

Tetra-*n*-butylammonium hexafluorophosphate
at 110 K

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Key indicators

Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.048
 wR factor = 0.130
Data-to-parameter ratio = 21.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The crystal structure of the title compound, $\text{C}_{16}\text{H}_{36}\text{N}^+\cdot\text{PF}_6^-$, has been precisely determined at *ca* 110 K, revealing a well ordered structure.

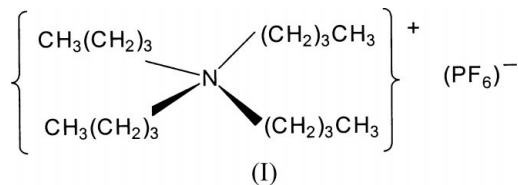
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Comment

Tetra-*n*-butylammonium hexafluorophosphate, (I), is an important reagent in organometallic chemistry, providing a convenient source of the PF_6^- anion. However, the structure of (I) has been poorly characterized in the past, primarily because of the pseudo-spherical shape and high propensity for rotational disorder of the anion, and the aliphatic nature of the cation. Earlier crystallographic determinations of (I), either in its pure form at 213 K [Cambridge Structural Database (Version 5.25; Allen, 2002) refcode NOFKEY; Angaridis *et al.*, 2001] or in its cocrystals with other compounds at 293 K (refcodes ROLQUE and ROLVOD; Tong *et al.*, 2001), had been concluded at relatively high R values of 0.07–0.09 and with geometric parameters of low precision. After submission of the original version of the present paper, we became aware of a more recent characterization of the title compound at *ca* 173 K, which appeared at first sight reasonably ordered, although the F atoms of the anion still exhibit large-amplitude displacements that may conceal excessive librational wagging (Schödel *et al.*, 2004). Moreover, these recent results were obtained from a poorly diffracting crystal [only 52% of the data are above the intensity threshold of $2\sigma(I)$] and relied on relatively low resolution data below $2\theta = 50^\circ$. The present report provides a considerably more precise determination of the title compound (Fig. 1), with an experimental data set measured at *ca* 110 K to $2\theta = 56.3^\circ$ and containing 3557 (out of 4839 unique) observations above $2\sigma(I)$ instead of 1754 (3379 unique) in the earlier determination by Schödel *et al.* (2004). Correspondingly, the standard uncertainties of the resulting geometric parameters are smaller than those quoted in the previous report, on average, by a factor of 2.



In the present structural model, the ammonium cation and the PF_6^- anion display perfectly ordered conformations. As found previously, in three of the four alkyl groups in the cation all torsion angles about the C–C bonds are *anti*. Only in the fourth arm is the C–C–C–C torsion angle *gauche*. However, a dramatic improvement of the PF_6^- description is evident in

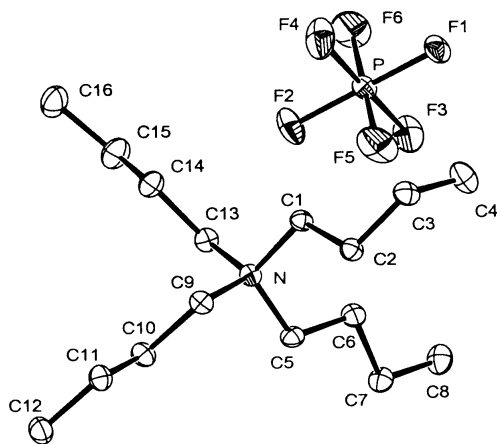


Figure 1
The structure of (I), showing the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

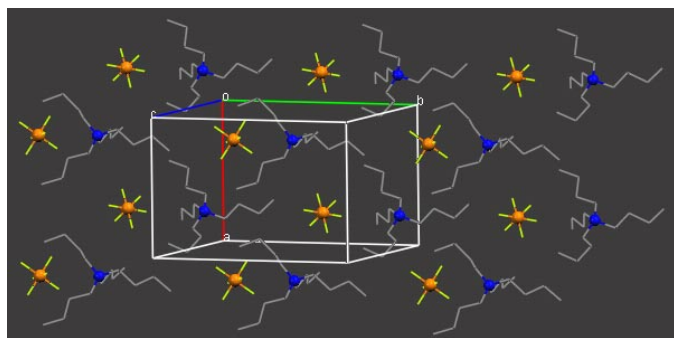


Figure 2
A section of the crystal structure parallel to the *ab* plane and contained within $z = 0.0\text{--}0.5$, showing the relative disposition of the cations and anions.

the present study. The PF_6^- anion is completely disordered at 213 K (Angaridis *et al.*, 2001), and it exhibits large-amplitude libration or partial dynamic disorder at 173 K, as indicated by the very large displacement parameters of the F atoms, with U_{eq} values in the range 0.0609 (6)–0.1228 (14) \AA^2 (Schödel *et al.*, 2004); the current U_{eq} values at 110 K range from 0.0320 (3) to 0.0582 (4) \AA^2 only. The apparent disorder/large-amplitude libration of PF_6^- at 173 K severely affects the reliability of the observed P–F bond distances in the refined structural model (Dunitz, 1979). Thus the corresponding bond lengths observed at 173 K appear severely shortened by libration effects, ranging from 1.504 (3) to 1.556 (2) \AA (Schödel *et al.*, 2004), compared with the more precise values obtained at 110 K, 1.5791 (13)–1.6000 (13) \AA . Similar, though less extreme, temperature-affected differences are observed consistently for other bond lengths: N–C = 1.486 (4)–1.493 (4) \AA at 173 K *versus* 1.515 (2)–1.529 (2) \AA at 110 K, and C–C = 1.478 (5)–1.497 (5) \AA at 173 K *versus* 1.516 (3)–1.531 (2) \AA at 110 K. Selected geometric parameters are given in Table 1.

