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Synthesis and crystal structure of N^1,N^2-dimethylethanedihydrazide

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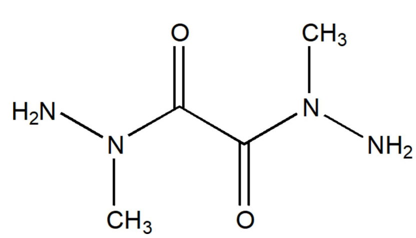
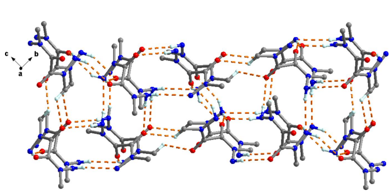
The title compound, N^1,N^2-dimethylethanedihydrazide, $C_4H_{10}N_4O_2$, was obtained by the methylation of oxalyl dihydrazide protected with phthalimide. The molecule is essentially non-planar with a dihedral angle between the two planar hydrazide fragments of 86.5 (2)°. This geometry contributes to the formation of a multi-contact three-dimensional supramolecular network *via* C—H···O, N—H···O and N—H···N hydrogen bonds.

1. Chemical context

For over a century, researchers have aimed to synthesize diverse heterocycles using well-established available methods. Currently, there is significant research interest in developing new methods for their synthesis, focusing on efficient and atom-economical routes (Favi, 2020; Pathan *et al.*, 2020). Among these novel synthetic approaches, the utilization of hydrazides stands out as one of the most appealing methods for synthesizing heterocyclic compounds such as pyrazoles, triazoles, oxadiazoles and pyridazines (Majumdar *et al.*, 2014; Mittersteiner *et al.*, 2021; Hosseini & Bayat, 2018; Khomenko *et al.*, 2022).

Organic acid hydrazides constitute a broad group of hydrazine derivatives containing the functional group –C(=O)NHNH$_2$. Therefore, this keen interest in hydrazide chemistry appears to arise not only from their diversity but also from the unique properties of these compounds. Acid hydrazides and their derivatives such as hydrazones possess biological activities including anticonvulsant (Angelova *et al.*, 2016), antidepressant (Ergenç *et al.*, 1998), anti-inflammatory (Kajal *et al.*, 2014), antimalarial (Walcourt *et al.*, 2004), antimycobacterial (Shalini *et al.*, 2019), anticancer (Witusik-Perkowska *et al.*, 2023; Küçükgüzel *et al.*, 2015) and antimicrobial (Hiremathad *et al.*, 2015; Popiołek *et al.*, 2022; Berillo & Dyusebaeva, 2022; Popiołek, 2021). Hydrazides are also bidentate ligands that can form chelate complexes (Ju *et al.*, 2023).





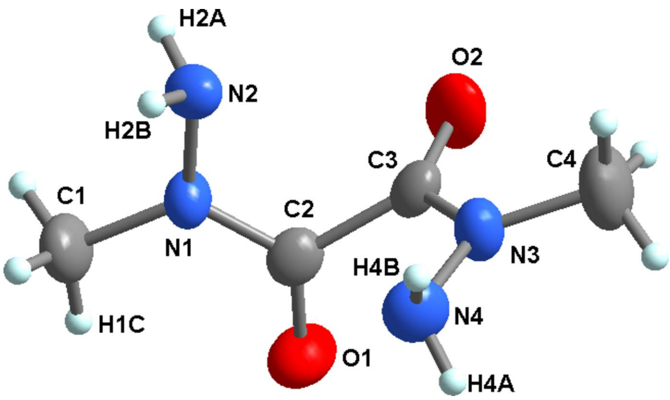


Figure 1
The molecular structure of the title compound with atom labeling and displacement ellipsoids drawn at the 50% probability level.

Considering the above, we report on the synthesis and crystal structure of a new alkylated oxalyl dihydrazide as an attractive synthon for the synthesis of biologically active organic compounds and metal complexes.

