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# Crystal structure analysis of 4-(7-fluoro-4-oxo-4H-chromen-3-yl)-2-(methylamino)-3-nitropyrano [3,2-c] chromen-5(4H)-one chloroform monosolvate

**R. Raja[1]*, S. Kandasamy[2], P. T. Perumal[2]**

[1]*Department of Physics, Presidency College (Autonomous), Chennai-600 005, India
[2]Organic Chemistry Division, CSIR Central Leather Research Institute, Adyar, Chennai-600 020, India

**Abstract:** The crystal structure of 4-(7-fluoro-4-oxo-4H-chromen-3-yl)-2-(methylamino)-3-nitropyrano [3,2-c] chromen-5(4H)-one ($C_{23}H_{14}Cl_3FN_2O_7$). The compound crystallizes in triclinic P-1 space group with unit cell parameters at 296(2) K as follows: a = 7.9788(5) Å, b = 11.5381(8) Å, c = 13.1235(8) Å, α = 87.568(3)°, β = 87.219(3)°, γ = 70.616(3)°. The fluoro-substituted benzene ring is approximately perpendicular to the mean plane of the 4H-benzo[h] chromene ring system [maximum deviation = -0.007 Å]. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares procedures to the final $R_1$ of 0.0554 using SHELXL programs.
**Key Words:** Chromene, nitropyran and crystal structure.

## Introduction

Chromene (Benzopyran) is one of the privileged medicinal pharmacophore which appears as an important structural component in natural compounds and generated great attention because of their interesting biological activity. It is known that certain natural and synthetic chromene derivatives possess important biological activities such as antitumor, antivascular[1], antimicrobial[2], antioxidant[3]. Chromene derivatives are very important heterocyclic compounds that have a variety of industrial, biological and chemical synthesis applications[4]. Against this background, the X-ray analysis of the title compound has been carried out to study its structural aspects.

## Experimental

### X-ray Structure Determination

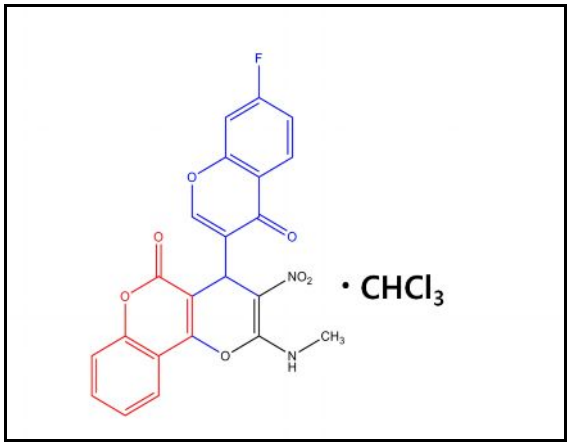
Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker[5] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at Department of chemistry, IIT, Chennai, India. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares procedures using the SHELXL programs[6]. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3[7]. The crystallographic data for the compound are listed in Table 1.

**Table 1: Crystal data and structure refinement of the titled compound**

| **Compound** | **Parameters** |
|---|---|
| Empirical formula | $C_{23}\ H_{14}\ Cl_3\ F\ N_2\ O_7$ |
| Formula weight | 555.71 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.9788(5) Å alpha = 87.568(3)° |
| | b = 11.5381(8) Å beta = 87.219(3)° |
| | c = 13.1235(8) Å gamma = 70.616(3)° |
| Volume | 1137.88(13) $Å^3$ |
| Z, Calculated density | 2, 1.622 $Mg/m^3$ |
| Absorption coefficient | 0.461 $mm^{-1}$ |
| F(000) | 564 |
| Crystal size | 0.30 x 0.25 x 0.20 mm |
| Theta range for data collection | 1.87 to 24.68 deg. |
| Limiting indices | -8<=h<=9, -13<=k<=13, -15<=l<=15 |
| Reflections collected / unique | 11312 / 3762 [R(int) = 0.0422] |
| Completeness to theta = 24.68 | 96.90% |
| Max. and min. transmission | 0.912 and 0.891 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3762 / 0 / 325 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indices [I>2sigma(I)] | **R1 = 0.0554**, wR2 = 0.1553 |
| R indices (all data) | R1 = 0.0737, wR2 = 0.1762 |
| Largest diff. peak and hole | 0.411 and -0.524 e. $Å^{-3}$ |

**Synthesis of the compound**

A solution of 4-Hydroxycoumarin (0.81g, 5mmol), 7-fluoro-4-oxo-4H-chromene-3-carbaldehyde (0.81g, 5mmol) and NMSM(0.74g, 5mmol) were selected as substrate to the reaction. Initially, the above three component coupling was carried out in EtOH at room temperature (2h) in the presence of piperidine (0.1eq), as a catalyst. Upon completion of the reaction, the mixture was filtered, and washed with ethanol to obtain desired product. The combination of ethanol piperidine has obtained excellent result in the experiments with short reaction time. The overall yield 90% was obtained. The resulting solution was subjected to crystallization by slow evaporation of the solvent for 48 hours resulting in the formation of single crystals. The scheme diagram is given below.




