Crystal Structure of 7-(Dimethylamino)-2H-1-benzopyran-2-one

Kanji KUBO,^{*†} Taisuke MATSUMOTO,^{**} and Haruko TAKECHI^{***}

^{*}Department of Life Science and Technology, Faculty of Engineering, Hokkai-Gakuen University, Asahimachi, Toyohira-ku, Sapporo 062-8605, Japan

^{**}Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

^{***}Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido 061-0293, Japan

The structure of 7-(dimethylamino)coumarin (**1**) was determined by X-ray crystallography. The structure of **1** contains two crystallographically independent molecules. The two molecules are almost planar. Intermolecular C-H...O, C-H... π , and π ... π interactions were observed in the crystal lattice.

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Coumarin derivatives have been found to be very useful as fluorescence materials and laser dyes, nonlinear optical materials and reagents, photorefractive materials, photo resists, intermediates for drug synthesis, luminescence materials, and analytical reagents.^{1,2} Although the fluorescence of the coumarin, itself, is weak, the introduction of a substituent group into coumarin increases the fluorescence intensity. Recently, we reported the synthesis and fluorescence properties of 7-(dimethylamino)coumarin and 7-(diethylamino)coumarin derivatives as fluoroionophores accessible for analytical purpose in the fields of analytical and biological chemistry.^{1,2} The crystal structures of 7-(diethylamino)coumarin³ have been reported. However the crystal structure of 7-(dimethylamino)coumarin (**1**) has not yet been reported. We now report on the crystal structure of **1** with the aim of the contributing to a deeper understanding of the substituent effect at 7-position of coumarin on the structure and crystal packing.

Compound (**1**) was synthesized by the reaction of 2-hydroxy-4-dimethylaminobenzaldehyde and carbethoxy-benzylidenetriphenylphosphorane in mesitylene, as reported in a previous paper.¹ Single crystals of **1** were grown in ethyl acetate at room temperature. Data collection and refinement parameters are listed in Table 1. The H atoms were positioned with the idealized geometry, and were refined to be isotropic ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$) using a riding model with C-H = 0.95 Å for aromatic H atoms and C-H = 0.98 Å for methyl H atoms.

Fig. 1 Chemical diagram of the title compound (**1**).

The selected bond distances and angles are collected in Table 2.

An ORTEP drawing of molecule of **1** is shown in Fig. 2. The structure of **1** contains two crystallographically independent molecules (A and B). The molecules are almost planar with a maximum deviation of $-0.216(3)$ Å for C11 in molecule A and $0.066(3)$ Å for C22 in B. The dihedral angles between the pyrone ring and the benzene ring are $2.5(1)^\circ$ for A and $2.0(1)^\circ$ for B, respectively. The dihedral angles between the benzene ring and the dimethylamino group are $10.3(1)^\circ$ for A and $2.0(1)^\circ$ for B.

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{11}\text{H}_{11}\text{NO}_2$	
Formula weight = 189.21	
$T = 113$ K	
Crystal system: Triclinic	Space group: $P\bar{1}$
$a = 6.601(2)$ Å	$\alpha = 79.89(2)^\circ$
$b = 7.433(2)$ Å	$\beta = 89.62(2)^\circ$
$c = 20.317(5)$ Å	$\gamma = 66.70(2)^\circ$
$V = 899.3(4)$ Å ³	$Z = 4$
$D_x = 1.397$ g/cm ³	
Radiation: Cu $K\alpha$ ($\lambda = 1.54187$ Å)	
$\mu(\text{Cu } K\alpha) = 7.920$ cm ⁻¹	$F(0\ 0\ 0) = 400$
Crystal size = $0.20 \times 0.20 \times 0.10$ mm ³	
No. of reflections collected = 11678	
No. of independent reflections = 3164	
θ range for data collection: 0.965 to 68.18°	
Data/Restraints/Parameters = 3164/0/257	
R indices [$I \geq 2\sigma(I)$]: $R1 = 0.0383$	
R indices (all data): $R1 = 0.0508$, $wR2 = 0.1461$	
Goodness-of-fit on $F^2 = 1.188$	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.22$ eÅ ⁻³	$(\Delta\rho)_{\text{min}} = -0.21$ eÅ ⁻³
Measurement: Rigaku RAXIS-RAPID diffractometer	
Data collection & cell refinement program: <i>CrystalClear</i>	
Data reduction program: <i>CrystalStructure 4.0</i>	
Structure solving program: <i>SIR2008</i>	
Structure refinement program: <i>Crystals</i>	
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[†] To whom correspondence should be addressed.
E-mail: kubo@lst.hokkai-s-u.ac.jp

