# Synthesis and X-ray structural investigations of 2-amino-7-methyl-4-(1-naphthyl)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3-carbonitrile and 2-amino-4-(1-naphthyl)-5-oxo-4*H*,5*H*pyrano[3,2-*c*]chromene-3-carbonitrile

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Synthesis and X-ray structural investigations have been carried out for the two title compounds  $C_{20}H_{14}N_2O_3$  (4) and  $C_{23}H_{14}N_2O_3 \cdot C_2H_3N$  (5). Compound 4 crystallizes in the monoclinic space group  $P2_1/n$ , with a = 7.0542(5), b = 8.822(1), c = 24.833(2) Å,  $\beta = 94.30(4)^\circ$ , V = 1541.0(4)Å<sup>3</sup>, and Z = 4. Compound **5** crystallizes with an acetonitrile solvent molecule in the monoclinic space group  $P2_1/n$ , with a = 11.075(1), b = 7.854(1), c = 22.703(2) Å,  $\beta = 90.67(1)^{\circ}$ , V = 1974.5(3) Å<sup>3</sup>, and Z = 4. In both molecules, the 4H-pyran ring adopts a flattened-boat conformation. The naphthalene substituent occupies a pseudo-axial position and the dihedral angle with the flat part of the pyran ring is equal to 94.6(3) in 4 and 76.8(3) $^{\circ}$  in 5. The mutual orientation of these fragments and the flatness of the heterocyclic rings lead to H...H intramolecular steric interactions: H4A...H18A 1.98 Å in 4 and 2.11 Å in 5. In the crystal of 4, intermolecular hydrogen bonds  $N-H\cdots O$ and  $C-H \cdots N$  link molecules into infinite tapes along the b axis. In the crystals of 5, intermolecular hydrogen bonds  $N-H \cdots O$  and  $C-H \cdots N$  link molecules into infinite layers parallel to the bc plane. In each case, the  $C-H \cdots N$  interaction can be considered to be a weak hydrogen bond. The acetonitrile molecules link via intermolecular weak  $C-H\cdots N$ hydrogen bonds to form infinite chains along the *b* axes.

**KEY WORDS:**  $\alpha,\beta$ -Unsaturated nitriles; 4H-pyran; crystal structure; conjugation; intermolecular H-bonds.

## Introduction

The present investigation is a continuation of our work that includes synthesis and structural studies of heterocyclic compounds, such as 4H- pyran derivatives<sup>1–7</sup> that can be obtained starting from different  $\alpha$ , $\beta$ -unsaturated nitriles.<sup>8,9</sup> Some 4H-pyran derivatives are potential bioactive compounds, such as adenosine receptor antagonists<sup>10</sup> and calcium antagonists.<sup>11</sup>

The investigated compounds were synthesized by the reaction of (1-naphthylmethylene) malononitrile **1** with 4-hydroxy-6-methyl-2pyrone **2** or **1** with 4-hydroxycoumarin **3** in accord with literature methods.<sup>6,7</sup> We report here the

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synthesis of both 4H-pyran derivatives and their full characterization by X-ray analysis (Scheme 1, Figs. 1 and 2). The structures of these compounds are not present in the Cambridge Structural Database.<sup>12</sup>

## **Experimental section**

### General methods for 4 and 5

A 50-mL round-bottom flask was charged with (1-naphthylmethylene)malononitrile **1** (0.61

g, 3.0 mmol) and 4-hydroxy-6-methyl-2-pyrone **2** (0.38 g, 3.0 mmol) or **1** (0.61 g, 3.0 mmol) and 4-hydroxycoumarin **3** (0.49 g, 3.0 mmol), 20 mL of ethanol and catalytic amounts of morpholine. The mixtures were boiled while stirring for 1–3 min and then allowed to cool. The precipitates were filtrated, washed with ethanol and then dried under vacuum. After recrystallization from 1:1 acetoni-trile/EtOH for **4** and from acetonitrile for **5**, 88% (0.88 g) and 85% (0.93 g) yields of pure products were obtained, respectively. The compounds had melting points of 248 and 242°C, respectively.



**Fig. 1.** View of the title molecule **4** with the atom-numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary small radius for clarity.



**Fig. 2.** View of the title molecule **5** and acetonitrile with the atom-numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary small radius for clarity.

The NMR for **4** follows: <sup>1</sup>H (300 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 8.35 (d, J = 7.4 Hz, 1H), 7.93 (dm, J = 7.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.54 (m, 2H), 7.45 (t, J = 8.1 Hz, 1H), 7.23 (d, J = 7.0 Hz, 1H), 7.13 (br s, 2H), 6.33 (d, J = 1 Hz, 1H), 5.27 (s, 1H), 2.23 (s, 3H); <sup>13</sup>C (75 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 162.79, 161.35, 158.53, 157.92, 140.88, 133.28, 130.96, 128.48, 127.35, 125.98, 125.76 (2C), 125.67, 123.41, 119.21, 101.38, 97.93, 58.56, 30.95, 19.28.

