[closo-1-CB\textsubscript{11}H\textsubscript{11}-1-Ph]\textsuperscript{-} as a structural element for ionic liquid crystals

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Dedicated to Professor Vladimir Bregadze on the occasion of his 75th birthday.

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\textbf{A B S T R A C T}

Ion pairs 2[Pyr] and 3[Pyr] containing [closo-1-CB\textsubscript{11}H\textsubscript{11}-1-Ph]\textsuperscript{-} as the structural element were synthesized and their liquid crystalline properties were investigated by thermal and optical methods. Their mesogenic behavior was compared to that of the analogous series 1[Pyr] having a COO linking group between the benzene ring and the cluster, and the observed structure–property relationships are discussed in the context of general trends in related non-ionic liquid crystals.

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1. Introduction

A recently developed method for C-arylation of the [closo-1-CB\textsubscript{9}H\textsubscript{10}]\textsuperscript{-} cluster [1] has opened up possibilities for synthesis of new materials with improved properties. One such class of materials are ionic liquid crystals (ILC), in which the mesogenic properties are driven by the anisometric anion. These compounds are capable of anisotropic cation transport [2–6] and are of interest for ion batteries [7] and solar cell applications [8]. In this context we have demonstrated that closo-carboranates [closo-1-CB\textsubscript{9}H\textsubscript{10}]\textsuperscript{-} (A, Fig. 1) and [closo-1-CB\textsubscript{11}H\textsubscript{12}]\textsuperscript{-} (B) are suitable structural elements for ILC, such as 1A and 1B in Fig. 1 [9–11], and ion pairs 1[Pyr] containing [closo-1-CB\textsubscript{11}H\textsubscript{12}]\textsuperscript{-} (B), exhibit SmA and nematic phases [11]. The new synthetic method [1] opens access to C-aryl derivatives of cluster B and enables synthesis of new series of ILC such as 2[Pyr] and 3[Pyr], including those lacking the ester group and, consequently, with increased chemical stability. The first two members of this new family of ILC, 2c[Pyr] and 2f[Pyr], were reported recently [1].

Here we describe the synthesis and characterization of mesogenic ion pairs 2[Pyr], derived from the [closo-1-CB\textsubscript{11}H\textsubscript{11}-1-Ph]\textsuperscript{-}, with the C\textsubscript{6}H\textsubscript{13} chain and one derivative 3c[Pyr] with double length of the alkyl chain. Properties of the new compounds are compared to those of series 1[Pyr] and are used for structure–property relationship analysis.
2. Results and discussion

2.1. Synthesis

Esters 1b, 1d, 2b, 2c, and 3c were prepared from appropriate carboxylic acids 4[NEt]–6[NMe]4. Thus, carboxylic acids were converted to acid chlorides with (COCl)2 and treated with appropriate phenol 7 or trans-4-pentylcyclohexanol [12] (8) to give desired esters as the [NEt]4+ salts (Scheme 1). The reaction with the cyclohexanol was conducted with five-fold excess alcohol and at high concentration and temperature to assure formation of the esters. Esters 2d[NMe4] and 2e[NMe4] were obtained by esterification of phenol 9[NMe4] with 4-pentylbenzyl chloride and trans-4-pentylcyclohexanecarbonyl chloride, respectively (Scheme 2). Finally, alkylation of phenol 9[NMe4] with tosylate 10 in DMF in the presence of K2CO3 resulted in derivative 2f[NMe4] isolated in 76% yield. The ion pairs 1[Pyr]–3[Pyr] were prepared by exchange of the [NEt]4+ or [NMe]4+ cation for N-butyl-4-heptyloxyprogundium [9,14] (Pyr) in a biphasic CH2Cl2/CH3OH system following the procedure previously reported for the preparation of ion pair 1a[Pyr] [11].


Preparation of iodoacid 11[NMe4] and iodo phenol 12[NMe4] is described elsewhere [11] and involves arylation of [closo-1-CB11H11-12-I] [NMe4]4+ [13] [NMe4]4+ substituted iodobenzene through a carboranylcopper reagent, followed by deprotection of acid or phenol functionality (Scheme 3).

Phenol 7e (Scheme 1) was obtained according to a literature procedure [17], while synthesis of 7b was reported before [18].

2.2. Liquid crystalline properties

Transition temperatures for compounds 1[Pyr] and 2[Pyr] are shown in Table 1. Phase structures were assigned by comparison of POM results with published textures for reference compounds [19].

