

p-Phenylenediamine and its dihydrate: two-dimensional isomorphism and mechanism of the dehydration process, and N—H···N and N—H··· π interactions

Agnieszka Czapiak, Hanna Konowalska and Maria Gdaniec*

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland
Correspondence e-mail: magdan@amu.edu.pl

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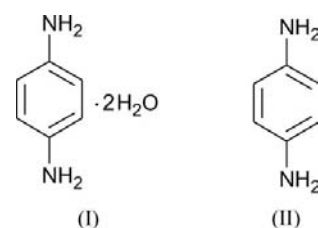
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p-Phenylenediamine can be obtained as the dihydrate, C₆H₈N₂·2H₂O, (I), and in its anhydrous form, C₆H₈N₂, (II). The asymmetric unit of (I) contains one half of the *p*-phenylenediamine molecule lying about an inversion centre and two halves of water molecules, one lying on a mirror plane and the other lying across a mirror plane. In (II), the asymmetric unit consists of one molecule in a general position and two half molecules located around inversion centres. In both structures, the *p*-phenylenediamine molecules are arranged in layers stabilized by N—H··· π interactions. The diamine layers in (I) are isostructural with half of the layers in (II). On dehydration, crystals of (I) transform to (II). Comparison of their crystal structures suggests the most plausible mechanism of the transformation process which requires, in addition to translational motion of the diamine molecules, in-plane rotation of every fourth *p*-phenylenediamine molecule by *ca* 60°. A search of the Cambridge Structural Database shows that the formation of hydrates by aromatic amines should be considered exceptional.

Comment

p-Phenylenediamine is a popular reagent in organic and coordination chemistry. This compound is quite soluble in water but is generally known in its anhydrous form. In the course of our work on cocrystal formation by aromatic diamines, aminophenols and diphenols, the previously unknown hydrated form of *p*-phenylenediamine emerged. To check whether formation of a hydrate by *p*-phenylenediamine can be considered exceptional among aromatic amines, recrystallizations of the two other phenylenediamine isomers from water have been carried out, always resulting in the known anhydrous form. The crystal structures of the three (*o*-, *m*- and *p*-) anhydrous phenylenediamines have already been

published (Betz *et al.*, 2008; Poveteva & Zvonkova, 1975; Stalhandske, 1981), with two of them, the *meta* (Betz *et al.*, 2008) and *para* (Poveteva & Zvonkova, 1975; Colapietro *et al.*, 1985) isomers, showing high-*Z'* structures. The above observations prompted us to take a closer look at the structures of primary aromatic amines deposited in the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002) and to analyse them from the point of view of hydrate formation. This paper, in addition to the crystal structure of *p*-phenylenediamine dihydrate, (I), reports the redetermination of the crystal structure of *p*-phenylenediamine, (II), at 130 K to provide more accurate positions of the amino H atoms.



The numbering scheme for (I) is shown in Fig. 1. The asymmetric unit contains one half of the *p*-phenylenediamine molecule, which is located around an inversion centre, and two halves of the water molecules. One water molecule has all its atoms on a mirror plane, whereas the other molecule lies across a mirror plane. The endocyclic bond angle at C1 of 118.17 (11)° is consistent with the electron-withdrawing character of the amino group. The water molecules are linked *via* O—H···O interactions into a C4 chain (Infantes & Motherwell, 2002), with one water molecule acting as a double donor and the other as a double acceptor of hydrogen bonding. *p*-Phenylenediamine molecules bridge these water chains by involving their amino groups as single donors and single acceptors in hydrogen bonding (Fig. 2*a* and Table 1). All these interactions generate a two-dimensional network of hydrogen

