

Polar hydrogen-bonded organic chains in 4,4'-bipyrazolium bromide and perchlorate monohydrates

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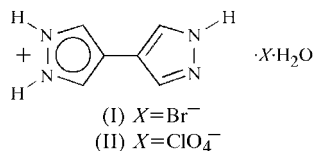
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4,4'-Bipyrazolium [or 4-(1*H*-pyrazol-4-yl)pyrazolium] bromide monohydrate, C₆H₇N₄⁺·Br⁻·H₂O, and 4,4'-bipyrazolium perchlorate monohydrate, C₆H₇N₄⁺·ClO₄⁻·H₂O, have closely related layered structures involving tight stacks of antiparallel N—H···N hydrogen-bonded polar bipyrazolium chains [N···N = 2.712 (3) and 2.742 (2) Å], which are crosslinked by hydrogen bonds with water molecules and counter-anions.

Comment

Pyrazole possesses self-complementary functionality and yields hydrogen-bonded polar chains when associated by 'head-to-tail' N—H···N hydrogen bonding (Foces-Foces *et al.*, 2000). The doubled number of hydrogen-bond donor (NH) and acceptor (N) sites (2:2) of 4,4'-bipyrazole allows the incorporation of this polar motif into a planar hydrogen-bonded network (Boldog *et al.*, 2001). However, the molecular symmetry of the 4,4'-bipyrazole molecule effects its situation



across a centre of inversion and this eliminates any overall polarity of the hydrogen-bonding directions. Double protonation of 4,4'-bipyrazole yields centrosymmetric dications, which act as donors of four N—H···X hydrogen bonds and which are unable to participate in self-association due to a lack of acceptor sites (Boldog, 2005). Unlike these cases, 4,4'-bipyrazolium monocations are inherently non-centrosymmetric and they retain both types of binding sites (NH and N), in a 3:1 ratio, allowing self-association and effective interchain interactions. Thus, singly protonated 4,4'-bipyrazole offers a special potential for the generation of polar hydrogen-bonded chains and their integration into an extended architecture. In this context, we have prepared two new salts of 4,4'-bipyrazole, (I) and (II), and present their structures here.

The structural results reveal the close resemblance of the crystalline salts (I) and (II). The bipyrazolium monocations have a nearly planar structure. The dihedral angle between the mean planes of the two heterocyclic fragments is 3.5 (1)° in (I) and 8.7 (1)° in (II) (Figs. 1 and 2). Protonation of the pyrazole ring results in the equivalence of atoms N1 and N2, and the corresponding pairs of bonds, *viz.* C1—N1/C3—N2 and C1—C2/C2—C3, are actually uniform in length, while bond C6—N4 (N) remains *ca.* 0.02 Å shorter than C4—N3 (NH). This reflects the greater delocalization of π -electron density within the frame of the pyrazolium moiety compared with the neutral pyrazole fragment. The N3—N4 bond lengths for the neutral pyrazole fragments are the same as for 4,4'-bipyrazole [1.345 (2) Å; Boldog *et al.*, 2001] or its complexes with metal ions [1.341 (2)–1.347 (2) Å; Boldog *et al.*, 2002], while the N1—N2 bonds for the protonated fragments are somewhat shortened and are comparable with the parameter for 4,4'-bipyrazolium diperchlorate [1.328 (3) Å; Boldog, 2005]. A similar result may be found from a comparison of the molecular geometries of pyrazole (la Cour & Rasmussen, 1973) and the pyrazolium cation (Ishida & Kashino, 2001) (N—N = 1.343 and 1.335 Å, respectively).

The bipyrazolium monocations in (I) and (II) associate in a uniform fashion, yielding polar chains with relatively strong

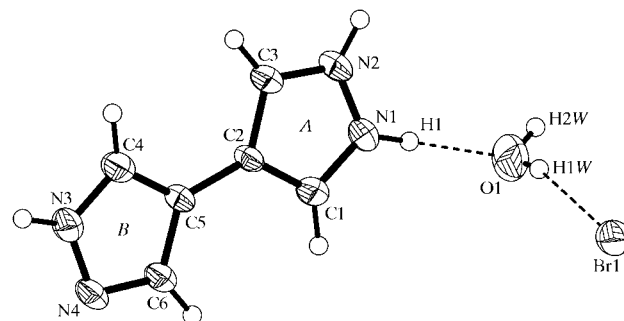


Figure 1

The structure of (I), showing the atom- and ring-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

