Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-(2-Ethoxyphenyl)-1-(3-nitrophenyl)-triaz-1-ene

Mohammad Reza Melardi,[a]* Atefeh Ghannadan,[a] Mitra Peyman,[a] Giuseppe Bruno[b] and Hadi Amiri Rudbari[b]

[a]Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran, and [b]Dipartimento di Chimica Inorganica, Universita di Messina, Messina, Italy
Correspondence e-mail: m.melardi@kiau.ac.ir

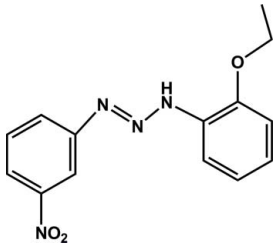
Received 4 November 2011; accepted 16 November 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.115; data-to-parameter ratio = 16.6.

The title compound, $C_{14}H_{14}N_4O_3$, exhibits a *trans* geometry about the N=N double bond in the triazene unit. The molecule is approximately planar (r.m.s. deviation = 0.044 Å for all non-H atoms). An intramolecular N—H···O hydrogen bond occurs. In the crystal, C—H···N hydrogen bonds lead to the formation of dimers which are, in turn, connected to each other by C—H···O hydrogen bonds, forming infinite chains of $R_2^2(8)$ graph-set motif.

Related literature

For aryl triazenes, their structural properties and metal complexes see: Meldola & Streatfield (1888); Leman *et al.* (1993); Chen *et al.* (2002); Vrieze & Van Koten (1987). For a similar structure with cyano instead of ethoxy groups, see: Melardi *et al.* (2008). For the synthesis and characterization of a similar structure with methoxy instead of ethoxy groups, see: Rofouei *et al.* (2006). For the synthesis and crystal structures of mercury(II) and silver(I) complexes with 1,3-bis(2-methoxyphenyl)triazene, see: Hematyar & Rofouei (2008) and Payehghadr *et al.* (2007), respectively. For hydrogen-bond patterns and related graph sets, see: Grell *et al.* (2002).



Experimental

Crystal data

$C_{14}H_{14}N_4O_3$ — M_r = 286.29
Triclinic, $P\overline{1}$
a = 6.7754 (4) Å
b = 7.5482 (4) Å
c = 14.0467 (7) Å
α = 99.057 (3)°
β = 102.479 (2)°
γ = 90.192 (3)°
V = 692.14 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.55 × 0.33 × 0.26 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.688, T_{max} = 0.746
26097 measured reflections
3178 independent reflections
2693 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.115
S = 1.06
3178 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.26	2.6130 (12)	105
C7—H2A···O3^{i}	0.97	2.55	3.4595 (18)	157
C10—H10···N3^{ii}	0.93	2.65	3.543 (3)	161

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2042).

References

Bruker (2005). *SAINT-Plus* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, N., Barra, M., Lee, I. & Chahal, N. (2002). *J. Org. Chem.* **67**, 2271–2277.
Grell, J. J., Bernstein, J. & Tinhofer, G. (2002). *Crystallogr. Rev.* **8**, 1–56.
Hematyar, M. & Rofouei, M. K. (2008). *Anal. Sci.* **24**, x117–x118.
Leman, J. T., Wilking, J. B., Cooling, A. J. & Barron, A. R. (1993). *Inorg. Chem.* **32**, 4324–4336.
Melardi, M. R., Khalili, H. R., Barkhi, M. & Rofouei, M. K. (2008). *Anal. Sci.* **24**, x281–x282.
Meldola, R. & Streatfield, F. W. (1888). *J. Chem. Soc.* **61**, 102–118.
Payehghadr, M., Rofouei, M. K., Morsali, A. & Shamsipur, M. (2007). *Inorg. Chim. Acta*, **360**, 1792–1798.
Rofouei, M. K., Shamsipur, M. & Payehghadr, M. (2006). *Anal. Sci.* **22**, x79–x80.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Vrieze, K. & Van Koten, G. (1987). In *Comprehensive Coordination Chemistry*. Oxford: Pergamon Press.

supporting information

Acta Cryst. (2011). E**67**, o3485 [https://doi.org/10.1107/S1600536811048781]

3-(2-Ethoxyphenyl)-1-(3-nitrophenyl)triaz-1-ene

Mohammad Reza Melardi, Atefeh Ghannadan, Mitra Peyman, Giuseppe Bruno and Hadi Amiri Rudbari

