

Hydrogen bonding in nitroaniline analogues: hydrogen-bonded sheets in 2-amino-4,6-dimethoxy-5-nitropyrimidine and π -stacked hydrogen-bonded sheets in 4-amino-2,6-dimethoxy-5-nitropyrimidine

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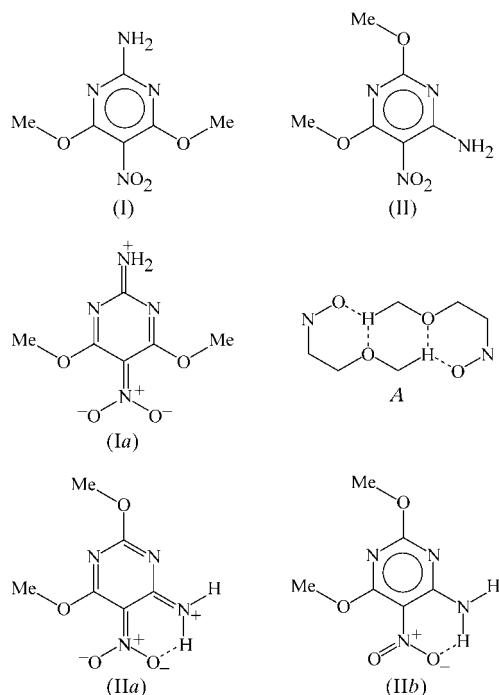
In 2-amino-4,6-dimethoxy-5-nitropyrimidine, $C_6H_8N_4O_4$, the molecules are linked by one $N-H\cdots N$ and one $N-H\cdots O$ hydrogen bond to form sheets built from alternating $R_2^2(8)$ and $R_6^6(32)$ rings. In isomeric 4-amino-2,6-dimethoxy-5-nitropyrimidine, $C_6H_8N_4O_4$, which crystallizes with $Z' = 2$ in $P\bar{1}$, the two independent molecules are linked into a dimer by two independent $N-H\cdots N$ hydrogen bonds. These dimers are linked into sheets by a combination of two-centre $C-H\cdots O$ and three-centre $C-H\cdots(O)_2$ hydrogen bonds, and the sheets are further linked by two independent aromatic π - π -stacking interactions to form a three-dimensional structure.

Comment

Supramolecular aggregation in simple C-substituted nitroanilines is dominated by $N-H\cdots O$ hydrogen bonds. In 4-nitroanilines containing no other hydrogen-bonding substituents, there are two dominant patterns of supramolecular aggregation. Either each molecule is linked to four other molecules by means of such hydrogen bonds, giving rise to two-dimensional (Tonogaki *et al.*, 1993; Glidewell *et al.*, 2002a) or three-dimensional (Ferguson *et al.*, 2001) hydrogen-bonded structures, or else the molecules are linked into chains *via* paired $N-H\cdots O$ hydrogen bonds which form an $R_2^2(6)$

(Bernstein *et al.*, 1995) motif (McWilliam *et al.*, 2001; Glidewell *et al.*, 2002a). The dominant motif in simple 2-nitroanilines is a combination of intramolecular $S(6)$ rings and simple $C(6)$ or $C_2^2(12)$ chains, depending upon whether Z' is 1 or 2 (Dhaneshwar *et al.*, 1978; Ellena *et al.*, 1996; Cannon *et al.*, 2001; Garden *et al.*, 2002).

However, where other hydrogen-bond acceptors are present, whether as a heteroatom within the aromatic ring or in a C-substituent, formation of $N-H\cdots N$ hydrogen bonds can effectively compete with $N-H\cdots O$ hydrogen-bond formation, leading to the production of very elegant sheets containing alternating large and small rings (Glidewell *et al.*, 2001; Glidewell *et al.*, 2002b). Continuing our exploration of this theme, we have now investigated two isomeric examples, namely 2-amino-4,6-dimethoxy-5-nitropyrimidine, (I), and 4-amino-2,6-dimethoxy-5-nitropyrimidine, (II), containing two additional types of potential hydrogen-bond acceptor, namely a pair of N atoms within the ring and a pair of O atoms in C-substituents.



