



Crystal structure and Hirshfeld surface analysis of 1-[(*E*)-2-(3-nitrophenyl)diazen-1-yl]naphthalen-2-ol

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Received 4 January 2023
Accepted 3 February 2023

Edited by A. Briceno, Venezuelan Institute of Scientific Research, Venezuela

This article is part of a collection of articles to commemorate the founding of the African Crystallographic Association and the 75th anniversary of the IUCr.

Keywords: azo dyes; X-ray diffraction; crystal structure; intermolecular interactions; Hirshfeld surface.

CCDC reference: 2239846

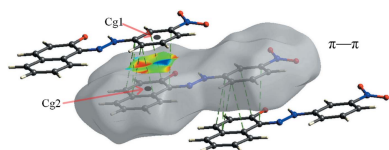
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The title compound, C₁₆H₁₁N₃O₃, belongs to the family of azo dyes. In the light of a single-crystal X-ray study, it is evident that of the tautomeric forms (azo-hydrazone), the hydrazone form is the predominant form in the solid state, namely, (1*E*)-1-[2-(3-nitrophenyl)hydrazin-1-ylidene]-1,2-dihydronaphthalen-2-one. The naphthol and benzene fragments attached to the –N=N– moiety adopt the *s-trans* conformation. Furthermore, the molecules are nearly coplanar, subtending a dihedral angle of 2.63 (5)°. An intramolecular N–H···O hydrogen bond occurs. There are only two types of intermolecular interactions in the crystal structure: strong hydrogen-bonding C–H···O interactions and π – π stacking interactions. The importance of C–H···O interactions in the molecular packing is reflected by the relatively high contributions (28.5%) made by O···H/H···O contacts to the Hirshfeld surface.

1. Chemical context

Azo compounds, which include the functional group $R-N=N-R'$ where R and R' can either be aryl or alkyl, aryl azo compounds being more common than aliphatic azo compounds (Christie, 2001), have striking colors. These colors, particularly reds, oranges, and yellows, are the result of π -electron delocalization through aromatic moieties (Debnath *et al.*, 2015; Ferreira *et al.*, 2013). They are therefore used as dyes, not only in textile colorants but in many other industrial fields for coloring different substrates, as printing inks, in biological reactions and in the cosmetics industry (Hunger, 2003; Ran *et al.*, 2022; Mathieu-Denoncourt *et al.*, 2014; Shi & Chen, 2014; Chudgar & Oakes, 2003; Benkhaya *et al.*, 2020).

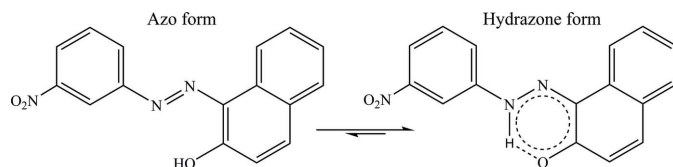
Detailed knowledge of molecular structures is essential for determining structure–function relationships and for a systematic approach to the design of new dyes. Structural information obtained from single-crystal X-ray diffraction analysis including conformation, stereochemistry, intra- and intermolecular interactions is related to the optical properties of azo dyes (Pavlović *et al.*, 2009). In the case of 1-phenylazo-2-naphthol derivatives, a strong hydrogen bond enhanced by resonance is established, inducing the azo (OH) \rightarrow hydrazone (NH) tautomeric displacement (Benosmane *et al.*, 2015; Bougueria, Benaouida *et al.*, 2013; Bougueria *et al.*, 2014). This is directly connected with the presence of at least one protic donor group in conjugation to the azo bridge (2-naphthol) (Antonov, 2016). As a part of our continuing interest in the



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synthesis and crystallography evaluation of azo-2 naphthol compounds, we embarked on the present crystallographic study and report herein the synthesis, molecular structure and Hirshfeld surface analysis of dye derived from 1-phenylazo-2-naphthol: (*E*)-1-(3-nitrophenylazo)-2-naphthol.



