



$[closo-1-CB_{11}H_{11}-1-Ph]^-$ as a structural element for ionic liquid crystals



Aleksandra Jankowiak^a, Junichiro Kanazawa^{a,b}, Piotr Kaszynski^{a,c,*}, Ryo Takita^b, Masanobu Uchiyama^b

^a Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

^b Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

^c Section of Heteroorganic Compounds, University of Łódź, Tamka 12, 91403 Łódź, Poland

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ABSTRACT

Ion pairs **2[Pyrr]** and **3[Pyrr]** containing $[closo-1-CB_{11}H_{11}-1-Ph]^-$ 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[Pyrr]** 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.

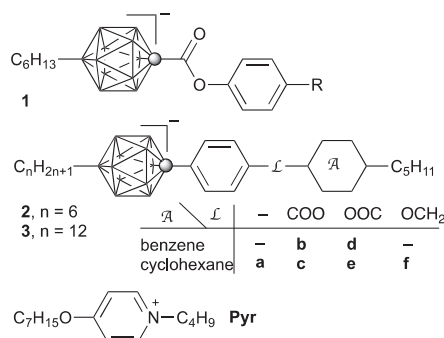
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1. Introduction

A recently developed method for C-arylation of the $[closo-1-CB_{11}H_{12}]^-$ 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*-carborates $[closo-1-CB_9H_{10}]^-$ (**A**, Fig. 1) and $[closo-1-CB_{11}H_{12}]^-$ (**B**) are suitable structural elements for ILC, such as **IA** and **IB** in Fig. 1 [9–11], and ion pairs **1[Pyrr]** containing $[closo-1-CB_{11}H_{12}]^-$ (**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[Pyrr]** and **3[Pyrr]**, including those lacking the ester group and, consequently, with increased chemical stability. The first two members of this new family of ILC, **2c[Pyrr]** and **2f[Pyrr]**, were reported recently [1].

Here we describe the synthesis and characterization of mesogenic ion pairs **2[Pyrr]**, derived from the $[closo-1-CB_{11}H_{11}-1-Ph]^-$, with the C_6H_{13} chain and one derivative **3c[Pyrr]** with double length of the alkyl chain. Properties of the new compounds are compared to those of series **1[Pyrr]** and are used for structure–property relationship analysis.



* Corresponding author. Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Box 1822 Station B, Nashville, TN 37235, USA. Tel.: +1 615 322 3458; fax: +1 615 343 1234.

E-mail addresses: aleksandra.jankowiak@Vanderbilt.Edu (A. Jankowiak), 1727407712@mail.ecc.u-tokyo.ac.jp (J. Kanazawa), piotr.kaszynski@vanderbilt.edu (P. Kaszynski), takita@mol.f.u-tokyo.ac.jp (R. Takita), uchiyama@mol.f.u-tokyo.ac.jp (M. Uchiyama).

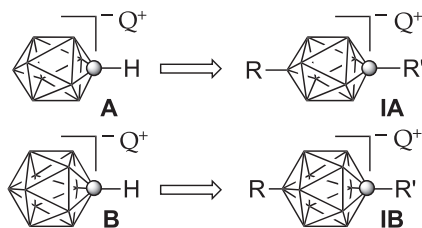


Fig. 1. The structures of the [closo-1-CB₉H₁₀]⁻ (A) and [closo-1-CB₁₁H₁₂]⁻ (B) clusters, and ion pairs of their 1,10- (IA) and 1,12-disubstituted (IB) derivatives with the counterion Q⁺. Each vertex represents a BH fragment and the sphere is a carbon atom.

2. Results and discussion

2.1. Synthesis

Esters **1b**, **1d**, **2b**, **2c**, and **3c** were prepared from appropriate carboxylic acids **4**[NET₄]⁺–**6**[NET₄]⁺. Thus, carboxylic acids were converted to acid chlorides with (COCl)₂ and treated with appropriate phenol **7** or *trans*-4-pentylcyclohexanol (**8**) to give desired esters as the [NET₄]⁺ 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-pentylbenzoyl chloride and *trans*-4-pentylcyclohexanecarbonyl chloride, respectively (Scheme 2). Finally, alkylation of phenol **9**[NMe₄]⁺ with tosylate **10** [13] 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 [NET₄]⁺ or [NMe₄]⁺ cation for *N*-butyl-4-heptyloxypyridinium [9,14] (Pyr) in a biphasic CH₂Cl₂/H₂O system following the procedure previously reported for the preparation of ion pair **1a**[Pyr] [11].

