Crystal structure and Hirshfeld surface analysis of 3-benzoyl-6-(1,3-dioxo-1-phenylbutan-2-yl)-2-hydroxy-2-methyl-4-phenylcyclohexane-1,1-dicarbonitrile

Farid N. Naghiyev, Victor N. Khrustalev, Ekaterina V. Dobrokhotova, Mehmet Akkurt, Ali N. Khalilov, Ajaya Bhattarai and Ibrahim G. Mamedov

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The central cyclohexane ring of the title compound, C₃₂H₂₈N₂O₄, adopts a chair conformation, with puckering parameters Qₐ = 0.618 (2) Å, θ = 176.72 (19)° and ϕ = 290 (3)°. In the crystal, molecules are linked by O—H···O, C—H···O and C—H···N hydrogen bonds, forming layers parallel to (100). These layers are linked by weak C—H···π interactions and van der Waals forces. A Hirshfeld surface analysis indicates that the contributions from the most prevalent interactions are H···H (41.2% contribution), C···H/H···C (20.3%), O···H/ H···O (17.8%) and N···H/H···N (10.6%).

1. Chemical context

Functionalized derivatives of carbo- and heterocyclic compounds are of great interest in the fields of organic synthesis, catalysis, materials science and medicinal chemistry (Zubkov et al., 2018; Shikhaliyev et al., 2019; Viswanathan et al., 2019; Gurbanov et al., 2020; Khalilov et al., 2021). In particular, β-dicarbonyl compounds are important chemical substrates for the construction of various classes of organic compounds (Kaur et al., 2021).

To the best of our knowledge, the interaction of β-dicarbonyl compounds with phenyl-allylidene-malononitriles leads to the formation of xanthene, benzo[b]pyran and pyridine derivatives (Bardasov et al., 2014; Amoozadeh et al., 2018). Interestingly, we discovered that in case of the reaction of one equivalent of phenyl-allylidene-malononitrile with two
equivalents of benzoylacetone at room temperature, a substituted cyclohexane derivative was the product. In the context of ongoing structural studies (Safavora et al., 2019; Aliyeva et al., 2011; Mamedov et al., 2022), we report here the crystal structure and Hirshfeld surface analysis of the title compound, 3-benzoyl-6-(1,3-dioxo-1-phenylbutan-2-yl)-2-hydroxy-2-methyl-4-phenylcyclohexane-1,1-dicarbonitrile.

2. Structural commentary

In the title compound (Fig. 1), the central cyclohexane ring (A: atoms C1–C6) adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) $Q_T = 0.618 (2)$ Å, $\theta = 176.72 (19)^\circ$ and $\phi = 290 (3)^\circ$. The phenyl (B: C11–C16; C: C21–C26; D: C27–C32) rings make dihedral angles of 78.23 (10), 83.20 (11) and 82.89 (10)$^\circ$, respectively, with the mean plane of the central cyclohexane ring. The dihedral angles between the phenyl rings are $B/C = 21.88 (10)^\circ$, $B/D = 21.88 (19)^\circ$ and $C/D = 73.64 (10)^\circ$. The C1–C7–C10–C11, C1–C7–C10–O2, C1–C7–C8–C9 and C1–C7–C8–O1 torsion angles are $-157.13 (16)$, $27.9 (2)$, $-73.6 (2)$ and $106.7 (2)^\circ$. The phenyl, benzoyl, hydroxy, cyano C2–C17$\equiv$N1 and 1,3-dioxo-1-phenylbutan-2-yl substituents all occupy equatorial sites, so that the cyano C2–C18$\equiv$N2 substituent necessarily occupies an axial site. There are five stereogenic centres and the chirality about the C1, C3, C4, C5 and C7 atoms are S, R, R, S and R, respectively. The values of the geometric parameters of the title compound are normal and compatible with those of related compounds compiled in the Database survey section (§S).