2. Structural commentary

The molecular structure of the title compound (Fig. 1) was solved in the orthorhombic space group $P2_12_12_1$. The N1–N2, C1–N1, C7–N2 and C8–O1 bond lengths are 1.312 (4), 1.394 (5), 1.330 (5) and 1.276 (5) Å, respectively, indicating that the dye compound has crystallized in the hydrazone tautomeric form (*i.e.* proton transfer from the naphthol group to the azo group); bond lengths and angles are within normal ranges and are comparable to those reported for other azo compounds (Benaouida *et al.*, 2013; Bouguerria, Benosmane *et al.*, 2013; Mili *et al.*, 2013; Xu *et al.*, 2010). The molecule adopts an *s*-trans conformation, with the two aryl groups residing on the opposite side of the azo group. The naphthol and benzene rings attached to the hydrazone group are almost coplanar, subtending a dihedral angle of 2.63 (5)°, indicating significant electron delocalization within the molecule. The molecular structure is stabilized by an intramolecular N–H···O hydrogen bond involving hydrogen atoms from the hydrazone groups (Table 1).

3. Supramolecular features

In the crystal, molecules are held together by strong intermolecular C–H···O hydrogen bonds (Table 1), forming parallel chains propagating along the *a*-axis direction (Fig. 2). Cohesion of the crystal structure is enhanced by the presence of π – π stacking interactions (Fig. 3), the most significant being

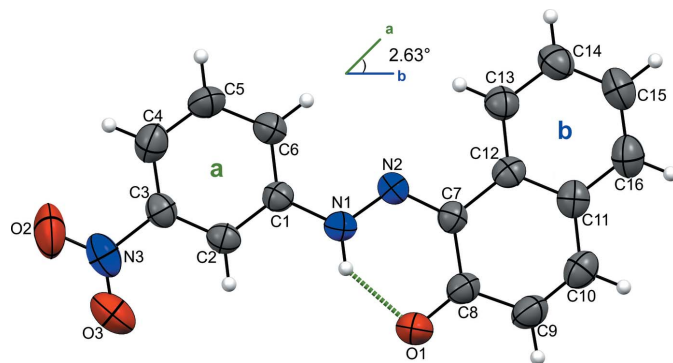


Figure 1
The molecular structure with the atom-labeling scheme. Displacement ellipsoids drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

Table 1
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–H1···O1	0.86 (3)	1.84 (3)	2.551 (4)	138 (3)
C2–H2···O1 ⁱ	0.93	2.43	3.312 (4)	157
C9–H9···O3 ⁱⁱ	0.93	2.62	3.303 (5)	130

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

between the benzene and naphthalene rings [$Cg1 \cdots Cg2(1+x, y, z) = 3.607 (2) \text{ \AA}$ where *Cg1* and *Cg2* are the centroids of the C1–C6 and C7–C12 rings, respectively].

4. Database survey

A search for 1-phenylazo-2-naphthol derivatives in the Cambridge Structural Database (CSD; Version 2022.3.0, last update November 2022; Groom *et al.*, 2016), revealed several examples of structurally similar azo-2-naphthol compounds prepared using different aromatic primary amines. The crystal structures of 1-[(*E*)-2-(5-chloro-2-hydroxyphenyl)hydrazin-1-ylidene]naphthalen-2(1*H*)-one (Bouguerria *et al.*, 2021), (4-aminosulfonylphenyl)[(2-oxidonaphthalen-1-yl)-imino]-azanium (Benosmane *et al.*, 2016), (*E*)-1-(4-fluorophenyl)-2-(2-oxidonaphthalen-1-yl)diazen-1-ium (Bouguerria *et al.*, 2017) have been reported, as well as the structural and optoelec-

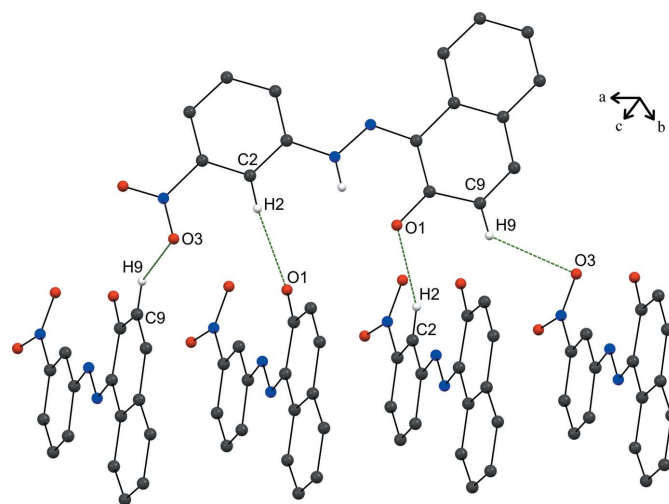


Figure 2
A view along the *c* axis of the crystal packing of the title compound. The C–H···O hydrogen bonds are shown as dashed lines (see Table 1 for details).

