Anion driven ionic liquid crystals: The effect of the connecting group in [closo-1-CB$_9$H$_{10}$]$^-$ derivatives on mesogenic properties

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Anion driven ionic liquid crystals: The effect of the connecting group in [closo-1-CB_{9}H_{10}]^- derivatives on mesogenic properties

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Replacement of the connecting CH_{2} group in ionic liquid crystal 1a[Pyr] with an oxygen atom in 1b[Pyr] resulted in significant destabilisation of the nematic and, to a greater extent, smectic A (SmA) phases, as established from binary mixture studies in 2a[Pyr]. Density functional theory (DFT) modelling of both anions suggests that the destabilisation results from the difference in charge distribution rather than conformational changes. Binary mixture studies demonstrated that all three ionic liquid crystals are compatible with a non-ionic benzoate nematic host 3a.

Keywords: ionic liquid crystals; boron clusters; synthesis

1. Introduction

Recently we demonstrated [1, 2] that boron clusters [closo-1-CB_{9}H_{10}]^- (A, Figure 1) and [closo-1-CB_{11}H_{12}]^- (B) are effective structural elements of ionic liquid crystals (ILCs). We have found that ion pairs that have a total of four rigid structural elements (rings and the monocarbaborate cage) exhibit liquid crystalline properties. This includes ion pairs 1a[Pyr] and 2a[Pyr], which exhibit SmA and, rarely observed in ILCs, nematic phases [2].

In continuing our interest in this class of materials we set out to study the effect of an alkyl chain modification on phase transition. Here we report the investigation of an effect of replacing of the connecting CH_{2} group in 1a[Pyr] with an oxygen atom in 1b[Pyr] on the mesogenic properties of ILCs derived from the [closo-1-CB_{9}H_{10}]^- cluster (A) and our efforts to prepare the sulfur analogue 1c[Pyr]. The results for the two derivatives, 1a[Pyr] and 1b[Pyr], are compared to those in an analogous series of non-ionic benzoate mesogens 3. Finally, we study binary mixtures of ILC 1[Pyr] in 2a[Pyr] and nematogen 3a.

2. Results and discussion

2.1 Synthesis

Esters 1–3 were obtained by esterification of 4-hexyloxy-4′-hydroxyazobenzene (4) [2] with acid chlorides prepared from appropriate carboxylic acids 5 and 6 and oxalyl dichloride (COCl)_{2} (Method A, Scheme 1). The ion pair 1b[NMe_{4}]^+, obtained from acid 5b[NMe_{4}] [3], was converted to 1b[Pyr] by cation exchange in a biphasic CH_{2}Cl_{2}/H_{2}O system, as described previously [1]. Ester 3c was prepared directly from carboxylic acid 6c and phenol 4 in the presence of N,N'-dicyclohexylcarbodiimide (DCC) (Method B).

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10-Pentyloxy carboxylic acid \(5b[NMe_4]\) was obtained by thermolysis of dinitrogen acid \([\text{closo-1-CB}_9\text{H}_8-1-\text{COOH}-10-\text{N}_2]\) (7) in dry pentanol followed by basic workup (Scheme 2) [3]. A similar approach to the preparation of 10-pentylsulfanyl acid \([\text{closo-1-CB}_9\text{H}_8-1-\text{COOH}-10-\text{SC}_5\text{H}_11]\) \((5c[NMe_4])\) was unsuccessful. The dinitrogen acid 7 was insoluble in pentanethiol and its methyl ester \([\text{closo-1-CB}_9\text{H}_8-1-\text{COO}Me-10-\text{N}_2]\) \((8)\) [4] was used instead. NMR analysis of the crude reaction mixture demonstrated the presence of several pentyl residues and at least two \(\text{closo-1-CB}_9\) species even after basic hydrolysis. In one instance, chromatographic separation of the crude mixture gave a low yield of the pentyl ester \([\text{closo-1-CB}_9\text{H}_8-1-\text{COOSC}_5\text{H}_11-10-\text{SC}_5\text{H}_11]\), which was characterised by HRMS technique. The results were reproducible in three runs and the preparation of acid 5c was not pursued further.

