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# 1,3-Dimethyl-5-(3-methylphenoxy)-1*H*-pyrazole-4-carbaldehyde

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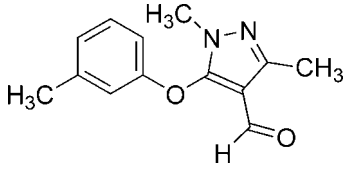
Key indicators: single-crystal X-ray study; $T$ = 113 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.057; $wR$ factor = 0.100; data-to-parameter ratio = 17.7.

There are two independent molecules in the asymmetric unit of the title compound, $C_{13}H_{14}N_2O_2$, in which the dihedral angles between the substituted phenyl ring and the pyrazole ring are 86.5 (2) and 82.3 (3)°. The crystal packing features weak intermolecular C—H···O interactions.

## Related literature

For the biological activity of pyrazole derivatives, see: Drabek (1992); Haga *et al.* (1990); Motoba *et al.* (1992); Watanabe *et al.* (2001).



## Experimental

### Crystal data

$C_{13}H_{14}N_2O_2$
$M_r$ = 230.26
Triclinic, $P\overline{1}$
$a$ = 7.9444 (16) Å
$b$ = 10.643 (3) Å
$c$ = 15.053 (3) Å
$\alpha$ = 107.732 (3)°
$\beta$ = 102.473 (5)°
$\gamma$ = 93.225 (7)°
$V$ = 1173.4 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 113 K
0.20 × 0.16 × 0.12 mm

### Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min}$ = 0.982, $T_{max}$ = 0.989
12386 measured reflections
5529 independent reflections
2226 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.064

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.100
$S$ = 1.02
5529 reflections
313 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.40 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C12—H12$A$···O4$^{i}$ | 0.98 | 2.57 | 3.488 (3) | 157 |
| C15—H15···O2$^{ii}$ | 0.95 | 2.58 | 3.315 (3) | 134 |

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2155).

## References

Drabek, J. (1992). DE Patent No. 4200742.
Haga, T., Toki, T., Koyanaqi, T., Okada, H., Imai, O. & Morita, M. (1990). Jpn Patent No. 02096568.
Motoba, K., Suzuki, T. & Uchida, M. (1992). *Pestic. Biochem. Physiol.* **43**, 37–44.
Rigaku (2008). *CrystalClear*. Rigaku Corporation, Toyko, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Watanabe, M., Kuwata, T., Okada, T., Ohita, S., Asahara, T., Noritake, T. & Fukuda, Y. (2001). Jpn Patent No. 2001233861.

# supporting information

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## 1,3-Dimethyl-5-(3-methylphenoxy)-1*H*-pyrazole-4-carbaldehyde

**Hong Dai, Hai-Jun Zhang, Lei Shi, Hai-Qin Sun and Yu-Jun Shi**

### S1. Comment

It is well known that compounds containing pyrazole ring have good bioactivities such as fungicidal, insecticidal, and herbicidal activities (Haga *et al.*, 1990; Motoba *et al.*, 1992; Watanabe *et al.*, 2001). They are widely applied in the field of plant protection (Drabek, 1992). In order to discover more biologically active pyrazole compounds, the title compound, (I), was synthesized and its crystal structure was determined (Fig.1). The dihedral angles between substituted phenyl ring and pyrazole ring in the two independent molecules are 86.5 (2) ° and 82.3 (3) °, respectively. The crystal packing displays weak intermolecular C—H···O interactions (Table 1).

### S2. Experimental

To a stirred solution of 1-methyl-3-methyl-5-chloro-1*H*-pyrazole- 4-carbaldehyde(30 mmol) and 3-methylphenol(48 mmol) in DMF(30 ml) was added potassium hydroxide(60 mmol) at room temperature. The resulting mixture was heated to 388 k for 6 h. Then the reaction solution was poured into cold water(100 ml) and extracted with ethyl acetate (3 *x* 60 ml). The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was recrystallized from ethyl acetate/petroleum ether to give colourless crystals.

### S3. Refinement

All H atoms were placed in calculated positions, with C–H = 0.95, and 0.98 ° A, and included in the final cycles of refinement using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(C).

