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A CRYSTAL PACKING - MELTING POINT CORRELATION FOR QUATERNARY AMMONIUM SALTS

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Abstract: The melting point of symmetrical quaternary ammonium salts $(C_nH_{2n+1})_4N^+ X^-$ exhibits a sudden drop as n, the alkyl chain length increases. The location of this discontinuity varies with the nature of the associated anion. Concommitant with the drop in melting point is a lowering of the space group symmetry. An explanation based upon relative cation and anion sizes is proposed.

Chickos's method for estimating the fusion energetics of solids has been adapted to handle "hydrocarbon-like" large quaternary cations. Extrapolation to small cations and comparison with melting points yields an estimate of the energy of the crystal structure change responsible for the melting point discontinuity.

INTRODUCTION

The free energy of fusion of a molecular crystal is a function of the enthalpy and entropy of fusion (Equation 1):-

$$\Delta G_{fusion} = (H_{liquid}-H_{solid}) - T_m(S_{liquid}-S_{solid}) \quad (1)$$

where T_m is the melting point of the crystal. Since intermolecular forces are greatest in the solid, whilst entropy is greatest in the liquid, the lattice energy will generally be the major contributor to

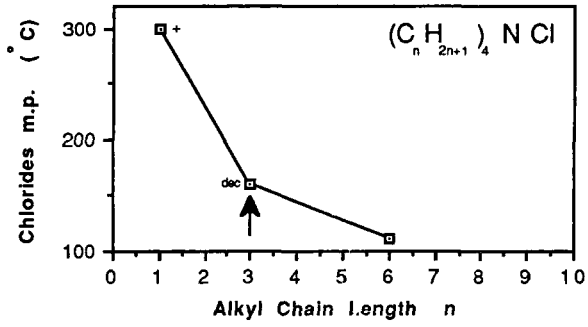
the enthalpy term, whereas the entropy term will be dominated by the state of the liquid. These assumptions underly the extensive work of Chickos et al[1-2], whose group additivity method effectively predicts fusion entropies for organic compounds. Fusion enthalpies can be estimated indirectly using Equation 2 :

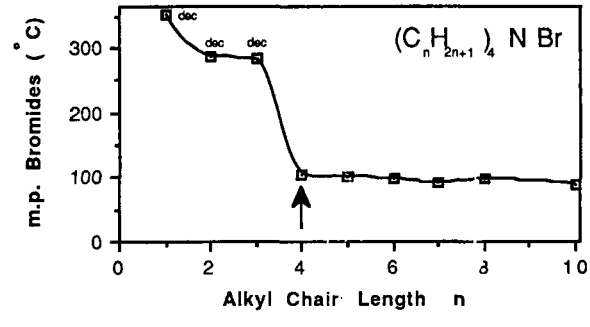
$$\Delta H_{fusion} = T_m \Delta S_{fusion} \qquad (2)$$

Chickos's work now allows estimates of ΔS_{fusion} and ΔH_{fusion} for linear, branched, cyclic and aromatic hydrocarbons, simple or substituted.

We recently became interested in the melting point behaviour of tetraalkylammonium salts, a class of charged organic species of the form $(C_nH_{2n+1})_4N^+ X^-$ to which the systematic work of specialists in this field[2-3] has not yet been applied. Our interest stems from the fact that as the chain length of the alkyl substituent is increased a sudden discontinuity occurs in the melting point[4a,5]. In fact the chain length at which this sudden drop in melting point occurs varies with the nature of the counter anion. This is shown in Figure 1, where the arrow indicates the smallest low-melting salt.

We have chosen to probe this phenomenon by combining a crystallographic study with energy estimates based on the approach of Chickos et al[1]. The work will be presented both as a qualitative study and as a preliminary quantitative analysis.





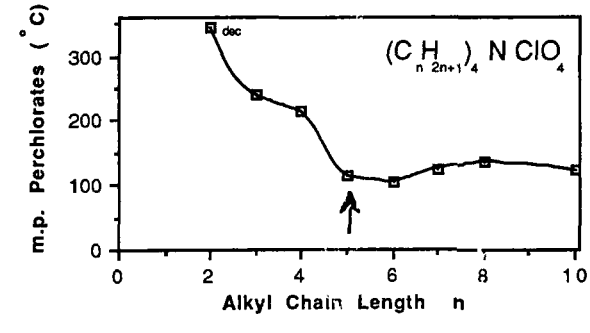


FIGURE 1 : Dependence of melting point on alkyl chain length for quaternary ammonium chlorides, bromides and perchlorates.

