# Air Stable Liquid Clathrates: Solid State Structure and Hydrocarbon Solubility of Organic Cation Triiodide Salts

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**Abstract.** A series of air and water stable organic cation triiodide salts have been prepared and characterized. Almost all of the salts isolated sustain liquid clathrate phases in the presence of benzene or toluene, the compositions of which were determined via $^1$H NMR spectroscopy. Two of the salts were also characterized via X-ray crystallography in order to determine the nature of any solid state interionic interactions (1-ethylpyridinium triiodide, monoclinic, $P2_1/c$, $a = 9.6031(7)$, $b = 15.129(3)$, $c = 8.8160(16)$ Å, $\beta = 104.192(11)°$, $Z = 4$, $R = 0.041$ for 2463 independent observed reflections; 1,2,4-trimethylpyridinium triiodide, orthorhombic, *Pbcm*, $a = 9.434(4)$, 20.176(4), 7.411(4) Å, $Z = 4$, $R = 0.045$ for 966 observed reflections).

## 1. Introduction

Organic cation alkylboride [1] and, particularly, haloaluminate salts [2, 3] have been subjects of recent attention as a result of their tendency to exist as ambient condition melts. Another interesting feature of these [1, 4–7] and other low melting salts such as [NBu$_4^n$][BF$_4$] [8] and a wide range of organic cation salts of trialkylaluminate [9] and complex hydrogen halide containing anions [10], is their ability to dissolve toluene and other liquid aromatic hydrocarbon compounds to afford binary liquid-liquid phases under ambient conditions. The denser of the binary phases, which is salt-rich and incorporates a fixed but non-stoichometric amount of hydrocarbon compound, has been termed 'liquid clathrate' by their discoverer, Atwood [9, 11]. Atwood's early work focused upon air and moisture sensitive trialkylaluminate salts, but recent work of several groups has concentrated upon expanding the range of known 'liquid clathrate' sustaining salts. Indeed, even organotransition metal anions have been utilized in this capacity [12, 13].

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Polyiodide salts have long been investigated from the point of view of solid state inclusion chemistry [14, 15] but not in the context of the liquid phase. The well-known salt 1-ethylpyridinium triiodide, $\mathbf{1^+I_3^-}$, melts at 45°C and was first reported in 1895 [16]. In this contribution we describe the hydrocarbon solubility properties of $\mathbf{1^+I_3^-}$ and a range of related triiodide, haloaluminate and alkylaluminate salts. We also report the solid state structures of $\mathbf{1^+I_3^-}$ and 1,2,4-trimethylpyridinium triiodide, $\mathbf{2^+I_3^-}$.

$$N-Et \qquad\qquad Me \quad Me-N-Me$$

$$1^+ \qquad\qquad\qquad\qquad 2^+$$

The crystal structures are discussed in the context of recent structural studies conducted upon low melting chloroaluminate salts and 'liquid clathrate' sustaining salts.

## 2. Experimental

### 2.1. SYNTHESIS AND CHARACTERIZATION OF SALTS AND LIQUID CLATHRATES

#### 2.1.1. *Synthesis of Organic Cation Iodide Salts*

All solvents were distilled under $N_2$ and dried over molecular sieves prior to use. The bases were purchased from Aldrich and used as supplied. In a typical reaction, 5.00 mL of iodomethane (80.3 mmol) was added to a solution of 11.00 mL of 4-t-butylpyridine (74.4 mmol) in approximately 70 mL of hexane. The mixture was refluxed for 20 hr and the resulting precipitate was vacuum filtered and washed with hexane. The identity of the product was confirmed using 60 MHz $^1$H (Varian EM-360) and 90.78 MHz $^{13}$C (Nicolet 360-NB) NMR spectroscopy. The reaction of pyridines with alkyl halides is a well-documented reaction [17] and has been used in the context of low melting salts [18]. All other iodide salts were prepared and characterized in a similar manner with the following exceptions: iodomethane with 2,4,6-trimethylpyridine, 2,4-dimethylpyridine, and 2-ethylpyridine utilized tetrahydrofuran as solvent; iodoethane was used in a large excess and refluxed for two days; iodobutane reactions employed refluxing octane as solvent.

#### 2.1.2. *Synthesis of Organic Cation Triiodide Salts and Their Benzene and Toluene 'Liquid Clathrates'*

The appropriate organic cation iodide salt and iodine (BDH) were combined in a 1 : 1 molar ratio in acetone under ambient conditions for 1 hour. Solvent removal *in vacuo* afforded the black or red-black triiodide salts quantitatively; however, salts were recrystallized from acetone/hexane prior to further use. The opaque black 'liquid clathrates' were prepared by stirring 1.00 g of the triiodide salt in 15.0 mL of benzene or toluene for 10 min. $^1$H NMR integrations were used to determine the aromatic content of the lower, 'liquid clathrate' phase.

(i) *1,2,4,6-Tetramethylpyridinium triiodide.* m.p. 93.0–95.5°C; $^1$H NMR (CDCl$_3$) $\delta$2.65(*s*, 3H), 2.92(*s*, 6H), 4.18(*s*, 3H), 7.62(*s*, 2H); aromatic content – benzene n/c, toluene 3.1 (n/c = no clathrate formation).

