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Crystal Structure of 2-amino-4-(4-hydroxyphenyl)-5, 10-dihydro-4H-benzo[*g*] chromene-3-carbonitrile

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Abstract: *The title compound 2-Amino-4-(4-Hydroxyphenyl)-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile crystallizes in monoclinic system, space group $P2_1/c$ with unit cell parameters: a=8.1258(5), b=11.8112(7), c=21.5768(16) Å, β=92.194(7)^o and Z=4. The crystal structure has been solved by direct methods and refined by full-matrix least squares procedures to a final R value of 0.1199 for 2629 observed reflections. In the crystal, molecules are linked via five intermolecular (N-H…N, N-H…O, O-H…O and C-H…O) hydrogen bonds. In addition, C-H...π and π-π interactions are also observed in crystal structure.*

Keywords- *Chromene, Single crystal, X-ray diffraction, Direct methods, Interactions.*

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I. Introduction

Benzochromenes represent an important class of organic compounds, which being the main components of many naturally occurring products, exhibit a broad spectrum of biological activities, including anticancer[1], anti-inflammatory[2], antimalarial[3] and pesticides activities[4-5]. In addition, they are valuable precursors used for the synthesis of cosmetics and pigments[6]. The benzo[*g*]chromenes constituting naphthoquinone structural motifs, which occur in a variety of natural products possess varied biological activities[7]. It has been reported that hydroxynaphthalene-1,4-dione derivatives are fluorescent compounds and have various applications such as, emitters for electroluminescent devices[8], molecular probes for biochemical research[9] and fluorescent whitening agents[10].

In view of the numerous biological and pharmacological applications associated with benzo[*g*]chromenes, the synthesis and crystal structure of 2-Amino-4-(4-Hydroxyphenyl)-5,10-dihydro-4*H*-benzo[*g*]chromene-3-carbonitrile is reported in this paper.

II. Experimental

2.1. Experimental procedure for the synthesis of 2-amino-4-(4-hydroxyphenyl)-5, 10-dihydro-4H-benzo[g] chromene-3-carbonitrile

A mixture of aryl aldehyde (1 mmol), malononitrile (1mmol), 2-Hydroxy-1,4-naphthoquinone (1 mmol), a catalytic amount of Et_3N (0.01 g, 0.10 mmol) were dissolved in CH_3CN (5 mL). This mixture was then sonicated for 10-15 min. After completion of the reaction (monitored by TLC method), the precipitated product was separated from reaction mixture by filtration and was washed with water and 5 ml hexane. The desired product was obtained without any further purification. Obtained product dried in air and obtained as orange powder. Single crystal of the purified product was grown from DMSO by slow evaporation method (M.P = 531-533 K). The reaction scheme for the synthesis of title compound is given in figure 1.

2.2. Structure solution and refinement

The structure was solved by direct methods using SHELXS97[11]. Five cycles of full-matrix least-squares refinement was carried out and it brought the final R-factor to 0.1199. All non-hydrogen atoms of the molecule were located in the best E-map and refined in anisotropic approximation. In the title molecule, carbon atoms (C21 & C22) and sulphur atom (S1) are thermally disordered. The thermal disorder could not be tackled and hence, it led to the large value of the R-factor. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with N-H=0.84 to 0.87 Å, C-H= 0.93 Å, and $U_{iso}(H)=1.5\ U_{eq}$ of the

attached C atoms for methyl groups and 1.2 U_{eq}(N, C) for other H atoms. The geometry of the molecule was calculated using WinGX[12], PARST[13] and PLATON[14] softwares.

Crystallographic information has been deposited with Cambridge Crystallographic Data Centre, CCDC number 1543477. This data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data is summarized in Table 1.

