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Synthesis and Crystal Structure of 5, 5-diphenyldihydrofuran-2(3H)-one (5)

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Abstract: *5,5-diphenyldihydrofuran-2(3H)-one(5) [$C_{16}H_{14}O_2$] crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell parameters: a=8.132(5), b=13.224(5), c=11.785(5) Å, β=101.445(5)° and Z=4. The crystal structure was solved by direct methods and refined by full matrix least-squares procedure to a final R value of 0.054 for 1651 observed reflections. Furan ring adopts envelope conformation. Two phenyl rings are almost perpendicular to each other [dihedral angle = 85.66(7)°]. Crystal packing is stabilized by C-H...O intra molecular and weak C-H...π interactions.*

Keywords: *Crystal structure, Direct methods, Furan, Hydrogen bonding.*

I. Introduction

Furan is one of the most important five-membered heterocyclic ring systems. Furan derivatives widely occur in nature and are gaining importance for their wide pharmacological activities such as antibacterial, antitumor, anti-inflammatory, antifungal, anticonvulsant, and analgesic [1-3]. Many of naturally occurring furan and their unnatural analogs are important precursors for the synthesis of natural products [4,5]. Furan derivatives are well known in many marine organisms [6], and some have important bioactivities, such as antitumor activity [7] and diabetes treatment activity [8,9].

II. Synthesis

Synthesis of 5, 5-diphenyldihydrofuran-2(3H)-one(5)is presented in scheme 1.

2.1 Experimental procedure for the synthesis of 1, 1-diphenylbutane-1, 4-diol (2)[10]

Bromobenzene (0.362 g, 2.32 mmol, 1.0 equiv.) in dry THF (10.0 mL) was added dropwise with the help of syringe to a stirred solution of crushed magnesium turnings (0.1112 g, 4.64 mmol, 2.0 equiv.) in dry THF (10 mL, freshly distilled from sodium/benzophenone) at room temperature for one hour under inert atmosphere. The prepared Grignard reagent solution (PhMgBr, 0.418 g, 2.3 mmol, 2.0 equiv.) was added dropwise through the cannula to the stirred solution of butyrolactone **1** (0.1 g, 1.16 mmol, 1.0 equiv.) in THF (10 mL) at 0 ^{o}C over 30 minutes. The combined reaction mixture was stirred at 0 °C for additional 2 h and then quenched by NH_4Cl (5 mL, saturated) and the organic layer was separated. The aqueous layer was again extracted with EtOAc (2 x 5 mL). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography (Hexane: EtOAc, 20:1 to 5:1) to give the desired 1, 1-diphenylbutane-1, 4-diol **(2)** as a white semi-solid (196 mg, 70% yield).

2.2 Experimental procedure for the synthesis of 5, 5-diphenyldihydrofuran-2(3H)-one (5) [11]

1,1-diphenylbutane-1, 4-diol **(2)** (100 mg, 4.13 mmol, 1.0 equiv.) solution in dichloromethane (2.0 mL) was added to a stirred solution of PCC (266 mg, 12.3 mmol, 3.0 equiv.) and celite (100 mg) in dichloromethane (2.0 mL) and stirred for 3 hrs at room temperature. The reaction was monitored by TLC till completion. Filter the reaction mixture over a pad of Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane: EtOAc = 90:10 to 70:30) to give the desired product **(5)** as a white solid (69 mg, 70% yield).

III. Experimental

A crystal of dimensions 0.20 × 0.15 × 0.15 mm was used for data collection on *X*'calibur CCD area-detector diffractometer, equipped with graphite monochromated Mo*Kα* radiation (λ=0.71073 Å)[12]. X-ray intensity data consisting of 5118 reflections were collected at 293(2) K and 2434 reflections were found unique. The intensities were measured by ω scan mode for θ ranges 3.5 to 26.0°. A total number of 1651 reflections were treated as observed $[I > 2\sigma(I)]$. Data were corrected for Lorentz-polarization and absorption factors. The crystal structure was solved by direct methods using SHELXS97[13] and refined by the full matrix least squares method using SHELXL97[13] present in the program suite WinGX.

All non-hydrogen atoms of the molecule were located in the best E-map. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C-H= 0.93-0.97 Å and U_{iso} = 1.2 U_{eq}(C), except for the methyl groups where $U_{iso}(H) = 1.5U_{eq}(C)$. The refinement cycles converged the structure to a final R- factor of 0.054 (wR (F^2) = 0.127) for the 1651 observed reflections. Residual electron densities ranges from -0.15 to 0.21 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)[14].

IV. Result And Discussion

An ORTEP[15] view of the structure with atomic labelling scheme is shown in Fig. 1. The geometry of the molecule was calculated using the PLATON[16] and PARST[17] software. Crystal data, along with data collection and structure refinement details are summarized in Table 1. Selected bond lengths, bond angles and torsion angles are given in Table 2. The geometry of intra molecular and C-H…π interactions is given in Table 3.

