Crystal structure and Hirshfeld surface analysis of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

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A new synthesis of the title compound, C19H21NO2, was developed with good yield and purity using the reaction of 4-hydroxy-3-methyl-2-butanone, benzaldehyde and ammonium acetate in glacial acetic acid as a solvent. The central piperidine ring adopts a chair conformation, and its least-squares basal plane forms dihedral angles of 85.71 (11) and 77.27 (11)° with the terminal aromatic rings. In the crystal, the molecules are linked by O—H···C and C—H···O hydrogen bonds into double ribbons. The Hirshfeld surface analysis shows that the most important contributions are from H···H (68%), C···H/ H···C (19%) and O···H/H···O (12%) interactions.

1. Chemical context

Many piperidine derivatives are found to possess pharmacological activity and are constituents of important drugs. Numerous biological effects including antiviral, antitumor, bactericidal, fungicidal and anti-inflammatory activities have been reported for these compounds (Kappe, 2000; Rameshkumar et al., 2003; Sasitha & John, 2021). In this work, a new protocol for the synthesis of diphenylpiperidin-4-one from 4-hydroxy-3-methyl-2-butanone, benzaldehyde and ammonium acetate under mild reaction conditions was developed. In addition, 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one was characterized by single crystal X-ray diffraction and studied by Hirshfeld surface analysis.

2. Structural commentary

The title compound, C19H21NO2, crystallizes in the space group Pna21 with one molecule in the asymmetric unit of the...
As shown in Fig. 1, it involves two terminal aromatic rings (C1–C6 and C14–C19) and a central piperidinone fragment (N1/C7–C10/C13/O1). The piperidine ring adopts a chair conformation, with the carbonyl O1 and the N-bound H1 atoms being in the equatorial positions. The least-squares basal plane of the piperidine ring (C7, C8, C10, C13) makes dihedral angles of 85.71 (11) and 77.27 (11)°, respectively, with the planes of the C1–C6 and C14–C19 aromatic rings.

3. Supramolecular features

In the crystal, molecules of the title compound are linked by strong O—H···O and weak C—H···O hydrogen bonds (Table 1) into double ribbons stretched along the c-axis direction (Fig. 2). Neighbouring molecules in the ribbon are related by the 2_1 screw axis. Besides this, the molecules are connected by N1—H1···C3 contacts into chains along the b-axis direction, thus layers perpendicular to the a axis are formed. No π–π or C—H···π interactions are present in this structure.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.42, update of May 2021; Groom et al., 2016) revealed several related structures, viz. dimethyl-3-(2-hydroxyethyl)-9-oxo-7-phenylethyl-6,8-diphenyl-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate (BACLUM; Caujolle et al., 1981), dimethyl-2,4-bis(2-methoxyphenyl)-3,7-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (REXNUD; Comba et al., 1997). In these three structures, the piperidine rings adopt a chair conformation, as in the title compound.

5. Hirshfeld surface analysis

The Hirshfeld surface analysis of the title compound was performed using Crystal Explorer 17 (Turner et al., 2017; Spackman & Jayatilaka, 2009). Fig. 3 shows the 3D surface mapped over dnorm over the range 0.5456 (red) to 1.6913 (blue) a.u. The large and small red spots indicate the O—H···O and C—H···O intermolecular interactions. The two-dimensional fingerprint plots, shown in Fig. 4, present all interactions and those delineated into H···H (68%), C···H/H···C (19%) and O···H/H···O (12%) components.
6. Synthesis and crystallization

The title compound was prepared (Fig. 5) according to the procedure reported in the literature for preparation of diphenylpiperidin-4-one (Kim & Tulemisova, 1997). To a mixture of 3.03 g (0.03 mol) of 4-hydroxy-3-methyl-2-butanone and 6.04 g (0.06 mol) of benzaldehyde in glacial acetic acid as a solvent, kept at 293–298 K until the initial keto alcohol disappears as indicated by TLC (1.5 h), 2.3 g (0.03 mol) of ammonium acetate was added. Then the mixture was stirred at the same temperature for 6–7 h. The formed white precipitate was separated and after acidification of the solution with 5% hydrochloric acid to pH 4, the hydrochlorides were converted to bases by neutralization with K₂CO₃ in a strongly basic reaction. After the extraction with diethyl ether of the by-product base (control of the completeness of extraction by TLC), the title compound was extracted with chloroform. After drying the chloroform extracts and distilling off the solvent, a white crystalline compound was obtained (5.95 g, 70%), readily soluble in chloroform, acetone, and hot ethanol (Fig. 5).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound H atom was refined freely. The O-bound H atom was located in a difference-Fourier map and refined with O—H = 0.82 Å, and with $U_{eq}(H) = 1.5U_{eq}(O)$. The C-bound H atoms were positioned geometrically (C—H = 0.93, 0.96, 0.97 and 0.98 Å for sp², hybridized, methyl, methylene and methine C atoms, respectively) and refined using a riding model, with $U_{eq}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(C)$ for methyl and other H atoms, respectively.

