

Structure of 2-chloro-*N*-(*p*-tolyl)propanamideRoderick C. Jones^{a*} and Brendan Twamley^b

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Received 15 August 2018

Accepted 1 October 2018

Edited by P. Dastidar, Indian Association for the Cultivation of Science, India

Keywords: crystal structure; API; continuous processing; biphasic.

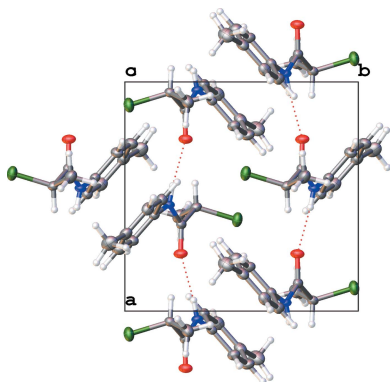
CCDC references: 1870782; 1870781

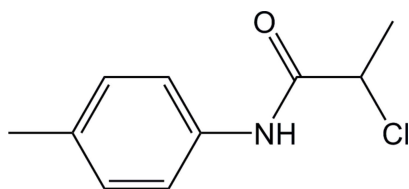
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Two independent samples of the title compound, alternatively 2-chloro-*N*-(4-methylphenyl)propanamide, C₁₀H₁₂ClNO, **1**, were studied using Cu *K*α, **1a**, and Mo *K*α, **1b**, radiation as part of a continuous crystallization study. The molecule crystallizes with disorder in the Cl/terminal methyl positions [occupancies for the major disorder component of 0.783 (2) in **1a** and 0.768 (2) in **1b**] and exhibits N–C bond lengths of 1.3448 (19), 1.344 (2) Å, C=O bond lengths of 1.2233 (18) and 1.2245 (19) Å and an acetamide moiety C–N–C–C torsion angle of 179.00 (13), 178.97 (14) ° for **1a** and **1b**, respectively. In the crystal, chains along the *a* axis are formed *via* N–H···O hydrogen bonds between acetamide groups, as well as C–H···O interactions. These chains arrange themselves into parallel running stacks which display weak C–Cl···O=C halogen bonding as well as weak C–H···π interactions.

1. Chemical context

The introduction of continuous processing has been a paradigm shift in safety and productivity in the synthesis and isolation of active pharmaceutical ingredients (APIs) in both industry and academic research (Mascia *et al.*, 2013 and Lee *et al.*, 2015 and references contained therein). A major focus of our current research is developing design and optimization strategies to deliver robust, scalable and tunable continuous processes for API manufacturing, which can deliver specific API characteristics (Power *et al.*, 2015; Zhao *et al.*, 2015; O'Mahony *et al.*, 2017; Simon *et al.*, 2018). As part of this work we have been examining the continuous crystallization of 2-chloro-*N*-(*p*-tolyl)propanamide, **1**, a key intermediate of α-thio-β-chloroacrylamides, a class of compound that has shown importance in the literature as synthetically viable APIs (Murphy *et al.*, 2007; Foley *et al.*, 2011; Kissane & Maguire, 2011) that can undergo transformations; such as Diels–Alder cycloadditions (Kissane *et al.*, 2010*a*), 1,3-dipolar cycloadditions (Kissane *et al.*, 2010*b*), sulfide group (Kissane *et al.*, 2010*c,d*) and nucleophilic substitution (Kissane *et al.*, 2011). To design and understand a continuous crystallization process for **1**, an extensive solubility study was conducted examining the compound's solubility characteristics in common organic solvents (Pascual *et al.*, 2017). During this study, an improved bi-phasic synthesis was developed and crystals from two different continuous crystallization process runs were isolated to detect and characterize any variability of the crystalline material produced. These samples, **1a** and **1b**, of 2-chloro-*N*-(*p*-tolyl)propanamide, see Fig. 1, are described herein.





2. Structural commentary

Compound **1a** and **1b** both crystallize with one molecule in the asymmetric unit in the orthorhombic space group *Pbca* and exhibit normal bond lengths and angles compared to similar compounds (2-chloro-*N*-phenylpropanamide, IQOHOL, Gowda *et al.*, 2003 and references below). The disorder observed in **1** between the methyl/chloro positions is similarly displayed in IQOHOL. The aryl ring-to-amide backbone plane is twisted with a C1–C7–N8–C9 torsion angle of 45.3 (2)° in **1a** and 45.6 (2)° in **1b** (Table 1).

