

## Glycine methyl ester hydrochloride

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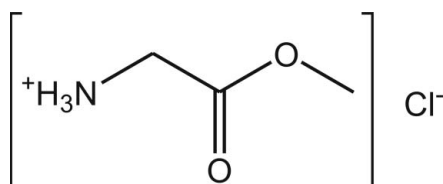
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Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.069;  $wR$  factor = 0.184; data-to-parameter ratio = 23.3.

The title compound [systematic name: (methoxycarbonylmethyl)ammonium chloride], crystallizes as a salt,  $\text{C}_3\text{H}_8\text{NO}_2^+\text{Cl}^-$ , with the charged species interacting mutually *via* strong and highly directional  $\text{N}^+\cdots\text{H}\cdots\text{Cl}^-$  hydrogen bonds which lead to the formation of a supramolecular tape running parallel to the  $c$  axis. Tapes close pack in the solid state mediated by multipoint recognition synthons based on weak  $\text{C}-\text{H}\cdots\text{O}$  interactions and van der Waals contacts between adjacent methyl groups.

### Related literature

For related structures, see: Handelsman-Benory *et al.* (1995). For detailed background to the role of hydrogen bonds in the supramolecular organization of organic crystals, see: Nangia & Desiraju (1998). For general background studies on crystal engineering approaches from our research group, see: Shi *et al.* (2008); Paz & Klinowski (2003); Paz *et al.* (2002). For a description of the Cambridge Structural Database, see: Allen (2002).



### Experimental

#### Crystal data

$\text{C}_3\text{H}_8\text{NO}_2^+\text{Cl}^-$   
 $M_r = 125.55$   
Monoclinic,  $P2_1/c$

$a = 8.352$  (2) Å  
 $b = 12.505$  (3) Å  
 $c = 5.6369$  (14) Å

$\beta = 99.730$  (9)°  
 $V = 580.3$  (2) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation

$\mu = 0.55$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.08 \times 0.02 \times 0.02$  mm

#### Data collection

Bruker X8 Kappa CCD APEXII diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.957$ ,  $T_{\max} = 0.989$

5189 measured reflections  
1539 independent reflections  
923 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.070$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$   
 $wR(F^2) = 0.184$   
 $S = 1.08$   
1539 reflections

66 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.05$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.55$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                                | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N1}-\text{H1A}\cdots\text{Cl1}^i$     | 0.91  | 2.52        | 3.269 (4)   | 140           |
| $\text{N1}-\text{H1B}\cdots\text{Cl1}^{ii}$  | 0.91  | 2.25        | 3.112 (4)   | 158           |
| $\text{N1}-\text{H1C}\cdots\text{Cl1}$       | 0.91  | 2.26        | 3.147 (4)   | 165           |
| $\text{C1}-\text{H1D}\cdots\text{Cl1}^{iii}$ | 0.99  | 2.69        | 3.448 (4)   | 133           |
| $\text{C1}-\text{H1E}\cdots\text{O2}^j$      | 0.99  | 2.51        | 2.928 (4)   | 105           |

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

We are grateful to Fundação para a Ciência e a Tecnologia (FCT, Portugal) for their general financial support and also for specific funding toward the purchase of the single-crystal diffractometer. SV wishes to acknowledge the Associated Laboratory CICECO for a research grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2539).

### References

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Shi, F.-N., Cunha-Silva, L., Sá Ferreira, R. A., Mafra, L., Trindade, T., Carlos, L. D., Paz, F. A. A. & Rocha, J. (2008). *J. Am. Chem. Soc.* **130**, 150–167.

**supplementary materials**

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## Glycine methyl ester hydrochloride

S. M. F. Vilela, F. A. Almeida Paz, J. P. C. Tomé, V. de Zea Bermudez, J. A. S. Cavaleiro and J. Rocha

### Comment

Following our interest in crystal engineering (Shi *et al.*, 2008; Paz & Klinowski, 2003; Paz *et al.*, 2002), we recently started to prepare novel organic ligands based on amino acid moieties, which can be ultimately employed as building units in the construction of multi-dimensional coordination polymers. Even though the latest release of the Cambridge Structural Database (CSD, Version of November 2008 with three updates; Allen, 2002) contains the remarkable number of 70 determinations of zwitterionic glycine, the structure of the title compound has never been reported to date. It is important to emphasize that crystallization of this compound is not trivial, typically leading to microcrystalline powders with needle-like crystal habit. Larger single crystals could only be obtained when a 1:1 chloroform:methanol mixture was used (Fig. 1).

