Si on considère l'ensemble de cette structure on peut voir que les atomes de soufre présentent un empilement hexagonal compact. Dans un tel empilement (de type wurtzite) les atomes de soufre laissent entre eux des cavités tétraédriques et des cavités octaédriques. Ici ces dernières sont vides. Toutefois dans une face de l'une d'entre elles se trouve un atome de cuivre: Cu(2). La moitié des cavités tétraédriques est occupée soit par du cuivre: Cu(1) et Cu(3), soit par de l'étain. Les autres tétraèdres de soufre sont vides.

La stéréochimie des chalcogénures riches en cuivre est encore peu connue. Dans les réseaux de chalcogénures, les atomes de cuivre sont généralement placés dans des cavités tétraédriques. Cependant, il arrive fréquemment que ces atomes ne soient pas au centre de l'environnement tétraédrique de chalcogènes et à la limite ils se trouvent dans l'une des faces du tétraèdre.

Nous remercions M le Professeur N. Rodier pour sa collaboration lors des mesures expérimentales.

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DL-Valine Hydrochloride*

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Abstract. $C_5H_{12}NO_2Cl$, $M_r = 153$, monoclinic, $P2_1/c$, $a = 11.722$ (4), $b = 7.007$ (3), $c = 11.143$ (4) Å, $\beta = 120° 32'$. Layers of isoconfigurational molecules are packed in the same way as in free amino acids. The structure has been determined by analogy with the optically active form and refined to an R of 0.063.

Introduction. It has been shown that structures of racemic and optically active pairs are often related: a plane of close-packed isoconfigurational molecules with the appropriate symmetry elements generates the two structures (Pedone & Benedetti, 1972; Benedetti, Pedone & Sirigu, 1973; Di Blasio, Pedone & Sirigu, 1975). This was verified for many pairs of free amino (and other) acids and also overcrowded halogenated compounds (Herbstein, Kapon & Merksamer, 1976). The structure of L-valine.HCl has been solved (Parthasarathy, 1966; Ando, Ashida, Sasada & Kakudo, 1967) and consists of layers of hydrogen-bonded molecules arranged so that polar groups and similarly the hydrocarbon side chains face each other. The structure of DL-valine.HCl also possesses this feature.

Crystals were grown from a dilute hydrochloric acid solution of the DL-amino acid. 845 non-zero independent reflexions were measured by an on-line single-crystal Siemens diffractometer. The cell dimensions

Table 1. *Comparison of crystallographic data for the* DL *and* L *forms of valine hydrochloride*

	DL-Valine.HCl	L-Valine.HCl*
Crystal system	Monoclinic	Monoclinic
a	11.722 (4) Å	10.394 Å
b	7.007 (3)	7.072
c	11.143 (4)	5.430
β	120° 32'	91° 42'
V	788.27 Å^3	399.0 Å^3
Z	4	2
Space group	$P2_1/c$	$P2_1$
D_x	1.29 g cm^{-3}	1.27 g cm^{-3}

* Ando, Ashida, Sasada & Kakudo (1967).

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* Based in part on the thesis of G. Napolitano, Università di Napoli, 1976.

Table 2. *Positional and thermal parameters*

Coordinates for non-hydrogen atoms are $\times 10^4$; those for H atoms are $\times 10^3$. Anisotropic temperature factor: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*) \times 10^{-2}]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	6203 (4)	2632 (5)	6151 (3)	742 (22)	277 (14)	420 (15)	120 (29)	771 (32)	79 (25)
O(2)	6911 (5)	207 (5)	5394 (5)	1335 (36)	200 (14)	883 (27)	246 (36)	1735 (57)	144 (31)
N	6109 (5)	5082 (5)	4254 (4)	567 (24)	282 (16)	471 (21)	149 (32)	679 (39)	195 (31)
C(1)	9047 (7)	1907 (9)	4911 (7)	711 (36)	493 (29)	596 (32)	321 (54)	770 (60)	60 (50)
C(2)	8315 (6)	3658 (7)	4972 (6)	585 (31)	338 (22)	454 (26)	99 (42)	654 (50)	49 (38)
C(3)	9062 (7)	4574 (10)	6407 (7)	673 (38)	611 (34)	625 (35)	−344 (59)	699 (63)	−511 (58)
C(4)	6849 (5)	3256 (7)	4454 (5)	531 (27)	245 (18)	360 (22)	61 (35)	550 (42)	−23 (32)
C(5)	6612 (6)	2023 (6)	5436 (5)	605 (29)	244 (19)	373 (21)	−53 (38)	574 (44)	−61 (33)
Cl	6620 (2)	7667 (2)	2224 (1)	632 (7)	227 (4)	407 (5)	−3 (10)	612 (10)	59 (9)