(ii) *1,2,4-Trimethylpyridinium triiodide.* m.p. 110.5–113.0°C; $^1$H NMR ((CD$_3$)$_2$CO) $\delta$2.73(*s*, 3H) 2.99(*s*, 3H), 4.50(*s*, 3H), 8.53(*m*, 3H); aromatic content – benzene 4.3, toluene n/c.

(iii) *1-Methyl-2-ethylpyridinium triiodide.* m.p. 38.5–39.5°C; $^1$H NMR ((CD$_3$)$_2$CO) $\delta$1.45(*t*,3H), 3.37(*q*, 2H), 4.57(*s*, 3H), 8.17(*d*, 2H), 8.67(*t*, 1H), 9.08(*d*, 1H); aromatic content – benzene 4.0, toluene 2.6.

(iv) *1-Methyl-4-t-butylpyridinium triiodide.* m.p. 91.5–92.0°C; $^1$H NMR (CDCl$_3$) $\delta$1.50(*s*, 9H), 4.58(*s*, 3H), 8.15(*d*, 2H), 8.83(*d*, 2H); aromatic content – benzene 5.5, toluene 3.3.

(v) *1-Methylpiperidinium triiodide.* m.p. liq.; $^1$H NMR ((CD$_3$)$_2$CO) $\delta$2.68(*m*, 13H), 7.87(*s*, 1H); aromatic content – benzene 3.1, toluene 2.1.

(vi) *1,3-Dimethylimidazolium triiodide.* m.p. 53.0–54.0°C; $^1$H NMR (CD$_3$)$_2$CO) $\delta$4.10(*s*, 6H), 7.72(*s*, 2H), 9.00(*s*, 1*H*); aromatic content – benzene 4.4, toluene 2.0.

(vii) *N-Methylcyclohexylammonium triiodide.* m.p. liq.; $^1$H NMR (CDCl$_3$) $\delta$1.67(*m*, 10H), 2.79(*m*, 4H), 6.54(*s*, 2H); aromatic content – benzene 2.6, toluene 1.3.

(viii) *1-Methylpyridinium triiodide.* m.p. 45.5–48.0°C; $^1$H NMR ((CD$_3$)$_2$CO) $\delta$4.75(*s*, 3H), 8.42(*t*, 2H), 8.88(*t*, 1H), 9.28(*d*, 2H); aromatic content – benzene 3.8, toluene 2.4.

(ix) *1-Ethyl-2,4,6-trimethylpyridinium triiodide.* m.p. 71.0–76.5°C; $^1$H NMR (CDCl$_3$) $\delta$1.55(*t*, 3H), 2.63(*s*, 3H), 2.97(*s*, 6H), 4.68(*q*, 2H), 7.67(*s*, 2H); aromatic content – benzene 4.7, toluene 3.6.

(x) *1-Ethyl-2,4-dimethylpyridinium triiodide.* m.p. 46.0–50.5°C; $^1$H NMR (CDCl$_3$) $\delta$1.38(*t*, 3H), 2.38(*s*, 3H), 2.49(*s*, 3H), 4.37(*q*, 2H), 7.40(*s*, 2H), 8.35(*d*, 1H); aromatic content – benzene 4.7, toluene 2.8.

(xi) *1,2-Diethylpyridinium triiodide.* m.p. 35.0–37.5°C; $^1$H NM ((CD$_3$)$_2$CO) $\delta$1.83(*m*, 6H), 3.46(*q*, 2H), 4.97(*q*, 2H), 8.27(*d*, 2H), 8.73(*t*, 1H), 9.21(*d*, 1H); aromatic content – benzene 4.7, toluene 3.0.

(xii) *1-Ethyl-4-t-butylpyridinium triiodide.* m.p. 88.0–91.5C; $^1$H NMR (CDCl$_3$) $\delta$1.45(*s*, 9H), 1.82(*t*, 3H), 4.80(*q*,2H), 8.13(*d*, 2H), 8.83(*d*, 2H); aromatic content – benzene 5.7, toluene 3.4.

(xiii) *1-Ethylpiperidinium triiodide.* m.p. liq.; $^1$H NMR (CDCl$_3$) $\delta$1.83(*m*, 9H), 3.35(*m*, 6H), 7.28(*s*, 1H); *analysis*: *found*: C, 16.76; H, 3.31; N, 2.91. *calcd.*: C, 16.99; H, 3.26; N, 2.83%. aromatic content – benzene 3.7, toluene 1.8.

(xiv) *1-Ethyl-2-methylimidazolium triiodide.* m.p. 32.0–33.5°C; $^1$H NMR (CDCl$_3$) $\delta$1.70(*t*, 3H), 4.13(*s*, 3H), 4.43(*q*, 2H), 7.38(*s*, 2H) 9.00(*s*, 1H); *analysis*: *found*: C, 14.71; H, 2.29; N, 5.70. *calcd.*: C, 14.65; H, 2.25; N, 5.70%. aromatic content – benzene 4.4, toluene 2.4.

