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Mesophases of Alkylammonium Salts. VI. The Crystal Structures of Tetra-n-butylammonium Bromide and Iodide

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Mesophases of Alkylammonium Salts. VI. The Crystal Structures of Tetra-*n*-butylammonium Bromide and Iodide

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The structures of tetra-*n*-butylammonium bromide, $N(C_4H_9)_4Br$ (abbreviated: 4Br) and tetra-*n*-butylammonium iodide, $N(C_4H_9)_4I$ (abbreviated:4I) have been determined. For 4Br: $Mw = 322.4$ Da, c-centered monoclinic space group C2/c, $a = 14.409(5)$ Å, $b = 13.901(2)$ Å, $c = 20.345(9)$ Å, $\beta = 110.18(3)$ Å, $V = 3729.4$Å^3, $Z = 8$, $Dc = 1.148$ g/cm^3, $F(000) = 1392$, $R = 0.098$ for 1311 reflections. For 4I: $Mw = 369.4$ Da, c-centered monoclinic space group C2, $a = 14.482(4)$ Å, $b = 14.318(4)$Å, $c = 19.975(7)$Å, $\beta = 110.86(2)$°, $V = 3870$Å^3, $Z = 8$, $Dc = 1.230$ g/cm^3, $F(000) = 1536$, $R = 0.142$ for 1899 reflections. The structure analysis shows that the n-butyl chains are distorted to different degrees from their all-*trans* conformations and are connected through the quaternary nitrogen with one or two *gauche*- bonds. The plastic crystalline mesophase for 4I seems to be possible because of a lower packing fraction that produces larger deviations of the bond-rotation angles from the intramolecular energy-minimum, not found for 4Br. The condis crystal mesophase for 4Br, in turn, may be due to a more intermeshing cation structure, possible because of the higher packing fraction with the Br^- anion. Higher homologues of the tetra-*n*-alkylammonium salts form only condis-crystal mesophases, lower homologues, only plastic-crystal mesophases. The low-temperature crystal structures of all salts of this homologous series contain similar cation conformations. The *n*-butyl and longer alkyl chains form layer-like crystals with methyl surfaces. The somewhat poor fit of computed and experimental structures does not arise from experimental error, but is due to static packing disorder.

Keywords: Tetra-n-butylammonium bromide, $N(C_4H_9)_4Br$, tetra-n-butylammonium iodide, $N(C_4H_9)_4I$, crystal structure, X-ray diffraction, plastic crystal, condis crystal, crystal disorder

1. INTRODUCTION

Tetra-*n*-butylammonium bromide, $N(C_4H_9)_4Br$ (abbreviated: 4Br) and tetra-*n*-butylammonium iodide, $N(C_4H_9)_4I$ (abbreviated: 4I) are ionic crystals composed of tetra-*n*-butylammonium cations and halide anions. They from part of a homologous series of symmetric alkylammonium halides. In our laboratory we are studying compounds that range in length of alkyl group from methyl to octadecyl.[1-5] Our past investigations were mainly concerned with questions about the types of mesophases possible for the various homologues and equilibrium and non-equilibrium disorder in the crystals. For

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crystals with small cations (alkyl groups from methyl to propyl), orientational motion of the whole cation is possible, i.e. plastic crystals are observed above a disordering transition.[2] For crystals with cations based on alkyl groups larger than butyl, only conformational motion is possible in the mesophases that are stable above the disordering transition temperature (T_d).[4] The two *n*-butyl compounds show an intermediate behavior. The iodide yields a plastic crystal on disordering at 394.0 K (with an entropy of disordering $\Delta S_d = 71.2\,JK^{-1}\,mol^{-1}$) and isotropization is observed at 420.6 K (with an isotropization entropy $\Delta S_i = 21.3\,JK^{-1}\,mol^{-1}$).[1] The corresponding bromide changes to a conformationally disordered crystal (condis crystal) at 367.0 K ($\Delta S_d = 41.2\,JK^{-1}\,mol^{-1}$), with a second, small disordering at 379.2 K ($\Delta S_d = 1.4\,JK^{-1}\,mol^{-1}$) and final isotropization at 493.9 K ($\Delta S_i = 37.6\,JK^{-1}mol^{-1}$).

The initial assignments of the high-temperature phases of 4I and 4Br were made on the basis of their entropies of transition.[1,6,7] While 4I develops conformational disorder and orientational disorder at T_d, 4Br starts only conformational disorder at T_d. Typical entropies of conformational disordering $7–12\,JK^{-1}\,mol^{-1}$ of bonds able to rotate ($28–48\,JK^{-1}\,mol^{-1}$ for 4I),[7] while the entropy of positional disordering of a simple binary salt A^+B^- is $21–26\,JK\,mol^{-1}$,[1] and the orientational disordering can yield $20-50\,JK^{-1}\,mol^{-1}$.[7] The isotropization of 4I shows clearly only positional disordering, typical for a plastic crystal. For 4Br, additional orientational disordering occurs at T_i, although some orientational disordering seems to be gained in the condis state, indicated by the extra transition and by an elevated heat capacity.[5] Solid state NMR and heat capacity measurements verified these assignments.[3,5]

The purpose of this paper is to shed some light on the possible structural reasons for this difference in mesophase behavior and to establish a base for the description of the structure of the longer-chain homologues. Powder X-ray studies that were carried out as a function of temperature could not be indexed at low temperatures for the 4Br and 4I crystals and at high temperatures for 4Br condis crystals.[8] The high-temperature form of 4I is clearly a plastic crystal and was indexed as simple cubic with six molecules per unit cell.[8]

2. EXPERIMENTAL

Sufficiently large crystals of the title compounds were obtained by recrystallization from aqueous solutions. The original samples of approximately 99% purity were purchased from Fluka Chemical Co. (980 South Second Street, Ronkonkoma, NY 11779). Both crystals were colorless, transparent, and of a platy morphology.

