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X-ray Crystallographic Structure of 3-(Propan-2-ylidene) benzofuran-2(3*H*)-one

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Abstract: 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one, $C_{11}H_{10}O_2$, crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 7.1869(3), b = 18.0636(10), c = 13.1656(7) Å, β= 96.763(3)°, V =1697.28(15) $Å^3$, Z = 8 (Z' = 2 independent molecules, A and B, per asymmetric unit), D_c = 1.363 g cm^{-3} and the linear absorption coefficient = 0.093 mm^{-1}. The crystal structure determination was carried out using MoKα X-ray data measured at 120(2) K. In the final refinement cycle the data/restraints/parameter ratios were 3827/0/239, the goodness-of-fit on F^2 = 1.019. Final R indices for [I>2sigma(I)] were R1 = 0.0517, wR2 = 0.1115 and R indices (all data) R1 = 0.1007, wR2 = 0.1354. The largest electron density difference peak and hole were 0.254 and -0.244 electrons $Å^{-3}$, respectively. The two independent molecules A and B have essentially identical bond lengths and angles and are highly planar, with rms deviation for all 12 non-H atoms of 0.0292 Å for molecule A and 0.0592 Å for molecule B. The two molecules in the asymmetric unit are assembled parallel to each other within 1.58(4)° with each of the six atoms of benzene ring A overlapping with one of the atoms in benzene ring B at a mean distance of 3.84(3) Å). The closest contacts between molecules A and B are C(12A)H---O(4B) = 3.521 Å and C(11B)H---O(4A) = 3.441 Å. The crystal structure is formed by infinite sheets of these assemblies all lying parallel to the (1 0 $\bar{1}$) plane. The presence of two independent molecules in the asymmetric unit provides an opportunity to examine the molecular geometry in detail by comparison. The benzene ring in both molecules A and B exhibits distortions as a result of the presence of the furan moiety. In particular, C(1)-C(6) = 1.369(2) Å in molecule A and 1.367(2) Å in molecule B are both significantly less than the average of the other 10 C-C bonds, 1.393(2), by about 12σ. Other examples of crystal structures are discussed where this effect is observed.

Keywords: Knoevenagel condensation; X-ray crystal structure; molecular geometry

1. Introduction

Recent interest in the Knoevenagel condensations of indol-2-one with aldehydes or ketones led to the report of a number of X-ray structures[1, 2] of the resulting 3-methylidene-1,3-dihydro-2*H*-indol-2-one compounds (**Figure 1**), which display intermolecular hydrogen bonding between the NH and C=O groups of neighbouring units. The aim, in this current study, is to compare the structure of the Knoevenagel condensation product of acetone with benzofuran-2(*3H*)-one as opposed to that with indolin-2-one since, in the former case, due to the lack of an NH group, no intermolecular H-bonding, of the type described above, is possible in the final product.

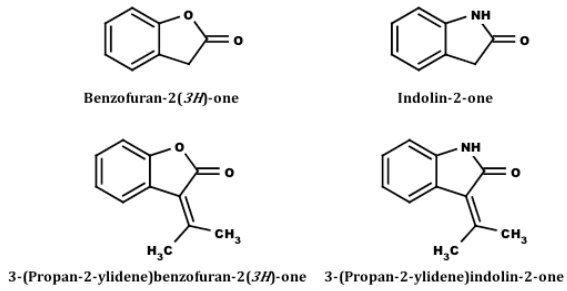

Figure 1. Knoevenagel condensation products.

2. Results and Discussion

Figure 2 shows the chemical scheme and crystallographic atom numbering for $C_{11}H_{10}O_2$ (**I**). **Figure 3** shows molecule A determined in the structure analysis and drawn with Visualizer, Discovery Studio (Release 3.5, Accelrys Inc., 2012).[3] ORTEP[4] and

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RASTER3D,[5] as implemented in WinGX, were used to prepare **Figure 4** which shows the relative disposition of molecules A and B depicted with their thermal ellipsoids at 50% probability.

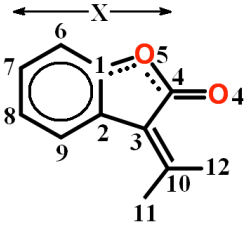

Figure 2. Schematic chemical structure and atom numbering for $C_{11}H_{10}O_2$ (**I**). The bonding shown is discussed. X denotes the region of geometry discussed in more detail.

