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

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The molecule of 2-benzyl-1,3-diphenylpropane-1,3-dione, $C_{22}H_{18}O_2$, 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 C—H$\cdots$O and π–π stacking interactions.

Comment

Insertion of a sterically demanding substituent into the α-position of a β-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 β-diketones, we have synthesized an α-substituted derivative of 1,3-diphenyl-propane-1,3-dione, Hdbm. The title compound, 2-benzyl-1,3-diphenylpropane-1,3-dione, α(Bzl)Hdbm, (I), is a potential bidentate monoanionic and neutral ligand for coordination to transition metal ions.

(I)
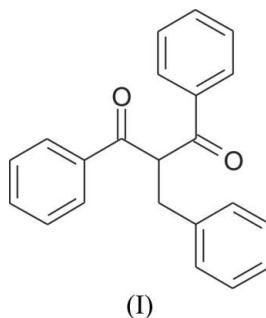
The asymmetric unit of (I) contains a single molecule which is located in a general position (Fig. 1) and which is best described as a distorted *U*;*cis*-diketo;*Z*,*Z* conformer (Emsley, 1984). Distortion of the molecule with respect to the ideal *U*-conformation involving atoms O1, C1, C2, C3 and O2 is best described in terms of torsion angles involving sets of atoms 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 *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 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, α(Bzl,Bzl)acac (Judaš & Kaitner, 1995).
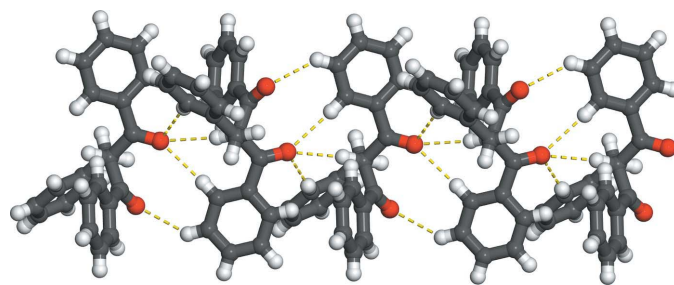
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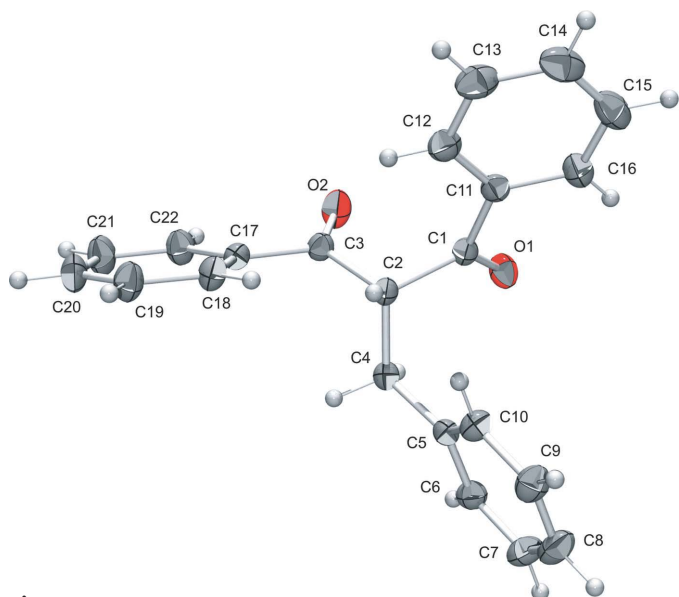
Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Figure 2
Ball-and-stick model representation showing the cooperative linking of the α(Bzl)Hdbm molecules of (I) into chains. C—H$\cdots$O interactions are shown as dashed lines.

Figure 3
Ball-and-stick model representation showing the linking of the chains into sheets *via* C—H$\cdots$O interactions (dashed lines).

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_α 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).
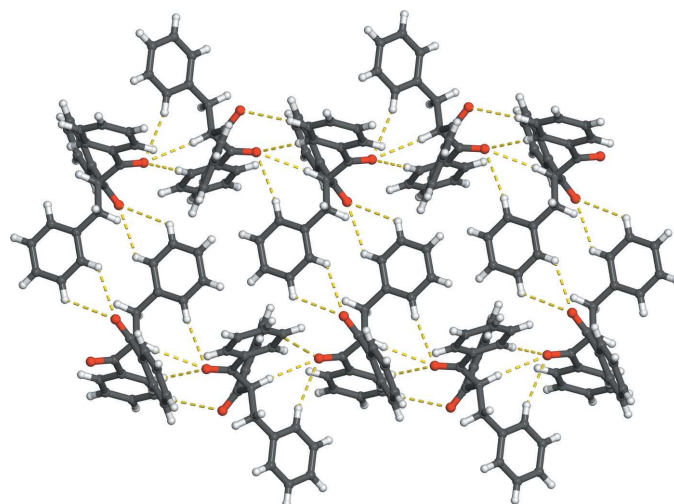
The molecules of (I) are connected by C—H$\cdots$O interactions (Table 1). Four such contacts, specifically C10—H10$\cdots$O2^i, C2—H2$\cdots$O2^i, C22—H22$\cdots$O2^i and C21—H21$\cdots$O1^i, cooperatively link the molecules into chains (Fig. 2; symmetry code as in Table 1). These chains of molecules are further linked into sheets by way of two distinct sets of C—H$\cdots$O interactions (Fig. 3). The sheets are interlinked by additional C—H$\cdots$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 $T_f = 373$ K with enthalpy of fusion $\Delta H_{fus} = 35.6$ kJ mol^{-1}. The second signal, related to boiling, has an onset temperature of $T_b = 583$ 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

$C_{22}H_{18}O_2$	$D_x = 1.221$ Mg m^{-3}
$M_r = 314.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 44
$a = 10.2935$ (6) Å	reflections
$b = 10.9060$ (6) Å	$\theta = 10.0$–16.6°
$c = 15.4090$ (7) Å	$\mu = 0.08$ mm^{-1}
$\beta = 98.562$ (4)°	$T = 298$ (1) K
$V = 1710.55$ (16) Å^3	Prism, colourless
$Z = 4$	$0.91 \times 0.80 \times 0.60$ mm

Data collection

Philips PW1100 diffractometer	$\theta_{max} = 27.0°$
ω scans	$h = -13 \rightarrow 13$
Absorption correction: none	$k = 0 \rightarrow 13$
3866 measured reflections	$l = 0 \rightarrow 19$
3733 independent reflections	3 standard reflections
2731 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.065$	intensity decay: 2.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.079P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.4571P]$
$wR(F^2) = 0.152$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3733 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
H-atom parameters constrained	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10$\cdots$O2^{i}	0.93	2.63	3.498 (2)	155
C2—H2$\cdots$O2^{i}	0.98	2.60	3.576 (2)	173
C22—H22$\cdots$O2^{i}	0.93	2.58	3.513 (2)	177
C21—H21$\cdots$O1^{i}	0.93	2.74	3.491 (3)	139
C6—H6$\cdots$O1^{ii}	0.93	2.72	3.401 (2)	131

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (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 $U_{iso}(H) = 1.2U_{eq}(C)$.

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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