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editing of the manuscript) MKG and SK; formal analysis, MKG, SK and ND; crystal-structure determination, MKG, SK and ND; validation, MKG, GBT and ES; project administration, MKG and SK. MKG thanks the Ministry of Education and Science of the Republic of Kazakhstan for financial support as a visiting professor at Atyrau State University.

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Crystal structure and Hirshfeld surface analysis of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

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Computing details

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA (Stoe & Cie, 2002); data reduction: X-RED (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT2017/1 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017/1 (Sheldrick, 2015b); molecular graphics: PLATON (Spek, 2020); software used to prepare material for publication: WinGX (Farrugia, 2012) and publCIF (Westrip, 2010).

3-(Hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

Crystal data

\[ \text{C}_{19}\text{H}_{21}\text{NO}_{2} \]

\[ M_r = 295.37 \]

Orthorhombic, \( Pna_2_1 \)

\( a = 17.3298 \) (8) Å

\( b = 14.1856 \) (7) Å

\( c = 6.5857 \) (3) Å

\( V = 1618.99 \) (13) Å\(^3\)

\( Z = 4 \)

\( F(000) = 632 \)

\( D_a = 1.212 \) Mg m\(^{-3}\)

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 17006 reflections

\( \theta = 1.9–31.5^\circ \)

\( \mu = 0.08 \) mm\(^{-1}\)

\( T = 296 \) K

Prism, colorless

0.72 × 0.57 × 0.33 mm

Data collection

Stoe IPDS 2
diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Detector resolution: 6.67 pixels mm\(^{-1}\)

rotation method scans

Absorption correction: integration

(X-RED32; Stoe & Cie, 2002)

\( T_{\text{min}} = 0.958, T_{\text{max}} = 0.973 \)

17314 measured reflections

4763 independent reflections

3441 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.042 \)

\( \theta_{\text{max}} = 31.2^\circ, \theta_{\text{min}} = 1.9^\circ \)

\( h = -24\rightarrow25 \)

\( k = -20\rightarrow20 \)

\( l = -7\rightarrow9 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R(F^2) = 0.041 \)

\( wR(F^2) = 0.096 \)

\( S = 1.01 \)

4763 reflections

204 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$$w = \frac{1}{\sigma(F_o^2) + (0.0515P)^2}$$  
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta \rho_{\text{max}} = 0.16 \text{ e} \ \text{Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.19 \text{ e} \ \text{Å}^{-3}$

**Absolute structure:** Flack $x$ determined using 1072 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons et al., 2013)

