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Three structures containing (*E*)-1,2-bis(benzimidazol-2-yl)ethene groups

Robert T. Stibrany, Harvey J. Schugar and Joseph A. Potenza*

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, USA
Correspondence e-mail: potenza@rutchem.rutgers.edu

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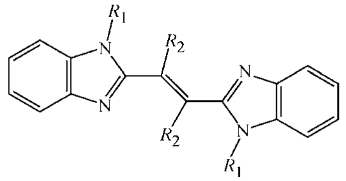
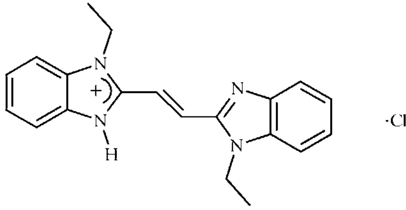
Two of the title compounds, namely (*E*)-1,2-bis(1-methylbenzimidazol-2-yl)ethene, $C_{18}H_{16}N_4$, (I*b*), and (*E*)-1,2-bis(1-ethylbenzimidazol-2-yl)ethene, $C_{20}H_{20}N_4$, (I*c*), consist of centrosymmetric *trans*-bis(1-alkylbenzimidazol-2-yl)ethene molecules, while 3-ethyl-2-[(*E*)-2-(1-ethylbenzimidazol-2-yl)-ethenyl]benzimidazol-1-ium perchlorate, $C_{20}H_{21}N_4^+\cdot ClO_4^-$, (II), contains the monoprotonated analogue of compound (I*c*). In the three structures, the benzimidazole and benzimidazolium moieties are essentially planar; the geometric parameters for the ethene linkages and their bonds to the aromatic groups are consistent with double and single bonds, respectively, implying little, if any, conjugation of the central C=C bonds with the nitrogen-containing rings. The C—N bond lengths in the N=C—N part of the benzimidazole groups differ and are consistent with localized imine C=N and amine C—N linkages in (I*b*) and (I*c*); in contrast, the corresponding distances in the benzimidazolium cation are equal in (II), consistent with electron delocalization resulting from protonation of the amine N atom. Crystals of (I*b*) and (I*c*) contain columns of parallel molecules, which are linked by edge-over-edge C—H$\cdots\pi$ overlap. The columns are linked to one another by C—H$\cdots\pi$ interactions and, in the case of (I*b*), C—H$\cdots$N hydrogen bonds. Crystals of (II) contain layers of monocations linked by π–π interactions and separated by both perchlorate anions and the protruding ethyl groups; the cations and anions are linked by N—H$\cdots$O hydrogen bonds.

Comment

The three compounds reported here, *viz*. (I*b*), (I*c*) and (II) (see scheme), were prepared as part of a project designed to extend our study of the chemistry of bis(imidazoles) and bis(benzimidazoles). Previously, we utilized compounds containing bis(imidazoles) as agents to study electron self-exchange (Knapp *et al.*, 1990), while systems containing bis(benzimidazoles) have been shown to behave as catalysts (Patil *et al.*, 2003; Stibrany *et al.*, 2003; Stibrany & Kacker, 2002; Stibrany, 2001), as geometrically constraining ligands (Stibrany *et al.*, 2004) and as proton sponges (Stibrany *et al.*, 2002). In the past, *trans*-1,2-bis(benzimidazol-2-yl)ethene compounds have been prepared directly from the condensation of maleic acid with an appropriate phenylenediamine (Dann *et al.*, 1973). The preparation of (I*a*) has been reported from the condensation of *rac*-malic acid at high temperature (403–468 K), but with little characterization (Siegrist & Ackermann, 1959). During our synthetic studies, we have found that malic acid-based derivatives, at ambient temperature, undergo facile dehydration during alkylation in the presence of excess NaH to yield *trans*-ethene products. Initial isolation of the *trans* isomer may be anticipated from the results obtained for the analogous molecule stilbene, whose *trans* isomer is reported to be stabilized by 4.59 kcal mol^{-1} over that of the *cis* isomer (Saltiel *et al.*, 1987). Isolation of *cis*- or (*Z*)-1,2-bis(benzimidazol-2-yl)ethene compounds will be explored in future investigations.