An overlay of the molecular structures of **1a** and **1b** without inversion and an r.m.s. fit of 0.040 Å is shown in Fig. 2. The data, collected using different sources (Cu *Kα* for **1a** and Mo *Kα* for **1b**), show remarkable similarity even down to the hydrogen-bonding metrics seen in Tables 2 and 3. Data were collected on crystals of a similar size and at 100 K. As can be seen in Table 1, a comparison between several bond lengths

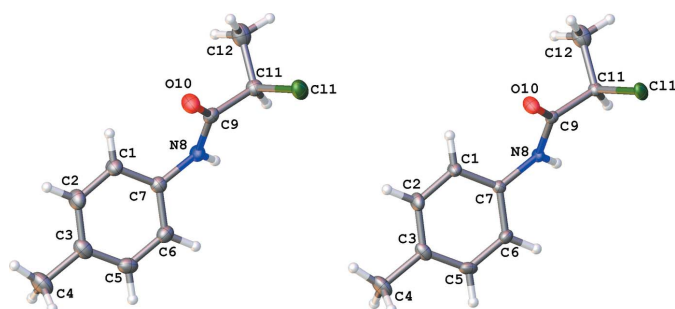


Figure 1
Molecular structures **1a** and **1b** showing the atom-numbering scheme. Only the major occupancy disorder components [**1a** 0.793 (4) and **1b** 0.768 (2)] of the C11 and C12 positions are shown. Displacement ellipsoids drawn at the 50% probability level.

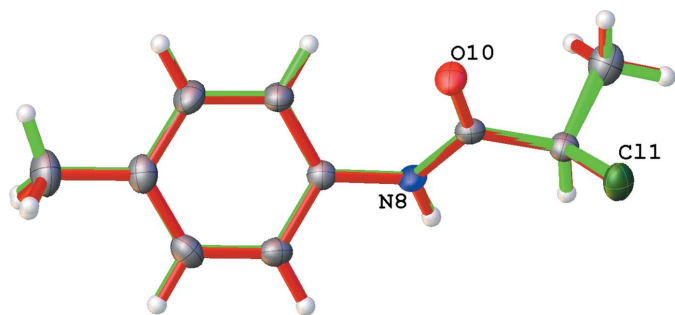


Figure 2
Overlay image of both molecules of 2-chloro-*N*-(*p*-tolyl)propanamide (**1a** is shown in red and **1b** in green) with an r.m.s. fit of 0.040 Å (no inversion). Displacement ellipsoids shown at the 50% probability level. Selected atom numbering only for clarity.

Table 1
Selected geometric parameters (Å, °) for **1a**, **1b** and IQOHOL.

	1a	1b	IQOHOL ^a
C11–C11	1.7861 (17)	1.7845 (18)	1.785 (16)
O10–C9	1.2233 (18)	1.2245 (19)	1.219 (15)
N8–C7	1.4226 (19)	1.421 (2)	1.421 (16)
N8–C9	1.3448 (19)	1.344 (2)	1.341 (16)
C9–C11	1.524 (2)	1.523 (2)	1.522 (18)
O10–C9–C11–C12	−60.4 (5)	−60.2 (6)	61.35 (1)
C9–N8–C7–C1	45.3 (2)	45.6 (2)	−44.19 (1)

and angles in **1a**, **1b** and IQOHOL show how the metrics are similar, even with data that was collected at room temperature (IQOHOL). The disorder occupancy is different in **1a**, **1b** and in IQOHOL, but to no great extent with the occupancy of the major component being 0.783 (2) for **1a**, 0.768 (2) for **1b** and for 0.899 IQOHOL.

3. Supramolecular features

In the extended structure there is, as expected, a strong amide hydrogen bond, between the N–H group and the ketone oxygen (N8···O10ⁱ, see Tables 2 and 3). This feature can be seen in many of the known phenylacetamides and the donor–acceptor distance in similar congeners below range from 2.8175 (8) Å (XIHMOQ; Gowda *et al.*, 2001) to the longer interaction in CEXPOK of 3.2576 (6) Å. The distance in IQOHOL is 2.8632 (6) Å, slightly longer than that found in **1**.

There is also a weaker interaction between the methine group and the ketone (C11–H11···O10ⁱ, see Tables 2 and 3). This type of chelate hydrogen bonding is also seen in

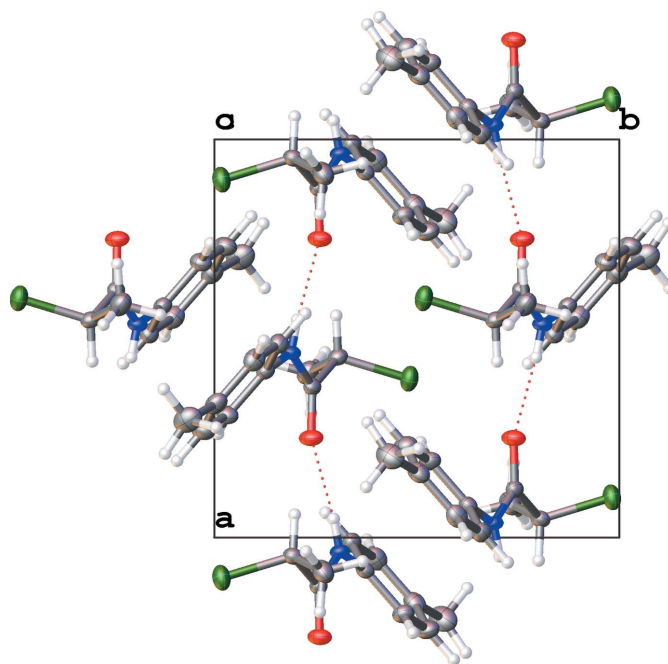


Figure 3
Hydrogen-bonding network represented by dotted lines of one layer in the cell viewed normal to the (001) plane. Displacement ellipsoids are shown at the 50% probability level.