(xv) *N-Ethylcyclohexylammonium    triiodide.* m.p.    liq.;    $^1$H NMR    (CDCl$_3$) $\delta$0.92($m$, 13H), 2.48($m$, 3H), 6.97($s$, 2H); aromatic content – benzene 2.3, toluene 1.8.

(xvi) *1-Ethylpyridinium    triiodide.* m.p.    45.0–46.0°C;    $^1$H NMR    ((CD$_3$)$_2$CO) $\delta$1.77($t$, 3H), 4.99($q$, 2H), 8.38($d$, 2H), 8.84($t$, 1H), 9.32($d$, 2H); aromatic content – benzene 4.3, toluene 2.7.

(xvii) *1-Butyl-2,4,6-trimethylpyridinium    triiodide.* m.p.    40.0–50.0°C;    $^1$H NMR (CDCl$_3$)  $\delta$1.53($m$, 7H), 2.65($s$, 3H), 2.95($s$, 6H), 4.53($t$, 2H), 7.67($s$, 2H); aromatic content – benzene 5.4, toluene 3.6.

(xviii) *1-Butyl-2,4-dimethylpyridinium    triiodide.* m.p.    41.0–42.5°C;    $^1$H NMR (CDCl$_3$)    $\delta$1.60($m$, 7H),    2.75($s$, 3H),    2.97($s$, 3H),    4.62($t$, 2H),    7.90($s$, 2H), 8.68($d$, 1H); aromatic content – benzene 5.0, toluene 4.4.

(xix) *1-Butyl-2-ethylpyridinium    triiodide.* m.p.    liq.;    $^1$H NMR    (CDCl$_3$) $\delta$1.20($t$, 3H),    1.52($m$, 4$H$),    1.73($t$, 3H),    3.47($q$, 2H),    4.84($t$, 2H),    8.29($d$, 2H), 8.80($t$, 1H), 9.07($d$, 1H); *analysis: found*: C, 24.11; H, 3.31; N, 2.63. *calcd.*: C, 24.24; H, 3.33; N, 2.57% aromatic content – benzene 5.3, toluene 3.7.

(xx) *1-Butyl-4-t-butylpyridinium    triiodide.* m.p.    49.0–53.0°C;    $^1$H NMR (CDCl$_3$) $\delta$1.52($s$, 9H),    1.62($m$, 16H),    4.76($t$, 2H),    8.23($d$, 2H),    8.93($d$, 2H);    aromatic content – benzene 6.7, toluene 4.9.

(xxi) *1-Butylpiperidinium    triiodide.* M.p.    39.5–41.5°C;    $^1$H NMR    (CDCl$_3$) $\delta$2.42($m$, 19H), 7.52($s$, 1H); *analysis: found*: C, 20.70; H, 3.85; N, 2.74. *calcd.*: C, 20.67; H, 3.86; N, 2.68%. aromatic content – benzene 5.0, toluene 2.8.

(xxii) *1-Butyl-3-methylimidazolium    triiodide.* m. p. liq.;    $^1$H NMR    (CDCl$_3$) $\delta$1.56($m$, 7H), 4.15($s$, 3H), 4.38($t$, 2H), 7.57($s$, 2H), 8.87($s$, 1H); *analysis: found*: C, 18.86; H, 2.99; N, 5.29. *calcd.*: C, 18.48; H, 2.91; N, 5.40%. aromatic content – benzene 4.9, toluene 3.1.

(xxiii) *N-Butylcyclohexylammonium    triiodide.* m.p.    liq.;    $^1$H NMR    (CDCl$_3$) $\delta$2.17($m$, 20H), 7.12($s$, 2H); *analysis: found*: C, 23.89; H, 4.41; N, 2.58. *calcd.*: C, 22.36; H, 4.13; N, 2.61%. aromatic content – benzene 4.4, toluene 2.2.

(xxiv) *1-Butylpyridinium    triiodide.* m.p. liq.; $^1$H NMR ((CD$_3$)$_2$CO)  $\delta$1.66($m$,7H), 4.91($t$, 2H), 8.33($t$, 2H), 8.81($t$, 1H), 9.23($d$, 2H); aromatic content – benzene 4.5, toluene 3.4.

### 2.1.3. *Synthesis of Organic Cation Haloaluminate Salts and Their Benzene and Toluene Based 'Liquid Clathrates'*

'Liquid clathrates' sustained by **1$^+$**[AlCl$_3$I] and **2$^+$**[AlCl$_3$I] were prepared via quantitative *in situ* generation of the appropriate salt in the presence of benzene or toluene. In a typical reaction, 0.50 g (2.1 mmol) of **1$^+$I$^-$** was suspended in approximately 20 mL of degassed benzene in a Schlenk tube under an atmosphere of dinitrogen. 0.28 g (2.1 mmol) of AlCl$_3$ (Aesar) was added to the suspension and the slurry was stirred for 15 min., at which point a colorless 'liquid clathrate' containing 4.8 moles of benzene per mole of cation had formed. The corresponding

toluene based 'liquid clathrate' contained 2.8 moles of aromatic whereas the 'liquid clathrates' sustained by $2^+[AlCl_3I]$ contained 4.3 and 3.0 moles of aromatic for benzene and toluene, respectively. Mixed halide haloaluminate salts have been reported in earlier studies [5, 18].