Carboxylic acid **6**[NET₄]⁺ was obtained by Negishi coupling [15,16] of iodo acid [closo-1-CB₁₁H₁₀-1-(4-C₆H₄COOH)-12-I]⁻ [NMe₄]⁺ (**11** [NMe₄]⁺) [1] with 12-fold excess dodecylzinc chloride in the presence of Pd(0) and PCy₃ ligand generated *in-situ* (Scheme 3), as described previously for the preparation of acids [closo-1-CB₁₁H₁₀-1-COOH-12-C₆H₁₃]⁻ [NMe₄]⁺ (**4**[NMe₄]⁺) [11] and [closo-1-CB₁₁H₁₀-1-(4-C₆H₄COOH)-12-C₆H₁₃]⁻ [NET₄]⁺ (**5**[NET₄]⁺) [1]. A similar Negishi coupling of iodo phenol [closo-1-CB₁₁H₁₀-1-(4-C₆H₄OH)-12-I]⁻ [NMe₄]⁺ (**12**[NMe₄]⁺) gave the hexyl phenol **9**[NMe₄]⁺ [1].

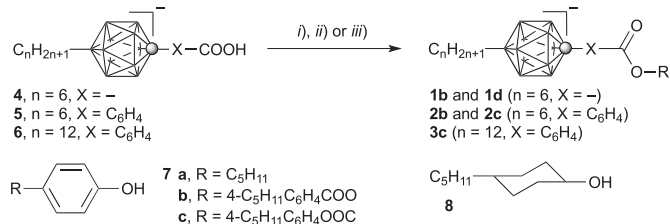
Preparation of iodo acid **11**[NMe₄]⁺ and iodo phenol **12**[NMe₄]⁺ is described elsewhere [1] and involves arylation of [closo-1-CB₁₁H₁₁-12-I]⁻ [NMe₄]⁺ (**13**[NMe₄]⁺) with substituted iodobenzene through a carbonylcopper reagent, followed by deprotection of acid or phenol functionality (Scheme 3).

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

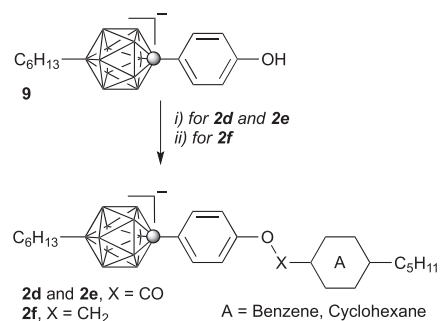
2.2. Liquid crystalline properties

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



Scheme 1. Reagents and conditions: i) (COCl)₂, cat. DMF, CH₂Cl₂; ii) ROH **7**, Pyr, CH₂Cl₂, rt; iii) ROH **8**, Pyr, 90 °C, 2 d.



Scheme 2. Reagents and conditions: i) C₅H₁₁-A-COCl, Pyr, CH₂Cl₂; ii) C₅H₁₁-Chx-CH₂OTs (**10**), K₂CO₃, DMF.

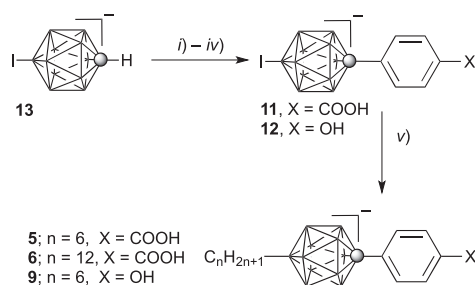
microdroplet (Fig. 2b), while the second phase was detected in some DSC scans (Fig. 3b). Nematic phase is rarely observed in ILC and ion pair **1b**[Pyr] represent the second example of a nematic ILC found among boron cluster derivatives [11].

Analysis of data in Table 1 demonstrates that moving the carboxylic 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 in 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 *T*_c 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



Scheme 3. Reagents and conditions: i) BuLi, THF; ii) Cul; iii) I-C₆H₄-X', Pd(OAc)₂, (o-MeOC₆H₄)₃P; iv) deprotection X' → X; v) C_nH_{2n+1}ZnCl, Pd₂(dba)₃, [HPCy₃]⁺[BF₄]⁻, THF.

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