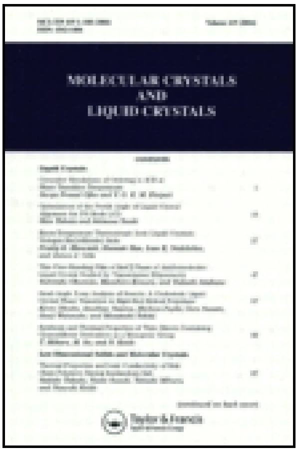

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Mesophases of Alkylammonium Salts. IV. Disorder and Motion in the High Homologs: A Solid State ^{13}C NMR Study on $(C_nH_{2n+1})_4NBr$, n = 8, 10, 12, and 18 and $[CH_3(CH_2)_{11}]_4NI$

J. Cheng [a] [b], A. Xenopoulos [a] [b] & B. Wunderlich [a] [b]
[a] Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600
[b] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37837-6797

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Mesophases of Alkylammonium Salts. IV. Disorder and Motion in the High Homologs: A Solid State ^{13}C NMR Study on $(C_nH_{2n+1})_4NBr$, $n = 8, 10, 12$, and 18 and $[CH_3(CH_2)_{11}]_4NI$

JINLONG CHENG, ALEXANDER XENOPOULOS and BERNHARD WUNDERLICH†

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197

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Conformational disorder and motion in crystals of some high homologs of symmetric tetra-*n*-alkylammonium halides, $(C_nH_{2n+1})_4NBr$, where $n = 8, 10, 12$, and 18, and $[CH_3(CH_2)_{11}]_4NI$, have been analyzed using solid state ^{13}C NMR over a wide range of temperatures covering all phase transitions seen by calorimetry. It is proven that this group of molecules cannot form plastic crystals. Their mesophases show only conformational disordering of C—C single bonds below isotropization. In most cases, the observed phase transitions in calorimetry can be correlated with abrupt changes of the chemical shift of certain carbon atoms in the alkyl chains. The bonds at the chain ends tend to become gradually conformationally mobile and disorder at temperatures much below the first observable transition. The increased mobility is revealed by a gradual up-field shifting of the resonance peaks with increasing temperature. This feature explains the entropy deficit in total entropy of fusion observed by calorimetry. Crystal structure changes can be coupled with a possible change in the nitrogen-to-anion distance, as shown by significant chemical shift changes of the inner-most carbon atoms. Orientational and positional disordering is only possible on isotropization (final step of melting).

Keywords: tetra-n-alkylammonium bromides and iodides, conformational disorder and motion, condis crystals, solid state ^{13}C NMR, thermal analysis

INTRODUCTION

The concepts of orientational and conformational motion and disorder were established through an extensive discussion of the entropy of fusion in the first paper of this series of publications.[1] Parallel and supplementary studies with solid state ^{13}C NMR on the details of motion and disorder have been carried out in the second

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and third paper of this series[2,3] for the low and intermediate homologs of symmetrical tetra-*n*-alkylammonium bromides and iodides with alkyl chain lengths up to seven contiguous carbon atoms. The present publication is a report on the longer homologs.

It was concluded for the low homologs, namely, $(C_nH_{2n+1})_4NX$, $n = 1, 2$, and 3 with X = Br and I, that conformational motion that would change the overall molecular geometry in the cation, i.e., motion about the bonds between two CH_2 groups (in the propyl chain) and between the N—C-bond (in the propyl and ethyl chains) are, for steric reasons, restricted to librations with angles smaller than those between two stable rotational isomers.[2] The final methyl groups, in turn, are involved in rotational motion about the C_3-axis already at low temperature. This motion, however, does not greatly disturb the molecular geometry. It is best described as a noncooperative, local hindered rotation that gets gradually excited outside (and below) the transition temperatures. These observations imply that below the isotropization temperature: (1) Only a plastic-crystal phase is possible for the low homologs, and (2) Three bonds (including CH_2—CH_3) should not be considered for the conformational disordering in intermediate homologs (for n = 4, 5, 6, and 7), as well as for the high homologs (for $n > 7$) studied in this paper.

Of the intermediate homologs,[3] only tetra-*n*-butylammonium iodide shows a plastic-crystal phase with conformational motion and disordering about the CH_2—CH_2CH_3-bond. All other molecules in this series have either no mesophase, and melt in one step, or they develop conformational disorder (giving a condis crystal) before isotropization. The conformational motion and disorder about all bonds was studied by multi-technique variable-temperature ^{13}C NMR and could be shown to occur either *gradually* starting from the alkyl chain ends or to take place *stepwise* at temperatures that coincide with the transitions observed in the DSC experiments.

In this fourth paper on the studies of mesophase of alkylammonium halides, we will continue to apply the same methods, namely, NMR and thermal analysis, to the higher homologs of tetra-*n*-alkylammonium bromides and iodides given in the title. We will correlate the prior reported entropy data[1] with the specific carbon atoms that undergo changes in their chemical shift at the phase transitions. Special attention will be paid to the process in which the conformational disordering occurs gradually over a wide range of temperatures, i.e., conformational disordering without entropy gain in a well-defined transition. This process can be followed: (1) by high-resolution solid state ^{13}C NMR through the gradual up-field shift of the ^{13}C resonance peaks with increasing temperature (γ-*gauche* effect); (2) by recognizing a deficit for the experimental total transition entropy of fusion when compared with empirical rules,[4,5] (3) by a detailed heat capacity study, in which a larger value than calculated from the vibrational heat capacity is observed within the temperature range of such gradual disordering, and (4) by the change of the X-ray diffraction patterns as a function of temperature as the alkyl chains become disordered. Research using the latter two methods is in progress and their results will be presented in the concluding papers of this series of publications.

The crystal structure may also change by rearrangement of the relative positions of the anions (Br or I). This more standard crystal-crystal transition is indicated by an abrupt change in the chemical shift of the inner-most carbon atoms, which are most predominantly influenced by the charge distribution. Details on the crystal structure are, of course, to be supplied by X-ray diffraction experiments which are in progress.

EXPERIMENTAL

The samples used in this paper are commercially produced bromides and iodides of $[CH_3(CH_2)_{n-1}]_4NBr$ with $n = 8$, 10, 12, and 18 from Fluka Chemical Corp., 980 South Second Street, Ronkonkoma, NY 11779, and $[CH_3(CH_2)_{11}]_4NI$ from Lancaster Synthesis Ltd., P.O. Box 1000, Windham, NH 03087. All samples had purities above 99% and were used as received. Solution NMR did not detect any proton and carbon containing impurities.