The asymmetric unit of the title compound, (I), is composed of a cationic glycinium methyl ester moiety and a chloride anion as depicted in Fig. 2. In the crystal structure, the three crystallographically independent N—H moieties are engaged in strong and highly directional [ $\angle(\text{DHA})$  greater than  $140^\circ$ ]  $\text{N}^+—\text{H}\cdots\text{Cl}^-$  hydrogen bonds with three symmetry-related  $\text{Cl}^-$  anions (Fig. 3). These interactions promote the formation of a tape of  $\text{C}_3\text{H}_8\text{NO}_2^+\text{Cl}^-$  moieties running parallel to the *c* axis. It is noteworthy to emphasize that the  $\text{N}^+—\text{H}\cdots\text{Cl}^-$  interactions can be divided into two families according to the registered  $d_{\text{D}\cdots\text{A}}$  distances: while the two outer interactions of the tape have interatomic distances ranging from 3.112 (4) to 3.112 (4) Å, the inner hydrogen bond is weaker with the corresponding value being 3.269 (4) Å. Indeed, FT—IR studies on the title compound support this assumption clearly revealing the presence of two stretching bands centered at *ca* 2628 and 2682  $\text{cm}^{-1}$  and attributed to two  $\nu(\text{N}^+—\text{H})$  families, respectively.

Hydrogen-bonded supramolecular  $\text{C}_3\text{H}_8\text{NO}_2^+\text{Cl}^-$  chains close pack in the solid state mediated by a combination multi-point recognition synthons involving weak  $\text{C}—\text{H}\cdots\text{O}$  hydrogen bonds (not shown; Nangia & Desiraju, 1998) and the need to effectively fill the available space (*i.e.*, van der Waals interactions; Fig. 4). This packing behavior is strikingly distinct from that reported by Handelsman-Benory *et al.* (1995): while in (I) all H atoms bound to nitrogen are engaged in  $\text{N}^+—\text{H}\cdots\text{Cl}^-$  interactions, in glycyl-glycyl-glycine methyl ester hydrochloride the N—H and C=O moieties from the middle of the chain establish further hydrogen bonding connections with neighboring molecules; the final connectivity of the compounds results in a three-dimensional network of strong and highly directional hydrogen bonds.

### Experimental

Glycine methyl ester hydrochloride (99% purity) was purchased from Sigma-Aldrich and used without further purification. Crystalline material suitable for single-crystal studies (Fig. 1) was isolated from the slow evaporation (at ambient temperature) of a 1:1 chloroform:methanol solution.

## supplementary materials

Fourier-Transform Infrared (FT—IR) spectra were obtained as KBr (Aldrich 99%+, FT—IR grade) pellets using a Mattson 7000 instrument. Selected FT—IR bands (in  $\text{cm}^{-1}$ ): overtone  $\nu(\text{C}=\text{O}) = 3400br,m$ ;  $\nu(\text{N}^+—\text{H}) = 2682m$  and  $2628m$ ;  $\nu(\text{C}=\text{O}) = 1749vs$ ;  $\nu_{asym}(\text{C}—\text{O}—\text{C}) = 1259vs$ .

### Refinement

Hydrogen atoms bound to nitrogen and carbon were located at their idealized positions and were included in the final structural model in riding-motion approximation with  $\text{C}—\text{H} = 0.98 \text{ \AA}$  and  $\text{N}—\text{H} = 0.91 \text{ \AA}$ . The isotropic thermal displacement parameters for these atoms were fixed at 1.2 (for the  $—\text{CH}_2—$  group) or 1.5 (for the pendant  $—\text{NH}_3^+$  and  $—\text{CH}_3$  moieties) times  $U_{eq}$  of the atom to which they are attached.

### Figures

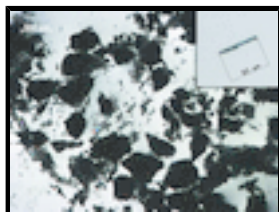


Fig. 1. Optical photographs of the (micro-)crystalline material composing the title compound. The inset shows the single-crystal used for data collection, emphasizing morphology (thin needle) and small crystal size. Optical photographs were taken on a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses and a digital high-resolution AxioCam MRc5 digital camera connected to a personal computer.

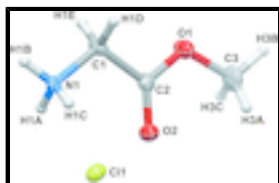


Fig. 2. Asymmetric unit of the title compound. Non-hydrogen atoms are represented as thermal displacement ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radii. The atomic labeling is provided for all atoms. Bond lengths and angles are provided in the following Tables.

