# 2-Methyl-1,2,4-triazolo[4,3-a]pyridin-2-ium tetrafluoroborate

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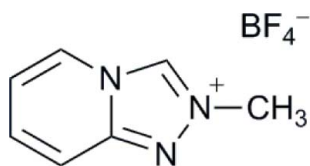Correspondence e-mail: swei1225@gmail.com, wq_ring@hotmail.com

In the title salt, $C_7H_8N_3^+ \cdot BF_4^-$, the 1,2,4-triazolo[4,3-a]pyridinium cation is planar [maximum deviation of 0.016 (2) Å for all non-H atoms]. The cation and anion constitute a tight ionic pair with an F···N [2.911 (4) Å] intermolecular attractive interaction. The ionic pairs form dimers via stacking interactions between inversion-related cations, the normal distance between the cation planes being 3.376 (5) Å. The dimers are packed in stacks along the a axis and linked via C—H···F hydrogen bond, forming a three-dimensional network.

## Related literature

For catalytic applications of triazoliums, see: Fisher *et al.* (2006); Enders *et al.* (2006); Wurz *et al.* (2012). For the synthesis of a related compound and for related structures, see: Ma *et al.* (2008); Wei *et al.* (2009).

## Experimental

### Crystal data

| | |
|---|---|
| $C_7H_8N_3^+ \cdot BF_4^-$ | $V = 1886.0$ (5) Å³ |
| $M_r = 220.97$ | $Z = 8$ |
| Orthorhombic, $Pbca$ | Mo $K\alpha$ radiation |
| $a = 7.1508$ (10) Å | $\mu = 0.15$ mm⁻¹ |
| $b = 12.3070$ (18) Å | $T = 296$ K |
| $c = 21.431$ (3) Å | $0.30 \times 0.20 \times 0.20$ mm |

### Data collection

| | |
|---|---|
| Oxford Diffraction Xcalibur Eos diffractometer | 14891 measured reflections |
| Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010) | 1903 independent reflections |
| | 1616 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.956$, $T_{max} = 0.970$ | $R_{int} = 0.027$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.077$ | 137 parameters |
| $wR(F^2) = 0.245$ | H-atom parameters constrained |
| $S = 1.05$ | $\Delta\rho_{max} = 0.74$ e Å⁻³ |
| 1903 reflections | $\Delta\rho_{min} = -0.50$ e Å⁻³ |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1···F4ⁱ | 0.93 | 2.18 | 3.086 (3) | 165 |
| C5—H5···F2ⁱⁱ | 0.93 | 2.38 | 3.169 (4) | 143 |
| C6—H6···F1ⁱⁱⁱ | 0.93 | 2.53 | 3.301 (5) | 141 |

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x - 1, y, z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KQ2005).

## References

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# supporting information

## 2-Methyl-1,2,4-triazolo[4,3-*a*]pyridin-2-ium tetrafluoroborate

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### S1. Comment

Recently, triazolium salts which can used as carbene precursors are widely using in organic catalysis for the formation of C—C bond reactions, such as benzoin reactions, Stetter reactions and Diels-Alder reactions (Fisher *et al.* 2006; Enders *et al.* 2006; Wurz *et al.* 2012), because of their good stability and excellent catalytic performance. Most research show that bicyclic 1,2,4-triazole carbene have excellent catalytic activity because they have weaker nucleophility than that of thiazole and imidazole carbene.

The crystal structure of the title compound shows that this salt containing the 1,2,4-triazolo[4,3-*a*]pyridinium cation and tetrafluoroborate anion. The cation adopts the planar structure (r.m.s. deviation is 0.009 Å). The cation and anion constitute a tight ionic pair by the N···F (2.911 (4) Å) intermolecular attractive interaction. The ionic pairs form centrosymmetrical dimers *via* the intermolecular stacking interactions between cations (the distance between the cation planes within the dimer is 3.376 (5) Å). The dimers are packed in stacks along the *a* axis and linked into three-dimensional framework by the C—H···F hydrogen bonds.
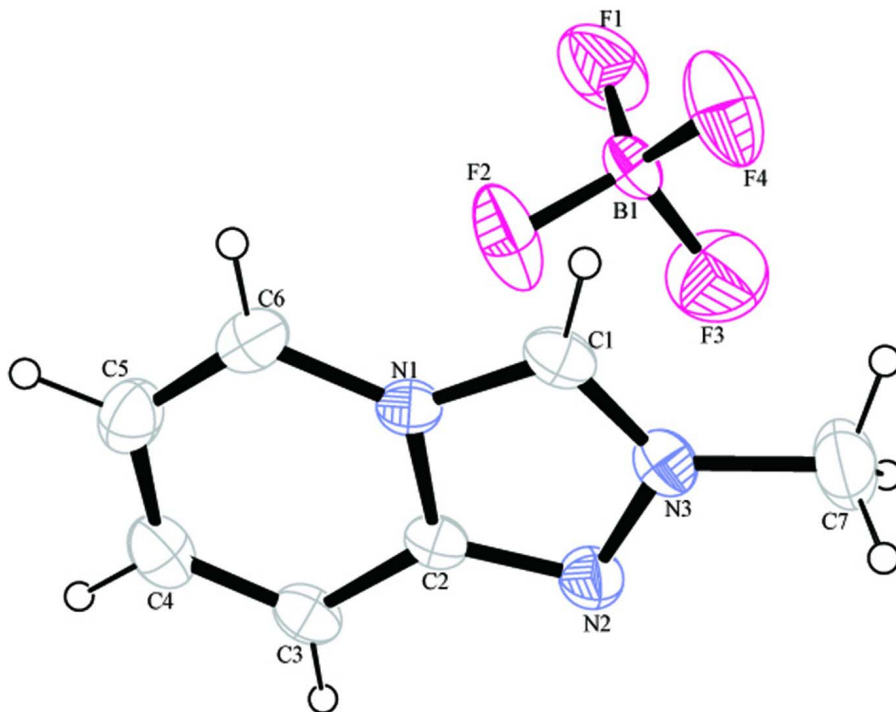
### S2. Experimental

