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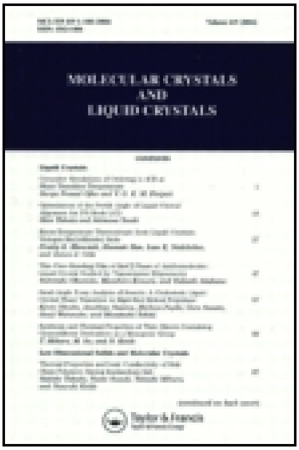

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Mesophases of Alkylammonium Salts II. Disorder and Motion in the Low Homologs: $[CH_3(CH_2)_{n-1}]NX$, n = 1, 2, 3 and X = Br and I Analyzed by Solid State ^{13}C NMR

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Mesophases of Alkylammonium Salts II. Disorder and Motion in the Low Homologs: $[CH_3(CH_2)_{n-1}]NX$, $n = 1, 2, 3$ and X = Br and I Analyzed by Solid State ^{13}C NMR†

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Disorder and motion in crystals of tetra-*n*-alkylammonium halides of short chain length alkyl groups, $[CH_3(CH_2)_{n-1}]_4NX$, where $n = 1, 2, 3$ and X = Br and I, have been analyzed based on solid state NMR. The solid-mesophase phase transitions involve orientational motion and disorder of the cation as a whole, so that the mesophases must be identified as plastic crystals. Except for the methyl rotation, the conformational motion, *i.e.*, the rotation about single-bonds, is limited to small-angle librations that do not reach other conformational isomers. The analyzed salts show, thus, a plastic-crystal mesophase without conformational disorder. The information on the disorder and motion, obtained initially by thermal analysis of the transition, agrees well with the more detailed NMR results.

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

INTRODUCTION

In the first paper of this series,[1] the first-order transitions in tetra-*n*-alkylammonium halides, $[CH_3(CH_2)_{n-1}]NX$, have been discussed based on the concept of conformational motion and disorder. The entropy changes for the orientational and conformational disordering for the short-, intermediate-, and long-chain tetra-*n*-alkyl ammonium salts was shown to follow the following respective approximations:

$$\Delta S_{\text{short}} = 44.9\ \text{JK}^{-1}\text{mol}^{-1} \qquad \text{for } n = 1, 2 \text{ and } 3,$$
$$\Delta S_{\text{inter}} = 44.9 + 9.5 \times (4n - 12)\ \text{JK}^{-1}\text{mol}^{-1} \qquad \text{for } n = 4\text{–}7,$$
$$\Delta S_{\text{long}} = 9.5 \times (4n - 12)\ \text{JK}^{-1}\text{mol}^{-1} \qquad \text{for } n \geq 8.$$

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where the value of 44.9 $JK^{-1}mol^{-1}$ is the average value of total entropy of disordering for tetraethyl- and tetra-*n*-propylammonium bromide as well as the iodides, see Table I, and is well within the range for orientational disordering of single, nonspherical motifs predicted by Walden's rule ($\Delta S_{\mathrm{orient}}$ = 20–50 $JK^{-1}mol^{-1}$).[2,3] The term 9.5 × (4*n* − 12) represents the contribution from conformational disordering. The variable *n* is the number of single bonds (including N—C) in the cation, diminished by 12 since there are 3 single bonds in each alkyl chain (total of 12 in four chains) that do not contribute to the entropy changes. These bonds include N—CH_2, NCH_2—CH_2, and CH_2—CH_3. The details will be discussed in this paper. The proportionality constant, 9.5 $JK^{-1}mol^{-1}$, is the typical entropy change associated with one single-bond that becomes conformationally disordered.[3-5]

The interpretation of these relations are: (1) In the short tetra-*n*-alkylammonium salts only orientational disordering to *plastic crystals* without conformational disordering is possible before fusion. The isotropization to the melt occurs for these salts within or above the sublimation or decomposition temperature range. (2) In the salts with intermediate alkyl-chain length both orientational and conformational disordering may be possible, leading either to conformationally disordered *plastic crystals* or to *condis crystals* that have no orientational disorder.[3,5] (3) In the long-chain tetra-*n*-alkylammonium salts, only *condis crystals* exist before isotropization to the melt. The disordering, particularly the conformational disordering, may occur to some degree in a gradual process. Such gradual acquisition of conformational entropy was first documented for the liquid crystal forming N,N′-*bis*-(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD).[6]

In this paper, we will focus on the disorder and motion in the mesophases of the short-chain tetra-*n*-alkylammonium halides derived from solution proton NMR and variable-temperature multi-technique solid state ^{13}C NMR, such as the temperature dependence of the chemical shift anisotropy powder patterns (VT-CSA) measured on static samples, high resolution spectra obtained under conditions of magic angle sample spinning (MAS) and high power proton decoupling with/without cross polarization (CP) transfer, and ^{13}C spin-lattice relaxation times (T_1) at some characteristic temperatures.

It will be shown that the motion and disorder in the mesophases of these short-chain tetra-*n*-alkylammonium salts is, indeed, orientational only. The motion about

TABLE I

Thermodynamic parameters of short-chain tetra-*n*-alkylammonium salts[a]

Salt	T_{tr} (K)	ΔS_{tr} ($JK^{-1}mol^{-1}$)	ΔS_{tr}^{tot} ($JK^{-1}mol^{-1}$)
Et_4NBr	448.3, 462.6	44.6, 3.2	47.8
Et_4NI	471.3	44.3	44.3
Pr_4NBr	382.2, 395.8	44.4, 0.9	45.3
Pr_4NI	225.4, 418.9	6.4, 35.8	42.2

a. Data are taken from Ref. 1 using measurements over temperature range from 130 to 550 K. Tetramethylammonium bromide and iodide show no transition in this temperature range.

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the single bonds, namely, N—CH_2, and NCH_2—CH_2 will be shown to be librational and, thus, does not introduce conformational disorder. The rotation about the —CH_3 bond is facile as in all similar structures and starts gradually already at very low temperature, so that for all practical purpose the —CH_3 can be treated as an isolated (noncooperative) hindered rotor and as is common practice its conformational disorder is ignored since its motion does not substantially change the shape of the cation. The mesophases of the short-chain tetra-*n*-alkylammonium salts are thus all plastic crystals without conformational disorder in the cation.

In subsequent analyses,[7] we will apply this result to the analysis of intermediate- and long-chain cations, for which the proposal of approximately $9.5 \times 12 = 114$ $JK^{-1}mol^{-1}$ was made to account for the deficit in conformational entropy of fusion. Thus, this paper serves as a basis in the effort to separate the well-known plastic crystalline states for the lower homologs from the condis states that exist in the intermediate and long-chain tetra-*n*-alkylammonium halides.

EXPERIMENTAL

The samples used in this paper have been described in detail in the previous publication.[1] They consisted of commercially produced bromides and iodides of $[CH_3(CH_2)_{n-1}]NX$ with $n = 1, 2,$ and 3. All samples had purities in the 99% range. Solution NMR did not detect any proton and carbon containing impurities.

For the measurement of ^1H NMR spectra in solution about 15 mg of the crystalline samples of each were dissolved in 5 ml of deuterated water. The dissolved samples were measured at room-temperature with a Bruker AC250 spectrometer, operating at 250.132 and 62.893 MHz for ^1H and ^{13}C, respectively. The chemical shifts for both ^1H and ^{13}C spectra were reported relative to DSS (4,4-dimethyl 4-silapentane sodium sulfonate) in D_2O.

