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N-(2-Bromoethyl)-4-piperidino-1,8-naphthalimide and *N*-(3-bromopropyl)-4-piperidino-1,8-naphthalimide

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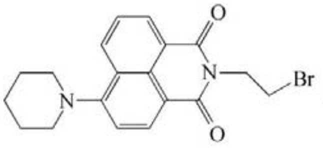
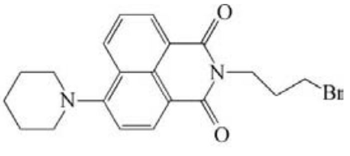
N-(2-Bromoethyl)-4-piperidino-1,8-naphthalimide, $C_{19}H_{19}BrN_2O_2$, (I), and *N*-(3-bromopropyl)-4-piperidino-1,8-naphthalimide, $C_{20}H_{21}BrN_2O_2$, (II), are an homologous pair of 1,8-naphthalimide derivatives. The naphthalimide units are planar and each piperidine substituent adopts a chair conformation. This study emphasizes the importance of π-stacking interactions, often augmented by other contacts, in determining the crystal structures of 1,8-naphthalimide derivatives.

Comment

1,8-Naphthalimides find widespread use in materials science, including use as dyes (Hirahara *et al.*, 1993), as markers in biomedical science (Stewart, 1981*a*,*b*) and as optical brighteners (Dorlars *et al.*, 1975). Our interest in these compounds centres on the incorporation of fluorescent naphthalimide units into molecular assemblies that contain both redox-active and fluorescent functionalities joined by conductive alkene or alkyne linkages (McAdam *et al.*, 2000, 2003, 2005), enamines (McAdam *et al.*, 2004) or sugar derivatives of the naphthalimides (Cavigiolo *et al.*, 2004), and the incorporation of fluorescent naphthalimides into polymeric systems (Dana *et al.*, 2007). Of particular recent interest is the use of fluorescent naphthalimides or polyaromatic hydrocarbons in the redox-triggered absorption of radiation in the near-IR region of the electromagnetic spectrum (McAdam *et al.*, 2003; Cuffe *et al.*, 2005). We report here the syntheses and crystal structures of an homologous pair of 1,8-naphthalimide derivatives, namely *N*-(2-bromoethyl)-4-piperidino-1,8-naphthalimide, (I), and *N*-(3-bromopropyl)-4-piperidino-1,8-naphthalimide, (II), prepared as precursors to the syntheses of ferrocene–naphthalimide and related poly *ad* systems (Tagg, 2008).



(I)



(II)

Each molecule comprises a 1,8-naphthalimide ring system, with a piperidino substituent at the 4-position of the naphthalene ring and with the N atom of the dicarboximide ring carrying a bromoethyl substituent in (I) (Fig. 1) and a bromopropyl substituent in (II) (Fig. 2). The naphthalimide units are essentially planar in each compound, with r.m.s. deviations from the mean planes through all 15 atoms, including the dicarboximide O atoms, of 0.048 Å for (I) and 0.019 Å for (II). The C13 and N2 substituents are displaced only slightly from these planes, *viz.* by 0.0278 (19) and −0.0807 (17) Å, respectively, in opposite directions for (I) and, somewhat more extensively, by 0.1108 (15) and 0.1224 (14) Å, but both in the same direction, for (II). The piperidine rings each adopt classical chair conformations, with Cremer & Pople (1975) puckering parameters of Q_2 = 0.0447 (15) Å, φ_2 = 178 (2)° and Q_3 = −0.5847 (15) Å for the N2/C15–C19 ring in (I), and Q_2 = 0.0186 (17) Å, φ_2 = 324 (5)° and Q_3 = 0.5808 (17) Å for the N2/C16–C20 ring in (II).

A search of the Cambridge Structural Database (Version 5.29, updated to January 2008; Allen, 2002) reveals 12 other naphthalimide derivatives with amine substituents in the 4-position and an alkyl chain with two or more C atoms on the

