5:1 and 2:1 cocrystals of 2,3,4,5,6-pentafluorophenol with phenazine

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2,3,4,5,6-Pentafluorophenol (pFp), unlike phenol, forms cocrystals with the weak heteroaromatic base phenazine (phz). Two types of cocrystals were prepared, (I) with a high content of pFp, 2,3,4,5,6-pentafluorophenol–phenazine (5/1), $5C_6HF_5O\cdot C_{12}H_8N_2$, and (II) with a 2:1 pFp–phz molar ratio, 2,3,4,5,6-pentafluorophenol–phenazine (2/1), $2C_6HF_5O\cdot C_{12}H_8N_2$. In both forms, homostacks are formed by the heterocyclic base and phenol molecules and no aryl–perfluoroaryl stacking interactions occur. The arrangement of the molecules in the crystal of (I) is determined by strong O—H$\cdots$N and O—H$\cdots$O hydrogen bonds, weak O—H$\cdots$F, C—H$\cdots$F and C—H$\cdots$O interactions, π–π stacking interactions between the phz molecules and C—F$\cdots\pi_F$ interactions within the pFp stacks. Among the specific interactions in (II) are a strong O—H$\cdots$N hydrogen bond, weak C—H$\cdots$F interactions and π–π stacking interactions between the phz molecules. In (I) and (II), the heterocyclic molecules are located around inversion centres and one of the symmetry-independent pFp molecules in (I) is disordered about an inversion centre. Remarkably, similar structural fragments consisting of six pFp stacks can be identified in cocrystal (I) and in the known orthorhombic polymorph of pFp with $Z' = 3$ [Gdaniec (2007). *CrystEngComm*, **9**, 286–288].

Comment

Phenazine (phz), a diaza-aromatic weak base, is considered to be a good supramolecular substrate as it can easily form complexes *via* metal coordination, hydrogen bonding and halogen bonding. The recognition process of phz can also occur *via* the use of weaker interactions involving its aromatic π system and C—H groups, thus making prediction of the stoichiometry and packing mode of its complexes more difficult. This fact is best illustrated by the molecular complexes formed by phz with polyphenols. Cocrystallization of phz with hydroquinone (HQ) and naphthalene-1,5-diol affords crystals in a 2:1 molar ratio, and cocrystals of stoichiometry 3:1 are formed with biphenyl-4,4′-diol (Thalladi *et al.*, 2000), *i.e.* the stoichiometry of these cocrystals does not conform with simple considerations of the hydrogen-bond requirements of the

cocrystal components. In turn, with phloroglucinol (phl), three nonsolvated crystalline forms with phz–phl molar ratios of 2:1, 7:4 and 3:2 are obtained (Sarma *et al.*, 2008), and only in this last cocrystal are the numbers of donor O—H groups and N-atom acceptors balanced. Importantly, all the above cocrystals share similar structural features, namely that the main network is constructed from phz stacks and that the phenolic molecules are accommodated in channels, where they interact with phz by O—H$\cdots$N hydrogen bonds, weak nonclassical hydrogen bonds and edge-to-face aromatic interactions.

Edge-to-face interactions are of primary importance in the formation of these channel-type structures (Thalladi *et al.*, 2000; Kadzewski & Gdaniec, 2006). Altering these interactions by lowering the electron density of the aromatic ring of the diphenol, through the exchange of C—H groups with C—F groups, destroys this channel-type structural motif and promotes the formation of mixed π-stacks (Czapik & Gdaniec, 2010), by analogy with the robust Ar–Ar^F packing motif found in arene–perfluoroarene systems (Collings *et al.*, 2002, and references therein).