The title compound was prepared according to the method of Ma *et al.* (Ma *et al.*, 2008) and Wei *et al.* (Wei *et al.*, 2009). A flame-dried round-bottomed flask equipped with a reflux condenser was charged with trimethyloxonium tetrafluoroborate (0.88 g, 6 mmol), 1-(pyridin-2-yl)hydrazine (0.55 g, 5 mmol), and chlorobenzene (20 ml). The mixture was then stirred for 30 min, followed by addition of trimethyl orthoformate (1.65 ml, 15 mmol). After being heated at 110 °C for 10 h, the reaction mixture was concentrated *in vacuo*. The resulting residue was recrystallized from acetone to give 2-Methylpyrido[1,2-*a*][1,2,4]-triazol-2-ium tetrafluoroborate as colorless crystal in 88% yield. Mp 171 - 173 °C. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 4.40 (s, 3 H), 7.44 (t, $J$ = 7.2 Hz, 1 H), 7.85 - 7.88 (m, 1 H), 7.96 (d, $J$ = 9.6 Hz, 1 H), 8.75 (d, $J$ = 7.8 Hz, 1 H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 40.7, 116.4, 119.8, 127.0, 134.9, 149.5. MS (ESI$^+$) *m/z* 133 [*M* - BF$_4$ - H]$^+$. Anal. Calcd for C$_7$H$_8$BF$_4$N$_3$: C, 38.05; H, 3.65; N, 19.02. Found: C, 37.96; H, 3.50; N, 19.25. Colourless crystals suitable for X-ray structural determination were grown by slow evaporation of a solution of the title compound in a petroleum ether/actone mixture (1:1, *v/v*) at room temperature.

### S3. Refinement

All H atoms were positioned geometrically and refined in the riding model approximation with C—H = 0.93 (CH$_3$) or 0.96 (CH) Å.

BF$_4^-$ is a tetrahedral anion, the central boron atom is surrounded by four neighboring fluorine atoms. Consequently, the thermal movement of boron atom is limited, but not for the ending fluorine atoms. Therefore, the $U_{eq}$ for the boron atom is low as compared to the neighboring fluorine atoms.

There are two relatively high positive peaks of 0.74 and 0.53 e/Å³ near the fluorine atoms of the $BF_4^-$ anion that indicate a slight disorder of the anion. However, due to the low contribution of the second component it was neglected.



**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

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*Crystal data*

| | |
|---|---|
| $C_7H_8N_3^+ \cdot BF_4^-$ | $F(000) = 896$ |
| $M_r = 220.97$ | $D_x = 1.556$ Mg m$^{-3}$ |
| Orthorhombic, *Pbca* | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 7.1508$ (10) Å | $\mu = 0.15$ mm$^{-1}$ |
| $b = 12.3070$ (18) Å | $T = 296$ K |
| $c = 21.431$ (3) Å | Block, colourless |
| $V = 1886.0$ (5) Å³ | $0.30 \times 0.20 \times 0.20$ mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Xcalibur Eos diffractometer | 14891 measured reflections |
| Radiation source: fine-focus sealed tube | 1903 independent reflections |
| Graphite monochromator | 1616 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 16.0874 pixels mm⁻¹ | $R_{int} = 0.027$ |
| $\omega$ scans | $\theta_{max} = 26.4°$, $\theta_{min} = 1.9°$ |
| Absorption correction: multi-scan | $h = -8 \rightarrow 8$ |
| (*CrysAlis PRO*; Oxford Diffraction, 2010) | $k = -15 \rightarrow 15$ |
| $T_{min} = 0.956$, $T_{max} = 0.970$ | $l = -26 \rightarrow 26$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.077$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.245$ | |
| $S = 1.05$ | H-atom parameters constrained |
| 1903 reflections | $w = 1/[\sigma^2(F_o^2) + (0.1597P)^2 + 1.099P]$ |
| 137 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.74$ e Å⁻³ |
| | $\Delta\rho_{min} = -0.50$ e Å⁻³ |

