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5-Acetyl-2-amino-6-methyl-4-(1-naphthyl)-4*H*-pyran-3-carbonitrile, methyl 6-amino-5-cyano-2-methyl-4-(1-naphthyl)-4*H*-pyran-3-carboxylate and *tert*-butyl 6-amino-5-cyano-2-methyl-4-(1-naphthyl)-4*H*-pyran-3-carboxylate

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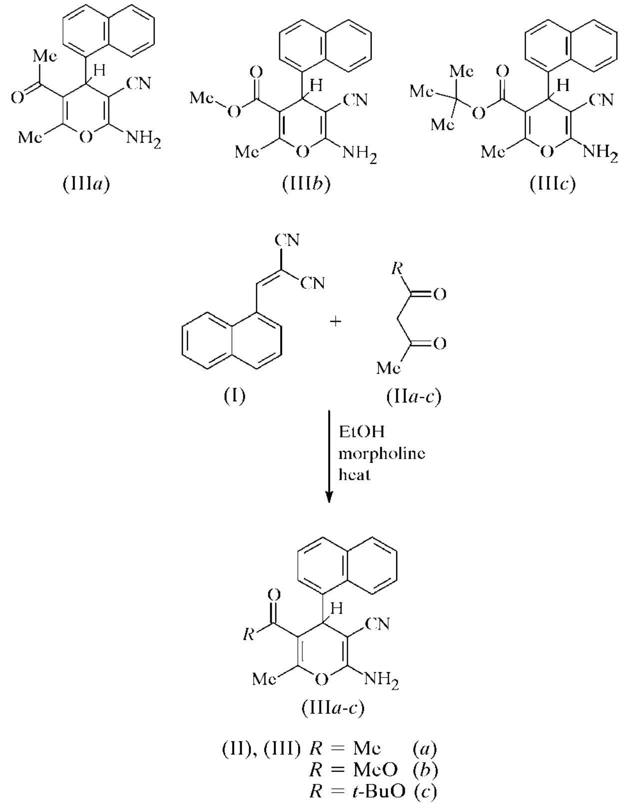
Syntheses and X-ray structural investigations have been carried out for the three title compounds, $C_{19}H_{16}N_2O_2$, (III*a*), $C_{19}H_{16}N_2O_3$, (III*b*), and $C_{22}H_{22}N_2O_3$, (III*c*), respectively. In molecules (III*a*) and (III*c*), the heterocyclic ring is practically flat, while in (III*b*) it adopts a flattened-boat conformation. In (III*b*) and (III*c*), the carbonyl group and a double bond of the heterocyclic ring are *anti*, but in (III*a*) they are *syn* and the carbonyl group participates in an intramolecular C—H···O hydrogen bond which forms a six-membered ring. In molecules (III*a*) and (III*c*), the dihedral angles between the naphthalene substituent and the flat heterocyclic ring are 96.4 (3) and 102.6 (3)°, respectively. In (III*b*), the dihedral angle between the pseudo-axial naphthalene bicycle and the flat part of the pyran ring is 81.6 (3)°. In the crystal structure of (III*a*), intermolecular N—H···N and N—H···O hydrogen bonds link the molecules into a three-dimensional framework. In (III*b*) and (III*c*), only one H atom of the NH_2 group takes part in an N—H···O hydrogen bond and infinite chains are formed along the *a* axis.

Comment

The present investigation of the title compounds, *viz*. (III*a*), (III*b*) and (III*c*) (see scheme), is a continuation of our work on the synthesis and structural study of heterocyclic compounds, such as 4*H*-pyran derivatives (Sharanina *et al.*, 1986; Klokol *et al.*, 1987; Nesterov & Viltchinskaia, 2001; Shestopalov *et al.*, 2002, 2003; Nesterov *et al.*, 2004), that can be obtained starting from different unsaturated nitriles (Nesterov *et al.*, 2001*a*,*b*). Some 4*H*-pyran derivatives are potential bioactive compounds, such as calcium antagonists (Suarez *et al.*, 2002).