III. Results And Discussion

The molecular structure containing atomic labeling is shown in figure 2 (ORTEP)[15]. The structural parameters, including bond distances and angles (Table 2) show a normal geometry and are in agreement with the values observed for related structures[16-17]. The C7=O1 and C10=O2 bond distance of 1.204(6) Å and 1.221(6) Å, respectively are of the double bond character. The lengthening of C=O bonds are probably due to the involvement of O1 and O2 in two different intermolecular interactions (C4-H4…O1 and N1-H25B…O2). The molecule consists of approximately three planar fragments; two phenyl rings (C&D) and chromene ring system (A&B). The chromene moiety is slightly folded [the dihedral angle between these planes (A&B) is 6.40 (1)˚]. The phenyl ring D is almost perpendicular to chromene moiety and phenyl ring C making dihedral angles of 89.29 (1)˚ and 88.25 (2)˚, respectively. All the rings are almost planar with maximum deviation of 0.1453 Å below the plane (for C12 atom of the chromene ring system). The amino and cyanide groups attached at C13 and C12, respectively are almost planar, as indicated by the torsion angle N1-C13-C12-C20 [=2.8 (9)˚]. In the crystal structure, adjacent molecules are interconnected through N1-H25A…N2, N1-H25B…O2, O4-H26A…O5, C4-H4…O1 and C15-H15…O5 intermolecular hydrogen bonds. It is worth mentioning that, the molecular packing in the crystal structure is stabilized by the above mentioned five intermolecular hydrogen bonds, of which N2, O2, O5, O1 and O5 work as hydrogen bond acceptors and N1, N1, O4, C4 and C15 work as hydrogen bond donors, respectively. Molecular packing in the unit cell viewed down the a-axis is shown in figure 3 (PLATON)[14]. The crystal structure is further stabilized by C-H…π and π-π interactions. Details of intermolecular C-H…π and π-π interactions are given in Table 3 and 4 respectively.

IV. Figures And Tables

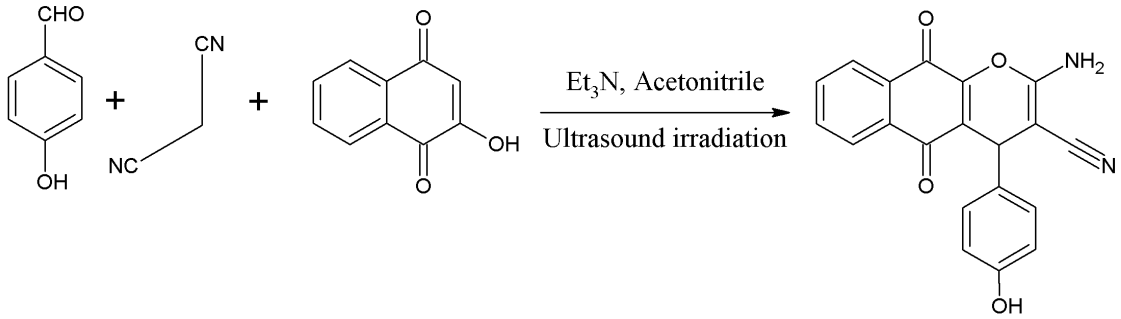

Figure 1: Reaction scheme.

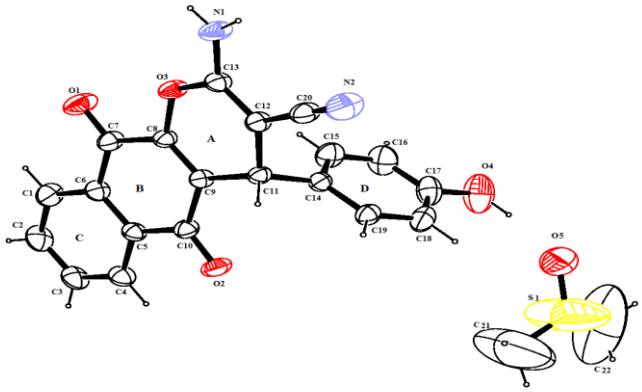

Figure 2: ORTEP plot of the molecular structure of 2-Amino-4-(4-Hydroxyphenyl)-5,10-dihydro-4*H*-benzo[*g*]chromene-3-carbonitrile with 40% probability thermal ellipsoids. H atoms are shown as small spheres of arbitrary radii.

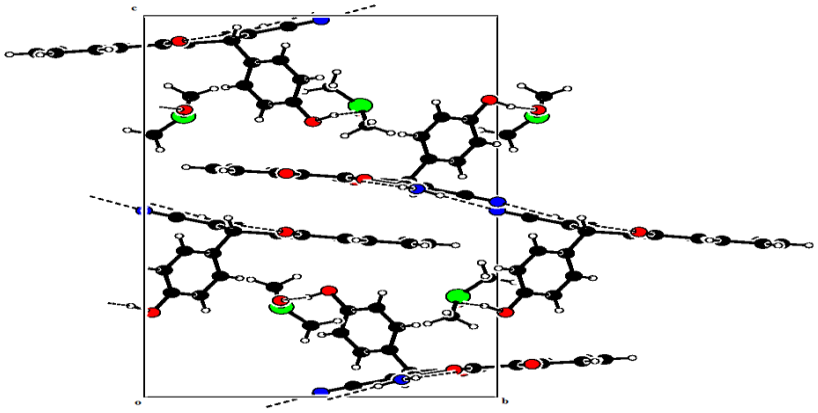

Figure 3: Molecular packing viewed down a-axis.