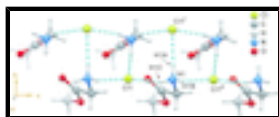


Fig. 3. Schematic representation of the  $\text{N}^+—\text{H}\cdots\text{Cl}^-$  hydrogen bonding interactions which lead to the formation of a one-dimensional supramolecular tape running parallel to the  $c$  axis. For details on the hydrogen bonding geometry see Table 1. Symmetry transformations used to generate equivalent atoms: (i)  $x, -y + 1/2, z + 1/2$ ; (ii)  $x, y, z + 1$ .

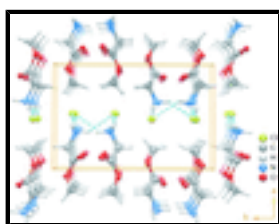


Fig. 4. Perspective view along the  $[001]$  direction of the crystal packing of the title compound.  $\text{N}^+—\text{H}\cdots\text{Cl}^-$  hydrogen bonds are represented as light-blue dashed lines.

### (methoxycarbonylmethyl)ammonium chloride

#### Crystal data

$\text{C}_3\text{H}_8\text{NO}_2^+\cdot\text{Cl}^-$

$M_r = 125.55$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 8.352(2) \text{ \AA}$

$F_{000} = 264$

$D_x = 1.437 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 793 reflections

$\theta = 3.0\text{--}24.8^\circ$

$b = 12.505 (3) \text{ \AA}$   
 $c = 5.6369 (14) \text{ \AA}$   
 $\beta = 99.730 (9)^\circ$   
 $V = 580.3 (2) \text{ \AA}^3$   
 $Z = 4$

$\mu = 0.55 \text{ mm}^{-1}$   
 $T = 150 \text{ K}$   
 Needle, colourless  
 $0.08 \times 0.02 \times 0.02 \text{ mm}$

### Data collection

Bruker X8 Kappa CCD APEXII diffractometer  
 Radiation source: fine-focus sealed tube  
 Monochromator: graphite  
 $T = 150 \text{ K}$   
 $\varphi$  scans  
 Absorption correction: Multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.957, T_{\max} = 0.989$   
 5189 measured reflections

1539 independent reflections  
 923 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.070$   
 $\theta_{\max} = 29.1^\circ$   
 $\theta_{\min} = 4.0^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -17 \rightarrow 16$   
 $l = -7 \rightarrow 7$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.069$   
 $wR(F^2) = 0.184$   
 $S = 1.08$   
 1539 reflections  
 66 parameters  
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 1.246P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.05 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.55 \text{ e \AA}^{-3}$   
 Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

| $x$ | $y$ | $z$ | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-----|-----|----------------------------------|
|-----|-----|-----|----------------------------------|

