



Temperature-dependent solid-state phase transition with twinning in the crystal structure of 4-methoxyanilinium chloride

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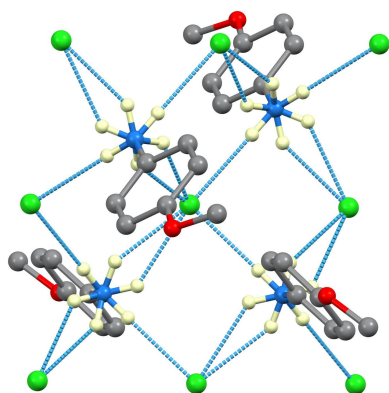
CCDC references: 2314991; 2314990

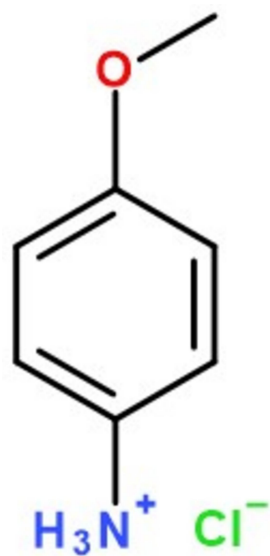
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At room temperature, the title salt, $C_7H_{10}NO^+ \cdot Cl^-$, is orthorhombic, space group $Pbca$ with $Z' = 1$, as previously reported [Zhao (2009). *Acta Cryst. E* **65**, o2378]. Between 250 and 200 K, there is a solid-state phase transition to a twinned monoclinic $P2_1/c$ structure with $Z' = 2$. We report the high temperature structure at 250 K and the low-temperature structure at 100 K. In the low-temperature structure, the $-NH_3$ hydrogen atoms are ordered and this group has a different orientation in each independent molecule, in keeping with optimizing $N-H \cdots Cl$ hydrogen bonding, some of which are bifurcated: these hydrogen bonds have $N \cdots Cl$ distances in the range 3.1201 (8)–3.4047 (8) Å. In the single cation of the high-temperature structure, the NH hydrogen atoms are disordered into the average of the two low-temperature positions and the $N \cdots Cl$ hydrogen bond distances are in the range 3.1570 (15)–3.3323 (18) Å. At both temperatures, the methoxy group is nearly coplanar with the rest of the molecule, with the $C-C-O-C$ torsion angles being $-7.0(2)^\circ$ at 250 K and $-6.94(12)$ and $-9.35(12)^\circ$ at 100 K. In the extended orthorhombic structure, (001) hydrogen-bonded sheets occur; in the monoclinic structure, the sheets propagate in the (010) plane.

1. Chemical context

4-Alkoxyacetanilides (4-AAs), represented by phenacetin, or *N*-(4-ethoxyphenyl)acetamide ($C_{10}H_{13}NO_2$), played a pivotal role in introducing synthetic fever reduction and non-opioid analgesics to the global pharmaceutical market in the early 1900s. The analgesic effects of 4-AAs result from their impact on the sensory tracts of the spinal cord, while their antipyretic actions predominantly occur in the brain, where they lower the temperature set point (Dalmann *et al.*, 2015; Flower & Vane, 1972). *In vivo*, the primary metabolic pathway involves oxidative *O*-dealkylation, producing *N*-(4-hydroxyphenyl)acetamide, $C_8H_9NO_3$, a clinically significant analgesic (Nohmi *et al.*, 1984). However, a minor fraction may undergo deacylation, leading to the formation of carcinogenic and kidney-damaging 4-alkoxyanilines Nohmi *et al.*, 1984; Prescott, 1980). This study centers on the crystal structure analysis of the title salt, 4-methoxyaniline hydrochloride (4-methoxyanilinium chloride or 4-MAC), **I**, aiming to expound not only its potential kidney-damaging properties but also provide structural data for exploring molecular targets through molecular docking and molecular dynamic simulations.





2. Structural commentary

At room temperature (298 K), **I** crystallizes in the orthorhombic space group $Pbca$ with one formula unit in the asymmetric unit. The cell dimensions are $a = 8.8778$ (5), $b = 8.4660$ (5), $c = 21.7236$ (11) Å and $V = 1632.73$ (16) Å³. Cooling the sample causes a solid-state phase transition to a twinned structure with lower symmetry and two formula units in the asymmetric unit. At 250 K, the structure is still orthorhombic, but at 200 K, the space group is monoclinic $P2_1/c$ with $a = 8.3772$ (11), $b = 21.715$ (3), $c = 8.8466$ (12) Å, $\beta = 90.039$ (4)° and $V = 1609.3$ (4) Å³. At $T = 100$ K, the monoclinic cell parameters are $a = 8.3039$ (6), $b = 21.6993$ (15), $c = 8.8495$ (6) Å, $\beta = 90.077$ (2)° and $V = 1594.58$ (19) Å³.