	R_1	R_2
(I*a*)	H	H
(I*b*)	Me	H
(I*c*)	Et	H
(I*d*)	Me	OH



(II)

The structures (I*b*) and (I*c*) (Figs. 1 and 2, respectively) contain centrosymmetric molecules, with the centers of symmetry located at the mid-points of the ethene fragments. In (I*b*), the planar methylbenzimidazole fragments are not mutually coplanar; a twist about the ethene linkage gives the molecule a slight stepped appearance in profile. Owing to the center of symmetry, the benzimidazole planes in molecules of (I*b*) are necessarily parallel; the distance between these planes

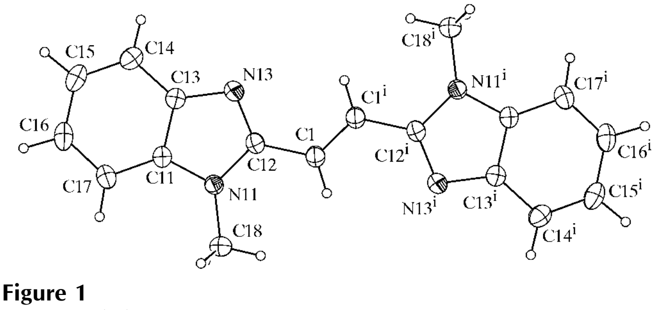


Figure 1
A view of (I*b*), showing 25% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (i) $-x, -y, -z$.]

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is 0.501 (3) Å. In (I*c*), the twist about the central ethene fragment is much smaller than that in (I*b*), as indicated by the interplanar spacing of 0.211 (4) Å, so that (I*c*), with the exception of the methyl groups of the ethyl moieties, which protrude on either side of the molecular plane, is very nearly planar.

Corresponding bond lengths in (I*b*) and (I*c*) (Table 3) for the benzimidazole and the ethene fragments are equivalent to each other within experimental error and agree well in general with those in (I*d*), the only example obtained from a search of the Cambridge Structural Database (CSD; Version 5.24; Allen, 2002) for a species containing a 1,2-bis(benzimidazol-2-yl)ethene substructure (CSD refcode TACWAV; Morkovnik *et al.*, 1995). In these three structures, the amine N11—C12 distances are longer than the imine N13═C12 distances, as expected. The ethene linkages C1═C1, while normal for C═C bonds of their type, are not all equal; in particular, the C1═C1′ distance in (I*d*) is significantly longer than those in (I*b*) and (I*c*), while the $\text{C}{=}\text{N}_{\text{imine}}$ distance in (I*d*) is slightly longer than those in (I*b*) and (I*c*). The differences in the 'ethene' and 'imine' lengths suggest the possibility of some electron delocalization between the ethene and benzimidazole fragments in (I*d*), possibly as a result of substitution at the C1 position in (I*d*). Lastly, we note that the C1—C12 distances in all three structures are comparable in length and are consistent with normal Csp^2—Csp^2 linkages.

In the perchlorate salt, (II) (Fig. 3), the monocation is effectively planar, except for the methyl groups. The imine N═C2 and amine N—C2 bond distances in the benzimidazole group (N11—C12 and N13═C12; Fig. 3) are not equal, with the 'imine' length shorter than the 'amine' length, as expected. These distances compare well with structures (I*b*)–(I*d*), as do the angles in the imidazole fragments with atoms C12, N11 and N13 as vertices (Table 3). In contrast, the related distances in the benzimidazolium moiety (N21—C22 and N23—C22) are essentially equal, as are the angles with atoms C22, N22 and N23 as vertices, consistent with protonation occurring exclusively at N23. Atom N23 participates in three hydrogen bonds (Table 2), *viz.* two interionic N—H⋯O bonds to two of the four O atoms of the ClO_4^- ion and one intraionic C—H⋯N bond involving ethene atom H1. The perchlorate ion shows little evidence of disorder, possibly as a result of stabilization by hydrogen bonding, and exhibits typical Cl—O bond lengths, which range from 1.380 (2) to 1.428 (3) Å; the longer Cl—O bonds are associated with the O atoms involved in hydrogen bonding. Finally, we note that the ethene linkage (C1═C2) in (II) is slightly shorter than those in (I*b*) and (I*c*), possibly as a result of the positive charge and/or the weak intraionic C—H⋯N interaction.

