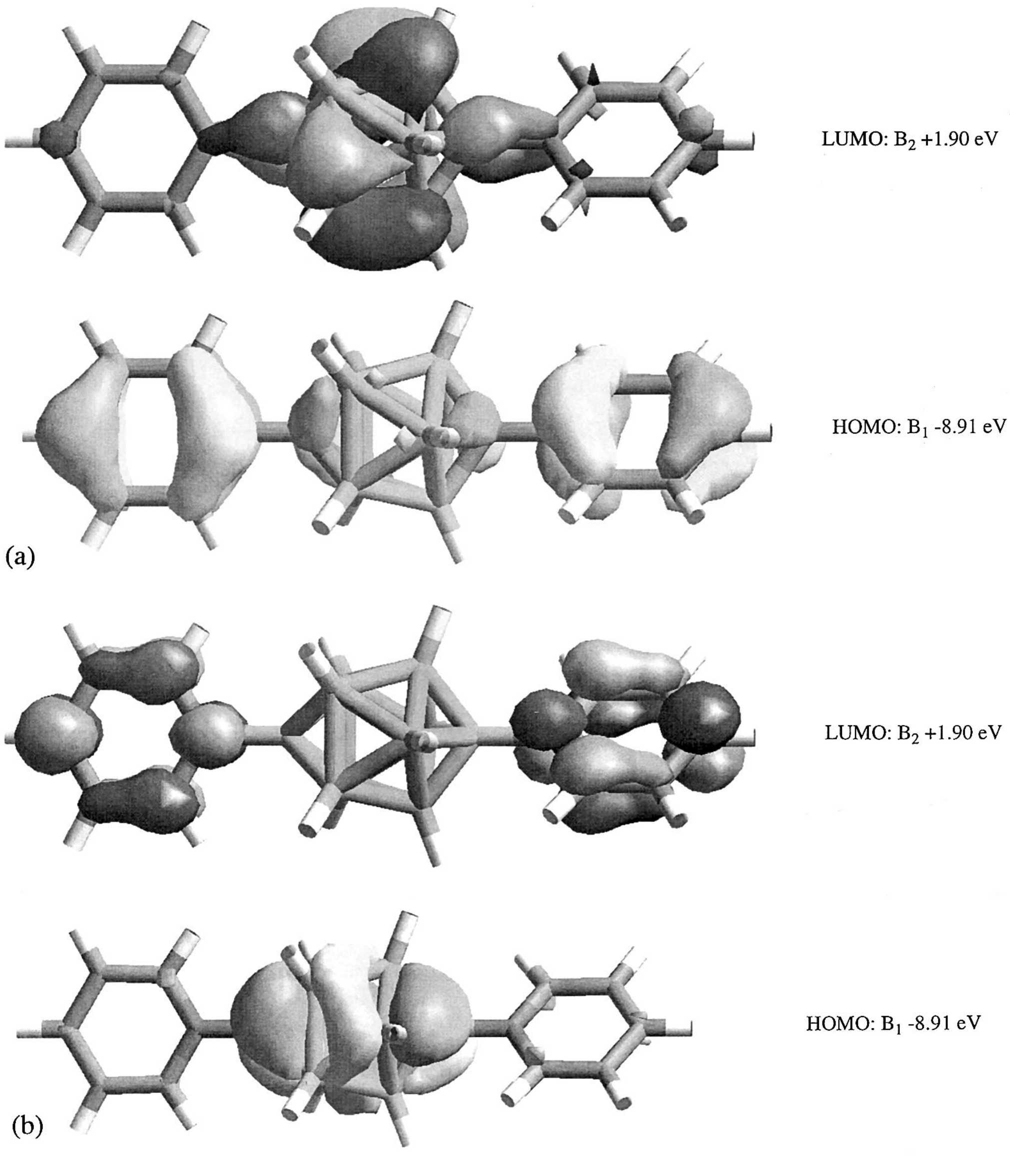


Fig. 8. A representation of the HOMO (lower row) and the LUMO (upper row) orbitals for 1,10-diphenyl-1,10-dicarba-*closo*-decaborane (a) and 1,10-dipyridine-*closo*-decaborane (b).

