



ISSN 1600-5368

Crystal structure of 2,7-diethoxy-1,8-bis(4-nitrobenzoyl)naphthalene

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Received 17 July 2014
Accepted 18 August 2014

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Edited by H. Ishida, Okayama University, Japan

Keywords: crystal structure; *peri*-aroyl-naphthalene; naphthalene diketone; non-coplanarly accumulated aromatic-rings structure; spatial organization

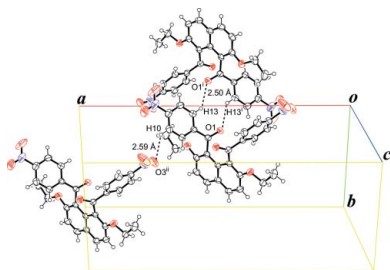
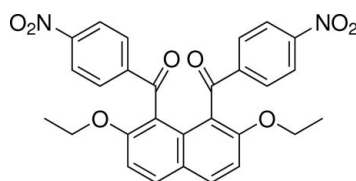
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The title compound, C₂₈H₂₂N₂O₈, possesses crystallographically imposed twofold symmetry, with the two central carbon atoms of the naphthalene unit lying on the rotation axis. The two benzoyl groups in the molecule are twisted away from the attached naphthalene unit with a C–C–C=O torsion angle of 49.05 (15)° between the naphthalene unit and the carbonyl group. The dihedral angle between the naphthalene ring system and the benzene ring is 77.17 (5)°. In the crystal, pairs of C–H···O=C hydrogen bonds link the molecules into a double-column structure along the *c* axis. The molecules are further linked by C–H···O=N hydrogen bonds, forming a three-dimensional network. C–H···π interactions between the methylene group and the naphthalene unit and π–π interactions between the naphthalene ring systems [centroid–centroid distances of 3.7858 (7)–3.7860 (7) Å] are also observed.

1. Chemical context

Molecules with non-coplanarly accumulated aromatic rings, such as biphenyl and binaphthyl derivatives, have been in the limelight as unique building blocks affording characteristic optical and electronic properties (Hatano *et al.*, 2013; Park *et al.*, 2010; Vaghi *et al.*, 2013) and asymmetric molecular environments (Bulman Page *et al.*, 2012; Jayalakshmi *et al.*, 2012; Kano *et al.*, 2006; Wang *et al.*, 2014). *peri*-Substituted naphthalenes have also much attention as characteristic aromatic ring core compounds and the structural analyses have been actively performed (Cohen *et al.*, 2004; Jing *et al.*, 2005).



In the course of our study on selective electrophilic aromatic arylation of 2,7-dimethoxynaphthalene, *peri*-aroyl-naphthalene compounds have proved to be formed regioselectively with the aid of a suitable acidic mediator (Okamoto & Yonezawa, 2009; Okamoto *et al.*, 2011). According to X-ray crystal analysis, the resulting 1,8-diaroylnaphthalene and 1-monoaroylnaphthalene compounds have non-coplanarly accumulated aromatic-ring structures in their crystals. The aroyl groups at the 1,8-positions (or 1-position) of the naphthalene ring system in the molecules are situated in a perpendicular fashion to the naphthalene ring system, as

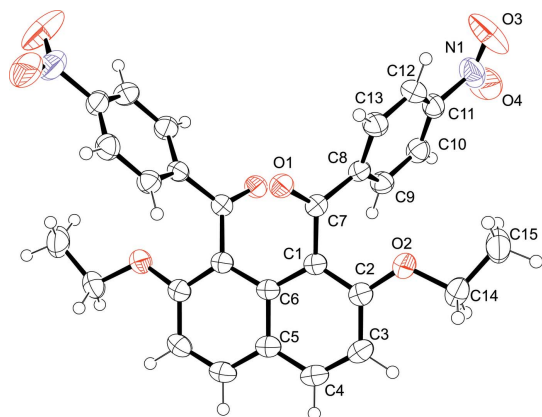


Figure 1
The molecular structure of the title compound with the atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

shown in 1,8-dibenzoyl-2,7-dimethoxynaphthalene (Nakaema *et al.*, 2008), 1,8-dibenzoyl-2,7-diethoxynaphthalene (Isogai *et al.*, 2013) and 1-(4-nitrobenzoyl)-2,7-dimethoxynaphthalene (Watanabe *et al.*, 2010). As a part of our continuous study on the molecular structures of this kind of molecules, the X-ray crystal structure of the title compound is reported here.

