

The Structures of LL- and *meso*-Diaminopimelic Acid Hydrochlorides

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The structures of the hydrochlorides of the LL and *meso* isomers of diaminopimelic acid were determined by direct methods. The cell constants are: LL-DAP: $a = 11.252$ (2), $b = 5.088$ (1), $c = 18.047$ (3) Å, $\beta = 94.22$ (1)°; *meso*-DAP: $a = 11.024$ (3), $b = 5.108$ (1), $c = 18.320$ (3) Å, $\beta = 97.11$ (2)°. The structures were refined to $R = 0.0295$ (LL) and 0.0391 (*meso*). The positions of all H atoms were determined. The results are compared with those of related amino acids.

Introduction

The isomers of 2,6-diaminopimelic acid, subsequently referred to as DAP (Work, 1950), are unique to the polymeric peptidoglycans present in walls of all bacteria except *Halobacteria*. These polymers are the structural components in bacterial cell walls which are strong enough to resist forces resulting from internal cellular osmotic pressure up to 20 atm. The peptidoglycans consist of long carbohydrate strands with repeating residues of the disaccharide, 1-4 β N-acetylglucosaminyl-*N*-acetylmuramic acid, linked together by short peptides. Any given peptidoglycan contains no more than four or five different amino acid residues, which alternate in optical enantiomorphism, unless glycine is involved. In every known example the terminal D-alanyl carboxyl group of the peptide attached to one glycan chain is bonded to the amino group of a diamino acid of a peptide attached to a contiguous chain. This diamino acid is most frequently DAP (in all Gram-negative bacteria for example) or L-lysine and much less frequently a variety of other amino acids (Schleifer & Kandler, 1972; Rogers, 1974). When DAP is involved it is commonly the *meso* isomer, but the LL and DD isomers may occur in some bacterial species.

Little is known about the conformation of peptidoglycans, but various hypothetical models have been proposed (Kelemen & Rogers, 1971; Oldmixon, Glauser & Higgins, 1974; Braun, Gnirke, Henning & Rehn, 1973; Formanek, Formanek & Wawra, 1974). Many of these models involve intermolecular association between the glycan chains, as in the

polymer of *N*-acetylglucosamine, chitin (Carlström, 1953). Some evidence in favour of this assumption has been obtained from an X-ray diffraction study of bacterial walls (Formanek *et al.*, 1974).

X-ray data are available for all the common amino acid residues of peptidoglycans except DAP. Since DAP acts as a cross-link, with both amino groups attached to the peptide, the conformation of the main chain is influenced by the conformational constraints on DAP. With an accurate knowledge of the molecular geometry it is possible to carry out conformational energy calculations and thus establish the most likely models for the cross-linkage. The present analysis was undertaken with this aim in view.

Experimental

The hydrochlorides of the two isomers of DAP were prepared by the method of Work (1950) and crystallized as colourless needles by evaporation from water–acetone solution at about pH 4. Crystal data and details of the data collection on a Syntex P2₁ four-circle diffractometer are given in Table 1. Cell constants were determined by least squares from 15 automatically centred reflexions. The intensities were corrected for absorption.

Structure determination and refinement

Both structures were solved by direct methods: LL-DAP with *SHELX* 76 (Sheldrick, 1976) and *meso*-DAP with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The Cambridge University IBM 370/165 computer was used for all calculations.

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Table 1. *Crystal data and intensity measurement*

	LL-DAP	meso-DAP
Formula	C ₇ H ₁₄ N ₂ O ₄ ·HCl	C ₇ H ₁₄ N ₂ O ₄ ·HCl
<i>M_r</i>	226.5	226.5
System	Monoclinic	Monoclinic
Space group	<i>I</i> 2	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i>	11.252 (2) Å	11.024 (3) Å
<i>b</i>	5.088 (1)	5.108 (1)
<i>c</i>	18.047 (3)	18.320 (3)
β	94.22 (1)°	97.11 (2)°
<i>U</i>	1030 Å ³	1024 Å ³
<i>D_c</i>	1.46 g cm ⁻³ (<i>Z</i> = 4)	1.47 g cm ⁻³ (<i>Z</i> = 4)
<i>F</i> (000)	476	476
μ (Cu <i>K</i> α)	31.3 cm ⁻¹	31.5 cm ⁻¹
Crystal size	0.43 × 0.20 × 0.06 mm	0.22 × 0.08 × 0.03 mm
Radiation	Graphite-monochromated Cu <i>K</i> α	
Scan method	2 θ / ω	
Scan range	2° plus calculated α_1/α_2 separation	
Scan rate	Between 1° and 29° min ⁻¹	
2 θ _{max}	118°	111°
Number of unique reflexions	854	1312