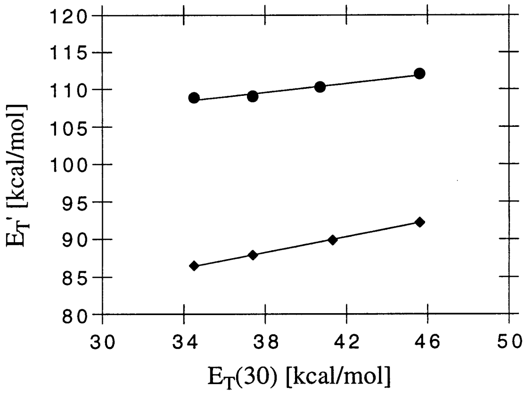


Fig. 9. Correlation between solvent polarity (E_T30 scale) and the charge transfer transition energy E'_T for 1-dinitrogen-10-(4-pentyl-1-quinuclidine)-*closo*-decaborane (**11**, circles) and 1-(4-heptyloxy-1-pyridine)-10-(4-pentyl-1-quinuclidine)-*closo*-decaborane (**21**, squares).

3. Liquid crystal properties

Investigation of compounds synthesized thus far does not allow for formulation of far reaching conclusions, but certain trends are beginning to emerge. The data strongly suggests that boron clusters are nematogenic (i.e. promote nematic phases). Table 3 compares transition temperatures for several pairs of 12- (**a**) and 10- (**b**) vertex carborane mesogens. Inspection of the table shows that in most cases where other rings are present, the choice of carborane has little effect on transition temperatures. For the pairs of homostructural carborane derivatives **13** [27], **19** [27], and **23** [34], the nematic-isotropic transitions are substantially higher for the 12-vertex compound. The largest difference of 90°C (for virtual nematic–isotropic transitions) is observed in the pair of single ring compounds **23a** and **23b** [34]. It has been postulated that these differences may have, in part, conformational origin (see Fig. 5, [27]).

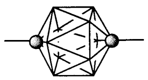
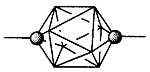
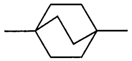
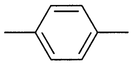
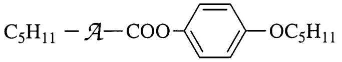
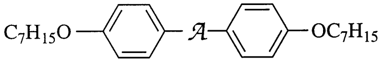
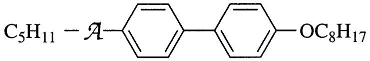
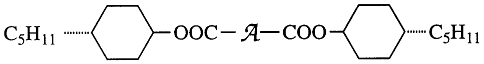
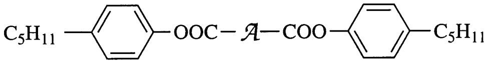
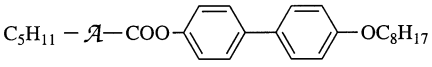
Generally, mesophase thermal stability of the boron cluster derivatives is lower than that for the bicyclo[2.2.2]octane and phenyl analogs. The only exceptions found so far are the series of homostructural one and two ring compounds **13** and **23**, in which the phenyl derivatives exhibit the lowest transition temperatures. The clearing temperatures show some dependence on the position of the carborane ring in the rigid core; a centrally located carborane cage appears less favorable than a terminal position e.g. **17a** versus **24a**. Substitution of carborane for phenyl significantly lowers the clearing temperature and profoundly destabilizes the smectic phases. For instance, the diester **18a** has a monotropic nematic–isotropic transition at 30°C [59] which is lower by about 150°C than the smectic–isotropic transition in the phenyl analog [64]. This smectic phase destabilization and lower mesophase stability presumably is due to ring size disparity and unfavorable broadening of the molecule by the bulky carborane cage. In the saturated esters **25**, however, the carborane and phenyl rings have similar effects on the mesophase stability and the observed N–I transitions are about 160°C [28]. Substituting phenol for cyclohexanol gives carborane ester **26a**, which has a lower clearing temperature of 114°C. A similar decrease in mesophase stability is predicted for the pair of bicyclo[2.2.2]octane analogs **25c** and **26c**. Conversely for the phenyl analogs the substitution increases the clearing point by about 15°C.