The structure consists of two phenyl (A and B) and furan(C) rings. The structural parameters, including bond distances and angles show a normal geometry [18]. The double bond character of the C16=O1 is confirmed by the respective distance of 1.188(3)Å. The bond distance O2-C16 [1.365(2)Å] lies within the normal range but bond distance O2-C7 [1.472(2)Å] is larger than the normal value of 1.368Å for furan ring(C). The two phenyl rings are almost perpendicular to each other with the torsion angle of 85.66(7)°. The plane of furan ring forms a dihedral angle of 46.89(9)° and 80.75(8)° with the plane of the phenyl rings A and B respectively. Furan ring (C) adopts an envelope conformation [asymmetric parameter ΔC_s=4.362] with atom C14 as the flap, deviating by 0.505(3)Å from the mean plane defined by atoms (C15/C16/O2/C7). Phenyl rings A and B are planar with maximum deviations for atom C6 [-0.0078(2) Å] and C11 [0.0021(3) Å], respectively.

Molecular packing in the unit cell viewed down the c-axis is shown in Fig.2. Molecular packing is stabilized by weak van der waals forces. Examination of non-bonded contacts reveals the presence of C-H…O intra-molecular hydrogen bond [C9-H9…O2] which results in the formation of a virtual five-membered ring with S(5) graph-set motif [19]. The existence of few weak C-H…π interactions help in stabilizing the structure.

V. Figures and Tables

Scheme 1: Synthesis of 5, 5-diphenyldihydrofuran-2(3H)-one(5).

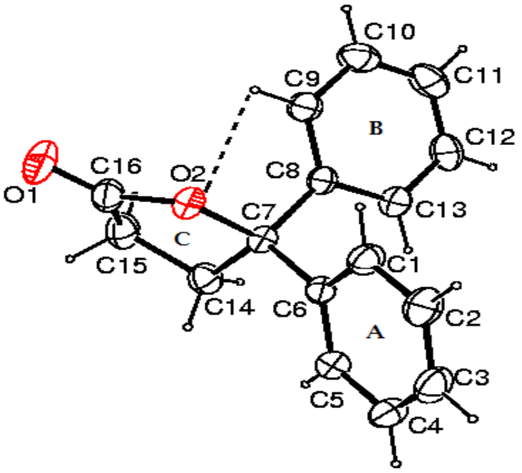

Figure1: ORTEP view of the molecule with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as small sphere of arbitrary radii.

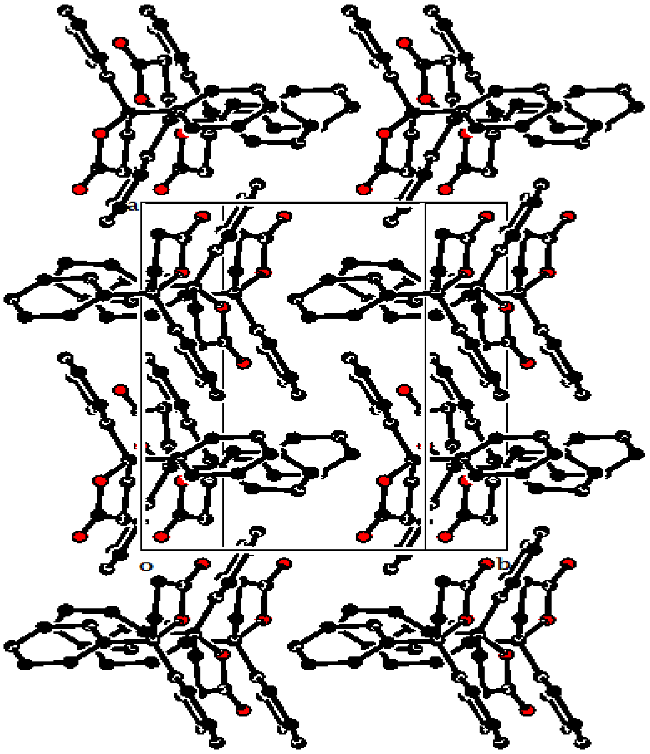

Figure 2: Packing diagram viewed down the c-axis.

Table1: Crystal and experimental Data.

Chemical formula	$C_{16}H_{14}O_2$
CCDC no.	1455201
M_r	238.27
Crystal system, space group	Monoclinic, $p2_1/c$
Temperature (K)	293
a, b, c (Å)	8.132 (5), 13.224 (5), 11.785 (5)
β (°)	101.445 (5)
V (Å^3)	1242.1 (10)
Z	4
F(000)	504
D_x (Mg m^{-3})	1.274
Radiation type	Mo $K\alpha$
No. of reflections for cell measurement	1292
θ range (°) for cell measurement	3.9–27.6
μ (mm^{-1})	0.08
Crystal size (mm)	0.20 × 0.15 × 0.15
T_{min}, T_{max}	0.863, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5118, 2434, 1651
R_{int}	0.032
θ values (°)	$\theta_{max} = 26.0$, $\theta_{min} = 3.5$
Range of h, k, l	$h = -6 \rightarrow 10$, $k = -15 \rightarrow 16$, $l = -14 \rightarrow 14$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.148, 1.06
No. of reflections	2434
No. of parameters	164
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.15

Table 2: Selected Bond Distances(Å), Bond Angles(°) and Torsion Angles(°).

