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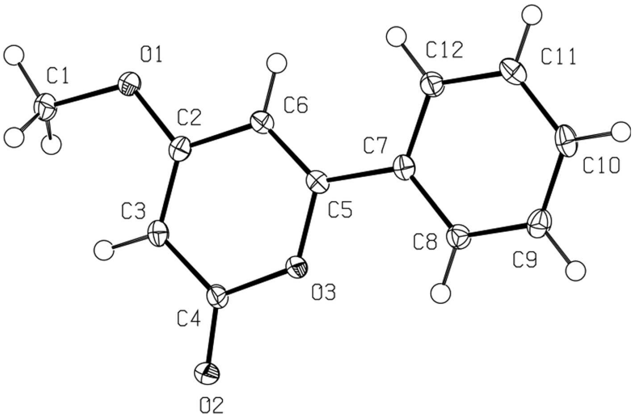
Crystal structure of 4-methoxy-6-phenyl-2*H*-pyran-2-one, $C_{12}H_{10}O_3$



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Abstract

$C_{12}H_{10}O_3$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2709(5)$ Å, $b = 7.3228(5)$ Å, $c = 9.4670(7)$ Å, $\alpha = 82.241(4)°$, $\beta = 88.161(3)°$, $\gamma = 70.192(5)°$, $V = 469.84(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0370$, $wR_{ref}(F^2) = 0.1082$, $T = 100(2)$ K.

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The structure of the title compound is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Block, colourless
Size:	$0.31 \times 0.19 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.1 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	27.4°, >97%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7509, 2090, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1871
$N(param)_{refined}$:	137
Programs:	Bruker programs [1], SHELX [2], WinGX and ORTEP [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.17895(13)	0.94151(12)	0.22094(9)	0.0166(2)
O2	0.51240(14)	0.26790(12)	0.37978(9)	0.0200(2)
O3	0.37392(12)	0.36424(12)	0.16552(9)	0.0147(2)
C1	0.22024(19)	1.00221(18)	0.35143(13)	0.0183(3)
H1A	0.161756	0.942809	0.431516	0.027*
H1B	0.164989	1.145165	0.345066	0.027*
H1C	0.362045	0.959930	0.366465	0.027*
C2	0.24864(16)	0.74773(16)	0.21294(12)	0.0132(2)
C3	0.34992(17)	0.60870(17)	0.31902(12)	0.0140(2)
H3	0.374911	0.645165	0.407108	0.017*
C4	0.41842(17)	0.40752(17)	0.29707(12)	0.0142(2)
C5	0.27170(16)	0.50579(17)	0.06034(12)	0.0126(2)
C6	0.20801(17)	0.69565(17)	0.07999(12)	0.0138(2)
H6	0.137029	0.793784	0.006591	0.017*
C7	0.24591(16)	0.42345(16)	−0.06846(12)	0.0130(2)
C8	0.29998(17)	0.22085(17)	−0.06696(13)	0.0153(2)
H8	0.349620	0.135928	0.018517	0.018*
C9	0.28166(18)	0.14262(17)	−0.18960(13)	0.0179(3)
H9	0.319447	0.004744	−0.187640	0.021*
C10	0.20837(18)	0.26540(19)	−0.31475(13)	0.0183(3)
H10	0.197045	0.211842	−0.398702	0.022*
C11	0.15155(18)	0.46725(19)	−0.31682(13)	0.0183(3)
H11	0.099773	0.551521	−0.402146	0.022*
C12	0.17006(17)	0.54647(17)	−0.19471(13)	0.0158(3)
H12	0.131109	0.684477	−0.197016	0.019*

Source of materials

The dianion of ethyl acetoacetate (1.83 g, 14.04 mmol) was formed by successive treatment of the substrate in THF (60 mL) with NaH (60% dispersion in mineral oil, 1.12 g, 28.0 mmol) and *n*-butyllithium (2.5 M in hexane, 9.2 mL, 23.20 mmol). Addition of ethyl benzoate (2.11 g, 14.04 mmol) to the reaction mixture yielded ethyl 3,5-dioxo-5-phenylpentanoate (3.15 g, 74% yield). Refluxing of ethyl 3,5-dioxo-5-phenylpentanoate (0.21 g, 0.9 mmol) and 1,8-diazobicyclo[5.4.0]undecan-7-ene (DBU, 0.16 g, 1.0 mmol) in benzene (5 mL) overnight, according to the method described by Cervello et al. [4], led to base-mediated cyclization to

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yield 4-hydroxy-6-phenyl-2*H*-pyran-2-one (98 mg, 74% yield). Methylation of the product (0.38 g, 2.0 mmol) with dimethyl sulfate (0.38 g, 3.0 mmol) in the presence of potassium carbonate (0.8 g, 6.0 mmol) afforded the product as a white solid. Colourless, block-shaped crystals were obtained by recrystallization from ethyl acetate. Yield: 98%; **m.p.** 223–225 °C; ^{1}**H NMR** ($CDCl_3$, 400 MHz): δ (ppm) = 3.85 (s, 3H), 5.54 (d, 1H, $J = 1.9$ Hz), 6.42 (d, 1H, $J = 1.9$ Hz), 7.43–7.45 (m, 3H), 7.79–7.81 (m, 2H); ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ (ppm) = 56.1, 88.6, 98.1, 125.8, 129.0, 131.1, 131.3, 160.3, 164.3, 171.4; Selected **IR** (neat) ν_{max} (cm^{-1}): 1706, 1631, 1557, 1271, 1219, 1009; **HR-MS** (ESI+) calcd. for $C_{12}H_{10}O_3$ $(M+Na)^+$ 202.0528 m/z, found 202.0532 m/z.

Experimental details

Molecular graphics were done using ORTEP-3 [3]. All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms and refined isotropically. The C—$H_{aromatic}$ and C—H_{methyl} bond distances were restrained to 0.95 Å and 0.98 Å with $U_{iso}(H_{aromatic}) = 1.2U_{eq}$ and $U_{iso}(H_{methyl}) = 1.5U_{eq}$ of parent atom, respectively.

Comment

2-Pyrones (α-pyrones) form an important class of natural products [5]. These compounds and their synthetic analogues are associated with a range of biological activities such as antiviral [6], antimalarial and antituberculosis [7] activities. The range of biological activities displayed by these compounds have stimulated investigations in the synthesis and structures of 2-pyrones.

There is one molecule present in the asymmetric unit of the title crystal structure. The molecular unit consists of phenyl and pyranonyl moieties, which confirms the synthesis of the title compound. The two moieties are not co-planar and have a C6—C5—C7—C12 torsion angle of 8.80(18)°. At least one non-classical intermolecular C3—H3···O2 hydrogen bond exists between two pyranonyl moieties of neighbouring molecules with C—H···O angle of 172° and H3···O2 distance of 2.44 Å (symmetry code: $-x+1, -y+1, -z+1$). This hydrogen bonding pattern forms an eight-membered ring with two donor and acceptor atoms. Offset $\pi\cdots\pi$ interactions between phenyl and pyranonyl moieties of neighboring molecules were also observed with a $\pi_{phenyl}\cdots\pi_{pyranonyl}$ distances of 3.677 Å. All geometric parameters are in the expected ranges.

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