Thermochimica Acta, 139 (1989) 205–217
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOLID–SOLID PHASE TRANSITIONS IN PHENALKYLAMMONIUM SALTS *

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(Received 6 June 1988)

ABSTRACT

Solid–solid phase transitions have been investigated in thirty phenalkylammonium salts, $C_6H_5C_nH_{2n}NH_3X$, where $n = 1$ to 10, and X = Cl, Br and NO_3, primarily by differential scanning calorimetry. The preparation and phase transition properties of these compounds are described.

INTRODUCTION

Solid–solid phase transitions in ammonium salts and substituted ammonium salts have been the subject of numerous recent experimental and theoretical studies. The transitions may be due to order–disorder of the ammonium group or of the substituent on the ammonium group. One family of substituents is alkyl chains, and monoalkyl ammonium halides have been studied by many techniques, such as differential scanning calorimetry [1–4], infrared spectroscopy [5], X-ray crystallography [6,7] and nuclear magnetic resonance [8–10].

The purpose of the present investigation was to determine whether phenalkylammonium salts of the general formula $C_6H_5C_nH_{2n}NH_3X$ ($n = 1$ to 10, and X = Cl, Br and NO_3, abbreviated PhC*n*X) undergo solid–solid phase transitions. These compounds were investigated primarily by differential scanning calorimetry (DSC).

Previous investigations of the phenalkylammonium salts of this same general formula have been limited to the $n = 0$ (anilinium) salts with X = Cl, Br and I (abbreviated PhX). The crystal structure of PhCl is known [11] and

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* Dedicated to Professor Edgar F. Westrum, Jr., in honour of his contributions to calorimetry and thermal analysis, and on the occasion of his 70th birthday.

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this compound also has been studied by NMR [12] and IR [13]. PhBr has been studied by neutron and X-ray diffraction [14,15], NMR [12], IR [13] and Raman spectroscopy [16], diffuse X-ray scattering [17], ^{79}Br NQR [18], dilatometry [19] and conduction calorimetry [20]. PhI has been studied by X-ray and neutron diffraction [21], NMR [12], ^{127}I NQR [19,22] and dilatometry [19]. These studies have shown that PhBr and PhI undergo solid–solid phase transitions while PhCl does not. The phase transitions in PhBr and PhI occur at 296.9 K and 241 K, respectively. PhBr and PhI are nearly isostructural in both phases while the structure of PhCl is different from either of those phases. Anilinium chloride forms a structure with the chlorines in a layer and the anilinium ions all point in the same direction with respect to the C–N bond direction [11]. The phenyl rings are packed together as tightly as possible leaving the chloride ions to arrange themselves equidistant from three nitrogens. The packing in PhBr (and PhI) can be described as layers occupied alternatively by Br (I) and anilinium ions. The anilinium ions interdigitate and point in opposite directions with respect to the C–N bond direction. Each nitrogen atom is surrounded by four Br in such a way that three of the Br are equidistant from the nitrogen while the fourth is farther away.

From diffuse X-ray scattering experiments [17], it was suggested that the phase transition in PhBr is due to the coupling of three mechanisms: orientational disorder of the ammonium group; elastic shear strain associated with a soft acoustical phonon mode; and internal displacement of ions connected with a soft optical mode [17]. Raman [16] and ultrasonic [23] experiments disproved the latter two mechanisms, and neutron diffraction studies indicated that the driving force for the ferroelastic phase transition in PhBr is the orientational disorder of the $-NH_3^+$ group between two energetically equivalent orientations, as well as small oscillations in the phenyl ring [15]. The low temperature and high temperature structures of PhI and PhBr are similar except for the disorder of the ammonium ions. In PhBr there is disorder between two orientations of equal probability; in PhI there are four orientations with pair-wise probabilities.

