

2-Amino-4-(1-naphthyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile and 2-amino-7,7-dimethyl-4-(1-naphthyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

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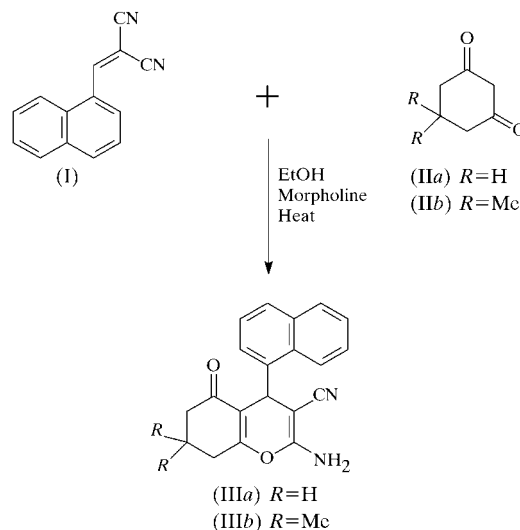
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Syntheses and X-ray structural investigations have been carried out for the two title compounds, $C_{20}H_{16}N_2O_2$, (IIIa), and $C_{22}H_{20}N_2O_2$, (IIIb). In (IIIa), the heterocyclic ring adopts a sofa conformation, while in (IIIb), the ring has a flattened boat conformation. In both molecules, the fused cyclohexenone ring adopts a sofa conformation. The dihedral angles between these two flat fragments are 3.5 (2) and 17.5 (2) $^\circ$ in (IIIa) and (IIIb), respectively. The dihedral angles between the pseudo-axial naphthalene substituents and the planes of the pyran rings are 90.9 (1) and 96.7 (1) $^\circ$, respectively. In the crystal structure of (IIIa), intermolecular $N-H\cdots N$ and $N-H\cdots O$ hydrogen bonds link the molecules into infinite tapes along the b axis, while molecules of (IIIb) form centrosymmetric dimers *via* $N-H\cdots N$ hydrogen bonds, with only one H atom of the NH_2 donor group taking part in hydrogen bonding.

Comment

The present investigation is a continuation of our work that includes syntheses and structural studies of unsaturated nitriles as potential non-linear optical materials (Nesterov *et al.*, 2001a,b) and heterocyclic compounds that can be obtained using such nitriles (Nesterov & Viltchinskaia, 2001). Some 4H-pyran derivatives are potential bioactive compounds, for instance, as calcium antagonists (Suarez *et al.*, 2002). Such heterocyclic compounds have structures similar to the well known 1,4-dihydropyridines (Triggle *et al.*, 1980; Bossert *et al.*, 1981; Kokubun & Reuter, 1984; Bossert & Vater, 1989; Wang *et al.*, 1989), which exhibit high bioactivities. Thus, there has been a growing interest in the structures of 4H-pyran derivatives (Bellanato *et al.*, 1987, 1988; Florencio & Garcia-Blanco, 1987; Lokaj *et al.*, 1990; Marco *et al.*, 1993).

Syntheses and X-ray structural investigations have been carried out for the title compounds, (IIIa) and (IIIb) (Figs. 1 and 2), which were synthesized from (1-naphthylmethylene)-malononitrile, (I) (Nesterov *et al.*, 2001a). Most of the geometric parameters in the two molecules (Tables 1 and 3) are very similar to the standard values (Allen *et al.*, 1987) and very close to previously reported data for similar 4H-pyran derivatives (Sharanina *et al.*, 1986; Klokol *et al.*, 1987; Martin-Leon *et al.*, 1990; Shestopalov *et al.*, 1991, 2002, 2003; Samet *et al.*, 1996; Kislyi *et al.*, 1999; Nesterov & Viltchinskaia, 2001; Suarez *et al.*, 2002).