Compounds in series 2[Pyr] and 3c[Pyr] exhibit a SmA phase identified by the characteristic textures observed in polarized light (Fig. 2a). In ester 2e[Pyr] and ether 2f[Pyr] the smectic phase is enantiotropic with a tendency for supercooling (Fig. 3a), while in the remaining esters the SmA phase is monotropic appearing as much as 26 K below melting for ester 2d[Pyr] (Table 1). Compounds in series 1[Pyr], including the newly synthesized phenyl benzoates 1b[Pyr] and 1d[Pyr], exhibit similar phase behavior. Surprisingly, ester 1b[Pyr] also displays a nematic phase above presumably a SmA phase. The former phase was observed in a supercooled microdroplet (Fig. 2b), while the second phase was detected in some DSC scans (Fig. 3b). Nematic phase is rarely observed in ILC and ion pair 1b[Pyr] represent the second example of a nematic ILC found among boron cluster derivatives [11].

Analysis of data in Table 1 demonstrates that moving the carbonyl group from the [closo-CB11] cluster in 1a[Pyr] to the benzene ring lowers the melting point by 70 K in 2c[Pyr]. Inversion of the direction of the carboxyl group in 2c[Pyr] significantly increases stability of the SmA by 47 K in 2e[Pyr]. In contrast, the same change of the COO group orientation in the benzene analogues 2b[Pyr] and 2d[Pyr] and also in 1b[Pyr] and 1d[Pyr] results in a much smaller increase of mesophase stability by 8 K and 22 K, respectively.

Replacement of the COO group in 2e[Pyr] with the CH2O group in 2f[Pyr] has little effect on the phase stability but significantly lowers the melting point by 31 K.

Compounds with the cyclohexyl ring appear to exhibit more stable SmA phase than their benzene analogues. Thus, replacement of the benzene ring with the cyclohexyl ring Moderately increases the SmA-I transition in the pair 2b[Pyr] and 2c[Pyr], while the same replacement on pairs 1d[Pyr] and 1e[Pyr], and 2d[Pyr] and 2e[Pyr] stabilizes the SmA phase by 46 K and 57 K, respectively.

A comparison of the clearing temperatures Tc in series 1[Pyr] and 2[Pyr] shows that insertion of a COO group between the [closo-1-CB11] and Ph groups increases stability of the mesophase by an
2-pyrrolidinethanol increases the nematic phase stability by 18 K for pairs of ethers. Non-ionic structurally related calamitic mesogens of the general head-to-tail molecular arrangement in the SmA phase in the average of 22 K with the smallest effect for the 1b[Pyr] pair (ΔTc = 18 K) and the largest for the 1d[Pyr] pair (ΔTc = 32 K).

Increasing the chain length has a desired effect on thermal properties of the Sma phase by 45 K leading to a broad rangeenantiotropic mesophase (Fig. 4). This change is presumably due to better matching of the length of substituents at the B(12) and C(1) positions of the [closo-CB11] cluster and consequently better filling space in head-to-tail molecular arrangement in the SmA phase in 3c than in 2c.

Structure–property relationships found in series 1[Pyr] and 2[Pyr] are consistent with trends observed for the N–I transition in non-ionic structurally related calamitic mesogens of the general structure 14 (Fig. 5) [20]. Thus, statistical analysis of the difference in TNI for 16 pairs of isostructural mesogenic esters 14a and 14b, and four pairs of ethers 14c shows that replacement of the benzene ring with cyclohexane increases the nematic phase stability by 18 ± 8 K, 20 ± 7 K and 46 ± 2 K, respectively. On the other hand, changing orientation of the ester group from ester of phenol to ester of cyclohexanol or replacement of the ArOCH2 group with a ArOOC group in cyclohexane derivatives 14d and 14e, significantly increases the N phase stability by about 40 K. Similarly, in isostructural analogues of p-carborane 15, that are closely related to 2d and 2e, the cyclohexyl derivative 15a exhibits higher stability of the nematic phase by 16 K than its benzene analogue 15b (Fig. 6) [21]. Finally, inserting a COO group between 4-pentylobicyclo[2.2.2]octane group and benzene ring in 14f increases the mesophase stability by 21 ± 8 K, which is nearly identical to that observed for three pairs 1[Pyr]/2[Pyr].