All solid state ^{13}C NMR measurements were made with a Nicolet NT 200 spectrometer operating at 200.07 and 50.31 MHz for ^1H and ^{13}C, respectively. The solid state probe was purchased from Doty Scientific, Inc., and has a design similar to that described in the literature.[6] The probe has variable temperature capability over the range of 120–430 K. Temperature calibration below and above 300 K was done by measuring the proton resonances of liquid methanol and ethylene glycol,[7] respectively, through the decoupler at various temperatures under the same spinning rate (4.5 kHz) as for the solid state ^{13}C NMR experiments. The cylindrical sample container (rotor) was made from a single crystal of Al_2O_3 (sapphire) and has a diameter of 5 mm. The end cap pairs used for the rotor were made from brown plastic Vespel® (Registered trademark for a DuPont polyimide). The sample was spun with nitrogen gas at 4.5 kHz at the magic angle for all measurements below 300 K. After stabilizing temperature and sample spinning rate, prior to each measurement, the probe was tuned and matched with a 2382 Spectrum Analyzer (100 Hz–400 MHz) made by Marconi Instruments.

In the stability region of crystals and condis crystals, the ^{13}C NMR spectra were measured with the combined techniques of *cross-polarization* (CP), *high-power decoupling of protons*, and *magic angle sample spinning* (MAS), known as CP-MAS. The spin-contact time was typically 1–3 ms. The 90° pulse-width for proton was 4.75 μs, which results in a decoupling field of about 53 kHz. At temperatures close to isotropization or in the melt in which rapid motion is present, the ^{13}C NMR spectra were measured with the pulse sequence for liquids, namely, one-pulse for ^{13}C with two-level decoupling of protons (BILEV). The pulse angle was chosen to be 40° (about 2 μs in pulse width) and relaxation delay of 5 s, which ensure adequate relaxing of the nuclear spins and, thus, faithful representation of the relationship between signal intensity and number of spins.

RESULTS

A selection of the variable-temperature ^{13}C NMR spectra recorded under magic-angle spinning with either cross-polarization (CP-MAS) or one-pulse for ^{13}C plus

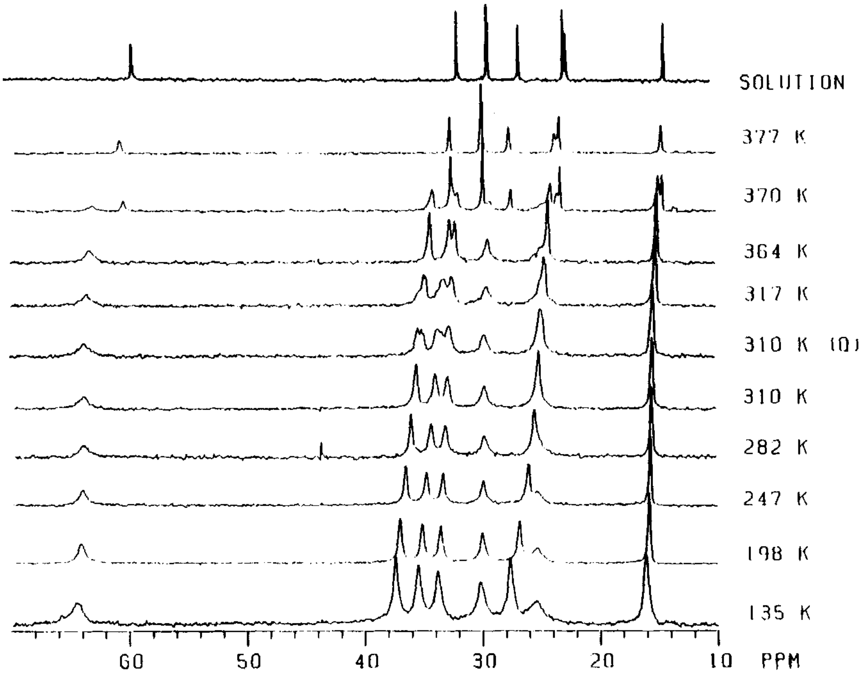

FIGURE 1 Variable-temperature NMR spectra of tetra-*n*-octylammonium bromide, $[CH_3(CH_2)_7]_4NBr$, as a function of temperature. The solution spectrum is shown at the top. Peak assignments and chemical shifts are given in Table I.

two-level decoupling of protons (BILEV) are shown in Figures 1–4 for $(C_nH_{2n+1})_4NBr$, $n = 8$, 10, 12, and 18, and Figures 5 and 6 for $[CH_3(CH_2)_{11}]_4NI$ at temperatures below and above 310 K, respectively.

For tetra-*n*-octylammonium bromide, all spectral lines are well resolved. The numbering of the carbon atoms starts always with C-1 for the carbon bonded to nitrogen and ends with C-8 for the methyl carbon. In Table I all measured chemical shift data are summarized. For longer alkyl chains the resonances for the carbon atoms in the middle of the chains overlap, i.e., their chemical shifts can only be indicated as a range. There are, however, always six carbon atoms (three at either chain end, i.e., C-*x*, C-*y*, C-*z*; and C-1, C-2, C-3) that can be uniquely resolved. Tables II–V contain lists of the chemical shifts for $(C_nH_{2n+1})_4NBr$, with $n = 10$, 12, and 18, and $[CH_3(CH_2)_{11}]_4NI$, respectively.

DISCUSSION

^{13}C Chemical Shift Values of the Crystalline Phase

The crystalline phase of tetra-*n*-alkylammonium halides is usually reached on sufficiently slow cooling. The ^{13}C CP-MAS NMR spectrum of the crystalline phase is characterized by the well separated resonances of the different carbon atoms (fingerprint). There are at least six carbon atoms in a sufficiently long alkyl chain that

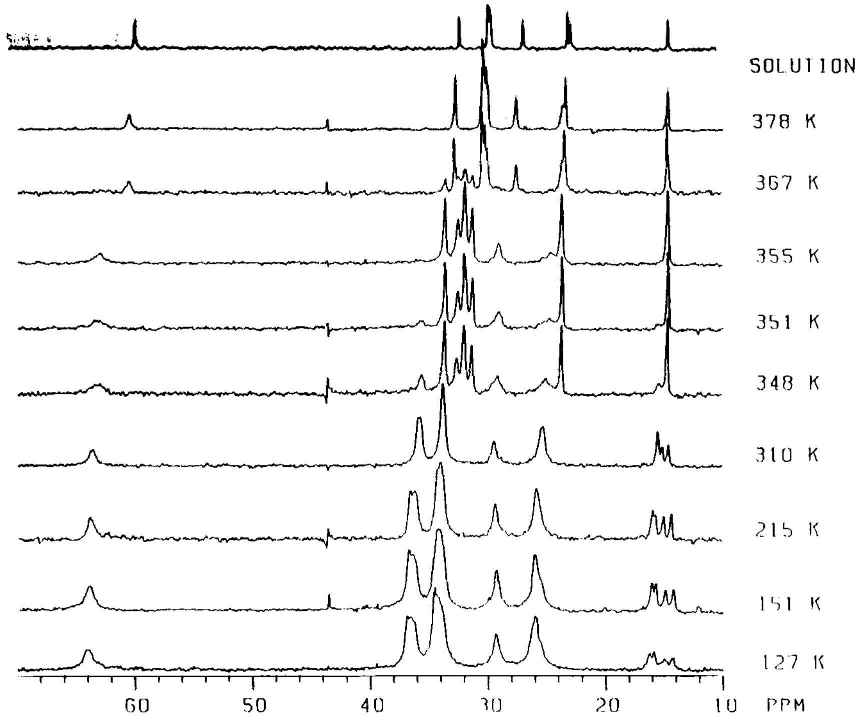

FIGURE 2 Variable-temperature NMR spectra of tetra-*n*-decylammonium bromide, $[CH_3(CH_2)_9]_4NBr$, as a function of temperature. The solution spectrum is shown at the top. Peak assignments and chemical shifts are given in Table II.

have distinguishable resonance peaks, as is shown in the low temperature spectra of Figures 1–5. These six carbon atoms can be identified by comparison with solution ^{13}C spectra, studied using two-dimensional NMR techniques[8] (three carbons close to the nitrogen as C-1, C-2, and C-3, and three at the chain end as C-x, C-y, and C-z being the methyl carbon atom).

