

A three-dimensional framework of π -stacked hydrogen-bonded chains in benzyl 4-chloro-3-nitrobenzoate, and chains of hydrogen-bonded rings in benzyl 4-nitrobenzoate, redetermined at 120 K

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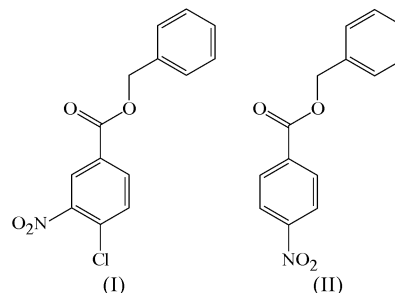
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Benzyl 4-chloro-3-nitrobenzoate, $C_{14}H_{10}ClNO_4$, crystallizes with $Z' = 2$ in the space group $P\bar{1}$. The molecules are linked by three independent $C-H\cdots O$ hydrogen bonds into chains of edge-fused $R_4^4(26)$ and $R_4^4(34)$ rings, and these chains are linked into a three-dimensional framework structure by aromatic π - π stacking interactions. In benzyl 4-nitrobenzoate, $C_{14}H_{11}NO_4$, the molecules are linked by two independent $C-H\cdots O$ hydrogen bonds into chains containing two types of $R_2^2(10)$ ring.

Comment

We report here the structures of benzyl 4-chloro-3-nitrobenzoate, (I) (Fig. 1), and benzyl 4-nitrobenzoate, (II) (Fig. 2), and compare their supramolecular structures with that in benzyl 3,5-dinitrobenzoate, (III) (Vasconcelos *et al.*, 2006). The structure of (II) was reported some years ago (Jones *et al.*, 1989) using diffraction data collected at ambient temperature, but there was no mention in that report of any direction-specific intermolecular interactions. Hence, we have redetermined this structure using diffraction data collected at 120 K and find in it significant hydrogen bonding which forms a chain of rings motif (Bernstein *et al.*, 1995). The unit-cell dimensions, space group and atomic coordinates for (II) indicate that no phase change occurs between ambient temperature and 120 K.

The conformations of the independent molecules are all different, as shown by the leading torsion angles (Table 1). While the ester moieties are essentially planar in each of (I) and (II), there are significant differences between the molecules, particularly as shown by the torsion angles about the



bonds $On11-Cn12$ and $Cn12-Cn21$ ($n = 1$ or 2) in (I) and the corresponding angles about the bonds $O11-C12$ and $C12-C21$ in both (II) and (III). In addition, while the nitro groups in (II) and (III) are almost coplanar with the adjacent aryl rings, in compound (I) the $C-NO_2$ planes make dihedral angles with the adjacent aryl rings of $45.2(2)^\circ$ in molecule 1 (defined by $n = 1$) and $34.4(2)^\circ$ in molecule 2 (defined by $n = 2$). The conformational differences between the two independent molecules in (I) are sufficient to preclude the occurrence of any additional symmetry. The bond lengths and angles in (I) show no unexpected features; those in (II) closely resemble the values reported at ambient temperature (Jones *et al.*, 1989).

The molecules of (I) are linked by three $C-H\cdots O$ hydrogen bonds (Table 2) to form a chain of edge-fused rings. Atom C15 acts as hydrogen-bond donor to atom O21 within the selected asymmetric unit (Fig. 1). Similarly, atom C25 at (x, y, z) acts as donor to atom O11 at $(1+x, 1+y, z)$, so generating by translation a $C_2^2(12)$ chain (Bernstein *et al.*, 1995)