### 2.1.4. Synthesis of $1^+[Al_2R_6I]$ (R = Me, Et) and Their Benzene and Toluene Sustained 'Liquid Clathrates'

'Liquid clathrates' sustained by salts of overall stoichiometry $1^+[Al_2R_6I]$ (R = Me, Et) were prepared via quantitative in situ generation of the appropriate salt in the presence of benzene or toluene. Anions of the general stoichiometry $[Al_2R_6X]^-$ are the prototypal 'liquid clathrate' parent anions and are known and structurally characterized for a wide variety of halides and pseudohalides [9, 11]. All reactions were conducted in a Vacuum Atmospheres inert atmosphere glove box under an atmosphere of Ar. In a typical reaction 0.50 g (2.1 mmol) of $1^+I^-$ was suspended in 10 ml of benzene. An amount of 0.40 mL (4.2 mmol) of $AlMe_3$ (Texas Alkyls) was added slowly with a syringe, spontaneously affording a colorless 'liquid clathrate' containing 6.8 moles of benzene per mole of cation. Using a similar procedure 'liquid clathrates' of composition $1^+[Al_2Me_6I]\cdot5.5$ toluene, $1^+[Al_2Et_6I]\cdot11.1$ benzene and $1^+[Al_2Et_6I]\cdot9.4$ toluene were prepared.

## 2.2. X-RAY CRYSTALLOGRAPHY

Red-black rectangular block crystals of $1^+I_3^-$ and $2^+I_3^-$ were sealed in thin-walled glass capillaries and mounted on an Enraf-Nonius CAD-4 diffractometer. In the case of $1^+I_3^-$ the space group was unambiguously determined to be $P2_1/c$ whereas for $2^+I_3^-$ systematic absences determined the space group to be either the centric Pbcm or acentric $Pca2_1$. Successful refinement of the structure of $2^+I_3^-$ was carried out in the centric space group Pbcm. Summaries of data collection and structure refinement parameters are presented in Table I. In the case of $1^+I_3^-$ hydrogen atoms were placed in calculated positions 1.08 Å from the appropriate carbon atoms and full-matrix least-squares refinement of nonhydrogen atoms with anisotropic temperature factors gave $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.041$ and $R_w = [\Sigma(w(F_0 - F_c)^2)/\Sigma wF_0^2]^{1/2} = 0.056$. For $2^+I_3^-$ geometrically constrained hydrogen atoms were placed in calculated postions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å$^2$. The methyl group hydrogen atoms were not included in the final refinement because of high thermal motion. Large amplitudes of thermal vibration were noted, especially for the methyl groups. Refinement was carried out in the acentric $Pca2_1$ to check out the possibility that freeing the ring from the constraints of a mirror plane could improve the refinement. Although the structure can be refined in $Pca2_1$, no lessening of the thermal motion for the methyl groups was noted. The centric Pbcm was therefore retained as the correct space group. Refinement of nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.045$ and $R_w = 0.045$. Programs used for $1^+I_3^-$ were MULTAN80 [20] and the NRCVAX system [21] whereaas SHELX [22] and SHELXS [23] were used for $2^+I_3^-$. Atomic scattering fractors were taken from Reference [24] . The final values of the positional parameters are given in Tables II and III for $1^+I_3^-$ and $2^+I_3^-$, respectively.

Table I. Crystal data and summary of intensity data collection and structure refinement.

| Compound | $1^+I_3^-$ | $2^+I_3^-$ |
|---|---|---|
| Color | red/black | red/black |
| Formula Wt. | 488.7 | 502.9 |
| Space Group | $P2_1/c$ | $Pbcm$ |
| Temp, °C | 20 | 20 |
| Cell constants[a] | | |
| $a$, Å | 9.6031(7) | 9.934(4) |
| $b$, Å | 15.129(3) | 20.176(4) |
| $c$, Å | 8.8160(16) | 7.411(4) |
| $\beta$, ° | 104.192(11) | – |
| Cell Volume, Å$^3$ | 1241.8 | 1411 |
| Z | 4 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 2.615 | 2.37 |
| $\mu_{calc}$, cm$^{-1}$ | 74.3 | 66.9 |
| Scan Type | $\theta/2\theta$ | $\theta/2\theta$ |
| Radiation | Mo$K_\alpha$ | Mo$K_\alpha$ |
| Max. Xtal Dimensions, mm | $0.30 \times 0.50 \times 0.65$ | $0.20 \times 0.30 \times 0.35$ |
| Scan Width, ° | $0.70 + 0.35 \tan \theta$ | $0.80 + 0.35 \tan \theta$ |
| Decay of Standards | +2% | +2% |
| Reflections Measured | 3601 | 1471 |
| $2\theta$ range, ° | 2–60 | 2–50 |
| Reflections Observed[b] | 2463 | 966 |
| Computer Programs[c] | NRCVAX | SHELX |
| Structure Solution | MULTAN | SHELXS |
| Number Parameters | 111 | 73 |
| Weights, $w$ | 0.0005 | 0.00006 |
| G.O.F. | 1.71 | 1.17 |
| R | 0.041 | 0.045 |
| $R_w$ | 0.056 | 0.045 |
| Final Diff. Map $(e/Å^3)$ | 1.0 | 1.5 |
| | (near I) | (near I) |

[a]Least-squares refinement of $((\sin \theta)/\lambda)^2$ for 25 reflections $\theta > 15°$.
[b]Corrections: Lorentz-polarization and absorption (empirical psi scan)
[c]Neutral scattering factors and anomalous dispersion corrections from reference [21].