The chemical shift assignments for the crystals of all available compounds at sufficiently low temperatures are given in Table VI. The prior reported data for tetra-*n*-hexyl- and heptyl compounds[3] are also included in this table. Except for some of the inner carbons in $[CH_3(CH_2)_{11}]_4NBr$ and $[CH_3(CH_2)_{17}]_4NBr$, the chemical shift values for a given carbon atom in different compounds are close enough to obtain the averages listed. Table VI contains also the average chemical shifts measured in $CDCl_3$ solution, which were determined using two-dimensional NMR techniques [namely proton homo-nuclear shift correlated (COSY) and ^{13}C-^{1}H shift correlated (XHCORR)].[8]

From Table VI, one observes the following: (1) The three carbon atoms on either end have often comparable values. The exceptions listed in Footnote d of Table VI may point to special crystal structures of these compounds. Such special crystal structure would also have to explain the double peaks of C-1 in 18Br and of all carbons in 12Br. (2) Comparisons of the average chemical shift values for the crystals in Table VI and those of solutions show that upon dissolution, the shielding

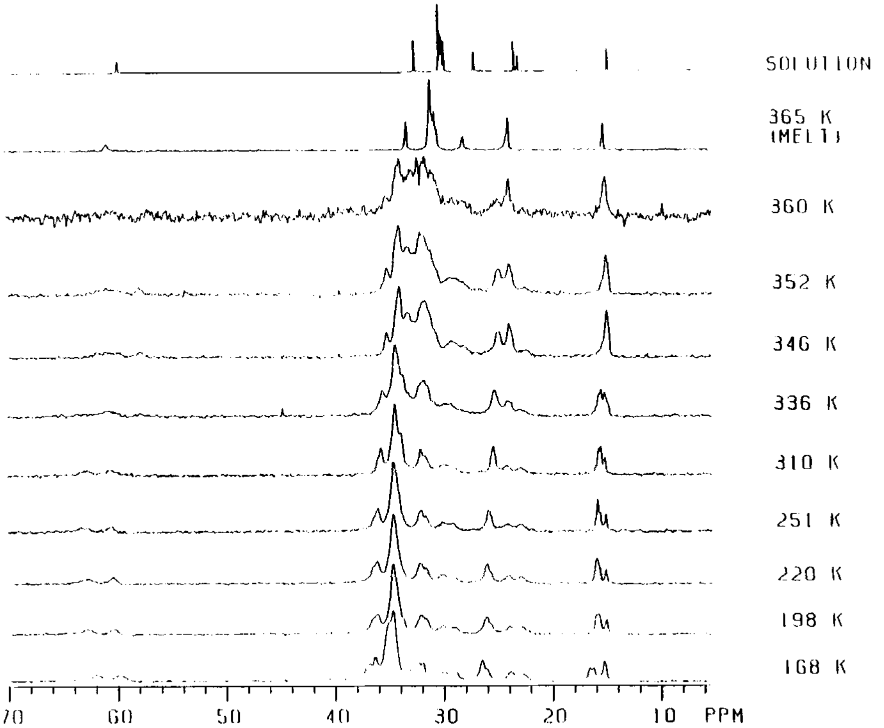

FIGURE 3 Variable-temperature NMR spectra of tetra-*n*-dodecylammonium bromide, $[CH_3(CH_2)_{11}]_4NBr$, as a function of temperature. The solution spectrum is shown at the top. Peak assignments and chemical shifts for C-1, C-2, C-3, C-4, through C-9, C-10, C-11, and C-12 are given in Table III.

of C-1 changes the most (−4.6 ppm), while for the rest of the carbon atoms the difference in chemical shift exhibits a maximum towards the middle of the chain. The large change of chemical shift for C-1 (which carries the largest positive charge) is due to the obvious change in distance between nitrogen and the anion on dissolution. The changes of chemical shift for the more neutral carbon atoms, C-2 through methyl carbon, should be caused mainly by conformational disorder which is present in solution, but largely absent in the crystalline phase due to crystallization to a mainly *trans* conformation. The trend that the carbon atoms at the middle of the chain have a maximum differential chemical shift is brought about because only they may have two γ-substituents that become partially *gauche* on dissolution. A more detailed discussion of the γ-*gauche* effect was given in Part III of this series of papers.[3] Since each of the γ-*gauche* substituents contributes a shielding effect of −5.2 ppm[9] for one *gauche*-bond γ to the carbon atom in question, the observed contribution of the γ-*gauche* effect in going from all-*trans* in the crystalline phase to the typically 40% *gauche* concentration in solution is about $-5.2 \times 0.4 \times 2 = -4.16$ ppm for two *gauche*-bonds γ to the analyzed carbon. The observed differences for C-4 through C-*w* between crystal and solution are, thus, expected to be about −4.16 ppm. For C-1, C-2, C-3, C-*x*, C-*y*, and C-*z* which have only one possible γ-*gauche* effect, the observed differences are expected to be closer to half