S1. Comment

Aryl triazenes have been studied for over 130 years for their interesting structural, anticancer, and reactivity properties. The first extensive investigation of the coordination chemistry of a triazene derivative (1,3 diphenyltriazene) was carried out in 1887 by Meldola (Meldola *et al.*, 1888). In the intervening years, numerous transition metal triazenide compounds have been studied (Leman *et al.*, 1993). Triazene compounds characterized by having a diazoamino group commonly adopt a *trans* configuration in the ground state (Chen *et al.*, 2002). The study of transition metal complexes containing 1,3-diaryltriazenide [RN═N—NR]- ligands has increased greatly in the past few years, because of their potential reactivity in relation to their several coordination modes (Vrieze *et al.*, 1987). We have recently reported the synthesis and characterization of the two molecules 1,3-bis(2-methoxyphenyl)triazene (Rofouei, *et al.*, 2006) and 1,3-bis(2-cyano-phenyl)triazene (Melardi, *et al.*, 2008).

The title compound, $C_{14}H_{14}N_4O_3$, is a related triazene compound. It exhibits a *trans* stereo chemistry of the N═N double bond, and the C9—N3—N2—N1 and C1—N1—N2—N3 torsion angles are -179.23 (9) and 177.91 (10)°, respectively which indicates the molecule is planar. The N1—N2 and N2—N3 bond distances are 1.3295 (13) and 1.2550 (14) Å, respectively, which indicates the presence of distinct single and double bonds between the nitrogen atoms. These values are in good agreement with the reported data for N—N and N═N bond distances (Hematyar, *et al.*, 2008; Payehghadr, *et al.* 2007). For example, in 1,3-bis(2-cyanophenyl)triazene, the N—N and N═N bond distances are 1.335 (5) and 1.289 (5) Å (Melardi, *et al.*, 2008). Individual molecules are mostly planar with an r.m.s. deviation from planarity of 0.044 Å for all non-hydrogen atoms. Every molecule in the molecular structure (Fig. 1) is connected to other unit by two distinct C—H···N hydrogen bonds to form dimers. The resultant dimers are then connected to each other by C—H···O hydrogen bonds to form infinite chains with $R^2_2(8)$ graph-set motifs (Grell *et al.*, 2002)) (Fig. 2). Unit cell diagram of the title compound is illustrated in Fig. 3.

S2. Experimental

The compound was prepared by the following method: A 100 ml flask was charged with 10 g of ice and 15 ml of water and then cooled to 273 k in an ice-bath. To this was added 2 mmol (0.344 g) of 3-nitroaniline and 2 mmol of hydrochloric acid (36.5%) and 2 ml of water. To thissolution was then added a solution containing $NaNO_2$ (2 mmol, 0.16 g) in 2 ml of water during a 15 min period. After mixing for 15 min, the obtained solution was added to a solution of 2 mmol (0.261 ml) of *o*-phenetidin and 2 ml of methanol and 2 ml of water.

After that a solution containing 36 mmol (2.95 g) of sodium acetate in 10 ml of water was added. After mixing for 24 h the orange product was filtered off and dissolved in DMSO. Recrystallization from DMSO afforded the product as an orange crystalline material. ^{1}H NMR (300MHZ, DMSO): 1.37(6*H*, CH_3), 4.12(4*H*, CH_2), 6.98–8.07 (8*H*, aromatic), 12.93(1*H*, NH). IR (KBr): 3326, 1484, 1468, 1253, 1046, 816 cm^{-1}