3. Supramolecular features

In the crystal, O–H···O hydrogen bonds of medium strength, and weaker C–H···O and C–H···N interactions link adjacent molecules, forming layers extending parallel to (100) (Table 1 and Figs. 2–4). These layers are connected by weak C–H·π interactions and van der Waals interactions (Table 1 and Fig. 5).
Various interatomic contacts are compiled in Table 2. Hydrogen bonding plays major roles in the crystal packing. Interactions suggest that van der Waals interactions and (10.6%) contacts are illustrated in Figs. 7. The other minor contributions to the Hirshfeld surface are (0.8%) and those delineated into H (0.8%) and O (17.8%) and N (1.0%) contributions. C (0.9%) O–H/H–O (17.8%) and N–H/H–N (10.6%) contacts are illustrated in Figs. 7(b)–(e), respectively. The other minor contributions to the Hirshfeld surface are from N–H/C–N (1.0%), C–C (0.9%), O–N/N–O (0.8%) and O–C/C–O (0.8%) contacts. The large number of H–N, C–H/H–C, O–H/H–O and N–H/H–N interactions suggest that van der Waals interactions and hydrogen bonding play major roles in the crystal packing. Various interatomic contacts are compiled in Table 2.

### 4. Hirshfeld surface analysis

A Hirshfeld surface for the title compound and its associated two-dimensional fingerprint plots were analyzed and calculated using *CrystalExplorer* (Version 17.5; Turner et al., 2017). Hirshfeld surfaces allow for the display of intermolecular interactions by using distinct colors and intensities to indicate short and long contacts, as well as the relative strengths of the interactions. The three-dimensional (3D) Hirshfeld surface of the title compound plotted over dnorm in the range from −0.5877 to +1.7202 a.u. is shown in Fig. 6. As discussed above, the O3–H3⋅⋅⋅O1 interactions play a key role in the molecular packing of the title compound.

The overall two-dimensional (2D) fingerprint plot [Fig. 7(a)] and those delineated into H⋅⋅⋅H (41.2% contribution), C⋅⋅⋅H/H⋅⋅⋅C (20.3%), O⋅⋅⋅H/H–O (17.8%) and N⋅⋅⋅H/H–N (10.6%) contacts are illustrated in Figs. 7(b)–(e), respectively. The other minor contributions to the Hirshfeld surface are from N–C/C–N (1.0%), C–C (0.9%), O–N/N–O (0.8%) and O–C/C–O (0.8%) contacts. The large number of H–N, C–H/H–C, O–H/H–O and N–H/H–N interactions suggest that van der Waals interactions and hydrogen bonding play major roles in the crystal packing. Various interatomic contacts are compiled in Table 2.

### 5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom et al., 2016) for the 2-hydroxy-2-methylecyclohexane-1,1-dicarbonitrile moiety revealed five structures closely related to the title compound: 3-cyano-4-hydroxy-2-(4-methylphenyl)-6-oxo-N-phenyl-4-(thiophen-2-yl)cyclohexane-1-carboxamide hydrate (CSD refcode UPOMOE; Naghiyev et al., 2021), 2RS,3SR,4RS,6SR-3-benzoyl-4-hydroxy-2,4,6-triphenylcyclohexane-1,1-dicarbonitrile (MEHMOCO1; Rodríguez et al., 2008), 3-(4-fluorobenzoyl)-4-(4-fluorophenyl)-4-hydroxy-2,6-diphenylcyclohexane-1,1-dicarbonitrile (SODHAW; Narayana et al., 2014), 5-cyano-2-hydroxy-2-methyl-N-phenyl-4-(pyridin-4-yl)-6-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (JUPHUA; Naghiyev et al., 2020) and 5-cyano-2-hydroxy-2-methyl-6-oxo-N-phenyl-4-(thiophen-2-yl)piperi-

