

Simple chains in methyl 3,5-dinitrobenzoate, isolated molecules in isopropyl 3,5-dinitrobenzoate, and a three-dimensional framework containing double and sextuple helices in benzyl 3,5-dinitrobenzoate, all at 120 K

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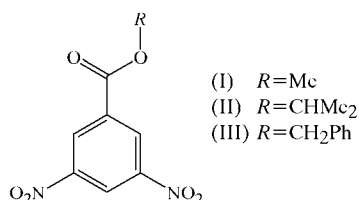
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Molecules of methyl 3,5-dinitrobenzoate, $C_8H_6N_2O_6$, are linked into $C(7)$ chains by a single nearly linear $C-H\cdots O$ hydrogen bond, but there are no direction-specific interactions in the structure of isopropyl 3,5-dinitrobenzoate, $C_{10}H_{10}N_2O_6$. In benzyl 3,5-dinitrobenzoate, $C_{14}H_{10}N_2O_6$, the molecules are linked by four independent $C-H\cdots O$ hydrogen bonds into a complex three-dimensional framework structure, in which it is possible to identify simple substructures in the form of cyclic centrosymmetric dimers, double helices and sextuple helices.

Comment

We report here the structures of methyl, isopropyl and benzyl 3,5-dinitrobenzoate, (I)–(III), respectively, derived from low-temperature diffraction data. It has been recognized since the early days of experimental organic chemistry that the 3,5-dinitrobenzoate esters of simple alcohols are crystalline solids



that are very readily purified and crystallized, and indeed these crystalline esters were for many decades utilized as an

aid to identification of such alcohols by means of their sharp and characteristic melting temperatures. The structures of a few of these esters have been the subject of isolated reports, including the ethyl ester (Hughes & Trotter, 1971) and the 2,2-dimethylbutyl ester, where $Z' = 2$ (Sax *et al.*, 1976); both of these structure determinations were based on the use of diffraction data collected at ambient temperature. More recently, the structures of the methyl ester, (I) (Jin & Xiao, 2000*b*), the *n*-propyl ester, where $Z' = 2$ (Jin & Xiao, 2005*c*), and the isopropyl ester, (II) (Jin & Xiao, 2005*a*), have been reported, also using diffraction data collected at ambient temperature. The structure of (I) was reported to contain π -stacked molecules related by translation along $[100]$, with intermolecular $C\cdots C$ contacts as short as 3.440 (4) Å, despite the a repeat vector of 4.5833 (15) Å; no hydrogen bonds were reported in this compound. Although the unit-cell dimensions, the space group and the atomic coordinates for (I) indicate that no phase change has occurred between ambient

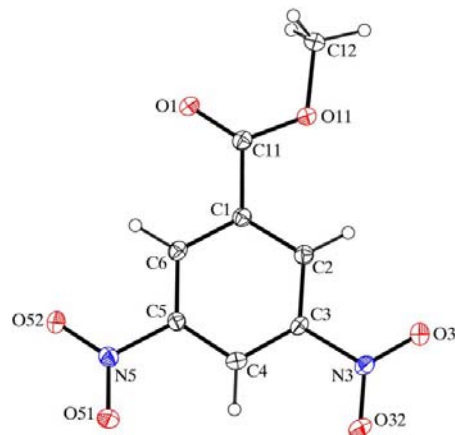


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

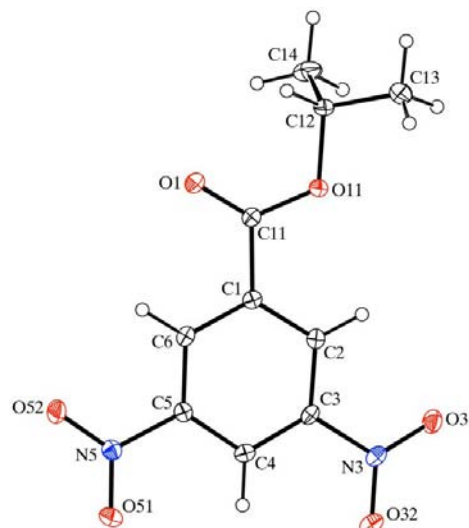


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

temperature and 120 K, we find no π - π stacking in (I); however, a nearly linear C—H \cdots O hydrogen bond is present, in contrast to the findings reported previously (Jin & Xiao, 2005b).

