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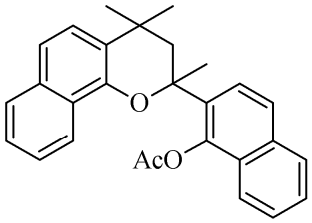
Single crystal X-ray structural characterization of the isomeric 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate (**1**) and 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthyl acetate (**2**) is described.



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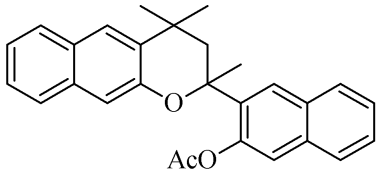

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Abstract:

Single crystal X-ray structure characterization of the isomeric 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate (**1**) and 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthyl acetate (**2**) is described. Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with all atoms situated in general positions. The isomeric compound **2** crystallizes in the centrosymmetric triclinic space group P-1 and its structure consists of two crystallographically independent molecules with all atoms located in general positions. In addition to intramolecular C-H···O bonding, **2** is involved in two intermolecular C-H···O interactions resulting in a one-dimensional H-bonded network.

Keywords: 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate, 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthyl acetate, naphthopyran, benzoflavans, crystal structure, structural isomers.

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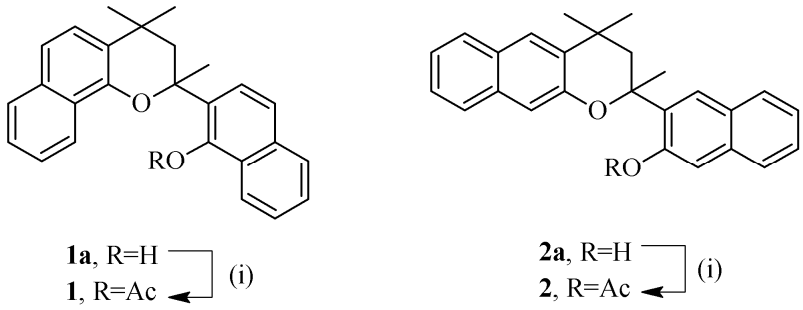
Introduction

Natural and synthetic flavans exhibit many important biological and pharmacological activities [1]. There are very few flavans having methyl substituents at 2- and 4-position of the pyran moiety. For example 2-(2'-hydroxy)-2,4',4,4,7-pentamethylflavan called inulavosin is the only naturally occurring flavan of this type having piscicidal activity and is also a melanogenesis inhibitor [2, 3]. There are no reports on natural or synthetic benzoflavans of any type. In view of this, study of benzoflavans was of interest, and we recently reported the synthesis of two new benzochromen-2-yl derivatives having methyl substituents in the pyran ring similar to inulavosin [4]. In the present work, we describe the X-ray structural characterization of the isomeric 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate **1** and 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthyl acetate **2** (Scheme 1) .



Scheme 1- Synthesis of **1** and **2**; (i) Ac_2O/pyridine

Experimental. The benzochromen-2-yl naphthols, 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthol (**1a**) and 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthol (**2a**) were prepared by literature procedure [4]. Treatment of (**1a**) or (**2a**) with acetic anhydride in the presence of pyridine afforded the title compounds **1** and **2** in good yield. IR spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000-400 cm^{-1}. The samples were prepared as KBr diluted pellets in the solid state. The benzochromen-2-yl naphthyl acetates **1** and **2** were crystallized for single crystal X-ray analysis by dissolving in hot hexane and standing at room temperature. Intensity data for **1** and **2** were collected on a Bruker (Smart Apex) CCD diffractometer using graphite-

monochromated Mo-K_α radiation. The data integration and reduction were processed with SAINTPLUS software [5]. An empirical absorption correction was applied to the collected reflections with SADABS [6]. The structure was solved with direct methods using SHELXS-97 and refinement was done against F^2 using SHELXL-97 [7]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The technical details of data acquisition and some selected refinement results for **1** and **2** are listed (Table 1).

< PLEASE PLACE TABLE 1 HERE >

CCDC 720451 (**1**) and CCDC 720452 (**2**) contain the supplementary crystallographic data for the structures reported and can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: (+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.

