

***N,N'*-Dimethylpyrazinediium bis(tetrafluoroborate) and *N,N'*-diethylpyrazinediium bis(tetrafluoroborate): new examples of anion– π triads**

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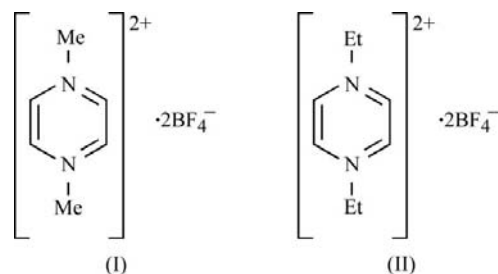
Crystallization of *N,N'*-dimethylpyrazinediium bis(tetrafluoroborate), $C_6H_{10}N_2^{2+} \cdot 2BF_4^-$, (I), and *N,N'*-diethylpyrazinediium bis(tetrafluoroborate), $C_8H_{14}N_2^{2+} \cdot 2BF_4^-$, (II), from dried acetonitrile under argon protection has permitted their single-crystal studies. In both crystal structures, the pyrazinediium dications are located about an inversion center (located at the ring center) and each pyrazinediium aromatic ring is π -bonded to two centrosymmetrically related BF_4^- anions. Strong anion– π interactions, as well as weak C–H...F hydrogen bonds, between BF_4^- and pyrazinediium ions are present in both salts.

Comment

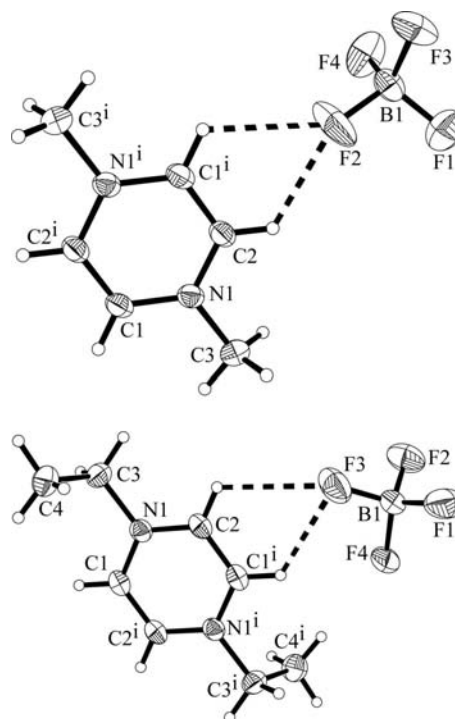
Investigations on the supramolecular chemistry of anion– π acid interactions are relevant to anion binding in biological systems (Gamez *et al.*, 2007), as well as to the design of new anion receptors (Beer *et al.*, 2001; Bianchi *et al.*, 1997). We demonstrated previously the charge-transfer (C–T) nature of anion– π interactions (Rosokha *et al.*, 2004). Such interactions play an important role in the stabilization of ternary anion– π complexes that are responsible for the direction of crystal growth of anions and π -acids into infinite chain structures (wires) (Han *et al.*, 2008; Lu *et al.*, 2009). We also suggested that one-dimensional molecular wires are derived from the ternary synthons of the donor (*D*, anion) and acceptor (*A*, aromatic π -acid). We further demonstrated that triad complexes (*DAD* or *ADA* triad synthons) can be isolated by charge modulation in cationic π -acid salts (Lu *et al.*, 2009).

In this communication, we turn to the anion– π interactions in *N,N'*-dimethylpyrazinediium bis(tetrafluoroborate), (I), and *N,N'*-diethylpyrazinediium bis(tetrafluoroborate), (II), which contain monoanionic tetrafluoroborate donors and dicationic R_2Pyz^{2+} π -acceptors [where *R* = Me for dimethylpyrazinediium in (I) and *R* = Et for diethylpyrazinediium in (II)]. *N,N'*-Dialkylated (diquaternized) pyrazinediiums are

strong electron acceptors with interesting redox properties (Hilgers *et al.*, 1994; Schmittl *et al.*, 2005). They are also important precursors for generating stable radical species (Kaim *et al.*, 1993). However, studies of the C–T behavior between pyrazinediium acceptors and various neutral donors in solution show no stable C–T band. The existence of stable anion– π triads $\{D^- \cdots A^{2+} \cdots D^-\}$ could be the main explanation for this observation. Unfortunately, so far, no crystal structures of dialkylpyrazinediium salts have been reported to confirm such an assumption.



