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# 1-Formyl-*r*-2,*c*-6-bis(4-methoxyphenyl)-*c*-3,*t*-3-dimethylpiperidin-4-one

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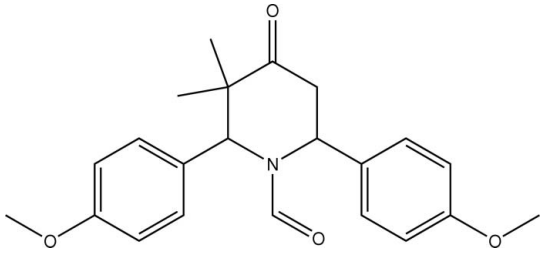
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.049; $wR$ factor = 0.142; data-to-parameter ratio = 25.6.

In the title compound, $C_{22}H_{25}NO_4$, the piperidine ring adopts a distorted boat conformation. The two benzene rings are approximately perpendicular to each other, making a dihedral angle of 86.2 (8)°. The crystal packing is stabilized by C—H···O and C—H···$\pi$ interactions.

## Related literature

For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995). For ring conformational analysis, see: Cremer & Pople (1975); Nardelli (1983).



## Experimental

### *Crystal data*

$C_{22}H_{25}NO_4$
$M_r$ = 367.43
Monoclinic, $P2_1/c$
$a$ = 11.7274 (3) Å
$b$ = 18.8556 (4) Å
$c$ = 9.7178 (3) Å
$\beta$ = 113.507 (1)°
$V$ = 1970.54 (9) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
0.25 × 0.20 × 0.20 mm

### *Data collection*

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min}$ = 0.979, $T_{max}$ = 0.983
26804 measured reflections
6250 independent reflections
4080 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.142
$S$ = 1.03
6250 reflections
244 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C5—H5$A$···O3$^{i}$ | 0.97 | 2.44 | 3.3446 (16) | 155 |
| C6—H6···O2$^{ii}$ | 0.98 | 2.41 | 3.3708 (16) | 168 |
| C18—H18···O1$^{iii}$ | 0.93 | 2.53 | 3.3018 (17) | 140 |
| C10—H10···$Cg1^{iv}$ | 0.93 | 2.90 | 3.6627 (17) | 140 |

Symmetry codes: (i) $x, y, z-1$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+2$. $Cg(1)$ is the centroid of the C16–C21 ring.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1983).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2903).

## References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2004). *SAINT* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

# supporting information

*Acta Cryst.* (2009). E**65**, o856 [doi:10.1107/S1600536809010010]

## 1-Formyl-*r*-2,*c*-6-bis(4-methoxyphenyl)-*c*-3,*t*-3-dimethylpiperidin-4-one

**T. Kavitha, S. Ponnuswamy, P. Sakthivel, K. Karthik and M. N. Ponnuswamy**

### S1. Comment

Piperidine, a basic component of the piper alkaloid piper nigrum is a monocyclic cyclohexane with a hetero atom affixed in the first position. The skeletal ring of piperidine is contained in the molecules of many synthetic and natural medicaments. A significant industrial application of piperidine is for the production of dipiperidinyl dithiuram tetra-sulfide, which can be used as a rubber vulcanization accelerator.

The piperidine ring adopts distorted boat conformation with puckering parameters (Cremer & Pople, 1975) q2 = 0.630 (1) Å, q3 =0.070 (1)Å and $\varphi$2= 87.2 (1)° and the asymmetry parameters $\Delta C_2$(N1) and $\Delta C_2$(C4) = 14.78 (12)Å (Nardelli, 1983). The angles between the best plane of the piperidine ring (N1,C3,C4,C6) and the phenyl rings (C8—C13 and C16—C21) are 84.17 (7)° and 80.70 (7)°, respectively. The two phenyl rings are approximately perpendicular to each other as can be seen from the dihedral angle of 86.23 (8)°. The methyl substituents C14 and C15 are oriented equatorially [N1—C2—C3—C14 =] -178.88 (11)° and axially [N1—C2—C3—C15 =] -59.52 (13) ° with respect to the piperidine ring. The sum of the bond angles around N1 atom (359.3°) indicates $sp^2$ hybridization.