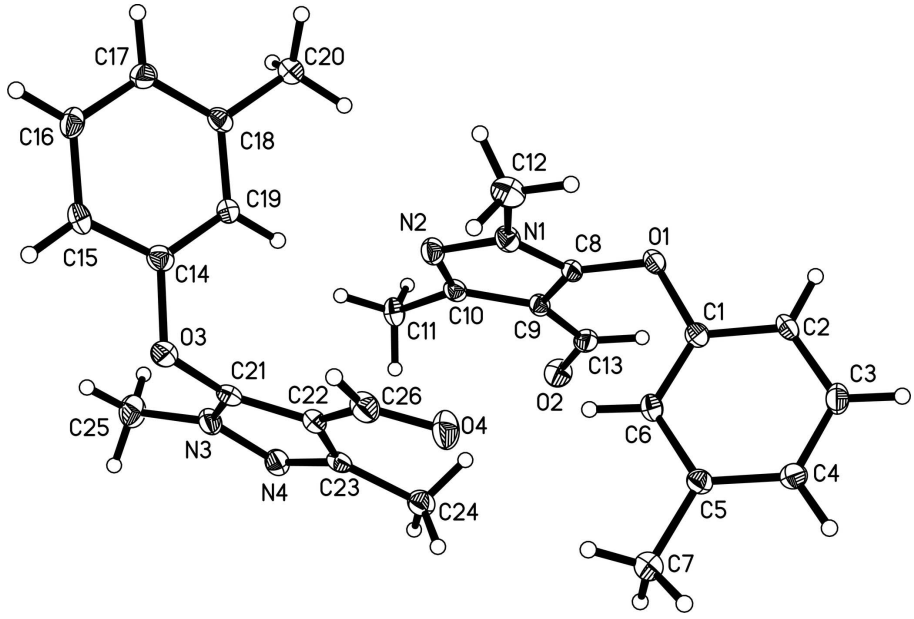


**Figure 1**

View of the title compound (I), with displacement ellipsoids drawn at the 30% probability level.

**1,3-Dimethyl-5-(3-methylphenoxy)-1*H*-pyrazole-4-carbaldehyde**

*Crystal data*

$C_{13}H_{14}N_2O_2$
$M_r = 230.27$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.9444\ (16)$ Å
$b = 10.643\ (3)$ Å
$c = 15.053\ (3)$ Å
$\alpha = 107.732\ (3)°$
$\beta = 102.473\ (5)°$
$\gamma = 93.225\ (7)°$
$V = 1173.4\ (5)$ Å$^3$
$Z = 4$
$F(000) = 488$
$D_x = 1.303$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4226 reflections
$\theta = 2.0–28.1°$
$\mu = 0.09$ mm$^{-1}$
$T = 113$ K
Prism, colourless
0.20 × 0.16 × 0.12 mm

*Data collection*

Rigaku Saturn724 CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm$^{-1}$
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min} = 0.982$, $T_{max} = 0.989$
12386 measured reflections
5529 independent reflections
2226 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.0°$
$h = -10\rightarrow10$
$k = -14\rightarrow14$
$l = -19\rightarrow19$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.100$
$S = 1.02$
5529 reflections
313 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
$w = 1/[\sigma^2(F_o^2) + (0.010P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{min} = -0.40$ e Å$^{-3}$