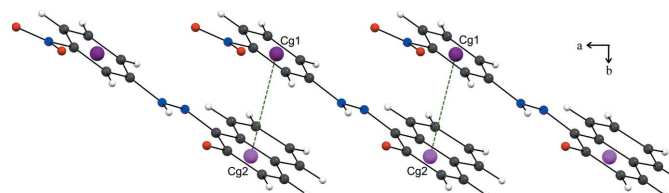


Figure 3
 π – π stacking interactions, view along the *c* axis of the stacked molecules. Dashed light-green lines indicate $Cg1 \cdots Cg2$ contacts.

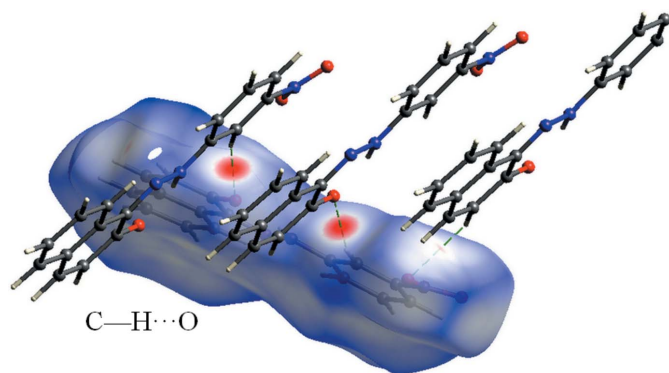


Figure 4
Hirshfeld surfaces mapped over d_{norm} in the range -0.23 \AA (red) to 1.23 \AA (blue).

tronic properties and theoretical investigation of a novel square-planar nickel (II) complex with an (*o*-tolylidiazanyl) naphthalen-2-yl ligand (Benosmane *et al.*, 2023) that exhibits structural diversity with interesting optoelectronic properties.

5. Hirshfeld surface analysis

The supramolecular interactions in the title structure were investigated quantitatively and visualized with *Crystal Explorer* (Spackman & Jayatilaka, 2009; McKinnon *et al.*, 2004). Fig. 4 shows the Hirshfeld surface mapped over d_{norm} in the range -0.2344 (red) a.u. to 1.2354 (blue) a.u. The donors and acceptors of intermolecular $\text{C}-\text{H}\cdots\text{O}$ closest interactions in the structure are seen as bright-red spots near the benzene-H2, naphthalene-H9, hydroxyl-O1 and nitro-O3 atoms. The Hirshfeld surface mapped over shape-index is shown in Fig. 5 where the triangles clearly illustrate the $\pi-\pi$ stacking interactions. The two-dimensional fingerprint plots are shown in Fig. 6. $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ interactions provide the largest contribution (28.5%) to the surface. The second largest contribution is from $\text{H}\cdots\text{H}$ contacts (26.4%). The presence of $\text{C}\cdots\text{C}$ interactions (6.1%), corresponding to $\pi-\pi$ stacking, is also important. Table 2 summarizes the percentage contributions of different types of contacts to the Hirshfeld surface.

6. Synthesis and crystallization

The title compound was obtained through the diazotization of 3-nitroaniline followed by a coupling reaction with 2-naphthol.

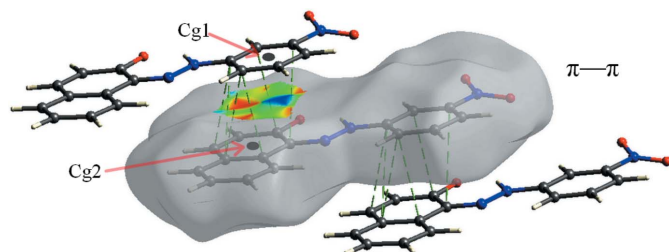


Figure 5
Three-dimensional Hirshfeld surface mapped over shape-index.