The mesophase polymorphism is identical for all pairs of carborane mesogens in Table 3. Most of them display nematic phases, and only the pair **27a** and **27b** exhibits a monotropic smectic C phase in addition to the nematic. Removing the ester linkage in **27a** leads to the appearance of a monotropic smectic A phase in **24a** (the 10-vertex analog has not been prepared). Analogs of many of these compounds having organic rings instead of carborane show very different mesophase polymorphisms. For example, carborane compounds **27a** and **27b** both exhibit smectic C and nematic phases. However, when the carborane cage is replaced with bicyclo[2.2.2]octane, such as in **27c**, smectic A, smectic B and other highly ordered smectic phases are observed in addition to the nematic and smectic C [29]. The bicyclo[2.2.2]octane analog also exhibits the smectic C phase at a temperature 100°C higher than for **27a** and **27b**, demonstrating a further example of smectic phase destabilization by carborane. Presumably the bulkier carboranes broaden molecules, reducing their ability to pack efficiently in the lamellar arrangements that characterize smectic phases.

Introduction of highly polar bonds between the cluster and the substituents in compounds of Type IV and V appears to significantly increase the thermal stability of liquid crystalline phases. For instance, the two-ring derivative **15** has a virtual isotropic transition at 137°C, and its 12-pentyl derivative **28** exhibits a smectic phase with the isotropic transition above the decomposition point at 260°C (Table 4, [56]). Interestingly, compound **28** has one of the highest clearing temperatures for two-ring liquid crystals which is much higher than that for homostructural compounds **13a** and **13c** (Table 3).

The tendency of monocarborane compounds to form high temperature mesophases can be attributed to the presence of a strong molecular dipole moment, but even derivatives of **1** in which two local dipole moments largely cancel each other exhibit enhanced stability of the LC phases. Diquinuclidine derivative

Table 3
Transition temperatures of some carborane-containing liquid crystals and their bicyclo[2.2.2]octyl and phenyl analogs[a]

	$\mathscr{A}$	Ref.	**a**	**b**	**c**	**d**
						
13	$C_7H_{15}-\mathscr{A}-\mathscr{A}-C_7H_{15}$	[27]	Cr 92 Cr 142 N 143 I	Cr 20 C 82 (N 81) I	Cr 47 S 226 I	Cr<20 S$_E$ 20 S$_{E'}$ 35 S$_B$ 61 I
14		[30]	Cr 34 N 36 I	na	Cr 49.5 N 93.5 I	Cr 70 N 81 I
17		[59]	Cr 97 N 99.5 I	Cr 73 N 105 I	na	S 232 ± 23 I[b]
19	$C_5H_{11}-\equiv-\mathscr{A}-\mathscr{A}-\equiv-C_5H_{11}$	[27]	Cr 93.5 Cr 95.5 [N -31] I	Cr 77 [N-73] I	na	Cr 67.5 S 86 I
23	$C_5H_{11}-\mathscr{A}-C_5H_{11}$	[34]	Cr 17 Cr 19 [N -18] I	Cr -3.5 [N-109] I	Cr -14 Cr -10 (N -24.5) I	Cr -49 [N -163] I
24		[28,31]	Cr 71 (S$_A$ 45) N 149 I	na	Cr 89.2 S$_B$ 189.9 S$_A$ 216.4 N 217.0 I	Cr 96.7 S$_E$ 194 S$_B$ 210.5 S$_A$ 221.5 I
25		[28]	Cr 150 N 160 I	na	N 202 ± 10 I[b]	Cr 104 N 165 I
26		[24]	Cr 104 N 114 I	na	Cr 98 N 173 I	Cr 155 N 181 I
27		[28,29]	Cr 80 (S$_C$ 40) N 167 I	Cr 58 (S$_C$ 46) N 153 I	Cr 68 S$_X$ 93 S$_B$ 130 S$_C$ 144 S$_A$ 185 N 219 I	N 185 ± 15 I[b]