The crystal structure at 250 K, shown in Fig. 1, closely aligns with the published structure (Zhao, 2009) except that we find disorder in the NH hydrogen atoms, while Zhao treated them as ordered. Using Zhao's intensity data, we do see evidence of a second orientation of the NH₃ group, and we also see it from our crystal when warmed to 298 K. The methoxy group in **I** is

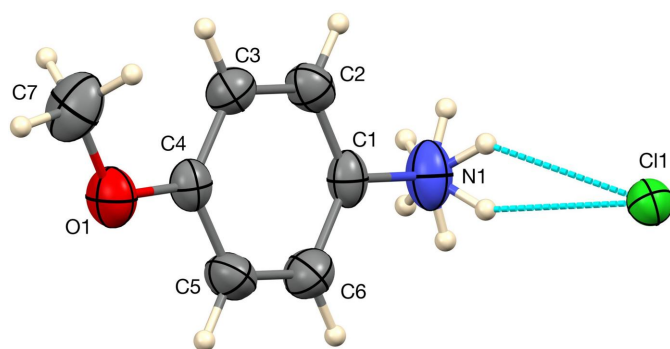


Figure 1

The asymmetric unit of the 250 K structure of **I**, with 50% displacement ellipsoids and hydrogen bonds indicated by blue dashed lines.

Table 1

Hydrogen-bond geometry (Å, °) for **I** at 250 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots Cl1^i$	0.90	2.43	3.3265 (18)	174
$N1-H2N\cdots Cl1^{ii}$	0.90	2.40	3.1915 (15)	147
$N1-H3N\cdots Cl1$	0.90	2.45	3.1570 (16)	135
$N1-H4N\cdots Cl1^{iii}$	0.90	2.43	3.3323 (18)	180
$N1-H5N\cdots Cl1$	0.90	2.36	3.1570 (15)	148
$N1-H6N\cdots Cl1^{ii}$	0.90	2.49	3.1915 (17)	136
$C6-H6\cdots Cl1^i$	0.94	2.82	3.6323 (16)	145

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

Table 2

Hydrogen-bond geometry (Å, °) for **I** at 100 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H11N\cdots Cl2$	0.880 (15)	2.279 (15)	3.1450 (8)	167.7 (13)
$N1-H12N\cdots Cl1^i$	0.870 (14)	2.573 (14)	3.2480 (7)	135.2 (13)
$N1-H12N\cdots Cl2^{ii}$	0.870 (14)	2.735 (15)	3.3797 (8)	132.1 (12)
$N1-H13N\cdots Cl1$	0.926 (15)	2.304 (16)	3.2080 (8)	165.0 (13)
$N2-H21N\cdots Cl1^{iii}$	0.901 (14)	2.487 (15)	3.2318 (8)	140.3 (12)
$N2-H21N\cdots Cl2^{iv}$	0.901 (14)	2.795 (14)	3.4047 (8)	126.2 (11)
$N2-H22N\cdots Cl1$	0.899 (14)	2.300 (15)	3.1916 (8)	171.3 (12)
$N2-H23N\cdots Cl2$	0.907 (15)	2.234 (15)	3.1201 (8)	165.5 (13)
$C2-H2\cdots Cl1$	0.95	2.98	3.7487 (8)	139
$C6-H6\cdots Cl2^{ii}$	0.95	2.77	3.6055 (8)	147

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

nearly coplanar with the rest of the molecule, with the torsion angle $C7-O1-C4-C3 = -7.0$ (2)°.

The asymmetric unit of the 100 K structure is shown in Fig. 2. The major difference between the two independent molecules is the conformation of the $-NH_3$ group, in which one molecule has one set of the disordered positions in the 250 K structure and the second has the other. As in the 250 K structure, the methoxy groups are twisted only slightly out of the planes of the aromatic rings, with $C7-O1-C4-C3$ and $C14-O2-C11-C10$ torsion angles of -6.94 (12) and -9.35 (12)°, respectively.

3. Supramolecular features

In both structures, the intermolecular interactions are predominantly $N-H\cdots Cl$ hydrogen bonds, as listed in Tables 1 and 2 and illustrated in Figs. 3 and 4. The $N\cdots Cl$ separations are in the range 3.1201 (8)–3.4047 (8) Å in the monoclinic 100 K

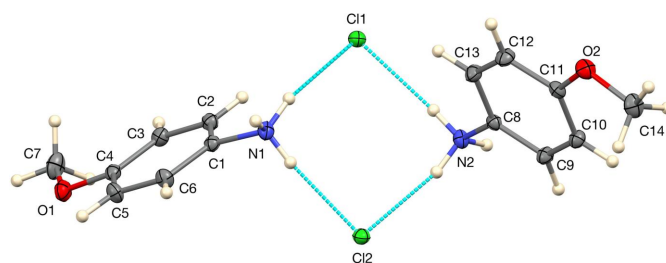


Figure 2

The asymmetric unit of the 100 K structure of **I**, with 50% displacement ellipsoids and hydrogen bonds indicated by blue dashed lines.