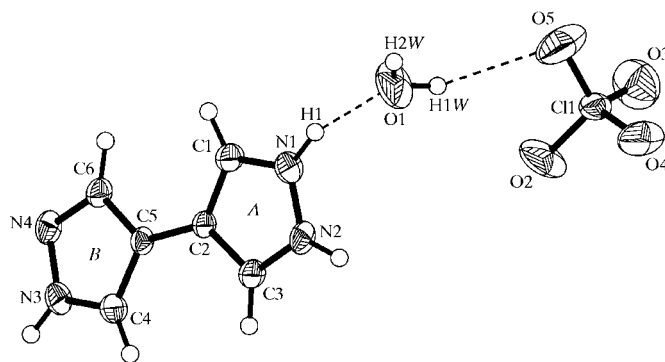


Figure 2

The structure of (II), showing the atom- and ring-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

hydrogen bonds [$N \cdots N = 2.712(3)$ and $2.742(2)$ Å, respectively], employing the only acceptor sites, N4, and the N2—H2 donor sites *trans* to them (Figs. 3 and 4). Owing to the cationic nature of the donor sites, these N—H \cdots N interactions are appreciably stronger than those observed for neutral species [$2.912(3)$ Å for pyrazole (la Cour & Rasmussen, 1973) and $2.886(2)$ Å for 4,4'-bipyrazole (Boldog *et al.*, 2001)].

Two bipyrazolium cations, related by inversion [symmetry codes: $(1-x, -y, 1-z)$ for (I) and $(-x, 1-y, 1-z)$ for (II)], afford tight π - π stacking, in which the interaction occurs between pairs of cationic (A) and neutral (B) pyrazole rings. Such a mode of stacking dictates an antiparallel alignment of the chains. Within the hydrogen-bonded layers (Figs. 3 and 4), the geometric parameters of π - π interactions (Janiak, 2000) are similar for (I) and (II) (Tables 3 and 6). For (I), both intra- and interlayer π - π stacking follow the A/B mode and are actually uniform in their geometry, while for (II), the inter-

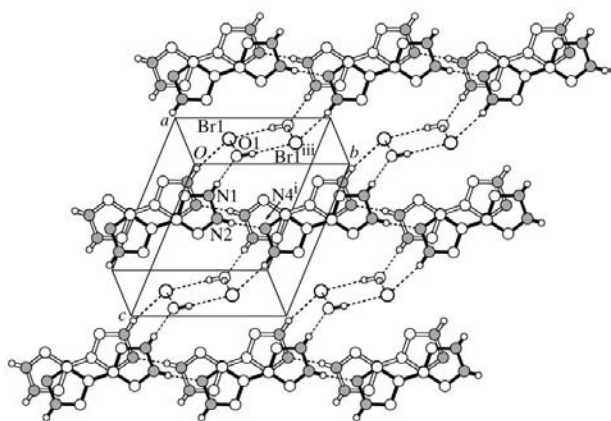


Figure 3
A perspective view of the structure of (I), showing NH and OH hydrogen bonds as dashed lines. N atoms are shaded grey. Note the antiparallel packing of the polar bipyrazolium chains. [Symmetry codes: (i) $x, 1+y, z$; (iii) $1-x, 1-y, -z$.]

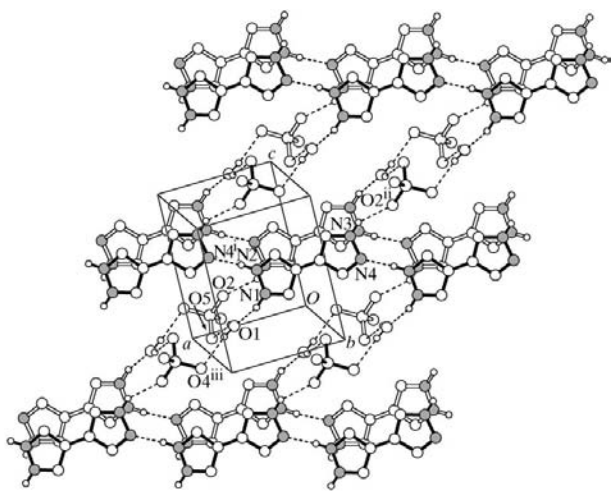


Figure 4
A perspective view of the structure of (II) showing NH and OH hydrogen bonds as dashed lines. N atoms are shaded grey. Note the antiparallel packing of the polar bipyrazolium chains. [Symmetry codes: (i) $1+x, y-1, z$; (ii) $-x, 1-y, 1-z$; (iii) $2-x, -y, -z$.]

layer interactions are supported by $B/B(-x, 2-y, 1-z)$ and $A/A(1-x, 1-y, 1-z)$ stacking modes.