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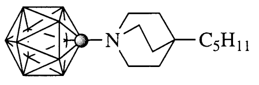
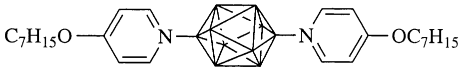
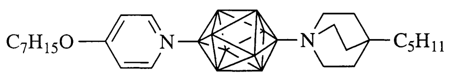
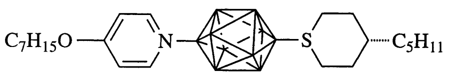
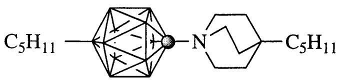
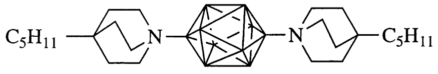
[a] Temperature in °C; Cr-crystal, S-smectic, N-nematic, I-isotropic. Data for non-carborane compounds were obtained from V. Vill, LiqCryst 3.1 database [5].

[b] Extrapolated using Vill's Liq Cryst 3.1 database [5].

Table 4
Transition temperatures of some cluster-containing liquid crystals[a]

	Compound	Ref.	Transition temperature
15		[59]	[N 137] I
20		[24]	Cr 205 N 225 I
21		[40]	Cr 142 Cr 234 S 285 I
22		[40]	Cr 105 N 158 I
28		[59]	Cr 128 S > 260 I
29		[40]	Cr > 320

[a] Temperature in °C; Cr-crystal, S-smectic, N-nematic, I-isotropic.

29 melts with decomposition at about 350°C. Dissymmetrization of **29** and substitution of pyridine for one quinuclidine residue in **21** lowers the melting point and introduces a smectic phase which becomes an isotropic liquid at 284°C with partial decomposition. Interestingly, the isotropic transition for **21** is roughly intermediate between those for dipyridine **20** and diquinuclidine **29** (Table 4). Substitution of thiacyclohexane for quinuclidine in **22** further lowers the melting and isotropic transition temperatures and replaces the smectic phase of **21** with a nematic phase [40].

Studies of phase diagrams revealed that the carborane and monocarborane-containing [56] liquid crystals exhibit ideal miscibility with all organic systems studied thus far [27,29–31,34]. This is remarkable considering that *closo*-boranes are inorganic, occasionally highly polar clusters (e.g. **15**). Results for binary mixtures of two out of three 10-vertex carborane derivatives with a nematic host show a somewhat poorer line fitting than for the 12-vertex analogs, which has been attributed to the unfavorable stereochemistry of the 10 vertex cage (vide supra) [27,34]. We have found that in most cases carborane-containing mesogens strongly destabilize the smectic order, but in rare instances the stability of smectic phases is enhanced [29,31]. In one case it has been postulated that the formation of molecular associates between the carborane and benzene analogs (**24a** and **24d**) is responsible for the stabilization of the S_E phase [31].

Demonstrating miscibility is crucial to potential application of these materials as commercial liquid crystals. Generally, 10–15 components are required to produce the correct combination of properties [37,65]. An example of such a binary phase diagram is given in Fig. 10 where ester **14a** has been mixed with 4-hexylbicyclo[2.2.2]octane-1-carboxylic acid 4-decyloxyphenyl ester and complete miscibility of the nematic phase is observed. For comparison we have also studied the binary mixture of bicyclo[2.2.2]octane analog **14c** and it can be seen that carborane-containing **14a** suppresses the smectic behavior in mixtures more effectively than **14c**.

