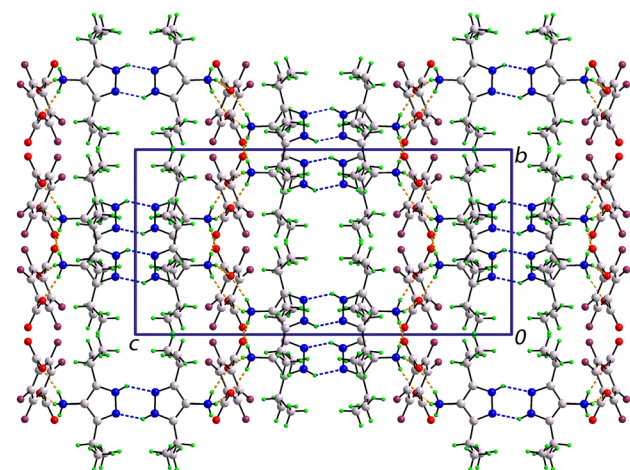
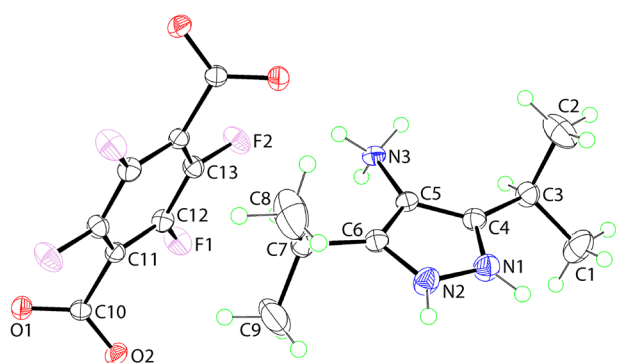


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# Crystal structure of bis(3,5-diisopropyl-1*H*-pyrazol-4-ammonium) tetrafluoroterephthalate, 2 [C<sub>9</sub>H<sub>18</sub>N<sub>3</sub>][C<sub>8</sub>F<sub>4</sub>O<sub>4</sub>]



**Table 1:** Data collection and handling.

|                                                                            |                                                                         |
|----------------------------------------------------------------------------|-------------------------------------------------------------------------|
| Crystal:                                                                   | Colourless prism                                                        |
| Size:                                                                      | 0.18 × 0.07 × 0.04 mm                                                   |
| Wavelength:                                                                | Mo K $\alpha$ radiation (0.71073 Å)                                     |
| $\mu$ :                                                                    | 0.11 mm <sup>-1</sup>                                                   |
| Diffractometer, scan mode:                                                 | Rigaku XtaLAB P200, $\omega$                                            |
| $\theta_{\max}$ , completeness:                                            | 29.7°, >99 %                                                            |
| $N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ : | 11,009, 3809, 0.026                                                     |
| Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :                    | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 3016                      |
| $N(\text{param})_{\text{refined}}$ :                                       | 200                                                                     |
| Programs:                                                                  | CRYSTALS <sup>PRO</sup> [1], Il Milione [2], SHELX [3], WinGX/ORTEP [4] |

## Abstract

2[C<sub>9</sub>H<sub>18</sub>N<sub>3</sub>][C<sub>8</sub>F<sub>4</sub>O<sub>4</sub>], monoclinic,  $I2/a$  (no. 15),  $a = 10.2282(4)$  Å,  $b = 11.9366(5)$  Å,  $c = 24.5548(12)$  Å,  $\beta = 98.948(4)^\circ$ ,  $V = 2961.4(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0456$ ,  $wR_{\text{ref}}(F^2) = 0.1217$ ,  $T = 178$  K.