The solid state ^{13}C NMR spectra were measured on the samples as received. All the measurements were made with a Nicolet NT 200 spectrometer operating at 200.07 and 50.31 MHz for ^1H and ^{13}C, respectively. A solid state probe, purchased from Doty Scientific, Inc., permitted variable temperature measurements. 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 with the rotor were made from brown plastic Vespel® (Registered trademark for a DuPont polyimide). The sample was spun at 4.5 kHz at the magic angle for all the ^{13}C MAS NMR measurements and kept static for the measurements of chemical shift anisotropy powder patterns. Prior to each measurement, after stabilizing temperature and sample spinning rate, the probe was tuned and matched with a 2382 Spectrum Analyzer (100 Hz–400 MHz) made by Marconi Instruments.

A sample of ethylene glycol was used for chemical-shift thermometry to calibrate the sample temperature above 300 K.[8] The calibration was done in the decoupler at sample spinning rates of 0 and 4.5 kHz. The 0 kHz-spinning rate was applied for the observations of CSA and 4.5 kHz for high resolution spectra of solids. The highest achievable temperature of the solid probe employed is 420 K.

The ^{13}C chemical shift values of the solid samples were referenced indirectly

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relative to TMS (tetramethylsilane) *via* hexamethylbenzene (the CH_3 resonance is 17.37 ppm). The spectrometer field drifting was estimated to be less than 0.05 ppm during a variable-temperature run.

The relaxation times of ^{13}C were measured using the conventional progressive saturation method (PS) for long T_1's (>15 s), and inversion recovery (IR) method for shorter T_1's. The broad band decoupling of the protons was maintained. During the variable delay and the recycle delay, a low decoupling power, *ca.* 1 W, was used to saturate the protons and reduce undesirable heating of the sample. During data acquisition, high power dipolar decoupling was used (*ca.* 25 W, corresponding to a 50 kHz field strength or 5 μs for the 90° proton pulse width). The 90° and 180° pulse widths for ^{13}C were 4.1 and 8.2 μs, respectively. At each temperature 10 to 20 experimental data points (variable delays) and 64 FIDs per each data point were collected to yield T_1 values with average errors of less than 8%. All the relaxation time measurements were done under the magic angle spinning conditions (spinning rate of 4.5 kHz). The variable temperature ^{13}C spectra were measured using the combined techniques of CP-MAS. The spin contact/lock time was typically 1–3 ms and the 90° pulse width for protons was 5.0 μs. When cross polarization becomes no longer possible within certain temperature range, the conventional method of one-pulse in ^{13}C channel with two level proton decoupling was used.

RESULTS

The entropies of first order transitions for all to us available samples have been given in the previous publication.[1] For reference, the data for the short-chain tetra-*n*-alkylammonium salts are collected in Table I. A detailed discussion on the experimental and calculated heat capacities of the salts studied in this paper will be given as part V of this series of papers.[9]

Full ^1H and ^{13}C NMR characterizations of $[CH_3(CH_2)_{n-1}]_4NX$ in solution were made, where $n = 1, 2, 3$; and $X = $ Br and I. The solution spectra were used to check the identities and purities of the samples used. Except for improved resolution the spectra are similar to those documented in the literature.[10,11] Of particular interest are the ^1H NMR spectra of the tetra-*n*-propylammonium halides. In Figure 1 the resonances of the protons bonded to C-1 (C-1 is the carbon bonded to the nitrogen) are plotted for all available salts.

For tetramethylammonium iodide the solid state ^{13}C CP-MAS NMR spectral parameters, namely, chemical shift (δ), line width (ΔH), and signal-to-noise ratio (S/N), were monitored as a function of temperature. As the temperature is increased from 308 to 424 K, δ increases from 56.40 to 57.09 ppm, while ΔH decreases from 54.97 to 35.30 Hz and S/N from 100 to 40 (arbitrary units). All changes are gradual.

The ^{13}C spin-lattice relaxation times, T_1, of tetramethylammonium bromide and iodide were measured from 311 to 397 K. The results are shown in Table II.

The variable temperature ^{13}C CP-MAS spectra of tetraethylammonium bromide are shown in Figure 2. Up to 358 K, the methylene carbon resonance shows an asymmetric doublet. At higher temperature the resonance changes to a broad, symmetric single peak and vanishes at 395 K. For the iodide, the room-temperature ^{13}C CP-MAS spectrum is plotted in Figure 3, together with the CSA powder pattern

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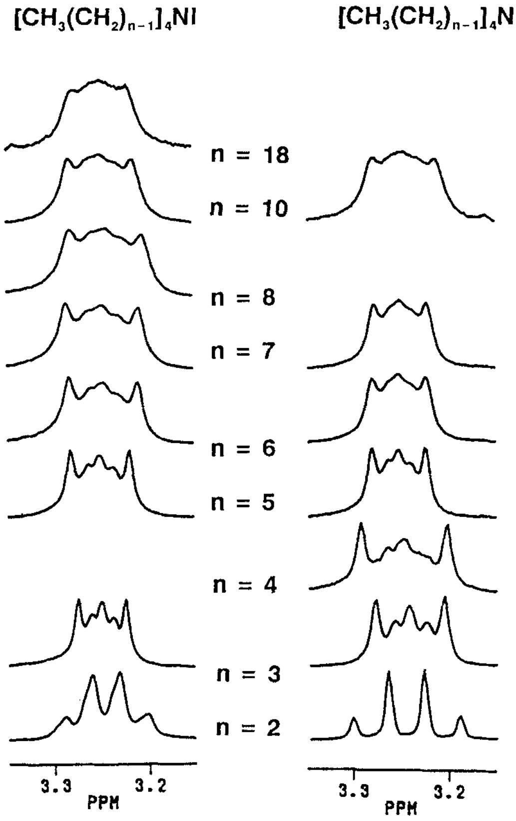

FIGURE 1 Section plots of the 250 MHz ^1H spectra for $N-CH_2$ protons in tetraethylammonium halides and higher homologs in either D_2O or $CDCl_3$ solution at room temperature.

of $(CH_3CH_2)_4NI$. The CSA powder pattern of $(CH_3)_4NI$ is also shown in Figure 3 (at the top) for comparison. An asymmetric doublet pattern of the methylene carbon, as seen in $(CH_3CH_2)_4NBr$, was not observed for the iodide. The ^{13}C T_1 for both tetraethylammonium salts are listed in Table III.

For tetra-*n*-propylammonium bromide at several chosen temperatures, the static ^{13}C NMR spectra, showing CSA powder patterns, are displayed in Figure 4. The variable-temperature high-resolution ^{13}C solid state NMR spectra obtained under conditions of MAS plus high power decoupling are reproduced in Figure 5. The ^{13}C T_1 of tetra-*n*-propylammonium bromide and iodide are listed in Table IV. The correlation time, τ_C, of the motion of an individual carbon in the alkyl groups can be evaluated using the commonly assumed expression for spin-lattice relaxation by dipole-dipole interaction:

$$\frac{1}{nT_{1C}} = \frac{\gamma_C^2\gamma_H^2 h^2}{40\pi^2 r^6}\left[\frac{\tau_C}{1 + (\omega_H - \omega_C)\tau_C^2} + \frac{3\tau_C}{1 + \omega_C^2\tau_C^2} + \frac{6\tau_C}{1 + (\omega_H + \omega_C)^2\tau_C^2}\right] \qquad (1)$$

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TABLE II

^{13}C spin-lattice relaxation times, T_1, of plastic crystalline Me_4NBr and Me_4NI[a]

Temperature (K)	Me_4NBr (ms)	Me_4NI (ms)
311	26.53	32.82
317	26.29	34.33
324	26.34	36.09
331	26.61	38.01
337	27.05	40.19
344	27.60	42.62
350	28.26	45.31
357	28.97	48.23
364	29.75	51.47
370	30.58	55.04
377	31.47	58.81
384	32.40	62.80
390	33.42	67.20
397	34.51	71.76

[a] Measured with inverse recovery method. Typical errors in T_1 are 8%.

