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# 3,3’-(p-tolylmethylene)bis(4-amino-2H-chromen-2-one): X-Ray Crystallographic Investigation and Crystal Structure

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## Abstract:

Coumarins(2H-chromen-2-one) are organic compound of naturally occurring photochemical found in many plants species and very well known for their biological activity, such as antibacterial, antioxidant, antifungal agent, anticancer, anticonvulsant and antiviral activities. In view of this prominence significance, we report here the novel coumarin derivative crystal structure of 3,3’-(p-tolylmethylene)bis(4-amino-2H-chromen-2-one) ($C_{26}H_{20}N_2O_4$). X-Ray crystallography technique is used to determine the crystal structure of title compound. It crystallizes in monoclinic space group $P2_1/c$ with Z=4. The crystallographic parameters are a= 11.6409(4) Ǻ, b= 10.7659 (4) Ǻ, c= 16.4917 (6) and β= 94.152 (3)°. The structure is refined up to R = 0.0612 for the 2812 observed reflections for 337 parameters. The molecule is linked into a three-dimensional framework by a combination of C-H…O, N-H…O and C-H… π hydrogen bonds and aromatic π-π stacking interactions.

*Keywords* — **2H-chromen-2-one, X-ray crystallography, Crystal structure, Molecular interactions**

## I. INTRODUCTION

The study of coumarins and their derivatives has attracted considerable attention from organic and medicinal chemists for many years as a large number of natural products contain this heterocyclic nucleus. Coumarins are very common type of secondary plant metabolites with a broad spectrum of biological activities. Bioactive compounds from fruits, vegetables, spices and herbs are widely considered to be valuable for human health [1–3]. Coumarins naturally present in many plants (primarily in angiosperms) possess anticoagulant, antimicrobial, antioxidant, anti-inflammatory, anti-allergic and anticancer properties [4,5]. They are widely used as additives in food, perfumes, cosmetics, pharmaceuticals [6], optical brighteners [6], dispersed fluorescent and laser dyes [7]. In view of the considerable importance of the coumarins, the present work is aimed to investigate and report a novel coumarin derivative crystal structure and its molecular interactions. The chemical structure of the title compound is shown in Fig. 1.

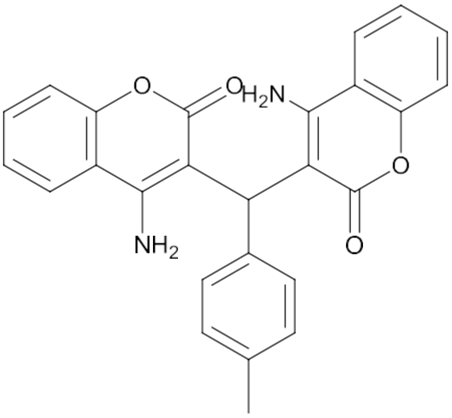

**Fig. 1:** The chemical structure of title compound

## II. MATERIALS AND METHODS

The synthesis of the title compound has been carried out and supplied by Prof. Brahmbhatt D. I. and the group, Department of Chemistry, Sardar Patel University, V.V. Nagar, Gujarat. The pure powder form of the synthesized compound is soluble in methanol, ethanol, dichloromethane and ethyl acetate etc. solvents. But good diffraction quality plate type single crystals are grown from dichloromethane solvent at room temperature 293(2) K by slow evaporation method. All diffraction measurements are performed using graphite monochromated MoKα radiation of wavelength 0.71073 Ǻ. The three dimensional X-ray intensity data are collected from the single crystal with θ ranging from 2.1º to 27.5º using ω-2θ scan mode on a KAPPA APEX II CCD diffractometer [8] at Department of Physics, Sardar Patel University.

## III. STRUCTURE SOLUTION AND REFINEMENT

The structure is solved by Direct methods with SHELXS-97 [9] programme. The Structure is refined by full matrix least squares on |F|2 with SHELXL-97 [10]. Programs SHELXL-97 and ORTEP-3 [11] built in with WinGX [12] software programme are used to prepare materials for publications. At this stage the hydrogen atoms are geometrically fixed and included in the refinement cycle which are allowed to ride on the corresponding non-hydrogen atoms with C-H = 0.86 – 1.08 Ǻ. The weighting scheme employed is of the type W =1/[s2(Fo2)+(0.2P)2] where P=(Fo2+2Fc2)/3. The title compound is crystallized into monoclinic system with P21/C space group with lattice parameters a=11.6409(4) Ǻ, b= 10.7659 (4) Ǻ, C= 16.4917 (6) and β=94.152 (3)°. The crystallographic data along with the intensity and refinement data are tabulated in Table 1. The ORTEP view of the title compound with the atom numbering scheme and displacement ellipsoids for non-H atoms are drawn at the 50% probability level is shown in Fig. 2. The intermolecular hydrogen bonding interactions and the molecular graphics are prepared using PLATON [13] software programme built in with WinGX software programme. The selected bond lengths and bond angles are mention in Table 2.