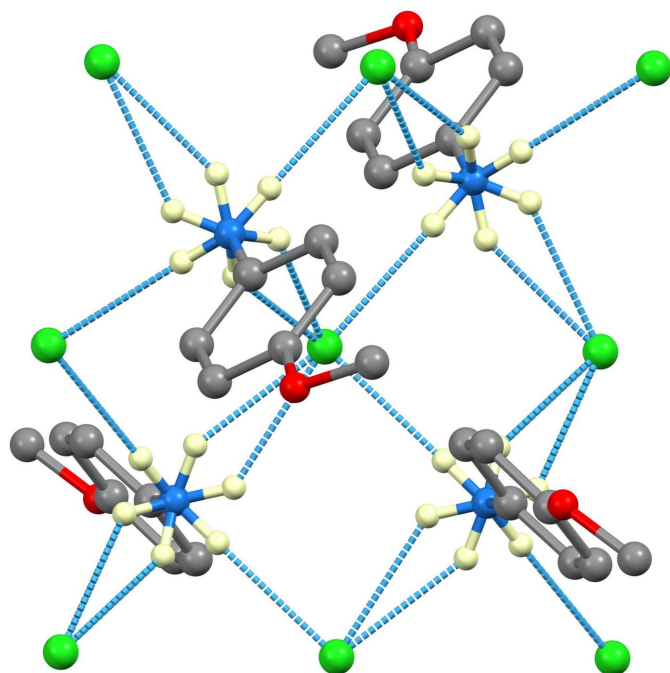


Figure 3
Hydrogen bonding in the 250 K structure of **I**.

structure and 3.1570 (15)–3.3323 (18) Å in the orthorhombic 250 K structure. In Fig. 4, it can be seen that for each NH₃ group, two of the H atoms are involved in direct hydrogen bonds and the third in a bifurcated N–H···(Cl,Cl) bond with two acceptors. The graph set (Etter *et al.*, 1990) patterns are centrosymmetric $R_4^2(8)$ rings and $R_2^2(4)$ rings. At 250 K, (001) sheets arise in the extended structure and at 100 K similar sheets propagate in the (010) plane, due to the change in unit-cell settings.

4. Database survey

A review of the literature revealed that the room temperature (298 K) structure of 4-methoxyanilinium chloride was previously reported (Zhao, 2009; Cambridge Structural Database refcode CUCTUQ). Similarly, the structure of 4-ethoxyanilinium chloride at 100 K has been documented (Fu, 2010; Hines *et al.*, 2023). However, these studies did not provide information on phase transitions and twinning.

5. Synthesis and crystallization

A saturated solution of the title compound, C₇H₁₀ClNO (CAS 20265-97-8 from AmBeed, Arlington Heights, IL, USA) in boiling water was allowed to pass through a short column of activated charcoal. The resulting colorless solution (eluent) was left to cool to room temperature and evaporate slowly in the dark. Pink laths of **I**, prepared through this process, were suitable for X-ray diffraction studies.