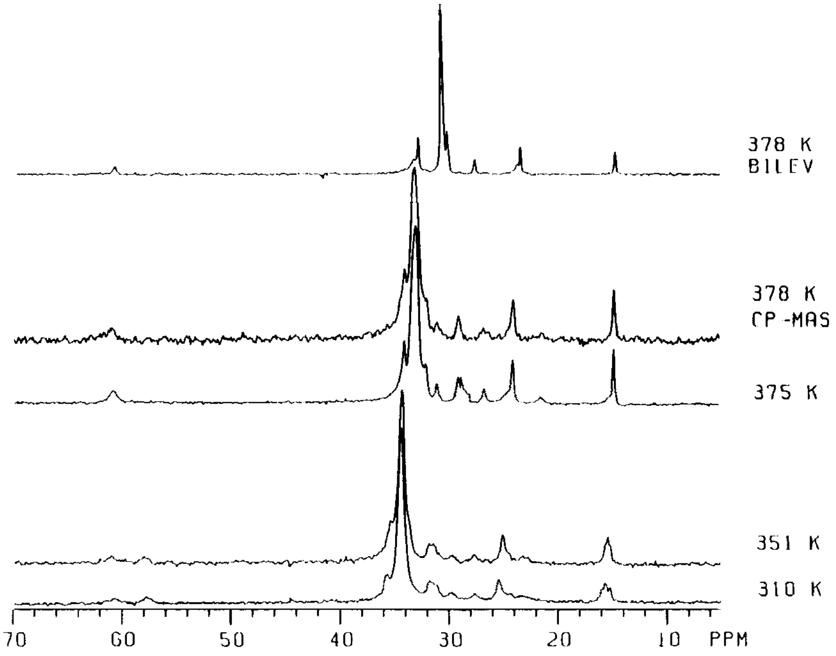

FIGURE 4 Variable-temperature NMR spectra of tetra-*n*-octadecylammonium bromide, $[CH_3(CH_2)_{17}]_4NBr$, as a function of temperature. At 378 K, two spectra were measured with BILEV and CP-MAS. Peak assignments and chemical shifts for C-1, C-2, C-3, carbons at the middle of the chain, C-16, C-17, and C-18 are given in Table IV.

of this value. Although this rule is not perfectly obeyed, it can in many cases give a satisfactory explanation of the motion and disorder.

Tetra-*n*-octylammonium Bromide

From calorimetry, the total entropy of fusion is 129.0 JK^{-1} mol^{-1}. According to the empirical fusion rules,[1,4,5] this value is less than expected by about: $[(\Delta S_{conf.} \times 4 \times 5) + \Delta S_{orient.} + (\Delta S_{pos.} \times 2)] - 129.0 = [(9.5 \pm 2.5) \times 4 \times 5 + (35 \pm 15) + (10.5 \pm 3.5) \times 2] - 129.0 = 116.6 \pm 24.5$ (in JK^{-1} mol^{-1}). The multiplier 4 accounts for the four alkyl chains per cation, the multiplier 5 for the five single C—C bonds that can be disordered,[2,3] and the multiplier 2 accounts for the positional disorder of both cation and anion. The entropy deficit of 116 JK^{-1} mol^{-1} may well be made up by conformational disordering of *three* bonds per alkyl chain ($9.5 \times 4 \times 3 = 114$ JK^{-1} mol^{-1}) that occurs outside of the transitions.

A detailed look at the changes of the chemical shifts is given by Figure 7. The atoms C-3 to C-8 show a continuous decrease in chemical shift below T_d (323 K). All atoms show a break at T_d and only C-1 and C-2 show irregular, almost constant chemical shifts between T_d and T_i (374 K). In the melt, C-1 to C-4 and C-8 show the expected decreases in chemical shift (see Table I), while C-5 to C-7 show 2–4 ppm larger chemical shifts than expected from the discussion of Table VI above. If one assumes that the extra chemical-shift changes originate from intermolecular sources and are changing largely parallel with the increase in motion in the vicinity

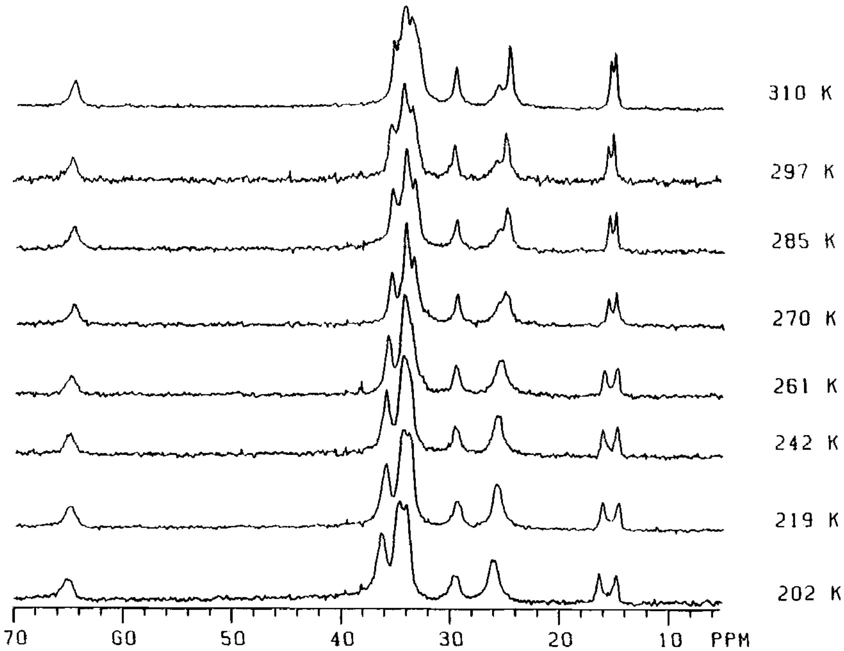

FIGURE 5 Variable-temperature NMR spectra of tetra-*n*-dodecylammonium iodide, $[CH_3(CH_2)_{11}]_4NI$, as a function of temperature. Peak assignments and chemical shifts for C-1, C-2, C-3, C-4 through C-9, C-10, C-11 and C-12 are given in Table V.

of the carbon atom in question, one can speculate that motion is introduced as follows: At about 150 K bonds C6—C7, C5—C6, and C4—C5 become gradually mobile with a decreasing degree of γ-concentrations in the sequence listed. Most of the change in chemical shift in C-5 to C-7 is, however, caused by intermolecular effects as judged from the smaller decreases for C-3, C-4, and C-8. For equal *gauche* concentrations in these three bonds equal γ-*gauche* effects are expected for C-3 to C-8. The transition at T_d brings (because of its small entropy) mainly a packing adjustment with further increase in the disorder about bonds C6—C7, C5—C6, and C4—C5 occurring above T_d. Only on isotropization are bonds C2—C3 and C3—C4 randomized as seen from the larger changes in chemical shift of C-5 and C-4 (affected by two bonds) as well as C-1 and C-2, and is expected from the entropy of isotropization of 118.0 JK^{-1} mol^{-1} [conformational: $(7-12) \times 4 \times 2 = 56-96$, orientational: 20–50, positional: $(7-14) \times 2 = 14-28$, all in JK^{-1} mol^{-1}].