Table 2

Hydrogen-bond geometry (Å, °) for **1a**.

Cg1 is the centroid of the C1–C6 ring.

<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>
N8–H8···O10 ⁱ	0.80 (2)	2.03 (2)	2.8295 (16)	174.8 (17)
C11–H11···O10 ⁱ	1.00	2.48	3.3574 (18)	146
C12–H12E···Cg1 ⁱⁱ	0.98	2.61	3.503 (11)	151

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

IQOHOL and XIHMOQ [$D \cdots A = 3.2699$ (8) and 2.8632 (6) Å respectively] The head-to-tail packing and the chelate hydrogen bonding allows an approximately linear arrangement of **1**, forming ribbons propagating along the [100] direction, see Fig. 3. Only IQOHOL and XIHMOQ exhibit similar characteristics with head-to-tail and approximately linear packing [0.21367 (6) and 3.5472 (14)° respectively, as measured by the amide OCN and aryl carbon plane normal to plane normal angle, compared to 1.80942 (8)° in **1a** and 1.71940 (13)° in **1b**].

There are other supramolecular interactions that assist in the packing of **1**. Complimenting the hydrogen bonding above, there is a weak C–Cl···Oⁱⁱ=Cⁱⁱ halogen bond between the terminal chlorine and the ketone, with distances of **1a**, 3.1761 (14) and **1b**, 3.1734 (18) Å [symmetry code: (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, z$]. A very weak example of a C–H···πⁱⁱⁱ interaction is also present in **1**, with the methyl group C12 directed towards the centroid of ring C1–C6 (see Tables 2 and 3).

Table 4

Experimental details.

	(1a)	(1b)
Crystal data		
Chemical formula	C ₁₀ H ₁₂ ClNO	C ₁₀ H ₁₂ ClNO
<i>M_r</i>	197.66	197.66
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.5119 (3), 9.6885 (4), 21.8439 (8)	9.5053 (6), 9.6793 (5), 21.8380 (13)
<i>V</i> (Å ³)	2013.05 (13)	2009.2 (2)
<i>Z</i>	8	8
Radiation type	Cu <i>Kα</i>	Mo <i>Kα</i>
<i>μ</i> (mm ^{−1})	3.03	0.34
Crystal size (mm)	0.27 × 0.14 × 0.10	0.25 × 0.11 × 0.1
Data collection		
Diffractometer	Bruker APEXII Kappa Duo	Bruker D8 Quest ECO
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.565, 0.753	0.702, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18191, 1892, 1819	19741, 2061, 1668
<i>R_{int}</i>	0.045	0.051
($\sin \theta/\lambda$) _{max} (Å ^{−1})	0.608	0.627
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.038, 0.103, 1.06	0.037, 0.089, 1.10
No. of reflections	1892	2061
No. of parameters	138	138
No. of restraints	2	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.29, −0.26	0.30, −0.31

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Table 3

Hydrogen-bond geometry (Å, °) for **1b**.

Cg1 is the centroid of the C1–C6 ring.

<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>
N8–H8···O10 ⁱ	0.83 (2)	2.00 (2)	2.8255 (18)	174.2 (19)
C11–H11···O10 ⁱ	1.00	2.48	3.353 (2)	146
C12–H12E···Cg1 ⁱⁱ	0.98	2.62	3.493 (13)	149

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

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.39, February 2018 update; Groom *et al.*, 2016) for similar systems (*R*-PhNHCOCH–, where *R* = H, methyl, halogen) yielded several similar substituted phenylacetamides: CLACTN (Subramanian, 1966), CLACTN01 (Gowda *et al.*, 2007a), CLACTN02 (Naumov *et al.*, 2007), CLACTN03 [Coles (née Huth) *et al.*, 2008], CEXPOK (Banks *et al.*, 1999), FOWYIA (Gowda *et al.*, 2009), IFALIK (Frohberg *et al.*, 2002), IQOHOL (Gowda *et al.*, 2003), JODQEZ (Si-shun Kang *et al.*, 2008), NIYYEB (Pathak *et al.*, 2014), NUWQUT (Hursthouse *et al.*, 2009), NUZBUF (Pal *et al.*, 1998), NUZBUF01 (Gowda *et al.*, 2001), RIYWIG (Gowda *et al.*, 2008), SALYIN (Chekhlov *et al.*, 1987), WINSUI (Gowda *et al.*, 2007b), XEKNEJ (Gupta *et al.*, 2017), XICMAY (Gowda *et al.*, 2007c), XIHMIK and XIHMOQ (Gowda *et al.*, 2001) and XIQNIV (Staples & Vidnovio, 2007).

