

A Structural Study of the β,β' -Triketone 3-Benzoyl-6-phenylhex-5-ene-2,4-dione

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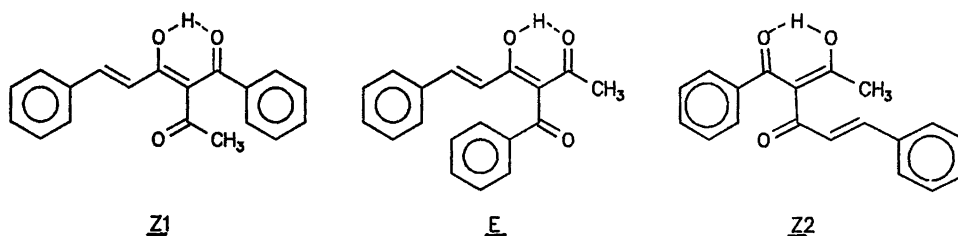
The crystal and molecular structure of 3-benzoyl-6-phenylhex-5-ene-2,4-dione has been determined at 121 K by X-ray crystallographic methods using 2782 reflections measured by counter methods. The crystals are monoclinic, space group $P2_1/n$ (No. 14). The structure was refined to a conventional R -factor of 0.046. The enol ring is clearly asymmetric, and the enol hydrogen is bonded to the oxygen atom next to the olefinic double bond. The molecular conformation and the intermolecular interactions are discussed.

In contrast with the well known β,β' -triketones, where two carbonyl groups take part in a cyclic system, their open chain analogues, the so-called triacylmethanes, have hardly been structurally characterised.¹ However, such compounds are repeatedly studied on account of their tautomeric capability in non-polar solvents.²

The structural investigation of the title compound was initiated for several reasons: first, because of the possibility for three different conformations, which all may establish a pseudoaromatic enol group stabilised by a strong $-\text{OH}-\text{O}=\text{C}$ hydrogen bond as illustrated in Scheme 1, it was of interest to study the preferred conformation of the molecule in the crystal phase. Secondly, it was of interest to study the enol ring geometry in relation to the rest of the molecule, i.e., finding the position of the hydrogen atom. Finally, because the enol group does not, in general, take part in intermolecular hydrogen bonding, it was of interest to study the weak intermolecular interactions between such pseudoaromatic groups as well as between ordinary aromatic moieties.

Experimental

The title compound is new and was prepared by C -acylation of benzoylacetone with cinnamoyl chloride following the general synthesis of α -acyl acetoacetic esters.³ It was isolated in 68% yield. Recrystallization from methanol gave pale yellow plate-shaped crystals with a melting point of 73–74 °C. The diffraction experiment was conducted using a crystal of dimensions: 0.8 × 0.4 × 0.3 mm and a collimator with a diameter of 1.2 mm. The unit cell dimensions were determined from 25 reflections in the 2Θ range 20–30°. The stability of the intensity measurements throughout the data collection was monitored by three test reflections after every hundred measurements. No systematic variation was observed and the test reflections were not used for correction of the data. The crystal structure was solved using the program system MITHRIL and refined by Fourier and least-squares calculations, whereby the positions of all atoms, including the hydrogen atoms, were determined. The refinement



Scheme 1.

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ended with a final conventional R -factor of 0.046 ($R_w = 0.044$). The experimental conditions and results are summarised in Table 1, the atomic coordinates are

Table 1. Crystal data and the experimental conditions.