Structural and chemical information related to cocrystallization of phz with polyphenols is abundant in the literature. However, no information is available on cocrystallization attempts with phenol itself. As our crystallization efforts revealed, this is most probably due to the negative outcome of these experiments, as we too were unable to cocrystallize these two compounds, despite numerous trials and a variety of applied conditions. Instead, we were more successful with 2,3,4,5,6-pentafluorophenol (pFp), which is 4.5 pK_a units more acidic than phenol (pK_a = 5.50 for pFp *versus* 9.95 for phenol), and we obtained two types of pFp–phz cocrystals with component ratios 5:1, (I), and 2:1, (II). Form (I), which is highly unstable in air, was obtained when phenazine was dissolved in molten pFp (m.p. 305 K), or from an *n*-heptane solution containing phz and a large excess of pFp. The stable form, (II), was obtained when phz and pFp were dissolved in *n*-heptane in a 1:2 molar ratio. When crystals of (I) were immersed in a drop of perfluoropolyether (PFO-XR75, Lancaster Synthesis), slow growth of (II) on the crystals of (I) was observed, with a complete transformation occurring overnight. The identification of the crystals formed after this transformation as form (II) was established by the measurement of the unit-cell parameters for a few single crystals resulting from the transformation.

(I) X = 5
(II) X = 2
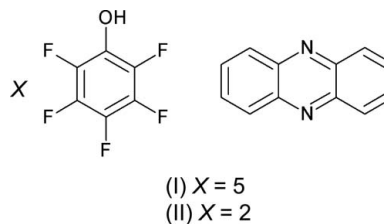
The molecular structure of the components of cocrystal (I) and the atom-numbering scheme are shown in Fig. 1. The asymmetric unit of (I) consists of one-half of the centrosymmetric phz molecule and 2.5 molecules of pFp, labelled *A*, *B*

organic compounds
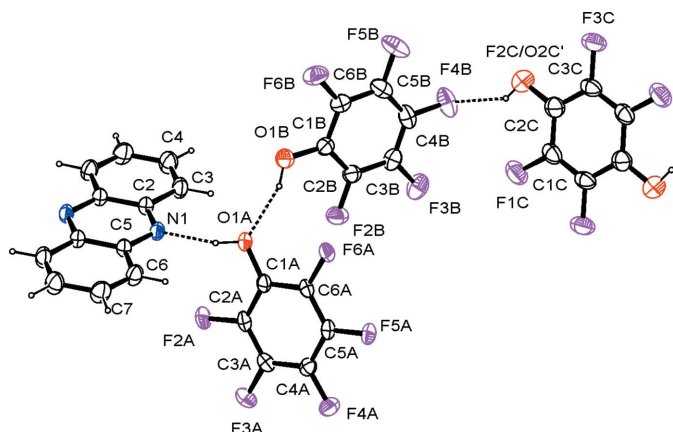
Figure 1
The components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and only atoms in the asymmetric unit are labelled. Disorder in molecule C is represented by two labels (F2C/O2C') given for one atomic position.

Figure 2
The crystal packing of (I), viewed along the b axis. O, F and N atoms are represented as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

and C. The pFp C molecule is disordered about an inversion centre in such a manner that atoms O2C' and F2C from the two disordered components are overlapping (Fig. 1). Identification of the OH group of the disordered pFp molecule was based mostly on molecular geometric features, namely it was expected that the endocyclic angle at the C atoms attached to the electron-donating OH group would be less than 120° (Domenicano *et al.*, 1975). As the C1C—C2C—C3C angle of 119.21 (19)° is significantly smaller than the remaining two angles [C1C—C3C—C2C^i = 120.32 (18)° and C3C—C1C—C2C^i = 120.47 (19)°; symmetry code: (i) $-x + 1, -y + 2, -z + 1$], it was concluded that the OH group is attached to atom C2C. In turn, analysis of the intermolecular contacts of the disordered pFp molecule indicated atoms C2C or C1C as the possible substitution sites. The two short intermolecular F1C···F3A($-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$) and F2$C$···F4$B$ contacts of 2.791 (2) and 2.948 (2) Å, respectively, might represent an O—H···F interaction. However, the latter, longer, contact appears to be more indicative of a generally weak O—H···F hydrogen bond, as the low propensity of organic fluorine to participate in classical hydrogen bonding is nowadays well recognized (Reichenbächer *et al.*, 2005, and references therein). Location of the OH group in the remaining two pFp molecules was straightforward and confirmed by the analysis of pFp molecular geometry and intermolecular interactions.

