

Crystal Structure of a Pyrrolyl-Substituted 4-Trifluoromethylcoumarin

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Crystal Structure of 7-(1*H*-pyrrol-1-yl)-4-trifluoromethyl-2*H*-1-benzopyran-2-one has been determined by X-ray diffraction. The crystal, C₁₄H₈NO₂F₃, belongs to space group *P*2₁/*n* with cell dimensions of *a* = 10.201(6) Å, *b* = 8.481(8) Å, *c* = 13.864(8) Å, β = 109.75(2)°. The final *R* value is 0.041 for 2602 reflections (*I* > 2.00σ(*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 6.98(4)°.

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Coumarin does not fluoresce, whereas coumarin derivatives substituted at the 7-position with an amino or hydroxy group are highly fluorescent. The latter type of coumarins are widely used as laser dyes, fluorescent probes, and optical brighteners.^{1,2} In this paper we report on the crystal structure of 7-(1*H*-pyrrol-1-yl)-4-trifluoromethyl-2*H*-1-benzopyran-2-one (I, see Figs. 1 and 2). This compound can be regarded as a modified 7-aminocoumarin with larger π -conjugation.

Compound I was synthesized in the following manner:³ a mixture of 0.7 g (3.0 mmol) of 7-amino-4-trifluoromethylcoumarin and 0.5 g (3.8 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 extracts were washed with a saturated solution of NaCl. After drying with anhydrous sodium sulfate, the crude product was put on a chromatography column packed with silica gel and eluted with a hexane/ethyl acetate mixture (4/1) (recrystallized from a water/methanol mixture and a hexane/ethyl acetate mixture): Yield 21%; Mp 142–144°C; MS *m/z* = 279 (M⁺); ¹H-NMR (500 MHz, CDCl₃) δ 7.84–7.81 (1H, d), 7.72–7.68 (2H, m), 7.54–7.50 (2H, t), 6.86 (1H, s), 6.39–6.38 (2H, t); IR (KBr, cm⁻¹) 3154, 3115, 1882, 1741, 1615, 1564, 1527, 1473; UV (λ_{\max} /nm ($\epsilon/10^4$ M⁻¹ cm⁻¹), C₂H₅OH) 346 (1.8), 240 (1.0), 202 (3.0); Found: C, 60.27; H, 2.88; N, 5.01%.

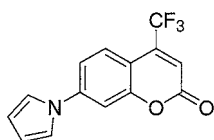


Fig. 1 Chemical structure of I.

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Calcd for C₁₄H₈F₃NO₂: C, 60.22; H, 2.88; N, 5.01%.

Pale-yellow crystals of I suitable for X-ray diffraction analysis were obtained by the slow evaporation of a hexane solution at room temperature. Data collections were performed at 123 K. All measurements were made on a Rigaku/MS Mercury CCD diffractometer with graphite-monochromated Mo *K*_α radiation

Table 1 Crystal and experimental data

| |
|--|
| Formula: C ₁₄ H ₈ NO ₂ F ₃ |
| Formula weight: 279.22 |
| Crystal system: monoclinic |
| <i>a</i> = 10.201(6) Å |
| <i>b</i> = 8.481(8) Å |
| <i>c</i> = 13.864(8) Å |
| β = 109.75(2)° |
| <i>V</i> = 1128(1) Å ³ |
| Space group: <i>P</i> 2 ₁ / <i>n</i> <i>Z</i> = 4 |
| <i>D</i> _{calc} = 1.643 g/cm ³ |
| <i>F</i> (0 0 0) = 568.00 |
| μ (Mo <i>K</i> _α) = 1.43 cm ⁻¹ |
| <i>T</i> = 123 K |
| $2\theta_{\max}$ = 61.0° with Mo <i>K</i> _α (0.7107 Å) |
| No. observations = 2602 (<i>I</i> > 2.00σ(<i>I</i>)) |
| No. variables = 213 |
| <i>R</i> , <i>R</i> _w = 0.041, 0.063 |
| Goodness-of-fit = 1.31 |
| (Δ /σ) _{max} = 0.000 |
| ($\Delta\rho$) _{max} = 0.30 e ⁻ /Å ³ |
| ($\Delta\rho$) _{min} = -0.19 e ⁻ /Å ³ |
| Diffractometer: Rigaku/MS Mercury CCD |
| Program system: teXsan |
| Structure determination: direct method (SIR88) |
| Refinement: full-matrix least-squares |