The packing of the molecules is controlled by C—H···O types of intermolecular interactions. The symmetry related molecules form a dimer with the graph-set motif of $R^2_2(16)$ (Bernstein *et al.*, 1995) through hydrogen bonds. Further a C—H··· $\pi$ interaction also leads to the formation of a dimer [C10—H10 = 0.9301 Å, H10···*Cg*(1) =2.9035 Å, C10···*Cg*(1) = 3.6627 (17) Å and C10—H10···*Cg*(1) = 139.71°, where *Cg*(1) is the centroid of the ring (C16—C21) at (1 - *x*,-*y*,2 - *z*)] .

### S2. Experimental

The ice-cold solution of acetic-formic anhydride was prepared from acetic anhydride (10 ml) and 85% formic acid (5 ml) and was added slowly to a cold solution of *r*-2, *c*-6-*bis*(4-methoxyphenyl)-*c*-3,*t*-3-dimethylpiperidine-4-one (1.69 g) in benzene (30 ml). The reaction mixture was stirred at room temperature for 5 hrs. The organic layer was separated, dried over anhydrous $Na_2SO_4$ and concentrated. The resulting mass was purified by crystallization from benzene-petroleum ether (333–353 K) in the ratio 1:1.

### S3. Refinement

H atoms were positioned geometrically (C—H=0.93–0.96 Å) and allowed to ride on their parent atoms, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H, 1.2$U_{eq}$(C) for other H atoms.