The X-ray experiments were carried out on a Nicolet R3m/V automatic diffractometer with graphite-monochromated Mo Kα-radiation. All of the parameters of the X-ray experiments are listed in Table 1.

3. RESULTS

The crystal structures were solved by the heavy-atom method. For the iodide there was little difficulty in finding the heavy atom positions since the two iodide ions have

TABLE I

Experimental parameters

$N(C_4H_9)_4I$	$N(C_4H_9)_4Br$
Mo Kα radiation	Mo Kα radiation
$\lambda = 0.71073$ Å	$\lambda = 0.71073$ Å
$Mw = 369.4$	$Mw = 322.4$
monoclinic C2	monoclinic C2/c
unit cell parameters:	
(24 reflections, $2\theta = 25.2° - 38.1°$)	(25 reflections, $2\theta = 25.1° - 33.9°$)
$a = 14.482$ (4) Å	$a = 14.409$ (5) Å
$b = 14.318$ (4) Å	$b = 13.901$ (2) Å
$c = 19.957$ (7) Å	$c = 20.345$ (9) Å
$\beta = 110.86$ (2)°	$\beta = 110.18$ (3)°
$z = 8$	$z = 8$
$R = 0.142$	$R = 0.098$
$V = 3870$ Å^3	$V = 3729.4$ Å^3
$Dc = 1.268$ g/cm^3	$Dc = 1.148$ g/cm^3
$\mu = 1.63$ mm^{-1}	$\mu = 2.17$ mm^{-1}
T= room temperature	T= room temperature
platy, transparent, colorless	platy, transparent, colorless
$0.3 \times 0.3 \times 0.3$ mm^3	$0.3 \times 0.3 \times 0.3$ mm^3
$F(000) = 1536$	$F(000) = 1392$

a distance which is nearly equal to half of the c-axis, therefore it added an extra pseudo-symmetric absence to the diffraction data. All of the non-hydrogen atoms were located by the difference Fourier synthesis and least-square refinement. We could not get as good a refinement as expected from a standard crystal, a fact that needs special attention. The final R-factor of the iodide was 0.142 for 1899 reflections. The determination of the bromide structure was somewhat easier. Both Patterson analysis and direct method gave the same result. The nitrogen and carbon atoms were revealed by difference Fourier synthesis and refinement following block and full matrix least-squares refinement. The final R was 0.098 for 1311 independent reflections. The refinement of the anisotropic temperature factor was only applied to iodine for 4I and to bromine for 4Br.

The positional parameters and isotropic or equivalent isotropic thermal parameters for tetra-*n*-butylammonium bromide and iodide are given in Tables 2 and 3. The bond lengths and angles of the tetra-*n*-butylammonium cation for both crystal structures are given in Tables 4 and 5. The molecular conformations with atom numberings are drawn in Figures 1 and 2. The packing is shown in Figures 3 and 4.

4. DISCUSSION

4.1 Cation Conformation and Crystal Structure

The cation conformations can be seen from Figures 1and 2. The *n*-butyl chains in both crystals have distorted, all-*trans*, planar zig-zag, fully extended conformations. For an

TABLE II

Positional parameters and equivalent isotropic thermal parameters for 4I

Atom	X	Y	Z	U
I1	0.4899(3)	0.0121	0.2266(2)	0.0450(22)
I2	0.5217(3)	0.4855(8)	0.2875(3)	0.0051(25)
N1	0.2432(30)	0.2526(32)	0.2610(26)	0.0081(80)
C1	0.1603(32)	0.1953(37)	0.2051(26)	0.0076(82)
C2	0.0915(36)	0.2682(46)	0.1566(40)	0.0287(87)
C3	−0.0041(48)	0.2056(50)	0.1150(34)	0.0288(90)
C4	−0.0852(40)	0.2515(41)	0.0564(29)	0.0943(94)
C5	0.2200(30)	0.3418(50)	0.2952(36)	0.0391(82)
C6	0.3185(40)	0.3786(51)	0.3608(36)	0.0296(80)
C7	0.2731(50)	0.4618(50)	0.3924(37)	0.0408(97)
C8	0.3408(57)	0.4838(53)	0.4520(42)	0.1041(91)
C9	0.3233(40)	0.3040(42)	0.2299(31)	0.0097(84)
C10	0.3140(61)	0.2698(61)	0.1615(49)	0.0535(79)
C11	0.3727(46)	0.3060(50)	0.1111(33)	0.0612(92)
C12	0.4071(39)	0.2409(40)	0.0584(29)	0.1002(95)
C13	0.3186(39)	0.1859(41)	0.2993(27)	0.0629(87)
C14	0.2863(41)	0.1384(50)	0.3546(40)	0.0347(87)
C15	0.3725(36)	0.0725(40)	0.4003(28)	0.0832(86)
C16	0.3357(46)	−0.0007(60)	0.4535(34)	0.1102(93)
N2	0.7397(40)	0.2613(37)	0.2529(27)	0.0063(85)
C17	0.6616(37)	0.3230(38)	0.2229(32)	0.0192(83)
C18	0.6940(42)	0.3961(57)	0.1719(43)	0.0606(94)
C19	0.6205(63)	0.4595(63)	0.1051(60)	0.0866(98)
C20	0.6479(34)	0.5298(40)	0.0474(26)	0.1162(89)
C21	0.8472(40)	0.3035(47)	0.2823(40)	0.0558(90)
C22	0.9271(51)	0.2486(48)	0.3484(36)	0.0798(94)
C23	1.0174(60)	0.3056(48)	0.3964(47)	0.0524(88)
C24	1.0960(70)	0.2422(54)	0.4529(50)	0.1160(92)
C25	0.7173(51)	0.1881(50)	0.3111(50)	0.0502(94)
C26	0.6862(47)	0.2657(47)	0.3523(51)	0.0708(88)
C27	0.6417(58)	0.2019(57)	0.3954(60)	0.0642(91)
C28	0.6022(70)	0.2735(67)	0.4322(57)	0.0669(90)
C29	0.7636(36)	0.2021(37)	0.2005(28)	0.0501(84)
C30	0.7001(52)	0.1349(48)	0.1473(40)	0.0518(86)
C31	0.7355(40)	0.0799(52)	0.1051(30)	0.0547(90)
C32	0.6368(61)	0.0347(53)	0.0642(42)	0.0961(94)