The NMR for **5** follows: <sup>1</sup>H (300 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 8.43 (d, J = 8.1 Hz, 1H), 7.95 (dm, J = 7.7 Hz, 2H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (tm, J = 7.0 Hz, 1H), 7.55 (m, 3H), 7.46 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.37 (br s, 2H), 7.32 (d, J = 7.0 Hz, 1H), 5.46 (s, 1H); <sup>13</sup>C (75 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 159.56, 157.87, 157.82, 153.81, 152.11, 140.71, 133.30, 132.93, 130.96, 128.48, 127.45, 126.10, 125.85, 125.76, 124.74, 123.44, 122.46, 119.13, 116.61, 112.98, 104.68, 58.56, 31.46.

# Crystallography

Single crystals of 4 and 5 were obtained by slow evaporation of their ethanol and acetonitrile solutions, respectively. Suitable colorless crystals of 4 and 5 with approximate dimensions  $0.60 \times 0.19 \times 0.13$  and  $0.48 \times 0.10 \times 0.08$  mm were found. Diffraction data for 4 and 5 were collected at -173°C on a RIGAKU R-AXIS RAPID diffractometer with graphite monochromator and CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54118$  Å) using a 0.8 mm collimator. Data collection, intensity integration, and absorption corrections were performed with the CrystalClear package.<sup>13</sup> A spherical-harmonics-based absorption correction was applied by deducing an absorption surface associated with the crystal, requiring that this surface minimize the difference in intensities between symmetry related reflections.

All non-hydrogen atoms of the structures were found by direct methods. Refinement was done by full-matrix least-squares first isotropically and then anisotropically for all non-H atoms using SHELXL97.<sup>14</sup> In **5**, the hydrogen atoms of the CH<sub>3</sub> group of the solvent acetonitrile molecule were found from a difference Fourier map and refined isotropically. All other H atoms in both structures were placed in geometrically calculated positions and introduced in the refinements using the riding approximation. The final difference map showed no unusual features, with no significant peaks above the general background. The crystal and structure determination data for **4** and **5** are summarized in Table 1.

#### **Results and discussion**

The X-ray investigations show that molecules 4 and 5 have slightly different structures, but most of the geometric parameters are very similar to the standard values<sup>15</sup> and are very close to our data.<sup>3–7</sup>

In both molecules the pyran ring adopts a flattened boat conformation: the O1 and C4 atoms are out of the C2/C3/C5/C9 plane (planar within 0.003(3) and 0.020(4) Å, respectively) by 0.041(3) and 0.043(3) Å in 4 and -0.117(4) and -0.220(4) Å in 5. The bending of the heterocyclic rings along the lines  $O1 \cdot \cdot \cdot C4$ ,  $C2 \cdot \cdot \cdot C9$ and  $C3 \cdot \cdot \cdot C5$  equals 4.0(3), 3.3(3) and 2.8(3)° in 4, and 15.8(3), 9.4(3) and 14.3(3)° in 5, respectively. Thus, the heterocyclic ring is more flattened in molecule 4. In both molecules, the bulky naphthalene substituent occupies a pseudoaxial position and the dihedral angle with the flat part of the pyran ring is equal to 94.6(3)and  $76.8(3)^{\circ}$ , respectively. The mutual orientation of these fragments and the flatness of the heterocyclic rings (especially in 4) lead to  $H \cdot \cdot \cdot H$ intramolecular steric interactions: H4A···H18A 1.98 Å in 4 and 2.11 Å in 5. These contacts are shorter than the sum of the van der Waals radii of the H atoms.<sup>16</sup> As we mentioned earlier for related compounds,<sup>6,7</sup> such steric hindrance causes elongation of the C4–C10 bond lengths to 1.556(3)and 1.542(4) Å, respectively, in comparison with neighboring  $Csp^3 - Csp^2$  distances that are only slightly longer or equal to the standard value.<sup>15</sup>

	4	5
CCDC deposit no.	256432	256433
Empirical formula	$C_{20}H_{14}N_2O_3$	$C_{23}H_{14}N_2O_3C_2H_3N$
Formula weight	330.33	407.42
Diffractometer	RIGAKU R-AXIS RAPID	RIGAKU R-AXIS RAPID
Temperature, K	100	100
Crystal system	Monoclinic	Monoclinic
Space group; Z	$P2_1/n; 4$	$P2_1/n; 4$
<i>a</i> (Å)	7.054(1)	11.075(1)
b (Å)	8.822(1)	7.854(1)
<i>c</i> (Å)	24.833(2)	22.703(2)
$\alpha$ (°)	90.00	90
$\beta$ (°)	94.30(4)	90.67(1)
γ (°)	90.00	90
Volume (Å <sup>3</sup> )	1541.0(3)	1974.6(3)
Density (g cm $^{-3}$ )	1.424	1.370
$\theta$ scan range	5.3-66.6	3.9-68.4
Absorbtion coefficient $(mm^{-1})$	0.80	0.75
R <sub>merge</sub>	0.059	0.063
Absorbtion correction factor	0.83-0.85	0.69-0.94
Total reflections	12402	12446
Independent reflections	2570	3495
Observed reflections $[F_o > 4\sigma (F_o)]$	2484	3224
Final R <sub>1</sub>	0.0605	0.0750
Final $wR_2$	0.1638	0.2428
Goodness of fit	1.046	1.048