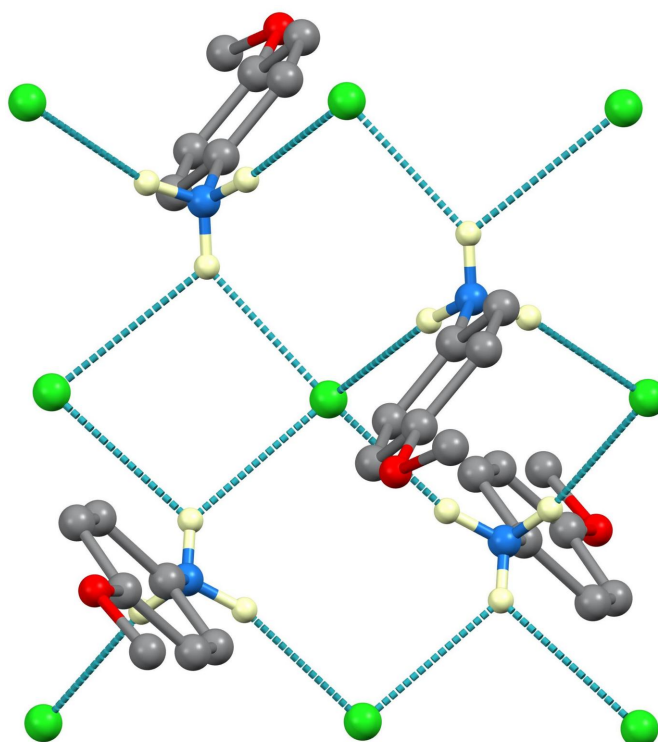


Figure 4
Hydrogen bonding in the 100 K structure of **I**.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For the structure at 250 K, all the H atoms were located in difference maps and those on carbon were relocated to geometrically idealized positions with C–H = 0.94 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aromatic C atoms and C–H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl group. The N-bound H atoms were idealized as six half-populated sites at 60° torsional intervals with N–H = 0.90 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ and the torsion angle was refined. For the structure at 100 K, the H atoms were handled similarly, except that C–H distances were fixed at 0.95 Å for aromatic C atoms and 0.98 Å for the methyl group, and the H atoms on N were ordered with their positions individually refined. The twin law for the monoclinic structure is (1 0 0, 0 –1 0, 0 0 –1) and the BASF parameter refined to 0.4484 (6).

Funding information

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Table 3
Experimental details.

	I at 250 K	I at 100 K
Crystal data		
Chemical formula	C ₇ H ₁₀ NO ⁺ ·Cl ⁻	C ₇ H ₁₀ NO ⁺ ·Cl ⁻
<i>M_r</i>	159.61	159.61
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	250	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8689 (4), 8.4361 (3), 21.7319 (9)	8.3039 (6), 21.6993 (15), 8.8495 (6)
α , β , γ (°)	90, 90, 90	90, 90.077 (2), 90
<i>V</i> (Å ³)	1625.96 (12)	1594.58 (19)
<i>Z</i>	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.40	0.41
Crystal size (mm)	0.34 × 0.31 × 0.15	0.43 × 0.41 × 0.21
Data collection		
Diffractometer	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.896, 0.942	0.873, 0.919
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	73425, 2717, 2019	48397, 10832, 9310
<i>R_{int}</i>	0.050	0.033
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.737	0.940
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.102, 1.08	0.033, 0.075, 1.06
No. of reflections	2717	10832
No. of parameters	93	202
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.24, -0.22	0.47, -0.28

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015), *SHELXL2018/1* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2024). E80, 58-61 [https://doi.org/10.1107/S2056989023010812]

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Computing details

4-Methoxyanilinium chloride (I_250K)

Crystal data

$C_7H_{10}NO^+ \cdot Cl^-$

$M_r = 159.61$

Orthorhombic, *Pbca*

$a = 8.8689$ (4) Å

$b = 8.4361$ (3) Å

$c = 21.7319$ (9) Å

$V = 1625.96$ (12) Å³

$Z = 8$

$F(000) = 672$

$D_x = 1.304$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9997 reflections

$\theta = 3.8$ – 27.4°

$\mu = 0.40$ mm⁻¹

$T = 250$ K

Lath fragment, pink

$0.34 \times 0.31 \times 0.15$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

TRIUMPH curved graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.896$, $T_{\max} = 0.942$

73425 measured reflections

2717 independent reflections

2019 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 31.6^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -13 \rightarrow 13$

$k = -12 \rightarrow 12$

$l = -32 \rightarrow 32$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.102$

$S = 1.08$

2717 reflections

93 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.6343P]$

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

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

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻³

Extinction correction: SHELXL-2017/1
(Sheldrick 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0070 (9)

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.