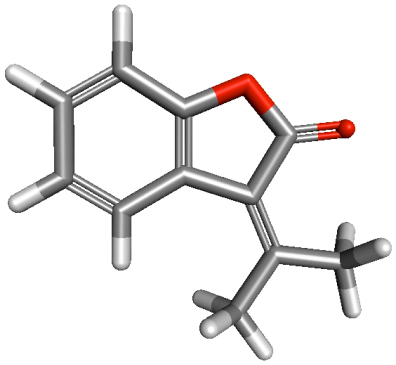

Figure 3. The 3-(propan-2-ylidene)benzofuran-2(*3H*)-one, $C_{11}H_{10}O_2$ (**I**) molecule A as determined by X-ray analysis (Drawn with Visualizer, Discovery Studio, Release 3.5, Accelrys Inc., 2012)[3] [http://accelrys.com/products/datasheets/whats-new-in-discovery-studio.pdf].

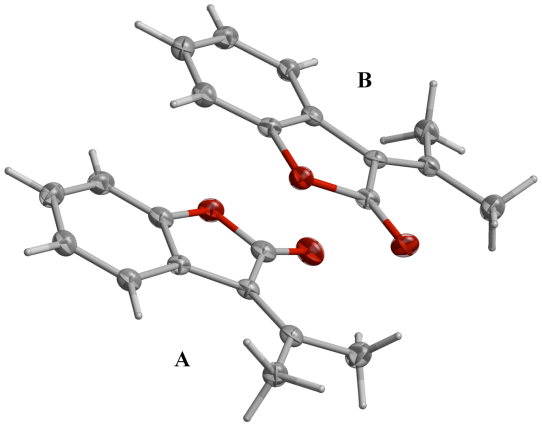

Figure 4. 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one (Ortep/Raster)[4,5], molecules A and B. The two molecules in the asymmetric unit are parallel within 1.67(6)° and the benzene rings overlap with a mean intermolecular distance of 3.84(3) Å between corresponding atoms. Thermal ellipsoids are shown at 50% probability.

2.1. Molecular Geometry

2.1.1. Bond lengths

Crystal data are summarized in **Table 1**. Bond lengths are determined to a precision of ± 0.002Å and bond angles to ± (0.2°). **Table 2** lists corresponding bond lengths in molecules A and B, respectively. These data indicate that there is a complete one to one agreement in bond length values. In the benzene ring all bond lengths are standard aromatic C-C bonds[6] except C(1)-C(6) which is 1.369(2)Å in molecule A and 1.367(2)Å in molecule B, which are both shorter by about 12σ than the standard value of 1.40 Å. This is possibly a result of the proximity of O(5) in the adjoining ring. In fact in the chain extending to the furan ring, i.e., C(6)-C(1)-O(5)-C(4), C(1)-O(5) = 1.391(2) Å in molecule A and 1.396(2) Å in molecule B, and O(5)-C(4) = 1.388(2) Å in molecule A and 1.395(2) Å in molecule B, this reduction in bond length is consistent with the presence of a delocalisation effect. This region is designated X in **Figure 2**.

Table 1. Crystal data and structure refinement for (**I**).

Identification code	2008src0248 CCDC804780
Empirical formula	$C_{11}H_{10}O_2$
Formula weight	174.20
Temperature	120(2) K
Wavelength (wtd. mean)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.1869(3) Å; α = 90° b= 18.0636(10)Å; β = 96.763(3)° c = 13.1656(7) Å; γ = 90°
Volume	1697.28(15) $Å^3$
Z	8 (2 molecules/asymmetric unit)
D_c	1.363 g cm^{-3}
Absorption coefficient	0.093 mm^{-1}
F(000)	736
Crystal size	0.44 x 0.30 x 0.08 mm^3
Theta range for data collection	3.07 to 27.48°.
Index ranges	-9<=h<=9, -23<=k<=23, -17<=l<=17
Reflections collected in total sphere	20306
Independent reflections	3827 [R(int) = 0.0800]
Completeness to theta = 27.48°	98.3 %
Max. and min. transmission	0.9926 and 0.9601
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	3827/0/239
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1149
R indices (all data)	R1 = 0.1007, wR2 = 0.1354
Largest diff. peak and hole	0.254 and-0.244 electrons $Å^{-3}$

2.1.2. Geometry Optimization

To investigate molecule A further its geometry was optimized in the program Visualizer, Discovery Studio (Release 4.0, Accelrys Inc., 2013).[7][http://accelrys.com/products/discovery-studio/] using the Smart Minimizer algorithm and conjugate gradient minimization criteria. The molecule was typed with the CHARMM forcefield[8] using the Partial Charge method.[9] After 2000 steps convergence was reached and the final potential energy of the molecule **I** was 61.5 kcal/mol. The results for molecules A and B bond lengths are listed in **Table 3**. These results show that the energy minimized molecular geometry is consistent with the shortening of bond C(1)-C(6) in both molecules A and B. Further examples of structures where such a short bond length feature may be present are noted below.