## supplementary materials

|     |              |             |              |             |
|-----|--------------|-------------|--------------|-------------|
| Cl1 | 0.47434 (13) | 0.11638 (8) | 0.24634 (19) | 0.0210 (3)  |
| C1  | 0.7947 (5)   | 0.0942 (3)  | 0.8596 (8)   | 0.0200 (10) |
| H1D | 0.7834       | 0.0155      | 0.8502       | 0.024*      |
| H1E | 0.8397       | 0.1135      | 1.0280       | 0.024*      |
| C2  | 0.9087 (5)   | 0.1308 (3)  | 0.6967 (8)   | 0.0190 (9)  |
| C3  | 1.1805 (6)   | 0.1209 (5)  | 0.6290 (10)  | 0.0348 (12) |
| H3A | 1.1348       | 0.1161      | 0.4573       | 0.052*      |
| H3B | 1.2733       | 0.0723      | 0.6660       | 0.052*      |
| H3C | 1.2163       | 0.1944      | 0.6682       | 0.052*      |
| N1  | 0.6341 (4)   | 0.1443 (3)  | 0.7897 (6)   | 0.0178 (8)  |
| H1A | 0.6452       | 0.2167      | 0.7915       | 0.027*      |
| H1B | 0.5683       | 0.1246      | 0.8954       | 0.027*      |
| H1C | 0.5895       | 0.1225      | 0.6390       | 0.027*      |
| O1  | 1.0566 (4)   | 0.0911 (3)  | 0.7714 (6)   | 0.0295 (8)  |
| O2  | 0.8701 (4)   | 0.1866 (3)  | 0.5246 (6)   | 0.0251 (8)  |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| Cl1 | 0.0258 (6)  | 0.0195 (5)  | 0.0182 (6)  | -0.0065 (5)  | 0.0049 (4)  | -0.0014 (5)  |
| C1  | 0.016 (2)   | 0.014 (2)   | 0.030 (3)   | -0.0018 (17) | 0.0031 (17) | 0.0025 (17)  |
| C2  | 0.021 (2)   | 0.0111 (19) | 0.026 (3)   | -0.0028 (16) | 0.0058 (17) | -0.0028 (18) |
| C3  | 0.020 (2)   | 0.040 (3)   | 0.047 (3)   | 0.000 (2)    | 0.013 (2)   | 0.003 (3)    |
| N1  | 0.0204 (19) | 0.0166 (18) | 0.017 (2)   | 0.0018 (14)  | 0.0050 (14) | -0.0001 (14) |
| O1  | 0.0223 (18) | 0.0313 (18) | 0.036 (2)   | 0.0042 (15)  | 0.0086 (14) | 0.0102 (16)  |
| O2  | 0.0268 (18) | 0.0239 (17) | 0.0253 (19) | 0.0024 (14)  | 0.0065 (14) | 0.0065 (14)  |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| C1—N1       | 1.472 (5) | C3—H3A      | 0.9800    |
| C1—C2       | 1.502 (6) | C3—H3B      | 0.9800    |
| C1—H1D      | 0.9900    | C3—H3C      | 0.9800    |
| C1—H1E      | 0.9900    | N1—H1A      | 0.9100    |
| C2—O2       | 1.194 (5) | N1—H1B      | 0.9100    |
| C2—O1       | 1.332 (5) | N1—H1C      | 0.9100    |
| C3—O1       | 1.461 (5) |             |           |
| N1—C1—C2    | 110.5 (4) | H3A—C3—H3B  | 109.5     |
| N1—C1—H1D   | 109.6     | O1—C3—H3C   | 109.5     |
| C2—C1—H1D   | 109.6     | H3A—C3—H3C  | 109.5     |
| N1—C1—H1E   | 109.6     | H3B—C3—H3C  | 109.5     |
| C2—C1—H1E   | 109.6     | C1—N1—H1A   | 109.5     |
| H1D—C1—H1E  | 108.1     | C1—N1—H1B   | 109.5     |
| O2—C2—O1    | 125.7 (4) | H1A—N1—H1B  | 109.5     |
| O2—C2—C1    | 124.2 (4) | C1—N1—H1C   | 109.5     |
| O1—C2—C1    | 110.1 (4) | H1A—N1—H1C  | 109.5     |
| O1—C3—H3A   | 109.5     | H1B—N1—H1C  | 109.5     |
| O1—C3—H3B   | 109.5     | C2—O1—C3    | 115.9 (4) |
| N1—C1—C2—O2 | -5.0 (6)  | O2—C2—O1—C3 | 0.9 (7)   |

N1—C1—C2—O1                      175.7 (3)                      C1—C2—O1—C3                      -179.7 (4)

*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—H1A $\cdots$ C11 <sup>i</sup>   | 0.91        | 2.52                | 3.269 (4)                  | 140                           |
| N1—H1B $\cdots$ C11 <sup>ii</sup>  | 0.91        | 2.25                | 3.112 (4)                  | 158                           |
| N1—H1C $\cdots$ C11                | 0.91        | 2.26                | 3.147 (4)                  | 165                           |
| C1—H1D $\cdots$ C11 <sup>iii</sup> | 0.99        | 2.69                | 3.448 (4)                  | 133                           |
| C1—H1E $\cdots$ O2 <sup>i</sup>    | 0.99        | 2.51                | 2.928 (4)                  | 105                           |