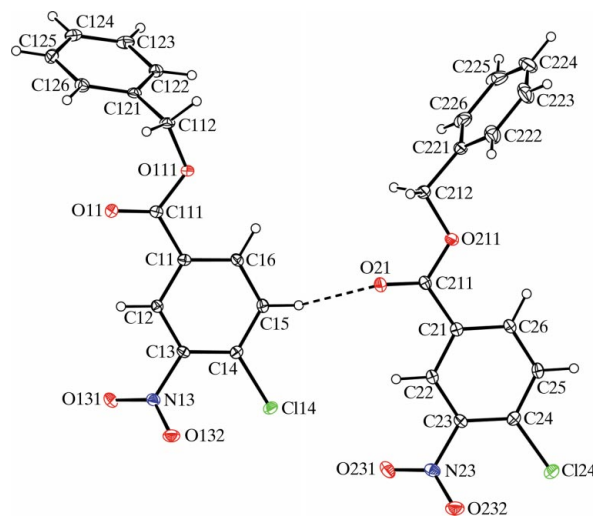


Figure 1

The two independent molecules in compound (I), showing the atom-labelling scheme and the $C-H\cdots O$ hydrogen bond (dashed line) within the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

running parallel to the [110] direction (Fig. 3). Antiparallel pairs of such chains, related to one another by inversion, are then linked by the final hydrogen bond, in which a nitro O atom is the acceptor (Table 2), and this then generates a chain of edge-fused rings, in which centrosymmetric $R_4^2(26)$ rings are centred at $(n, n - \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and centrosymmetric $R_4^2(34)$ rings are centred at $(n + \frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 3).

The hydrogen-bonded chains (Fig. 3) are linked into (001) sheets by means of several π - π stacking interactions. The rings C11–C16 in the type 1 molecules at (x, y, z) and $(-x, -y, 1 - z)$ are parallel, with an interplanar spacing of 3.457 (2) Å

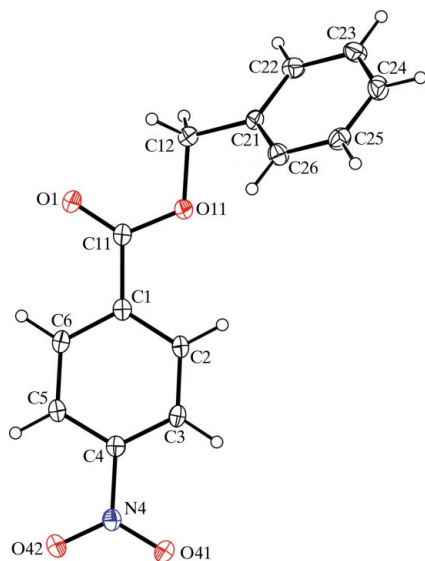


Figure 2
A molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

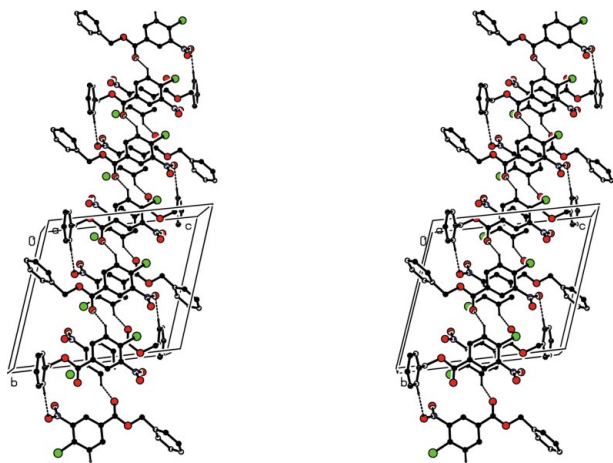


Figure 3
A stereoview of part of the crystal structure of compound (I), showing a hydrogen-bonded chain of edge-fused rings along [110]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

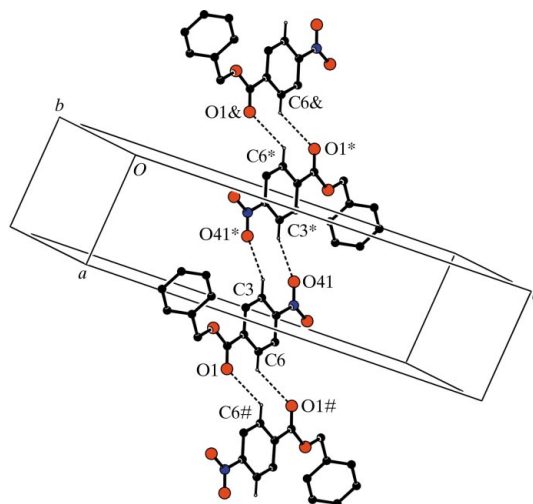


Figure 4
Part of the crystal structure of compound (II), showing the formation of a chain of rings along $[2\bar{1}0]$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(3 - x, -y, 1 - z)$ and $(-2 + x, 1 + y, z)$, respectively.

