

Methyl 4-(3-chloropropoxy)-5-methoxy-2-nitrobenzoate

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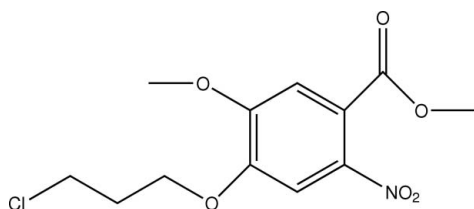
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.065; wR factor = 0.162; data-to-parameter ratio = 14.1.

The asymmetric unit of the title compound, $\text{C}_{12}\text{H}_{14}\text{ClNO}_6$, contains two crystallographically independent molecules, in which the benzene rings are oriented at a dihedral angle of 9.12 (3)°. In the crystal structure, weak intermolecular C—H...O hydrogen bonds link the molecules into a three-dimensional network.

Related literature

For general background, see: Knesl *et al.* (2006). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{14}\text{ClNO}_6$	$V = 2799.7$ (10) Å ³
$M_r = 303.69$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 23.150$ (5) Å	$\mu = 0.30$ mm ⁻¹
$b = 15.013$ (3) Å	$T = 294$ K
$c = 8.0700$ (16) Å	$0.30 \times 0.20 \times 0.20$ mm
$\beta = 93.42$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	5096 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	2874 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.916$, $T_{\max} = 0.943$	$R_{\text{int}} = 0.038$
5208 measured reflections	3 standard reflections
	frequency: 120 min
	intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$	362 parameters
$wR(F^2) = 0.162$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.40$ e Å ⁻³
5096 reflections	$\Delta\rho_{\text{min}} = -0.30$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10B...O4 ⁱ	0.97	2.58	3.336 (7)	135
C13—H13B...O9 ⁱⁱ	0.96	2.41	3.211 (6)	141
C21—H21A...O5 ⁱⁱⁱ	0.96	2.48	3.243 (5)	136
C24—H24A...O9 ^{iv}	0.97	2.59	3.276 (6)	128

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2642).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Knesl, P., Roeseling, D. & Jordis, U. (2006). *Molecules*, **11**, 286–297.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

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Methyl 4-(3-chloropropoxy)-5-methoxy-2-nitrobenzoate

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Comment

As part of our ongoing studies on quinazoline derivatives (Knesl *et al.*, 2006), we report herein the crystal structure of the title compound.

The asymmetric unit of the title compound contains two crystallographically independent molecules (Fig. 1), in which the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Rings A (C3-C8) and A' (C15-C20) are, of course, planar and they are oriented at a dihedral angle of A/A' = 9.12 (3)°.

In the crystal structure, weak intermolecular C-H...O hydrogen bonds (Table 1) link the molecules into a three dimensional network (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, a solution of methyl 4-(3-chloro- propoxy)-3-methoxybenzoate (19 mmol) in acetic acid (20 ml) was added dropwise to nitric acid (98%, 4.5 ml) at 273-278 K. The mixture was stirred for 1 h at room temperature, and then for 2 h at 323 K. After the reaction was completed, the reaction mixture was poured into ice/water (130 ml), and then extracted with trichloromethane (20 ml). The combined organic phases were collected, washed with saturated sodium bicarbonate (20 ml), brine (20 ml), dried (Na₂SO₄) and decolorized (charcoal). Trichloromethane was then removed under reduced pressure to give a yellow oil, which was crystallized from ethyl acetate/petroleum ether to afford the product as light yellow crystals (m.p. 337 K). Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

Refinement

H atoms were positioned geometrically, with C-H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

Figures

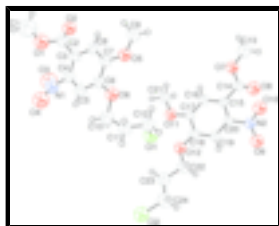


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme.

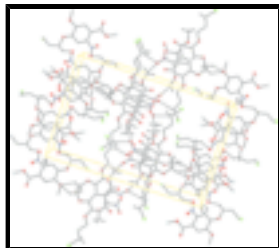


Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding are omitted.