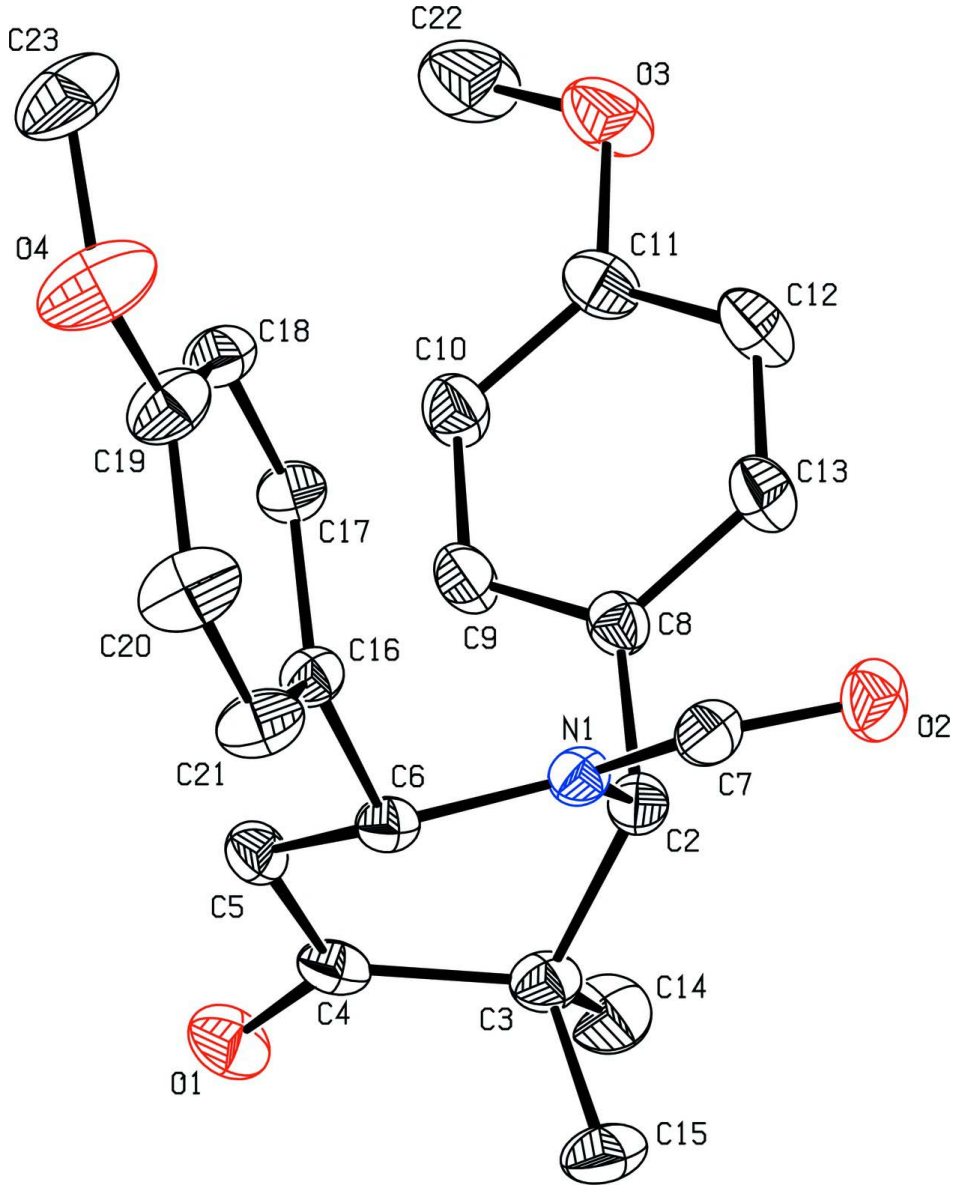


**Figure 1**

*ORTEP* plot of the molecule showing that the thermal ellipsoids are drawn at 30% probability level. H atoms have been omitted for clarity.

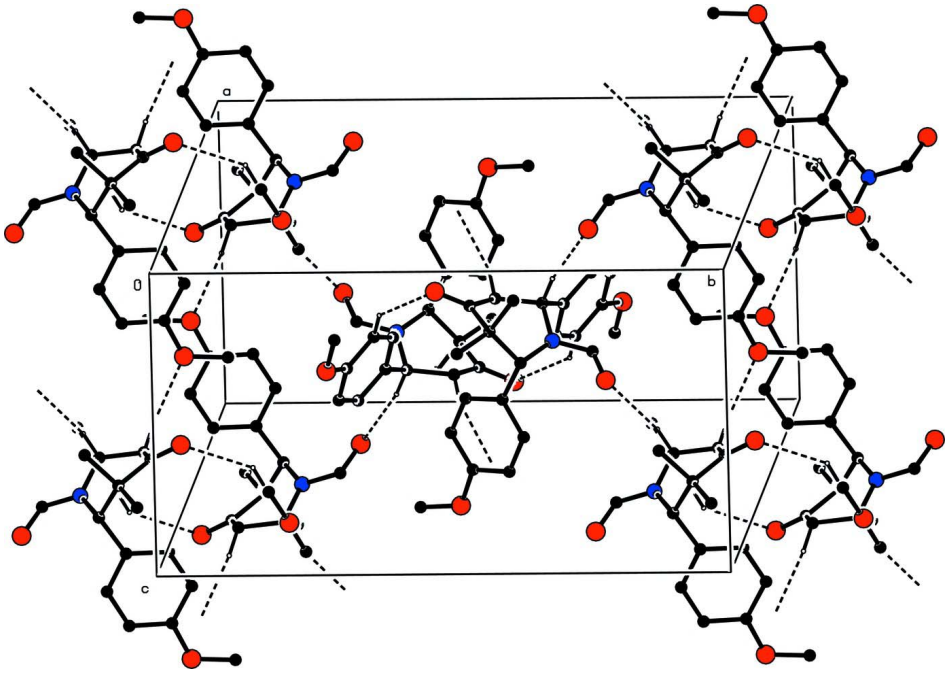


**Figure 2**

The molecular packing of the compound viewed down the *b* axis is shown. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

### 1-Formyl-r-2,c-6-bis(4-methoxyphenyl)-c-3,t-3-dimethylpiperidin-4-one

*Crystal data*

$C_{22}H_{25}NO_4$
$M_r = 367.43$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.7274\ (3)$ Å
$b = 18.8556\ (4)$ Å
$c = 9.7178\ (3)$ Å
$\beta = 113.507\ (1)°$
$V = 1970.54\ (9)$ Å$^3$
$Z = 4$
$F(000) = 784$
$D_x = 1.239$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6250 reflections
$\theta = 2.2–31.0°$
$\mu = 0.09$ mm$^{-1}$
$T = 293$ K
Block, colourless
0.25 × 0.20 × 0.20 mm