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)
C11	0.74847 (4)	0.51434 (4)	0.52125 (2)	0.03992 (12)	
O1	0.65326 (14)	0.80202 (15)	0.20491 (5)	0.0514 (3)	
N1	0.52441 (19)	0.75043 (18)	0.45535 (6)	0.0547 (4)	
H1N	0.584233	0.818422	0.475901	0.082*	0.5
H2N	0.427238	0.776832	0.461481	0.082*	0.5
H3N	0.540574	0.651270	0.469129	0.082*	0.5
H4N	0.450464	0.679260	0.461773	0.082*	0.5
H5N	0.607459	0.720851	0.476193	0.082*	0.5
H6N	0.494123	0.846412	0.468545	0.082*	0.5
C1	0.55894 (17)	0.75820 (17)	0.38936 (7)	0.0388 (3)	
C2	0.48090 (17)	0.66401 (19)	0.34891 (7)	0.0427 (3)	
H2	0.408003	0.592462	0.363560	0.051*	
C3	0.51002 (17)	0.67476 (19)	0.28628 (7)	0.0406 (3)	
H3	0.456473	0.610978	0.258349	0.049*	
C4	0.61767 (17)	0.77925 (17)	0.26521 (6)	0.0371 (3)	
C5	0.6976 (2)	0.8710 (2)	0.30673 (8)	0.0481 (4)	
H5	0.772702	0.940379	0.292416	0.058*	
C6	0.6681 (2)	0.8615 (2)	0.36875 (7)	0.0484 (4)	
H6	0.721776	0.924909	0.396768	0.058*	
C7	0.5863 (2)	0.6992 (3)	0.16061 (8)	0.0638 (5)	
H7A	0.611485	0.590164	0.170382	0.096*	
H7B	0.624205	0.725123	0.119973	0.096*	
H7C	0.477664	0.712315	0.161343	0.096*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.03990 (18)	0.04090 (19)	0.03894 (18)	−0.00135 (14)	−0.00086 (16)	0.00395 (13)
O1	0.0576 (7)	0.0614 (7)	0.0351 (6)	0.0028 (6)	0.0091 (5)	0.0037 (5)
N1	0.0653 (9)	0.0622 (9)	0.0364 (7)	0.0194 (7)	0.0085 (6)	0.0064 (6)
C1	0.0407 (7)	0.0429 (7)	0.0328 (6)	0.0138 (6)	0.0038 (6)	0.0053 (6)
C2	0.0373 (7)	0.0436 (8)	0.0473 (8)	−0.0006 (6)	0.0065 (6)	0.0055 (6)
C3	0.0375 (8)	0.0435 (8)	0.0407 (7)	0.0009 (6)	0.0001 (6)	−0.0035 (6)
C4	0.0375 (7)	0.0391 (7)	0.0347 (7)	0.0073 (6)	0.0040 (6)	0.0036 (5)
C5	0.0484 (9)	0.0496 (9)	0.0463 (9)	−0.0129 (7)	0.0036 (7)	0.0052 (7)
C6	0.0528 (9)	0.0504 (9)	0.0419 (8)	−0.0056 (7)	−0.0049 (7)	−0.0028 (7)
C7	0.0643 (12)	0.0896 (14)	0.0374 (8)	0.0102 (11)	0.0031 (8)	−0.0106 (9)

Geometric parameters (Å, °)

O1—C4	1.3615 (17)	C2—C3	1.388 (2)
O1—C7	1.425 (2)	C2—H2	0.9400
N1—C1	1.4679 (19)	C3—C4	1.378 (2)
N1—H1N	0.9000	C3—H3	0.9400
N1—H2N	0.9000	C4—C5	1.384 (2)
N1—H3N	0.9000	C5—C6	1.375 (2)
N1—H4N	0.9000	C5—H5	0.9400
N1—H5N	0.9000	C6—H6	0.9400
N1—H6N	0.9000	C7—H7A	0.9700
C1—C2	1.372 (2)	C7—H7B	0.9700
C1—C6	1.377 (2)	C7—H7C	0.9700
C4—O1—C7	117.88 (14)	C4—C3—C2	119.77 (14)
C1—N1—H1N	109.5	C4—C3—H3	120.1
C1—N1—H2N	109.5	C2—C3—H3	120.1
H1N—N1—H2N	109.5	O1—C4—C3	124.81 (14)
C1—N1—H3N	109.5	O1—C4—C5	115.46 (14)
H1N—N1—H3N	109.5	C3—C4—C5	119.73 (13)
H2N—N1—H3N	109.5	C6—C5—C4	120.60 (15)
C1—N1—H4N	109.5	C6—C5—H5	119.7
C1—N1—H5N	109.5	C4—C5—H5	119.7
H4N—N1—H5N	109.5	C5—C6—C1	119.28 (15)
C1—N1—H6N	109.5	C5—C6—H6	120.4
H4N—N1—H6N	109.5	C1—C6—H6	120.4
H5N—N1—H6N	109.5	O1—C7—H7A	109.5
C2—C1—C6	120.83 (14)	O1—C7—H7B	109.5
C2—C1—N1	119.65 (14)	H7A—C7—H7B	109.5
C6—C1—N1	119.51 (15)	O1—C7—H7C	109.5
C1—C2—C3	119.76 (14)	H7A—C7—H7C	109.5
C1—C2—H2	120.1	H7B—C7—H7C	109.5
C3—C2—H2	120.1		
C6—C1—C2—C3	-1.2 (2)	C2—C3—C4—C5	1.0 (2)
N1—C1—C2—C3	177.97 (14)	O1—C4—C5—C6	178.05 (15)
C1—C2—C3—C4	0.4 (2)	C3—C4—C5—C6	-1.5 (2)
C7—O1—C4—C3	-7.0 (2)	C4—C5—C6—C1	0.7 (3)
C7—O1—C4—C5	173.48 (15)	C2—C1—C6—C5	0.7 (2)
C2—C3—C4—O1	-178.58 (14)	N1—C1—C6—C5	-178.52 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots Cl1 ⁱ	0.90	2.43	3.3265 (18)	174
N1—H2N \cdots Cl1 ⁱⁱ	0.90	2.40	3.1915 (15)	147
N1—H3N \cdots Cl1	0.90	2.45	3.1570 (16)	135
N1—H4N \cdots Cl1 ⁱⁱⁱ	0.90	2.43	3.3323 (18)	180