exactly *trans* conformation, the rotation angles should be 180° for each appropriate C—C bond. From the list of torsional angles of Table 6, one can calculate an average of 11° deviation from 180° for the rotatable C—C bonds in 4I, but only 3° in 4Br. The zig-zag-planes of the *n*-butyl groups do not continue through the quaternary nitrogen. In 4I, the sequences C4—C12 and C8—C16 for N1, and C20—C32 and C24 – C28 for N2 are interrupted by two close-to-*gauche* conformations at the nitrogen. The other four possible sequences have one *trans* and one *gauche* conformation at the nitrogen. Assuming the ideal rotational isomers have *trans* and *gauche* conformations with 180° and 60°, respectively, the average deviation of the 3 × 8 possible angles about the two different nitrogens from the ideal angles in 13.9°. For 4Br, the double-*gauche* conformations about the nitrogen are also in the sequences C4—C12 and C8—C16 and the 3 × 4 deviations average to only 5.5°. There is thus no question that the iodide contains

TABLE III

Positional parameters and equivalent isotropic thermal parameters for 4Br

Atom	X	Y	Z	U
Br_1	0.7382(2)	0.0013(3)	0.4780(2)	0.0025(20)
N1	0.4930(13)	0.2528(11)	0.4937(8)	0.0334(21)
C1	0.4476(13)	0.3074(12)	0.5442(9)	0.0212(34)
C2	0.4253(13)	0.2427(16)	0.5964(10)	0.0471(55)
C3	0.3772(16)	0.3024(16)	0.6386(13)	0.0529(71)
C4	0.3554(15)	0.2442(19)	0.7048(9)	0.0522(91)
C5	0.4213(20)	0.1693(17)	0.4464(13)	0.0566(42)
C6	0.4593(15)	0.1246(17)	0.3988(11)	0.0427(43)
C7	0.3823(16)	0.0488(15)	0.3618(10)	0.0431(56)
C8	0.4152(20)	−0.0034(22)	0.3084(13)	0.0764(72)
C9	0.5916(12)	0.1997(12)	0.5400(9)	0.0188(33)
C10	0.6687(13)	0.2644(14)	0.5946(10)	0.0337(58)
C11	0.7640(16)	0.2045(19)	0.6395(12)	0.0601(60)
C12	0.8370(19)	0.2718(24)	0.6786(10)	0.0589(74)
C13	0.5229(18)	0.3337(17)	0.4514(15)	0.0542(38)
C14	0.4358(15)	0.3751(15)	0.3945(11)	0.0378(54)
C15	0.4754(17)	0.4412(17)	0.3536(12)	0.0579(57)
C16	0.3864(20)	0.4905(20)	0.2947(13)	0.0748(75)

conformationally distorted chains. The more distorted chains should correspond to a poorer packing in the iodide. The bond angles and lengths in Tables 4 and 5 show also considerable spreads. Again, 4Br has less deviations from strain-free bond angles and lengths than 4I.

The densities and unit cell volumes of the two crystals, listed in Table 1 support the poorer-packing hypothesis for 4I. Using typical van der Waals radii,[9] the packing fraction of 4Br is 0.682, relative to 0.680 for 4I. Although the difference is small, it must be kept in mind that the van der Waals volumes of the eight I^- and Br^- ions in the unit cells are only 337.7 and 248.5Å^3, respectively, compared to the 2294.4 Å^3 of the eight cations. The overall magnitude of the packing fraction is less than found, for example in poly(ethylene) (0.70).[9] The densities are by far less than eight known compounds with similar halogen-to-(carbon + nitrogen + oxygen) composition, but without the branching of four hydrocarbon chains that occurs at the quaternary nitrogen (1.45 to 1.61 g/cm^3).[10]

The 4Br and 4I crystals form layer-like structures with their prominent planes normal to the crystallographic *c*-direction (see Figures 3 and 4; to fill-in the motifs left out for clarity, see also the schematic of Figure 5). The heavy-atom anions are placed in gaps of stacks of tetra-*n*-butylammonium cations in direction [100]. Each anion is surrounded by eight *n*-butyl chains from four neighboring cations in the stack. The mean distance from a halide anion to the nearest nitrogen atom is about 5 Å (ionic radii: Br^- = 1.95 Å, I^- = 2.16 Å; van der Waals radii: N = 1.55 Å, C = 1.7 Å). This structure furnishes the reason for the observed preferential crystal growth normal to the *c*-direction and the resulting lamellar morphology.

