

Crystal Structure of a Pyrrolyl-Substituted 4-Methylcoumarin

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The crystal structure of 7-(1H-pyrrol-1-yl)-4-methyl-2H-1-benzopyran-2-one was determined by X-ray diffraction. The crystal, C₁₄H₁₁NO₂, belongs to space group C2/c with cell dimensions $a = 17.74(1)\text{Å}$, $b = 7.343(3)\text{Å}$, $c = 16.242(6)\text{Å}$, $\beta = 92.349(9)^\circ$. The final R value is 0.047 for 2301 reflections ($I > 2.00\sigma(I)$). The coumarin and the pyrrole moieties are almost coplanar. The dihedral angle between the least-squares planes of the aromatic ring and the pyrrolyl group is $3.74(5)^\circ$.

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7-Aminocoumarin derivatives are highly fluorescent and are used as laser dyes and fluorescent probes.¹⁻³ Substituted 7-aminocoumarins form an important class of laser dyes for the blue-green region. In this paper we report on the crystal structure of 7-(1H-pyrrol-1-yl)-4-methyl-2H-1-benzopyran-2-one (I, see Figs. 1 and 2). This compound can be regarded as a modified 7-aminocoumarin with a larger π -conjugation.

Compound I was synthesized in the following manner:⁴ a

mixture of 1.0 g (5.7 mmol) of 7-amino-4-methylcoumarin and 0.9 g (6.8 mmol) of 2,5-dimethoxytetrahydrofuran was refluxed at 120°C in 20 ml of acetic acid for 1 h. After a 2% aqueous solution of NaOH was added, the organic layer was extracted with CHCl₃. The combined extract was washed with a saturated solution of NaCl. Followed by drying with anhydrous sodium

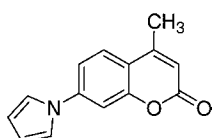


Fig. 1 Chemical structure of I.

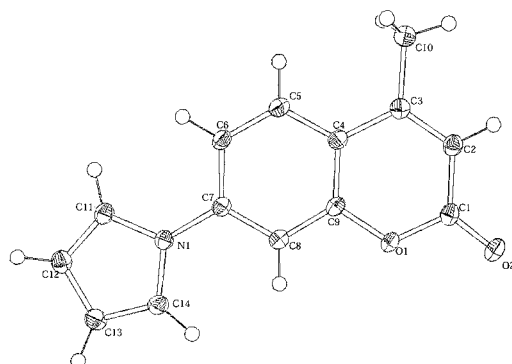


Fig. 2 Molecular structure of I along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 1 Crystal and experimental data

Formula: C ₁₄ H ₁₁ NO ₂
Formula weight: 225.25
Crystal system: monoclinic
$a = 17.74(1)\text{Å}$
$b = 7.343(3)\text{Å}$
$c = 16.242(6)\text{Å}$
$\beta = 92.349(9)^\circ$
$V = 2114(1)\text{Å}^3$
Space group: C2/c $Z = 8$
$D_{\text{calc}} = 1.415\text{ g/cm}^3$
$F(0\ 0\ 0) = 944.00$
$\mu(\text{Mo } K\alpha) = 0.95\text{ cm}^{-1}$
$T = 123\text{ K}$
$2\theta_{\text{max}} = 60.9^\circ$ with Mo $K\alpha$ (0.71070 Å)
No. observations = 2301 ($I > 2.00\sigma(I)$)
No. variables = 198
$R, R_w = 0.047, 0.070$
Goodness-of-fit = 1.21
$(\Delta/\sigma)_{\text{max}} = 0.000$
$(\Delta\rho)_{\text{max}} = 0.31\text{ e}^{-}/\text{Å}^3$
$(\Delta\rho)_{\text{min}} = -0.24\text{ e}^{-}/\text{Å}^3$
Diffractometer: Rigaku/MSM Mercury CCD
Program system: teXsan
Structure determination: direct method (SIR88)
Refinement: full-matrix least-squares

CCDC 607185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

atom	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	0.04823(5)	0.2625(1)	0.56952(6)	1.48(2)
O(2)	-0.06460(5)	0.3479(1)	0.52155(6)	1.83(2)
N(1)	0.28974(6)	0.1073(1)	0.68802(7)	1.34(2)
C(1)	-0.00635(7)	0.2705(2)	0.50682(8)	1.45(2)
C(2)	0.01039(7)	0.1830(2)	0.42949(8)	1.52(2)
C(3)	0.07643(7)	0.0966(2)	0.41779(7)	1.39(2)
C(4)	0.13284(7)	0.0936(2)	0.48447(8)	1.33(2)
C(5)	0.20418(7)	0.0117(2)	0.48051(8)	1.52(2)
C(6)	0.25596(7)	0.0146(2)	0.54643(8)	1.51(2)
C(7)	0.23736(7)	0.1012(2)	0.62019(8)	1.27(2)
C(8)	0.16671(7)	0.1815(2)	0.62613(8)	1.36(2)
C(9)	0.11622(7)	0.1779(2)	0.55885(8)	1.28(2)
C(10)	0.09128(8)	0.0038(2)	0.33783(8)	1.78(2)
C(11)	0.36241(7)	0.0371(2)	0.69059(8)	1.50(2)
C(12)	0.39304(7)	0.0631(2)	0.76837(8)	1.71(2)
C(13)	0.33816(7)	0.1521(2)	0.81574(8)	1.72(2)
C(14)	0.27557(7)	0.1773(2)	0.76523(8)	1.59(2)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha).$$