N1—H5N···Cl1	0.90	2.36	3.1570 (15)	148
N1—H6N···Cl1 ⁱⁱ	0.90	2.49	3.1915 (17)	136
C6—H6···Cl1 ⁱ	0.94	2.82	3.6323 (16)	145

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

4-Methoxyanilinium chloride (I_100K)

Crystal data

$C_7H_{10}NO^+Cl^-$	$F(000) = 672$
$M_r = 159.61$	$D_x = 1.330 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 8.3039 (6) \text{ \AA}$	Cell parameters from 9875 reflections
$b = 21.6993 (15) \text{ \AA}$	$\theta = 3.4\text{--}41.5^\circ$
$c = 8.8495 (6) \text{ \AA}$	$\mu = 0.41 \text{ mm}^{-1}$
$\beta = 90.077 (2)^\circ$	$T = 100 \text{ K}$
$V = 1594.58 (19) \text{ \AA}^3$	Needle fragment, pink
$Z = 8$	$0.43 \times 0.41 \times 0.21 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD diffractometer	48397 measured reflections
Radiation source: fine-focus sealed tube	10832 independent reflections
TRIUMPH curved graphite monochromator	9310 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.033$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 41.9^\circ, \theta_{\text{min}} = 1.9^\circ$
$T_{\text{min}} = 0.873, T_{\text{max}} = 0.919$	$h = -15 \rightarrow 15$
	$k = -40 \rightarrow 40$
	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.1702P]$
$wR(F^2) = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} = 0.001$
10832 reflections	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
202 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
0 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. Refined as a 2-component twin

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.46961 (2)	0.52412 (2)	0.74414 (2)	0.01433 (3)
Cl2	1.00704 (2)	0.51981 (2)	0.75416 (2)	0.01431 (3)
O1	0.81503 (9)	0.79863 (3)	0.36295 (8)	0.01972 (12)
N1	0.75005 (10)	0.54837 (3)	0.50236 (8)	0.01524 (11)

H11N	0.8313 (18)	0.5382 (6)	0.5613 (16)	0.023*
H12N	0.7496 (18)	0.5254 (6)	0.4219 (16)	0.023*
H13N	0.6580 (18)	0.5390 (6)	0.5566 (17)	0.023*
C1	0.75955 (9)	0.61391 (3)	0.46333 (8)	0.01282 (11)
C2	0.66656 (10)	0.65590 (4)	0.54219 (9)	0.01463 (13)
H2	0.592916	0.642048	0.616899	0.018*
C3	0.68159 (10)	0.71877 (4)	0.51130 (9)	0.01510 (12)
H3	0.618985	0.747903	0.565734	0.018*
C4	0.78835 (10)	0.73857 (3)	0.40075 (9)	0.01439 (12)
C5	0.87901 (11)	0.69542 (4)	0.31922 (10)	0.01746 (14)
H5	0.949889	0.708935	0.241833	0.021*
C6	0.86556 (10)	0.63310 (4)	0.35115 (10)	0.01644 (13)
H6	0.928009	0.603820	0.297051	0.020*
C7	0.71299 (15)	0.84409 (4)	0.43121 (12)	0.02472 (19)
H7A	0.600193	0.834617	0.408214	0.037*
H7B	0.739987	0.884893	0.391123	0.037*
H7C	0.729058	0.843809	0.540940	0.037*
O2	0.69262 (8)	0.20673 (3)	0.82982 (8)	0.01905 (11)
N2	0.73702 (9)	0.45944 (3)	0.94929 (8)	0.01440 (11)
H21N	0.7316 (18)	0.4677 (6)	1.0489 (16)	0.022*
H22N	0.6576 (18)	0.4795 (6)	0.9008 (16)	0.022*
H23N	0.8253 (18)	0.4776 (6)	0.9085 (16)	0.022*
C8	0.72962 (9)	0.39304 (3)	0.91915 (8)	0.01249 (11)
C9	0.82458 (10)	0.35313 (4)	1.00292 (9)	0.01498 (12)
H9	0.895113	0.368738	1.078368	0.018*
C10	0.81599 (10)	0.28992 (3)	0.97583 (9)	0.01480 (12)
H10	0.880248	0.262235	1.033186	0.018*
C11	0.71267 (9)	0.26745 (3)	0.86417 (9)	0.01383 (12)
C12	0.61959 (10)	0.30835 (4)	0.77920 (10)	0.01777 (14)
H12	0.550715	0.293062	0.702026	0.021*
C13	0.62716 (10)	0.37124 (4)	0.80690 (10)	0.01671 (13)
H13	0.563053	0.399067	0.749807	0.020*
C14	0.80131 (12)	0.16348 (4)	0.89757 (11)	0.02172 (16)
H14A	0.912339	0.174734	0.872250	0.033*
H14B	0.778211	0.122036	0.859247	0.033*
H14C	0.787721	0.164090	1.007547	0.033*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01254 (6)	0.01532 (6)	0.01511 (7)	-0.00041 (5)	-0.00015 (8)	0.00016 (6)
Cl2	0.01256 (6)	0.01453 (6)	0.01584 (7)	-0.00127 (5)	-0.00072 (8)	-0.00022 (6)
O1	0.0248 (3)	0.0133 (2)	0.0211 (3)	-0.0012 (2)	-0.0017 (2)	0.0031 (2)
N1	0.0200 (3)	0.0126 (2)	0.0132 (3)	-0.0018 (2)	-0.0019 (2)	0.00002 (19)
C1	0.0144 (3)	0.0126 (2)	0.0114 (3)	-0.0006 (2)	-0.0012 (2)	-0.0003 (2)
C2	0.0154 (3)	0.0155 (3)	0.0130 (3)	-0.0001 (2)	0.0007 (2)	-0.0002 (2)
C3	0.0168 (3)	0.0149 (3)	0.0136 (3)	0.0019 (2)	-0.0001 (2)	-0.0010 (2)
C4	0.0158 (3)	0.0133 (3)	0.0140 (3)	-0.0011 (2)	-0.0034 (2)	0.0009 (2)

