

Red, orange and yellow crystals of 4,5-bis(4-methoxyphenyl)-2-(3-nitro- phenyl)-1*H*-imidazole

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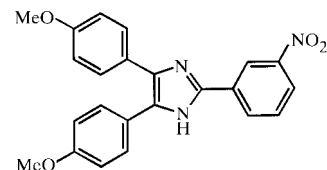
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Red non-solvate crystals of the title compound from ethanol, $C_{23}H_{19}N_3O_4$, orange solvate crystals from *tert*-butanol, $C_{23}H_{19}N_3O_4 \cdot C_4H_{10}O$, yellow solvate crystals from dioxane–water, $C_{23}H_{19}N_3O_4 \cdot 0.5C_4H_8O_2$, and intense yellow solvate crystals from benzene–*N,N'*-dimethylformamide,

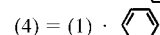
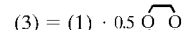
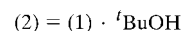
$C_{23}H_{19}N_3O_4 \cdot C_6H_6$, differ from each other in their molecular conformation and hydrogen-bonding scheme. The bathochromic shifts of the crystal color are explained by the molecular planarity and charge-transfer effect among the imidazole molecules.

Comment

4,5-Bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-imidazole crystallizes in different colored states on changing the solvent (Sakaino *et al.*, 1996). Recently, we reported yellow solvate



(1)



crystals from ethyl acetate. The guest solvent molecules were lost without destruction of the network of host imidazole