Compounds (I) and (II) were prepared according to the literature procedure of Curphey *et al.* (1972) and were recrystallized in both cases as colourless crystals from dried acetonitrile. As shown in Fig. 1, the asymmetric unit of each salt contains half the pyrazinediium dication and one BF_4^- anion. The pyrazinediium dication is located about an inversion center in both salts. The pyrazine rings experience an average increase of the aromatic C–N bond lengths of

**Figure 1**

Displacement ellipsoid plots of (I) [top, symmetry code: (i) $-x, -y + 1, -z$] and (II) [bottom, symmetry code: (i) $-x + 1, -y + 2, -z + 1$] at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

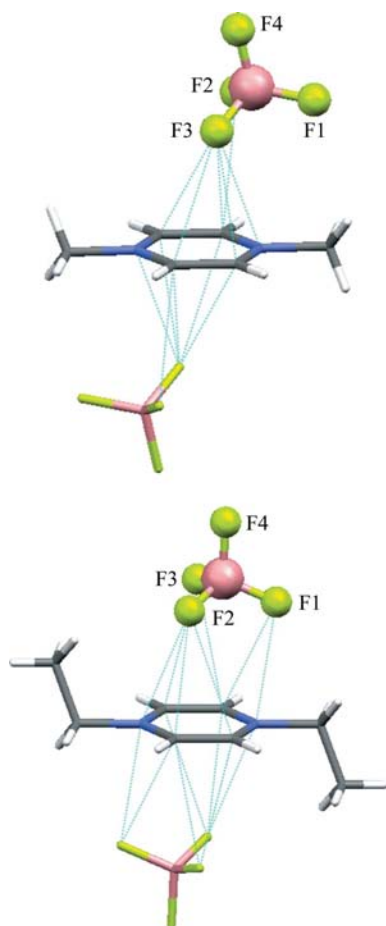


Figure 2
The π -bonding of BF_4^- anions to $\text{Me}_2\text{Pyz}^{2+}$ [in (I), top] and $\text{Et}_2\text{Pyz}^{2+}$ [in (II), bottom].

~ 0.025 Å and the aromatic C–C bonds increase by ~ 0.013 Å relative to the neutral parent molecule (Wheatley, 1957).

The anion– π interaction patterns are illustrated in Fig. 2. In both compounds, each cationic π -acceptor is π -bonded with two BF_4^- anions, which sit centrosymmetrically above and below the aromatic ring of the cation to form a *DAD* triad. Careful examination of the modes of approach of the BF_4^- anions to the π -acceptors reveals some differences. In compound (I), a head-to-face mode can be identified since only one of the four F atoms of the anion (F3) bonds strongly with the π -acceptor ring. In (II), a face-to-face mode can be identified since three F atoms (F1, F2 and F3) of the anion intimately bond with the π -acceptor ring on the ring surface. The relevant distances (Berryman *et al.*, 2007) of closest F to aromatic C atoms, F to center-of-ring (d_{centroid}) and F to plane-of-ring (d_{plane}) are summarized in Tables 2 and 4 for (I) and (II), respectively. The closest F to center-of-ring (d_{centroid}) distances in (I) and (II) are 2.71 and 2.82 Å, respectively. From a literature survey (Mooibroek *et al.*, 2008) of all available crystal data involving BF_4^- – π interactions, these two contact distances (d_{centroid}) represent unique examples of strong BF_4^- – π interactions.

Weak C–H \cdots F hydrogen-bond interactions are also found among these triad units. The anions form several contacts with

H atoms of the pyrazinedium cation that are less than the sum of the van der Waals radii of hydrogen (1.2 Å) and fluorine (1.5 Å). The hydrogen-bonding information is summarized in Tables 1 and 3 for (I) and (II), respectively. It is worth noting here that there are bifurcated C–H \cdots F hydrogen bonds in both compounds. For example, in compound (I), atom F2 bonds to both H1(–C1) and H2(–C2) of the same molecule. The C–H \cdots F interactions complete the three-dimensional supramolecular network.