The packing of the CH_3-groups in the (001) lamellar surfaces were confirmed by atomic force microscopy (AFM).[11] The (001) surfaces were imaged with atomic

TABLE IV

Bond lengths and angles for 4I

N1 C1	1.55(6)	N2—C17	1.39(6)
N1 C5	1.54(5)	N2—C21	1.57(7)
N1 C9	1.67(7)	N2—C25	1.68(7)
N1 C13	1.45(7)	N2—C29	1.48(7)
C1 C2	1.53(5)	C17—C18	1.64(8)
C2 C3	1.61(6)	C18—C19	1.65(7)
C3 C4	1.48(4)	C19—C20	1.68(7)
C5 C6	1.64(5)	C21—C22	1.61(7)
C6 C7	1.59(6)	C22—C23	1.55(6)
C7 C8	1.29(5)	C23—C24	1.57(7)
C9 C10	1.41(6)	C25—C26	1.54(6)
C10—C11	1.62(8)	C26—C27	1.54(6)
C11 C12	1.61(7)	C27—C28	1.49(6)
C13 C14	1.51(7)	C29—C30	1.49(7)
C14 C15	1.57(6)	C30—C31	1.38(7)
C15 C16	1.69(8)	C31—C32	1.52(6)
C1 N1 C5	121(4)	C17—N2—C21	117(4)
C1 N1 C9	115(3)	C17—N2—C25	111(4)
C1 N1 C13	106(4)	C17—N2—C29	115(3)
C5 N1 C9	115(6)	C21—N2—C25	113(3)
C5 N1 C13	123(5)	C21 N2—C29	92(5)
C9 N1 C13	91(5)	C25—N2—C29	107(4)
N1 C1 C2	105(5)	N2—C17—C18	108(5)
C1 C2 C3	101(5)	C17—C18—C19	127(6)
C2 C3 C4	117(6)	C18—C19—C20	130(6)
N1 C5 C6	111(5)	N2—C21—C22	116(5)
C5 C6 C7	101(5)	C21 C22—C23	117(6)
C6 C7 C8	105(6)	C22 C23 C24	112(6)
N1 C9 C10	102(5)	N2 C25 C26	95(6)
C9 C10 C11	127(6)	C25 C26 C27	98(6)
C10 C11 C12	125(6)	C26 C27 C28	100(6)
N1 C13 C14	108(5)	N2 C29 C30	129(6)
C13 C14 C15	108(6)	C29 C30 C31	122(7)
C14 C15 C16	112(6)	C30 C31 C32	95(6)

resolution and gave almost square arrays of 5.2 × 5.4 and 5.3 × 5.5 Å for 4I and 4Br, respectively, in close agreement with the X-ray structure.

4.2 Disorder in the Tetra-*n*-butylammonium Salts

The reliability factors *R* for both crystal structures (Table I) are larger than normally acceptable. The relatively poor fit is not based on experimental error. Parallel experiments in a different laboratory yielded similar poor fits to any assumed structure.[12] The same is true for the deviations of the bond lengths, bond angles, and rotation angles. The possible explanations for these observations are the presence of either dynamic or static disorder. In the case of dynamic disorder, there should be unusually large temperature factors, associated with two or more different positions sampled by the same atoms, creating an artificially large thermal ellipsoid. The electron density map must in this case be distinctly non-spherical for the atoms involved in the

TABLE V

Bond lengths and angles for 4I

N1—C1	1.592(28)	C6—C7	1.512(28)
N1—C5	1.630(27)	C7—C8	1.494(38)
N1—C9	1.563(21)	C9—C10	1.551(23)
N1—C13	1.565(31)	C10—C11	1.594(28)
C1—C2	1.477(30)	C11—C12	1.405(31)
C2—C3	1.504(31)	C13—C14	1.507(28)
C3—C4	1.683(35)	C14—C15	1.484(32)
C5—C6	1.389(30)	C15—C16	1.557(31)
C1—N1—C5	115.0(1.7)	N1—C5—C6	113.7(1.5)
C1—N1—C9	106.6(1.2)	C5—C6—C7	105.9(2.0)
C1—N1—C13	104.6(1.5)	C6—C7—C8	111.5(2.1)
C5—N1—C9	106.8(1.4)	N1—C9—C10	115.1(1.4)
C5—N1—C13	115.2(1.6)	C9—C10—C11	111.1(1.6)
C9—N1—C13	108.3(1.5)	C10—C11—C12	108.4(2.2)
N1—C1—C2	114.4(1.5)	N1—C13—C14	112.7(1.9)
C1—C2—C3	108.6(1.6)	C13—C14—C15	107.3(1.9)
C2—C2—C4	115.5(1.8)	C14—C15—C16	109.6(2.0)

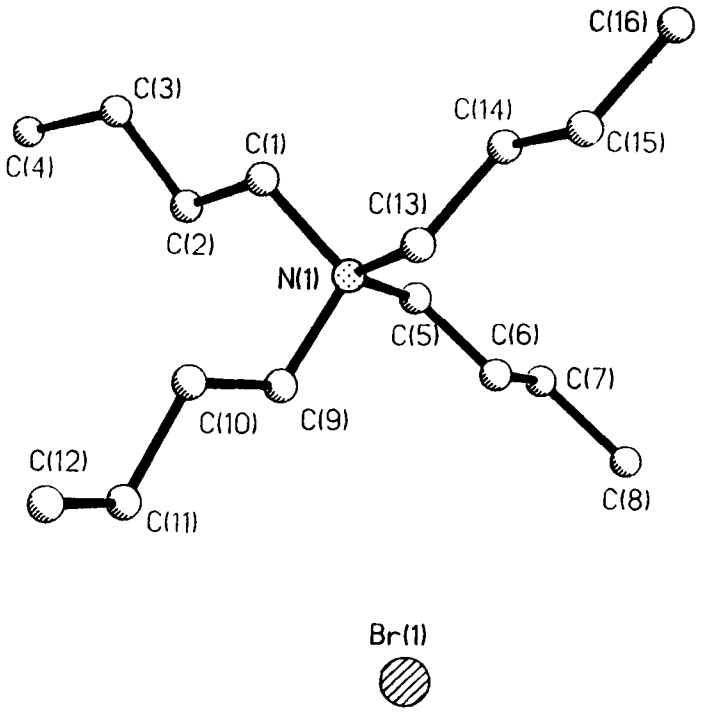

FIGURE 1 Structure of the motif of 4Br.