Table II. Final fraction coordinates for $1^+I_3^-$.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| I(1) | 0.15398(5) | 0.81488(3) | 0.99602(5) |
| I(2) | −0.13793(5) | 0.84911(4) | 1.02957(7) |
| I(3) | 0.44039(6) | 0.77346(4) | 0.96230(7) |
| N(1) | 0.2852(6) | 0.4828(4) | 0.1243(7) |
| C(2) | 0.2419(9) | 0.4051(5) | 0.0517(10) |
| C(3) | 0.1455(9) | 0.4046(5) | 0.0922(10) |
| C(4) | 0.0973(9) | 0.4851(5) | −0.1635(10) |
| C(5) | 0.1402(8) | 0.5622(4) | −0.0882(10) |
| C(6) | 0.2358(8) | 0.5598(4) | 0.0527(9) |
| C(7) | 0.3928(9) | 0.4840(5) | 0.2729(9) |
| C(8) | 0.5396(10) | 0.4955(7) | 0.2462(11) |

Table III. Final fractional coordinates for $2^+I_3^-$.

| Atom | $x$ | $y$ | $z$ |
|------|-----|-----|-----|
| I(1) | 0.3265(1) | 0.13423(6) | 0.7500 |
| I(2) | 0.01953(9) | 0.11241(5) | 0.7500 |
| I(3) | −0.2850(1) | 0.09019(8) | 0.7500 |
| N(1) | 0.321(1) | −0.1012(7) | 0.7500 |
| C(1) | 0.314(2) | −0.1679(9) | 0.7500 |
| C(2) | 0.173(2) | −0.1929(9) | 0.7500 |
| C(3) | 0.044(2) | −0.1536(9) | 0.7500 |
| C(4) | 0.064(2) | −0.0878(8) | 0.7500 |
| C(5) | 0.207(2) | −0.061(1) | 0.7500 |
| C(6) | 0.459(1) | −0.0669(9) | 0.7500 |
| C(7) | 0.442(2) | −0.211(1) | 0.7500 |
| C(8) | −0.101(2) | −0.185(1) | 0.7500 |

## 3. Results and Discussion

The triiodide salts prepared in this study were typified by their characteristic black or red-black appearance and their low melting properties; indeed, eight of the salts were found to be ambient condition melts and many of the others melted below 50°C. The possibility that some of the lower melting salts were actually oils resulting from mixtures of polyiodide salts seems low as a result of the microanalysis conducted upon several representative salts and the two X-ray crystal structure determinations. The ensuing discussion is subdivided for the sake of clarity:

### 3.1. HYDROCARBON SOLUBILITY

The majority of the triiodide salts investigated were found to sustain the 'liquid clathrate' effect spontaneously when contacted with excess benzene or toluene. The 'liquid clathrates' thereby formed appeared quite typical [9, 11] in that they were observed to be immiscible with excess aromatic hydrocarbon, contained non-stoichiometric quantities of hydrocarbon, were quite free flowing, and tended to incorporate a greater molar quantity of benzene vs. toluene. The similarity between the triiodide sustained 'liquid clathrates' and more traditional analogues is also supported by the observation that the $AlCl_3I^-$ salts of both $1^+$ and $2^+$ also sustain the 'liquid clathrate' effect, as do the $[Al_2R_6I]^-$ (R = Me, Et) salts of $1^+$. As might be expected from size considerations the iodohexaethyldialuminate sustained 'liquid clathrates' were observed to incorporate the greatest quantity of aromatic hydrocarbon compound. Organic cation triiodide salts therefore appear to complement existing 'liquid clathrate' sustaining anions, particularly as the former are considerably more resistant to both air and moisture than the latter.

