

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Dimethyl 3,5-diethyl-1*H*-pyrrole-2,4-dicarboxylate

Gui-Fen Lu, Wen-Sheng Lin, Wei-Hua Zhu and Zhong-Ping Ou*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China

Correspondence e-mail: zpou2011@126.com

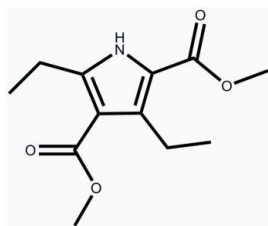
Received 29 June 2011; accepted 15 July 2011

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.118; data-to-parameter ratio = 14.7.

The title pyrrole derivative, $\text{C}_{12}\text{H}_{17}\text{NO}_4$, consists of a pyrrole ring with two diagonally attached methoxycarbonyl groups and two diagonally attached ethyl groups. The two carbonyl groups are approximately in the same plane as the pyrrole ring, making dihedral angles of 3.50 (19) and 6.70 (19)°. In the crystal, adjacent molecules are assembled into dimers in a head-to-head mode by pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For applications of polysubstituted pyrroles, see: Brockmann & Tour (1995); Guillard *et al.* (2001); Trofimov *et al.* (2004). For related structures, see: Takaya *et al.* (2001). For background to complexes of pyrrole derivatives, see: Fan *et al.* (2008); Ou *et al.* (2009); Paixão *et al.* (2003); Yamamoto *et al.* (1986).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{17}\text{NO}_4$
 $M_r = 239.27$
 Monoclinic, $P2_1/c$
 $a = 4.4697$ (7) Å
 $b = 14.616$ (2) Å

$c = 19.784$ (3) Å
 $\beta = 90.467$ (2)°
 $V = 1292.4$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.09$ mm⁻¹
 $T = 298$ K

0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.982$, $T_{\max} = 0.991$
 6296 measured reflections
 2285 independent reflections
 1977 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.118$
 $S = 1.08$
 2285 reflections
 155 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1N}\cdots\text{O4}^i$ | 0.85 | 2.07 | 2.8773 (15) | 160 |

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

This work was supported by the Natural Science Foundation of China (No. 21001054) and the Natural Science Fund for Colleges and Universities in Jiangsu Province (No. 10KJB150003)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2335).

References

- Brockmann, T. W. & Tour, J. M. (1995). *J. Am. Chem. Soc.* **117**, 4437–4447.
 Bruker (2001). *SAINTE-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Fan, H., Peng, J. N., Hamann, M. T. & Hu, J. F. (2008). *Chem. Rev.* **108**, 264–287.
 Guillard, R., Gross, C. P., Bolze, F., Jerome, F., Ou, Z. P., Shao, J. G., Fischer, J., Weiss, R. & Kadish, K. M. (2001). *Inorg. Chem.* **40**, 4845–4855.
 Ou, Z. P., Zhu, W. H., Zhou, F., Zhao, X. F. & Ji, X. L. (2009). *Fine Chem.* **26**, 609–612.
 Paixão, J. A., Ramos Silva, M., Matos Beja, A., Sobral, A. J. F. N., Lopes, S. H. & Rocha Gonsalves, A. M. d'A. (2003). *Acta Cryst.* **E59**, o94–o96.
 Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Takaya, H., Kojima, S. & Murahashi, S. I. (2001). *Org. Lett.* **3**, 421–424.
 Trofimov, B. A., Sobenina, L. N., Demenev, A. P. & Mikhaleva, A. (2004). *Chem. Rev.* **104**, 2481–2506.
 Yamamoto, N., Machida, K., Taga, T. & Ogoshi, H. (1986). *Acta Cryst.* **C42**, 1573–1576.

supporting information

Acta Cryst. (2011). E67, o2097 [doi:10.1107/S1600536811028352]

Dimethyl 3,5-diethyl-1*H*-pyrrole-2,4-dicarboxylate

Gui-Fen Lu, Wen-Sheng Lin, Wei-Hua Zhu and Zhong-Ping Ou

S1. Comment

Polysubstituted pyrroles have been paid much attention because of their wide application in the preparation of porphyrin (Trofimov *et al.*, 2004), corrole (Guilard *et al.*, 2001), and as monomers for polymer chemistry (Brockmann & Tour, 1995). In particular, 2-(alkoxycarbonyl)pyrrole derivatives have attracted intense interest in the design and synthesis of functional materials (Fan *et al.*, 2008). The title compound was synthesized as a precursor to corrole compounds.

