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Highly quadrupolar derivatives of the [*closo*-$B_{10}H_{10}$]$^{2-}$ anion: Investigation of liquid crystalline polymorphism in an homologous series of 1,10-bis(4-alkoxypyridinium) zwitterions

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ABSTRACT

A series of pyridinium bis-zwitterions [*closo*-$B_{10}H_8$-1,10-2 (4-ROC_5H_4N)] (**1[n]**) was obtained in 55–60% yield by reacting [*closo*-$B_{10}H_8$-1,10-2(IPh)] (**3**) with 4-alkoxypyridines and the resulting derivatives were analyzed for their liquid crystalline properties. Optical, thermal and XRD analyses revealed the formation of a nematic and rare lamellar phases, $\mathrm{Lam_{Cr}}$, driven by dipolar interactions. Upon elongation of the terminal alkoxy chain, the nematic phase is gradually replaced by the lamellar polymorphism. The solid-state structures of **1[8]**, **1[12]** and **1[16]** were established by single crystal XRD: **1[8]** $P2_1/c$, Z = 4, a = 12.6009 (2) Å, b = 20.7889 (2) Å, c = 12.61150 (10) Å, β = 103.9910 (10)°; **1[12]** P-1, Z = 2, a = 9.6262 (2) Å, b = 12.0464 (2) Å, c = 17.9226 (3) Å, α = 80.5940 (10)°, β = 83.0700 (10)°, γ = 74.9860 (10)°; **1[16]** P-1, Z = 2, a = 9.6827 (3) Å, b = 11.6711 (5) Å, c = 22.8486 (7) Å, α = 77.416 (3)°, β = 86.925 (2)°, γ = 66.202 (4)°.

1. Introduction

The ready availability of the [*closo*-$B_{10}H_{10}$]$^{2-}$ anion (**A**, Fig. 1) and its reasonably well developed chemistry [1] have been exploited in preparation of bio-conjugates for e.g. BNCT therapy [2,3]. On the other hand, the 3D σ-aromaticity of the cluster [4], along with high electronic polarization [5] and a relatively high lying HOMO [6,7], allow for strong interactions with π-aromatic substituents [8] and effective charge transfer (CT) phenomena [9–12], which are of interest for functional materials. The negative charge of the boron cage **A** can be compensated with two onium substituents in positions 1 and 10 leading to highly quadrupolar derivatives **B** [13] (Fig. 1). We have investigated electronically dissymmetric derivatives **B** that exhibit directional photoinduced CT, non-linear optical (NLO) properties, electrooptical switching, and liquid crystalline behavior [12]. We have also demonstrated one example of a symmetric 1,10-bispyridinium derivative **1[7]** (Fig. 2) exhibiting a strong cage-to-pyridine photoinduced CT band and nematic [14] behavior [10,12]. Since derivatives **1[n]** have strong local dipole moments, we expected to observe lamellar phases in higher homologues in this series.

Herein we report the preparation of six members of a homologous series **1[n]** (n = even, Fig. 2) and investigate their phase behavior with optical, thermal, and powder XRD methods augmented with DFT calculations. In addition, we report solid-state structures of three homologs.

2. Results and discussion

2.1. Synthesis

The previously reported [12] synthesis of **1[7]** involving the bisdinitrogen derivative **2** [9] was inefficient, giving the desired product in about 4% yield for two steps from the parent anion **A**

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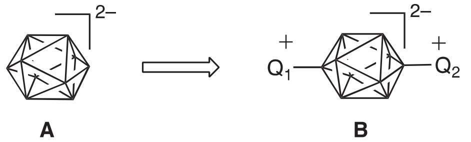


Fig. 1. The structure of the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion (**A**) and linear quadrupolar derivatives **B**. Each unsubstituted vertex represents a B–H fragment.

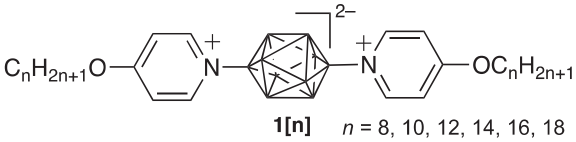


Fig. 2. The structure of liquid crystalline derivatives **1[n]**.

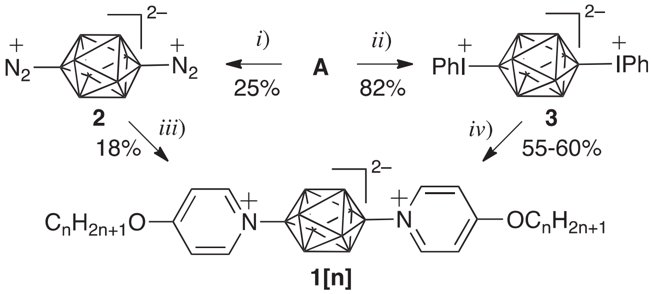
(Scheme 1). Therefore, for the preparation of higher homologues **1[n]** we used a recently discovered method [15], which takes advantage of an efficient nucleophilic substitution in bisiodonium zwitterion **3** (Scheme 1). The overall yield for this new, two-step sequence is about 48%, which is an order of magnitude more efficient than the previous method.

