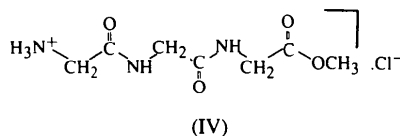


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MeGly<sub>3</sub> forms an infinite puckered sheet of hydrogen-bonded molecules related by a screw axis. Each molecule is held in the crystal structure by four hydrogen bonds involving NH<sub>3</sub><sup>+</sup>, NH and two CO groups.

### Comment

During a study of solid-state reactions of polypeptide esters, diglycyl-glycine methyl ester hydrochloride (MeGly<sub>3</sub>), (IV), was prepared according to the procedures of Sluyterman & Kooistra (1952) and Sluyterman & Veenedaal (1952). Its crystal structure was determined by single-crystal X-ray diffraction.



Diglycyl-glycine has seven rotational degrees of freedom (apart from C—NH<sub>3</sub> rotation); however, its conformation is determined mainly by strong intramolecular interactions such as the conjugation between the lone-pair electrons of an N atom and a neighbouring carbonyl group. This strong interaction favors a planar N—C(C)=O moiety and the number of free rotations is reduced to five. The molecule has several donors and acceptors of hydrogen bonds and the conformation of the molecule in the solid state is, therefore, also determined by intermolecular hydrogen bonds. A few crystal structures of compounds containing the diglycyl-glycine skeleton are known. Only three do not include metal cations (in the latter compounds the conformation is strongly influenced by interactions with the cation). The conformation and the hydrogen-bonding patterns have been compared for glycyl-glycyl-glycine hydrochloride, (I) (Lalitha & Subramanian, 1982), sarcosyl-glycyl-glycine, (II) (Glusker, Carrel, Berman, Gallen & Peck, 1977), glycyl-glycyl-glycine, (III) (Srikrishnan, Winiewicz & Parthasarathy, 1982), and the methyl ester of (I), the subject of the present study, (IV).

The expected most stable conformation is the same as found for alkanes, namely all-*trans*. Some torsion angles in compounds (I)–(IV) are compared in Table 3. Most of the torsion angles indicate the all-*trans* conformation found in alkanes. There are four exceptions that should be noted. In these cases, atoms are involved that are not constrained by the intramolecular interaction mentioned above (the resulting torsion angles are marked by a † in Table 3).

Each of the four compounds, (I)–(IV), includes three identical hydrogen-acceptor groups (C=O), two identical hydrogen-donor groups (NH) and a third which is either NH<sub>3</sub><sup>+</sup> or CH<sub>3</sub>NH<sub>2</sub><sup>+</sup>. The conformation of the molecule in the crystal and the possibility of hydrogen-bond

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## Hydrogen Bonding in Glycyl-glycyl-glycine Methyl Ester Hydrochloride

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### Abstract

The structure of the title compound, C<sub>7</sub>H<sub>14</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup>.Cl<sup>−</sup> (MeGly<sub>3</sub>), is described and compared to those of other compounds having the diglycyl-glycine moiety. Although the molecular structure of MeGly<sub>3</sub> is similar to that of the parent acid, its crystal structure is different.

formation are closely related, and play the dominant role in determining the packing and the symmetry relationships between the molecules. There are several possible hydrogen-bonding patterns; one of these will be mentioned because it could provide four hydrogen bonds between two molecules. When two molecules are related by an inversion center, the formation of four hydrogen bonds can be anticipated. However, if the two molecules adopt the all-*trans* conformation and are coplanar, then the two central methylene groups will be too close. Therefore, such a pattern is not formed. Dimers are formed in three cases, either through a crystallographic inversion center or through a pseudo-inversion center, with the formation of only two strong hydrogen bonds between the end groups [ $\text{H}_3\text{N}^+\cdots\text{O}=\text{C}$  in (I) and  $\text{RH}_2\text{N}^+\cdots\text{O}=\text{C}$  in (II)]. In two cases, (I) and (II), the molecules undergo conformational changes from all-*trans* by rotation about bonds that are not restricted by the conjugation mentioned above. The result is the formation of dimers packed face-to-face. In compound (I), each molecule forms a second dimer (through an inversion center) through hydrogen bonds between the central  $\text{NH}\cdots\text{O}=\text{C}$  groups, so that all hydrogen donors and hydrogen acceptors are involved in hydrogen bonding. In one case, (III), there are two crystallographically independent molecules, both adopting the all-*trans* conformation, which, therefore, cannot form dimers related by an inversion center. Instead, the two independent molecules form dimers related by a pseudo-inversion center [ $\text{H}_3\text{N}^+\cdots\text{O}=\text{C}$  2.925 (6) and 2.939 (6) Å]. In the crystal structure of MeGly<sub>3</sub>, (IV), the molecules form an infinite puckered sheet of hydrogen-bonded molecules related