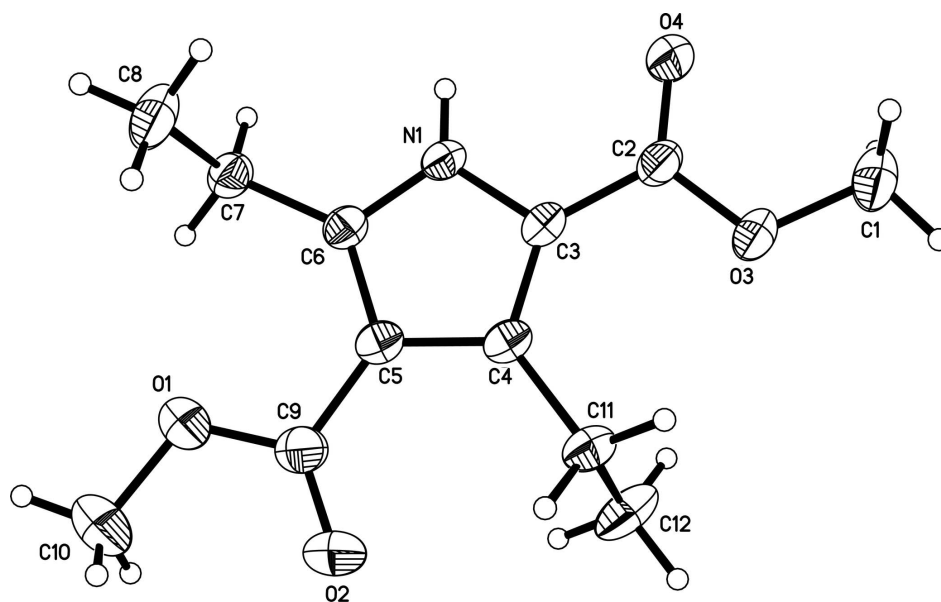
As shown in Fig. 1, the compound has a five-membered pyrrole ring as skeleton and four substituents. Two diagonally related methoxycarbonyl groups and two diagonally related ethyl substituents are attached to the pyrrole ring. Pairs of intermolecular N1—H1n \cdots O4ⁱ (symmetry code *i*: $-x + 1, -y, -z + 1$) hydrogen bonds assemble adjacent molecules in a head-to-head manner, as shown in Fig. 2. All bond distances are in the normal range for this type of compound, as reported by Yamamoto *et al.* (1986).

S2. Experimental

The title compound was synthesized from methyl 3-oxopentanoate by a Knorr-type reaction according to the method reported by Ou *et al.* (2009). Single crystals were grown from ethyl alcohol by slow evaporation.

S3. Refinement

All the non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 . All the H atoms except H1n were placed in calculated positions with C—H distances of 0.93 and 0.96 Å, and were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H1n was found in a difference map, and included using a riding model with a bond length restrained to 0.84 (1) Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