**CCDC no.:** 2314073

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of material

Under an argon atmosphere, the reaction of 4-amino-3,5-diisopropyl-1-pyrazole (0.0312 g, 0.187 mmol) in anhydrous tetrahydrofuran (5 mL) with tetrafluoroterephthalic acid (0.0284 g, 0.119 mmol) in anhydrous tetrahydrofuran (6 mL) was conducted overnight at room temperature. The undissolved powders were filtered off and after evaporation *in vacuo*, the obtained white powders were collected. The colourless crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation at room temperature from anhydrous methanol (0.0252 g, 0.044 mmol, 47 % yield). Anal. Calcd. for C<sub>26</sub>H<sub>36</sub>F<sub>4</sub>N<sub>6</sub>O<sub>4</sub>: C 54.54, H 6.34, N 14.68 %. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz):  $\delta$  1.29 (d, 24H,  $J = 7$  Hz, CH(CH<sub>3</sub>)), 3.07

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ ).

| Atom             | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------------------|--------------|--------------|--------------|----------------------------------|
| F1               | 0.46906 (8)  | 0.64920 (7)  | 0.30490 (4)  | 0.0325 (2)                       |
| F2               | 0.23735 (8)  | 0.54260 (7)  | 0.29369 (4)  | 0.0313 (2)                       |
| O1               | 0.51208 (9)  | 0.96155 (8)  | 0.28513 (4)  | 0.0264 (2)                       |
| O2               | 0.59978 (9)  | 0.81696 (9)  | 0.24651 (4)  | 0.0269 (2)                       |
| N1               | 0.20840 (13) | 0.31259 (11) | 0.05303 (5)  | 0.0284 (3)                       |
| H1N <sup>a</sup> | 0.226 (3)    | 0.279 (3)    | 0.0232 (9)   | 0.034*                           |
| N2               | 0.20424 (13) | 0.42611 (11) | 0.05144 (5)  | 0.0278 (3)                       |
| H2N <sup>a</sup> | 0.219 (3)    | 0.456 (3)    | 0.0203 (8)   | 0.033*                           |
| N3               | 0.16216 (11) | 0.37577 (10) | 0.19246 (5)  | 0.0194 (2)                       |
| H3N              | 0.1127 (15)  | 0.4354 (11)  | 0.2012 (7)   | 0.029*                           |
| H4N              | 0.1233 (16)  | 0.3129 (10)  | 0.2037 (7)   | 0.029*                           |
| H5N              | 0.2432 (11)  | 0.3751 (14)  | 0.2140 (6)   | 0.029*                           |
| C1               | 0.2776 (2)   | 0.08617 (15) | 0.08653 (8)  | 0.0434 (4)                       |
| H1A              | 0.241164     | 0.088712     | 0.047194     | 0.065*                           |
| H1B              | 0.279576     | 0.008395     | 0.099416     | 0.065*                           |
| H1C              | 0.367632     | 0.116622     | 0.092205     | 0.065*                           |
| C2               | 0.05064 (18) | 0.11107 (15) | 0.11199 (9)  | 0.0473 (5)                       |
| H2A              | −0.002307    | 0.158114     | 0.132963     | 0.071*                           |
| H2B              | 0.051567     | 0.033970     | 0.125767     | 0.071*                           |
| H2C              | 0.011883     | 0.112345     | 0.072902     | 0.071*                           |
| C3               | 0.19116 (14) | 0.15562 (12) | 0.11873 (6)  | 0.0260 (3)                       |
| H3               | 0.229318     | 0.149323     | 0.158658     | 0.031*                           |
| C4               | 0.19271 (13) | 0.27756 (11) | 0.10349 (6)  | 0.0220 (3)                       |
| C5               | 0.17765 (12) | 0.37296 (11) | 0.13466 (5)  | 0.0187 (3)                       |
| C6               | 0.18635 (13) | 0.46552 (11) | 0.10081 (5)  | 0.0212 (3)                       |
| C7               | 0.17959 (15) | 0.58883 (12) | 0.11206 (6)  | 0.0260 (3)                       |
| H7               | 0.178006     | 0.597683     | 0.152453     | 0.031*                           |
| C8               | 0.0544 (2)   | 0.64013 (16) | 0.08236 (12) | 0.0641 (7)                       |
| H8A              | 0.051607     | 0.631626     | 0.042496     | 0.096*                           |
| H8B              | 0.052135     | 0.719917     | 0.091576     | 0.096*                           |
| H8C              | −0.022117    | 0.602334     | 0.093618     | 0.096*                           |
| C9               | 0.3014 (2)   | 0.64917 (16) | 0.09940 (12) | 0.0636 (7)                       |
| H9A              | 0.380657     | 0.614668     | 0.120271     | 0.095*                           |
| H9B              | 0.297208     | 0.728159     | 0.109881     | 0.095*                           |
| H9C              | 0.305187     | 0.643782     | 0.059856     | 0.095*                           |
| C10              | 0.50604 (12) | 0.86825 (11) | 0.26286 (5)  | 0.0199 (3)                       |
| C11              | 0.37346 (12) | 0.80635 (11) | 0.25539 (5)  | 0.0192 (3)                       |
| C12              | 0.36218 (12) | 0.70010 (11) | 0.27668 (6)  | 0.0214 (3)                       |
| C13              | 0.24181 (13) | 0.64536 (11) | 0.27148 (6)  | 0.0210 (3)                       |