The hydrogen-bonded chains retain two NH functions per bipyrazole block and donate a set of N—H \cdots O and N—H \cdots Br hydrogen bonds to finite hydrogen-bonded anion-water assemblies $[(H_2O)_2(X)_2]^{2-}$ [X is Br in (I) or ClO_4 in (II)]. These lie across centres of inversion and unite pairs of antiparallel bipyrazolium chains into layers. Such centrosymmetric 2:2 anion-water aggregates have also been observed for acetylcarnitine hydrochloride monohydrate (Destro & Heyda, 1977). The water molecules tend to accept bonds from the cationic pyrazole fragment, while the anions are bound to the neutral pyrazole site (Tables 2 and 4). Hydrogen bonds of the type N—H \cdots Br in (I) [$3.312(2)$ Å] are only slightly weaker than the hydrogen bonding observed in pyrazolium bromides (3.17 – 3.22 Å; Foces-Foces *et al.*, 1997).

A number of directional C—H \cdots O(X) interactions observed in (I) and (II) could be attributed to a weaker hydrogen bond (Desiraju & Steiner, 1999). The protonation evidently enhances the CH acidity of the pyrazole ring and, as a result, the C—H \cdots O(X) interactions donated by the cationic pyrazole fragment are appreciably shorter. Thus, in (II), the cationic pyrazolium fragment supports three weak C—H \cdots O bonds [$C \cdots O = 3.267(3)$ – $3.386(3)$ Å], while the shortest C—H \cdots O contact donated by the neutral pyrazole fragment is longer [$3.502(3)$ Å]. Similar directional C—H \cdots O hydrogen bonding [$C \cdots O = 3.201(3)$ Å] also occurs for the pyrazolium cation in the salt with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (Ishida & Kashino, 2001). The shortest C \cdots Br separation in (I) is also observed for the cationic pyrazolium fragment (Table 2) and is comparable with the typical C—H \cdots Br bond in acetylenes (3.72 Å; Steiner, 1998).

Thus, the 4,4'-bipyrazolium monocations of (I) and (II) produce polar hydrogen-bonded chains by direct association. The mode of the intercation stacking, however, effects an antiparallel alignment of the chains and this mitigates against bulk polarity of the structure. We intend to investigate a series of related systems in order to resolve this problem.

Experimental

4,4'-Bipyrazole was prepared by condensation of 1,1,2,2-ethane-tetracarbaldehyde and hydrazine (Trofimenko, 1964). Recrystallization of the compound from hot 10% aqueous HBr or hot 10% aqueous $HClO_4$ afforded large colourless prisms of salts (I) and (II), respectively.

Compound (I)

Crystal data

$C_6H_7N_4^+ \cdot Br^- \cdot H_2O$
 $M_r = 233.08$
 Triclinic, $P\bar{1}$
 $a = 7.1352(11)$ Å
 $b = 8.505(2)$ Å
 $c = 9.056(2)$ Å
 $\alpha = 112.52(3)^\circ$
 $\beta = 108.53(3)^\circ$
 $\gamma = 97.31(3)^\circ$
 $V = 461.5(3)$ Å³

$Z = 2$
 $D_x = 1.677$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 22 reflections
 $\theta = 12.1$ – 17.8°
 $\mu = 4.41$ mm⁻¹
 $T = 223(2)$ K
 Prism, colourless
 $0.25 \times 0.23 \times 0.22$ mm

Data collection

| | |
|---|------------------------------------|
| Enraf–Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.017$ |
| Non-profiled ω -2 θ scans | $\theta_{\text{max}} = 27.9^\circ$ |
| Absorption correction: ψ scan (North <i>et al.</i> , 1968) | $h = -9 \rightarrow 9$ |
| $T_{\text{min}} = 0.321$, $T_{\text{max}} = 0.379$ | $k = -11 \rightarrow 10$ |
| 2879 measured reflections | $l = -10 \rightarrow 11$ |
| 2204 independent reflections | 3 standard reflections |
| 1611 reflections with $I > 2\sigma(I)$ | frequency: 120 min |
| | intensity decay: none |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.0613P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.072$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.02$ | $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$ |
| 2204 reflections | $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$ |
| 109 parameters | |
| H-atom parameters constrained | |

