Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1967). **23**, 172

The crystal structure of L-valine hydrochloride.

By O. Ando, T. Ashida, Y. Sasada* and M. Kakudo, *Institute for Protein Research, Osaka University, Kita-ku, Osaka, Japan*

(*Received* 4 *February* 1967 *and in revised form* 13 *March* 1967)

The crystal structure of L-valine hydrochloride was determined with the intensity data collected on a single-crystal diffractometer. Some significant differences in the conformation of the carboxyl group and the features of the hydrogen bonding were found between our result and that obtained by Parthasarathy using Weissenberg intensity data.

L-Valine is one of the essential amino acids, and the crystal structure determination of its hydrochloride based on photographic data has been already reported by Parthasarathy (1966). We have also determined independently the crystal structure of the same compound by the X-ray diffractometer method. There exist, however, some differences between the results of these investigations concerning the conformation of the carboxyl group and the hydrogen bonding features.

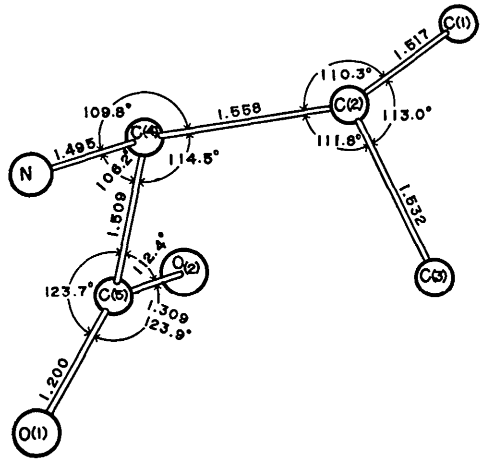

Fig. 1. The bond distances (Å) and the bond angles in the valine molecule.

Throughout this work the X-ray experiments were done on a General Electric XRD-5 diffractometer with Mo $K\alpha$ radiation. The unit-cell dimensions are: $a=10·394$, $b=7·072$, $c=5·430$ Å and $\beta=91·42°$; the space group is $P2_1$, and two units of $C_5H_{12}NO_2Cl$ are in a unit cell. A total of 1027 reflexions with 2θ less than 56° were collected. Corrections for absorption and extinction were not applied in this work.

The crystal structure was solved by the heavy atom method, and the structural parameters were refined by the least-squares method using a block-diagonal matrix approximation. The hydrogen atoms were found on the difference Fourier synthesis and were included in the refinement. The final R value is 0·068 excluding the non-observed reflexions. The final parameters are listed in Tables 1–3. The averaged estimated standard deviation of the positional parameters of C, N and O is 0·006 Å (Parthasarathy's value, 0·011 Å).

Table 1. *The final atomic coordinates and their standard deviations*, σ (in 10^{-3} Å)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl	0·1500	2	0·2500	3	0·2843	1
O(1)	0·1219	4	0·7463	7	1·1225	4
O(2)	0·2236	6	0·5318	5	0·9027	5
N	0·1111	5	0·9996	6	0·7655	5
C(1)	0·4090	7	0·7265	11	0·5712	7
C(2)	0·3336	6	0·8893	7	0·6784	6
C(3)	0·3967	7	0·9709	9	0·9132	7
C(4)	0·1917	6	0·8288	6	0·7197	6
C(5)	0·1738	6	0·6994	6	0·9371	6

Table 2. *The thermal parameters and their standard deviations* ($\times 10^{-4}$)

The thermal parameters are of the form $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cl	117	1	198	3	333	4	18	5	9	4	139	9
O(1)	133	5	202	9	285	12	6	17	55	12	69	28
O(2)	216	8	183	11	474	22	71	17	218	21	138	29
N	90	5	187	11	303	17	27	14	42	14	137	25
C(1)	119	7	287	22	408	24	107	25	43	21	6	45
C(2)	91	6	213	15	314	21	4	16	51	18	87	32
C(3)	95	7	324	23	465	29	−88	22	−19	22	−109	45
C(4)	91	6	204	14	209	16	−8	15	27	15	−16	26
C(5)	87	5	168	14	303	19	16	14	−4	16	23	26

---

* Present address: Faculty of Science, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo.