4-Pentylsulfanylenzoic acid \((6c)\) [5] was prepared in 44% yield by nucleophilic aromatic substitution of 4-fluorobenzoate salt with pentanethiolate in dimethyl sulfoxide (DMSO) (Scheme 3), under conditions [6] that promote the SRN1 mechanism [7]. This reaction appears to be cleaner than previously reported synthesis of this acid through diazotisation of 4-aminobenzoic acid [5] and more straightforward than multistep preparation from 4-bromothiophenol [8].

2.2 Mesomorphic properties

The transition temperatures and enthalpies of the newly prepared compounds were determined by differential scanning calorimetry (DSC). The phase types were identified by observed microscopic textures in polarised light and the results are shown in Table 1. Analysis of benzoates 3 demonstrated that all three esters form exclusively a nematic phase. This is consistent with the highly nematogenic properties of azobenzene derivatives and exclusive formation of nematic phases by all known [9] alkoxybenzoate esters of alkoxyazophenol, even by those with long alkyl chains [10, 11]. In series 3 the highest clearing temperature is observed for the pentyloxy derivative 3b \((T_{NI} = 233^\circ\text{C})\), while replacement of the connecting O atom with a CH\(_2\) group or S atom lowers the \(T_{NI}\) by about 30 K. The observed trend in \(T_{NI}\) for series 3, O >> CH\(_2\) > S, is the same as in another series of structurally similar mesogens 9 [12, 13] and is consistent with generally higher clearing temperatures for alkoxy derivatives than for their alkyl analogues. However, an opposite trend is observed in bicyclo[2.2.2]octane derivatives in which 4-butoxybicyclo[2.2.2]octane derivatives have lower \(T_{NI}\) values by about 15 K compared with the 4-pentylbicyclo[2.2.2]octane analogues [14]. Results for 10-pentyloxy derivative 1b[Pyr] were surprising. The ion pair had a lower melting point than the 10-hexyl analogue 1a[Pyr] (Table 1) and no mesogenic properties even on cooling by about 35 K below melting. Interestingly, the polymorph obtained from the melt had a lower melting point by 19 K. The mesogenic properties of 1b[Pyr] were investigated in binary mixtures with ILC 2a[Pyr], which was previously used in similar studies [2].
Table 1. Transition temperatures (°C) and enthalpies (kJ mol⁻¹) for selected compounds.

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<td>Cr 134 (SmA 133) N 144 I⁻</td>
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<td>b -O-</td>
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<td>c -S-</td>
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² Obtained on heating. Cr, crystal; SmA, smectic A; N, nematic; I, isotropic. ⁶ Cr–Cr transition at 32°C. ¹ Ref. [2]. ⁴ Heating rate 0.5 K min⁻¹. For a heating 10 K min⁻¹ Cr–Cr transition at 84°C, melting at 86°C, partial crystallization followed by another melting at 91°C. ⁴ Cr–Cr transition at 76°C (21.6 kJ mol⁻¹). ¹ Cr–Cr transition at 109°C (15.4 kJ mol⁻¹).

Figure 3. A plot of N–I (dots) and SmA–N (squares) transition temperatures for binary mixtures of 1a[Pyr] (black solid) and 1b[Pyr] (grey dotted) in 2a[Pyr] as a function of mole fraction.

2.3 Binary mixtures

Virtual transition temperatures for the non-mesogenic ion pair 1b[Pyr] and, for comparison purposes, also for 1a[Pyr] were extrapolated from low concentration solutions in 2a[Pyr]. For both additives the phase transition temperatures changed linearly with respect to the composition of the mixture, as shown in Figure 3, which demonstrates ideal miscibility of the components. The least square fitting lines have high correlation factor (r² > 0.99), and the extrapolated temperatures have uncertainty of ±1 K.

The virtual transition temperatures [TNI] and [TAN] established for ion pair 1a[Pyr] were 2 K lower than those for enantiotropic transitions in the pure material (Table 2). Results for the pentyloxy ion pair 1b[Pyr] showed that the nematic phase is less stable by 65 K than that in hexyl analogue 1a[Pyr], while the extrapolated smectic A–nematic (SmA–N) transition temperature [TAN] is 100 K lower relative to that in 1a[Pyr].