CCDC 606660 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

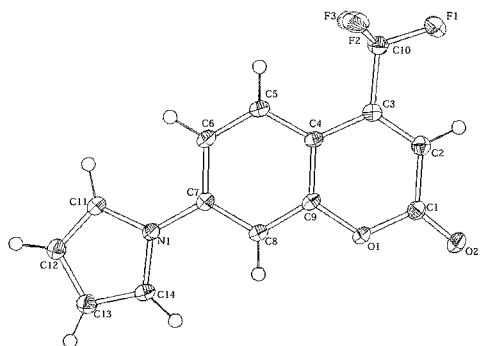


Fig. 2 Molecular structure of I along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

($\lambda = 0.7107 \text{ \AA}$). 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 located by a difference Fourier synthesis, and their positional and isotropic displacement parameters were refined. All calculations were performed using the teXsan crystallographic software package.

Table 1 lists the crystal data and experimental conditions. Figure 2 illustrates an ORTEP diagram of the molecule with the atomic-labeling scheme. The final position parameters are given in Table 2.

In the crystal lattice, coumarin molecules related by an inversion center are stacked by strong π -interactions with the C(7)···C(14)ⁱ distances of 3.357(2) Å. Stacks of molecules are further interconnected by the F(2)···F(3)ⁱⁱ short contacts of 2.911(1) Å. [symmetry code: (i) $-x + 1, -y + 2, -z$; (ii) $-x + 1/2, y + 1/2, -z + 1/2$] 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 6.98(4)°. The sum of the bond angles around N(1) is 359.89°. 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.⁴ The N(1)–C(11) and N(1)–C(14) bonds in I are 1.386(2) and 1.389(1) Å, respectively. These bonds are significantly shorter

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

| Atom | x | y | z | $B_{eq}(\text{\AA}^2)$ |
|-------|-------------|-------------|-------------|------------------------|
| F(1) | 0.12106(8) | 0.33429(10) | 0.13915(6) | 2.18(2) |
| F(2) | 0.21001(9) | 0.55592(9) | 0.20548(6) | 2.27(2) |
| F(3) | 0.34309(8) | 0.35575(9) | 0.21239(6) | 2.07(2) |
| O(1) | 0.26307(8) | 0.58926(10) | -0.13179(6) | 1.43(2) |
| O(2) | 0.09446(9) | 0.4272(1) | -0.21773(7) | 1.88(2) |
| N(1) | 0.66948(10) | 0.8968(1) | 0.03056(7) | 1.27(2) |
| C(1) | 0.1650(1) | 0.4762(1) | -0.13460(9) | 1.43(2) |
| C(2) | 0.1542(1) | 0.4273(1) | -0.03687(9) | 1.51(2) |
| C(3) | 0.2437(1) | 0.4821(1) | 0.05210(9) | 1.34(2) |
| C(4) | 0.3545(1) | 0.5898(1) | 0.05393(8) | 1.23(2) |
| C(5) | 0.4595(1) | 0.6459(1) | 0.14162(9) | 1.44(2) |
| C(6) | 0.5619(1) | 0.7460(1) | 0.13423(9) | 1.41(2) |
| C(7) | 0.5633(1) | 0.7961(1) | 0.03776(8) | 1.21(2) |
| C(8) | 0.4597(1) | 0.7435(1) | -0.05061(8) | 1.29(2) |
| C(9) | 0.3589(1) | 0.6411(1) | -0.04114(8) | 1.23(2) |
| C(10) | 0.2294(1) | 0.4313(1) | 0.15255(9) | 1.61(2) |
| C(11) | 0.7846(1) | 0.9463(1) | 0.11138(9) | 1.67(2) |
| C(12) | 0.8669(1) | 1.0341(2) | 0.07235(10) | 1.87(2) |
| C(13) | 0.8011(1) | 1.0399(1) | -0.03605(9) | 1.69(2) |
| C(14) | 0.6808(1) | 0.9550(1) | -0.05996(9) | 1.46(2) |

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

than the corresponding bond [1.40 Å] in *N*-methylpyrrole.⁵ This finding suggests a π -conjugation between the pyrrole and coumarin rings.

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