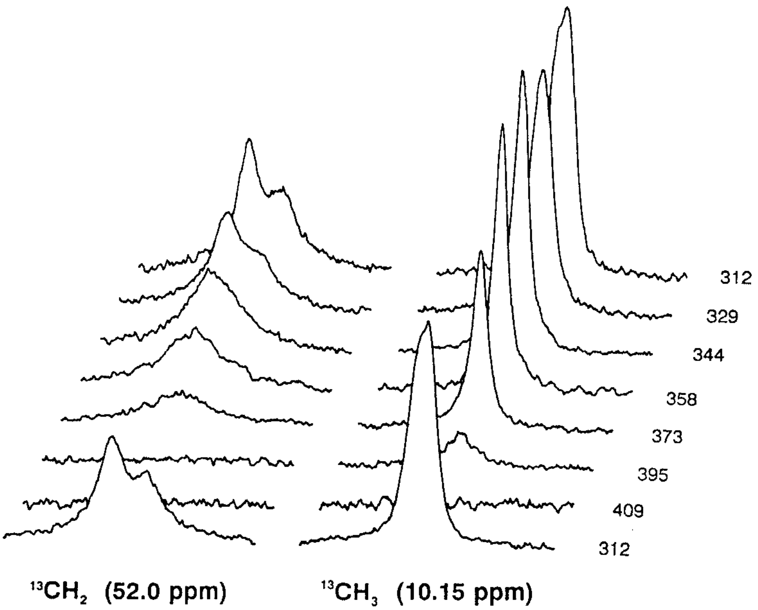

FIGURE 2 Variable temperature 50.3 MHz ^{13}C CP-MAS spectra of solid tetraethylammonium bromide below the disordering transition. Plotted regions are: 56–48 ppm and 14–6 ppm for the methylene and methyl carbons, respectively. Temperatures are (starting from top): 312, 329, 344, 358, 373, 395, 409, and again 312 K measured after cooling from 409 K.

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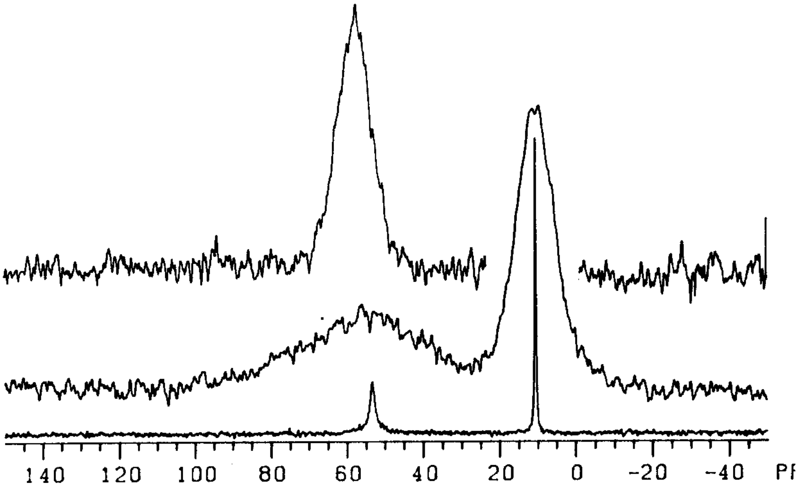

FIGURE 3 Room-temperature 50.3 MHz solid state ^{13}C NMR spectra of tetraethylammonium iodide. Bottom spectrum: CP-MAS; middle: CSA powder pattern measured with CP. The CSA powder pattern for tetramethylammonium iodide is shown on the top for comparison.

TABLE III

^{13}C spin-lattice relaxation times, T_1 (in s), of $(CH_3CH_2)_4NBr$ and $(CH_3CH_2)_4NI$[a]

$(CH_3CH_2)_4NBr$			$(CH_3CH_2)_4NI$		
T (K)	$^{13}CH_2$	$^{13}CH_3$	*T* (K)	$^{13}CH_2$	$^{13}CH_3$
312	14.3	1.69	308	33.6	2.8
329	14.2	1.98	336	21.9	3.5
344	17.4	2.28	358	16.3	4.3
373	17.4	3.09	380	14.4	5.9
395	20.8	3.43	402	4.5	7.3
409	7.94	3.83			

[a] Measured with the progressive saturation method. The errors in T_1 are typically 5%.

where n is the number of directly bonded protons, h is Planck's constant, γ_C and γ_H are the carbon and proton magnetogyric ratios, respectively, r is the distance between interacting ^{13}C and ^1H, ω_C and ω_H are the ^{13}C and ^1H resonance frequencies. The results of the calculations are also listed in Table IV.

For tetra-*n*-propylammonium iodide, a series of the variable temperature ^{13}C NMR MAS spectra from 312 to 433 K were obtained with Bloch-decay and high-power decoupling of protons and are shown in Figure 6a. The MAS spectra from 177 to 312 K were obtained with CP-MAS and are shown in Figure 6b. The rates of cross polarization transfer at 308 and 408 K are shown in Figures 7 and 8, respectively, in which a series of ^{13}C CP-MAS spectra are plotted as a function of spin-contact times.

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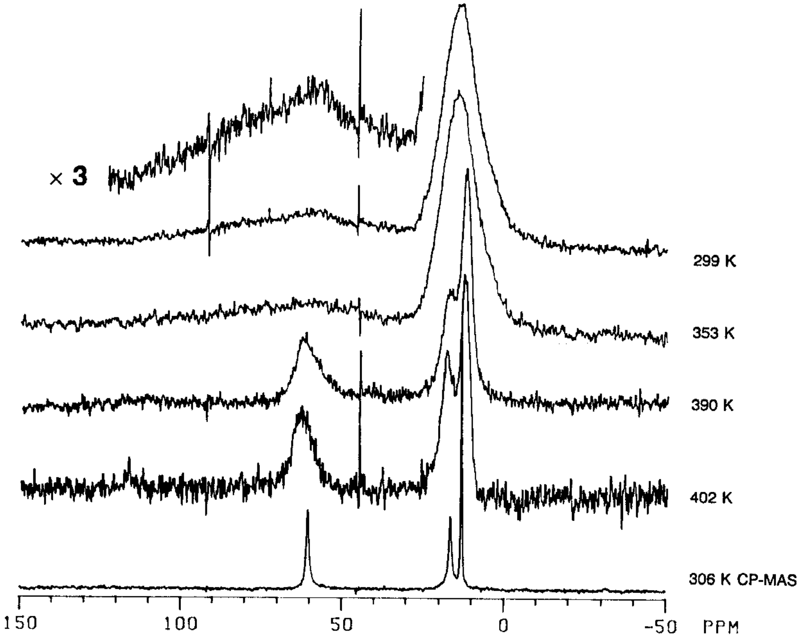

FIGURE 4 Variable temperature 50.3 MHz ^{13}C CSA powder patterns of tetra-*n*-propylammonium bromide. The temperatures are listed along with each spectrum. The bottom plot is the CP-MAS spectrum at 306 K to indicate the isotropic positions for all the resonances. Spectra at 299 and 353 K were obtained with CP, while above the phase transition of 382.2 K the spectra were measured with Bloch decay.