5. Synthesis and crystallization

A solution of α -chloropropionyl chloride (1.16 mL, 12 mmol, 1.2 equiv.) in toluene (30 mL) was added dropwise (with extreme caution) to a vigorously stirred bi-phasic suspension of *p*-toluidine (1.07 g, 10 mmol) in toluene (50 mL) and 40 mL of aqueous NaOH (1.20 g, 30 mmol, 3 equiv.) at 273 K. After the addition was complete, the biphasic suspension was warmed to room temperature and stirred vigorously for 1 h. The organic phase was separated, and the aqueous layer extracted with ethyl acetate (3×15 mL). The organic layers were then combined, dried with Na₂SO₄, filtered and the solvent removed under vacuum. The resulting off-white solid was collected and washed thoroughly with cold cyclohexane (1.89 g, 96%). Single crystals for X-ray analysis were grown by slow evaporation of a toluene solution at room temperature. Spectroscopic data for the obtained product matched that reported in the literature (Pascual *et al.*, 2017).

¹H NMR (300 MHz, CDCl₃): δ 8.21 (*s*, 1H), 7.42 (*d*, *J* = 8.2 Hz, 2H), 7.15 (*d*, *J* = 8.2 Hz, 2H), 4.54 (*q*, *J* = 7.1 Hz, 1H), 2.13 (*s*, 3H), 1.83 (*d*, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 134.4, 134.0, 129.1, 119.7, 55.9, 22.4, 20.5. MS (EI) *m/z* 197 [M]⁺, [¹²C₁₀H₁₂³⁵Cl¹⁴N¹⁶O 197]. HRMS (EI) *m/z* Found: [M]⁺ 197.0604, [C₁₀H₁₂ClNO]⁺ requires 197.0607.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. In both **1a** and **1b**, C11/C11a and C12/C12a were modelled as disordered over two positions using restraints (DFIX for C11–C12, C11–C12a distances) and constraints (EADP, Cl atoms). The occupancy was allowed to refine with a population parameter of **1a** = 0.783 (2), and **1b** = 0.768 (2). The amide N–H H atom was located in a difference-Fourier map and freely refined. H atoms bonded to carbon were placed with idealized geometry and refined using a riding model with C–H = 0.95 Å aromatic, C–H = 0.90 Å methine, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C–H = 0.98 Å methyl with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Acknowledgements

RCJ would like to thank Professor Brian Glennon for the use of the lab and experimental assistance.

Funding information

Funding for this research was provided by: Synthesis and Solid State Pharmaceutical Center (SSPC); Science Foundation Ireland (grant No. SFI, 12/RC/2275).

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supporting information

Acta Cryst. (2018). E74, 1584-1588 [https://doi.org/10.1107/S2056989018013889]

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Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

2-Chloro-*N*-(4-methylphenyl)propanamide (1a)

Crystal data

$C_{10}H_{12}ClNO$

$M_r = 197.66$

Orthorhombic, *Pbca*

$a = 9.5119$ (3) Å

$b = 9.6885$ (4) Å

$c = 21.8439$ (8) Å

$V = 2013.05$ (13) Å³

$Z = 8$

$F(000) = 832$

$D_x = 1.304$ Mg m⁻³

Cu *Kα* radiation, $\lambda = 1.54178$ Å

Cell parameters from 9895 reflections

$\theta = 4.1$ – 69.6°

$\mu = 3.03$ mm⁻¹

$T = 100$ K

Irregular, clear colourless

$0.27 \times 0.14 \times 0.10$ mm

Data collection

Bruker APEXII Kappa Duo
diffractometer

Radiation source: microfocus sealed X-ray tube,
Incoatec *Iμs*

Mirror optics monochromator

Detector resolution: 7.9 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.565$, $T_{\max} = 0.753$

18191 measured reflections

1892 independent reflections

1819 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 69.7^\circ$, $\theta_{\min} = 4.1^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -26 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.103$

