

# Structures of 1-hydrophenanthroimidazoles: building blocks in the synthesis of expanded-ring bis(imidazoles)

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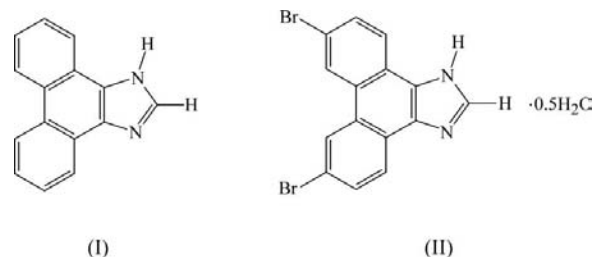
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The structures of 1*H*-phenanthro[9,10-*d*]imidazole, C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>, (I), and 3,6-dibromo-1*H*-phenanthro[9,10-*d*]imidazole hemihydrate, C<sub>15</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub>·0.5H<sub>2</sub>O, (II), contain hydrogen-bonded polymeric chains linked by columns of  $\pi$ - $\pi$  stacked essentially planar phenanthroimidazole monomers. In the structure of (I), the asymmetric unit consists of two independent molecules, denoted (Ia) and (Ib), of 1*H*-phenanthro[9,10-*d*]imidazole. Alternating molecules of (Ia) and (Ib), canted by 79.07 (3)°, form hydrogen-bonded zigzag polymer chains along the *a*-cell direction. The chains are linked by  $\pi$ - $\pi$  stacking of molecules of (Ia) and (Ib) along the *b*-cell direction. In the structure of (II), the asymmetric unit consists of two independent molecules of 3,6-dibromo-1*H*-phenanthro[9,10-*d*]imidazole, denoted (IIa) and (IIb), along with a molecule of water. Alternating molecules of (IIa), (IIb) and water form hydrogen-bonded polymer chains along the [110] direction. The donor-acceptor distances in these N(imine)···H—O(water)···H—N(amine) hydrogen bonds are the shortest thus far reported for imidazole amine and imine hydrogen-bond interactions with water. Centrosymmetrically related molecules of (IIa) and (IIb) alternate in columns along the *a*-cell direction and are canted by 48.27 (3)°. The present study provides the first examples of structurally characterized 1*H*-phenanthroimidazoles.

## Comment

Bis(imidazoles) and bis(benzimidazoles) are versatile species with numerous applications. Structurally, they have been used as geometrically constraining ligands (Stibrany *et al.*, 2004) and in the formation of metal-organic copolymers (Stibrany & Potenza, 2008). Functionally, they have been shown to act as proton sponges (Stibrany *et al.*, 2002), and when complexed to copper, as polymerization catalysts (Stibrany *et al.*, 2003; Stibrany & Kacker, 2002). Analytically, they have been used as agents in the study of electron transfer (Knapp *et al.*, 1990),

and fluorinated versions have been used as <sup>19</sup>F NMR probes to study the active sites of copper polymerization catalysts (Stibrany, 2003). In the present study, we have investigated the structures of 1*H*-phenanthroimidazoles, *i.e.* expanded-ring imidazoles, as potential building blocks for bis(phenanthroimidazoles). We have previously shown that 1-methylbenzimidazole can be used in the synthesis of bis(benzimidazole) ketones, which were found to be useful ligands for the chelation of metals (Gorun *et al.*, 1996).



Crystals of 1*H*-phenanthro[9,10-*d*]imidazole, (I), contain two independent molecules, (Ia) and (Ib), in the asymmetric unit, linked by N(amine)—H···N(imine) hydrogen bonds (Fig. 1 and Table 1). Analysis of the structure reveals a

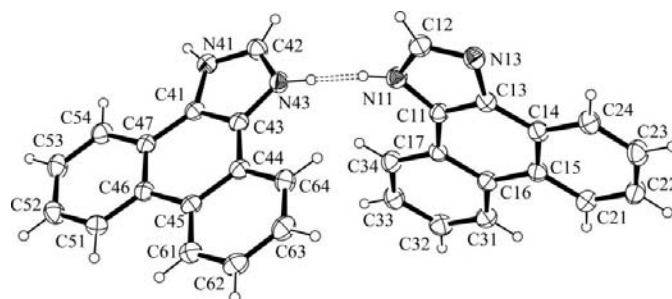


Figure 1

A view of the asymmetric unit of (I), showing the atom-numbering scheme for the repeat unit of molecules (Ia) and (Ib). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent the superimposed N11—H11···H43 and N43—H43···N11 hydrogen bonds.

