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Determination of the Anomalous Scattering Factor $\Delta f''$ for Chlorine

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Measurements of the Bijvoet inequality for the *c* zone of L-tyrosine hydrochloride are reported. The measured values of the Bijvoet inequality vary between half and twice the calculated value, but there is a good agreement in sign in almost all cases. These large variations between the observed values and those calculated from the structure are explained by the possible errors in the atomic coordinates and errors in the measurement of the Bijvoet inequality. The imaginary part of $\Delta f''$ for chlorine for Cu $K\alpha$ is estimated to be $0{\cdot}67 \pm 0{\cdot}21$. The absolute configuration of L-tyrosine is also obtained.

1. Introduction

During recent years, the anomalous dispersion method of measuring the phases of X-ray reflections has proved to be successful in elucidating the structure of non-centric crystals (Ramachandran and Raman, 1956, Raman, 1959, Doyne, Pepinsky & Watanabé, 1957). This method of estimating the phases depends on measuring the difference in intensity between pairs of inverse reflections **H** (*hkl*) and $\overline{\mathbf{H}}$ ($\bar{h}\bar{k}\bar{l}$) produced by the imaginary component $\Delta f''$ of the atomic scattering factor. Since the value of ΔI depends on $\Delta f''$, the estimated value of the phase angle also depends on the actual value of $\Delta f''$ used. The values ordinarily used are those calculated by Hönl (James, 1954) or by Dauben and Templeton (1955), the former using the wave-mechanical theory and the latter a semi-theoretical method. It seems desirable now to determine experimentally the values of $\Delta f''$ for the following reasons. The measurements on $NaClO_3$ (Ramachandran and Chandrasekharan, 1957) indicated that there was not very good agreement between the magnitude of $(\Delta I/I)_{\text{th.}}$ and $(\Delta I/I)_{\text{exp.}}$ although the sign of the two agreed in most cases. Harrison, Jeffrey and Townsend (1958) found in their measurements of anomalous dispersion effects in ZnO a peculiar periodic variation, which cannot be explained by using a common value of $\Delta f''$ for each Zn atom. They concluded that, if more than one identical anomalous scatterer occurs in the unit cell, it may be necessary to compute the anomalous crystal structure factor directly.* Bijvoet while determining the absolute configuration of $NaBrO_3$ found that it gave an exactly opposite configuration to that of its isomorphous pair $NaClO_3$ and suspected that the occurrence of more than two identical anomalous scatterers in the unit cell was the cause of this (personal communication to Prof. G. N. Ramachandran). Thus it appears that two types of experimental study of the anomalous dispersion effects are needed:

(i) One is to find out accurately the value of $\Delta f''$ using simple compounds like ZnS. This can then be used to test the conclusions of wave-mechanical theory, for example to see whether there is any dependence of $\Delta f''$ on $(\sin \theta/\lambda)$.

(ii) Secondly, it is necessary to find out whether the values of $\Delta f''$ so obtained can be directly carried over to more complicated structures containing a number of identical anomalous scatterers in the unit cell.

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* We have now received the information from Dr J. R. Townsend that only certain crystals of ZnO exhibit this anomaly regarding the Bijvoet inequality and therefore the peculiar results reported earlier require reassessment.

Regarding the first part, the recent experimental study of ZnS by Townsend, Jeffrey and Panagis (1959) has yielded values of $\Delta f''_{\mathrm{Zn}}$ in good agreement with the wave-mechanical conclusions of Hönl. The present investigation shows that even when the crystal is more complex, with two identical anomalous scatterers and a number of non-anomalous scatterers per unit cell, the wave-mechanical value of Hönl or that of Dauben and Templeton for $\Delta f''$ can, in general, be used.

2. Experimental details

The crystal chosen for the present investigation was L-tyrosin hydrochloride, whose structure was solved by Srinivasan (1959) by the differnce-Patterson method. The crystallographic data for this compound are:

$$a = 11·07,\quad b = 9·03,\quad c = 5·09\ \text{Å}$$
$$\beta = 91·8°$$

Space group $P2_1$, two molecules per unit cell, μ (linear absorption coefficient) for Cu $K\alpha$ radiation $= 35$ cm.$^{-1}$. Final R-value obtained for [001] projection $= 10·3\%$.