<sup>a</sup>Occupancy: 0.5.

(sept, 4H,  $J = 7 \text{ Hz}$ ,  $\text{CH}(\text{CH}_3)$ ), NH not observed. IR (KBr,  $\text{cm}^{-1}$ ): 3239 s  $\nu(\text{N-H})$ , 2973 s  $\nu(\text{C-H})$ , 1624 s  $\nu(\text{C=O})$ , 1606 s  $\nu(\text{C=O})$ , 1367 s, 986 s, 742 s.

## 2 Experimental details

The C-bound H atoms were geometrically placed ( $\text{C-H} = 0.98\text{--}1.00 \text{ \AA}$ ) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$ . The N-bound H atoms were located in a difference Fourier map and refined with  $\text{pyrazolyl-N-H} = 0.88 \pm 0.01 \text{ \AA}$  and  $\text{ammonium-N-H} = 0.91 \pm 0.01 \text{ \AA}$  with  $U_{\text{iso}}(\text{H}) = 1.2$  and

$1.5U_{\text{eq}}(\text{N})$ , respectively. Owing to poor agreement, one reflection, i.e. (1 1 0), being affected by the beam-stop, was omitted from the final cycles of refinement.

## 3 Comment

Covalent organic frameworks (COFs) are a new class of materials having two- or three-dimensional architectures resulting from the reactions between organic precursors being characterised by strong covalent bonds between the original precursors to afford porous and stable crystalline materials [5]. Recent interest has focussed upon in the construction of COFs through imine=C=N bond formation through the reaction of an aromatic amine with a carbonyl compound, such as an aldehyde, and by imide C–N bond formation by the reaction of an aromatic amine with a carbonyl compound, such as a carboxylic acid or an acid anhydride [6]. With this in mind, recent reports have described the crystal structures of products obtained from the reactions of 4-amino-3,5-diisopropyl-1-pyrazole ( $\text{L}^1\text{HpzNH}_2$ ) [7] and of 4-amino-3,5-dimethyl-1-pyrazole ( $\text{L}^0\text{HpzNH}_2$ ) [8] with benzene-1,4-dicarboxaldehyde (terephthalaldehyde) [9, 10]. These studies were complemented by the structure determination of the product of the reaction between  $\text{L}^0\text{HpzNH}_2$  with tetrafluoroterephthalic acid, through imide=C–N bond formation, motivated by the desire to improve solubility in normal organic solvents [11]. However, the obtained product proved to be a salt, i.e.  $\{(\text{4-ammonium-3,5-dimethyl-1-pyrazole})_2\text{-(tetrafluoroterephthalate)}\}$  [11]; this salt is later referred to as “(II)”. Herein, the structure of title compound was obtained by the reaction of the more electron-donating isopropyl substituted precursor,  $\text{L}^1\text{HpzNH}_2$ , with tetrafluoroterephthalic acid in anhydrous tetrahydrofuran solution. However, this reaction, too, resulted in a salt, (I).