The structures were refined by *SHELX 76* (Sheldrick, 1976). Positional parameters were refined for all atoms including H, and the heavy atoms were allowed anisotropic temperature factors. A single isotropic temperature factor was refined for the H atoms of each structure. In both refinements all the measured data* were used, the function minimized being $\sum w|F_o - k|F_c||^2$, where $w = [\sigma^2(F_o) + 0.001F_o^2]$. For LL-DAP, $R = 0.0295$, $R_w = 0.0321$; and for meso-DAP, $R = 0.0391$, $R_w = 0.0389$, where $R = \sum |F_o - k|F_c|/\sum |F_o|$ and $R_w = \sum w^{1/2}|F_o - k|F_c|/\sum w^{1/2}|F_o|$. The final atomic parameters are listed in Table 2 (for LL-DAP) and Table 3 (for meso-DAP).

Discussion

Molecular geometry

The numbering schemes are shown in Figs. 1 and 2, and the bond lengths and angles in Tables 4 and 5. In both structures the amino groups are protonated, as is one of the carboxylic acid groups. Equivalent bond lengths between heavy atoms in the two isomers are equal within experimental error, the largest discrepancy being about twice the estimated standard deviation. Some of the discrepancies between the bond angles in the two isomers are significant and appear to be a consequence of the slightly different hydrogen-bonding schemes. The mean bond lengths in the two structures are: C—C 1.527 (LL-DAP) and 1.521 Å (meso-DAP),

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32802 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atom coordinates (× 10⁴) for LL-DAP*

	For H atoms $U = 36 (2) \times 10^{-3} \text{ \AA}^2$.		
	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	4199 (1)	4371 (1)	8307 (1)
O(1)	2525 (2)	-4611 (5)	11903 (1)
O(2)	1198 (2)	-2705 (7)	11100 (1)
O(3)	1079 (2)	4082 (6)	8113 (1)
O(4)	5 (2)	3298 (7)	9079 (2)
N(1)	2303 (2)	-396 (7)	8282 (1)
H(311)	2854 (36)	923 (111)	8244 (21)
H(312)	2808 (37)	-1798 (110)	8325 (22)
H(313)	1920 (30)	-511 (105)	7866 (21)
N(2)	3943 (2)	-454 (8)	11953 (1)
H(321)	4385 (36)	1637 (109)	11987 (22)
H(322)	3587 (30)	-263 (111)	12380 (19)
H(323)	4353 (36)	1068 (110)	11928 (21)
C(1)	2196 (3)	-2865 (7)	11460 (2)
C(2)	3044 (2)	-655 (7)	11306 (1)
H(121)	2602 (30)	1033 (103)	11333 (18)
C(3)	3708 (3)	-1190 (7)	10607 (2)
H(131)	4211 (32)	454 (97)	10632 (19)
H(132)	4171 (33)	-3050 (89)	10684 (19)
C(4)	2926 (3)	-1672 (8)	9893 (2)
H(141)	2285 (29)	-3187 (92)	10026 (20)
H(142)	3453 (28)	-2106 (90)	9483 (18)
C(5)	2228 (3)	754 (7)	9625 (2)
H(151)	1664 (29)	1160 (92)	10018 (18)
H(152)	2801 (31)	2218 (94)	9528 (19)
C(6)	1506 (3)	303 (7)	8877 (2)
H(161)	983 (33)	1173 (91)	8831 (19)
C(7)	828 (3)	2790 (8)	8645 (2)
H(441)	578 (31)	4066 (101)	8981 (19)