and a ring-centroid separation of 3.763 (2) Å, corresponding to a ring offset of 1.485 (2) Å. These two molecules lie in adjacent chains offset along the [100] direction. Similarly, the rings C21–C26 in the type 2 molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are parallel, with an interplanar spacing of 3.397 (2) Å, a ring-centroid separation of 3.782 (2) Å and a ring offset of 1.662 (2) Å, and this interaction links the hydrogen-bonded chains along [010]. Finally, the rings C121–C126 in the molecules at (x, y, z) and $(-x, -y, 2 - z)$ have an interplanar spacing of 3.530 (2) Å, with a ring-centroid separation of 3.845 (2) Å and a ring offset of 1.523 (2) Å. This stacking interaction links the hydrogen-bonded chains along the [011] direction, and the combination of interactions linking these chains along [100], [010] and [011] suffices to generate a three-dimensional structure.

The supramolecular structure of compound (II) is much simpler than that of (I) and is based on the action of just two C–H...O hydrogen bonds (Table 3). Atom C3 in the nitrated ring of the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O41 of the molecule at $(1 - x, 1 - y, 1 - z)$, so forming by inversion an $R_2^2(10)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. At the same time, atom C6 at (x, y, z) acts as donor to ester atom O1 of the molecule at $(3 - x, -y, 1 - z)$, so forming a second $R_2^2(10)$ motif, this time centred at $(\frac{3}{2}, 0, \frac{1}{2})$. Propagation of these two hydrogen bonds then generates a $C_2^2(12)[R_2^2(10)][R_2^2(10)]$ chain of rings running parallel to the $[2\bar{1}0]$ direction (Fig. 4).

The supramolecular structures of compounds (I) and (II) contrast strongly with that of closely related compound (III), where four independent C–H...O hydrogen bonds link the molecules into a three-dimensional hydrogen-bonded framework in which it is possible to identify substructures in the form of double and sextuple helices (Vasconcelos *et al.*, 2006).

Experimental

Samples of the esters (I) and (II) were prepared from benzyl alcohol and the appropriate substituted benzoic acid following a general procedure (Vogel, 1977). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol. Analysis for compound (I) (m.p. 341–342 K), ^1H NMR (CDCl_3): δ 5.39 (s, 2H, CH_2), 7.37–7.46 (m, 5H, Ph), 7.64 (d, 1H, $J = 8.4$ Hz, H6), 8.18 (1H, dd, $J = 2.0$ and 8.4 Hz, H2), 8.52 (1H, d, $J = 2.0$ Hz, H5); ^{13}C NMR (CDCl_3): δ 67.8, 126.6, 128.4, 128.6, 128.8, 130.1, 131.8, 132.2, 133.7, 135.1, 148.0, 163.6. Analysis for compound (II) (m.p. 239–340 K), ^1H NMR (CDCl_3): δ 5.41 (s, 2H, CH_2), 7.35–7.48 (m, 5H, Ph), 8.23 (2H, d, $J = 9.0$ Hz, H2 and H6), 8.28 (2H, d, $J = 9.0$ Hz, H3 and H5); ^{13}C NMR (CDCl_3): δ 67.7, 123.6, 128.5, 128.7, 128.8, 130.8, 135.3, 135.5, 150.6, 164.5.

Table 1

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

	(I) $n = 1$	(I) $n = 2$	(II) $n = \text{nil}$	(III) $n = \text{nil}$
$\text{Cn1} - \text{Cn11} - \text{On11} - \text{Cn12}$	−169.62 (11)	−178.05 (12)	−176.24 (17)	177.03 (12)
$\text{Cn11} - \text{On11} - \text{Cn12} - \text{Cn21}$	−84.35 (16)	176.07 (13)	159.40 (18)	93.65 (16)
$\text{On11} - \text{Cn12} - \text{Cn21} - \text{Cn22}$	−66.31 (18)	−85.93 (18)	136.8 (2)	89.93 (7)

Note: data for compound (III) are taken from Vasconcelos *et al.* (2006).

