Crystal structure of methyl 1,3-benzoxazole-2-carboxylate

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The title compound, C9H7NO3, crystallizes in the monoclinic (P21) space group. In the crystal, the almost planar molecules display a flattened herringbone arrangement. Stacking molecules are slipped in the lengthwise and widthwise directions and are linked by π–π interactions [d(Cg–Cg) = 3.6640 (11) Å]. The structure is characterized by strong C—H–N and weak C—H–O hydrogen bonds, and further stabilized by C–O–C interactions.

1. Chemical context

Benzoxazoles are common in natural products and represent an important class of key structural motifs, often incorporated as building blocks in ligands to target a variety of receptors and enzymes in medicinal chemistry studies (Demmer & Bunch, 2015; Kamal et al., 2020). They are also a scaffold of prime importance for fluorescent probes and materials (Carayon & Fery-Forgues, 2017; Fery-Forgues & Vanucci-Bacqué, 2021). Methyl-1,3-benzoxazole-2-carboxylate (1) belongs to this family and much attention has been paid to its preparation.

This compound was first prepared by a multi-step synthesis starting from 2,3-dioxo-1,4-benzoxazine (Dickoré et al., 1970) and 2-cyanobenzoxazole (Möller, 1970), but it can be obtained much more simply from condensation of 2-aminophenol with methyl 2,2,2-trimethoxyacetate (Musser, Hudec et al., 1984; Koshelev et al., 2019). It has been synthesized in high yields by direct carboxylation of benzoxazole using carbon dioxide (CO2) as a naturally abundant and renewable C1 source, with (Zhang et al., 2010; Inomata et al., 2012) or without any metal catalyst (Vechorkin et al., 2010; Fenner & Ackermann, 2016). Recently, it has been produced by oxidative cyclization of glycine catalysed by copper (Liu et al., 2021) or induced by irradiation with visible light (Zhu et al., 2021). The molecule is commercially available. It has been used to complex europium, resulting in a very efficient electroluminescent layer for applications in the field of organic light-emitting diodes (OLEDs) (Koshelev et al., 2019). Used as a synthetic inter-
mediate, methyl-1,3-benzoxazole-2-carboxylate has led to various pharmacologically active agents with anti-allergic (Musser, Brown et al., 1984), anti-microbial (Vodela et al., 2013) and neuro-anti-inflammatory (Shang et al., 2020) activity, to name just a few.

2. Structural commentary

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1$ and exhibits the expected bond lengths and angles for a benzoxazole. The N1—C1 bond, which corresponds to a double bond, is significantly shorter [1.293 (2) Å] than the other bonds (>1.36 Å) of the oxazole cycle. The molecule is almost planar [N1—C1—C2—O3 = $-6.7$ (2)°]. The heterocyclic and carbonyl oxygen atoms O1 and O2, respectively, are located on the same side with respect to the long axis of the molecule.

3. Supramolecular features

In the crystal structure, molecules are displayed according to the γ packing type, i.e. a flattened herringbone featuring stacks of parallel, translationally related molecules (Desiraju et al., 1989; Campbell et al., 2017) (Fig. 2). Neighboring molecules situated in almost perpendicular planes (84.4°) are linked through C—H···N interactions between the heterocyclic nitrogen atom N1 and H9 of an adjacent molecule and weak C—H···O hydrogen bonds between O2 and one hydrogen

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

**Figure 2**
C—H···N and C—H···O hydrogen bonds (blue dotted lines).

**Figure 3**
π–π and C—O···π interactions (green dotted lines). Orange balls represent the ring centroids $Cg$. 

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Poirot et al. • C$_9$H$_7$NO$_3$
When the latter is a phenyl group, the molecule is almost azolylcarbonyl moiety may be linked to an aromatic group. When the benzoxazole and phenyl derivative moieties are attached via a benzoic acid that is involved in many intermolecular interactions.

Finally, the benzoxazolylcarbonyl moiety may be linked to an aromatic group, which may be rather bulky like a bornane-aliphatic moiety, which may be smaller like a morpholine moiety (JAXMED; Xing et al., 2017). In contrast, this angle almost reaches 71° with a benzoic acid that is involved in many intermolecular interactions (DEJGEE; Ling et al., 1999), and when the benzoxazole and phenyl derivative moieties are attached via a flexible linker (KONTEP; Deng et al., 2019).

