Journal of the Iranian Chemical Society, Vol. 3, No. 1, March 2006, pp. 46-50.

JOURNAL OF THE
Iranian
Chemical Society

The Crystal Structure of *tert*-Butyl Coumarin-3-carboxylate

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(Received 5 November 2005, Accepted 3 December 2005)

The crystal structure of *tert*-butyl coumarin-3-carboxylate has been determined. This compound crystallizes in the triclinic space group P-1 with cell parameters a = 5.8038(9) Å, b = 9.3022(16) Å, c = 12.421(2) Å, β = 97.107(5)°, V = 610.71(17) Å^3, D_{calc} = 1.339 mg m^{-3}, and Z = 2. The final R value is 0.0593 for 2396 reflections. The adjacent molecules form a cyclic dimer by intermolecular hydrogen bonds of type C=O…H with their carbonyl group and the hydrogen on C(3).

Keywords: Coumarin, X-ray structure, Single crystal, Hydrogen bond

INTRODUCTION

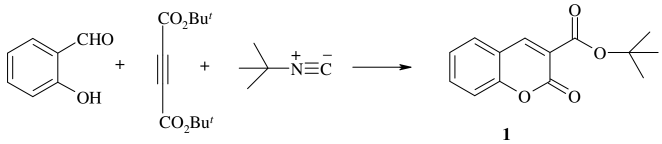
The coumarin ring system has a central position in various classes of naturally occurring compounds [1,2]. Coumarin derivatives, such as warfarin and trioxsalen, have a variety of potent bioactivities, and are being used clinically for curing platelet coagulation and leucoderma, respectively [3]. In this study, an X-ray analysis of *tert*-butyl coumarin-3-carboxylate (**1**) was undertaken in order to determine its crystal structure and inherent conformation.

EXPERIMENTAL

tert-Butyl coumarin-3-carboxylate (**1**) was synthesized in 90% yield from the reaction between *tert*-butyl isocyanide and di-*tert*-butyl acetylenedicarboxylate in the presence of 2-hydroxybenzaldehyde [4] (Fig. 1).

X-ray Diffraction Analysis

Crystallographic data and the refinement procedures are given in Table 1. The single crystals were grown from a CHCl$_3$/Et$_2$O solution. A colorless needle-shaped crystal having the dimensions of 0.30 × 0.20 × 0.05 mm was mounted on a glass fiber and used for data collection. The measurements were made with graphite-monochromatized Mo Kα radiation at 120 K. Intensities were corrected for Lorenz and polarization effects. The structure was solved by direct methods and expanded by Fourier techniques. All of the non-hydrogen atoms were refined anisotropically, and all of the hydrogens were fixed as a riding model over their heavier atoms. The molecular structure drawn by ORTEP-III is given in Fig. 2.



1

Fig. 1. Synthesis and chemical structure of *tert*-butyl coumarin-3-carboxylate (**1**).

RESULTS AND DISCUSSION

The molecular structure of **1**, showing the atom numbering

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Table 1. Crystal Data and Structure Refinement for Compound **1**

Empirical formula	$C_{14}H_{14}O_4$
Formula weight	246.25
Temperature	120 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 5.8038 (9) Å
	b = 9.3022 (16) Å
	c = 12.421 (2) Å
	β = 97.107 (5)°
Cell volume	610.71 (17) $Å^3$
Z	2
D_C	1.339 mg m^{-3}
Absorption coefficient (Mo Kα)	0.098 mm^{-1}
F (000)	260
Crystal size	0.30 × 0.20 × 0.05 mm
θ range for data collection	1.78 to 30.02°
Limiting indices	-8<=h<=8, -13<=k<=12, -17<=l<=17
Reflections collected	7236
Independent reflections	3499 [R(int) = 0.0272]
Completeness to θ = 30.02°	98.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.962 and 0.638
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3499/0/219
Goodness-of-fit on F^2	1.094
Final R indices [for 2396 rfln with $I>2\sigma(I)$]	R1 = 0.0593, wR2 = 0.0416
R indices (all data)	R1 = 0.0838, wR2 = 0.1532
Largest diff. peak and hole	0.568 and –0.250 e. $Å^{-3}$

