

4,4'-(Azinodimethylene)dipyridinium bis(tetrafluoroborate) and 4-[(4-pyridylmethylene)hydrazonomethyl]pyridinium perchlorate: two different hydrogen-bonding motifs

Mohamed Ghazzali,^{a*} Vratislav Langer,^a Lars Öhrström^a and Morsy Abu-Youssef^b

^aDepartment of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and ^bDepartment of Chemistry, Faculty of Science, Alexandria University, PO 426-21321, Alexandria, Egypt
Correspondence e-mail: mghazz@chalmers.se

Received 28 March 2007

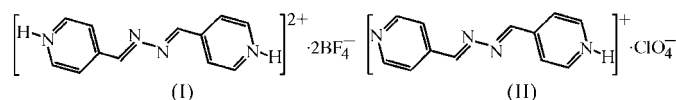
Accepted 30 March 2007

Online 28 April 2007

In the crystal structures of the title compounds, $C_{12}H_{12}N_4^{2+} \cdot 2BF_4^-$, (I), and $C_{12}H_{11}N_4^+ \cdot ClO_4^-$, (II), respectively, infinite two- and one-dimensional architectures are built up *via* N—H...F [in (I)] and conventional N—H...N [in (II)] hydrogen bonding. The N—N single bond in (I) lies on a crystallographic centre of symmetry; as a result, the two pyridinium rings are parallel. In (II), the pyridinium and pyridyl ring planes are inclined with a dihedral angle of 14.45 (3)°.

Comment

Neutral 1,2-bis(4-pyridylmethylene)hydrazine has been known as an antitumour precursor (Hirayama *et al.*, 1980) as well as an analytical reagent for the determination of Fe^{2+} concentration in solution (Luque de Castro & Valcarcel, 1978). Recent interest in this and related molecules stems from their use as linear organic mono- or bidentate bridging ligands in the crystal engineering of multidimensional coordination polymers (Ciurtin *et al.*, 2001; Patra & Goldberg, 2003; Kennedy *et al.*, 2005; Granifo *et al.*, 2006). The characterization of 1,2-bis(4-pyridylmethylene)hydrazine (El-Rayyes & Katrib, 1983) and its crystal structure (Shanmuga



Sundara Raj *et al.*, 2000; Ciurtin *et al.*, 2001), as well as the crystal structure of 4,4'-(azinodimethylene)dipyridinium bis(perchlorate) (Chen *et al.*, 1997), have been reported. The geometric features of the non-isostructural compounds 4,4'-azinodimethylene)dipyridinium bis(tetrafluoroborate), (I), and 4-[(4-pyridylmethylene)hydrazonomethyl]pyridinium perchlorate, (II), are discussed here.

The N1—N1ⁱ [symmetry code: (i) $-x, -y + 2, -z + 2$] and N1=C1 bond distances in (I), and N1A—N1B, N1A=C1A and N1B=C1B in (II), are longer than those of the diperchlorate salt [1.400 (4) and 1.260 (4) Å; Chen *et al.*, 1997] but agree well with those reported for the 4,4'-(azinodimethylene)dipyridinium chloranilate dichloromethane disolvate [1.411 (6) and 1.278 (5) Å; Kennedy & Waterson, 2003] (Table 1). Perspective drawings of compounds (I) and (II), together with the atomic numbering schemes, are shown in Figs. 1 and 2, respectively.

The two pyridine rings in (I) are parallel, with an interplanar distance of 0.104 (2) Å, and form a dihedral angle of 1.21 (9)° with the mean plane of the —CH=N—N=CH— zigzag-like spacer, which exhibits an ideal antiperiplanar conformation with a torsion angle of 180° and the N—N bond lying on a crystallographic centre of symmetry. In (II), the molecule has no crystallographic centre of symmetry, the two ring planes are inclined by an angle of 14.45 (3)° and the antiperiplanar —CH=N—N=CH— spacer exhibits a torsion angle of -170.34 (2)°.