The IR spectrum of (I) features a new characteristic absorption band at  $3239 \text{ cm}^{-1}$ , assigned to N–H stretching. Further, the sharp N–H<sub>2</sub> stretching band of the  $\text{L}^1\text{HpzNH}_2$  precursor, at  $3374 \text{ cm}^{-1}$ , disappeared [7]. In addition, new C=O stretching bands, at  $1624$  and  $1606 \text{ cm}^{-1}$ , are clearly shifted from the C=O stretching band, at  $1700 \text{ cm}^{-1}$ , of tetrafluoroterephthalic acid. The observed bands in the IR spectrum of (I) very closely resemble those of the previously reported salt,  $\{(\text{4-ammonium-3,5-dimethyl-1-pyrazole})_2\text{-(tetrafluoroterephthalate)}\}$ , i.e.  $3197 \text{ s } \nu(\text{N-H})$ ,  $1639 \text{ s}$  and  $1607 \text{ cm}^{-1} \text{ s } \nu(\text{C=O})$  [11]. The expected signals in  $^1\text{H}$  NMR spectrum of (I) were observed at  $1.29 \text{ ppm}$  (methyl–H) and  $3.07 \text{ ppm}$  (methine–H), the latter of which are shifted downfield compound to those of  $\text{L}^1\text{HpzNH}_2$  at  $2.97 \text{ ppm}$ . A detailed determination of the structural details of (I) in the solid-state was achieved through X-ray crystallography.

The molecular structures of the constituents of salt (I) are shown in the upper view of the figure (50 % displacement ellipsoids; unlabelled atoms are related by the symmetry operation  $0.5 - x, 1.5 - y, 0.5 - z$ ). The H1n and H2n atoms are statistically disordered over the N1 and N2 atoms. The asymmetric-unit comprises a 4-ammonium-3,5-diisopropyl-1-pyrazole cation, in a general position, and half a 2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate dianion, as this is located about an inversion centre.

The closeness in the C10–O1, O2 bond lengths [1.2380(16) & 1.2551(16) Å] confirms that proton transfer occurred during co-crystallisation; see below for further comment. The angles subtended at the N1 atom [C4–N1–N2 = 109.30(12)°] is equivalent to that subtended at the N2 atom [C6–N2–N1 = 109.44(11)°], confirming each of the N1 and N2 atoms is partially protonated. In the methyl analogue of (I), i.e. (II), the comparable angles were disparate at 113.09(9) and 104.80(9)° [11], with the former corresponding to the protonated pyrazolyl–N atom.

The pyrazolyl ring is planar to  $\pm 0.004(1)$  Å and an evaluation of the bond lengths within the five-membered ring is consistent with the significant delocalisation of  $\pi$ -electron density over the five atoms. Thus, the C4–N1 [1.3407(18) Å] and C6–N2 [1.3393(17) Å] bond lengths are experimentally equivalent as are the C4–C5 [1.3938(19) Å] and C5–C6 [1.3937(18) Å] bonds; N1–N2 = 1.3561(18) Å. This observation provides further support for the protonation at each nitrogen site of the pyrazolyl ring.

The dianion deviates from planarity with the carboxylate residues being splayed with respect to the phenyl ring as the dihedral angle between the respective least-squares planes is 55.99(8)°. This result contrasts the near perpendicular relationship observed in (II), i.e. 83.14(6)° [11].