3. Summary and conclusions

We have demonstrated that [closo-1-CB11H11-1-Ph]– group is a viable structural element of ionic liquid crystals. The removal of the esters linking group between the cluster and the benzene ring in series 1[Pyr] destabilizes the mesophase by about 20 K, but leads to more chemically stable derivatives, such as 2f[Pyr] that are resistant to hydrolytic conditions. Increasing the length of the chain has a favorable effect on phase stability and range, which is important for further optimization of properties.

Structure–property relationships observed in series 1[Pyr] and 2[Pyr] follow those established for non-ionic liquid crystals, which provides good design tool for new mesogens with desired properties.

4. Experimental section

4.1. General procedures

NMR spectra were obtained at 400 MHz (1H) and 128 MHz (13B) in CD3CN. Chemical shifts were referenced to the solvent (δ 1H, 1.93 ppm) or to an external sample of B(OH)3 in MeOH (δ 13B, 18.1 ppm). Mass spectrometry was acquired in the ESI mode. Optical microscopy and phase identification was performed using a PZO “Biolar” polarized microscope equipped with a HCS250 Insect hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (0.3–1 mg) and a heating rate of 5 K min−1 under a flow of nitrogen gas. For DSC and combustion analyses, each compound was additionally purified by filtering solutions in CH2Cl2 to remove particles, followed by recrystallization from appropriate solvent until constant transition temperatures. The resulting crystals were dried in vacuum at ambient temperature.

4.2. Synthesis of esters 1[NEt4]–3c[NEt4]. General procedure

NMR spectra were obtained at 400 MHz (1H) and 128 MHz (13B) in CD3CN. Chemical shifts were referenced to the solvent (δ 1H, 1.93 ppm) or to an external sample of B(OH)3 in MeOH (δ 13B, 18.1 ppm). Mass spectrometry was acquired in the ESI mode. Optical microscopy and phase identification was performed using a PZO “Biolar” polarized microscope equipped with a HCS250 Insect hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (0.3–1 mg) and a heating rate of 5 K min−1 under a flow of nitrogen gas. For DSC and combustion analyses, each compound was additionally purified by filtering solutions in CH2Cl2 to remove particles, followed by recrystallization from appropriate solvent until constant transition temperatures. The resulting crystals were dried in vacuum at ambient temperature.

Table 1
Transition temperatures (°C) and enthalpies (kJ/mol, in parentheses) for 1[Pyr] and 2[Pyr].

<table>
<thead>
<tr>
<th>L</th>
<th>A</th>
<th>1[Pyr]</th>
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<td></td>
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<td>C1</td>
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<td></td>
<td>a</td>
<td>Chx</td>
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<td></td>
<td>b</td>
<td>Ben</td>
<td>Cr 104 (SmA 87 N 93)1/3 (64.4) (0.7) (1.7)</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>Chx</td>
<td>Cr 108 (SmA 92)1/3 (45.4) (3.9)</td>
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<tr>
<td></td>
<td>d</td>
<td>Ben</td>
<td>Cr 125 (SmA 115)1/3 (47.7) (3.6)</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>Chx</td>
<td>Cr 136 SmA 139 (56.9)</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>Chx</td>
<td>Cr 105 SmA 141 (40.9) (7.7)</td>
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* Transition temperatures obtained on heating.
* Monotropic transition.
* Obtained on cooling.
* Ref. [1].
* Combined enthalpy.

![Fig. 2. Optical textures of a SmA phase for 2f[Pyr] (a) and a nematic phase for 1b[Pyr] in a supercooled microdroplet (b). Magnification x50.](image)
[closo-1-CB\textsubscript{11}H\textsubscript{10}-1-C\textsubscript{6}H\textsubscript{4}COOH-12-C\textsubscript{12}H\textsubscript{25}]\textsuperscript{+} \text{[NMe\textsubscript{4}]\textsuperscript{+}} \text{[6(NEt\textsubscript{4})]} (0.12 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2 mL), oxalyl chloride (COCl\textsubscript{2}) (0.15 mmol) was dissolved in excess SOCl\textsubscript{2} (2 mL), pyridine (24 mg, 0.3 mmol) was added followed by phenol (102 mg, 0.6 mmol) was added and the reaction mixture was stirred at ambient temperature overnight. For the preparation of esters \textit{2b[NEt\textsubscript{4}]}, crude acid chloride was dissolved in pyridine (48 mg, 0.6 mmol), trans-pentylcyclohexanol [12] (102 mg, 0.6 mmol) was added and the reaction mixture was stirred at 90 °C for 2 days followed by removal of volatiles in vacuo. The resulting reaction mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} and washed twice with 10% HCl. The organic layer was separated, and the aqueous layer was extracted (CH\textsubscript{2}Cl\textsubscript{2}). Combined CH\textsubscript{2}Cl\textsubscript{2} layers were dried (Na\textsubscript{2}SO\textsubscript{4}) and solvent evaporated giving a white crystalline solid product. Further purification was achieved by repeating recrystallization from EtOH/H\textsubscript{2}O mixtures (3–5×), and ACO\textsubscript{Et}/n-hexane mixtures (2×) providing pure product as white crystalline material.

