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Alkyl-chain disorder in tetraisohexyl-ammonium bromide

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Tetraisohexylammonium bromide [systematic name: tetrakis-(4-methylpentyl)azanium bromide], $C_{24}H_{52}N^+\cdot Br^-$, is a powerful structure II clathrate hydrate crystal-growth inhibitor. The crystal structure, in the space group $P3_221$, contains one ammonium cation and one bromide anion in the asymmetric unit, both on general positions. At 100 K, the ammonium cation exhibits one ordered isohexyl chain and three disordered isohexyl chains. At 250 K, all four isohexyl chains are disordered. In an effort to reduce the disorder in the alkyl chains, the crystal was thermally cycled, but the disorder remained, indicating that it is dynamic in nature.

Comment

Gas hydrates are ice-like clathrates that are formed at high pressure and low temperature from water or water/hydrocarbon mixtures, and they are a serious problem in the oil and gas industries due to their ability to cause blockages. Low-dosage hydrate inhibitors are a recent alternative to thermodynamic hydrate inhibitors and can be divided into two classes, *viz.* kinetic inhibitors and anti-agglomerants. A major breakthrough in this area of research was the development of quaternary ammonium surfactant anti-agglomerants with tributyl or tripentyl head groups (Kelland, 2006). Searches of the Cambridge Structural Database (CSD, Version 5.32, including November 2010 and February 2011 updates; Allen, 2002; Bruno *et al.*, 2002) show that many quaternary ammonium halide structures have been reported, both as hydrate clathrates (*e.g.* Feil & Jeffrey, 1961; McMullan *et al.*, 1963; Lipkowski *et al.*, 1994, 2002; Shimada *et al.*, 2005; Komarov *et al.*, 2007; Wang *et al.*, 2009) and without solvent as *n*-propyl (Yoshida *et al.*, 1994), *n*-butyl (Wang *et al.*, 1995; Prukała *et al.*, 2007), *n*-pentyl (Szafranska *et al.*, 2000), *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl (Abdallah *et al.*, 1999) ammonium halides. However, despite its industrial importance, the structure of the title compound, (I), has not been reported and, remarkably, the tetraisohexylammonium cation does not

appear in the CSD at all. The most closely related compound is tetraisopentylammonium bromide, which is reported as the hydrate clathrate (Wang *et al.*, 2009).

(I)
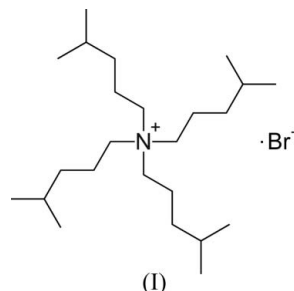
Compound (I) was found to form soft greasy soap-like crystals which gave poor-quality diffraction data and were consequently challenging to work with. Almost no diffraction was seen with a conventional Mo radiation X-ray source. However, reasonable data could be obtained using a Cu microfocus instrument. Initially, the chosen crystal was placed directly in a cold stream (Cosier & Glazer, 1986) at 100 K. The space group was determined to be $P3_221$ and the structure was solved. Examination of the difference map indicated disorder in three of the four alkyl chains.