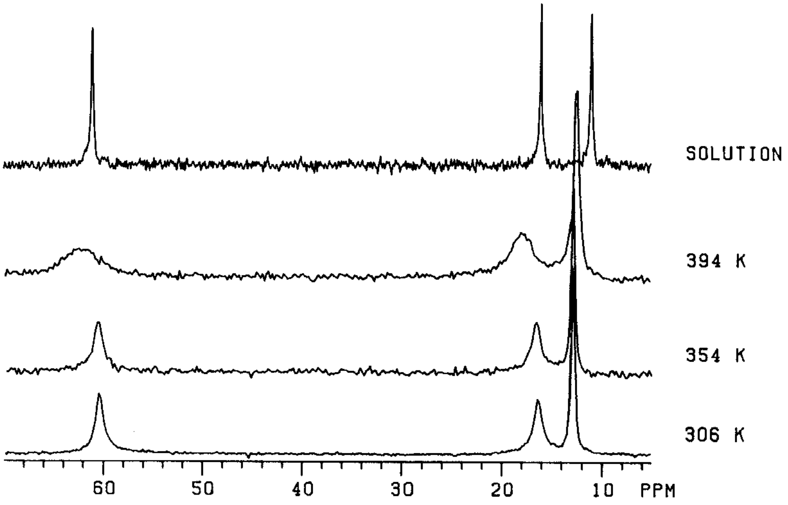

FIGURE 5 Variable temperature 50.3 MHz ^{13}C NMR MAS (spinning rate 4.5 KHz) NMR spectra of tetra-*n*-propylammonium bromide with CP at 306 and 354 K, without CP at 394 K. The solution spectrum is reproduced at the top for reference.

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TABLE IV

^{13}C spin-lattice relaxation time, T_1 (in s), and calculated correlation time, τ_C (in parentheses) of tetra-*n*-propylammonium bromide and iodide[a]

T (K)	C-1	C-2	C-3 (methyl)
$(CH_3CH_2CH_2)_4NBr$			
306	33.2 ±2.1 (47.9 μs)	22.4 ±1.6 (32.3 μs)	1.57 ±0.11 (14.9 ps)
354	30.4 ±1.9 (43.7 μs)	20.0 ±1.5 (28.8 μs)	1.04 ±0.10 (22.1 ps)
394	0.154 ±0.002 (157 ps)	0.250 ±0.004 (94.6 ps)	1.16 ±0.03 (20.0 ps)
$(CH_3CH_2CH_3)_4NI$			
322	3.31 ±0.35 (0.477 μs)	3.42 ±0.51 (0.493 μs)	1.20 ±0.25 (19.4 ps)
433	0.230 ±0.02 (103 ps)	0.42 ±0.04 (55.8 ps)	1.95 ±0.07 (12.0 ps)

[a] Measurements at 354 K and below were done with progressive saturation method, and at 394 and 433 K with inverse recovery. Calculations were made according to Eq. (1). Correlation times were assumed to be on the long-time side of the T_1 minimum at 354 K and below; on the short-time side of the T_1 minimum at 394 and 433 K, as well as for methyl carbons at all temperatures.

DISCUSSIONS

Tetramethylammonium Bromide and Iodide

The thermal and structural information on tetramethylammonium chloride, bromide, and iodide has been summarized in a review by Parsonage and Staveley.[12] These salts have the *a priori* possibilities of rotation of the methyl group, orientational motion of the cation as a whole about one or more axes, and diffusion through the crystal. The former two are considered to be more important in the solid state. The orientational motion of the whole cation in both salts was detected at room temperature by the proton linewidth (second moment) and proton spin-lattice relaxation (wide-line NMR).[12] The orientational motion of the cation was considered to be random, therefore, the crystal must be classified as a plastic crystal.

The experimental evidence for the orientational motion of the cation generated in this research is given by the temperature dependence of three ^{13}C CP-MAS NMR parameters for tetramethylammonium iodide, namely, the chemical shift (δ), linewidth (ΔH), and signal-to-noise ratio (S/N). The chemical shift value increases by 0.4 ppm from 308 to 424 K, but the change is only half of the linewidth at 308 K (1.1 ppm), indicating that the packing remains the same. The other two parameters, ΔH and S/N, decrease continuously and considerably with increasing the temperature. These latter two parameters determine the overall NMR signal intensity, *i.e.*, the area under the peak. The decrease of the integrated signal in a ^{13}C CP-MAS NMR spectrum was shown to be caused by the increased molecular motion as the temperature is increased.[13] The motion that influences the NMR signal intensity between 300 and 400 K is mainly the orientational motion of the cation. The methyl rotation has a much lower activation energy and its motional frequency shows little change as a function of temperature in this high temperature region, *i.e.*, the methyl rotation does not contribute to the change of the NMR spin-relaxation related parameters.

The correlation times and activation energies of the orientational motion of the

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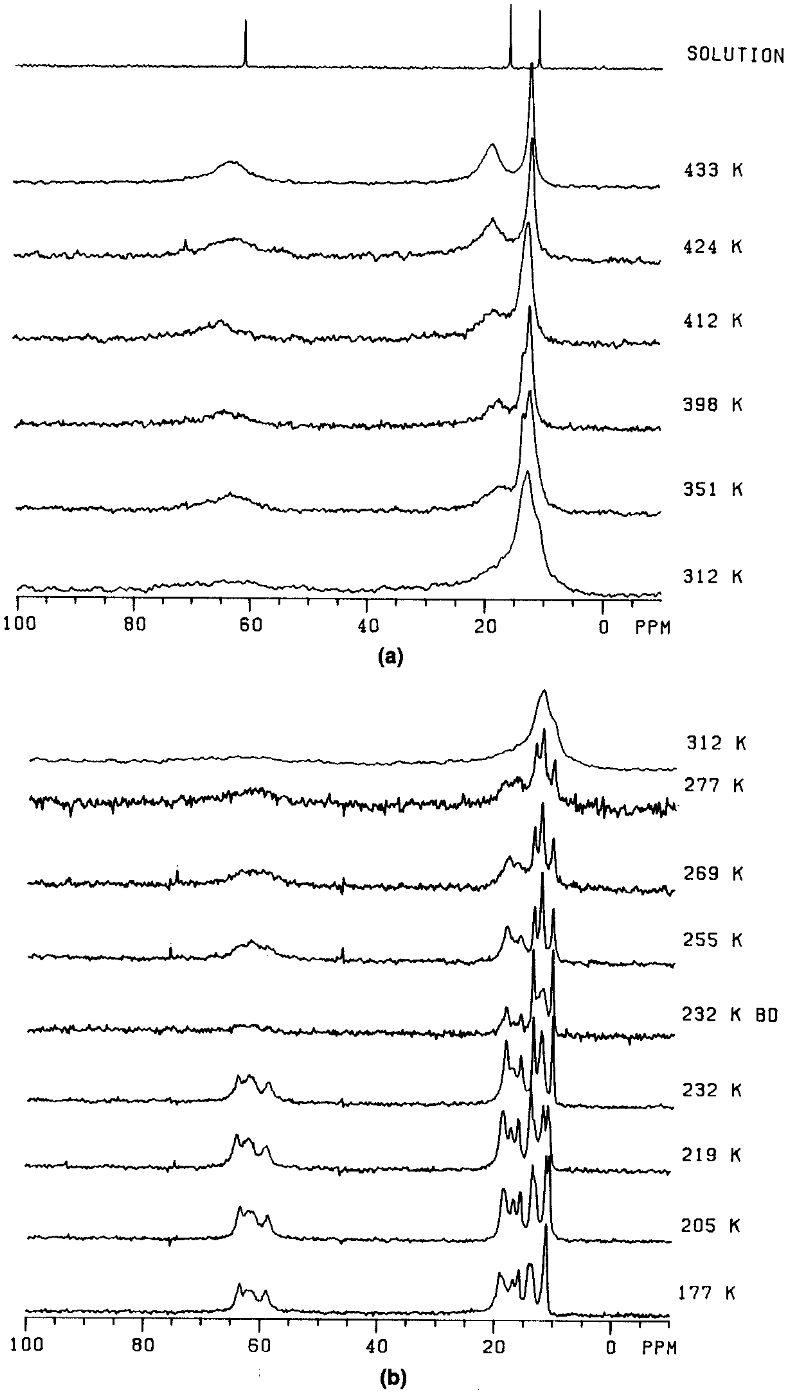

FIGURE 6 (a) Variable temperature 50.3 MHz ^{13}C NMR MAS (spinning rate 4.5 KHz) spectra of tetra-*n*-propylammonium iodide without CP. Temperatures are listed. (b) Same as Figure 6a, but at lower temperatures.