### 4.3. Preparation of \textit{1[Pyr]}–\textit{3[Pyr]} General procedure

The ion pair \textit{1[NEt\textsubscript{4}]}, \textit{2[NEt\textsubscript{4}]}, or \textit{3[NEt\textsubscript{4}]} was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and N-butyl-4-heptyloxypyridinium bromide [9] (2.0 equiv) was added resulting in formation of a precipitate. Water was added and the biphasic system was stirred vigorously until all the precipitate had dissolved. The CH\textsubscript{2}Cl\textsubscript{2} layer was separated, and the aqueous layer was extracted with additional CH\textsubscript{2}Cl\textsubscript{2}. The CH\textsubscript{2}Cl\textsubscript{2} layers were combined, dried (Na\textsubscript{2}SO\textsubscript{4}), evaporated and the resulting product was passed through a short silica gel plug (CH\textsubscript{2}Cl\textsubscript{2}) giving a white crystalline solid product. Further purification was achieved by repeating recrystallization from EtOH/H\textsubscript{2}O mixtures (3–5×), and ACO\textsubscript{Et}/n-hexane mixtures (2×) providing pure product as white crystalline material.

### 4.3.1. Ester \textit{1b[Pyr]}

Obtained in 55% overall yield according to Method A: \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN) \( \delta \) 0.40–2.50 (m, 10H, B-H), 0.47–0.58 (m, 2H, B-Ch\textsubscript{2}H), 0.88 (t, J = 6.7 Hz, 3H, CH\textsubscript{3}2), 0.91 (t, J = 6.8 Hz, 6H, CH\textsubscript{3}2), 0.96 (t, J = 7.4 Hz, 3H, CH\textsubscript{3}2), 1.13–1.41 (m, 20H, CH\textsubscript{2}2), 1.42–1.50 (m, 20H, CH\textsubscript{2}2), 1.60–1.68 (m, 2H, CH\textsubscript{2}2), 1.77–1.92 (m, 4H, CH\textsubscript{2}2), 2.64 (t, J = 7.8 Hz, 2H, Benz-CH\textsubscript{2}CH\textsubscript{2}), 4.29 (t, J = 6.7 Hz, 2H, O-CH\textsubscript{2}2), 4.31 (t, J = 8.1 Hz, 2H, N=CH\textsubscript{2}), 7.13 (d, J = 8.5 Hz, 2H, Benz-H\textsubscript{2}), 7.19 (d, J = 8.7 Hz, 2H, Benz-H\textsubscript{2}), 7.28 (d, J = 8.5 Hz, 2H, Benz-H\textsubscript{2}), 7.34 (d, J = 7.4 Hz, 2H, Pyr-H), 8.17 (d, J = 8.7 Hz, 2H, Benz-H\textsubscript{2}), 8.39 (d, J = 7.3 Hz, 2H, Pyr-H); \textsuperscript{13}C \textsuperscript{(1)}H NMR (100 MHz, CD\textsubscript{3}CN) \( \delta \) 13.8, 14.4, 14.5, 14.6, 20.0, 21.2 (br), 23.2, 23.3, 23.6, 26.3, 29.2, 29.6, 31.2, 31.3, 31.7, 32.2, 32.5, 32.9, 33.6, 33.8, 36.6, 60.6, 72.4, 114.8, 123.3, 123.9, 127.7, 129.8, 131.0, 146.4, 149.6, 149.7, 150.8, 163.8, 166.1, 167.6, 171.7. Anal. Caled for C\textsubscript{22}H\textsubscript{77}N\textsubscript{11}O\textsubscript{5}: C, 64.02; H, 8.95; N, 1.78. Found: C, 64.32; H, 8.95; N, 1.82.