Table 2

Distribution of individual intermolecular interactions based on Hirshfeld surface analysis.

Contact type	Percentage contribution
$\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$	28.5
$\text{H}\cdots\text{H}$	26.4
$\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$	26.0
$\text{C}\cdots\text{C}$	6.1
$\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$	4.8
$\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$	3.8
$\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$	2.2

A solution of hydrochloric acid (12 *M*) and 6 mL of water were added to 3-nitroaniline (0.02 mol) at 273 K. Sodium nitrite solution (0.02 mol, in 10 mL of water) was added dropwise to the cooled mixture and stirred for 15 min. To the formed diazonium salt was added dropwise an aqueous solution of 2-naphthol (0.02 mol in 100 mL of water) containing sodium hydroxide (16 mL). The mixture was then allowed to stir for 1 h at 273 K. The resulting red precipitate was filtered and washed several times with distilled water and dried in air. Red needle-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution at room temperature (yield 85.4%).

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atom of hydrazo group was localized in a difference-Fourier map and refined with $\text{N}-\text{H} = 0.86$ (3) \AA with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The other hydrogen atoms were placed in calculated positions with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and refined using a riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

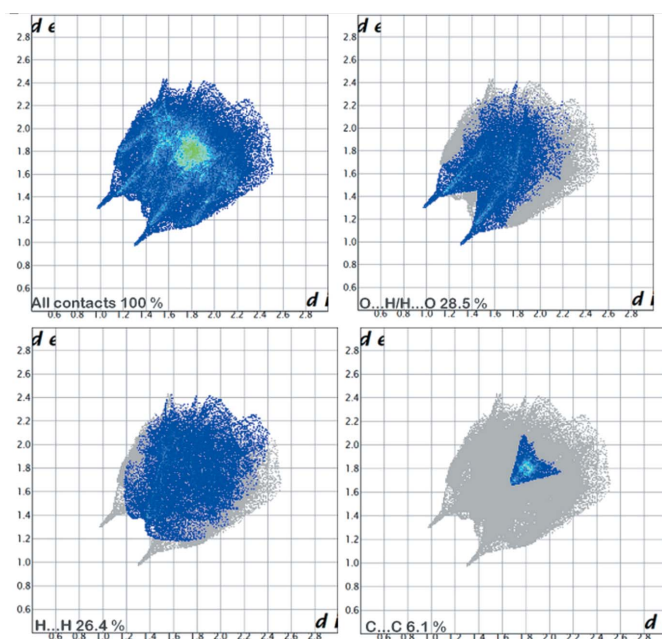


Figure 6
Two-dimensional fingerprint plots.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₁₁ N ₃ O ₃
<i>M_r</i>	293.28
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0981 (9), 14.485 (2), 15.389 (2)
<i>V</i> (Å ³)	1359.3 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.10
Crystal size (mm)	0.50 × 0.30 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	12470, 2803, 1342
<i>R</i> _{int}	0.113
(sin θ/λ) _{max} (Å ⁻¹)	0.626
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> [<i>F</i> ²], <i>S</i>	0.041, 0.087, 0.81
No. of reflections	2803
No. of parameters	203
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.12, -0.13
Absolute structure	Flack (1983), 5026 Friedel pairs
Absolute structure parameter	-2.4 (10)

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *WinGX* publication routines (Farrugia, 2012).

Acknowledgements

We thank all researchers of the CHEMS Research Unit of the University of Constantine Algeria for the valuable assistance they have provided us throughout the realization of this work.