2. Structural commentary

The title molecule lies on a crystallographic twofold axis running through atoms C5 and C6 of the naphthalene unit so that the asymmetric unit consists of one half-molecule (Fig. 1). In the molecule, two aryl groups are non-coplanar attached to the naphthalene ring system. The torsion angles of the benzene ring and the naphthalene ring system with the ketonic carbonyl moiety (O1–C7–C8–C13 and C6–C1–C7–O1) are 26.83 (17) and 49.05 (15)°, respectively. The dihedral angle between the benzene ring and the naphthalene ring system is 77.17 (5)°. The benzene ring and the nitro group are approximately coplanar with a dihedral angle of 5.0 (2)°.

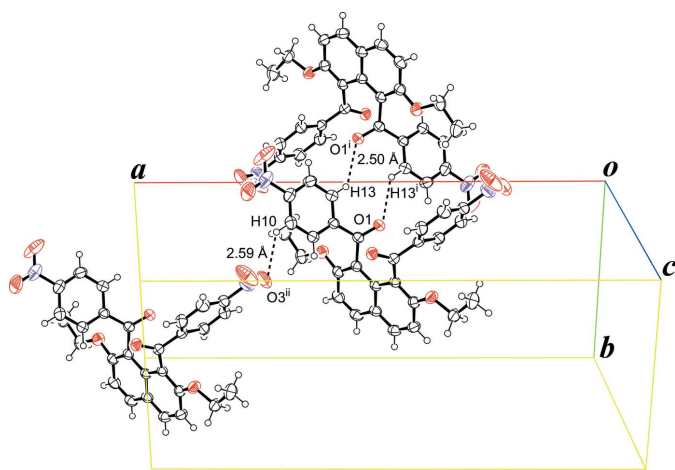


Figure 2
A crystal packing view of the title compound, showing the intermolecular C–H...O=C and C–H...O=N interactions. [Symmetry codes: (i) $1-x, -y, -z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$].

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

*Cg*1 and *Cg*2 are the centroids of the six-membered C1–C6 and C1^v–C4^v/C5/C6 rings, respectively. [Symmetry code: (v) $-x+1, y, -z+\frac{1}{2}$]

| <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> |
|-------------------------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13–H13...O1 ⁱ | 0.95 | 2.50 | 3.2129 (17) | 132 |
| C10–H10...O3 ⁱⁱ | 0.95 | 2.59 | 3.360 (2) | 138 |
| C14–H14 <i>B</i> ... <i>Cg</i> 1 ⁱⁱⁱ | 0.99 | 2.81 | 3.6284 (15) | 140 |
| C14–H14 <i>B</i> ... <i>Cg</i> 2 ^{iv} | 0.99 | 2.81 | 3.6284 (15) | 140 |