Methyl 4-(3-chloropropoxy)-5-methoxy-2-nitrobenzoate

Crystal data

$C_{12}H_{14}ClNO_6$

$M_r = 303.69$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 23.150 (5) \text{ \AA}$

$b = 15.013 (3) \text{ \AA}$

$c = 8.0700 (16) \text{ \AA}$

$\beta = 93.42 (3)^\circ$

$V = 2799.7 (10) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1264$

$D_x = 1.441 \text{ Mg m}^{-3}$

Melting point: 337 K

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10\text{--}13^\circ$

$\mu = 0.30 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Needle, yellow

$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294 \text{ K}$

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.916$, $T_{\max} = 0.943$

5208 measured reflections

5096 independent reflections

2874 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 25.3^\circ$

$\theta_{\min} = 1.6^\circ$

$h = 0 \rightarrow 27$

$k = 0 \rightarrow 18$

$l = -9 \rightarrow 9$

3 standard reflections

every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.162$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 1.915P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$S = 1.03$ $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 5096 reflections $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$
 362 parameters Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.0049 (6)
 Secondary atom site location: difference Fourier map

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.26534 (6)	0.48992 (8)	0.29390 (17)	0.0758 (4)
C12	0.30461 (6)	0.79461 (8)	0.6560 (2)	0.0888 (5)
O1	-0.10537 (13)	0.2705 (2)	0.1972 (5)	0.0846 (11)
O2	-0.05735 (14)	0.1596 (2)	0.3282 (4)	0.0714 (9)
O3	-0.06317 (19)	0.3963 (3)	0.4296 (5)	0.1081 (15)
O4	-0.05061 (16)	0.5014 (2)	0.2559 (6)	0.0970 (13)
O5	0.13459 (12)	0.23218 (18)	0.0445 (4)	0.0559 (8)
O6	0.14060 (12)	0.40304 (18)	0.0445 (4)	0.0593 (8)
O7	0.40610 (12)	0.06586 (17)	0.5910 (4)	0.0558 (8)
O8	0.48185 (14)	0.1024 (2)	0.7607 (4)	0.0740 (10)
O9	0.53876 (12)	0.3392 (2)	0.6019 (4)	0.0637 (9)
O10	0.51561 (13)	0.2122 (2)	0.4944 (4)	0.0694 (9)
O11	0.28231 (11)	0.33078 (17)	0.7787 (4)	0.0528 (7)
O12	0.34201 (12)	0.46634 (17)	0.7009 (4)	0.0538 (8)
N1	-0.04080 (17)	0.4270 (3)	0.3109 (6)	0.0687 (11)
N2	0.50447 (14)	0.2793 (2)	0.5715 (4)	0.0466 (8)
C1	-0.1592 (2)	0.2271 (5)	0.2275 (9)	0.124 (3)
H1A	-0.1907	0.2607	0.1761	0.185*
H1B	-0.1635	0.2237	0.3449	0.185*
H1C	-0.1593	0.1681	0.1816	0.185*
C2	-0.05727 (18)	0.2299 (3)	0.2610 (6)	0.0554 (11)
C3	-0.00469 (17)	0.2813 (3)	0.2209 (5)	0.0477 (10)
C4	0.00118 (18)	0.3722 (3)	0.2282 (5)	0.0495 (10)
C5	0.04788 (18)	0.4163 (3)	0.1691 (5)	0.0542 (11)
H5A	0.0498	0.4781	0.1724	0.065*