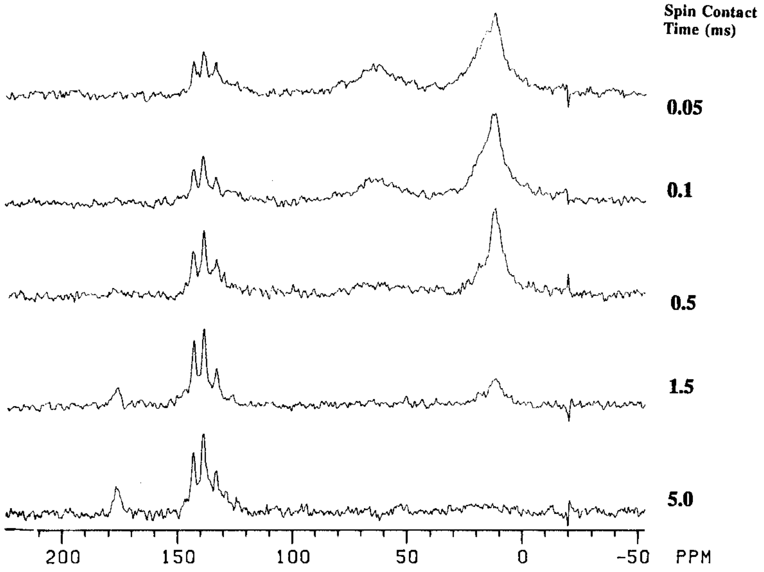

FIGURE 7 Change of ^{13}C CP-MAS spectra of Pr_4NI as a function of spin-contact times (in ms) at room temperature. A maximum in intensity *vs.* the contact time could not be attained. The signals between 120 and 180 ppm are from a referencing compound, tetraphenylborate sodium.

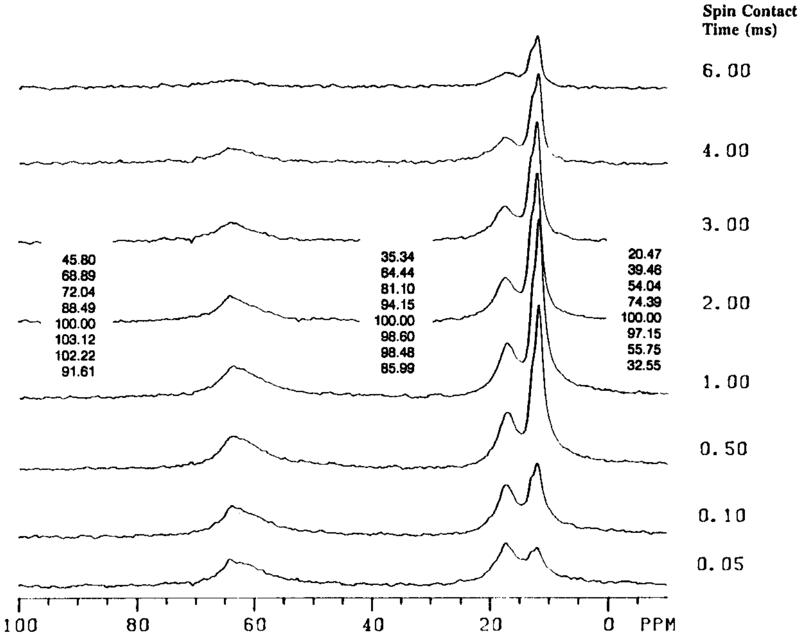

FIGURE 8 Change of ^{13}C CP-MAS spectra of Pr_4NI as a function of spin-contact times (in ms) at 408 K. Maxima in intensity *vs.* the contact time could be attained at contact times of 0.5, 1.0, and 1.0 ms for C-1, C-2, and C-3, respectively (see data printed in the figure).

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cation in tetramethylammonium bromide and iodide can be obtained from the temperature dependence of the T_1 data listed in Table II. The correlation times τ_C of $(CH_3)_4NBr$ decreases from 3.0 ns to 0.74 ns as the temperature is increased from 311 K to 397 K. Within the same temperature range, τ_C of $(CH_3)_4NI$ decreases from 0.85 ns to 0.23 ns. The shorter τ_C's indicate a faster orientational motion in the iodide than in the bromide. The relationship between τ_C and temperature can be fitted into a simple equation to give the activation energy, E_a:

$$\tau_C = \tau_0 \exp(E_a/RT) \tag{2}$$

in which T is the experimental temperature. Fits to the logarithmic form of Equation (2) lead to $\tau_0 = 5.0$ ps and $E_a = 16.5$ kJ/mol for the bromide and $\tau_0 = 2.2$ ps and $E_a = 15.4$ kJ/mol for the iodide. Within the experimental error (8%), the activation energies are the same for both cases. The activation energies obtained in this work are lower than those given for the same compounds in the literature, 35 and 33.5 kJ/mol for the bromide and iodide, respectively, see Reference 12. They are, however, more in line with the activation energies for rotation of a series of tetramethyl compounds with central atoms of varying size: $(CH_3)_4C$, 4.2 kJ/mol; $(CH_3)_4Si$, 31 kJ/mol; $(CH_3)_4Ge$, 46–64 kJ/mol.[14]

Tetraethylammonium Bromide and Iodide

As indicated in Table I, each of these two salts has a strong solid-mesophase transition (at 448.3 and 471.3 K, respectively, outside the high-temperature capability of our NMR probe) with entropy changes of 44.6 and 44.3 $JK^{-1}mol^{-1}$. These values are well within the range of entropy changes for orientational disordering: 20–50 $JK^{-1}mol^{-1}$, as given before by Walden's rule,[2,3] indicating that the cations should be orientationally disordered above the phase transition.

The most decisive information on the orientational order of the cations of iodide at ambient temperature is given by the X-ray data on the crystal structure. Wait and Powell[15] could show that the cation in projection forms a Nordic cross (swastika) with the bond angle $N—CH_2—CH_3$ approximately 12° larger than the normal tetrahedral angle. This large distortion in the valence angle in the solid state results in a large decrease in chemical shifts of the methyl carbons of both compounds on dissolution in a solvent, such as D_2O (in the solid state at 308 K the chemical shifts of the methyl carbon are 10.15 and 10.00 ppm for the bromide and iodide, respectively, while in D_2O solution they decrease to 7.10 and 7.17 ppm, respectively).

Other experimental evidence that the cation is orientationally ordered below the phase transition comes from the analysis of the NMR spectra. The asymmetric doublet pattern from the methylene carbon in $(CH_3CH_2)_4NBr$ below 348 K, shown in Figure 2, is due to the ^{14}N quadrupole effect on the ^{13}C-^{14}N dipolar coupling. Such phenomena is usually observable for ^{13}C atoms bonded to such ^{14}N atoms, *e.g.*, $—NO_2$, $—NH_2$, $>NH$, $>N—$, $—NH_3^+$, and $—CN$.[16–18] The asymmetric doublet pattern indicates thus that the inner part of the cation cannot have a tetrahedral symmetry. By increasing the temperature, the symmetry increases and as the electric field gradient at the ^{14}N nucleus vanishes, the splitting pattern disappears. The initial absence of such asymmetric doublet pattern in Figure 3, for the iodide

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indicates that the cation of iodide has the high symmetry already at room temperature.