sulfate, the crude product was put on a chromatography column packed with silica gel and eluted with a hexane/ethyl acetate mixture (3/1) (recrystallized from a water/methanol mixture and a hexane/ethyl acetate mixture): Yield 54%; Mp 188 – 189°C; MS $m/z = 225$ (M^+); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.65 – 7.63 (1H, d), 7.36 – 7.26 (2H, m), 7.17 – 7.16 (2H, t), 6.41 – 6.40 (2H, t), 6.26 (1H, s), 2.45 (3H, s); IR (KBr, cm^{-1}) 3131, 3112, 1829, 1768, 1718, 1612, 1565, 1521, 1476, 1436; UV ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4$ $\text{M}^{-1} \text{cm}^{-1}$), $\text{C}_2\text{H}_5\text{OH}$) 329 (1.9), 237 (1.3), 202 (3.5); Found: C, 74.46; H, 4.93; N, 6.30%. Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: C, 74.65; H, 4.92; N, 6.24%.

Colorless crystals of I suitable for X-ray diffraction analysis were obtained by the slow evaporation of an ethanol solution at room temperature. Data collections were performed at 123 K. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71070 \text{ \AA}$). The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically. All calculations were performed using the teXsan crystallographic software package.

Table 1 lists the crystal data and the experimental conditions. Figure 2 illustrates an ORTEP diagram of the molecule along with the atomic-labeling scheme. The final position parameters are given in Table 2, and selected bond lengths, bond angles and torsion angles are listed in Table 3.

Table 3 Selected bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$)

C(4)	C(5)	1.405(2)	C(5)	C(6)	1.382(2)				
C(6)	C(7)	1.408(2)	C(7)	C(8)	1.392(2)				
C(8)	C(9)	1.385(2)	C(4)	C(9)	1.400(2)				
C(11)	C(12)	1.368(2)	C(12)	C(13)	1.424(2)				
C(13)	C(14)	1.366(2)	N(1)	C(7)	1.413(2)				
N(1)	C(11)	1.388(2)	N(1)	C(14)	1.388(2)				
C(5)	C(4)	C(9)	116.8(1)	C(4)	C(5)	C(6)	122.0(1)		
C(5)	C(6)	C(7)	119.7(1)	C(6)	C(7)	C(8)	119.6(1)		
C(7)	C(8)	C(9)	119.5(1)	C(4)	C(9)	C(8)	122.5(1)		
C(7)	N(1)	C(14)	125.3(1)	C(7)	N(1)	C(11)	126.3(1)		
C(11)	N(1)	C(14)	108.2(1)	N(1)	C(7)	C(8)	119.9(1)		
N(1)	C(7)	C(6)	120.5(1)						
N(1)	C(7)	C(6)	C(5)	-179.4(1)	N(1)	C(7)	C(8)	C(9)	178.8(1)
N(1)	C(11)	C(12)	C(13)	-0.1(1)	N(1)	C(14)	C(13)	C(12)	-0.1(1)
C(6)	C(7)	N(1)	C(11)	1.5(2)	C(6)	C(7)	N(1)	C(14)	-175.2(1)
C(7)	N(1)	C(11)	C(12)	-177.1(1)	C(7)	N(1)	C(14)	C(13)	177.2(1)
C(8)	C(7)	N(1)	C(11)	-178.5(1)	C(8)	C(7)	N(1)	C(14)	4.8(2)
C(11)	N(1)	C(14)	C(13)	0.1(1)	C(12)	C(11)	N(1)	C(14)	0.0(1)

Estimated standard deviations in the least significant figure are given in parentheses.

The coumarin and the pyrrole moieties are almost coplanar. The dihedral angle between the least-squares planes of the aromatic ring and the pyrrolyl group is $3.74(5)^\circ$. The sum of bond angles around N(1) is 359.8° . This value indicates that the nitrogen is sp^2 -hybridized. The geometry of an aromatic ring in I is similar to that of bicyclic coumarins.⁵ In the crystal lattice, coumarin molecules related by an inversion center are stacked by strong π -interactions with the $\text{C}(1)\cdots\text{C}(3)^i$ distances of $3.230(2)\text{\AA}$.

[symmetry code: (i) $-x, -y, 1 - z$]

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