Table 2. 1-Benzofuran-2(3*H*)-one: bond lengths [Å] and angles [°] for molecules (**I**) A and B.

Bond Lengths		
Bond	*(I)A*	*(I)B*
C(1)-C(2)	1.392(2)	1.395(2)
C(2)-C(3)	1.471(2)	1.469(2)
C(3)-C(10)	1.350(2)	1.349(2)
C(10)-C(11)	1.492(2)	1.494(2)
C(10)-C(12)	1.503(2)	1.494(2)
C(3)-C(4)	1.489(2)	1.479(2)
O(4)-C(4)	1.204(2)	1.204(2)
C(4)-O(5)	**1.388(2)**	**1.395(2)**
O(5)-C(1)	**1.391(2)**	**1.396(2)**
C(1)-C(6)	**1.369(2)**	**1.367(2)**
C(6)-C(7)	1.393(2)	1.398(2)
C(7)-C(8)	1.390(2)	1.391(2)
C(8)-C(9)	1.389(2)	1.389(2)
C(9)-C(2)	1.398(2)	1.397(2)
Bond Angles		
C(1)-C(2)-C(3)	106.5(2)	106.7(2)
C(2)-C(3)-C(10)	130.8(2)	129.8(2)
C(3)-C(10)-C(11)	122.3(2)	121.4 (2)
C(3)-C(10)-C(12)	122.8(2)	123.4(2)
C(11)-C(10)-C(12)	115.0(2)	115.2(2)
C(2)-C(3)-C(4)	104.9(2)	105.1(2)
C(3)-C(4)-O(4)	132.5 (2)	132.6(2)
C(3)-C(4)-O(5)	108.4(2)	108.6(2)
O(4)-C(4)-O(5)	119.2(2)	118.7(2)
C(4)-O(5)-C(1)	**108.2(2)**	**108.4(2)**
C(6)-C(1)-O(5)	123.5(2)	123.7(2)
C(6)-C(1)-C(2)	**124.6(2)**	**124.6(2)**
C(1)-C(6)-C(7)	**116.7(2)**	**116.7(2)**
C(6)-C(7)-C(8)	120.9(2)	120.6(2)
C(7)-C(8)-C(9)	121.1(2)	121.4 (2)
C(8)-C(9)-C(2)	119.1(2)	118.9(2)

Features in region X, **Figure 2**, are in **bold**.

2.1.3. Bond angles

Table 2 lists corresponding bond angles in molecule A and B, respectively. These data indicate that there is a complete one to one agreement in bond angle values. Of the bond angles in the benzene ring C(1)-C(6)-C(7) = 116.7(2)° in both molecules, is significantly less than 120° and may be associated with the unusually short bond length C(1)-C(6) discussed above. The molecular geometry of the two independent molecules A and B is practically identical, as revealed by application of the AUTOFIT routine in PLATON[10] using Molfit with Quaternion Transformation.[11]

Table 3. 3-(Propan-2-ylidene) benzofuran-2(*3H*)-one (**I**): X-ray bond lengths [Å] for molecules A and B and molecules A and B after minimization in the Visualizer (Discovery Studio, Relase 4.0, Accelrys Inc., 2013).