Syntheses and X-ray structural investigations have been carried out for compounds (III*a*), (III*b*) and (III*c*) (Figs. 1–3), which were synthesized by the reaction of (1-naphthylmethylene)malononitrile, (I) (Nesterov *et al.*, 2001*a*), with a 1,3-diketone or *β*-ketoesters, (II). Most of the geometric parameters in the molecules (Tables 1, 3 and 5) are very similar to the standard values (Allen *et al.*, 1987), and are very close to our data from analogous compounds (Nesterov &



(II), (III) *R* = Me (*a*)
R = MeO (*b*)
R = *t*-BuO (*c*)

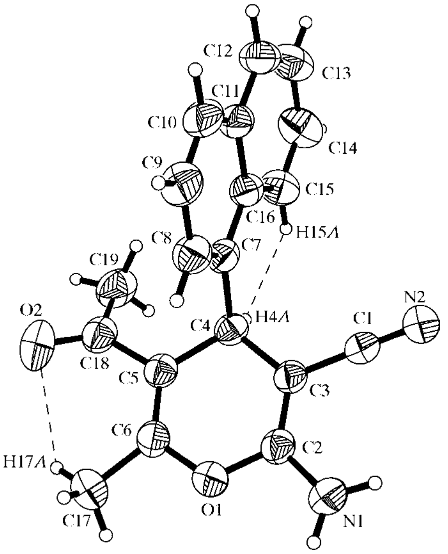


Figure 1
A view of the molecule of (III*a*), showing the atom numbering used. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the weak intramolecular C—H···O hydrogen bond and the short intramolecular steric H···H interaction.

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Viltchinskaia, 2001; Nesterov *et al.*, 2004) and to the literature data cited in previous work.

The X-ray analyses showed that the molecules of all three title compounds have slightly different structures. The pyran ring in (III*a*) and (III*c*) is practically flat [planar to within 0.009 (3) and 0.013 (3) Å, respectively]. However, in (III*b*) it adopts a flattened boat conformation; atoms O1 and C4 are displaced out of the C2/C3/C5/C6 plane [planar to within 0.017 (3) Å] by −0.106 (3) and −0.208 (3) Å, respectively. The bending of the pyran ring of (III*b*) along the lines O1$\cdots$C4, C2$\cdots$C6 and C3$\cdots$C5 is 14.7 (3), 8.8 (3) and 13.8 (3)°, respectively.

In molecules (III*a*) and (III*c*), the dihedral angles between the bulky naphthalene substituent and the pyran ring are 96.4 (3) and 102.6 (3)°, respectively. In (III*b*), the naphthalene substituent occupies a pseudo-axial position and the dihedral angle it makes with the flat part of the pyran rings is 81.6 (3)°. The mutual orientation of these fragments and the flatness of the heterocyclic rings lead to H$\cdots$H intramolecular steric interactions: H4*A*$\cdots$H15*A* = 2.06 Å in (III*a*), 2.06 Å in (III*b*) and 2.04 Å in (III*c*). These contacts are shorter than the sum of the van der Waals radii of H atoms (Rowland & Taylor, 1996). As mentioned previously by us for related compounds (Nesterov *et al.*, 2004), such steric hindrance causes elongation of the C4—C7 bond lengths to 1.540 (2), 1.536 (3) and 1.530 (3) Å, respectively, in comparison with the neighbouring Csp^3—Csp^2 distances, which are only slightly longer than or equal to the standard value (Allen *et al.*, 1987).

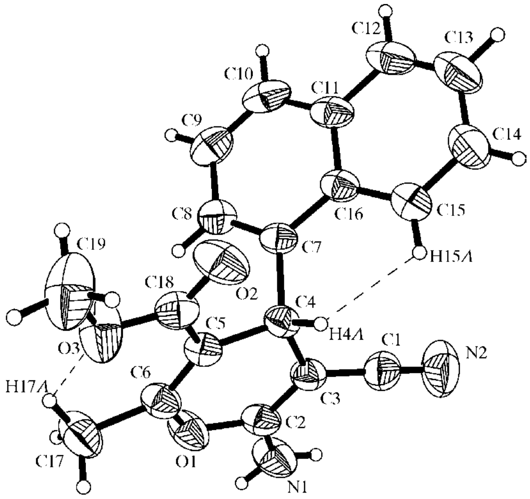

Figure 2
A view of the molecule of (III*b*), showing the atom numbering used. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the weak intramolecular C—H$\cdots$O hydrogen bond and the short intramolecular steric H$\cdots$H interaction.

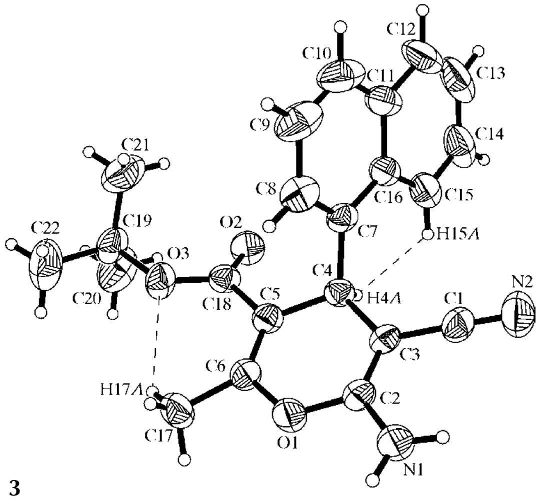

Figure 3
A view of the molecule of (III*c*), showing the atom numbering used. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the weak intramolecular C—H$\cdots$O hydrogen bond and the short intramolecular steric H$\cdots$H interaction.