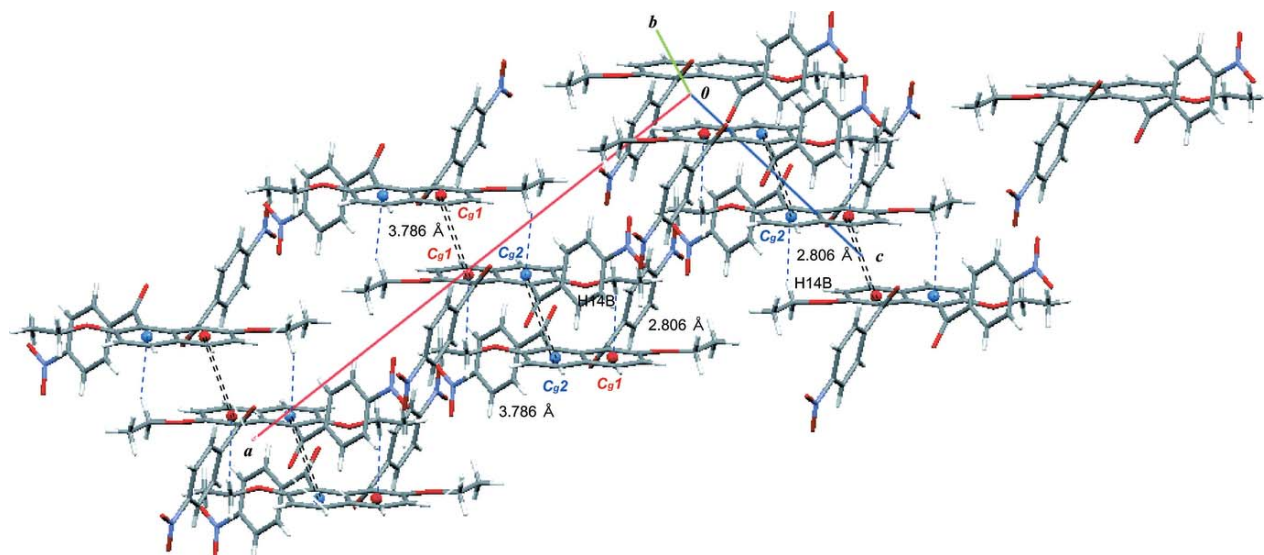
Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $-x, -y, -z+1$.

3. Supramolecular features

In the crystal, the molecular packing of the title compound is mainly stabilized by a pair of C–H...O=C hydrogen bonds between the benzene ring and the ketonic carbonyl group (C13–H13...O1ⁱ; details and symmetry code in Table 1), which make an $R_2^2(10)$ ring motif (Fig. 2). The molecules are stacked through these interactions in a double-column along the *c* axis. The molecules are also linked by C–H...O=N interactions between the benzene ring and the nitro group (C10–H10...O3ⁱⁱ; Table 1), forming a three-dimensional network and thus resulting in the interpenetration of the naphthalene unit into the adjacent double-column. π – π interactions between the interpenetrating naphthalene ring systems are observed; the interplanar distance is 3.5326 (4) Å and the centroid–centroid distances are 3.7860 (7), 3.7859 (7) and 3.7858 (7) Å, respectively, for *Cg*1...*Cg*1^{vi}, *Cg*1...*Cg*2^{vii} and *Cg*2...*Cg*2^{viii}, where *Cg*1 and *Cg*2 are the centroids of the six-membered C1–C6 and C1^v–C4^v/C5/C6 rings, respectively [symmetry codes: (v) $-x+1, y, -z+\frac{1}{2}$; (vi) $-x+1, -y+1, -z$; (vii) $x, -y+1, z-\frac{1}{2}$; (viii) $-x+1, -y+1, -z+1$]. C–H... π interactions between the methylene group and the naphthalene ring system (C14–H14*B*...*Cg*1ⁱⁱⁱ and C14–H14*B*...*Cg*2^{iv}; Table 1 and Fig. 3) are also observed.

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update May 2014; Allen, 2002) showed 39 and 29 structures containing the 1,8-diaroynaphthalene (including 1,8-dialkanoylnaphthalene) and 1,8-diaroyl-2,7-dialkoxynaphthalene units, respectively. The title compound has a non-coplanarly accumulated aromatic-rings structure, as found in the nitro group-free 1,8-dibenzoylnaphthalene homologues and the nitro-group-bearing 1-benzoylnaphthalene homologue, *viz.* 1,8-dibenzoyl-2,7-dimethoxynaphthalene (Nakaema *et al.*, 2008) and 1,8-dibenzoyl-2,7-diethoxynaphthalene (Isogai *et al.*, 2013), and 2,7-dimethoxy-1-(4-nitrobenzoyl)-naphthalene (Watanabe *et al.*, 2010). The dihedral angle between the benzene ring and the naphthalene ring system [77.17 (5)°] is close to those of the three homologues [68.42 (5) and 71.69 (5)° for 1,8-dibenzoyl-2,7-diethoxynaphthalene; 83.59 (5)° for 1,8-dibenzoyl-2,7-dimethoxynaphthalene; 61.97 (5)° for 1-(4-nitrobenzoyl)-2,7-dimethoxynaphthalene].