2. Structural commentary

The title compound crystalizes in the orthorhombic Sohncke space group $P2_12_12_1$ with four formula units per unit cell (Fig. 1). The crystal structure does not show other tautomeric forms. Bond lengths and angles are given in Table 1. The geometrical parameters are comparable to the values found in methylsemicarbazide (Szimhardt & Stierstorfer, 2018) and oxalyl dihydrazide (Quaeyhaegens *et al.*, 1990). The methyl hydrazide core [–C(═O)N(–CH_3)NH_2] is almost planar (r.m.s. deviation = 0.022 Å). The torsion angles around the N1—C2 and N3—C3 bonds are N2—N1—C2—O1 = 175.1 (4)°, C1—N1—C2—O1 = −1.2 (5)°, N4—N3—C3—O2 = 174.8 (4)°, and C4—N3—C3—O2 = −1.4 (6)°. The methyl hydrazide fragments are almost perpendicular to each other [the dihedral angle between the two moieties is 86.5 (2)°]. The torsion angles around the C2—C3 bond are O1—C2—C3—O2 = 89.9 (4), O1—C2—C3—N3 = −81.4 (4), N1—C2—C3—O2 = −83.2 (4), and N1—C2—C3—N3 = 105.5 (4)°.

3. Supramolecular features

In the crystal, each molecule forms chains along the *a*-axis direction with two neighboring ones *via* N—H···O hydrogen bonds (Table 2, Fig. 2). Neighboring chains form a 3D supramolecular network *via* C—H···O, N—H···O and N—H···N hydrogen-bonding contacts (Table 2, Fig. 3).

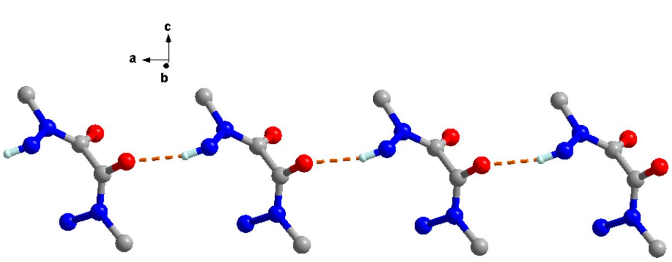


Figure 2
One-dimensional chains along the *a*-axis direction formed by N—H···O hydrogen bonding.

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.231 (4)	N3—N4	1.414 (4)
O2—C3	1.233 (4)	N3—C3	1.319 (4)
N1—N2	1.412 (4)	N3—C4	1.460 (4)
N1—C1	1.460 (4)	C2—C3	1.511 (5)
N1—C2	1.331 (4)		
N2—N1—C1	119.9 (3)	O1—C2—N1	123.8 (3)
C2—N1—N2	117.6 (3)	O1—C2—C3	118.2 (3)
C2—N1—C1	122.4 (3)	N1—C2—C3	117.7 (3)
N4—N3—C4	120.5 (3)	O2—C3—N3	124.1 (4)
C3—N3—N4	117.3 (3)	O2—C3—C2	118.7 (3)
C3—N3—C4	122.1 (4)	N3—C3—C2	116.5 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···O1^{i}	0.96	2.58	3.042 (4)	110
N2—H2*A*···O2^{ii}	0.87 (5)	2.13 (5)	2.977 (4)	164 (4)
N2—H2*B*···O2^{iii}	0.90 (3)	2.35 (3)	3.182 (4)	155 (3)
N4—H4*A*···O1^{iv}	0.79 (4)	2.30 (4)	3.075 (5)	169 (4)
N4—H4*B*···N2^{v}	0.99 (5)	2.38 (5)	3.367 (5)	170 (4)

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

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, last update November 2021; Groom *et al.*, 2016) confirmed that the title compound has not previously been published. A search for the N—N—C(═O)—C(═O)—N—N fragment gave oxalyl dihydrazide (CSD refcode VIPKIO; Quaeyhaegens *et al.*, 1990), its salts: EREQOK (Wu, 2021), NEXMIP (Xu *et al.*, 2018), MIDNOG (Devi *et al.*, 2018), VUHYUU and VUHZAB (Fischer *et al.*, 2014), ZIBBIX and ZIBDAR (Fischer *et al.*, 2013), and Schiff bases derived from it as the closest analogues: CUQPAF (Drexler *et al.*, 1999), HIRHIB (Singh *et al.*, 2013), IYACUH (Ran *et al.*, 2011), KUTREX (Kaluderović *et al.*, 2010), LORQEP (Bi *et al.*,

