

Hydrogen bonding in substituted nitroanilines: hydrogen-bonded sheets in 4-iodo-3-nitroaniline

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In the title compound, C₆H₅IN₂O₂, the nitro group is disordered over two sets of sites, each with 0.5 occupancy, and the amino N atom is pyramidal. The molecules are linked into sheets by a combination of three-centre N—H···(O)₂ hydrogen bonds involving alternative pairs of O-atom sites and two-centre N—H···N hydrogen bonds involving the pyramidal amino group.

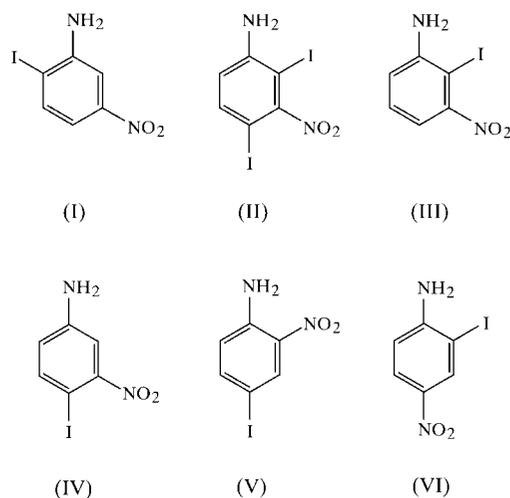
Comment

We have recently reported the molecular and supramolecular structures of a number of iodonitroanilines, no two of which exhibit in their supramolecular structures the same pattern of N—H···O hydrogen bonds, iodo–nitro interactions or aromatic π – π stacking interactions (Garden, Glidewell *et al.*, 2001; McWilliam *et al.*, 2001, Garden *et al.*, 2002).

Iodination of 3-nitroaniline using a solution of K[ICl₂] in methanol as the iodinating agent (Larsen *et al.*, 1956; Garden, Torres *et al.*, 2001) gave, in addition to 2-iodo-5-nitroaniline, (I), and 2,4-diiodo-3-nitroaniline, (II), a third compound in very low yield. This is presumably an intermediate in the formation of (II), *viz.* either 2-iodo-3-nitroaniline, (III), or more plausibly 4-iodo-3-nitroaniline, (IV), but it had not been isolated when the structures of (I) and (II) were reported (Garden *et al.*, 2002). This intermediate has now been isolated and crystallized and we report here the molecular and supramolecular structures of this product, 4-iodo-3-nitroaniline, (IV). The supramolecular structure proves to be different from any of those adopted by its isomers (I), (V) and (VI).

The O atoms of the nitro group in (IV) are disordered over two sets of sites of equal occupancy (Fig. 1). The nitro groups

defined by atoms O3A and O3B on the one hand and O3C and O3D on the other are both twisted out of the plane of the aryl ring by *ca* 13° and *ca* 35°, respectively, such that the dihedral angle between the two nitro-group planes is *ca* 48°. However, despite their equal occupancies, the occupation of the two alternative sets of sites cannot be entirely random. In order to avoid a very short contact of 2.518 (12) Å between atoms O3C and O3D in the molecules at (*x*, *y*, *z*) and (*x*, 1 + *y*, *z*), respectively, adjacent molecular sites related by translation along [010] cannot both accommodate the nitro-group orientation involving atoms O3C and O3D. Since both orientations must occur with equal frequency in a given [010] stack, there must be a strict alternation along [010] of the occupation of the two alternative sets of sites. Hence, there must be perfect correlation of the occupancies along any one [010] stack, although without any necessary correlation of the occupancies in any given [010] stack with those in the neighbouring stacks. Accordingly, the structure is correctly described in terms of the present unit cell with *Z* = 4, rather than of a larger unit cell with *Z* = 8.



The amino N atom is pyramidal, as judged by the locations of the corresponding H atoms found from difference maps. Consistent with this, the C1–N1 distance of 1.388 (5) Å is typical of C_{aryl}–NH₂ distances involving pyramidal nitrogen (mean value 1.394 Å and lower quartile value 1.385 Å; Allen *et al.*, 1987), rather than of those involving planar N (mean value 1.355 Å and upper quartile value 1.372 Å). The remaining bond distances show no unusual values.

The supramolecular structure of compound (IV) is determined by a combination of an asymmetric three-centre N—H···(O)₂ hydrogen bond and a two-centre N—H···N hydrogen bond (Table 1). However, X—H··· π (arene) hydrogen bonds (*X* is C or N), intermolecular iodo–nitro interactions and aromatic π – π stacking interactions are all absent.

