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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Abdallah, David J. , Lu, Liangde , Cocker, T. Matthew , Bachman, Robert E. and Weiss, Richard G.(2000) 'The crystalline and liquid crystalline structures of benzyl-tri-octadecylammonium bromide complete the puzzle: how do Group VA halide salts with one-four long n-alkyl chains pack?', Liquid Crystals, 27: 6, 831 — 837

To link to this Article: DOI: 10.1080/026782900202327

URL: http://dx.doi.org/10.1080/026782900202327

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 6, 831–837

The crystalline and liquid crystalline structures of benzyl-tri-octadecylammonium bromide complete the puzzle: how do Group VA halide salts with one–four long *n*-alkyl chains pack?

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(*Received 17 November 1999; accepted 14 January 2000*)

The first single crystal structure of a Group VA halide salt with three equivalent long *n*-alkyl chains, benzyltrioctadecylammonium bromide (BzN18Br), is reported. It consists of alternating interdigitated and non-interdigitated regions of alkyl chains separated by ionic planes. Two chains per molecule are paired and extend to one side in a non-interdigitated region. The third chain is on the opposite side of the ionic plane and pairs intermolecularly to form an adjacent, interdigitated region. The thickness of two nearly extended molecules defines the bilayer unit—two ionic planes flanked by a region with intramolecularly paired chains and separated by an interdigitated chain region. Powder X-ray diffraction and optical microscopy data of liquid crystalline BzN18Br are consistent with an enantiotropic smectic A_2 (SmA_2) phase: the three *n*-alkyl chains of each molecule are projected from one side of an ionic plane, and head groups of neighbouring molecules are oriented head-to-head, in a non-interdigitated bilayer assembly. The structure of BzN18Br fills an important gap in our knowledge about the crystal packing of ammonium and phosphonium salts with one–four equivalent long *n*-alkyl chains. A comparison of their packing arrangements is made and the transitional nature of the BzN18Br structures is demonstrated. Although salts with one, two, or three long *n*-alkyl chains form SmA_2 phases, each is distinctive in its molecular packing. A large molecular reorganization accompanies the crystal-to-liquid crystal transition of BzN18Br.

1. Introduction

Molecules composed of one–four long *n*-alkyl chains attached to a Group VA cationic centre (N or P) and a halide anion are prototypical amphiphiles. They offer a wide variety of molecular structures. Yet, their packing modes in neat and lyotropic phases should be related by virtue of their similarities, a hydrophobic tail and a small ionic head group. This contention has been borne out by extensive studies on lyotropic phases of molecules of this type, especially when the group VA element is attached to one or two long chains [1–4]; the models of Israelachvili and others predict well their packing in lyotropic phases [5]. Although the packing of the neat phases of these salts with one [6–9] or two [10, 11] long chains has also been investigated, salts with three or four long chains have been virtually ignored until recently [12]. Here, we report the first crystalline structure of a Group VA halide salt with *three* long *n*-alkyl chains, benzyltrioctadecylammonium bromide (BzN18Br, figure 1), and compare its packing with that of the liquid crystalline phase. In addition, a comparative overview

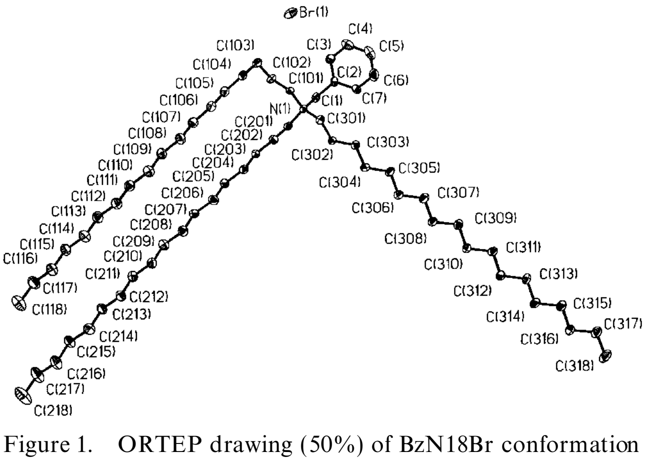

Figure 1. ORTEP drawing (50%) of BzN18Br conformation in its crystalline phase.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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of the packing arrangements of salts with one–four long *n*-alkyl chains in their neat crystalline and liquid crystalline phases is presented.