Compound	3-benzoyl-6-phenylhex-5-ene-2,4-dione
Melting point/K	346–347
Formula	$C_{19}H_{16}O_3$
Crystal system	Monoclinic
$a/\text{\AA}$	5.627(1)
$b/\text{\AA}$	34.136(7)
$c/\text{\AA}$	7.999(1)
$\beta/^\circ$	104.01(1)
Cell volume/ \AA^3	1490.9
Experimental temp./K	121
Space group	$P2_1/n$ (No. 14)
Molecular weight/Da	292.33
No. of molecules per cell (Z)	4
Wavelength/ \AA	0.71069 Mo-K α
Density/ g cm^{-3}	1.31
Crystal dimensions/mm	$0.8 \times 0.4 \times 0.3$
Diffractometer	Nicolet
Scan mode	ω
Scan speed/ $^\circ \text{min}^{-1}$	3.0
Scan range/ $^\circ$	0.8
Background count time	0.7
2θ range	4.0–60.0
No. of independent meas.	4480
No. observed [$i > 3.0\sigma(i)$]	2782
Test reflections	3
COR	0.02
Corr. for var. in test refl.	None
Corr. for absorption	None
Corr. for sec. ext.	None
Method of structure det.	MITHRIL
Method of refinement	Fourier/LSR
$R = \sum F_o - F_c / \sum F_o $	0.046
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	0.044
$S = [\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$	2.12

given in Table 2, and the bond lengths and angles in Table 3.

Discussion

The molecular structure, the atomic numbering and some of the bond lengths are given in Fig. 1. The molecule exists in a conformation where the 6-phenylhex-5-ene-2,4-dione moiety is almost planar, and the bond lengths indicate the conjugated character of the C1–O3 chain. However, the dihedral angles along the chain (C2–C1–C7–C8: -2.7° , C1–C7–C8–C9: -177.6° , C7–C8–C9–C10: 175° , C8–C9–C10–C18: -2.4° , C9–C10–C18–O3: 7.1° and C9–C10–C18–C19: -174.7°) give the molecule a slight left-hand twist when projected along the hexene chain.

The plane of phenyl ring I (C1–C6) makes an angle of 7° with the plane of the enol ring and 68° with the plane of phenyl ring II. The latter makes an angle of 73° with the enol ring plane. The shortest intramolecular distance between rings I and II is found between HC2 and C13: $3.34(2) \text{\AA}$.

The atoms in the enol ring deviate less than 0.004\AA from the mean plane defined by the five non-hydrogen atoms. The distance between the oxygen atoms in the enol ring is 2.445\AA and the geometry of the enol ring clearly supports the position of the hydrogen atom and its bonding to the O1 oxygen atom, as found in the difference maps. The bond length O1–H was found to be $1.04(3) \text{\AA}$.

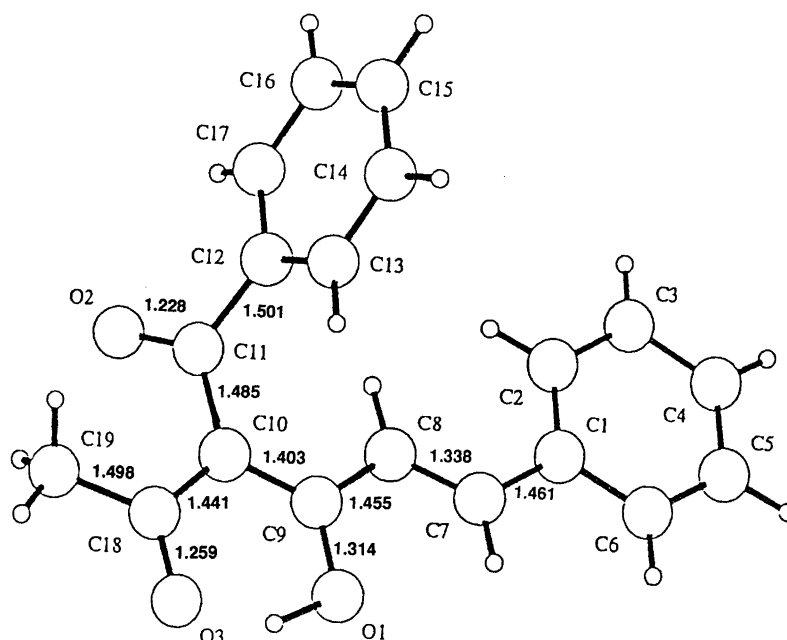


Fig. 1. Molecular structure with numbering of the atoms.