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C6	0.09190 (17)	0.3675 (3)	0.1046 (5)	0.0474 (10)
C7	0.08873 (17)	0.2742 (3)	0.1040 (5)	0.0463 (10)
C8	0.04040 (17)	0.2321 (3)	0.1598 (5)	0.0476 (10)
H8A	0.0380	0.1702	0.1564	0.057*
C9	0.1376 (2)	0.1372 (3)	0.0606 (6)	0.0626 (12)
H9A	0.1721	0.1159	0.0133	0.094*
H9B	0.1043	0.1109	0.0033	0.094*
H9C	0.1384	0.1213	0.1759	0.094*
C10	0.1491 (2)	0.4975 (3)	0.0631 (7)	0.0645 (13)
H10A	0.1494	0.5140	0.1794	0.077*
H10B	0.1182	0.5297	0.0031	0.077*
C11	0.2060 (2)	0.5190 (3)	-0.0057 (6)	0.0638 (13)
H11A	0.2128	0.5825	0.0057	0.077*
H11B	0.2037	0.5053	-0.1234	0.077*
C12	0.25688 (19)	0.4705 (3)	0.0750 (6)	0.0612 (12)
H12A	0.2918	0.4893	0.0241	0.073*
H12B	0.2521	0.4071	0.0553	0.073*
C13	0.4229 (2)	-0.0264 (3)	0.6021 (7)	0.0748 (15)
H13A	0.3962	-0.0617	0.5344	0.112*
H13B	0.4226	-0.0458	0.7154	0.112*
H13C	0.4611	-0.0332	0.5638	0.112*
C14	0.43940 (17)	0.1222 (3)	0.6788 (5)	0.0433 (10)
C15	0.41457 (15)	0.2145 (2)	0.6687 (4)	0.0367 (9)
C16	0.35887 (16)	0.2280 (2)	0.7183 (5)	0.0409 (9)
H16A	0.3365	0.1790	0.7442	0.049*
C17	0.33587 (16)	0.3122 (2)	0.7300 (5)	0.0397 (9)
C18	0.36847 (16)	0.3871 (2)	0.6871 (5)	0.0415 (9)
C19	0.42370 (16)	0.3744 (2)	0.6376 (5)	0.0418 (9)
H19A	0.4460	0.4231	0.6098	0.050*
C20	0.44601 (15)	0.2890 (2)	0.6293 (4)	0.0378 (9)
C21	0.24745 (17)	0.2586 (3)	0.8302 (5)	0.0521 (11)
H21A	0.2108	0.2811	0.8613	0.078*
H21B	0.2667	0.2292	0.9235	0.078*
H21C	0.2414	0.2171	0.7404	0.078*
C22	0.3705 (2)	0.5435 (3)	0.6460 (6)	0.0567 (11)
H22A	0.3781	0.5384	0.5295	0.068*
H22B	0.4070	0.5523	0.7096	0.068*
C23	0.3290 (2)	0.6207 (3)	0.6738 (7)	0.0680 (14)
H23A	0.2931	0.6108	0.6080	0.082*
H23B	0.3201	0.6222	0.7897	0.082*
C24	0.3531 (2)	0.7046 (3)	0.6292 (8)	0.0895 (18)
H24A	0.3629	0.7024	0.5141	0.107*
H24B	0.3885	0.7149	0.6969	0.107*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0858 (9)	0.0698 (8)	0.0709 (8)	-0.0107 (7)	-0.0018 (7)	-0.0109 (7)