Table 2 (*cont.*)

	x	y	z	B
H(1)N	630 (6)	586 (9)	361 (7)	5 (2)
H(2)N	619 (6)	569 (9)	500 (6)	4 (1)
H(3)N	505 (5)	489 (8)	376 (5)	3 (1)
H(4)C(3)	1015 (6)	475 (10)	663 (7)	5 (2)
H(5)C(3)	901 (6)	341 (10)	712 (6)	5 (2)
H(6)C(3)	857 (8)	544 (12)	662 (9)	10 (3)
H(7)C(1)	1019 (7)	226 (10)	533 (8)	7 (2)
H(8)C(1)	856 (8)	112 (12)	398 (8)	8 (2)
H(9)C(1)	911 (6)	98 (9)	567 (6)	5 (2)
H(10)C(2)	841 (6)	459 (9)	422 (6)	4 (1)
H(11)C(4)	644 (5)	253 (7)	350 (5)	2 (1)
H(12)O(2)	681 (7)	−31 (10)	605 (7)	6 (2)

were derived by least squares from a number of high-order reflexions and are reported in Table 1, together with the data of the L form.

The structure was determined on the hypothesis that the *ba* plane of the optically active form was retained in the racemic form, almost coincident with the plane *b*, (**a** + **c**)/2.

R for this first trial model was 0·30. The structure was refined by least squares[*] with anisotropic thermal parameters for the heavy atoms and isotropic ones for H. The final *R* for the observed reflexions is 0·063.[†]

The weighting scheme was that suggested by Cruickshank & Pilling (1961).

The final atomic coordinates and thermal factors are reported in Table 2.

Discussion. The dimensions of the molecule are reported in Table 3. They agree with those for DL-valine (Mallikarjunan & Rao, 1969) and L-valine (Torii & Iitaka, 1970) except the parameters involving the carboxylic group, which agree with those found in the L-hydrohalide monohydrate (Rao, 1969) and the anhydrous compound, in which the molecule takes a cationic form. As expected, the L and DL forms consist of layers of hydrogen-bonded molecules with the same configuration; the difference in the arrangement within a layer is significant but still small. Fig. 1 shows the layer for both structures; layers are joined by hydrogen bonds, related by centres of symmetry in the DL form and by translation in the optically active form. The racemic form, as usual, has the better packing (1·29 compared with 1·27 g cm^{-3}) owing to the close approach of methyl groups through the operation of centres of symmetry ($CH_3\cdots CH_3$ = 3·43 Å, and the H atoms are almost staggered, while the shortest $CH_3\cdots CH_3$ distance in the L form is 3·80 Å between molecules related by a 2_1 axis). Also, in the racemic form four H atoms are involved in hydrogen-bond formation. The packing along **b** is shown in Fig. 2 and the environment around the N and Cl atoms in Fig. 3. The Cl ion is involved in four hydrogen bonds. One of the H atoms of the NH_3^+ group seems to be involved in a bifurcated hydrogen bond, being equally distant from a Cl and an O atom. The geometrical parameters are reported in Table 4. Around the Cl ion, in a sphere of

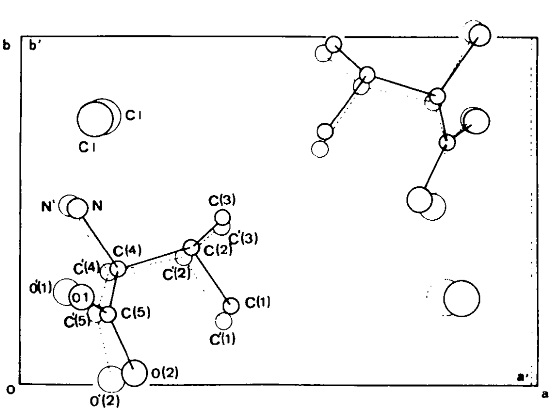

Fig. 1. Plane of isoconfigurational molecules in L-valine.HCl (continuous lines) and DL-valine.HCl [broken lines, **a'** = (**a** + **c**)/2].