*Data collection*

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.979$, $T_{max} = 0.983$
26804 measured reflections
6250 independent reflections
4080 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 31.0°$, $\theta_{min} = 2.2°$
$h = -16\rightarrow16$
$k = -27\rightarrow26$
$l = -14\rightarrow14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.142$
$S = 1.03$
6250 reflections
244 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
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.3342P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.19$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C2 | 0.17408 (11) | 0.62041 (6) | 0.40308 (14) | 0.0338 (3) |
| H2 | 0.1120 | 0.6538 | 0.4087 | 0.041* |
| C3 | 0.10682 (11) | 0.57637 (7) | 0.25999 (14) | 0.0381 (3) |
| C4 | 0.19953 (12) | 0.53109 (7) | 0.22723 (13) | 0.0363 (3) |
| C5 | 0.33023 (12) | 0.55897 (7) | 0.27795 (15) | 0.0366 (3) |
| H5A | 0.3623 | 0.5459 | 0.2036 | 0.044* |
| H5B | 0.3812 | 0.5353 | 0.3709 | 0.044* |
| C6 | 0.34585 (11) | 0.63892 (6) | 0.30324 (13) | 0.0323 (2) |
| H6 | 0.3138 | 0.6621 | 0.2048 | 0.039* |
| C7 | 0.28230 (12) | 0.73249 (7) | 0.42790 (15) | 0.0398 (3) |
| H7 | 0.3400 | 0.7599 | 0.4081 | 0.048* |
| C8 | 0.22360 (11) | 0.58092 (7) | 0.55153 (14) | 0.0352 (3) |
| C9 | 0.26574 (13) | 0.51168 (7) | 0.57097 (15) | 0.0429 (3) |
| H9 | 0.2638 | 0.4863 | 0.4880 | 0.052* |
| C10 | 0.31075 (14) | 0.47894 (8) | 0.70986 (16) | 0.0446 (3) |
| H10 | 0.3396 | 0.4325 | 0.7196 | 0.054* |
| C11 | 0.31275 (14) | 0.51526 (8) | 0.83330 (15) | 0.0446 (3) |
| C12 | 0.26964 (16) | 0.58424 (8) | 0.81650 (17) | 0.0530 (4) |
| H12 | 0.2700 | 0.6092 | 0.8993 | 0.064* |
| C13 | 0.22628 (14) | 0.61613 (8) | 0.67819 (16) | 0.0462 (3) |
| H13 | 0.1979 | 0.6627 | 0.6690 | 0.055* |
| C14 | 0.00369 (14) | 0.53174 (9) | 0.2744 (2) | 0.0553 (4) |
| H14A | −0.0532 | 0.5621 | 0.2953 | 0.083* |
| H14B | 0.0393 | 0.4983 | 0.3548 | 0.083* |
| H14C | −0.0400 | 0.5067 | 0.1822 | 0.083* |