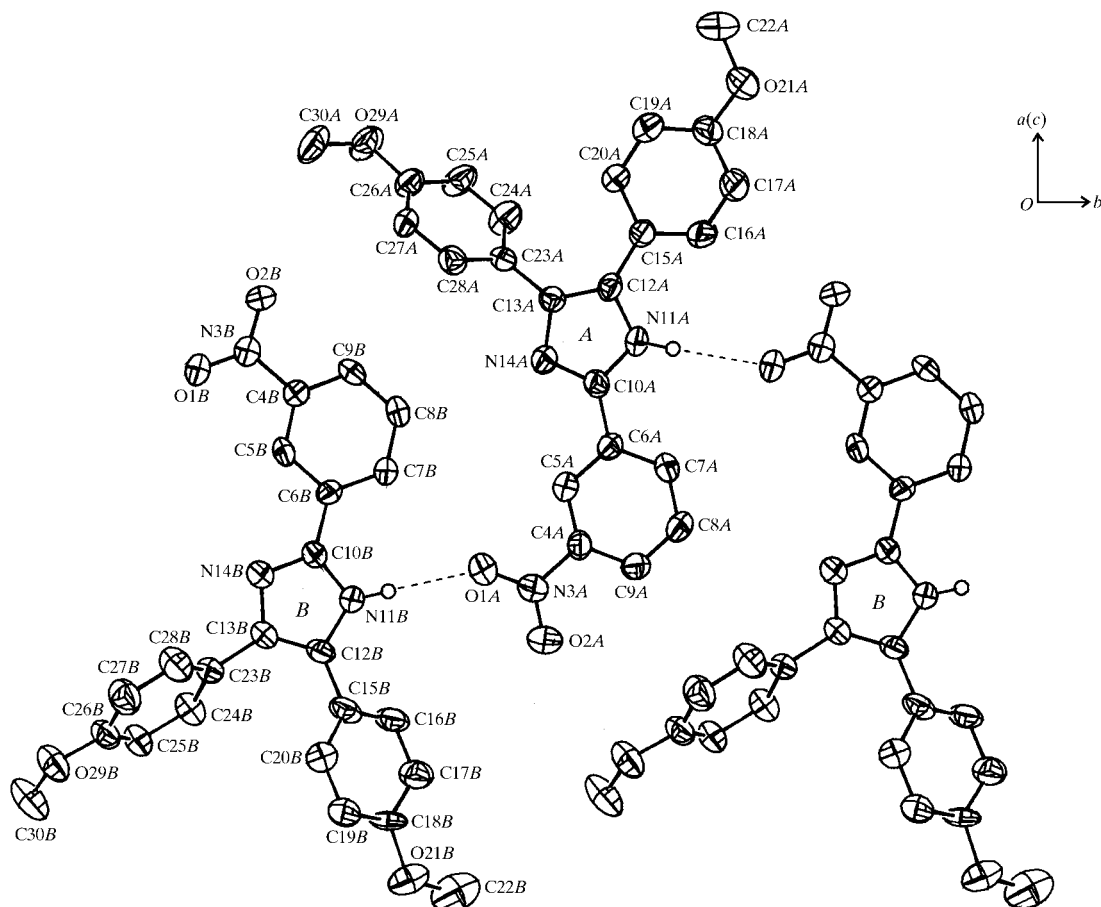


Figure 1

The molecular structure of (1) showing 50% probability displacement ellipsoids (ORTEP; Johnson, 1976). For clarity, only one of the disordered positions of O2*B* and C15*B*–C22*B*, and only the H atom of the N–H group, are included. The dashed lines show the hydrogen bonding.

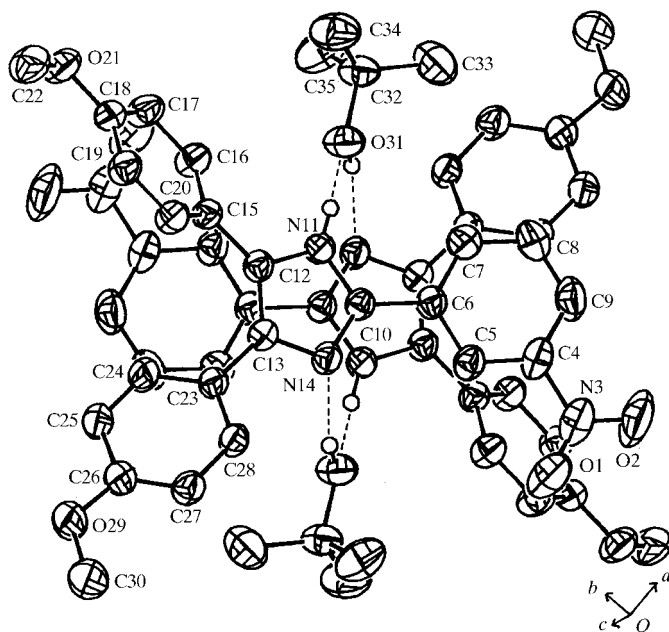


Figure 2

The molecular arrangement of (2) showing 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976). For clarity, only the H atom of the N–H group is included, with dashed lines showing the hydrogen bonding.

molecules upon heating at 353 K under 2 Torr (1 Torr = 133.322 Pa) (Inouye *et al.*, 1999). Here, we wish to report four other crystals: red non-solvate crystals from ethanol, (1), orange solvate crystals from *tert*-butanol, (2), yellow solvate crystals from dioxane–water, (3), and intense yellow solvate crystals from benzene–*N,N'*-dimethylformamide (10:1), (4).

The numbering of the host molecule is the same in all crystals. Fig. 1 represents the molecular structure of (1). Two independent molecules (designated *A* and *B*) were found in (1) and they differ in the conformation of the molecules, as shown by the dihedral angle between the imidazole ring (C10 to N14, designated I) and three benzene rings (C4 to C9, II; C15 to C20, III; and C23 to C28, IV). In molecule *A*, I/II = 3.8 (3), I/III = 4.5 (4), and I/IV = 62.5 (2)°. In molecule *B*, I/II = 7.5 (4), I/III = 31.7 (5) and 15.0 (8) (1:1), and I/IV = 55.9 (2)°. The host molecules lie as a sheet and are connected through a weak hydrogen bond between N11–H11 and the O1 atom of the nitro group (see Table 1). The imidazole ring of molecule *A* in a sheet faces the nitrophenyl ring of molecules *A* and *B* in the upper and lower sheets, respectively. The short intermolecular distances between the imidazole ring and the nitrophenyl ring are $C6A-C12A(1-x, 1-y, 1-z) = 3.515$ (8) and $C4A-C10B(\frac{1}{2}-x, \frac{1}{2}+y, 1-z) = 3.481$ (8) Å, respectively. The molecular planarity and intermolecular charge-transfer effect from the imidazole ring to the nitrophenyl ring may cause the bathochromic shift of the color. Two host molecules in (2) are arranged to have a center of symmetry and are connected with each other by two *tert*-butanol molecules. The O31–H31 of *tert*-butanol bonds to N14 of the imidazole, while O31 bonds to H11–N11 of the imidazole (see Fig. 2 and Table 2). The dihedral angles between the rings are I/II = 10.2 (2), I/III = 40.2 (2) and I/IV = 29.7 (1)°. The facing of the imidazole ring