Table 3. *Atom coordinates (× 10⁴) for meso-DAP*

	For H atoms $U = 48 (2) \times 10^{-3} \text{ \AA}^2$.		
	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	4224 (1)	5549 (1)	8288 (1)
O(1)	2571 (2)	4646 (3)	11905 (1)
O(2)	1241 (2)	3258 (4)	10969 (1)
O(3)	1031 (2)	3836 (4)	8211 (1)
O(4)	28 (2)	2693 (4)	9120 (1)
N(1)	2332 (2)	526 (5)	8291 (1)
H(311)	1915 (28)	510 (58)	7842 (19)
H(312)	2742 (27)	1947 (67)	8387 (15)
H(313)	2866 (28)	866 (63)	8319 (15)
N(2)	3869 (2)	-312 (5)	11963 (1)
H(321)	4375 (29)	1622 (67)	12012 (15)
H(322)	3454 (27)	254 (60)	12385 (17)
H(323)	4340 (29)	1098 (64)	11934 (15)
C(1)	2214 (2)	3083 (5)	11407 (1)
C(2)	2975 (2)	674 (5)	11293 (1)
H(121)	2456 (27)	757 (61)	11244 (15)
C(3)	3683 (3)	864 (61)	10627 (1)
H(131)	4293 (28)	2303 (63)	10753 (14)
H(132)	4031 (27)	802 (63)	10582 (15)
C(4)	2932 (3)	1431 (6)	9887 (1)
H(141)	2480 (26)	3036 (64)	9920 (15)
H(142)	3456 (27)	1758 (60)	9526 (16)
C(5)	2019 (3)	675 (5)	9612 (1)
H(151)	1420 (27)	722 (58)	9937 (15)
H(152)	2471 (25)	2386 (62)	9673 (14)
C(6)	1425 (2)	273 (5)	8823 (1)
H(161)	865 (27)	1558 (60)	8710 (15)
C(7)	783 (2)	2332 (5)	8686 (1)
H(441)	497 (28)	4069 (64)	9071 (16)

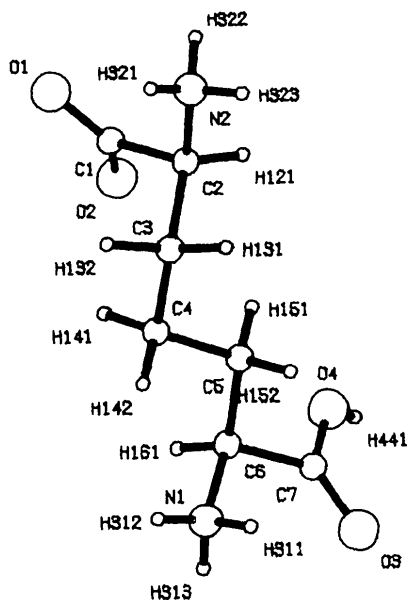
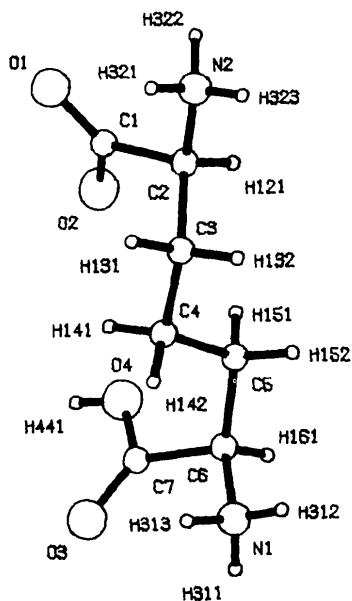


Fig. 1. Molecular structure and numbering scheme for LL-DAP.

Fig. 2. Molecular structure and numbering scheme for *meso*-DAP.