The results clearly demonstrated that the CH₂→O substitution markedly destabilises both mesophases in 1b[Pyr] and has a particularly strong effect on the smectic phase. This effect cannot be attributed only to the difference in conformational properties of acids 5a and 5b. Theoretical analysis at the B3LYP/6-31G(d,p) level of theory [15] demonstrated

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<td>2a[Pyr]</td>
<td>SmA 130 N 135 I⁻</td>
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² Obtained on heating. SmA, smectic A; N, nematic; I, isotropic. ² Ref. [2].
that the C(1)-carboxyl and B(10)-hexyl chain adopt a staggered orientation with respect to the \{closo-1-CB_{10}\} cage in the conformational minimum. Consequently, the ideal dihedral angle between the planes of the two substituents is 45° and all conformers of acid 5a are chiral (Figure 4). In contrast, density functional theory (DFT) analysis of the 10-vertex acid 5b revealed that the substituent is eclipsed relative to the cage resulting in a C1-symmetry of the molecule. Such higher symmetry conformational minimum observed in 5b is expected to have favourable impact on mesophase stability; however, contrary to these expectations, the mesophase in its ester 1b[Pyr] is significantly destabilised. Thus, the origin of this destabilisation likely lies elsewhere, for example, in charge distribution in the anions.

Previous studies demonstrated unusually high basicity of the amino group attached to a boron atom in closo-carboranates [4, 16]. A similar increase of basicity is observed for pentyloxy derivative 5b, which easily protonates at the oxygen atom giving a zwitterionic oxonium acid 5b[H]+ [3]. Analysis of natural charges (obtained from natural bond orbital (NBO) analysis of the self-consistent field (SCF) wavefunction within Gaussian 09) [17] indeed shows that the cage in acid 5b has smaller overall negative charge by -0.19e than in acid 5a and the B(10)-oxygen atom has a substantial negative charge of -0.70e (Figure 4). This difference in charge distribution and localisation of a substantial negative charge on the oxygen atom may lead to strong coulombic interactions with the pyridinium and ion alignment unfavourable for the formation of a mesophase. This is consistent with the observed particularly strong destabilisation of the smectic phase (Table 2).

The three ILCs, 1a[Pyr], 1b[Pyr] and 2a[Pyr], were also investigated as additives to non-ionic hexylbenzoate mesogen 3a (Table 2 and Figure 5). The ion pairs were fully miscible with the nematic host and the N–I transition temperature exhibits approximately linear dependence on concentration (r^2 > 0.97). For concentrations >8 mol\% SmA phase induction was observed in all three binary systems. It can be estimated that the nematic phase is replaced completely with SmA at concentrations of about 32–35 mol\% for the 10-vertex derivatives, 1a[Pyr] and 1b[Pyr] (Figure 5), and at even lower concentrations, of about 20 mol\%, for 2a[Pyr]. The nematic–isotropic (N–I) transition temperatures extrapolated from mixtures with 3a are higher than those obtained for pure ion pairs 1a[Pyr] and 2a[Pyr] by 8 K and 13 K, respectively, and have uncertainty of ±4 K. In contrast, the \[T_{NI}\] extrapolated for 1b[Pyr] is significantly lower, by 22 K, than that extrapolated from binary mixtures with 2a[Pyr] (Table 2). These results demonstrate particularly good compatibility of nematic 1a[Pyr] and 2a[Pyr] with a non-ionic host, which is consistent with our previous findings for miscibility of ionic and non-ionic smectogens [2]. The lower value for \[T_{NI}\] extrapolated for 1b[Pyr] from 3a than from ILC 2a[Pyr] again indicates significant disruption of molecular organisation in the phase and is consistent with the postulated unfavourable cation–anion interactions in 1b[Pyr] compared with its analogue 1a[Pyr].

3. Conclusions

The results demonstrated that replacement of the CH₂ connecting group in 1a[Pyr] with an oxygen atom in 1b[Pyr] markedly destabilises the mesophase. The pentyloxy derivative 1b[Pyr] also has a lower than expected \[T_{NI}\] temperature extrapolated from a non-ionic host, indicating significant disruption
of the molecular organisation in the nematic phase. Computational analysis suggests that the effect is due to unusually high basici

ty of the connecting oxygen atom and consequently less favourable interactions between the anion and pyridinium cation. These

results indicate that heteroatom connecting and presumably linking groups (such as COO) should be avoided in designing high mesophase stability ILC derived from closo-borates.

All three ionic liquid crystals 1a[Pyr], 1b[Pyr] and 2a[Pyr] are compatible and miscible with non-ionic mesogen 3a, which is consistent with our previous find-
ing and important for designing anisotropic materials for electrolyte applications.