Finally, the benzoxazolylcarbonyl moiety may be linked to an aliphatic moiety, which may be rather bulky like a bornane-1,2-sultam moiety (BAKRIQ; Piątek et al., 2011), or smaller like a morpholine moiety (JAXMED; Xing et al., 2017).

In both cases, the network is structured by an interaction between the carbonyl oxygen of one molecule and the hydrogen atom borne by the C7 carbon of a neighbouring molecule. Finally, the framework closest to that of the title compound is an isopropyl 4-acetyl-5-hydroxy-1,3-benzoxazole-2-carboxylate (MIMZUG; Tangellamudi et al., 2018). In this molecule, the hydroxyl and the acetyl substituents form intramolecular hydrogen bonds while the carbonyl oxygen of one molecule interacts with the isopropyl group of the neighbouring one to form some kind of dimer. In general, planar molecules tend to assemble in layers (AGESUD; Boga et al., 2018; MIMZUG; Tangellamudi et al., 2018) and even in ribbons (JAXMED; Xing et al., 2017).

### 5. Synthesis and crystallization

The title compound was synthesized according to a variant of the procedure described by Jacobs et al. (2017) (Fig. 4). To a mixture of 5-aminophenol (1.09 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in anhydrous tetrahydrofuran (40 mL) at 263 K was added slowly methyl oxalyl chloride (1.34 g, 0.011 mol). The mixture was stirred at room temperature for 3 h and then cooled onto an ice–water bath. Triphenylphosphine (5.64 g, 0.0215 mol), disopropyl azodicarboxylate (2.25 g, 0.011 mol) and tetrahydrofuran (50 mL) were then added. The solution was allowed to stir at room temperature for 16 h and concentrated in vacuo. The crude product was purified by column chromatography (SiO2, petroleum ether/dichloromethane 70/30 until 60/40) to give a white solid (1.2 g) in 83% yield. 1H NMR (300 MHz, CDCl3): δ = 7.90 (dd, J = 7.9, 1.5, 0.8 Hz, 1H), 7.67 (dd, J = 8.1, 1.2, 0.8 Hz, 1H), 7.57–7.44 (m, 2H), 4.10 (s, 3H). 13C NMR (75 MHz, CDCl3): δ = 156.9, 152.5, 150.9, 140.5, 128.2, 125.8, 122.2, 111.7, 53.7.

Single crystals of the title compound, suitable for X-ray analysis, were grown by slow evaporation of a dichloromethane solution.

### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were fixed geometrically.
Table 4
Experimental details.

| Crystal data | C$_{9}$H$_{7}$NO$_{3}$ |
|----------------|----------------------|
| $M_r$ | 177.16 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 193 |
| a, b, c (Å) | 6.8165 (3), 4.4676 (2), 13.2879 (6) |
| $\beta$ (°) | 95.1319 (16) |
| $V$ (Å$^3$) | 403.04 (3) |
| $Z$ | 2 |
| Radiation type | Mo $K_{\alpha}$ |
| $\mu$ (mm$^{-1}$) | 0.11 |
| Crystal size (mm) | 0.40 × 0.30 × 0.10 |
| Data collection | Bruker D8-Venture Photon III detector |
| Absorption correction | Multi-scan (SADABS) |
| $T_{min}$ - $T_{max}$ | 0.698, 0.746 |
| No. of measured, independent and observed | 9084, 1954, 1860 |
| $R_{int}$ | 0.022 |
| $\sin \theta/\lambda_{max}$ (Å$^{-1}$) | 0.667 |
| Refinement | |
| $R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, $S$ | 0.030, 0.077, 1.10 |
| No. of reflections | 1954 |
| No. of parameters | 119 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å$^{-3}$) | 0.20, -0.16 |

Computer programs: APEX3 and SAINT (Bruker, 2018). SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), SHELXTL (Sheldrick, 2008), Mercury (Macrae et al., 2020), PLATON (Spek 2020) and pubICIF (Westrip 2010).