Bond	X-ray Structure		Minimized Structure	
	(I)A	(I)B	A	B
C(1)-C(2)	1.392(2)	1.395(2)	1.402	1.402
C(2)-C(3)	1.471(2)	1.469(2)	1.489	1.488
C(3)-C(10)	1.350(2)	1.349(2)	1.359	1.358
C(10)-C(11)	1.492(2)	1.494(2)	1.515	1.514
C(10)-C(12)	1.503(2)	1.494(2)	1.516	1.516
C(3)-C(4)	1.489(2)	1.479(2)	1.503	1.501
O(4)-C(4)	1.204(2)	1.204(2)	1.225	1.224
C(4)-O(5)	1.388(2)	1.395(2)	1.337	1.337
O(5)-C(1)	1.391(2)	1.396(2)	1.461	1.460
C(1)-C(6)	**1.369(2)**	**1.367(2)**	**1.367**	**1.366**
C(6)-C(7)	1.393(2)	1.398(2)	1.394	1.394
C(7)-C(8)	1.390(2)	1.391(2)	1.396	1.394
C(8)-C(9)	1.389(2)	1.389(2)	1.398	1.398
C(9)-C(2)	1.398(2)	1.397(2)	1.375	1.375

2.2. Crystal Packing

The two molecules in the asymmetric unit are assembled parallel to each other within 1.58(4)° with each of the six atoms of benzene ring A overlapping with one of the atoms in benzene ring B at a mean distance of 3.84(3) Å); **Table 4(a)** and **Figure 5(a)**. The closest contacts between molecules A and B are C(12A)H---O(4B) = 3.521 Å and C(11B)H---O(4A) = 3.441 Å , **Table 4(b)** and **Figures 5(b)** and **(c)**. The crystal structure is formed by infinite sheets of these assemblies all lying parallel to the (1 0 $\bar{1}$) plane, **Figure 6**.

Table 4(a). Intermolecular C...C distances in the asymmetric unit (Å).

C(1A)...C(9B)	3.853
C(2A)...C(2B)	3.848
C(6A)...C(8B)	3.798
C(7A)...C(7B)	3.804
C(8A)...C(6B)	3.837
C(9A)...C(1B)	3.886

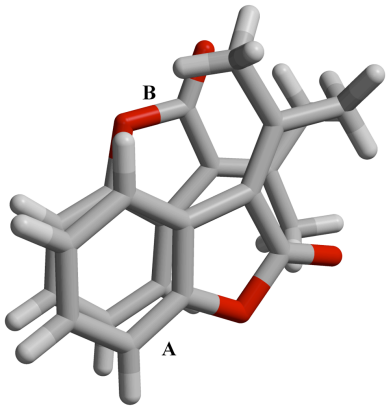

Figure 5(a). 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one mode of overlapping of molecules A and B (Ortep/Raster)[4,5]. The two molecules in the asymmetric unit are parallel within 1.58(4)°

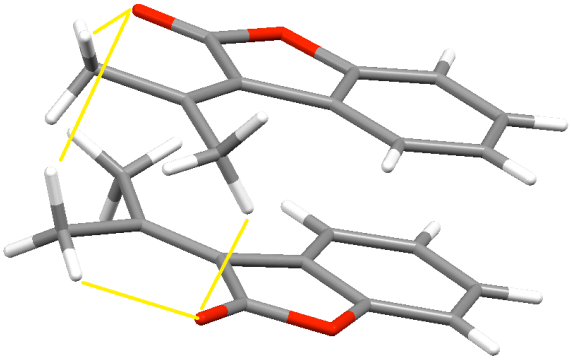

Figure 5(b). 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one, overlapping of molecules A and B. The short CH---O contacts as listed in Table 4 are indicated. Benzene – benzene distances range from 3.597 Å for C3(A) --- C3(B) to 3.886 Å for C1(A) --- C1(B); (Drawn with Mercury)[5].

Further Examples of Structures where Chain X Exhibits Delocalisation

In order to further investigate the delocalization effect observed in **(I),** molecules A and B, the corresponding bond in 2,3-diphenyl-5-methyl-1-benzofuran $C_{21}H_{16}O_1$

(**II**),[12] **Figure 7a** and 3-(1-phenylmeth-(*E*)-ylidene)-*3H*-benzofuran-2-one **(III)**,[13] **Figure 7b** was noted. Bond lengths in chain X for molecules (**I**), (**II**) and (**III**) are listed in **Table 5**. The delocalization in bond C(1)–C(6), evident in all 4 molecules listed here, is less prominent in molecule (**II**).