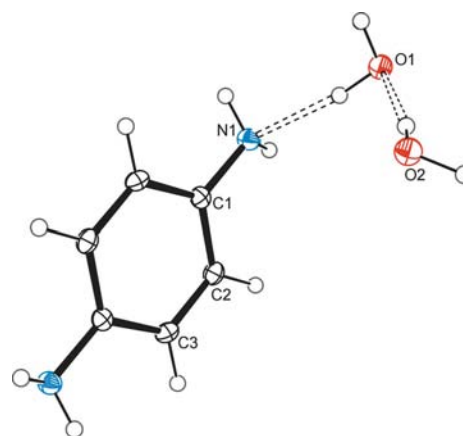
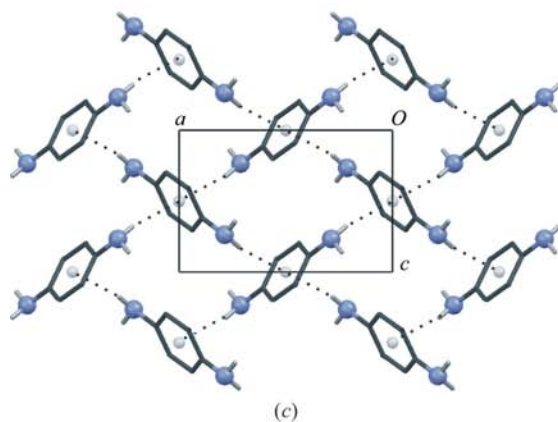
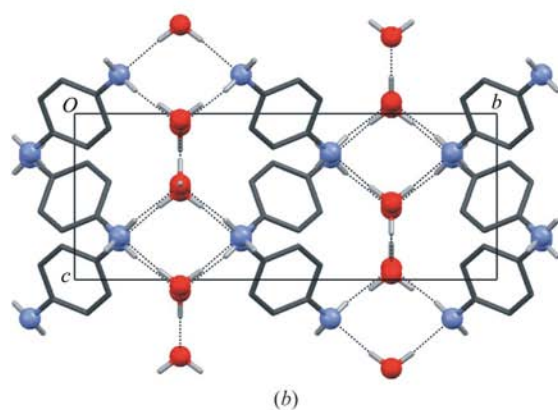
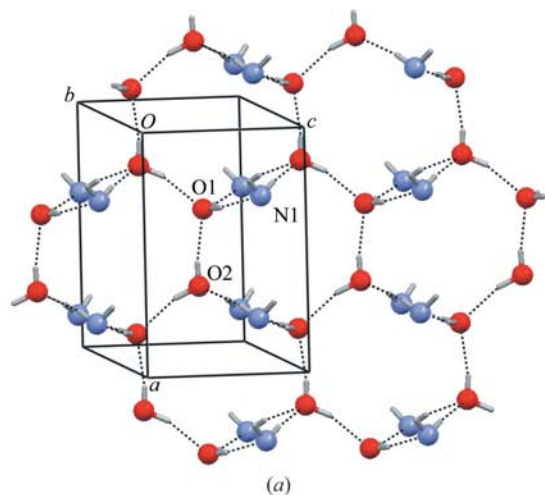
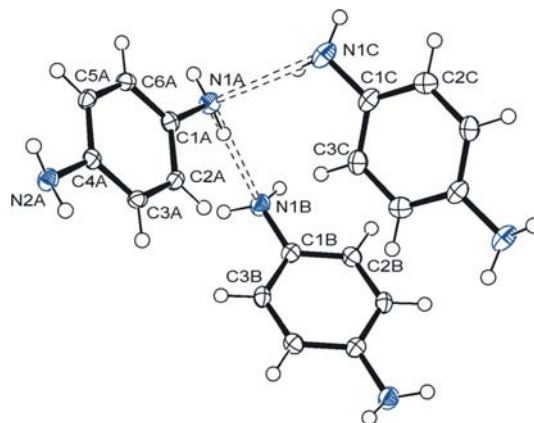


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the symmetry-unique atoms are labelled (water O atoms lie on mirror planes). Hydrogen bonds are shown as dashed lines.

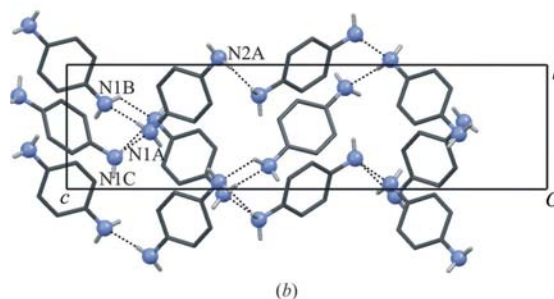
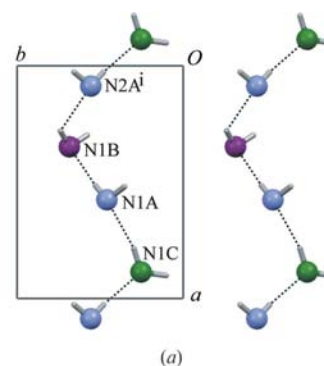
**Figure 2**

(a) The two-dimensional hydrogen-bond network of (I) formed by water molecules and primary amino groups (the ring atoms have been omitted for clarity). Hydrogen bonds are shown as dotted lines. (b) A projection of the crystal structure along the *a* axis. (c) N—H $\cdots\pi$ interactions in the (010) layers of *p*-phenylenediamine molecules.

bonds parallel to (010) and a three-dimensional network of hydrogen-bonded molecules (Fig. 2b). The *p*-phenylenediamine molecules in (I) are arranged in a herringbone motif into (010) layers. The amino H atom not involved in strong interactions with the water molecules forms an N—H $\cdots\pi$ interaction with an adjacent benzene ring, with an H $\cdots\pi$ distance of 2.48 (2) Å. Each benzene ring accepts two such interactions (Fig. 2c). It should be emphasized here that there

**Figure 3**

The molecular 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. Only the symmetry-equivalent atoms are labelled. Hydrogen bonds are shown as dashed lines.