X-ray analysis shows that the molecules of (IIIa) and (IIIb) have slightly different molecular structures. The pyran ring in (IIIa) adopts a sofa conformation; atom C4 lies 0.100 (1) Å out of the O1/C2/C3/C5/C10 plane [planar within 0.003 (1) Å] and the dihedral angle between this plane and the C3–C5 plane is 6.5 (2) $^\circ$. However, (IIIb) has a flattened boat conformation; atoms O1 and C4 deviate from the C2/C3/C5/C10 plane [planar within 0.015 (2) Å] by 0.186 (2) and

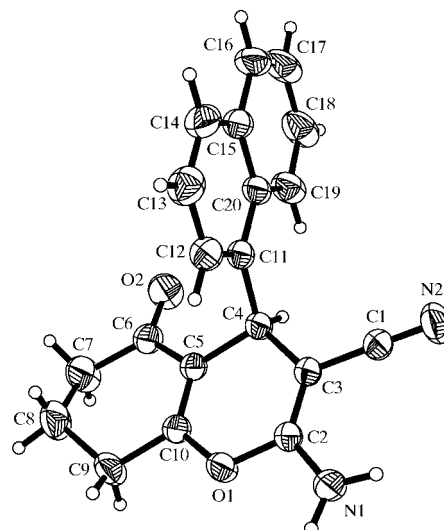


Figure 1
A view of (IIIa), showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

0.340 (2) Å, respectively, and the heterocycle bends along the O1...C4, C2...C10 and C3...C5 lines by 24.5 (2), 15.1 (2) and 22.0 (2)°, respectively. Our previous work and literature data show that the pyran ring is flexible but usually adopts a flattened boat conformation.

In both molecules, the fused cyclohexanone ring adopts a sofa conformation; in (IIIa) and (IIIb), the C8 atoms lie 0.572 (1) and 0.620 (2) Å, respectively, out of the C7/C6/C5/C10/C9 planes [planar within 0.005 (1) and 0.040 (1) Å, respectively]. The dihedral angles between the pyran and cyclohexanone rings are 3.5 (2) and 17.5 (2)°, respectively. In both molecules, the bulky naphthalene substituents occupy

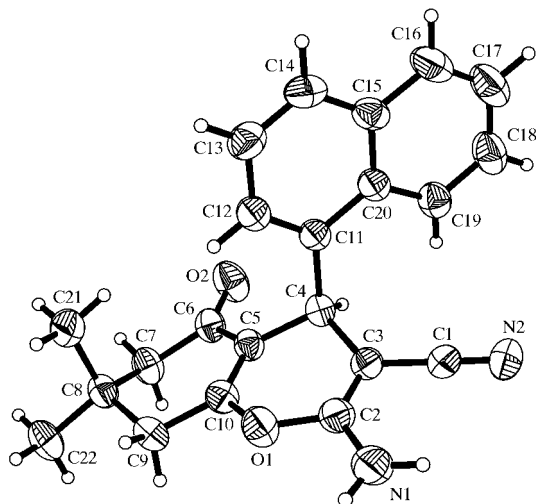


Figure 2
A view of (IIIb), showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

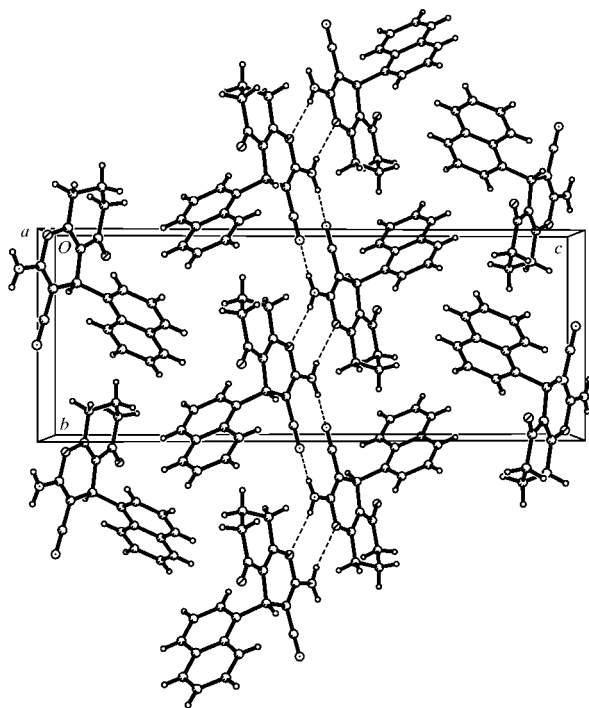


Figure 3
A projection of the crystal packing of (IIIa) along the *a* axis.