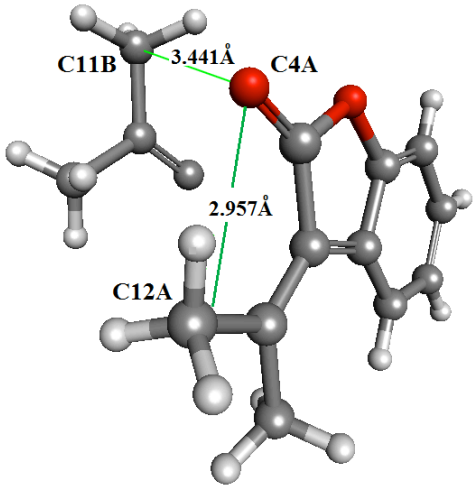

Figure 5(c). 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one, details of the intra molecular CH---O contact in Molecule A and between Molecule A and Molecule B. Essentially equivalent contacts occur within Molecule B and between Molecule B---A (Drawn with Visualizer, Discovery Studio, Release 3.5, Accelrys Inc., 2012)[3] [http://accelrys.com/products/datasheets/whats-new-in-discovery-studio.pdf].) see also **Table 4**.

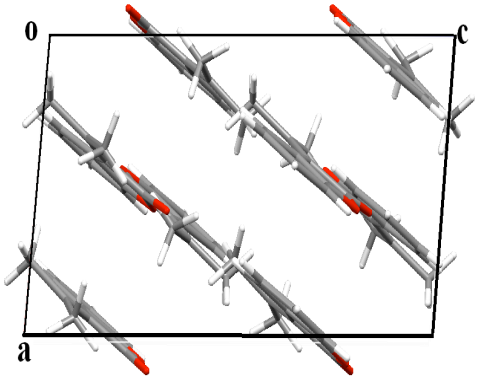

Figure 6. 3-(Propan-2-ylidene)benzofuran-2(3*H*)-one crystal packing viewed along **b**. The molecular planes are parallel to (1 0 $\bar{1}$). (Drawn with Mercury)[5].

Table 4(b). Possible hydrogen bonds [Å and deg.]

D-H...A	d(D-H) Å	d(H...A) Å	d(D...A) Å	<(DHA) deg
C(12A)-H(11A)...O(4A)*	0.98	*2.20*	*2.957(2)**	*132.6*
C(12A)-H(11C)...O(4B)	0.98	*2.80*	3.521(2)	*131.4*
C(11B)-H(11D)...O(4A)	0.98	*2.73*	3.441(2)	*130.2*
C(12B)-H(11G)...O(4B)*	0.98	*2. 25*	3.001(2)*	*132.3*
C(8A)-H(7)...O(4B)#1	0.95	*2.75*	3.412(2)	*127.5*
C(9A)-H(8)...O(5B)#1	0.95	*2.86*	3.798(2)	*168.4*
C(9A)-H(8)...O(4B)#1	0.95	*2.84*	3.452(2)	*122.8*
C(11A)-H(10A)...O(5B)#1	*0.98*	*3.00*	3.459(2)	*110.1*
C(7B)-H(106)...O(4B)#2	0.95	*2.85*	3.798(2)	*176.8*
C(11B)-H(11F)...O(5A)#3	*0.98*	*2.75*	3.241(2)	*111.7*
C(9B)-H(108)...O(4A)#3	0.95	*2.70*	3.414(2)	*132.3*

*C...O distance is less than the sum of the van der Waals radii; Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x,y+1/2,-z+1/2; #3 -x+1,-y,-z+1

3. Experimental

3-(Propan-2-ylidene)benzofuran-2(3*H*)-one(**I**), $C_{11}H_{10}O_2$, was provided by the Trost laboratory[14] and crystallized from dichloromethane/hexane by vapour diffusion.

3.1. Data Collection

A colourless crystal plate fragment of size 0.44 × 0.30 × 0.08 mm^3 was mounted on a glass fibre and flash frozen to 120 K. Intensities were collected, using monochromated MoKα radiation, λ = 0.71073 Å, with a Bruker-Nonius *Kappa* CCD camera, employing ϕ and ω scans to cover an asymmetric unit. Programs used were: unit cell determination with the program DirAx;[15] data collection was controlled by Collect;[16] data reduction and cell refinement were carried out using the program Denzo;[17] an absorption correction was made with SADABS.[18, 19] An Oxford Cryosystems "Cryostreams" 700,[20] enabled the data to be collected at 120 K. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions a = 7.1869(3), b = 18.0636(10), c = 13.1656(7) Å, β = 96.763(3)°, V = 1697.28(15) Å^3, $Z = 8$ (Z' = 2), D_c = 1.363 g cm^{-3} and linear absorption coefficient = 0.093 mm^{-1}. The crystal structure determination was carried out using MoKα X-ray data measured at 120(2) K. In total 20306 integrated reflections were collected, reducing to an asymmetric unit data set of 3827 [R(int) = 0.080], and completeness of data to theta = 27.48° of 98.3 % corresponding to a resolution of 0.770 Å. There was no significant variation in intensity of reference reflections during the course of data collection.