It is often postulated that rapid or 'quench' cooling can cause dynamic motion to freeze in multiple disordered components to form a metastable structure, whereas slow cooling in such systems enables dynamic components to find a single global optimum position and achieve a more stable state. To test this in (I), the single crystal was warmed to 300 K and after a few minutes was cooled back to 250 K (at a rate of 120 K h^{-1}), where a second data set was collected. The crystal
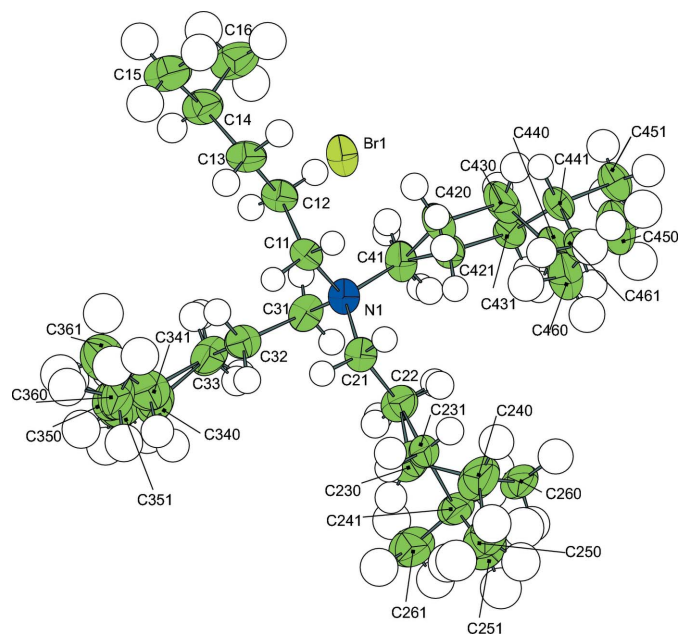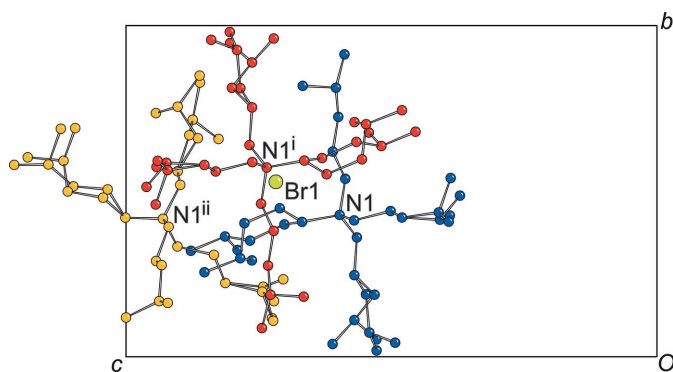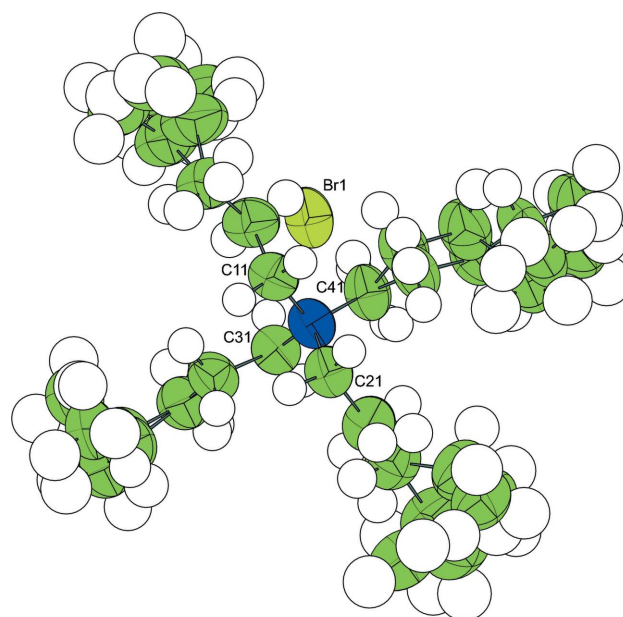