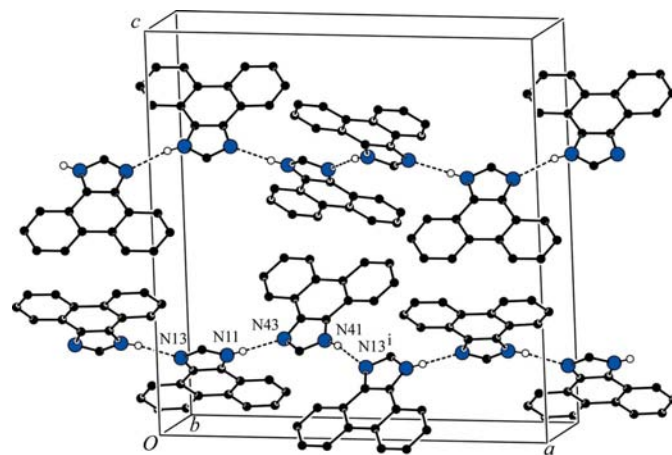
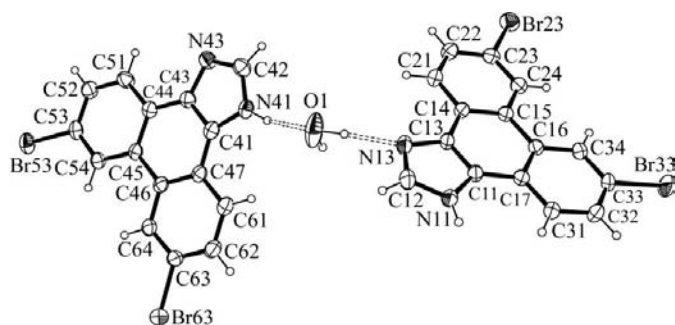


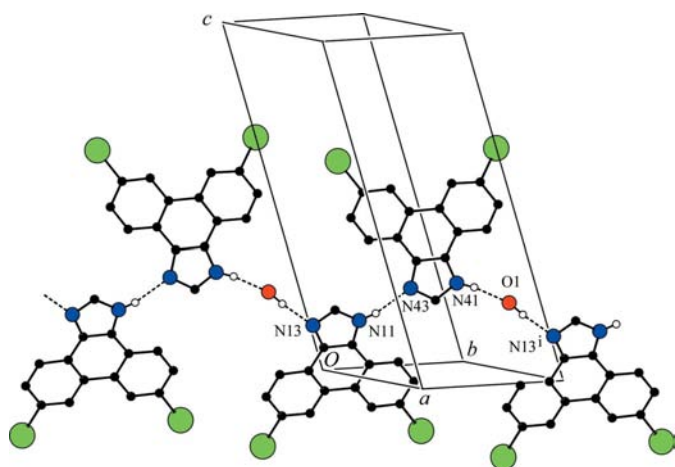
Figure 2

A view of the packing of (I) approximately along the *b* axis, showing the hydrogen-bonded polymer chains (dashed lines). See Table 1 for symmetry code.



**Figure 3**

A view of the asymmetric unit of (II), showing the atom-numbering scheme for the repeat unit of (IIa), water and (IIb). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.



**Figure 4**

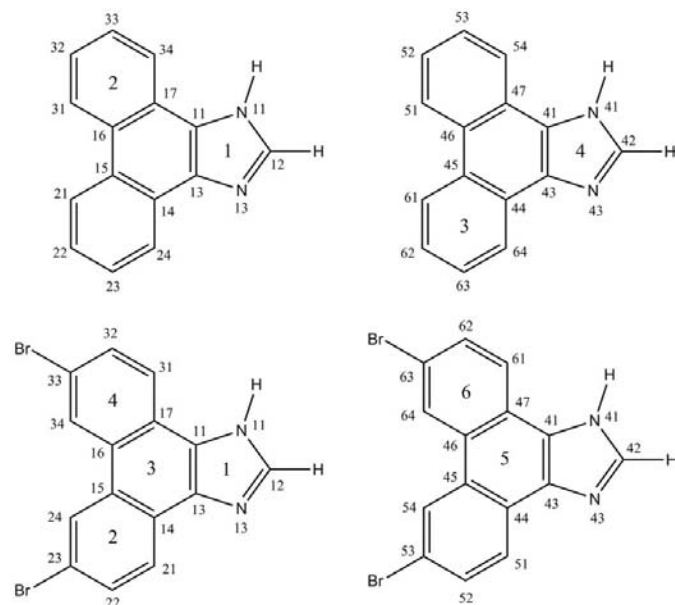
A view of the packing of (II), showing the hydrogen-bonded polymer chains (dashed lines). See Table 2 for symmetry code.