3.2. X-ray Structure Analysis

The crystal structure was solved by Direct Methods (SHELXS-86) and refined using SHELXL-97[21, 22] both implemented in the WinGX system of programs.[23] Non-hydrogen atoms were refined anisotropically by full-matrix least squares methods. All H atoms were set geometrically and refined in riding mode. Geometrical calculations were made with the programs PARST and PLATON[10] as implemented in WinGX. In the final refinement cycle there were 3827 data to 239 parameters, resulting in a final goodness-of-fit on F^2 of 1.019. Final R indices for [I>2sigma(I)] were R1 = 0.0517, wR2 = 0.1149 and R indices (all data) R1 = 0.1007, wR2 = 0.1354. The largest and smallest difference electron density regions were +0.254 and -0.244 electrons Å^{-3}, respectively. Crystal data are summarized in **Table 1**.

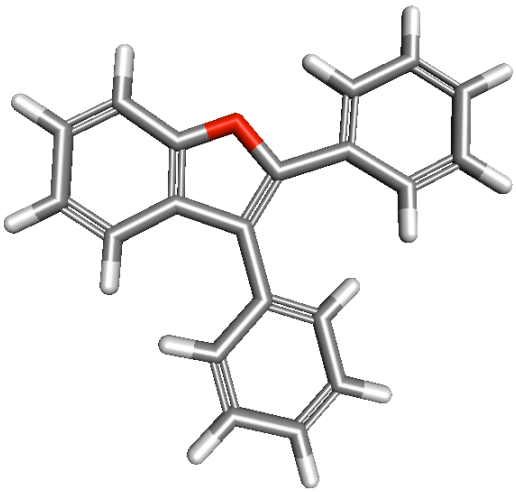

Figure 7a. *2,3-Diphenyl-5-methyl-1-benzofuran* $C_{21}H_{16}O_1$ **(II)**[6] determined by X-ray analysis (Drawn with Visualizer, Discovery Studio, Release 3.5, Accelrys Inc.,2012)[3] [http://accelrys.com/products/datasheets/whats-new-in-discovery-studio.pdf].

Table 5. Bond lengths [Å] in the chain C(4)-O(5)-C(1)-C(6) in 1-benzofuran-2-one (**I**) molecules A and B and the corresponding values in molecules (**II**) and (**III**).

Bond	(I)A	(I)B	(II)	(III)
C(4)-O(5)	1.388(2)	1.395(2)	1.398(4)	1.381(3)
O(5)-C(1)	1.391(2)	1.396(2)	1.380(4)	1.398(3)
C(1) C(6)	**1.369(2)**	**1.367(2)**	**1.378(4)**	**1.362(3)**
C(6)-C(7)	1.393(2)	1.398(2)	1.386(4)	1.387(3)

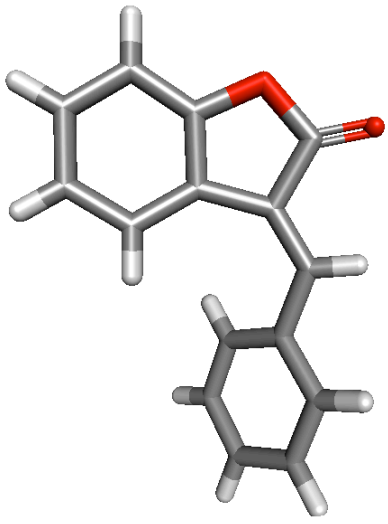

Figure 7b. 3-(1-Phenylmeth-(E)-ylidene)-3*H*-benzofuran-2-one *$C_{21}H_{16}O_1$* ***(III)***[7] *determined in the X-ray analysis (Drawn with Visualizer, Discovery Studio, Release 3.5, Accelrys Inc., 2012)[3] [http://accelrys.com/products/datasheets/whats-new-in-discovery-studio.pdf].*

Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 804780. Copies of available material can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0) 1223-336033 or e-mail: data request @ccdc.cam.ac.uk). X-ray diffraction data were measured at the UK National Crystallographic Service, Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.[24]

References

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