Crystal structure of 8-methoxy-2-oxo-2*H*-chromene-3-carboxylic acid, $C_{11}H_8O_5$

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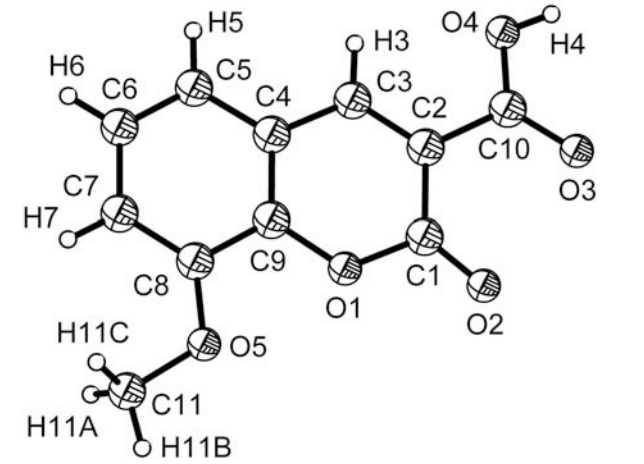

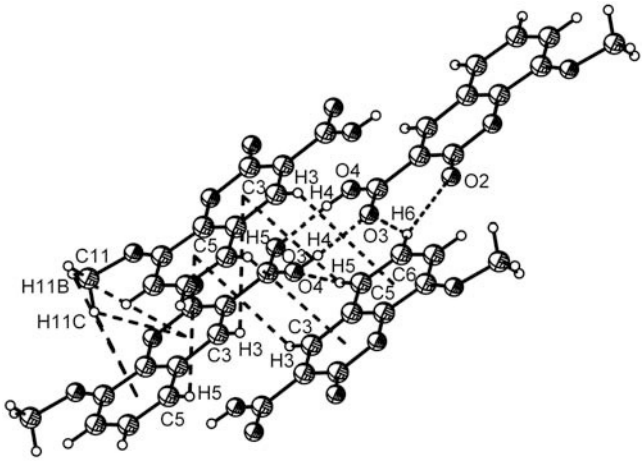

Abstract

$C_{11}H_8O_5$, monoclinic, $P12_1/c1$ (no. 14), a = 5.1525(6) Å, b = 19.922(2) Å, c = 9.458(1) Å, β = 100.468(1)°, V = 954.7 Å^3, Z = 4, $R(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.100, T = 296 K.

Source of material

8-Methoxy-2-oxo-2*H*-chromene-3-carboxylic acid was synthesized according to the reported method [1]. Chemicals used for the synthesis were commercially available of AR grade, and were used as received without further purification. The yellow crystals of the title compound were obtained by slowly evaporating of ethanol solution at room temperature. The crystalline product thus was filtered, washed with ethanol and dried. Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol.

Experimental details

The hydrogen atoms were placed geometrically and refined using a riding model with d(C—H) = 0.93 Å (aromatic) or 0.96 Å (methyl), U_{iso}(H) = 1.2 U_{eq}(C) or U_{iso}(H) = 1.5 U_{eq}(C) and d(O—H) = 0.82 Å (carboxyl), U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

The title crystal structure is built up from $C_{11}H_8O_5$ molecules (figure, top). Only one kind of hydrogen bond is generated in the crystal packing (O4–H4···O3^{i}, symmetry code i: 2–x,1–y,1–z). The donor-acceptor distance is 1.818(1) Å with the bond angle 167.0(1)°. The hydrogen bonds connect each two molecules into a dimer. The prevalent interactions observed in the crystal are intermolecular C–H···π interactions established only between the parallel molecules. There are four kinds of type-V [2] C–H···π interactions generated between the aromatic hydrogen atoms and the corresponding π-system (figure, bottom): C3–H3···π^{i} (C4/C5/C6/C7/C8/C9), C5–H5···π^{i} (C1/C2/C3/C4/C9/O1), C3–H3···π^{ii} (C1/C2/C3/C4/C9/O1, symmetry code ii: –1+x,y,z), and C5–H5···π^{ii} (C1/C2/C3/C4/C9/O1). There is no π···π interaction estabilished, which is usual between parallel π-systems. Other C–H···π interactions are observed between the methyl hydrogen atoms and the corresponding π-system: C11–H11C···π^{iii} (C4/C5/C6/C7/C8/C9, symmetry code iii: x,y,z), C11–H11C···π^{iii} (C1/C2/C3/C4/ C9/O1), C11–H11B···π^{iii} (C1/C2/C3/C4/C9/O1), and C11–H11B···π^{iii} (C4/C5/C6/C7/C8/C9). The geometry of C11–H11C···π is a typical for a type-III interactions, in which the hydrogen atom is directly above the centre of the ring, but for the C–H bond points to the ring carbon. The geometry of other three C–H···π interactions belong to type V and VI. In the present crystal structure, weak C5–H5···O4^{i}, C6–H6···O3^{iv} and C6–H6···O2^{iv} interactions are also observed (symmetry code iv: x,y,1+z). The distances H···O are 2.766(1) Å (H5···O4^{i}), 2.758(1) Å (H6···O3^{iv}), and 2.436(1) Å (H6···O2^{iv}). The C···O contacts range from 3.31 to 3.68 Å, which is well inside the interval 3.0 to 4.0 Å, based on a survey of over 100 structures [3]. The C–H···O angles range from 139.2° to 167.3°, which is also in agreement with [3]. Although parallel molecules are found in the crystal, they are not packed layer by layer. The packing is like in the wall, in which the molecules is brick-like and they are bricked by various kinds of intermolecular interactions.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.25 × 0.41 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.23 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7127, 1770
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1570
$N(param)_{refined}$:	147
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.7844	0.4607	0.3851	0.039
H(5)	4*e*	0.6623	0.4379	0.6308	0.048
H(6)	4*e*	0.3978	0.3816	0.7625	0.053
H(7)	4*e*	0.0763	0.3076	0.6522	0.050
H(11A)	4*e*	–0.0871	0.2082	0.5093	0.077
H(11B)	4*e*	–0.3285	0.2137	0.3823	0.077
H(11C)	4*e*	–0.2932	0.2662	0.5079	0.077
H(4)	4*e*	1.0378	0.5113	0.1215	0.071