Table 2. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for all atoms.

Atom	x	y	z	U_{eq}^a
O1	1.2618(2)	0.0628(0)	0.2855(2)	0.035
O2	1.0120(2)	0.1754(0)	0.5125(2)	0.038
O3	1.5794(2)	0.0948(0)	0.5065(2)	0.037
C1	0.5783(3)	0.0571(0)	-0.0729(2)	0.028
C2	0.3868(3)	0.0837(1)	-0.0934(2)	0.034
C3	0.1699(3)	0.0783(1)	-0.2174(3)	0.042
C4	0.1407(4)	0.0455(1)	-0.3216(3)	0.043
C5	0.3273(4)	0.0186(1)	-0.3036(2)	0.045
C6	0.5451(3)	0.0242(1)	-0.1798(2)	0.037
C7	0.8116(3)	0.0618(1)	0.0539(2)	0.029
C8	0.8806(3)	0.0919(1)	0.1618(2)	0.028
C9	1.1227(3)	0.0940(0)	0.2785(2)	0.028
C10	1.2072(3)	0.1263(0)	0.3847(2)	0.027
C11	1.0551(3)	0.1620(0)	0.3804(2)	0.028
C12	0.9666(3)	0.1838(0)	0.2140(2)	0.026
C13	1.0890(3)	0.1813(1)	0.0817(2)	0.030
C14	1.0151(4)	0.2041(1)	-0.0657(2)	0.038
C15	0.8160(4)	0.2290(1)	-0.0820(2)	0.039
C16	0.6929(3)	0.2314(1)	0.0479(3)	0.039
C17	0.7679(3)	0.2092(1)	0.1956(2)	0.033
C18	1.4415(3)	0.1238(1)	0.5076(2)	0.031
C19	1.5331(4)	0.1558(1)	0.6342(3)	0.039
HO1	1.424(5)	0.069(1)	0.377(3)	0.089(8)
HC2	0.408(3)	0.106(1)	-0.021(2)	0.036(5)
HC3	0.042(4)	0.097(1)	-0.232(2)	0.048(6)
HC4	-0.003(4)	0.041(1)	-0.405(3)	0.049(6)
HC5	0.303(4)	-0.004(1)	-0.376(3)	0.060(6)
HC6	0.677(3)	0.005(1)	-0.167(2)	0.043(5)
HC7	0.932(3)	0.041(1)	0.054(2)	0.039(5)
HC8	0.772(3)	0.113(1)	0.164(2)	0.040(5)
HC13	1.227(3)	0.164(0)	0.094(2)	0.027(4)
HC14	1.101(3)	0.202(1)	-0.161(3)	0.051(6)
HC15	0.770(3)	0.244(1)	-0.183(2)	0.039(5)
HC16	0.557(3)	0.249(1)	0.039(2)	0.042(5)
HC17	0.685(3)	0.211(1)	0.283(2)	0.037(5)
HC191	1.423(4)	0.158(1)	0.713(3)	0.064(7)
HC192	1.522(4)	0.181(1)	0.579(3)	0.071(7)
HC193	1.692(5)	0.151(1)	0.696(3)	0.076(8)

^a $U_{eq} = (U11 + U22 + U33)/3$ for anisotropic atoms.