Compounds (I) and (II) crystallize in space groups $P2_1/c$ and $P\bar{1}$ with $Z' = 1$ and 2, respectively. In (I) (Fig. 1), both methoxy groups have their methyl C atoms essentially in the plane of the pyrimidine ring, such that both methyl groups are directed away from the nitro substituent. This conformation matches that of the analogous 2-amino-4,6-dimethoxy-5-nitrosopyrimidine (Glidewell *et al.*, 2002). Although there is no crystallographic symmetry relating the two halves of the molecule across the $N2\cdots N5$ line, the corresponding dimensions for the two halves (Table 1) are very similar. Both of the exocyclic C—N distances are very short for their types (Allen *et al.*, 1987), while the N—O distances are long. The $N1-C6$ and $N3-C4$ distances are significantly shorter than the $N1-C2$ and $C2-N3$ distances, and these observations, taken

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together, point to the charge-separated form (Ia) as an important contributor to the overall molecular–electronic structure.

The two independent molecules in (II) (Fig. 2) have identical conformations and in each the C–O bonds of the two methoxy groups are almost parallel. The intramolecular distances in the two molecules (Table 3) are very similar. As observed in (I), the exocyclic C–N bonds are short for their types but, in contrast with (I), in each molecule of (II) there is a significant difference between the two N–O bond lengths, with that involved in the characteristic intramolecular $S(6)$ hydrogen-bonded motif being the longer in each molecule. These observations, together with the pattern of C–N distances within the rings, point to (IIa) and (IIb) as important contributors to the overall molecular–electronic structure. The nitro groups in (II) are almost coplanar with the adjacent pyrimidine rings, presumably influenced by the intramolecular hydrogen bonds. In (I), the nitro group is twisted out of the ring plane by *ca* 30° (Tables 1 and 3).

The supramolecular structure of (I) is generated by just two hydrogen bonds, one each of the N–H···N and N–H···O types (Table 2). The amino atom N2 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H2A, to ring atom N1 in the molecule at $(1 - x, -y, 1 - z)$, so generating a centrosymmetric $R_2^2(8)$ ring centred at $(\frac{1}{2}, 0, \frac{1}{2})$ (Fig. 3). The same atom N2 also acts as a donor, but this time *via* atom H2B, to nitro atom O51 in the molecule at $(-x, y - \frac{1}{2}, \frac{1}{2} - z)$, and propagation of this hydrogen bond produces a $C(8)$ chain running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(0, y, \frac{1}{4})$. The combination of $R_2^2(8)$ rings and $C(8)$ chains generates a $(10\bar{2})$ sheet, built from alternating centrosymmetric $R_2^2(8)$ and $R_6^6(32)$ rings and incorporating the $C(8)$ chains along $(0, y, \frac{1}{4})$ and $(1, -y, \frac{3}{4})$ (Fig. 3).

Neither of the methoxy substituents participates directly in the hydrogen-bonding arrangement but, in each molecule, the two methoxy groups are directed into the interior of a

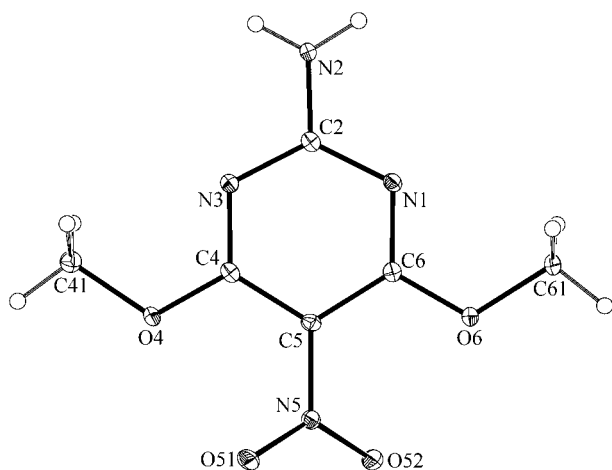


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

different $R_6^6(32)$ ring, such that four methoxy groups are directed into each of these rings, effectively occupying the whole interior of these rings. Thus, it may well be that these methoxy groups act as templates for the formation of the $R_6^6(32)$ rings, just as in 3-trifluoromethyl-4-nitroaniline there are pairs of CF_3 groups lying within hydrogen-bonded $R_4^4(32)$ rings (Glidewell *et al.*, 2002a). There are neither C–H··· π (arene) hydrogen bonds nor aromatic π – π -stacking interactions in the structure of (I), which thus depends solely on hard hydrogen bonds as the only direction-specific interactions.