**Results and Discussion**

The symmetric unit of the title compound is shown in Fig. 1. The pyran ring (O3/C8-C12) is very similar to a Screw-Boat conformation with puckering parameters[8], Q = 0.181(3), ϴ = 101.2(9)° and ϕ = 8.9(9)°.

The chromene rings O1 and O6 atoms are deviating from the mean plane of (O1/C1-C9) and (O7/C14-C22) by 0.015 and 0.005Å, respectively. The pyran ring is almost orthogonal to the chromene rings, making a dihedral angle of 7.4(1) and 90.1(1)°. The methylamino group (N2/C13) is slightly twisted from the attached pyran ring (O3/C8-C12) with the torsion angle C11-C12-N2-C13 of -174.4(3)°. An intramolecular N2---H2...O4 hydrogen bond generates an S(6) ring motif.

In the crystal, molecules are linked via N---H...O hydrogen bonds, forming $R^2_2(12)$ rings and it forms chain running parallel to the b-axis (Fig 2 & Table 2). The crystal packing is further stabilized by C---H...O and C---H...$\pi$ intermolecular interactions (Fig 3). The selected bond lengths and angles are listed in table 3 and 4, respectively.

**Table 2: Hydrogen-bond geometry [Å]**

| Distance (Å) | | | | Angle (°) |
|---|---|---|---|---|
| D—H…A | D—H | H…A | D…A | D—H…A |
| N2---H2…O4$^{i}$ | 0.86 | 2.20 | 2.926(3) | 142 |
| C6---H6…O6$^{ii}$ | 0.93 | 2.44 | 3.113(4) | 129 |
| C13---H13C…Cg4$^{iii}$ | 61 | 2.93 | 3.655 | 134 |

**Symmetry code: i) 1-x,2-y,1-z**
**ii) 2-x,1-y,1-z**
**iii) 2-x,1-y,1-z**

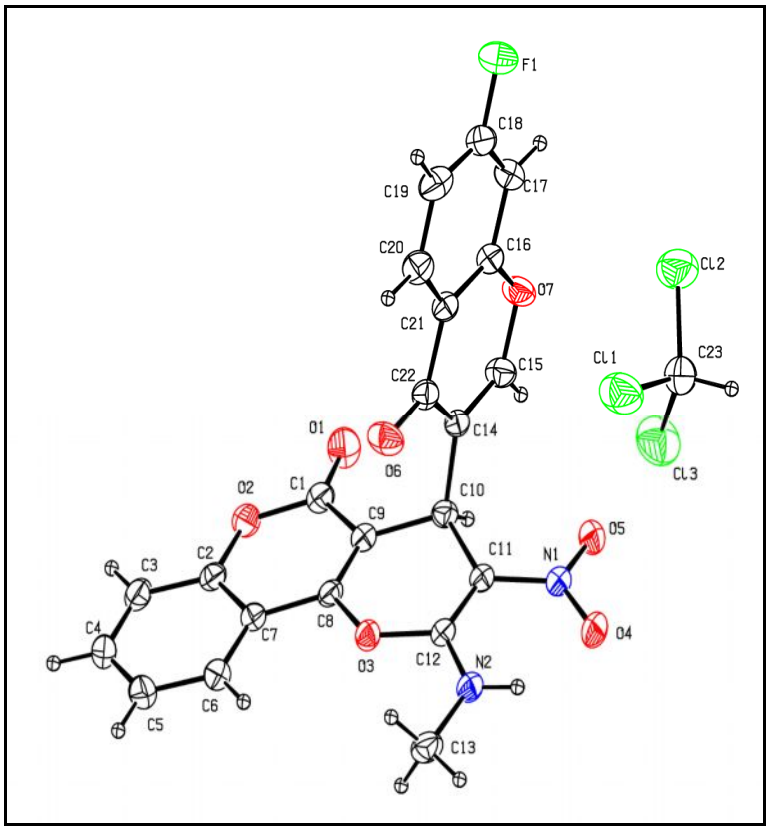



**Fig.1. The molecular structure of the title compound, with the atom-numbering scheme. The displacement ellipsoids are drawn at 30% probability level. H atoms are shown as spheres of arbitrary radius.**