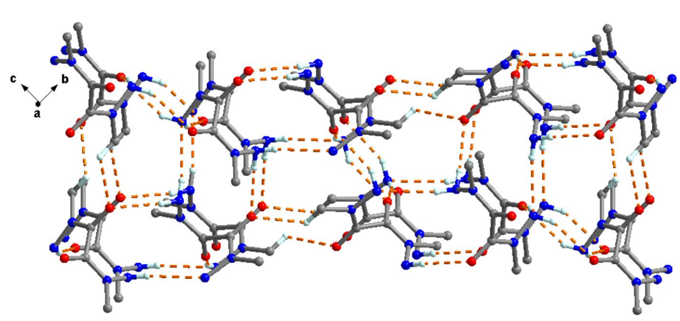


Figure 3
A view normal to plane (100) of the crystal structure of the title compound, showing the three-dimensional supramolecular hydrogen-bonding network.

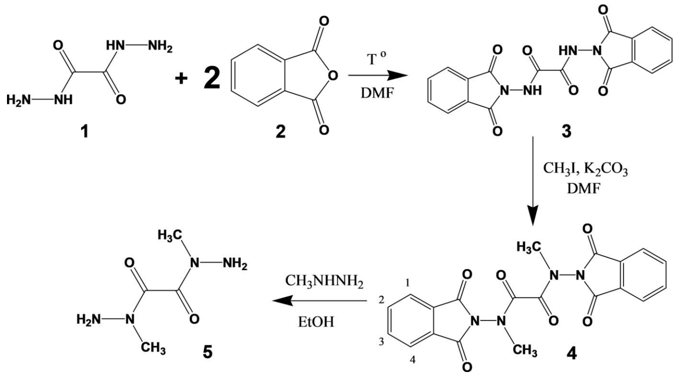


Figure 4
Synthesis of the title compound.

2009), NAJWUT (Singh *et al.*, 2016), NEQQOQ (Zhu *et al.*, 2006), RIRTET (Singh *et al.*, 2014), SUYWUG (Galvão *et al.*, 2016), UMIZUN (El-Asmy *et al.*, 2015), ZOLQUP and ZOLRAW (Fries *et al.*, 2019). For compound ZOLQOJ (Fries *et al.*, 2019), the fragment is part of a ring structure. Notably, a strictly planar structure is observed for the molecules oxalyl dihydrazide VIPKIO and dimethyl oxalate DMEOXA (Dougill & Jeffrey, 1953).

A search for the methyl hydrazide moiety gave methylsemicarbazide (XIBFEW; Szimhardt & Stierstorfer, 2018). Its geometric parameters agree well with those of the title compound. Further searches also revealed two structural analogues with a second non-hydrogen substituent at the amide-nitrogen atom: *N*,*N*,*N*′,*N*′-tetramethyloxamide and *N*,*N*,*N*′,*N*′-tetramethylmonothiooxamide (TMOXAM and TMTHOX, respectively; Adiwidjaja & Voss, 1977). These two crystal structures have a different packing and belong to monoclinic space groups. However, they exhibit very similar geometries in terms of the rotation of the molecule fragments around the central C—C bond. The O═C—C═O(S) torsion angles are 105.1 (2) and 89.6 (2)°, respectively.

5. Synthesis and crystallization

The title compound (**5**) was obtained according to the reaction scheme shown in Fig. 4.

***N*,*N*'-bis(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)ethanediamide** (3): compound **3** was synthesized from the commercially available precursors (Enamine Ltd.) according to the following method: 12.45 g (84 mmol, 2 eq.) of phthalic anhydride (**2**) were dissolved in 125 ml of DMF and 4.96 g (42 mmol, 1 eq.) of oxalyl dihydrazide (**1**) were added to the boiling solution. The obtained mixture was refluxed for 5 h. Upon cooling, precipitation of the product was observed. It was filtered off and dried. White powder; yield 73%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05–8.15 (*m*, 4H, 4-Ph), 11.57 (*br*, 1H, NH).