2. A comparative overview of packing in the neat anisotropic phases of Group VA halide salts with one, two, or four long *n*-alkyl chains

Crystalline ammonium salts with *one* long *n*-alkyl chain pack in interdigitated layers in which the alkyl chains adopt all-*transoid* (extended) conformations (figure 2, **n** = 1) [13–22]. The cationic groups orient head-to-head and are staggered within thin ionic layers containing the counter-ion. The nitrogen atoms of molecules with chains projecting on one side of an ionic layer are coplanar and are offset slightly from those in a near plane of molecules whose chains are projected in the opposing direction. The long *n*-alkyl chains tilt when necessary to make a projection onto the ionic plane that is comparable to the cross-sectional area of the head group (cationic centre and anion). At elevated temperatures, chains melt prior to complete dissociation of the head groups, resulting in a smectic A_2 (SmA_2) phase [23].

In the crystalline state, chains of ammonium bromide salts with *two* methyl groups and two equivalent long *n*-alkyl chains are neither fully extended nor interdigitated (figure 2, **n** = 2) [24–26]. One chain has two consecutive *gauche* bends near the cationic centre, so that intramolecular dispersive interactions between the chains are maximized. Consequently, the paired chains can accommodate a space comparable to the head group without interdigitation. The head groups themselves pack in a manner analogous to that in the salts with one long *n*-alkyl chain, resulting in the formation of a bilayer structure. Both the ammonium and corresponding phosphonium salts form SmA_2 phases, but with less interdigitation due to greater spatial constraints in the lipophilic regions [10, 11].

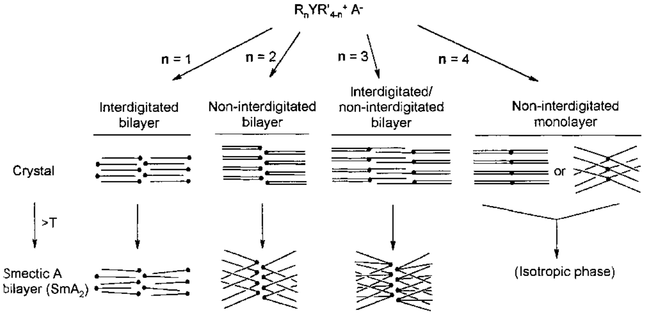

Figure 2. Cartoon of the solid state and liquid crystalline packing of long chain quaternary ammonium and phosphonium salts with one–four long *n*-alkyl groups. $R = H(CH_2)_x$– where $x \geq 10$, R' = 'small' substituent (i.e., $R' = H(CH_2)_y$– where $y \leq 4$ or benzyl), A = halide and Y = nitrogen or phosphorus. In the actual crystal structures, the alkyl chains extend into the hydrophobic region at a non-orthogonal angle with respect to the layer interfacial planes.

Recently, we investigated the packing of crystalline ammonium and phosphonium salts with *four* equivalent long *n*-alkyl groups [12]. In this case, the head groups are located in a plane at the centre of each monolayer (figure 2, **n** = 4) and are less staggered than the charged centres of salts with one or two long *n*-alkyl chains. When *n*-alkyl groups have $\gtrsim 12$ carbon atoms, they are paired *intra*molecularly (i.e. two coparallel adjacent chains on each side of an ionic plane). Groups with $\lesssim 12$ carbon atoms pair *inter*molecularly but, again, with two chains on each side of the ionic layer. None of the salts with four long *n*-alkyl groups examined thus far is liquid crystalline.

3. Experimental

The synthesis of BzN18Br has already been described [27]. A colourless plate (from benzene by slow evaporation) of approximately $0.4 \times 0.4 \times 0.12\,mm^3$ was mounted on a glass fibre using epoxy cement. All aspects of the data collection were performed on a Siemens P4/RA diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å) at 173 (± 2) K. The unit cell parameters were determined by a least-squares analysis of 36 random, carefully centred reflections which were well distributed in reciprocal space ($9.0° \leq 2\theta \leq 25.0°$). Instrument and crystal stability were verified by monitoring three check reflections every 100 data points. No measurable decay was detected. The data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved using direct methods and refined against F^2 using the SHELXLT/PC v5.1 software suite and X-SEED software [28]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions using a standard riding model and thermal parameters proportional to the non-hydrogen atom to which they are attached. Important crystallographic parameters are collected in table 1. Full details, including atomic positions and anisotropic displacement parameters (see supplementary materials), have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

The powder diffraction pattern of BzN18Br in a sealed 1 mm capillary (Charles Supper Company, Natick, MA) was obtained on an Inel CPS 120 diffractometer using Cu_α radiation and a home-built sample thermostatting unit. A theoretical powder diffraction pattern was generated from the single crystal data using the Lazy Pulverix [29] program included with the X-SEED software.