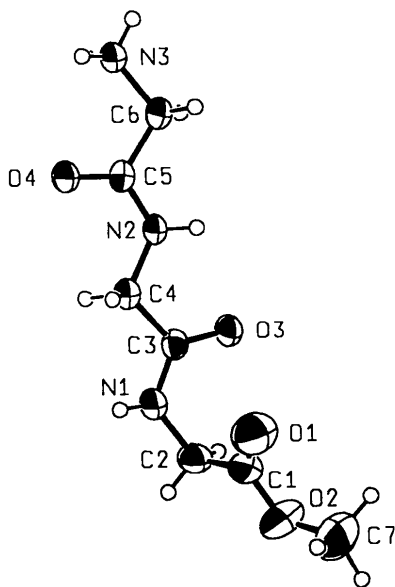


Fig. 1. View of compound (IV) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

by a screw axis. The hydrogen bonds are  $\text{H}_3\text{N}^+\cdots\text{O}=\text{C}$  [2.883 (4) Å] and  $\text{HN}\cdots\text{O}=\text{C}$  [2.973 (4) Å] and are shown in Fig. 2.

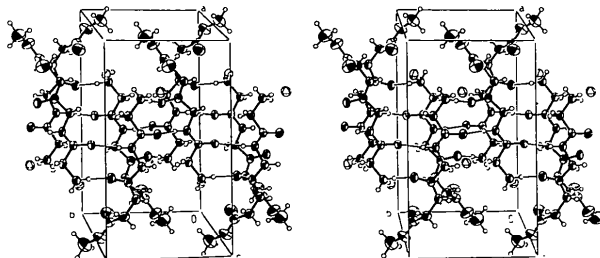


Fig. 2. Stereoscopic view of the crystal packing with the hydrogen-bonding interactions indicated.

## Experimental

Diglycyl-glycine methyl ester hydrochloride was prepared by allowing a solution of 4 mmol of triglycine, 60 ml of 2,2-dimethoxypropane and 4 ml of 32% HCl to stand for 20 h. Colorless elongated crystals were obtained by crystallization from an ether-ethanol solution.

### Crystal data

$\text{C}_7\text{H}_{14}\text{N}_3\text{O}_4\cdot\text{Cl}^-$   
 $M_r = 239.66$   
 Monoclinic  
 $P2_1/c$   
 $a = 15.011 (8) \text{ \AA}$   
 $b = 8.862 (4) \text{ \AA}$   
 $c = 9.068 (4) \text{ \AA}$   
 $\beta = 107.50 (2)^\circ$   
 $V = 1150.5 (4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.384 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 2.8\text{--}12.8^\circ$   
 $\mu = 0.332 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Plate  
 $0.3 \times 0.3 \times 0.1 \text{ mm}$   
 Colorless