The important aspects of motion and disorder in tetra-*n*-octylammonium bromide are thus: (1) It forms a well-ordered crystal at low temperatures (below 150 K) as indicated by the typical values of ^{13}C chemical shifts. (2) Most of the entropy of fusion (90%) is observed at the isotropization. (3) The difference between the experimental entropy of fusion and that predicted (deficit of entropy of fusion) is comparable to the entropy change of 3 bonds per alkyl chain that become conformationally disordered below T_i. (4) If one realizes the fact that the long alkyl-chain tetra-*n*-alkylammonium salts lose their orientational and positional order at iso-

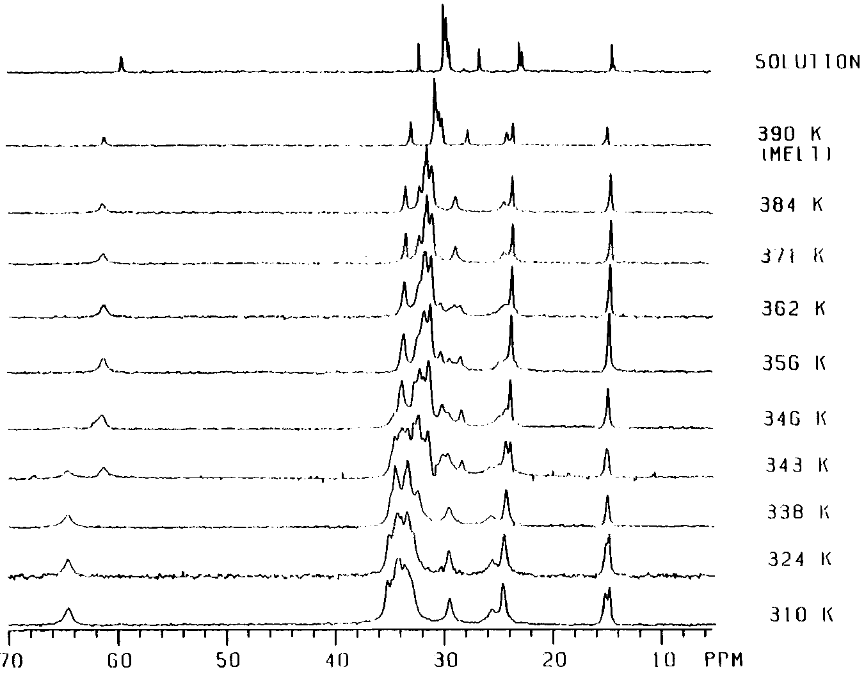

FIGURE 6 Same as Figure 5, but for the high-temperature range from 310 to 390 K. The solution spectrum is shown at the top. Assignments are given in Table V.

tropization only, these observations then suggest that this salt exists as a condis mesophase below isotropization with 3 bonds disordered. It is probable that the already-disordered bonds are those at the chain end, namely, C4—C5, C5—C6, and C6—C7. The conformational disordering is seen to be a rather gradual process over a temperature range from as low as 150 K. (5) The phase transition at 323 K does not introduce additional major disorder and can be looked upon as a change in crystal structure between two condis crystals.

It is hoped that detailed heat capacity and X-ray diffraction studies in progress can resolve the remaining problems of this interesting salt.

Tetra-*n*-decylammonium Bromide

The ^{13}C NMR spectra, plotted in Figure 2, show only small changes below the disordering transition (T_d = 348.6 K, with ΔS_d = 160.8 JK^{-1} mol^{-1}), suggesting that major disordering occurs only at and above T_d. The entropy change corresponds to 4 bonds per alkyl chain becoming disordered. These four bonds can be proven by the γ-*gauche* effect to be those at the chain end, namely, C5—C6, C6—C7, C7—C8, and C8—C9. Comparison between the spectra at 310 and 351 K shows that the chemical shifts for C-1, C-2, and C-3 remain constant, while the others change by different amounts (see Table II). The chemical shift change for C-4 (-1.3 ppm) is due to the disordering about the bond C5—C6, the changes of C-5 and C-6 (-1.8 ppm) are due to the bonds C6—C7 and C7—C8, respectively;

TABLE I

Chemical shifts (in ppm) of tetra-*n*-octylammonium bromide, $[CH_3(CH_2)_7]_4NBr$, as a function of temperature[a]

T (K)	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
135	64.4	25.3	30.0	33.7	35.3	37.3	27.6	16.0
150	64.2	25.5	30.0	33.6	35.3	37.2	27.3	15.9
185	64.0	25.3	29.9	33.5	35.1	36.9	26.9	15.8
198	64.0	25.3	29.9	33.4	35.0	36.8	26.7	15.7
218	63.9	25.3	29.8	33.3	34.9	36.7	26.4	15.7
231	63.8	25.3	29.8	33.3	34.8	36.6	26.3	15.6
247	63.8	25.3	29.8	33.2	34.6	36.4	26.0	15.6
282	63.7	25.2	29.7	33.0	34.2	35.9	25.4	15.5
298	63.7	25.2	29.7	32.8	33.9	35.6	25.2	15.4
306	63.7	25.1	29.7	32.8	33.8	35.4	25.1	15.4
310	63.6	25.0	29.6	32.7	33.8	35.4	25.0	15.4
317	63.4	24.7	29.4	32.4	33.0	34.7	24.6	15.1
Disordering Transition: T_d = 323 K, ΔS_d = 11 $JK^{-1}mol^{-1}$								
325	63.3	24.7	29.4	32.3	33.0	34.7	24.5	15.1
335	63.6	24.7	29.4	32.3	33.0	34.6	24.4	15.0
349	63.3	24.8	29.3	32.2	32.8	34.4	24.3	15.0
364	63.2	24.9	29.3	32.1	32.5	34.2	24.2	14.9
367	63.1	24.7	29.2	32.0	32.5	34.1	24.1	14.9
Isotropization: T_i = 374 K, ΔS_i = 118 $JK^{-1}mol^{-1}$								
377	60.6	23.7	27.6	29.9	29.9	32.6	23.3	14.6
Solut.	59.3	22.4	26.4	29.1	29.1	31.6	22.6	14.1

[a]Based on the spectra of Figure 1 and additional spectra at *T* = 150, 185, 218, 231, 298, 306, 325, 335, 349, and 367 K. Data for the solution are taken from Reference 8.

the C-7 (−4.4 ppm) shows uniquely effects due to two *gauche*-bonds C5—C6 and C8—C9; the change of C-8 (−2.1 ppm) is due to C6—C7; C-9 (−1.7 ppm) due to C7—C8; and finally C-10 (−0.71 ppm) is due to C8—C9. Although the change for the methyl carbon (C-10) is small, its resonance pattern changes from four lines to one, a clear indication of averaging over different crystal positions. The smaller change for C-4 permits further up-field shifting at higher temperatures discussed in the next paragraph. In contrast to the octyl compound the changes in the decyl cation are abrupt at the transition instead of gradual before the transition.