EXPERIMENTAL

Preparation of phenalkylammonium salts

All compounds investigated ($C_6H_5C_nH_{2n}NH_3X$; $X = Cl$, Br, NO_3) were prepared from the corresponding phenalkylamines ($C_6H_5C_nH_{2n}NH_2$). Benzylamine, 2-phenylethylamine, 3-phenylpropylamine and 4-phenylbutylamine were purchased from Aldrich and used as received. The longer chain amines, 5-phenylpentylamine through to 10-phenyldecylamine, were not commercially available and therefore were synthesized as described below from the conversion of the phenalkylcarboxylic acid to the acid chloride, then to the amide, and then to the amine [24]. The amine was converted to the chloride, bromide or nitrate.

Approximately 0.01–0.02 mol of finely divided phenalkylcarboxylic acid (Columbia Organic Chemicals) was placed in a round-bottomed flask equipped with a teflon-coated stirring bar and reflux condenser with a $CaCl_2$ drying tube. Twice the stoichiometric requirement of purified [25] thionyl chloride was added all at once. The mixture stirred for 10 min at room temperature and then the flask was immersed in a water bath maintained at 60 ° C. After approximately 2 h, the conversion to the acid chloride was found to be complete as confirmed by IR. Excess $SOCl_2$ was removed by vacuum distillation and the solution was cooled to room temperature.

A solution containing 8 ml of concentrated ammonium hydroxide (28 wt.%) and 100 ml of benzene was placed in a 250 ml round-bottomed flask and chilled in an ice bath until the benzene layer became cloudy. With vigorous stirring, the acid chloride was added drop-wise while maintaining the solution in the ice bath during this very exothermic reaction, which produced a white precipitate. After the addition of the acid chloride was complete, the solution was stirred for 1 h and allowed to warm to room temperature. The solution was warmed further in a hot water bath in order to dissolve the amide in the benzene layer, and the aqueous layer was separated. The benzene solution was washed three times with 50 ml portions of distilled water in order to remove the ammonium chloride by-product. The solution was concentrated to about half-volume using a rotary evaporator and then it was cooled to 8 ° C. The amide precipitated out and was suction-filtered and dried in a desiccator. The crude product was dissolved in anhydrous diethyl ether, filtered and then recrystallized from benzene–diethyl ether.

The phenalkylamines were prepared by the reduction of the phenalkylamides using lithium aluminium hydride. A 3-neck 500 ml round-bottomed flask containing a teflon-coated stirring bar was equipped with a double surface reflux condenser and a dry nitrogen gas blanket. Using a powder funnel, 0.05 mol of $LiAlH_4$ was added, quickly followed by 90 ml of $LiAlH_4$-dried diethyl ether. While maintaining the nitrogen blanket, the solution was refluxed gently for 30 min. After cooling to room temperature, 0.02 mol of amide in 60 ml of anhydrous tetrahydrofuran (THF) was slowly added using a 100 ml pressure-equalizing dropping funnel; the addition took 2 h. This was followed by a rinse with 25 ml of THF. The solution was allowed to reflux for 6 h, then the heat was turned off and the solution was stirred for 12 h. The excess $LiAlH_4$ was decomposed by a solution of 15 ml of distilled water and 40 ml of THF which was added slowly from a dropping funnel with vigorous stirring over the course of 3 h. After the decomposition was complete, most of the lithium and aluminium salts were removed by gravity filtration. The precipitate was washed several times with diethyl ether and then most of the solvent was removed from the filtrate under reduced pressure. By repeated addition of anhydrous ethanol and evaporation, the water was removed from the filtrate through the ethanol/water azeotrope. Diethyl ether was added to the amine and the solution was gravity-filtered in order to remove other solid impurities. The diethyl ether in the filtrate was removed under reduced pressure, leaving the amine.