| References |
|----------------|
| Boga, C., Bordoni, S., Casarin, L., Micheletti, G. & Monari, M. (2018). | Molecules, 23, 171. |
| Boominathan, S. S. K., Hu, W.-P., Senadi, G. C., Vandavasi, J. K. & Wang, J.-J. (2014). | Chem. Commun., 50, 6726-6728. |
| Bruker (2018). APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA. |
| Campbell, J. E., Yang, J. & Day, G. M. (2017). | J. Mater. Chem. C, 5, 7574-7584. |
| Carayon, C. & Ferry-Forgues, S. (2017). | Photochem. Photobiol. Sci., 16, 1020-1035. |
| Demmer, C. S. & Bunch, L. (2015). | Eur. J. Med. Chem., 97, 778-785. |
| Deng, S., Chen, H., Ma, X., Zhou, Y., Yang, K., Lan, Y. & Song, Q. (2019). | Chem. Sci., 10, 6828-6833. |
| Desiraju, G. R. & Gavezzotti, A. (1989). | Acta Cryst. B45, 473-482. |
| Dickoré, K., Sasse, K. & Bode, K.-D. (1970). | Justus Liebigs Ann. Chem., 733, 70-87. |
| | |
| Fenner, S. & Ackermann, L. (2016). | Green Chem., 18, 3804-3807. |
| Ferry-Forgues, S. & Vanucci-Bacqué, C. (2021). | Top. Curr. Chem. (Z.), 379, 32. |
| Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). | Acta Cryst. B72, 171-179. |
| Iaseo, O., Novitchi, G., Jeanneau, E., Tommasino, J. B., Roques, N. & Luneau, D. (2012). | Inorg. Chem., 51, 2588-2596. |
| Inomata, H., Ogata, K., Fukuzawa, S. & Hou, Z. (2012). | Org. Lett. 14, 3986-3989. |
| Jacobs, L., de Kock, C., Taylor, D., Pelly, S. C. & Blackie, M. A. L. (2018). | Bioorg. Med. Chem. 26, 5730-5741. |
| Kamal, U., Javed, N. M. & Arun, K. (2020). | Asia. J. Pharm. Clin. Res. pp. 28-41. |
| Koshelev, D. S., Chikineva, T. Y., Kozevnikova (Khudoleeva), V. Y., Medvedko, A. V., Vashchenko, A. A., Goloveskin, A. S., Tsymbarenko, D. M., Averin, A. A., Meschkov, A., Scheper, U., Vatsadze, S. Z. & Utochnikova, V. V. (2019). | Dyes Pigments, 170, 107604. |
| Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). | J. Appl. Cryst. 48, 3-10. |
| Lim, I., Osowska, K., Armitage, J. A., Martin, B. R. & Miljanić, O. S. (2012). | CrystEngComm, 14, 6152-6162. |
| Ling, K.-Q., Cai, H., Ye, J.-H. & Xu, J.-H. (1999). | Tetrahedron, 55, 1707-1716. |
| Liu, S., Zhu, Z.-Q., Hu, Z.-Y., Tang, J. & Yuan, E. (2021). | Org. Biomol. Chem. 19, 1616-1619. |
| 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. |
| Möller, H. (1971). | Justus Liebig’s Ann. Chem., 749, 1-11. |
| Musser, J. H., Brown, R. E., Loew, B., Bailey, K., Jones, H., Kahn, R., Huang, F., Khandwala, A., Leibowitz, M. & Sonnino-Goldman, P. (1984). | J. Med. Chem. 27, 121-125. |
| Musser, J. H., Hudec, T. T. & Bailey, K. (1984). | Synth. Commun. 14, 947-953. |
| Osowska, K. & Miljanić, O. S. (2010). | Chem. Commun., 46, 4276-4278. |
| Pijetek, A. M., Sadowska, A., Chapuis, C. & Jurczak, J. (2011). | Helv. Chim. Acta, 94, 2141-2167. |
| Shang, Y., Hao, Q., Jiang, K., He, M. & Wang, J. (2020). | Bioorg. Med. Chem. Lett. 30, 127118. |
| Sheldrick, G. M. (2008). | Acta Cryst. A64, 112-122. |
| Sheldrick, G. M. (2015a). | Acta Cryst. A71, 3-8. |
| Sheldrick, G. M. (2015b). | Acta Cryst. A71, 3-8. |
| Spek, A. L. (2020). | Acta Cryst. E76, 1-11. |
| Tangellamudi, N. D., Shinde, S. B., Pooledanda, V., Godugu, C. & Balasubramanian, S. (2018). | Bioorg. Med. Chem. Lett. 28, 3639-3647. |
| Vechorkin, O., Hirt, N. & Hu, X. (2010). | Org. Lett. 12, 3567-3569. |
| Vodeola, S., Mekala, R. V. R., Danda, R. R. & Kodhati, V. (2013). | Chin. Chem. Lett. 24, 625-628. |
| Westrip, S. P. (2010). | J. Appl. Cryst. 43, 920-925. |
| Xing, Q., Lv, H., Xia, C. & Li, F. (2017). | Chem. Commun. 53, 6914-6917. |
| Zhang, L., Cheng, J., Ohishi, T. & Hou, Z. (2010). | Angew. Chem. Int. Ed. 49, 8670-8673. |
| Zhu, Z.-Q., Liu, S., Hu, Z.-Y., Xie, Z.-B., Tang, J. & Le, Z.-G. (2021). | Adv. Synth. Catal. 363, 2568-2572. |
Crystal structure of methyl 1,3-benzoxazole-2-carboxylate