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**Table 1**

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<th>Distance (Å)</th>
<th>Symmetry operation</th>
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<tr>
<td>H9A⋅⋅⋅H6A</td>
<td>2.39</td>
<td>1 − x, 1 − y, − z</td>
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<tr>
<td>O4⋅⋅⋅H15</td>
<td>2.73</td>
<td>−1 + x, y, z</td>
</tr>
<tr>
<td>H19B⋅⋅⋅N1</td>
<td>2.77</td>
<td>1 − x, 1 − y, 1 − z</td>
</tr>
<tr>
<td>H26⋅⋅⋅H31</td>
<td>2.57</td>
<td>−x, 1/2 + y, −1 + z</td>
</tr>
<tr>
<td>C25⋅⋅⋅C24</td>
<td>3.367</td>
<td>−x, −y, 1 − z</td>
</tr>
<tr>
<td>H29⋅⋅⋅H23</td>
<td>2.41</td>
<td>x, −1/2 + y, −1 + z</td>
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<tr>
<td>H13⋅⋅⋅H15</td>
<td>2.36</td>
<td>2 − x, 1/2 + y, 1/2 − z</td>
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**Table 2**

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<tr>
<td>H13⋅⋅⋅H15</td>
<td>2.36</td>
<td>2 − x, 1/2 + y, 1/2 − z</td>
</tr>
</tbody>
</table>

**Symmetry codes:** (i) −x + 1, y − 1/2, −z + 1/2 (ii) −x + 1, y + 1/2, −z + 1/2 (iii) x + 1, y, z.
dine-3-carboxamide methanol solvate (JUPJOW; Naghiyev et al., 2020).

In the crystal of UPOMOE, the central cyclohexane ring adopts a chair conformation. Molecules are linked by N—H⋯O, C—H⋯O and C—H⋯N hydrogen bonds, forming layers parallel to (100), which interact via the van der Waals forces between them.

In the crystal of MEHMOC01, the molecules are linked into complex sheets by two C—H⋯O hydrogen bonds and three C—H⋯N hydrogen bonds.

In the crystal of SODHAW, molecules are linked via pairs of O—H⋯N hydrogen bonds, forming inversion dimers. The dimers are linked via C—H⋯N and C—H⋯O hydrogen bonds, forming chains parallel to [001]. C—H⋯F hydrogen bonds link the chains into sheets lying parallel to (100).

In JUPHUA, the crystal structure is stabilized by an extensive hydrogen-bonding network defined by N—H⋯N, O—H⋯N and C—H⋯O interactions with graph-set motifs C(9), C(8), C₂(32) and R₂(8), with base vectors [100], [011] and [110] for the 3D network. In JUPJOW, the crystal structure is also stabilized by an extensive hydrogen-bonding network of N—H⋯O, O—H⋯O and O—H⋯N interactions, where the methanol molecule participate with neighbouring molecules with graph-set motifs C(4), C₂(10), C₂(28), R₂(8) and R₂(36), with base vectors [010], [100] and [001] for the 3D network. For JUPHUA and JUPJOW, another non-covalent weak interaction is also observed, specifically a chalcogen⋯π interaction (ca 3.6 Å) in JUPHUA between the thiophenyl sulfur fragment and the phenyl ring and a hydrogen⋯π interaction (ca 3.2 Å) in JUPJOW between the methyl group on the piperidone ring and the phenyl ring.

6. Synthesis and crystallization

To a solution of 2-(3-phenylallylidene)malononitrile (0.92 g, 5 mmol) and benzoylacetone (1.68 g, 10 mmol) in benzene (25 ml), 3–4 drops of 1-methylpiperazine were added and the mixture was stirred for 10 min and kept at room temperature.
for 72 h. Benzene (15 ml) was then removed from the reaction mixture by distillation, which was left overnight. The crystals which formed were separated by filtration and recrystallized from an ethanol–water (1:1 v/v) solution (yield 41%; m.p. 514–515 K).