The crystal packing of (I), viewed along the b axis, is shown in Fig. 2. The phz molecules are arranged *via* π–π interactions into stacks that are completely surrounded by eight stacks formed separately by the three symmetry-independent pFp molecules. All the stacks extend along [010] and the distance between the benzene ring centroids for all pFp stacks is 4.5223 (2) Å, *i.e.* equal to unit-cell parameter b. Such a large value of the centroid-to-centroid distance points to a scant overlapping of the pFp aromatic π-systems and thus to a significant slipping of these molecules within the stacks. To optimize the electrostatic interactions, the F atoms are located above and below the electron-deficient aromatic ring of pFp,
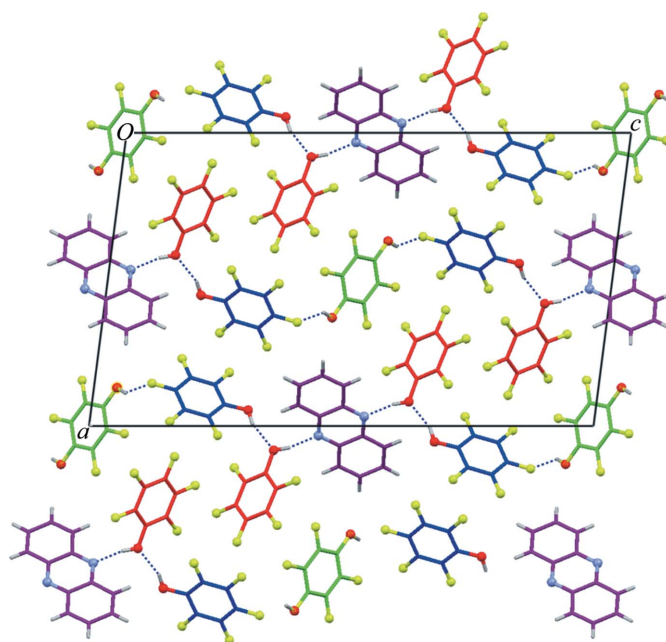
with C—F···Cg distances in the range 3.264–3.309 Å for stacks composed of pFp molecules A and C, and 3.502–3.515 Å for stacks of B molecules. The stacks formed by phz molecules are also slipped, although in this case the slipping leads to an overlap of the π-systems of the electron-deficient pyrazine fragment and the electron-rich benzene fragment, with a centroid–centroid distance of 3.791 Å. However, the slipping of phz molecules in the stack is too small to expose one of the phz benzene rings to aryl–perfluoroaryl interactions, and the Ar–Ar^F synthon is not observed in (I). Strong O—H···N and O—H···O hydrogen bonds connect the phz molecules and pFp molecules A and B into centrosymmetric heteropentamers, with A molecules acting as donors in an O—H···N interaction and as acceptors in an O—H···O hydrogen bond (Table 1 and Fig. 2). Molecule A, which forms a dihedral angle of 72.25 (8)° with the phz molecule, is additionally involved in a C—H···F interaction with another phz molecule (Table 1), thus bridging two neighbouring molecules in the phz stack. Each of the phz C—H groups forms a short contact with the electronegative O or F atoms of the pFp molecules (Table 1).