The crystals were prepared in the manner described by Srinivasan (1956) and fine needles with [001] as needle axis were obtained. A crystal of thickness less than 0·2 mm. and with a fairly circular cross-section was chosen for study. As the crystal was slightly hygroscopic, it was enclosed in a Lindeman-glass capillary and sealed.

Cu $K\alpha$ radiation was used for the present study and accurate intensity measurements were made with a Unicam S–25 single-crystal goniometer, converted into a Geiger-counter spectrometer by means of the accessory S–32. Some modifications were made in this instrument to reduce the angular speed of the rotation to about $\frac{1}{4}°$ per minute, and also for the fine adjustment of the angular setting of the Geiger counter. As a result of these improvements, it was possible to set the counter quickly for any desired value of 2θ. Further, the collimator given by the manufacturers was also replaced by one giving a smaller background. The Geiger counter used was Mullard MX–118. A counting rate meter was used for the initial settings of the crystal and the counter and a scale of 128 was employed for measuring the integrated intensities of reflections. The X-ray unit used was Philips 1009 and it was found that measurements were reproducible to 5%.

For the c zone, the reflections $hk0$ and $\bar{h}k0$ are equivalent so that two pairs of reflections, viz., $hk0$, $\bar{h}\bar{k}0$ and $\bar{h}k0$, $h\bar{k}0$ can be studied. Further, two settings are possible for the Geiger counter for each reflection, namely at an angle 2θ on either side of the X-ray beam. Thus in all eight observations are possible for each reflection, giving four measurements of the Bijvoet inequality. The mutual agreement among these four showed that the effect of crystal shape, if any, was not important. The final values af $(\Delta I/I)$ was obtained as an average of the four values.

3. Results

(a)Calculation of $\Delta f''$

The theoretical value of $(\Delta I/I)$ was obtained using the relevant formula for this space group, namely,

$$(\Delta I/I)_{\mathrm{th.}} = 4A_{\mathrm{Cl}}''B/|F|^2 \qquad (1)$$

where $|F|^2$ is the mean intensity of two inverse reflections, which may, for all practical purposes, be put equal to the value calculated without including $\Delta f_{\mathrm{Cl}}''$ and $B = |F| \sin \alpha$ where α is the phase angle. (The derivation of equation (1) is given in Appendix I.) The calculations were made using the data of Viervoll and Øgrim (1949) for the scattering factors and the

Table 1. *Comparison of calculated and measured Bijvoet inequalities*

hkl	$\left(\frac{\Delta I}{I}\right)\%_{\mathrm{exp.}}$	$\left(\frac{\Delta I}{I}\right)\%_{\mathrm{th.}}$
110	2·1	3·8
310	0·8	4·0
410	0·7	0·6
510	7·5	11·2
610	−3·9	−4·7
710	5·4	0·0
810	0·4	−7·1
910	−5·1	−7·0
020	−16·9	−19·0
120	3·6	10·4
220	−17·8	−24·2
320	0·6	0·0
420	11·6	−16·2
520	14·2	20·0
620	0·0	−8·6
720	4·8	5·6
820	−6·4	−8·2
920	1·6	0·0
11,2,0	9·0	−7·4
12,2,0	0·0	0·0
130	−13·3	−18·6
230	0·0	−4·1
330	1·7	0·0
430	5·8	−4·1
530	18·4	14·8
630	0·0	3·6
830	0·0	−12·5
930	33·9	32·3
10,3,0	3·3	8·0
040	8·8	9·5
140	18·6	15·0
240	1·6	−8·0
340	1·2	0·0
440	40·6	23·4
540	18·7	−8·0
640	3·2	0·0
740	−3·8	−6·6
10,4,0	9·1	−6·8
11,4,0	3·0	−4·7
150	−12·8	−16·0
250	−17·4	−15·2
350	0·5	0·0
450	−2·1	0·0
750	6·9	10·3
850	7·1	0·0
950	−1·0	0·0
060	−1·1	−3·4
160	−5·3	−8·3
260	16·4	12·8
360	2·1	0·0
460	−23·8	−26·2
560	−20·9	−41·8
660	−12·3	7·2
760	9·0	14·4
860	−1·0	6·8
960	25·0	11·3
10,6,0	12·7	14·2
11,6,0	−35·9	−28·0
170	20·9	44·0
270	24·3	14·2
370	21·0	14·5
470	0·6	0·0
570	−6·6	−12·0
770	−2·1	1·0
870	−7·6	−15·0
10,7,0	−9·5	−18·4
080	11·0	12·8
180	−7·1	−16·3
280	−22·5	−24·0
380	1·4	0·0
480	−4·3	−15·3
580	−14·3	−12·4
680	35·3	20·3
190	−59·3	−30·8
290	19·7	25·8
390	3·2	0·0
490	10·9	0·0
590	3·9	−10·0
690	12·5	6·0
1,10,0	18·9	20·0
4,10,0	−1·3	0·0
5,10,0	−12·2	−10·2
1,11,0	−8·4	−34·0
2,11,0	−35·9	−46·0
200	0·0	0·0
400	0·0	0·0
600	0·0	0·0
800	0·0	0·0