Figure 3

A crystal packing view of the title compound, showing the intermolecular C–H··· π interactions (dashed lines) and π – π interactions (double dashed lines).

On the other hand, the torsion angle between the carbonyl group and the benzene ring is different from the homologues, *i.e.*, the title compound [$26.83(17)^\circ$] > 1-(4-nitrobenzoyl)-2,7-dimethoxynaphthalene [$-13.29(17)^\circ$] >> 1,8-dibenzoyl-2,7-diethoxynaphthalene [$1.58(17)^\circ$ and $1.44(17)^\circ$] > 1,8-dibenzoyl-2,7-dimethoxynaphthalene [$0.4(2)^\circ$]. Although the C–H···O=C interactions between the benzene ring and the ketonic carbonyl group are observed in all of four homologues, the C–H···O=N interaction is observed only in the title compound.

5. Synthesis and crystallization

To a 10 ml flask, 4-nitrobenzoic acid (3.96 mmol, 735 mg), aluminium chloride (4.35 mmol, 580 mg) and methyl chloride (3.0 ml) were placed and stirred at 273 K. To reaction mixture thus obtained, 2,7-diethoxynaphthalene (0.6 mmol, 130 mg) was added. After the reaction mixture was stirred at 273 K for 48 h, it was poured into ice-cold water (10 ml). The aqueous layer was extracted with CHCl_3 (10 ml \times 3). The combined extracts were washed with 2 M aqueous NaOH followed by washing with brine. The organic layers thus obtained were dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure to give cake. The crude product was purified by reprecipitation (CHCl_3 /methanol) (isolated yield 27%). Finally, the isolated product was crystallized from CHCl_3 -hexane (*v/v* = 2:1) to give single crystals.

^1H NMR (300 MHz, CDCl_3): δ 0.91 (6H, *t*, J = 5.2 Hz), 3.98 (4H, *q*, J = 5.2 Hz), 7.18 (2H, *d*, J = 6.9 Hz), 7.91 (4H, *d*, J = 6.6 Hz), 8.00 (2H, *d*, J = 6.9 Hz), 8.26 (4H, *d*, J = 6.6 Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 14.39, 64.90, 111.96, 119.88, 123.50, 125.48, 129.74, 130.82, 133.44, 144.19, 150.06, 156.77, 197.28; IR (KBr cm^{-1}): 1662 (C=O), 1603, 1515, 1472 (Ar, naphthalene), 1229 (=C–O–C); HRMS (*m/z*): [$M + \text{H}$] $^+$ Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_8$, 515.1410; found, 515.1449; m.p. = 556.4–568.5 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference Fourier map and were subsequently refined as riding atoms, with C–H = 0.95 (aromatic), 0.98 (methyl) and 0.99 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The positions of methyl H atoms were rotationally optimized.

Table 2

Experimental details.

| | |
|----------------------------------------------------------------------------|--------------------------------------------------|
| Crystal data | |
| Chemical formula | $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_8$ |
| M_r | 514.48 |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Temperature (K) | 193 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 23.5359 (16), 10.2522 (5), 10.3605 (11) |
| β ($^\circ$) | 97.257 (14) |
| <i>V</i> (Å 3) | 2479.9 (3) |
| <i>Z</i> | 4 |
| Radiation type | Cu $K\alpha$ |
| μ (mm $^{-1}$) | 0.86 |
| Crystal size (mm) | 0.50 \times 0.40 \times 0.20 |
| Data collection | |
| Diffractometer | Rigaku R-Axis RAPID |
| Absorption correction | Numerical (NUMABS; Higashi, 1999) |
| T_{min} , T_{max} | 0.674, 0.847 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 21420, 2272, 2118 |
| R_{int} | 0.044 |
| ($\sin \theta/\lambda$) $_{\text{max}}$ (Å $^{-1}$) | 0.602 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i> | 0.037, 0.101, 1.02 |
| No. of reflections | 2272 |
| No. of parameters | 175 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å $^{-3}$) | 0.21, –0.26 |

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *CrystalStructure* (Rigaku, 2010), *SIR2004* (Burla *et al.*, 2007), *SHELXL97* (Sheldrick, 2008) and *ORTEPIII* (Burnett & Johnson, 1996).