In the crystal of (I), all potential hydrogen bond acceptors and donors participate in charge-assisted hydrogen-bonding interactions. The cations associate about a 2-fold axis via pyrazolyl–N–H...N(pyrazolyl) hydrogen bonds [N1–H1n...N1<sup>i</sup>: H1n...N1<sup>i</sup> = 2.12(2) Å, N1...N1<sup>i</sup> = 2.8628(18) Å with angle at H1n = 142(3)° and N2–H2n...N2<sup>i</sup>: H2n...N2<sup>i</sup> = 2.07(2) Å, N2...N2<sup>i</sup> = 2.8273(18) Å with angle at H2n = 144(3)° for symmetry operation (i):  $1/2 - x, y, -z$ ] leading to six-membered  $\{\cdots\text{HNN}\}_2$  synthons. In the lower view of the figure, only one of each of the disordered pairs of hydrogen bonds is shown in the view in projection down the  $a$ -axis of the unit-cell contents of (I). The ammonium–N–H atoms form hydrogen bonds with carboxylate–O atoms derived from three different di-anions to construct a three-dimensional framework. One ammonium–N–H atom connects to the carboxylate–O1 atom [N3–H3n...O1<sup>ii</sup>: H3n...O1<sup>ii</sup> = 1.841(15) Å, N3...O1<sup>ii</sup> = 2.7486(15) Å with angle at H3n = 169.7(14)° for (ii):  $0.5 - x, 1.5 - y, 0.5 - z$ ] while two ammonium–N–H atoms

connect to disparate carboxylate–O2 atoms [N3–H4n...O2<sup>iii</sup>: H4n...O2<sup>iii</sup> = 1.909(14) Å, N3...O2<sup>iii</sup> = 2.7793(16) Å with angle at H3n = 158.9(15)° and N3–H5n...O2<sup>iv</sup>: H5n...O2<sup>iv</sup> = 1.875(13) Å, N3...O2<sup>iv</sup> = 2.7445(15) Å with angle at H5n = 158.7(15)° for (iii):  $-0.5 + x, 1 - y, z$  and (iv):  $1 - x, -0.5 + y, 1/2 - z$ ]. The participation of the carboxylate–O2 atom in two hydrogen bonds as opposed to the single hydrogen bond involving the carboxylate–O1 atom explains the slight lengthening of the C10–O2 bond compared with the C10–O1 bond (see above). Globally, the packing comprises alternating layers of anions and cations stacked along the  $c$ -axis.

A complementary analysis of the molecular packing to the above was achieved through the calculation of the Hirshfeld surfaces as well as of the full and delineated two-dimensional fingerprint plots employing Crystal Explorer 21 [12] and standard procedures [13]. The calculations were based on the two-molecule aggregate shown in the upper view of the figure, i.e. with the full di-anion, the most prominent contacts in the crystal of (I) are H...H [40.8 %] followed by H...O/O...H [21.7 %] and H...F/F...H [20.3 %]. Significant contributions to the surface contacts are also made by H...C/C...H [8.0 %] and O...F/F...O [4.3 %] with smaller contributions from H...N/N...H [2.9 %] and F...F [1.0 %]. When the calculations were performed on the individual components of (I), rather different contributions are evident, as anticipated. The cation has significantly greater contributions to the Hirshfeld surface from H...H contacts, at 62.7 %, compared to (I), with concomitantly diminished contributions from H...O/O...H [12.9 %] and H...F/F...H [11.2 %]. Small increases are seen in H...C/C...H [8.7 %] and H...N/N...H [4.5 %] contacts. Lacking hydrogen atoms, the di-anion has a vastly different spread of contributors to the surface contacts, with the most prominent being H...O/O...H [36.4 %] and H...F/F...H [34.7 %] followed by H...C/C...C [16.6 %] and O...F/F...O [8.4 %] contacts. Smaller contributions are made by F...F [2.0 %] and C...O/O...C [1.9 %] contacts.