On isotropization, the spectra in Figure 2 show large changes in the resonance positions for C-1, C-2, and C-3, indicating conformational disordering about the bonds C2—C3, C3—C4, and C4—C5, respectively. Other carbon atoms, for ex-

TABLE II

Chemical shifts (in ppm) of tetra-*n*-decylammonium bromide, $[CH_3(CH_2)_9]_4NBr$, as a function of temperature[a]

<table>
<tr><th>T (K)</th><th>C-1</th><th>C-2</th><th>C-3</th><th colspan="2">C-4 to C-6</th><th colspan="2">C-7, C-8</th><th>C-9</th><th>C-10</th></tr>
<tr><td>127</td><td>63.8</td><td>25.3</td><td>29.2</td><td colspan="2">34.0 ±0.5[b]</td><td colspan="2">36.6 ±0.2</td><td>25.9</td><td>14.3 – 16.2[c]</td></tr>
<tr><td>310</td><td>63.5</td><td>25.3</td><td>29.4</td><td colspan="2">33.8 ±0.3</td><td colspan="2">35.7 ±0.2</td><td>25.3</td><td>14.6 – 15.5</td></tr>
<tr><td colspan="10">Disordering Transition: T_d = 349 K, ΔS_d = 161 JK^{-1}mol^{-1}</td></tr>
<tr><td></td><td>C-1</td><td>C-2</td><td>C-3</td><td>C-4</td><td>C-5, C-6</td><td>C-7</td><td>C-8</td><td>C-9</td><td>C-10</td></tr>
<tr><td>351</td><td>63.3</td><td>24.7</td><td>29.0</td><td>32.5</td><td>31.9</td><td>31.3</td><td>33.6</td><td>23.6</td><td>14.7</td></tr>
<tr><td>355</td><td>62.8</td><td>24.6</td><td>29.0</td><td>32.4</td><td>31.9</td><td>31.2</td><td>33.5</td><td>23.6</td><td>14.6</td></tr>
<tr><td colspan="10">Isotropization: T_i = 363 K, ΔS_i = 102 JK^{-1}mol^{-1}</td></tr>
<tr><td></td><td>C-1</td><td>C-2</td><td>C-3</td><td colspan="3">C-4 to C-7</td><td>C-8</td><td>C-9</td><td>C-10</td></tr>
<tr><td>378</td><td>60.4</td><td>23.5</td><td>27.5</td><td colspan="3">30.3, 30.0, 29.9</td><td>32.7</td><td>23.3</td><td>14.6</td></tr>
<tr><td>Solut.</td><td>59.3</td><td>22.4</td><td>26.4</td><td colspan="3">29.4, 29.2, 29.2</td><td>31.8</td><td>22.6</td><td>14.1</td></tr>
</table>

[a] Spectra of Figure 2.
[b] Errors indicate an approximate linewidth of the broad peak.
[c] Showing the range of multiple lines.

ample, C-4 to C-8, undergo further up-field changes in the chemical shift (but with relatively smaller amplitudes), indicating perhaps further increase in the *gauche* content in the corresponding bonds. A comparison between the spectra of melt and solution in Figure 2 reveals that there is still an about 1 ppm difference in the chemical shift values for the inner carbon atoms, such as C-1, C-2, C-3, and perhaps C-4, but there is almost no difference for the chain-end atoms, such as C-9 and C-10. The reason may be that the inner-bonds have less *gauche* concentrations or mobility and different charge distributions in the molecules of the melt.

From this analysis, it is concluded that tetra-*n*-decylammonium bromide forms a well-ordered crystal phase below T_d = 348 K, a condis phase between T_d = 348 K and T_i = 363 K with only four bonds disordered per alkyl chain, and finally a melt above T_i with all bonds except N—C1, C1—C2, and C9—C10 contributing to conformational disorder. Disordering seems to occur stepwise only.

Tetra-*n*-dodecylammonium Bromide and Iodide

Bromide. The observed total entropy of fusion for tetra-*n*-dodecylammonium bromide (341 JK^{-1} mol^{-1}) is within the expected range of 286–510 JK^{-1} mol^{-1}. The large uncertainty of the empirical rules for such long alkyl chains, however, leaves the possibility of disordering of 2–3 bonds per alkyl chain outside of the transitions.

Below the lowest transition temperature (225 K), the ^{13}C NMR spectra show double peaks for each distinguishable carbon from C-1 to C-11, while for the methyl carbon, C-12, four lines are clearly evident (Figure 3). This complicated spectrum proves non-equivalency among the four alkyl chains, i.e., a low symmetry of the

TABLE III

Chemical shifts (in ppm) of tetra-*n*-dodecylammonium bromide, $[CH_3(CH_2)_9]_4NBr$, as a function of temperature[a]

T (K)	C-1	C-2	C-3	Middle	C-10	C-11	C-12
168	62.0 59.9[b]	23.7 22.7	29.9 28.9	34.5 −31.8[c]	36.7 36.2	26.4 26.0	16.5 −15.2
220	62.5 60.2	23.8 22.7	29.9 29.3	34.4 −31.5	35.9	25.8	15.7 −14.9
Transition: T_d = 225 K, ΔS_d = 6.4 $JK^{-1}mol^{-1}$							
310	62.5 60.5	23.9 22.6	29.7 29.1	34.2 −31.4	35.4	25.1	15.4 −14.8
336	60.5 57.8	23.8 22.6	29.0	34.1 −31.6	35.3	25.0	15.2 −14.9
346	60.5 57.7	23.7	29.0	33.8 −31.4	35.0	24.6	14.7
Overlapping Transitions: (347 K, 363 K) with ΔS (128, 207 $JK^{-1}mol^{-1}$)							
365 (melt)	60.4	23.4	27.3	30.5 −30.0	32.7	23.4	14.6
Solut.	59.3	22.4	26.5	29.7 −29.2	31.9	22.7	14.1

[a] Spectra of Figure 3.

[b] Two values are given for the same carbon atom with two peaks.

[c] Two values separated by a " – " indicates the range, for details see Figure 3.

TABLE IV

Chemical shifts (in ppm) of tetra-*n*-octadecylammonium bromide, $[CH_3(CH_2)_{17}]_4NBr$, as a function of temperature[a]

T	C-1	C-2	C-3	middle	C-16	C-17	C-18
310	60.5, 57.7[b]	24.2, 23.1	27.5	34.2[c]	35.5	25.3	15.9–15.1
351	60.8, 57.9	24.2, 23.1	27.6	34.2	35.2	25.0	15.3
Overlapping Transitions: (375, 380 K), with ΔS = (227, 329 $JK^{-1}mol^{-1}$)							
375	60.7	24.5, 21.4	26.6	32.9	33.9	24.0	14.7
378[d]	60.8	24.0	26.7	33.0	34.0	24.0	14.7
378[e]	60.6	23.6	27.5	30.5	32.7	23.3	14.6

[a] Spectra of Figure 4.

[b] Two values are given for the same carbon atom with two peaks.

[c] Indicates the strongest peak in Figure 4.

[d] Measured with CP-MAS pulse sequence.

[e] Measured with BILEV pulse sequence.