C12	0.0811 (9)	0.0518 (7)	0.1376 (13)	0.0225 (6)	0.0417 (9)	0.0179 (8)
O1	0.049 (2)	0.095 (3)	0.111 (3)	-0.0011 (18)	0.0157 (19)	0.046 (2)
O2	0.071 (2)	0.066 (2)	0.079 (2)	-0.0029 (17)	0.0184 (18)	0.0170 (19)
O3	0.124 (3)	0.119 (3)	0.087 (3)	0.048 (3)	0.053 (3)	0.017 (3)
O4	0.088 (3)	0.059 (2)	0.148 (4)	0.018 (2)	0.037 (2)	0.006 (2)
O5	0.0529 (18)	0.0488 (17)	0.068 (2)	-0.0020 (14)	0.0179 (15)	-0.0026 (15)
O6	0.0515 (18)	0.0475 (17)	0.080 (2)	-0.0126 (14)	0.0128 (16)	-0.0039 (15)
O7	0.0585 (18)	0.0382 (15)	0.069 (2)	0.0053 (14)	-0.0072 (15)	-0.0044 (15)
O8	0.064 (2)	0.064 (2)	0.089 (2)	0.0219 (17)	-0.0301 (19)	-0.0083 (18)
O9	0.0436 (17)	0.071 (2)	0.078 (2)	-0.0114 (16)	0.0142 (15)	-0.0192 (17)
O10	0.062 (2)	0.060 (2)	0.089 (2)	0.0059 (16)	0.0290 (18)	-0.0250 (18)
O11	0.0425 (16)	0.0458 (16)	0.072 (2)	0.0063 (13)	0.0190 (14)	-0.0015 (15)
O12	0.0547 (18)	0.0370 (15)	0.072 (2)	0.0082 (13)	0.0231 (15)	0.0010 (14)
N1	0.062 (3)	0.070 (3)	0.075 (3)	0.008 (2)	0.011 (2)	0.000 (2)
N2	0.041 (2)	0.051 (2)	0.049 (2)	0.0044 (17)	0.0083 (16)	-0.0039 (18)
C1	0.048 (3)	0.155 (6)	0.171 (7)	-0.014 (4)	0.023 (4)	0.067 (5)
C2	0.048 (3)	0.068 (3)	0.052 (3)	0.001 (2)	0.014 (2)	0.001 (2)
C3	0.044 (2)	0.056 (3)	0.043 (2)	0.004 (2)	0.0049 (19)	0.001 (2)
C4	0.046 (2)	0.055 (3)	0.048 (3)	0.005 (2)	0.005 (2)	-0.008 (2)
C5	0.052 (3)	0.045 (2)	0.065 (3)	-0.001 (2)	-0.003 (2)	-0.003 (2)
C6	0.043 (2)	0.051 (3)	0.048 (3)	-0.005 (2)	0.000 (2)	-0.001 (2)
C7	0.048 (3)	0.046 (2)	0.044 (2)	-0.002 (2)	0.000 (2)	-0.006 (2)
C8	0.050 (3)	0.044 (2)	0.049 (3)	-0.005 (2)	0.006 (2)	0.001 (2)
C9	0.063 (3)	0.049 (3)	0.078 (3)	-0.001 (2)	0.017 (2)	-0.006 (2)
C10	0.060 (3)	0.042 (2)	0.092 (4)	-0.007 (2)	0.002 (3)	0.003 (2)
C11	0.073 (3)	0.047 (3)	0.071 (3)	-0.014 (2)	0.004 (3)	0.005 (2)
C12	0.058 (3)	0.059 (3)	0.067 (3)	-0.009 (2)	0.013 (2)	-0.007 (2)
C13	0.082 (4)	0.036 (2)	0.106 (4)	0.005 (2)	0.001 (3)	0.000 (3)
C14	0.044 (2)	0.046 (2)	0.041 (2)	0.004 (2)	0.0054 (19)	-0.0019 (19)
C15	0.038 (2)	0.039 (2)	0.033 (2)	0.0017 (17)	0.0013 (17)	-0.0016 (17)
C16	0.041 (2)	0.036 (2)	0.046 (2)	-0.0013 (17)	0.0048 (18)	0.0002 (18)
C17	0.036 (2)	0.044 (2)	0.040 (2)	0.0053 (18)	0.0084 (17)	-0.0025 (18)
C18	0.046 (2)	0.039 (2)	0.041 (2)	0.0089 (19)	0.0060 (18)	-0.0043 (18)
C19	0.049 (2)	0.039 (2)	0.039 (2)	-0.0025 (18)	0.0081 (18)	-0.0030 (18)
C20	0.035 (2)	0.044 (2)	0.035 (2)	0.0052 (17)	0.0059 (16)	-0.0034 (17)
C21	0.046 (2)	0.058 (3)	0.053 (3)	-0.004 (2)	0.013 (2)	-0.004 (2)
C22	0.068 (3)	0.040 (2)	0.063 (3)	0.007 (2)	0.016 (2)	0.001 (2)
C23	0.074 (3)	0.046 (3)	0.087 (4)	0.006 (2)	0.030 (3)	-0.001 (3)
C24	0.080 (4)	0.061 (3)	0.131 (5)	0.013 (3)	0.036 (4)	-0.002 (3)

Geometric parameters (Å, °)

C11—C12	1.789 (5)	C9—H9A	0.9600
C12—C24	1.778 (5)	C9—H9B	0.9600
O1—C2	1.345 (5)	C9—H9C	0.9600
O1—C1	1.439 (5)	C10—C11	1.496 (6)
O2—C2	1.187 (5)	C10—H10A	0.9700
O3—N1	1.208 (5)	C10—H10B	0.9700
O4—N1	1.218 (5)	C11—C12	1.500 (6)