dispersion corrections $\Delta f_{\mathrm{Cl}}''=0{\cdot}23$, $\Delta f_{\mathrm{Cl}}''=0{\cdot}66$ were obtained from James' book (1954). No temperature correction need be applied if it is assumed that all atoms have the same Debye-Waller factor. The values of $(\Delta I/I)_{\mathrm{th.}}$ and $(\Delta I/I)_{\mathrm{exp.}}$ are listed in Table 1.

A comparison of the theoretical and experimental values in Table 1 shows that while the observed value varies between half and twice the calculated value, there is a good agreement in sign in almost all cases. In a few cases where the signs disagree, the calculated or measured value of the Bijvoet inequality is small and hence this disagreement is not significant. Since no systematic deviation is observed between theory and experiment with the Bragg angle θ, it appears to be more convenient to study the variation of $(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}$ rather than that of $(\Delta I/I)_{\mathrm{exp.}}$, for $(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}$ is expected to be a constant. Hence $\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}$ was calculated from the formula

$$(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}/(\Delta f_{\mathrm{Cl}}'')_{\mathrm{th.}}=(\Delta I/I)_{\mathrm{exp.}}/(\Delta I/I)_{\mathrm{th.}}$$

or

$$(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}=0{\cdot}66\,(\Delta I/I)_{\mathrm{exp.}}/(\Delta I/I)_{\mathrm{th.}} \qquad (2)$$

and the values so obtained are listed in Table 2, and the data are plotted in Fig. 1. It is seen from this graph that the agreement with the theoretically expected value of 0·66 is good at low $\sin\theta$ values, but at higher values of $\sin\theta$ the experimental points are more widely distributed. So far no allowance has been made for any possible error in $(\Delta I/I)_{\mathrm{th.}}$ and $(\Delta I/I)_{\mathrm{exp.}}$ and the possibility of the way how errors can arise in $(\Delta I/I)_{\mathrm{exp.}}$ and $(\Delta I/I)_{\mathrm{th.}}$ is discussed in the following sections.

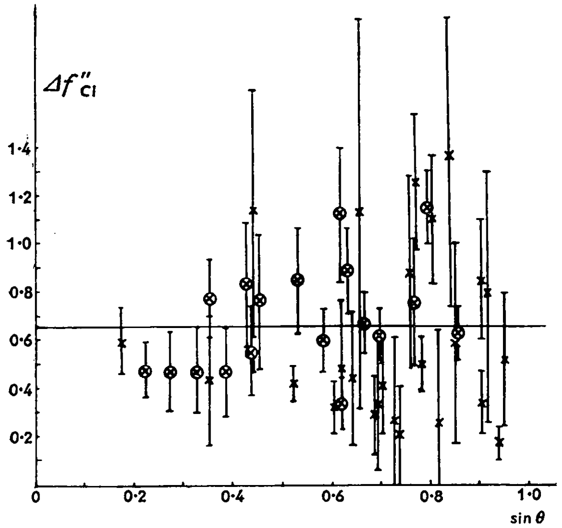

Fig. 1. Plot of $\Delta f_{\mathrm{Cl}}''$ against $\sin\theta$.
○ represents points for which $|F|>5$, $(\Delta I/I)>10\%$.