***N*^{1},*N*^{2}-dimethylethanedihydrazide (5):** 11.0 g (79.7 mmol, 3 eq.) of K_2CO_3 and 3.65 ml (58.6 mmol, 2.2 eq.) of CH_3I were added to a solution containing 10.0 g (26.5 mmol, 1 eq.) of compound **3** in 50 ml DMF. The reaction mixture was stirred for 6 h at room temperature. The inorganic precipitate was filtered off, the filtrate was evaporated and the residue was stirred in water, filtered off and dried in air. Yield: 9.9 g.

The crude precipitate of **4** (4 g, 9.8 mmol, 1 eq.) obtained from the previous step was refluxed with 1.1 ml (20.6 mmol, 2.1 eq.) of methylhydrazine in ethanol for 6 h. The precipitate was filtered off, ethanol was evaporated and the residue was recrystallized from 2-propanol and dried in air. The title compound was isolated as a white solid. Crystals suitable for X-ray analysis were obtained during the recrystallization. White powder; yield 84%. LC–MS (ESI) *m*/*z* 147 (MH^+) . IR (ATR, ν, cm^{-1}) : ν 3290, 3214, 1672, 1616, 1414, 1386, 1234, 1066, 1014, 870, 782, 762. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.90*, 2.95 and 3.00* (*s*, 3H, CH_3), 4.68, 4.85* and 4.93* (*s*, 2H, NH_2). *Minor signals indicate hindered rotation about the (O)C—N bond.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_4H_{10}N_4O_2$
M_r	146.16
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, *b*, *c* (Å)	6.0356 (5), 7.6501 (6), 15.7851 (14)
V (Å^3)	728.84 (10)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.11
Crystal size (mm)	0.25 × 0.2 × 0.15
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.975, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2356, 1279, 1014
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.050, 0.093, 1.04
No. of reflections	1279
No. of parameters	107
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.12
Absolute structure	Flack *x* determined using 280 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter	−0.7 (10)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For the NH_2 group, the hydrogen atoms were placed from a difference-Fourier map and refined freely. The CH_3 hydrogen atoms were placed geometrically and refined as riding with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