The chloride salts of the amines were prepared either by passing HCl gas through an ether solution of the amine, or by neutralizing an ether/ethanol solution of the amine using aqueous HCl. The salts precipitated on cooling and were recrystallized from diethyl ether/ethanol or isopropanol/hexane. The bromide salts were prepared by neutralization with aqueous HBr. The

TABLE 1

Properties of compounds of the general formula $C_6H_5C_nH_{2n}NH_3X$

X	*n*	Appearance	Melting point (° C)
Cl	1	White platelets	269–270
Cl	2	White platelets	d * > 222
Cl	3	White platelets	d > 179
Cl	4	White platelets	158–159
Cl	5	White platelets	d > 141
Cl	6	White platelets	117–118
Cl	7	White platelets	d > 122
Cl	8	White platelets	115–116
Cl	9	White platelets	128–130
Cl	10	White platelets	123–127
Br	1	White needles	223–224
Br	2	White needles	262–263
Br	3	White platelets	d > 140
Br	4	White platelets	147–148
Br	5	White platelets	d > 117
Br	6	White platelets	126–127
Br	7	White platelets	127–128
Br	8	White platelets	121–122
Br	9	White platelets	131–132
Br	10	White platelets	122–123
NO_3	1	Flat needles	136–138
NO_3	2	White needles	151–153
NO_3	3	White platelets	66–68
NO_3	4	White needles	104–105
NO_3	5	White needles	64–66
NO_3	6	White needles	81–82
NO_3	7	White needles	67–68
NO_3	8	White needles	71–72
NO_3	9	White needles	75–76
NO_3	10	White needles	77–78

* d >, decomposes above.

nitrate salts were prepared by neutralization of an ether solution of the amine with a solution of nitric acid in ether. The precipitates were washed several times with ether and recrystallized from isopropanol and ether. Properties of the chlorides, bromides and nitrate salts prepared are summarized in Table 1.

Differential scanning calorimetry

All differential scanning calorimetry experiments above room temperature (300–450 K) were performed either on a Perkin–Elmer DSC-1, with a data acquisition system controlled by an IBM-PC [26], or a Perkin–Elmer DSC-4. The melting point of indium was used for enthalpy and temperature calibration. The sub-ambient (120–300 K) results were obtained on a Perkin–Elmer DSC-2C, calibrated with the solid–solid phase transition and melting point of cyclohexane. The accuracy in the transition temperatures (taken as onset temperatures) is ±2 K and in the enthalpies is ±10%. Typical sample sizes for DSC runs were 1–10 mg, and all scans were in N_2 at heating rates of 5 K min^{-1}.

Adiabatic calorimetry

Adiabatic calorimetry was used to measure the heat capacity of one of these samples as a function of temperature ($80 \text{ K} < T < 380 \text{ K}$). These measurements were carried out by the DC heat-pulse technique, as described in detail elsewhere [27,28].

RESULTS AND DISCUSSION

Concerning specific phenalkylammonium salts

Summaries of the thermodynamic data of the solid–solid phase transitions observed from differential scanning calorimetry experiments on the phenalkylammonium chlorides, bromides and nitrates, $C_6H_5C_nH_{2n}NH_3X$, are given in Tables 2, 3 and 4, respectively. The comments and discussion in this section enlarge on observations concerning the specific compounds in this series.

The temperature of the solid–solid phase transition in PhC1Cl is close to the melting point of $PhClNO_3$, suggesting that the PhC1Cl phase transition may involve sufficient conformational disorder to cause breakdown of the $PhC1NO_3$ crystal lattice. The temperature of the minimum in the T_1 relaxation for anilinium chloride [12] agrees quite well with the temperature of the PhC1Cl solid–solid phase transition, which suggests that it is due to a reorientation of the $-NH_3^+$ group, but the high entropy change ($\sim 1.2R$) suggests that more is happening, possibly increased disorder of the methyl-

TABLE 2

Summary of thermodynamic data for phenalkylammonium chlorides, $C_6H_5C_nH_{2n}NH_3Cl$

n	T_{tr} (K)	ΔH_{tr} (kJ mol^{-1})	$\Delta S_{tr}/R$	Notes
1	416 *	4.41	1.28	
	416 +	4.24	1.23	
2	392 *	7.70	2.36	
	389 +	7.59	2.35	
	432	3.23	0.90	
3	343	6.22	2.18	
	368	4.24	1.39	
4	243	4.03	2.00	See text
	274	0.65	0.29	
	295	0.27	0.19	
5	359	19.5	6.58	
6	265 *	0.28	0.12	
	320 *	10.0	3.76	
	338 *	1.08	0.38	
	353 *	0.50	0.17	
	319 +	0.04	0.02	
	338 +	1.17	0.41	
	345 +	0.55	0.19	
7	319 *	22.6	8.5	
	310 +	10.1	3.9	
8	333 *	7.25	2.62	
	347 *	2.79	0.97	
	332 +	7.02	2.54	
	347 +	2.85	0.99	
9	320	10.0	3.82	
	331	7.59	2.54	
10	357	17.7	6.0	
	368	7.2	2.4	

* Only seen on the initial scan of a virgin sample.