4. Experimental

4.1 Characterisation

1H NMR spectra were obtained at 400 MHz in CDCl3 and referenced to the solvent, unless specified otherwise. Optical microscopy and phase identifi-
cation were performed using a PZO 'Biolar' polarised microscope equipped with a HCS400 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures and enthalpies were obtained using small sam-

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4.2 Binary mixtures

Binary mixtures were prepared by dissolving both components in small amounts of dry acetonitrile (MeCN), subsequent evaporation of the solvent and drying the resulting homogenous material at 130°C for several hours. The hot homogenous mixture was transferred to an aluminium pan and analysed by DSC. Transition temperatures of the mixtures were taken as peak temperature on the second heating cycle. The transition temperatures were extrapolated to pure additive by fixing the intercept of the fitting line at the peak transition temperature of the host.

4.3 Synthesis

4.3.1 General procedures for the synthesis of esters

4.3.1.1 Method A. Carboxylic acid (1 mmol) was dissolved in anhydrous dichloromethane (CH2Cl2) (5 mL), (COCl)2 (0.26 mL, 3 mmol) and a catalytic amount of N,N-dimethylformamide (DMF) were added. The reaction mixture was stirred for 15 min and evaporated to dryness in vacuo. The residue was dissolved in anhydrous CH2Cl2 (10 mL) and triethylamine (NEt3) (0.21 mL, 1.5 mmol) and 4-hydroxy-4’-(hexyloxy)azobenzene [2] (4, 328 mg, 1.1 mmol) were added. The reaction mixture was stirred overnight, washed with 10% HCl, organic layer dried (Na2SO4) and the solvent removed. The crude material was passed through a short silica gel plug (CH2Cl2) giving the ester as an orange crystalline solid. The resulting ester was purified further by recrystallisation.

4.3.1.2 Method B. Carboxylic acid (1 mmol) was dissolved in anhydrous CH2Cl2 (10 mL), 4-Hydroxy-4’-(hexyloxy)azobenzene [2] (4, 328 mg, 1.1 mmol), DCC (309 mg, 1.5 mmol) and catalytic amounts of 4-dimethylaminopyridine were added. The reaction mixture was stirred overnight, washed with 10% HCl, organic layer dried (Na2SO4) and the solvent removed. The crude material was purified as described in Method A.

Ester of [closo-1-CB10H10-COOH-10-OC6H13]- acid Pyr salt (1b[Pyr]). Ester 1b[NMe4], obtained from 5b[NMe4] [3] using Method A, was dissolved in CH2Cl2 and N-butyl-4-heptyloxypyridinium bromide [1] (1.0 equivalent) 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 CH2Cl2 layer was separated, and the aqueous layer was extracted with additional CH2Cl2. The CH2Cl2 layers were combined, dried (Na2SO4) and evaporating giving a yellow crystalline solid of 1b[Pyr]. Crude product was purified on a silica gel column (CH2Cl2/MeCN, 2:1) and then recrystallised repeatedly from ethyl acetate/hexane. The resulting crystals were dried in vacuum at ambient temperature.

Ester of 4-C6H13C6H4COOH (3a). Obtained using Method A and recrystallised from ethanol/ethyl acetate: 1H NMR (400 MHz, CDCl3) δ 0.90 (t, J = 7.0 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H), 1.29–1.40 (m, 8H), 1.42–1.58 (m, 8H), 1.78–1.92 (m, 8H), 7.34 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 7.5 Hz, 2H); 13C NMR (128 MHz, CDCl3) δ –28.4 (d, J = 150 Hz, 4B), –20.0 (d, J = 162 Hz, 4B), 53.2 (s, 1B). Analysis calculated for C41H68B9N3O5: C, 63.11; H, 8.78; N, 5.39. Found: C, 62.89; H, 8.59; N, 5.36%.

Ester of 4-C8H11C4H4COOH (3a). Obtained using Method A and recrystallised from ethanol/ethyl acetate: 1H NMR (400 MHz, CDCl3) δ 0.90 (t, J = 7.0 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H), 1.29–1.40 (m,
1.45–1.52 (m, 2H), 1.66 (quint, J = 7.5 Hz, 2H), 1.83 (quint, J = 7.1 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H). Analysis calculated for C_{12}H_{18}N_{2}O_{3}S: C, 76.34; H, 7.82; N, 5.76%. Found: C, 71.41; H, 7.13; N, 5.63%.