A CRYSTALLOGRAPHIC APPROACH TO MELTING POINT TRENDS

The behaviour shown in Figure 1 suggests that when the cation becomes very large relative to the anion, the efficiency of crystal packing is impaired, and a relatively weak structure of low melting point is obtained. For the chloride anion such a situation is probably reached with a tetrapropyl cation. The bromide anion can pack efficiently, forming a high-melting solid, with cations up to and including tetrapropylammonium, whereas its tetrabutyl salt is low-melting. The behaviour of iodides (not shown) and perchlorates is similarly explained, with their tetrapentyl salts being the first of the low-melting series.

Further support for this idea may be obtained from the crystal structures of tetraalkylammonium salts[4b]. Only a few of these containing simple anions are available, since crystallographic research on compounds containing this type of cation has involved their use as counter-cation in the study of complex[6] or unsymmetrical anions[7]. The data summarized in Table I indicate the prevalence of high-symmetry tetragonal structures, reminiscent of ionic packing. All the compounds listed here as having such symmetry have high melting points. No crystal structures have been published for the low-melting salts with simple small anions. Many of these are highly unstable with respect to their hydrates; for instance tetraethylammonium chloride monohydrate[10] was crystallised unwittingly from anhydrous chloroform-ether! Quaternary fluorides[14] and hydroxides[15] tend to form water-rich polyhedral clathrates. These facts can be taken to infer low stability of the anhydrous parent structure containing these small anions.

TABLE I : Crystal symmetry of tetraalkylammonium salts.

Compound	Space Group	System	Ref.
Tetramethylammonium Chloride	P4/nmm	Tetragonal	8
Tetramethylammonium Bromide	P4/nmm	Tetragonal	8
Tetramethylammonium Iodide	P4/nmm	Tetragonal	8
Tetramethylammonium Perchlorate	P4/nmm	Tetragonal	9
Tetraethylammonium Chloride Monohydrate	C2/c	Monoclinic	10
Tetraethylammonium Iodide	$I\bar{4}$	Tetragonal	11
Tetrapropylammonium Bromide	$I\bar{4}$	Tetragonal	12
Tetrabutylammonium AuI_2	C2/c	Monoclinic	13

Combining the ideas raised so far we would now like to explore a further hypothesis. This is that if compounds in the low-melting group can be crystallised, they will tend to have improved their packing by shifting to a hydrocarbon-like, lower symmetry structure. Table I does include two salts of lower symmetry. Both unfortunately have anions that are neither monoatomic nor symmetrical. Figure 2 illustrates schematically the ionic-style packing observed where the cation and anion are of similar size, compared with the proposed "hydrocarbon-like" packing (Figure 3) that we might expect where the cation is very large and intermolecular alkyl chain interactions are important in fixing crystal architecture:

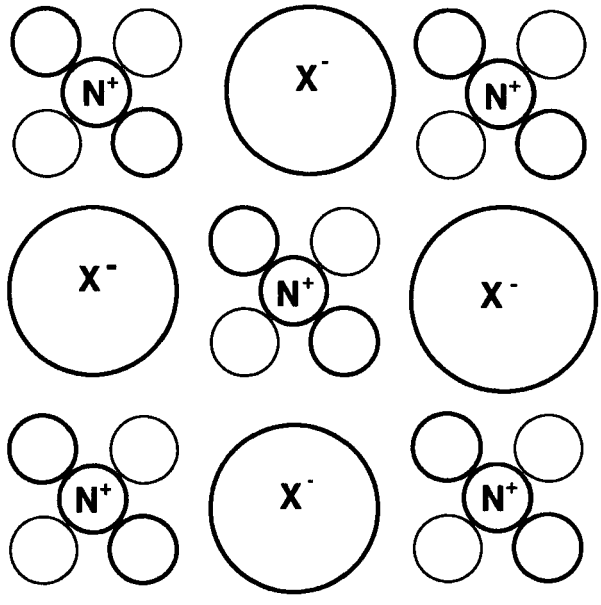


FIGURE 2: Ionic-style packing of a quaternary salt (schematic).