\(^1\)H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm): 6 1.74 (s, 3H, CH<sub>3</sub>), 2.01 (t, 2H, CH<sub>2</sub>), 2.12 (s, 3H, COCH<sub>3</sub>), 3.47 (d, 1H, CH), 3.52 (s, 1H, OH), 4.08 (m, 1H, 4H), 4.62 (d, 1H, CH), 4.86 (d, 1H, CH), 7.12–7.78 (m, 15H, 15Ar-H). \(^{13}\)C NMR (75 MHz, DMSO-d<sub>6</sub>, ppm): 6 24.28 (CH<sub>3</sub>), 30.36 (COCH<sub>3</sub>), 34.42 (CH<sub>2</sub>), 39.41 (CH), 45.49 (CH), 56.46 (C<sub>tert</sub>), 57.01 (CH), 60.85 (CH), 81.92 (O—C<sub>tert</sub>), 111.37 (CN), 111.81 (CN), 125.94 (CH<sub>arom</sub>), 127.22 (2CH<sub>arom</sub>), 127.86 (2CH<sub>arom</sub>), 128.90 (2CH<sub>arom</sub>), 128.98 (2CH<sub>arom</sub>), 129.31 (2CH<sub>arom</sub>), 130.35 (2CH<sub>arom</sub>), 132.52 (CH<sub>arom</sub>), 133.85 (CH<sub>arom</sub>), 135.44 (C<sub>arom</sub>), 138.49 (C<sub>arom</sub>), 141.22 (C<sub>arom</sub>), 194.97 (C—CO), 195.93 (C—CO), 200.21 (C—CO).

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Due to large differences between calculated and observed intensities, about 40 reflections were omitted from the refinement. The H atom of the OH group was located in a difference map and its positional parameters were allowed to refine freely [O3—H3 = 0.93 (3) Å], with \(U_{eq}(H) = 1.5 U_{eq}(O)\). All H atoms bound to C atoms were positioned geometrically and refined as riding, with C—H = 0.95 (aromatic), 0.99 (methylene), 1.00 (methine) and 0.98 Å (methyl), with \(U_{eq}(H) = 1.5 U_{eq}(C)\) for methyl H atoms and 1.2\(U_{eq}(C)\) for the others.

Acknowledgements

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Funding information

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Crystal structure and Hirshfeld surface analysis of 3-benzoyl-6-(1,3-dioxo-1-phenylbutan-2-yl)-2-hydroxy-2-methyl-4-phenylcyclohexane-1,1-dicarbonitrile

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Computing details

Data collection: CrystAlis PRO (Rigaku OD, 2021); cell refinement: CrystAlis PRO (Rigaku OD, 2021); data reduction: CrystAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

3-Benzoyl-6-(1,3-dioxo-1-phenylbutan-2-yl)-2-hydroxy-2-methyl-4-phenylcyclohexane-1,1-dicarbonitrile

Crystal data

C32H28N2O4
Mr = 504.56
Monoclinic, P21/c
a = 13.9798 (3) Å
b = 11.8411 (2) Å
c = 15.7406 (3) Å
β = 91.901 (2)°
V = 2604.21 (9) Å3
Z = 4
F(000) = 1064
Dx = 1.287 Mg m−3
Cu Kα radiation, λ = 1.54184 Å
Cell parameters from 52541 reflections
θ = 3.1–79.4°
µ = 0.69 mm−1
T = 100 K
Prism, colourless
0.09 × 0.06 × 0.06 mm

Data collection

Rigaku XtaLAB Synergy Dualflex HyPix
diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan
(CrysAlis PRO; Rigaku OD, 2021)
Tmin = 0.933, Tmax = 0.949
77914 measured reflections
5618 independent reflections
5497 reflections with I > 2σ(I)
Rint = 0.110
θmax = 80.3°, θmin = 4.7°
h = −17→17
k = −14→12
l = −20→20

Refinement

Refinement on F2
Least-squares matrix: full
R[F2 > 2σ(F2)] = 0.074
wR(F2) = 0.187
S = 1.11
5618 reflections
348 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
supporting information

\[ w = 1/\sigma^2(F_o^2) + (0.0869P)^2 + 2.2708P \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

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

\( \Delta \rho_{\text{max}} = 0.54 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.33 \text{ e Å}^{-3} \)

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)

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## Atomic displacement parameters (Å²)

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supporting information
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C8—C7—C10—C11  83.3 (2)  C8—C7—C10—C11  127 (3)
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Hydrogen-bond geometry (Å, º)

$C_g 4$ is a centroid of the C27–C32 phenyl ring.

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</tbody>
</table>

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

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