References

- Antonov, L. (2016). *Tautomerism: Concepts and Applications in Science and Technology*. Weinheim: Wiley-VCH.
- Benaouida, M. A., Chetioui, S. & Bouaoud, S. E. (2013). *Acta Cryst. E* **69**, o867–o868.
- Benkhaya, S., M'rabet, S. & El Harfi, A. (2020). *Heliyon*, **6**, e03271–e03296.
- Benosmane, A., Benaouida, M. A., Mili, A., Bouchoul, A. & Merazig, H. (2015). *Acta Cryst. E* **71**, o303.
- Benosmane, A., Gündüz, B., Benaouida, M. A., Boukentoucha, C. & Merzig, H. (2023). *J. Mol. Struct.* **1273**, 134254–134266.
- Benosmane, A., Rouag, D. A., Mili, A., Merazig, H. & Benaouida, M. A. (2016). *IUCrData*, **1**, x160658.
- Bougueria, H., Benaouida, M. A., Bouacida, S. & Bouchoul, A. el kader (2013). *Acta Cryst. E* **69**, o1175–o1176.
- Bougueria, H., Benosmane, A., Benaouida, M. A., Bouchoul, A. E. K. & Bouaoud, S. E. (2013). *Acta Cryst. E* **69**, o1052.
- Bougueria, H., Chetioui, S., Bensegueni, M. A., Djukic, J.-P. & Benarous, N. (2021). *Acta Cryst. E* **77**, 672–676.
- Bougueria, H., Chetioui, S., Mili, A., Bouaoud, S. E. & Merazig, H. (2017). *IUCrData*, **2**, x170039.
- Bougueria, H., Mili, A., Benosmane, A., Bouchoul, A. el kader & Bouaoud, S. (2014). *Acta Cryst. E* **70**, o225.
- Bruker (2012). *APEX2*, *SAINT* and *SADABS*. BrukerAXS Inc, Madison, Wisconsin, USA.
- Christie, R. M. (2001). *Colour Chemistry*. Cambridge: Royal Society of Chemistry.
- Chudgar, R. J. & Oakes, J. (2003). *Azo Dyes*. In *Kirk–Othmer Encyclopedia of Chemical Technology*. Hoboken, NJ: John Wiley & Sons, Inc.
- Debnath, D., Roy, S., Li, B.-H., Lin, C.-H. & Misra, T. K. (2015). *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **140**, 185–197.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Ferreira, G. R., Garcia, H. C., Couri, M. R. C., Dos Santos, H. F. & de Oliveira, L. F. C. (2013). *J. Phys. Chem. A*, **117**, 642–649.
- Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.
- Hunger, K. (2003). *Industrial Dyes: Chemistry, properties, Applications*. Weinheim: Wiley-VCH.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Mathieu-Denoncourt, J., Martyniuk, C. J., de Solla, S. R., Balakrishnan, V. K. & Langlois, V. S. (2014). *Environ. Sci. Technol.* **48**, 2952–2961.
- McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Cryst. B* **60**, 627–668.
- Mili, A., Benosmane, A., Benaouida, M. A., Bouchoul, A. & Bouaoud, S. E. (2013). *Acta Cryst. E* **69**, o1498.
- Pavlović, G., Racané, L., Čičak, H. & Tralić-Kulenović, V. (2009). *Dyes Pigments*, **83**, 354–362.
- Ran, J., Pryazhnikova, V. G. & Telegin, F. Y. (2022). *Colorants*, **1**, 280–297.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Shi, J. & Chen, L. (2014). *Anal. Methods*, **6**, 8129–8135.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Xu, J.-J., Li, J., Pi, M. & Jin, C.-M. (2010). *Acta Cryst. E* **66**, o1752.

supporting information

Acta Cryst. (2023). E79, 142-145 [https://doi.org/10.1107/S2056989023001068]

Crystal structure and Hirshfeld surface analysis of 1-[(*E*)-2-(3-nitrophenyl)-diazen-1-yl]naphthalen-2-ol

