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X-Ray Crystallographic Investigation and Crystal Structure of 3,3'-((3,4dimethoxyphenyl)methylene)bis(4-amino-8methyl-2H-chromen-2-one)

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ABSTRACT: The coumarin(2H-chromen-2-one) and its derivatives are important class of heterocyclic compounds with wide range of biological activities. Considering the importance of these group of compounds, authors have investigated the novel derivative namely 3,3'-((3,4-dimethoxyphenyl)methylene)bis(4-amino-8-methyl-2H-chromen-2-one)(C₂₉H₂₆N₂O₆). The crystal structure is determined using X-Ray crystallographic technique. The title compound crystallizes in monoclinic space group P2₁/cwith Z=4. The crystallographic parameters are a= 13.223(9), b= 16.987(12), c= 11.1964(8) and β = 106.37°. The stability of the structure is due to weak but significant C-H...O, N-H...O, π - π , and C-H... π interactions observed in the molecular packing of the title compound.

KEYWORDS: Coumarin, X-ray crystallography, Crystal structure, Molecular interactions

I. INTRODUCTION

Coumarins classified as a member of thebenzopyrones family of compounds, consisting of a benzene ringjoined to a pyrone ring. Coumarins constitute one of the major classes of naturally occurring compounds, andhaving deep interest in the field of chemistry. It also works as biologically active agent. Coumarin represents the core structure of several molecules of pharmaceuticalimportance. Coumarins has been reported to serve as antibacterial[1-4], anti-oxidant[5,6], anti-inflammatory[7,8], anticoagulant[8] and antitumour[9,10] agents. They are widely used as additives in food, perfumes, cosmetics, pharmaceuticals[11], optical brighteners[11], dispersed fluorescent and laser dyes[12].

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.



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Fig. 1: The chemical structure of title compound

II. MATERIALS AND METHODS

To carry out crystallographic investigation of compound using X-Ray diffraction technique, good diffraction quality square type single crystals are grown from dichloromethane with toluenesolvent at room temperature 293(2) K by slow evaporation method. All diffraction measurements are performed using graphite monochromated MoK α radiation of wavelength 0.71073 $\dot{}$. The three dimensional X-ray intensity data are collected from the single crystal with θ ranging from 1.26° to 27.56° using ω -2 θ scan mode on a KAPPA APEX II CCD diffractometer[13] at Department of Physics, Sardar Patel University.

III. STRUCTURE SOLUTION AND REFINEMENT

The structure is solved by Direct methods with SHELXS-97[14]programme. The Structure is refined by full matrix least squares on $|F|^2$ with SHELXL-97[15]. Programs SHELXL-97 and ORTEP-3[16] built in with WinGX[17]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 = 0.93 – 0.98 '. 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/Cspace group with lattice parameters a=13.223(9) b=16.987(12), c=11.964(8)Å and β =106.37°. The crystallographic data along with the intensity and refinement data are summarized in Table 1. The ORTEP diagram of the molecule showing 50% probability of the displacement ellipsoids is depicted in Fig. 2. The intermolecular hydrogen bonding interactions and the molecular graphics are prepared using PLATON[18]software programme. The selected bond lengths and bond angles are listed in Table 2.



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Fig. 2: ORTEP view of the title molecule, showing 50 % probability displacement ellipsoids

Table 1: The crystallographic	e data along with the intensi	ty and refinement detail

Chemical Name	3,3'-((3,4-dimethoxyphenyl)methylene)bis(4-amino-8-		
	methyl-2H-chromen-2-one)		
Chemical formula	$C_{29}H_{26}N_2O_6$		
Formula weight	498.52		
Crystal system, Space group	Monoclinic, P2 ₁ /c		
Temperature (K)	293 K		
Wavelength (Å)	0.71073		
a (Å)	13.223 (9)		
b (Å)	16.987 (12)		
c (Å)	11.196 (8)		
α (°)	90		
β (°)	106.37 (2)		
γ (°)	90		
Volume (Å ³)	2413.1 (3) Å ³		
Ζ	4		
Calculated density (Mg m ⁻³),	1.372 Mg m^{-3}		