$S = 1.06$

1892 reflections

138 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.2115P]$

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

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

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

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. The terminal chloro/methyl groups are disordered and overlap with an occupancy of 78:22%. The disorder was modelled with restraints (DFIX) and constraints (EADP for the Cl atoms).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.60104 (11)	0.01803 (8)	0.42660 (5)	0.0298 (2)	0.783 (2)
Cl1A	0.6006 (11)	0.2847 (11)	0.3649 (4)	0.0328 (12)	0.217 (2)
O10	0.74965 (11)	0.26055 (12)	0.48882 (5)	0.0281 (3)	
N8	0.53542 (13)	0.31060 (13)	0.52846 (6)	0.0208 (3)	
H8	0.453 (2)	0.2949 (17)	0.5247 (7)	0.016 (4)*	
C1	0.69159 (16)	0.46725 (17)	0.58476 (7)	0.0257 (4)	
H1	0.7392	0.4906	0.5480	0.031*	
C2	0.73137 (17)	0.52711 (18)	0.63985 (8)	0.0303 (4)	
H2	0.8067	0.5915	0.6402	0.036*	
C3	0.66349 (18)	0.49513 (17)	0.69457 (8)	0.0286 (4)	
C4	0.7043 (2)	0.5651 (2)	0.75375 (9)	0.0408 (5)	
H4A	0.7236	0.4951	0.7850	0.061*	
H4B	0.6272	0.6246	0.7675	0.061*	
H4C	0.7888	0.6212	0.7471	0.061*	
C5	0.55361 (18)	0.40046 (17)	0.69264 (7)	0.0286 (4)	
H5	0.5058	0.3771	0.7294	0.034*	
C6	0.51263 (16)	0.33958 (16)	0.63802 (7)	0.0253 (3)	
H6	0.4374	0.2751	0.6376	0.030*	
C7	0.58167 (15)	0.37290 (16)	0.58389 (7)	0.0208 (3)	
C9	0.62129 (15)	0.25772 (15)	0.48554 (7)	0.0204 (3)	
C11	0.54665 (16)	0.19425 (16)	0.43058 (7)	0.0223 (3)	
H11	0.4426	0.1988	0.4369	0.027*	0.783 (2)
H11A	0.4428	0.2050	0.4358	0.027*	0.217 (2)
C12A	0.582 (2)	0.0409 (11)	0.4215 (10)	0.035 (2)	0.217 (2)
H12A	0.5437	-0.0127	0.4558	0.053*	0.217 (2)
H12B	0.6838	0.0290	0.4197	0.053*	0.217 (2)
H12C	0.5395	0.0084	0.3831	0.053*	0.217 (2)
C12	0.5856 (12)	0.2688 (11)	0.3711 (4)	0.035 (2)	0.783 (2)
H12D	0.6871	0.2610	0.3641	0.053*	0.783 (2)
H12E	0.5597	0.3664	0.3743	0.053*	0.783 (2)
H12F	0.5350	0.2266	0.3368	0.053*	0.783 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0401 (5)	0.0204 (4)	0.0290 (4)	0.0037 (2)	-0.0030 (3)	-0.0030 (3)
Cl1A	0.034 (2)	0.036 (2)	0.0278 (15)	-0.0036 (14)	-0.0033 (13)	0.0100 (13)

O10	0.0158 (6)	0.0365 (7)	0.0320 (6)	0.0011 (5)	0.0005 (4)	-0.0073 (5)
N8	0.0125 (6)	0.0255 (7)	0.0244 (6)	-0.0016 (5)	0.0002 (5)	-0.0020 (5)
C1	0.0207 (7)	0.0299 (8)	0.0266 (8)	-0.0025 (6)	0.0027 (6)	-0.0026 (6)
C2	0.0215 (8)	0.0348 (9)	0.0347 (9)	-0.0034 (7)	-0.0014 (7)	-0.0071 (7)
C3	0.0281 (8)	0.0310 (8)	0.0266 (8)	0.0070 (7)	-0.0060 (7)	-0.0037 (6)
C4	0.0409 (10)	0.0500 (11)	0.0315 (9)	0.0061 (9)	-0.0089 (8)	-0.0112 (9)
C5	0.0332 (8)	0.0295 (8)	0.0233 (7)	0.0048 (7)	0.0034 (6)	0.0033 (6)
C6	0.0242 (7)	0.0230 (7)	0.0286 (8)	-0.0005 (6)	0.0032 (6)	0.0016 (6)
C7	0.0181 (7)	0.0215 (7)	0.0229 (7)	0.0032 (6)	-0.0005 (5)	-0.0003 (6)
C9	0.0182 (7)	0.0195 (7)	0.0235 (7)	0.0001 (5)	0.0010 (5)	0.0024 (6)
C11	0.0175 (7)	0.0244 (8)	0.0250 (7)	0.0020 (6)	0.0010 (5)	-0.0016 (6)
C12A	0.034 (3)	0.030 (3)	0.042 (4)	0.006 (2)	-0.007 (2)	-0.005 (2)
C12	0.034 (3)	0.030 (3)	0.042 (4)	0.006 (2)	-0.007 (2)	-0.005 (2)

Geometric parameters (Å, °)