**Absolute structure parameter:** 0.8 (5)

**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 ($\text{Å}^2$)**

| $x$     | $y$     | $z$     | $U_{\text{eq}}$ |
|---------|---------|---------|-----------------|
| O1      | -0.52068 (8) | -0.46901 (9) | -0.4103 (2) | 0.0600 (4) |
| O2      | -0.60074 (9) | -0.40945 (10) | -0.0228 (2) | 0.0610 (4) |
| H2      | -0.565229 | -0.447609 | -0.026638 | 0.091* |
| N1      | -0.58527 (9) | -0.20075 (10) | -0.4826 (2) | 0.0446 (3) |
| C14     | -0.69489 (10) | -0.21260 (11) | -0.2492 (3) | 0.0421 (4) |
| C9      | -0.54765 (10) | -0.39351 (11) | -0.4587 (3) | 0.0417 (4) |
| C13     | -0.61836 (10) | -0.25456 (10) | -0.3131 (3) | 0.0396 (3) |
| H13     | -0.582802 | -0.250220 | -0.197803 | 0.048* |
| C6      | -0.47125 (11) | -0.16339 (12) | -0.6872 (3) | 0.0483 (4) |
| C10     | -0.62508 (9) | -0.36075 (11) | -0.3756 (3) | 0.0388 (3) |
| C11     | -0.64790 (12) | -0.42148 (12) | -0.1929 (3) | 0.0482 (4) |
| H11A    | -0.700646 | -0.406616 | -0.155468 | 0.058* |
| H11B    | -0.646451 | -0.487258 | -0.233009 | 0.058* |
| C7      | -0.50597 (10) | -0.22790 (12) | -0.5292 (3) | 0.0453 (4) |
| H7      | -0.474939 | -0.224784 | -0.404983 | 0.054* |
| C19     | -0.74209 (11) | -0.16475 (13) | -0.3861 (3) | 0.0515 (4) |
| H19     | -0.725854 | -0.156467 | -0.519485 | 0.062* |
| C8      | -0.50769 (11) | -0.32968 (13) | -0.6060 (3) | 0.0484 (4) |
| H8A     | -0.534221 | -0.331932 | -0.735585 | 0.058* |
| H8B     | -0.455272 | -0.351604 | -0.626845 | 0.058* |
| C12     | -0.68510 (11) | -0.37561 (13) | -0.5433 (3) | 0.0508 (4) |
| H12A    | -0.674874 | -0.333097 | -0.653506 | 0.076* |
| H12B    | -0.735741 | -0.363652 | -0.490172 | 0.076* |
| H12C    | -0.682287 | -0.439401 | -0.591446 | 0.076* |
| C15     | -0.72036 (12) | -0.22177 (14) | -0.0520 (3) | 0.0555 (5) |
| H15     | -0.688985 | -0.251458 | 0.043011 | 0.067* |
| C18     | -0.81260 (13) | -0.12956 (14) | -0.3257 (4) | 0.0638 (6) |
| H18     | -0.843205 | -0.097262 | -0.418500 | 0.077* |
| C1      | -0.51207 (14) | -0.13749 (15) | -0.8595 (4) | 0.0630 (5) |
| H1A     | -0.562927 | -0.157131 | -0.875089 | 0.076* |
| C17     | -0.83831 (13) | -0.14174 (16) | -0.1288 (4) | 0.0692 (6) |
| H17     | -0.886403 | -0.119157 | -0.089324 | 0.083* |
| C3      | -0.40316 (15) | -0.05295 (15) | -0.9865 (4) | 0.0730 (7) |
| H3      | -0.379964 | -0.017017 | -1.087645 | 0.088* |
|   | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|---|------|------|------|------|------|------|
|O1 | 0.0654 (9) | 0.0459 (7) | 0.0686 (9) | 0.0199 (6) | 0.0128 (8) | 0.0080 (6) |
|O2 | 0.0811 (10) | 0.0618 (7) | 0.0400 (7) | 0.0271 (7) | −0.0050 (7) | 0.0015 (6) |
|N1 | 0.0489 (8) | 0.0368 (6) | 0.0480 (9) | 0.0024 (6) | 0.0031 (7) | 0.0004 (6) |
|C14| 0.0454 (9) | 0.0369 (7) | 0.0439 (7) | 0.0037 (7) | −0.0020 (8) | −0.0021 (6) |
|C9 | 0.0468 (9) | 0.0383 (7) | 0.0399 (8) | 0.0044 (7) | −0.0039 (7) | −0.0052 (6) |
|C13| 0.0428 (9) | 0.0376 (7) | 0.0383 (8) | 0.0038 (6) | −0.0031 (7) | 0.0005 (7) |
|C6 | 0.0484 (10) | 0.0428 (8) | 0.0537 (11) | −0.0033 (7) | 0.0038 (9) | −0.0028 (8) |
|C10| 0.0424 (8) | 0.0370 (7) | 0.0372 (8) | 0.0030 (6) | −0.0040 (7) | 0.0002 (6) |
|C11| 0.0524 (10) | 0.0425 (8) | 0.0495 (10) | 0.0046 (7) | 0.0047 (9) | 0.0050 (7) |
|C7 | 0.0448 (9) | 0.0468 (8) | 0.0441 (9) | −0.0011 (7) | −0.0013 (8) | −0.0006 (8) |
|C19| 0.0549 (11) | 0.0475 (9) | 0.0521 (10) | 0.0092 (8) | −0.0043 (9) | 0.0034 (8) |
|C8 | 0.0478 (10) | 0.0465 (9) | 0.0509 (10) | 0.0044 (8) | 0.0061 (8) | −0.0008 (8) |
|C12| 0.0536 (11) | 0.0482 (9) | 0.0507 (10) | 0.0017 (8) | −0.0117 (9) | −0.0064 (8) |
|C15| 0.0594 (11) | 0.0600 (10) | 0.0471 (11) | 0.0121 (9) | 0.0023 (9) | 0.0022 (9) |
|C18| 0.0584 (12) | 0.0527 (10) | 0.0803 (16) | 0.0175 (9) | −0.0110 (11) | 0.0034 (11) |
|C1 | 0.0735 (14) | 0.0611 (11) | 0.0544 (12) | −0.0208 (10) | −0.0075 (11) | 0.0033 (10) |
|C17| 0.0518 (12) | 0.0604 (11) | 0.0954 (19) | 0.0141 (10) | 0.0101 (13) | −0.0121 (12) |
|C3 | 0.0806 (16) | 0.0533 (10) | 0.0851 (18) | 0.0009 (10) | 0.0272 (14) | 0.0154 (12) |
|C16| 0.0682 (13) | 0.0748 (13) | 0.0632 (14) | 0.0105 (11) | 0.0176 (12) | −0.0050 (11) |
|C2 | 0.0980 (17) | 0.0631 (12) | 0.0540 (13) | −0.0150 (12) | −0.0030 (12) | 0.0060 (11) |
|C5 | 0.0459 (12) | 0.0746 (14) | 0.0940 (19) | −0.0035 (10) | −0.0049 (12) | 0.0283 (14) |
|C4 | 0.0533 (13) | 0.0824 (16) | 0.119 (3) | −0.0099 (11) | 0.0055 (15) | 0.0365 (17) |