C—N 1.492 and 1.488 Å, C—H 1.02 and 0.96 Å, and N—H 0.88 and 0.90 Å. The average length of the C—C bonds at the ends of the molecules is 1.516 Å, close to the accepted value for C(sp^3)—C(sp^2) bonds (1.509 ± 0.003 Å) (Bartell & Bonham, 1960). The average length of the remaining C—C bonds is 1.528 Å, close to the usual value for C(sp^3)—C(sp^3) bonds (1.533 ± 0.003 Å) (Bartell, 1959). The average length of the bonds involving C(4) is slightly less (1.522 Å) than that

Table 4. Bond lengths (Å) with standard deviations in parentheses

		LL DAP	<i>meso</i> DAP
C(1)	O(1)	1.235 (5)	1.239 (4)
C(1)	O(2)	1.257 (5)	1.261 (4)
C(7)	O(3)	1.215 (5)	1.217 (4)
C(7)	O(4)	1.282 (5)	1.282 (4)
C(2)	N(2)	1.491 (4)	1.489 (4)
C(6)	N(1)	1.492 (5)	1.487 (4)
C(1)	C(2)	1.514 (6)	1.518 (5)
C(2)	C(3)	1.538 (6)	1.531 (6)
C(3)	C(4)	1.525 (6)	1.526 (6)
C(4)	C(5)	1.523 (7)	1.515 (6)
C(5)	C(6)	1.541 (6)	1.525 (6)
C(6)	C(7)	1.520 (7)	1.513 (6)
N(1)	H(311)	0.92 (5)	0.89 (4)
N(1)	H(312)	0.91 (5)	0.86 (3)
N(1)	H(313)	0.84 (4)	0.92 (3)
N(2)	H(321)	0.78 (5)	0.87 (4)
N(2)	H(322)	0.90 (4)	0.95 (3)
N(2)	H(323)	0.90 (5)	0.89 (3)
O(4)	H(441)	0.77 (4)	0.87 (3)
C(2)	H(121)	1.00 (5)	0.93 (3)
C(3)	H(131)	1.01 (5)	1.00 (3)
C(3)	H(132)	1.08 (4)	0.94 (3)
C(4)	H(141)	1.10 (4)	0.96 (3)
C(4)	H(142)	1.00 (3)	0.94 (3)
C(5)	H(151)	1.01 (4)	0.94 (3)
C(5)	H(152)	1.01 (4)	1.00 (3)
C(6)	H(161)	0.95 (4)	0.91 (3)

of the neighbouring bonds (1.534 Å). The C—O bonds are influenced by hydrogen bonding and are discussed below.

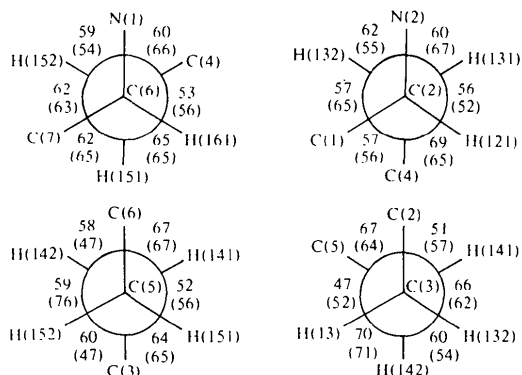
The major conformational difference between the two isomers is best illustrated by Figs. 1 and 2, which show that the molecular backbones are very similar except in the region of C(6); in the two isomers this atom can be considered to have opposite chirality and it is not surprising that it is closely associated with the conformational differences between the molecules. The close correspondence in the backbone conformation from C(1) to C(6) is confirmed by the torsion angles (Table 6, Fig. 3). The maximum difference in torsion angles is 5°. In neither compound is the carbon backbone fully extended, in contrast to L-lysine hydrochloride dihydrate (Wright & Marsh, 1962) which has all the C atoms and the terminal N atom in the same plane, yet differs chemically from the molecules reported here only by the absence of one of the carboxylic acid groups. DL-Lysine hydrochloride (Bhaduri & Saha, 1974) also has a planar carbon chain. In LL-DAP the carbon chain is only extended about C(5)—C(6) and C(4)—C(5), and in *meso*-DAP only C(4)—C(5) has a staggered conformation; all the other bonds in the carbon chain have *gauche* conformations, illustrated in the Newman projections in Fig. 3. These conformational differences from L-lysine can be attributed to the constraints placed on the molecules by the more complex hydrogen bonding, involving a larger number of polar atoms.