Figure 1
The molecular structure of (I) at 100 K after rapid (quench) cooling, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
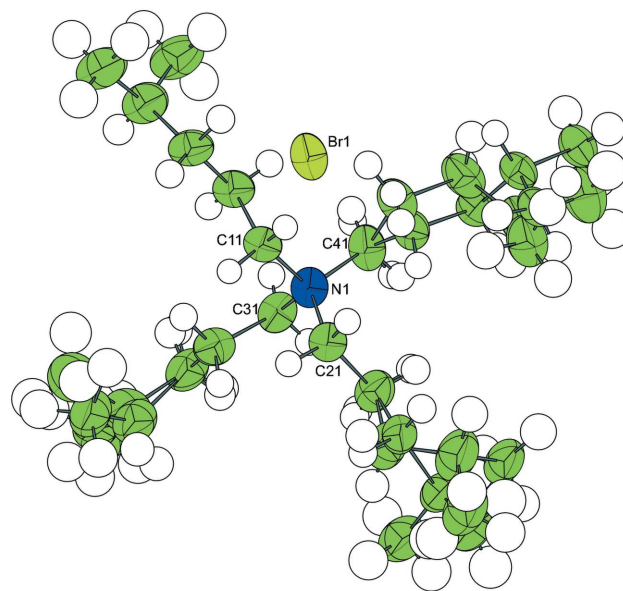
Figure 2
A partial packing diagram for (I), viewed along the *a* axis, showing the symmetry relationships between the ammonium cations surrounding the bromide anion. The N1 cation (blue in the electronic version of the paper) is related to the N1^i cation (red) by a 2_1 screw axis parallel to *a*, and related to the N1^{ii} cation (orange) by a 3_2 screw axis parallel to *c*. The N1^{ii} and N1^i cations are related by a twofold rotation parallel to *b*. [Symmetry codes: (i) $x - y + 1, -y + 1, -z + \frac{4}{3}$; (ii) $-x + y + 1, -x + 1, z + \frac{1}{3}$.]

was then further cooled to 100 K (at a rate of 120 K h^{-1}), where a third data collection was carried out for comparison. All three data collections were carried out in an identical manner and indexed on the same orientation matrix so that the first structure solution at 100 K could be used as the starting point for all refinements.

The structure of (I) consists of one ammonium cation and one bromide anion in the asymmetric unit (Fig. 1), both on general positions. Each bromide anion is surrounded by three cations, two of which are related by a twofold screw axis and the third related to the other two by a twofold rotor and a threefold screw axis, respectively (Fig. 2). Initially, each structure was refined without disorder and with anisotropic displacement parameters (ADPs) for each isohexyl group. The two structures at 100 K showed very little difference, so the disorder was modelled for the first 100 K data set and that model transferred to the other 100 K refinement. The model consisted of one ordered alkyl group (C11–C16), two where the terminal 3–5 atoms wagged (C31–C36 and C41–C46), and one where the end group wagged and is also rotated (C21–C26). On refinement against the data at 250 K, it was clear that the alkyl group that was ordered at 100 K (C11–C16) also appeared disordered. Although all of the ADPs increased in size between 100 and 250 K, the nature of the disorder showed little sign of change in the two wagging alkyl chains (C31–C36 and C41–C46; Fig. 3). A slight change in the orientation of the chain defined by atoms C21–C26 was observed. It is of note that the highest density of short contacts is between the minor component of the terminal methyl groups of this chain and their symmetry equivalents, suggesting that there is a correlation between disorder in neighbouring molecules. At 250 K, there are additional contacts between the C21–C26 chain and the C11–C16 chain that is ordered at 100 K. It is possible, therefore, that the disorder seen in the C11–C16 chain at 250 K is correlated with increased motion in the C21–C26 chain.

Figure 3
The molecular structure of (I) after slow cooling (*a*) to 250 K and (*b*) to 100 K, with displacement ellipsoids drawn at the 50% probability level.

In conclusion, in the case of this compound, the structure accessed by flash cooling to 100 K is the same as that achieved by a slower cooling regime. This suggests that the disorder at 100 K is dynamic in nature.

Experimental

Isohexyl bromide (3.96 g, 24 mmol), powdered K$_2$CO$_3$ (3.31 g, 24 mmol) and isohexylamine hydrochloride (1.00 g, 7.27 mmol) were refluxed in isobutyronitrile (20 ml) for 5 d. The solution was filtered and the solvent removed *in vacuo* to leave an off-white solid (52% yield). Crystals were grown from an ethyl acetate–diethyl ether mixture (1:1 *v/v*) cooled to 243 K over a period of 24 h. NMR data

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were recorded on a Varian 300 MHz instrument. ^{1}H NMR (CDCl$_3$): δ 0.92 (doublet, 6H), 1.31 (quartet, 2H), 1.66 (multiplet, 1H), 1.67 (multiplet, 2H), 3.39 (multiplet, 2H). ^{13}C NMR (CDCl$_3$): δ 20.14, 22.27, 27.44, 35.16, 59.45.