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

Fig. 1

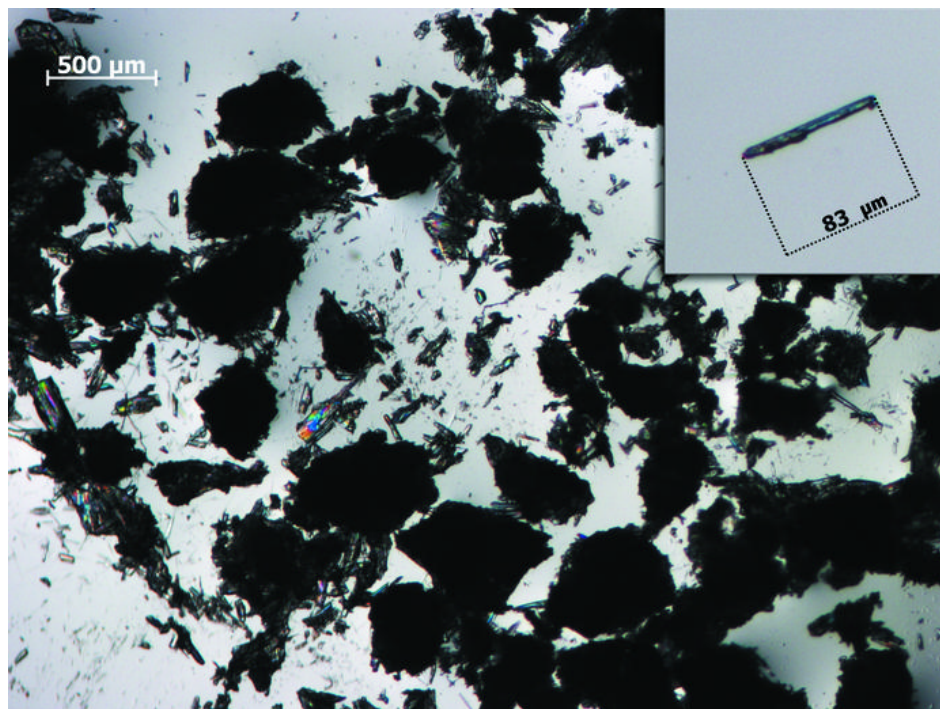




Fig. 2

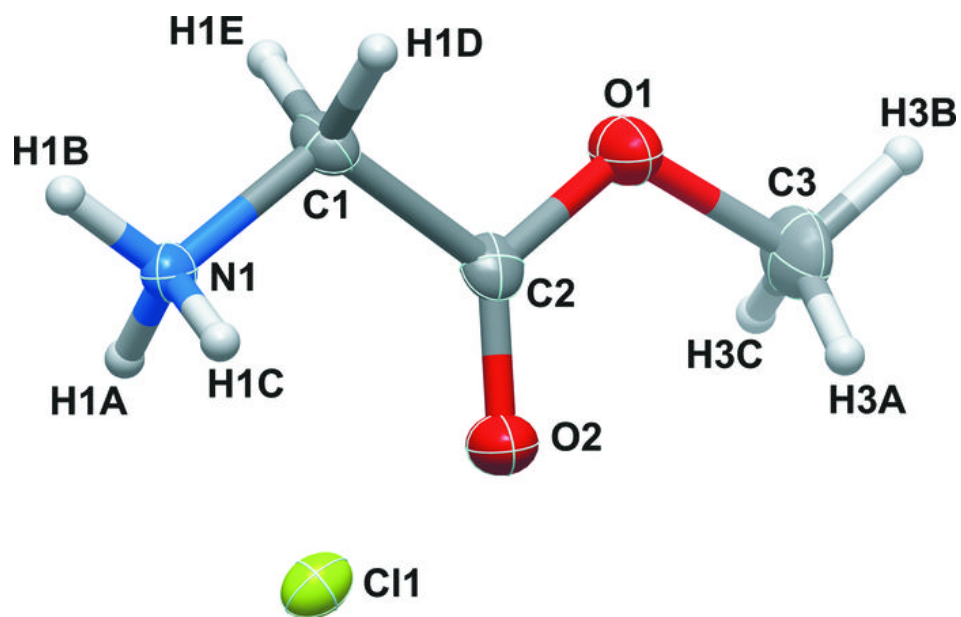


Fig. 3

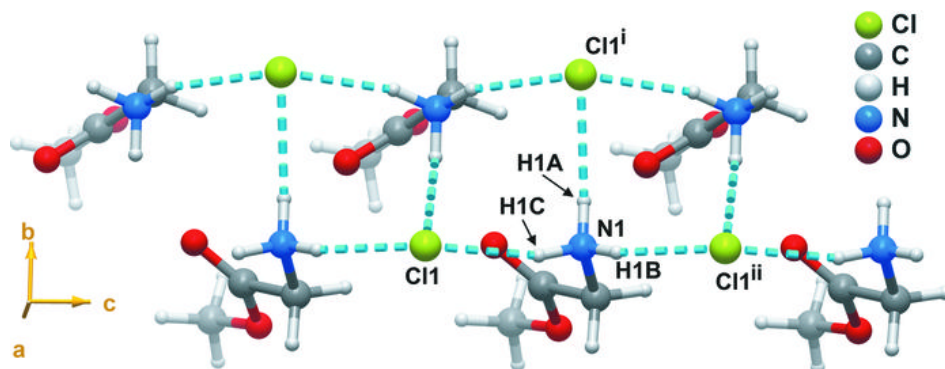


Fig. 4

