

Structural and conformational studies of 1,4-bis(phenacyloxy)benzene

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ABSTRACT

The title compound crystallizes with the orthorhombic space group *Pbca*. The dihedral angle between the central benzene and the phenyl ring is $77.74(2)^\circ$. The atom O2 is deviated by $0.037(2)^\circ$ from the remaining of the atoms in the central benzene ring. The dihedral angle between the benzene ring and the phenacyloxy ring is $77.59(1)^\circ$. The atom O1 is deviated by $0.032(1)^\circ$ from the remaining of the atoms in the group C1-C8. The C7-O1 to the phenacyl system assumes a synperiplanar conformation with respect to the O2-C8 bond [O2-C8-C7-O1 of $-6.4(4)^\circ$]. The C8-C7-O1-C1 fragment of phenacyl substituent is flat and approximately perpendicular to the central benzene. The phenyl ring is twisted by $6.61(1)^\circ$ from C8-C7-O1-C1 plane.

INTRODUCTION

The phenacyl derivatives have proved to be an important reagent for protecting carboxyl functions during synthesis in presence of other esters [6]. Phenacyl groups are used as protected carboxylic acids in organic synthesis [5]. They are generally solids, soluble in common solvents, easy to prepare, purify and handle [7]. They are stable to acidic conditions and therefore are suitable for orthogonal protection of the carboxyl group.

In order to study and explain the behaviour of phenacyl group with benzene, the title compound was subjected to an X-ray crystallographic study. The chemical scheme of the molecule of the compound is given in **Fig. 1**

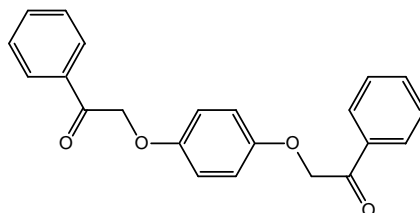


Fig. 1

MATERIALS AND METHODS

Hydroquinone (0.05g , 4.5×10^{-3} mol), triethylamine (0.909g , 9×10^{-3} mol) phenacyl bromide (1.79g , 0.009 mol) were dissolved in minimum amount of methanol. This solution was added slowly in 25 ml of micellar solution (sodium lauryl sulphate [0.6g , 2.08×10^{-3} mol] in methanol water (70-30 v/v). The reaction mixture was stirred well for

about 10h at room temperature. This solid product appeared was filtered, washed with water and then with petroleum ether. The solid was dried well, recrystallized from ethyl acetate, yield 1.2g (77%), melting point 115-117°C.

Intensity Data Collection

X-ray data were collected on a Bruker AXS (Kappa APEX2) [4] CCD area detector using ω and Ψ scan mode. A small crystal of size $0.28 \times 0.24 \times 0.16$ mm was chosen and its quality was checked using polarizing microscope. Cell refinement and data reduction were carried out by using APEX2/SAINT-NT [4]. Sets of three standard reflections were monitored for every one hour of exposure during the data collection and there was no noticeable change in the intensity observed. A total of 5358 reflections were collected resulting in 876 independent reflections of which 694 had $I > 2\sigma(I)$, were considered as observed. The intensities were corrected for Lorentz and polarization effects. Absorption corrections were made with SADABS [4] using multi scan mode.

Structure Solution and Refinement

Analysis over the crystal data and unit cell parameters revealed the following systematic absences: $hk0$ for $h=2n+1$, $h0l$ for $l=2n+1$, and $0kl$ for $k=2n+1$. Therefore the space group orthorhombic **Pbca** was unambiguously assigned.