$^+$ Observed on successive scans.

ene group and the phenyl ring. When plates of PhC1Cl were heated through the phase transition on a hot stage microscope, volume changes were observed, suggesting that the changes that do occur are first order.

No solid–solid phase transitions were observed in PhC1Br, in contrast with the anilinium series discussed earlier.

Benzylammonium nitrate ($PhC1NO_3$) displayed one solid–solid phase transition with approximately the same entropy change as anilinium bromide ($\sim 0.5R$) which suggests that the phase transition may involve similar hydrogen-bonding changes.

At room temperature, PhC2Cl and PhC2Br have the same chain structures [29,30]. The backbone of the structure is formed of chains consisting of a hydrogen-bonded network of ammonium groups and halide ions, with the

TABLE 3

Summary of thermodynamic data for phenalkylammonium bromides, $C_6H_5C_nH_{2n}NH_3Br$

n	T_{tr} (K)	ΔH_{tr} (kJ mol^{-1})	$\Delta S_{tr}/R$	Notes
1	No transitions observed			
2	347	6.68	2.31	See text
3	357	10.8	3.63	
	402	0.11	0.03	
4	353	9.6	3.25	
	393	1.4	0.43	
5	345	17.6	6.1	
6	334	14.4	5.2	
7	324 *	9.5	3.53	
	332 $^+$	9.3	3.46	
8	380 *	13.6	4.30	
	356 $^+$	0.69	0.23	
	379 $^+$	12.1	3.83	
9	310 *	9.23	3.57	
	309 $^+$	8.93	3.48	
10	331 *	10.5	3.81	
	364/372 *	16.0	5.2	
	321/324 $^+$	14.2	5.3	
	366/372 $^+$	16.0	5.2	

* Only seen on the initial scan of a virgin sample.

$^+$ Observed on successive scans.

TABLE 4

Summary of thermodynamic data for phenalkylammonium nitrates, $C_6H_5C_nH_{2n}NH_3NO_3$

n	T_{tr} (K)	ΔH_{tr} (kJ mol^{-1})	$\Delta S_{tr}/R$
1	227	0.90	0.48
2	337 *	11.3	4.02
	320 $^+$	7.28	2.73
	369/371	1.05	0.42
3	No solid–solid phase transitions observed		
4	338 *	19.6	6.99
	336 $^+$	19.1	6.83
5	No solid–solid phase transitions observed		
6	330 *	22.0	8.00
	320/330 $^+$	21.7	7.9
7	No solid–solid phase transitions observed		
8	335 *	23.2	8.33
	334 $^+$	23.0	8.29
9	No solid–solid phase transitions observed		
10	No solid–solid phase transitions		

* Only seen on the initial scan of a virgin sample.

$^+$ Observed on successive scans.