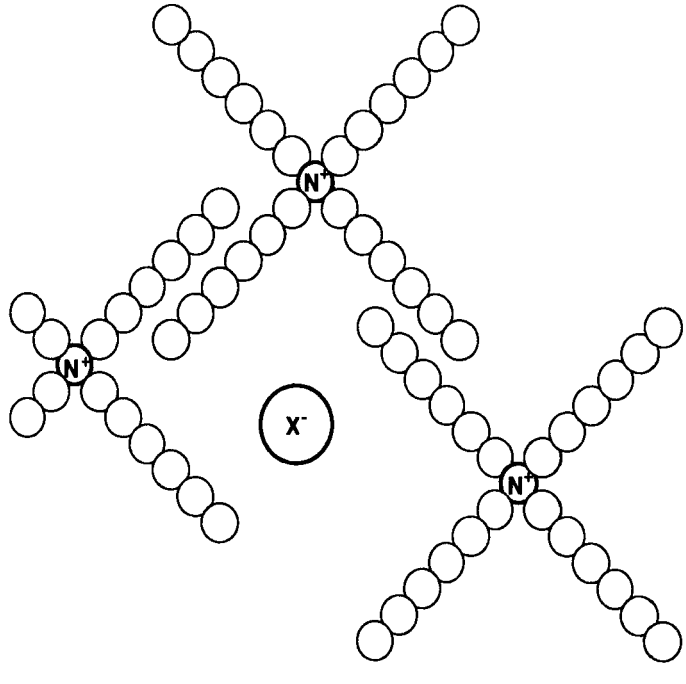


FIGURE 3: Hydrocarbon-like packing of a quaternary salt (schematic).

To further investigate the packing argument we undertook the single crystal structure determination of the low-melting tetrabutylammonium bromide (TBuAB), which we would predict as belonging to a low-symmetry crystal system . The structure was in fact found to be monoclinic (space group C2/c) - a low symmetry structure - in accordance with our prediction[16]. This contrasts sharply with the tetragonal $I\bar{4}$ structure of the tetrapropyl analogue (TPrAB). The change in structure is accompanied by a drop in melting point of 180 °C (see Figure 1)!

The monoclinic TBuAB structure can be viewed approximately perpendicular to its a-b plane to give a projection (Figure 4b) which is similar to the view on the a-b plane of the high-symmetry TPrAB structure (Figure 4a)[12]. On comparing the structures two differences are apparent:-

In TPrAB the four cations are in fact alternately above and below the plane, forming a tetrahedron, whereas in the TBuAB structure they lie in a common plane, with a concommitant expansion of the cell dimensions in that plane. Secondly the best plane through the carbon atoms of the alkyl chain is nearly perpendicular to the paper in TPrAB but has become approximately parallel to the paper in TBuAB. Note that the axial relation a=b is roughly retained in the monoclinic structure.

Based upon the above analysis we suggest that TBuAB shares the fundamental tendency of these salts for tetragonal symmetry; however the relative sizes of anion and cation make such a structure unfavourable, leading to the distortions observed. Qualitatively the $I\bar{4}$ packing would have led to unfavourable intermolecular interactions, involving either alkyl chain overlap, or dimensional expansion to the point where much electrostatic stabilisation would be lost and where the anion would "rattle" inside a cavity.