Acknowledgements

This work was supported by the Ogasawara Foundation for the Promotion of Science Engineering, Tokyo, Japan.

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supporting information

Acta Cryst. (2014). E70, 138-141 [doi:10.1107/S1600536814018674]

Crystal structure of 2,7-diethoxy-1,8-bis(4-nitrobenzoyl)naphthalene

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Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku, 2010); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

2,7-Diethoxy-1,8-bis(4-nitrobenzoyl)naphthalene

Crystal data

$C_{28}H_{22}N_2O_8$

$M_r = 514.48$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 23.5359$ (16) Å

$b = 10.2522$ (5) Å

$c = 10.3605$ (11) Å

$\beta = 97.257$ (14)°

$V = 2479.9$ (3) Å³

$Z = 4$

$F(000) = 1072$

$D_x = 1.378$ Mg m⁻³

Cu *K* α radiation, $\lambda = 1.54187$ Å

Cell parameters from 1640 reflections

$\theta = 3.8$ – 67.5 °

$\mu = 0.86$ mm⁻¹

$T = 193$ K

Block, yellow

$0.50 \times 0.40 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer

Radiation source: rotating anode

Graphite monochromator

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: numerical
(*NUMABS*; Higashi, 1999)

$T_{\min} = 0.674$, $T_{\max} = 0.847$

21420 measured reflections

2272 independent reflections

2118 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 68.2$ °, $\theta_{\min} = 3.8$ °

$h = -28 \rightarrow 27$

$k = -12 \rightarrow 12$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.101$