Table 5. Bond angles ($^{\circ}$) with standard deviations in parentheses

	LL-DAP	meso-DAP
O(1) C(1) O(2)	126.6 (4)	126.2 (3)
O(1) C(1) C(2)	119.4 (3)	119.6 (3)
O(2) C(1) C(2)	114.1 (4)	114.2 (3)
C(1) C(2) N(2)	108.0 (3)	107.9 (3)
N(2) C(2) C(3)	108.2 (3)	108.3 (3)
C(1) C(2) C(3)	111.7 (4)	113.8 (3)
C(2) C(3) C(4)	115.9 (3)	116.5 (3)
C(3) C(4) C(5)	113.0 (4)	115.2 (3)
C(4) C(5) C(6)	112.6 (4)	114.1 (3)
C(5) C(6) C(7)	109.8 (4)	114.4 (3)
C(5) C(6) N(1)	111.1 (3)	111.4 (3)
C(7) C(6) N(1)	108.5 (3)	107.8 (3)
C(6) C(7) O(3)	121.8 (4)	122.2 (3)
C(6) C(7) O(4)	111.7 (4)	111.7 (3)
O(3) C(7) O(4)	126.5 (4)	126.1 (3)
H(313) N(1) H(311)	107 (4)	107 (4)
H(312) N(1) H(311)	99 (3)	113 (3)
H(313) N(1) H(312)	107 (4)	109 (3)
C(6) N(1) H(311)	109 (3)	107 (2)
C(6) N(1) H(312)	122 (3)	108 (2)
C(6) N(1) H(313)	111 (2)	112 (2)
H(323) N(2) H(321)	110 (4)	105 (3)
H(322) N(2) H(321)	110 (4)	108 (2)
H(323) N(2) H(322)	102 (4)	112 (3)
C(2) N(2) H(321)	114 (3)	110 (2)
C(2) N(2) H(322)	111 (2)	110 (2)
C(2) N(2) H(323)	110 (2)	112 (2)
H(121) C(2) C(1)	108 (2)	108 (2)
C(3) C(2) H(121)	118 (2)	110 (2)
H(121) C(2) N(2)	102 (3)	109 (2)
H(132) C(3) C(2)	108 (2)	105 (2)
H(132) C(3) H(131)	117 (3)	114 (2)
C(2) C(3) H(131)	97 (2)	105 (2)
C(4) C(3) H(131)	117 (2)	110 (2)
C(4) C(3) H(132)	102 (2)	106 (2)
H(141) C(4) C(3)	106 (2)	109 (2)
H(142) C(4) C(3)	109 (2)	110 (2)
H(142) C(4) H(141)	116 (3)	105 (2)
C(5) C(4) H(141)	108 (2)	107 (2)
C(5) C(4) H(142)	105 (2)	109 (2)
H(151) C(5) C(4)	106 (2)	107 (2)
H(152) C(5) C(4)	109 (2)	106 (2)
H(152) C(5) H(151)	114 (3)	106 (2)
H(151) C(5) C(6)	109 (2)	110 (2)
H(152) C(5) C(6)	105 (2)	112 (2)
H(161) C(6) N(1)	98 (2)	106 (2)
H(161) C(6) C(5)	118 (2)	109 (2)
H(161) C(6) C(7)	110 (2)	108 (2)
H(441) O(4) C(7)	127 (3)	120 (2)

Table 6. Torsion angles ($^{\circ}$) not shown in the Newman projections

	LL-DAP	meso-DAP
N(1) O(6) C(7) O(3)	10	0
C(5) C(6) C(7) O(3)	-112	124
C(5) C(6) C(7) O(4)	68	-56
N(1) C(6) C(7) O(4)	171	179
C(7) C(6) C(5) C(4)	180	-56
C(6) C(5) C(4) C(3)	-176	-171
N(2) C(2) C(1) O(1)	22	16
C(3) C(2) C(1) O(1)	-96	-105
C(3) C(2) C(1) O(2)	84	76
N(2) C(2) C(1) O(2)	-158	-164
N(2) C(2) C(3) O(4)	-175	-176

Fig. 3. Newman projections. Torsion angles ($^{\circ}$) for LL-DAP and, in parentheses, for meso-DAP.Table 7. Selected non-bonded distances (\AA) in LL-DAP