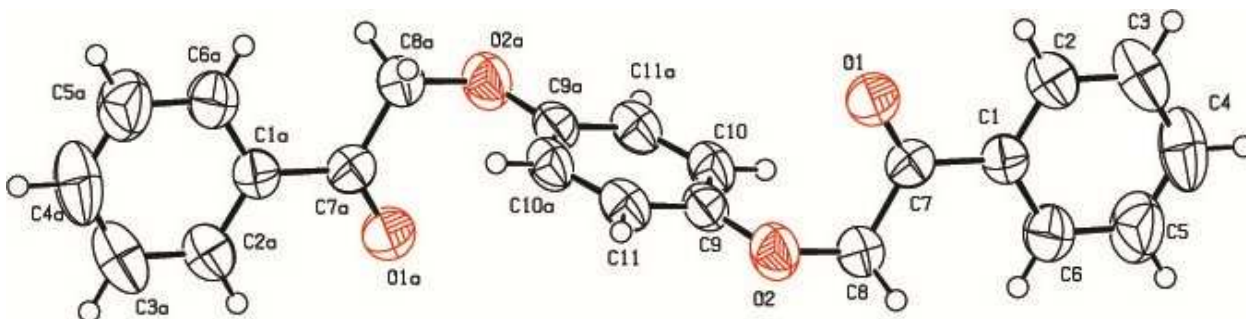


Fig 1.2 The ORTEP diagram of the molecule showing the displacement ellipsoids of all non hydrogen atoms at 30% probability level

Refinement was carried out using the program SHELXL97 [10]. All the non-hydrogen atoms were refined with anisotropic factor. At this stage, the difference Fourier map revealed all hydrogen atoms. After checking their presence in difference map, H atoms were positioned geometrically with C-H distances in the range C-H = 0.93Å-0.97Å. They were allowed to ride on their parent atoms with isotropic displacement parameter $U_{iso}(H)=1.2U_{eq}(C)$ for other H-atoms in the riding model approximation. The refinement was completed at $R=0.031$ for 694 reflections.

The weighting scheme [12] adopted during the final cycle of refinement is

$$w = 1 / [s^2 (Fo^2) + (0.1000P)^2]$$

where $P = (Fo^2 + 2Fo^2) / 3$

The geometric calculations were performed using the PARST[8,9] and PLATON [11]. The crystal data and refinement parameters are summarized in **Table 1.1**.

RESULTS AND DISCUSSION

The ORTEP diagram of the molecule showing the displacement ellipsoids of all non hydrogen atoms at 30% probability level is shown in the **Fig. 1.2**. The molecular structure contains central benzene ring which is linked to the phenacyloxy ring. The asymmetric unit contains only the half of the molecule. The fractional atomic coordinates of non hydrogen atoms and their isotropic and anisotropic temperature factors are analyzed..

Molecular Geometry and Conformation

The torsion angles involving all the non hydrogen atoms are given in **Table 1.2**. All the bond lengths and angles show normal values [1,2] (Cambridge Structural Database, Version 5.27).

The dihedral angle between the central benzene and the phenyl ring is $77.74(2)^\circ$. The atom O2 is deviated by $0.037(2)$ from the remaining of the atoms in the central benzene ring. The dihedral angle between the benzene ring and the phenacyloxy ring is $77.59(1)^\circ$. The atom O1 is deviated by $0.032(1)$ from the remaining of the atoms in the group C1-C8. The C7=O1 to the phenacyl system assumes a synperiplanar conformation with respect to the O2-C8 bond [O2-C8-C7-O1 of $-6.4(4)^\circ$]. The C8-C7-O1-C1 fragment of phenacyl substituent is flat and approximately perpendicular to the central benzene. The phenyl ring is twisted by $6.61(1)^\circ$ from C8-C7-O1-C1 plane.

The torsion angles C10-C9-O2-C8 [$6.0(4)^\circ$], O2-C8-C7-O1 [$-6.4(4)^\circ$], O1-C7-C1-C6 [$177.4(3)^\circ$] and C9-O2-C8-C7 [$77.3(3)^\circ$] determine the orientation of the phenyl ring through O2-C8-C7-O1 group. The torsion angle O1-C7-C1-C6 indicates the conjugation with the benzoyl fragment. The orientation of other half of the molecule outside the asymmetric unit is also observed to conform the molecular structure of the compound.

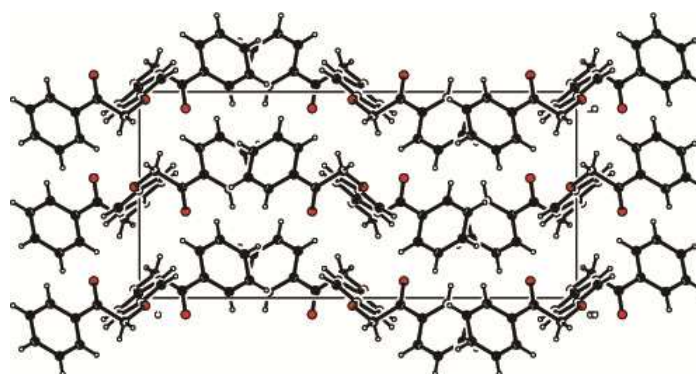


Fig 1.3 The packing of molecules form a chain along C axis.