Another inconsistency relates to the unit-cell volumes determined for the title structure at 213 (2063.7 \AA^3), 173 (1914.9 \AA^3) and 110 K (2021.2 \AA^3). The 1914.9 \AA^3 value looks outstandingly low, as no apparent phase transition has been

found in our study on cooling or heating the crystals. In order to confirm the latter observation we remeasured the unit-cell dimensions from another well shaped crystal of (I) characterized by low mosaicity (*ca* 0.4°) at different temperatures from 110 to 240 K (Table 2). These results are based on data collected on 50 1° φ -scan frames, comprising about 3500 (1950 unique) reflections. The results show that the unit cell of the compound expands gradually (along all three axes) on heating the crystal, from 2019.6 \AA^3 at 110 K to 2087.9 \AA^3 at 240 K. They are in agreement with the 213 K data (Angaridis *et al.*, 2001), but not with the 173 K results (Schödel *et al.*, 2004). It is not clear whether the shortened bond lengths in the 173 K study are entirely a libration effect or whether the unit cell anomaly also contributes.

Finally, the crystal packing of (I) can be described as composed of sheets of alternating cations and anions (Fig. 2), stabilized by Coulombic as well as by van der Waals interactions.

Experimental

The title compound was crystallized from acetonitrile.

Crystal data

$\text{C}_{16}\text{H}_{36}\text{N}^+\text{PF}_6^-$	$D_x = 1.273 \text{ Mg m}^{-3}$
$M_r = 387.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4658 reflections
$a = 9.5559 (2) \text{ \AA}$	$\theta = 2.0\text{--}28.2^\circ$
$b = 13.8885 (5) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$c = 15.2346 (5) \text{ \AA}$	$T = 110 (2) \text{ K}$
$\beta = 91.557 (2)^\circ$	Thin plate, colorless
$V = 2021.15 (11) \text{ \AA}^3$	$0.35 \times 0.25 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.043$
φ and ω scans	$\theta_{\text{max}} = 28.2^\circ$
Absorption correction: none	$h = -12 \rightarrow 12$
17998 measured reflections	$k = -17 \rightarrow 18$
4839 independent reflections	$l = -20 \rightarrow 20$
3557 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.7302P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
4839 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
221 parameters	
H-atom parameters constrained	

Table 1

Unit-cell dimensions of (I) at different temperatures.

T (K)	a (\AA)	b (\AA)	c (\AA)	β ($^\circ$)	V (\AA^3)
110	9.555 (3)	13.887 (2)	15.226 (4)	91.57 (1)	2019.6 (9)
120	9.558 (4)	13.889 (3)	15.237 (4)	91.54 (1)	2022.1 (10)
150	9.591 (4)	13.910 (3)	15.303 (4)	91.32 (1)	2041.0 (11)
180	9.607 (4)	13.920 (3)	15.358 (4)	91.14 (1)	2053.5 (11)
210	9.628 (4)	13.932 (3)	15.422 (4)	90.94 (1)	2068.2 (11)
240	9.659 (5)	13.948 (3)	15.499 (5)	90.75 (2)	2087.9 (13)
213 ^a	9.621 (1)	13.923 (1)	15.410 (1)	90.92 (1)	2063.7 (2)
173 ^b	9.406 (2)	13.593 (2)	19.982 (3)	91.37 (2)	1914.9 (6)

Notes: (a) Angaridis *et al.* (2001); (b) Schödel *et al.* (2004).

Table 2
Selected geometric parameters (Å, °).

P–F5	1.5791 (13)	P–F6	1.6000 (13)
P–F3	1.5884 (12)	N–C9	1.515 (2)
P–F4	1.5933 (12)	N–C1	1.524 (2)
P–F2	1.5985 (11)	N–C13	1.525 (2)
P–F1	1.5981 (11)	N–C5	1.529 (2)
N–C1–C2–C3	173.68 (13)	N–C9–C10–C11	178.68 (13)
C1–C2–C3–C4	–70.8 (2)	C9–C10–C11–C12	179.79 (15)
N–C5–C6–C7	–168.00 (13)	N–C13–C14–C15	177.72 (15)
C5–C6–C7–C8	177.64 (14)	C13–C14–C15–C16	174.88 (17)

H atoms were placed in idealized positions, with C–H = 0.98–0.99 Å. They were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and

MERCURY (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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