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Absorption coefficient (mm ⁻¹)	0.10 mm^{-1}
F(000)	1048
θ range for data collection (°)	1.24° to 27.56°
Limiting indices	$-18 \le h \le 18; -24 \le k \le 24; -16 \le l \le 16$
Reflections collected/unique	7372/3982
Refinement method	Full Matrix Least Square of F ²
Data/restrains/parameters	7372/0/334
Goodness-of-fit (S)	1.3660
Final R indices	R1 = 0.1302
Largest diff. peak and hole (e $Å^{-3}$)	1.12 and -0.49
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—C7	1.349 (11)	O5—C26	1.391 (10)
O1—C8	1.327 (10)	O5—C28	1.300 (13)
O2—C8	1.250 (9)	O6—C25	1.363 (7)
O3—C15	1.394 (11)	O6—C29	1.408 (11)
O3—C16	1.400 (9)	N1-C10	1.298 (7)
O4—C16	1.249 (8)	N2—C13	1.271 (9)
Atoms	Bond angles (°)	Atoms	Bond angles (°)
C7—O1—C8	122.0 (6)	N2—C13—C12	123.3 (8)
C15—O3—C16	117.2 (6)	N2—C13—C14	115.8 (7)
C26—O5—C28	122.2 (8)	O3—C15—C20	107.6 (7)
C25—O6—C29	114.9 (6)	O3—C15—C14	122.7 (7)
O1—C7—C6	119.7 (7)	O3—C16—C12	121.7 (5)
O1—C7—C2	111.4 (7)	O3—C16—O4	111.4 (5)
O1—C8—O2	114.9 (6)	O4—C16—C12	126.9 (6)
O1—C8—C9	121.2 (6)	O6—C25—C24	127.4 (6)
O2—C8—C9	123.9 (7)	O6—C25—C26	115.9 (6)
N1—C10—C6	115.9 (6)	O5—C26—C25	113.9 (6)
N1—C10—C9	124.1 (6)	O5—C26—C27	124.3 (7)



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IV. RESULTS AND DISCUSSION

In the title molecule, both the fused rings 1 and 2, (O1-C8-C9-C10-C6-C5-C4-C3-C2-C7) and (O3-C16-C12-C13-C14-C17-C18-C19-C20-C21), are almost planner. The angle between phenyl ring and pyrone is 2.5(4)° in fused ring1 while that in fused ring 2 is $4.3(4)^\circ$. The two fused ring system are oriented at $60.8(3)^\circ$ to each other. The central phenyl ring which is bridging the two fused ring system is rotated at 68.3(3)° to ring 1 and by 65.6(3)° to ring 2 respectively. In the fused rings 1 and 2, pyrone ring is puckered in ring 2 with ring puckering parameters[19]Puckering Amplitude (Q) =0.092(8)Å, $\theta = 107(4)^{\circ}$ and $\varphi = 45(5)^{\circ}$. Few selected torsional angles defining the molecular conformations about significant bonds are C9-C11-C12-C13= 93.8(6)°, C9-C11-C22-C27= 156.2(5)°, C12-C11-C22-C23= -166.0(5)°. The torsional anglesC28-O5-C26-C27= 8.9(15)° and C29-O6-C25-C26= 179.9(7)° reveal that the both methoxy group are at CIS conformation with respect to phenyl ring. Analysis of the hydrogen bonding pattern of the title molecule shows the presence of C-H... π , π - π , C-H...O and N-H...O intermolecular hydrogen bond interactions in the structure. The C-H... π interaction involving the C28 via H28B to the centroid Cg4 of symmetry related methyl phenyl ring offused ring-2, where C18-H28B...Cg (4) (ii) =3.508(13) Å, is of type I[20]as mention by Malone et al., 1997 contributing to the stability of the molecular structure (Fig. 3). Further the centroid Cg2 of the pyrone ring of fused ring 2is connected by π - π interactions with the centroid Cg5of symmetry related phenyl ring of the molecule (x,1/2-y,1/2+z) with Cg-Cg separation distance of 4.219(4) Å(Fig. 4). The Intra and intermolecular hydrogen bond interactions are summarized in Table 3. Intramolecular hydrogen bonds are formed via N1-H1D...O4 and N2-H2B...O2 in which oxygen atoms acts as an acceptor. In addition, intermolecular hydrogen bond interactions are formed as C11-H11...O4, C29-H29C...O1 and N2-H2B...O4 with symmetry related molecule (x, 1/2-y, -1/2+z) (Fig. 5). All these weak but significant hydrogen bond interactions play important role for molecular stability.