TABLE 1.1 Crystal data and structure refinement for 1,4-Bis(Phenacyloxy) benzene

Identification code	PS13
Empirical formula	C ₈₈ H ₇₂ O ₁₆
Formula weight	1385.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbc _a
Unit cell dimensions	a = 9.1737(10) Å α = 90°
b = 9.5382(7) Å β = 90°	
c = 20.199(2) Å γ = 90°	
Volume	1767.4(3) Å ³
Z, Calculated density	1, 1.302 Mg/m ³
Absorption coefficient	0.089 mm ⁻¹
F(000)	728
Crystal size	0.28 × 0.24 × 0.14 mm
Theta range for data collection	2.02 to 20.46°
Limiting indices	-8 < h < 9, -9 < k < 9, -17 < l < 19
Reflections collected / unique	5358 / 876 [R(int) = 0.0327]
Completeness to theta = 20.46	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	876 / 0 / 118
Goodness-of-fit on F ²	1.223
Final R indices [I > 2σ(I)]	R1 = 0.0313, wR2 = 0.0971
R indices (all data)	R1 = 0.0504, wR2 = 0.1320
Largest diff. peak and hole	0.166 e.Å ⁻³ and -0.189 e.Å ⁻³

Hydrogen Bonding

The packing of the molecules form a zig zag chain along c-axis as shown in the **Fig. 1.3**.

One intermolecular C-H...π hydrogen bonding interaction is observed in the structure. The molecular structure is stabilized by C6-H6...Cg2 interactions [where the Cg2 is the centroid of the central benzene ring C9-C10-C11-C9a-C10a-C11a]. The atom H6 is separated by a distance of 2.95 Å from the centroid of the ring Cg2 which is less than

the sum of the van der Waals radii. [C6...Cg2 = 3.851(3), symmetry codes: $^{-1/2+x, 1/2-y, -z}$ and $^{3/2-x, -1/2+y, z}$ respectively]. The hydrogen bonding geometry is given in the **Table 1.3**.

TABLE 1.2 Torsion angles ($^{\circ}$) for non-hydrogen atoms of compound with esd's in parentheses

Atom	Angle
C6-C1-C2-C3	-0.2(4)
C7-C1-C2-C3	178.5(3)
C1-C2-C3-C4	-0.7(5)
C2-C3-C4-C5	1.4(6)
C3-C4-C5-C6	-1.2(6)
C4-C5-C6-C1	0.3(6)
C2-C1-C6-C5	0.4(5)
C7-C1-C6-C5	-178.3(3)
C2-C1-C7-O1	-1.3(4)
C6-C1-C7-O1	177.4(3)
C2-C1-C7-C8	179.5(2)
C6-C1-C7-C8	-1.8(4)
C9-O2-C8-C7	77.3(3)
O1-C7-C8-O2	-6.4(4)
C1-C7-C8-O2	172.8(2)
C8-O2-C9-C10	6.0(4)
C8-O2-C9-C11	-176.3(2)
O2-C9-C10-C11 ⁱ	178.1(2)
C11-C9-C10-C11 ⁱ	0.6(5)
C10-C9-C11-C10 ⁱ	-0.6(5)
O2-C9-C11-C10 ⁱ	-178.4(2)

Symmetry code: (i) = $-x+2, -y+1, -z$

TABLE 1.3 Hydrogen bonding geometry (\AA , $^{\circ}$) (D-donor; A-acceptor; H-hydrogen) for compound

Interactions	D...H	H...A	D...A	D-H...A
Intermolecular				
C6-H6...Cg2 ⁱ	0.9300	2.95	3.851(3)	165
C6-H6...Cg2 ⁱⁱ	0.9300	2.95	3.851(3)	165

Symmetry code: (i) = $^{-1/2+x, 1/2-y, -z}$; (ii) = $^{3/2-x, -1/2+y, z}$.

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