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O5—C7	1.348 (5)	C11—H11A	0.9700
O5—C9	1.433 (5)	C11—H11B	0.9700
O6—C6	1.363 (4)	C12—H12A	0.9700
O6—C10	1.438 (5)	C12—H12B	0.9700
O7—C14	1.322 (5)	C13—H13A	0.9600
O7—C13	1.440 (5)	C13—H13B	0.9600
O8—C14	1.189 (4)	C13—H13C	0.9600
O9—N2	1.215 (4)	C14—C15	1.501 (5)
O10—N2	1.220 (4)	C15—C20	1.382 (5)
O11—C17	1.352 (4)	C15—C16	1.388 (5)
O11—C21	1.427 (4)	C16—C17	1.377 (5)
O12—C18	1.346 (4)	C16—H16A	0.9300
O12—C22	1.417 (5)	C17—C18	1.409 (5)
N1—C4	1.464 (5)	C18—C19	1.375 (5)
N2—C20	1.465 (5)	C19—C20	1.385 (5)
C1—H1A	0.9600	C19—H19A	0.9300
C1—H1B	0.9600	C21—H21A	0.9600
C1—H1C	0.9600	C21—H21B	0.9600
C2—C3	1.493 (6)	C21—H21C	0.9600
C3—C4	1.372 (5)	C22—C23	1.530 (5)
C3—C8	1.393 (5)	C22—H22A	0.9700
C4—C5	1.377 (6)	C22—H22B	0.9700
C5—C6	1.381 (5)	C23—C24	1.432 (6)
C5—H5A	0.9300	C23—H23A	0.9700
C6—C7	1.402 (5)	C23—H23B	0.9700
C7—C8	1.384 (5)	C24—H24A	0.9700
C8—H8A	0.9300	C24—H24B	0.9700
C2—O1—C1	115.8 (4)	C11—C12—C11	112.7 (3)
C7—O5—C9	118.0 (3)	C11—C12—H12A	109.0
C6—O6—C10	117.4 (3)	C11—C12—H12A	109.0
C14—O7—C13	115.8 (3)	C11—C12—H12B	109.0
C17—O11—C21	118.2 (3)	C11—C12—H12B	109.0
C18—O12—C22	118.3 (3)	H12A—C12—H12B	107.8
O3—N1—O4	124.0 (4)	O7—C13—H13A	109.5
O3—N1—C4	118.3 (4)	O7—C13—H13B	109.5
O4—N1—C4	117.6 (4)	H13A—C13—H13B	109.5
O9—N2—O10	124.0 (3)	O7—C13—H13C	109.5
O9—N2—C20	117.9 (3)	H13A—C13—H13C	109.5
O10—N2—C20	118.2 (3)	H13B—C13—H13C	109.5
O1—C1—H1A	109.5	O8—C14—O7	125.0 (4)
O1—C1—H1B	109.5	O8—C14—C15	124.2 (4)
H1A—C1—H1B	109.5	O7—C14—C15	110.7 (3)
O1—C1—H1C	109.5	C20—C15—C16	117.3 (3)
H1A—C1—H1C	109.5	C20—C15—C14	123.7 (3)
H1B—C1—H1C	109.5	C16—C15—C14	118.6 (3)
O2—C2—O1	123.7 (4)	C17—C16—C15	121.6 (3)
O2—C2—C3	125.6 (4)	C17—C16—H16A	119.2
O1—C2—C3	110.5 (4)	C15—C16—H16A	119.2
C4—C3—C8	118.0 (4)	O11—C17—C16	125.1 (3)