(*b*) *Errors in the measurement of Bijvoet inequality*:

An estimate of the error in the measured value of the Bijvoet inequality can be made. In the expression

$$(\Delta I/I)=(I-\bar{I})/(\tfrac{1}{2}(I+\bar{I})) \qquad (3)$$

I and $\bar{I}$ are the intensities of a pair of inverse reflections and are subjected to standard deviations $\sigma(I)$ and $\sigma(\bar{I})$ respectively. In general it is found that $\sigma(I)$ is nearly equal to $\sigma(\bar{I})$ and that $\sigma(I)$ varies from 3% for strong and medium reflections to 5% for weak reflections. Treating I and $\bar{I}$ as two independent variables it can be readily shown that the fractional error in the expression in equation (3) is given by

$$\begin{aligned}\sigma(\Delta I/I)/(\Delta I/I)\\ &=(\sqrt{2}\sigma(I)/\Delta I)(1+(\Delta I/I)^2)^{1/2}\approx\sqrt{2}\sigma(I)/\Delta I \qquad (4)\end{aligned}$$

From equation (2) it can be seen that the fractional error of $(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}$ due to the inaccuracy in the measurement will be equal to that of $(\Delta I/I)_{\mathrm{exp.}}$ and hence

$$\sigma_1(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')=\sqrt{2}\sigma(I)/\Delta I \qquad (5)$$

The fractional standard errors so obtained are given in Table 3.

(*c*) *Effect of errors in the atomic parameters*:

Although the atomic coordinates in the structure are not explicitly mentioned in equation (2), it is obvious that they would vitally come into the calculation of $\Delta f''$ from the value of $(\Delta I/I)$. In equation (2), they are implicitly contained in $(\Delta I/I)_{\mathrm{th.}}$ in the denominator. Making use of the expression for this from equation (1), we have

$$\begin{aligned}\Delta f_{\mathrm{Cl}}''&=(0{\cdot}66|F|^2/(4A_{\mathrm{Cl}}''B))(\Delta I/I)_{\mathrm{exp.}}\\ &=(|F|/8\sin\alpha\cos\alpha_{\mathrm{Cl}})(\Delta I/I)_{\mathrm{exp.}} \qquad (6)\end{aligned}$$

where α is the phase angle of the total structure factor and $\alpha_{\mathrm{Cl}}=2\pi\mathbf{H}.\mathbf{r}_{\mathrm{Cl}}$, $\mathbf{r}_{\mathrm{Cl}}$ being the coordinate of the chlorine atom.

Now, the error in α_{Cl} can be considered to be negligible as the heavy atom position is in general known to a much higher accuracy than the other atoms. Consequently, the errors in the value of $\Delta f_{\mathrm{Cl}}''$ would arise essentially from the errors arising in $|F|$ and $\sin\alpha$ from the inaccuracy in the knowledge of atomic coordinates. The problem of evaluating the standard deviations of these quantities, given the standard deviations of atomic coordinates, is a more general one and is considered in another paper (Parthasarathy, 1960). Assuming that the errors in the atomic coordinates are isotropic, i.e., the position of the jth atom is distributed spherically around its mean position with a root mean square radius $\sigma(|\mathbf{r}_j|)$ ($=\sigma_{rj}$ say in Å) it can be shown that the standard error of $|F(hk0)|$ is given by

$$\sigma(|F|)=(2\pi^2N/3)^{1/2}(f\sigma_r/d) \qquad (7)$$

where N is the number of atoms in the unit cell, d is the spacing of the reflection, and, for convenience, we have denoted the factor $[\langle f_j^2\sigma_{rj}^2\rangle_{av.}]^{1/2}$ (i.e., the square root of the mean of the product $f_j^2\sigma_{rj}^2$ for

Table 2. *Calculation of* $(\Delta f'')_{\mathrm{Cl}}$, $\sigma(|F|)/|F|$ and $\sigma_2(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$