The molecule of (I) (Fig. 1) is effectively planar, apart from the H atoms of the methyl group, as shown by the leading torsion angles (Table 3). In (II) and (III) (Figs. 2 and 3), the ester fragment up to and including atom C12 is effectively coplanar with the adjacent aryl ring, but in (III) in particular, the remaining torsion angles indicate a markedly non-planar conformation. The bond distances show no unusual values, but in each compound the internal angles at atoms C3 and C5, which are *ipso* to the nitro groups, are significantly larger than the corresponding angle at C2, which is *ipso* to the ester group.

There are no direction-specific intermolecular interactions in the structure of (II), but the molecules of (I) are linked into simple $C(7)$ chains by a single C—H \cdots O hydrogen bond (Table 1). Atom C4 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O1 in the molecule at $(\frac{3}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, so forming a $C(7)$ (Bernstein *et al.*, 1995) chain running parallel to the $[301]$ direction and generated by the n -glide plane at $y = \frac{3}{4}$ (Fig. 4). Two such chains, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent chains; in particular, C—H \cdots π (arene) hydrogen bonds and aromatic π - π stacking interactions are both absent. The shortest ring-centroid separation, which involves the molecules at (x, y, z) and $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, is 5.670 (2) Å and is clearly too large for effective π - π stacking.

The molecules of (III) are linked by four independent C—H \cdots O hydrogen bonds (Table 2) into a three-dimensional framework of considerable complexity. However, it is possible to identify several simple substructures, each generated by a limited number of hydrogen bonds. The formation of the framework is most simply analysed in terms of one finite zero-

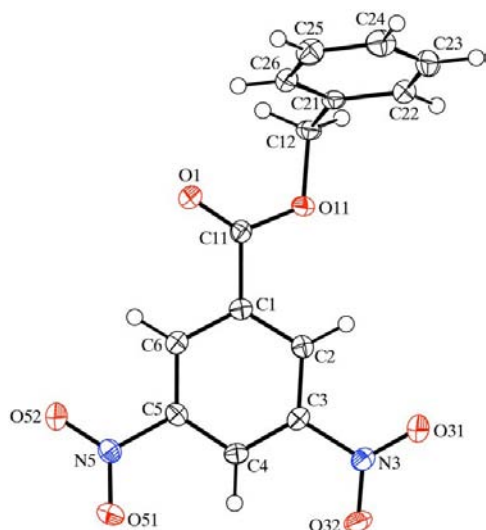


Figure 3

The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

dimensional motif, which can be regarded as the basic building block; this motif is formed by the concerted action of two of the hydrogen bonds and two independent chain motifs, each containing a single hydrogen bond, one of which generates a double helix while the other generates a sextuple helix.

In the first substructure, atoms C6 and C12 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atoms O1 and O52 in the molecule at $(1 - x, 1 - y, -z)$, so gener-

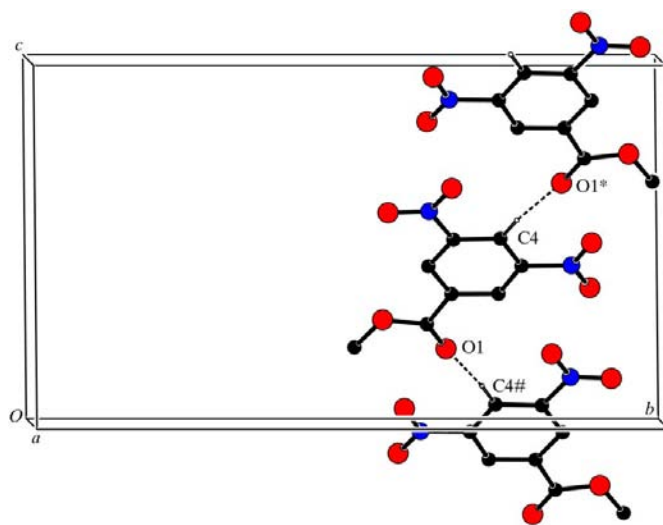


Figure 4

Part of the crystal structure of (I), showing the formation of a $C(7)$ chain along $[301]$. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{3}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(-\frac{3}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, respectively.