### 4.3.2. Ester \textit{3d[Pyr]}

Obtained in 56% overall yield according to Method A: \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN) \( \delta \) 0.40–2.50 (m, 10H, B-H), 0.47–0.58 (m, 2H, B-
(d, 9.46; N, 1.85. (128 MHz, CDCl3) 0.41 (t, J = 7.8 Hz, 2H, Benz-CN) 2.50 (m, 10H, B-{C19}) 6.9 Hz, 2H, O-{C14}); 3.05 (t, J = 7.6 Hz, 2H, CH2); 3.37 (m, 2H, CH2); 1.92 (m, 6H, C-{C0}); 1.84 (m, 4H, CH2). 2.64 (t, J = 7.6 Hz, 2H, Benz-CN); 4.29 (t, J = 6.6 Hz, 2H, O-CN); 4.31 (t, J = 7.5 Hz, 2H, N-C{C0}); 7.11 (d, J = 8.5 Hz, 2H, Benz-CN); 2.72 (d, J = 8.4 Hz, 2H, Benz-CN); 3.23 (d, J = 7.5 Hz, 2H, Pyr-CN); 11B[1] (128 MHz, CDCl3) δ = 13.4 (5B), –11.6 (5B); 3.9 (br, 1B). Anal. Calcld for C4H3BN2O5: C, 66.20; H, 9.48; N, 1.88. Found: C, 66.42; H, 9.46; N, 1.85.

4.3.5. Ester 2[Pyr]

Obtained in 87% overall yield according to Method B: [1H NMR (400 MHz, CDCl3) δ 0.4–2.5 (m, 10H, B-H), 0.45–0.55 (m, 2H, B-Ch2), 0.87–0.93 (m, 6H, CH3) 0.88 (t, J = 6.9 Hz, 3H, CH3) 0.96 (t, J = 7.4 Hz, 3H, CH3) 0.98–1.06 (m, 2H, CH2), 1.12–1.59 (29H, CH and CH2) 1.80–1.91 (m, 6H, CH3) 2.09–2.12 (m, 2H, CH2) 2.46 (tt, J1 = 12.2 Hz, J2 = 3.6 Hz, 1H, CH–COO) 4.29 (t, J = 6.9 Hz, 2H, O–CH2) 4.31 (t, J = 7.5 Hz, 2H, N-CH2) 6.81 (d, J = 8.8 Hz, 2H, Benz-H) 7.33 (d, J = 7.5 Hz, 2H, Pyr-H) 7.50 (d, J = 8.8 Hz, 2H, Benz-H) 8.39 (d, J = 7.5 Hz, 2H, Pyr-H); 11B[1] (128 MHz, CDCl3) δ = 13.3 (5B), –11.7 (5B); 3.4 (1B). Anal. Calcld for C4H3BN2O5: C, 65.66; H, 10.21; N, 1.87. Found: C, 65.77; H, 10.20; N, 1.94.

4.3.6. Ester 3[Pyr]

Obtained in 28% overall yield according to Method A: [1H NMR (400 MHz, CDCl3) δ 0.40–2.50 (m, 10H, B-H), 0.50–0.63 (m, 2H, B-Ch2), 0.86–0.92 (m, 3H, CH3) 0.96 (t, J = 7.4 Hz, 3H, CH3) 1.00–1.11 (m, 2H, CH2) 1.13–1.41 (m, 37H, CH and CH2) 1.42–1.52 (m, 4H, CH20) 1.78–1.92 (m, 6H, CH2) 2.00–2.08 (m, 2H, CH2) 4.29 (t, J = 6.6 Hz, 2H, O-CH3) 4.31 (t, J = 7.5 Hz, 2H, N-CH3) 4.81 (tt, J1 = 11.1 Hz, J2 = 4.4 Hz, 1H, CH–OOC) 7.34 (d, J = 7.5 Hz, 2H, Pyr-H) 7.59 (d, J = 8.6 Hz, 2H, Benz-H) 7.74 (d, J = 8.5 Hz, 2H, Benz-H).
[14] $^{13}$C NMR (100 MHz, CD$_3$CN) δ 13.7, 14.3, 19.8, 23.2, 26.2, 29.0, 29.5, 32.3, 33.6, 60.1, 72.3, 114.7, 146.8, 171.5