### 3.2. SOLID-STATE STRUCTURE

Room temperature haloaluminate ionic liquids have been widely investigated from an electrochemical perspective [2, 3]. However, recent spectroscopic [25–29], theo-
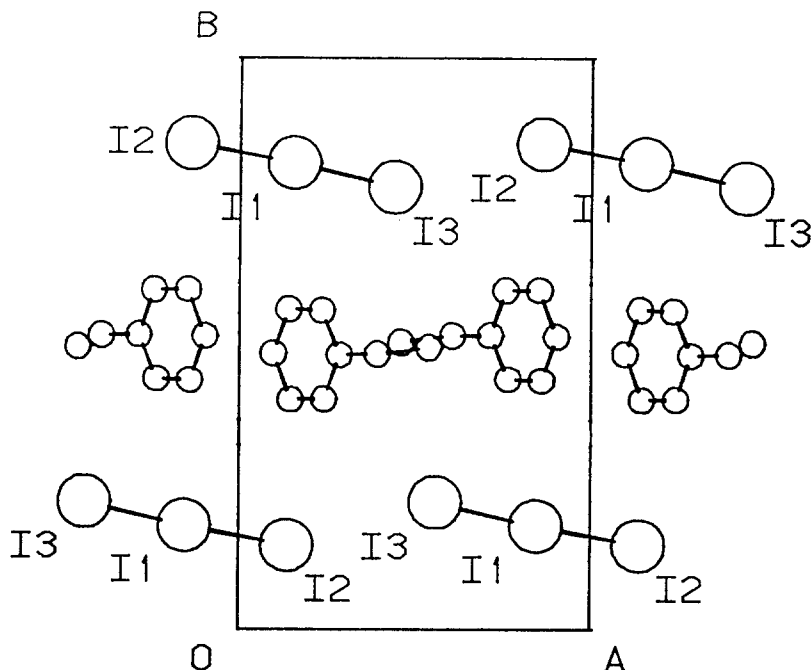
Fig. 1. SNOOPI [35] cell packing plot for $1^+I_3^-$ illustrating triiodide anions stacking in the direction of the $a$-axis.

retical [25], X-ray diffraction [30] and, in the case of model compounds, X-ray crystallographic [6, 31, 32] techniques have been employed by various groups in order to gain information about the structure of the liquid phase. A particular focus of these studies has been on whether or not any ordering via cation–anion attractions occurs in the liquid phase. The X-ray structures presented herein do indeed reveal some degree of ordering in the solid state, however the ordering arises from anion–anion interaction. Figures 1 and 2 are cell-packing plots and they illustrate how the triiodide anions dispose themselves in linear chains parallel to the $a$-axes. The I$\cdots$I contacts of 4.1088(8) and 3.772(1) Å, for $1^+I_3^-$ and $2^+I_3^-$, respectively, are both shorter than the sum of the van der Waals radii for I, 4.30 Å [33]. This study therefore contrasts with the recent studies upon haloaluminate ionic liquids, in which ion-pairing or complex formation via cation–anion C–H$\cdots$Cl hydrogen bonding was suggested for so-called 'basic' (AlCl$_3$ : Cl$^-$ ratio of less than 1.0) melts. However, our observations are not at all unexpected for triiodide salts [14, 15], for which the tendency to order has even resulted in investigations in the context of superconducting solids [34]. Another interesting feature of the structures is that cations in $1^+I_3^-$ stack quite differently from those in $2^+I_3^-$, as illustrated by Figures 1 and 2. In the case of the former, the cations pack horizontally so that they are roughly perpendicular to the triiodide chains whereas for the latter the cations pack exactly parallel to the triiodide chains as all atoms lie in crystallographic mirror planes. There is therefore an appearance that cavities are present in the
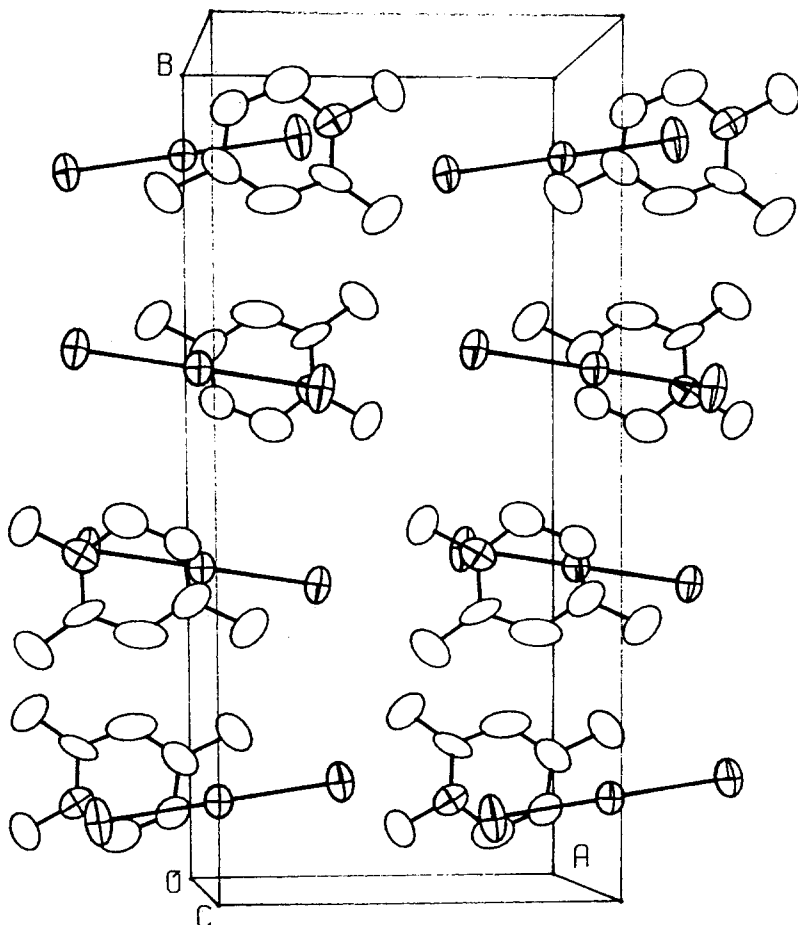
Fig. 2. ORTEP [36] cell packing plot for $2^{+}I_{3}^{-}$ illustrating triiodide anions stacking in the direction of the $a$-axis.