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

| | | | |
|-------------|-------------|----------|-------------|
| N1–C1 | 1.334 (3) | C1–C2 | 1.389 (3) |
| N1–N2 | 1.340 (3) | C2–C3 | 1.392 (3) |
| N2–C3 | 1.333 (3) | C2–C5 | 1.452 (3) |
| N3–C4 | 1.338 (3) | C4–C5 | 1.375 (3) |
| N3–N4 | 1.351 (3) | C5–C6 | 1.397 (3) |
| N4–C6 | 1.335 (3) | | |
| | | | |
| C1–N1–N2 | 109.23 (19) | C3–C2–C5 | 128.01 (19) |
| C3–N2–N1 | 108.32 (18) | N2–C3–C2 | 109.2 (2) |
| C4–N3–N4 | 111.97 (18) | N3–C4–C5 | 107.6 (2) |
| C6–N4–N3 | 104.60 (18) | C4–C5–C6 | 104.28 (19) |
| N1–C1–C2 | 108.8 (2) | C4–C5–C2 | 128.0 (2) |
| C1–C2–C3 | 104.45 (18) | C6–C5–C2 | 127.7 (2) |
| C1–C2–C5 | 127.55 (19) | N4–C6–C5 | 111.6 (2) |
| | | | |
| C1–C2–C5–C4 | 176.8 (2) | | |

Table 2

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

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------------|-------|--------------|--------------|----------------|
| N1–H1 \cdots O1 | 0.90 | 1.80 | 2.680 (3) | 165 |
| N2–H2 \cdots N4 ⁱ | 0.90 | 1.82 | 2.712 (3) | 173 |
| N3–H3 \cdots Br1 ⁱⁱ | 0.90 | 2.43 | 3.312 (2) | 165 |
| O1–H1W \cdots Br1 | 0.85 | 2.48 | 3.311 (2) | 165 |
| O1–H2W \cdots Br1 ⁱⁱⁱ | 0.85 | 2.53 | 3.315 (2) | 154 |
| C1–H1A \cdots Br1 ^{iv} | 0.96 | 2.84 | 3.795 (3) | 174 |
| C4–H4A \cdots O1 ^v | 0.96 | 2.56 | 3.503 (4) | 169 |

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

Table 3

 π - π contacts (\AA , $^\circ$) for (I).

| Group 1/Group 2 | IPD [†] (\AA) | CCD [‡] (\AA) | SA [§] ($^\circ$) |
|--|-----------------------------------|-----------------------------------|------------------------------|
| Ring A/Ring B ^{ii¶} (layer) | 3.366 (4) | 3.630 (5) | 22.0 (2) |
| Ring A/Ring B ^{vi} (interlayer) | 3.254 (4) | 3.691 (5) | 28.2 (2) |

[†] IPD is the interplanar distance (distance from one plane to the neighbouring centroid). [‡] CCD is the centre-to-centre distance (distance between ring centroids). [§] SA is the slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000). [¶] Rings A and B are labelled according to Fig. 1. Symmetry codes: (ii) $1 - x, -y, 1 - z$; (vi) $-x, -y, 1 - z$.

Compound (II)

Crystal data

$\text{C}_6\text{H}_7\text{N}_4^+ \cdot \text{ClO}_4^- \cdot \text{H}_2\text{O}$
 $M_r = 252.62$
 Triclinic, $P\bar{1}$
 $a = 7.7691$ (7) \AA
 $b = 7.9578$ (11) \AA
 $c = 9.826$ (2) \AA
 $\alpha = 69.941$ (18) $^\circ$
 $\beta = 70.380$ (10) $^\circ$
 $\gamma = 65.393$ (8) $^\circ$
 $V = 505.43$ (14) \AA^3
 $Z = 2$

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.862$, $T_{\text{max}} = 0.926$
 2565 measured reflections
 2397 independent reflections
 1830 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.113$
 $S = 1.05$
 2397 reflections
 145 parameters
 H-atom parameters constrained