Within the asymmetric unit of (II) (Fig. 2), there are two independent N–H···O hydrogen bonds (Table 4), each generating an $S(6)$ motif, and there are two independent N–H···N hydrogen bonds, which together generate a pseudo-centrosymmetric $R_2^2(8)$ ring. However, a search of possible additional symmetry revealed none. These dimeric units are then linked into sheets *via* a series of two C–H···O hydrogen bonds (Table 4). Methoxy atom C121 in the type 1 molecule

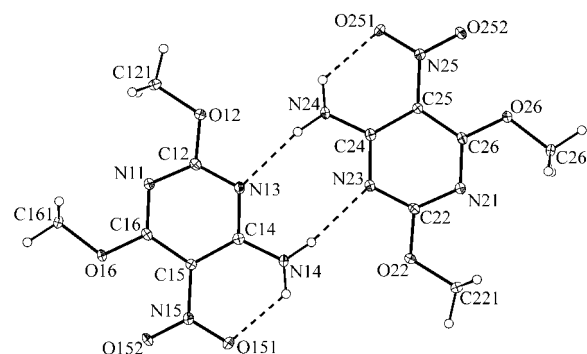


Figure 2

A view of the two independent molecules of (II), showing the atom-labelling scheme and the N–H···N hydrogen bonds within the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

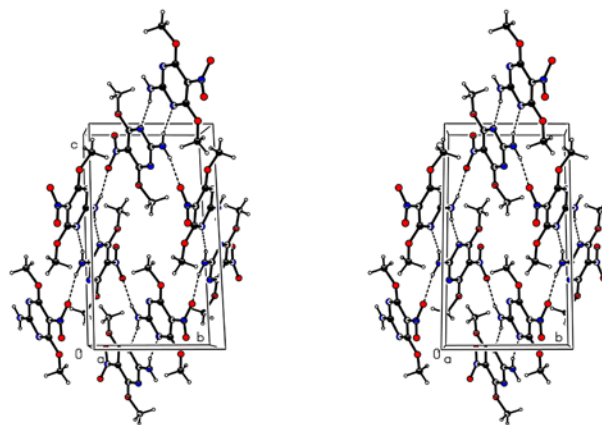


Figure 3

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $(10\bar{2})$ sheet built from $R_2^2(8)$ and $R_6^6(32)$ rings.

(containing atoms N11 *etc.*) at (x, y, z) acts as a hydrogen-bond donor, *via* atom H12B, to nitro atom O151 in the type 1 molecule at $(x, 1 + y, z)$, while atom C221 in the type 2 molecule (containing atoms N21 *etc.*) at (x, y, z) similarly acts as a donor, *via* atom H22B, to nitro atom O251 at $(x, y - 1, z)$. In this manner, a chain of edge-fused $R_2^2(8)$ and $R_6^0(22)$ rings running parallel to $[010]$ is generated by translation (Fig. 4).

Similarly, methoxy atom C161 in the type 1 molecule at (x, y, z) forms, *via* atom H16B, a planar three-centre C—H \cdots (O) $_2$ hydrogen bond, in which the two acceptors are methoxy atom O26 and nitro atom O252, both in the type 2 molecule at $(x, y - 1, 1 + z)$. Methoxy atom C261 at (x, y, z) forms, *via* atom H26B, another such three-centre system, where the acceptors are methoxy atom O16 and nitro atom O152 at $(x, 1 + y, z - 1)$. The combination of these two three-centre interactions generates a tricyclic $R_2^1(6)R_2^2(6)R_2^3(6)$ motif containing the unusual pseudo-anthracene synthon *A* (see *Scheme*), and propagation of this motif by translation generates a chain running parallel to the $[01\bar{1}]$ direction (Fig. 5).

The combination of the $[010]$ (Fig. 4) and $[01\bar{1}]$ chains (Fig. 5) generates a sheet parallel to (100) , and adjacent sheets are linked to form a three-dimensional structure by two independent aromatic π - π -stacking interactions involving type 1 molecules only. The pyrimidine ring of the type 1 molecule at (x, y, z) forms stacking interactions with the

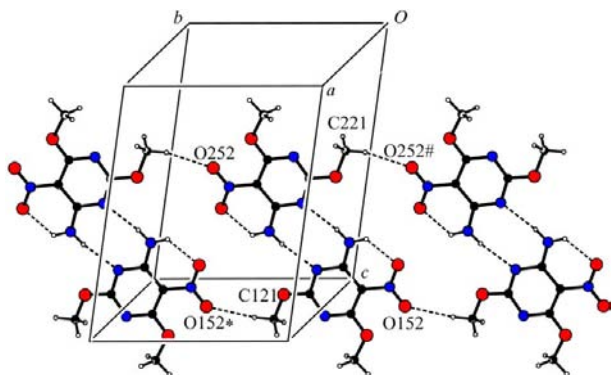


Figure 4

Part of the crystal structure of (II), showing the formation of an edge-fused chain of $R_2^2(8)$ and $R_6^0(22)$ rings along $[010]$. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, y - 1, z)$, respectively.