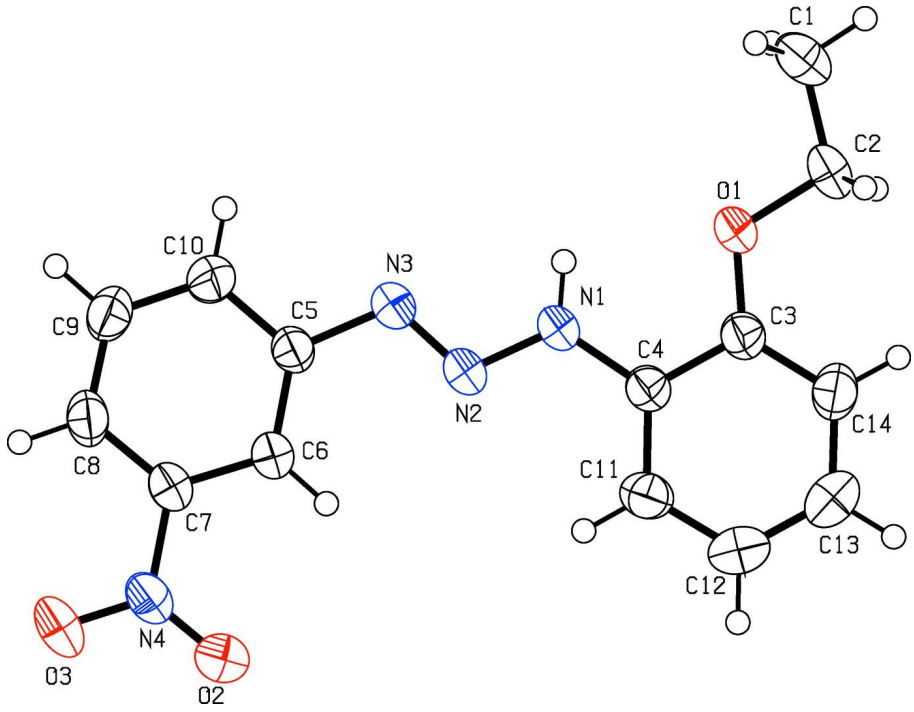


Figure 1

Molecular structure of the title compound. Thermal ellipsoids are drawn at the 50% probability level.

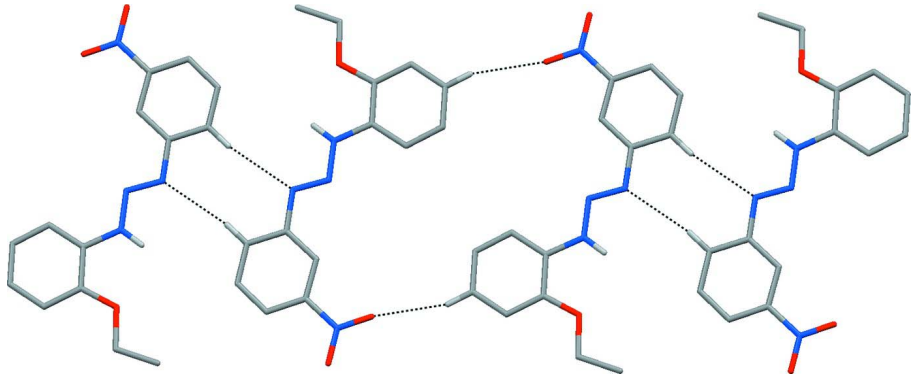


Figure 2

C—H···N and C—H···O hydrogen bonds connect the different units into chains with $R^2_2(8)$ graph-set motifs