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.3959(3)	0.37661(7)	0.1329(1)	0.0372(7)	0.0435(8)	0.0271(7)	–0.0051(6)	0.0120(6)	0.0004(6)
C(2)	4*e*	0.6080(2)	0.42137(7)	0.2008(1)	0.0304(6)	0.0345(7)	0.0303(7)	0.0008(5)	0.0085(5)	0.0025(5)
C(3)	4*e*	0.6494(3)	0.43188(7)	0.3441(1)	0.0330(7)	0.0329(7)	0.0320(7)	–0.0011(5)	0.0059(5)	0.0008(5)
C(4)	4*e*	0.4921(3)	0.40014(7)	0.4352(1)	0.0360(7)	0.0338(7)	0.0282(7)	0.0026(5)	0.0078(5)	0.0020(5)
C(5)	4*e*	0.5312(3)	0.40917(8)	0.5852(2)	0.0481(8)	0.0427(8)	0.0293(7)	–0.0004(6)	0.0068(6)	–0.0013(6)
C(6)	4*e*	0.3740(3)	0.37515(8)	0.6636(2)	0.0553(9)	0.0536(9)	0.0259(7)	0.0053(7)	0.0119(6)	0.0032(6)
C(7)	4*e*	0.1783(3)	0.33084(8)	0.5968(2)	0.0454(8)	0.0495(9)	0.0352(8)	0.0045(7)	0.0190(6)	0.0107(6)
C(8)	4*e*	0.1346(3)	0.32112(7)	0.4492(2)	0.0347(7)	0.0371(7)	0.0357(7)	0.0020(6)	0.0106(6)	0.0055(6)
C(9)	4*e*	0.2949(3)	0.35675(6)	0.3695(1)	0.0338(7)	0.0344(7)	0.0260(6)	0.0031(5)	0.0089(5)	0.0029(5)
C(10)	4*e*	0.7784(3)	0.45531(7)	0.1115(1)	0.0319(7)	0.0357(7)	0.0312(7)	–0.0002(5)	0.0087(5)	0.0026(5)
C(11)	4*e*	–0.2023(3)	0.23872(8)	0.4492(2)	0.0436(8)	0.0468(9)	0.066(1)	–0.0056(7)	0.0189(7)	0.0161(8)
O(1)	4*e*	0.2508(2)	0.34567(5)	0.22442(9)	0.0395(5)	0.0454(6)	0.0268(5)	–0.0105(4)	0.0100(4)	–0.0011(4)
O(2)	4*e*	0.3318(2)	0.36349(7)	0.0082(1)	0.0651(8)	0.092(1)	0.0285(6)	–0.0375(7)	0.0152(5)	–0.0099(6)
O(3)	4*e*	0.7349(2)	0.44790(6)	–0.0227(1)	0.0494(6)	0.0662(7)	0.0311(6)	–0.0163(5)	0.0143(5)	0.0007(5)
O(4)	4*e*	0.9657(2)	0.49106(6)	0.1793(1)	0.0455(6)	0.0598(7)	0.0383(6)	–0.0203(5)	0.0106(5)	0.0038(5)
O(5)	4*e*	–0.0497(2)	0.28061(6)	0.3717(1)	0.0474(6)	0.0528(7)	0.0439(6)	–0.0152(5)	0.0141(5)	0.0051(5)

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References

1. Bigi, F.; Chesini, L.; Maggi, R.; Sartori, G.: Montmorillonite KSF as an Inorganic, Water Stable, and Reusable Catalyst for the Knoevenagel Synthesis of Coumarin-3-carboxylic Acids. J. Org. Chem. **64** (1999) 1033-1035.
2. Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J.: X–H···π (phenyl) interactions theoretical and crystallographic observations. J. Chem. Soc. Faraday Trans. **93** (1997) 3429-3436.
3. Desiraju, G. R.: The C–H···O hydrogen bond in crystals: What is it? Acc. Chem. Res. **24** (1991) 290-296.
4. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
6. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.