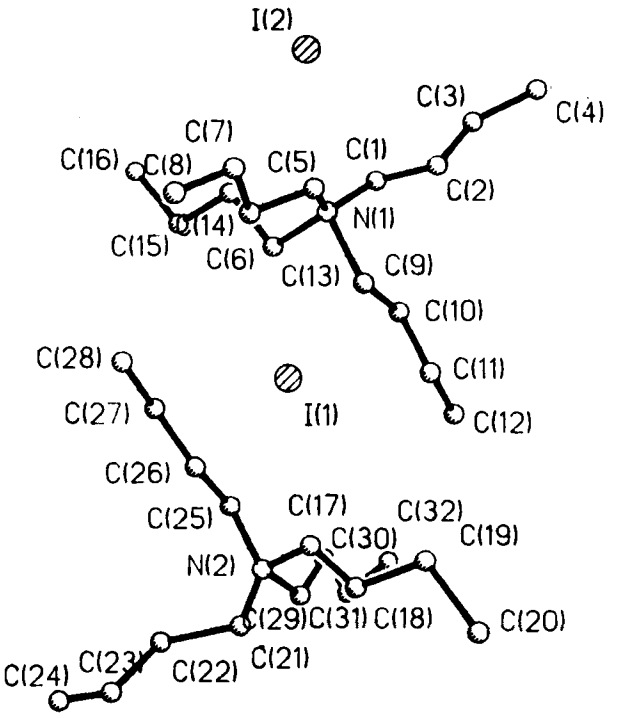

FIGURE 2 Structure of the double-motif of 4I.

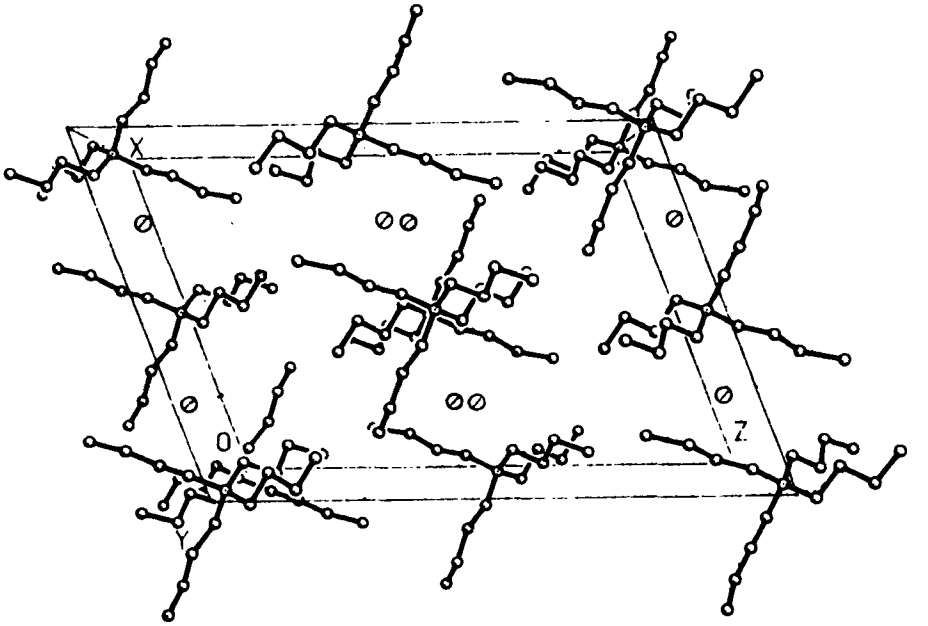

FIGURE 3 Packing in 4Br. Projection along the *b*-axis.

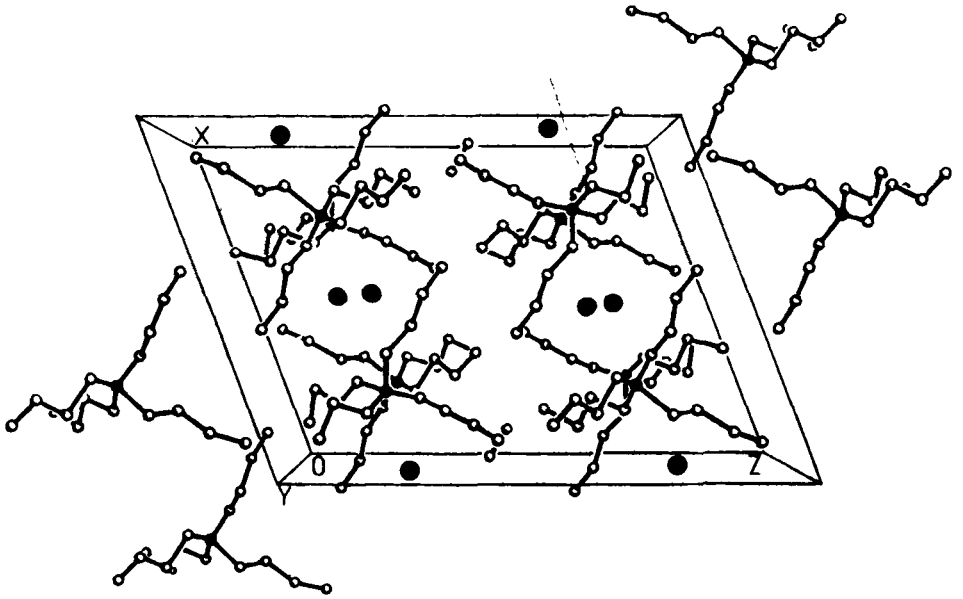

FIGURE 4 Packing in 4I, Projection along *b*-axis.