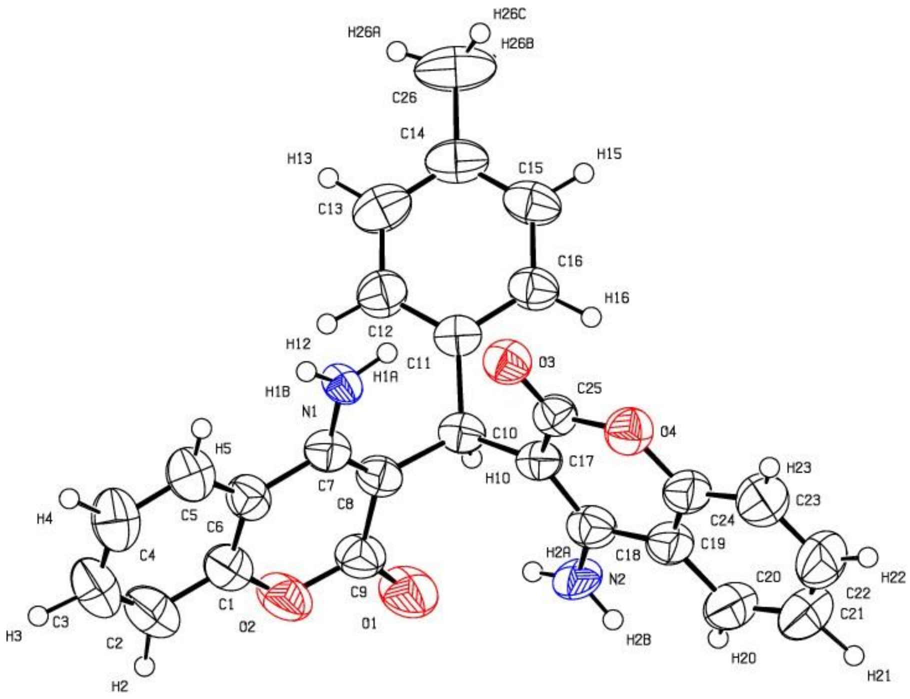

**Fig. 2:** ORTEP view of the title molecule with the atom numbering scheme and displacement ellipsoids for non-H atoms are drawn at the 50% probability level

**Table 1:** The crystallographic data along with the intensity and refinement detail

| | |
|---|---|
| Chemical Name | 3,3’-(p-tolylmethylene)bis(4-amino-2H-chromen-2-one) |
| Chemical formula | $C_{26}H_{20}N_2O_4$ |
| Formula weight | 424.44 |
| Crystal system, Space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 293 K |
| Wavelength (Å) | 0.71073 |
| a (Å) | 11.6409(4) Å |
| b (Å) | 10.7659 (4) Å |
| c (Å) | 16.4917 (6) Å |
| α (°) | 90 |
| β (°) | 94.152 (3)° |
| γ (°) | 90 |
| Volume (Å3) | 2061.39 (13)  Å3 |
| Z | 4 |
| Calculated density (Mg m-3), | 1.368 Mg $m^{-3}$ |
| Absorption coefficient (mm-1) | 0.09 $mm^{-1}$ |
| F(000) | 888 |
| θ range for data collection (°) | 2.1° to 27.5° |
| Limiting indices | $-15 \leq h \leq 14; -13 \leq k \leq 14; -21 \leq l \leq 21$ |
| Reflections collected/unique | 4732/ 2812 |
| Refinement method | Full Matrix Least Square of $\|F\|^2$ |
| Data/restrains/parameters | 4732/ 0/ 337 |
| Goodness-of-fit (S) | 1.058 |
| Final R indices | R1 = 0.062 |
| Largest diff. peak and hole (e Å-3 ) | 0.394 and -0.523 |
| Software used to solve the structure | SHELXS-97 |
| Software used to refine the structure | SHELXL-97 |
| Software used for Molecular Graphics | PLATON |

