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Arene–arene stacking in the revised structure of 2,2′-bipyridinium hexafluorophosphate

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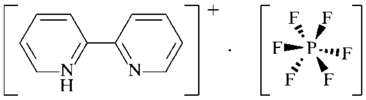
The title compound, $C_{10}H_9N_2^+\cdot PF_6^-$, crystallizes in space group $P2_1/c$ in a supercell doubled along *b*, rather than in the previously reported polar space group *Pc* [Milani, Anzilutti, Vicentini, Santi, Zangrando, Geremia & Mestroni (1997). *Organometallics*, **16**, 5064–5075]. This new structure determination provides a more appropriate description of intra- and intermolecular parameters. The crystal packing is dominated by shifted π-stacked arrangements of adjacent aromatic moieties.

Comment

As has been pointed out by Marsh (1995) and by Marsh *et al.* (2002), in some detail, derivation of space lattices based solely on data collected by conventional automated diffractometers bears some risk. Superstructure arrangements, in which the true structure is based on small but systematic deviations from a more symmetric substructure and that require a unit cell larger than that of the substructure, may go unnoticed. Missing the true translational symmetry will impose an artificially averaged structure upon the subsequent refinement. Nevertheless, the indication of such a mistake in the course of structure refinement may be slight.

While trying to identify a by-product, we came across such an example. Since we failed to identify the compound by comparing its cell parameters, as determined by powder diffractometry, with entries in the Cambridge Structural Database (CSD, Release 5.22 of October 2001; Allen *et al.*, 1983), a single-crystal structure determination was undertaken. This showed the compound to be 2,2′-bipyridinium hexafluorophosphate, (I), for which a crystal structure was previously described (Milani *et al.*, 1997; CSD reference code NOXXED) in space group *Pc*, with a unit cell of half the true size [$a = 6.1758\ (4)$, $b = 13.120\ (3)$ and $c = 7.255\ (4)$ Å, and $\beta = 100.74\ (3)°$; Fig. 2].

There were several indications of a problem in the original refinement, which were unfortunately ignored. The refinement could only be performed with isotropic displacement parameters for the C atoms. In contrast with what was claimed in the publication, the bond lengths and angles were not in the expected range for aromatic bonds. For instance, while C1—C2 was unusually long (1.500 Å), C2—C3 was far too short (1.210 Å). Also, probably because of intramolecular hydrogen bonding (Table 2), all reported *cisoid* bipyridinium structures appear to be bent around the midpoint of the C5—C6 bond; the angles on the nitrogen side are considerably smaller than those on the carbon side. For the related 2,2′-bipyridinium tetraphenylborate, angles of 115.4 and 113.6° *versus* 126.8 and 123.3° were reported (Bakshi *et al.*, 1996; CSD reference code ZUTAT). However, Milani *et al.* (1997) found angles of 121.5 and 113.3° *versus* 119.8 and 121.7°; because of the unrealistically high symmetry imposed in their refinement, the expected kink disappeared. The interplanar angle between the pyridine rings in the cation is quite similar in both the previous and the present refinement; Milani reports 12.98°, while we find a value of 13.50°. The torsion around C5—C6 is, in any case, a rather soft parameter, and consequently this interplanar angle adjusts to the packing requirements and varies considerably for the examples included in the CSD (*e.g.* for 2,2′-bipyridinium tetraphenylborate, a value of 5.27° was observed).


(I)

In correcting the structure, significant changes in bond lengths and angles result (Table 1). Refinement with the true translational symmetry cures all the above-mentioned intramolecular shortcomings of the initial refinement. The H atom attached to atom N1 is clearly visible in the difference map

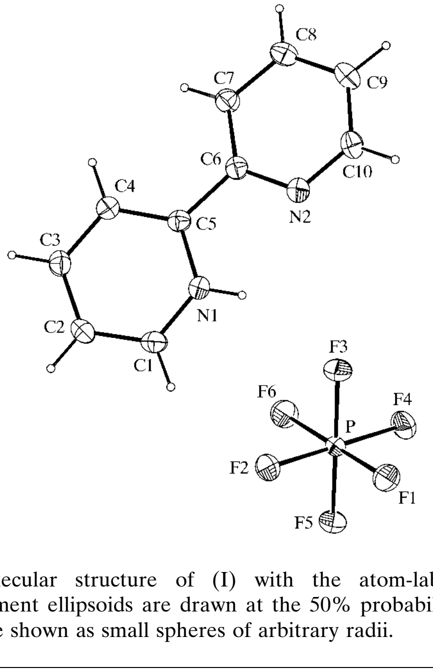


Figure 1
The molecular structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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and the assignment of N1 as being protonated is unambiguous when choosing the correct cell.