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.8036 (2) | 0.24450 (16) | 0.10860 (11) | 0.0294 (5) |
| O2 | 0.7737 (2) | 0.60698 (17) | 0.33053 (12) | 0.0382 (5) |
| O3 | 0.0347 (2) | 0.00932 (17) | 0.28476 (11) | 0.0328 (5) |
| O4 | 0.2005 (2) | 0.11940 (17) | 0.05903 (12) | 0.0425 (5) |
| N1 | 0.6563 (3) | 0.1553 (2) | 0.19874 (14) | 0.0278 (6) |
| N2 | 0.5999 (3) | 0.1925 (2) | 0.28185 (14) | 0.0294 (6) |
| N3 | 0.0942 (3) | 0.2408 (2) | 0.35725 (15) | 0.0303 (6) |
| N4 | 0.1457 (3) | 0.3542 (2) | 0.33896 (14) | 0.0297 (6) |
| C1 | 0.7095 (3) | 0.2757 (2) | 0.02854 (17) | 0.0241 (6) |
| C2 | 0.8041 (3) | 0.2834 (2) | −0.03652 (16) | 0.0274 (7) |
| H2 | 0.9235 | 0.2712 | −0.0258 | 0.033* |
| C3 | 0.7187 (3) | 0.3095 (2) | −0.11844 (17) | 0.0321 (7) |
| H3 | 0.7797 | 0.3156 | −0.1651 | 0.038* |
| C4 | 0.5444 (3) | 0.3268 (2) | −0.13217 (17) | 0.0301 (7) |
| H4 | 0.4875 | 0.3453 | −0.1883 | 0.036* |
| C5 | 0.4513 (3) | 0.3177 (2) | −0.06618 (17) | 0.0255 (6) |
| C6 | 0.5371 (3) | 0.2912 (2) | 0.01631 (16) | 0.0256 (6) |
| H6 | 0.4767 | 0.2840 | 0.0630 | 0.031* |
| C7 | 0.2610 (3) | 0.3341 (2) | −0.08065 (16) | 0.0341 (7) |
| H7A | 0.2039 | 0.2766 | −0.0529 | 0.051* |
| H7B | 0.2067 | 0.3093 | −0.1496 | 0.051* |
| H7C | 0.2488 | 0.4271 | −0.0488 | 0.051* |
| C8 | 0.7308 (3) | 0.2600 (3) | 0.18420 (17) | 0.0256 (7) |
| C9 | 0.7234 (3) | 0.3731 (2) | 0.25874 (17) | 0.0223 (6) |
| C10 | 0.6415 (3) | 0.3234 (3) | 0.31759 (17) | 0.0255 (6) |
| C11 | 0.5998 (3) | 0.4000 (2) | 0.40987 (15) | 0.0320 (7) |
| H11A | 0.5401 | 0.3387 | 0.4337 | 0.048* |
| H11B | 0.5243 | 0.4661 | 0.3986 | 0.048* |
| H11C | 0.7077 | 0.4452 | 0.4577 | 0.048* |