Table 3. *The final parameters of hydrogen atoms*

	x	y	z	B	Bonded to
H(1)	0·133	1·094	0·659	3·3	N
H(2)	0·027	0·964	0·766	1·7	N
H(3)	0·126	1·073	0·936	6·1	N
H(4)	0·208	0·459	1·035	4·4	O(2)
H(5)	0·165	0·735	0·581	0·3	C(4)
H(6)	0·337	0·979	0·530	3·3	C(2)
H(7)	0·365	1·074	1·010	7·6	C(3)
H(8)	0·381	0·865	1·037	3·9	C(3)
H(9)	0·478	1·017	0·887	4·8	C(3)
H(10)	0·434	0·631	0·695	4·9	C(1)
H(11)	0·488	0·780	0·552	4·1	C(1)
H(12)	0·370	0·664	0·458	2·3	C(1)

$\langle\sigma(x)\rangle=0{\cdot}07$ $\langle\sigma(y)\rangle=0{\cdot}08$ $\langle\sigma(z)\rangle=0{\cdot}07$ Å
$\langle\sigma(B)\rangle=1{\cdot}9$ Å^2

There are significant differences between the temperature factors of the two investigations; the differences may be due to the neglect of absorption. Significant differences are also found in the positional parameters. For example, the difference in x of O(1) is 10σ; x of O(2), 9σ; y of O(1), 12σ; z of O(2), 8σ; z of C(5), 7σ, where the σ's are the standard deviations in our result. It is interesting that all these atoms belong to the carboxyl group; the differences resulted in a large deviation of the configuration of the carboxyl group. Most of the differences of the bond lengths and angles are, however, not significant considering the experimental accuracies. The bond lengths and angles in the valine molecule are shown in Fig. 1; the averages of their standard deviations are 0·009 Å and 0·6° (Parthasarathy's values, 0·018 Å and 1·5°).

Parthasarathy suggested the possible existence of a bifurcated hydrogen bond among N, Cl″ and O(1″) (see Fig. 3 of Parthasarathy's paper). In the present study, however, only the N–H(2)···Cl″ contact seems to be a hydrogen bond, while N···O(1″) seems to be a normal ionic contact, because the H(2)···O(1″) distance of 2·60 Å corresponds to a normal van der Waals contact, and H(2) is too far from the line of N···O(1″), though the distance of N···O(1″) corresponds to that of the weakest hydrogen bond. The N···O(1″) distance is 2·99 Å in Parthasarathy's result but 3·06 Å in ours. The atoms, N, H(2), Cl″ and O(1″), are roughly coplanar, and they are shown in Fig. 2. Many examples have been reported in which four negatively charged atoms approach a protonated amino group within hydrogen-bonding distances and only three of them are hydrogen-bonded.

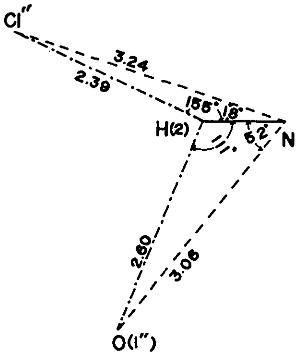

Fig. 2. The environment of the H(2) atom. The contact between H(2) and O(1″) does not seem to be a hydrogen bond.

We express our thanks to Dr R. Parthasarathy and to Professors R. Srinivasan and G. N. Ramachandran for their kind suggestion to present this paper. The authors' thanks are also due to the Matsunaga Science Foundation for financial support.

References

Parthasarathy, R. (1966). *Acta Cryst.* **21**, 422.

Acta Cryst. (1967). **23**, 173

Application of the molecular replacement equations to the heavy atom technique.

By Michael G. Rossmann,
Department of Biological Sciences, Purdue University, Lafayette, Indiana, U.S.A.

(*Received* 9 *September* 1966)

A set of non-linear phase equations is derived. The coefficients depend on the knowledge of structure amplitudes and the position of some 'heavy atoms'. An approximate set of phases based on structure factor calculations using the known heavy atoms can then be refined to satisfy the equations exactly. Thus non-heavy-atom structural information can be derived without interpretation of heavy-atom based Fourier maps which may require chemical information and intuition.

Main & Rossmann (1966) and Main (1967) have shown that the use of the molecular replacement equations may lead to a satisfactory solution of the phase problem whenever the asymmetric unit can be divided into different parts with related structures. Let us now divide the unit cell into a known (heavy-atom) and unknown part.

Let the structure factor of reflexion $\mathbf{p}$ of the known part of the cell be $\mathbf{f}_p$. Then by definition,

$$\mathbf{f}_p=\int_U \varrho(\mathbf{x})\exp\{2\pi i\mathbf{p}\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,, \tag{1}$$

where the integral is taken over the volume U of the known part of the cell, and $\varrho(\mathbf{x})$ is the total electron density distribution within the cell.

But

$$\varrho(\mathbf{x})=\frac{1}{V}\sum_h \mathbf{F}_h\exp\{-2\pi i\mathbf{h}\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,. \tag{2}$$

Hence by substituting (2) in (1) we have

$$\mathbf{f}_p=\frac{1}{V}\sum_h \mathbf{F}_h\int_U\exp\{2\pi i(\mathbf{p}-\mathbf{h})\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,.$$