| | | | | |
|---|---|---|---|---|
| C15 | 0.04780 (14) | 0.62642 (8) | 0.12465 (17) | 0.0513 (4) |
| H15A | −0.0123 | 0.6563 | 0.1401 | 0.077* |
| H15B | 0.0076 | 0.5989 | 0.0351 | 0.077* |
| H15C | 0.1114 | 0.6553 | 0.1143 | 0.077* |
| C16 | 0.48138 (11) | 0.65875 (6) | 0.38343 (14) | 0.0332 (3) |
| C17 | 0.55115 (11) | 0.63584 (7) | 0.52784 (14) | 0.0368 (3) |
| H17 | 0.5134 | 0.6082 | 0.5770 | 0.044* |
| C18 | 0.67579 (12) | 0.65292 (7) | 0.60132 (16) | 0.0418 (3) |
| H18 | 0.7212 | 0.6366 | 0.6982 | 0.050* |
| C19 | 0.73163 (13) | 0.69426 (8) | 0.52933 (19) | 0.0511 (4) |
| C20 | 0.66322 (15) | 0.71813 (10) | 0.3859 (2) | 0.0623 (5) |
| H20 | 0.7008 | 0.7464 | 0.3375 | 0.075* |
| C21 | 0.53942 (14) | 0.70045 (8) | 0.31376 (17) | 0.0488 (4) |
| H21 | 0.4943 | 0.7168 | 0.2168 | 0.059* |
| C22 | 0.3775 (2) | 0.41457 (10) | 0.9928 (2) | 0.0736 (5) |
| H22A | 0.4042 | 0.4023 | 1.0969 | 0.110* |
| H22B | 0.4416 | 0.4027 | 0.9590 | 0.110* |
| H22C | 0.3032 | 0.3887 | 0.9349 | 0.110* |
| C23 | 0.92890 (16) | 0.68961 (11) | 0.7357 (3) | 0.0787 (6) |
| H23A | 1.0117 | 0.7079 | 0.7651 | 0.118* |
| H23B | 0.9311 | 0.6387 | 0.7350 | 0.118* |
| H23C | 0.8951 | 0.7053 | 0.8056 | 0.118* |
| N1 | 0.27207 (9) | 0.66443 (5) | 0.38626 (11) | 0.0321 (2) |
| O1 | 0.17227 (10) | 0.47451 (5) | 0.16419 (12) | 0.0515 (3) |
| O2 | 0.22263 (10) | 0.76191 (5) | 0.48956 (13) | 0.0524 (3) |
| O3 | 0.35310 (13) | 0.48797 (6) | 0.97457 (12) | 0.0646 (3) |
| O4 | 0.85343 (11) | 0.71456 (8) | 0.59033 (17) | 0.0816 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C2 | 0.0292 (5) | 0.0337 (6) | 0.0364 (6) | −0.0019 (5) | 0.0109 (5) | −0.0052 (5) |
| C3 | 0.0320 (6) | 0.0379 (6) | 0.0374 (7) | −0.0076 (5) | 0.0065 (5) | −0.0049 (5) |
| C4 | 0.0435 (7) | 0.0340 (6) | 0.0260 (6) | −0.0071 (5) | 0.0080 (5) | −0.0030 (5) |
| C5 | 0.0382 (6) | 0.0353 (6) | 0.0354 (6) | −0.0023 (5) | 0.0137 (5) | −0.0077 (5) |
| C6 | 0.0317 (6) | 0.0327 (6) | 0.0288 (6) | −0.0019 (5) | 0.0081 (5) | −0.0006 (4) |
| C7 | 0.0364 (6) | 0.0301 (6) | 0.0448 (7) | −0.0007 (5) | 0.0076 (6) | −0.0040 (5) |
| C8 | 0.0340 (6) | 0.0369 (6) | 0.0361 (6) | −0.0041 (5) | 0.0155 (5) | −0.0055 (5) |
| C9 | 0.0548 (8) | 0.0413 (7) | 0.0374 (7) | 0.0031 (6) | 0.0234 (6) | −0.0050 (5) |
| C10 | 0.0556 (8) | 0.0411 (7) | 0.0425 (7) | 0.0052 (6) | 0.0252 (7) | 0.0025 (6) |
| C11 | 0.0527 (8) | 0.0492 (8) | 0.0360 (7) | −0.0079 (6) | 0.0220 (6) | −0.0009 (6) |
| C12 | 0.0787 (11) | 0.0465 (8) | 0.0418 (8) | −0.0045 (7) | 0.0323 (8) | −0.0108 (6) |
| C13 | 0.0609 (9) | 0.0382 (7) | 0.0454 (8) | −0.0004 (6) | 0.0275 (7) | −0.0072 (6) |
| C14 | 0.0413 (8) | 0.0585 (9) | 0.0620 (10) | −0.0193 (7) | 0.0162 (7) | −0.0103 (8) |
| C15 | 0.0406 (7) | 0.0506 (8) | 0.0431 (8) | −0.0029 (6) | −0.0039 (6) | −0.0003 (6) |