The main differences between the two methods are a) the degree of selectivity of the electrophilic substitution of the anion **A**, and b) the mechanism for replacement of the leaving group in the intermediate. The formation of **2** is not selective for the apical positions of the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion and the isolated low yield reflects the formation of the undesired and unstable equatorial isomers. In contrast, the electrophilic phenyliodine(III) species appears to be most selective electrophile for substitution of *closo*-borane anions including **A** and exclusive formation of **3** [15]. Also the mechanism for substitution is more efficient for iodonium zwitterions, such as **3**, proceeding through a 10-I-3 intermediate [15]. In contrast, replacement of the N_2 leaving groups in **2** most likely involves a heterolysis and formation of a highly reactive boronium ylide [9,12]. The reaction of **2** with a nucleophilic solvent is efficient for small molecules (e.g. pyridine) [9]. However, it becomes more problematic with substituted nucleophiles, such as long chain 4-alkoxypyridines, when the nucleophilic center is “diluted” and side reactions with the alkyl chain (C-H insertion) [9] are dominant.

The required 4-alkoxypyridines were obtained as described previously [12] and in another report [16].

2.2. Molecular and crystal structures

Colorless crystals of **1[8]**, **1[12]** and **1[16]** were obtained by slow cooling of MeCN solutions, and their solid-state structures were determined by low temperature single crystal X-ray analysis. Results are detailed in Tables 1 and 2 and shown in Figs. 3–5.



Scheme 1. Synthesis of derivatives **1[n]**. Reagents and conditions: *i*) ref [9]; *ii*) $PhI(OAc)_2$, 70% AcOH, 0 °C, 1 h then rt, 1 h, ref [15]; *iii*) 4-Alkoxypyridine 120 °C, overnight, ref [12]; *iv*) 4-Alkoxypyridine 80 °C, overnight.

The bispyridinium zwitterion **1[8]** crystallizes in a monoclinic $P2_1/c$ space group with a unit cell containing four molecules, while the two higher homologues, **1[12]** and **1[16]**, form triclinic crystals with two molecules in the unit cell (Table 1). Molecular geometry analysis revealed that the $\{closo\text{-}B_{10}\}$ cage has typical dimensions in all three derivatives (Fig. 3) and data for **1[8]** are shown in Table 2. For instance, the B–N bonds in **1[8]** are 1.525 (1) and 1.523 (1) Å, which are shorter than those in two similar pyridinium derivatives, **4[7]** (1.541 (6) and 1.533 (5) Å) [12] and **5[NEt₄]** (1.530 (3) Å) [17] (Table 2, Fig. 4). Further analysis of data in Table 2 demonstrates that substitution of the B (10) apex with an electron-accepting group in **5[NEt₄]** affects bonding in the cluster. Thus, substitution with the pyridinium fragment contracts the B (10)–B and B (1)–B bonds and expands the equatorial B–B bonds.

This effect appears to be stronger for the more electronegative sulfonium substituent in **4[7]** (Table 2). Consequently, the B (1) ··· B (10) separation diminishes from 3.657 (4) Å in **5[NEt₄]** to 3.618 (1) Å in **1[8]** and to 3.593 (6) in **4[7]**. The observed trend in substituent effect on cage dimensions is consistent with those observed previously [18].

Orientation of the pyridine ring in pyridinium zwitterions of the $\{closo\text{-}B_{10}\}$ cage varies from staggered to nearly eclipsed in spite the preference for the former conformation, according to DFT calculations. Thus, pyridine rings in **1[8]** adopt an approximately staggered conformation with respect to the boron cage with the torsion angles of about 42°, for the B (1) apex, and 37° for the B (10) apex, which results in a 57° angle between planes defined by the pyridine rings. A similar, nearly staggered orientation of the pyridine rings is found for **1 [12]** (32° and 42°, the pyridine ring interplanar angle 28°). In contrast, in the **1[16]** homolog, the pyridine rings nearly eclipse the B–B bonds which results in small torsion angle (4° and 10°), while the pyridine ring interplanar angle is 41°. For comparison, in the sulfonium analogue **4[7]** and the monopyridinium derivative **5[NEt₄]** the pyridine rings adopt a nearly eclipsed conformation with the torsion angles of 7° and 16° in two unique molecules of the former and 20° in the latter derivative. These results demonstrate that the torsion potential for the Pyridine–$\{closo\text{–}B_{10}\}$ bond is shallow and the angle may deviate substantially from the ideal value of 45°.

Structural analysis of alkyl substituents revealed that the longer chains are better organized in the crystal structures than the shorter ones. Thus, one of the octyloxy chains in **1[8]** is in an all-*trans* conformation and coplanar with the pyridine ring, while the second chain exhibits a gauche conformation around the C (3)–C (4) and C (6)–C (7) bonds with positional disorder of the C (6), C (7) and C (8) atoms. The occupancy of the two sites is 72.7 (3)% for the major and 27.3 (3)% for the minor conformer. Similar results are found for the heptyl chains in **1[7]** [19], which exhibit gauche conformations in each alkyl chain of both molecules in the asymmetric unit cell and position disorder in one of them [20]. In contrast, in higher homologs, **1[12]** and **1[16]**, each alkyl chain shows a gauche conformation around the C (1)–C (2) bond giving rise to the S molecular shape with coplanar alkyl chains (Fig. 5). No positional disorder is observed in these homologs.

Analysis of the packing diagram of **1[8]** (Fig. 5) demonstrates that the negatively charged $\{closo\text{-}B_{10}\}$ cage is surrounded by four positively charged pyridinium rings in the equatorial position, which can be described as a square-planar coordination. The average distance between ring centroids and the cage center is 6.34 Å. The pyridine C (3)–H atoms and two equatorial boron atoms are in close contacts separated by distances of 0.181 Å and 0.139 Å, respectively, less than the sum of van der Waals radii. Crystal packing of **1[12]** and **1[16]** exhibits similar, but less regular

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