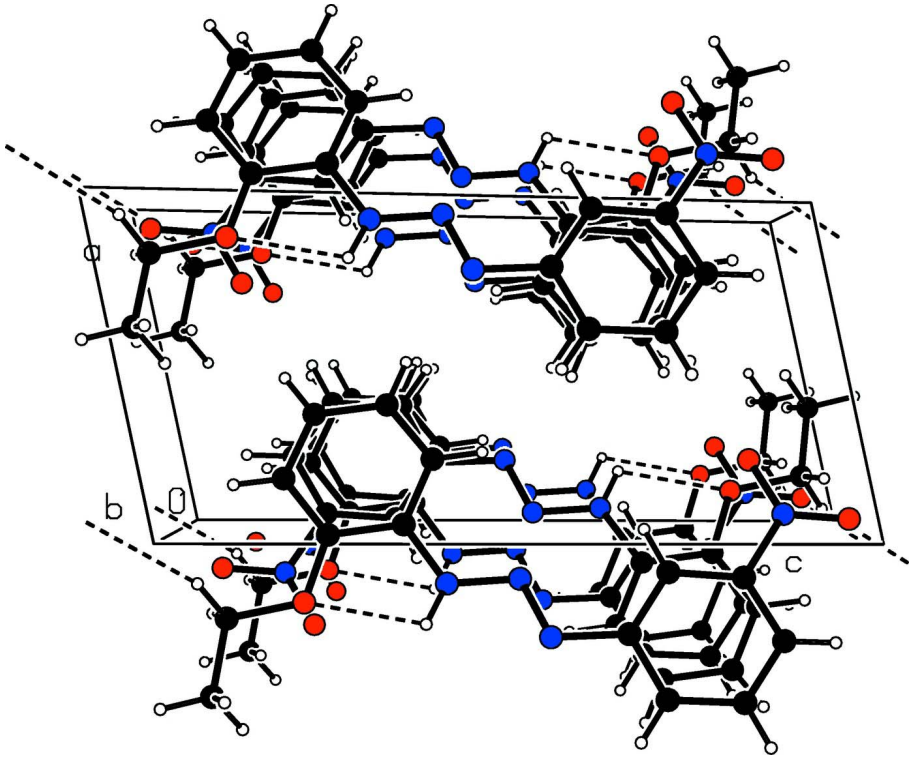


Figure 3

Unit cell packing diagram of the title compound, hydrogen bonding are shown as dashed lines.

3-(2-Ethoxyphenyl)-1-(3-nitrophenyl)triaz-1-ene

Crystal data

$C_{14}H_{14}N_4O_3$
M_r = 286.29
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 6.7754 (4) Å
b = 7.5482 (4) Å
c = 14.0467 (7) Å
α = 99.057 (3)°
β = 102.479 (2)°
γ = 90.192 (3)°
V = 692.14 (6) Å^3
Z = 2
F(000) = 300
D_x = 1.374 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9946 reflections
θ = 2.7–31.1°
μ = 0.10 mm^{-1}
T = 293 K
Irregular, colourless
0.55 × 0.33 × 0.26 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.688, T_{max} = 0.746
26097 measured reflections
3178 independent reflections
2693 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −8→8
k = −9→9
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.115$
$S = 1.06$
3178 reflections
191 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
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.145P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.14363 (13)	0.78956 (13)	0.80767 (6)	0.0496 (2)
O2	−0.25541 (16)	0.75287 (19)	0.17852 (8)	0.0775 (4)
O3	−0.09609 (19)	0.67215 (19)	0.06405 (7)	0.0772 (4)
N1	0.08879 (15)	0.75248 (15)	0.61555 (7)	0.0463 (3)
H1	0.1969	0.7224	0.6532	0.056*
N2	0.07393 (15)	0.72890 (13)	0.51841 (7)	0.0405 (2)
N3	0.22616 (15)	0.65698 (14)	0.49393 (7)	0.0452 (2)
N4	−0.10788 (17)	0.69283 (16)	0.15046 (7)	0.0510 (3)
C8	0.3938 (2)	0.7498 (2)	0.94857 (10)	0.0657 (4)
H1A	0.3911	0.6227	0.9261	0.099*
H1B	0.4296	0.7732	1.0195	0.099*
H1C	0.4919	0.8082	0.9226	0.099*
C7	0.1898 (2)	0.8201 (2)	0.91353 (9)	0.0539 (3)
H2A	0.0890	0.7591	0.9376	0.065*
H2B	0.1895	0.9476	0.9383	0.065*
C2	−0.03776 (17)	0.84559 (16)	0.76042 (8)	0.0408 (3)
C1	−0.06778 (17)	0.82518 (15)	0.65747 (8)	0.0388 (2)
C9	0.21578 (17)	0.63226 (15)	0.39086 (8)	0.0383 (2)
C14	0.05175 (17)	0.67526 (15)	0.32130 (8)	0.0385 (2)
H6	−0.0627	0.7236	0.3402	0.046*
C13	0.06377 (18)	0.64406 (15)	0.22357 (8)	0.0404 (3)
C12	0.2299 (2)	0.57199 (18)	0.19153 (9)	0.0488 (3)
H8	0.2329	0.5523	0.1248	0.059*
C11	0.3909 (2)	0.53033 (18)	0.26185 (10)	0.0529 (3)
H9	0.5049	0.4818	0.2425	0.063*