Compound (I) at 100 K, quenched

Crystal data

$C_{24}H_{52}N^+ \cdot Br^-$	$Z = 6$
$M_r = 434.59$	Cu $K\alpha$ radiation
Trigonal, $P3_221$	$\mu = 2.04$ mm^{-1}
$a = 15.12762$ (13) Å	$T = 100$ K
$c = 21.0223$ (2) Å	$0.15 \times 0.14 \times 0.07$ mm
$V = 4166.31$ (6) Å^3	

Data collection

Oxford Diffraction SuperNova Dual diffractometer with Cu at zero and an Atlas detector	89102 measured reflections
	5781 independent reflections
	5591 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011) $T_{min} = 0.57$, $T_{max} = 0.87$	$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.114$	$\Delta\rho_{max} = 0.46$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.60$ e Å^{-3}
5781 reflections	Absolute structure: Flack (1983), with 2550 Friedel pairs
347 parameters	
648 restraints	Flack parameter: -0.02 (2)

Compound (I) at 250 K

Crystal data

$C_{24}H_{52}N^+ \cdot Br^-$	$Z = 6$
$M_r = 434.59$	Cu $K\alpha$ radiation
Trigonal, $P3_221$	$\mu = 1.93$ mm^{-1}
$a = 15.4995$ (2) Å	$T = 250$ K
$c = 21.1346$ (3) Å	$0.15 \times 0.14 \times 0.07$ mm
$V = 4397.06$ (12) Å^3	

Data collection

Oxford Diffraction SuperNova Dual diffractometer with Cu at zero and Atlas detector	94951 measured reflections
	6128 independent reflections
	4391 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011) $T_{min} = 0.60$, $T_{max} = 0.87$	$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.178$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 0.96$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
6128 reflections	Absolute structure: Flack (1983), with 2710 Friedel pairs
366 parameters	
864 restraints	Flack parameter: -0.03 (3)

Compound (I) at 100 K, cooled slowly

Crystal data

$C_{24}H_{52}N^+ \cdot Br^-$	$Z = 6$
$M_r = 434.59$	Cu $K\alpha$ radiation
Trigonal, $P3_221$	$\mu = 2.05$ mm^{-1}
$a = 15.1327$ (3) Å	$T = 100$ K
$c = 20.9326$ (4) Å	$0.15 \times 0.14 \times 0.07$ mm
$V = 4151.30$ (13) Å^3	

Data collection

Oxford Diffraction SuperNova Dual diffractometer with Cu at zero and Atlas detector	88138 measured reflections
	5768 independent reflections
	5336 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011) $T_{min} = 0.59$, $T_{max} = 0.87$	$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.128$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
$S = 0.98$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
5768 reflections	Absolute structure: Flack (1983), with 2546 Friedel pairs
347 parameters	
648 restraints	Flack parameter: -0.01 (3)

Analysis of the Flack x (Flack, 1983; Flack & Bernardinelli, 2000) and Hooft y parameters (Hooft *et al.*, 2008) within *CRYSTALS* (Betteridge *et al.*, 2003; Thompson & Watkin, 2009, 2011) indicated that the crystal had spontaneously resolved and was enantiopure in the space group $P3_221$. The disorder was modelled by splitting atoms with prolate anisotropic displacement parameters (ADPs) into two components; the naming convention used involved appending a 1 or 0 to the index number, such that C26 became C260 and C261 *etc*. To ensure a sensible geometry for the disordered model, the bond distances and angles along the isohexyl chains were restrained to be the same, with s.u. values of 0.01 Å and 0.1°, respectively, and the ADPs of the disordered atoms were restrained to be similar, with an s.u. value of 0.01 Å^2. The H atoms were generally visible in difference maps, but were positioned geometrically then initially refined with soft restraints to the geometry and isotropic ADPs, after which the displacement parameters were fixed and the positions were refined with riding constraints (Cooper *et al.*, 2010).

For all thermal regimes, data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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