disorder, something that was not observed. Both of the title compounds show, in addition, heat capacities at room temperature that are close to the values calculated from their vibrational spectrum, leaving little room for conformational or rotational disorder.[5] Major disordering occurs only at higher temperature (367 K for 4Br and 394 K for 4I). A further check of presence of the possibility of dynamic disorder was made by attempting to reduce the difficulties in structure refinement by repeating the diffraction experiment at low temperature (173 K). At this temperature any type of thermally-activated, dynamic disorder should be removed or at least be reduced. The low-temperature diffraction data, however, gave the same results as the room temperature experiments.

The explanation for the excessively large reliability factors R in the structure refinement are thus more likely caused by static disorder, set up during crystallization of the two compounds. We expect that in the studied crystals the same atoms of cations related by symmetry may occupy somewhat different positions in different unit cells. Since this is more so in the iodide ($R = 0.142$) than in the bromide ($R = 0.098$), it seems likely that the strain in the torsional angle leads to several (or many) slightly different conformations with the same overall shape for packing in the ionic lattice. The different cation structure are probably too similar in conformational energy to change at lower temperature. The average atomic positions detected by X-ray diffraction are spread, thus, over larger ranges of positions in the unit cell. Since this kind of static disorder is not contributed by thermal motion of the atoms, it can also not be decreased by lowering the temperature.

TABLE VI

Torsion angles

			$N(C_4H_9)_4I$		
N1	C1	C2	C3	−165.8	C1—C2—C3—C4	−174.0
N1	C5	C6	C7	−173.6	C5—C6—C7—C8	168.0
N1	C9	C10	C11	175.8	C9—C10—C11—C12	145.9
N1	C13	C14	C15	−175.2	C13—C14—C15—C16	−168.8
C5	N1	C1	C2	41.6	C1—N1—C5—C6	171.3
C9	N1	C1	C2	−72.3	C9—N1—C5—C6	−64.7
C13	N1	C1	C2	−169.7	C13—N1—C5—C6	38.3
C1	N1	C9	C10	−32.7	C1—N1—C13—C14	−79.9
C5	N1	C9	C10	−141.3	C5—N1—C13—C14	67.9
C13	N1	C9	C10	94.9	C9—N1—C13—C14	163.9
N2	C17	C18	C19	158.3	C17—C18—C19—C20	−175.3
N2	C21	C22	C23	−157.0	C21—C22—C23—C24	−173.0
N2	C25	C26	C27	167.7	C25—C26—C27—C28	−175.5
N2	C29	C30	C31	−175.6	C29—C30—C31—C32	−177.9
C21	N2	C17	C18	43.8	C17—N2—C21—C22	150.4
C21	N2	C17	C18	175.8	C25—N2—C21—C22	48.5
C29	N2	C17	C18	−63.1	C29—N2—C21—C22	−90.3
C17	N2	C25	C26	−49.2	C17—N2—C29—C30	−58.7
C25	N2	C25	C26	85.6	C21—N2—C29—C30	179.7
C29	N2	C25	C26	−175.0	C25—N2—C29—C30	65.1
			$N(C_4H_9)_4Br$		
N	C1	C2	C3	−178.0	C1—C2—C3—C4	−175.3
N1	C5	C6	C7	−179.4	C5—C6—C7—C8	−179.4
N1	C9	C10	C11	−179.0	C9—C10—C11—C12	169.9
N1	C13	C14	c15	−173.4	C13—C14—C15—C16	−178.3
C5	N1	C1	C2	59.8	C1—N1—C9—C10	−51.9
C9	N1	C1	C2	57.1	C5—N1—C9—C10	−175.1
C13	N1	C1	C2	−173.0	C13—N1—C9—C10	61.5
C1	N1	C5	C6	176.0	C1—N1—C13—C14	−71.3
C9	N1	C5	C6	−64.8	C5—N1—C13—C14	51.2
C13	N1	C5	C6	54.5	C9—N1—C13—C14	170.1

The disorder appears also in the angular distribution of the diffraction data. The statistics of the distribution of diffraction intensity decreases quickly with increasing angle 2θ. In other words, the temperature factors are much larger at larger angles than in typical well-ordered crystals. In the range of 2θ from 45° to 50°, there are only few observable diffraction peaks that have intensities above three standard deviations of the background and can contribute to the structure determination. This kind of intensity distribution is a typical manifestation of irregular distribution of atoms in the lattice.