The amino atom N1 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* atom H1A, to O atoms in the molecule at ($\frac{1}{2} + x$, $\frac{3}{2} - y$, $\frac{1}{2} + z$), either to both O3A and O3B in one orientation of the nitro group, or to both O3C and O3D in

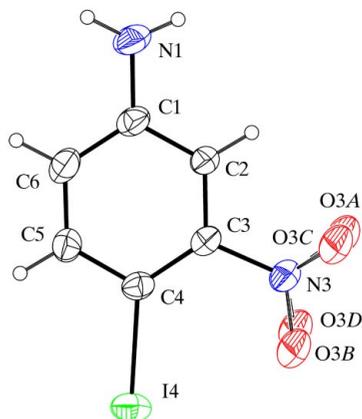


Figure 1

The molecule of (IV), showing the atom-labelling scheme and the disordered O atoms. Displacement ellipsoids are drawn at the 30% probability level.

the other orientation. No matter which pair of O-atom sites is occupied, the molecules at (x, y, z) and $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ are linked by a nearly planar three-centre interaction. Propagation of this interaction then produces a $C(7)[R_1^2(4)]$ (Bernstein *et al.*, 1995) chain of rings running parallel to the [101] direction and generated by the n -glide plane at $y = \frac{3}{4}$ (Fig. 2).

The [101] chains are linked by the nearly linear two-centre $N-H \cdots N$ hydrogen bond, in which amino atom N1 in the molecule at (x, y, z) acts as donor, *via* atom H1B, to atom N1 in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, thereby forming a $C(2)$ chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{3}{4})$ (Fig. 3). The combination of the [101] and [010] chains generates a $(10\bar{1})$ sheet (Fig. 4) in the form of a (4,4)-net (Batten & Robson, 1998).

It is of interest to compare very briefly the rather simple supramolecular structure of compound (IV) with those of the

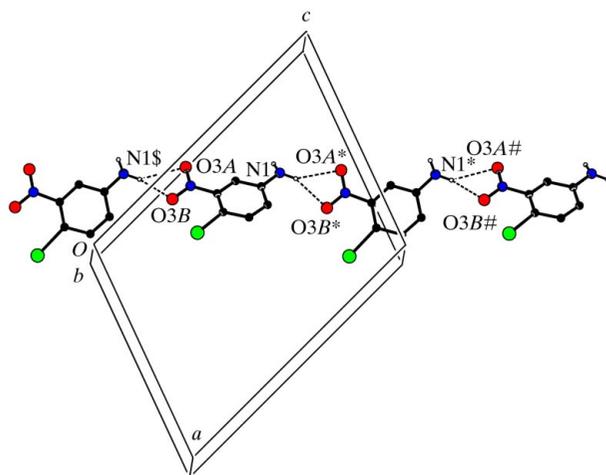


Figure 2

Part of the crystal structure of (IV), showing the formation of the hydrogen-bonded chain of rings along [101]. For the sake of clarity, H atoms bonded to C atoms have been omitted, and only one pair of O atoms, O3A and O3B, is shown. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, $(1 + x, y, 1 + z)$ and $(x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2})$, respectively.

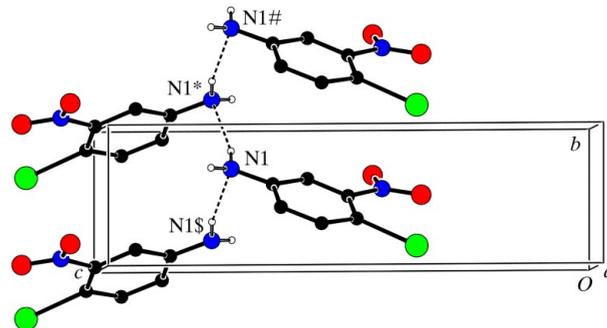


Figure 3

Part of the crystal structure of (IV), showing the formation of the hydrogen-bonded chain along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted, and only one orientation of the disordered nitro group is shown. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, $(x, 1 + y, z)$ and $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z)$, respectively.

isomers (I), (V) and (VI). In (I), hydrogen-bonded dimers are linked into sheets by two-centre iodo–nitro interactions, and these sheets are linked into a three-dimensional framework by aromatic π - π stacking interactions (Garden *et al.*, 2002). In compound (V), where $Z' = 2$, each of the two independent molecules forms sheets *via* a combination of $N-H \cdots O$ hydrogen bonds and two-centre iodo–nitro interactions, but there are no direction-specific interactions between the two types of sheet (Garden *et al.*, 2002). Compound (VI) forms two polymorphs and in each a combination of hydrogen bonds and