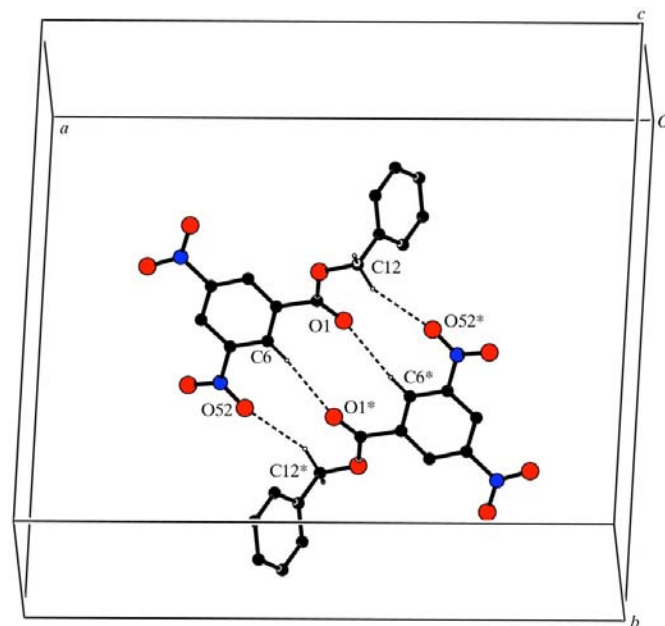


Figure 5

Part of the crystal structure of (III), showing the formation of a centrosymmetric dimer. For the sake of clarity, H atoms bonded to C atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, -z)$.

ating a centrosymmetric dimer centred at $(\frac{1}{2}, \frac{1}{2}, 0)$, in which inversion-related pairs of hydrogen bonds generate $R_2^2(10)$ and $R_2^2(18)$ rings (Fig. 5). In the second substructure, this time one-dimensional as opposed to zero-dimensional, atom C2 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom O32 in the molecule at $(1 - y, -\frac{1}{2} + x, \frac{1}{2} + z)$, while atom C2 at $(1 - y, -\frac{1}{2} + x, \frac{1}{2} + z)$ in turn acts as a donor to atom O32 at $(\frac{3}{2} - x, \frac{1}{2} - y, 1 + z)$. Propagation of this hydrogen bond thus generates a $C(5)$ helical chain running parallel to the $[001]$ direction and generated by the 4_2 screw axis along $(\frac{3}{4}, \frac{1}{4}, z)$ (Fig. 6). Because the screw axis is of the 4_2 type, this chain links the molecules at (x, y, z) and $(x, y, 2 + z)$, so that complete definition of this substructure requires two coaxial helices offset by a unit translation along $[001]$.

The combination of this helical chain (Fig. 6) with the centrosymmetric dimer motif (Fig. 5) then links each helical chain to four adjacent helical chains; for example, the helix along $(\frac{3}{4}, \frac{1}{4}, z)$ is directly linked in this way to those along

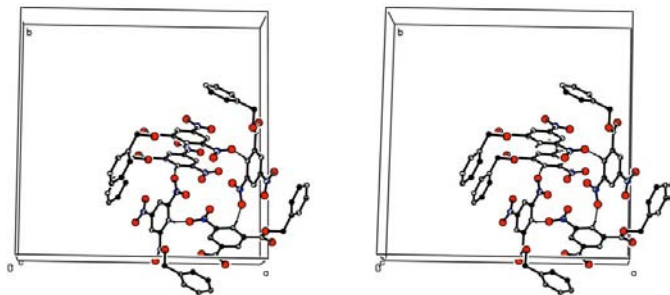


Figure 6
A stereoview of part of the crystal structure of (III), showing a hydrogen-bonded helical $C(5)$ chain generated by the 4_2 screw axis along $(\frac{3}{4}, \frac{1}{4}, z)$ and forming one strand of a double helix. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