phenalkyl groups perpendicular to the chain. The chains are held together by van der Waals forces. Within the chain each N atom forms three strong approximately linear hydrogen bonds with three neighbouring halogen atoms, and each halogen receives three hydrogen bonds from three different donors. The resulting hydrogen-bonding scheme resembles a zig-zag chain of halogens held together by hydrogen bonds. The phenalkyl groups on neighbouring chains do not interdigitate, in contrast with compounds such as *n*-decylammonium chloride (C10Cl) [6]. From X-ray structural studies, the magnitudes of the thermal coefficients of PhC2Cl were found to increase in the order: chlorine, nitrogen, alkyl chain, phenyl [29]. The occurrence of two phase transitions in PhC2Cl (at 392 K and 432 K) and the thermal coefficient results suggest that one of the phase transitions may be due to disorder of the phenalkyl group or to onset of rotation of the phenyl group, and that the second transition could be due to disorder of the alkyl chain and/or a change in hydrogen-bonding. The lower temperature phase transition of PhC2Cl was observed on a hot stage microscope; during the phase transition striations moved across the crystal at an angle of approximately 60° to the plate edge. The total entropy change of the transitions in PhC2Cl ($\sim 3.3R$) is approximately three times that of PhC1Cl ($\sim 1.2R$). The phenalkyl group or the phenyl group may not have as much freedom to move in PhC1Cl owing to its proximity to the ammonium group and to the high cohesive forces between the phenalkyl groups because of packing; this may in turn restrict the motion of the ammonium group leading to a higher transition temperature and a lower entropy change, as observed.

Phenethylammonium bromide (PhC2Br) displayed a very odd behaviour. The initial DSC scan displayed multiple peaks over a range of approximately 30 K (330–360 K). After the sample was cooled to room temperature, a subsequent scan through the transition showed an increase in the average transition temperature, and a reduction in the fine structure and enthalpy of the transition. The transition disappeared when scanned a third time but reappeared if the sample was allowed to remain at room temperature for at least two days; even then the enthalpy of the transition was only about 60% of the initial value. Subsequent experiments with the low temperature DSC indicated the following: the thermal hysteresis ΔT, the difference between the temperature of the transition measured in the heating mode and in the cooling mode, increased upon thermal cycling ($\Delta T \sim 60$ K after the first cycle and ~ 140 K after 5 cycles); the fine structure of the transition decreased with increased cycling; the average transition temperature on heating increased and the average transition temperature on cooling decreased with the number of cycles. The phase transition was observed on a hot stage microscope; PhC2Br undergoes a first-order phase transition, in which the crystal completely shatters—the most dramatic of any of the observed phase changes in these salts. When the shattered crystal was recycled, the small crystallites shattered again at a slightly higher temperature. This indicates that the thermodynamics of the phase transition depend on the particle-size. In addition, DSC experiments indicated that a single crystal produced multiple peaks, whereas a sample ground to a powder yielded a DSC trace with much less fine structure. After a few cycles with large crystals, the average particle size is uniform and they transform at about the same temperature and the thermal fine structure disappears.

This type of behaviour is rare but not unique. The phase transition in hydrazinium sulphate was reported to have a particle-size dependence on the transition temperature [31]. It was observed that the transition occurred over a 40 K temperature range, that the phase transition moves to successively lower temperatures (when measured in the cooling mode) upon repeated thermal cycling and that the fine structure in the DTA peak gradually disappeared upon repeated thermal cycling. Similar observations have been reported for studies on the phase transitions in NH_4NO_3 [32,33].

The effect of particle size on the thermodynamics and thermal hysteresis of solid–solid phase transitions has been investigated in a number of compounds [34]. It was concluded that on heating, the transition temperature increases with a decrease in particle size, and that the thermal hysteresis increases with a decrease in particle size. Recent investigations of the solid–solid phase transition of hexamethylbenzene using an adiabatic calorimeter in the cooling mode have suggested that there is a "memory effect" in which each crystallite of the specimen has a specific (and different) transition temperature [35].

It has been stated that in order for hysteresis to appear at least part of the solid–solid phase transition must occur isothermally (i.e. partly first-order), and that the hysteresis is confined to the isothermal part of the change [36]. Because there must be an isothermal component to the phase transition, there must be an associated volume change, and the magnitude of the hysteresis is proportional to the volume change [36,37]. The proportionality between the magnitude of the thermal hysteresis and the volume change of the transition has been confirmed by dilatometry experiments with ammonium halides [36].