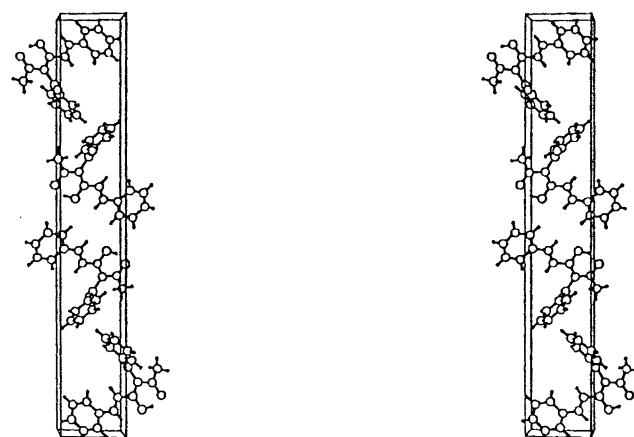


Fig. 2. Stereoscopic view of the molecular packing in the unit cell.

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations for non-hydrogen atoms.

Distance		Distance	
O1–C9	1.314(2)	O2–C11	1.228(2)
O3–C18	1.259(3)	C1–C2	1.390(3)
C1–C6	1.397(3)	C1–C7	1.461(3)
C2–C3	1.386(3)	C3–C4	1.381(3)
C4–C5	1.376(3)	C5–C6	1.390(3)
C7–C8	1.338(3)	C8–C9	1.455(3)
C9–C10	1.403(3)	C10–C11	1.485(3)
C10–C18	1.441(3)	C11–C12	1.501(3)
C12–C13	1.398(3)	C12–C17	1.394(3)
C13–C14	1.391(3)	C14–C15	1.386(3)
C15–C16	1.384(3)	C16–C17	1.382(3)
C18–C19	1.498(3)		
Angle		Angle	
C2–C1–C6	118.0(2)	C2–C1–C7	123.3(2)
C6–C1–C7	118.6(2)	C1–C2–C3	121.3(2)
C2–C3–C4	119.8(2)	C3–C4–C5	120.1(2)
C4–C5–C6	120.2(2)	C1–C6–C5	120.7(2)
C1–C7–C8	127.3(2)	C7–C8–C9	122.2(2)
O1–C9–C8	116.3(2)	O1–C9–C10	120.0(2)
C8–C9–C10	123.7(2)	C9–C10–C11	121.5(2)
C9–C10–C18	118.9(2)	C11–C10–C18	119.5(2)
O2–C11–C10	121.2(2)	O2–C11–C12	119.1(2)
C10–C11–C12	119.5(2)	C11–C12–C13	121.5(2)
C11–C12–C17	119.2(2)	C13–C12–C17	119.2(2)
C12–C13–C14	120.4(2)	C13–C14–C15	119.5(2)
C14–C15–C16	120.4(2)	C15–C16–C17	120.3(2)
C12–C17–C16	120.2(2)	O3–C18–C10	120.7(2)
O3–C18–C19	117.6(2)	C10–C18–C19	121.7(2)
C18–C19–C19	117.6(2)		

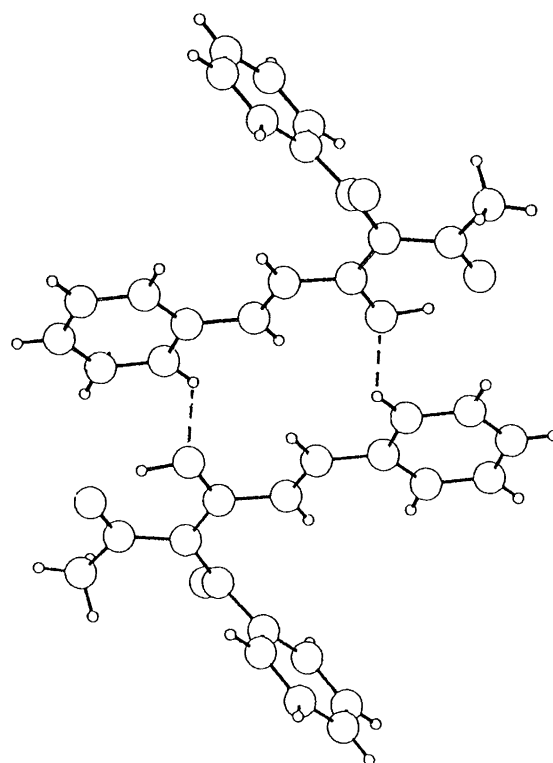


Fig. 3. Intermolecular interaction over a centre of symmetry.

