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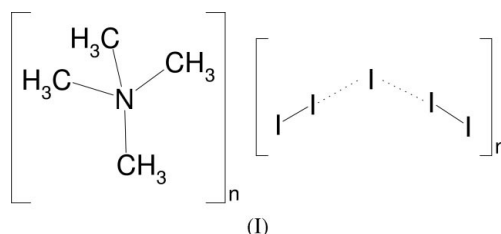
Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(I) = 0.001 \text{ \AA}$
R factor = 0.052
wR factor = 0.143
Data-to-parameter ratio = 45.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tetramethylammonium pentafluorophosphate

The title compound, $C_4H_{12}N^+ \cdot PF_6^-$, consists of V-shaped PF_6^- ions which are linked to adjacent PF_6^- ions to form a flat square mesh normal to (001), with four P atoms on each edge. The tetramethylammonium ions are located at the centre of each square.

Comment

Various polyiodide ions are known, with the most frequently reported being I_3^- and I_5^- (Kloo *et al.*, 2000; Blake *et al.*, 1998). The structures of a number of tetraorganoammonium salts of I_5^- are in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) at the Chemical database service of the EPSRC (Fletcher *et al.*, 1996), including those of [EtMe-Ph₂N]I₅ (213550, refcode FIQLAS; Tebbe & Loukili, 1999), {2[Me₂Ph₂N][I₅]₂·I₂} (161933, ZIVXOR; Tebbe & Gilles, 1996a), [EtMe₃N]I₅ (Loukili & Tebbe, 1999), [Pr¹Me₂PhN]I₅·I₂ (195990, PAZQEM; Tebbe & Loukili, 1998), [Pr₄N]I₅ (Tebbe & Gilles, 1996b) and [Me₄N]I₅ (130287, DULZOZ; Tsvetkov *et al.*, 1986). However, only the data for cell dimensions and space group are provided for [Me₄N]I₅ in the CSD. The structure of [Me₄N]I₅ had also featured in earlier studies (Broekema *et al.*, 1959; Hach & Rundle, 1951), while a listing of cell dimensions and the space group for [Me₄N]I₅, with a reference to a dissertation (Loukili, 1998), were provided by Loukili & Tebbe (1999).Tetraorganoammonium polyiodides are generally prepared from [R₄N]I and the requisite number of molar equivalents of iodine in solvents such as methanol. Tetramethylammonium pentafluorophosphate was isolated in this study from aqueous solutions of [Me₄N]I and SnI₂ (equimolar) in water, the co-product being yellow-brown hydrated tin(IV) oxide. Similar reactions between [Me₄N]X and SnX₂ (X = Cl or Br) in contrast simply led to [Me₄N][SnX₃].The refinement of the carbon displacement parameters for the tetramethylammonium ion gave very high values, suggesting disorder. This was modelled using two superimposed orientations of the molecule *via* the *SHELX PART* instruction. The C atoms could not be refined anisotropically, but the final ratio of the two orientations was 85:15. However,Received 6 March 2001
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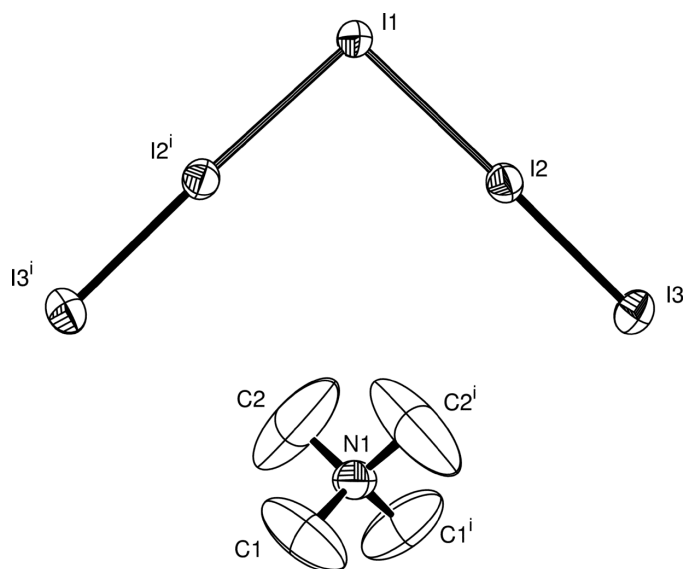