**Geometric parameters (Å, ″)**

|   | O1—C9  | 1.211 (2) | 0.9300 |
|---|--------|-----------|--------|
|O2| 1.397 (2) | C8—H8A | 0.9700 |
|O2—H2 | 0.8200 | C8—H8B | 0.9700 |
|N1—C7 | 1.460 (2) | C12—H12A | 0.9600 |
|N1—C13 | 1.469 (2) | C12—H12B | 0.9600 |
|N1—H1 | 0.90 (3) | C12—H12C | 0.9600 |
|C14—C15 | 1.378 (3) | C15—C16 | 1.385 (3) |
|C14—C19 | 1.394 (3) | C15—H15 | 0.9300 |
|C14—C13 | 1.513 (2) | C18—C17 | 1.382 (4) |
|C9—C8 | 1.497 (3) | C18—H18 | 0.9300 |

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### Supporting Information

| Bond        | Distance (Å) |
|-------------|--------------|
| C9—C10      | 1.522 (2)    |
| C13—C10     | 1.566 (2)    |
| C13—H13     | 0.9800       |
| C6—C5       | 1.378 (3)    |
| C6—C1       | 1.387 (3)    |
| C6—C7       | 1.511 (3)    |
| C10—C12     | 1.532 (3)    |
| C10—C11     | 1.531 (2)    |
| C11—H11A    | 0.9700       |
| C7—C8       | 1.530 (3)    |
| C7—H7       | 0.9800       |
| C19—C18     | 1.379 (3)    |
| C11—O2—H2  | 109.5        |
| C7—N1—C13  | 112.98 (14)  |
| C7—N1—H1   | 113.2 (19)   |
| C13—N1—H1  | 107 (2)      |
| C15—C14—C19| 117.87 (17)  |
| C15—C14—C13| 120.38 (16)  |
| C19—C14—C13| 121.74 (17)  |
| O1—C9—C8   | 121.79 (16)  |
| O1—C9—C10  | 121.04 (16)  |
| C8—C9—C10  | 117.15 (14)  |
| N1—C13—C14 | 110.43 (13)  |
| N1—C13—C10 | 109.24 (13)  |
| C14—C13—C10| 112.72 (13)  |
| N1—C13—H13 | 108.1        |
| C14—C13—H13| 108.1        |
| C10—C13—H13| 108.1        |
| C5—C6—C1   | 117.8 (2)    |
| C5—C6—C7   | 120.78 (19)  |
| C1—C6—C7   | 121.40 (17)  |
| C9—C10—C12 | 107.29 (14)  |
| C9—C10—C11 | 109.78 (14)  |
| C12—C10—C11| 108.28 (15)  |
| C9—C10—C13 | 108.82 (13)  |
| C12—C10—C13| 111.86 (13)  |
| C11—C10—C13| 110.75 (14)  |
| O2—C11—C10 | 114.21 (15)  |
| O2—C11—H11A| 108.7        |
| C10—C11—H11A| 108.7       |
| O2—C11—H11B| 108.7        |
| C10—C11—H11B| 108.7       |
| H11A—C11—H11B| 107.6       |
| N1—C7—C6   | 111.10 (15)  |
| N1—C7—C8   | 107.46 (14)  |
| C6—C7—C8   | 110.59 (16)  |

