ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

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SINGLE CRYSTAL X-RAY ANALYSIS OF ISOMERIC 2-(2,4,4-TRIMETHYL-3,4-DIHYDRO-2*H*-BENZO[*h*]CHROMEN-2-YL)-1-NAPHTHYL ACETATE AND 3-(2,4,4-TRIMETHYL-3,4-DIHYDRO-2*H*-BENZO[*g*]CHROMEN-2-YL)-2-NAPHTHYL ACETATE

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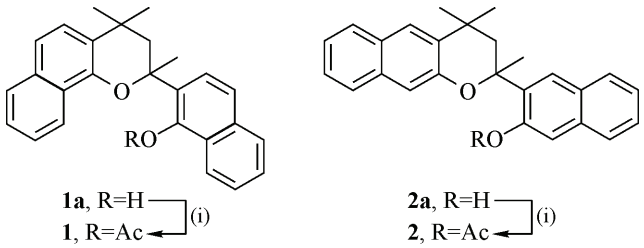
Single crystal X-ray structure characterization of isomeric 2-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl)-1-naphthyl acetate (**1**) and 3-(2,4,4-trimethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-yl)-2-naphthyl acetate (**2**) is described. Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with all atoms situated in general positions. 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.

K e y w o r d s: 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.

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-positions 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, the 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 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

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 the literature procedure [4]. Treatment of (**1a**) or (**2a**) with acetic anhydride in the presence of pyridine afforded 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. Benzochromen-2-yl naphthyl acetates **1** and **2** were crystallized for the 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 MoK_α radiation. The data integration and reduction were processed with the SAINT-PLUS software [5]. An empirical absorption correction was applied to the collected reflections with SADABS [6]. The structure was solved by direct methods using SHELXS-97 and refinement was made against F^2 using SHELXL-97 [7]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were introduced in the 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 in Table 1.

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, °C	168	136
Formula weight, $g \cdot mol^{-1}$	410.49	410.514
Temperature, K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, P-1
Unit cell dimensions a, b, c, Å; α, β, γ, deg.	16.1468(17), 9.8267(10), 15.2787(16); β = 114.129(2)	10.3830(10), 14.8633(15), 15.5292(15); 76.510(2), 84.871(2), 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	0.30×0.22×0.06	0.38×0.30×0.22
θ range for data collection, deg.	1.38 to 26.02	1.75 to 26.06
Index ranges	$-19 \le h \le 19$, $-12 \le k \le 12$, $18 \le l \le 18$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-19 \le l \le 19$
Reflections collected	22385	23756
Independent reflections	4353 [R(int) = 0.0457]	8898 [R(int) = 0.0296]
Completeness to θ, deg.	26.02 = 99.8 %	26.06 = 99.1 %
Refinement method	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 [$I > 2\sigma(I)$]	$R1$ = 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, $e \cdot Å^{-3}$	0.152 and –0.151	0.279 and –0.275
CCDC No.	720451	720452