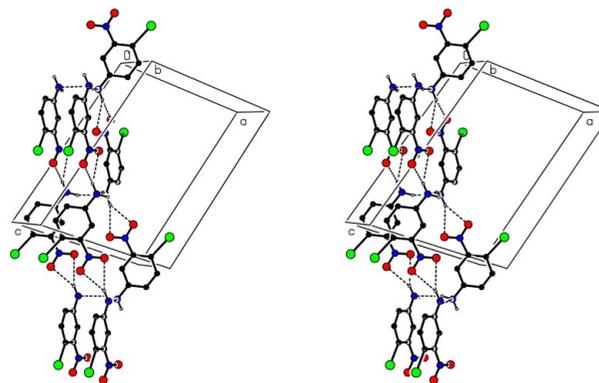


Figure 4

A stereoview of part of the crystal structure of (IV), showing the formation of the $(10\bar{1})$ sheet resulting from the combination of [101] and [010] chains. For the sake of clarity, H atoms bonded to C atoms have been omitted, and only one orientation of the disordered nitro group is shown.

iodo–nitro interactions generates sheets, which are linked by aromatic π - π stacking interactions into bilayers in the triclinic polymorph and into a three-dimensional framework in the orthorhombic polymorph (McWilliam *et al.*, 2001). It is striking that iodo–nitro interactions are present in the structures of each of compounds (I), (V) and (VI), but that these interactions are absent from the structure of (IV).

Experimental

For the preparation of (IV), a solution of K[ICl₂] (2.5 ml, 2 M) in water was added to a solution of 3-nitroaniline (10 mmol) in MeOH (18 ml). The reaction mixture was left at room temperature for a few hours, then heated to boiling and diluted with water (10 ml). The precipitate which formed on cooling was collected, washed with cold 50% aqueous methanol, and recrystallized from 50% aqueous methanol to give a cocrystallized mixture of 2-iodo-5-nitroaniline, (I), and 4-iodo-3-nitroaniline, (IV). These compounds were separated by column chromatography on silica gel using hexane–CH₂Cl₂ (1:1 v/v) as eluant. 4-Iodo-3-nitroaniline (0.60 g, 45% yield based on K[ICl₂]; m.p. 414–415 K) was recrystallized from aqueous methanol. ¹H NMR (CDCl₃/DMSO-*d*₆, δ): 4.90 (2H, *br, s*, NH₂), 6.62 (1H, H6, *dd*, *J* = 2.7 and 8.6 Hz), 7.20 (1H, H2, *d*, *J* = 2.7 Hz), 7.62 (1H, H5, *d*, *J* = 8.7 Hz); ¹³C NMR (CDCl₃/DMSO-*d*₆, δ): 67.6 (C–I), 110.7 (CH), 119.6 (CH), 141.1 (CH), 148.5 (C–NH₂), 153.1 (C–NO₂).

Crystal data

C ₆ H ₅ IN ₂ O ₂	Mo Kα radiation
<i>M_r</i> = 264.02	Cell parameters from 2848 reflections
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	<i>a</i> = 2.6–32.5°
<i>a</i> = 12.5174 (7) Å	<i>b</i> = 4.2601 (3) Å
<i>b</i> = 4.2601 (3) Å	<i>c</i> = 16.0042 (9) Å
<i>c</i> = 16.0042 (9) Å	<i>β</i> = 111.580 (1)°
<i>β</i> = 111.580 (1)°	<i>V</i> = 793.61 (8) Å ³
<i>V</i> = 793.61 (8) Å ³	<i>Z</i> = 4
<i>Z</i> = 4	<i>D_x</i> = 2.210 Mg m ⁻³
<i>D_x</i> = 2.210 Mg m ⁻³	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2848 independent reflections
<i>φ/ω</i> scans	1971 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 2000)	<i>R</i> _{int} = 0.028
<i>T</i> _{min} = 0.456, <i>T</i> _{max} = 0.819	<i>θ</i> _{max} = 32.5°
8259 measured reflections	<i>h</i> = -17 → 18
	<i>k</i> = -4 → 6
	<i>l</i> = -22 → 24

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.2861P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.00	$\Delta\rho_{max} = 1.10 \text{ e } \text{Å}^{-3}$
2848 reflections	$\Delta\rho_{min} = -0.85 \text{ e } \text{Å}^{-3}$
100 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bonding geometry (Å, °).