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

(*E*)-1-[2-(3-Nitrophenyl)hydrazin-1-ylidene]-1,2-dihydronaphthalen-2-one

Crystal data

$C_{16}H_{11}N_3O_3$	$F(000) = 608$
$M_r = 293.28$	$D_x = 1.433 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2ac 2ab	Cell parameters from 1342 reflections
$a = 6.0981 (9) \text{ \AA}$	$\theta = 2.7\text{--}18.9^\circ$
$b = 14.485 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 15.389 (2) \text{ \AA}$	$T = 296 \text{ K}$
$V = 1359.3 (3) \text{ \AA}^3$	Needle, red
$Z = 4$	$0.50 \times 0.30 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	1342 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{\text{int}} = 0.113$
Graphite monochromator	$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.7^\circ$
phi and ω scans	$h = -7 \rightarrow 7$
12470 measured reflections	$k = -18 \rightarrow 18$
2803 independent reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.087$	$W = 1/[\Sigma^2(FO^2) + (0.0223P)^2]$ WHERE $P = (FO^2 + 2FC^2)/3$
$S = 0.81$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2803 reflections	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
203 parameters	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
1 restraint	
Primary atom site location: structure-invariant direct methods	

Extinction correction: shelxl

Absolute structure: Flack (1983), 5026 Friedel
pairs
Absolute structure parameter: -2.4 (10)*Special details*

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1440 (4)	0.7501 (2)	0.56438 (19)	0.0628 (11)
O2	1.2087 (6)	0.4813 (3)	0.5013 (2)	0.0970 (16)
O3	0.9538 (5)	0.5490 (2)	0.4279 (2)	0.0808 (11)
N1	0.3939 (5)	0.6367 (2)	0.6436 (2)	0.0463 (12)
N2	0.2663 (5)	0.6417 (2)	0.7121 (2)	0.0428 (11)
N3	1.0269 (7)	0.5166 (3)	0.4945 (3)	0.0623 (17)
C1	0.5740 (6)	0.5775 (3)	0.6452 (2)	0.0403 (12)
C2	0.7054 (6)	0.5749 (2)	0.5720 (2)	0.0437 (12)
C3	0.8870 (6)	0.5181 (3)	0.5725 (3)	0.0457 (12)
C4	0.9420 (6)	0.4646 (3)	0.6429 (3)	0.0597 (17)
C5	0.8071 (7)	0.4677 (3)	0.7151 (3)	0.0603 (17)
C6	0.6243 (6)	0.5242 (3)	0.7173 (3)	0.0490 (14)
C7	0.0931 (6)	0.6974 (3)	0.7091 (3)	0.0397 (12)
C8	0.0303 (6)	0.7519 (3)	0.6340 (3)	0.0480 (16)
C9	-0.1635 (6)	0.8064 (3)	0.6396 (3)	0.0583 (17)
C10	-0.2879 (7)	0.8059 (3)	0.7116 (3)	0.0567 (16)
C11	-0.2361 (6)	0.7522 (3)	0.7869 (3)	0.0470 (14)
C12	-0.0426 (6)	0.6988 (3)	0.7871 (3)	0.0417 (12)
C13	0.0082 (6)	0.6472 (3)	0.8611 (3)	0.0503 (16)
C14	-0.1283 (7)	0.6474 (3)	0.9321 (3)	0.0580 (17)
C15	-0.3181 (7)	0.6989 (3)	0.9312 (3)	0.0627 (17)
C16	-0.3733 (7)	0.7510 (3)	0.8599 (3)	0.0623 (17)
H1	0.357 (6)	0.667 (2)	0.5978 (18)	0.063 (15)*
H2	0.67210	0.61060	0.52350	0.0530*
H4	1.06630	0.42750	0.64210	0.0720*
H5	0.83990	0.43110	0.76300	0.0720*
H6	0.53620	0.52640	0.76660	0.0590*
H9	-0.20470	0.84290	0.59260	0.0700*
H10	-0.41370	0.84220	0.71260	0.0680*
H13	0.13610	0.61220	0.86230	0.0600*
H14	-0.09250	0.61260	0.98090	0.0700*
H15	-0.40990	0.69840	0.97940	0.0750*