pseudo-axial positions, forming dihedral angles with the flat moieties of the pyran rings of 90.9 (1) and 96.7 (1)°, respectively. This mutual orientation of these fragments and the flatness of the heterocyclic rings leads to intramolecular H4A...H19A steric interactions [2.01 Å in (IIIa) and 2.17 Å in (IIIb)]. These contacts are shorter than the sum of the van der Waals radii of two H atoms (Rowland & Taylor, 1996), especially in the case of (IIIa). In addition, (IIIb) contains a short intramolecular contact [C1...C19 = 3.160 (2) Å] that is shorter than the sum of the van der Waals radii (Rowland & Taylor, 1996). These steric hindrances cause elongation of the C4—C11 bond lengths to 1.534 (3) and 1.539 (2) Å in (IIIa) and (IIIb), respectively, whereas the neighboring Csp^3 — Csp^2 distances are only slightly longer than the standard value (Allen *et al.*, 1987).

As we described previously for related compounds (Sharina *et al.*, 1986; Klokol *et al.*, 1987; Shestopalov *et al.*, 1991, 2002, 2003; Samet *et al.*, 1996; Kislyi *et al.*, 1999; Nesterov & Viltchinskaja, 2001), there is conjugation between NH_2 donor and CN acceptor groups *via* the C2=C3 double bond. Thus, in both molecules, the C2—N1 distances are shorter than the average conjugated C—N single-bond length (1.370 Å) found in the Cambridge Structural Database (Allen, 2002). However, variations of other bond lengths in these flat fragments are less distinct.

In the crystal structure of (IIIa), intermolecular N—H...N and N—H...O hydrogen bonds link molecules into infinite tapes along the *b* axis (Fig. 3), while molecules of (IIIb) form centrosymmetric dimers *via* N—H...N hydrogen bonds (Fig. 4), involving only one H atom of the NH_2 donor group (Tables 2 and 4). These dimers are further linked by weak C—H...O contacts along the *a* axis.

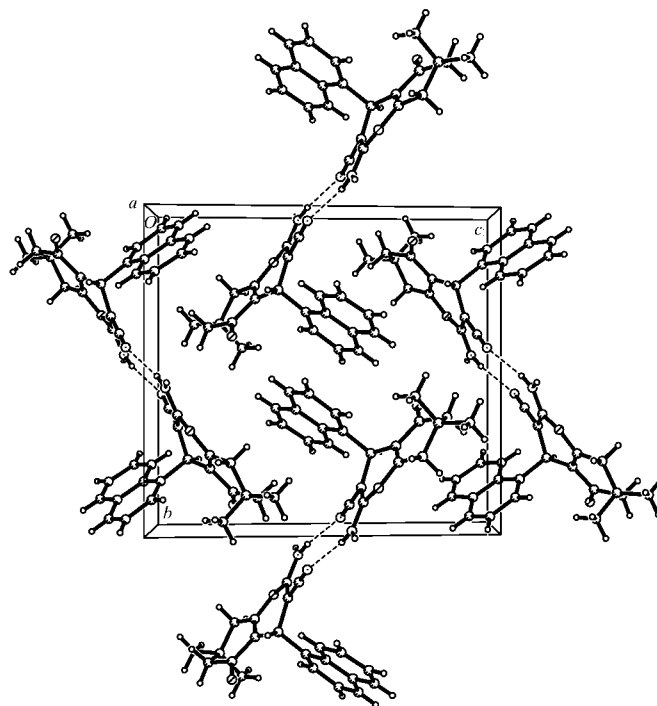


Figure 4
A projection of the crystal packing of (IIIb) along the *a* axis.