The parallel molecular stacks in (I) are arranged along the *b* axis (Fig. 3), maintained *via* π – π stacking at an interplanar distance of 3.335 (3) Å and supported by a bifurcated N—H...F hydrogen bond building up an extended two-dimensional architecture along the (100) plane and S-like molecular

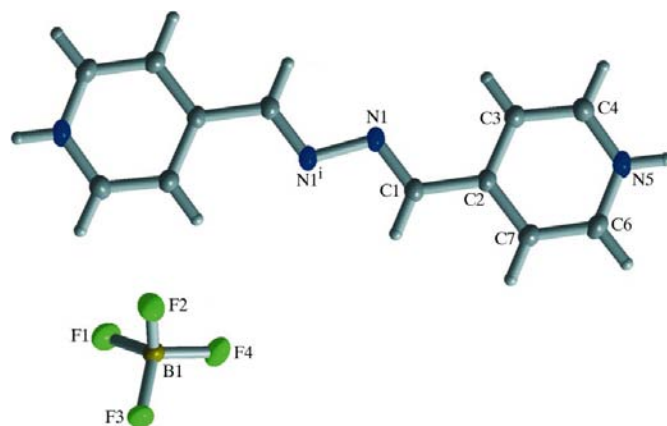


Figure 1

A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code (i) and symmetry code used to generate unlabelled atoms: $-x, -y + 2, -z + 2$.]

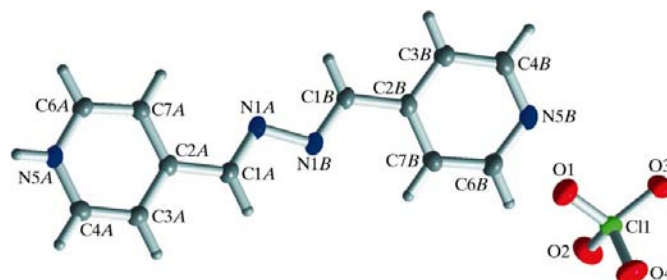


Figure 2

A perspective drawing of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

sheets along the c axis. On the first-level graph set, as defined by Bernstein *et al.* (1995) and Grell *et al.* (1999), $D(2)$ and $D_2^2(16)$ finite patterns are formed *via* hydrogen bonds a and b , respectively (see Table 2 and Fig. 5). On the second-level

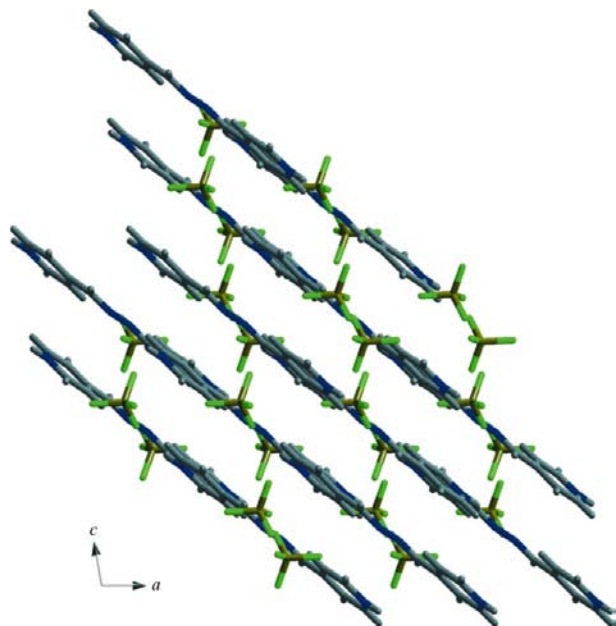


Figure 3
The packing pattern of (I), projected along the b axis.

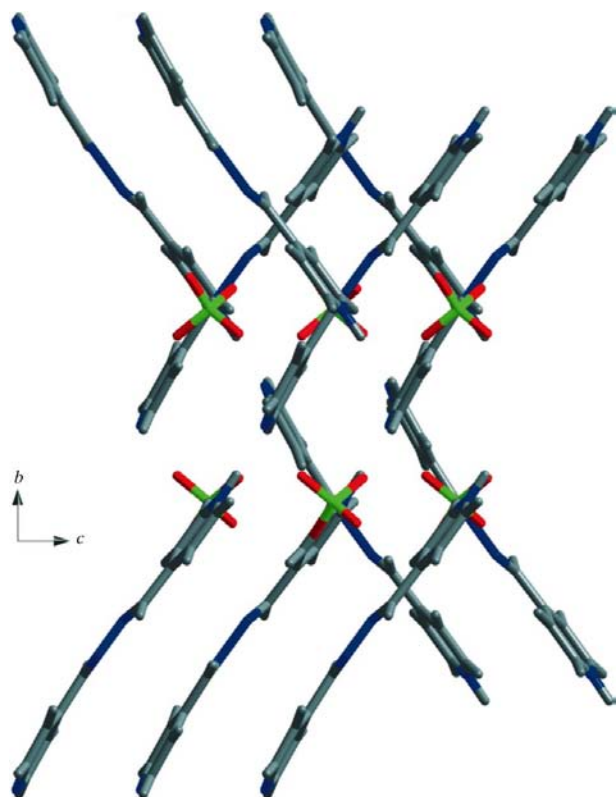


Figure 4
The packing pattern of (II), projected along the a axis.

