Synthesis and Crystal Structure of Pyrano-[3,2-*c*]-chromene Derivative

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The title compound was synthesized and the structure was investigated by X-ray crystallography. The compound crystallizes in the triclinic crystal class in the space group $P\bar{1}$ with cell parameters $a = 7.794(5)\text{\AA}$, $b = 11.736(1)\text{\AA}$, $c = 12.422(1)\text{\AA}$, $\alpha = 112.27(2)^\circ$, $\beta = 97.383(5)^\circ$, $\gamma = 103.876(5)^\circ$, $Z = 2$. The structure exhibits intermolecular hydrogen bonds of the type N-H...O and N-H...N.

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4-Hydroxy coumarin serves as a powerful tool for constructing 3,4-positionally fused heterocyclic systems.¹ The scaffolds, composed of three skeletal rings including coumarin and fused pyran skeleton, possess anti-bacterial,² coronary dilatatory, anti-coagulant and anti-viral activity. Earlier our research group prepared many derivatives of the fused heterocycles at the C3-C4 position of coumarin to study their anti-HIV activity; the compounds exhibited good antimicrobial activity. This observation has further led us to work on synthetic aspects of the fused benzopyran system at the 3,4 positions. We present here the synthesis and structure of the title molecule. The molecule is being assessed for biological activity.

Preparation of (3-phenoxybenzyl)melanonitrile. In a clean dry beaker, 3-phenoxy benzaldehyde (0.01 mol) was taken and cooled to 5°; then, melanonitrile (0.01 mol) was added dropwise along with piperidine (3 to 4 drops) as a base catalyst. After thorough mixing and keeping at room temperature, the reaction mass was poured into ice cold water, filtered, washed with water, dried and recrystallised from methanol. The yield was 85–87%.

Preparation of 2-amino-5-oxo-4-(3-phenoxyphenyl)-4H,5H-pyrano-[3,2-*c*]chromene-3-carbonitrile. A mixture of 4-hydroxycoumarin (0.01 mol) and melanonitrile (0.01 mol) in ethanol (25 ml) and piperidine (6 to 7 drops as a base catalyst) was refluxed on a steam bath for 3 to 4 h. The solvent was then removed by treating in a rotary evaporator, and the product was washed with chilled methanol and filtered. The solid product was crystallized from DMF. The yield was 25% with a melting

point of 225°C.

Method of crystallization. 2-Amino-5-oxo-4-(3-phenoxyphenyl)-4H,5H-pyrano[3,2-*c*]chromene-3-carbonitrile (0.5 g) was taken in 10 ml of DMF. One gram of charcoal was added and heated for 2 to 3 min. The solution was filtered while hot through Whatmann 42 filter paper and corked using a filter paper. The solution was kept in a corked flask, which led to slow evaporation of the solvent. This gave good single crystals that were then washed with chilled ethanol. A schematic diagram of the molecule is shown in Fig. 1.

A single crystal of the title compound with dimensions of 0.3 × 0.3 × 0.2 mm was chosen for X-ray diffraction studies. The data were collected on a DIPLabo Image Plate system with graphite monochromated Mo K_α radiation. Thirty six frames of data were collected in the oscillation mode with an oscillation range of 5° and processed using Denzo.³ The reflections were merged with Scalepack. All of the frames could be indexed

Fig. 1 Schematic diagram.

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Table 1 Crystal data and structure refinement table

CCDC 294991	
Empirical formula	C ₂₅ H ₁₆ N ₂ O ₄
Formula weight	408.40
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ $Z = 2$
Cell dimensions	
	$a = 7.794(5)\text{\AA}$, $b = 11.736(1)\text{\AA}$, $c = 12.422(1)\text{\AA}$
	$\alpha = 112.27(2)^\circ$, $\beta = 97.383(5)^\circ$, $\gamma = 103.876(5)^\circ$
Volume	989.90(14) Å ³
D_c	1.370 Mg/m ³
$\theta_{\max}$	32.49°
R	0.0664
Data/restraints/parameters	5807/0/281
$(\Delta/\sigma)_{\max}$	0.000
$(\Delta\rho)_{\max}$	0.444 e Å ⁻³
$(\Delta\rho)_{\min}$	-0.283 e Å ⁻³
Refinement method	Full-matrix least-squares on F^2
Measurement	DIPLabo Kappa
Program system	Denzo
Structure determination	SHELXS-97
Refinement	full-matrix: SHELXL-97

Fig. 2 ORTEP drawing of the molecule at 50% probability.

Table 2 Selected bond lengths (Å) and bond angles (°)

Atoms	Length	Atoms	Length
O1-C2	1.381(2)	C10-N18	1.333(2)
O9-C10	1.3733(17)	O15-C14	1.208(2)
C8-C7	1.443(2)	C16-N17	1.145(2)
O9-C8	1.210(2)	O25-C21	1.395(2)
C11-C12-C19	110.35(13)	N18-C10-O9	109.59(13)
C13-C12-C19	114.69(12)	C20-C19-C12	118.67(15)
O15-C14-O1	116.33(16)	C26-O25-C21	117.45(14)
N18-C10-C11	129.20(14)	C27-C26-O25	117.52(19)

using primitive triclinic lattice. The structure was solved by direct methods using SHELXS-97.⁴ The structure was refined by a full-matrix least squares method with anisotropic temperature factors for non-hydrogen atoms using SHELXL-97.⁴ The hydrogen atoms were fixed at chemically acceptable positions and were refined with isotropic temperature factors. The crystal and experimental details are given in Table 1. An ORTEP drawing of the molecule at 50% probability is shown in Fig. 2. Table 2 gives selected bond lengths and bond angles of the non-hydrogen atoms.

The pyran ring [2] of the coumarin is planar, while the other pyran ring [3] adopts a flattened boat conformation with the atoms O9 and C12 deviating from the Cremer and Pople plane defined by atoms (C8 C10 C11 C13) by 0.1213(16)Å and

0.1545(18) Å, respectively. The value of the puckering amplitude,⁵ (Q) is 0.2469(18) Å. The torsion angle about C13 C12 C19 C24 being 32.2° reflects +*syn*-clinal confirmation of the phenyl ring [4] w.r.t the pyran ring [3]. The dihedral angle between the phenyl ring [4] and the fused benzopyran moiety (O1–C14) is 89.85(9)°, indicating that they are almost perpendicular to each other while that about the phenyl rings [4 & 5] bridged by the oxygen is 71.93(13)°. The torsion angle about C21 O25 C26 C31 is –52.3(3)°. The structure exhibits intermolecular hydrogen bonds of the type N–H...N and N–H...O. The intermolecular hydrogen bonds are N(18)–H(19A)...N(17) (3.035(3) Å, 163.1(3)°), N(18)–H(19B)...O(15) (2.913(2) Å, 164.78(2)°) with symmetry codes (1 – x, 1 – y, –z) and (–1 + x, y, z), respectively. The packing of the molecules exhibit layered stacking when viewed down the *a*-axis. These layers are linked *via* hydrogen bonds, which in turn form a linear polymeric chain.

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