Results and discussion. The title compounds **1** and **2** were isolated as colorless and greenish crystalline solids respectively. The IR spectrum gave intense signal at 1769 (compound **1**) and 1757 cm^{-1} (compound **2**) which can be assigned for the carbonyl stretching vibration $\upsilon_{(C=O)}$. The peak at around 1500 cm^{-1} in both compounds can be assigned for the aromatic C-C stretching vibration while the signal at ~ 750 cm^{-1} is indicative of the presence of ortho-disubstituted aromatic compound. The C-O stretching vibration was observed at around 1199 cm^{-1} in both compounds. Compounds **1** and **2** which dissolve in common organic solvents are positional isomers and differ in terms of the disposition of the naphthalene moiety with respect to the pyran unit.

Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with all atoms situated in general positions. The observed bond angles and bond distances are in the normal range. The observed dihedral angle of 78.87^o for (C2-O1-C13-C17) in **1** indicates that the naphthopyran moiety is nearly perpendicular to the naphthalene moiety carrying the acetate group. A scrutiny of the crystal structure reveals that the ester oxygen O2 in compound **1** is involved in two weak H-bonding interactions both of which are intramolecular (Fig. 1). The O2···H16B and

O2···H12B distances of 2.630 and 2.327 Å accompanied by CHO angles of 117 and 124 ^{o} are indicative of weak C-H···O interactions (Table 2). The pyran oxygen atom O1 and the carbonyl oxygen O3 are not involved in H-bonding. Further no intermolecular H-bonds are observed in this compound.

< PLEASE PLACE FIGURE 1 & TABLE 2 HERE >

The isomeric acetate **2** crystallizes in the centrosymmetric triclinic space group P-1. The structure consists of two crystallographically independent molecules of **2** with all atoms in both molecules situated in general positions (Fig. 2). The observed bond angles and bond distances are in the normal range. In compound **2** the carbon atom (C1) of naphthopyran moiety is linked to the carbon atom (C14) of naphthalene moiety carrying the acetate group via a (C1-O2-C13-C14) dihedral angle of 87.03^{o} indicating that both the moieties are almost perpendicular. An analysis of the crystal structure reveals that four oxygen atoms are involved in H-bonding. It is interesting to note that the ester oxygen atoms O1 and O4 in each independent molecule exhibit intramolecular interactions and this behaviour is similar to that observed for **1**. The intramolecular hydrogen bonds are comparatively weaker as evidenced by smaller values of the DHA angles (Table 2). In addition the pyran oxygen atom O3 and the carbonyl oxygen O5 function as H-acceptors and are involved in intermolecular H-bonding. The C7-H7···O5 interaction leads to a one dimensional hydrogen bonded network extending along *a* axis. The C25-H25A···O3 interaction serves as a crosslink in the network (Fig. 3). In summary, the structural characterization of the isomeric benzochromene acetates **1** and **2** are reported.

< PLEASE PLACE FIGURES 2 & 3 HERE >

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Table 1: Technical details and selected refinement results for **1** and **2**

Identification Code	**1**	**2**
Empirical formula	$C_{28}H_{26}O_3$	$C_{28}H_{26}O_3$
Melting point	168 ^oC	136^oC
Formula weight	410.49 g mol^{-1}	410.514 g mol^{-1}
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, P-1
Unit cell dimensions (Å, ^{o})	a = 16.1468(17) b = 9.8267(10) c = 15.2787(16) β = 114.129(2)	a = 10.3830(10) . b = 14.8633(15) c = 15.5292(15) α = 76.510(2) β = 84.871(2) γ = 76.846(2)
Volume ($Å^3$)	2212.5(4)	2267.6(4)
Z	4	4
Density (calculated) (mg / m^3)	1.232	1.202
Absorption coefficient (mm^{-1})	0.079	0.077
F(000)	872	872
Crystal size (mm^3)	0.30 x 0.22 x 0.06	0.38 x 0.30 x 0.22
Theta range for data collection	1.38 to 26.02^o	1.75 to 26.06^o
Index ranges	$-19\leq h\leq 19$, $-12\leq k\leq 12$, $18\leq l\leq 18$	$-12\leq h\leq 12$, $-18\leq k\leq 18$, $-19\leq l\leq 19$
Reflections collected	22385	23756
Independent reflections	4353 [R(int) = 0.0457]	8898 [R(int) = 0.0296]
Completeness to theta	26.02^o = 99.8 %	26.06^o = 99.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4353 / 0 / 284	8898 / 0 / 567
Goodness-of-fit on F^2	1.007	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1066	R1 = 0.0648, wR2 = 0.1386
R indices (all data)	R1 = 0.0835, wR2 = 0.1243	R1 = 0.1041, wR2 = 0.1567
Largest diff. peak and hole	0.152 and -0.151 e. $Å^{-3}$	0.279 and -0.275 e. $Å^{-3}$
CCDC No.	720451	720452

