

Crystal structure of (*E*)-1-methyl-2-[2-(2-methoxyphenyl)ethenyl]-4-nitro-1*H*-imidazole

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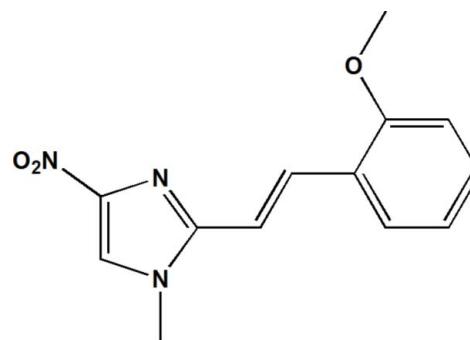
In the asymmetric unit of the title compound, C₁₃H₁₃N₃O₃, the 2-(2-methoxyphenyl)ethenyl unit is connected to the methyl-nitroimidazole 1-methyl-4-nitro-1*H*-imidazole moiety. The molecule is quasi-planar and the planes of the two rings form a dihedral angle of 0.92 (11)°. The crystal packing can be described as layers parallel to the (011) plane, stabilized by intermolecular C—H...O hydrogen bonding, resulting in the formation of an infinite three-dimensional network linking these layers. Strong π – π stacking interactions are observed, *viz.* benzene–benzene, imidazole–imidazole and benzene–imidazole rings, with centroid–centroid distances of 3.528 (2), 3.457 (2) and 3.544 (2) Å, respectively. Intensity statistics indicated twinning by non-merohedry, with refined weights of the twin components of 0.3687:0.6313.

Keywords: crystal structure; hydrogen bonding; π – π stacking interactions; nitroimidazoles,.

CCDC reference: 1015965

1. Related literature

For the synthesis and applications of this important class of compounds, see: Hori *et al.* (1997); Bourdin-Trunz *et al.* (2011). For our previous work on imidazole derivatives, see: Alliouche *et al.* (2014); Zama *et al.* (2013); Bahnous *et al.* (2012).



2. Experimental

2.1. Crystal data

| | |
|---|---|
| C ₁₃ H ₁₃ N ₃ O ₃ | $\gamma = 76.182 (17)^\circ$ |
| $M_r = 259.26$ | $V = 604.7 (2) \text{ \AA}^3$ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 7.9339 (18) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 8.1994 (19) \text{ \AA}$ | $\mu = 0.10 \text{ mm}^{-1}$ |
| $c = 10.452 (3) \text{ \AA}$ | $T = 150 \text{ K}$ |
| $\alpha = 68.877 (17)^\circ$ | $0.19 \times 0.12 \times 0.08 \text{ mm}$ |
| $\beta = 75.037 (17)^\circ$ | |

2.2. Data collection

| | |
|---|--|
| Bruker APEXII diffractometer | 5177 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2002) | 5177 independent reflections |
| $T_{\min} = 0.754$, $T_{\max} = 1.000$ | 3712 reflections with $I > 2\sigma(I)$ |

2.3. Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.088$ | 176 parameters |
| $wR(F^2) = 0.282$ | H-atom parameters constrained |
| $S = 1.06$ | $\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$ |
| 5171 reflections | $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$ |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|-------|-------------|-------------|---------------|
| C3–H3...O2 ⁱ | 0.93 | 2.45 | 3.271 (4) | 147 |
| C4–H4B...O1 ⁱⁱ | 0.96 | 2.53 | 3.465 (5) | 165 |
| C6–H6...O3 | 0.93 | 2.31 | 2.685 (4) | 103 |
| C6–H6...N2 | 0.93 | 2.60 | 2.935 (4) | 102 |

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

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5400).

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supporting information

Acta Cryst. (2014). E70, o966–o967 [doi:10.1107/S1600536814017206]

Crystal structure of (*E*)-1-methyl-2-[2-(2-methoxyphenyl)ethenyl]-4-nitro-1*H*-imidazole

Hayette Alliouche, Abdelmalek Bouraiou, Sofiane Bouacida, Hocine Merazig and Ali Belfaitah