<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–H1A...O3A ⁱ	0.88	2.50	3.265 (8)	146
N1–H1A...O3B ⁱ	0.88	2.35	3.148 (8)	150
N1–H1A...O3D ⁱ	0.88	2.58	3.298 (8)	140
N1–H1A...O3C ⁱ	0.88	2.46	3.295 (8)	158
N1–H1B...N1 ⁱⁱ	0.88	2.25	3.105 (6)	164

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

The space group *P*2₁/*n* was uniquely assigned from the systematic absences. All H atoms were located from difference maps. H atoms bonded to C atoms were treated as riding atoms along the bisectors of the external angles of the aryl ring, with C–H distances of 0.93 Å. The sites of the H atoms bonded to atom N1 showed clearly the pyramidal geometry of the amino group; these H atoms were allowed to ride at the sites found from the difference maps, with the N–H distances constrained to 0.88 Å. For all H atoms, *U*_{iso}(H) = 1.2*U*_{eq}(C,N). It was found necessary to assign equal anisotropic displacement parameters to the partial O-atom sites in order to achieve satisfactory refinements of the O atoms. When the site-occupancy factors of the O atoms in the alternative orientations of the nitro group were then refined, they gave values of 0.51 (3) and 0.49 (3); these occupancies were all thereafter fixed at 0.50.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

X-ray data were collected at the University of Aberdeen; the authors thank the University of Aberdeen for funding the purchase of the diffractometer. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. SLG and JLW thank CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1211). Services for accessing these data are described at the back of the journal.

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supporting information

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Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

4-iodo-3-nitroaniline

Crystal data

$C_6H_5IN_2O_2$

$M_r = 264.02$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 12.5174$ (7) Å

$b = 4.2601$ (3) Å

$c = 16.0042$ (9) Å

$\beta = 111.580$ (1)°

$V = 793.61$ (8) Å³

$Z = 4$

$F(000) = 496$

$D_x = 2.210$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2848 reflections

$\theta = 2.6$ – 32.5 °

$\mu = 3.99$ mm⁻¹

$T = 291$ K

Plate, colourless

$0.50 \times 0.05 \times 0.05$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed X-ray tube

Graphite monochromator

ϕ/ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2000)

$T_{\min} = 0.456$, $T_{\max} = 0.819$

8259 measured reflections

2848 independent reflections

1971 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 2.6$ °

$h = -17 \rightarrow 18$

$k = -4 \rightarrow 6$

$l = -22 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.107$

$S = 1.00$

2848 reflections

100 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.2861P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
I4	0.28665 (2)	0.16650 (6)	0.356645 (15)	0.06100 (12)	
O3A	0.0122 (6)	0.682 (2)	0.4378 (5)	0.0840 (15)	0.50
O3B	0.0796 (6)	0.538 (2)	0.3416 (5)	0.0840 (15)	0.50
O3C	0.0469 (6)	0.833 (2)	0.4266 (6)	0.0840 (15)	0.50
O3D	0.0510 (6)	0.376 (2)	0.3657 (5)	0.0840 (15)	0.50
N1	0.3297 (3)	0.7166 (11)	0.7327 (2)	0.0707 (10)	
N3	0.0928 (3)	0.5822 (9)	0.4213 (2)	0.0567 (8)	
C1	0.3197 (3)	0.6074 (10)	0.6485 (2)	0.0521 (8)	
C2	0.2173 (3)	0.6486 (9)	0.5757 (2)	0.0460 (7)	
C3	0.2052 (2)	0.5254 (9)	0.49309 (19)	0.0436 (6)	
C4	0.2922 (3)	0.3615 (8)	0.4779 (2)	0.0455 (7)	
C5	0.3944 (3)	0.3240 (10)	0.5519 (3)	0.0563 (9)	
C6	0.4073 (3)	0.4401 (12)	0.6344 (2)	0.0598 (10)	
H1A	0.3986	0.7221	0.7752	0.085*	
H1B	0.2745	0.8462	0.7316	0.085*	
H2	0.1570	0.7589	0.5828	0.055*	
H5	0.4552	0.2172	0.5446	0.068*	
H6	0.4761	0.4068	0.6824	0.072*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I4	0.0921 (2)	0.04963 (16)	0.04865 (15)	0.00516 (12)	0.03457 (13)	0.00129 (10)
O3A	0.056 (2)	0.112 (5)	0.065 (2)	0.007 (2)	-0.0015 (17)	-0.016 (3)
O3B	0.056 (2)	0.112 (5)	0.065 (2)	0.007 (2)	-0.0015 (17)	-0.016 (3)
O3C	0.056 (2)	0.112 (5)	0.065 (2)	0.007 (2)	-0.0015 (17)	-0.016 (3)
O3D	0.056 (2)	0.112 (5)	0.065 (2)	0.007 (2)	-0.0015 (17)	-0.016 (3)
N1	0.0607 (18)	0.103 (3)	0.0408 (15)	-0.0103 (19)	0.0096 (13)	-0.0162 (18)
N3	0.0464 (15)	0.073 (2)	0.0440 (15)	-0.0001 (15)	0.0084 (12)	-0.0019 (14)
C1	0.0466 (16)	0.066 (2)	0.0384 (14)	-0.0117 (15)	0.0097 (12)	-0.0046 (14)
C2	0.0407 (14)	0.0572 (19)	0.0378 (13)	-0.0006 (14)	0.0117 (11)	-0.0030 (14)
C3	0.0429 (14)	0.0466 (17)	0.0371 (13)	-0.0054 (13)	0.0095 (11)	0.0022 (13)
C4	0.0556 (17)	0.0443 (16)	0.0369 (13)	-0.0003 (14)	0.0175 (12)	0.0044 (13)
C5	0.0477 (16)	0.069 (2)	0.0506 (18)	0.0112 (17)	0.0157 (14)	0.0104 (18)
C6	0.0455 (16)	0.079 (3)	0.0461 (17)	-0.0011 (18)	0.0066 (13)	0.0106 (18)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.388 (5)	N3—O3A	1.211 (9)
C1—C2	1.390 (4)	N3—O3D	1.223 (8)
C1—C6	1.393 (6)	N3—O3C	1.232 (9)