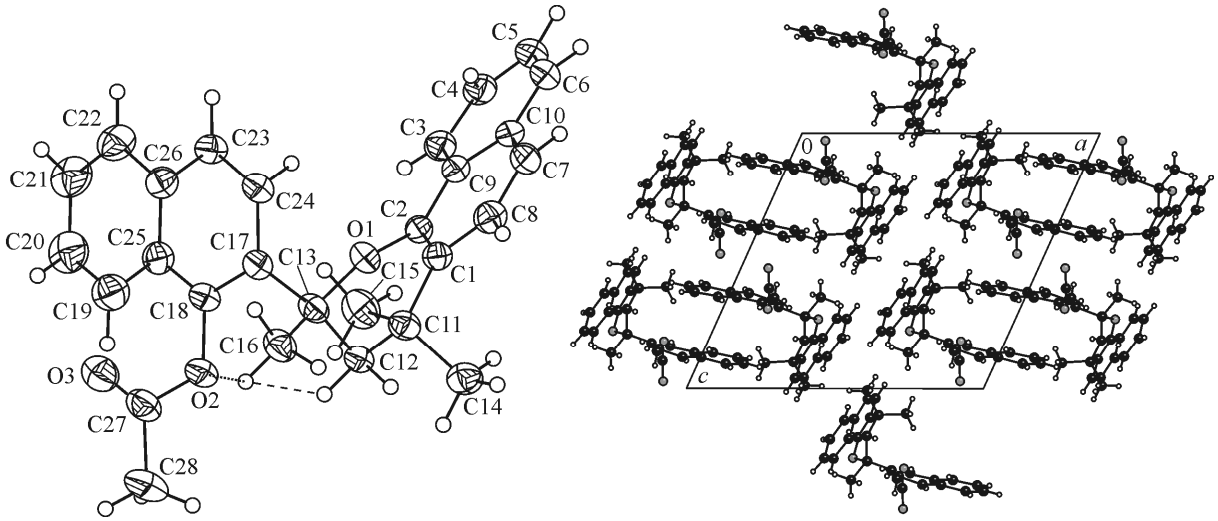


Fig. 1. Crystal structure of **1** showing the atom-labeling scheme.
Displacement ellipsoids are drawn at the 30 % probability level, except for the H atoms that are shown as circles of an arbitrary radius. Intramolecular H-bonding is shown by broken lines (left). A view of crystallographic packing of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

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 e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Title compounds **1** and **2** were isolated as colorless and greenish crystalline solids respectively. The IR spectrum gave intense signal at 1769 cm^{-1} (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 to the aromatic C—C stretching vibration, while the signal at ~750 cm^{-1} is indicative of the presence of the *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.

T a b l e 2

Hydrogen bond geometry (Å, deg.) *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*

The observed dihedral angle of 78.87° 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 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 Å and 2.327 Å accompanied by CHO angles of 117° and 124° are indicative of weak C—H···O interactions (Table 2). The pyran oxygen atom O1 and carbonyl oxygen O3 are not involved in H-bonding. Further no intermolecular H-bonds are observed in this compound.

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 the naphthopyran moiety is linked to the carbon atom (C14) of the naphthalene moiety, carrying the acetate group via the (C1—O2—C13—C14) dihedral angle of 87.03°, indicating that both moieties are almost perpendicular. An analysis of the crystal