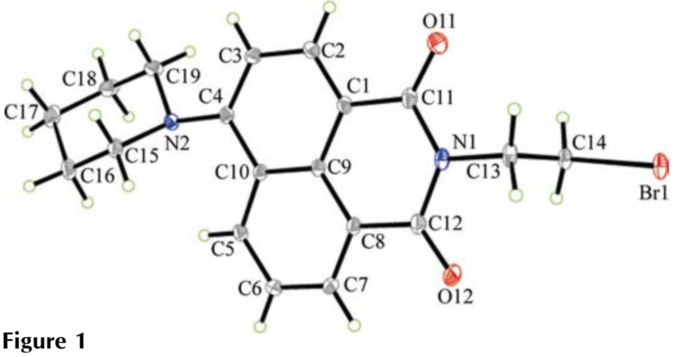


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

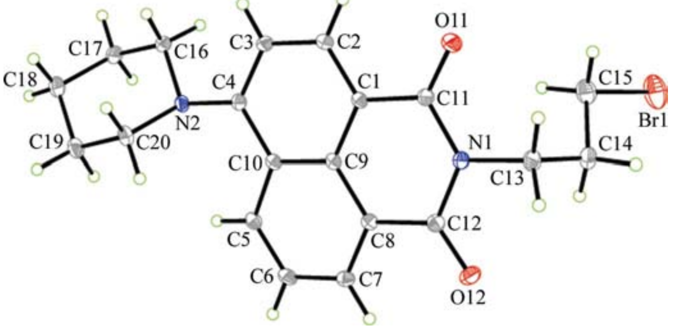


Figure 2
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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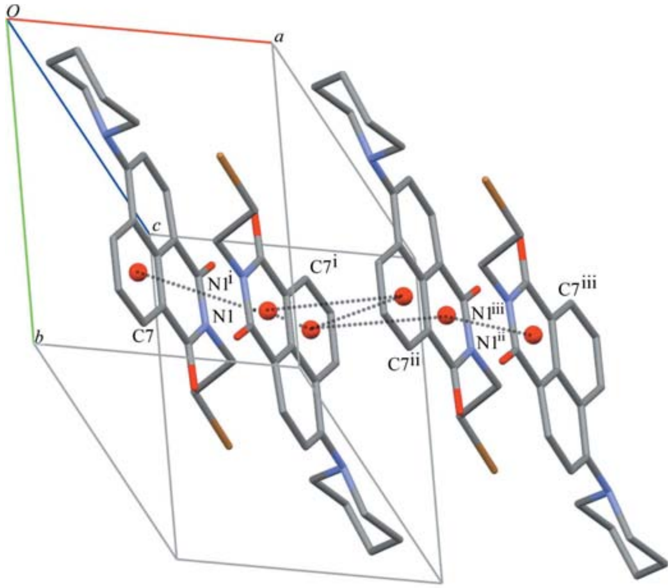

Figure 3
The π-stacking along *a* for (I). Spheres represent ring centroids and centroid–centroid interactions are shown as dotted lines. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 2, -y + 1, -z + 1$.]

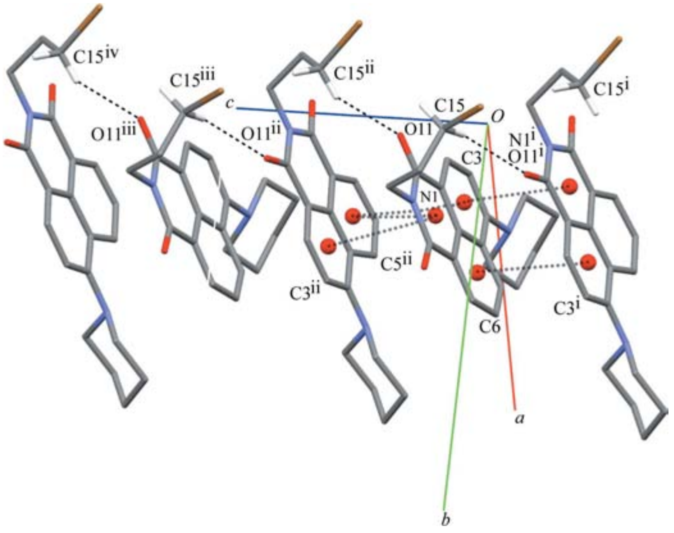

Figure 5
The π–π stacking of (II), augmented by C—H$\cdots$O hydrogen bonds (dashed lines). Spheres represent ring centroids and centroid–centroid interactions are shown as dotted lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x, y, z + 1$; (iv) $x, -y + \frac{1}{2}, z + \frac{3}{2}$.]