Table 1. Crystal data for BzN18Br.

Empirical formula	$C_{61}H_{118}BrN$
Formula weight	945.47
Temperature	173(2) K
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	$a = 8.0809(9)$ Å $b = 8.3425(7)$ Å $c = 50.276(6)$ Å $\alpha = 87.850(7)°$ $\beta = 89.335(8)°$ $\gamma = 62.513(7)°$
Volume	3004.6(6) $Å^3$
Z	2
Theta range for data collection	2.03° to 20.00°
Index ranges	$-1 \leqslant h \leqslant 7$, $-7 \leqslant k \leqslant 8$, $-48 \leqslant l \leqslant 48$
Reflections collected	7203
Independent reflections	5594 [R(int) = 0.0400]
Completeness to theta = 20.00°	99.90%
Data/restraints/parameters	5594/0/568
Goodness-of-fit on F^2	1.06
Final R indices [1 > 2sigma(1)]	$R1 = 0.0461$, $wR2 = 0.0927$
R indices (all data)	$R1 = 0.0851$, $wR2 = 0.1078$

Thermally-induced phase changes were followed by differential scanning calorimetry (DSC; TA 2910 DSC cell base interfaced to a TA Thermal Analyst 3100 controller) and polarizing optical microscopy (Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage and an Omega HH21 Microprocessor thermometer connected to a J-K-T thermocouple). Samples for optical microscopy were sandwiched between glass slides. Samples (3–5 mg) were placed in open aluminum pans for DSC analyses. A steady stream of nitrogen flowed through the cell. Sample heating rate was 5°C $\min^{-1}$; the cooling rate was uncontrolled and depended on the difference between the sample and ambient temperatures.

4. Results

4.1. *Crystal structure and packing of BzN18Br*

At the molecular level, BzN18Br has the shape of a bent rod. Two of its long alkyl chains are paired (figure 1), as in salts with two [24–26] or four [12] long *n*-alkyl chains. Consecutive *gauche* bends between C102–C103 and C103–C104 allow one chain to be projected parallel and adjacent to another all-*transoid* chain (C201 to C218). The third, non-paired chain is in an all-*transoid* conformation and is projected along an axis nearly perpendicular to the paired chains; the angle between the two all-*transoid* chains is 93.2°.

Two molecules define the thickness of one bilayer unit. It comprises two adjacent non-interdigitated regions flanked by one interdigitated segment (figure 3); except for the interface between the adjacent non-interdigitated regions, boundaries within a unit are defined by an ionic plane. The packing within non-interdigitated segments is reminiscent of *intra*molecularly paired chains in Group VA salts with two or four long *n*-alkyl chains [12, 24–26]; the intermolecularly paired chains of the interdigitated segments are like the structures of salts with one long *n*-alkyl group [13–22], including the monohydrate of benzyldodecyldimethylammonium bromide [19]. Spacings between ionic planes alternate between 19.8 Å (an interdigitated segment) and 30.4 Å (two non-interdigitated segments). Their sum constitutes the length of the *c*-axis in a unit cell (table 1).

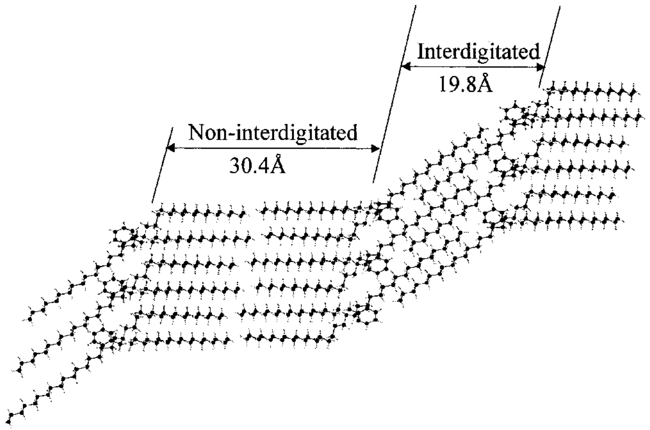

Figure 3. Molecular packing of crystalline BzN18Br.