$\sin\theta$	*hkl*	$(\Delta f'')_{\mathrm{Cl}}$	$\|F\|$	$\sigma(\|F\|)/\|F\|$ (%)	$\sigma_2(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ (%)
0·170	020	0·59	26·0	—	—
0·217	220	0·48	8·9	6·5	7·4
0·265	130	0·47	13·5	3·0	4·6
0·319	420	0·47	12·0	5·5	9·1
0·346	140	0·77	17·0	3·3	5·2
0·348	510	0·44	9·0	7·6	15·6
0·378	520	0·47	9·0	7·3	17·7
0·423	530	0·83	6·1	10·4	21·9
0·429	150	0·55	9·6	6·0	9·2
0·434	440	1·14	3·8	15·0	44·5
0·444	250	0·76	8·4	6·3	19·8
0·514	160	0·42	14·5	3·2	9·3
0·525	260	0·84	10·0	4·7	6·4
0·575	460	0·60	7·0	6·4	7·6
0·597	170	0·32	3·8	11·0	12·7
0·607	270	1·13	7·6	5·5	14·0
0·610	560	0·33	5·0	7·0	14·4
0·613	910	0·48	23·0	2·4	5·9
0·626	370	0·89	12·8	3·3	5·7
0·634	750	0·44	8·7	5·2	13·7
0·650	660	1·13	6·5	6·6	59·1
0·659	930	0·67	6·8	6·9	11·8
0·681	180	0·29	9·9	3·8	6·2
0·682	570	0·33	6·2	10·2	10·1
0·691	280	0·62	5·4	6·9	7·7
0·693	760	0·41	9·6	4·2	7·7
0·722	10,3,0	0·27	9·8	4·5	14·8
0·730	480	0·21	6·3	4·4	7·8
0·756	10,4,0	0·88	10·4	6·2	9·9
0·757	580	0·76	5·4	5·6	24·0
0·766	190	1·26	2·9	11·4	17·8
0·774	290	0·50	4·0	8·1	17·7
0·789	680	1·15	7·8	4·4	7·6
0·792	960	1·11	4·3	8·6	10·2
0·808	590	0·26	4·3	7·2	14·8
0·834	690	1·37	5·0	5·9	12·7
0·845	10,6,0	0·59	2·9	11·7	46·6
0·850	1,10,0	0·63	8·3	3·3	3·7
0·898	10,7,0	0·34	4·4	6·9	13·4
0·900	11,6,0	0·85	3·5	8·8	19·6
0·912	5,10,0	0·79	3·9	7·1	31·1
0·934	1,11,0	0·17	2·5	9·9	10·6
0·944	2,11,0	0·52	2·5	9·8	13·4

the individual atoms) by $(f\sigma_r)$. In practice, σ_{rj}^2 are inversely proportional to Z_j^2, Z_j being the number of electrons in an atom j, so that $(f\sigma_r)$ is nearly the same for all the atoms. The value of $(f\sigma_r)$ can be obtained from the values of σ_x and σ_y for the atomic positions in Ångströms given by Srinivasan (1959). Since the monoclinic angle β is very nearly equal to 90°, it can be taken that $\sigma_x=\sigma_y=\sigma_z=\sigma_r/\sqrt{3}$ and the average of σ_r for C, N and O comes out as $\sqrt{3}\times 0{\cdot}018$ Å. The value of $(f\sigma_r)$ was then obtained by taking the value of f for a nitrogen atom from the table, and the fractional errors $\sigma(|F|)/|F|$ so obtained are given in Table 2. It is also readily shown that the fractional error of the expression $(|F|^2/B)$ in equation (6) is

$$\sigma(|F|^2/B)/(|F|^2/B)=(2\pi^2N/3)^{1/2}((f\sigma_r)/Bd) \qquad (8)$$

Since, as already stated, the error in α_{Cl} is negligible, the fractional error of $(\Delta f_{\mathrm{Cl}}'')_{\mathrm{exp.}}$ will be equal to that of $(|F|^2/B)$ and hence

$$\sigma_2(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')=(2\pi^2N/3)^{1/2}(f\sigma_r/Bd) \qquad (9)$$

The fractional errors so obtained are also given in Table 2. It will be noticed that in general the errors increase with $(\sin\theta/\lambda)$ as expected from the factor $1/d$ in equation (9). They are also particularly large for those reflections with B small, i.e., with phase angles nearly 0° or 180°. From equations (5) and (9) the total fractional standard error $\sigma_{\mathrm{tot.}}(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ can be calculated from the formula

$$\sigma_{\mathrm{tot.}}^2=\sigma_1^2+\sigma_2^2 \qquad (10)$$

and the values of $\sigma_{\mathrm{tot.}}(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ so obtained are listed in Table 3. These have been applied to the observed data in Fig. 1 and are shown by the spreads of the vertical lines associated with each point.