C11—C11	1.7861 (17)	C5—H5	0.9500
C11A—C11	1.758 (8)	C5—C6	1.387 (2)
O10—C9	1.2233 (18)	C6—H6	0.9500
N8—H8	0.80 (2)	C6—C7	1.391 (2)
N8—C7	1.4226 (19)	C9—C11	1.524 (2)
N8—C9	1.3448 (19)	C11—H11	1.0000
C1—H1	0.9500	C11—H11A	1.0000
C1—C2	1.388 (2)	C11—C12A	1.536 (9)
C1—C7	1.389 (2)	C11—C12	1.532 (7)
C2—H2	0.9500	C12A—H12A	0.9800
C2—C3	1.394 (2)	C12A—H12B	0.9800
C3—C4	1.511 (2)	C12A—H12C	0.9800
C3—C5	1.391 (2)	C12—H12D	0.9800
C4—H4A	0.9800	C12—H12E	0.9800
C4—H4B	0.9800	C12—H12F	0.9800
C4—H4C	0.9800		
C7—N8—H8	118.0 (12)	O10—C9—N8	123.83 (14)
C9—N8—H8	116.7 (12)	O10—C9—C11	121.34 (13)
C9—N8—C7	124.55 (13)	N8—C9—C11	114.82 (13)
C2—C1—H1	120.3	C11—C11—H11	109.6
C2—C1—C7	119.47 (15)	C11A—C11—H11A	109.2
C7—C1—H1	120.3	C9—C11—C11	106.80 (10)
C1—C2—H2	119.2	C9—C11—C11A	107.8 (4)
C1—C2—C3	121.63 (16)	C9—C11—H11	109.6
C3—C2—H2	119.2	C9—C11—H11A	109.2
C2—C3—C4	121.00 (16)	C9—C11—C12A	113.1 (8)
C5—C3—C2	117.95 (15)	C9—C11—C12	111.4 (5)
C5—C3—C4	121.02 (16)	C12A—C11—C11A	108.3 (9)
C3—C4—H4A	109.5	C12A—C11—H11A	109.2
C3—C4—H4B	109.5	C12—C11—C11	109.8 (4)
C3—C4—H4C	109.5	C12—C11—H11	109.6

H4A—C4—H4B	109.5	C11—C12A—H12A	109.5
H4A—C4—H4C	109.5	C11—C12A—H12B	109.5
H4B—C4—H4C	109.5	C11—C12A—H12C	109.5
C3—C5—H5	119.4	H12A—C12A—H12B	109.5
C6—C5—C3	121.17 (15)	H12A—C12A—H12C	109.5
C6—C5—H5	119.4	H12B—C12A—H12C	109.5
C5—C6—H6	120.0	C11—C12—H12D	109.5
C5—C6—C7	120.01 (15)	C11—C12—H12E	109.5
C7—C6—H6	120.0	C11—C12—H12F	109.5
C1—C7—N8	121.58 (14)	H12D—C12—H12E	109.5
C1—C7—C6	119.77 (14)	H12D—C12—H12F	109.5
C6—C7—N8	118.63 (14)	H12E—C12—H12F	109.5
O10—C9—C11—C11	59.49 (17)	C2—C1—C7—C6	0.1 (2)
O10—C9—C11—C11A	-59.4 (4)	C2—C3—C5—C6	0.0 (2)
O10—C9—C11—C12A	60.2 (10)	C3—C5—C6—C7	0.0 (2)
O10—C9—C11—C12	-60.4 (5)	C4—C3—C5—C6	177.74 (16)
N8—C9—C11—C11	-121.40 (12)	C5—C6—C7—N8	-178.85 (14)
N8—C9—C11—C11A	119.7 (4)	C5—C6—C7—C1	0.0 (2)
N8—C9—C11—C12A	-120.7 (10)	C7—N8—C9—O10	-1.9 (2)
N8—C9—C11—C12	118.7 (5)	C7—N8—C9—C11	179.00 (13)
C1—C2—C3—C4	-177.66 (16)	C7—C1—C2—C3	-0.1 (3)
C1—C2—C3—C5	0.1 (3)	C9—N8—C7—C1	45.3 (2)
C2—C1—C7—N8	178.89 (14)	C9—N8—C7—C6	-135.93 (15)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C1—C6 ring.

<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>
N8—H8...O10 ⁱ	0.80 (2)	2.03 (2)	2.8295 (16)	174.8 (17)
C11—H11...O10 ⁱ	1.00	2.48	3.3574 (18)	146
C12—H12E...Cg1 ⁱⁱ	0.98	2.61	3.503 (11)	151

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

(1b)

Crystal data

C₁₀H₁₂ClNO

M_r = 197.66

Orthorhombic, *Pbca*

a = 9.5053 (6) Å

b = 9.6793 (5) Å

c = 21.8380 (13) Å

V = 2009.2 (2) Å³

Z = 8

F(000) = 832

D_x = 1.307 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 6677 reflections

θ = 2.8–26.5°

μ = 0.34 mm⁻¹

T = 100 K

Fragment, clear colourless

0.25 × 0.11 × 0.1 mm

Data collection

Bruker D8 Quest ECO diffractometer	$T_{\min} = 0.702$, $T_{\max} = 0.745$
Radiation source: sealed X-ray tube, Siemens, KFF Mo 2K -90 C	19741 measured reflections
Graphite monochromator	2061 independent reflections
Detector resolution: 5.12 pixels mm ⁻¹	1668 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{\text{int}} = 0.051$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 3.5^\circ$
	$h = -11 \rightarrow 9$
	$k = -12 \rightarrow 12$
	$l = -26 \rightarrow 27$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 1.4949P]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\max} < 0.001$
2061 reflections	$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
138 parameters	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
2 restraints	
Primary atom site location: dual	