two-site H-atom disorder, corresponding to overlapping N(imine)···H—N(amine) and N(amine)—H···N(imine) bonds and their associated molecules. Occupancy factors for the two H atoms, which were refined and constrained to sum to 1, were 0.60 (3) and 0.40 (3). These data and the structure described below are consistent with racemic twinning in which the twins are related by rotation of 180° about the *a* unit-cell axis. We describe the structure below using the major component (60% occupancy) twin.

In the structure of (I), alternating molecules of (Ia) and (Ib) are essentially planar, canted by 79.07 (3)°, and linked by the hydrogen bonds mentioned above to create zigzag polymeric chains which extend along the *a*-cell direction (Fig. 2). In these chains, molecules of (Ia) and (Ib) stack along the *b*-cell direction to yield columns in which the phenanthroimidazole planes are separated by interplanar distances consistent with  $\pi$ – $\pi$  interactions, which have been taken as inter-ring contacts less than 3.8 Å (Janiak, 2000). The inter-ring contacts are listed in Table 3 and the several rings are enumerated in the second scheme. In each column, the planes of the rings are canted with respect to the *ac* plane such that, when viewed down the *a* axis along the polymer chains, the phenanthroimidazole

columns appear as a criss-cross array of molecules of (Ia) and (Ib) in profile.

Crystals of 3,6-dibromo-1*H*-phenanthro[9,10-*d*]imidazole hemihydrate, (II), contain a water molecule and two independent phenanthroimidazole molecules, (IIa) and (IIb), in the asymmetric unit (Fig. 3). The water molecule acts as both a donor (O—H) and an acceptor (O) to form two hydrogen bonds (Table 2), one to the N(amine) H atom of molecule (IIb) and the other to the N(imine) atom of molecule (IIa). In (II), the N···O distances (Table 2) in the N(imine)···H—O(H<sub>2</sub>O)···H—N(amine) fragments are shorter than the corresponding N(imine)···O(H<sub>2</sub>O) and N(amine)···O(H<sub>2</sub>O) distances in similar hydrogen-bond networks, in which they are in the ranges 2.770–2.914 and 2.802–2.946 Å, respectively, for the imine and amine linkages [Cambridge Structural Database (CSD), Version 5.30; Allen, 2002] (Botana *et al.*, 2007; Freire *et al.*, 2003; Fridman *et al.*, 2006; Meng *et al.*, 2006; Molina *et al.*, 1998; Zhang *et al.*, 2005). In (II), the hydrogen bonds lead to polymer chains consisting sequentially of molecules of (IIa), (IIb) and water. These hydrogen-bond chains extend along the [110] direction (Fig. 4), while centrosymmetrically related molecules of molecules (IIa) and (IIb) stack in columns along the *a*-axis direction. The planes of (IIa) and (IIb) are canted by 48.27 (3)°. In the structure of (II), there are four  $\pi$ – $\pi$  interactions and two short atom-to-ring interactions (Table 3; see also second scheme). In Table 3, the angles reported along with the *C<sub>g</sub>* interactions are the dihedral angles between these planes. The *C<sub>g</sub>*–atom interactions are defined by *C<sub>g</sub>*···C—X, where X = H or Br.



Compounds (I) and (II) are technically defined as extended-ring imidazole systems. The title compounds, which are 1,2-dihydro-substituted, are the first such compounds to be structurally characterized. A total of 22 crystal structures containing phenanthroimidazoles reported in the CSD contain aromatic substitution at the 2-position. Synthetically, aromatic aldehydes facilitate the formation of phenanthroimidazole ring systems.