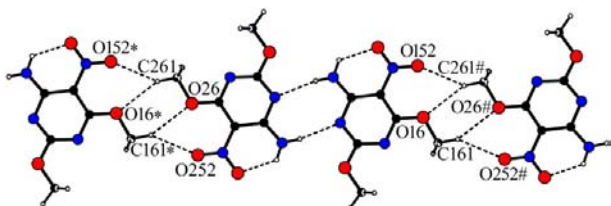


Figure 5

Part of the crystal structure of (II), showing the formation of a chain of rings along $[01\bar{1}]$. For the sake of clarity, the unit-cell box has been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1 + y, z - 1)$ and $(x, y - 1, 1 + z)$, respectively.

corresponding rings at both $(-x, -y, 2 - z)$ and $(1 - x, -y, 2 - z)$. The centroid separations are 3.462 (2) and 3.414 (2) Å, the interplanar spacings are 3.269 (2) and 3.241 (2) Å, and the centroid offsets are 1.140 (2) and 1.073 (2) Å, respectively. The combined effect of these two interactions is the generation of a π -stacked chain running parallel to the $[100]$ direction (Fig. 6), linking the hydrogen-bonded (100) sheets.

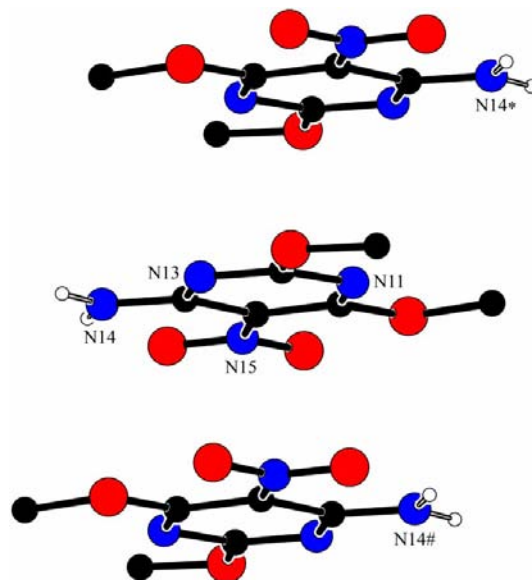


Figure 6

Part of the crystal structure of (II), showing the formation of a π -stacked chain of type 1 molecules along $[100]$. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, -y, 2 - z)$ and $(-x, -y, 2 - z)$, respectively. For the sake of clarity, the unit-cell box and H atoms bonded to C atoms have been omitted.

The structural role of the methoxy substituents thus appears to be entirely different between (I) and (II). In (I), these substituents appear to act as templates for the formation of large hydrogen-bonded rings, while in (II), they link dimeric units into sheets.

Experimental

Samples of (I) and (II) were prepared by oxidation of the corresponding nitroso compounds (Marchal *et al.*, 2002) with 3-chloroperoxybenzoic acid (1.1 molar equivalents) in acetonitrile solution. After recrystallization from ethyl acetate, the products had melting points of 462 [for (I)] and 452 K [for (II)]. Spectroscopic analysis for (I), $^1\text{H NMR}$ (δ , DMSO- d_6 , p.p.m.): 3.91 (*s*, 6H, O—CH $_3$), 7.65 (*bs*, 2H, NH $_2$, exchanges with D $_2$ O); $^{13}\text{C NMR}$ (δ , DMSO- d_6 , p.p.m.): 54.6, 112.2, 160.7, 163.5. Spectroscopic analysis for (II), $^1\text{H NMR}$ (δ , DMSO- d_6 , p.p.m.): 3.88 (*s*, 3H, O—CH $_3$), 3.93 (*s*, 3H, O—CH $_3$), 8.33 (*bs*, 2H, NH $_2$, exchanges with D $_2$ O); $^{13}\text{C NMR}$ (δ , DMSO- d_6 , p.p.m.): 54.8, 54.9, 111.6, 160.1, 163.3, 165.9. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethyl acetate [for (I)] or diethyl ether [for (II)].