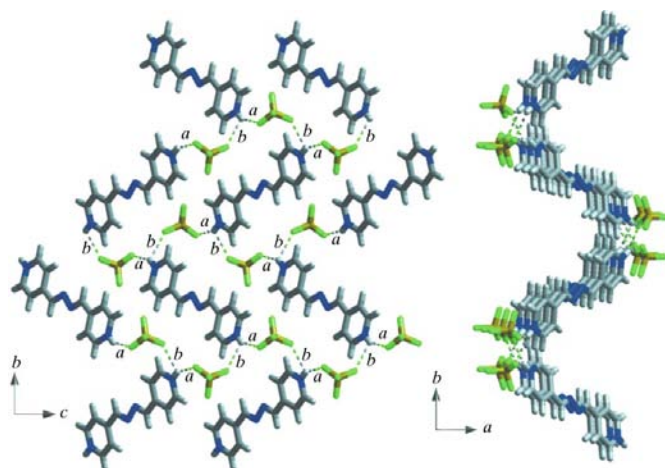


Figure 5
The hydrogen-bonding pattern of (I) along the a and c axes, with hydrogen bonds shown as dashed lines. For notation, see Table 2.

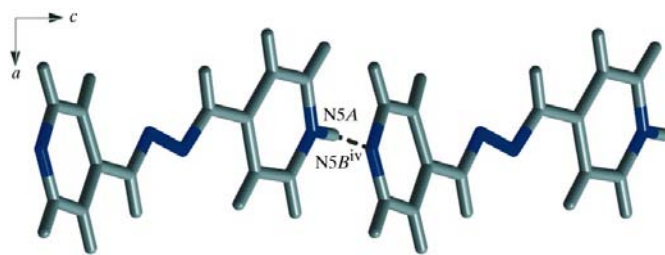


Figure 6
The hydrogen-bonding chains of (II) along the b axis, with hydrogen bonds shown as dashed lines. For symmetry code, see Table 3.

graph set, $C_2^1(4)$ and $C_2^2(17)$ chains and an $R_6^6(43)$ ring can be recognized.

In (II), no profound π - π stacking exists. However, the zigzag-like molecular stacks built up along the a -axis direction (Fig. 4) are cemented by a conventional $N-H \cdots N^{IV}$ hydrogen bond (Table 3 and Fig. 6), giving rise to an infinite one-dimensional $C(13)$ chain along the vector $[01\bar{1}]$. Assignments and graph-set analyses were performed using *PLUTO* (Motherwell *et al.*, 1999).

Experimental

For the preparation of compound (I), $Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol; Aldrich), $NH_2NH_2 \cdot H_2O$ (1 mmol; Aldrich) and pyridine-4-carboxaldehyde (2 mmol; Aldrich) were stirred under an N_2 flow in EtOH (95%) at 350–355 K for 2 h. The resulting solution was allowed to cool, and was then filtered and the filtrate evaporated at room temperature for a few days. Yellow crystals were collected by filtration, washed with MeOH and dried *in vacuo*.

For the preparation of compound (II), 1,2-bis(4-pyridylmethylene)hydrazine (1 mmol), prepared as described by El-Rayyes & Katrib (1983), was added to an ethanolic solution of $Fe(ClO_4)_2 \cdot H_2O$ (1 mmol; Aldrich). The solution was stirred at 350–355 K for 1 h. The resulting solution was cooled, filtered and the filtrate evaporated at room temperature for a few days. Red crystals were collected by filtration, washed with MeOH and dried *in vacuo*.