Benzyl groups are parallel and displaced. The separation between identical carbon atoms on neighbouring benzyl groups is 8.3 Å, the length of the *b*-axis. It is much longer than the separation between parallel stacked and displaced aromatic rings that engage in detectable aromatic–aromatic interactions (*c*. 4.50 Å) [30]; π-π interactions do not contribute appreciably to stabilization of the structure. The distance of the centre of the bromide counter-ion from a hydrogen nucleus (H-C3) at an *ortho* position of a benzyl group, 2.79 Å, is much shorter than the sum of the van der Waals radii of bromide and hydrogen (3.13 Å) [31]. There may be hydrogen-bonding interactions [32].

The rings are located within the interdigitated region and are in contact with the methyl terminus of a chain from an oppositely oriented molecule. The closest contact distance, 4.16 Å, is between a *meta* carbon atom of a ring and a (C118) methyl carbon atom. A close contact distance (3.9 Å) is also observed between the *meta* carbon atom of a ring and the terminal methyl carbon atom of an oppositely oriented molecule in the solid state of benzyldodecyldimethylammonium bromide monohydrate [19]. The distance between two terminal methyl atoms (C218 to C318 of oppositely oriented molecules) at the interface between two non-interdigitated layer segments is 5.37 Å.

X-ray powder diffraction patterns of BzN18Br in its crystalline and liquid crystalline phases are displayed in figure 4. The similarity between the X-SEED-generated (from data obtained at − 100°C on the single crystal) and measured (from data at 70°C) powder diffraction patterns is compelling evidence that no phase transitions occur between ambient temperature and the temperature at which the single crystal diffraction data were collected.

4.2. *The liquid crystalline structure and packing of BzN18Br*

The phase assignment of BzN18Br is based on X-ray powder diffraction, DSC and optical microscopy [33]. Both BzN18Br and its phosphorus analogue, benzyltrioctadecylphosphonium bromide (BzP18Br), form a SmA_2 phase [33]. Their layer spacings (*d*) are the same within experimental error: 28.9 Å for BzP18Br at 76°C; 28.5 Å for BzN18Br at 90°C.

Although BzP18Br is much more stable to heat, the range of the liquid crystalline phase of BzN18Br (12.5°; $T_{Cr\text{-}SmA_2}$ 78.3°C) is larger than that of BzP18Br (8°; $T_{Cr\text{-}SmA_2}$ 70.8°C). Only the solid–SmA_2 and SmA_2–isotropic transitions are observed in the thermogram of recrystallized BzN18Br, figure 5 (*a*). Transition enthalpies and entropies for the SmA_2–isotropic transition are similar to those of BzP18Br (table 2) and many other related ammonium [27] and phosphonium [33] salts with three long *n*-alkyl groups. The second heating thermogram of BzN18Br contains an additional endothermic transition, figure 5 (*b*). When heated to 140°C, BzN18Br exhibits a broad exothermic transition centred around 130°C and corresponding to what we believe is a Hofmann-type elimination reaction.

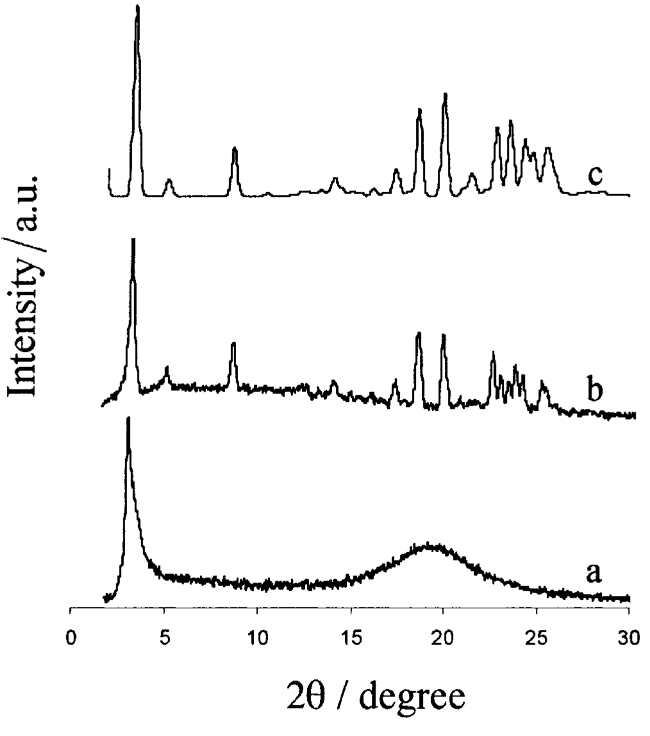

Figure 4. XRD of BzN18Br at (*a*) 90°C (liquid crystal) and (*b*) 70°C (crystal). (*c*) The simulated powder pattern from single crystal diffraction data at − 100°C; see text.