Table 2: Hydrogen bond geometry (Å, ^{o}) for **1** and **2**

D-H···A	d(H···A)	D(D···A)	<DHA	Symmetry code
Compound **1**				
C12-H12B···O2	2.327	2.997	124	x, y, z
C16-H16B···O2	2.630	3.201	117	x, y, z
Compound **2**				
C7-H7···O5	2.523	3.423	163	1+x, y, z
C25-H25A···O3	2.604	3.563	179	1+x, y, z
C26-H26B···O1	2.512	3.091	119	x, y, z
C12-H12B···O1	2.343	3.005	125	x, y, z
C38-H38A···O4	2.368	3.017	124	x, y, z

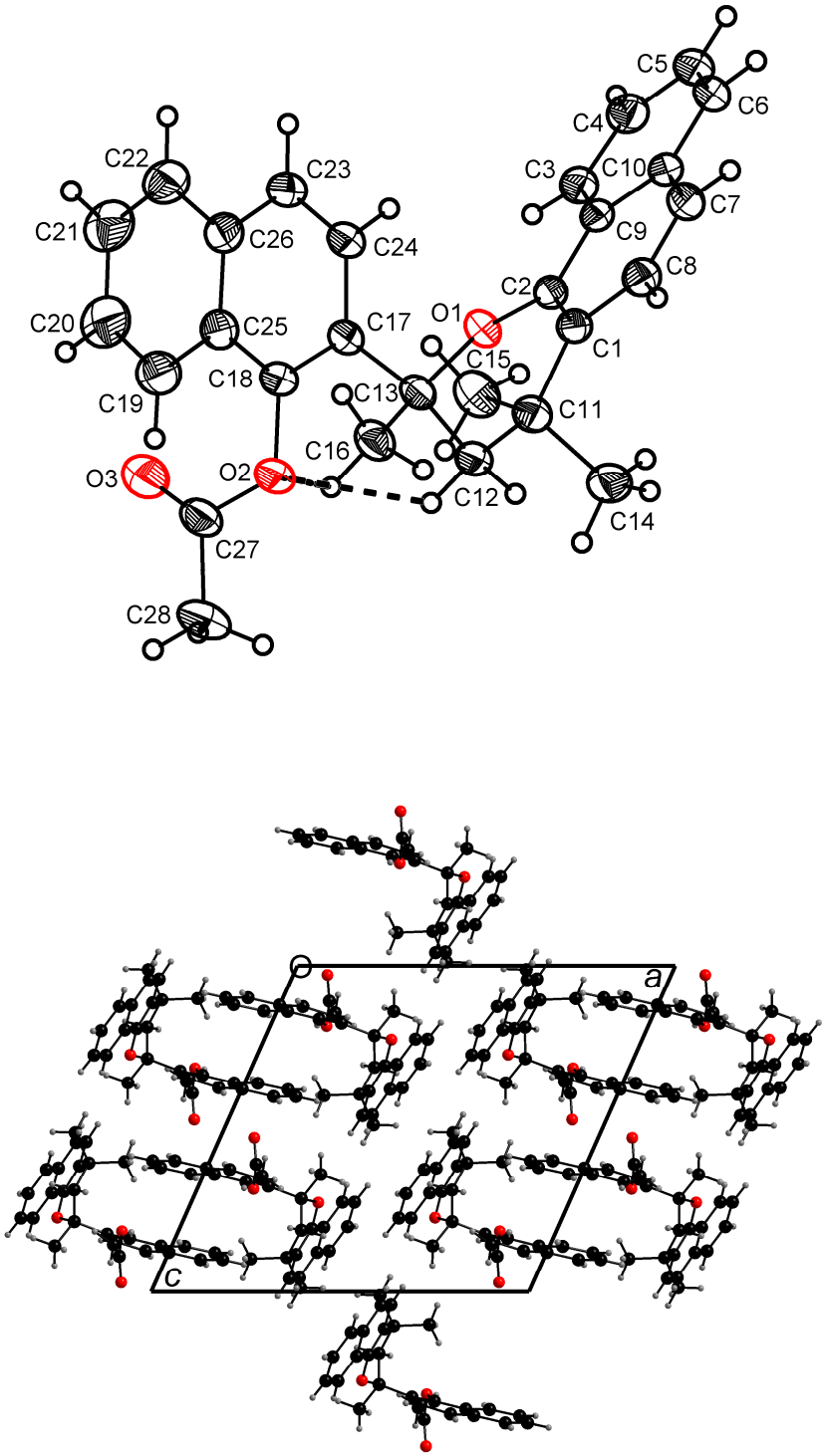

Figure 1. The crystal structure of **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines (top). A view of the crystallographic packing of **1** along *b* axis (bottom). For clarity the intramolecular H-bonding is not shown.