H16 -0.50180 0.78550 0.86010 0.0750*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0707 (19)	0.0686 (19)	0.0491 (18)	0.0118 (17)	0.0061 (17)	0.0121 (18)
O2	0.059 (2)	0.125 (3)	0.107 (3)	0.023 (2)	0.021 (2)	-0.022 (2)
O3	0.093 (2)	0.095 (2)	0.0545 (19)	-0.014 (2)	0.019 (2)	-0.002 (2)
N1	0.047 (2)	0.054 (2)	0.038 (2)	0.0038 (18)	-0.0002 (19)	0.0050 (19)
N2	0.0433 (19)	0.0452 (19)	0.0399 (18)	0.0002 (17)	0.0032 (17)	-0.0004 (17)
N3	0.062 (3)	0.065 (3)	0.060 (3)	-0.012 (2)	0.016 (3)	-0.018 (2)
C1	0.039 (2)	0.043 (2)	0.039 (2)	-0.0021 (19)	-0.002 (2)	0.000 (2)
C2	0.047 (2)	0.042 (2)	0.042 (2)	-0.006 (2)	0.000 (2)	0.002 (2)
C3	0.046 (2)	0.046 (2)	0.045 (2)	-0.004 (2)	0.004 (2)	-0.006 (2)
C4	0.052 (3)	0.053 (3)	0.074 (3)	0.006 (2)	0.003 (3)	0.000 (3)
C5	0.064 (3)	0.054 (3)	0.063 (3)	0.009 (2)	0.002 (3)	0.019 (3)
C6	0.051 (2)	0.053 (3)	0.043 (2)	0.000 (2)	0.003 (2)	0.005 (2)
C7	0.041 (2)	0.037 (2)	0.041 (2)	0.000 (2)	-0.001 (2)	-0.004 (2)
C8	0.051 (3)	0.044 (2)	0.049 (3)	0.005 (2)	-0.004 (2)	0.004 (2)
C9	0.064 (3)	0.049 (3)	0.062 (3)	0.011 (2)	-0.006 (3)	0.008 (2)
C10	0.057 (3)	0.047 (2)	0.066 (3)	0.007 (2)	-0.005 (3)	-0.004 (3)
C11	0.043 (2)	0.043 (2)	0.055 (3)	-0.004 (2)	-0.001 (2)	-0.009 (3)
C12	0.042 (2)	0.042 (2)	0.041 (2)	-0.003 (2)	-0.008 (2)	-0.004 (2)
C13	0.050 (3)	0.055 (3)	0.046 (2)	0.000 (2)	-0.002 (2)	-0.003 (2)
C14	0.062 (3)	0.067 (3)	0.045 (3)	-0.001 (3)	0.003 (2)	-0.002 (3)
C15	0.058 (3)	0.071 (3)	0.059 (3)	0.000 (3)	0.015 (3)	-0.010 (3)
C16	0.057 (3)	0.058 (3)	0.072 (3)	0.005 (3)	0.010 (3)	-0.010 (3)

Geometric parameters (Å, °)

O1—C8	1.276 (5)	C10—C11	1.431 (6)
O2—N3	1.225 (6)	C11—C16	1.401 (6)
O3—N3	1.212 (5)	C11—C12	1.411 (5)
N1—N2	1.312 (4)	C12—C13	1.397 (6)
N1—C1	1.394 (5)	C13—C14	1.374 (6)
N2—C7	1.330 (5)	C14—C15	1.377 (6)
N3—C3	1.473 (6)	C15—C16	1.374 (6)
C1—C2	1.383 (5)	C2—H2	0.9300
C1—C6	1.386 (6)	C4—H4	0.9300
N1—H1	0.86 (3)	C5—H5	0.9300
C2—C3	1.380 (5)	C6—H6	0.9300
C3—C4	1.374 (6)	C9—H9	0.9300
C4—C5	1.383 (6)	C10—H10	0.9300
C5—C6	1.383 (6)	C13—H13	0.9300
C7—C8	1.451 (6)	C14—H14	0.9300
C7—C12	1.458 (6)	C15—H15	0.9300
C8—C9	1.424 (5)	C16—H16	0.9300
C9—C10	1.343 (6)		