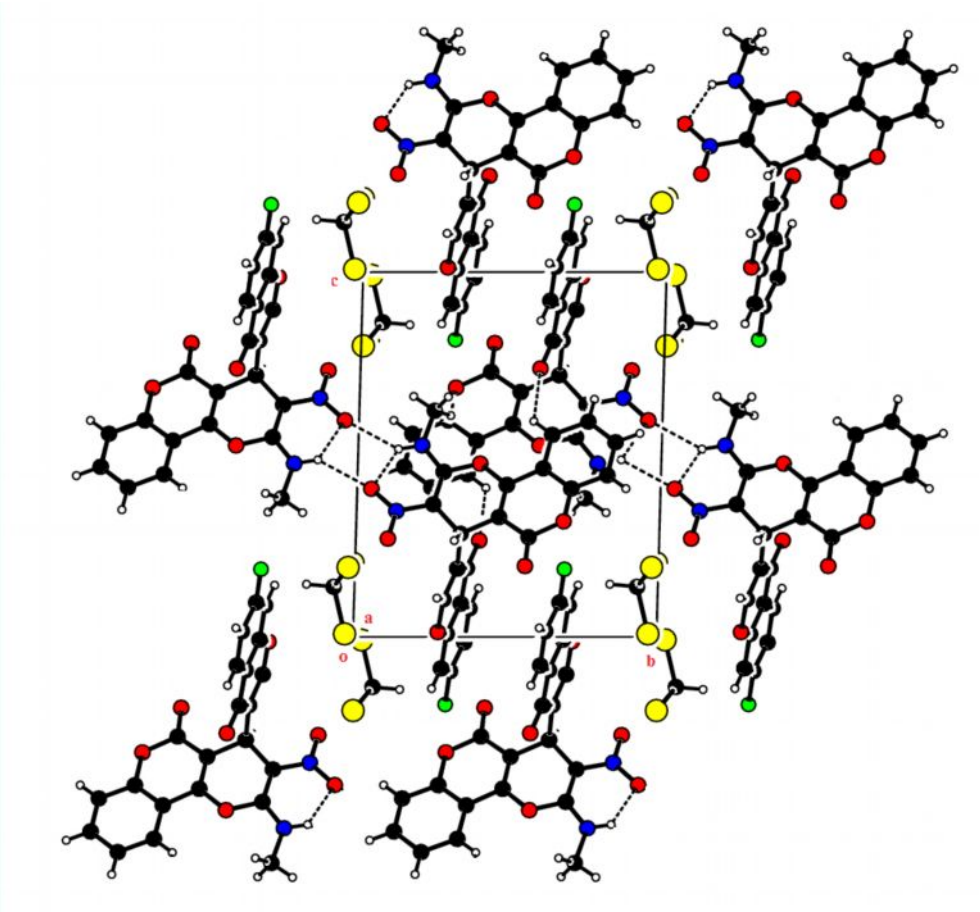



**Fig.2. The crystal packing of the title compound, viewed along a axis, showing N2---H2...O4 hydrogen bonds producing $R^2_2(12)$ chains parallel to b axis. The hydrogen bonds are shown as dashed lines (see Table 2 for details).**