dicarboximide N atom (Banthia & Samanta, 2005, 2006; Banthia & Paul, 2005; Bardajee *et al.*, 2006; Baughman *et al.*, 1995; Shi *et al.*, 2005; Gunnlaugsson *et al.*, 2003, 2005; Qin *et al.*, 2007). In contrast, the structures of only two other 4-piperidinonaphthalimide derivatives have been reported previously (McAdam *et al.*, 2003, 2005). Bond-length variations within the dicarboximide ring are consistent with significant delocalization over the naphthalimide unit. However, predictably (Easton *et al.*, 1992; Batchelor *et al.*, 1997), delocalization does not extend to the alkyl substituent, as evidenced by N1—C13 bond distances of 1.4667 (17) and 1.472 (2) Å for (I) and (II), respectively. These values compare with the corresponding average distance of 1.482 Å found for the 12 related naphthalimide derivatives using *VISTA* (CCDC, 1994). In contrast, the C4—N2 bonds from the naphthalene ring to the piperidine N atom are relatively short [1.4005 (17) Å for (I) and 1.411 (2) Å for (II)], suggesting some delocalization between the naphthalene and piperidine units. However, these distances are somewhat longer than the average value of 1.365 Å in the related *N*-alkyl-4-amidonaphthalimide derivatives, but compare somewhat more closely with the values of 1.4088 (19) and 1.376 (4) Å found for the two other reported 4-piperidinonaphthalimides (McAdam *et al.*, 2003, 2005).

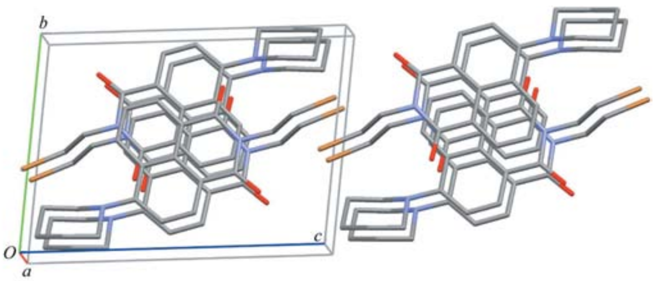

Figure 4
The crystal packing of (I), viewed down *a*, showing the three-dimensional network structure generated by π–π stacking interactions. H atoms have been omitted for clarity.

Naphthalimide compounds are well known to aggregate through π-stacking interactions in the solid state (McAdam *et al.*, 2000; Sarma *et al.*, 2007; Reger *et al.*, 2005) and this often results in poor solubility and difficulty in obtaining crystalline materials (Keeling *et al.*, 2003; Figueiredo *et al.*, 2005). Offset π–π interactions are major contributors to the packing in both (I) and (II). However, such interactions are supported differently, despite the close relationship between these structures.

For (I), offset π–π interactions form head-to-tail dimers *via* inversion-related $Cg1\cdots Cg3^{i}$ [3.6442 (8) Å] and $Cg3\cdots Cg3^{i}$ [3.6923 (8) Å] contacts [symmetry code: (i) $-x, -y + 1, -z + 1$; *Cg*1 and *Cg*3 are the centroids of the N1/C1/C8/C11/C12 and C5–C10 rings, respectively]. Pairs of dimers are further aggregated through weaker $Cg3\cdots Cg1^{ii}$ [3.9078 (8) Å] contacts [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$], forming columns down *a* (Fig. 3). The crystal packing in (I) is further stabilized by weak nonclassical C14—H14*A*$\cdots$Br1 contacts [C14$\cdots$Br1($-x, -y + 1, -z + 2$) = 3.8729 (13) Å] that result in the formation of inversion-related dimers. These contacts generate an $R_2^2(6)$ graph-set motif (Bernstein *et al.*, 1995). The overall three-dimensional network structure generated by molecules of (I) is shown in Fig. 4.

In the crystal packing of (II), pairs of molecules are arranged in an obverse fashion through head-to-head offset π-stacking interactions that involve all three rings of the