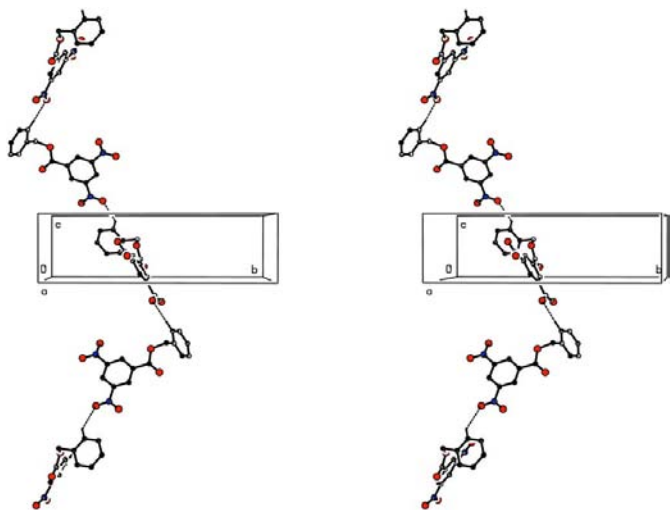


Figure 7
A stereoview of part of the crystal structure of (III), showing a hydrogen-bonded helical $C(11)$ chain generated by the 4_2 screw axis along $(\frac{3}{4}, \frac{1}{4}, z)$ and forming one strand of a sextuple helix. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

$(\frac{1}{4}, \frac{3}{4}, z)$, $(\frac{5}{4}, \frac{3}{4}, z)$, $(\frac{1}{4}, -\frac{1}{4}, z)$ and $(\frac{5}{4}, -\frac{1}{4}, z)$, so forming a continuous three-dimensional framework. Because of the double-helical nature of the $[001]$ chain, there are in fact two such frameworks, intimately interwoven.

In addition, there is a fourth $C-H \cdots O$ hydrogen bond, whose action in isolation is to generate a sextuple helix of $C(11)$ chains (Fig. 7), but which in combination with the first chain-forming hydrogen bond links the two interwoven frameworks into a single continuous structure. Atom C22 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom O51 in the molecule at $(1 - y, -\frac{1}{2} + x, \frac{3}{2} + z)$, and atom C22 at $(1 - y, -\frac{1}{2} + x, \frac{3}{2} + z)$ likewise acts as a donor to atom O51 at $(\frac{3}{2} - x, \frac{1}{2} - y, 3 + z)$, and thence *via* $(\frac{1}{2} + y, 1 - x, \frac{9}{2} + z)$ to $(x, y, 6 + z)$, so generating the sextuple helix. At the same time, atom C2 in the molecule at $(1 - y, -\frac{1}{2} + x, \frac{3}{2} + z)$ acts as a hydrogen-bond donor to atom O32 in the molecule at $(\frac{3}{2} - x, \frac{1}{2} - y, 2 + z)$, thereby linking the two coaxial $C(5)$ helices along $(\frac{3}{4}, \frac{1}{4}, z)$ and hence linking the two frameworks.

Experimental

Samples of compounds (I)–(III) were prepared from 3,5-dinitrobenzoic acid according to a published procedure (Vogel, 1977). The compounds had the expected NMR and IR spectra, and the melting points were in agreement with those reported previously (Vogel, 1977). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol.

Compound (I)

Crystal data

$C_8H_6N_2O_6$
 $M_r = 226.15$
 Monoclinic, $P2_1/n$
 $a = 4.5664$ (4) Å
 $b = 18.727$ (2) Å
 $c = 10.8416$ (10) Å
 $\beta = 101.787$ (6)°
 $V = 907.57$ (15) Å³
 $Z = 4$

$D_x = 1.655$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2070 reflections
 $\theta = 2.9$ – 27.6°
 $\mu = 0.14$ mm⁻¹
 $T = 120$ (2) K
 Lath, colourless
 $0.52 \times 0.12 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.935$, $T_{\max} = 0.997$
 9551 measured reflections
 2070 independent reflections

1319 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 $\theta_{\max} = 27.6^\circ$
 $h = -5 \rightarrow 5$
 $k = -24 \rightarrow 24$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.174$
 $S = 1.09$
 2070 reflections
 146 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.2307P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C4-H4 \cdots O1^i$	0.95	2.46	3.399 (3)	171