**Table 2:** The selected bond lengths (Å) and bond angles(°)

| Atoms | Bond lengths (Å) | Atoms | Bond lengths (Å) |
|---|---|---|---|
| O1—C9 | 1.223 (4) | O4—C24 | 1.375 (3) |
| O2—C1 | 1.376 (4) | O4—C25 | 1.361 (3) |
| O2—C9 | 1.359 (3) | N1—C7 | 1.317 (3) |
| O3—C25 | 1.226 (3) | N2—C18 | 1.324 (3) |
| **Atoms** | **Bond angles (°)** | **Atoms** | **Bond angles (°)** |
| C1—O2—C9 | 121.1 (2) | O1—C9—C8 | 125.0 (2) |
| C24—O4—C25 | 121.3 (19) | N2—C18—C17 | 124.1 (2) |
| O2—C1—C2 | 116.6 (3) | N2—C18—C19 | 115.4 (2) |
| O2—C1—C6 | 121.2 (2) | O4—C24—C23 | 117.1 (2) |
| N1—C7—C8 | 124.9 (2) | O4—C24—C19 | 121.2 (2) |
| N1—C7—C6 | 114.9 (19) | O4—C25—C17 | 119.3 (2) |
| O2—C9—C8 | 119.6 (2) | O3—C25—O4 | 115.2 (2) |
| O1—C9—O2 | 115.4 (2) | O3—C25—C17 | 125.5 (2) |

## IV. RESULTS AND DISCUSSION

By investigating both the fused rings 1 and 2, (O2-C1-C2-C3-C4-C5-C6-C7-C8-C9) and (O4-C25-C17-C18-C19-C20-C21-C22-C23-C24), are found almost planner. The angle between phenyl ring and pyrone is 4.01(13)° in fused ring1 while it is 4.32(15)° in fused ring 2 . Both these fused ring system are oriented at 55.71(9)° to each other. The central phenyl ring which is joining the two fused ring system is rotated at 65.06(11)° to ring 1 and by 66.20(11)° to ring 2 respectively. In both the fused ring system 1 and 2, pyrone ring is puckered with ring puckering parameters [14] Puckering Amplitude (Q) = 0.089(3) Å , $\theta$ = 104.9(19)° and $\varphi$ = 82.0(16)° and Puckering Amplitude (Q) = 0.086(2) Å , $\theta$ = 104.9(14)° and $\varphi$ = 60.0(17)° respectively. Few selected torsional angles defining the molecular conformations about significant bonds are C25-C17-C10-C11= 50.1(3)°, C7-C8-C10-C11= -50.8(3)° and C8-C10-C11-C12= -22.8(3)°. The crystal packing is governed by diverse set of weak intermolecular interactions. The Intra and intermolecular hydrogen bond interactions along with $\pi$-$\pi$ and C-H…$\pi$ are summarized in Table 3. Intramolecular hydrogen bond interactions are found via N1-H1A…O3 and N2-H2A…O1 bounds the molecule. In addition carbon atom C2 of fused ring 1 via H2 acts as a potential donor to O4 atom of symmetry related molecule (-1/2+x,1/2-y,1/2+z) and also carbon atom C10 via H10 acts as potential donor to O3 atom of symmetry related molecule (3/2-x,-1/2+y,1/2-z) forming a network of intermolecular hydrogen bond interactions gives the stability to structure(Fig. 3). Further the centroid Cg2 of the pyrone ring of fused ring 2 is connected by $\pi$-$\pi$ interactions with the centroid Cg4 of symmetry related phenyl ring of the molecule (3/2-x,1/2+y,1/2-z) with Cg-Cg separation distance of 3.546(14) Å (Fig. 4) is off-centric. The C-H…$\pi$ interaction of type-III [15], involves carbon atom C5 of fused ring 1 via H5 to centroid of the phenyl ring Cg(5) of fused ring 2 of symmetry related molecule (3/2-x,-1/2+y,1/2-z) gives further stability to molecule. Thus molecular stability is due to all these hydrogen bond interactions along with week but significant $\pi$…$\pi$ stacking interactions.