| C16 | 0.0305 (5) | 0.0305 (6) | 0.0351 (6) | −0.0017 (4) | 0.0094 (5) | 0.0001 (5) |
| C17 | 0.0337 (6) | 0.0379 (6) | 0.0359 (6) | −0.0024 (5) | 0.0108 (5) | 0.0017 (5) |
| C18 | 0.0347 (6) | 0.0400 (7) | 0.0406 (7) | 0.0003 (5) | 0.0042 (5) | −0.0002 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C19 | 0.0328 (7) | 0.0457 (8) | 0.0640 (10) | −0.0071 (6) | 0.0081 (7) | 0.0027 (7) |
| C20 | 0.0453 (8) | 0.0647 (10) | 0.0719 (11) | −0.0151 (7) | 0.0182 (8) | 0.0234 (9) |
| C21 | 0.0437 (8) | 0.0492 (8) | 0.0470 (8) | −0.0054 (6) | 0.0113 (6) | 0.0152 (6) |
| C22 | 0.1037 (15) | 0.0640 (11) | 0.0502 (10) | 0.0027 (10) | 0.0277 (10) | 0.0144 (8) |
| C23 | 0.0342 (8) | 0.0782 (13) | 0.0957 (15) | −0.0048 (8) | −0.0036 (9) | 0.0030 (11) |
| N1 | 0.0293 (5) | 0.0279 (5) | 0.0341 (5) | −0.0019 (4) | 0.0076 (4) | −0.0031 (4) |
| O1 | 0.0621 (6) | 0.0396 (5) | 0.0481 (6) | −0.0136 (5) | 0.0169 (5) | −0.0155 (4) |
| O2 | 0.0531 (6) | 0.0367 (5) | 0.0643 (7) | 0.0024 (4) | 0.0204 (5) | −0.0136 (5) |
| O3 | 0.1002 (9) | 0.0585 (7) | 0.0396 (6) | 0.0004 (6) | 0.0326 (6) | 0.0052 (5) |
| O4 | 0.0371 (6) | 0.0867 (9) | 0.0976 (10) | −0.0224 (6) | 0.0023 (6) | 0.0220 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C2—N1 | 1.4785 (15) | C12—H12 | 0.9300 |
| C2—C8 | 1.5181 (18) | C13—H13 | 0.9300 |
| C2—C3 | 1.5395 (17) | C14—H14A | 0.9600 |
| C2—H2 | 0.9800 | C14—H14B | 0.9600 |
| C3—C4 | 1.5128 (19) | C14—H14C | 0.9600 |
| C3—C14 | 1.5250 (19) | C15—H15A | 0.9600 |
| C3—C15 | 1.541 (2) | C15—H15B | 0.9600 |
| C4—O1 | 1.2081 (15) | C15—H15C | 0.9600 |
| C4—C5 | 1.5053 (18) | C16—C21 | 1.3811 (18) |
| C5—C6 | 1.5267 (17) | C16—C17 | 1.3818 (17) |
| C5—H5A | 0.9700 | C17—C18 | 1.3847 (18) |
| C5—H5B | 0.9700 | C17—H17 | 0.9300 |
| C6—N1 | 1.4791 (15) | C18—C19 | 1.375 (2) |
| C6—C16 | 1.5117 (16) | C18—H18 | 0.9300 |
| C6—H6 | 0.9800 | C19—O4 | 1.3648 (17) |
| C7—O2 | 1.2211 (17) | C19—C20 | 1.377 (2) |
| C7—N1 | 1.3365 (16) | C20—C21 | 1.378 (2) |
| C7—H7 | 0.9300 | C20—H20 | 0.9300 |
| C8—C9 | 1.3821 (18) | C21—H21 | 0.9300 |
| C8—C13 | 1.3877 (18) | C22—O3 | 1.410 (2) |
| C9—C10 | 1.3831 (19) | C22—H22A | 0.9600 |
| C9—H9 | 0.9300 | C22—H22B | 0.9600 |
| C10—C11 | 1.3734 (19) | C22—H22C | 0.9600 |
| C10—H10 | 0.9300 | C23—O4 | 1.415 (2) |
| C11—O3 | 1.3621 (17) | C23—H23A | 0.9600 |
| C11—C12 | 1.381 (2) | C23—H23B | 0.9600 |
| C12—C13 | 1.372 (2) | C23—H23C | 0.9600 |
| | | | |
| N1—C2—C8 | 111.15 (9) | C3—C14—H14A | 109.5 |
| N1—C2—C3 | 110.11 (10) | C3—C14—H14B | 109.5 |
| C8—C2—C3 | 117.24 (10) | H14A—C14—H14B | 109.5 |
| N1—C2—H2 | 105.8 | C3—C14—H14C | 109.5 |
| C8—C2—H2 | 105.8 | H14A—C14—H14C | 109.5 |
| C3—C2—H2 | 105.8 | H14B—C14—H14C | 109.5 |
| C4—C3—C14 | 111.76 (11) | C3—C15—H15A | 109.5 |