4.3 High-temperature Crystal Forms

It was found in Ref. [8] by powder difraction, that the structure of 4I above its disordering transition to a plastic crystal changes to simple cubic with the lattice

parameter $a = 14.78$ Å and $Z = 6$. A single-crystal analysis of the high-temperature phase could not be performed because it was not possible to heat the crystal without cracking. In an effort to elucidate the relationship of the room-temperature crystal to the plastic crystal we derived the schematic of Figure 5. In the plastic crystal, where the whole cations rotate cooperatively, they might be represented by interpenetrating spheres, the inner parts of these spheres are indicated in the figure. A high-temperature structure with minimal displacement of the ions from the low-temperature structure can be drawn schematically as structure (C). Comparing this structure with the similarly represented low-temperature crystals (B), the plastic crystal should be a primitive cubic structure. The powder diffraction data suggest also a primitive cubic unit cell, but with $Z = 6$. This must be taken as an indication that the shape of the rotating cation is more complicated and may require cooperative motion of neighboring cations. Further work on this problem is in progress.[8]

4.4 Structures of Other Tetra-*n*-alkylammonium Salts

Of the other members of the series of tetra-*n*-alkylammonium halides, crystal structures have only been determined for tetraethylammonium iodide (2I),[13] tetra-*n*-propylammonium bromide (3Br),[14] and tetra-*n*-propylammonium iodide (3I).[15] A summary of their crystallographic parameters is listed in Table 7, the packings in the crystal can be seen in Figures 6 and 7, and a comparison of the thermodynamic parameters of the

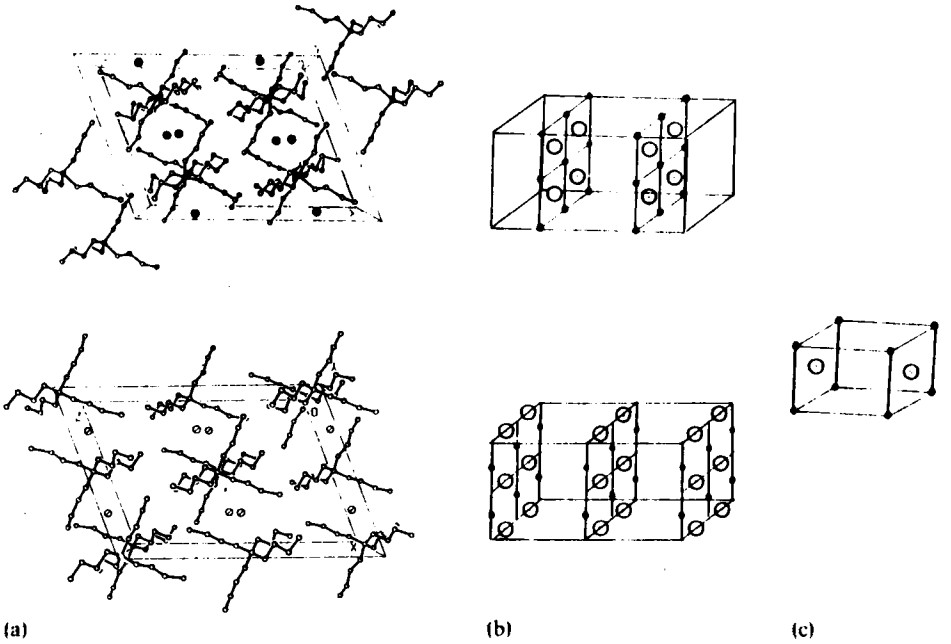

FIGURE 5 Relationship of the low-temperature crystals of 4Br and 4I to the high-temperature plastic crystal of 4I.

disordering transitions is given in Table 8. Again, for most of the crystal structures the R value is rather large and may indicate disorder in the packing of the motifs. All compounds of Table 7 have a high-temperature plastic crystal phase; 3I and 3Br are identical in structure to 4I, and 2I is face-centered-cubic.[8] The right 3I structure represents the low-temperature crystal (see Table 7), the left, the room-temperature structure (both with similar densities).

Although most of the crystal structures are different, the cation conformation is the same. Starting with the ethylammonium, it consists, as the inner part of 4I and 4Br, of two opposing pairs of ethyl groups, being linked through the N by two *gauche* conformations. All other paths from one outer carbon to the other are one *gauche* and one *trans* conformation. The structure can be visualized as two CH_3—C-*t*-N-*g*-C—CH_3 chains crossing at right angles at the N with the *gauche*-bonds turning the C—CH_3 to minimize the interactions. Using a molecular modelling program,[16] the conformation of minimum intramolecular interaction was calculated for an isolated cation (disregarding its charge). The conformation was identical to the one found in the experiments with the rotation angles deviating an average of 7.8° from the unhindered *gauche* and *trans* angles. The 2I experimental deviations are 5.8°, in close agreement with the intramolecualr equilibrium conformation. Similarly, 3I shows a deviation of 6.2°. These values must be compared with the value of 13.9°, derived above for 4I. The 3Br shows for the inner rotation angles a deviation of only 2.7°, comparable to the value of 5.5° for the experimental data for 4Br for the same rotations.

The two outer (C—C) rotation angles for the butyl groups at their energy minimum in the cation were also calculated. Their average deviation from 180° was 3.1°, to be compared to the experimental values of 4.7° and 3.0° in 3Br and 4Br, respectively. Again, the experimental value for 4I is exceptional with 11°, as shown above.