In their crystal structures, molecules of (I*b*) and (I*c*) form columns parallel to the *a*-axis direction. Molecules within the columns are tilted, as in a slipped deck of cards, with the result that the molecules in a given column are linked to one another primarily by edge-over-edge C—H⋯π interactions. The interplanar spacings between molecules within the columns are 3.5107 (15) and 3.250 (2) Å for (I*b*) and (I*c*), respectively, values typical of π-system interactions (Janiak, 2000). In both structures, the columns of molecules are arranged in an offset herring-bone pattern, and are linked by C—H⋯π and N—H⋯π interactions to complete the packing. In addition, (I*b*) contains an intermolecular C—H⋯N hydrogen bond (Table 1). From their calculated densities (see *Crystal data* sections), crystals of (I*c*) are considerably less dense than (I*b*), implying a more open structure for (I*c*), despite the similarity of the two structures. Crystals of (II) consist of layers of monocations parallel to the (100) planes, centered about the planes $z = 0$ and $z = \frac{1}{2}$, and separated by ethyl groups and perchlorate anions. Within the cation layer centered about $z = 0$, individual cations are arranged in offset lines parallel to [110] (Fig. 4) to yield a two-dimensional array of cations, all of which are connected by π–π interactions among the aromatic fragments. For the fragments with the greatest overlap, benzimidazole–benzimidazole and benzimidazolium–benzimidazolium interplanar spacings are 3.379 (9) and 3.428 (3) Å, respectively. About the $z = \frac{1}{2}$ plane (not shown), the cations are arranged with their planes parallel to $[1\bar{1}0]$. Together, these

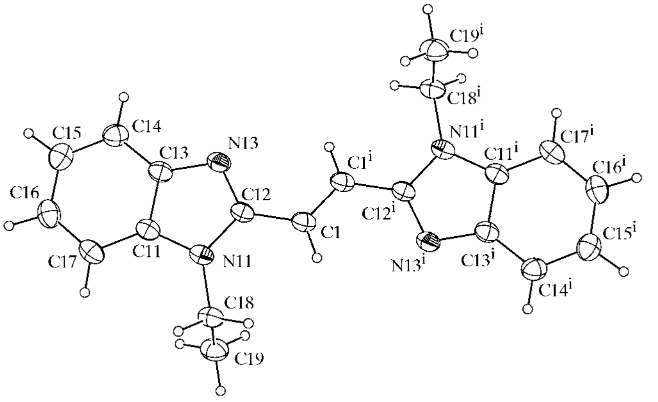

Figure 2
A view of (I*c*), showing 25% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (i) −*x*, −*y*, −*z*.]

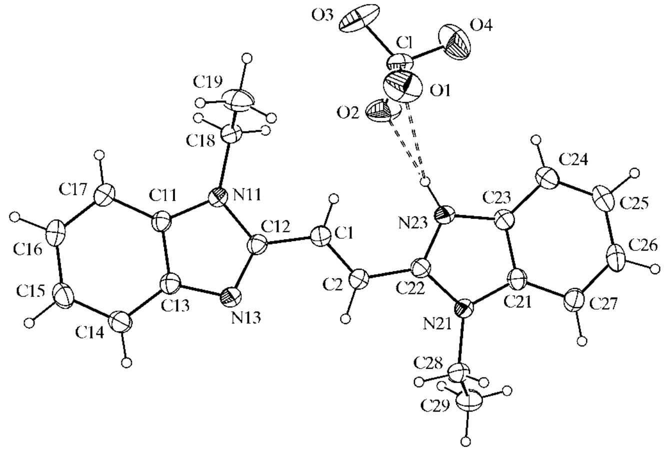

Figure 3
A view of (II), showing 25% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen bonds are indicated by dashed lines.