### Bond Angles (°)

| Angle       | Value          |
|-------------|----------------|
| C9—C8—C7   | 111.45 (15)    |
| C9—C8—H8A  | 109.3          |
| C7—C8—H8A  | 109.3          |
| C9—C8—H8B  | 109.3          |
| C7—C8—H8B  | 109.3          |
| C10—C12—H12B| 109.5         |
| C10—C12—H12C| 109.5         |
| C10—C12—H12A| 109.5         |
| H8A—C8—H8B| 108.0          |
| C14—C13—H13| 119.3          |
| C14—C13—H13| 119.3          |
| C19—C18—C17| 120.7 (2)      |
| C19—C18—H18| 119.6          |
| C14—C15—H15| 119.3          |
| C14—C15—H15| 119.3          |
| C16—C15—H15| 119.3          |
| C5—C6—C7   | 121.80 (17)    |
| C2—C1—C6   | 120.8 (2)      |
| C2—C1—H1A  | 119.6          |
| C6—C1—H1A  | 119.6          |
| C6—C1—H17  | 119.6          |
| C6—C1—H17  | 119.6          |
| C18—C17—H17| 120.5          |
| C18—C17—H17| 120.5          |
| C18—C17—C14| 118.9 (2)      |
| C18—C17—C14| 118.9 (2)      |
| C18—C17—C16| 118.9 (2)      |
| C18—C17—C16| 118.9 (2)      |
| C1—C2—H2A  | 120.2          |
| C1—C2—H2A  | 120.2          |
| C1—C2—H2A  | 120.2          |
| C3—C2—H2A  | 120.1 (3)      |
| C4—C5—C6   | 121.1 (2)      |
| C4—C5—C6   | 121.1 (2)      |
| C4—C5—C6   | 121.1 (2)      |
| C4—C5—C6   | 121.1 (2)      |

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| Bond                  | Angle (°) |
|----------------------|-----------|
| N1—C7—H7            | 109.2     |
| C6—C7—H7            | 109.2     |
| C8—C7—H7            | 109.2     |
| C18—C19—C14         | 120.7 (2) |
| C18—C19—H19         | 119.7     |
| C14—C19—H19         | 119.7     |
| C7—N1—C13—C14       | 170.51 (14)|
| C7—N1—C13—C10       | −64.98 (17) |
| C15—C14—C13—N1      | −152.01 (17) |
| C19—C14—C13—N1      | 28.7 (2) |
| C15—C14—C13—C10     | 85.5 (2) |
| C19—C14—C13—C10     | −93.80 (19) |
| O1—C9—C10—C12       | −102.5 (2) |
| C8—C9—C10—C12       | 75.99 (19) |
| O1—C9—C10—C11       | 15.0 (2) |
| C8—C9—C10—C11       | −166.55 (15) |
| O1—C9—C10—C13       | 136.33 (17) |
| C8—C9—C10—C13       | −45.2 (2) |
| N1—C13—C10—C9       | 50.76 (17) |
| C14—C13—C10—C9      | 173.93 (15) |
| N1—C13—C10—C12      | −67.59 (18) |
| C14—C13—C10—C12     | 55.57 (19) |
| N1—C13—C10—C11      | 171.52 (14) |
| C14—C13—C10—C11     | −65.32 (18) |
| C9—C10—C11—O2       | 67.49 (18) |
| C12—C10—C11—O2      | −175.68 (14) |
| C13—C10—C11—O2      | −52.70 (19) |
| C13—N1—C7—C6        | −173.39 (15) |
| C13—N1—C7—C8        | 65.51 (18) |
| C5—C6—C7—N1         | 137.2 (2) |

**Hydrogen-bond geometry (Å, °)**

| D—H···A   | D—H  | H···A  | D···A   | D—H···A |
|-----------|------|-------|--------|---------|
| O2—H2···O1<sup>i</sup> | 0.82 | 2.05  | 2.8194 (18) | 156 |
| C8—H8A···O2<sup>ii</sup> | 0.97 | 2.47  | 3.379 (3)   | 155 |
| N1—H1···C3<sup>iii</sup> | 0.90 (3) | 2.75 (3) | 3.605 (2)   | 161 (3) |

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