Analysis of the crystal packing showed that there is only one intermolecular steric contact in (IIIa). This contact, C13...C18(1 - x, y, z), is shorter than the sum of the van der Waals radii (Rowland & Taylor, 1996). The other geometric parameters in the investigated molecules have standard values (Allen *et al.*, 1987).

Experimental

Compounds (IIIa) and (IIIb) were obtained by the reaction of (1-naphthylmethylene)malononitrile, (I) (Nesterov *et al.*, 2001a), with 1,3-diketones (IIa) and (IIb) according to a literature procedure (Nesterov & Viltchinskaja, 2001). The precipitates were isolated and recrystallized from acetonitrile [m.p. 501 K, yield 95% for (IIIa); m.p. 484 K, yield 92% for (IIIb)]. Crystals were grown by slow isothermic evaporation of CH₃CN solutions of (IIIa) and (IIIb). For (IIIa), ¹H NMR (DMDO-*d*₆, 300 MHz): δ 8.38 (*d*, 1H, *J* = 8.1 Hz), 7.91 (*dd*, 1H, *J* = 7.7, 1.5 Hz), 7.76 (*d*, 1H, *J* = 8.1 Hz), 7.56 (*td*, 1H, *J* = 6.6, 1.5 Hz), 7.51 (*td*, 1H, *J* = 6.6, 1.1 Hz), 7.43 (*t*, 1H, *J* = 7.5 Hz), 7.24 (*dd*, 1H, *J* = 7.4, 1.1 Hz), 6.95 (*br s*, 2H, NH₂), 5.14 (*s*, 1H, H4), 2.68 (*m*, 2H, H6), 2.25 (*m*, 2H, H8), 1.95 (*m*, 2H, H7); ¹³C NMR (CDCl₃, 75 MHz): δ 195.9 (C5), 164.8 (C8A), 158.4 (C2), 142.0, 133.3, 130.7, 128.3, 126.9, 125.8 (2C), 125.6, 124.9, 123.6 (naphthalene), 119.7 (CN), 114.5 (C4A), 58.8 (C3), 36.3 (C6), 30.0 (C4), 26.5 (C8), 19.9 (C7). For (IIIb), ¹H NMR (DMDO-*d*₆, 300 MHz): δ 8.36 (*d*, 1H, *J* = 8.5 Hz), 7.91 (*dd*, 1H, *J* = 7.4, 1.8 Hz), 7.76 (*d*, 1H, *J* = 8.1 Hz), 7.56 (*td*, 1H, *J* = 7.0, 1.5 Hz), 7.51 (*td*, 1H, *J* = 6.6, 1.1 Hz), 7.44 (*t*, 1H, *J* = 7.7 Hz), 7.23 (*d*, 1H, *J* = 7.4 Hz), 6.96 (*br s*, 2H, NH₂), 5.13 (*s*, 1H, H4), 2.58 (*s*, 2H, H6), 2.23 (*d*, 1H, H8A, *J* = 16.2 Hz), 2.06 (*d*, 1H, H8B, *J* = 15.8 Hz), 1.05 (*s*, 3H, CH₃), 0.98 (*s*, 3H, CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 195.7 (C5), 162.7 (C8A), 158.4 (C2), 141.9, 133.3, 130.7, 128.3, 126.9, 125.8, 125.63, 125.56, 125.1, 123.6 (naphthalene), 119.6 (CN), 113.4 (C4A), 58.9 (C3), 50.0 (C6), 39.8 (C8), 31.8 (C7), 30.1 (C4), 28.4 (CH₃), 27.0 (CH₃).

Compound (IIIa)

Crystal data

C₂₀H₁₆N₂O₂
M_r = 316.35
 Monoclinic, *P*₂₁/*n*
a = 6.4410 (13) Å
b = 9.6330 (19) Å
c = 24.911 (5) Å
 β = 92.98 (3)°
V = 1543.5 (5) Å³
Z = 4

D_x = 1.361 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 12–13°
 μ = 0.09 mm⁻¹
T = 295 (2) K
 Prism, colorless
 0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ/2θ scans
 3619 measured reflections
 3318 independent reflections
 2287 reflections with *I* > 2σ(*I*)
R_{int} = 0.061

θ_{max} = 27.0°
h = 0 → 8
k = 0 → 12
l = -31 → 31
 3 standard reflections every 97 reflections intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.051
wR(*F*²) = 0.157
S = 1.05
 3318 reflections
 217 parameters
 H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.085*P*)² + 0.45*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.33 e Å⁻³
 Δρ_{min} = -0.24 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (IIIa).