S1. Comment

Nitroimidazoles are a class of N-heterocyclic compounds which have a wide range of applications in the drug synthesis (Hori, *et al.*, 1997) In fact, Metronidazole (Flagyl) and related N-1 substituted 5-nitroimidazoles such as Tinidazole (Fasigyne), Ornidazole (Tiberal) and Secnidazole (Secnol) still commonly used in medicine. Despite their fewer biological activities compared with 5-nitroimidazoles, a number of 4-nitroimidazoles were reported to exhibit antileishmanial, antiamebic and anti-parasitic activities (Bourdin-Trunz, *et al.* 2011). However, only some limited investigations have been carried out using methyl iodide (Alliouche, *et al.* 2014). In previous work, we have reported the synthesis and structure determination of some new heterocyclic compounds bearing an imidazole unit (Zama, *et al.*, 2013; Bahnous, *et al.*, 2012). Herein, we describe the synthesis and the structure determination of (*E*)-1-methyl-2-[(2-methoxyphenyl)-1-ethenyl]-4-nitroimidazole resulting from the intramolecular transposition reaction of its 5-nitro isomer in the presence of catalytic amounts of methyl iodide in nitrobenzene. The molecular geometry and the atom-numbering scheme of (I) are shown in Fig. 1. In the asymmetric unit of title compound the methoxyphenyl-1-ethenyl unit is linked to methyl-nitroimidazole moiety. The molecule is quasi-planar and the two rings of phenyl and imidazol form a dihedral angle of 0.92 (11)°. The crystal packing can be described as layers parallel to (011) plane, along the *a* axis (Fig. 2). It is stabilized by intermolecular hydrogen bond C—H...O, resulting in the formation of an infinite three-dimensional network linking these layers together and reinforcing cohesion in the structure (Fig. 2). Hydrogen-bonding parameters are listed in Table 1. Strong π - π stacking interactions are observed between phenyl-phenyl, imidazol-imidazol and phenyl-imidazol rings, distances centroid-centroid are C_g — C_g = 3.528 (2), 3.457 (2) and 3.544 (2) Å respectively. The crystal used was a non-merohedral twin, the refined ratio of twin components being 0.3687:0.6313.

S2. Experimental

The title compound was obtained as a yellow-green solid in 83% of yield by heating a solution of (*E*)-1-methyl-2-[(2-methoxyphenyl)-1-ethenyl]-5-nitroimidazole in nitrobenzene at 160°C during 24 h in the presence of catalytic amount of CH₃I. Suitable crystal of compound (I) was obtained by slow evaporation from a water/methanol solution at room temperature, and X-ray crystallographic analysis confirmed the structural assignment (Fig. 1).

S3. Refinement

All non-H atoms were refined with anisotropic atomic displacement parameters. All H atoms were localized on Fourier maps but introduced in calculated positions and treated as riding on their parent C or N atom. (with C—H = 0.93 and 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5$ or 1.2 (carrier atom).