C10	0.38486 (19)	0.55994 (17)	0.36067 (9)	0.0466 (3)
H10	0.4946	0.5313	0.4074	0.056*
C6	−0.24781 (19)	0.87423 (17)	0.60219 (10)	0.0483 (3)
H11	−0.2686	0.8599	0.5337	0.058*
C5	−0.3968 (2)	0.94460 (18)	0.64873 (11)	0.0551 (3)
H12	−0.5176	0.9778	0.6114	0.066*
C4	−0.3679 (2)	0.96581 (19)	0.74939 (12)	0.0565 (3)
H13	−0.4688	1.0137	0.7801	0.068*
C3	−0.1888 (2)	0.91623 (19)	0.80575 (10)	0.0514 (3)
H14	−0.1701	0.9304	0.8741	0.062*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0446 (5)	0.0738 (6)	0.0283 (4)	0.0085 (4)	0.0058 (3)	0.0050 (4)
O2	0.0549 (6)	0.1304 (11)	0.0483 (6)	0.0282 (6)	0.0088 (5)	0.0206 (6)
O3	0.0823 (8)	0.1176 (10)	0.0321 (5)	0.0152 (7)	0.0110 (5)	0.0155 (5)
N1	0.0432 (5)	0.0665 (7)	0.0277 (5)	0.0103 (5)	0.0052 (4)	0.0068 (4)
N2	0.0437 (5)	0.0473 (5)	0.0295 (5)	0.0021 (4)	0.0061 (4)	0.0060 (4)
N3	0.0461 (5)	0.0557 (6)	0.0329 (5)	0.0094 (4)	0.0074 (4)	0.0064 (4)
N4	0.0537 (6)	0.0657 (7)	0.0329 (5)	0.0009 (5)	0.0067 (4)	0.0096 (5)
C8	0.0646 (9)	0.0905 (11)	0.0386 (7)	0.0041 (8)	0.0004 (6)	0.0152 (7)
C7	0.0621 (8)	0.0705 (9)	0.0284 (6)	0.0037 (6)	0.0093 (5)	0.0069 (5)
C2	0.0415 (6)	0.0438 (6)	0.0360 (6)	−0.0011 (5)	0.0081 (4)	0.0035 (5)
C1	0.0398 (6)	0.0399 (6)	0.0357 (6)	0.0002 (4)	0.0072 (4)	0.0047 (4)
C9	0.0437 (6)	0.0379 (6)	0.0334 (5)	0.0025 (4)	0.0091 (4)	0.0058 (4)
C14	0.0408 (6)	0.0418 (6)	0.0338 (5)	0.0020 (4)	0.0103 (4)	0.0054 (4)
C13	0.0457 (6)	0.0422 (6)	0.0334 (6)	−0.0005 (5)	0.0083 (5)	0.0074 (4)
C12	0.0604 (7)	0.0534 (7)	0.0368 (6)	0.0060 (6)	0.0199 (5)	0.0068 (5)
C11	0.0557 (7)	0.0566 (8)	0.0524 (7)	0.0155 (6)	0.0247 (6)	0.0094 (6)
C10	0.0468 (6)	0.0493 (7)	0.0452 (6)	0.0114 (5)	0.0108 (5)	0.0109 (5)
C6	0.0466 (6)	0.0521 (7)	0.0434 (7)	0.0028 (5)	0.0024 (5)	0.0093 (5)
C5	0.0421 (6)	0.0523 (7)	0.0693 (9)	0.0062 (5)	0.0057 (6)	0.0137 (6)
C4	0.0476 (7)	0.0547 (8)	0.0704 (9)	0.0072 (6)	0.0228 (6)	0.0055 (6)
C3	0.0521 (7)	0.0577 (7)	0.0460 (7)	0.0018 (6)	0.0186 (6)	0.0019 (6)

Geometric parameters (Å, º)

O1—C2	1.3672 (14)	C1—C6	1.3828 (16)
O1—C7	1.4327 (14)	C9—C14	1.3886 (15)
O2—N4	1.2153 (15)	C9—C10	1.3898 (16)
O3—N4	1.2192 (14)	C14—C13	1.3760 (15)
N1—N2	1.3295 (13)	C14—H6	0.9300
N1—C1	1.3948 (15)	C13—C12	1.3824 (17)
N1—H1	0.8600	C12—C11	1.3782 (19)
N2—N3	1.2550 (14)	C12—H8	0.9300
N3—C9	1.4165 (14)	C11—C10	1.3803 (18)
N4—C13	1.4658 (16)	C11—H9	0.9300

C8—C7	1.493 (2)	C10—H10	0.9300
C8—H1A	0.9600	C6—C5	1.3813 (19)
C8—H1B	0.9600	C6—H11	0.9300
C8—H1C	0.9600	C5—C4	1.368 (2)
C7—H2A	0.9700	C5—H12	0.9300
C7—H2B	0.9700	C4—C3	1.386 (2)
C2—C3	1.3840 (17)	C4—H13	0.9300
C2—C1	1.3996 (16)	C3—H14	0.9300