In summary, we report here the first crystal structures of dialkylpyrazinedium salts. The preservation of *DAD* triads is found in both salts owing to weak C–H \cdots F hydrogen bonding as well as the presence of strong electrostatic anion–cation interactions. Strong anion– π bonding in both triads effectively protects the dicationic π -acceptor from forming stable C–T complexes with additional electron donors in solution.

Experimental

The title dialkylpyrazinedium salts were prepared according to the literature procedure of Curphey *et al.* (1972) and were recrystallized from dried acetonitrile under argon protection. Crystals are extremely sensitive to moisture and turned black after a few hours under ambient conditions.

Compound (I)

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{BF}_4^-$
 $M_r = 283.78$
 Monoclinic, $P2_1/c$
 $a = 5.6227$ (14) Å
 $b = 14.884$ (4) Å
 $c = 6.7419$ (17) Å
 $\beta = 103.557$ (4)°

$V = 548.5$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.20$ mm⁻¹
 $T = 173$ (2) K
 $0.14 \times 0.14 \times 0.10$ mm

Data collection

Bruker SMART diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2003)
 $T_{\text{min}} = 0.776$, $T_{\text{max}} = 1.000$
 (expected range = 0.761–0.980)

5874 measured reflections
 1617 independent reflections
 1331 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
C1–H1 \cdots F2 ⁱ	0.95	2.43	2.973 (2)	116
C2–H2 \cdots F2	0.95	2.26	2.892 (2)	124
C1–H1 \cdots F3 ⁱⁱ	0.95	2.32	3.081 (2)	136
C2–H2 \cdots F4 ⁱⁱⁱ	0.95	2.58	3.053 (2)	111

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x + 1, y, z - 1$; (iii) $x + 1, y, z$.

Table 2

F atoms of BF_4^- – π interaction modes to $\text{Me}_2\text{Pyz}^{2+}$.

F atom	Closest F–C distance (Å)	d_{centroid} (Å)	d_{plane} (Å)
F2	3.06	3.69	2.93
F3	3.00	2.71	2.69

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.131$
 $S = 1.08$
 1617 reflections

83 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$\text{C}_8\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{BF}_4^-$
 $M_r = 311.83$
 Monoclinic, $P2_1/n$
 $a = 9.324 (3) \text{ \AA}$
 $b = 6.2281 (17) \text{ \AA}$
 $c = 11.987 (4) \text{ \AA}$
 $\beta = 102.346 (7)^\circ$

$V = 680.0 (4) \text{ \AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.17 \text{ mm}^{-1}$
 $T = 173 (2) \text{ K}$
 $0.20 \times 0.14 \times 0.12 \text{ mm}$

Data collection

Bruker SMART diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.383$, $T_{\max} = 1.000$
 (expected range = 0.375–0.980)

7346 measured reflections
 2000 independent reflections
 1272 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.167$
 $S = 1.09$
 2000 reflections

92 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Table 3

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C2}-\text{H2} \cdots \text{F2}^i$	0.95	2.51	3.090 (2)	119
$\text{C1}-\text{H1} \cdots \text{F3}^{ii}$	0.95	2.35	2.999 (2)	126
$\text{C2}-\text{H2} \cdots \text{F3}$	0.95	2.53	3.082 (2)	117
$\text{C1}-\text{H1} \cdots \text{F4}^{ii}$	0.95	2.31	3.225 (2)	161

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

Table 4

F atoms of BF_4^- – π interaction modes to $\text{Et}_2\text{Pyz}^{2+}$.

F atom	Closest F–C distance (\AA)	d_{centroid} (\AA)	d_{plane} (\AA)
F1	3.06	3.38	2.79
F2	3.02	2.82	2.80
F3	3.09	3.57	2.88

The unexpectedly wide range of multi-scan absorption corrections for (II) was traced to the incorporation of a correction for minor crystal movement during one run of frames. Carbon-bound H atoms were placed in calculated positions ($\text{C}-\text{H} = 0.95\text{--}0.99 \text{ \AA}$) and included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ values set at $1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

For both compounds, data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Bruker, 2003); program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: XP (Bruker, 1999); software used to prepare material for publication: SHELXTL and XCIF (Bruker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3186). Services for accessing these data are described at the back of the journal.

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