| | | | | |
|---|---|---|---|---|
| C12 | 0.6303 (3) | 0.0156 (2) | 0.13985 (17) | 0.0377 (8) |
| H12A | 0.6849 | 0.0053 | 0.0860 | 0.056* |
| H12B | 0.5054 | −0.0155 | 0.1149 | 0.056* |
| H12C | 0.6830 | −0.0372 | 0.1791 | 0.056* |
| C13 | 0.7929 (3) | 0.5060 (3) | 0.26952 (18) | 0.0313 (7) |
| H13 | 0.8587 | 0.5164 | 0.2259 | 0.038* |
| C14 | 0.1617 (3) | −0.0619 (3) | 0.32283 (16) | 0.0274 (7) |
| C15 | 0.0930 (3) | −0.1703 (2) | 0.34139 (16) | 0.0294 (7) |
| H15 | −0.0289 | −0.1912 | 0.3313 | 0.035* |
| C16 | 0.2095 (3) | −0.2481 (2) | 0.37553 (16) | 0.0298 (7) |
| H16 | 0.1670 | −0.3246 | 0.3881 | 0.036* |
| C17 | 0.3865 (3) | −0.2146 (2) | 0.39111 (16) | 0.0296 (7) |
| H17 | 0.4643 | −0.2684 | 0.4145 | 0.035* |
| C18 | 0.4526 (3) | −0.1037 (2) | 0.37326 (16) | 0.0252 (6) |
| C19 | 0.3373 (3) | −0.0259 (2) | 0.33883 (15) | 0.0249 (6) |
| H19 | 0.3792 | 0.0510 | 0.3266 | 0.030* |
| C20 | 0.6461 (3) | −0.0664 (2) | 0.39066 (16) | 0.0320 (7) |
| H20A | 0.6958 | −0.0195 | 0.4593 | 0.048* |
| H20B | 0.6672 | −0.0084 | 0.3535 | 0.048* |
| H20C | 0.7009 | −0.1472 | 0.3704 | 0.048* |
| C21 | 0.0920 (3) | 0.1315 (3) | 0.28273 (19) | 0.0287 (7) |
| C22 | 0.1413 (3) | 0.1701 (3) | 0.21237 (18) | 0.0250 (6) |
| C23 | 0.1758 (3) | 0.3107 (3) | 0.25212 (18) | 0.0268 (7) |
| C24 | 0.2314 (3) | 0.4080 (2) | 0.20729 (17) | 0.0327 (7) |
| H24A | 0.2286 | 0.4987 | 0.2485 | 0.049* |
| H24B | 0.1522 | 0.3915 | 0.1440 | 0.049* |
| H24C | 0.3499 | 0.3978 | 0.1999 | 0.049* |
| C25 | 0.0481 (3) | 0.2495 (3) | 0.44694 (16) | 0.0417 (8) |
| H25A | −0.0006 | 0.1613 | 0.4440 | 0.063* |
| H25B | −0.0385 | 0.3111 | 0.4571 | 0.063* |
| H25C | 0.1521 | 0.2821 | 0.5003 | 0.063* |
| C26 | 0.1513 (3) | 0.0825 (3) | 0.11980 (19) | 0.0350 (7) |
| H26 | 0.1175 | −0.0100 | 0.1050 | 0.042* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0228 (11) | 0.0443 (12) | 0.0271 (10) | 0.0118 (9) | 0.0112 (8) | 0.0153 (9) |
| O2 | 0.0450 (13) | 0.0302 (12) | 0.0371 (11) | 0.0036 (10) | 0.0104 (10) | 0.0076 (10) |
| O3 | 0.0224 (11) | 0.0375 (12) | 0.0437 (12) | 0.0048 (9) | 0.0077 (9) | 0.0208 (10) |
| O4 | 0.0511 (14) | 0.0431 (13) | 0.0393 (12) | 0.0058 (10) | 0.0263 (10) | 0.0116 (10) |
| N1 | 0.0281 (14) | 0.0296 (14) | 0.0244 (12) | 0.0053 (11) | 0.0086 (11) | 0.0055 (11) |
| N2 | 0.0295 (14) | 0.0351 (14) | 0.0256 (13) | 0.0052 (11) | 0.0107 (11) | 0.0100 (11) |
| N3 | 0.0255 (14) | 0.0421 (15) | 0.0279 (13) | 0.0077 (12) | 0.0114 (11) | 0.0140 (12) |
| N4 | 0.0258 (14) | 0.0330 (14) | 0.0307 (13) | 0.0028 (11) | 0.0083 (11) | 0.0100 (12) |
| C1 | 0.0238 (17) | 0.0238 (15) | 0.0240 (14) | 0.0034 (12) | 0.0067 (12) | 0.0063 (12) |
| C2 | 0.0215 (16) | 0.0336 (17) | 0.0306 (15) | 0.0078 (13) | 0.0135 (12) | 0.0099 (13) |
| C3 | 0.0399 (19) | 0.0322 (17) | 0.0311 (15) | 0.0071 (14) | 0.0191 (13) | 0.0126 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 0.0325 (18) | 0.0335 (17) | 0.0271 (15) | 0.0107 (14) | 0.0082 (13) | 0.0122 (13) |
| C5 | 0.0249 (17) | 0.0253 (15) | 0.0266 (15) | 0.0062 (12) | 0.0077 (12) | 0.0074 (13) |
| C6 | 0.0268 (17) | 0.0283 (16) | 0.0229 (14) | 0.0044 (13) | 0.0108 (12) | 0.0066 (12) |
| C7 | 0.0307 (18) | 0.0389 (18) | 0.0353 (16) | 0.0066 (14) | 0.0093 (13) | 0.0143 (14) |
| C8 | 0.0182 (16) | 0.0387 (18) | 0.0262 (15) | 0.0080 (13) | 0.0074 (13) | 0.0172 (14) |
| C9 | 0.0176 (15) | 0.0266 (15) | 0.0226 (14) | 0.0014 (12) | 0.0045 (12) | 0.0086 (12) |
| C10 | 0.0200 (16) | 0.0331 (16) | 0.0229 (14) | 0.0057 (13) | 0.0042 (12) | 0.0089 (13) |
| C11 | 0.0333 (17) | 0.0374 (18) | 0.0274 (15) | 0.0030 (14) | 0.0147 (13) | 0.0086 (14) |
| C12 | 0.0386 (19) | 0.0305 (17) | 0.0364 (16) | 0.0054 (14) | 0.0074 (14) | 0.0014 (14) |
| C13 | 0.0240 (17) | 0.0394 (18) | 0.0343 (17) | 0.0042 (14) | 0.0048 (13) | 0.0190 (15) |
| C14 | 0.0274 (18) | 0.0315 (17) | 0.0240 (15) | 0.0078 (13) | 0.0080 (13) | 0.0079 (13) |
| C15 | 0.0255 (17) | 0.0360 (17) | 0.0284 (15) | 0.0030 (14) | 0.0138 (13) | 0.0083 (13) |
| C16 | 0.0387 (19) | 0.0278 (16) | 0.0275 (15) | 0.0036 (14) | 0.0160 (13) | 0.0103 (13) |
| C17 | 0.0342 (18) | 0.0299 (16) | 0.0302 (15) | 0.0112 (14) | 0.0129 (14) | 0.0131 (13) |
| C18 | 0.0238 (16) | 0.0290 (16) | 0.0224 (14) | 0.0073 (13) | 0.0088 (12) | 0.0052 (13) |
| C19 | 0.0223 (16) | 0.0290 (16) | 0.0272 (14) | 0.0047 (12) | 0.0087 (12) | 0.0126 (13) |
| C20 | 0.0308 (18) | 0.0351 (17) | 0.0356 (16) | 0.0095 (13) | 0.0132 (13) | 0.0150 (14) |
| C21 | 0.0162 (16) | 0.0374 (18) | 0.0376 (17) | 0.0087 (13) | 0.0064 (13) | 0.0188 (15) |
| C22 | 0.0214 (16) | 0.0289 (16) | 0.0281 (15) | 0.0073 (13) | 0.0097 (12) | 0.0107 (13) |
| C23 | 0.0166 (16) | 0.0350 (17) | 0.0305 (15) | 0.0082 (13) | 0.0049 (12) | 0.0130 (14) |
| C24 | 0.0309 (17) | 0.0314 (17) | 0.0380 (16) | 0.0083 (14) | 0.0116 (13) | 0.0116 (14) |
| C25 | 0.046 (2) | 0.057 (2) | 0.0274 (16) | 0.0085 (16) | 0.0162 (14) | 0.0173 (15) |
| C26 | 0.0320 (18) | 0.0327 (18) | 0.0411 (18) | 0.0060 (14) | 0.0140 (15) | 0.0092 (15) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C8 | 1.356 (3) | C11—H11A | 0.9800 |
| O1—C1 | 1.415 (2) | C11—H11B | 0.9800 |
| O2—C13 | 1.224 (3) | C11—H11C | 0.9800 |
| O3—C21 | 1.364 (3) | C12—H12A | 0.9800 |
| O3—C14 | 1.422 (3) | C12—H12B | 0.9800 |
| O4—C26 | 1.224 (3) | C12—H12C | 0.9800 |
| N1—C8 | 1.330 (3) | C13—H13 | 0.9500 |
| N1—N2 | 1.372 (3) | C14—C19 | 1.374 (3) |
| N1—C12 | 1.458 (3) | C14—C15 | 1.378 (3) |
| N2—C10 | 1.325 (3) | C15—C16 | 1.395 (3) |
| N3—C21 | 1.344 (3) | C15—H15 | 0.9500 |
| N3—N4 | 1.377 (3) | C16—C17 | 1.382 (3) |
| N3—C25 | 1.451 (3) | C16—H16 | 0.9500 |
| N4—C23 | 1.326 (3) | C17—C18 | 1.387 (3) |
| C1—C6 | 1.369 (3) | C17—H17 | 0.9500 |
| C1—C2 | 1.375 (3) | C18—C19 | 1.392 (3) |
| C2—C3 | 1.388 (3) | C18—C20 | 1.511 (3) |
| C2—H2 | 0.9500 | C19—H19 | 0.9500 |
| C3—C4 | 1.386 (3) | C20—H20A | 0.9800 |
| C3—H3 | 0.9500 | C20—H20B | 0.9800 |
| C4—C5 | 1.382 (3) | C20—H20C | 0.9800 |
| C4—H4 | 0.9500 | C21—C22 | 1.367 (3) |