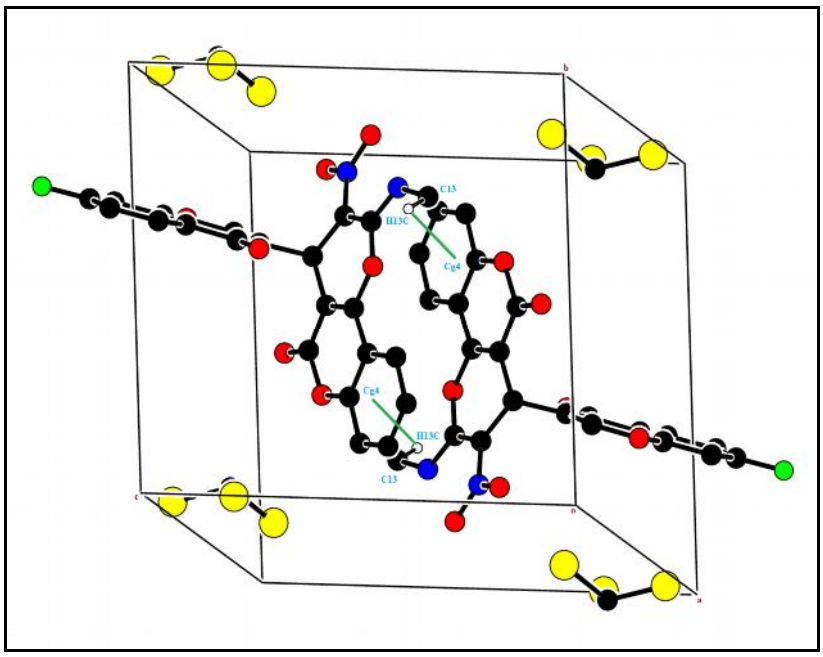



**Fig.3. The crystal packing of the title compound, viewed along a axis, showing C---H…$\pi$ hydrogen bonds intermolecular interactions.**

**Table 3: Selected Bond lengths (Å)**

| Atom | Length |
|---|---|
| C(1)-O(1) | 1.199(4) |
| C(1)-O(2) | 1.381(4) |
| C(1)-C(9) | 1.452(4) |
| C(2)-O(2) | 1.371(4) |
| C(2)-C(3) | 1.379(4) |
| C(2)-C(7) | 1.396(4) |
| C(3)-C(4) | 1.371(5) |
| C(3)-H(3) | 0.93 |
| C(4)-C(5) | 1.388(5) |
| C(4)-H(4) | 0.93 |
| C(5)-C(6) | 1.379(4) |
| C(5)-H(5) | 0.93 |
| C(6)-C(7) | 1.393(4) |
| C(6)-H(6) | 0.93 |
| C(7)-C(8) | 1.436(4) |
| C(8)-C(9) | 1.328(4) |
| C(8)-O(3) | 1.386(3) |
| C(9)-C(10) | 1.507(4) |
| C(10)-C(11) | 1.503(4) |
| C(10)-C(14) | 1.522(4) |
| C(10)-H(10) | 0.98 |
| C(11)-N(1) | 1.379(4) |
| C(11)-C(12) | 1.383(4) |
| C(12)-N(2) | 1.320(4) |
| C(12)-O(3) | 1.354(3) |
| C(13)-N(2) | 1.443(4) |

**Table 4: Selected Bond angles (º)**

| Atom | Angle |
|---|---|
| O(1)-C(1)-O(2) | 117.0(3) |
| O(1)-C(1)-C(9) | 125.5(3) |
| O(2)-C(1)-C(9) | 117.5(3) |
| O(2)-C(2)-C(3) | 118.0(3) |
| O(2)-C(2)-C(7) | 121.2(3) |
| C(3)-C(2)-C(7) | 120.7(3) |
| C(4)-C(3)-C(2) | 119.1(3) |
| C(4)-C(3)-H(3) | 120.4 |
| C(2)-C(3)-H(3) | 120.4 |
| C(3)-C(4)-C(5) | 121.5(3) |
| C(3)-C(4)-H(4) | 119.3 |
| C(5)-C(4)-H(4) | 119.3 |
| C(6)-C(5)-C(4) | 119.4(3) |
| C(6)-C(5)-H(5) | 120.3 |
| C(4)-C(5)-H(5) | 120.3 |
| C(5)-C(6)-C(7) | 120.1(3) |
| C(5)-C(6)-H(6) | 119.9 |
| C(7)-C(6)-H(6) | 119.9 |
| C(6)-C(7)-C(2) | 119.2(3) |
| C(6)-C(7)-C(8) | 125.0(3) |
| C(2)-C(7)-C(8) | 115.8(3) |
| C(9)-C(8)-O(3) | 122.8(2) |
| C(9)-C(8)-C(7) | 124.0(3) |
| O(3)-C(8)-C(7) | 113.1(2) |
| C(8)-C(9)-C(1) | 119.0(3) |
| C(8)-C(9)-C(10) | 122.7(2) |

## Conclusion

The crystal structure analysis of a novel Chromen-5(4H) compound was studied using x-ray diffraction method. In the crystal, molecules are linked via N---H...O hydrogen bonds, forming $R^2_2(12)$ rings motif and it forms chains. The crystal packing is further stabilized by C---H...O and C---H...$\pi$ intermolecular interactions.

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