O(3) Cl(1)	3.505	N(1) Cl(1)	3.228
H(311) Cl(1)	2.315	H(312) Cl(1a)	2.502
H(142) Cl(1a)	2.948	H(152) Cl(1)	3.008
O(1) Cl(1b)	3.769	N(2) Cl(1c)	3.280
H(321) Cl(1b)	2.658	H(323) Cl(1c)	2.400
H(132) Cl(1b)	2.813	O(3) Cl(1d)	3.505
N(1) Cl(1d)	3.221	H(313) Cl(1d)	2.382
H(121) O(1e)	2.447	H(441) O(1f)	2.699
O(1) O(1g)	3.336	N(2) O(1g)	2.770
H(322) O(1g)	1.893	C(1) O(1g)	3.380
C(2) O(1g)	3.381	O(4) O(2f)	2.451
C(6) O(2h)	3.409	H(161) O(2h)	2.587
C(7) O(2f)	3.289	H(441) O(2f)	1.787
H(312) O(3a)	2.866	H(161) O(3a)	2.746
N(2) O(3i)	3.077	H(321) O(3i)	2.707
N(1) O(3d)	3.223	O(4) O(4h)	3.324
C(1) O(4j)	3.246	C(1) O(4j)	3.246
H(151) O(4h)	2.795	C(1) H(322k)	2.631
H(441) C(1f)	2.484		

Key to symmetry operations relating designated atoms to reference atoms at (x,y,z)

(a)	$x, 1.0 + y, z$	(g)	$0.5 - x, 0.5 + y, 2.5 - z$
(b)	$1.0 - x, -1.0 + y, 2.0 - z$	(h)	$-x, y, 2.0 - z$
(c)	$1.0 - x, y, 2.0 - z$	(i)	$0.5 + x, -0.5 + y, 0.5 + z$
(d)	$0.5 - x, -0.5 + y, 1.5 - z$	(j)	$-x, -1.0 + y, 2.0 - z$
(e)	$x, 1.0 + y, z$	(k)	$0.5 - x, -0.5 + y, 2.5 - z$
(f)	$x, 1.0 + y, 2.0 - z$		

Molecular packing and hydrogen bonding

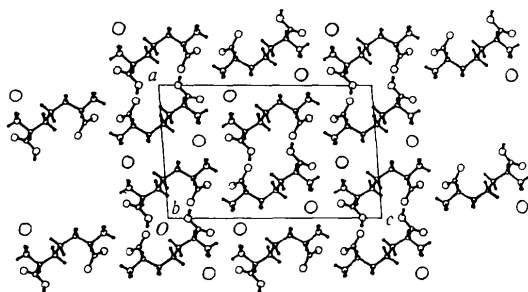
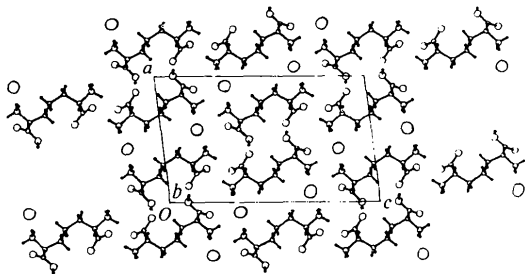
The intermolecular distances of interest are given in Tables 7 and 8. The molecular packing in the plane perpendicular to the unique axis in both structures is shown in Figs. 4 and 5. The fractional coordinates of all heavy atoms in the reference molecules of the two structures are approximately the same, except for Cl(1), O(3), O(4), N(1) and C(7). These five atoms have similar x and z coordinates in both crystals, but the y coordinates have opposite signs. The largest discrepancy between equivalent atoms in the two structures is about 0.3 \AA , after negation of y if necessary. Because space groups $I2$ and $P2_1/n$ both