C5	0.0187 (3)	0.0169 (3)	0.0168 (3)	-0.0015 (3)	0.0047 (3)	0.0013 (3)
C6	0.0182 (3)	0.0150 (3)	0.0161 (3)	0.0007 (2)	0.0037 (3)	-0.0010 (2)
C7	0.0372 (6)	0.0143 (3)	0.0226 (4)	0.0052 (3)	-0.0034 (4)	0.0003 (3)
O2	0.0220 (3)	0.0129 (2)	0.0222 (3)	-0.0016 (2)	-0.0008 (2)	-0.0029 (2)
N2	0.0182 (3)	0.0126 (2)	0.0124 (3)	-0.0008 (2)	0.0008 (2)	0.00002 (19)
C8	0.0136 (3)	0.0124 (2)	0.0115 (3)	-0.0012 (2)	0.0008 (2)	-0.0003 (2)
C9	0.0166 (3)	0.0149 (3)	0.0134 (3)	-0.0003 (2)	-0.0026 (3)	-0.0014 (2)
C10	0.0169 (3)	0.0139 (3)	0.0136 (3)	0.0007 (2)	-0.0013 (2)	-0.0006 (2)
C11	0.0147 (3)	0.0129 (3)	0.0139 (3)	-0.0023 (2)	0.0023 (2)	-0.0014 (2)
C12	0.0193 (3)	0.0160 (3)	0.0180 (4)	-0.0021 (2)	-0.0055 (3)	-0.0018 (2)
C13	0.0181 (3)	0.0153 (3)	0.0167 (3)	-0.0010 (2)	-0.0050 (3)	0.0011 (2)
C14	0.0280 (4)	0.0136 (3)	0.0236 (4)	0.0022 (3)	0.0032 (3)	-0.0011 (3)

Geometric parameters (Å, °)

O1—C4	1.3636 (10)	O2—C11	1.3624 (9)
O1—C7	1.4343 (12)	O2—C14	1.4330 (11)
N1—C1	1.4655 (10)	N2—C8	1.4667 (10)
N1—H11N	0.880 (15)	N2—H21N	0.901 (14)
N1—H12N	0.870 (14)	N2—H22N	0.899 (14)
N1—H13N	0.926 (15)	N2—H23N	0.907 (15)
C1—C2	1.3838 (11)	C8—C9	1.3856 (11)
C1—C6	1.3915 (11)	C8—C13	1.3900 (11)
C2—C3	1.3971 (11)	C9—C10	1.3941 (11)
C2—H2	0.9500	C9—H9	0.9500
C3—C4	1.3893 (12)	C10—C11	1.3957 (11)
C3—H3	0.9500	C10—H10	0.9500
C4—C5	1.4020 (12)	C11—C12	1.3961 (11)
C5—C6	1.3860 (11)	C12—C13	1.3879 (11)
C5—H5	0.9500	C12—H12	0.9500
C6—H6	0.9500	C13—H13	0.9500
C7—H7A	0.9800	C14—H14A	0.9800
C7—H7B	0.9800	C14—H14B	0.9800
C7—H7C	0.9800	C14—H14C	0.9800
C4—O1—C7	117.24 (7)	C11—O2—C14	117.60 (7)
C1—N1—H11N	109.9 (9)	C8—N2—H21N	111.7 (8)
C1—N1—H12N	111.4 (9)	C8—N2—H22N	111.0 (8)
H11N—N1—H12N	110.1 (13)	H21N—N2—H22N	109.5 (12)
C1—N1—H13N	112.4 (8)	C8—N2—H23N	112.8 (8)
H11N—N1—H13N	105.7 (12)	H21N—N2—H23N	110.2 (13)
H12N—N1—H13N	107.2 (13)	H22N—N2—H23N	101.1 (12)
C2—C1—C6	121.11 (7)	C9—C8—C13	121.13 (7)
C2—C1—N1	119.33 (7)	C9—C8—N2	119.54 (7)
C6—C1—N1	119.53 (7)	C13—C8—N2	119.32 (7)
C1—C2—C3	119.63 (8)	C8—C9—C10	119.60 (7)
C1—C2—H2	120.2	C8—C9—H9	120.2
C3—C2—H2	120.2	C10—C9—H9	120.2