Using thermodynamic arguments and considering the effect of strain on the free energies of the two phases, it has been shown that [38]

$$\Delta S_{\mathrm{tr}}\ \Delta T_{\mathrm{h}} = \Delta V_{\mathrm{tr}}\ \Delta P_{\mathrm{h}} \qquad (1)$$

where ΔS_{tr} is the entropy change of the transition, ΔT_{h} is the temperature range of the hysteresis, ΔV_{tr} is the volume change of the transition and ΔP_{h} is the range of pressure of the hysteresis. Equation (1) bears a remarkable resemblance to the Clapeyron equation. Although it has not been possible to test the validity of this equation here because the ΔP_{h} values are not known, eqn. (1) does indicate a direct variation of the hysteresis with the volume change, as observed.

During the DSC investigations $PhC2NO_3$ was observed to undergo three

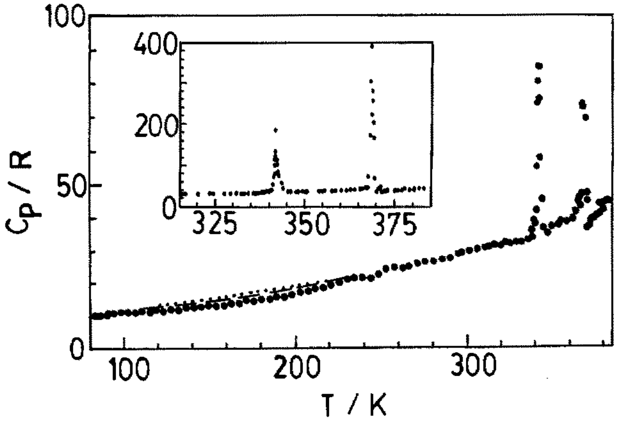

Fig. 1. The molar heat capacity of $C_6H_5CH_2CH_2CH_2NH_3Cl$ as a function of temperature. The circles represent the heat capacity in run 1; the dashed line represents run 2; the dotted line represents run 3.

solid–solid phase transitions. The transition at 337 K had a very large associated entropy change which indicates that there is considerable increase in disorder. When needles of $PhC2NO_3$ were heated through the phase transitions slight birefringent changes were observed.

Our DSC experiments indicated that PhC3Cl undergoes two solid–solid phase transitions and that PhC3Br undergoes one phase transition. The transitions can be observed on a hot-stage microscope and all of the transitions show observable crystal modifications at the transition temperature. In PhC3Cl, the lower transition corresponded to curling of the plates and the upper phase transition corresponded to movement of striations across the crystal at an angle of about 60° to the plate edge. In one case, it was possible to observe the meeting of two striations, and the formation of a crack at the junction. In PhC3Br, the phase transition corresponded to a curling of the crystal.

The heat capacity of 9.9573 g of PhC3Cl was measured from 82 to 383 K using adiabatic calorimetry; the results are shown graphically in Fig. 1. Two solid–solid phase transitions were observed; one at 341.9 ± 0.2 K and the other at 368.6 ± 0.2 K. The low temperature heat capacity increased after the compound was cycled through the phase transition which suggests that there was some disorder frozen in. In addition, the time required for thermal relaxation following the heat pulse in the region of the low temperature phase transition was exceptionally long. For example, a small pulse of electrical energy (~ 60 J) was not thermally equilibrated after 2 h (typical relaxation times were approximately 15–20 min for this calorimeter in this temperature range). After the phase transition was transversed, the relaxation times returned to normal. This suggests poor thermal conduction during the phase transition; the curling of the crystallites may cause the sample to pull away from the heat source, thus increasing the relaxation time.

DSC experiments showed that this irreversible reconstruction did not affect the entropy or temperature of the phase transition, within the error of the DSC experiment. The large, similar, total entropy changes in PhC3Cl and PhC3Br suggest that the crystal structures undergo similar large modifications at the transitions; this also is supported by visual results. The low melting point of $PhC3NO_3$ (339 K), which is near the temperature of the solid–solid phase transitions of PhC3Cl and PhC3Br, suggests that the disorder in the nitrate salt is sufficient to cause melting of the complex.

There is a dramatic drop in the melting point (or decomposition temperature) when the cation reaches the phenpropylammonium ion. At three alkyl carbons, the phenalkylammonium cation has gained sufficient momentum with its disorder to weaken the attractive binding forces of the lattice.