Owing to the high pFp content in the phz–pFp (5/1) cocrystal, (I), we decided to check whether any similar structural motif could be identified between the crystal packing of pFp molecules in this cocrystal and in the polymorphic forms of pFp. In fact, as shown in Fig. 3, in the orthorhombic $P2_12_12_1$ pFp polymorph (Gdaniec, 2007), which like (I) contains three symmetry-independent molecules, a group of six pFp stacks with an arrangement strongly resembling that of the six stacks in (I) can be identified. The stacks in the orthorhombic polymorph are slightly more slipped than in (I), as the distance between the benzene ring centroids
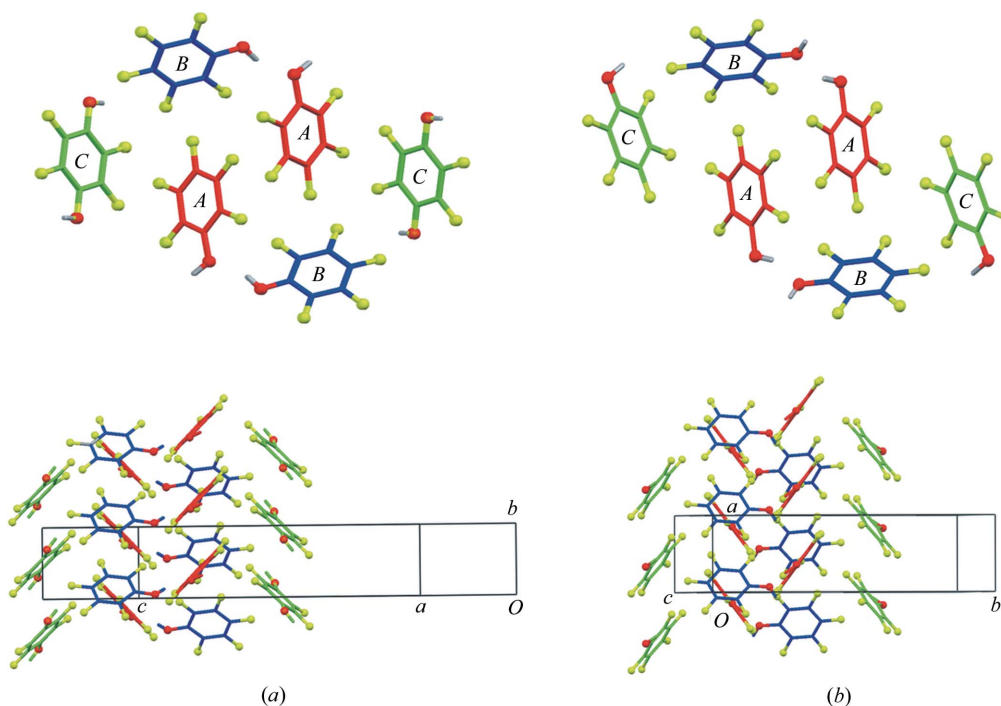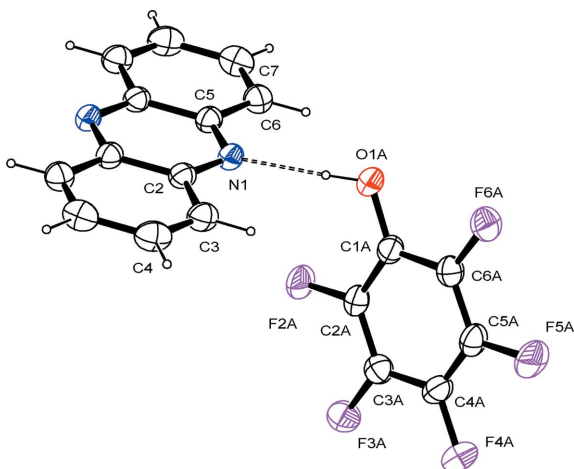
Figure 3
The similar fragments of the crystal structures, consisting of six stacks of pFp molecules, in (a) (I) and (b) the orthorhombic polymorph (Gdaniec, 2007).

increases to 5.1398 (9) Å, *i.e. ca* 0.6 Å longer than in cocrystal (I). The arrangement of these stacks is mostly directed by close-packing forces and not by strong intermolecular inter-actions, as the helical hydrogen-bond motif observed in the orthorhombic polymorph of pFp is no longer present in (I), and the O—H···O interactions join only two pairs of stacks within this hexameric stack cluster.