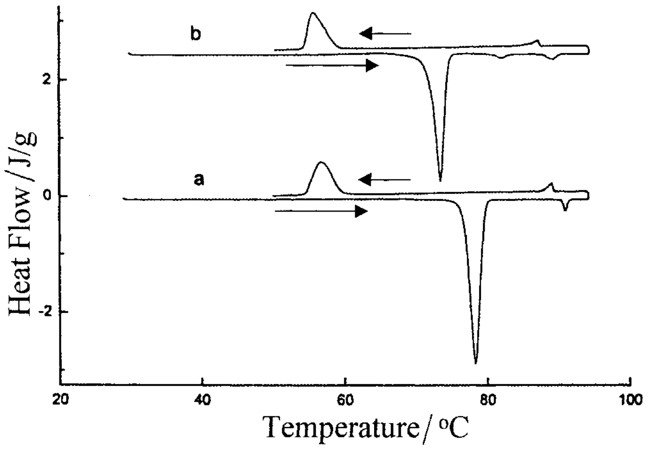

Figure 5. Thermograms of BzN18Br: (*a*) first heat/cool cycle; (*b*) second heat/cool cycle.

The polarized optical micrograph of BzN18Br, taken just below the SmA_2–isotropic transition at 90°C, has an oily streak texture (figure 6). Homeotropic alignment is achieved when samples are cooled from the isotropic phase.

5. Discussion

No structures in the Cambridge Structural Database were found for compounds consisting of a halide anion and three long *n*-alkyl chains (≥ 10 carbon atoms) attached to a charged tetrahedral Group VA atomic centre. The anion of the only remotely related structure found, tridecylmethylammonium bis[4,5-dimercapto-1,3-dithiol-2-thionato(2-)-*S*4,*S*5]aurate(1-) [34], is much too large for this salt to be a reasonable member of the molecular class we seek. For this reason, and to determine the packing requirements of salts that are intermediate in structure between the interdigitated bilayered (**n** = 1) or less/non-interdigitated (**n** = 2) and monolayered (**n** = 4) compounds, we have attempted to examine the molecular packing arrangement of crystalline salts with *three* long *n*-alkyl groups and one short alkyl or benzyl group. Because attempts to make diffraction quality single crystals of these molecules had been largely unsuccessful, we have focused on their liquid crystalline phases [33]. The analysis of the molecular structure and packing of BzN18Br reported here fills a gap in our knowledge about the dependence of the crystal packing of Group VA halide salts on the number of long *n*-alkyl groups.

Table 2. Transition temperatures, enthalpies (ΔH), and entropies (ΔS) from DSC thermograms of Bz*Y*18Br.

		1st Cycle						
		heating		cooling		2nd heating		
Y	Transition	T/°C[a]	ΔH/kJ mol^{-1}	T/°C[a]	$-\Delta H$/kJ mol^{-1}	T/°C[a]	ΔH/kJ mol^{-1}	ΔS[b]/J mol-*T*/K
N[c]	Solid–Solid	—[e]	—	—	—	73.4	113.3	
	Solid–SmA$_2$	78.3	145.5	56.6	97.5	81.9	3.0	
	SmA$_2$–Isotropic	90.9	3.8	88.8	3.8	89	3.7	10.3
P[d]	Solid–Solid	37.1	− 1.3	59.7	100.2	—	—	—
	Solid–SmA$_2$	70.8	117.7	64.6	23.3	70.5	124.5	—
	SmA$_2$–Isotropic	78.8	3.8	78.1	4.3	78.3	3.7	11.4

[a] Peak onset.
[b] Calculated from the averaged ΔH and *T* based on the first cooling and second heating thermograms.
[c] Ref. [27].
[d] Ref. [33].
[e] No transition observed.