## Experimental

1*H*-Phenanthro[9,10-*d*]imidazole, (I), was prepared according to the procedure of Steck & Day (1943). Phenanthroquinone (2.08 g, 9.99 mmol), hexamethylenetetramine (2.80 g, 20.0 mmol) and ammonium acetate (15.5 g) were placed in a 250 ml round-bottomed flask. The solids were suspended in glacial acetic acid and refluxed for 1 h. The mixture was cooled and neutralized with concentrated ammonium hydroxide, followed by the addition of water to precipitate the product fully. The product was collected by filtration, washed with water and dried to a constant weight in a vacuum oven to give the product as an off-white solid (yield 2.01 g, 92.2%; m.p. 564 K). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>, 298 K): δ 8.86 (*br m*, 2H), 8.51 (*br m*, 2H), 8.37 (*s*, 1H), 7.72 (*br m*, 2H), 7.64 (*br m*, 2H); <sup>13</sup>C NMR (CD<sub>3</sub>SOCD<sub>3</sub>): δ 139.6, 136.2, 127.9, 127.8, 127.4, 125.4, 124.3, 122.0; *R*<sub>F</sub> = 0.38 (ethyl acetate/silica). Single crystals of (I) were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution of the compound (m.p. 581 K). Crystals of 3,6-dibromo-1*H*-phenanthro[9,10-*d*]imidazole hemihydrate, (II), were prepared by following a procedure similar to that for (I). 3,6-Dibromophenanthro-9,10-quinone (2.08 g, 5.68 mmol) (Schmidt & Eitel, 1932; Bhatt, 1964), hexamethylenetetramine (1.59 g, 11.34 mmol) and ammonium acetate (14.0 g) were placed in a 250 ml round-bottomed flask. The solids were suspended in glacial acetic acid and refluxed for 1 h. The mixture was cooled and neutralized with concentrated ammonium hydroxide, followed by the addition of water to precipitate the product fully. The product was collected by filtration, washed with water and dried to constant weight in a vacuum oven to give anhydrous (II) as a pale-gray solid (yield 2.02 g, 94.4%; m.p. 546 K). <sup>1</sup>H NMR (400 MHz, 323 K, CD<sub>3</sub>SOCD<sub>3</sub>): δ 8.85 (*s*, 2H), 8.19 (*d*, *J* = 6.4 Hz, 2H), 8.04 (*s*, 1H), 7.78 (*dd*, *J* = 1.8 and 8.6 Hz, 2H); <sup>13</sup>C NMR (CD<sub>3</sub>SOCD<sub>3</sub>, 323 K): δ 139.7, 139.5, 130.6, 128.6, 126.7, 124.3, 119.1. *R*<sub>F</sub> = 0.37 (ethyl acetate/silica). Single crystals of (II) were obtained by slow evaporation from a DMSO solution of the compound [m.p. 453 (opaque), 572 (soften) and 583 K (melt)]. The hemihydrate formed owing to the adventitious presence of water in the DMSO.

## Compound (I)

### Crystal data

C <sub>15</sub> H <sub>10</sub> N <sub>2</sub>	<i>V</i> = 2033.5 (5) Å <sup>3</sup>
<i>M</i> <sub>r</sub> = 218.25	<i>Z</i> = 8
Orthorhombic, <i>Pna</i> 2 <sub>1</sub>	Mo <i>K</i> α radiation
<i>a</i> = 19.559 (3) Å	<i>μ</i> = 0.09 mm <sup>-1</sup>
<i>b</i> = 5.2321 (8) Å	<i>T</i> = 298 K
<i>c</i> = 19.871 (3) Å	0.47 × 0.37 × 0.10 mm

### Data collection

Bruker SMART CCD area-detector diffractometer	18138 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Blessing, 1995)	2095 independent reflections
<i>T</i> <sub>min</sub> = 0.856, <i>T</i> <sub>max</sub> = 1.000 (expected range = 0.849–0.991)	1803 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.035

**Table 1**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11...N43	0.86	2.16	3.018 (3)	173
N41—H41...N13 <sup>i</sup>	0.86	2.28	3.129 (3)	168
N13—H13...N41 <sup>ii</sup>	0.86	2.28	3.129 (3)	167
N43—H43...N11	0.86	2.16	3.018 (3)	175

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

**Table 2**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11...N43	0.86	2.05	2.892 (5)	165
N41—H41...O1	0.86	1.87	2.702 (5)	164
O1—H2O...N13 <sup>i</sup>	0.91 (10)	1.83 (10)	2.731 (8)	172 (13)

Symmetry code: (i) *x* + 1, *y* + 1, *z*.

**Table 3**

Geometric parameters of *Cg*...*Cg* and *Cg*...atom interactions (Å, °).

*Cg*(I)1, *Cg*(I)2, *Cg*(I)3 and *Cg*(I)4 are the centroids of the N11/C11/C13/N13/C12, C16/C17/C34/C33/C32/C31, C44/C45/C61–C64 and N41/C41/C43/N43/C42 rings of (I), respectively, and *Cg*(II)1, *Cg*(II)2, *Cg*(II)3, *Cg*(II)4, *Cg*(II)5 and *Cg*(II)6 are the centroids of the N11/C11/C13/N13/C12, C16/C17/C31–C34, C11/C13–C17, C14/C15/C24/C23/C22/C21, C41/C43–C47 and C46/C47/C61–C64 rings of (II), respectively.