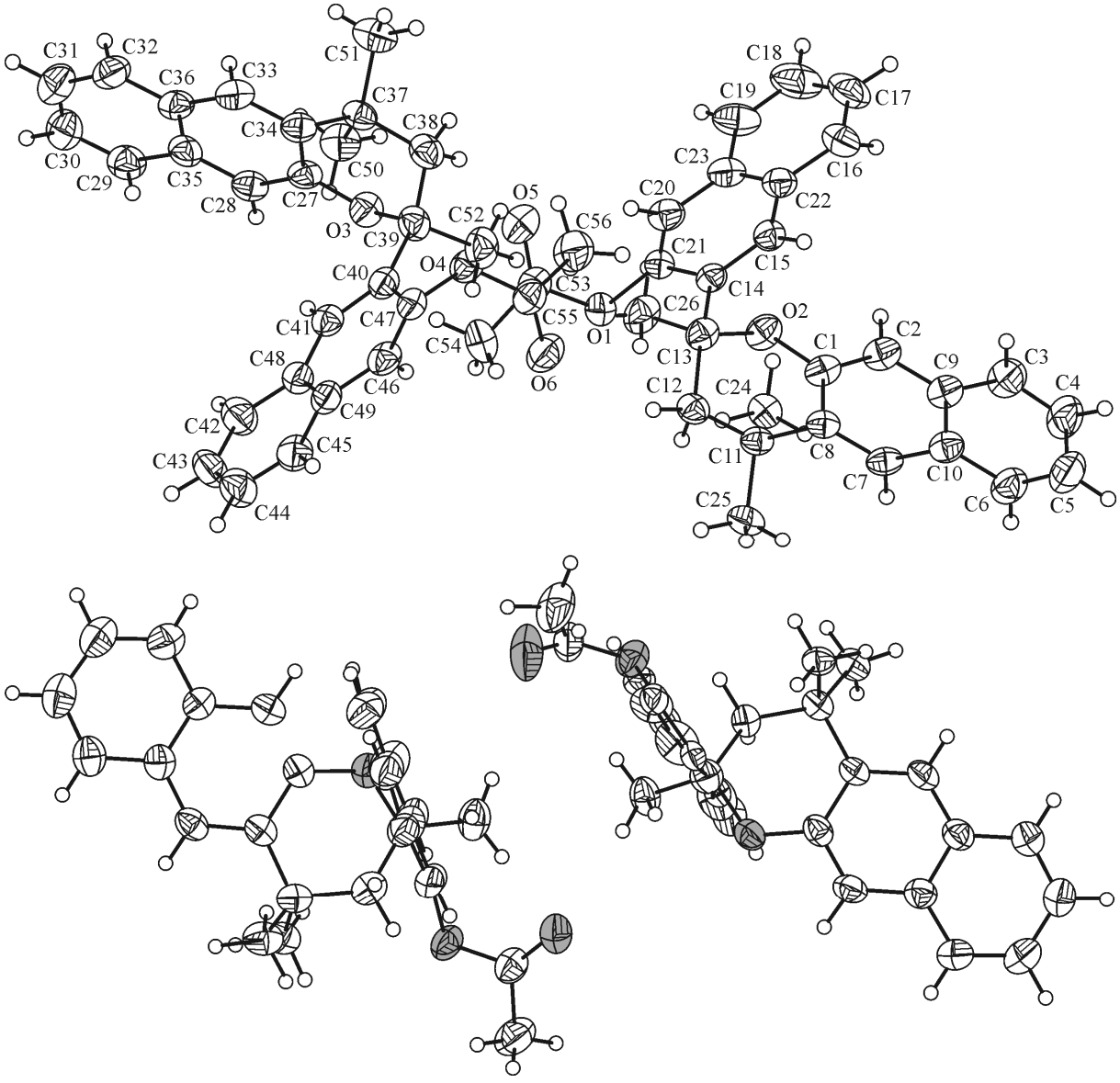


Fig. 2. Crystal structure of **2** showing the atom-labeling scheme.
Displacement ellipsoids are drawn at the 30 % probability level, except for the H atoms that are shown as circles of an arbitrary radius. (top). A view showing the two independent molecules of **2**. The naphthalene moiety carrying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

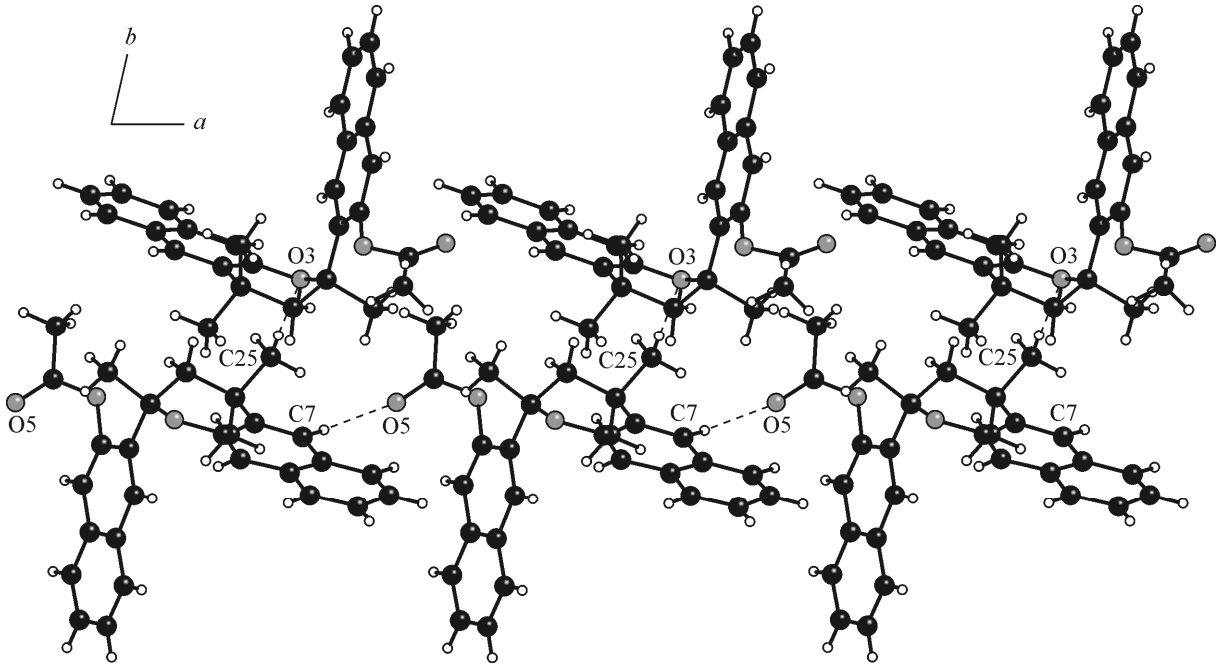


Fig. 3. View along *c* showing the intermolecular C7—H7···O5 and C25—H25···O3 H-bonds resulting in a one-dimensional network for **2**

structure reveals that four oxygen atoms are involved in H-bonding. It is interesting to note that ester oxygen atoms O1 and O4 in each independent molecule exhibit intramolecular interactions, and this behavior 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 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 the *a* axis. The C25—H25A···O3 interaction serves as a crosslink in the network (Fig. 3). In summary, the structural characterization of isomeric benzochromene acetates **1** and **2** are reported.

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