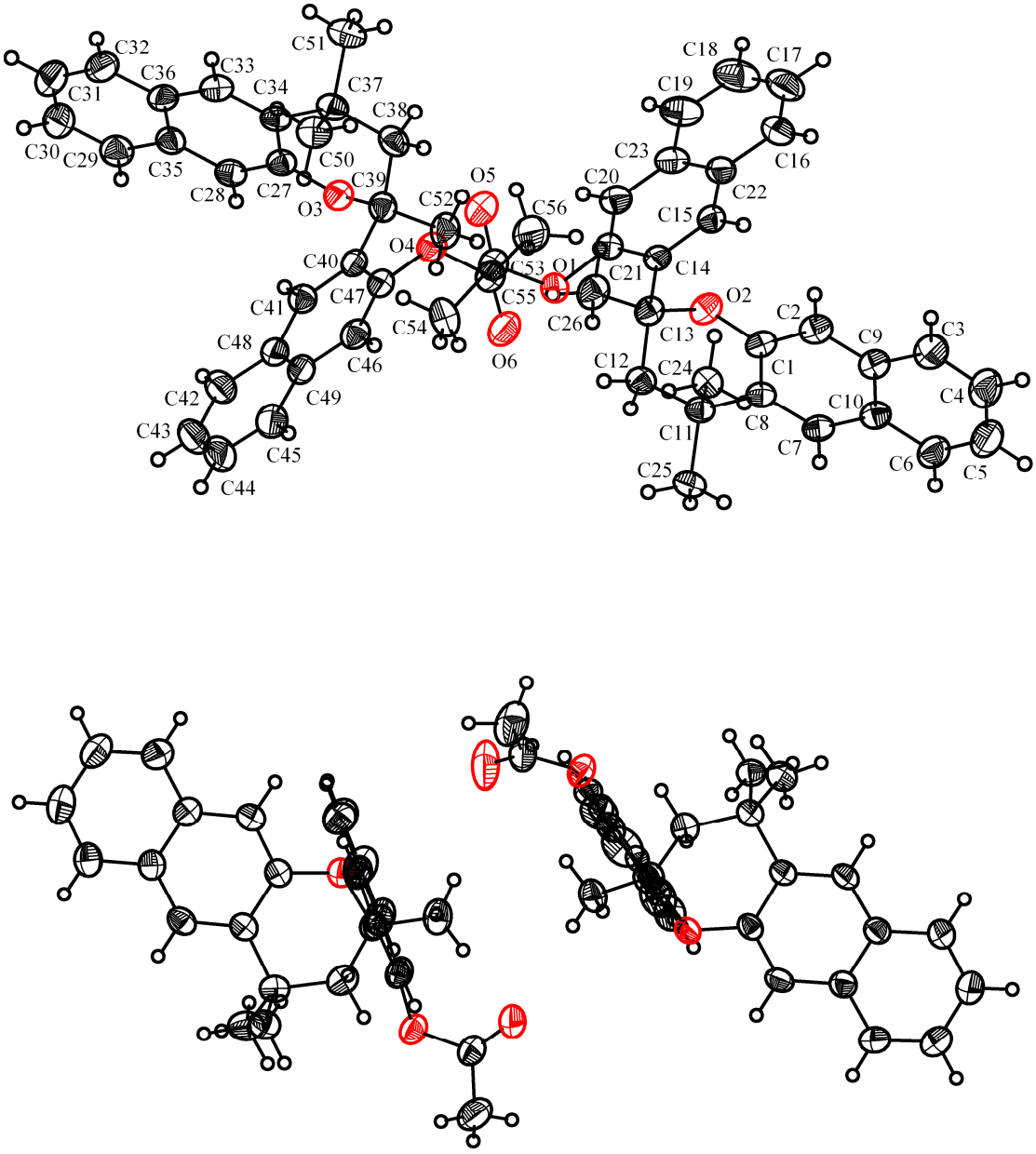

Figure 2. The crystal structure of **2** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are shown as circles of arbitrary radius (top). A view showing the two independent molecules of **2**. The naphthalene moiety