Table IV. Interatomic distances (Å) and angles (°) for $1^{+}I_{3}^{-}$.

*Distances*

| | | | |
|---|---|---|---|
| I(1)–I(2) | 2.9360(7) | I(1)–I(3) | 2.9063(7) |
| N(1)–C(2) | 1.354(9) | C(3)–C(4) | 1.397(11) |
| N(1)–C(6) | 1.355(9) | C(4)–C(5) | 1.355(11) |
| N(1)–C(7) | 1.456(10) | C(5)–C(6) | 1.352(11) |
| C(2)–C(3) | 1.375(12) | C(7)–C(8) | 1.495(12) |

*Angles*

| | | | |
|---|---|---|---|
| I(2)–I(1)–I(3) | 177.704(22) | C(2)–C(3)–C(4) | 119.0(7) |
| C(2)–N(1)–C(6) | 119.7(7) | C(3)–C(4)–C(5) | 120.2(7) |
| C(2)–N(1)–C(7) | 120.3(6) | C(4)–C(5)–C(6) | 118.9(7) |
| C(6)–N(1)–C(7) | 119.9(6) | N(1)–C(6)–C(5) | 122.2(6) |
| N(1)–C(2)–C(3) | 120.0(7) | N(1)–C(7)–C(8) | 110.3(6) |

Table V. Interatomic distances (Å) and angles (°) for $2^+I_3^-$.

| Distances | | | |
|---|---|---|---|
| I(1)–I(2) | 2.929(1) | I(2)–I(3) | 2.907(1) |
| N(1)–C(1) | 1.35(2) | N(1)–C(5) | 1.34(2) |
| N(1)–C(6) | 1.48(2) | C(1)–C(2) | 1.43(2) |
| C(1)–C(7) | 1.48(2) | C(2)–C(3) | 1.45(2) |
| C(3)–C(4) | 1.34(2) | C(3)–C(8) | 1.50(2) |
| C(4)–C(5) | 1.45(2) | | |

| Angles | | | |
|---|---|---|---|
| I(1)–I(2)–I(3) | 179.76(2) | C(1)–N(1)–C(5) | 125(2) |
| C(1)–N(1)–C(6) | 120(1) | C(5)–N(1)–C(6) | 115(2) |
| N(1)–C(1)–C(2) | 113(2) | N(1)–C(1)–C(7) | 123(2) |
| C(2)–C(1)–C(7) | 124(2) | C(1)–C(2)–C(3) | 126(2) |
| C(2)–C(3)–C(4) | 115.(2) | C(2)–C(3)–C(8) | 122(2) |
| C(4)–C(3)–C(8) | 123(2) | C(3)–C(4)–C(5) | 120(2) |
| N(1)–C(5)–C(4) | 121(2) | | |

lattice of $1^+I_3^-$, however this is not borne out by the calculated densities which reveal that $1^+I_3^-$ is more dense than $2^+I_3^-$. The absence of any significant cation–anion interactions precludes simple rationalization of the packing phenomenon. Intraionic bond distances and angles are presented in Tables IV and V. The I—I distances within the triiodide anions are quite symmetric but not equivalent to one another. $1^+I_3^-$ exhibits distances of 2.9360(7) and 2.9063(7) Å whereas the corresponding distances in $2^+I_3^-$ are 2.929(1) and 2.907(1) Å. The bond distances themselves and their inequality are quite typical of crystallographically characterized triiodide salts [37]. All other bond distances and angles are also within expected ranges.

## 4. Conclusions

In summary, we may draw three conclusions from this study that bear relevance to low temperature ionic liquid chemistry. First, there appears to be a correlation between the melting point of a salt and its ability to dissolve in aromatic hydrocarbon media to yield binary liquid–liquid phases or 'liquid clathrates'. Second, the range of salts that exhibit 'liquid clathrate' behavior is clearly not limited to a select group of ions but appears to be quite general. Finally, the nature of interionic interactions in the solid phase of low melting salts would appear to be weak and unpredictable, as recently suggested by our studies upon organic cation tetrachloroaluminate salts [6. 7, 32]. Further investigations into the solid-state and hydrocarbon solubility properties of low melting salts are under way in our laboratories.