Table 8. Selected non-bonded distances (Å) in *meso*-DAP

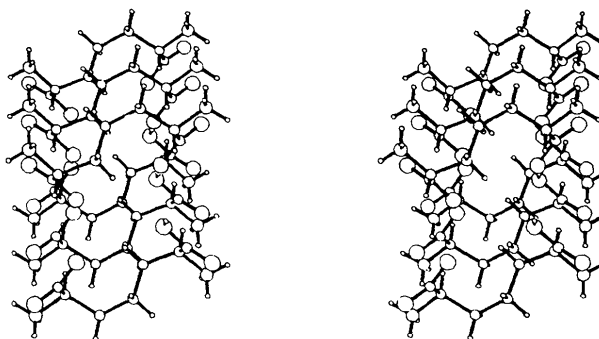
O(3)—Cl(1a)	3.519	N(1)—Cl(1a)	3.289
H(312)—Cl(1)	2.482	H(313)—Cl(1a)	2.370
H(142)—Cl(1a)	2.868	O(1)—Cl(1b)	3.624
N(2)—Cl(1c)	3.284	H(321)—Cl(1b)	2.631
H(323)—Cl(1c)	2.401	H(131)—Cl(1b)	2.792
O(3)—Cl(1d)	3.527	N(1)—Cl(1d)	3.174
H(311)—Cl(1d)	2.285	H(323)—O(1e)	2.917
H(121)—O(1e)	2.638	H(441)—O(1f)	2.800
N(2)—O(1g)	2.784	H(322)—O(1g)	1.851
O(4)—O(2f)	2.458	C(6)—O(2h)	3.374
H(161)—O(2h)	2.614	C(7)—O(2f)	3.287
H(441)—O(2f)	1.590	H(312)—O(3e)	2.855
H(161)—O(3e)	2.539	N(2)—O(3i)	3.121
H(321)—O(3i)	2.687	C(1)—O(4f)	3.290
H(121)—O(4h)	2.854	H(151)—O(4h)	2.648
C(1)—H(322j)	2.659	H(441)—C(1f)	2.461

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z)

(a) $x, -1.0 + y, z$	(f) $-x, -1.0 - y, 2.0 - z$
(b) $1.0 - x, -y, 2.0 - z$	(g) $0.5 - x, 0.5 + y, 2.5 - z$
(c) $1.0 - x, 1.0 - y, 2.0 - z$	(h) $-x, -y, 2.0 - z$
(d) $0.5 - x, -0.5 + y, 1.5 - z$	(i) $0.5 + x, -0.5 - y, 0.5 + z$
(e) $x, 1.0 + y, z$	(j) $0.5 - x, -0.5 + y, 2.5 - z$

Fig. 4. Packing diagram for LL-DAP, projected down **b**.Fig. 5. Packing diagram for *meso*-DAP, projected down **b**.

reduce to plane group $p2$ when projected down **b** and molecules of LL-DAP and *meso*-DAP are almost identical when viewed in this direction, there is little difference between the packing of the molecules in the *ac* planes of the two structures.

Fig. 6. Stereoview of *meso*-DAP showing pairs of molecules related by an inversion centre.

The greatest difference concerns the way in which the molecules are connected by hydrogen bonding between O(2) and O(4). In *meso*-DAP the molecules are associated in distinct pairs related by a crystallographic inversion centre (Fig. 6); in LL-DAP the molecules form infinite intertwined helices related by crystallographic twofold axes parallel to **b** (Fig. 7). Despite this difference the O(2)—O(4) bonds are geometrically very similar, with H attached to O(4) and O—O distances of 2.45 and 2.45 Å for LL-DAP and *meso*-DAP respectively. Although very short these are not symmetric hydrogen bonds of the type usually found in salts of carboxylic acids. Because only one of the carboxylic acid groups is protonated, there are several types of C—O bonds. The C(7)—O(4) bonds are longest (1.282 and 1.282 Å), approaching the normal C—O single-bond length in carboxylic acids (1.30 Å), and consequently the C(7)—O(3) bonds are the shortest (1.215 and 1.217 Å), close to the normal C—O double-bond length in carboxylic acids (1.21 Å). The other C—O bonds are of intermediate length, indicating that the negative charge is delocalized over the O(1)—C(1)—O(2) fragment, although the C(1)—O(2) bonds are slightly longer (1.257 and 1.261 Å) than the C(1)—O(1) bonds (1.235 and 1.239 Å). An analogous situation is found in the structure of diglycine hydrochloride (Hahn, 1960) in which the asymmetric unit contains one HCl molecule and two amino acid residues, one of which is protonated, joined by an O—O hydrogen bond. This structure and the two reported here contrast strongly with di-*L*-leucine hydrochloride (Golič & Hamilton, 1972) in which the two leucine molecules are joined by one symmetric hydrogen bond and each molecule has one long and one short C—O bond. In LL-DAP and *meso*-DAP O(1) and N(2) are joined by intermolecular hydrogen bonds (O—N distances 2.77 and 2.78 Å) which are weaker than those between O(2) and O(4) and account for the slightly greater double-bond character of the C(1)—O(1) compared with the C(1)—O(2) bonds.

