2-Benzyl-1,3-diphenylpropane-1,3-dione

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Key indicators

- Single-crystal X-ray study
- \( T = 298 \) K
- Mean \( \sigma(C-C) = 0.003 \) Å
- \( R \) factor = 0.051
- \( wR \) factor = 0.152
- Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of 2-benzyl-1,3-diphenylpropane-1,3-dione, \( \text{C}_{22}\text{H}_{18}\text{O}_{2} \), being a diketo tautomer, shows different stereochemistry from that of the closed-ring cis-ketoenol tautomer of the parent 1,3-diphenylpropane-1,3-dione. The molecular packing involves \( \text{C—H} \cdot \cdot \cdot \text{O} \) and \( \pi—\pi \) stacking interactions.

Comment

Insertion of a sterically demanding substituent into the \( \alpha \)-position of a \( \beta \)-diketone molecule affects its ligating properties and the keto–enol equilibrium. As part of a study of the effects of benzyl substitution on the structures of \( \beta \)-diketones, we have synthesized an \( \alpha \)-substituted derivative of 1,3-diphenylpropane-1,3-dione, \( \text{Hdbm} \). The title compound, 2-benzyl-1,3-diphenylpropane-1,3-dione, \( \alpha(\text{Bzl})\text{Hdbm} \; \text{(I)} \), is a potential bidentate monoanionic and neutral ligand for coordination to transition metal ions.

The asymmetric unit of (I) contains a single molecule which is located in a general position (Fig. 1) and which is best described as a distorted \( \text{Ucis-diketo,Z,Z} \) conformer (Emsley, 1984). Distortion of the molecule with respect to the ideal \( \text{U} \)-conformation involving atoms \( \text{O1, C1, C2, C3 and O2} \) is best described in terms of torsion angles involving sets of atoms \( \text{O1/C1/C2/C3 and O2/C3/C2/C1} \). The angles are \( -90.42 (18) \) and \( 25.69 (23) \)°, respectively. Such a conformation of the molecule is dictated by steric hindrance related to the presence of the large benzyl group, which prevents the molecule from adopting the closed-ring conformation characteristic for the \( \text{cis-ketoenol tautomer} \).

The bond angles about atom C2, to which two benzoyl and one benzyl groups are bonded, do not show any significant deviations from those expected for an \( sp^3 \)-hybridized C atom. A larger discrepancy from the standard tetrahedral value is observed in the angle \( \text{C2—C4—C5} \) [114.7 (2)°] and may be explained by steric effects. Notably, similar deviations were observed in the analogous compound 3,3-dibenzylpentane-2,4-dione, \( \alpha(\text{Bzl,Bzl})\text{acac} \) (Judasˇ & Kaitner, 1995).
The planes defined by the terminal phenyl rings (C11–C16 and C17–C22) are twisted with respect to the planes defined by neighbouring carbonyl groups and the C/C atom (O1/C1/C2 and O2/C3/C2) by 19.56 (17) and 26.97 (8), respectively. Such values are larger than those observed in any known polymorph of the parent compound 1,3-diphenylpropane-1,3-dione (Hdbm) (Williams, 1966; Hollander et al., 1973; Kaitner & Meštrović, 1993).

The molecules of (I) are connected by C—H· · ·O interactions (Table 1). Four such contacts, specifically C10—H10· · ·O2i, C2—H2· · ·O2i, C22—H22· · ·O2i and C21—H21· · ·O1i, cooperatively link the molecules into chains (Fig. 2; symmetry code as in Table 1). These chains of molecules are further linked into sheets by way of two distinct sets of C—H· · ·O interactions (Fig. 3). The sheets are interlinked by additional C—H· · ·O interactions and are presumably stabilized by π–π stacking interactions between the terminal phenyl rings at a distance of 3.55 Å.