Table 3: Intra and intermolecular N-H...O, C-H...O, π ... π andC-H... π interactions (distances in Å, angles in °)

A. Hydrogen bond interactions										
D-HA	d(D-H) °		d (D-A) °		d (H- A) °		((D-HA)°		
N1—H1D…O4(i)	0.860		2.595(8)	1.918		3(6)		135.00	
N2—H2B····O2(i)	0.860		2.711(10)	2.007(6)			138.00		
C11-H11O4(ii)	0.980		3.527(7)			2.585(5)		161.05		
C29-H29CO1(ii)	0.960		3.849(11)			2.931(6)		160.48		
N2-H2BO4(ii)	0.860		3.269(9)			2.686(5)			126.29	
B. π - π interaction										
Cg(I)- Cg(J)	Cg(I)Cg(J)		α	β		γ	Cg(I)P °		Cg(J)P °	
Cg(2) - Cg(5)(iii)	4.219(4)		23.2(3)	8.9		24.6 -3.8		36(3)	4.167(3)	
C. C-H <i>π</i> interaction										
C- H(I)Cg (J)	d(H-Cg) °	(d(C-Cg) °	С-Н	C	g(°)	γ (°)	НР	Туре	
C28-H28BCg(4)(ii)	2.580		3.508(13)	163			8.33	2.55	Ι	
D. Symmetry Code										
(i)x,y,z; (ii) x, $1/2$ -y, $-1/2$ +z; (iii)x, $1/2$ -y, $1/2$ +z.										
Note:Cg(2), Cg(4) and Cg(5) represents the centroid of (O3-C15-C14-C13-C12-C16), (C14-C15-C20-C19-C18-C17)										
and (C22-C23-C24-C25-C26-C27) respectively.										



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Fig. 4: Molecular packing diagram of π - π interaction



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V. CONCLUSION

The title compound characterized by single crystal X-ray diffraction technique and its three dimensional structures is worked out. The stability of the molecule is given by the hydrogen bond C-H...O and N-H...O interactions. The contribution of π - π and C-H... π interactions also plays significant role in molecular stability.

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REFERENCES

[1] Ukhov, S. V.; Kon'shin, M. E. and Odegova, T. F. Synthesis and antimicrobial activity of 2-iminocoumarin-3-carboxyli c acid amides. Pharm. Chem. J. 2001, 35, 364-365.

- [2] AbdElhafez, O. M.; El Khrisy, E. A.; Badria, F. and Fathy, A. M. Arch. Pharm. Res. 2003, 26, 686-696.
 [3] Basanagouda, M.; Kulkarni, M. V.; Sharma, D.; Gupta, V. K.; Sandhyarani, P. and Sasal, V. P. J. Chem. Sci. 2009, 121, 485–495.
- [4] Liu, X.; Dong, M.; Chen, X.; Jiang, M.; Lv, X. and Zhou, J. ApplMicrobiolBiotechnol. 2008, 78, 241–247.
 [5] Trapkov, V. A.; Parfenov, E.A. and Smirnov, L. D. Pharm. Chem. J. 1996, 30, 445-447.
- [6] Vukovic, N.; Sukdolak, S.; Solujic, S. and Niciforovic, N. Arch. Pharm. Res. 2010,33, 5-15.
- [7] Emmanuel-Giota, A.A.; Fylaktakidou, K.C.; Hadjipavlou-Litina, D.J.; Litinas, K.E. and Nicolaides, D.N. J. Heterocyclic Chem. 2001,38, 717-722.
- [8] Hamdi, N. and Dixneuf, P. H. Synthesis of Triazole and Coumarin Compounds. Topics in Heterocyclic Chemistry, Springer-Verlag, Berlin Heidelberg, 2007.
- [9] Wang, M.; Wang, L.; Li, Y. and Li, Q. Trans. Met. Chem. 2001, 26, 307-310.
- [10]Marchenko, M. M.; Kopyl'chuk, G. P.; Shmarakov, I. A; Ketsa, O. V. and Kushnir, V. N Pharm.Chem. J. 2006, 40, 1296-297.
- [11] O'Kennedy, R.; Thornes, R. D. Coumarins: Biology, Applications and mode of action; John Wiley & Sons: Chichester, 1997.
- [12] Zabradnik, M. The Production and Application of Fluorescent Brightening Agents; John Wiley & Sons: New York, 1992.
- [13] Bruker (2008). APEX2andSAINT.Bruker AXS Inc., Madison, Wisconsin, USA.
- [14]Sheldrick, G. M. (2008). Acta Cryst.A64, 112-122
- [15] Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- [16] Farrugia, L. J. (1997). J. Appl. Cryst., 30, 565
- [17]L. J. Farrugia, J. Appl. Cryst. (1999), 32, 837-838.
- [18] Spek, A. L. 2009. Structure validation in chemical crystallography, ActaCrystallographica, D65, pp.148-155
 [19] D. Cremer& J.A. Pople, J.Amer.Chem.Soc., 97, (1975), 1354-1358.
- [20]J. F. Malone, C. M. Murray, M. H. Charlton, R. Docherty and A. J. Lavrry (1997), Journal of Chemical Society, Vol. 93 (19), 3429-3436.