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Computing details
Data collection: APEX3 (Bruker, 2018); cell refinement: SAINT (Bruker, 2018); data reduction: SAINT (Bruker, 2018); program(s) used to solve structure: SHELXTL (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae et al., 2020); software used to prepare material for publication: PLATON (Spek 2020) and publCIF (Westrip 2010).

Methyl 1,3-benzoxazole-2-carboxylate

Crystal data
C₉H₇NO₃  
Formula  
Mr = 177.16  
Monoclinic, P2₁  
a = 6.8165 (3) Å  
b = 4.4676 (2) Å  
c = 13.2879 (6) Å  
β = 95.1319 (16)°  
V = 403.04 (3) Å³  
Z = 2  

F(000) = 184  
Dₐ = 1.460 Mg m⁻³  
Mo Kα radiation, λ = 0.71073 Å  
θ = 3.3–28.2°  
μ = 0.11 mm⁻¹  
T = 193 K  
Plate, colourless  
0.40 × 0.30 × 0.10 mm

Data collection
Bruker D8-Venture Photon III detector  
diffraactomter  
Radiation source: Fine-focus sealed tube  
Phi and ω scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  
T_min = 0.698, T_max = 0.746  
9084 measured reflections

1954 independent reflections  
1860 reflections with I > 2σ(I)  
R_{int} = 0.022  
θ_{max} = 28.3°, θ_{min} = 3.3°  
h = −8→9  
k = −5→5  
l = −17→17