Figure 1
The title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

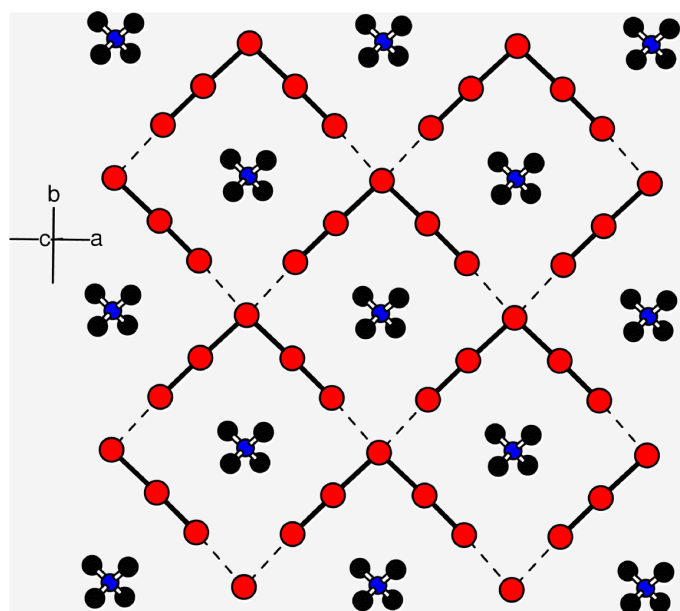


Figure 2
View normal to (001) showing the pentaiodine mesh and the location of the tetramethylammonium ions.

the R value was not improved (5.75% compared to 5.14% for the ordered model) and thus the ordered model has been retained for this report.

The structure of the title compound, (I) (Fig. 1), consists of isolated tetramethylammonium ions and I_5^- ions. The I_5 units are linked *via* longer I—I bonds to form a square mesh normal to (001) (Fig. 2), with I1 coordinated to two I2 atoms at 3.1514 (8) Å and two I3 at 3.6453 (9) Å [symmetry codes: (i) $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$], which are within the van der Waals radius sum of 3.96 Å. The tetramethylammonium ions are located at the centre of each square.

This square mesh is similar to that found in $(EtMe_3N)I_5$ (Loukili & Tebbe, 1999); however, in this case, the mesh is flat and parallel to [010], whereas in $(EtMe_3N)I_5$ there is significant puckering, likely caused by the relative location of the cation. These are the only such square-mesh formations to be reported to date; other pentaiodide networks form herringbone, F-shaped and linear conformations, and in a few cases isolated I_5^- anions.

Many pentaiodides are reported in the literature. In addition, pentaiodide ions may form as part of a more complex polyiodide framework. This is clearly seen in the work of Tebbe and co-workers, in which the V angle varies from 83.51° in $(EtMe_3N)I_5$ (Loukili & Tebbe, 1999) to 119.60° in bipyridinium heptaiodide, $(C_{10}H_9N_2)I_7$ (Tebbe & Bittner, 1995), whereas the 'straight limb' angle varies from 172.09° in $(Me_2-Ph_2N)_3I_{13}$ (Tebbe & Gilles, 1996a) to 179.57° in $(UrEt)_2I_8$ (Grafe-Kavoosian *et al.*, 1998). Bond lengths in the V motif can be divided into the outer (shorter) and inner (longer). The outer bond lengths range from 2.739 to 2.873 Å, whereas the inner range from 2.975 to 3.460 Å. There is, evidently, a significant (0.1 Å) gap between these values which supports the alternative description of the pentaiodide unit as $[2(I_2) \cdot I]^-$.

Experimental

An equimolar solution of NMe_4I and SnI_2 in water was maintained at 368 K for 2 h with stirring. The initial orange-coloured solution initially produced a near-black coloured precipitate which slowly redissolved to be replaced by a pale-yellow precipitate. The reaction mixture was filtered and green-black crystals of the title compound were deposited from the filtrate on standing. M.p. 398–400 K; literature value 399–400 K (Gama & Filguieras, 1989). Analysis: C 6.68, H 1.99, N 1.83%; calculated for $C_4H_{12}N^+I_5^-$: C 6.78, H 1.71, N 1.98%.

Crystal data

$C_4H_{12}N^+I_5^-$
 $M_r = 708.64$
 Monoclinic, $C2/c$
 $a = 13.3110$ (10) Å
 $b = 13.5395$ (11) Å
 $c = 8.8727$ (7) Å
 $\beta = 107.801$ (2)°
 $V = 1522.5$ (2) Å³
 $Z = 4$

$D_x = 3.092$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2244 reflections
 $\theta = 2.4$ – 29.4 °
 $\mu = 10.17$ mm⁻¹
 $T = 296$ (2) K
 Prism, dark purple
 $0.60 \times 0.50 \times 0.50$ mm

Data collection

Bruker SMART 1000 Area CCD diffractometer
 φ - ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{min} = 0.742$, $T_{max} = 0.906$
 4712 measured reflections

2182 independent reflections
 1622 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$
 $\theta_{max} = 30.9$ °
 $h = -10 \rightarrow 18$
 $k = -18 \rightarrow 18$
 $l = -12 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.143$
 $S = 1.05$
 2182 reflections
 48 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0740P)^2 + 6.1215P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.48$ e Å⁻³
 $\Delta\rho_{min} = -1.47$ e Å⁻³
 Extinction correction: SHELXL
 Extinction coefficient: 0.00143 (18)

The maximum residual electron density was $1.48 \text{ e } \text{\AA}^{-3}$ at 0.89 \AA from I3; all residuals $>0.8 \text{ e } \text{\AA}^{-3}$ were within 1 \AA of I atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP-3* (Farrugia, 1999); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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