$D_x = 1.660 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 23 reflections
 $\theta = 7.0$ – 14.5°
 $\mu = 0.39 \text{ mm}^{-1}$
 $T = 223$ (2) K
 Prism, colourless
 $0.22 \times 0.20 \times 0.20 \text{ mm}$

$R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 27.9^\circ$
 $h = -9 \rightarrow 10$
 $k = 0 \rightarrow 10$
 $l = -12 \rightarrow 12$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.2131P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

Table 4

Selected geometric parameters (\AA , $^\circ$) for (II).

| | | | |
|-------------|--------------|----------|-------------|
| N1–N2 | 1.326 (2) | C1–C2 | 1.380 (2) |
| N1–C1 | 1.334 (2) | C2–C3 | 1.391 (2) |
| N2–C3 | 1.325 (2) | C2–C5 | 1.455 (2) |
| N3–C4 | 1.336 (2) | C4–C5 | 1.380 (2) |
| N3–N4 | 1.346 (2) | C5–C6 | 1.403 (2) |
| N4–C6 | 1.326 (2) | | |
| | | | |
| N2–N1–C1 | 109.35 (15) | C3–C2–C5 | 126.95 (15) |
| C3–N2–N1 | 108.55 (14) | N2–C3–C2 | 109.13 (15) |
| C4–N3–N4 | 112.22 (15) | N3–C4–C5 | 107.16 (16) |
| C6–N4–N3 | 105.09 (14) | C4–C5–C6 | 104.26 (15) |
| N1–C1–C2 | 108.57 (16) | C4–C5–C2 | 127.51 (15) |
| C1–C2–C3 | 104.40 (15) | C6–C5–C2 | 128.22 (15) |
| C1–C2–C5 | 128.63 (15) | N4–C6–C5 | 111.27 (16) |
| | | | |
| C1–C2–C5–C4 | –173.36 (19) | | |

Table 5

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

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|-------|--------------|--------------|----------------|
| N1–H1 \cdots O1 | 0.90 | 1.81 | 2.665 (2) | 159 |
| N2–H2 \cdots N4 ⁱ | 0.90 | 1.85 | 2.742 (2) | 174 |
| N3–H3 \cdots O2 ⁱⁱ | 0.90 | 2.07 | 2.871 (2) | 148 |
| O1–H1W \cdots O5 | 0.85 | 2.40 | 3.193 (3) | 155 |
| O1–H2W \cdots O4 ⁱⁱⁱ | 0.85 | 2.13 | 2.966 (3) | 168 |
| C1–H1A \cdots O5 ^{iv} | 0.96 | 2.38 | 3.297 (3) | 160 |
| C3–H3A \cdots O2 ^v | 0.96 | 2.51 | 3.267 (3) | 136 |
| C3–H3A \cdots O4 ^{vi} | 0.96 | 2.44 | 3.386 (3) | 169 |

Symmetry codes: (i) $x + 1, y - 1, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $2 - x, -y, -z$; (iv) $1 - x, 1 - y, -z$; (v) $1 - x, -y, 1 - z$.

Table 6
 π - π contacts (\AA , $^\circ$) for (II).

| Group 1/Group 2 | | IPD [†] (\AA) | CCD [‡] (\AA) | SA [§] ($^\circ$) |
|-------------------------------|--------------|-----------------------------------|-----------------------------------|------------------------------|
| Ring A/Ring B ⁱⁱ ¶ | (layer) | 3.216 (4) | 3.623 (4) | 27.4 (2) |
| Ring A/Ring A ^{vi} | (interlayer) | 3.390 (4) | 3.944 (4) | 30.7 (2) |
| Ring B/Ring B ^{vii} | (interlayer) | 3.323 (3) | 3.445 (4) | 15.3 (2) |

[†] IPD is the interplanar distance (distance from one plane to the neighbouring centroid). [‡] CCD is the centre-to-centre distance (distance between ring centroids). [§] SA is the slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000). [¶] Rings A and B are labelled according to Fig. 2. Symmetry codes: (ii) $-x, 1-y, 1-z$; (vi) $1-x, 1-y, 1-z$; (vii) $-x, 2-y, 1-z$.

All H atoms were located from difference maps and refined as riding, with O—H distances constrained to 0.85 \AA , N—H distances constrained to 0.90 \AA and C—H distances constrained to 0.96 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); publication software: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1085). Services for accessing these data are described at the back of the journal.

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