N2—N1—C1	119.2 (3)	C11—C12—C13	118.7 (4)
N1—N2—C7	118.5 (3)	C7—C12—C11	118.7 (4)
O2—N3—O3	124.5 (4)	C7—C12—C13	122.5 (4)
O2—N3—C3	117.4 (4)	C12—C13—C14	120.9 (4)
O3—N3—C3	118.1 (4)	C13—C14—C15	120.2 (4)
N1—C1—C2	117.3 (3)	C14—C15—C16	120.8 (4)
N1—C1—C6	122.1 (3)	C11—C16—C15	120.1 (4)
C2—C1—C6	120.6 (4)	C1—C2—H2	121.00
N2—N1—H1	118 (2)	C3—C2—H2	121.00
C1—N1—H1	122 (2)	C3—C4—H4	121.00
C1—C2—C3	118.5 (3)	C5—C4—H4	121.00
N3—C3—C4	119.5 (4)	C4—C5—H5	119.00
N3—C3—C2	118.0 (4)	C6—C5—H5	119.00
C2—C3—C4	122.5 (4)	C1—C6—H6	120.00
C3—C4—C5	118.0 (4)	C5—C6—H6	120.00
C4—C5—C6	121.2 (4)	C8—C9—H9	119.00
C1—C6—C5	119.2 (4)	C10—C9—H9	119.00
C8—C7—C12	119.9 (3)	C9—C10—H10	118.00
N2—C7—C8	124.6 (4)	C11—C10—H10	118.00
N2—C7—C12	115.5 (4)	C12—C13—H13	120.00
C7—C8—C9	118.2 (4)	C14—C13—H13	120.00
O1—C8—C9	120.9 (4)	C13—C14—H14	120.00
O1—C8—C7	120.9 (3)	C15—C14—H14	120.00
C8—C9—C10	121.1 (4)	C14—C15—H15	120.00
C9—C10—C11	123.1 (4)	C16—C15—H15	120.00
C12—C11—C16	119.4 (4)	C11—C16—H16	120.00
C10—C11—C12	119.0 (4)	C15—C16—H16	120.00
C10—C11—C16	121.6 (4)		
C1—N1—N2—C7	-179.0 (3)	C12—C7—C8—C9	0.7 (6)
N2—N1—C1—C2	-179.4 (3)	N2—C7—C12—C11	-176.4 (4)
N2—N1—C1—C6	-0.7 (5)	N2—C7—C12—C13	1.7 (6)
N1—N2—C7—C8	1.8 (6)	C8—C7—C12—C11	1.3 (6)
N1—N2—C7—C12	179.4 (3)	C8—C7—C12—C13	179.4 (4)
O2—N3—C3—C2	165.7 (4)	O1—C8—C9—C10	177.6 (4)
O2—N3—C3—C4	-13.5 (6)	C7—C8—C9—C10	-1.5 (6)
O3—N3—C3—C2	-15.4 (6)	C8—C9—C10—C11	0.4 (7)
O3—N3—C3—C4	165.5 (4)	C9—C10—C11—C12	1.7 (7)
N1—C1—C2—C3	178.9 (3)	C9—C10—C11—C16	-177.9 (4)
C6—C1—C2—C3	0.0 (6)	C10—C11—C12—C7	-2.5 (6)
N1—C1—C6—C5	-179.2 (4)	C10—C11—C12—C13	179.4 (4)
C2—C1—C6—C5	-0.4 (6)	C16—C11—C12—C7	177.2 (4)
C1—C2—C3—N3	-179.4 (4)	C16—C11—C12—C13	-1.0 (6)
C1—C2—C3—C4	-0.3 (6)	C10—C11—C16—C15	-179.8 (4)
N3—C3—C4—C5	180.0 (4)	C12—C11—C16—C15	0.6 (6)
C2—C3—C4—C5	0.8 (6)	C7—C12—C13—C14	-177.4 (4)
C3—C4—C5—C6	-1.2 (6)	C11—C12—C13—C14	0.7 (6)

C4—C5—C6—C1	1.0 (6)	C12—C13—C14—C15	-0.1 (7)
N2—C7—C8—O1	-0.9 (6)	C13—C14—C15—C16	-0.3 (7)
N2—C7—C8—C9	178.2 (4)	C14—C15—C16—C11	0.0 (7)
C12—C7—C8—O1	-178.4 (4)		

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—H1...O1	0.86 (3)	1.84 (3)	2.551 (4)	138 (3)
C2—H2...O1 ⁱ	0.93	2.43	3.312 (4)	157
C9—H9...O3 ⁱⁱ	0.93	2.62	3.303 (5)	130

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