towards the nitrophenyl ring [$N11-C6(-x, 1-y, -z) = 3.554$ (4) Å] may cause a slight bathochromic shift of the color. In (3), on the other hand, dioxane connects two host molecules by intermolecular hydrogen bonds between the O31 atom and H11–N11 to have a center of symmetry at the center of dioxane (see Fig. 3 and Table 3). The dihedral angles between the rings are I/II = 7.0 (1), I/III = 77.9 (1) and I/IV = 12.4 (1)°. The packing pattern of (4) is shown in Fig. 4. The dihedral angles between the rings are I/II = 14.0 (2), I/III = 36.5 (1) and I/IV = 42.9 (1)°. The host molecules in (4) are connected directly through intermolecular hydrogen bonds between N11–H11 and the N14 atom of the imidazole ring (see Fig. 4 and Table 4). These arrangements were similar to the ethyl acetate solvate crystals (Inouye *et al.*, 1999). However, (4) is centrosymmetric, while the latter is chiral. The guest benzene molecules in (4) form a column structure in the holes along the $[10\bar{1}]$ axis.

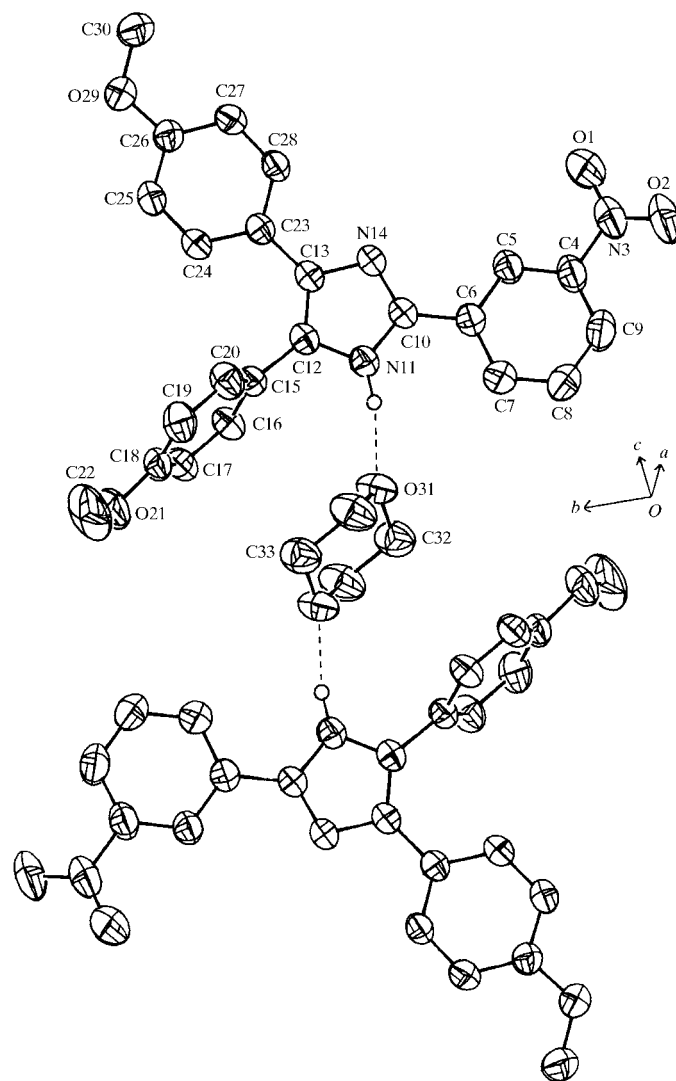


Figure 3

The molecular structure of (3) showing 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976). For clarity, only the H atom of the N–H group is included, with dashed lines showing the hydrogen bonding.