When compared to the comparable analysis conducted on the three-molecule aggregate in the non-isostructural methyl analogue (II) [11], several trends are apparent. First and foremost amongst these trends is the greater contribution of H...H contacts in the crystal of (I) cf. (II) [23.5 %], an observation correlated with the greater number of hydrogen atoms in the cation. While, to a first approximation, the contributions from the H...O/O...H and H...F/F...H contacts in (I) and (II) [i.e. 23.8 and 19.8 %, respectively] are the same, there is a greater range and more significant contributions from other surface contacts in (II), reflecting, for example, the presence of  $\pi\cdots\pi$  interactions.

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## References

1. Rigaku Oxford Diffraction. *CrysAlis<sup>PRO</sup>*, Rigaku Corporation: Oxford, UK, 2021.
2. Burla M. C., Caliendo R., Camalli M., Carrozzini B., Cascarano G. L., De Caro L., Giacovazzo C., Polidori G., Siliqi D., Spagna R. IL MILIONE: a suite of computer programs for crystal structure solution of proteins. *J. Appl. Crystallogr.* 2007, 40, 609–613.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
4. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, 45, 849–854.
5. Côté A. P., Benin A. I., Ockwig N. W., O’Keeffe M., Matzger A. J., Yaghi O. M. Porous, crystalline, covalent organic frameworks. *Science* 2005, 310, 1166–1170.
6. Diercks C. S., Yaghi O. M. The atom, the molecule, and the covalent organic framework. *Science* 2017, 355, eaa1585.
7. Fujisawa K., Ageishi K., Okano M., Tiekink E. R. T. The crystal structure of 3,5-bis(propan-2-yl)-1H-pyrazol-4-amine,  $\text{C}_9\text{H}_{17}\text{N}_3$ . *Z. Kristallogr. N. Cryst. Struct.* 2022, 237, 1055–1057.
8. Infantes L., Foces-Foces C., Claramunt R. M., López C., Elguero J. Aminopyrazoles and their conjugated acids. An X-ray study of 3,5-dimethyl-4-aminopyrazole and the picrate of 3(5)-aminopyrazole. *J. Heterocycl. Chem.* 1999, 36, 595–600.
9. Fujisawa K., Ageishi K., Tiekink E. R. T. Crystal structure of  $[N(E),N'(E)]$ - $N,N'$ -(1,4-phenylenedimethyldiylidene)bis-3,5-bis(propan-2-yl)-1H-pyrazol-4-amine,  $\text{C}_{26}\text{H}_{36}\text{N}_6$ . *Z. Kristallogr. N. Cryst. Struct.* 2023, 238, 973–976.
10. Fujisawa K., Ageishi K., Harakuni S., Tiekink E. R. T. Crystal structure of  $[N(E),N'(E)]$ - $N,N'$ -(1,4-phenylenedimethyldiylidene)bis-3,5-dimethyl-1H-pyrazol-4-amine di-methanol solvate,  $\text{C}_{18}\text{H}_{20}\text{N}_6 \cdot 2(\text{CH}_3\text{OH})$ . *Z. Kristallogr. N. Cryst. Struct.* 2023, 238, 1005–1008.
11. Fujisawa K., Harakuni S., Ageishi K., Tiekink E. R. T. Crystal structure of bis(3,5-dimethyl-1H-pyrazol-4-ammonium) tetrafluoroterephthate, 2  $[\text{C}_5\text{H}_{10}\text{N}_3][\text{C}_8\text{F}_4\text{O}_4]$ . *Z. Kristallogr. N. Cryst. Struct.* 2023, 238, 1017–1020.
12. Spackman P. R., Turner M. J., McKinnon J. J., Wolff S. K., Grimwood D. J., Jayatilaka D., Spackman M. A. CrystalExplorer: a program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Crystallogr.* 2021, 54, 1006–1011.
13. Tan S. L., Jotani M. M., Tiekink E. R. T. Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr.* 2019, E75, 308–318.