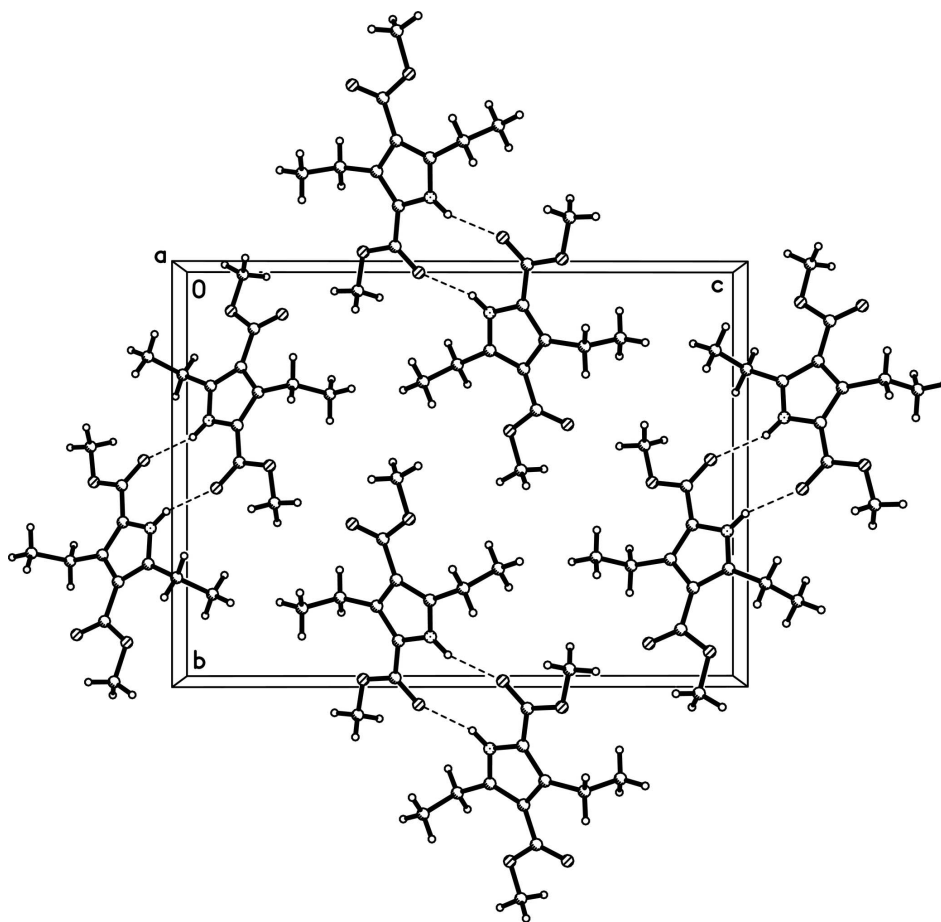


Figure 2

The two-dimensional supramolecular configuration, viewed down the *a* axis.

Dimethyl 3,5-diethyl-1*H*-pyrrole-2,4-dicarboxylate*Crystal data*C₁₂H₁₇NO₄*M_r* = 239.27Monoclinic, *P*2₁/*c*Hall symbol: -*P* 2ybc*a* = 4.4697 (7) Å*b* = 14.616 (2) Å*c* = 19.784 (3) Å

β = 90.467 (2)°

V = 1292.4 (4) Å³*Z* = 4*F*(000) = 512*D_x* = 1.230 Mg m⁻³Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3745 reflections

θ = 2.8–27.4°

μ = 0.09 mm⁻¹*T* = 298 K

Block, colorless

0.20 × 0.15 × 0.10 mm

*Data collection*Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2003)*T_{min}* = 0.982, *T_{max}* = 0.991

6296 measured reflections

2285 independent reflections

1977 reflections with *I* > 2σ(*I*)*R_{int}* = 0.037θ_{max} = 25.0°, θ_{min} = 1.7°*h* = -5→5*k* = -15→17*l* = -23→21*Refinement*Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.041*wR*(*F*²) = 0.118*S* = 1.08

2285 reflections

155 parameters

1 restraint

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0619*P*)² + 0.1775*P*]where *P* = (*F_o*² + 2*F_c*²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.15 e Å⁻³Δρ_{min} = -0.16 e Å⁻³Extinction correction: *SHELXL97* (Sheldrick,
2008), *F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.110 (8)