In general, the trend of the errors in the observed data are explained by the possible errors in the measured value of the Bijvoet inequality and the atomic coordinates and there seems to be no indication of a variation of $\Delta f''$ with the scattering angle θ.

Table 3. *Calculation of* $\sigma_1(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ *and* $\sigma_{\mathrm{tot.}}(\Delta f_{\mathrm{Cl}}'')/\Delta f_{\mathrm{Cl}}'')$

hkl	*I*	$\sigma(I)$	ΔI	$\sigma_1(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ (%)	$\sigma_{\mathrm{tot.}}(\Delta f_{\mathrm{Cl}}'')/(\Delta f_{\mathrm{Cl}}'')$ (%)
020	292·43	8·77	49·27	25·1	25·1
220	44·72	1·34	7·98	23·8	24·9
130	84·22	2·53	11·17	32·0	32·3
420	30·21	0·91	3·62	35·4	36·5
140	68·05	1·96	12·47	22·2	22·8
510	15·72	0·47	1·16	57·4	59·5
520	20·94	0·63	2·47	36·0	40·1
530	5·52	0·17	1·01	23·1	32·4
150	15·18	0·46	1·94	33·2	34·4
440	2·18	0·11	0·89	16·3	47·3
250	12·84	0·39	2·23	24·4	31·4
160	23·90	0·07	1·27	8·0	12·3
260	11·56	0·34	1·89	25·1	25·9
460	5·83	0·17	1·39	17·8	19·3
170	0·75	0·38	0·16	33·6	35·9
270	4·27	0·13	1·04	17·1	22·1
560	2·11	0·08	0·44	27·0	30·6
910	40·27	1·21	2·18	78·3	78·5
370	10·30	0·31	2·15	20·3	21·1
750	6·39	0·19	0·44	62·1	63·6
660	2·11	0·08	0·44	26·6	64·8
930	2·23	0·07	0·75	12·4	17·1
180	10·55	0·32	0·75	59·3	57·9
570	2·00	0·06	0·13	64·2	65·0
760	6·67	0·20	0·60	46·8	47·4
10,3,0	5·80	0·17	0·19	126·8	127·0
480	1·72	0·05	0·07	98·6	98·9
10,4,0	6·60	0·20	0·60	46·8	47·8
580	1·90	0·06	0·30	28·3	37·1
190	0·20	0·01	0·13	15·0	23·3
290	0·64	0·03	0·13	15·0	23·2
680	4·14	0·12	1·46	12·0	14·2
960	0·89	0·04	0·22	22·4	24·6
590	1·47	0·06	0·06	146·5	147·3
690	1·96	0·08	0·25	44·9	46·7
10,6,0	1·14	0·04	0·14	42·4	63·0
1,10,0	4·12	0·12	0·86	20·3	24·7
10,7,0	2·13	0·06	0·20	36·2	38·6
11,6,0	1·49	0·08	0·54	19·5	27·6
5,10,0	0·74	0·04	0·09	58·0	65·8
1,11,0	1·79	0·09	0·44	28·8	30·7
2,11,0	1·20	0·06	0·15	56·2	57·8

Consequently, it was assumed that there was no such variation and the best value af $\Delta f''$ was obtained as below.

(*d*) *Best value for* $\Delta f''$

Out of all the measured values, particularly reliable measurements were chosen which satisfied the following conditions:

(i) $(\Delta I/I)_{\mathrm{exp.}}$ should be greater than 10%
(ii) $(\Delta I/I)_{\mathrm{th.}}$ should be greater than 10%
(iii) $|F|$ value should be greater than 5.

Conforming to these restrictions, there are about fifteen reflections and the corresponding values of $\Delta f_{\mathrm{Cl}}''$ are represented in Fig. 1 by circles. Using these values only, an average of $\Delta f_{\mathrm{Cl}}''$ was calculated, which came out to be $0{\cdot}67 \pm 0{\cdot}21$, in agreement with the wave-mechanical value of 0·66.