Compound (I)*Crystal data*

$C_6H_8N_4O_4$
 $M_r = 200.16$
 Monoclinic, $P2_1/c$
 $a = 7.3443$ (2) Å
 $b = 7.8437$ (2) Å
 $c = 14.9129$ (4) Å
 $\beta = 109.9470$ (13)°
 $V = 807.54$ (4) Å³
 $Z = 4$

$D_x = 1.646$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1835 reflections
 $\theta = 3.0$ – 27.5°
 $\mu = 0.14$ mm⁻¹
 $T = 120$ (2) K
 Block, yellow
 $0.50 \times 0.40 \times 0.15$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
 $T_{\min} = 0.936$, $T_{\max} = 0.985$
 6065 measured reflections

1835 independent reflections
 1569 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 9$
 $k = -9 \rightarrow 10$
 $l = -19 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.110$
 $S = 1.00$
 1835 reflections
 129 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.2772P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

N1—C2	1.3515 (17)	C2—N2	1.3299 (16)
C2—N3	1.3515 (16)	C5—N5	1.4367 (16)
N3—C4	1.3167 (16)	N5—O51	1.2368 (14)
C4—C5	1.4076 (18)	N5—O52	1.2287 (14)
C5—C6	1.4151 (17)	C4—O4	1.3265 (15)
C6—N1	1.3244 (16)	C6—O6	1.3273 (15)
C4—C5—N5—O51	−29.94 (17)	N1—C6—O6—C61	3.10 (17)
C6—C5—N5—O51	149.95 (12)	N3—C4—O4—C41	2.14 (16)

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots N1 ⁱ	0.88	2.26	3.1210 (16)	165
N2—H2B \cdots O51 ⁱⁱ	0.88	2.13	2.9951 (15)	166

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.**Compound (II)***Crystal data*

$C_6H_8N_4O_4$
 $M_r = 200.16$
 Triclinic, $P\bar{1}$
 $a = 6.8427$ (2) Å
 $b = 9.9742$ (5) Å
 $c = 13.2752$ (5) Å
 $\alpha = 79.007$ (2)°
 $\beta = 75.577$ (3)°
 $\gamma = 72.547$ (2)°
 $V = 830.46$ (6) Å³

$Z = 4$
 $D_x = 1.601$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3699 reflections
 $\theta = 3.2$ – 27.5°
 $\mu = 0.14$ mm⁻¹
 $T = 120$ (1) K
 Block, colourless
 $0.40 \times 0.25 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
 $T_{\min} = 0.946$, $T_{\max} = 0.978$
 12 543 measured reflections

3699 independent reflections
 2510 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -12 \rightarrow 12$
 $l = -17 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.135$
 $S = 1.02$
 3699 reflections
 257 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0779P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 3

Selected geometric parameters (Å, °) for (II).

N11—C12	1.3333 (19)	N21—C22	1.3348 (19)
C12—N13	1.3201 (19)	C22—N23	1.3212 (19)
N13—C14	1.3497 (19)	N23—C24	1.3522 (19)
C14—C15	1.429 (2)	C24—C25	1.433 (2)
C15—C16	1.416 (2)	C25—C26	1.420 (2)
C16—N11	1.3341 (19)	C26—N21	1.323 (2)
C14—N14	1.3292 (18)	C24—N24	1.3266 (19)
C15—N15	1.4362 (19)	C25—N25	1.4254 (19)
N15—O151	1.2411 (16)	N25—O251	1.2456 (16)
N15—O152	1.2153 (17)	N25—O252	1.2255 (16)
C12—O12	1.3259 (18)	C22—O22	1.3304 (18)
C16—O16	1.3199 (17)	C26—O26	1.3215 (17)
C14—C15—N15—O151	−0.4 (2)	C24—C25—N25—O251	−4.9 (2)
C16—C15—N15—O151	179.95 (13)	C26—C25—N25—O251	175.77 (13)
N11—C12—O12—C121	−3.7 (2)	N21—C22—O22—C221	0.2 (2)
N11—C16—O16—C161	−1.36 (19)	N21—C26—O26—C261	−2.44 (19)

Table 4

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N14—H14B \cdots O151	0.88	2.00	2.624 (2)	127
N24—H24B \cdots O251	0.88	2.01	2.630 (2)	126
N14—H14A \cdots N23	0.88	2.16	3.027 (2)	169
N24—H24A \cdots N13	0.88	2.14	3.010 (2)	170
C121—H12B \cdots O152 ⁱ	0.98	2.42	3.378 (2)	165
C221—H22B \cdots O252 ⁱⁱ	0.98	2.44	3.394 (2)	165
C161—H16B \cdots O26 ⁱⁱⁱ	0.98	2.54	3.438 (2)	153
C161—H16B \cdots O252 ⁱⁱⁱ	0.98	2.50	3.356 (2)	146
C261—H26B \cdots O16 ^{iv}	0.98	2.54	3.441 (2)	152
C261—H26B \cdots O152 ^{iv}	0.98	2.48	3.338 (2)	146

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

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1599). Services for accessing these data are described at the back of the journal.

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