### Data collection

Philips PW1100 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1925 measured reflections  
 1806 independent reflections  
 1421 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0488$   
 $\theta_{\text{max}} = 23.99^\circ$   
 $h = -17 \rightarrow 16$   
 $k = 0 \rightarrow 10$   
 $l = 0 \rightarrow 10$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.0484$   
 $wR(F^2) = 0.1541$   
 $S = 1.045$   
 1806 reflections  
 192 parameters  
 H atoms refined isotropically  
 $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.745$   
 $\Delta\rho_{\text{max}} = 0.223 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.202 \text{ e \AA}^{-3}$   
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
Cl1	0.2157 (1)	0.0875 (1)	0.3753 (1)	0.052 (1)
O1	0.8448 (2)	0.4361 (4)	0.7673 (4)	0.084 (1)
O2	0.9236 (2)	0.5259 (4)	0.6148 (5)	0.095 (1)
O3	0.6372 (2)	0.4483 (2)	0.5403 (3)	0.047 (1)
O4	0.4635 (2)	0.0496 (2)	0.6888 (3)	0.050 (1)
N1	0.7355 (2)	0.2605 (3)	0.5288 (4)	0.050 (1)
N2	0.5189 (2)	0.2664 (3)	0.6281 (4)	0.049 (1)
N3	0.3067 (2)	0.1741 (3)	0.7209 (4)	0.043 (1)
C1	0.8598 (2)	0.4416 (4)	0.6448 (5)	0.056 (1)
C2	0.8068 (3)	0.3573 (5)	0.5041 (5)	0.056 (1)
C3	0.6598 (2)	0.3144 (3)	0.5558 (3)	0.038 (1)
C4	0.6007 (2)	0.1986 (3)	0.6029 (4)	0.044 (1)
C5	0.4588 (2)	0.1866 (3)	0.6752 (3)	0.035 (1)
C6	0.3823 (2)	0.2757 (3)	0.7105 (4)	0.042 (1)
C7	0.9801 (4)	0.6212 (10)	0.7402 (14)	0.138 (3)

Table 2. Selected geometric parameters (Å, °)

O1—C1	1.199 (5)	N2—C5	1.315 (4)
O2—C1	1.305 (4)	N2—C4	1.445 (4)
O2—C7	1.465 (9)	N3—C6	1.473 (4)
O3—C3	1.231 (3)	C1—C2	1.487 (6)
O4—C5	1.220 (3)	C3—C4	1.500 (4)
N1—C3	1.322 (4)	C5—C6	1.506 (4)
N1—C2	1.441 (4)		
C1—O2—C7	117.2 (5)	O3—C3—C4	121.7 (3)
C3—N1—C2	122.2 (3)	N1—C3—C4	114.9 (3)
C5—N2—C4	121.7 (3)	N2—C4—C3	111.3 (3)
O1—C1—O2	124.8 (4)	O4—C5—N2	123.0 (3)
O1—C1—C2	125.0 (3)	O4—C5—C6	121.6 (3)
O2—C1—C2	110.2 (4)	N2—C5—C6	115.4 (2)
N1—C2—C1	113.4 (3)	N3—C6—C5	110.2 (2)
O3—C3—N1	123.4 (3)		

Table 3. Comparison of torsion angles (°) in compounds (I)–(IV)

	(I)	(II)	(IIIa)	(IIIb)	(IV)
N3—C6—C5—N2	164.8	158.5	-149.9	-161.8	164.9 (3)
C6—C5—N2—C4	172.1	-178.2	-176.7	176.1	174.5 (3)
C5—N2—C4—C3	-153.3	-72.1†	177.6	-165.9	-177.7 (3)
N2—C4—C3—N1	159.7	163.7	-171.5	174.5	-179.2 (3)
C4—C3—N1—C2	-178.5	-176.2	-178.5	-176.1	-170.9 (3)
C3—N1—C2—C1	-80.1†	85.5†	172.8	172.8	68.5(5)†
N1—C2—C1—O1	172.7	177.5	-172.6	-168.8	177.7 (6)

† The atoms involved in these angles are not constrained by intermolecular interactions.

The metric symmetry of the title compound is orthorhombic but the diffraction symmetry and systematic extinctions are compatible only with monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c*.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1258). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## An Indanyl Precursor to a Chiral Spiro Compound

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## Abstract

The dimer of  $\alpha$ -indanylcabene obtained after UV irradiation of the lithium salt of the tosylhydrazone of 1-indanone in benzene is *trans*- $\alpha,\alpha'$ -dehydrobiindanyl, (C<sub>9</sub>H<sub>8</sub>)<sub>2</sub>. The asymmetric unit is planar within  $\pm 0.02$  Å; the two halves are related by a center of symmetry and joined by a double bond.

## Comment

In an attempt to prepare a spiro compound with a chiral spiro atom resulting from enantioselective migration during pinacol rearrangement, we sought to make a *vic*-glycol as a precursor. If the *vic*-glycol is locked into the proper conformation by hydrogen bonding, the enantioselective migration might be facilitated. Thus, from alkene to epoxide to *vic*-glycol seemed a likely route. The alkene chosen for the mock-up study was *trans*- $\alpha,\alpha'$ -dehydrobiindanyl, (I).