The molecular structure of the molecules in (II) is shown in Fig. 4. The asymmetric unit of this (2/1) cocrystal consists of one-half of a phz molecule and one pFp molecule. The crystal components are connected into discrete heterotrimers *via* O—H···N hydrogen bonding (Table 2 and Fig. 5), and the stoi-

chiometry of (II) agrees with that predicted from hydrogen-bonding considerations. The O—H···N hydrogen bond between the phenol molecule and the heteroaromatic base is longer in (II) than in (I), probably reflecting the absence of a co-operative effect on hydrogen bonding in the former. Nevertheless, the geometry of the O1A—H1A···N1 inter-action in both cocrystals is within the range of hydrogen bonds formed by phz with strong carboxylic and dihalogenoanilic acids (Pedireddi *et al.*, 1996; Senthil Kumar *et al.*, 2002; Gdaniec & Połoński, 2007; Gotoh *et al.*, 2007; Kumai *et al.*, 2007). As in (I), the phz molecules in (II) are arranged into π-stacks extending along the *a* axis and are completely surrounded by stacks of pFp molecules (Fig. 5). The dihedral

Figure 4
The components of (II), showing the atom-numbering scheme. Displace-ment ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Only atoms in the asymmetric unit are labelled.
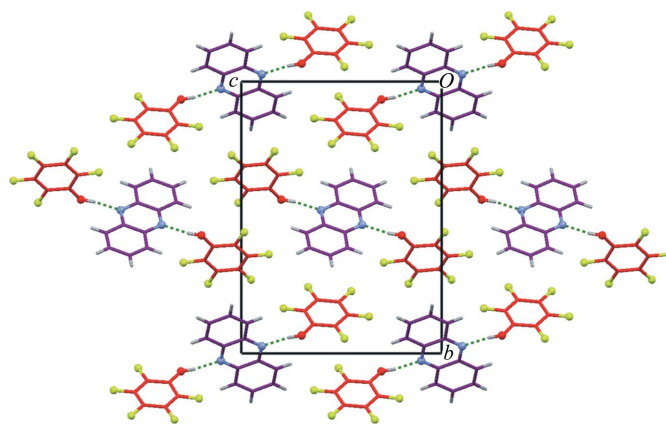
Figure 5
The crystal packing of (II), viewed along the *a* axis. O, F and N atoms are represented as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

angles formed between the mean planes of the phz molecules and those of the pFp molecules in adjacent stacks are 83.48 (3) and 4.49 (8)°, respectively, with the pFp molecules in the latter case being virtually coplanar with the heteroaromatic base. In effect, the crystal structure of (II) can be seen as composed of slightly corrugated (001) molecular layers, themselves composed of nearly parallel aromatic molecules (Fig. 5), with face-to-face stacking interactions arranging the heterocyclic molecules into homostacks and C—H···F interactions directing the packing of pFp molecules relative to phz. As in (I), the Ar–Ar^F stacking synthon is not observed in this cocrystal, as the closest distance between the centroids of the fluorinated phenyl ring and the phz benzene ring is *ca* 4.597 Å.

In summary, in the 5:1 and 2:1 cocrystals formed by pFp and phz, each heterocyclic molecule is linked *via* strong O—H···N hydrogen bonds to two pFp molecules strongly inclined to the phz mean plane. The pFp and phz molecules form separate strongly slipped stacks and no aryl–perfluoroaryl interactions are observed. The absence of the Ar–Ar^F stacking synthon in the two crystalline forms is quite unexpected, given that this robust synthon is present in cocrystals formed by 2,3,5,6-tetrafluorohydroquinone with phz and quinoxaline (Czapik & Gdaniec, 2010), and in 1:1 cocrystals formed by phz with pentafluoroiodobenzene *via* C—I···N halogen bonds (Cinčić *et al.*, 2008).