Refinement
Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.030  
wR(F²) = 0.077  
S = 1.10  
1594 reflections  
119 parameters  
1 restraint  
Primary atom site location: dual  
Hydrogen site location: inferred from neighbour sites  
H-atom parameters constrained  
w = 1/[σ(Fo^2) + (0.0432P)^2 + 0.0403P]  
where P = (Fo^2 + 2Fc^2)/3  
(Δσ)_{max} < 0.001  
Δρ_{max} = 0.20 e Å⁻³  
Δρ_{min} = −0.16 e Å⁻³
Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| Atom | x     | y     | z     | Uiso/Un eq |
|------|-------|-------|-------|------------|
| O1   | 0.25255 (16) | 0.3885 (3) | 0.69933 (9) | 0.0329 (3) |
| O2   | 0.43981 (19) | -0.0004 (3) | 0.57993 (9) | 0.0382 (3) |
| O3   | 0.73220 (17) | 0.2017 (3) | 0.63833 (9) | 0.0341 (3) |
| N1   | 0.54541 (19) | 0.5493 (3) | 0.77177 (10) | 0.0277 (3) |
| C1   | 0.4528 (2) | 0.3789 (4) | 0.70473 (12) | 0.0296 (3) |
| C2   | 0.5378 (2) | 0.1703 (4) | 0.63294 (12) | 0.0297 (3) |
| C3   | 0.8319 (3) | 0.0125 (4) | 0.57015 (13) | 0.0381 (4) |
| H3A  | 0.794777 | -0.196824 | 0.579791 | 0.057* |
| H3B  | 0.974729 | 0.034297 | 0.584461 | 0.057* |
| H3C  | 0.793506 | 0.072127 | 0.500188 | 0.057* |
| C4   | 0.2149 (2) | 0.5919 (4) | 0.77264 (12) | 0.0291 (3) |
| C5   | 0.3947 (2) | 0.6919 (4) | 0.81779 (11) | 0.0273 (3) |
| C6   | 0.4014 (2) | 0.9009 (4) | 0.89607 (13) | 0.0347 (4) |
| H6   | 0.522730 | 0.971603 | 0.928121 | 0.042* |
| C7   | 0.2220 (3) | 0.9998 (4) | 0.92465 (14) | 0.0401 (4) |
| H7   | 0.220300 | 1.141802 | 0.977785 | 0.048* |
| C8   | 0.0429 (3) | 0.8959 (5) | 0.87719 (15) | 0.0406 (4) |
| C9   | -0.076652 | 0.971435 | 0.898830 | 0.049* |
| H9   | 0.0342 (2) | 0.6878 (5) | 0.80018 (14) | 0.0370 (4) |

Atomic displacement parameters (Å²)

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|------|-----|-----|-----|-----|-----|-----|
| O1   | 0.0259 (5) | 0.0362 (6) | 0.0359 (6) | -0.0064 (5) | -0.0013 (4) | 0.0001 (5) |
| O2   | 0.0406 (6) | 0.0349 (6) | 0.0380 (6) | -0.0087 (5) | -0.0024 (5) | -0.0035 (5) |
| O3   | 0.0315 (6) | 0.0342 (6) | 0.0364 (6) | -0.0025 (5) | 0.0009 (4) | -0.0061 (5) |
| N1   | 0.0241 (6) | 0.0274 (6) | 0.0312 (6) | -0.0017 (5) | 0.0008 (4) | 0.0002 (5) |
| C1   | 0.0288 (7) | 0.0286 (7) | 0.0311 (7) | -0.0048 (6) | 0.0007 (6) | 0.0048 (6) |
| C2   | 0.0329 (8) | 0.0264 (7) | 0.0292 (7) | -0.0042 (6) | -0.0006 (6) | 0.0039 (6) |
| C3   | 0.0384 (9) | 0.0380 (10) | 0.0381 (8) | 0.0030 (8) | 0.0047 (7) | -0.0042 (8) |
| C4   | 0.0259 (7) | 0.0305 (8) | 0.0308 (7) | -0.0049 (6) | 0.0010 (5) | 0.0063 (6) |
| C5   | 0.0233 (7) | 0.0278 (7) | 0.0306 (7) | -0.0019 (6) | 0.0013 (5) | 0.0057 (6) |
| C6   | 0.0311 (8) | 0.0357 (8) | 0.0366 (8) | -0.0030 (7) | -0.0006 (6) | -0.0014 (7) |
| C7   | 0.0438 (10) | 0.0370 (9) | 0.0407 (9) | 0.0020 (8) | 0.0096 (7) | -0.0015 (8) |
| C8   | 0.0302 (8) | 0.0431 (10) | 0.0505 (10) | 0.0040 (8) | 0.0146 (7) | 0.0107 (9) |
| C9   | 0.0220 (7) | 0.0429 (9) | 0.0461 (9) | -0.0035 (7) | 0.0032 (6) | 0.0104 (8) |