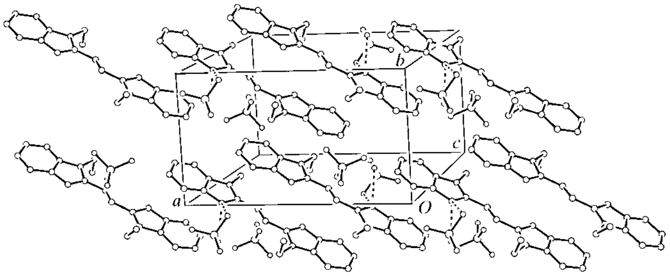

Figure 4
A view, centered about the plane $z = 0$, of the structure of (II). Hydrogen bonds between the cations and anions are indicated by dashed lines. H atoms have been omitted for clarity.

two symmetry-related layers create a structure in which, in projection along the *c* axis, the cations appear as a crisscrossed array. As noted above, the anions are stabilized in the crystal structure by hydrogen bonds to the protonated N atom; these linkages are shown as dashed lines in Fig. 4.

Experimental

Compounds (I*b*) and (I*c*) were prepared from *rac*-1,2-bis(1*H*-benzimidazol-2-yl)-1-hydroxyethane (Taffs *et al.*, 1961). Alkylation was effected according to a reported method (Stibrany *et al.*, 2004). Under N_2, NaH (6 molar equivalents) was added to a mixture of *rac*-1,2-bis(1*H*-benzimidazol-2-yl)-1-hydroxyethane in dry dimethyl sulfoxide. After a reaction time of 30 min, the appropriate alkyl iodide (2 molar equivalents) was added dropwise. After an additional 30 min, the product was precipitated with water, collected by filtration and recrystallized to give products in >90% yield. Crystals of (I*b*) (m.p. 574 K) were obtained by slow evaporation of an ethanol/triethylorthoformate mixture (1:1 *v*/*v*, 10 ml) containing (I*b*) (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (*s*, 2H), 7.81 (*m*, 2H), 7.33 (*m*, 6H), 3.97 (*s*, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 149.1, 143.4, 135.2, 123.2, 123.0, 120.6, 119.6, 109.4, 29.8. $R_F = 0.20$ (ethyl acetate/silica). Crystals of (I*c*) (m.p. 504 K) were obtained by slow evaporation of an acetone/2-propanol mixture (1:1 *v*/*v*, 10 ml) containing (I*c*) (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (*s*, 2H), 7.83 (*m*, 2H), 7.33 (*m*, 6H), 4.44 (*q*, $J = 7.3$ Hz, 4H), 1.52 (*t*, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 149.1, 143.4, 135.2, 123.2, 123.0, 120.6, 119.7, 109.6, 38.4, 15.8. $R_F = 0.54$ (ethyl acetate/silica). Crystals of (II) [m.p. 538 (soften) and 549 K (decomposition)] were obtained by addition of perchloric acid (1 molar equivalent) to a solution of 1,2-bis(1-ethylbenzimidazol-2-yl)ethene in a mixture of ethanol and triethylorthoformate (9:1 *v*/*v*). Bright yellow blocks precipitated overnight. IR (KBr pellet, cm^{-1}): 1641 (*s*), 1385 (*m*), 1122 (*s*), 1108 (*sh*), 1059 (*m*), 746 (*m*).

Compound (I*b*)

Crystal data

$C_{18}H_{16}N_4$
$M_r = 288.35$
Monoclinic, $P2_1/n$
$a = 6.2517$ (2) Å
$b = 12.0363$ (5) Å
$c = 9.9464$ (3) Å
$\beta = 102.927$ (3)°
$V = 729.47$ (4) Å^3
$Z = 2$

$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 886 reflections
$\theta = 2.7$–24.8°
$\mu = 0.08$ mm^{-1}
$T = 297$ (1) K
Prism, pale yellow
$0.43 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.852$, $T_{\max} = 1.00$
5056 measured reflections

1273 independent reflections
1118 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25.0°$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.111$
$S = 1.00$
1273 reflections
117 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.1265P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I*b*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18*C*···N13$^{\rm ii}$	0.96	2.61	3.560 (2)	169

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

Compound (I*c*)

Crystal data

$C_{20}H_{20}N_4$
$M_r = 316.40$
Monoclinic, $P2_1/c$
$a = 5.1789$ (4) Å
$b = 11.2713$ (8) Å
$c = 14.4525$ (9) Å
$\beta = 94.905$ (5)°
$V = 840.55$ (10) Å^3
$Z = 2$