Table 1: Crystallographic characteristics and the X-ray-data collection and structure-refinement parameters for $C_{20}H_{12}N_2O_4.C_2H_6OS$.

System, sp. gr., *Z*	monoclinic, $P2_1/c$, 4
a, *b*, *c* Å	8.1258(5), 11.8112(7), 21.5768(2)
β deg	92.194(7)
V, Å^3	2069.3(2)
D_x g.cm^{-3}	1.356
Radiation, λ, Å	Mo*Kα*, 0.71073
μ, mm^{-1}	0.193
T, K	293(2)
Sample size, mm	0.30 X 0.20 X 0.10
Diffractometer	*X' calibur* CCD area-detector diffractometer
Scan mode	ω scan
Absorption correction,	multi-scan,
T_{min}, T_{max}	0.79394, 1.00000
θ_{max}, deg	26.00
h, *k*, *l* ranges	$-10 \le h \le 9$ $-14 \le k \le 11$ $-26 \le l \le 16$
Number of reflections:	
measured/unique (*N*1),	8184/4043
R_{int}/with $I > 2\sigma(I)$ (*N*2)	0.0263/2629
Refinement method	Full matrix least squares on F^2
Number of refined parameters	286
R1/wR2	0.1199/ 0.3038
S	1.045
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.454/-1.614
Programs	SHELXS97 [11], SHELXL97 [11], PARST [13], PLATON [14], ORTEP [15]

Table 2: Bond distances d, Å, bond angles ω, deg, and torsion angles, τ, deg

Bond Distances		**Bond Distances**	
O1-C7	1.204(6)	O4-C17	1.363(7)
O2-C10	1.221(6)	C9-C10	1.471(6)
O3-C8	1.366(5)	C9-C11	1.511(6)
O3-C13	1.378(5)	C11-C12	1.514(6)
N1-C13	1.332(6)	C11-C14	1.539(6)
N2-C20	1.148(7)	C17-C18	1.384(8)
C12-C13	1.348(6)	C16-C17	1.379(9)
C5-C10	1.483(7)	C8-C9	1.327(6)
C5-C6	1.392(7)	C6-C7	1.485(7)
C7-C8	1.497(6)	C12-C20	1.409(7)
Bond Angles		**Bond Angles**	
C8-O3-C13	117.6(3)	N2-C20-C12	178.2(6)

C9-C8-O3	124.7(4)	N1-C13-C12	128.2(4)
C8-C9-C10	120.0(4)	C12-C13-O3	121.7(4)
O3-C8-C7	111.3(4)	N1-C13-O3	110.1(4)
O2-C10-C9	120.4(4)	O1-C7-C6	122.8(4)
O2-C10-C5	120.9(4)	O1-C7-C8	121.1(4)
C8-C9-C11	122.1(4)	O4-C17-C16	118.2(6)
C10-C9-C11	117.8(4)	O4-C17-C18	122.8(6)
C9-C11-C14	112.4(4)	C12-C11-C14	111.6(4)
C9-C11-C12	108.4(4)	C9-C8-C7	124.0(4)
Torsion Angles		**Torsion Angles**	
C13-O3-C8-C9	-9.8(7)	C12-C11-C14-C15	-73.4(6)
C13-O3-C8-C7	170.0(4)	C8-O3-C13-N1	-173.0(4)
O3-C8-C9-C10	176.9(4)	C20-C12-C13-N1	2.8(9)
O2-C10-C9-C11	4.1(7)	C11-C12-C13-N1	-174.6(5)
O1-C7-C8-O3	1.2(8)	C20-C12-C11-C14	-66.7(6)
O1-C7-C6-C5	179.2(5)	C20-C12-C11-C9	169.0(4)
O3-C8-C9-C11	-0.3(8)	C9-C11-C14-C19	-134.0(4)
O1-C7-C6-C1	-1.0(9)	C13-C12-C20-N2	146.0(2)
O1-C7-C8-C9	-173.1(5)	C11-C12-C20-N2	-37.0(2)
O2-C10-C5-C4	-6.1(7)	C15-C16-C17-O4	-179.5(6)
O2-C10-C9-C8	-173.2(5)	C19-C18-C17-O4	179.7(6)