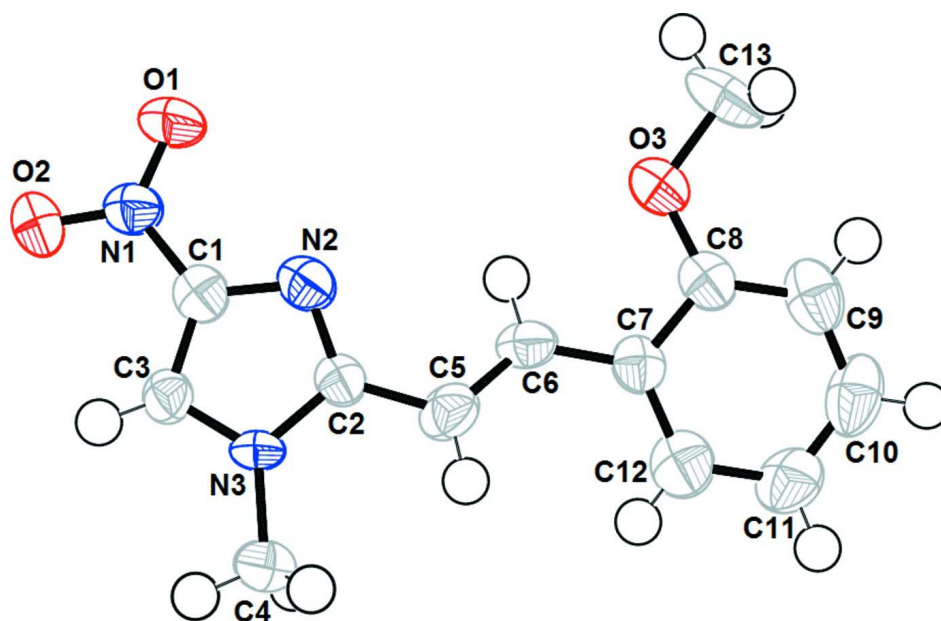
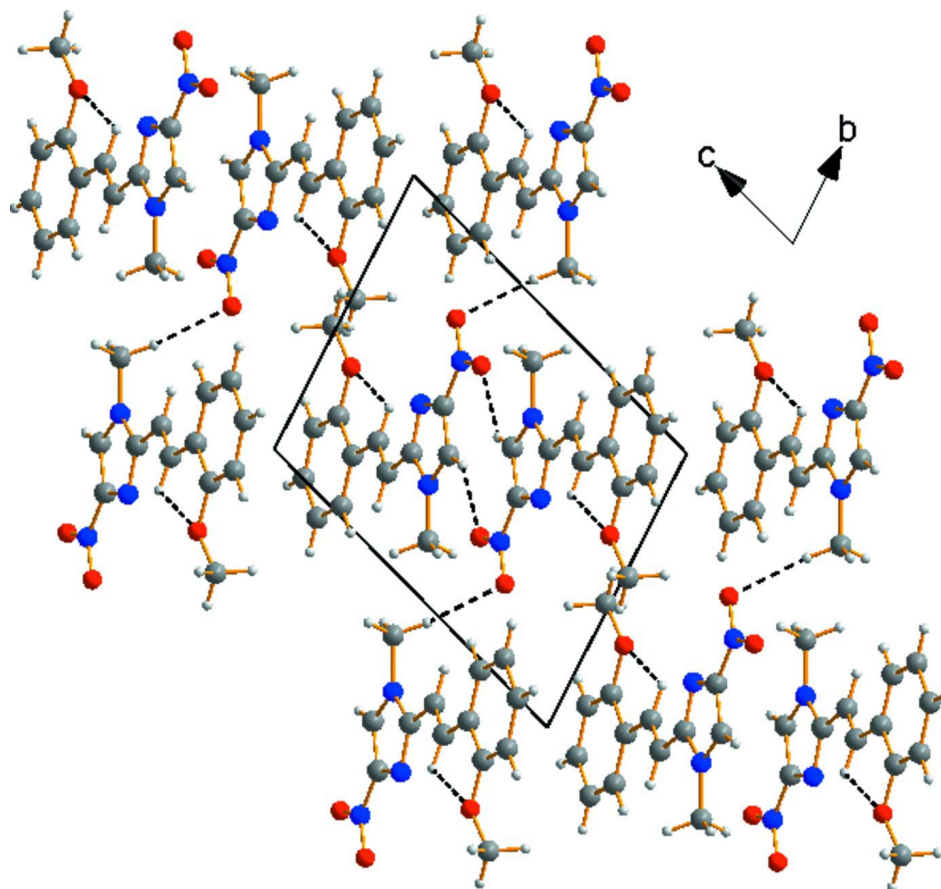


Figure 1

The structure of the title compound with the atomic labelling scheme. Displacement are drawn at the 50% probability level.

**Figure 2**

A diagram of the layered crystal packing of (I) viewed down the a axis and showing hydrogen bond [C—H \cdots O] as dashed line.

1-Methyl-2-[(*E*)-2-(2-methoxyphenyl)ethenyl]-4-nitro-1*H*-imidazole

Crystal data

$C_{13}H_{13}N_3O_3$

$M_r = 259.26$

Triclinic, $P\bar{1}$

$a = 7.9339$ (18) Å

$b = 8.1994$ (19) Å

$c = 10.452$ (3) Å

$\alpha = 68.877$ (17)°

$\beta = 75.037$ (17)°

$\gamma = 76.182$ (17)°

$V = 604.7$ (2) Å³

$Z = 2$

$F(000) = 272$

$D_x = 1.424$ Mg m⁻³

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

Cell parameters from 1356 reflections

$\theta = 2.7$ – 24.6 °

$\mu = 0.10$ mm⁻¹

$T = 150$ K

Block, yellow

$0.19 \times 0.12 \times 0.08$ mm

Data collection

Bruker APEXII
diffractometer

Graphite monochromator

CCD rotation images, thin slices scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2002)