The most severe warning signal that something was wrong with the original space-group assignment came from the ambiguous value for the Flack parameter (Flack, 1983). Milani *et al.* (1997) state that an attempt to evaluate the absolute configuration did not produce satisfactory results. Perpendicular to the *c* axis, the structure consists of layers of bipyridinium cations. In the incorrect small cell, all cations point in the same direction, and thus a large dipole moment would develop in the polar structure. In the correct supercell, however, adjacent rows of molecules point in opposite directions and, of course, no net dipole moment is present in the centrosymmetric space group.

Additionally, the orientation of the anions in both refinements differs significantly (Fig. 2). The orientation in the small cell is clearly an artefact of an averaged orientation. The intermolecular hydrogen bonding (Table 2) is, of course, affected by this.

The crystal-packing pattern is also interesting with respect to the non-covalent intermolecular interactions, which are important for the molecular recognition and self-assembly processes leading to molecular aggregates. Within the above-mentioned bipyridinium layers, the arene moieties are lined up in parallel and adjacent molecules are shifted by 5.1 Å. The intermolecular interaction is controlled by so called 'π–π interactions'. This shifted π-stacked arrangement, and the short perpendicular distances between the ring centroids and the parallel aromatic plane (3.286 Å), are in line with this view.

Both experimental (Cozzi *et al.*, 1993) and simulation (Jorgensen & Severance, 1990) work shows that most 'π–π interactions' are dominated by electrostatics (multipole–multipole). The inherent polarity of aromatic systems stems from the electron-rich core being surrounded by an electron-poor torus of H atoms. This electrostatic description accounts for the energetic preference for shifted π-stacked arrangements observed with the packing of (I). The frequently observed alternative π–π interaction is T-shaped (Desiraju & Gavezzotti, 1989), but this type is not encountered in the current structure.

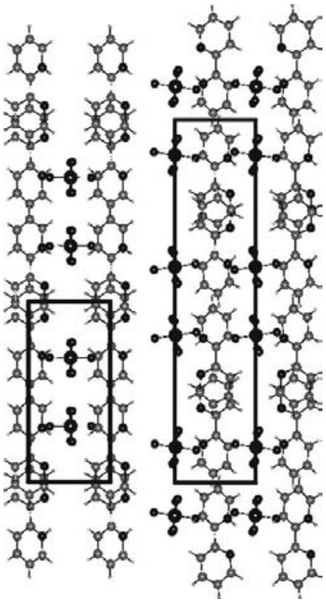

Figure 2
A comparison of the molecular packing of (I) (viewed along *c*) when refined in the original small cell (left) and the correct supercell (right). Note the significantly different orientation of the anions.

Experimental

The first crystal was isolated as a by-product in a synthesis of [Ru(bpy)$_3$](PF$_6$)$_2$. Since this crystal was stained and of low quality, pure 2,2′-bipyridinium hexafluorophosphate was subsequently synthesized according to the method of Milani *et al.* (1997). Suitable single crystals of (I) were obtained by recrystallization from methanol by slow evaporation of the solvent.

Crystal data

$C_{10}H_9N_2^+\cdot PF_6^-$
$M_r = 302.16$
Monoclinic, $P2_1/c$
$a = 6.1072$ (4) Å
$b = 26.0105$ (14) Å
$c = 7.1380$ (5) Å
$\beta = 101.416$ (9)°
$V = 1111.45$ (13) Å^3
$Z = 4$
$D_x = 1.806$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 3.0$–25.8°
$\mu = 0.32$ mm^{-1}
$T = 123$ (2) K
Prism, colourless
0.24 × 0.20 × 0.14 mm

Data collection

Stoe IPDS diffractometer
Rotation scans
11 182 measured reflections
2093 independent reflections
1766 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 25.8°$
$h = -7 \rightarrow 7$
$k = -31 \rightarrow 31$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R(F) = 0.029$
$wR(F^2) = 0.091$
$S = 1.05$
2093 reflections
175 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.2024P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.3352 (17)	C4—C5	1.3858 (18)
N1—C5	1.3505 (17)	C5—C6	1.4777 (18)
N2—C6	1.3453 (17)	C6—C7	1.3908 (18)
N2—C10	1.3320 (17)	C7—C8	1.3852 (18)
C1—C2	1.3761 (18)	C8—C9	1.3826 (18)
C2—C3	1.3894 (18)	C9—C10	1.3915 (18)
C3—C4	1.3865 (18)		
N1—C5—C6	115.86 (11)	C5—C6—C7	122.34 (11)
C4—C5—C6	126.06 (11)	N2—C6—C5	114.25 (11)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···F3	0.827 (18)	2.297 (17)	3.0424 (14)	150.1 (16)
N1—H1···N2	0.827 (18)	2.251 (18)	2.6345 (15)	108.6 (14)

H atoms on C atoms were calculated in their ideal positions and refined using a riding model, with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$. The H atom on atom N1 was identified in a difference Fourier map and refined freely, but also with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm N1)$.

Data collection: *IPDS* (Stoe & Cie, 1999); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1500). Services for accessing these data are described at the back of the journal.

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