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References

Adiwidjaja, G. & Voss, J. (1977). *Chem. Ber.* **110**, 1159–1166.
Angelova, V., Karabeliov, V., Andreeva–Gateva, P. A. & Tchekalarova, J. (2016). *Drug Dev. Res.* **77**, 379–392.
Berillo, D. A. & Dyusebaeva, M. A. (2022). *Saudi Pharm. J.* **30**, 1036–1043.
Bi, W.-T., Hu, N.-L. & Bi, J.-H. (2009). *Acta Cryst.* E**65**, o782.
Devi, A., Dharavath, S. & Ghule, V. D. (2018). *ChemistrySelect*, **3**, 4501–4504.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Dougill, M. W. & Jeffrey, G. A. (1953). *Acta Cryst.* **6**, 831–837.
Drexler, K., Dehne, H. & Reinke, H. (1999). *CSD Communication* (CCDC 137595, refcode CUQPAF). CCDC, Cambridge, England.
El-Asmy, A., Jeragh, B. & Ali, M. (2015). *Chem. Cent. J.* **9**, 69.
Ergenç, N., Günay, N. S. & Demirdamar, R. (1998). *Eur. J. Med. Chem.* **33**, 143–148.
Favi, G. (2020). *Molecules*, **25**, 10–13.
Fischer, D., Klapötke, T. M. & Stierstorfer, J. (2014). *J. Energetic Mater*. **32**, 37–49.
Fischer, N., Klapötke, T. M., Reymann, M. & Stierstorfer, J. (2013). *Eur. J. Inorg. Chem.* pp. 2167–2180.
Fries, M., Mertens, M., Teske, N., Kipp, M., Beyer, C., Willms, T., Valkonen, A., Rissanen, K., Albrecht, M. & Clarner, T. (2019). *ACS Omega*, **4**, 1685–1689.
Galvão, A. M., Carvalho, M. F. N. N. & Ferreira, A. S. D. (2016). *J. Mol. Struct.* **1108**, 708–716.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Hirematahad, A., Patil, M. R., Chand, K., Santos, M. A. & Keri, R. S. (2015). *RSC Adv.* **5**, 96809–96828.
Hosseini, H. & Bayat, M. (2018). *Cyanoacetohydrazides.* In *Synthesis of Heterocyclic Compounds.* Cham, Switzerland: Springer International Publishing.
Ju, H., Zhu, Q. L., Zuo, M., Liang, S., Du, M., Zheng, Q. & Wu, Z. L. (2023). *Chem. Eur. J.* **29**, e202300969.
Kajal, A., Bala, S., Sharma, N., Kamboj, S. & Saini, V. (2014). *Int. J. Med. Chem.* **2014**, 1–11.
Kaluderović, G. N., Mohamad Eshkourfu, R. O., Gómez-Ruiz, S., Mitić, D. & Andelković, K. K. (2010). *Acta Cryst.* E**66**, o904–o905.
Khomenko, D. M., Doroshchuk, R. O., Ohorodnik, Y. M., Ivanova, H. V., Zakharchenko, B. V., Raspertova, I. V., Vaschenko, O. V., Dobrydnev, A. V., Grygorenko, O. O. & Lampeka, R. D. (2022). *Chem. Heterocycl. C.* **58**, 116–128.
Küçükgüzel, G. Ş., Koç, D., Çıkla–Süzgün, P., Özsavcı, D., Bingöl–Özakpınar, Ö., Mega–Tiber, P., Orun, O., Erzincan, P., Sağ–Erdem, S. & Şahin, F. (2015). *Arch. Pharm.* **348**, 730–742.
Majumdar, P., Pati, A., Patra, M., Behera, R. K. & Behera, A. K. (2014). *Chem. Rev.* **114**, 2942–2977.
Mittersteiner, M., Bonacorso, H. G., Martins, M. A. P. & Zanatta, N. (2021). *Eur. J. Org. Chem.* pp. 3886–3911.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Pathan, S. I., Chundawat, N. S., Chauhan, N. P. S. & Singh, G. P. (2020). *Synth. Commun.* **50**, 1251–1285.
Popiołek, Ł. (2021). *Int. J. Mol. Sci.* **22**, 9389.
Popiołek, Ł., Tuszyńska, K. & Biernasiuk, A. (2022). *Biomed. Pharmacother.* **153**, 113302.
Quaeyhaegens, F., Desseyn, H. O., Bracke, B. & Lenstra, A. T. H. (1990). *J. Mol. Struct.* **238**, 139–157.
Ran, X., Zhang, P., Qu, S., Wang, H., Bai, B., Liu, H., Zhao, C. & Li, M. (2011). *Langmuir*, **27**, 3945–3951.
Rigaku, OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Shalini, Johansen, M. D., Kremer, L. & Kumar, V. (2019). *Chem. Biol. Drug Des.* **94**, 1300–1305.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* C**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* A**71**, 3–8.
Singh, D. P., Allam, B. K., Singh, K. N. & Singh, V. P. (2014). *RSC Adv.* **4**, 1155–1158.
Singh, D. P., Allam, B. K., Singh, R., Singh, K. N. & Singh, V. P. (2016). *RSC Adv.* **6**, 15518–15524.
Singh, D. P., Raghuvanshi, D. S., Singh, K. N. & Singh, V. P. (2013). *J. Mol. Catal. A Chem.* **379**, 21–29.
Szimhardt, N. & Stierstorfer, J. (2018). *Chem. A Eur. J.* **24**, 2687–2698.
Walcourt, A., Loyevsky, M., Lovejoy, D. B., Gordeuk, V. R. & Richardson, D. R. (2004). *Int. J. Biochem. & Cell. Biol.* **36**, 401–407.
Witusik-Perkowska, M., Głowacka, P., Pieczonka, A. M., Świderska, E., Pudlarz, A., Rachwalski, M., Szymańska, J., Zakrzewska, M., Jaskólski, D. J. & Szemraj, J. (2023). *Cells*, **12**, 1906.
Wu, B. (2021). *CSD Communication* (CCDC 2079326, refcode EREQOK). CCDC, Cambridge, England.
Xu, Y., Lin, Q., Wang, P. & Lu, M. (2018). *Chem. Asian J.* **13**, 924–928.
Zhu, L.-N., Li, C.-Q., Li, X.-Z. & Li, R. (2006). *Acta Cryst.* E**62**, o4603–o4605.