Ester of 4-C_{6}H_{11}SC_{6}H_{4}COOH (3c). Obtained using Method B and recrystallised from ethanol/ethyl acetate: ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, J = 7.0 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.33–1.54 (m, 10H), 1.74 (quint, J = 7.4 Hz, 2H), 1.83 (quint, J = 8.0 Hz, 2H), 3.02 (t, J = 7.4, 2H), 4.05 (t, J = 6.6 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 8.10 (d, 8.6 Hz, 2H). Analysis calculated for C_{10}H_{18}N_{2}O_{3}: C, 73.74; H, 7.43; N, 5.73. Found: C, 73.61; H, 7.27; N, 5.70%.

Ester of 4-C_{6}H_{11}SC_{6}H_{4}COOH (3e). Obtained using Method B and recrystallised from ethanol/ethyl acetate: ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, J = 7.0 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.33–1.54 (m, 10H), 1.74 (quint, J = 7.4 Hz, 2H), 1.83 (quint, J = 8.0 Hz, 2H), 3.02 (t, J = 7.4, 2H), 4.05 (t, J = 6.6 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 8.10 (d, 8.6 Hz, 2H). Analysis calculated for C_{10}H_{18}N_{2}O_{3}: C, 73.74; H, 7.43; N, 5.73. Found: C, 73.41; H, 7.13; N, 5.63%.

4.3.2 Attempted preparation of [closo-1-C_{6}B_{9}H_{5}I-COOH-10-SC_{6}H_{11}] ^{+}[NMe_{4}]^{-} (5c[NMe_{4}])

A solution of methyl ester [closo-1-C_{6}B_{9}H_{5}I-COOMe-10-N_{2}] [4] (8, 0.081 g, 0.40 mmol) and 1-pentanethiol (2 mL) was heated at 110°C for 8 h. The reaction mixture was cooled and excess 1-pentanethiol was removed in vacuo (40°C, 2 mm Hg), leaving the crude product as a yellow viscous oil. The material was washed with hot hexane and solvents were removed. The resulting oily mixture was partitioned between 10% HCl and ether, the organic layer was dried (Na_{2}SO_{4}) and solvent removed. The residue was separated on silica gel and the first fraction (6.5 mg, 5% yield) eluted with CH_{2}Cl_{2} contained mainly [closo-1-C_{6}B_{9}H_{5}I-COSMe_{11}10-HSC_{6}H_{11}]: ^1H NMR (CD_{2}Cl_{2}) δ -20.1 (4B), -14.7 (4B), 33.5 (1B). HRMS, m/z calculated for C_{12}H_{30}B_{9}O_{2}S_{2}: 353.2576; found: m/z 353.2549.

Further elution of the column with CH_{2}Cl_{2}/MeCN (4:1) gave 7 mg of a more polar fraction in which the main component had a mass of 632 daltons.

4.3.3 Synthesis of 4-C_{2}H_{11}SC_{6}H_{4}COOH (6c) [5]

1-Pentanethiol (4.42 mL, 0.036 mol) was added dropwise to a suspension of hexane-washed NaH (1.73 g, 0.072 mol) in anhydrous DMSO (100 mL) under argon. After 1 h, 4-fluorobenzoic acid (5.04 g, 0.036 mol) dissolved in DMSO (100 mL) was added slowly. The reaction mixture was stirred at 100°C overnight. After cooling, the nearly solid reaction mixture was suspended in H_{2}O and KOH was added to the mixture to ensure basic pH. The solution was filtered and the filtrate acidified. The resulting precipitate was filtered, washed with water and dried to give 5.53 g of an off-white solid. The crude product was recrystallised (aqueous EtOH) to give 3.67 g (46% yield) of acid 6c as an off-white solid: mp 112–113°C (lit.[5] mp 113°C); ^1H NMR (CDCl_3, 400 MHz) δ 7.36 (d, J = 7.2 Hz, 3H), 1.36 (sext, J = 7.2 Hz, 2H), 1.41–1.48 (m, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 3.00 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.6 Hz, 2H).

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References


[17] Obtained from NBO analysis of the SCF wavefunction within Gaussian 09.