C4—C3—C2	125.8 (4)	O11—C17—C18	114.9 (3)
C8—C3—C2	116.1 (4)	C16—C17—C18	120.0 (3)
C3—C4—C5	122.7 (4)	O12—C18—C19	125.6 (4)
C3—C4—N1	120.8 (4)	O12—C18—C17	115.6 (3)
C5—C4—N1	116.4 (4)	C19—C18—C17	118.8 (3)
C4—C5—C6	119.2 (4)	C18—C19—C20	119.8 (3)
C4—C5—H5A	120.4	C18—C19—H19A	120.1
C6—C5—H5A	120.4	C20—C19—H19A	120.1
O6—C6—C5	124.9 (4)	C15—C20—C19	122.3 (3)
O6—C6—C7	115.7 (4)	C15—C20—N2	120.1 (3)
C5—C6—C7	119.4 (4)	C19—C20—N2	117.5 (3)
O5—C7—C8	124.8 (4)	O11—C21—H21A	109.5
O5—C7—C6	115.3 (3)	O11—C21—H21B	109.5
C8—C7—C6	119.9 (4)	H21A—C21—H21B	109.5
C7—C8—C3	120.6 (4)	O11—C21—H21C	109.5
C7—C8—H8A	119.7	H21A—C21—H21C	109.5
C3—C8—H8A	119.7	H21B—C21—H21C	109.5
O5—C9—H9A	109.5	O12—C22—C23	105.3 (3)
O5—C9—H9B	109.5	O12—C22—H22A	110.7
H9A—C9—H9B	109.5	C23—C22—H22A	110.7
O5—C9—H9C	109.5	O12—C22—H22B	110.7
H9A—C9—H9C	109.5	C23—C22—H22B	110.7
H9B—C9—H9C	109.5	H22A—C22—H22B	108.8
O6—C10—C11	107.0 (4)	C24—C23—C22	111.8 (4)
O6—C10—H10A	110.3	C24—C23—H23A	109.2
C11—C10—H10A	110.3	C22—C23—H23A	109.2
O6—C10—H10B	110.3	C24—C23—H23B	109.2
C11—C10—H10B	110.3	C22—C23—H23B	109.2
H10A—C10—H10B	108.6	H23A—C23—H23B	107.9
C10—C11—C12	114.8 (4)	C23—C24—C12	112.4 (4)
C10—C11—H11A	108.6	C23—C24—H24A	109.1
C12—C11—H11A	108.6	C12—C24—H24A	109.1
C10—C11—H11B	108.6	C23—C24—H24B	109.1
C12—C11—H11B	108.6	C12—C24—H24B	109.1
H11A—C11—H11B	107.5	H24A—C24—H24B	107.9
C1—O1—C2—O2	5.3 (7)	C13—O7—C14—O8	1.8 (6)
C1—O1—C2—C3	179.9 (5)	C13—O7—C14—C15	-175.1 (3)
O2—C2—C3—C4	-143.1 (5)	O8—C14—C15—C20	53.4 (6)
O1—C2—C3—C4	42.5 (6)	O7—C14—C15—C20	-129.7 (4)
O2—C2—C3—C8	41.7 (6)	O8—C14—C15—C16	-119.6 (5)
O1—C2—C3—C8	-132.8 (4)	O7—C14—C15—C16	57.4 (5)
C8—C3—C4—C5	3.9 (6)	C20—C15—C16—C17	-0.8 (5)
C2—C3—C4—C5	-171.3 (4)	C14—C15—C16—C17	172.6 (4)
C8—C3—C4—N1	-171.9 (4)	C21—O11—C17—C16	3.3 (6)
C2—C3—C4—N1	12.9 (7)	C21—O11—C17—C18	-177.7 (3)
O3—N1—C4—C3	33.0 (7)	C15—C16—C17—O11	-179.4 (3)
O4—N1—C4—C3	-147.6 (4)	C15—C16—C17—C18	1.6 (6)
O3—N1—C4—C5	-143.1 (5)	C22—O12—C18—C19	6.2 (6)
O4—N1—C4—C5	36.3 (6)	C22—O12—C18—C17	-174.6 (4)