(*e*) *Absolute configuration of* L-*tyrosine*:

Incidentally, the absolute configuration of L-tyrosine hydrochloride was found out by using the standard procedure, which has been outlined by a number of workers (for instance, Raman, 1958) and is shown in Fig. 2. The configuration determined agrees with that assigned to the L-amino acids by chemists, according to the standard Fisher convention.

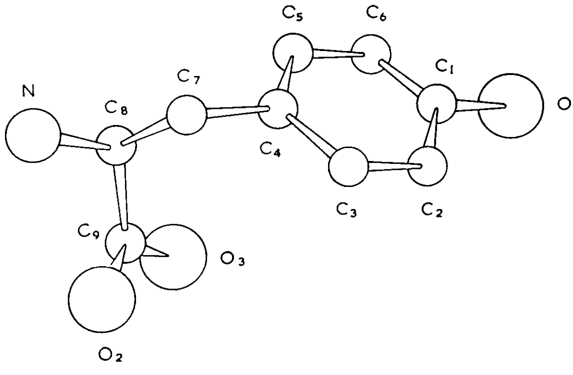

Fig. 2. Absolute configuration of L-tyrosine.

4. Conclusions

It has been shown that, although large variations often occur between the observed values of $(\Delta I/I)$ and those calculated from the structure, these can be reasonably explained by the possible errors in the measured value of the Bijvoet inequality and in atomic coordinates. It should be mentioned that the crystal structure used for the study had a fairly good accuracy (standard error in the coordinates of the light atoms was less than 0·02 Å), and yet large deviations by as much as a factor of 2 occur for weak reflectione at large values of $\sin\theta$. This is in agreement with theory (equation (9)) which shows that the error is particularly accentuated by both these factors, namely, high Bragg angle as well as the weakness of the reflection.

It is not quite certain that all the observed errors can be explained in this way and that no other cause is operative in modifying the anomalous scattering (imaginary component) of the chlorine atoms. However, if such an effect is operative in tyrosine hydrochloride, it is obvious that it does not materially matter for medium and strong reflections as shown by the reasonable agreement between theory and the experiment of the selected data mentioned in the last section. Consequently, the anomalous dispersion method can be confidently used for crystals like tyrosine hydrochloride which contain a large number of other atoms besides the anomalous scatterers. The mutual influence of the anomalous scatterers, if any, is likely to be small in such crystals because they are well separated.

It is very reassuring to report that in more than 90% of these cases, the sign of $\Delta f''$ obtained was correct. This means that the phase measured by the anomalous dispersion method would not be in error by more than ±90° in all these cases. The error would be much less in a majority of these cases. It appears desirable to study the distribution of errors in the phase angle obtained by the anomalous dispersion method. This is under investigation.

APPENDIX I

Since the structure belongs to the space group $P2_1$ there are only two chlorine atoms in the unit cell. The origin on the two-fold axis may therefore be chosen to be midway between the two chlorine atoms. Then the structure factor F may be written in the form

$$F=F_{Cl}+F_R \tag{A1}$$

in which F_{Cl} would be real, equal to A_{Cl}, if anomalous dispersion effects were neglected; but if they are included,

$$F_{Cl}=A_{Cl}+iA_{Cl}'' \tag{A2}$$

where

$$A_{Cl}''=2\Delta f_{Cl}''\cos\alpha_{Cl} \tag{A3}$$

and $\alpha_{Cl}=2\pi\mathbf{H}.\mathbf{r}_{Cl}$, $\mathbf{r}_{Cl}$ being the coordinate of the chlorine atom. Writing

$$F_R=A_R+iB_R \tag{A4}$$

we have

$$F=(A_R+A_{Cl})+i(A_{Cl}''+B_R) \tag{A5}$$

For the inverse reflection,

$$\overline{F}_R=A_R-iB_R$$

but

$$\overline{F}_{Cl}=A_{Cl}+iA_{Cl}''$$

so that

$$\overline{F}=(A_R+A_{Cl})+i(A_{Cl}''-B_R) \tag{A6}$$

Combining (A5) and (A6), we have

$$\Delta|F|^2=|F|^2-|\overline{F}|^2=4A_{Cl}''B_R=4A_{Cl}''B \tag{A7}$$

as $B_{Cl}=0$. Equation (1) follows from (A7).

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