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Synthesis and crystal structure of *N*[1],*N*[2]-dimethylethanedihydrazide

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Computing details

N[1],*N*[2]-Dimethylethanedihydrazide

Crystal data

$C_4H_{10}N_4O_2$
M_r = 146.16
Orthorhombic, $P2_12_12_1$
a = 6.0356 (5) Å
b = 7.6501 (6) Å
c = 15.7851 (14) Å
V = 728.84 (10) Å^3
Z = 4
F(000) = 312
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 809 reflections
θ = 2.6–21.5°
μ = 0.11 mm^{-1}
T = 293 K
Prism, clear light colourless
0.25 × 0.2 × 0.15 mm

Data collection

Xcalibur, Eos diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.0797 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.975, T_{max} = 1.000
2356 measured reflections
1279 independent reflections
1014 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°, θ_{min} = 2.6°
$h = -4 \rightarrow 7$
$k = -6 \rightarrow 9$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.093
S = 1.04
1279 reflections
107 parameters
6 restraints
Primary atom site location: dual
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}
Absolute structure: Flack x determined using 280 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: −0.7 (10)

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)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.3495 (5)	−0.6601 (3)	−0.39158 (16)	0.0534 (8)
O2	−0.1053 (4)	−0.3057 (4)	−0.38063 (17)	0.0565 (8)
N1	−0.5715 (5)	−0.4389 (3)	−0.43410 (17)	0.0356 (8)
N2	−0.6265 (6)	−0.2617 (4)	−0.4206 (2)	0.0390 (8)
N3	−0.2831 (5)	−0.3723 (4)	−0.2592 (2)	0.0418 (8)
N4	−0.4758 (7)	−0.4508 (6)	−0.2252 (2)	0.0510 (10)
C1	−0.7056 (7)	−0.5453 (5)	−0.4913 (2)	0.0520 (11)
H1A	−0.703336	−0.494920	−0.546990	0.078*
H1B	−0.855356	−0.549500	−0.470930	0.078*
H1C	−0.646056	−0.661570	−0.493510	0.078*
C2	−0.4040 (6)	−0.5050 (5)	−0.3896 (2)	0.0357 (9)
C3	−0.2571 (6)	−0.3787 (4)	−0.3421 (2)	0.0359 (9)
C4	−0.1283 (7)	−0.2793 (5)	−0.2043 (3)	0.0661 (13)
H4C	−0.188175	−0.166675	−0.190369	0.099*
H4D	0.010785	−0.264855	−0.232939	0.099*
H4E	−0.105945	−0.345315	−0.153239	0.099*
H2A	−0.763 (8)	−0.255 (5)	−0.404 (2)	0.061 (14)*
H4A	−0.537 (7)	−0.378 (5)	−0.199 (2)	0.053 (15)*
H2B	−0.621 (6)	−0.208 (5)	−0.471 (2)	0.056 (14)*
H4B	−0.432 (9)	−0.548 (7)	−0.187 (3)	0.12 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0640 (19)	0.0427 (15)	0.0536 (18)	0.0182 (15)	−0.0038 (16)	−0.0062 (13)
O2	0.0318 (15)	0.084 (2)	0.0542 (18)	−0.0106 (15)	0.0054 (15)	0.0102 (15)
N1	0.0346 (17)	0.0386 (16)	0.0335 (17)	0.0029 (15)	−0.0068 (15)	−0.0064 (14)
N2	0.0321 (19)	0.0372 (18)	0.048 (2)	0.0026 (17)	0.0011 (18)	0.0011 (17)
N3	0.0361 (18)	0.051 (2)	0.0377 (19)	−0.0037 (18)	−0.0046 (16)	−0.0015 (15)
N4	0.058 (3)	0.056 (2)	0.039 (2)	−0.002 (2)	0.0052 (19)	−0.002 (2)
C1	0.060 (3)	0.055 (2)	0.041 (2)	−0.005 (2)	−0.013 (2)	−0.011 (2)
C2	0.037 (2)	0.043 (2)	0.0267 (19)	0.0058 (19)	0.0072 (19)	−0.0023 (17)
C3	0.029 (2)	0.044 (2)	0.035 (2)	0.0081 (19)	−0.0022 (18)	0.0048 (18)
C4	0.057 (3)	0.084 (3)	0.057 (3)	−0.008 (3)	−0.017 (3)	−0.015 (3)