Symmetry code: (i) $x + \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

Compound (II)

Crystal data

$C_{10}H_{10}N_2O_6$	$D_x = 1.494 \text{ Mg m}^{-3}$
$M_r = 254.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2596 reflections
$a = 9.7037 (3) \text{ \AA}$	$\theta = 3.8\text{--}27.5^\circ$
$b = 5.7152 (2) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$c = 20.4739 (9) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 95.504 (2)^\circ$	Block, colourless
$V = 1130.22 (7) \text{ \AA}^3$	$0.42 \times 0.40 \times 0.38 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2596 independent reflections
φ and ω scans	2045 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.031$; $\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.944$, $T_{\text{max}} = 0.954$	$h = -12 \rightarrow 12$
10022 measured reflections	$k = -7 \rightarrow 7$
	$l = -24 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.2191P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
2596 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
165 parameters	
H-atom parameters constrained	

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (III).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$C2\text{---}H2\cdots O32^{\text{ii}}$	0.95	2.52	3.460 (2)	170
$C6\text{---}H6\cdots O1^{\text{iii}}$	0.95	2.57	3.493 (2)	164
$C12\text{---}H12A\cdots O52^{\text{iii}}$	0.99	2.56	3.474 (2)	154
$C22\text{---}H22\cdots O51^{\text{iv}}$	0.95	2.57	3.360 (2)	140

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

Compound (III)

Crystal data

$C_{14}H_{10}N_2O_6$	Mo $K\alpha$ radiation
$M_r = 302.24$	Cell parameters from 3000 reflections
Tetragonal, $P4_2/n$	$\theta = 3.1\text{--}27.5^\circ$
$a = 20.8531 (5) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 6.0377 (2) \text{ \AA}$	$T = 120 (2) \text{ K}$
$V = 2625.50 (12) \text{ \AA}^3$	Needle, colourless
$Z = 8$	$0.22 \times 0.06 \times 0.04 \text{ mm}$
$D_x = 1.529 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD diffractometer	3000 independent reflections
φ and ω scans	2413 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.053$; $\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.978$, $T_{\text{max}} = 0.995$	$h = -27 \rightarrow 26$
18873 measured reflections	$k = -16 \rightarrow 27$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 1.5651P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
3000 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
199 parameters	
H-atom parameters constrained	

Table 3

Selected angles and torsion angles ($^\circ$) for compounds (I)–(III).

	(I)	(II)	(III)
$C6\text{---}C1\text{---}C2$	120.2 (2)	120.34 (11)	120.82 (14)
$C2\text{---}C3\text{---}C4$	123.3 (2)	123.34 (11)	122.94 (15)
$C4\text{---}C5\text{---}C6$	123.3 (2)	122.58 (12)	123.37 (15)
$C2\text{---}C1\text{---}C11\text{---}O11$	2.0 (3)	-6.24 (16)	15.2 (2)
$C1\text{---}C11\text{---}O11\text{---}C12$	179.74 (19)	-176.88 (9)	177.03 (12)
$C11\text{---}O11\text{---}C12\text{---}C13$	-	152.12 (12)	-
$C11\text{---}O11\text{---}C12\text{---}C14$	-	-85.33 (13)	-
$C11\text{---}O11\text{---}C12\text{---}C21$	-	-	93.65 (16)
$O11\text{---}C12\text{---}C21\text{---}C22$	-	-	89.93 (7)
$C2\text{---}C3\text{---}N3\text{---}O31$	0.2 (3)	-4.88 (16)	9.1 (2)
$C4\text{---}C5\text{---}N5\text{---}O51$	4.2 (3)	6.13 (16)	7.5 (2)

For each of compounds (I) and (II), the space group $P2_1/n$ was uniquely assigned from the systematic absences. For compound (III), the space group $P4_2/n$ was uniquely assigned from the systematic absences, and the setting adopted had the origin coincident with a centre of inversion. All H atoms were located in difference maps and then treated as riding atoms, with C–H distances of 0.95 (aromatic), 0.98 (methyl), 0.99 (CH_2) or 1.00 \AA (aliphatic CH), and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups.

For all compounds, data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1889). Services for accessing these data are described at the back of the journal.

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