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## References

1. R. R. Singh and K. S. Pitzer: *J. Am. Chem. Soc.* **110**, 8723 (1988).
2. C. L. Hussey: *Adv. Molten Salt Chem.* **5**, 185 (1983).
3. J. S. Wilkes: *A Bibliography of Room Temperature Chloroaluminate Molten Salts*, F. J. Seiler Research Laboratory Report FJSRL-TMN-84-006, U.S. Air Force Academy, December 1984.
4. D. R. Bond, G. E. Jackson, H. C. Joao, M. N. Hofmeyr, T. A. Modro and L. R. Nassimbeni: *J. Chem. Soc., Chem. Commun.*, 1910 (1989).
5. F. H. Hurley and T. P. Wier: *J. Electrochem. Soc.* **98**, 203 (1951).
6. M. V. Gaudet, M. J. Zaworotko and P. S. White: *Inorg. Chem.* **28**, 1191 (1989).
7. R. H. Dubois, M. J. Zaworotko and P. S. White: *Inorg. Chem.* **28**, 2019 (1989).
8. C. J. Pickett: *J. Chem. Soc., Chem. Commun.*, 323 (1985).
9. J. L. Atwood: *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1984, vol I, p. 375.
10. M. V. Gaudet, D. C. Peterson and M. J. Zaworotko: *J. Incl. Phenom.* **6**, 425 (1988).
11. J. L. Atwood: *Recent Developments in Separation Science*, vol III, CRC Press, Cleveland, 195 (1977).
12. A. Alvanipour, H. Zhang and J. L. Atwood: *J. Organomet. Chem.* **358**, 295 (1988).
13. R. H. Dubois: B.Sc. Honours Thesis, Saint Mary's University, Halifax, Nova Scotia, Canada, 1989.
14. F. H. Herbstein, G. M. Reisner and W. Schwotzer: *J. Incl. Phenom.* **3**, 173 (1985).
15. M. Noltmeyer and W. Saenger: *J. Am. Chem. Soc.* **102**, 2710 (1980).
16. A. B. Prescott and P. F. Trowbridge: *J. Am. Chem. Soc.* **17**, 859 (1895).
17. R. J. Fessenden and J. S. Fessenden: *Organic Chemistry*, 2nd Edition, Willard Grant Press, Boston, 755 (1982).
18. D. S. Newman, R. T. Tillack, D. P. Morgan and W.-C. Wan: *J. Electrochem. Soc.* **124**, 856 (1977).
19. J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung: *J. Am. Chem. Soc.* **101**, 3776 (1979).
20. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson: 'MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Differaction Data'; Universities of York, England and Louvain, Belgium, 1980.
21. E. J. Gabe, F. L. Lee and Y. LePage: The NRCVAX Crystal Structure System. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; G. M. Sheldrick, C. Kruger and R. Goddard, eds., pp 167–174. Clarendon Press, Oxford (1985).
22. G. M. Sheldrick: 'SHELX76, a system of computer programs for X-ray structure determination as locally modified at Northern Illinois University'; University of Cambridge, England (1976).
23. G. M. Sheldrick, 'SHELXS', in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; G. M. Sheldrick, C. Kruger and R. Goddard, eds., pp 175–189. Clarendon Press, Oxford (1985).
24. *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, England, vol IV (1974); distributor Kluwer, Dordrecht, The Netherlands.
25. K. M. Dieter, C. J. Dymek, Jr., N. E. Heimer, J. W. Rovang and J. S. Wilkes: *J. Am Chem. Soc.* **110**, 2722 (1988).
26. S. Tait and R. A. Osteryoung: *Inorg. Chem.* **23**, 4353 (1984).
27. T. A. Zawodzinski, Jr., R. Kurland and R. A. Osteryoung: *J. Phys. Chem.* **91**, 962 (1987).
28. A. A. Fannin, Jr., L. A. King, J. A. Levisky and J. S. Wilkes: *J. Phys. Chem.* **88**, 2609 (1984).
29. D. S. Newman, R. T. Tillack, D. P. Morgan and W.-C. Wan: *J. Electrochem. Soc.* **124**, 856 (1977).
30. S. Takahashi, N. Koura, M. Murase and H. Ohno: *J. Chem. Soc., Faraday Trans. 2* **82**, 49 (1986).
31. A. K. Abdul-Sala, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon and J. A. Zora: *J. Chem. Soc., Chem. Commun.* 1753 (1986).
32. M. J. Zaworotko, T. S. Cameron, A. Linden and K. C. Sturge: *Acta Crystallogr.* **C45**, 996 (1989).

33. F. A. Cotton and G. W. Wilkinson: in *Advanced Inorganic Chemistry*, 3rd edition, Wiley Interscience (1972), p. 120.

34. T. J. Emge, H. H. Wang, M. A. Beno, P. C. W. Leung, M. A. Firestone, H. C. Jenkins, J. D. Cook, K. D. Carlson, J. M. Williams, E. L. Venturini, L. J. Azevedo and J. E. Schriber: *Inorg. Chem.* **24,** 1736 (1985).

35. E. K. Davies: 'Chemgraf Suite', Chemical Crystallography Laboratory, 9 Parks Road, Oxford, England, January 1983.

36. C. K. Johnson: 'ORTEP'; Report ORNL-3794 revised; Oak Ridge National Laboratory, Oak Ridge, TN (1965).

37. R. C. Teitelbaum, T. J. Marks and C. K. Johnson: *J. Am. Chem. Soc.* **102**, 2986 (1980), and references therein.