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[*] All computations were performed on a Univac 1106 computer (Immirzi, 1967).

[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32153 (7pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond distances* (Å), *angles* (°) *and dihedral angles of the* DL *and* L *forms of valine*. HCl

The mean values of bond distances and angles involving H atoms are C—H = 1·09 (9), N—H = 0·99 (8) Å; H—C—H = 109 (5), H—N—H = 106 (3)°. The *trans* configuration corresponds to a torsion angle of 180°.

	DL	L		DL	L		DL	L
O(1)—C(5)	1·197 (6)	1·200	O(1)—C(5)—O(2)	124·6 (2)	123·9	O(1)—C(5)—C(4)—N	−15·7	−11·0
O(2)—C(5)	1·327 (6)	1·309	O(1)—C(5)—C(4)	123·7 (2)	123·7	O(1)—C(5)—C(4)—C(2)	106·3	110·2
N—C(4)	1·497 (8)	1·495	O(2)—C(5)—C(4)	111·7 (2)	112·4	O(2)—C(5)—C(4)—N	163·3	170·3
C(1)—C(2)	1·519 (9)	1·517	N—C(4)—C(2)	110·6 (2)	109·8	O(2)—C(5)—C(4)—C(2)	−74·7	−68·4
C(2)—C(3)	1·521 (13)	1·532	N—C(4)—C(5)	106·7 (2)	106·2	C(5)—C(4)—C(2)—C(1)	71·1	74·4
C(2)—C(4)	1·535 (11)	1·558	C(1)—C(2)—C(3)	110·6 (3)	113·0	C(5)—C(4)—C(2)—C(3)	−55·5	−52·2
C(4)—C(5)	1·528 (10)	1·509	C(1)—C(2)—C(4)	112·7 (2)	110·3	N—C(4)—C(2)—C(3)	64·3	67·2
			C(2)—C(4)—C(5)	114·2 (3)	114·5	N—C(4)—C(2)—C(1)	190·9	193·8
			C(3)—C(2)—C(4)	114·2 (2)	111·8			

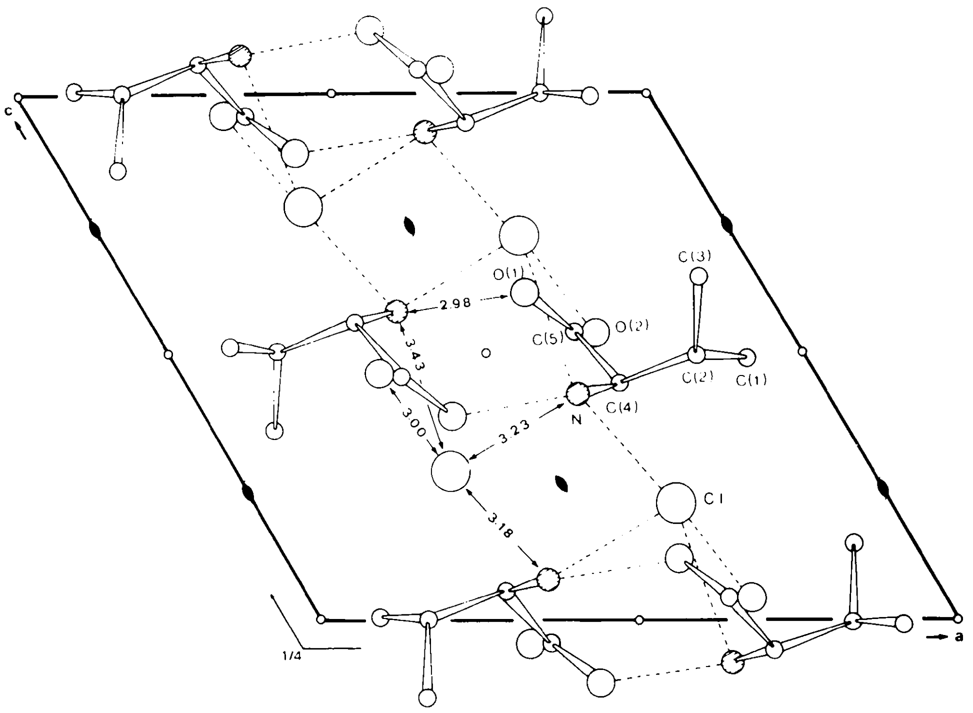

Fig. 2. Packing of DL-valine. HCl viewed along **b**.