| | | | |
|---|---|---|---|
| C5—C6 | 1.398 (3) | C22—C23 | 1.418 (3) |
| C5—C7 | 1.508 (3) | C22—C26 | 1.443 (3) |
| C6—H6 | 0.9500 | C23—C24 | 1.492 (3) |
| C7—H7A | 0.9800 | C24—H24A | 0.9800 |
| C7—H7B | 0.9800 | C24—H24B | 0.9800 |
| C7—H7C | 0.9800 | C24—H24C | 0.9800 |
| C8—C9 | 1.388 (3) | C25—H25A | 0.9800 |
| C9—C10 | 1.408 (3) | C25—H25B | 0.9800 |
| C9—C13 | 1.437 (3) | C25—H25C | 0.9800 |
| C10—C11 | 1.498 (3) | C26—H26 | 0.9500 |
| | | | |
| C8—O1—C1 | 117.58 (19) | H12A—C12—H12C | 109.5 |
| C21—O3—C14 | 117.0 (2) | H12B—C12—H12C | 109.5 |
| C8—N1—N2 | 111.3 (2) | O2—C13—C9 | 125.1 (3) |
| C8—N1—C12 | 128.9 (2) | O2—C13—H13 | 117.5 |
| N2—N1—C12 | 119.8 (2) | C9—C13—H13 | 117.5 |
| C10—N2—N1 | 105.0 (2) | C19—C14—C15 | 123.2 (2) |
| C21—N3—N4 | 110.9 (2) | C19—C14—O3 | 122.7 (2) |
| C21—N3—C25 | 128.5 (2) | C15—C14—O3 | 114.0 (2) |
| N4—N3—C25 | 120.6 (2) | C14—C15—C16 | 117.4 (2) |
| C23—N4—N3 | 104.8 (2) | C14—C15—H15 | 121.3 |
| C6—C1—C2 | 123.6 (2) | C16—C15—H15 | 121.3 |
| C6—C1—O1 | 122.0 (2) | C17—C16—C15 | 120.3 (2) |
| C2—C1—O1 | 114.3 (2) | C17—C16—H16 | 119.9 |
| C1—C2—C3 | 117.5 (2) | C15—C16—H16 | 119.9 |
| C1—C2—H2 | 121.2 | C16—C17—C18 | 121.2 (2) |
| C3—C2—H2 | 121.2 | C16—C17—H17 | 119.4 |
| C4—C3—C2 | 120.0 (2) | C18—C17—H17 | 119.4 |
| C4—C3—H3 | 120.0 | C17—C18—C19 | 118.8 (2) |
| C2—C3—H3 | 120.0 | C17—C18—C20 | 121.3 (2) |
| C5—C4—C3 | 121.6 (2) | C19—C18—C20 | 119.8 (2) |
| C5—C4—H4 | 119.2 | C14—C19—C18 | 119.0 (2) |
| C3—C4—H4 | 119.2 | C14—C19—H19 | 120.5 |
| C4—C5—C6 | 118.5 (2) | C18—C19—H19 | 120.5 |
| C4—C5—C7 | 122.3 (2) | C18—C20—H20A | 109.5 |
| C6—C5—C7 | 119.2 (2) | C18—C20—H20B | 109.5 |
| C1—C6—C5 | 118.7 (2) | H20A—C20—H20B | 109.5 |
| C1—C6—H6 | 120.6 | C18—C20—H20C | 109.5 |
| C5—C6—H6 | 120.6 | H20A—C20—H20C | 109.5 |
| C5—C7—H7A | 109.5 | H20B—C20—H20C | 109.5 |
| C5—C7—H7B | 109.5 | N3—C21—O3 | 119.8 (2) |
| H7A—C7—H7B | 109.5 | N3—C21—C22 | 108.6 (2) |
| C5—C7—H7C | 109.5 | O3—C21—C22 | 131.5 (3) |
| H7A—C7—H7C | 109.5 | C21—C22—C23 | 104.0 (2) |
| H7B—C7—H7C | 109.5 | C21—C22—C26 | 125.8 (3) |
| N1—C8—O1 | 120.9 (2) | C23—C22—C26 | 130.2 (3) |
| N1—C8—C9 | 108.3 (2) | N4—C23—C22 | 111.7 (2) |
| O1—C8—C9 | 130.8 (3) | N4—C23—C24 | 119.8 (2) |