The CSA powder pattern of the methylene carbon in $(CH_3CH_2)_4NI$, shown in the middle plot in Figure 3, indicates a broad, asymmetrical feature, indicating the methylene carbon is rigid, *i.e.*, neither a conformational motion about the N—C bonds, nor orientational motion of the cation as a whole could exist at room temperature. The methyl group, on the other hand, shows a much narrower and more symmetric peak due to the fast rotation about its C_3 axis. The CSA pattern for $(CH_3)_4NI$ (the top spectrum in Figure 3) shows narrower linewidth caused by the methyl rotation and additional orientational motion.

The orientational motion for a plastic crystal at T_d, the crystal-plastic crystal disordering transition temperature, is typically 5×10^{-9} s and decreases to about 2×10^{-12} s at the melting temperature.[19] The correlation times for the methylene carbons, calculated from the T_1 data of Table III, indicate a motion of correlation time in the range of μs at ambient temperatures, *i.e.*, 150–170 K below the solid-mesophase transition. At about 405 K, a temperature close to the transition, the correlation time is still much longer than is typical for plastic crystals. Therefore, we surmise that the motion below T_d detected in this research is not orientational motion. A slow libration within or of the cation may be possible, but the libration must be limited to an angle that is sufficiently small so that no other orientational or conformational isomer is reached, since these would be forbidden by the X-ray and entropy of transition data.

Examination of molecular models also reveals that the ethyl chains are sterically hindered about the bond between nitrogen and C-1. It seems possible that concerted rotations about all four N—C bonds may occur, but, again the amplitude must be limited, since rotations over large angles would lead to contradictions with other experimental evidences. The impossibility for the conformational motion can be extended also to temperatures above the phase transition, so that the solid-mesophase transition consists only of orientational disordering to the plastic crystalline state without disordering about the N—C bonds.

Tetra-*n*-propylammonium Bromide

Tetra-*n*-propylammonium bromide was studied in the room-temperature crystalline phase and in the high-temperature mesophase with solid state ^{13}C NMR with and without magic angle spinning (MAS). Figure 4 shows the powder patterns of ^{13}C NMR spectra below the first solid-mesophase transition temperature (T_{d1} = 382.2 K with an entropy change of 44.4 J/K mol) at 299 and 353 K, above T_{d1}, at 390 K, and above the second transition temperature (T_{d2} = 395.8 K, with an entropy change of 0.9 J/K mol) at 402 K. The CP-MAS spectrum, which eliminates the CSA interactions for nuclei of spin $\frac{1}{2}$, was obtained at 306 K and is shown at the bottom of Figure 4 to indicate the isotropic positions for all three carbon resonances. Below T_{d1}, the spectra feature broad, asymmetric resonances only. The magnified C-1 resonance at 299 K clearly shows a powder pattern that has three non-identical principal values in the chemical shift anisotropy (CSA) tensor, indicating that C-1 is rigid. The signals of C-2 and C-3 are broadened and overlapping, also due to the chemical shift anisotropy interactions. The width of the C-2 and C-3 peaks

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are, however, much less than for C-1 because of the methyl rotation that partially averages the CSA interaction. As the temperature is increased to 390 K, higher than T_{d1}, no signals can be detected with the CP sequence, indicating a fast motion (see analysis for tetra-*n*-propylammonium iodide below). The appearances of the powder spectra at 390 and 402, obtained with the Bloch decay pulse sequence, are very different from that at lower temperatures. The C-1 resonance changes from asymmetric at 299 and 353 K to an axially symmetric CSA powder pattern at 390 K. The axial symmetry in the CSA powder pattern indicates explicitly that rotation about one preferred molecular axis has started. The CSA interactions for C-2 and C-3 are reduced so much that their resonances are clearly resolved. As the temperature is further increased to 402 K, above T_{d2}, the spectral linewidths becomes further reduced and more symmetric, indicating that the molecular orientational motion becomes more isotropic.

The variable-temperature MAS ^{13}C NMR spectra are shown in Figure 5. Below T_{d1} the spectra obtained with CP at 306 and 354 K are almost identical in terms of chemical shifts and linewidth. While above T_{d1} the signals, again, become undetectable with the CP. The MAS spectrum at 394 K, measured with Bloch decay, shows two drastic changes compared to that at lower temperatures: (1) The linewidths for all carbons have increased. For C-1, it increases from 0.9 to 4.8 ppm (1 ppm = 50.31 Hz). This heterogeneous linewidth broadening is due to a distribution of the environments for the nuclei resulting from orientational disordering (more detailed discussion on the mechanisms of line broadening is given for the case of tetra-*n*-propylammonium iodide, below). (2) The chemical shifts change by 1.8, 1.3, and -0.6 ppm for C-1, C-2, and C-3, respectively, on going through the transition. This global change in chemical shift clearly indicates a change in the packing connected with the orientational disordering.

The conformational motion, *i.e.*, rotation about a single bond in a linear paraffinic chain can be investigated by the difference in the ^{13}C relaxation times between the two directly bonded carbon atoms.[20–22] It follows that the larger the difference in the T_1's between the two bonded carbon atoms, the faster is the conformational motion about the bond.

The ^{13}C T_1 of a series of tetra-*n*-alkylammonium perchlorates $(ClO_4)^-$, with alkyl chain length ranging from 1 to 8 carbon atoms, have been measured in CD_3OD solutions by Coletta *et al.*[23] They showed that in the tetra-*n*-hexylammonium cation the relaxation times are 0.25 and 0.30 s for C-1 and C-2, respectively, and in tetra-*n*-octylammonium cation, the difference between the T_1 of C-1 and C-2 is even smaller, (T_1 is 0.25 and 0.26 s, respectively). Conversion of the T_1 data to the correlation times of the motion, according to Equation (1), indicates that C-1 and C-2 have the same mobility. This can only be due to the orientational and translational motion of the cation in solution as a whole (molecular tumbling), in other words, the rotation about the bond between C-1 and C-2 is virtually absent. The T_1 values for C-3 and C-4 in these two compounds, on the other hand, increase to 0.5 and more than 1 second, respectively, indicating increased motion about C—C is possible as one approaches the chain ends. (In solution, the motion is at the fast extreme and the correlation time of the motion is at the short side of the T_1-minimum predicted by Equation (1), therefore, a larger T_1 corresponds to a

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faster motion). The T_1 values of C-1 and C-2 in the smaller tetra-*n*-alkylammonium cations analyzed were also very similar to each other compared to C-2 and C-3, and any other sequential, directly bonded carbon pair closer to the chain end.[23] This observation that the rotation about C1–C2 is hindered in the liquid, must naturally be extended to the solid state, as will be shown in the following. The motion about the innermost N—C bonds is even more hindered for obvious steric reasons.

The information on the conformational motion about the single bonds in tetra-*n*-propylammonium bromide is contained in the ^{13}C spin-lattice relaxation times, T_1 shown in Table IV. Below the disordering transition, T_1 for C-1 and C-2 is long (20–35 s), indicating slow motion ($\tau_C \approx 10^{-5}$ s) in both CH_2-groups. The difference in the correlation time, τ_C, between C-1 and C-2 is much less than between C-2 and C-3. If one considers the fact that the shortening of T_1 of C-2 relative to C-1 is largely due to the magnetic field fluctuations induced by the methyl rotation, the difference in actual motion between C-1 and C-2 is even less. As the temperature is increased above T_{d1}, T_1 of C-1 and C-2 decreases drastically to about 0.2 s. The difference in T_1 is still somewhat smaller between C-1 and C-2 than between C-2 and C-3, indicating that the bond between C-1 and C-2 is still rigid. The increase in the difference of T_1 between C-1 and C-2 at higher temperatures is caused by a librational motion about C1–C2, similar to that in the N—C bonds of the tetraethylammonium bromide and iodide. The correlation time for C-1 and C-2 at 394 K is on the order of 10^{-10} s, typical for plastic crystals.[19] While the T_1 of the methyl carbon remain almost the same, as expected.