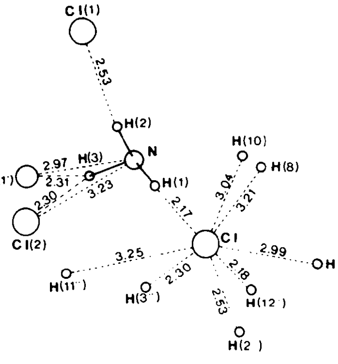

Fig. 3. The environment of N and Cl⁻ viewed along **b**.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°) (*see also Fig.* 3)

N···O(1′)	2·97	N—H(3)···O(1′)	118·5
N···Cl	3·18	N—H(3)···Cl(2)	143·5
N···Cl(1)	3·43	N—H(1)···Cl	176·1
N···Cl(2)	3·23	N—H(2)···Cl(1)	175·2
H(1)···Cl	2·17	O(1′)···N—H(3)	42·9
H(2)···Cl(1)	2·53	Cl(2)···N—H(3)	25·0
H(3)···Cl(2)	2·30	O(2′)—H(12′)···Cl	153·9
H(3)···O(1′)	2·31	Cl···N···Cl(1)	114·8
		Cl···N···Cl(2)	115·5
		Cl(1)···N···Cl(2)	112·0
		O(1′)···N···Cl(1)	66·3
		O(1′)···N···Cl	94·1
		O(1′)···N···Cl(2)	67·4

radius 3·3 Å, there are four other H atoms that belong to CH and CH_3 groups.

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Methylchlorophyllide A Dihydrate

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Abstract. Monoclinic, $P2_1$, $a = 8{\cdot}76\,(1)$, $b = 25{\cdot}86\,(3)$, $c = 8{\cdot}47\,(1)$ Å, $\beta = 119{\cdot}20\,(5)°$; $C_{36}H_{36}O_5N_4Mg\,.\,2H_2O$, $M_r = 665{\cdot}06$; $Z = 2$, $D_m = 1{\cdot}30$; $D_x = 1{\cdot}32$ g cm^{-3}. A net of hydrogen bonds gives rise to the formation of layers of chlorophyllide molecules, very similar to those found in crystals of ethylchlorophyllide A and B [Strouse, *Proc. Natl. Acad. Sci. US* (1974), **71**, 325–328; Chow, Serlin & Strouse, *J. Amer. Chem. Soc.* (1975), **97**, 7230–7237; Kratky & Dunitz, *Acta Cryst.* (1975), **B31**, 1586–1589].

Introduction. Crystals grown by slow evaporation from acetone/10% water under exclusion of oxygen were frequently twinned.* Intensities from a crystal fragment 0·5 x 0·3 x 0·05 mm were measured on an automated four-circle diffractometer (Hilger & Watts Y290) with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), yielding 2398 independent reflexions in the range $\theta \leq 23°$. The data were processed to yield 1950 reflexions with intensity significantly above background[$|F_o| > \sigma(|F_o|)$]. No absorption correction was applied [μ(Mo $K\alpha$) = 1·158 cm^{-1}].

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). All 308 reflexions with $|E| > 1{\cdot}4$ were included in the phase-determining process with 64 sets of starting phases. The E map calculated with phases from the solution with the best figures of merit contained 34 peaks forming a chemically reasonable pattern. After two cycles of least-squares refinement ($R = 0{\cdot}29$), an F_o synthesis showed eight more atoms, which were included in four further cycles ($R = 0{\cdot}19$). A second F_o synthesis then yielded the positions of the remaining six atoms.

After two cycles of full-matrix least-squares refinement with isotropic temperature factors for all atoms ($R = 0{\cdot}11$), H atoms were included at calculated positions. The orientations of the terminal CH_3 groups were estimated from an $(F_o - F_c)$ synthesis. Three cycles of block-diagonal least-squares refinement with anisotropic temperature factors for the peripheral atoms reduced R to 0·089, with H atom contributions included in F_c but not refined.

At this stage, scrutiny of the data revealed that the $(|F_o|-|F_c|)$ values for reflexions measured at χ settings around 0° or 90° were systematically negative, suggesting that the corresponding intensities had been only partially recorded. The reflexions in question were remeasured with a larger collimator for the detector. Refinement was then continued with a separate scale factor for the set of 487 remeasured reflexions.

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