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| C8—C9—C10 | 103.7 (2) | C22—C23—C24 | 128.5 (2) |
| C8—C9—C13 | 125.1 (3) | C23—C24—H24A | 109.5 |
| C10—C9—C13 | 131.2 (2) | C23—C24—H24B | 109.5 |
| N2—C10—C9 | 111.8 (2) | H24A—C24—H24B | 109.5 |
| N2—C10—C11 | 120.3 (2) | C23—C24—H24C | 109.5 |
| C9—C10—C11 | 128.0 (2) | H24A—C24—H24C | 109.5 |
| C10—C11—H11A | 109.5 | H24B—C24—H24C | 109.5 |
| C10—C11—H11B | 109.5 | N3—C25—H25A | 109.5 |
| H11A—C11—H11B | 109.5 | N3—C25—H25B | 109.5 |
| C10—C11—H11C | 109.5 | H25A—C25—H25B | 109.5 |
| H11A—C11—H11C | 109.5 | N3—C25—H25C | 109.5 |
| H11B—C11—H11C | 109.5 | H25A—C25—H25C | 109.5 |
| N1—C12—H12A | 109.5 | H25B—C25—H25C | 109.5 |
| N1—C12—H12B | 109.5 | O4—C26—C22 | 124.5 (3) |
| H12A—C12—H12B | 109.5 | O4—C26—H26 | 117.8 |
| N1—C12—H12C | 109.5 | C22—C26—H26 | 117.8 |