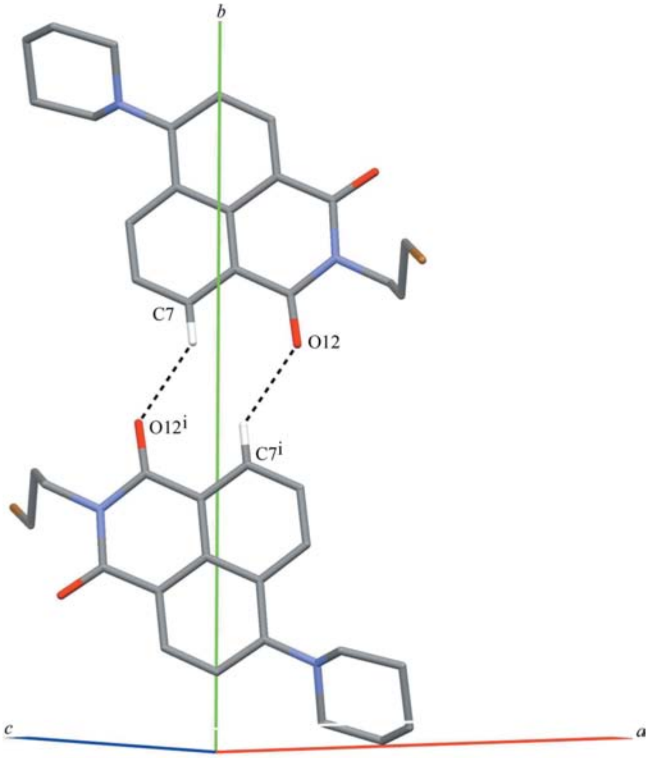

Figure 6
Centrosymmetric dimers of (II) formed by C—H···O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $-x, -y+1, -z$.]

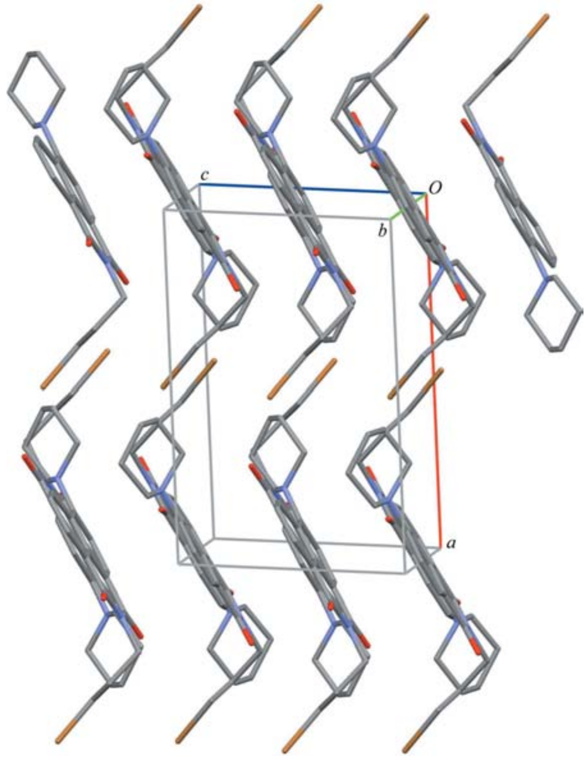

Figure 7
The π–π stacking of (II), viewed down the b axis. H atoms have been omitted for clarity.

naphthalimide unit [$Cg4\cdots Cg5^{\rm iii}$ = 3.4956 (9) Å, $Cg4\cdots Cg6^{\rm iii}$ = 3.8629 (9) Å and $Cg5\cdots Cg6^{\rm iii}$ = 3.4896 (9) Å; symmetry code: (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; $Cg5$, $Cg6$ and $Cg7$ are the centroids of the N1/C1/C8/C11/C12, C1–C4/C9/C10 and C5–C10 rings, respectively]. These contacts form extended columns down c and are augmented by C15—H15B···O11 interactions (Fig. 5). Pairs of molecules also form centrosymmetric dimers, with an $R_2^2(10)$ graph-set motif, through C7—H7···O12 hydrogen bonds (Fig. 6). These link adjacent molecules in each π-stacked column to form zigzag chains along a (Fig. 7).