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| C4—C3—C2 | 110.01 (10) | C3—C15—H15B | 109.5 |
| C14—C3—C2 | 110.73 (11) | H15A—C15—H15B | 109.5 |
| C4—C3—C15 | 106.37 (11) | C3—C15—H15C | 109.5 |
| C14—C3—C15 | 108.28 (12) | H15A—C15—H15C | 109.5 |
| C2—C3—C15 | 109.55 (11) | H15B—C15—H15C | 109.5 |
| O1—C4—C5 | 120.22 (12) | C21—C16—C17 | 117.89 (12) |
| O1—C4—C3 | 122.55 (12) | C21—C16—C6 | 120.70 (11) |
| C5—C4—C3 | 117.22 (10) | C17—C16—C6 | 121.41 (11) |
| C4—C5—C6 | 116.02 (11) | C16—C17—C18 | 121.78 (12) |
| C4—C5—H5A | 108.3 | C16—C17—H17 | 119.1 |
| C6—C5—H5A | 108.3 | C18—C17—H17 | 119.1 |
| C4—C5—H5B | 108.3 | C19—C18—C17 | 119.24 (13) |
| C6—C5—H5B | 108.3 | C19—C18—H18 | 120.4 |
| H5A—C5—H5B | 107.4 | C17—C18—H18 | 120.4 |
| N1—C6—C16 | 111.21 (9) | O4—C19—C18 | 124.49 (15) |
| N1—C6—C5 | 110.49 (10) | O4—C19—C20 | 115.74 (14) |
| C16—C6—C5 | 111.18 (10) | C18—C19—C20 | 119.77 (13) |
| N1—C6—H6 | 107.9 | C19—C20—C21 | 120.42 (14) |
| C16—C6—H6 | 107.9 | C19—C20—H20 | 119.8 |
| C5—C6—H6 | 107.9 | C21—C20—H20 | 119.8 |
| O2—C7—N1 | 125.80 (13) | C20—C21—C16 | 120.90 (14) |
| O2—C7—H7 | 117.1 | C20—C21—H21 | 119.6 |
| N1—C7—H7 | 117.1 | C16—C21—H21 | 119.6 |
| C9—C8—C13 | 116.76 (12) | O3—C22—H22A | 109.5 |
| C9—C8—C2 | 125.00 (11) | O3—C22—H22B | 109.5 |
| C13—C8—C2 | 118.23 (12) | H22A—C22—H22B | 109.5 |
| C8—C9—C10 | 122.10 (12) | O3—C22—H22C | 109.5 |
| C8—C9—H9 | 118.9 | H22A—C22—H22C | 109.5 |
| C10—C9—H9 | 118.9 | H22B—C22—H22C | 109.5 |
| C11—C10—C9 | 119.78 (13) | O4—C23—H23A | 109.5 |
| C11—C10—H10 | 120.1 | O4—C23—H23B | 109.5 |
| C9—C10—H10 | 120.1 | H23A—C23—H23B | 109.5 |
| O3—C11—C10 | 124.75 (14) | O4—C23—H23C | 109.5 |
| O3—C11—C12 | 116.01 (12) | H23A—C23—H23C | 109.5 |
| C10—C11—C12 | 119.23 (13) | H23B—C23—H23C | 109.5 |
| C13—C12—C11 | 120.24 (13) | C7—N1—C2 | 119.04 (10) |
| C13—C12—H12 | 119.9 | C7—N1—C6 | 118.42 (10) |
| C11—C12—H12 | 119.9 | C2—N1—C6 | 121.82 (9) |
| C12—C13—C8 | 121.86 (13) | C11—O3—C22 | 117.96 (12) |
| C12—C13—H13 | 119.1 | C19—O4—C23 | 118.02 (14) |
| C8—C13—H13 | 119.1 | | |