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| C8—N1—N2—C10 | 0.3 (3) | C8—C9—C13—O2 | 173.5 (2) |
| C12—N1—N2—C10 | −179.72 (19) | C10—C9—C13—O2 | −9.2 (4) |
| C21—N3—N4—C23 | −0.5 (3) | C21—O3—C14—C19 | −13.2 (3) |
| C25—N3—N4—C23 | −179.5 (2) | C21—O3—C14—C15 | 167.3 (2) |
| C8—O1—C1—C6 | −14.8 (3) | C19—C14—C15—C16 | −1.9 (4) |
| C8—O1—C1—C2 | 167.7 (2) | O3—C14—C15—C16 | 177.68 (19) |
| C6—C1—C2—C3 | 0.6 (4) | C14—C15—C16—C17 | 1.1 (4) |
| O1—C1—C2—C3 | 178.1 (2) | C15—C16—C17—C18 | −0.1 (4) |
| C1—C2—C3—C4 | 0.0 (4) | C16—C17—C18—C19 | −0.1 (4) |
| C2—C3—C4—C5 | −0.4 (4) | C16—C17—C18—C20 | 179.7 (2) |
| C3—C4—C5—C6 | 0.3 (4) | C15—C14—C19—C18 | 1.6 (4) |
| C3—C4—C5—C7 | −179.1 (2) | O3—C14—C19—C18 | −177.9 (2) |
| C2—C1—C6—C5 | −0.7 (4) | C17—C18—C19—C14 | −0.6 (4) |
| O1—C1—C6—C5 | −178.0 (2) | C20—C18—C19—C14 | 179.6 (2) |
| C4—C5—C6—C1 | 0.2 (4) | N4—N3—C21—O3 | −176.2 (2) |
| C7—C5—C6—C1 | 179.6 (2) | C25—N3—C21—O3 | 2.7 (4) |
| N2—N1—C8—O1 | 176.58 (19) | N4—N3—C21—C22 | −0.4 (3) |
| C12—N1—C8—O1 | −3.4 (4) | C25—N3—C21—C22 | 178.5 (2) |
| N2—N1—C8—C9 | −0.9 (3) | C14—O3—C21—N3 | −91.8 (3) |
| C12—N1—C8—C9 | 179.1 (2) | C14—O3—C21—C22 | 93.5 (3) |
| C1—O1—C8—N1 | 103.3 (3) | N3—C21—C22—C23 | 1.0 (3) |
| C1—O1—C8—C9 | −79.9 (3) | O3—C21—C22—C23 | 176.2 (2) |
| N1—C8—C9—C10 | 1.1 (3) | N3—C21—C22—C26 | −178.3 (2) |
| O1—C8—C9—C10 | −176.1 (2) | O3—C21—C22—C26 | −3.2 (5) |
| N1—C8—C9—C13 | 179.0 (2) | N3—N4—C23—C22 | 1.2 (3) |
| O1—C8—C9—C13 | 1.8 (4) | N3—N4—C23—C24 | 178.74 (19) |
| N1—N2—C10—C9 | 0.4 (3) | C21—C22—C23—N4 | −1.4 (3) |
| N1—N2—C10—C11 | −179.8 (2) | C26—C22—C23—N4 | 177.9 (2) |
| C8—C9—C10—N2 | −0.9 (3) | C21—C22—C23—C24 | −178.7 (2) |
| C13—C9—C10—N2 | −178.7 (2) | C26—C22—C23—C24 | 0.6 (4) |
| C8—C9—C10—C11 | 179.3 (2) | C21—C22—C26—O4 | −177.9 (3) |

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| C13—C9—C10—C11 | 1.6 (4) | C23—C22—C26—O4 | 2.9 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12*A*···O4$^{i}$ | 0.98 | 2.57 | 3.488 (3) | 157 |
| C15—H15···O2$^{ii}$ | 0.95 | 2.58 | 3.315 (3) | 134 |

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) *x*−1, *y*−1, *z*.