The C=O group has interesting orientational preferences relative to the C5=C6 double bond in the title compounds. In (III*b*) and (III*c*), the groups are *anti* [‘*transoid*’; C6—C5—C18—O2 torsion angles of 176.9 (2) and −154.6 (3)°, respectively]. However, in (III*a*) they are *syn* [‘*cisoid*’; C6—C5—C18—O2 torsion angle of 34.9 (3)°]. In the latter case, a short intramolecular contact (O2$\cdots$H17*A* = 2.32 Å) is present which connects the atoms into a six-membered ring. According to literature data (Desiraju & Steiner, 1999), this contact can be considered to be a weak hydrogen bond, with

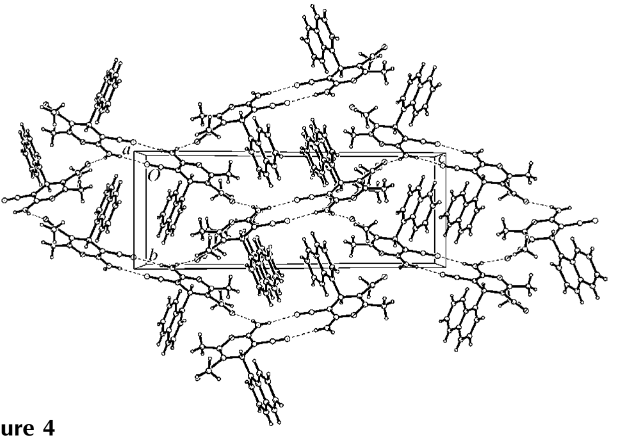

Figure 4
A projection of the crystal packing of (III*a*) along the *a* axis. Dashed lines indicate intermolecular N—H$\cdots$N and N—H$\cdots$O hydrogen bonds.

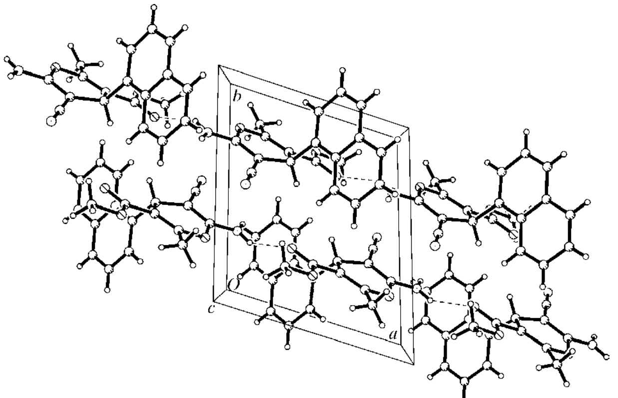

Figure 5
A projection of the crystal packing of (III*b*) along the *c* axis. Dashed lines indicate intermolecular N—H$\cdots$O hydrogen bonds.

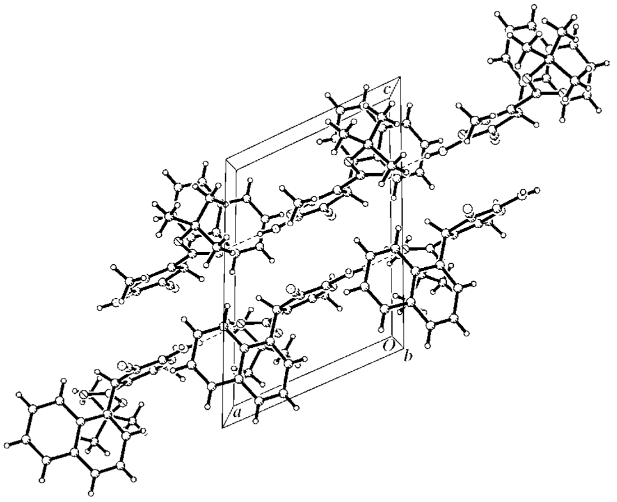

Figure 6
A projection of the crystal packing of (III*c*) along the *b* axis. Dashed lines indicate intermolecular N—H···O hydrogen bonds.