N1—H1A	0.88	N3—O3B	1.239 (8)
N1—H1B	0.88	C4—C5	1.396 (5)
C2—C3	1.379 (5)	C4—I4	2.089 (3)
C2—H2	0.93	C5—C6	1.363 (6)
C3—C4	1.388 (5)	C5—H5	0.93
C3—N3	1.472 (4)	C6—H6	0.93
N1—C1—C2	119.8 (4)	O3C—N3—O3B	108.3 (7)
N1—C1—C6	122.2 (3)	O3A—N3—C3	121.4 (4)
C2—C1—C6	117.9 (3)	O3D—N3—C3	118.7 (5)
C1—N1—H1A	118.2	O3C—N3—C3	115.2 (4)
C1—N1—H1B	113.7	O3B—N3—C3	120.4 (4)
H1A—N1—H1B	122.5	C3—C4—C5	116.3 (3)
C3—C2—C1	119.8 (3)	C3—C4—I4	127.1 (2)
C3—C2—H2	120.1	C5—C4—I4	116.7 (3)
C1—C2—H2	120.1	C6—C5—C4	121.7 (4)
C2—C3—C4	122.9 (3)	C6—C5—H5	119.2
C2—C3—N3	115.0 (3)	C4—C5—H5	119.2
C4—C3—N3	122.1 (3)	C5—C6—C1	121.4 (3)
O3A—N3—O3D	104.1 (6)	C5—C6—H6	119.3
O3D—N3—O3C	126.0 (5)	C1—C6—H6	119.3
O3A—N3—O3B	118.2 (5)		
N1—C1—C2—C3	-176.5 (4)	C4—C3—N3—O3B	-13.8 (8)
C6—C1—C2—C3	-0.1 (5)	C2—C3—C4—C5	0.5 (5)
C1—C2—C3—C4	-0.7 (5)	N3—C3—C4—C5	-179.9 (3)
C1—C2—C3—N3	179.7 (3)	C2—C3—C4—I4	-179.4 (3)
C2—C3—N3—O3A	-11.7 (8)	N3—C3—C4—I4	0.3 (5)
C4—C3—N3—O3A	168.6 (7)	C3—C4—C5—C6	0.5 (6)
C2—C3—N3—O3D	-143.1 (6)	I4—C4—C5—C6	-179.6 (3)
C4—C3—N3—O3D	37.3 (7)	C4—C5—C6—C1	-1.3 (7)
C2—C3—N3—O3C	33.2 (7)	N1—C1—C6—C5	177.4 (4)
C4—C3—N3—O3C	-146.5 (6)	C2—C1—C6—C5	1.1 (6)
C2—C3—N3—O3B	165.9 (6)		

Hydrogen-bond geometry (Å, °)

<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—H1A...O3A ⁱ	0.88	2.50	3.265 (8)	146
N1—H1A...O3B ⁱ	0.88	2.35	3.148 (8)	150
N1—H1A...O3D ⁱ	0.88	2.58	3.298 (8)	140
N1—H1A...O3C ⁱ	0.88	2.46	3.295 (8)	158
N1—H1B...N1 ⁱⁱ	0.88	2.25	3.105 (6)	164

Symmetry codes: (i) $x+1/2, -y+3/2, z+1/2$; (ii) $-x+1/2, y+1/2, -z+3/2$.