TABLE VII

Crystallographic parameters of other tetra-*n*-alkylammonium salts

	$N(C_2H_5)_4I$	$N(C_3H_7)_4Br$	$N(C_3H_7)_4I$	$N(C_3H_7)_4I$
radiation	Cu Kα	Cu Kα	Mo Kα	Mo Kα
λ, Å	1.5418	1.5418	0.71073	0.71073
Mw	257.2	266.1	313.3	313.3
method	Weissenberg	Weissenberg	Rigaku Diff.	Rigaku Diff.
system	tetragonal	tetragonal	orthorhombic	orthorhombic
space group	$I\bar{4}$	$I\bar{4}$	$P\,n\,a\,2_1$	$P\,2_1\,2_1\,2_1$
a, Å	8.87(2)	8.24(1)	14.845(4)	14.037(5)
b, Å	8.87(2)	8.24(1)	11.941(2)	11.716(1)
c, Å	6.95(2)	10.92(1)	9.302(1)	9.302(1)
V, $Å_3$	546.8	741.4	1587	1530
Z	2	2	4	4
R	0.094	0.177	0.088	0.028
Dc, g/cm³	1.56	1.192	1.36	1.36
T, *K*	room temp	room temp	298	173
	mean bond distances in Å:			
N—C	1.55(9)	1.55(4)	1.56(3)	1.529(6)
C—C	1.55(9)	1.55(7)	1.51(3)	1.517(8)

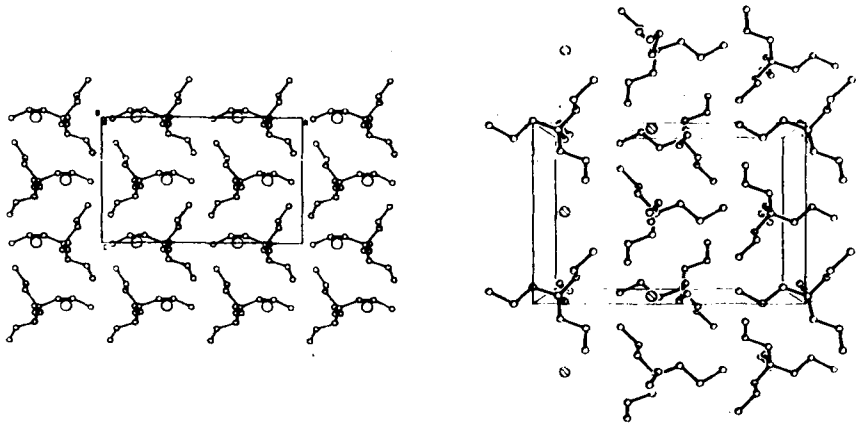

FIGURE 6 Packing in 3I. Projection along the *b*-axis with the *c*-axis vertical. Left, at room temperature. Right at low temperature.

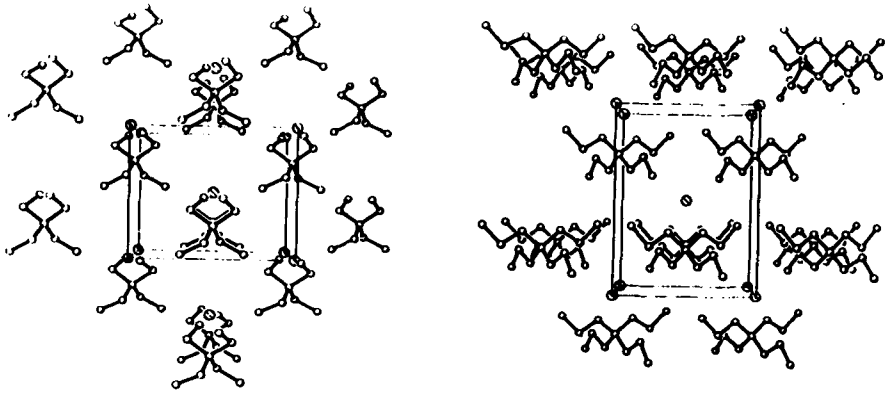

FIGURE 7 Packing of 2I (left) and 3Br (right), projections along the *b*-axis with the *c*-axis vertical. The structure of 2I is recalculated since the original literature contains only a 2-dimensional representation.

With this information, it may now be of interest to speculate on the reason for the transition to a plastic crystal in the case of 4I, and a condis crystal for 4Br, Note that solid state NMR revealed that the N—C and its adjacent C—C bond are not capable of rotational mobility in propyl and higher homologues, even in the melt.[2-4] In 4Br, the next C—C bond becomes mobile 367 K without initiating rotation of the cation as a whole, as is observed at 394 K for 4I. We assume that the better packing in 4Br is achieved by a closer interpenetration of cation and anion. This better packing and interpenetration would hinder rotation of the total cation, but permit rotation of the C—CH_3 about bonds like C(2)—C(3) (see Figure 1). In 4I, the packing is sufficiently poorer so that it is easier to create conformational and orientational disorder and mobility simultaneously.

TABLE VIII

Parameters for the disordering transitions of tetra-*n*-alkylammonium salts

	T_d[a] (K)		ΔS_d[a] (JK^{-1}mol^{-1})	
2Br	448.3	462.6	44.6	3.2
2I	471.3		44.3	
3Br	382.2	395.8	44.4	0.9
3I	225.4	418.9	6.4	35.8
4Br	367.0	393.9	41.2	1.4
4I	394.0		71.2	

[a] Two values indicate two transitions. The smaller one produces only a structure change without major effect on the disorder and motion of the cations.

5. CONCLUSIONS

The crystal structures of the room-temperature polymorphs of tetra-*n*-alkylammonium iodide and bromide have been determined. The homologous series of these interesting salts retains the same inner structure of the cation for all members and extends the layer structure, that is first prominent with the butyl salts, by adding all-*trans* sequences of CH_2-groups. Static packing disorder reduces the precision that can be achieved in structure determination, particulary for 4I. Finally, the different mesophases for 4I and 4Br are traced to differences in packing fractions, linked to major deviations of the torsional angles in 4I from the intramolecular cation energy minimum.

Acknowledgements

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