$T_{\min} = 0.754$, $T_{\max} = 1.000$

5177 measured reflections

5177 independent reflections

3712 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0$

$\theta_{\max} = 25.3$ °, $\theta_{\min} = 2.7$ °

$h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.088$
 $wR(F^2) = 0.282$
 $S = 1.06$
 5171 reflections
 176 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
 $w = 1/[\sigma^2(F_o^2) + (0.1745P)^2 + 0.1919P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.045 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|------------|-------------|----------------------------------|
| O1 | 0.4178 (3) | 0.2400 (3) | 0.2786 (3) | 0.0256 (6) |
| O3 | 1.0969 (3) | 0.6148 (3) | 0.0846 (2) | 0.0219 (6) |
| O2 | 0.1531 (3) | 0.2922 (3) | 0.3961 (3) | 0.0238 (6) |
| N1 | 0.3026 (4) | 0.3303 (4) | 0.3420 (3) | 0.0167 (7) |
| N2 | 0.5059 (3) | 0.5331 (4) | 0.2979 (3) | 0.0162 (7) |
| N3 | 0.3292 (3) | 0.7076 (3) | 0.4156 (3) | 0.0134 (6) |
| C1 | 0.3460 (4) | 0.4809 (4) | 0.3545 (3) | 0.0142 (7) |
| C2 | 0.4934 (4) | 0.6726 (4) | 0.3362 (3) | 0.0125 (7) |
| C5 | 0.6299 (4) | 0.7796 (5) | 0.3004 (3) | 0.0172 (8) |
| H5 | 0.6018 | 0.8867 | 0.319 | 0.021* |
| C6 | 0.7973 (4) | 0.7279 (4) | 0.2408 (3) | 0.0151 (7) |
| H6 | 0.8198 | 0.6187 | 0.2261 | 0.018* |
| C7 | 0.9464 (4) | 0.8227 (4) | 0.1968 (3) | 0.0139 (7) |
| C8 | 1.1027 (4) | 0.7634 (4) | 0.1144 (3) | 0.0159 (8) |
| C13 | 1.2438 (4) | 0.5580 (5) | -0.0106 (4) | 0.0273 (9) |
| H13C | 1.2622 | 0.6542 | -0.0961 | 0.041* |
| H13A | 1.22 | 0.4604 | -0.0296 | 0.041* |
| H13B | 1.3478 | 0.5214 | 0.0299 | 0.041* |
| C4 | 0.2711 (4) | 0.8439 (5) | 0.4845 (3) | 0.0196 (8) |
| H4A | 0.1465 | 0.8508 | 0.5215 | 0.029* |
| H4B | 0.2948 | 0.9563 | 0.418 | 0.029* |