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 > σ(*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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|---------------|--------------|----------------------------------|
| C1 | 1.0716 (4) | -0.06793 (13) | 0.67868 (10) | 0.0771 (5) |
| H1A | 1.1839 | -0.0662 | 0.7202 | 0.116* |
| H1B | 1.2038 | -0.0808 | 0.6419 | 0.116* |
| H1C | 0.9220 | -0.1149 | 0.6812 | 0.116* |
| C2 | 0.7645 (3) | 0.02789 (10) | 0.61180 (6) | 0.0485 (4) |
| C3 | 0.6201 (3) | 0.11655 (9) | 0.60495 (6) | 0.0429 (3) |
| C4 | 0.6275 (3) | 0.19623 (9) | 0.64214 (6) | 0.0428 (3) |
| C5 | 0.4354 (3) | 0.25896 (9) | 0.60761 (6) | 0.0440 (3) |
| C6 | 0.3161 (3) | 0.21461 (9) | 0.55064 (6) | 0.0422 (3) |
| C7 | 0.1103 (3) | 0.24441 (10) | 0.49502 (7) | 0.0504 (4) |
| H7A | -0.0305 | 0.2888 | 0.5126 | 0.060* |
| H7B | -0.0030 | 0.1920 | 0.4789 | 0.060* |
| C8 | 0.2772 (4) | 0.28646 (14) | 0.43641 (8) | 0.0753 (5) |
| H8A | 0.1370 | 0.3043 | 0.4018 | 0.113* |
| H8B | 0.4146 | 0.2425 | 0.4184 | 0.113* |
| H8C | 0.3857 | 0.3393 | 0.4519 | 0.113* |
| C9 | 0.3744 (3) | 0.35270 (11) | 0.62967 (7) | 0.0548 (4) |
| C10 | 0.1230 (6) | 0.49089 (14) | 0.60468 (13) | 0.1063 (8) |
| H10A | 0.0056 | 0.5182 | 0.5692 | 0.159* |
| H10B | 0.2992 | 0.5270 | 0.6126 | 0.159* |
| H10C | 0.0071 | 0.4882 | 0.6453 | 0.159* |
| C11 | 0.8015 (3) | 0.21297 (11) | 0.70625 (7) | 0.0530 (4) |
| H11A | 0.8638 | 0.2765 | 0.7077 | 0.064* |
| H11B | 0.9803 | 0.1754 | 0.7062 | 0.064* |
| C12 | 0.6215 (4) | 0.19160 (16) | 0.76897 (8) | 0.0802 (6) |
| H12A | 0.7415 | 0.2033 | 0.8085 | 0.120* |
| H12B | 0.5628 | 0.1284 | 0.7683 | 0.120* |
| H12C | 0.4463 | 0.2296 | 0.7698 | 0.120* |
| N1 | 0.4307 (2) | 0.12986 (7) | 0.55029 (5) | 0.0439 (3) |
| H1N | 0.3918 | 0.0897 | 0.5207 | 0.053* |
| O1 | 0.2088 (3) | 0.39946 (8) | 0.58509 (7) | 0.0858 (4) |
| O2 | 0.4557 (3) | 0.38626 (9) | 0.68180 (7) | 0.0867 (4) |
| O3 | 0.9285 (3) | 0.01959 (7) | 0.66768 (5) | 0.0619 (3) |
| O4 | 0.7364 (3) | -0.03336 (7) | 0.57103 (5) | 0.0725 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|-------------|-------------|-------------|
| C1 | 0.0872 (12) | 0.0737 (11) | 0.0700 (11) | 0.0164 (9) | -0.0229 (9) | 0.0148 (9) |
| C2 | 0.0557 (8) | 0.0537 (8) | 0.0361 (7) | -0.0007 (6) | -0.0071 (6) | 0.0027 (6) |
| C3 | 0.0452 (7) | 0.0510 (8) | 0.0324 (6) | -0.0027 (6) | -0.0039 (5) | 0.0028 (5) |
| C4 | 0.0428 (7) | 0.0518 (7) | 0.0337 (6) | -0.0065 (5) | 0.0008 (5) | -0.0004 (5) |
| C5 | 0.0448 (7) | 0.0501 (7) | 0.0370 (7) | -0.0040 (6) | 0.0018 (5) | -0.0018 (5) |
| C6 | 0.0426 (7) | 0.0485 (7) | 0.0356 (7) | -0.0011 (5) | 0.0022 (5) | 0.0011 (5) |
| C7 | 0.0499 (7) | 0.0581 (8) | 0.0430 (7) | 0.0065 (6) | -0.0060 (6) | -0.0012 (6) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C8 | 0.0784 (11) | 0.0967 (13) | 0.0507 (9) | 0.0129 (10) | -0.0038 (8) | 0.0251 (9) |
| C9 | 0.0604 (9) | 0.0543 (8) | 0.0497 (8) | -0.0030 (7) | 0.0003 (7) | -0.0054 (7) |
| C10 | 0.144 (2) | 0.0585 (11) | 0.1155 (18) | 0.0297 (12) | -0.0188 (16) | -0.0147 (12) |
| C11 | 0.0521 (8) | 0.0635 (9) | 0.0432 (8) | -0.0057 (7) | -0.0091 (6) | -0.0072 (6) |
| C12 | 0.0775 (12) | 0.1278 (17) | 0.0351 (8) | -0.0093 (11) | -0.0089 (7) | -0.0013 (9) |
| N1 | 0.0515 (7) | 0.0469 (6) | 0.0332 (6) | -0.0012 (5) | -0.0062 (5) | -0.0037 (4) |
| O1 | 0.1210 (11) | 0.0572 (7) | 0.0788 (8) | 0.0254 (7) | -0.0276 (8) | -0.0122 (6) |
| O2 | 0.1163 (11) | 0.0700 (8) | 0.0733 (8) | 0.0097 (7) | -0.0253 (7) | -0.0288 (6) |
| O3 | 0.0770 (7) | 0.0614 (7) | 0.0468 (6) | 0.0075 (5) | -0.0213 (5) | 0.0043 (5) |
| O4 | 0.1030 (9) | 0.0579 (7) | 0.0560 (7) | 0.0185 (6) | -0.0278 (6) | -0.0112 (5) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|---------------|-------------|
| C1—O3 | 1.446 (2) | C7—H7B | 0.9700 |
| C1—H1A | 0.9600 | C8—H8A | 0.9600 |
| C1—H1B | 0.9600 | C8—H8B | 0.9600 |
| C1—H1C | 0.9600 | C8—H8C | 0.9600 |
| C2—O4 | 1.2109 (17) | C9—O2 | 1.1959 (18) |
| C2—O3 | 1.3270 (16) | C9—O1 | 1.335 (2) |
| C2—C3 | 1.453 (2) | C10—O1 | 1.444 (2) |
| C3—C4 | 1.3779 (19) | C10—H10A | 0.9600 |
| C3—N1 | 1.3816 (16) | C10—H10B | 0.9600 |
| C4—C5 | 1.4266 (19) | C10—H10C | 0.9600 |
| C4—C11 | 1.5024 (18) | C11—C12 | 1.517 (2) |
| C5—C6 | 1.4017 (17) | C11—H11A | 0.9700 |
| C5—C9 | 1.464 (2) | C11—H11B | 0.9700 |
| C6—N1 | 1.3404 (17) | C12—H12A | 0.9600 |
| C6—C7 | 1.4935 (18) | C12—H12B | 0.9600 |
| C7—C8 | 1.514 (2) | C12—H12C | 0.9600 |
| C7—H7A | 0.9700 | N1—H1N | 0.8457 |
| O3—C1—H1A | 109.5 | C7—C8—H8C | 109.5 |
| O3—C1—H1B | 109.5 | H8A—C8—H8C | 109.5 |
| H1A—C1—H1B | 109.5 | H8B—C8—H8C | 109.5 |
| O3—C1—H1C | 109.5 | O2—C9—O1 | 121.51 (15) |
| H1A—C1—H1C | 109.5 | O2—C9—C5 | 125.79 (15) |
| H1B—C1—H1C | 109.5 | O1—C9—C5 | 112.69 (13) |
| O4—C2—O3 | 122.75 (13) | O1—C10—H10A | 109.5 |
| O4—C2—C3 | 123.61 (12) | O1—C10—H10B | 109.5 |
| O3—C2—C3 | 113.64 (12) | H10A—C10—H10B | 109.5 |
| C4—C3—N1 | 108.11 (12) | O1—C10—H10C | 109.5 |
| C4—C3—C2 | 134.03 (12) | H10A—C10—H10C | 109.5 |
| N1—C3—C2 | 117.86 (11) | H10B—C10—H10C | 109.5 |
| C3—C4—C5 | 106.00 (11) | C4—C11—C12 | 112.50 (12) |
| C3—C4—C11 | 126.77 (13) | C4—C11—H11A | 109.1 |
| C5—C4—C11 | 127.23 (12) | C12—C11—H11A | 109.1 |
| C6—C5—C4 | 108.15 (12) | C4—C11—H11B | 109.1 |
| C6—C5—C9 | 127.00 (13) | C12—C11—H11B | 109.1 |