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| N1—C2—C3—C4 | 57.08 (13) | C2—C8—C13—C12 | −179.98 (13) |
| C8—C2—C3—C4 | −71.28 (13) | N1—C6—C16—C21 | −120.55 (13) |
| N1—C2—C3—C14 | −178.88 (11) | C5—C6—C16—C21 | 115.87 (14) |
| C8—C2—C3—C14 | 52.76 (15) | N1—C6—C16—C17 | 59.60 (15) |
| N1—C2—C3—C15 | −59.52 (13) | C5—C6—C16—C17 | −63.98 (15) |
| C8—C2—C3—C15 | 172.12 (11) | C21—C16—C17—C18 | −0.8 (2) |

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| C14—C3—C4—O1 | 26.68 (18) | C6—C16—C17—C18 | 179.06 (12) |
| C2—C3—C4—O1 | 150.13 (12) | C16—C17—C18—C19 | 0.5 (2) |
| C15—C3—C4—O1 | −91.31 (15) | C17—C18—C19—O4 | 179.89 (15) |
| C14—C3—C4—C5 | −152.76 (12) | C17—C18—C19—C20 | 0.1 (2) |
| C2—C3—C4—C5 | −29.32 (15) | O4—C19—C20—C21 | 179.76 (17) |
| C15—C3—C4—C5 | 89.25 (13) | C18—C19—C20—C21 | −0.4 (3) |
| O1—C4—C5—C6 | 158.68 (12) | C19—C20—C21—C16 | 0.2 (3) |
| C3—C4—C5—C6 | −21.86 (16) | C17—C16—C21—C20 | 0.4 (2) |
| C4—C5—C6—N1 | 44.33 (14) | C6—C16—C21—C20 | −179.41 (15) |
| C4—C5—C6—C16 | 168.32 (10) | O2—C7—N1—C2 | 5.3 (2) |
| N1—C2—C8—C9 | −96.55 (14) | O2—C7—N1—C6 | 175.84 (12) |
| C3—C2—C8—C9 | 31.31 (17) | C8—C2—N1—C7 | −93.80 (13) |
| N1—C2—C8—C13 | 84.08 (14) | C3—C2—N1—C7 | 134.58 (12) |
| C3—C2—C8—C13 | −148.07 (12) | C8—C2—N1—C6 | 96.04 (12) |
| C13—C8—C9—C10 | −1.2 (2) | C3—C2—N1—C6 | −35.59 (14) |
| C2—C8—C9—C10 | 179.46 (13) | C16—C6—N1—C7 | 51.11 (14) |
| C8—C9—C10—C11 | 0.9 (2) | C5—C6—N1—C7 | 175.08 (11) |
| C9—C10—C11—O3 | 178.92 (14) | C16—C6—N1—C2 | −138.67 (11) |
| C9—C10—C11—C12 | −0.1 (2) | C5—C6—N1—C2 | −14.70 (15) |
| O3—C11—C12—C13 | −179.56 (15) | C10—C11—O3—C22 | −9.8 (2) |
| C10—C11—C12—C13 | −0.5 (2) | C12—C11—O3—C22 | 169.20 (16) |
| C11—C12—C13—C8 | 0.2 (2) | C18—C19—O4—C23 | 2.2 (3) |
| C9—C8—C13—C12 | 0.6 (2) | C20—C19—O4—C23 | −178.04 (18) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C5—H5*A*···O3$^{i}$ | 0.97 | 2.44 | 3.3446 (16) | 155 |
| C6—H6···O2$^{ii}$ | 0.98 | 2.41 | 3.3708 (16) | 168 |
| C18—H18···O1$^{iii}$ | 0.93 | 2.53 | 3.3018 (17) | 140 |
| C10—H10···*Cg*1$^{iv}$ | 0.93 | 2.90 | 3.6627 (17) | 140 |

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