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. The terminal chloro/methyl groups are disordered and overlap with an occupancy of 77:23%. The disorder was modelled with restraints (DFIX) and constraints (EADP for the Cl atoms).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.60085 (14)	0.01841 (9)	0.42661 (6)	0.0233 (2)	0.768 (2)
Cl1A	0.5999 (11)	0.2831 (11)	0.3648 (4)	0.0253 (12)	0.232 (2)
O10	0.74993 (12)	0.26099 (13)	0.48878 (5)	0.0217 (3)	
N8	0.53537 (14)	0.31069 (14)	0.52838 (6)	0.0141 (3)	
H8	0.450 (2)	0.2946 (19)	0.5248 (9)	0.019 (5)*	
C1	0.69140 (18)	0.46745 (18)	0.58487 (8)	0.0186 (4)	
H1	0.7389	0.4913	0.5481	0.022*	
C2	0.73115 (18)	0.52705 (19)	0.63992 (8)	0.0236 (4)	
H2	0.8064	0.5916	0.6404	0.028*	
C3	0.66346 (19)	0.49466 (19)	0.69465 (8)	0.0217 (4)	
C4	0.7041 (2)	0.5647 (2)	0.75373 (9)	0.0331 (5)	
H4A	0.6236	0.6170	0.7695	0.050*	
H4B	0.7829	0.6278	0.7462	0.050*	
H4C	0.7323	0.4949	0.7838	0.050*	
C5	0.5537 (2)	0.39994 (18)	0.69253 (8)	0.0220 (4)	
H5	0.5059	0.3763	0.7293	0.026*	
C6	0.51244 (18)	0.33931 (18)	0.63806 (8)	0.0187 (4)	
H6	0.4370	0.2750	0.6376	0.022*	
C7	0.58171 (16)	0.37265 (16)	0.58381 (7)	0.0140 (3)	

C9	0.62137 (16)	0.25791 (16)	0.48549 (7)	0.0135 (3)	
C11	0.54663 (17)	0.19470 (17)	0.43051 (8)	0.0158 (3)	
H11	0.4425	0.1995	0.4367	0.019*	0.768 (2)
H11A	0.4426	0.2044	0.4357	0.019*	0.232 (2)
C12A	0.585 (3)	0.0413 (12)	0.4233 (12)	0.033 (3)	0.232 (2)
H12A	0.5527	-0.0098	0.4595	0.049*	0.232 (2)
H12B	0.6867	0.0317	0.4191	0.049*	0.232 (2)
H12C	0.5383	0.0041	0.3867	0.049*	0.232 (2)
C12	0.5869 (14)	0.2707 (13)	0.3713 (4)	0.033 (3)	0.768 (2)
H12D	0.6883	0.2615	0.3643	0.049*	0.768 (2)
H12E	0.5625	0.3687	0.3752	0.049*	0.768 (2)
H12F	0.5355	0.2303	0.3368	0.049*	0.768 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0348 (6)	0.0136 (3)	0.0214 (4)	0.0023 (3)	-0.0026 (3)	-0.0033 (3)
C11A	0.032 (2)	0.027 (2)	0.0167 (16)	0.0008 (15)	-0.0042 (14)	0.0061 (13)
O10	0.0104 (6)	0.0306 (7)	0.0242 (7)	0.0017 (5)	0.0004 (5)	-0.0076 (5)
N8	0.0078 (7)	0.0183 (7)	0.0161 (7)	-0.0014 (5)	-0.0005 (6)	-0.0017 (6)
C1	0.0156 (8)	0.0216 (9)	0.0185 (9)	-0.0030 (7)	0.0031 (6)	-0.0029 (7)
C2	0.0166 (9)	0.0273 (10)	0.0268 (10)	-0.0046 (7)	-0.0006 (7)	-0.0077 (8)
C3	0.0216 (9)	0.0238 (9)	0.0196 (9)	0.0063 (7)	-0.0061 (7)	-0.0040 (7)
C4	0.0351 (11)	0.0407 (12)	0.0234 (10)	0.0051 (9)	-0.0089 (8)	-0.0098 (9)
C5	0.0293 (10)	0.0222 (9)	0.0145 (8)	0.0042 (7)	0.0041 (7)	0.0040 (7)
C6	0.0195 (8)	0.0166 (8)	0.0201 (9)	-0.0017 (7)	0.0029 (7)	0.0015 (7)
C7	0.0130 (8)	0.0144 (8)	0.0145 (8)	0.0023 (6)	0.0001 (6)	-0.0001 (6)
C9	0.0124 (8)	0.0131 (7)	0.0151 (8)	0.0007 (6)	0.0012 (6)	0.0014 (6)
C11	0.0125 (7)	0.0179 (8)	0.0169 (8)	0.0009 (6)	0.0018 (6)	-0.0017 (7)
C12A	0.028 (3)	0.031 (4)	0.039 (5)	0.009 (3)	-0.007 (3)	-0.006 (3)
C12	0.028 (3)	0.031 (4)	0.039 (5)	0.009 (3)	-0.007 (3)	-0.006 (3)