| | | | | |
|-----|------------|------------|------------|------------|
| H4C | 0.3339 | 0.814 | 0.5591 | 0.029* |
| C3 | 0.2328 (4) | 0.5873 (4) | 0.4277 (3) | 0.0139 (7) |
| H3 | 0.117 | 0.5778 | 0.4744 | 0.017* |
| C9 | 1.2469 (4) | 0.8506 (5) | 0.0702 (3) | 0.0207 (8) |
| H9 | 1.349 | 0.81 | 0.0154 | 0.025* |
| C10 | 1.2392 (5) | 0.9970 (5) | 0.1072 (3) | 0.0233 (8) |
| H10 | 1.3369 | 1.0544 | 0.0781 | 0.028* |
| C11 | 1.0871 (4) | 1.0600 (5) | 0.1876 (3) | 0.0211 (8) |
| H11 | 1.0818 | 1.1602 | 0.2116 | 0.025* |
| C12 | 0.9434 (4) | 0.9723 (5) | 0.2317 (3) | 0.0199 (8) |
| H12 | 0.8418 | 1.0144 | 0.2863 | 0.024* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0232 (13) | 0.0238 (14) | 0.0331 (14) | −0.0046 (11) | 0.0055 (11) | −0.0199 (12) |
| O3 | 0.0169 (13) | 0.0238 (14) | 0.0257 (13) | −0.0036 (10) | 0.0029 (10) | −0.0135 (11) |
| O2 | 0.0142 (13) | 0.0280 (15) | 0.0313 (14) | −0.0066 (11) | 0.0037 (11) | −0.0154 (12) |
| N1 | 0.0173 (15) | 0.0150 (15) | 0.0183 (14) | −0.0021 (12) | −0.0013 (12) | −0.0077 (12) |
| N2 | 0.0144 (14) | 0.0181 (15) | 0.0159 (14) | −0.0007 (12) | −0.0022 (11) | −0.0070 (12) |
| N3 | 0.0139 (14) | 0.0113 (14) | 0.0162 (13) | −0.0006 (11) | −0.0005 (11) | −0.0083 (11) |
| C1 | 0.0135 (16) | 0.0166 (17) | 0.0122 (16) | −0.0007 (13) | −0.0053 (13) | −0.0032 (13) |
| C2 | 0.0120 (16) | 0.0162 (17) | 0.0099 (14) | −0.0020 (13) | −0.0029 (13) | −0.0043 (13) |
| C5 | 0.0170 (18) | 0.0181 (17) | 0.0207 (17) | −0.0027 (14) | −0.0072 (14) | −0.0086 (15) |
| C6 | 0.0155 (17) | 0.0144 (17) | 0.0177 (16) | 0.0010 (14) | −0.0055 (13) | −0.0084 (14) |
| C7 | 0.0154 (17) | 0.0165 (17) | 0.0089 (15) | −0.0037 (14) | −0.0028 (13) | −0.0018 (13) |
| C8 | 0.0143 (17) | 0.0193 (18) | 0.0134 (16) | −0.0016 (14) | −0.0034 (14) | −0.0047 (14) |
| C13 | 0.0200 (19) | 0.033 (2) | 0.0253 (19) | 0.0037 (17) | 0.0043 (15) | −0.0167 (17) |
| C4 | 0.0171 (17) | 0.0219 (18) | 0.0232 (17) | −0.0021 (15) | −0.0010 (14) | −0.0137 (15) |
| C3 | 0.0126 (17) | 0.0178 (18) | 0.0129 (15) | −0.0037 (14) | −0.0026 (13) | −0.0058 (13) |
| C9 | 0.0150 (17) | 0.029 (2) | 0.0163 (17) | −0.0043 (15) | −0.0043 (14) | −0.0036 (15) |
| C10 | 0.026 (2) | 0.030 (2) | 0.0173 (17) | −0.0148 (16) | −0.0081 (15) | −0.0020 (16) |
| C11 | 0.0237 (19) | 0.025 (2) | 0.0201 (17) | −0.0062 (16) | −0.0086 (15) | −0.0092 (16) |
| C12 | 0.0187 (18) | 0.025 (2) | 0.0176 (17) | −0.0039 (15) | −0.0067 (14) | −0.0068 (15) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|----------|-----------|
| O1—N1 | 1.241 (3) | C7—C8 | 1.406 (4) |
| O3—C8 | 1.375 (4) | C8—C9 | 1.383 (5) |
| O3—C13 | 1.429 (4) | C13—H13C | 0.96 |
| O2—N1 | 1.236 (3) | C13—H13A | 0.96 |
| N1—C1 | 1.415 (4) | C13—H13B | 0.96 |
| N2—C2 | 1.317 (4) | C4—H4A | 0.96 |
| N2—C1 | 1.354 (4) | C4—H4B | 0.96 |
| N3—C3 | 1.339 (4) | C4—H4C | 0.96 |
| N3—C2 | 1.380 (4) | C3—H3 | 0.93 |
| N3—C4 | 1.464 (4) | C9—C10 | 1.372 (5) |
| C1—C3 | 1.380 (4) | C9—H9 | 0.93 |