$S = 1.02$

2272 reflections

175 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

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 1.320P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0031 (2)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{iso}^*/U_{eq} |
|------|-------------|---------------|---------------|--------------------|
| O1 | 0.48373 (3) | 0.18553 (8) | 0.10345 (8) | 0.0365 (2) |
| O2 | 0.60134 (4) | 0.37631 (9) | 0.01960 (9) | 0.0428 (3) |
| O3 | 0.72391 (7) | -0.19473 (16) | 0.10952 (14) | 0.0991 (6) |
| O4 | 0.76491 (5) | -0.08350 (14) | 0.27145 (16) | 0.0812 (4) |
| N1 | 0.72522 (6) | -0.10377 (14) | 0.18632 (14) | 0.0584 (4) |
| C1 | 0.53601 (5) | 0.37563 (12) | 0.16932 (11) | 0.0305 (3) |
| C2 | 0.57104 (5) | 0.44716 (13) | 0.09761 (11) | 0.0347 (3) |
| C3 | 0.57153 (5) | 0.58479 (13) | 0.10108 (12) | 0.0397 (3) |
| H3 | 0.5962 | 0.6327 | 0.0528 | 0.048* |
| C4 | 0.53620 (5) | 0.64790 (13) | 0.17435 (12) | 0.0396 (3) |
| H4 | 0.5359 | 0.7406 | 0.1746 | 0.048* |
| C5 | 0.5000 | 0.58029 (16) | 0.2500 | 0.0346 (4) |
| C6 | 0.5000 | 0.44053 (16) | 0.2500 | 0.0303 (4) |
| C7 | 0.53051 (5) | 0.23260 (12) | 0.14003 (11) | 0.0306 (3) |
| C8 | 0.58275 (5) | 0.14797 (11) | 0.15282 (11) | 0.0325 (3) |
| C9 | 0.63069 (5) | 0.17560 (12) | 0.24136 (12) | 0.0368 (3) |
| H9 | 0.6313 | 0.2522 | 0.2932 | 0.044* |
| C10 | 0.67737 (5) | 0.09281 (13) | 0.25474 (13) | 0.0415 (3) |
| H10 | 0.7099 | 0.1102 | 0.3164 | 0.050* |
| C11 | 0.67537 (6) | -0.01629 (13) | 0.17554 (14) | 0.0422 (3) |
| C12 | 0.62879 (6) | -0.04532 (13) | 0.08520 (14) | 0.0455 (3) |
| H12 | 0.6288 | -0.1204 | 0.0314 | 0.055* |
| C13 | 0.58214 (6) | 0.03741 (13) | 0.07495 (13) | 0.0410 (3) |
| H13 | 0.5494 | 0.0187 | 0.0143 | 0.049* |
| C14 | 0.64361 (6) | 0.43699 (15) | -0.04805 (14) | 0.0458 (3) |
| H14A | 0.6698 | 0.4913 | 0.0121 | 0.055* |
| H14B | 0.6252 | 0.4930 | -0.1193 | 0.055* |
| C15 | 0.67573 (7) | 0.32734 (18) | -0.10160 (18) | 0.0615 (4) |
| H15A | 0.6952 | 0.2756 | -0.0297 | 0.074* |
| H15B | 0.7041 | 0.3631 | -0.1535 | 0.074* |
| H15C | 0.6488 | 0.2717 | -0.1567 | 0.074* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O1 | 0.0325 (5) | 0.0357 (5) | 0.0403 (5) | -0.0042 (3) | 0.0003 (3) | -0.0047 (4) |
| O2 | 0.0451 (5) | 0.0403 (5) | 0.0458 (5) | -0.0028 (4) | 0.0167 (4) | 0.0027 (4) |
| O3 | 0.1189 (12) | 0.1059 (12) | 0.0720 (9) | 0.0757 (10) | 0.0100 (8) | -0.0127 (8) |
| O4 | 0.0517 (7) | 0.0739 (9) | 0.1132 (11) | 0.0221 (6) | -0.0077 (7) | 0.0084 (8) |
| N1 | 0.0580 (8) | 0.0581 (8) | 0.0623 (8) | 0.0231 (6) | 0.0198 (7) | 0.0154 (7) |
| C1 | 0.0301 (6) | 0.0293 (6) | 0.0306 (6) | -0.0002 (4) | -0.0027 (5) | 0.0010 (4) |
| C2 | 0.0338 (6) | 0.0353 (7) | 0.0338 (6) | -0.0014 (5) | -0.0004 (5) | 0.0012 (5) |
| C3 | 0.0414 (7) | 0.0351 (7) | 0.0418 (7) | -0.0071 (5) | 0.0024 (5) | 0.0071 (5) |
| C4 | 0.0463 (7) | 0.0276 (6) | 0.0427 (7) | -0.0031 (5) | -0.0033 (6) | 0.0033 (5) |
| C5 | 0.0370 (9) | 0.0294 (9) | 0.0349 (8) | 0.000 | -0.0050 (7) | 0.000 |
| C6 | 0.0304 (8) | 0.0282 (8) | 0.0300 (8) | 0.000 | -0.0047 (6) | 0.000 |
| C7 | 0.0327 (6) | 0.0323 (6) | 0.0266 (5) | -0.0025 (5) | 0.0024 (4) | -0.0004 (5) |
| C8 | 0.0334 (6) | 0.0291 (6) | 0.0354 (6) | -0.0036 (5) | 0.0058 (5) | -0.0004 (5) |
| C9 | 0.0364 (6) | 0.0340 (7) | 0.0393 (6) | -0.0015 (5) | 0.0024 (5) | -0.0027 (5) |
| C10 | 0.0346 (7) | 0.0444 (8) | 0.0447 (7) | 0.0002 (5) | 0.0017 (5) | 0.0042 (6) |
| C11 | 0.0394 (7) | 0.0388 (7) | 0.0507 (7) | 0.0082 (5) | 0.0140 (6) | 0.0090 (6) |
| C12 | 0.0502 (8) | 0.0351 (7) | 0.0528 (8) | 0.0026 (6) | 0.0129 (6) | -0.0074 (6) |
| C13 | 0.0385 (7) | 0.0377 (7) | 0.0464 (7) | -0.0029 (5) | 0.0036 (5) | -0.0085 (6) |
| C14 | 0.0384 (7) | 0.0536 (8) | 0.0463 (7) | -0.0059 (6) | 0.0094 (6) | 0.0084 (6) |
| C15 | 0.0469 (8) | 0.0731 (11) | 0.0686 (10) | 0.0035 (7) | 0.0238 (7) | 0.0044 (8) |