Tetra-*n*-propylammonium Iodide

The measurement of a high resolution ^{13}C MAS NMR spectrum in the vicinity of room temperature was initially attempted using the CP method. The cross-polarization efficiency using a normal spin contact time of 1–3 ms was, however, very poor, as shown in Figure 7. The reason for the insufficient cross-polarization *i.e.*, weak signals in a CP-MAS experiment, is that the cross-polarization time constant, T_{CH}, is equal or larger than the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho H}$.[13]

The relationship between signal intensity and spin-contact time, as shown in Figure 7, indicates that no maximum in the CP rate can be attained, suggesting that a short $T_{1\rho H}$ is the reason for the insufficient cross-polarization. If the shortening of $T_{1\rho H}$ is due to a kHz motion, then by changing the temperature, the rate of motion can be increased, which should yield a longer $T_{1\rho H}$ and a maximum in the signal intensity *vs.* spin-contact time. This is demonstrated in Figure 8 at 408 K, just below the major disordering transition temperature of 418.9 K, in which the maximum CP rates can be accomplished at 0.5 ms for C-1, and 1 ms for C-2 and C-3.

Another reason that may reduce $T_{1\rho H}$ is the presence of paramagnetic impurities. To verify their absence, solution ^1H and ^{13}C NMR spectra were recorded. No impurities could be found at detectable levels. This initial motivation of purity checking has, however, lead to a rather interesting finding: the proton solution spectrum of $(CH_3CH_2CH_2)_4NI$, shown in Figure 1, shows an unexpected splitting

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pattern arising from the N—CH_2 protons. It is centered at 3.23 ppm and consists of a weak triplet inside a strong doublet. This pattern is common to all salts when the alkyl chain length becomes equal to or longer than three carbon atoms. The same resonance patterns are also observed for almost all tetraalkyls in solution.[10,11] In contrast, the spectrum of the C-1 protons in tripropylamine, $(CH_3CH_2CH_2)_3N$, shows the expected triplet.

The splitting of the two C-1 protons, H-1a and H-1b, is caused by the spin-spin scalar coupling or J-coupling (through chemical bonds) with the two protons attached to C-2. The coupling between H-1a and the two H-2's must thus be different from that between H-1b and the two H-2's, which is impossible if the rotation about the bond C1–C2 were free.

The splitting pattern of H-1's shows little change even on heating the solution up to 423 K, the temperature limit of our ^{1}H NMR probe, see Figure 9. The downfield drifting (about 12 Hz) of all resonance lines (but not the solvent signal at 2.48 ppm) as a function of temperature in Figure 9 is a good indication of the fact that there is an acceleration of tumbling of the molecule as a whole as the temperature is increased. Thus, the peculiar pattern on the C-1 protons in tetra-*n*-alkylammonium cations is additional evidence that the rotation about C1–C2 is hindered.

To understand this splitting better, a spin simulation was made by assuming a specific average conformation in the bond between C-1 and C-2. The result for the conformation shown in Figure 10, and the coupling constants, J_{HH}, given in Table V is reproduced in Figure 11. The conformation proposed in Figure 10 permits some librational motion about C1–C2 of small amplitude. The hindrance should

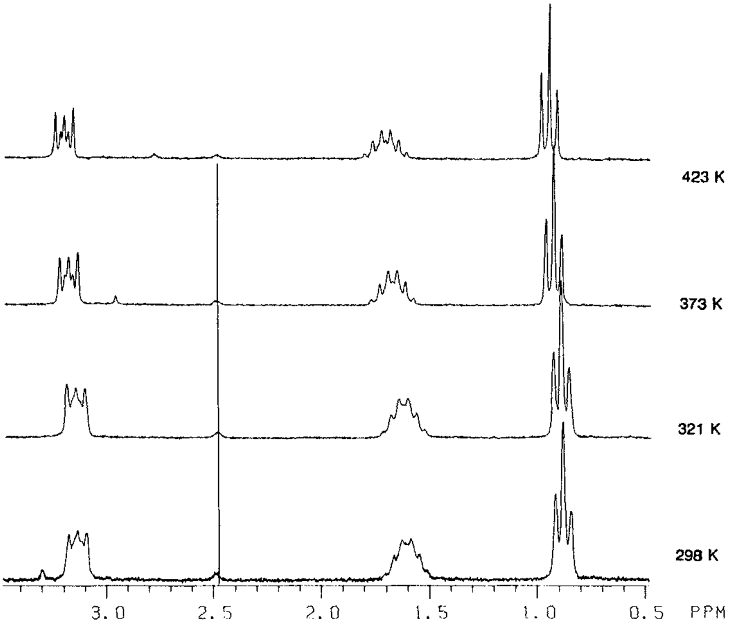

FIGURE 9 Variable temperature solution (in dimethylsulfoxide DMSO-d_6) ^{1}H NMR of tetra-*n*-propylammonium iodide. The peak at about 2.48 ppm is due to DMSO.

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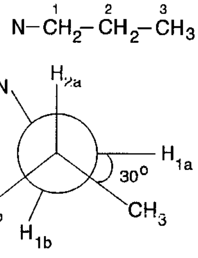

FIGURE 10 Newman projection of a particular equilibrium conformation in a propyl chain in Pr_4NX, X = Br and I. Notice that the dihedral angle between H-1a and H-2a is 90° which yields no coupling.

TABLE V

^1H spin-spin coupling constants, J_{HH}, (in Hz), of tetra-*n*-propylammonium iodide[a]

	H-1a	H-1b	H-2a	H-2b	CH_3
H-2a	0.10	3.5	-	0.00	7.3
H-2b	17.2	3.5	0.00	-	7.3

[a] The values were measured based on a proton spectrum in D_2O solution at room temperature.

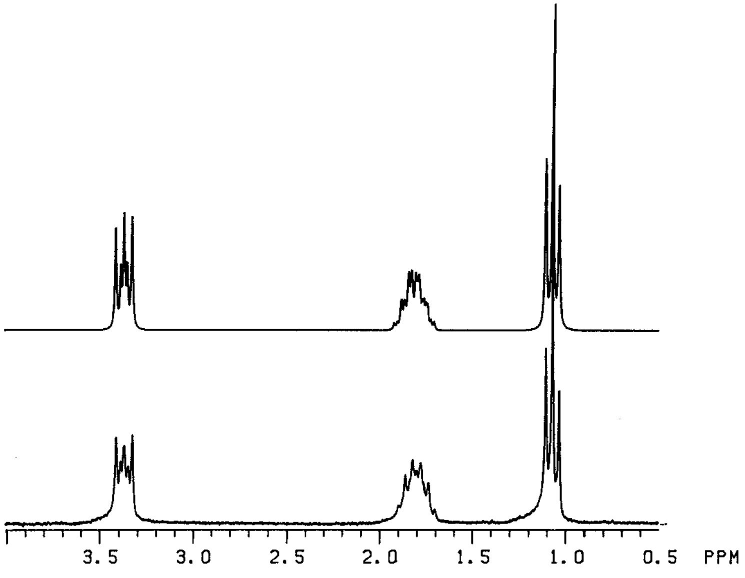

FIGURE 11 Simulated (top trace) and measured (bottom trace) ^1H spectra of Pr_4NI in D_2O. The 7-spin simulation was based on the data given in Table V, and consistent with the conformation shown in Figure 10.

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arise from inter-alkyl chain (intramolecular) steric interactions, similar to that in the N—C bond of the tetraethylammonium ion.