O1–C2	1.370 (2)	N2–C1	1.143 (3)
O1–C10	1.384 (2)	C1–C3	1.417 (2)
O2–C6	1.215 (2)	C2–C3	1.341 (3)
N1–C2	1.353 (2)		
C2–O1–C10	118.46 (14)	C2–C3–C4	123.70 (16)
N2–C1–C3	178.9 (2)	C1–C3–C4	118.78 (15)
C3–C2–N1	128.06 (17)	O2–C6–C5	120.05 (18)
C3–C2–O1	122.50 (17)	O2–C6–C7	121.70 (18)
N1–C2–O1	109.40 (16)	C5–C6–C7	118.20 (17)
C2–C3–C1	117.36 (17)		
C2–C3–C4–C5	-7.6 (3)	C3–C4–C5–C10	8.1 (3)
C2–C3–C4–C11	114.1 (2)	C3–C4–C11–C12	-57.8 (2)

Table 2

Hydrogen-bonding geometry (Å, °) for (IIIa).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1A...N2 ⁱ	0.86	2.22	3.016 (3)	153
N1–H1B...O1 ⁱⁱ	0.86	2.38	3.226 (3)	170

Symmetry codes: (i) 2 - x, 1 - y, -z; (ii) 2 - x, -y, -z.

Compound (IIIb)

Crystal data

C₂₂H₂₀N₂O₂
M_r = 344.40
 Monoclinic, *P*₂₁/*n*
a = 7.456 (3) Å
b = 14.854 (7) Å
c = 16.133 (9) Å
 β = 96.16 (2)°
V = 1776.4 (15) Å³
Z = 4

D_x = 1.288 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 13–14°
 μ = 0.08 mm⁻¹
T = 298 (2) K
 Prism, colorless
 0.55 × 0.45 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ/2θ scans
 4563 measured reflections
 4255 independent reflections
 3299 reflections with *I* > 2σ(*I*)
R_{int} = 0.015

θ_{max} = 28.0°
h = 0 → 9
k = 0 → 19
l = -21 → 21
 3 standard reflections every 97 reflections intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.132
S = 1.08
 4255 reflections
 237 parameters
 H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.06*P*)² + 0.4*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.24 e Å⁻³
 Δρ_{min} = -0.18 e Å⁻³

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SHELXTL* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

Table 3
Selected geometric parameters (Å, °) for (IIIb).

O1—C2	1.3695 (18)	N2—C1	1.147 (2)
O1—C10	1.3821 (17)	C1—C3	1.414 (2)
O2—C6	1.2228 (18)	C2—C3	1.352 (2)
N1—C2	1.345 (2)		
C2—O1—C10	117.57 (11)	C1—C3—C4	119.86 (13)
N2—C1—C3	178.0 (2)	O2—C6—C5	120.70 (13)
N1—C2—C3	128.74 (14)	O2—C6—C7	121.98 (13)
N1—C2—O1	109.98 (13)	C5—C6—C7	117.25 (12)
C3—C2—O1	121.28 (13)	C5—C10—O1	122.49 (12)
C2—C3—C1	118.51 (14)	C5—C10—C9	126.53 (13)
C2—C3—C4	121.63 (12)	O1—C10—C9	110.97 (12)
C2—C3—C4—C5	−27.62 (17)	C3—C4—C5—C10	24.51 (17)
C2—C3—C4—C11	97.34 (15)	C3—C4—C11—C12	−99.52 (15)

Table 4
Hydrogen-bonding geometry (Å, °) for (IIIb).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots N2 ⁱⁱⁱ	0.86	2.19	3.033 (2)	166

Symmetry code: (iii) $1 - x, -y, 1 - z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1213). Services for accessing these data are described at the back of the journal.

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