Experimental

For the preparation of (I), N-(2-hydroxyethyl)-4-piperidino-1,8-naphthalimide (Lei *et al.*, 2005) and 4-piperidinonaphthalic anhydride (Kupriyan *et al.*, 2004) were prepared by published or modified literature methods. PBr_3 (0.87 ml, 9.24 mmol) in tetrahydrofuran (THF, 10 ml) was added to a mixture of N-(2-hydroxyethyl)-4-piperidino-1,8-naphthalimide (1.00 g, 3.08 mmol) and pyridine (0.75 ml, 9.24 mmol) in THF (20 ml) and heated at 323 K for 16 h. The mixture was poured into ice–water, extracted with chloroform and dried over magnesium sulfate. Column chromatography (SiO_2, CH_2Cl_2) yielded 0.71 g (60%) of (I) and recrystallization from CH_2Cl_2–EtOH (1:1 v/v) gave yellow crystals suitable for X-ray analysis. Analysis calculated for $C_{19}H_{19}BrN_2O_2$: C 58.93, H 4.95, N 7.23%; found: C 58.94, H 4.98, N 7.12%; ESI–MS: 409.05 [calculated $(M + Na)^+$ = 409.05]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75 (m, 2H, pip. H), 1.89 (m, 4H, pip. H), 3.24 [t (J = 5 Hz), 4H, pip. H], 3.66 [t (J = 7 Hz), 2H, –CH_2—Br], 4.60 [t (J = 7 Hz), 2H, N—CH_2–], 7.18 [d (J = 8 Hz), naphth. H3], 7.68 [dd (J = 8, 7 Hz), naphth. H6], 8.41 [dd (J = 8, 1 Hz), naphth. H5], 8.51 [d (J = 8 Hz), naphth. H2], 8.58 [dd (J = 7, 1 Hz), naphth. H7]; IR (KBr): $\nu_{C=O}$ 1693, 1654 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (ε) 414 (11400); emission (CH_2Cl_2): λ_{flu} 519 nm, φ_f 0.46. For the preparation of (I), 4-piperidinonaphthalic anhydride (1.00 g, 3.55 mmol) and 3-bromopropylamine hydrobromide (1.55 g, 7.10 mmol) were refluxed in propan-2-ol (50 ml) in the presence of Et_3N (2 ml) for 10 h. The mixture was washed with saturated aqueous NaCl and extracted with chloroform. Column chromatography (SiO_2, CH_2Cl_2) yielded 0.42 g (30%) of (II) and recrystallization from CH_2Cl_2–MeOH (1:1 v/v) gave yellow crystals suitable for X-ray analysis. Analysis calculated for $C_{20}H_{21}BrN_2O_2$: C 59.86, H 5.28, N 6.98%; found: C 60.09, H 5.32, N 6.99%; ESI–MS: 423.07 [calculated $(M + Na)^+$ = 423.07]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (m, 2H, pip. H), 1.89 (m, 4H, pip. H), 2.32 [qt (J = 7 Hz), 2H, N—CH_2—CH_2–], 3.24 [t (J = 5 Hz), 4H, pip. H], 3.49 [t (J = 7 Hz), 2H, –CH_2—Br], 4.31 [t (J = 7 Hz), 2H, N—CH_2–], 7.18 [d (J = 8 Hz), naphth. H3], 7.68 [dd (J = 9, 8 Hz), naphth. H6], 8.39 [dd (J = 8, 1 Hz), naphth. H5], 8.50 [d (J = 8 Hz), naphth. H2], 8.57 [dd (J = 7, 1 Hz), naphth. H7]; IR (KBr): $\nu_{C=O}$ 1686, 1648 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (ε) 412 (11400); emission (CH_2Cl_2): λ_{flu} 518 nm, φ_f 0.51.

Compound (I)

Crystal data

$C_{19}H_{19}BrN_2O_2$
M_r = 387.27
Triclinic, $P\overline{1}$
a = 7.3476 (4) Å
b = 9.3218 (5) Å
c = 12.2905 (6) Å
α = 82.039 (3)°
β = 84.205 (2)°
γ = 74.937 (3)°
V = 803.19 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.57 mm^{-1}
T = 90 (2) K
0.56 × 0.46 × 0.12 mm

Table 1
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O12^{i}	0.95	2.47	3.250 (2)	140
C15—H15B···O11^{ii}	0.99	2.50	3.369 (2)	147

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

Data collection

Bruker–Nonius APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2005)
$T_{\min} = 0.326$, $T_{\max} = 0.734$

13527 measured reflections
4650 independent reflections
4402 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.067$
$S = 1.07$
4650 reflections

217 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.71$ e Å^{-3}

Compound (II)

Crystal data

$C_{20}H_{21}BrN_2O_2$
$M_r = 401.30$
Monoclinic, $P2_1/c$
$a = 12.4165$ (3) Å
$b = 17.7709$ (5) Å
$c = 7.9618$ (2) Å
$\beta = 94.569$ (1)°

$V = 1751.21$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.36$ mm^{-1}
$T = 90$ (2) K
0.62 × 0.14 × 0.04 mm

Data collection

Bruker–Nonius APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2005)
$T_{\min} = 0.201$, $T_{\max} = 0.911$

30759 measured reflections
5571 independent reflections
4434 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.02$
5571 reflections

226 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.99$ e Å^{-3}

All H atoms for both structures were positioned geometrically and refined using a riding model, with C—H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: *APEX2* (Bruker 2005); cell refinement: *APEX2* and *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *TITAN2000* (Hunter & Simpson, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *TITAN2000*; molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3024). Services for accessing these data are described at the back of the journal.

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