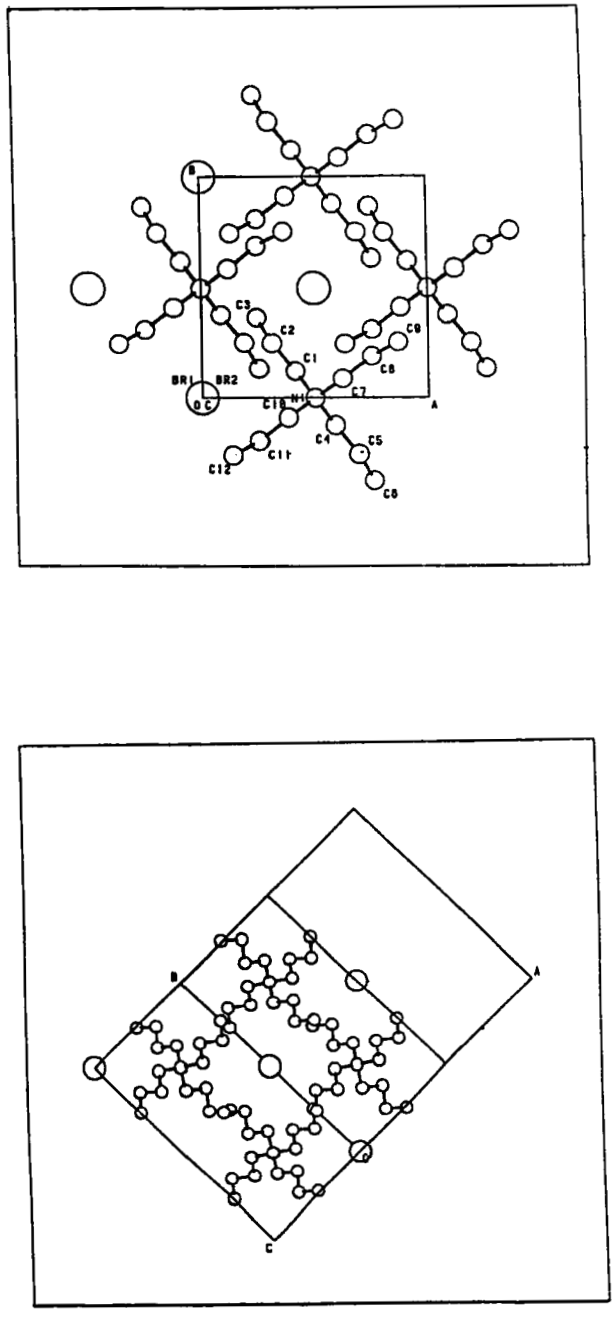


FIGURE 4: (a) Tetrapropylammonium bromide (tetragonal) viewed on the a-b plane. (b) Tetrabutylammonium bromide (monoclinic) in a similar orientation.

UNDERLYING ASSUMPTIONS IN A QUANTITATIVE APPROACH TO MELTING POINT INTERPRETATION

Whilst the sharp break in melting point behaviour shown in Figure 1 is qualitatively impressive, it is superimposed upon a downward trend with increasing alkyl chain length, due to increasing cation-anion separation and the increasingly "organic" character of the salt. In a quantitative study it is desirable to correct for this by subtracting a theoretical melting point-alkyl chain length profile that does not include a change in crystal structure.

A preliminary treatment can be based upon the approach of Chickos et al[1-2], which can predict fusion entropy and enthalpy for branched hydrocarbon solids, in which only van der Waals interactions operate. Using this starting point we have analysed the quaternary ammonium bromides on the basis of the following first-order assumptions:-

(a) The entropy of any symmetrical tetraalkylammonium cation can be modelled by the entropy of an uncharged quaternary hydrocarbon analogue.

(b) The contribution of the bromide ion to fusion entropy is independent of the nature of the cation.

(c) For the low-melting salts, packing of their large cations directs the overall structure. Thus for tetrahexyl and larger cations lattice energy is mostly fixed by the van der Waals contributions.

(d) For a given packing symmetry the electrostatic contribution to lattice energy will vary smoothly with alkyl chain length n.

ANALYTICAL PROCEDURE FOR ESTIMATION OF FUSION ENERGETICS

Our analytical procedure was carried out in the following stages:-

1) Using group contribution data for uncharged quaternary hydrocarbon models[1], fusion entropies were estimated for the range of quaternary cations. This is valid even for small cations according to assumption a.
2) A fixed contribution was added for the entropy of the bromide ion (assumption b). A figure of 2.0 e.u. was chosen, which is half the calculated entropy of fusion of rubidium bromide[17].
3) From the calculated entropies and published melting points, fusion enthalpies were calculated using equation 2, and will be termed "semi-empirical" parameters.
4) The above fusion enthalpies of the "hydrocarbon-like" salts (tetrahexyl-, heptyl-, octyl-, and decylammonium bromides) were found to fit by linear regression to an empirical relation shown as equation 3, where n is alkyl chain length and ΔH_{fusion} is in kcal/mole:-

$$\Delta H_{fusion} = 3.169\, n + 1.45 \qquad (3)$$

This relation describes members of similar lattice structure, in which hydrocarbon interactions are presumed to play an important role in determining the crystal structure (assumption c).
5) Next, equation 3 is applied beyond the conditions for which it was derived to the small cations of the high-melting group to predict enthalpies and hence melting points. These are denoted "hydrocarbon-like" parameters and Table II compares these "hydrocarbon-like" predictions to "semi-empirical" parameters derived from the true melting point. The difference between the sets of parameters can be interpreted as the extra stabilisation energy due to electrostatic and packing effects.