**Table 3:** Intra and intermolecular N-H…O, C-H…O, π…π and C-H…π interactions (distances in Å, angles in ◦)

**A. Hydrogen bond interactions**

| D-H...A | d(D-H ) Å | d (H- A) Å | d (D-A) Å | (D-H...A)° |
|---|---|---|---|---|
| N1-H1A….O3(i) | 0.86 | 1.93 | 2.617(2) | 136 |
| N2-H2A….O1(i) | 0.86 | 1.96 | 2.684(3) | 141 |
| C2-H2…O4(ii) | 1.07 | 2.32 | 3.224(4) | 141 |
| C10-H10…O3(iii) | 0.97 | 2.54 | 3.386(3) | 146 |

**B. π - π interaction**

| Cg(I)- Cg(J) | Cg(I)…Cg(J)Å | α | β | γ | Cg(I)…P Å | Cg(J)…P Å |
|---|---|---|---|---|---|---|
| Cg(2) - Cg(4)(iv) | 3.546(14) | 12.34(12) | 13.6 | 5.2 | -3.5310(9) | 3.328(4) |

**C. C-H…π interaction**

| C- H(I)…Cg (J) | d(H-Cg) Å | d(C-Cg) Å | C-H…Cg(°) | γ (°) | H…P Å | Type |
|---|---|---|---|---|---|---|
| C5-H5…Cg(5)(iii) | 2.900 | 3.648(4) | 143(3) | 16.69 | -2.78 | III |

**D. Symmetry Code**

**(i)** x,y,z; **(ii)** -1/2+x,1/2-y,1/2+z; **(iii)** 3/2-x,-1/2+y,1/2-z; **(iv)** 3/2-x,1/2+y,1/2-z.

**Note:** Cg(2), Cg(4), and Cg(5) represents the centroid of the rings (O4-C25-C17-C18-C19-C24), (C11-C12-C13-C14-C15-C16) and (C19-C20-C21-C22-C23-C24) respectively.