In both structures the Cl⁻ ion is hydrogen-bonded to five N atoms [average Cl—N distances 3.31 (LL-DAP)

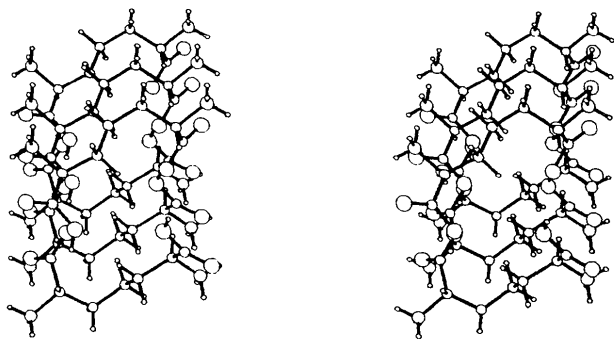


Fig. 7. Stereoview of LL-DAP showing intertwined helices.

and 3.30 Å (*meso*-DAP); average Cl—H distances 2.45 (LL-DAP) and 2.43 Å (*meso*-DAP)]. There is considerable variation in the strength of these bonds: the minimum Cl—N distance is 3.17 and the maximum 3.47 Å. The Cl—H—N angle varies from 160 to 180° and generally decreases as the Cl—N distance increases. The coordination round the Cl⁻ ion is similar to that in di-L-leucine (Golič & Hamilton, 1972), with the Cl atom close to the centre of a rectangle formed by four H atoms, the fifth [H(313) for LL-DAP, H(311) for *meso*-DAP] being at the apex of a distorted square pyramid. In both structures the apical atom forms the shortest hydrogen bond to Cl, although the Cl...H(311)—N(1) bond in LL-DAP is only slightly longer. There are no hydrogen bonds to the base side of the pyramid, but in both structures there are van der Waals contacts to the H atoms bonded to C(3) and C(4).

All seven H atoms attached to polar atoms in these structures take part in hydrogen bonding, as do all the heavy polar atoms except O(3), which is the closest O atom to the Cl (3.5 Å) and is 3.08 Å from N(2).

The relationship between the two structures

Pedone & Benedetti (1972) pointed out the close relationship which may exist between crystals of racemic and optically active forms of the same compound. The similarity of such pairs of crystals was ascribed to the formation of layers of molecules of one sense (D or L), and the stacking of these layers (possibly with some modification) either alternately to form the racemic crystal, or with layers of the same sense to produce the optically active crystal. Simpson & Marsh (1966) compared the structure of L-alanine with that of DL-alanine (Donohue, 1950) and found that reversing the columns of D molecules in the latter crystal gave the coordinates of the former. In diaminopimelic acid the two asymmetric centres are in the same molecule and so it is not obvious how the coordinates of one form can be derived from the other, as was done to solve the (–) form of *trans*-1,2-cyclopentanedicarboxylic acid after the (+) form had been solved (Benedetti,

Corradini & Pedone, 1972). Nevertheless the actual derivation of one structure from the other is simple and involves only the negation of the *y* coordinates of four atoms in the molecule and the Cl ion. Even this transformation is unnecessary if the asymmetric unit is taken not as a complete molecule, but as the molecule minus four atoms [O(3), O(4), N(1), and C(7)], plus these four atoms and the Cl ion related by a twofold axis (for LL-DAP) or an inversion centre (for *meso*-DAP). The layer structure of *meso*-DAP is not retained in LL-DAP because the two asymmetric centres are in the same molecule and when the sense of one of the centres is altered the hydrogen-bonded molecular pairs of *meso*-DAP are replaced by the infinite chains of LL-DAP perpendicular to the molecular plane (Figs. 6 and 7).

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