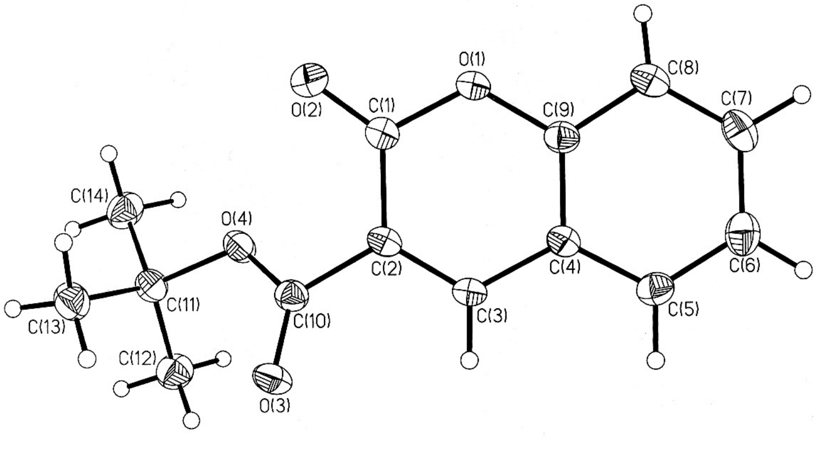

Fig. 2. The molecular structure of **1** along with the labeling atoms. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles for Compound **1**

O(1)-C(9)	1.3689 (17)	O(4)-C(11)	1.4778 (17)
O(1)-C(1)	1.3827 (17)	C(1)-C(2)	1.463 (2)
O(2)-C(1)	1.2024 (18)	C(2)-C(3)	1.344 (2)
O(1)-C(9)	1.2099 (17)	C(2)-C(10)	1.4952 (19)
O(4)-C(10)	1.3340 (17)	C(3)-C(4)	1.4367 (19)
C(9)-O(1)-C(1)	122.78 (11)	C(1)-C(2)-C(10)	119.73 (12)
C(10)-O(4)-C(11)	120.93 (11)	C(2)-C(3)-C(4)	120.84 (13)
O(2)-C(1)-O(1)	116.88 (13)	O(1)-C(9)-C(8)	117.40 (13)
O(2)-C(1)-C(2)	127.04 (13)	O(1)-C(9)-C(4)	121.23 (13)
O(1)-C(1)-C(2)	116.08 (12)	O(3)-C(10)-O(4)	125.98 (13)
C(3)-C(2)-C(1)	121.28 (13)	O(3)-C(10)-C(2)	122.94 (13)
C(3)-C(2)-C(10)	118.98 (13)		
C(9)-O(1)-C(1)-O(2)	176.03 (13)	C(1)-O(1)-C(9)-C(4)	-1.0 (2)
C(9)-O(1)-C(1)-C(2)	-3.13 (19)	C(7)-C(8)-C(9)-O(1)	-179.38 (13)
O(2)-C(1)-C(2)-C(3)	-173.12 (14)	C(3)-C(4)-C(9)-O(1)	2.49 (19)
O(1)-C(1)-C(2)-C(3)	5.94 (19)	C(3)-C(4)-C(9)-C(8)	-176.65 (12)
O(2)-C(1)-C(2)-C(10)	8.1 (2)	C(3)-O(4)-C(10)-O(3)	0.7 (2)
O(1)-C(1)-C(2)-C(10)	-172.87 (11)	C(11)-O(4)-C(10)-C(2)	177.05 (11)
C(1)-C(2)-C(3)-C(4)	-4.6 (2)	C(3)-C(2)-C(10)-O(3)	40.98 (19)
C(10)-C(2)-C(3)-C(4)	174.21 (11)	C(1)-C(2)-C(10)-O(3)	-140.17 (14)
C(2)-C(3)-C(4)-C(9)	0.36 (19)	C(3)-C(2)-C(10)-O(4)	-135.52 (13)
C(2)-C(3)-C(4)-C(5)	-176.13 (13)	C(1)-C(2)-C(10)-O(4)	43.32 (16)
C(9)-C(4)-C(5)-C(6)	0.5 (2)		

scheme is shown in Fig. 2. Selected bond lengths, bond angles, and torsion angles of **1** are listed in Table 2. Bond lengths and bond angles in the coumarin moiety of **1** are typical for coumarin derivatives [5]. The heterocyclic ring is distorted by about 5º, but the phenylene moiety is nearly planar. The ester carbonyl group is about 41º out of the plane of the heterocyclic ring system. There are no significant differences in bond distance and bond angles compared with other carboxylic acid esters [6,7]. All the other bond lengths fall within the expected range.