Experimental

Phenazine (phz) and 2,3,4,5,6-pentafluorophenol (pFp) were purchased from Aldrich. Yellow rhomboid cocrystals of (I) were obtained by dissolving phz in molten pFp or by adding phenazine to a solution of a ten molar excess of pFp in *n*-heptane. Needle-shaped crystals of the more stable form, (II), were obtained from an *n*-heptane solution containing phz and pFp in a 1:2 molar ratio. Form (II) was also obtained by slow decomposition of (I).

Compound (I)

Crystal data

$5C_6HF_5O \cdot C_{12}H_8N_2$	$V = 1984.35 (15)$ Å^3
$M_r = 1100.54$	$Z = 2$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
$a = 16.1015 (7)$ Å	$\mu = 1.82$ mm^{-1}
$b = 4.5223 (2)$ Å	$T = 130$ K
$c = 27.4753 (12)$ Å	$0.2 \times 0.05 \times 0.03$ mm
$\beta = 97.315 (4)°$	

Data collection

Oxford SuperNova diffractometer	13006 measured reflections
Absorption correction: multi-scan	4098 independent reflections
(*CrysAlis PRO*; Oxford	3460 reflections with $I > 2\sigma(I)$
Diffraction, 2009)	$R_{int} = 0.035$
$T_{min} = 0.671$, $T_{max} = 1.000$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of
$wR(F^2) = 0.115$	independent and constrained
$S = 1.08$	refinement
4098 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
342 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···N1	0.89 (3)	1.79 (3)	2.6693 (18)	167 (3)
O1B—H1B···O1A	0.84 (3)	1.93 (3)	2.7358 (19)	159 (3)
O2C'—H1C···F4B	0.85	2.21	2.948 (2)	146
C6—H6···F2A^i	0.95	2.37	3.209 (2)	147
C7—H7···F2C/O2C^{ii}	0.95	2.49	3.350 (2)	151
C4—H4···F5B^{iii}	0.95	2.52	3.349 (2)	145
C4—H4···O1B^{iv}	0.95	2.70	3.199 (2)	114
C3—H3···O1B^{iv}	0.95	2.62	3.158 (2)	116

Symmetry codes: (i) $x, y + 1, z$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y - \frac{3}{2}, -z + \frac{1}{2}$; (iv) $x, y - 1, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···N1	0.88 (3)	1.85 (3)	2.7192 (18)	172 (3)
C4—H4···F5A^i	0.95	2.54	3.441 (2)	158
C6—H6···F2A^{ii}	0.95	2.47	3.276 (2)	142

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

Compound (II)

Crystal data

$2C_6HF_5O \cdot C_{12}H_8N_2$	$V = 1062.03 (10)$ Å^3
$M_r = 548.34$	$Z = 2$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
$a = 4.9045 (3)$ Å	$\mu = 1.53$ mm^{-1}
$b = 17.1342 (10)$ Å	$T = 130$ K
$c = 12.6397 (6)$ Å	$0.4 \times 0.02 \times 0.02$ mm
$\beta = 90.931 (5)°$	

Data collection

Oxford SuperNova diffractometer	10876 measured reflections
Absorption correction: multi-scan	2186 independent reflections
(*CrysAlis PRO*; Oxford	1939 reflections with $I > 2\sigma(I)$
Diffraction, 2009)	$R_{int} = 0.039$
$T_{min} = 0.366$, $T_{max} = 1.000$	Standard reflections: 0

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of
$wR(F^2) = 0.126$	independent and constrained
$S = 1.11$	refinement
2186 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
176 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}

H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.95 Å, and were refined as riding on their carrier atoms, with U_{iso}(H) = $1.2U_{eq}$(C). The H atoms of the O—H groups, except for H2C in (I), were located in electron-density difference maps and freely refined. In (I), atoms O2C and F2C were given an occupancy of 0.5 and refined as having identical coordinates and displacement parameters. Atom H2C was located in an electron-density difference map and the O2C—H2C distance constrained to 0.85 Å. It was refined as riding on O2C, with U_{iso}(H) = $1.2U_{eq}$(O).

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows*

(Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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