**Figure 4**

(a) Chains of hydrogen bonds formed by primary amino groups (the ring atoms have been omitted for clarity) in (II). Hydrogen bonds are shown as dotted lines. (b) A projection of the crystal structure along the *a* axis. [Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.]

is no direct hydrogen-bond interaction between the amino groups in (I). The crystals of (I) are unstable and in air they lose the water molecules and are transformed into the known anhydrous form of *p*-phenylenediamine; this was confirmed by powder diffractograms of a partially decomposed sample of (I).

The asymmetric unit of (II) contains one molecule in a general position (molecule *A*) and two halves of *p*-phenylenediamine molecules located on two different sets of inversion centres (molecules *B* and *C*) (Fig. 3). The endocyclic bond angles at atoms C1A, C4A, C1B and C1C are all significantly

smaller than 120° [$117.57(10)$ – $118.04(10)^\circ$] and the C–N bond lengths are in the range $1.4065(13)$ – $1.4151(14)$ Å. The four symmetry-independent primary amino groups are connected *via* N–H···N hydrogen bonds into a polymeric chain extending along [100] (Table 2 and Fig. 4*a*), with each amino group acting as a single donor and a single acceptor in the hydrogen bonding. These N–H···N interactions generate a three-dimensional network of *p*-phenylenediamine molecules (Fig. 4*b*). An alternative depiction of the crystal structure of (II) shows it to be composed of a set of two different (001) molecular layers, one layer composed solely of *A* molecules and the second layer composed of centrosymmetric *B* and *C* molecules. The metric parameters of these layers [$a = 8.3020(2)$ Å, $b = 5.8970(1)$ Å and $\gamma = 90^\circ$] resemble those of the (010) layers in (I) [$a = 8.8599(8)$ Å, $c = 5.8952(4)$ Å and $\beta = 90^\circ$], and closer inspection of the two structures reveals that the layers of *A* molecules in (II) are virtually isostructural with the (010) layers of *p*-phenylenediamine molecules in (I), with the aromatic systems accepting two N–H··· π interactions (Table 2). The layers of *B* and *C* molecules have a different structure, with the benzene ring of the *C* molecules accepting two N–H··· π interactions from the N–H group of the *B* molecule, whereas the aromatic system of *B* is not involved in this type of interaction.

As indicated above, the dehydration process of (I) results in form (II) of *p*-phenylenediamine. Taking into account the extent of the structural similarities between the two crystalline forms, we suggest a mechanism of transformation between the hydrated and anhydrous forms. In the most plausible mechanism that we can propose, the structure of every second (010) layer of *p*-phenylenediamine molecules in (I) remains unaltered by the dehydration process. When water molecules start to leave the crystal, hydrogen bonds are broken and the amino groups ‘seek’ new donors and acceptors among the primary amino groups located on the surface of a neighbouring layer. The hydrogen-bond network of (I) cannot be fully reconstructed, as the number of NH₂ groups on the surface of the neighbouring layer is half the number of water molecules located in the interlayer space, and the acceptor–donor abilities of a primary amino group are different from those of water molecules. The proposed mechanism of dehydration of (I) is illustrated in Fig. 5. When the dehydration process begins, the stacks of *B* molecules running along the *a* axis move in the direction indicated by the arrow in Fig. 5 to replace two water molecules in a chain of hydrogen bonds with their NH₂ group. Because each water molecule occupies a special position of multiplicity 2 in the crystal structure, stoichiometrically this means a substitution of one water molecule per one amino group. This movement is accompanied by a concerted reorientation of the *C* molecules also arranged into stacks along the *a* axis. All *C* molecules within one stack rotate in the same direction by *ca* 60° around the axis approximately perpendicular to their aromatic ring plane. On this rearrangement, their NH₂ groups replace another pair of water molecules and a polymeric chain of N–H···N hydrogen bonds is formed, extending along the *a* axis and incorporating all amino groups as single donors and single acceptors. This