Geometric parameters (Å, °)

| | | | |
|--------------------|-------------|------------|-------------|
| O1—C7 | 1.2181 (14) | C7—C8 | 1.4970 (16) |
| O2—C2 | 1.3546 (15) | C8—C13 | 1.3903 (17) |
| O2—C14 | 1.4298 (15) | C8—C9 | 1.3904 (17) |
| O3—N1 | 1.224 (2) | C9—C10 | 1.3813 (18) |
| O4—N1 | 1.2188 (19) | C9—H9 | 0.9500 |
| N1—C11 | 1.4698 (17) | C10—C11 | 1.385 (2) |
| C1—C2 | 1.3872 (17) | C10—H10 | 0.9500 |
| C1—C6 | 1.4278 (14) | C11—C12 | 1.381 (2) |
| C1—C7 | 1.4997 (17) | C12—C13 | 1.3809 (19) |
| C2—C3 | 1.4116 (19) | C12—H12 | 0.9500 |
| C3—C4 | 1.3584 (19) | C13—H13 | 0.9500 |
| C3—H3 | 0.9500 | C14—C15 | 1.500 (2) |
| C4—C5 | 1.4105 (15) | C14—H14A | 0.9900 |
| C4—H4 | 0.9500 | C14—H14B | 0.9900 |
| C5—C4 ⁱ | 1.4105 (15) | C15—H15A | 0.9800 |
| C5—C6 | 1.433 (2) | C15—H15B | 0.9800 |
| C6—C1 ⁱ | 1.4278 (14) | C15—H15C | 0.9800 |
| C2—O2—C14 | 120.70 (11) | C10—C9—C8 | 120.65 (12) |
| O4—N1—O3 | 123.69 (14) | C10—C9—H9 | 119.7 |
| O4—N1—C11 | 118.84 (14) | C8—C9—H9 | 119.7 |
| O3—N1—C11 | 117.46 (15) | C9—C10—C11 | 118.03 (12) |