Acta Cryst. (2021). E77, 1078-1081 sup-2
**Geometric parameters (Å, °)**

|   |   |   |   |
|---|---|---|---|
| O1—C1 | 1.3610 (19) | C4—C9 | 1.384 (2) |
| O1—C4 | 1.373 (2) | C4—C5 | 1.390 (2) |
| O2—C2 | 1.200 (2) | C5—C6 | 1.395 (2) |
| O3—C2 | 1.3281 (19) | C6—C7 | 1.385 (3) |
| O3—C3 | 1.452 (2) | C6—H6 | 0.9500 |
| N1—C1 | 1.293 (2) | C7—C8 | 1.402 (3) |
| N1—C5 | 1.395 (2) | C7—H7 | 0.9500 |
| C1—C2 | 1.488 (2) | C8—C9 | 1.380 (3) |
| C3—H3A | 0.9800 | C8—H8 | 0.9500 |
| C3—H3B | 0.9800 | C9—H9 | 0.9500 |
| C3—H3C | 0.9800 |

|   |   |   |   |
|---|---|---|---|
| C1—O1—C4 | 103.51 (12) | C9—C4—C5 | 123.92 (17) |
| C2—O3—C3 | 115.17 (14) | C4—C5—N1 | 108.64 (15) |
| C1—N1—C5 | 103.74 (13) | C4—C5—C6 | 120.36 (15) |
| N1—C1—O1 | 116.33 (15) | N1—C5—C6 | 131.00 (14) |
| N1—C1—C2 | 128.06 (14) | C7—C6—C5 | 116.58 (16) |
| O1—C1—C2 | 115.61 (13) | C7—C6—H6 | 121.7 |
| O2—C2—O3 | 126.82 (17) | C5—C6—H6 | 121.7 |
| O2—C2—C1 | 123.11 (16) | C6—C7—C8 | 121.71 (18) |
| O3—C2—C1 | 110.07 (14) | C6—C7—H7 | 119.1 |
| O3—C3—H3A | 109.5 | C8—C7—H7 | 119.1 |
| O3—C3—H3B | 109.5 | C9—C8—C7 | 122.32 (17) |
| H3A—C3—H3B | 109.5 | C9—C8—H8 | 118.8 |
| O3—C3—H3C | 109.5 | C8—C9—C7 | 115.10 (16) |
| H3A—C3—H3C | 109.5 | C8—C9—H9 | 122.4 |
| O1—C4—C9 | 128.30 (15) | C4—C9—H9 | 122.4 |
| O1—C4—C5 | 107.78 (14) |

|   |   |   |   |
|---|---|---|---|
| C5—N1—C1—O1 | 0.05 (19) | C9—C4—C5—N1 | 179.93 (15) |
| C5—N1—C1—C2 | −179.34 (15) | O1—C4—C5—C6 | −179.61 (14) |
| C4—O1—C1—C4 | 0.03 (18) | C9—C4—C5—C6 | 0.2 (2) |
| C4—O1—C1—C2 | 179.50 (13) | C1—N1—C5—C4 | −0.11 (17) |
| C3—O3—C2—O2 | 1.7 (2) | C1—N1—C5—C6 | 179.60 (17) |
| C3—O3—C2—C1 | −178.99 (13) | C4—C5—C6—C7 | −0.2 (2) |
| N1—C1—C2—O2 | 172.61 (18) | N1—C5—C6—C7 | −179.92 (16) |
| O1—C1—C2—O2 | −6.8 (2) | C5—C6—C7—C8 | −0.1 (3) |
| N1—C1—C2—O3 | −6.7 (2) | C6—C7—C8—C9 | 0.6 (3) |
| O1—C1—C2—O3 | 173.92 (14) | C7—C8—C9—C4 | −0.6 (3) |
| C1—O1—C4—C9 | −179.89 (17) | O1—C4—C9—C8 | 180.00 (16) |
| C1—O1—C4—C5 | −0.10 (16) | C5—C4—C9—C8 | 0.2 (3) |
| O1—C4—C5—N1 | 0.14 (17) |
| $D$—H···$A$ | D—H | H···$A$ | D···$A$ | D—H···$A$ |
|------------|------|---------|----------|-----------|
| C9—H9···N1<sup>i</sup> | 0.95 | 2.53 | 3.377 (2) | 149 |
| C3—H3C···O2<sup>ii</sup> | 0.98 | 2.65 | 3.389 (2) | 133 |

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

*Hydrogen-bond geometry ($\AA$, °)