carrying the acetate group is orthogonal to the naphthopyran moiety (bottom).

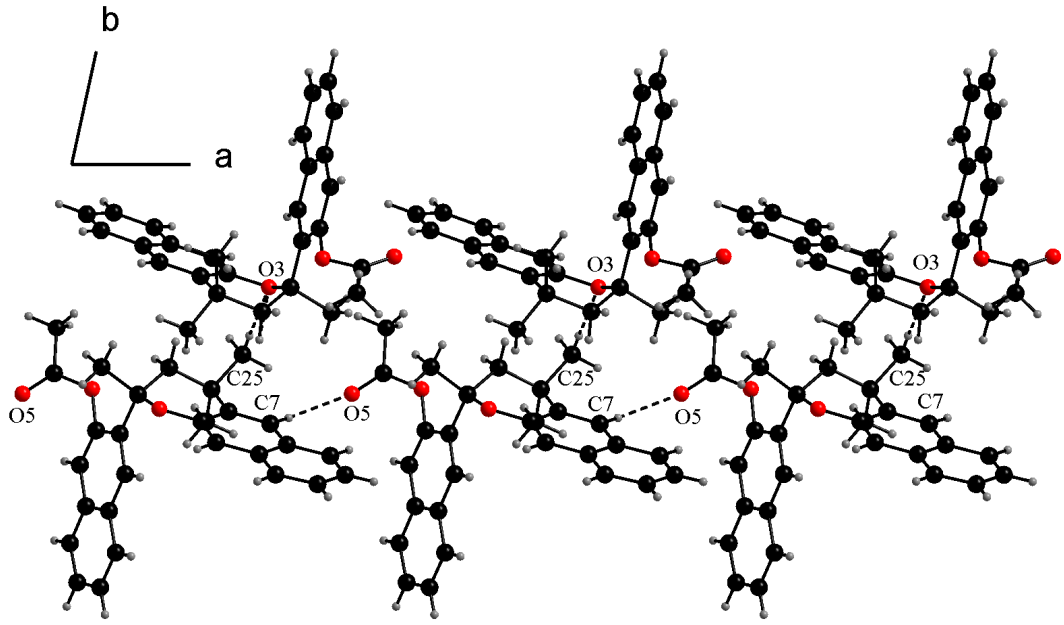

Figure 3. A view along *c* showing the intermolecular H-bonds C7-H7···O5 and C25-H25···O3 resulting in a one-dimensional network for **2**.