parameters C17···O2 = 2.894 (3) Å, C17—H17*A* = 0.96 Å and C17—H17*A*···O2 = 118°. As seen in Figs. 2 and 3, in (III*b*) and (III*c*), the O3 atoms of the ester groups have favourable orientations for the formation of short intramolecular contacts with the CH_3 groups of the heterocyclic ring. The O3···H17*A* distances are 2.15 and 2.26 Å, respectively. These contacts can also be considered to be weak hydrogen bonds, with parameters C17···O3 = 2.792 (3) Å, C17—H17*A* = 0.96 Å and C17—H17*A*···O3 = 123° in (III*b*), and C17···O3 = 2.837 (3) Å, C17—H17*A* = 0.96 Å and C17—H17*A*···O3 = 118° in (III*c*). In each case, the hydrogen bond connects the atoms into a six-membered ring.

Similar to what we observed in related compounds (Nesterov & Viltchinskaia, 2001; Nesterov *et al.*, 2004), in all three title compounds there is conjugation between the donor NH_2 and the acceptor CN groups *via* the C2═C3 double bond.

In the crystal structure of (III*a*), the active H atoms of the NH_2 group participate in intermolecular N—H···N and N—H···O hydrogen bonds, linking the molecules into a three-dimensional framework (Fig. 4 and Table 2). However, in the crystals of (III*b*) and (III*c*), only one H atom of the NH_2 group is involved in an N—H···O hydrogen bond, forming infinite chains along the *a* axis (Figs. 5 and 6, and Tables 4 and 6).

Analysis of the crystal packing of all three compounds shows that there are intermolecular steric C···C contacts between atoms of the naphthalene substituents of neighbouring molecules which are less than the sum of the van der Waals radii of C (Rowland & Taylor, 1996). Such contacts probably play a role in the orientation of bulky substituents in the molecule and can be considered as π–π interactions. The remaining geometrical parameters in the title compounds have standard values (Allen *et al.*, 1987).

Experimental

The title compounds were obtained by the reaction of (1-naphthylmethylene)malononitrile, (I) (Nesterov *et al.*, 2001*a*), with acetylacetone, (II*a*), methyl acetylacetate, (II*b*), and *tert*-butyl acetylacetate, (II*c*), respectively, according to the literature procedure of Nesterov & Viltchinskaia (2001) and Nesterov *et al.* (2004). The precipitates were isolated and recrystallized from acetonitrile [m.p. 468 K and yield 75% for (III*a*); m.p. 453 K and yield 79% for (III*b*); m.p. 479 K and yield 85% for (III*c*)]. All three compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy; these data are available in the archived CIF. The crystals of all three compounds were grown by slow isothermic evaporation of acetonitrile solutions.

Compound (III*a*)

Crystal data

$C_{19}H_{16}N_2O_2$
$M_r = 304.34$
Monoclinic, $P2_1/n$
$a = 7.8630$ (16) Å
$b = 8.5960$ (17) Å
$c = 23.227$ (5) Å
$\beta = 96.64$ (3)°
$V = 1559.4$ (6) Å^3
$Z = 4$
$D_x = 1.296$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.09$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ/2θ scans
3267 measured reflections
3035 independent reflections
2151 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\max} = 26.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -28 \rightarrow 28$
3 standard reflections every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.123$
$S = 1.07$
3035 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (III*a*).

O2—C18	1.217 (2)	C3—C4	1.521 (2)
N1—C2	1.349 (2)	C4—C5	1.513 (2)
N2—C1	1.143 (2)	C4—C7	1.540 (2)
C1—C3	1.408 (3)	C5—C6	1.325 (3)
C2—C3	1.348 (3)	C5—C18	1.497 (3)
N1—C2—C3	127.98 (17)	C5—C4—C7	111.19 (14)
O1—C2—C3	122.20 (16)	C3—C4—C7	110.62 (14)
C2—C3—C1	118.38 (17)	C6—C5—C4	123.05 (16)
C2—C3—C4	122.85 (16)	C5—C6—C17	129.78 (19)
C5—C4—C3	109.40 (14)		
C2—C3—C4—C7	121.95 (18)	C6—C5—C18—C19	−143.94 (19)
C3—C4—C7—C8	−69.8 (2)	C4—C5—C18—C19	33.3 (2)
C6—C5—C18—O2	34.9 (3)		

Table 2
Hydrogen-bonding geometry (Å, °) for (III*a*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2$^{\rm i}$	0.86	2.54	3.374 (2)	165
N1—H1*B*···N2$^{\rm ii}$	0.86	2.18	3.016 (2)	166