C2—O1—C7	117.63 (9)	C10—C9—N3	115.61 (10)
N2—N1—C1	121.19 (9)	C13—C14—C9	117.92 (11)
N2—N1—H1	119.4	C13—C14—H6	121.0
C1—N1—H1	119.4	C9—C14—H6	121.0
N3—N2—N1	112.29 (9)	C14—C13—C12	123.37 (11)
N2—N3—C9	113.57 (9)	C14—C13—N4	117.84 (10)
O2—N4—O3	122.79 (12)	C12—C13—N4	118.78 (10)
O2—N4—C13	118.69 (10)	C11—C12—C13	117.71 (11)
O3—N4—C13	118.52 (11)	C11—C12—H8	121.1
C7—C8—H1A	109.5	C13—C12—H8	121.1
C7—C8—H1B	109.5	C12—C11—C10	120.67 (11)
H1A—C8—H1B	109.5	C12—C11—H9	119.7
C7—C8—H1C	109.5	C10—C11—H9	119.7
H1A—C8—H1C	109.5	C11—C10—C9	120.44 (11)
H1B—C8—H1C	109.5	C11—C10—H10	119.8
O1—C7—C8	108.27 (11)	C9—C10—H10	119.8
O1—C7—H2A	110.0	C5—C6—C1	119.94 (12)
C8—C7—H2A	110.0	C5—C6—H11	120.0
O1—C7—H2B	110.0	C1—C6—H11	120.0
C8—C7—H2B	110.0	C4—C5—C6	120.46 (12)
H2A—C7—H2B	108.4	C4—C5—H12	119.8
O1—C2—C3	125.54 (11)	C6—C5—H12	119.8
O1—C2—C1	115.09 (10)	C5—C4—C3	120.27 (12)
C3—C2—C1	119.37 (11)	C5—C4—H13	119.9
C6—C1—N1	123.10 (11)	C3—C4—H13	119.9
C6—C1—C2	119.87 (11)	C2—C3—C4	120.09 (12)
N1—C1—C2	117.02 (10)	C2—C3—H14	120.0
C14—C9—C10	119.88 (10)	C4—C3—H14	120.0
C14—C9—N3	124.50 (10)		

C1—N1—N2—N3	−177.91 (10)	O2—N4—C13—C14	−2.37 (18)
N1—N2—N3—C9	−179.23 (9)	O3—N4—C13—C14	177.30 (12)
C2—O1—C7—C8	−179.64 (12)	O2—N4—C13—C12	178.57 (13)
C7—O1—C2—C3	−5.71 (19)	O3—N4—C13—C12	−1.77 (18)
C7—O1—C2—C1	175.15 (11)	C14—C13—C12—C11	−0.2 (2)
N2—N1—C1—C6	1.14 (18)	N4—C13—C12—C11	178.81 (12)
N2—N1—C1—C2	−179.72 (10)	C13—C12—C11—C10	0.1 (2)
O1—C2—C1—C6	178.70 (11)	C12—C11—C10—C9	0.1 (2)
C3—C2—C1—C6	−0.50 (18)	C14—C9—C10—C11	−0.06 (19)

O1—C2—C1—N1	−0.47 (16)	N3—C9—C10—C11	−179.95 (11)
C3—C2—C1—N1	−179.67 (11)	N1—C1—C6—C5	179.66 (12)
N2—N3—C9—C14	−2.50 (17)	C2—C1—C6—C5	0.54 (19)
N2—N3—C9—C10	177.40 (11)	C1—C6—C5—C4	−0.2 (2)
C10—C9—C14—C13	−0.07 (17)	C6—C5—C4—C3	−0.2 (2)
N3—C9—C14—C13	179.82 (10)	O1—C2—C3—C4	−179.01 (12)
C9—C14—C13—C12	0.20 (18)	C1—C2—C3—C4	0.1 (2)
C9—C14—C13—N4	−178.82 (10)	C5—C4—C3—C2	0.3 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	2.26	2.6130 (12)	105
C7—H2*A*···O3^{i}	0.97	2.55	3.4595 (18)	157
C10—H10···N3^{ii}	0.93	2.65	3.543 (3)	161

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.