TABLE II: Semi-empirical versus hydrocarbon-like enthalpy and melting point values for quaternary bromides.

Salt	Fusion enthalpy (kcal/mole)		Melting point (°C)	
	Semi-empirical	Hydrocarbon-like	Literature[5]	Hydrocarbon-like
TMeAB	>6.42	4.62	>350	175
TEtAB	9.71	7.79	288	131
TPrAB	15.73	10.96	283	114
TBuAB	14.02	14.12	103	106
TPeAB	17.32	17.29	101	100
THxAB	20.52	20.46	98	97
THpAB	23.34	23.66	90	95
TOcAB	27.12	26.83	97	93
TDcAB	33.05	33.14	89	90

The enthalpy data are also presented in graphical form in Figure 5 showing the difference between the semi-empirical (ΔH_{empir}) and hydrocarbon-like values ($\Delta H_{hydrocb}$). The derivation of these data ensured that the mean difference between the two lines for chain lengths n=6-10 must be close to zero. The data extrapolate very well to n=5 and n=4, however a sudden extra stabilisation of the solid is apparent on moving from the butyl to the propyl salt. This cannot be due to an increase of ionic character in the general sense, because electrostatic energy contribution should increase smoothly with a decrease in n and a reduction in the cation-anion separation (assumption d). For this reason we may infer that the increased fusion enthalpy and melting point of the tetrapropyl salt is mostly a direct consequence of the change of crystal structure. A tentative figure of about 5 kcal/mole can be ascribed to the energy gain of the tetragonal structure compared with "hydrocarbon-like packing for the tetrapropyl salt.

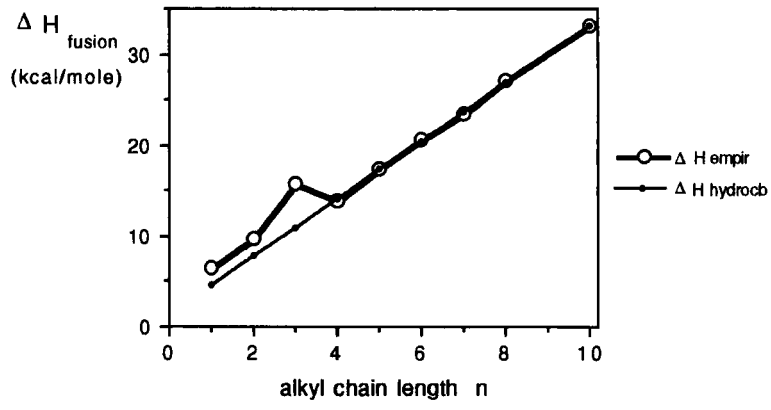


FIGURE 5: Anomalous stabilisation of short-chain quaternary salts compared with hydrocarbon-like trend prediction.

DISCUSSION

This predicted and observed change in crystal structure may indeed be due to alkyl chain packing restrictions in the tetrabutyl salt, as we have surmised. This interpretation cannot be quantified by the data because the change in molecular packing brings a concommitant change in charge distribution within the unit cell. An additional factor to be considered is that of disorder. It is known that disorder in a crystal can lead to both melting point increase and higher apparent crystal symmetry[18]. The TBuAB structure is certainly not disordered, nor was disorder reported in the case of TPrAB, although the latter is an old, photographic determination. Moreover the two structures differ not only in overall cell symmetry but also in molecular packing modes. Similarly, tetraethylammonium iodide[11] was not reported as disordered . Disorder was reported for the perchlorate ion in

tetramethylammonium perchlorate[9]. This is however an extreme structure with regard to the present discussion and is rather like that shown in Figure 2. On the evidence so far available, we suggest alkyl chain packing restrictions and not disorder as the major cause of the melting point discontinuities described. It is however interesting to speculate that the potential for disorder could coincide with, and be due to, the cessation of alkyl chain "tangling" when the cation/anion size ratio drops below a critical value.

Several of the questions raised and some quantitative issues are presently under study, using lattice energy minimisation calculations to assess the coulombic and van der Waals contributions to the structures of tetrapropyl- and tetrabutylammonium bromides.

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