Experimental

The title compound was synthesized from 1,3-diphenylpropane-1,3-dione and benzyl bromide via the method of Kalyanam et al. (1979). The resulting crude product was recrystallized twice from hot ethanol. Thermal analysis (thermogravimetric analysis and differential scanning calorimetry) of the pure product were carried out using Mettler thermal analysis modules. The calorimetric thermogram exhibited two endothermic signals. The first signal is the sharper and stronger of the two and corresponds to the melting. The onset temperature of the first signal is \( T_\text{f} = 373 \) K with enthalpy of fusion \( \Delta H_\text{fus} = 35.6 \text{ kJ mol}^{-1} \). The second signal, related to boiling, has an onset temperature of \( T_\text{b} = 583 \) K. No degradation of the sample during melting and boiling processes was detectable by thermal analysis methods. Single crystals of (I) suitable for the diffraction experiment were obtained by slow evaporation of a solution of the compound in acetic acid.

Crystal data

\[
C_{22}H_{18}O_2 \\
M_r = 314.36 \\
\text{Monoclinic, } P2_1/n \\
a = 10.2935 (6) \text{ Å} \\
b = 10.9060 (6) \text{ Å} \\
c = 15.4090 (7) \text{ Å} \\
\beta = 98.562 (4) \\
V = 1710.55 (16) \text{ Å}^3 \\
Z = 4
\]

\[
D_r = 1.221 \text{ Mg m}^{-3} \\
\text{Mo } K\alpha \text{ radiation} \\
\text{Cell parameters from 44} \\
\text{reflections} \\
\theta = 10.0–16.6^\circ \\
\mu = 0.08 \text{ mm}^{-1} \\
T = 298 (1) \text{ K} \\
\text{Prism, colourless} \\
Z = 4 \\
\theta_{\text{max}} = 27.0^\circ \\
k = -13 \rightarrow 13 \\
l = 0 \rightarrow 19 \\
3 \text{ standard reflections} \\
frequency: 60 \text{ mm}^{-1} \\
\text{intensity decay: 2.8%}
\]

Refinement

Refinement on \( F^2 \)

\[
R(I^2 > 2\sigma(I^2)) = 0.051 \\
wR(I^2) = 0.152 \\
S = 1.03 \\
3733 \text{ reflections} \\
217 \text{ parameters} \\
H-\text{atom parameters constrained}
\]

\[
w = 1/[\sigma^2(I^2) + (0.079P)^2 + 0.4371P] \\
\text{where } P = (F^2 + 2F_c^2)/3 \\
(\Delta \sigma)_{\text{max}} < 0.001 \\
\Delta \rho_{\text{max}} = 0.26 \text{ e Å}^{-3} \\
\Delta \rho_{\text{min}} = -0.17 \text{ e Å}^{-3}
\]


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C_{22}H_{18}O_2
Table 1
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10—H10···O2i</td>
<td>0.93</td>
<td>2.63</td>
<td>3.498 (2)</td>
<td>155</td>
</tr>
<tr>
<td>C2—H2···O2i</td>
<td>0.98</td>
<td>2.60</td>
<td>3.576 (2)</td>
<td>173</td>
</tr>
<tr>
<td>C22—H22···O2i</td>
<td>0.93</td>
<td>2.58</td>
<td>3.513 (2)</td>
<td>177</td>
</tr>
<tr>
<td>C21—H21···O1i</td>
<td>0.93</td>
<td>2.74</td>
<td>3.491 (3)</td>
<td>139</td>
</tr>
<tr>
<td>C6—H6···O1i</td>
<td>0.93</td>
<td>2.72</td>
<td>3.401 (2)</td>
<td>131</td>
</tr>
</tbody>
</table>

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

The positions of all H atoms were calculated, with C—H distances of 0.93 for phenyl, 0.97 for methylene and 0.98 Å for methine H atoms. The H atoms were included in the refinement using the riding-model approximation, with Uiso(H) = 1.2Ueq(C).

Data collection: STADI4 (Stoe & Cie, 1995); cell refinement: STADI4; data reduction: X-RED (Stoe & Cie, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997), MERCURY (Version 1.2.1; Bruno et al., 2002), RasTop (Valadon, 2004) and POV-Ray (Version 3.6; Persistence of Vision, 2004); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References