Geometric parameters (Å, °)

C11—C11	1.7845 (18)	C5—H5	0.9500
C11A—C11	1.746 (8)	C5—C6	1.383 (2)
O10—C9	1.2245 (19)	C6—H6	0.9500
N8—H8	0.83 (2)	C6—C7	1.393 (2)
N8—C7	1.421 (2)	C9—C11	1.523 (2)
N8—C9	1.344 (2)	C11—H11	1.0000
C1—H1	0.9500	C11—H11A	1.0000
C1—C2	1.386 (2)	C11—C12A	1.536 (9)
C1—C7	1.389 (2)	C11—C12	1.535 (7)
C2—H2	0.9500	C12A—H12A	0.9800
C2—C3	1.393 (3)	C12A—H12B	0.9800
C3—C4	1.508 (2)	C12A—H12C	0.9800
C3—C5	1.390 (3)	C12—H12D	0.9800
C4—H4A	0.9800	C12—H12E	0.9800

C4—H4B	0.9800	C12—H12F	0.9800
C4—H4C	0.9800		
C7—N8—H8	117.6 (13)	O10—C9—N8	123.83 (15)
C9—N8—H8	117.2 (14)	O10—C9—C11	121.43 (14)
C9—N8—C7	124.44 (14)	N8—C9—C11	114.73 (14)
C2—C1—H1	120.2	C11—C11—H11	109.7
C2—C1—C7	119.60 (16)	C11A—C11—H11A	109.5
C7—C1—H1	120.2	C9—C11—C11	106.68 (12)
C1—C2—H2	119.2	C9—C11—C11A	108.4 (4)
C1—C2—C3	121.64 (17)	C9—C11—H11	109.7
C3—C2—H2	119.2	C9—C11—H11A	109.5
C2—C3—C4	120.96 (17)	C9—C11—C12A	111.1 (9)
C5—C3—C2	117.83 (16)	C9—C11—C12	110.8 (5)
C5—C3—C4	121.17 (17)	C12A—C11—C11A	108.8 (10)
C3—C4—H4A	109.5	C12A—C11—H11A	109.5
C3—C4—H4B	109.5	C12—C11—C11	110.2 (5)
C3—C4—H4C	109.5	C12—C11—H11	109.7
H4A—C4—H4B	109.5	C11—C12A—H12A	109.5
H4A—C4—H4C	109.5	C11—C12A—H12B	109.5
H4B—C4—H4C	109.5	C11—C12A—H12C	109.5
C3—C5—H5	119.3	H12A—C12A—H12B	109.5
C6—C5—C3	121.41 (16)	H12A—C12A—H12C	109.5
C6—C5—H5	119.3	H12B—C12A—H12C	109.5
C5—C6—H6	120.0	C11—C12—H12D	109.5
C5—C6—C7	119.94 (16)	C11—C12—H12E	109.5
C7—C6—H6	120.0	C11—C12—H12F	109.5
C1—C7—N8	121.71 (14)	H12D—C12—H12E	109.5
C1—C7—C6	119.58 (15)	H12D—C12—H12F	109.5
C6—C7—N8	118.69 (14)	H12E—C12—H12F	109.5
O10—C9—C11—C11	59.75 (18)	C2—C1—C7—C6	0.4 (2)
O10—C9—C11—C11A	-58.9 (4)	C2—C3—C5—C6	0.1 (3)
O10—C9—C11—C12A	60.5 (11)	C3—C5—C6—C7	0.2 (3)
O10—C9—C11—C12	-60.2 (6)	C4—C3—C5—C6	177.51 (17)
N8—C9—C11—C11	-121.32 (14)	C5—C6—C7—N8	-178.85 (15)
N8—C9—C11—C11A	120.0 (4)	C5—C6—C7—C1	-0.4 (2)
N8—C9—C11—C12A	-120.6 (11)	C7—N8—C9—O10	-2.1 (3)
N8—C9—C11—C12	118.7 (6)	C7—N8—C9—C11	178.97 (14)
C1—C2—C3—C4	-177.50 (17)	C7—C1—C2—C3	-0.2 (3)
C1—C2—C3—C5	0.0 (3)	C9—N8—C7—C1	45.6 (2)
C2—C1—C7—N8	178.82 (16)	C9—N8—C7—C6	-136.01 (17)

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

Cg1 is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N8—H8 \cdots O10 ⁱ	0.83 (2)	2.00 (2)	2.8255 (18)	174.2 (19)

C11—H11…O10 ⁱ	1.00	2.48	3.353 (2)	146
C12—H12E…Cg1 ⁱⁱ	0.98	2.62	3.493 (13)	149

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