Compound (I)

Crystal data

$\text{C}_{14}\text{H}_{10}\text{ClNO}_4$
 $M_r = 291.68$
 Triclinic, $P\bar{1}$
 $a = 7.3497$ (2) Å
 $b = 12.8535$ (3) Å
 $c = 14.5334$ (4) Å
 $\alpha = 109.976$ (1) $^\circ$
 $\beta = 94.028$ (1) $^\circ$
 $\gamma = 92.551$ (1) $^\circ$
 $V = 1283.73$ (6) Å 3

$Z = 4$
 $D_x = 1.509$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 5729 reflections
 $\theta = 2.9$ – 27.5 $^\circ$
 $\mu = 0.31$ mm $^{-1}$
 $T = 120$ (2) K
 Plate, colourless
 $0.40 \times 0.20 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.867$, $T_{\text{max}} = 0.988$
 25854 measured reflections

5890 independent reflections
 4941 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 27.5$ $^\circ$
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.100$
 $S = 1.02$
 5890 reflections
 361 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.6918P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.34$ e Å $^{-3}$

Table 2

Hydrogen-bond geometry (Å, $^\circ$) for (I).

$D - \text{H} \cdots A$	$D - \text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D - \text{H} \cdots A$
$\text{C15} - \text{H15} \cdots \text{O21}$	0.95	2.39	3.187 (2)	141
$\text{C25} - \text{H25} \cdots \text{O11}^i$	0.95	2.44	3.235 (2)	142
$\text{C126} - \text{H126} \cdots \text{O232}^{ii}$	0.95	2.40	3.345 (2)	176

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

Compound (II)

Crystal data

$\text{C}_{14}\text{H}_{11}\text{NO}_4$
 $M_r = 257.24$
 Monoclinic, $P2_1/n$
 $a = 6.1574$ (6) Å
 $b = 7.4487$ (6) Å
 $c = 26.341$ (3) Å
 $\beta = 93.362$ (3) $^\circ$
 $V = 1206.0$ (2) Å 3
 $Z = 4$

$D_x = 1.417$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 2487 reflections
 $\theta = 2.9$ – 27.5 $^\circ$
 $\mu = 0.11$ mm $^{-1}$
 $T = 120$ (2) K
 Plate, colourless
 $0.28 \times 0.20 \times 0.03$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.979$, $T_{\text{max}} = 0.997$
 10597 measured reflections

2672 independent reflections
 1957 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 27.6$ $^\circ$
 $h = -7 \rightarrow 7$
 $k = -8 \rightarrow 9$
 $l = -34 \rightarrow 34$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.138$
 $S = 1.08$
 2672 reflections
 172 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.8562P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.22$ e Å $^{-3}$

Table 3

Hydrogen-bond geometry (Å, $^\circ$) for (II).

$D - \text{H} \cdots A$	$D - \text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D - \text{H} \cdots A$
$\text{C3} - \text{H3} \cdots \text{O41}^i$	0.95	2.50	3.387 (2)	156
$\text{C6} - \text{H6} \cdots \text{O1}^{ii}$	0.95	2.59	3.273 (2)	129

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 3, -y, -z + 1$.

Crystals of compound (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the structure analysis. For compound (II), the space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C–H distances of 0.95 (aromatic) or 0.99 Å (CH_2), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: COLLECT (Nonius, 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: SK3011). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Jones, P. G., Dólle, A., Kirby, A. J. & Parker, J. K. (1989). *Acta Cryst.* **C45**, 234–237.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Vasconcelos, T. R. A., de Souza, M. V. N., Wardell, S. M. S. V., Wardell, J. L., Low, J. N. & Glidewell, C. (2006). *Acta Cryst.* **C62**, o26–o29.
- Vogel, A. I. (1977). *Elementary Practical Organic Chemistry*, Part 2, *Qualitative Organic Analysis*, 2nd ed., p. 75. London: Longmans.