Table 2 Selected bond distances and bond angles ($\text{\AA}$, $^\circ$)

C1-C2	1.442(5)	C12-C13	1.439(5)
C2-C3	1.347(5)	C13-C14	1.347(5)
C3-C4	1.427(4)	C14-C15	1.426(4)
C4-C5	1.408(5)	C15-C16	1.401(4)
C4-C9	1.393(5)	C15-C20	1.402(5)
C5-C6	1.367(4)	C16-C17	1.370(4)
C6-C7	1.416(5)	C17-C18	1.416(5)
C7-C8	1.416(5)	C18-C19	1.412(4)
C8-C9	1.376(4)	C19-C20	1.378(4)
O1-C1	1.383(4)	O3-C12	1.384(4)
O1-C9	1.391(4)	O3-C20	1.384(4)
O2-C1	1.218(4)	O4-C12	1.217(4)
N1-C7	1.367(4)	N2-C18	1.368(4)
N1-C10	1.456(4)	N2-C21	1.457(4)
N1-C11	1.455(5)	N2-C22	1.450(5)
C7-N1-C10	120.1(3)	C18-N2-C21	120.6(3)
C7-N1-C11	120.6(3)	C18-N2-C22	120.6(3)
C10-N1-C11	118.6(3)	C21-N2-C22	118.7(3)

Table 3 Hydrogen bond geometry ($\text{\AA}$, $^\circ$) of **1**

D-H...A	D-H	H...A	D...A	D-H...A
C3-H3...O2 ⁱ	0.95	2.465	3.399(4)	167
C5-H5...O1 ⁱ	0.95	2.656	3.562(4)	159
C10-H10A...O4 ⁱ	0.98	2.583	3.555(4)	171
C10-H10B...O4 ⁱⁱ	0.98	2.536	3.404(4)	148
C11-H11B...C12	0.98	2.858	3.777(5)	157
C14-H14...O4 ⁱ	0.95	2.475	3.419(5)	172
C16-H16...O3 ⁱ	0.95	2.654	3.575(4)	163
C21-H21B...O2 ⁱⁱⁱ	0.98	2.593	3.535(4)	161
C21-H21C...O2 ^{iv}	0.98	2.622	3.519(4)	152
C22-H22A...O2	0.98	2.625	3.417(4)	138
C22-H22C...O2 ⁱⁱⁱ	0.98	2.593	3.533(4)	160

for B, respectively.

As shown in Table 2, the bond lengths and angles in the coumarin ring system in both molecules are normal, and are in good agreement with those observed in 7-(diethylamino) coumarin,³ 7-(diethylamino)-3-(dimethylamino)coumarin,⁴ methyl 4-(7-(diethylamino)-2-oxo-2H-1-benzopyran-3-yl) benzoate,⁵ 7-(diethylamino)-3-((4-ethoxycarbonyl)thiazol-2-yl) coumarin,⁶ and 7-(diethylamino)-3-phenylcoumarin.⁶ The N atom of the dimethylamine group has a planar environment. The N1-C7 and N3-C18 bond lengths are close to that of the value (1.355 $\text{\AA}$)⁷ observed for a Csp^2-Nsp^2 bond. This means that the dimethylamino group substituted at the C7 position effects the conjugation system of coumarin. The angle between the planes of the two molecules is $1.8(1)^\circ$.

Intermolecular C-H... π and C-H...O interactions are observed in the crystal structure of **1** (Table 3 and Fig. 3), with distances that are typical for those types of interactions: C-H... π interaction = 2.8 – 3.1 $\text{\AA}$ ⁴⁻⁶ and C-H...O interaction = 2.4 – 2.7 $\text{\AA}$.⁴⁻⁶

Intermolecular π ... π interactions between the coumarin planes are shown in Fig. 3. The distance between the intermolecular coumarin planes is 3.376(4) $\text{\AA}$ for C7...C14, which is within the range associated with π ... π interactions (3.3 – 3.8 $\text{\AA}$).^{5,6}

The occurrence of these weak C-H...O, CH... π , and π ... π

Fig. 2 ORTEP structure of **1**, showing 50% probability ellipsoids. Fig. 3 Intermolecular C-H...O, CH... π , and π ... π interactions in **1**. Symmetry codes: (i) $x+1, y, z$ (ii) $1-x, 1-y, 2-z$ (iii) $1-x, 1-y, 1-z$ (iv) $x+1, y-1, z$.

interactions builds up a three-dimensional network.

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