*Special details*

**Experimental**. Absorption correction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19, empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| F1 | 0.7647 (5) | 0.2546 (3) | 0.66913 (12) | 0.1094 (10) |
| F2 | 0.5247 (4) | 0.3344 (2) | 0.61787 (11) | 0.1026 (10) |
| F3 | 0.7464 (5) | 0.4320 (3) | 0.66199 (16) | 0.1321 (13) |
| F4 | 0.5444 (4) | 0.3483 (3) | 0.72252 (10) | 0.1119 (10) |
| N1 | 0.1517 (3) | 0.41555 (15) | 0.59033 (9) | 0.0398 (5) |
| N2 | 0.3053 (3) | 0.57217 (18) | 0.59455 (10) | 0.0500 (6) |
| N3 | 0.2503 (3) | 0.53825 (19) | 0.65195 (10) | 0.0500 (6) |
| C1 | 0.1599 (4) | 0.4458 (2) | 0.65054 (11) | 0.0476 (6) |
| H1 | 0.1110 | 0.4084 | 0.6845 | 0.057* |
| C2 | 0.2444 (3) | 0.49487 (18) | 0.55689 (11) | 0.0395 (6) |
| C3 | 0.2603 (3) | 0.4838 (2) | 0.49127 (12) | 0.0486 (7) |
| H3 | 0.3203 | 0.5364 | 0.4674 | 0.058* |
| C4 | 0.1859 (4) | 0.3948 (2) | 0.46456 (13) | 0.0564 (8) |
| H4 | 0.1952 | 0.3859 | 0.4216 | 0.068* |
| C5 | 0.0940 (5) | 0.3147 (2) | 0.50043 (15) | 0.0599 (8) |
| H5 | 0.0454 | 0.2538 | 0.4805 | 0.072* |
| C6 | 0.0751 (4) | 0.3243 (2) | 0.56234 (15) | 0.0544 (7) |
| H6 | 0.0130 | 0.2718 | 0.5856 | 0.065* |
| C7 | 0.2944 (6) | 0.6039 (3) | 0.70666 (15) | 0.0775 (10) |
| H7A | 0.2205 | 0.6690 | 0.7061 | 0.116* |
| H7B | 0.4247 | 0.6227 | 0.7061 | 0.116* |
| H7C | 0.2671 | 0.5632 | 0.7438 | 0.116* |
| B1 | 0.6389 (4) | 0.3369 (3) | 0.66829 (12) | 0.0498 (7) |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| F1 | 0.126 (2) | 0.124 (2) | 0.0777 (16) | 0.0613 (17) | −0.0112 (13) | 0.0018 (12) |
| F2 | 0.0934 (17) | 0.150 (2) | 0.0640 (13) | 0.0390 (15) | −0.0291 (11) | −0.0343 (13) |
| F3 | 0.121 (3) | 0.133 (2) | 0.142 (3) | −0.044 (2) | −0.0029 (18) | 0.0240 (19) |
| F4 | 0.0957 (18) | 0.191 (3) | 0.0492 (12) | −0.0054 (18) | 0.0215 (11) | −0.0277 (13) |
| N1 | 0.0366 (10) | 0.0397 (10) | 0.0431 (10) | 0.0044 (8) | 0.0029 (7) | 0.0056 (7) |
| N2 | 0.0533 (12) | 0.0509 (12) | 0.0456 (12) | −0.0067 (9) | 0.0023 (9) | 0.0053 (9) |
| N3 | 0.0536 (13) | 0.0574 (13) | 0.0389 (11) | 0.0006 (10) | 0.0010 (8) | 0.0016 (9) |
| C1 | 0.0477 (14) | 0.0564 (14) | 0.0386 (12) | 0.0048 (11) | 0.0060 (9) | 0.0102 (10) |
| C2 | 0.0329 (10) | 0.0455 (12) | 0.0401 (13) | 0.0038 (8) | 0.0022 (8) | 0.0082 (9) |
| C3 | 0.0420 (13) | 0.0621 (15) | 0.0416 (13) | 0.0070 (11) | 0.0045 (10) | 0.0087 (11) |
| C4 | 0.0525 (15) | 0.0716 (18) | 0.0452 (14) | 0.0193 (13) | 0.0003 (11) | −0.0086 (12) |
| C5 | 0.0613 (17) | 0.0502 (15) | 0.0682 (18) | 0.0065 (12) | −0.0054 (14) | −0.0129 (12) |
| C6 | 0.0544 (15) | 0.0413 (12) | 0.0674 (17) | −0.0007 (11) | 0.0006 (13) | 0.0023 (11) |
| C7 | 0.096 (3) | 0.088 (2) | 0.0488 (16) | −0.0100 (19) | −0.0080 (17) | −0.0151 (15) |
| B1 | 0.0478 (16) | 0.0710 (19) | 0.0305 (12) | 0.0042 (13) | 0.0016 (10) | 0.0002 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| F1—B1 | 1.356 (4) | C2—C3 | 1.418 (4) |
| F2—B1 | 1.355 (3) | C3—C4 | 1.345 (4) |
| F3—B1 | 1.407 (5) | C3—H3 | 0.9300 |
| F4—B1 | 1.352 (3) | C4—C5 | 1.412 (5) |
| N1—C1 | 1.344 (3) | C4—H4 | 0.9300 |
| N1—C2 | 1.380 (3) | C5—C6 | 1.339 (4) |
| N1—C6 | 1.386 (3) | C5—H5 | 0.9300 |
| N2—C2 | 1.322 (3) | C6—H6 | 0.9300 |
| N2—N3 | 1.357 (3) | C7—H7A | 0.9600 |
| N3—C1 | 1.309 (4) | C7—H7B | 0.9600 |
| N3—C7 | 1.459 (4) | C7—H7C | 0.9600 |
| C1—H1 | 0.9300 | | |
| | | | |
| C1—N1—C2 | 106.3 (2) | C6—C5—C4 | 121.7 (3) |
| C1—N1—C6 | 131.1 (2) | C6—C5—H5 | 119.2 |
| C2—N1—C6 | 122.5 (2) | C4—C5—H5 | 119.2 |
| C2—N2—N3 | 103.7 (2) | C5—C6—N1 | 117.4 (2) |
| C1—N3—N2 | 112.9 (2) | C5—C6—H6 | 121.3 |
| C1—N3—C7 | 127.4 (2) | N1—C6—H6 | 121.3 |
| N2—N3—C7 | 119.7 (3) | N3—C7—H7A | 109.5 |
| N3—C1—N1 | 106.5 (2) | N3—C7—H7B | 109.5 |
| N3—C1—H1 | 126.7 | H7A—C7—H7B | 109.5 |
| N1—C1—H1 | 126.7 | N3—C7—H7C | 109.5 |
| N2—C2—N1 | 110.5 (2) | H7A—C7—H7C | 109.5 |
| N2—C2—C3 | 130.4 (2) | H7B—C7—H7C | 109.5 |
| N1—C2—C3 | 119.1 (2) | F4—B1—F2 | 112.8 (3) |
| C4—C3—C2 | 118.0 (2) | F4—B1—F1 | 113.4 (3) |