Geometric parameters (Å, º)

O1—C2	1.231 (4)	N4—H4A	0.79 (4)
O2—C3	1.233 (4)	N4—H4B	0.99 (5)

N1—N2	1.412 (4)	C1—H1A	0.9599
N1—C1	1.460 (4)	C1—H1B	0.9601
N1—C2	1.331 (4)	C1—H1C	0.9600
N2—H2A	0.87 (4)	C2—C3	1.511 (5)
N2—H2B	0.89 (4)	C4—H4C	0.9600
N3—N4	1.414 (4)	C4—H4D	0.9600
N3—C3	1.319 (4)	C4—H4E	0.9601
N3—C4	1.460 (4)		
N2—N1—C1	119.9 (3)	H1A—C1—H1B	109.5
C2—N1—N2	117.6 (3)	H1A—C1—H1C	109.5
C2—N1—C1	122.4 (3)	H1B—C1—H1C	109.5
N1—N2—H2A	109 (3)	O1—C2—N1	123.8 (3)
N1—N2—H2B	108 (2)	O1—C2—C3	118.2 (3)
H2A—N2—H2B	106 (4)	N1—C2—C3	117.7 (3)
N4—N3—C4	120.5 (3)	O2—C3—N3	124.1 (4)
C3—N3—N4	117.3 (3)	O2—C3—C2	118.7 (3)
C3—N3—C4	122.1 (4)	N3—C3—C2	116.5 (3)
N3—N4—H4A	107 (3)	N3—C4—H4C	109.4
N3—N4—H4B	109 (3)	N3—C4—H4D	109.6
H4A—N4—H4B	109 (4)	N3—C4—H4E	109.4
N1—C1—H1A	109.6	H4C—C4—H4D	109.5
N1—C1—H1B	109.5	H4C—C4—H4E	109.5
N1—C1—H1C	109.4	H4D—C4—H4E	109.5
O1—C2—C3—O2	89.9 (4)	N4—N3—C3—O2	174.8 (4)
O1—C2—C3—N3	−81.4 (4)	N4—N3—C3—C2	−14.4 (5)
N1—C2—C3—O2	−83.2 (4)	C1—N1—C2—O1	−1.2 (5)
N1—C2—C3—N3	105.5 (4)	C1—N1—C2—C3	171.6 (3)
N2—N1—C2—O1	175.1 (4)	C4—N3—C3—O2	−1.4 (6)
N2—N1—C2—C3	−12.2 (4)	C4—N3—C3—C2	169.4 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···O1^{i}	0.96	2.58	3.042 (4)	110
N2—H2*A*···O2^{ii}	0.87 (5)	2.13 (5)	2.977 (4)	164 (4)
N2—H2*B*···O2^{iii}	0.90 (3)	2.35 (3)	3.182 (4)	155 (3)
N4—H4*A*···O1^{iv}	0.79 (4)	2.30 (4)	3.075 (5)	169 (4)
N4—H4*B*···N2^{v}	0.99 (5)	2.38 (5)	3.367 (5)	170 (4)

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