The ^{13}C T_1's measured in the solid state below and above the major disordering transition (T_d = 418.9 K) are listed in Table IV. The data show similar T_1 values for C-1 and C-2, indicating little motion about the bond between C-1 and C-2. The large difference in T_1 for both C-1 and C-2 between 322 and 433 K is due to the increase in overall motion in the cation, *i.e.*, the presence of orientational motion at 433 K. Below the disordering transition, the iodide has a shorter T_1 than the bromide. This will be elucidated in the following through other NMR techniques. Above T_d, both iodide and bromide have similar relaxation times for the respective carbon atoms, indicative of a similar motional state in both cases. The methyl carbons show a slight increase in T_1 going through the transition for both the propyl compounds.

Figure 6a shows that the chemical shifts for all carbons change very little (<0.6 ppm) as a function of temperature, even through the phase transition at 418.9 K. This behavior is quite different from tetra-*n*-propylammonium bromide where changes are observed in the chemical shift at the transition for all carbons (Figure 5). Only above the highest disordering transition can similarity in the ^{13}C MAS NMR spectra be found for iodide and bromide. The constancy in chemical shift of tetra-*n*-propylammonium iodide indicates that neither the packing of the cations nor the conformations about the bonds have changed from 312 to 433 K.

Another feature of the solid state ^{13}C MAS NMR spectra in Figure 6a is its broadness of the peaks. The room temperature spectrum (the bottom trace in Figure 6a) shows rather broad signals for all the carbons in the propyl chain. The most up-field peak has a linewidth of about 7 ppm at half-height and consists of the resonances of two carbons, C-2 and C-3 (C-3 is the methyl carbon) (compared to 0.9, 0.9 and 0.4 ppm for the linewidth of C-1, C-2, and C-3 in the bromide). As the temperature is increased, the separation between the resonances of C-2 and C-3 is possible, but the linewidths are still large (at 412 K the linewidths are 10, 6.5, and 2.8 ppm for C-1, C-2 and C-3, respectively).

It was shown that a distinction could be made between two kinds of solids in which molecular motion is slow based on their line broadening in solid state ^{13}C MAS NMR.[24,25] The first is a crystalline system and the second consists of glassy polymers below glass transition temperatures, T_g. The disordered, rigid solids give rise to broad ^{13}C resonance from 2 to 8 ppm in linewidth, due to variability of molecular environments (disorder). The rigid, crystalline materials, on the other hand, have narrow ^{13}C resonance lines of 0.2–0.8 ppm in width, because all chemically equivalent carbons have similar environments (well-packed and ordered).

Tetra-*n*-propylammonium iodide samples at room temperature fulfills the class of glass-below-T_g, in which the motion is slow (≤kHz). Since conformational disorder was shown above not to be possible, the line broadening must be caused by orientational disorder. This conclusion drawn from the NMR observations is in agreement with the somewhat smaller entropy change at the major orientational disordering transitions for the iodide (35.8 JK^{-1}mol^{-1} at 418.9 K) than for the bromide (45.3 JK^{-1}mol^{-1} at 448.3 K). In fact, a continuous change in the ^{13}C MAS NMR spectrum of the iodide (Figures 6a, 6b) begins at T_{d1} (225.4 K), in

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contrast to the bromide, in which the MAS spectra show no change below the major orientational transition (see Figure 5 at 306 and 354 K). Only as the temperature is decreased below T_{d1}, the linewidth of ^{13}C CP-MAS NMR spectrum of the iodide is narrowed to a value that is comparable to that of the crystalline phase of the bromide at room temperature. Most interestingly, the low temperature spectra measured from 177 K to 232 K exhibit multiple lines for chemically equivalent carbons (Figure 6b). The peaks at 59.0–63.3 ppm (216 Hz of largest separation) are due to C-1, 15.9–19.1 ppm (160 Hz in largest separation) due to C-2, and 11.3–14.1 ppm (140 Hz in largest separation) are from C-3. There are four resonance lines for each of the three carbon atoms in the propyl chain within this temperature range, which must correspond to four distinguishable chains in every cation. An intermolecular inequivalence would introduce much smaller changes in chemical shift, especially for the innermost carbons. The inequivalency agrees with the molecular structure, determined by X-ray, in which the four N—C bonds of the different propyl chains have different lengths.[26] The reason for the different bond lengths is traced to the fact that the four C-1's are in different proximity to the iodide.[26]

Additional details can be seen in the C-3 resonances of Figure 6b in the spectra from 177 to 232 K. The C-3 peaks (11.3 and 14.1 ppm at 177 K) change their splitting pattern as the temperature is increased. The inner two lines approach each other and overlap to become a strong single line as the temperature is increased to 232 K. In this low temperature range (177–232 K) the signals for C-1 and C-2 remain unchanged, indicating that only the methyl groups of the cation are in motion.

Between 232 and 255 K, the spectrum undergoes an overall broadening of which the C-1 and C-2 carbon resonances are most affected. The degradation in the resolution, or coalescence of the multiple lines of C-1 and C-2, indicates a motion that has generated a distribution of orientations, and corresponds to the phase transition centered at 225.4 K with an entropy change of 6.4 $JK^{-1}mol^{-1}$ and a volume increase of 2.5% in unit cell.[26] A further increase in temperature causes the orientational motion to have a rate comparable to that of the signal separation at low temperature (200 Hz). At this point (about 312 K) the NMR signals of C-1 and C-2 are further broadened and no longer observable. A comparison between the measured and the calculated heat capacities in the temperature region between the two transitions shows that the former is higher than the latter, confirming that orientational disordering is being developed. Details about the heat capacities and X-ray diffraction of the tetra-*n*-alkylammonium salts will be published later in this series of publications.[9] Since most of the orientational disordering is completed at 418.7 K (35.8 $JK^{-1}mol^{-1}$) and atomic coordinates can still be measured by X-ray, the motion detected at about 232 K must consist of librational jumps about a preferred orientation so that orientational order is largely maintained. The nature and rate (200 Hz) of libration of the cation as a whole permits a X-ray structure determination to give definite atomic positions within the cation, even at room temperature.[26]

The signals for C-1 and C-2 emerge again at $T \geq 424$ K, (Figure 6a) and appear

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as single lines, indicating the presence of an isotropic orientational motion faster than 1/200 Hz $\approx 10^{-3}$ s in correlation time. This estimation on the rate of motion by the peak separation agrees with the result obtained from the ^{13}C cross-polarization behaviors, shown above.

In summary, in the solid state of tetra-*n*-propylammonium bromide and iodide the only possible types of large-amplitude motion are the orientational motion of the cation as a whole and the well-known methyl rotation. The former occurs in one step in the bromide, and in two steps in the iodide. Other potential conformational motion, *i.e.*, rotation about the bonds between N and C-1, and between C-1 and C-2 are not possible for steric reasons, and proven by the ^{13}C spin-lattice relaxation times and proton spin simulation. The second conclusion made here agrees with the assumption made by Coker *et al.*,[27] based solely on the examination of models. These results will be extended to the tetra-*n*-alkylammonium cations with longer chains.[7]

CONCLUSIONS

The low homologs of tetra-*n*-alkylammonium halide crystals can only show orientational disordering. The disordering may be completed in one or more steps. Above the major disordering transition temperatures, the cations form plastic crystals. Except for the methyl groups, full rotations about single bonds are restricted for steric reasons, even in the liquid state. Some large amplitude motion about the single bonds $N—CH_2$ and $CH_2—CH_2$ must be librations with an angle too small to reach other conformational isomers. These bonds, therefore, do not contribute to conformational entropy changes at the phase transitions. Thus, including the bonds $CH_2—CH_3$, there are 3 bonds in each alkyl chain of 3 or more carbon atoms, or 12 in total of four chains, that contribute little to the overall entropy change on transition to the mesophase.

Acknowledgments

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