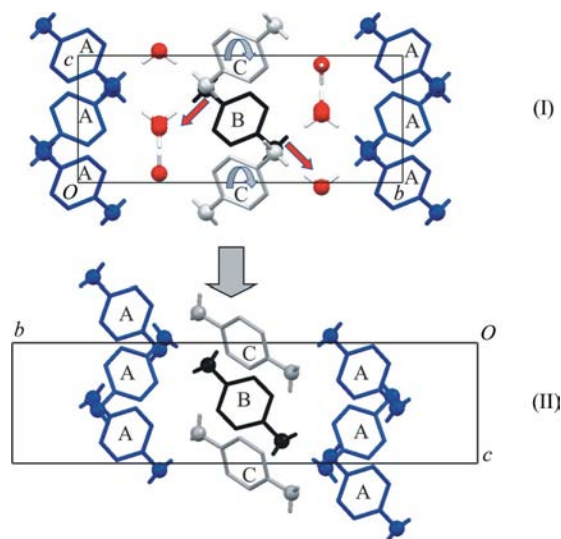


Figure 5

The proposed mechanism for the transformation of (I) into (II). One set of arrows show the direction of rotation of the *C* molecules, and the other set indicates pairs of water molecules replaced by the amino groups of the *B* molecules.

mechanism requires substantial rearrangement of only 25% of the amine molecules in the crystal structure, whereas the remaining 75% of molecules undergo mainly translational motion. The above transformation should be seen as a cooperative structure reconstruction, with both events, *viz.* translation and rotation of the diamine molecules, occurring at the same time.

In recent years, several papers dealing with the factors responsible for the formation of organic crystal hydrates have been published (Infantes & Motherwell, 2002; Infantes *et al.*, 2003, 2007). The formation of the hydrate by *p*-phenylenediamine should be considered rather exceptional in the light of our survey of the CSD, which gave 80 structures of compounds with at least one primary amino group and with only C and H atoms in the remaining part of the molecule [$C_nH_m(NH_2)_x$]. Among these structures, 48 were formed by aromatic, 27 by aliphatic and four by vinyl amines, and one by a mixed aromatic/aliphatic amine. The same search requesting additionally the presence of a water molecule in the crystal structure gave 23 hydrates but only one of them was formed by an aromatic amine, with one molecule of water included per three tetraamine molecules (CSD refcode RARROS; Laliiberté *et al.*, 2005). The search shows that inclusion of water molecules in the crystal structures of primary aromatic mono- and polyamines is less feasible than in the case of their aliphatic analogues.

It is well known that both aliphatic and aromatic primary amines cocrystallize easily with a variety of mono- and dialcohols (Ermer & Eling 1994; Hanessian *et al.*, 1994; Loehlin *et al.*, 1998; Loehlin & Okasako, 2007), as predicted from the saturated hydrogen-bond principle introduced by Ermer & Eling (1994). In the complementary alcohol/amine system, the total number of donor H atoms matches the number of acceptor lone pairs, whereas primary amines alone show an excess of donor H atoms and a deficit of hydrogen-

bond acceptors. The inclusion of self-complementary water molecules into the amine crystal structure leaves the unfavourable balance of donors and acceptors unchanged. However, on inclusion of water molecules into the crystal structures of aliphatic primary amines, stronger O—H···N and N—H···O hydrogen bonds can be formed substituting for weaker N—H···N interactions, and thus the enthalpic factor starts to play a promoting role in hydrate formation. In turn, primary aromatic amines are weak bases and have lower proton affinity. Thus, to accept a hydrogen bond their amine N atom has to adopt an sp^3 hybridization at the expense of the conjugation energy of its lone pair with the aromatic ring π -system. Moreover, in aromatic amines the ratio of hydrogen-bond donors to acceptors is improved compared with aliphatic amines, as an aromatic ring with its electron-donating amine substituents becomes almost as good a hydrogen-bond accepting group as the aromatic amino group. Analysis of the intermolecular interactions in 48 aromatic amine structures in the CSD shows that N—H··· π interactions are abundant and often competitive with respect to N—H···N hydrogen bonding. For example, 19 of the analysed structures show no N—H···N interactions, whereas only three of them do not have any short N—H··· π contacts. By way of contrast, there is only one early structure (CSD refcode MTOLID; Fowweather, 1952) where N—H···N hydrogen bonds can be postulated but no N—H··· π interactions are possible, considering the arrangement of molecules within the crystal structure.

In the case of the anhydrous form of *p*-phenylenediamine, (II), only one N—H group of the four symmetry-independent NH₂ substituents is not involved in any of the specific interactions discussed above. However, cocrystallization of *p*-phenylenediamine with water molecules not only allows this molecule to adopt the packing mode in which stronger O—H···O, O—H···N and N—H···O interactions replace weaker N—H···N hydrogen bonds, but also all donors and all acceptors, including the electron-rich aromatic π system, contribute to the crystal stabilization energy. In our opinion, this is the explanation for this unusual case of hydrate formation by an aromatic amine.