Structure	<i>Cg</i>	<i>Cg</i> /Atom	Distance	Angle
(I)	<i>Cg</i> (I)1	<i>Cg</i> (I)2 <sup>i</sup>	3.581 (2)	2.8 (2)
(I)	<i>Cg</i> (I)3	<i>Cg</i> (I)4 <sup>i</sup>	3.604 (2)	2.8 (2)
(II)	<i>Cg</i> (II)1	<i>Cg</i> (II)2 <sup>iii</sup>	3.594 (3)	1.0 (3)
(II)	<i>Cg</i> (II)3	<i>Cg</i> (II)4 <sup>iii</sup>	3.689 (3)	1.7 (2)
(II)	<i>Cg</i> (II)4	<i>Cg</i> (II)2 <sup>iii</sup>	3.631 (3)	2.5 (3)
(II)	<i>Cg</i> (II)5	<i>Cg</i> (II)6 <sup>iv</sup>	3.536 (3)	2.5 (2)
(II)	<i>Cg</i> (II)4	C42—H42 <sup>v</sup>	2.89 (1)	159
(II)	<i>Cg</i> (II)6	C53—Br53 <sup>v</sup>	3.639 (2)	86.1 (1)

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

## Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.043	1 restraint
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.112	H-atom parameters constrained
<i>S</i> = 1.00	Δρ <sub>max</sub> = 0.22 e Å <sup>-3</sup>
2095 reflections	Δρ <sub>min</sub> = -0.12 e Å <sup>-3</sup>
308 parameters	

## Compound (II)

### Crystal data

C <sub>15</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> ·0.5H <sub>2</sub> O	<i>γ</i> = 104.109 (5)°
<i>M</i> <sub>r</sub> = 385.04	<i>V</i> = 1347.9 (5) Å <sup>3</sup>
Triclinic, <i>P</i> 1̄	<i>Z</i> = 4
<i>a</i> = 8.415 (2) Å	Mo <i>K</i> α radiation
<i>b</i> = 10.139 (2) Å	<i>μ</i> = 6.00 mm <sup>-1</sup>
<i>c</i> = 17.227 (4) Å	<i>T</i> = 298 K
α = 101.683 (4)°	0.40 × 0.37 × 0.19 mm
β = 101.398 (5)°	

### Data collection

Bruker SMART CCD area-detector diffractometer	12857 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Blessing, 1995)	5330 independent reflections
<i>T</i> <sub>min</sub> = 0.359, <i>T</i> <sub>max</sub> = 1.000 (expected range = 0.115–0.320)	3658 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.040

## Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.047	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.128	Δρ <sub>max</sub> = 1.29 e Å <sup>-3</sup>
<i>S</i> = 1.00	Δρ <sub>min</sub> = -0.77 e Å <sup>-3</sup>
5330 reflections	
360 parameters	
2 restraints	

The C-bound H atoms were positioned geometrically using a riding model, with C—H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The H

atoms of the water molecule in (II) were located in a difference Fourier map and were allowed to refine with O—H distance restraints. In (II), the N—H hydrogens were located in a difference Fourier map and were subsequently refined isotropically.

Friedel pairs in (I) were merged. Disordered atoms H11 and H43 (Fig. 1), which participate in the N—H...N hydrogen bonds, were located in a difference Fourier map. Their occupancy factors were constrained to add to unity and refined to 0.60 (3) and 0.40 (3). Refinement of the two-site model reduced the weighted *R* factor, *wR*<sup>2</sup>(all), from 0.116 for the one-site model to 0.112. In several other structures containing benzimidazole units incapable of forming hydrogen bonds, residuals (*Q* peaks) were located 0.44–0.88 Å from the imine N atoms and in the planes of the imidazole rings, and were refined for comparison with the present structure. Refinement as H atoms decreased the *R* factors in some instances and increased them in others. In imidazole-containing structures, approximate differences between the C2—N(amine) and C2—N(imine) bond lengths are 0.04 Å for systems with no amine–imine hydrogen bonding, while for dialkyl-substituted imidazolium ions, there is essentially no difference within experimental error. In the present structure, the difference is 0.020 Å, which is not inconsistent with the two-site disordered model described above. Taken together, these data provide moderate support for the disordered/twinned model.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3095). Services for accessing these data are described at the back of the journal.

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