An anisotropic refinement using SHELXL-97 was started at this stage and R1 finally converged at 0.0593. The hydrogen atoms were placed at calculated positions and were not refined. Table 3 gives the details of the final coordinates and equivalent thermal parameters of non-hydrogen atoms.

There are two molecules in an asymmetric unit (see Fig. 3). The structure has intermolecular hydrogen bonds between the ester carbonyl group and the vinylic proton of the heterocyclic moiety of **1** (see Fig. 3 and Table 4).

Supplementary Material

CCDC-247583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallography Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Non-Hydrogen Atoms with RSDs' in Parentheses for **1**. *U*eq is Defined as One Third of the Trace of the Orthogonalized *U*ij Tensor

	x	*y*	*z*	*U*eq
O(1)	2404 (2)	6714 (1)	5102 (1)	23 (1)
O(2)	2336 (2)	8843 (1)	6574 (1)	33 (1)
O(3)	8477 (2)	11362 (1)	6403 (1)	25 (1)
O(4)	7086 (2)	10449 (1)	7730 (1)	24 (1)
C(1)	3471 (3)	8208 (2)	5883 (1)	22 (1)
C(2)	5860 (2)	8853 (2)	5764 (1)	20 (1)
C(3)	6846 (3)	8086 (2)	4878 (1)	20 (1)
C(4)	5655 (2)	6551 (2)	4065 (1)	20 (1)
C(5)	6649 (3)	5657 (2)	3167 (1)	24 (1)
C(6)	5433 (3)	4155 (2)	2453 (1)	30 (1)
C(7)	3242 (3)	3533 (2)	2637 (1)	28 (1)
C(8)	2220 (3)	4385 (2)	3518 (1)	24 (1)
C(9)	3442 (3)	5898 (2)	4228 (1)	21 (1)
C(10)	7263 (2)	10379 (2)	6654 (1)	21 (1)
C(11)	8415 (3)	11817 (2)	8761 (1)	24 (1)
C(12)	11068 (3)	11948 (2)	8812 (2)	30 (1)
C(13)	7619 (3)	13284 (2)	8746 (2)	30 (1)
C(14)	7650 (3)	11368 (2)	9756 (1)	31(1)

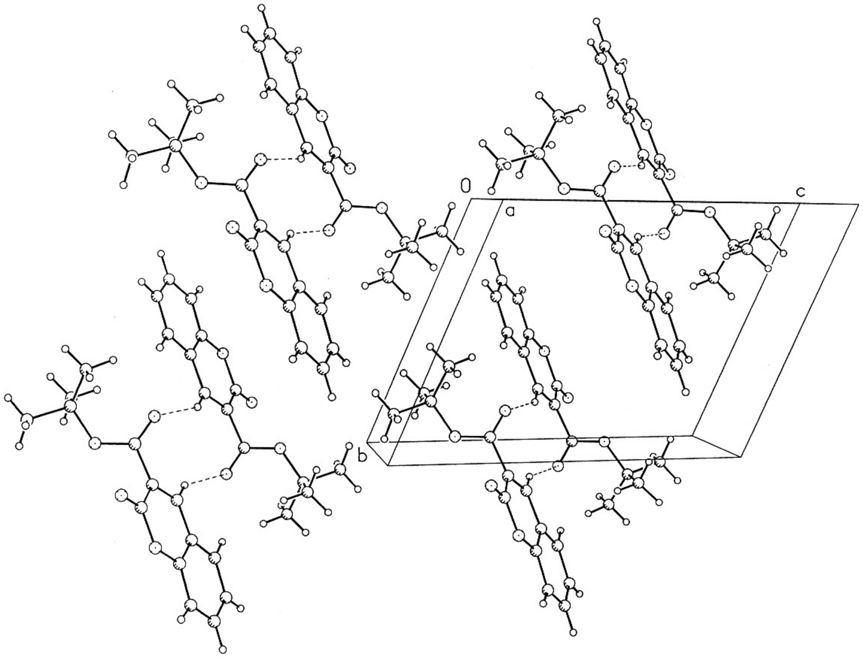

Fig. 3. The unit cell showing hydrogen bonding in **1**.

Table 4. Hydrogen Bonds for Compound **1** (Å and °)

D-H…A	D (D-H)	d (H…A)	D (D…A)	< (DHA)
C3-H3…O3_#1	0.93 (2)	2.53 (2)	3.36 (2)	151.3 (1.4)

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