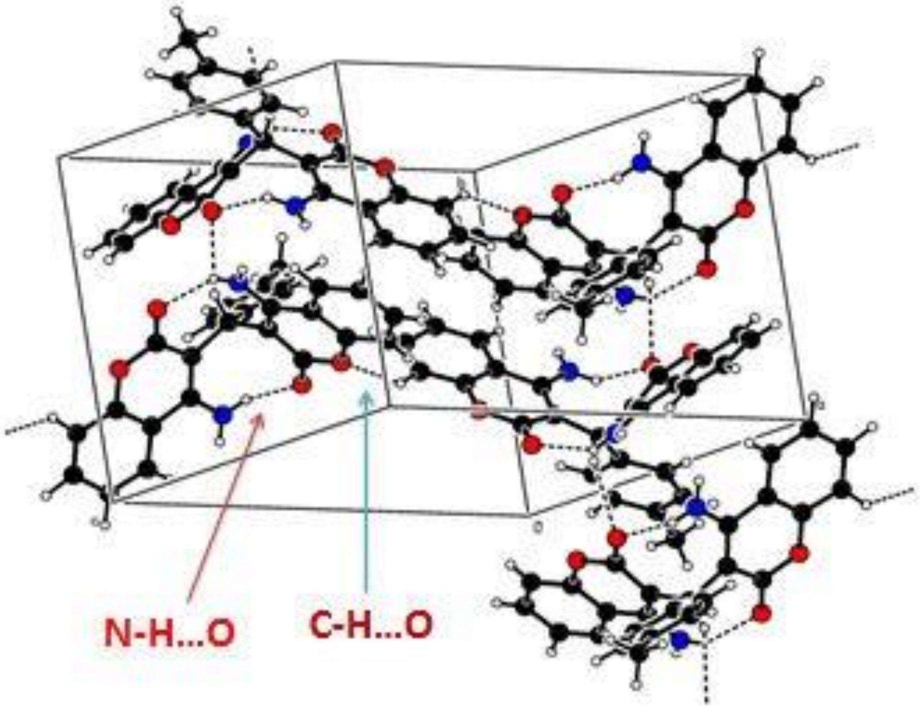

**Fig. 3:** N-H…O and C-H…O interactions in the molecule

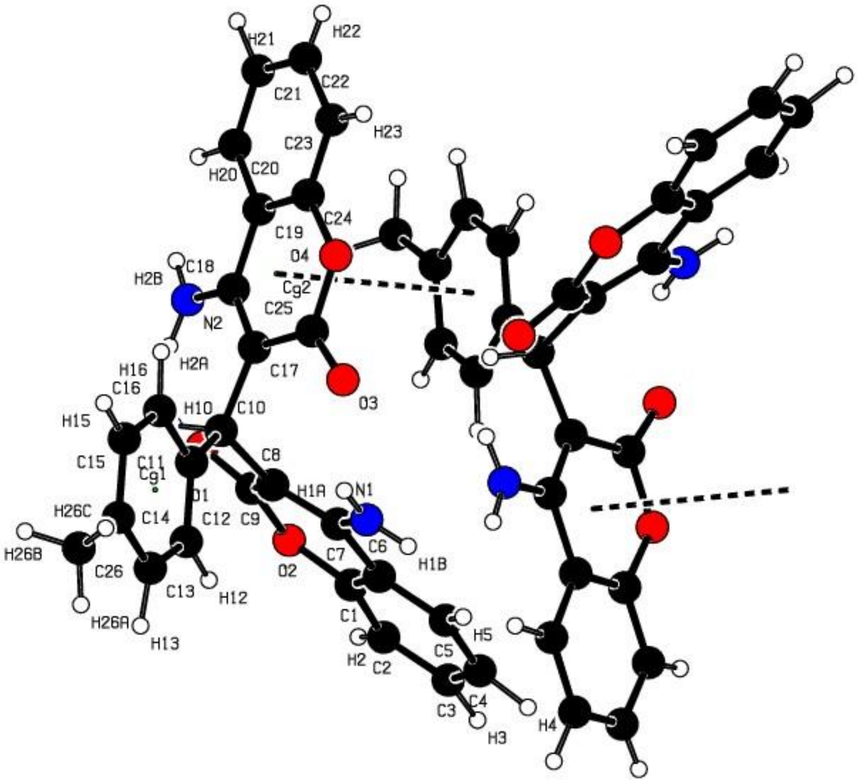

**Fig. 4:** π- π interaction in the title molecule

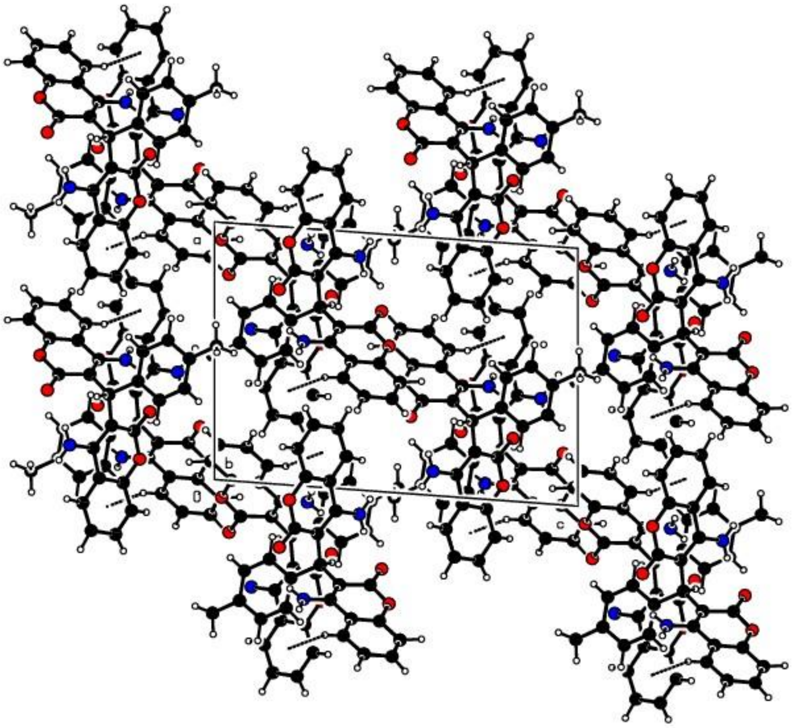

**Fig. 5:** Molecular packing view of C-H… π interaction in the molecule

## V. CONCLUSION

The title compound characterized by single crystal X-ray diffraction technique and its three dimensional structures is worked out. The crystal structure is stabilized by intermolecular interactions into a three dimensional framework by combination of C-H…O, N-H…O, C-H…$\pi$ and $\pi$-$\pi$ bond interactions.

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