C4—C3—C2	119.81 (7)	C9—C10—C11	119.78 (7)
C4—C3—H3	120.1	C9—C10—H10	120.1
C2—C3—H3	120.1	C11—C10—H10	120.1
O1—C4—C3	124.91 (7)	O2—C11—C10	124.79 (7)
O1—C4—C5	115.12 (7)	O2—C11—C12	115.29 (7)
C3—C4—C5	119.96 (7)	C10—C11—C12	119.91 (7)
C6—C5—C4	120.22 (8)	C13—C12—C11	120.33 (7)
C6—C5—H5	119.9	C13—C12—H12	119.8
C4—C5—H5	119.9	C11—C12—H12	119.8
C5—C6—C1	119.26 (7)	C12—C13—C8	119.23 (7)
C5—C6—H6	120.4	C12—C13—H13	120.4
C1—C6—H6	120.4	C8—C13—H13	120.4
O1—C7—H7A	109.5	O2—C14—H14A	109.5
O1—C7—H7B	109.5	O2—C14—H14B	109.5
H7A—C7—H7B	109.5	H14A—C14—H14B	109.5
O1—C7—H7C	109.5	O2—C14—H14C	109.5
H7A—C7—H7C	109.5	H14A—C14—H14C	109.5
H7B—C7—H7C	109.5	H14B—C14—H14C	109.5
C6—C1—C2—C3	-1.43 (12)	C13—C8—C9—C10	-0.84 (12)
N1—C1—C2—C3	176.47 (7)	N2—C8—C9—C10	179.11 (7)
C1—C2—C3—C4	0.67 (12)	C8—C9—C10—C11	0.36 (12)
C7—O1—C4—C3	-6.94 (12)	C14—O2—C11—C10	-9.35 (12)
C7—O1—C4—C5	173.41 (8)	C14—O2—C11—C12	171.16 (8)
C2—C3—C4—O1	-178.79 (8)	C9—C10—C11—O2	-178.87 (8)
C2—C3—C4—C5	0.84 (12)	C9—C10—C11—C12	0.60 (12)
O1—C4—C5—C6	178.02 (8)	O2—C11—C12—C13	178.42 (8)
C3—C4—C5—C6	-1.65 (12)	C10—C11—C12—C13	-1.10 (13)
C4—C5—C6—C1	0.91 (13)	C11—C12—C13—C8	0.63 (13)
C2—C1—C6—C5	0.63 (12)	C9—C8—C13—C12	0.35 (13)
N1—C1—C6—C5	-177.26 (8)	N2—C8—C13—C12	-179.60 (8)

Hydrogen-bond geometry (Å, °)

<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>
N1—H11 <i>N</i> ...Cl2	0.880 (15)	2.279 (15)	3.1450 (8)	167.7 (13)
N1—H12 <i>N</i> ...Cl1 ⁱ	0.870 (14)	2.573 (14)	3.2480 (7)	135.2 (13)
N1—H12 <i>N</i> ...Cl2 ⁱⁱ	0.870 (14)	2.735 (15)	3.3797 (8)	132.1 (12)
N1—H13 <i>N</i> ...Cl1	0.926 (15)	2.304 (16)	3.2080 (8)	165.0 (13)
N2—H21 <i>N</i> ...Cl1 ⁱⁱⁱ	0.901 (14)	2.487 (15)	3.2318 (8)	140.3 (12)
N2—H21 <i>N</i> ...Cl2 ^{iv}	0.901 (14)	2.795 (14)	3.4047 (8)	126.2 (11)
N2—H22 <i>N</i> ...Cl1	0.899 (14)	2.300 (15)	3.1916 (8)	171.3 (12)
N2—H23 <i>N</i> ...Cl2	0.907 (15)	2.234 (15)	3.1201 (8)	165.5 (13)
C2—H2...Cl1	0.95	2.98	3.7487 (8)	139
C6—H6...Cl2 ⁱⁱ	0.95	2.77	3.6055 (8)	147

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