Compound (I)

Crystal data

$C_{12}H_{12}N_4^{2+} \cdot 2BF_4^-$
 $M_r = 385.88$
 Monoclinic, $P2_1/c$
 $a = 5.1056$ (3) Å
 $b = 16.5856$ (10) Å
 $c = 9.6587$ (6) Å
 $\beta = 99.962$ (1)°
 $V = 805.56$ (8) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.16$ mm⁻¹
 $T = 153$ (2) K
 $0.46 \times 0.26 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{min} = 0.588$, $T_{max} = 0.981$
 14300 measured reflections
 2925 independent reflections
 2154 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.119$
 $S = 1.00$
 2925 reflections
 118 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.48$ e Å⁻³
 $\Delta\rho_{min} = -0.19$ e Å⁻³

Compound (II)

Crystal data

$C_{12}H_{11}N_4^+ \cdot ClO_4^-$
 $M_r = 310.70$
 Orthorhombic, $Pca2_1$
 $a = 15.0896$ (6) Å
 $b = 11.5525$ (5) Å
 $c = 7.8694$ (3) Å
 $V = 1371.81$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 153$ (2) K
 $0.18 \times 0.12 \times 0.08$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{min} = 0.795$, $T_{max} = 0.976$
 18851 measured reflections
 3440 independent reflections
 2994 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.082$
 $S = 1.00$
 3440 reflections
 190 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.24$ e Å⁻³
 $\Delta\rho_{min} = -0.21$ e Å⁻³
 Absolute structure: Flack (1983),
 with 1594 Friedel pairs
 Flack parameter: -0.02 (5)

H atoms were allowed for isotropically and were constrained to ideal geometry using an appropriate riding model, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

For both compounds, data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Sheldrick, 2003); program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXTL.

This work was supported by the Swedish Research Council (VR) and the Swedish International Development Agency (SIDA) through a Swedish Research Links Programme (VR grant Nos. 348-2002-6879 and 348-2004-5473).

Table 1

Comparison of selected bond distances (Å) for (I) and (II).

Bond	Bond distance	Compound
N1—N1 ⁱ	1.409 (2)	(I)
N1=C1	1.276 (1)	(I)
N1A—N1B	1.410 (2)	(II)
N1A=C1A	1.275 (2)	(II)
N1B=C1B	1.273 (2)	(II)

Symmetry code: (i) $-x, -y + 2, -z + 2$.

Table 2

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

Label	D—H...A	D—H	H...A	D...A	D—H...A
a	N5—H5...F4 ⁱⁱⁱ	0.88	2.01	2.8183 (12)	152
b	N5—H5...F2 ⁱⁱ	0.88	2.50	3.0320 (12)	119

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

Table 3

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

D—H...A	D—H	H...A	D...A	D—H...A
N5A—H5A...N5B ^{iv}	0.88	1.84	2.715 (2)	174

Symmetry code: (iv) $x, y - 1, z + 1$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3115). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Brandenburg, K. (2006). *DIAMOND*. Release 3.1d. Crystal Impact GbR, Bonn, Germany. URL: <http://www.crystalimpact.com/diamond>.
 Bruker (2003). *SMART* (Version 5.63), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
 Chen, W., Liu, C.-M., Li, D.-G. & You, X.-Z. (1997). *Acta Cryst.* **C53**, 1499–1501.
 Ciurtin, D. M., Dong, Y.-B., Smith, M. D., Barclay, T. & zur Loye, H.-C. (2001). *Inorg. Chem.* **40**, 2825–2834.
 El-Rayyes, N. R. & Katrib, A. H. (1983). *J. Chem. Eng. Data*, **28**, 132–134.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Granifo, J., Garland, M. T. & Baggio, R. (2006). *Acta Cryst.* **C62**, m56–m59.
 Grell, J., Bernstein, J. & Tinhofer, G. (1999). *Acta Cryst.* **B55**, 1030–1043.
 Hirayama, T., Watanabe, M., Akazawa, C., Ishigami, M., Fujikawa, F., Kasahara, T., Otsuka, M., Nishida, N. & Mizuno, D. (1980). *Yakugaku Zasshi*, **100**, 1225–1234. (In Japanese.)
 Kennedy, A. R., Brown, K. G., Graham, D., Kirkhouse, J. B., Kittner, M., Major, C., McHugh, C. J., Murdoch, P. & Smith, W. E. (2005). *New J. Chem.* **29**, 826–832.
 Kennedy, A. R. & Waterson, F. R. N. (2003). *Acta Cryst.* **C59**, o613–o615.
 Luque de Castro, M. D. & Valcarcel, M. (1978). *Anal. Lett.* **11**, 1–12.
 Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* **B55**, 1044–1056.
 Patra, G. K. & Goldberg, I. (2003). *Cryst. Growth Des.* **3**, 321–329.
 Shanmuga Sundara Raj, S., Fun, H.-K., Zhang, J., Xiong, R.-G. & You, X.-Z. (2000). *Acta Cryst.* **C56**, e274–e275.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.