Experimental

The hydrated form, (I), was obtained by slow evaporation of an aqueous solution of *p*-phenylenediamine to give large colourless tabloid crystals. The crystal used for X-ray measurements was pale-pink and was obtained serendipitously during the cocrystal screening. Crystals of (II) were obtained by evaporation of an ethanol–chloroform mixture.

Compound (I)

Crystal data

C ₆ H ₈ N ₂ ·2H ₂ O	$V = 784.76$ (11) Å ³
$M_r = 144.18$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 8.8599$ (8) Å	$\mu = 0.09$ mm ⁻¹
$b = 15.0248$ (14) Å	$T = 130$ K
$c = 5.8952$ (4) Å	$0.5 \times 0.4 \times 0.2$ mm

Data collection

Kuma KM-4 CCD κ -geometry diffractometer	3790 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	830 independent reflections
$T_{\min} = 0.929$, $T_{\max} = 0.980$	662 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	75 parameters
$wR(F^2) = 0.086$	All H-atom parameters refined
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.17$ e Å ⁻³
830 reflections	$\Delta\rho_{\text{min}} = -0.17$ e Å ⁻³

Table 1

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

Cg is the centroid of the aromatic ring.

<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>
N1—H1N1···O2 ⁱ	0.877 (16)	2.153 (17)	3.0120 (14)	166.1 (13)
O1—H1O1···N1 ⁱⁱ	0.894 (17)	1.978 (17)	2.8629 (13)	170.2 (14)
O2—H2O2···O1 ⁱⁱⁱ	0.95 (3)	1.92 (3)	2.8383 (19)	164 (2)
O2—H1O2···O1	0.83 (3)	1.97 (3)	2.7925 (19)	169 (3)
N1—H2N1···Cg ^{iv}	0.912 (16)	2.48 (2)	3.383 (2)	169 (2)

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

Compound (II)

Crystal data

C ₆ H ₈ N ₂	$V = 1112.09$ (4) Å ³
$M_r = 108.14$	$Z = 8$
Monoclinic, <i>P2₁/c</i>	Mo $K\alpha$ radiation
$a = 8.3020$ (2) Å	$\mu = 0.08$ mm ⁻¹
$b = 5.8970$ (1) Å	$T = 130$ K
$c = 22.7600$ (5) Å	$0.45 \times 0.4 \times 0.25$ mm
$\beta = 93.579$ (2)°	

Data collection

Oxford Diffraction Xcalibur E diffractometer	9761 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	2269 independent reflections
$T_{\min} = 0.973$, $T_{\max} = 0.980$	1811 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$\Delta\rho_{\text{max}} = 0.21$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.15$ e Å ⁻³
2269 reflections	
178 parameters	

Table 2

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

CgA and *CgC* are the centroids of the aromatic rings in molecules *A* and *C*, respectively.

<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>
N1A—H1NA···N1B	0.902 (13)	2.336 (14)	3.2366 (14)	176.1 (11)
N2A—H4NA···N1C ⁱ	0.893 (13)	2.271 (13)	3.1609 (14)	174.1 (11)
N1B—H2NB···N2A ⁱⁱ	0.904 (14)	2.512 (13)	3.2074 (13)	134.1 (11)
N1C—H2NC···N1A	0.914 (14)	2.347 (14)	3.2218 (14)	160.0 (12)
N1A—H2NA···CgA ⁱⁱ	0.905 (15)	2.57 (2)	3.361 (2)	146 (2)
N2A—H3NA···CgA ⁱ	0.898 (14)	2.53 (2)	3.311 (2)	145 (2)
N1B—H1NB···CgC ⁱⁱⁱ	0.869 (15)	2.95 (2)	3.666 (2)	151 (2)

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

In (I), all H atoms were located in electron-density difference maps and freely refined (coordinates and isotropic displacement parameters). In (II), all H atoms were identified in difference Fourier maps, but for the refinement all C-bound H atoms were placed in calculated positions, with C–H = 0.93 Å, and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All N-bound H atoms were freely refined (coordinates and isotropic displacement parameters).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007) for (I); *CrysAlis Pro* (Oxford Diffraction, 2009) for (II). Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007) for (I); *CrysAlis Pro* for (II). Data reduction: *CrysAlis RED* for (I); *CrysAlis Pro* for (II). For both compounds, 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.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3154). Services for accessing these data are described at the back of the journal.

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