Three solid–solid phase transitions were observed for PhC4Cl and the observed enthalpy change of each was dependent on the length of time that the sample was allowed to remain at room temperature. On the first DSC scan in the heating mode, the endotherm at 243 K was followed by a small exotherm, which disappeared on successive scans; in addition, on successive scans, the enthalpy of the transition at 243 K decreased steadily while the enthalpy of the transitions at 274 K and 295 K increased steadily. After three scans, the enthalpy of the transition at 243 K was approximately half its initial value, the enthalpy of the transitions at 274 K and 295 K had approximately doubled, while the total transition enthalpy and entropy had decreased. After allowing the sample to remain at 293 K for 2 days, this sequence of events was reproducible.

General comments concerning the phenalkylammonium salts

The low melting points of all of the nitrate salts, which are close in temperature to the solid–solid phase transitions observed in the chloride and bromide salts, suggest that solid state disorder requires stabilization by a hydrogen-bonding network, and that breakdown of the lattice occurs in the nitrates. In some cases (namely, PhC2, PhC4, PhC6 and PhC8), the nitrate salts showed high entropy solid–solid phase transitions before melting which implies that the packing can allow for this. Dramatic drops in the entropies of the phase transitions on subsequent scans mean that the process is partly irreversible.

There were no linear dependences of the thermodynamic properties of the solid–solid phase transitions as a function of the number of carbons in the alkyl chain in the phenalkylammonium salts, as has been observed in alkyl chain melting in other environments [39]. The alkyl chains in the portion of the phenalkyl series examined may be too short for general trends to be observed (it is hard to “wash out” the end group effect of a large end group such as a phenyl) and/or there may be sufficient changes in the crystal structure as methylene groups are added to change the thermodynamic behaviour.

As is often seen with melting of alkyl chains, there seems to be an odd-even effect in the nitrate salts: PhC2, PhC4, PhC6 and PhC8 all displayed solid–solid phase transitions, whereas the odd numbered salts did not; they melted. It is interesting that the solid–solid phase transitions in PhC2, PhC4, PhC6 and PhC8 nitrate salts occur at nearly the same temperature (~ 336 K), i.e. the temperatures of the phase transitions are controlled by the phenyl group or the nitrate ion, independent of the length of the alkyl chain.

The odd-numbered chain length phenalkylammonium bromide salts also show a general trend, in that the transition temperature decreases as the alkyl chain length increases. A decrease in the thermal energy required to cause disorder indicates that the cohesive forces between neighbouring phenalkylammonium ions are weakened. The packing of the phenyl groups may force the alkyl chain into a high energy conformation and decrease the inter-alkyl chain attractive potentials and thereby reduce the amount of thermal energy required to cause disorder.

Further experiments using other techniques are required in order to understand the exact nature of the processes that occur in the solid–solid phase transitions of each of these compounds. There are three possible sources of disorder: hydrogen-bonding changes, disorder of the alkyl group and disorder of the phenyl group. These can take place separately or collectively, depending on factors such as the strength of the hydrogen bonds, the hydrogen's position with respect to the anions (linear, bifurcated or trifurcated hydrogen bonds) and the amount of accessible room for the phenyl group and for the alkyl chain. The extent of disorder will be controlled by the cohesive forces of the lattice and detailed knowledge of the crystal structures would be beneficial to understanding the thermodynamic behaviour. The thermodynamic changes at the phase transitions are greatly affected by the packing of the phenyl group. This is clearly seen in the results from experiments on the phenalkylammonium nitrates and bromides. The even numbered $\mathrm{PhC}n\mathrm{NO}_3$ salts display solid–solid phase transitions, whereas the odd numbered salts melt, and the $\mathrm{PhC}n\mathrm{Br}$ salts with the odd numbered $n \geqslant 5$ show a steady decrease in temperature of transition.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge helpful discussions with and access to data prior to publication from Professors T.S. Cameron, O. Knop, R.E. Wasylishen, and Dr. S. Roe and M. Grewel. We also wish to thank Professor D. Gilson for arranging for the use of the sub-ambient DSC, and J. Leiper for assistance. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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