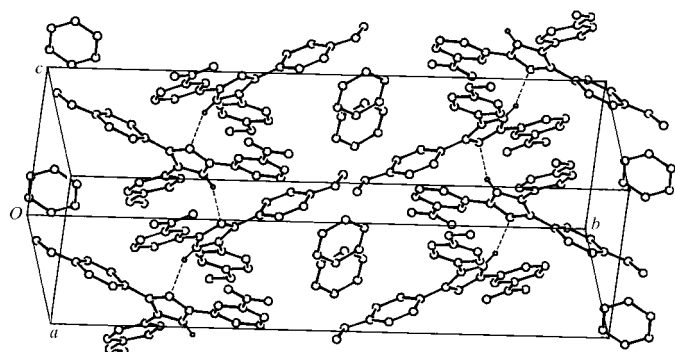


Figure 4
Packing pattern of (4) (ORTEP; Johnson, 1976), with dashed lines showing the hydrogen bonding.

Experimental

Crystals (1) to (4) were obtained from the respective solutions. Compound (1): thin red plates from ethanol; found: C 68.87, H 4.77, N 10.56%; calculated for $C_{23}H_{19}N_3O_4$: C 68.81, H 4.77, N 10.47%. Compound (2): orange needles from *tert*-butanol saturated at 353 K; found: C 68.15, H 6.12, N 8.79%; calculated for $C_{23}H_{19}N_3O_4 \cdot C_4H_{10}O$: C 68.19, H 6.16, N 8.84%. Compound (3): yellow needles from dioxane–water (3:1); found: C 67.33, H 5.16, N 9.45%; calculated for $C_{23}H_{19}N_3O_4 \cdot 0.5C_4H_8O_2$: C 67.40, H 5.20, N 9.43%. Compound (4): intense yellow needles from benzene–DMF (10:1); found: C 72.32, H 5.26, N 8.80%; calculated for $C_{23}H_{19}N_3O_4 \cdot C_6H_6$: C 72.63, H 5.26, N 8.76%.

Compound (1)

Crystal data

$C_{23}H_{19}N_3O_4$
 $M_r = 401.41$
Monoclinic, $P2_1/a$
 $a = 21.004$ (5) Å
 $b = 13.061$ (3) Å
 $c = 14.441$ (4) Å
 $\beta = 98.266$ (11)°
 $V = 3920.5$ (17) Å³
 $Z = 8$
 $D_x = 1.360$ Mg m⁻³
 $D_m = 1.34$ (2) Mg m⁻³

D_m measured by flotation
in aqueous KI solution
Mo $K\alpha$ radiation
Cell parameters from 25
reflections
 $\theta = 9.97$ – 13.77°
 $\mu = 0.095$ mm⁻¹
 $T = 293$ (2) K
Plate, red
 $0.35 \times 0.25 \times 0.04$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
12 374 measured reflections
11 950 independent reflections
3236 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.093$

$\theta_{max} = 30.50^\circ$
 $h = -29 \rightarrow 29$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 3.7%

Table 1

Hydrogen-bonding geometry (Å, °) for (1).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11A–H11A \cdots O1B ⁱ	0.87 (6)	2.30 (6)	3.135 (6)	161 (5)
N11B–H11B \cdots O1A	0.85 (6)	2.35 (7)	3.190 (7)	170 (6)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.086$
 $wR(F^2) = 0.221$
 $S = 1.067$
11 945 reflections
675 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.1751P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = -0.001$
 $\Delta\rho_{max} = 0.291$ e Å⁻³
 $\Delta\rho_{min} = -0.315$ e Å⁻³

Compound (2)

Crystal data

$C_{23}H_{19}N_3O_4 \cdot C_4H_{10}O$
 $M_r = 475.53$
Monoclinic, $P2_1/n$
 $a = 15.331$ (3) Å
 $b = 18.419$ (3) Å
 $c = 8.8318$ (14) Å
 $\beta = 97.401$ (8)°
 $V = 2473.2$ (7) Å³
 $Z = 4$
 $D_x = 1.277$ Mg m⁻³
 $D_m = 1.30$ (2) Mg m⁻³

D_m measured by flotation in aqueous KI solution
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.34$ – 13.80°
 $\mu = 0.089$ mm⁻¹
 $T = 293$ (2) K
Needle, orange
 $0.40 \times 0.20 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
7957 measured reflections
7523 independent reflections
3296 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.030$

$\theta_{max} = 30.47^\circ$
 $h = -21 \rightarrow 21$
 $k = 0 \rightarrow 26$
 $l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 3.5%