Bond distances(Å)		Bond angles(°)	
O1—C16	1.188 (3)	O2—C7—C8	108.24 (15)
O2—C16	1.365 (2)	O1—C16—O2	121.1 (2)
O2—C7	1.472 (2)	O1—C16—C15	129.4 (2)
C6—C7	1.522 (3)	O2—C16—C15	109.48 (18)
C7—C8	1.520 (3)	O2—C7—C14	102.80 (15)
C7—C14	1.531 (3)	C6—C7—C8—C13	59.9 (2)
C14—C15	1.509 (3)	C16—O2—C7—C8	95.61 (18)
		C1—C6—C7—O2	−55.6 (2)
		C14—C7—C8—C13	−70.4 (2)

Table 3: Hydrogen bonding geometery (e.s.d.'s are given in parentheses)

D–H…A	D–H(Å)	H…A(Å)	D…A(Å)	D–H…A(°)
C9-H9…O2	0.93	2.38	2.75(3)	103.0
C2-H2…Cg3^{i}	0.93	2.89	3.76(4)	155.6
C3-H3…Cg3^{ii}	0.93	3.26	3.73(4)	113.4
C4-H4…Cg3^{ii}	0.93	3.49	3.78(4)	110.9
C12-H12…Cg2^{iii}	0.93	2.89	3.71(4)	147.1
C15-H15A…Cg2^{iv}	0.97	2.77	3.69(4)	159.8

Symmetry codes: (i) 2-x,-y,1-z (ii) 2-x, -1/2+y, 1/2-z (iii) 1+x,y,z (iv) 2-x,1/2+y,1/2-z
Cg2 and Cg3 are the centroids of the rings (C1-C6) and (C8-C13).

VI. Conclusion

5, 5-diphenyldihydrofuran-2(3H)-one(5) has been synthesized from 1, 1-diphenylbutane-1, 4-diol (2) at room temperature. The residue was purified by silica gel column chromatography to give the final product as a white solid. The structure was characterized by single crystal X-ray diffraction to a final R-factor of 0.0574. The two phenyl rings (A and B) are almost perpendicular to each other with the torsion angle of 85.66(7)°. Furan ring C adopts envelope conformation. Crystal packing is stabilized by Intra-molecular [C9-H9…O2] and C-H…π interactions.

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References

[1] V. Anupam, S. N. Pandeya and S. Shweta, Int. J. Res. Ayurveda Pharm., 2, 2011, 1110–1116.
[2] S. Subhadramma, B. P. Siddaraju, C. Naveen, J. Saravanan and D. Gayathri, Acta Cryst., E71, 2015(a), o455–o456.
[3] S. Subhadramma, B. P. Siddaraju, N. Chandra, J. Saravanan and D. Gayathri, Acta Cryst., E71, 2015(b), o568–o569.
[4] S. Greve and W. Friedrichsen, Prog. Heterocycl. Chem., 12, 2000, 134–160.
[5] H. Hu, Acta Cryst., E64, 2008, o1534.
[6] D. J. Faulkner, Nat. Prod. Rep., 18, 2001, 1–49.
[7] P. Phuwapraisirsan, S. Matsunaga, R. W. M. V. Soest and N. Fusetani, Tetrahedron Lett., 45, 2004, 2125–2127.
[8] B. Y. Hwang, J. H. Lee, J. B. Nam, H. S. Kim, Y. S. Hong and J. J. Lee, J.Nat. Prod., 65, 2002, 616–617.
[9] X. C. Zeng, L. H. Li and Y. Z. Cen, Acta Cryst. E62, 2006, o3254–o3255.
[10] S.B. Yang, F.F. Gan, G.J. Chen, P.F. Xu, Synlett., 16, 2008, 2532.
[11] E. J. Corey, J. W. Suggs, Tetrahedron Lett. 16, 1975, 2647.
[12] Oxford Diffraction. CrysAlis PRO. Oxford Diffraction Ltd, Yarnton, England ,2010.
[13] G. M. Sheldrick, Acta Cryst., A64, 2008, 112.
[14] International Tables for X-ray Crystallography, Tables 4.2.6.8 and 6.1.1.4, A J C Wilson, Editor, Boston, Kluwer Academic Press, Vol. C, 1992.
[15] L. J. Farrugia, J. Appl. Cryst., 45, 2012, 849.
[16] A. L. Spek, Acta Cryst., D65, 2009, 148.
[17] M . Nardelli, J. Appl. Cryst., 28, 1995, 659.
[18] F. H. Allen, O. Kennard, D. G. Watson, et al., J. Chem. Soc., Perkin Trans. 2, 1987, S1–19.
[19] J. Bernstein, R. E. Davis, L. Shimoni and N. L. Chang, Angew. Chem.Int. Ed. Engl. 34, 1995, 1555.