| | | | |
|----------------------------------------|--------------|-----------------|--------------|
| C2—C1—C6 | 120.28 (12) | C9—C10—H10 | 121.0 |
| C2—C1—C7 | 116.77 (10) | C11—C10—H10 | 121.0 |
| C6—C1—C7 | 122.12 (11) | C12—C11—C10 | 122.71 (12) |
| O2—C2—C1 | 115.43 (11) | C12—C11—N1 | 118.54 (13) |
| O2—C2—C3 | 123.23 (11) | C10—C11—N1 | 118.75 (13) |
| C1—C2—C3 | 121.22 (12) | C11—C12—C13 | 118.37 (12) |
| C4—C3—C2 | 119.13 (12) | C11—C12—H12 | 120.8 |
| C4—C3—H3 | 120.4 | C13—C12—H12 | 120.8 |
| C2—C3—H3 | 120.4 | C12—C13—C8 | 120.41 (12) |
| C3—C4—C5 | 122.13 (12) | C12—C13—H13 | 119.8 |
| C3—C4—H4 | 118.9 | C8—C13—H13 | 119.8 |
| C5—C4—H4 | 118.9 | O2—C14—C15 | 105.65 (12) |
| C4 ⁱ —C5—C4 | 121.13 (16) | O2—C14—H14A | 110.6 |
| C4 ⁱ —C5—C6 | 119.43 (8) | C15—C14—H14A | 110.6 |
| C4—C5—C6 | 119.43 (8) | O2—C14—H14B | 110.6 |
| C1—C6—C1 ⁱ | 124.45 (15) | C15—C14—H14B | 110.6 |
| C1—C6—C5 | 117.77 (7) | H14A—C14—H14B | 108.7 |
| C1 ⁱ —C6—C5 | 117.77 (7) | C14—C15—H15A | 109.5 |
| O1—C7—C1 | 120.12 (10) | C14—C15—H15B | 109.5 |
| O1—C7—C8 | 119.87 (11) | H15A—C15—H15B | 109.5 |
| C1—C7—C8 | 120.00 (9) | C14—C15—H15C | 109.5 |
| C13—C8—C9 | 119.81 (12) | H15A—C15—H15C | 109.5 |
| C13—C8—C7 | 118.22 (11) | H15B—C15—H15C | 109.5 |
| C9—C8—C7 | 121.96 (11) | | |
| | | | |
| C14—O2—C2—C1 | -173.03 (10) | C2—C1—C7—C8 | 58.11 (14) |
| C14—O2—C2—C3 | 10.93 (18) | C6—C1—C7—C8 | -132.34 (10) |
| C6—C1—C2—O2 | -176.93 (8) | O1—C7—C8—C13 | 26.83 (17) |
| C7—C1—C2—O2 | -7.18 (14) | C1—C7—C8—C13 | -151.79 (11) |
| C6—C1—C2—C3 | -0.81 (16) | O1—C7—C8—C9 | -151.86 (12) |
| C7—C1—C2—C3 | 168.94 (11) | C1—C7—C8—C9 | 29.52 (17) |
| O2—C2—C3—C4 | 174.63 (11) | C13—C8—C9—C10 | -1.34 (19) |
| C1—C2—C3—C4 | -1.18 (18) | C7—C8—C9—C10 | 177.33 (11) |
| C2—C3—C4—C5 | 1.68 (18) | C8—C9—C10—C11 | 1.42 (19) |
| C3—C4—C5—C4 ⁱ | 179.81 (13) | C9—C10—C11—C12 | -0.4 (2) |
| C3—C4—C5—C6 | -0.19 (13) | C9—C10—C11—N1 | 178.57 (12) |
| C2—C1—C6—C1 ⁱ | -177.76 (11) | O4—N1—C11—C12 | -175.30 (14) |
| C7—C1—C6—C1 ⁱ | 13.05 (7) | O3—N1—C11—C12 | 3.6 (2) |
| C2—C1—C6—C5 | 2.24 (11) | O4—N1—C11—C10 | 5.7 (2) |
| C7—C1—C6—C5 | -166.95 (7) | O3—N1—C11—C10 | -175.35 (14) |
| C4 ⁱ —C5—C6—C1 | 178.24 (8) | C10—C11—C12—C13 | -0.8 (2) |
| C4—C5—C6—C1 | -1.76 (8) | N1—C11—C12—C13 | -179.72 (12) |
| C4 ⁱ —C5—C6—C1 ⁱ | -1.76 (8) | C11—C12—C13—C8 | 0.9 (2) |
| C4—C5—C6—C1 ⁱ | 178.24 (8) | C9—C8—C13—C12 | 0.2 (2) |
| C2—C1—C7—O1 | -120.50 (12) | C7—C8—C13—C12 | -178.56 (12) |
| C6—C1—C7—O1 | 49.05 (15) | C2—O2—C14—C15 | 169.06 (11) |

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

*Cg*1 and *Cg*2 are the centroids of the six-membered C1–C6 and C1^v–C4^v/C5/C6 rings, respectively. [Symmetry code: (v) $-x+1, y, -z+1/2$.]

| <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> |
|-----------------------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C13—H13 \cdots O1 ⁱⁱ | 0.95 | 2.50 | 3.2129 (17) | 132 |
| C10—H10 \cdots O3 ⁱⁱⁱ | 0.95 | 2.59 | 3.360 (2) | 138 |
| C14—H14 <i>B</i> \cdots <i>Cg</i> 1 ^{iv} | 0.99 | 2.81 | 3.6284 (15) | 140 |
| C14—H14 <i>B</i> \cdots <i>Cg</i> 2 ^v | 0.99 | 2.81 | 3.6284 (15) | 140 |

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