Table 2

Hydrogen-bonding geometry (Å, °) for (2).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11–H11 \cdots O31	0.90 (4)	2.08 (4)	2.915 (4)	155 (3)
O31–H31 \cdots N14 ⁱ	0.90 (4)	2.09 (6)	2.930 (4)	156 (5)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.193$
 $S = 0.869$
7523 reflections
377 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1826P)^2 + 0.6023P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = -0.001$
 $\Delta\rho_{max} = 0.231$ e Å⁻³
 $\Delta\rho_{min} = -0.235$ e Å⁻³

Compound (3)

Crystal data

$C_{23}H_{19}N_3O_4 \cdot 0.5C_4H_8O_2$
 $M_r = 445.46$
Triclinic, $P\bar{1}$
 $a = 9.510$ (2) Å
 $b = 13.236$ (4) Å
 $c = 9.168$ (2) Å
 $\alpha = 104.651$ (13)°
 $\beta = 92.624$ (15)°
 $\gamma = 85.83$ (2)°
 $V = 1113.1$ (5) Å³
 $Z = 2$
 $D_x = 1.329$ Mg m⁻³

$D_m = 1.32$ (2) Mg m⁻³
 D_m measured by flotation in aqueous KI solution
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 11.40$ – 13.78°
 $\mu = 0.094$ mm⁻¹
 $T = 293$ (2) K
Plate, yellow
 $0.40 \times 0.40 \times 0.10$ mm

Table 3
Hydrogen-bonding geometry (Å, °) for (3).

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...O31	0.93 (2)	1.96 (2)	2.878 (2)	168 (2)

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
7159 measured reflections
6768 independent reflections
4190 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

$\theta_{\text{max}} = 30.49^\circ$
 $h = -13 \rightarrow 13$
 $k = -18 \rightarrow 18$
 $l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 0.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.139$
 $S = 1.061$
6768 reflections
377 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2 + 0.2048P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.243 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.229 \text{ e \AA}^{-3}$

Compound (4)

Crystal data

$\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_4 \cdot \text{C}_6\text{H}_6$
 $M_r = 479.52$
Monoclinic, $P2_1/c$
 $a = 9.614 (2) \text{ \AA}$
 $b = 29.011 (5) \text{ \AA}$
 $c = 8.984 (2) \text{ \AA}$
 $\beta = 91.933 (10)^\circ$
 $V = 2504.3 (9) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.272 \text{ Mg m}^{-3}$
 $D_m = 1.25 (2) \text{ Mg m}^{-3}$

D_m measured by flotation in aqueous KI solution
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 11.34\text{--}13.78^\circ$
 $\mu = 0.086 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
Needle, intense yellow
 $0.40 \times 0.40 \times 0.30 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
7687 measured reflections
7270 independent reflections
3320 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 29.96^\circ$
 $h = -13 \rightarrow 13$
 $k = 0 \rightarrow 40$
 $l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 0.9%

Table 4
Hydrogen-bonding geometry (Å, °) for (4).

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...N14 ⁱ	0.92 (4)	2.06 (4)	2.933 (3)	158 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.191$
 $S = 0.941$
7258 reflections
379 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1839P)^2 + 0.8562P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.235 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.282 \text{ e \AA}^{-3}$

Disorder is found in (1) and (4). In (1), one of the methoxyphenyl rings (C15B–C22B:C15C–C22C = 0.54:0.46) and O2B and O2C (0.54:0.46) in molecule *B* were disordered and treated under the constraints that corresponding bond lengths in both conformations were similar to each other within an s.u. of 0.01 Å. C15C to C22C were refined isotropically. In (4), the guest benzene molecules (C31A–C36A:C31B–C36B = 0.70:0.30) were disordered and treated as ideal hexagons (C–C = 1.390 and C–H = 0.93 Å with *U*'s of H atoms being set at 1.2 times those of the attached non-H atoms). C31B to C36B were refined isotropically. The positions of aromatic H, NH and OH were refined in the final calculations. The methyl H atoms were calculated geometrically (C–H = 0.96 Å and *U*'s were set at 1.5 times those of the attached non-H atoms).

For all compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1099). Services for accessing these data are described at the back of the journal.

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