TABLE V

Chemical shifts (in ppm) of tetra-*n*-dodecylammonium iodide, $[CH_3(CH_2)_{11}]_4NI$, as a function of temperature[a]

T (K)	C-1	C-2	C-3	Middle	C-10	C-11	C-12
202	64.9	26.0	29.5	34.4–33.8[b]	36.1	26.0	16.3, 14.7[c]
270	64.6	25.6	29.4	34.1–33.4	35.4	25.0	15.5, 14.8
Transition: T_d = 284 K, ΔS_d = 12.3 $JK^{-1}mol^{-1}$							
285	64.6	25.71	29.4	34.1–33.3	35.3	24.8	15.4, 14.8
310	64.4	25.6	29.4	34.1–33.5	35.1	24.5	15.2, 14.8
338	64.4	25.6	29.4	34.1–32.2	34.5	24.1	14.8
Overlapping Transitions: (343, 351, 365 K) with ΔS (12.6, 109, 15.1 $JK^{-1}mol^{-1}$)							
346	61.2	24.6	29.2	32.0–29.9	33.6	23.6	14.7
362	61.1	24.2	28.8	31.5–30.1	33.4	23.5	14.5
384	61.2	24.2	28.7	32.0-30.8	33.2	23.4	14.4
Isotropization: T_i = 389 K, ΔS_i = 122 $JK^{-1}mol^{-1}$							
390	60.9	23.8	27.4	30.4–30.0	32.6	23.2	14.5
Solut.	59.4	22.5	26.4	29.7–29.2	32.0	22.7	14.1

[a] Spectra of Figures 5 and 6.

[b] Two values separated by a "–" indicates the range, for details see Figures 5 and 6.

[c] Two values are given for the same carbon atom with two peaks.

cation. The spectra below and above the 225 K transition do not indicate any significant change. The transition must thus be a solid-solid transition without major change in mobility and relative packing of the motifs of the crystal. The rather low entropy of transition is in accord with such interpretation.

Examining the wider range of temperature, from 168 K to 346 K (just below the second transition temperature on heating), reveals that: (1) The methyl carbon (C-12) resonance undergoes a coalescence from four-lines to a single line. (2) The chemical shift values for C-11 decrease gradually from 26.4/26.0 ppm (doublet) to 24.6 ppm (single peak). (3) Similar to C-11, C-10 also experiences such gradual change (from a double peak of 36.7/36.2 ppm to single line of 35.0 ppm). (4) Changes for the carbons in the middle of the alkyl chain, and even more for the innermost carbon atoms, are less. These observations suggest that the chain ends undergo, indeed, a gradual disordering below the major transition temperature.

The onset of the overlapping transitions from 347 to 363 K is reflected by the obvious up-field shifting of the carbon atoms in the middle of the chain, as shown from the spectra from 336 to 352 K. These carbons resonate at about 34 ppm at 336 K, while at 352 K an enhancement in the intensity of the peak at about 31.5 ppm is apparent. The change of about −2.5 ppm can again be explained by the γ-*gauche* effect. Unfortunately, due to the serious overlapping between the resonances of carbon atoms in the middle of the dodecyl chain, it is difficult to make a quantitative evaluation of the bonds that have become *gauche*.

TABLE VI

Chemical shifts (in ppm) of some tetra-*n*-alkylammonium bromides and iodides at low temperatures and in $CDCl_3$ solutions

Salts[a]/ T (K)	C-1	C-2	C-3	C-4 to C-w[e]	C-x[e]	C-y[e]	C-z[e,f]
6Br/148[b]	63.6	25.1	29.8		34.3	25.9	16.1
6I/308[b]	64.4	25.0	29.5		33.7	25.5	15.6
7Br/308[b]	63.2	25.1	29.7	32.5	35.6	25.1	15.8
7I/180[b]	64.4	25.2	29.3	32.8	36.2	26.2	16.4
8Br/135	64.4	25.3	30.0	35.3, 33.7	37.3	27.6	16.0
10Br/127	63.8	25.3	29.2	33.5–36.5	36.8	25.9	15.2
12Br/168	62.0, 59.9	23.7, 22.7	29.9, 28.9	31.8–35.0	36.7, 36.2	26.4, 26.0	15.9
12I/202	64.9	26.0	29.5	34.4–33.8	36.1	26.0	15.5
18Br/310	60.5, 57.7	24.2, 23.1	27.5	29.6–34.2	35.5	25.3	15.5
Average	64.0 ±0.5[d]	25.3 ±0.3[d]	29.6 ±0.3[d]	29.6–36.5	35.8 ±1.2	26.0 ±0.7	15.8 ±0.4
Average[c] (Solut.)	59.3 ±0.1	22.4 ±0.1	26.3 ±0.1	28.8–29.8	31.7 ±0.3	22.6 ±0.1	14.0 ±0.1
Diff. Average[g]	4.6	2.9	3.2	0.8–6.7	4.1	3.4	1.8

[a] The names of each salts are abbreviated as mX, in which m is the number of the carbon atoms in an *n*-alkyl chain, X stands for either Br or I.

[b] Data for $6X$ and $7X$ are taken from Reference 3.

[c] Data for solution are taken from Reference 8.

[d] The average values for C-1 and C-2 do not include 12Br and 18Br, for C-3 not 18Br.

[e] C-w, C-x, C-y, and C-z stand for the last four carbon atoms in an alkyl chain, C-z is the methyl carbon.

[f] The methyl carbons show multiple lines in many cases, but for convenience the values in this table were taken as the average. For details see respective tables.

[g] The differential value is taken as the average (crystal) *minus* average (solution).

Upon isotropization (363 K), the peaks of the carbon atoms in the middle (at about 34 and 31.5 ppm) move further down-field to 30.5–29.98 ppm, as indicated in Figure 3 and Table III. The inner-most carbon atoms also show changes. The double-peak of C-1 becomes a singlet in the melt, the C-2 signal decreases by 1.4 ppm, and C-3 changes from a rather broad peak centered at about 29 ppm to a sharp one at 27.3 ppm.

Another interesting feature in this salt is the change of the C-1 resonance. The double-peak undergoes a up-field shifting between 310 and 336 K, a temperature range where no transition is observable in the DSC experiment. This change is probably associated with a crystal structure change in which the distance between the nitrogen and bromide is altered. Similar up-field shifting of the C-1 resonance in the octyl- and decyl-compounds were only observed on isotropization, as shown in Figures 1 and 2.

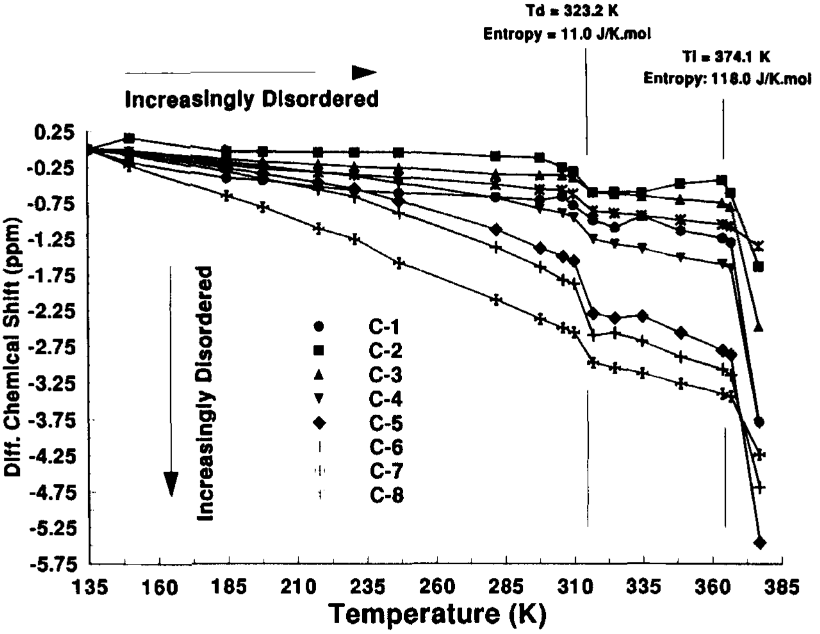

FIGURE 7 Plots of differential chemical shifts for all carbon atoms in tetra-*n*-octylammonium bromide (chemical shift at *T minus* the chemical shift at 135 K). The transition temperatures observed by DSC are marked by the two vertical lines, and are also listed in the figure along with the entropy changes.