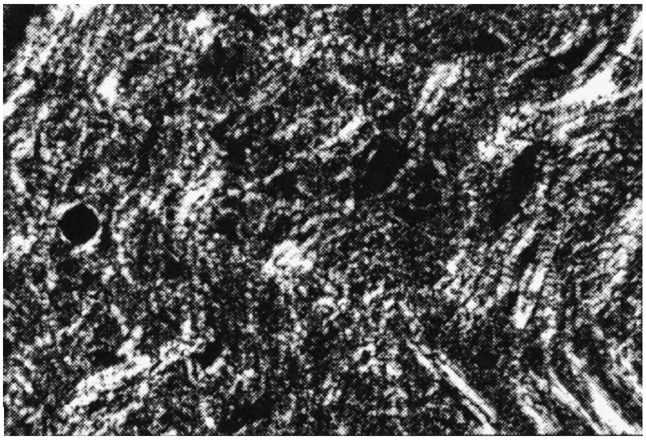

Figure 6. Optical micrograph (200×) of BzN18Br between crossed-polars at 90°C (first heating).

The preferred lowest energy conformations of *n*-alkyl chains in unconstrained environments and in many crystalline phases are all-*transoid* [35–37]. However, crystallized chains of appreciable length, such as those in polyethylene, tend to bend at regularly spaced intervals [38, 39]. Similarly, some bending of alkyl chains occurs in the crystalline phases of long-chained tetraalkylammonium [12], tetraalkylphosphonium [12], and dimethyldialkylammonium salts [24–26], as well as in the crystal of BzN18Br. In each case, the driving force behind bending is maximization of intramolecular chain pairing.

However, BzN18Br cannot adopt a molecular packing arrangement like that in ammonium salts with one, two, or four long *n*-alkyl chains due to the disparity between the cross-sectional areas of the head groups and their chains [5]. A non-interdigitated or interdigitated bilayered packing arrangement for BzN18Br would require *many gauche* bends to project its three long chains along the same direction. In addition, any non-interdigitated monolayer arrangement would have to include excessive amounts of free volume. To avoid either of these energetically unfavourable situations, intramolecular pairs of chains are projected above and intermolecular pairs are projected below charged centres localized in two closely spaced planes. Each pair makes a tilt angle of 36° with respect to the ionic plane so that its cross-sectional area matches the area of its head group.

Solid-to-liquid crystalline phase transitions of amphiphiles like BzN18Br occur when chains melt within lipophilic microphase regions prior to destruction of the ionic planes of the head groups [40]. In principle, melting of chains in the interdigitated and non-interdigitated segments prior to loss of ionic planes could transform crystalline BzN18Br to its liquid crystalline phase without a large change in overall molecular packing. However, significant reorganization does occur: in the liquid crystalline phase; the three long chains are projected from one side of an ionic plane, and non-interdigitated bilayers are formed [33].

Thus, segregation of ionic groups in planes is retained in both the crystalline and liquid crystalline packing motifs of all of the Group VA halide salts, regardless of the number of long *n*-alkyl groups. The detailed nature of the packing and whether a liquid crystalline phase can form depend upon such factors as: (1) overall molecular shape; (2) the area of the ionic (head) group (including the anion); (3) the type of shorter groups(s); and (4) the lengths and number of long *n*-alkyl groups [33].

6. Conclusions

The crystal structure of BzN18Br provides the last part of the answer to the long standing question, 'how do ammonium (and phosphonium) halide salts with one–four long *n*-alkyl groups pack in their neat anisotropic phases?' The crystalline structure is very different from any of its analogues, but combines elements of their packing arrangements. It incorporates both the interdigitation of salts with one long *n*-alkyl chain, and the non-interdigitation of salts with two or four chains. Each lamella requires stacking of two molecule units. BzN18Br combines elements of salts with one or two long *n*-alkyl chains and with four long chains. Ionic planes separate interdigitated and non-interdigitated chain regions. Upon melting to its smectic A_2 liquid crystalline phase, BzN18Br becomes a non-interdigitated bilayered assembly.

As is clear from figure 2, the crystalline phase of BzN18Br is a unique and transitional structure within the series, and its transformation to a smectic phase requires much more molecular reorganization than is needed by the salts with one or two long chains.

Although there is no evidence to conclude that the molecular packing of BzN18Br is representative of the crystalline Group VA halide salts with three long *n*-alkyl groups, it is quite likely that others will be organized in a similar manner. Regardless, the structure presented here and its comparison with other molecules of the class, but containing one, two, or four long chains, provide insights into why they adopt very different crystalline motifs while yielding (except for the salts with four long alkyl chains) smectic A_2 liquid-crystalline phases.

We thank the National Science Foundation for its support of this research. D.J.A. is very grateful to the Achievement Rewards for College Scientists Foundation (ARCS) for a fellowship. We also thank Prof. Timothy Swager of Massachusetts Institute of Technology for the use of a powder diffractometer.

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