$D_x = 1.250$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1011 reflections
$\theta = 3.4$–24.6°
$\mu = 0.08$ mm^{-1}
$T = 298$ (1) K
Prism, colorless
$0.50 \times 0.31 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.740$, $T_{\max} = 1.00$
5645 measured reflections

1464 independent reflections
1193 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 25.0°$
$h = -6 \rightarrow 6$
$k = -13 \rightarrow 12$
$l = -17 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.156$
$S = 1.00$
1464 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0976P)^2 + 0.1481P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N23—H23···O2	0.88 (3)	2.08 (3)	2.925 (3)	161 (3)
N23—H23···O1	0.88 (3)	2.54 (3)	3.276 (4)	141 (3)
C1—H1···N23	0.89 (3)	2.62 (3)	2.908 (3)	100 (2)

Compound (II)

Crystal data

$C_{20}H_{21}N_4^+\cdot ClO_4^-$
$M_r = 416.86$
Monoclinic, $P2_1/c$
$a = 14.3810\ (5)$ Å
$b = 8.3007\ (3)$ Å
$c = 16.4788\ (6)$ Å
$\beta = 91.561\ (3)^\circ$
$V = 1966.38\ (12)$ Å^3
$Z = 4$
$D_x = 1.408$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 862 reflections
$\theta = 2.8$–23.5°
$\mu = 0.23$ mm^{-1}
$T = 297\ (1)$ K
Block, yellow
$0.42 \times 0.33 \times 0.23$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.828$, $T_{\max} = 0.948$
14 068 measured reflections
3452 independent reflections
2725 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25.1^\circ$
$h = -17 \rightarrow 17$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.148$
$S = 1.00$
3452 reflections
324 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0892P)^2 + 0.7662P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Table 3
Comparison of selected bond lengths (Å) and angles (°) in the bis(benzimidazol-2-yl)ethene fragments of (I*b*), (I*c*), (I*d*) and (II) .

Bond	(I*b*)	(I*c*)	(I*d*)	(II)	
C1—C1	1.329 (3)	1.332 (4)	1.368 (3)	1.316 (3)	Protonated
C1—C12	1.4532 (19)	1.440 (3)	1.451 (2)	1.445 (3)	1.438 (3)
N11—C12	1.3727 (17)	1.376 (3)	1.371 (2)	1.376 (3)	1.346 (3)
N13—C12	1.3203 (18)	1.321 (3)	1.337 (2)	1.321 (3)	1.337 (3)
N11—C11	1.3772 (16)	1.381 (3)	1.386 (2)	1.378 (3)	1.395 (3)
N13—C13	1.3819 (18)	1.377 (3)	1.382 (2)	1.379 (3)	1.376 (3)
C11—C13	1.3996 (19)	1.404 (3)	1.405 (6)	1.401 (3)	1.390 (3)
C11—C17	1.388 (2)	1.395 (3)	1.388 (2)	1.392 (3)	1.387 (3)
C13—C14	1.399 (2)	1.391 (3)	1.399 (2)	1.396 (3)	1.391 (3)
C14—C15	1.369 (2)	1.372 (4)	1.383 (3)	1.376 (4)	1.373 (4)
C16—C17	1.374 (2)	1.368 (4)	1.386 (3)	1.373 (4)	1.376 (4)
C15—C16	1.397 (3)	1.391 (4)	1.405 (3)	1.399 (4)	1.393 (4)
N11—C12—C13	112.94 (12)	112.26 (18)	112.4 (1)	113.5 (2)	108.18 (19)
C12—N11—C11	106.52 (11)	106.89 (16)	106.5 (1)	105.92 (18)	108.85 (18)
C12—N13—C13	104.84 (11)	105.54 (18)	105.6 (1)	104.51 (18)	110.16 (19)

In the three structures, H atoms were located in difference electron-density maps, but in some cases the ethylene and methyl H atoms did not refine smoothly. These atoms were subsequently positioned geometrically and refined using a riding model, with C—H distances of 0.93–0.96 Å and $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(C) for methyl H atoms and $1.2U_{\rm eq}$(C) for the other H atoms.

For all compounds, data collection: *SMART WNT/2000* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; structure solution: *SHELXS97* (Sheldrick, 1990); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1255). Services for accessing these data are described at the back of the journal.

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