 Table 1. Structure Determination Summary for 4 and 5

In both molecules, the dihedral angle between the flat part of the pyran ring and the fused pyron heterocycle in 4 and the fused coumarin heterocycle in 5 is small. This angle value is

Fable         2.         Selection           Mol         Mol         Mol	cted Bond E ecules 4 and 5	istances in
Bond	4	5
D(1) - C(2) $D(1) - C(9)$ $N(1) - C(2)$ $C(2) - C(3)$ $C(3) - C(1)$ $C(3) - C(4)$ $C(1) - N(2)$ $C(4) - C(5)$ $C(4) - C(5)$ $C(4) - C(10)$ $C(5) - C(6)$ $C(5) - C(6)$ $C(5) - C(9)$ $C(6) - O(3)$ $D(3) - C(7)$	$\begin{array}{c} 1.382(3)\\ 1.382(3)\\ 1.342(2)\\ 1.354(3)\\ 1.423(3)\\ 1.515(4)\\ 1.155(3)\\ 1.502(3)\\ 1.556(3)\\ 1.437(3)\\ 1.356(3)\\ 1.388(3)\\ 1.374(3)\\ 1.374(3)\\ 1.242(2)\end{array}$	$\begin{array}{c} 1.384(3)\\ 1.368(3)\\ 1.339(4)\\ 1.346(4)\\ 1.428(4)\\ 1.516(4)\\ 1.516(4)\\ 1.511(4)\\ 1.542(4)\\ 1.445(4)\\ 1.343(4)\\ 1.370(3)\\ 1.378(3)\\ 1.378(3)\end{array}$
C(8) - C(9)	1.421(3)	1.447(4)

5.3(3) and  $7.1(3)^{\circ}$ , respectively. Due to the near planarity, it is possible to predict conjugation throughout both rings. According to Table 2, the



**Fig. 3.** Projection of the crystal packing of **4** along the *a* axis. Dashed lines are intermolecular  $N-H\cdots O$  and  $C-H\cdots N$  H-bonds.

Table 3. Hydrogen-Bond Parameters for 4

D-H	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	<dha< th=""><th><math display="block">d(D{\cdots}A)</math></th><th>А</th></dha<>	$d(D{\cdots}A)$	А
N(1)-H(1B)	0.88	2.05	145	2.820(3)	$\begin{array}{l} O(2) \ [x, 1 + y, z] \\ N(2) \ [0.5 - x, \\ -0.5 + y, 0.5 - z] \end{array}$
C(20)-H(20C)	0.98	2.55	155	3.463(3)	

bond length distributions show an alternation of single C–C and double C=C bond lengths and also elongation of C=O bonds in comparison with normal values.<sup>15</sup> Such bond lengths are consistent with the idea of extensive conjugation in these systems.

In both molecules, only one H-atom of the NH<sub>2</sub> group is involved in a N–H···O intermolecular hydrogen bond. In the crystal of 4, intermolecular hydrogen bonds N–H···O and C–H···N link molecules into infinite tapes along the *b* axis (Fig. 3; Table 3). In the crystals of 5, intermolecular hydrogen bonds N–H···O and C–H···N link molecules into infinite layers parallel to the *bc* plane (Fig. 4; Table 4). In both cases, according to literature data,<sup>17</sup> the C–H···N in-



**Fig. 4.** Projection of the crystal packing of **5** along the *a* axis (showed only one layer of molecules). Dashed lines are intermolecular  $N-H \cdots O$  and  $C-H \cdots N$  H-bonds.

Table 4. Hydrogen-Bond Parameters for 5

D-H	d(D-H)	$D(H{\cdot}{\cdot}{\cdot}A)$	<dha< th=""><th><math display="block">d(D{\cdots}A)</math></th><th>А</th></dha<>	$d(D{\cdots}A)$	А
N(1) = H(1B) C(22) = H(22A)	0.88	2.08	158	2.914(3)	O(2) [x, y - 1, z] N(2) [-0.5 + x]
C(22) = H(22A) C(2S) = H(1SC)	1.1(3)	2.32	159(1)	3.448(4)	N(2) [-0.5 + x, 0.5 - y, 0.5 + z] N(1S) [0.5 - x, 0.5 - x]
C(2S)-H(1SC)	1.1(3)	2.41(3)	159(1)	3.448(4)	N(1S) [0.5 - x, 0.5 + y, 0.5 - z]

teractions can be considered to be weak H-bonds. The acetonitrile molecules are linked via weak  $C-H\cdots N$  intermolecular hydrogen bonds that form infinite chains along the *b* axes (Fig. 4; Table 4).

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**Supplementary material** CCDC 256432 & 256433 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html of from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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#### 922

#### Nesterov, Wiedenfeld, Nesterova, and Daniels

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