| | | | |
|-------------|------------|---------------|------------|
| C2—C5 | 1.445 (5) | C10—C11 | 1.386 (5) |
| C5—C6 | 1.351 (5) | C10—H10 | 0.93 |
| C5—H5 | 0.93 | C11—C12 | 1.382 (5) |
| C6—C7 | 1.455 (5) | C11—H11 | 0.93 |
| C6—H6 | 0.93 | C12—H12 | 0.93 |
| C7—C12 | 1.394 (5) | | |
| | | | |
| C8—O3—C13 | 117.1 (3) | O3—C13—H13A | 109.5 |
| O2—N1—O1 | 122.5 (3) | H13C—C13—H13A | 109.5 |
| O2—N1—C1 | 119.0 (3) | O3—C13—H13B | 109.5 |
| O1—N1—C1 | 118.4 (3) | H13C—C13—H13B | 109.5 |
| C2—N2—C1 | 103.9 (3) | H13A—C13—H13B | 109.5 |
| C3—N3—C2 | 108.4 (2) | N3—C4—H4A | 109.5 |
| C3—N3—C4 | 124.7 (3) | N3—C4—H4B | 109.5 |
| C2—N3—C4 | 126.7 (3) | H4A—C4—H4B | 109.5 |
| N2—C1—C3 | 112.9 (3) | N3—C4—H4C | 109.5 |
| N2—C1—N1 | 123.0 (3) | H4A—C4—H4C | 109.5 |
| C3—C1—N1 | 124.1 (3) | H4B—C4—H4C | 109.5 |
| N2—C2—N3 | 111.1 (3) | N3—C3—C1 | 103.7 (3) |
| N2—C2—C5 | 125.9 (3) | N3—C3—H3 | 128.1 |
| N3—C2—C5 | 123.0 (3) | C1—C3—H3 | 128.1 |
| C6—C5—C2 | 121.7 (3) | C10—C9—C8 | 120.0 (3) |
| C6—C5—H5 | 119.2 | C10—C9—H9 | 120 |
| C2—C5—H5 | 119.2 | C8—C9—H9 | 120 |
| C5—C6—C7 | 127.7 (3) | C9—C10—C11 | 120.6 (3) |
| C5—C6—H6 | 116.1 | C9—C10—H10 | 119.7 |
| C7—C6—H6 | 116.1 | C11—C10—H10 | 119.7 |
| C12—C7—C8 | 117.2 (3) | C12—C11—C10 | 119.2 (3) |
| C12—C7—C6 | 123.3 (3) | C12—C11—H11 | 120.4 |
| C8—C7—C6 | 119.5 (3) | C10—C11—H11 | 120.4 |
| O3—C8—C9 | 124.8 (3) | C11—C12—C7 | 121.9 (3) |
| O3—C8—C7 | 114.1 (3) | C11—C12—H12 | 119 |
| C9—C8—C7 | 121.1 (3) | C7—C12—H12 | 119 |
| O3—C13—H13C | 109.5 | | |
| | | | |
| C2—N2—C1—C3 | 0.3 (3) | C13—O3—C8—C9 | -6.8 (5) |
| C2—N2—C1—N1 | -178.3 (3) | C13—O3—C8—C7 | 173.6 (3) |
| O2—N1—C1—N2 | -179.5 (3) | C12—C7—C8—O3 | 179.6 (3) |
| O1—N1—C1—N2 | 1.5 (4) | C6—C7—C8—O3 | -0.6 (4) |
| O2—N1—C1—C3 | 2.0 (5) | C12—C7—C8—C9 | -0.1 (5) |
| O1—N1—C1—C3 | -176.9 (3) | C6—C7—C8—C9 | 179.8 (3) |
| C1—N2—C2—N3 | 0.1 (3) | C2—N3—C3—C1 | 0.6 (3) |
| C1—N2—C2—C5 | -179.2 (3) | C4—N3—C3—C1 | -175.4 (3) |
| C3—N3—C2—N2 | -0.5 (3) | N2—C1—C3—N3 | -0.5 (3) |
| C4—N3—C2—N2 | 175.4 (3) | N1—C1—C3—N3 | 178.1 (3) |
| C3—N3—C2—C5 | 178.9 (3) | O3—C8—C9—C10 | -179.3 (3) |
| C4—N3—C2—C5 | -5.3 (5) | C7—C8—C9—C10 | 0.3 (5) |
| N2—C2—C5—C6 | -10.8 (5) | C8—C9—C10—C11 | -0.7 (5) |

| | | | |
|--------------|------------|----------------|------------|
| N3—C2—C5—C6 | 170.0 (3) | C9—C10—C11—C12 | 0.8 (5) |
| C2—C5—C6—C7 | 178.6 (3) | C10—C11—C12—C7 | -0.5 (5) |
| C5—C6—C7—C12 | 11.0 (5) | C8—C7—C12—C11 | 0.1 (5) |
| C5—C6—C7—C8 | -168.8 (3) | C6—C7—C12—C11 | -179.7 (3) |

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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| C3—H3...O2 ⁱ | 0.93 | 2.45 | 3.271 (4) | 147 |
| C4—H4B...O1 ⁱⁱ | 0.96 | 2.53 | 3.465 (5) | 165 |
| C6—H6...O3 | 0.93 | 2.31 | 2.685 (4) | 103 |
| C6—H6...N2 | 0.93 | 2.60 | 2.935 (4) | 102 |

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