Iodide. A series of transitions was reported for this salt as shown in Table V. The data in parentheses indicate overlapping transitions. Unlike the bromide discussed above, the total entropy of fusion for the iodide (271 JK^{-1} mol^{-1}) is clearly below the expected range of 286–510 JK^{-1} mol^{-1}.

The resonances of carbon atoms at the chain end undergo a clearly noticeable continuous change from 202 to 310 K. The separation of the doublet of C-12 (methyl carbon) decreases from 1.57 ppm at 202 K to 0.41 ppm at 310 K; C-11 initially superimposes with C-2 at 26.0 ppm at 202 K, but shifts to 24.5 ppm at 310 K (while C-2 remains at the same position); C-10 also undergoes a gradual, up-field change from 36.1 to 35.1 ppm. Because of the chemical shift changes in C-12, C-11, and C-10, the resonances of their γ-substituents C-9, C-8, and C-7, respectively, undergo similar changes (γ-*gauche* effect) as evidenced by the noticeable change in the overlapping signal at about 32 ppm. The gradual changes in the three chain end atoms and their γ-substituents, thus, explain the entropy deficit. The peaks for the inner-most carbon atoms remain unchanged.

The transition at 284.1 K shows an entropy change of only 12.3 JK^{-1} mol^{-1}, which is much less than that for the conformational disordering of even one bond per alkyl chain (about 38 JK^{-1} mol^{-1}). This transition is, nevertheless, reflected by the change in resonances of carbon atoms in the middle of the chain, as can be seen from the up-field shifting of the peaks at about 34.5 ppm in going through the transition. A transition involving mainly changes in cation packing is the likely explanation.

From 310 K to 343 K, although no transition is observable in the DSC experiment, the line shape of the peak arising from the carbons in the middle of the chain at about 34 ppm undergoes further gradual change (see Figure 6). Above 343 K, the overlapping endotherms observed in the DSC correspond to a gradual change in the peaks of around 31.5 ppm (middle of the chain) shown in the spectra from 346 to 371 K (Figure 6). The 343 K transition may also involve a crystal-structure change, as indicated by a rather large up-field shifting in the peak for C-1 (changes from 64.4 ppm at 338 K to 61.2 ppm at 346 K).

Finally, the comparison between the spectra at 384 and 390 K shows that on isotropization (389 K) another stepwise up-field shifting of the peaks for the middle of the chain is introduced. It is interesting to see that the signals for C-1 and C-2 change by -0.3, -0.4 ppm only, but C-3 by -1.3 ppm. This behavior may indicate that the bonds C2—C3 and C3—C4 are still rigid even in the melt of 390 K, and may also be used to explain the entropy deficit. With increasing of the temperature, the signals of C-1 and C-2 are expected to become more shielded (smaller chemical shifts).

In summary, the dodecyl compounds of bromide and iodide start to show gradual conformational disordering at the chain ends at temperatures below the reported transitions. The disordering and isotropization transitions observed in the DSC experiments can be linked with the stepwise conformational disordering about the bonds in the middle of the chain (C-4 through C-9). Below the isotropization, both salts may have a crystal structure change involving the rearrangement of the distances between nitrogen and the anion, as indicated by the large abrupt change in the C-1 resonance.

Tetra-*n*-octadecylammonium Bromide

Below the transition of 375 K, the low temperature ^{13}C NMR spectrum, similar to tetra-*n*-dodecylammonium bromide, shows double peaks for the inner-most carbons, C-1 and C-2 (see Figure 4 at 310 K), indicating the low symmetry of the cation. The carbon atoms at the chain end, on the other hand, behave as expected for a well-ordered crystal in terms of multiplicity and chemical shift values. The spectra obtained at 310 and 351 K show no obvious difference except for rather small changes of resonance pattern for the methyl carbon (C-18) and a slight up-field shifting of C-17 and C-16 by about -0.4 ppm (see Table IV). The strongest peak containing approximately 8–10 carbons (out of the total of 18) moves very little. Thus, the conformational disordering below the phase transition is small.

At the phase transition (375 K), major change is found for the strongest peak between 351 and 375 K. A decrease from 34.2 to 33.0 ppm can be linked to the observed entropy change of 227 JK^{-1} mol^{-1}. The signals of C-1 changing from two lines at 351 K to a single sharp peak at 375 K is, again, indicative of the rearrangement of ions (caused by a crystal structure change). Isotropization is indicated by yet another obvious change (-2.5 ppm) for the strongest peak between the two spectra measured with different pulse sequence (BILEV and CP-MAS), both at 378 K. The top spectrum in Figure 4 was obtained using BILEV method which shows mainly the liquid signals, while the CP-MAS spectrum shows only the solid signals.

Thus, in tetra-*n*-octadecylammonium bromide, only stepwise conformational disordering is observed. The phase transitions are mainly caused by the conformational changes in the middle of the alkyl chains. The entropy contribution from the gradual conformational disordering about the bonds at chain end is small.

CONCLUSION

The high homologs of symmetric tetra-*n*-alkylammonium bromides and iodides form well-ordered crystal phases at sufficiently low temperature, indicated by their typical ^{13}C NMR spectra (fingerprint) and unique chemical shift values.

Conformational motion and disordering starts from the chain ends either gradually or stepwise. Gradual conformational changes at the chain end are found for tetra-*n*-octylammonium bromide, tetra-*n*-dodecylammonium bromide, and tetra-*n*-dodecylammonium iodide, while a stepwise change is seen for the bromides of tetra-*n*-decylammonium and tetra-*n*-octadecylammonium. As the temperature is increased further, the bonds in the middle of the chain become disordered in steps within the mesophase-transition detected in the DSC experiments. Finally, isotropization occurs with all remaining types of disordering, i.e., positional, orientational, and conformational.

Crystal structure changes, indicated by a large up-field shifting of the C-1 resonance, occurs below isotropization in the cases of tetra-*n*-butylammonium bromide, tetra-*n*-hexylammonium bromide, and tetra-*n*-heptylammonium iodide, as shown in previous papers,[3] and the bromide and iodide of tetra-*n*-dodecylammonium and bromide of tetra-*n*-octadecylammonium, shown in this paper.

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