Table 3: Hydrogen bonding geometry (e.s.d`s in parentheses)

D–H…A	D–H(Å)	H…A(Å)	D…A(Å)	D–H…A(°)
N1-H25A…N2^{i}	0.87(7)	2.23(7)	3.088(7)	170(6)
N1-H25B…O2^{ii}	0.84(6)	2.19(6)	3.015(6)	169(6)
O4-H26A…O5^{iii}	1.02(11)	1.67(12)	2.636(10)	158(11)
C4-H4…O1^{iv}	0.93	2.55	3.411(6)	155
C15-H15…O5^{v}	0.93	2.60	3.477(10)	158
C15-H15…Cg1^{vi}	0.93	2.82	3.146(6)	101.57

Symmetry code: (i) 2-x, -y, 1-z (ii) 1+x, y, z (iii) -x, -1/2+y, 1/2-z (iv) -1+x, y, z (v) 1+x, y, z
(vi) x, y, z

*Cg1 represents the centre of gravity of ring A of chromene ring system

Table 4: Geometry of π–π interactions*

CgI…CgJ	CgI…CgJ (Å)	CgI…P(Å)	α(°)	β(°)	Δ(Å)
Cg1…Cg4^{i}	3.9969(3)	0.438	86.43	49.23	3.97

Symmetry code: (i) x, y, z
* Cg1 and Cg4 represent the centre of gravity of ring A of chromene ring system and phenyl ring D, respectively.

V. Conclusions

Benzochromenes represent an important class of organic compounds, which being the main components of many naturally occurring products, exhibit a broad spectrum of biological activities. They are most widely used as anticancer, anti-inflammatory and pesticides. In view of the numerous biological and pharmacological applications associated with Benzo[*g*]chromenes, we report the synthesis and crystal structure of the novel title compound.

The molecular structures have been determined by using X-ray diffraction techniques. The result of the single-crystal X-ray structure analysis establishes the molecular and crystal structural aspects of this compound and its molecular packing has been established by the presence of inter-molecular hydrogen bonds and van der Waals forces.

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Refrences

[1]. M. Ough, A. Lewis, E. A. Bey, J. Gao, J. M. Ritchie, W. Bornmann, D. A. Boothman, L. W. Oberley and j. j. Cullen, *Canc. Biol. Ther*., *4*, 2005, 95-102.
[2]. D. O. Moon, Y. H. Choi, N. D. Kim, Y. M. Park and G. Y. Kim, *Int. Immunopharmacol*., *7*, 2007, 506-514.
[3]. P. S. Elisa, E. B. Ana, A. G. Ravelo, D. J. Yapu and A. G. Turba, *Chem. Biodiversity*, *2*, 2005, 264-274.
[4]. A. M. Shestopalov, Y. M. Emelianova and V. N. Nesterov, *Russ. Chem. Bull*., *52*, 2003, 1164-1171.
[5]. A. Shaabani, R. Ghadari, S. Ghasemi, M. Milad Pedarpour, A. H. Rezayan, A. Sarvary and N. S. Weng, *J. Comb. Chem.*, *11*, 2009, 956-959.
[6]. A. M. El-Maghraby, *Org Chem Int.*, 2014.
[7]. M. K. Jitender, M. Devanshi and C. Ankita, *Synth. Commun*., *42*, 2012, 3211-3219.
[8]. K. Hunger, Industrial Dyes, Wiley, Weinheim, 2003.
[9]. A. Dmitry and A. Pavel, *Chem. Commun.*, *12*, 2003, 1394-1395.
[10]. E. Belgodere, R. Bossio, S. Chimichi, V. Passini and R. Pepino, *Dyes Pigm*., *4*, 1985, 59.
[11]. G. M. Sheldrick, *ActaCryst*., *A64*, 2008, 112.
[12]. L. J. Farrugia, *J. Appl. Cryst.*, *32*, 1999, 837.
[13]. M. Nardelli, *J. Appl. Cryst.*, *28*, 1995, 659.
[14].] A. L. Spek, *ActaCryst., D65*, 2009, 148.
[15]. L. J. Farrugia, *J. Appl. Cryst.*, *30*, 2012, 565.
[16]. J. Zhang, X. Zhang, S. Yan, N. Ma and S. Tu, *ActaCryst.*, *E65*, 2009, o5.
[17]. D. K. Sharma, A. Jayashree, B. Narayana, B. K. Sarojini, S. Anthal and Rajni Kant, *Bul. Las. Spect. Soc. Ind*., *23*, 2017, 91-98.

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