| | | | |
|------------|-------------|---------------|-------------|
| C4—C5—C9 | 124.85 (12) | H11A—C11—H11B | 107.8 |
| N1—C6—C5 | 106.78 (11) | C11—C12—H12A | 109.5 |
| N1—C6—C7 | 119.92 (12) | C11—C12—H12B | 109.5 |
| C5—C6—C7 | 133.28 (13) | H12A—C12—H12B | 109.5 |
| C6—C7—C8 | 112.23 (12) | C11—C12—H12C | 109.5 |
| C6—C7—H7A | 109.2 | H12A—C12—H12C | 109.5 |
| C8—C7—H7A | 109.2 | H12B—C12—H12C | 109.5 |
| C6—C7—H7B | 109.2 | C6—N1—C3 | 110.97 (11) |
| C8—C7—H7B | 109.2 | C6—N1—H1N | 124.6 |
| H7A—C7—H7B | 107.9 | C3—N1—H1N | 124.4 |
| C7—C8—H8A | 109.5 | C9—O1—C10 | 116.33 (15) |
| C7—C8—H8B | 109.5 | C2—O3—C1 | 116.55 (12) |
| H8A—C8—H8B | 109.5 | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|---------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1N \cdots O4 ⁱ | 0.85 | 2.07 | 2.8773 (15) | 160 |

Symmetry code: (i) $-x+1, -y, -z+1$.