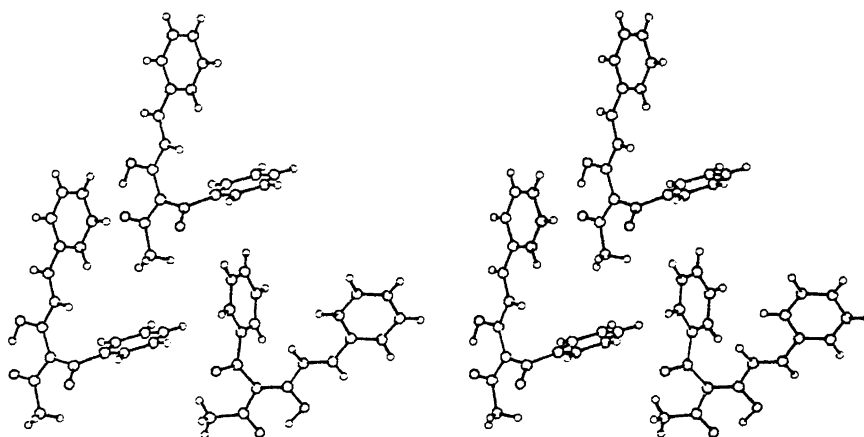


Fig. 4. Stereo drawing of aromatic interaction.

The conformation of the molecules in the crystal phase, the *E*-conformation in Scheme 1, allows conjugation from ring I through three double bonds including the C = O in the enol ring. Steric relations forbid coplanarity between the benzoyl moiety and the rest of the molecule, and the dihedral angle C9–C10–C11–O2 of 126.6° may indicate a larger repulsion between the two double bonds C9 = C10 and C11 = O2 than between the C10–C18 and C11 = O2 bonds. The C10–C11 distance of 1.485 \AA is close to that reported for an unconjugated sp^2 – sp^2 bond.⁴ Surprisingly, the benzoyl group itself is not quite planar as the torsion angle O2–C11–C12–C17 is -23.9° and the bond lengths C11–O2 and C11–C12 are 1.228 \AA and 1.501 \AA , respectively, indicating no conjugation in this group. This non-planarity may be a result of an optimal value for the dihedral angle about the C10–C11 bond and steric interaction between ring II and the C8–C10 part of the molecule (HC13–C10: 2.69 \AA , C8–C13: 2.98 \AA).

The packing of the molecules is depicted in Figs. 2 and 4, which indicate the same types of intermolecular interaction as found in 4-benzyl-1,7-diphenylhepta-1,6-diene-3,5-dione,⁵ i.e. interactions between aromatic groups and between the enol groups and phenyl ring hydrogens.

Along the *b*-axis the molecules are connected through interactions between ring II in neighbouring molecules. The C15–H bond points to a point between C13 and C17, the distance from HC15 to these two atoms being

$3.18(2) \text{ \AA}$ whereas the distance to C12 is found to be $2.99(2) \text{ \AA}$. The angle between the planes of the interacting rings is 85.7° . The shortest contacts between the molecular double layers interconnected in this way occur between the phenyl-ring hydrogen HC6 and the hydroxy oxygen in the enol group (O1) in a molecule related by a centre of symmetry, the distance being $2.55(2) \text{ \AA}$ (Fig. 3). Along the *a/c* diagonal there is a stacking of the enol- and the phenyl-rings, the distance between the ring planes being 3.28 \AA and the angle between the planes being 7.5° . This stacking, as well as the interactions between the aromatic moieties within the molecular double layers, are clearly illustrated in the stereographic drawing in Fig. 4.

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