| | | | |
|---|---|---|---|
| C4—C3—H3 | 121.0 | F2—B1—F1 | 113.2 (3) |
| C2—C3—H3 | 121.0 | F4—B1—F3 | 105.6 (3) |
| C3—C4—C5 | 121.4 (3) | F2—B1—F3 | 105.8 (3) |
| C3—C4—H4 | 119.3 | F1—B1—F3 | 105.1 (3) |
| C5—C4—H4 | 119.3 | | |
| | | | |
| C2—N2—N3—C1 | −0.2 (3) | C1—N1—C2—C3 | 179.2 (2) |
| C2—N2—N3—C7 | 179.7 (3) | C6—N1—C2—C3 | 0.8 (3) |
| N2—N3—C1—N1 | −0.3 (3) | N2—C2—C3—C4 | 179.2 (3) |
| C7—N3—C1—N1 | 179.8 (3) | N1—C2—C3—C4 | −0.9 (3) |
| C2—N1—C1—N3 | 0.7 (3) | C2—C3—C4—C5 | 0.2 (4) |
| C6—N1—C1—N3 | 179.0 (2) | C3—C4—C5—C6 | 0.7 (4) |
| N3—N2—C2—N1 | 0.7 (3) | C4—C5—C6—N1 | −0.9 (4) |
| N3—N2—C2—C3 | −179.5 (2) | C1—N1—C6—C5 | −177.9 (3) |
| C1—N1—C2—N2 | −0.9 (2) | C2—N1—C6—C5 | 0.1 (4) |
| C6—N1—C2—N2 | −179.3 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C1—H1···F4[i] | 0.93 | 2.18 | 3.086 (3) | 165 |
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