supplementary materials

C3—C4—C5—C6	-2.3 (7)	O11—C17—C18—O12	0.2 (5)
N1—C4—C5—C6	173.7 (4)	C16—C17—C18—O12	179.3 (3)
C10—O6—C6—C5	5.8 (6)	O11—C17—C18—C19	179.4 (3)
C10—O6—C6—C7	-172.0 (4)	C16—C17—C18—C19	-1.5 (6)
C4—C5—C6—O6	-179.1 (4)	O12—C18—C19—C20	179.7 (4)
C4—C5—C6—C7	-1.4 (6)	C17—C18—C19—C20	0.6 (6)
C9—O5—C7—C8	-9.0 (6)	C16—C15—C20—C19	-0.2 (5)
C9—O5—C7—C6	172.0 (4)	C14—C15—C20—C19	-173.2 (4)
O6—C6—C7—O5	0.3 (5)	C16—C15—C20—N2	-178.3 (3)
C5—C6—C7—O5	-177.6 (4)	C14—C15—C20—N2	8.7 (6)
O6—C6—C7—C8	-178.8 (3)	C18—C19—C20—C15	0.3 (6)
C5—C6—C7—C8	3.3 (6)	C18—C19—C20—N2	178.4 (3)
O5—C7—C8—C3	179.3 (4)	O9—N2—C20—C15	-150.4 (4)
C6—C7—C8—C3	-1.7 (6)	O10—N2—C20—C15	30.4 (5)
C4—C3—C8—C7	-1.8 (6)	O9—N2—C20—C19	31.4 (5)
C2—C3—C8—C7	173.8 (4)	O10—N2—C20—C19	-147.8 (4)
C6—O6—C10—C11	177.8 (4)	C18—O12—C22—C23	178.5 (4)
O6—C10—C11—C12	-58.2 (5)	O12—C22—C23—C24	177.8 (5)
C10—C11—C12—C11	-57.8 (5)	C22—C23—C24—C12	178.6 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10B \cdots O4 ⁱ	0.97	2.58	3.336 (7)	135
C13—H13B \cdots O9 ⁱⁱ	0.96	2.41	3.211 (6)	141
C21—H21A \cdots O5 ⁱⁱⁱ	0.96	2.48	3.243 (5)	136
C24—H24A \cdots O9 ^{iv}	0.97	2.59	3.276 (6)	128

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, y-1/2, -z+3/2$; (iii) $x, y, z+1$; (iv) $-x+1, -y+1, -z+1$.

Fig. 1

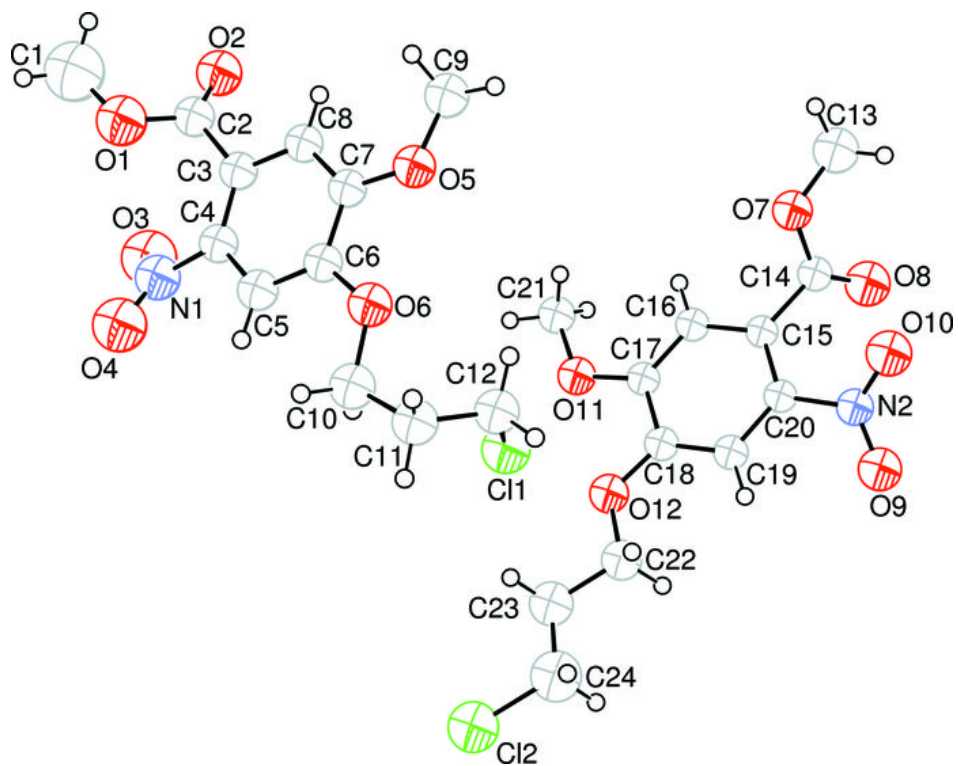


Fig. 2