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

Compound (III*b*)

Crystal data

$C_{19}H_{16}N_2O_3$
$M_r = 320.34$
Triclinic, $P\overline{1}$
$a = 8.3150\ (17)$ Å
$b = 10.283\ (2)$ Å
$c = 10.793\ (2)$ Å
$\alpha = 112.38\ (3)^\circ$
$\beta = 96.66\ (3)^\circ$
$\gamma = 103.83\ (3)^\circ$
$V = 806.3\ (4)$ Å^3
$Z = 2$
$D_x = 1.319$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.09$ mm^{-1}
$T = 295\ (2)$ K
Prism, colourless
0.45 × 0.40 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
4108 measured reflections
3841 independent reflections
1923 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\rm max} = 28.0^\circ$
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.172$
$S = 1.02$
3841 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.1P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III*b*).

O2—C18	1.207 (3)	C3—C4	1.512 (3)
N1—C2	1.341 (3)	C4—C5	1.510 (3)
N2—C1	1.138 (3)	C4—C7	1.536 (3)
C1—C3	1.414 (3)	C5—C6	1.337 (3)
C2—C3	1.345 (3)	C5—C18	1.468 (3)
N1—C2—C3	127.5 (2)	C5—C4—C3	109.19 (17)
C3—C2—O1	122.2 (2)	C5—C4—C7	111.85 (18)
C2—C3—C1	117.9 (2)	C3—C4—C7	111.26 (18)
C2—C3—C4	121.8 (2)	C6—C5—C4	122.8 (2)
C1—C3—C4	120.21 (19)	C5—C6—C17	131.2 (2)
C2—C3—C4—C7	−106.0 (2)	C6—C5—C18—O2	176.9 (2)
C3—C4—C7—C8	82.8 (2)	C6—C5—C18—O3	−1.8 (3)
C19—O3—C18—C5	178.3 (2)		

Compound (III*c*)

Crystal data

$C_{22}H_{22}N_2O_3$
$M_r = 362.42$
Triclinic, $P\overline{1}$
$a = 8.4940\ (17)$ Å
$b = 10.938\ (2)$ Å
$c = 11.844\ (2)$ Å
$\alpha = 104.69\ (3)^\circ$
$\beta = 109.84\ (3)^\circ$
$\gamma = 102.30\ (3)^\circ$
$V = 945.6\ (5)$ Å^3
$Z = 2$
$D_x = 1.273$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.09$ mm^{-1}
$T = 295\ (2)$ K
Prism, colourless
0.50 × 0.40 × 0.30 mm

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2$^{\rm i}$	0.86	2.14	2.919 (3)	150

Symmetry code: (i) $1 + x, y, z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
4336 measured reflections
4054 independent reflections
2361 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.135$
$\theta_{\rm max} = 27.0^\circ$
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.187$
$S = 1.02$
4054 reflections
248 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III*c*).

O2—C18	1.210 (3)	C3—C4	1.521 (3)
N1—C2	1.342 (3)	C4—C5	1.505 (3)
N2—C1	1.144 (3)	C4—C7	1.530 (3)
C1—C3	1.410 (3)	C5—C6	1.329 (3)
C2—C3	1.344 (3)	C5—C18	1.489 (3)
N1—C2—C3	127.7 (2)	C5—C4—C3	109.68 (18)
C3—C2—O1	123.0 (2)	C5—C4—C7	110.79 (18)
C2—C3—C1	118.1 (2)	C3—C4—C7	111.01 (18)
C2—C3—C4	122.4 (2)	C6—C5—C4	123.5 (2)
C1—C3—C4	119.5 (2)	C5—C6—C17	131.3 (2)
C2—C3—C4—C7	120.0 (2)	C6—C5—C18—O2	−154.6 (3)
C3—C4—C7—C8	−82.2 (3)	C6—C5—C18—O3	28.3 (3)

Table 6
Hydrogen-bonding geometry (Å, °) for (IIIc).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2$^{\rm i}$	0.86	2.22	3.071 (3)	171

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

For all three title compounds, H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H distances of 0.93 Å for aromatic H, 0.96 Å for CH_3, and 0.98 Å for CH, and N—H distances of 0.86 Å for NH_2 groups. In the cases of (III*b*) and (III*c*), the quality of the crystals was not very good and this is probably a reason for the high $R_{\rm int}$ values. Another reason is likely to be the high thermal motion of the terminal C atoms, especially in (III*c*).

For all three compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1162). Services for accessing these data are described at the back of the journal.

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