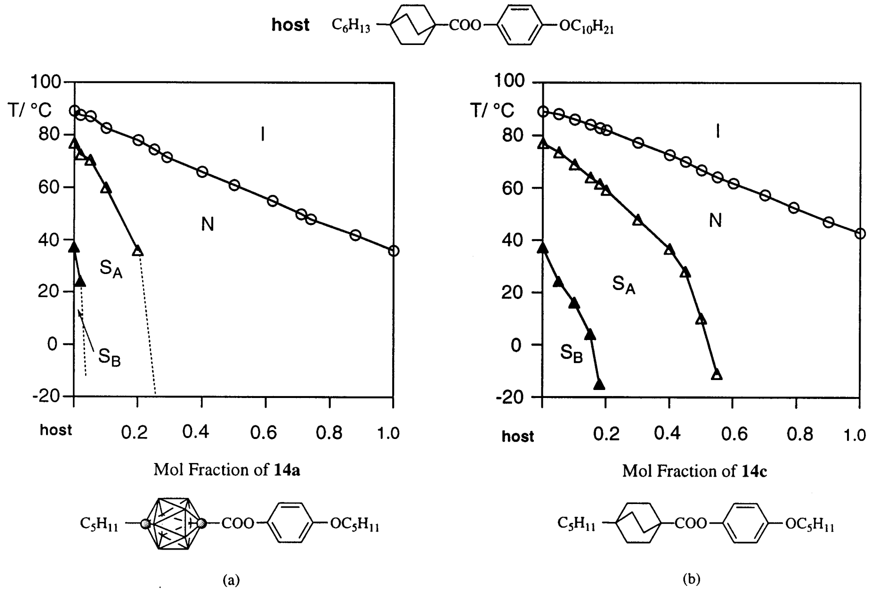


Fig. 10. Binary phase diagrams for 4-hexylbicyclo[2.2.2]octane-1-carboxylic acid 4-decyloxyphenyl ester and (a) 12-pentyl-*p*-carborane-1-carboxylic acid 4-pentyloxyphenyl ester (**14a**) and (b) 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid 4-pentyloxyphenyl ester (**14c**). The lines are guides to the eye.

We have studied 4-pentyloxyphenyl 12-pentyl-*p*-carborane-1-carboxylic ester (**14a**) in some detail and compared its liquid crystal properties with organic analogs (Table 3, [30]). These compounds are of particular interest, since the cyclohexane esters are currently used in display devices [37]. In addition to measuring the liquid crystal transition temperatures, we have measured other properties important for potential device application. Dielectric measurements for **14a** show the small negative dielectric anisotropy of − 1.3 expected for an ester. As stated previously, ester **14a** is unusual in that it exhibits a high average refractive index, yet low birefringence (Table 2). This combination of properties cannot be achieved using organic fragments alone.

The unique attributes of the boron *closo* clusters can provide new information on the intermolecular forces that stabilize liquid crystal phases. For example, it is possible to synthesize pairs of compounds that are isoelectronic and essentially isosteric but with very different polar and quadrupolar properties using borane and carborane analogs. Such molecular systems are very rare, and they have been used in extensive modeling of phase behavior as a function of molecular polarity and quadrupolar interactions [66]. The analog to 1,10-diphenylcarborane derivative **17a** (Table 3) is 1,10-dipyridinedecaborane derivative **20**. Replacement of the C–C links in **17a** with isosteric polar B–N links in **20** dramatically increases the stability of the nematic phase by 120°C presumably because the stronger, intermolecular dipole–dipole associations increase the orientational ordering.

Further study of such isosteric molecular systems will shed more light on the role of the polar interactions in stabilization of liquid crystalline phases.

4. Conclusions

Boron *closo* clusters are effective structural elements for liquid crystal materials and fully compatible with typical organic structures. Combination of the stereoelectronic attributes of the clusters with those of typical organic rings leads to inorganic–organic hybrid materials that can exhibit properties that are not possible using organic fragments alone. For instance, highly polar yet UV transparent liquid crystals can be obtained. On the other hand, by judicious choice of the cluster and substituents, the electronic absorption in the UV region can be controlled and mesogens with potential NLO properties obtained. In general the carborane-containing mesogens show a preference for the formation of nematic phases and can be used to suppress smectic phases in mixtures.

The clusters provide a unique opportunity to address fundamental aspects of the liquid crystal phenomenon. In our work we have begun to probe the role of the conformational energy hypersurface and the polar and quadrupolar effects in liquid crystal behavior. While the results collected thus far are very encouraging, for both theoretical and practical aspects the question as to whether or not these materials are technologically viable remains unanswered, and studies are continuing in our laboratories.

Acknowledgements

Support for this project has been provided by the Petroleum Research Fund (PRF-G 28742), NSF CAREER grant (DMR-9703002), and the National Research Council under the Collaboration in Basic Science and Engineering Program (COBASE).

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