Table 2. *Coordinates for* C_7, C_8 *and* C_9 *hydrazides*

	C_7		C_8		C_9
	x (Å)	z (Å)	x (Å)	z (Å)	y (Å)
C_1	3·56	1·57	0·33	1·57	1·57
C_2	3·13	2·85	0·94	2·87	0·96
C_3	3·88	4·11	0·39	4·12	1·48
C_4	3·46	5·38	0·97	5·37	0·98
C_5	4·21	6·65	0·44	6·64	1·67
C_6	3·78	7·91	1·03	7·92	0·92
C_7	4·28*	9·25*	0·44	9·20	1·60
C_8	—	—	1·13*	10·60*	0·95
C_9	—	—	—	—	1·99*
O	4·28*	9·25*	1·13*	10·60*	1·99*
N_1	5·16	10·00	1·66*	11·29*	0·91
N_2	5·97	11·18	2·41	12·48	1·24

* Not resolved in F projection.

C_8 hydrazides and $\{0kl\}$ for C_9 hydrazide. The Δd_{001} values indicate that the chains are very nearly normal to (001). Bragg–Lipson charts were used to determine the approximate structure. Electron densities were computed at units of $a/60$, $b/30$ and $c/120$ using Patterson–Tunell strips. The third F syntheses on (010) for C_7 and C_8 hydrazides (116 and 98 terms respectively) are shown in Fig. 2, and the first F synthesis on (100) for C_9 hydrazide (50 terms) is shown in Fig. 3. Approximate coordinates derived from these projections are listed in Table 2.

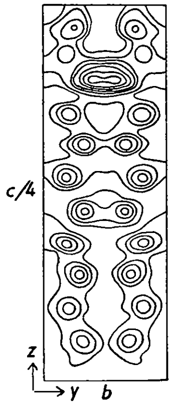

Fig. 3. Projection on (100) for C_9 hydrazide. Contours at arbitrary intervals of electron density.

Although these results are preliminary and not very accurate, some conclusions can be reached. The structures of these compounds with either an even or odd number of carbon atoms in the chain appear almost the same in (010) projection. There seem to be no consistent irregularities in bond lengths along the chains, nor do the rather short chains appear to deviate from linearity.

The C_8 and C_9 hydrazides have been chosen for further study and three-dimensional integrated data have been collected for the C_9 compound.

The authors express appreciation to Mr Clifford Roth and Dr Wayne Chen, who performed most of the numerical work, and to the Agnes H. Anderson Fund for support of the early part of this work.

Reference

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* 3, 210.

Acta Cryst. (1953). **6**, 301

Anisotropic temperature factors in *hkl* structure-factor calculations.

By D. R. Holmes, *Imperial Chemical Industries Ltd, Plastics Division, Research Department, Welwyn Garden City, Herts., England*

(*Received* 13 *October* 1952 *and in revised form* 1 *December* 1952)

In recent crystal-structure analyses it has been found necessary to apply anisotropic temperature factors, either to the structure factors as a whole (Hughes, 1941) or to the structure-factor contributions of particular atoms (Cochran, 1951*a*). Effects closely similar to those of asymmetric thermal vibrations are produced on the observed structure factors of crystals containing atoms whose electron clouds show appreciable departures from spherical symmetry owing to their bonding arrangements. Difference syntheses (Cochran, 1951*b*) enable one to find the direction of maximum thermal vibration (or maximum departure from spherical electron density) and the magnitude of the constants involved, and Cochran himself has shown how to apply anisotropic temperature factors in two-dimensional structure-factor calculations. The purpose of this note is to show that, by making certain assumptions about the symmetry of the electron-density clouds, such factors may easily be applied to the calculations of general *hkl* structure factors required by accurate crystal-structure analyses. The analysis given applies only to cases in which the vibration ellipsoid of the atom (or electron-density ellipsoid) is an ellipsoid of revolution. The ellipsoid is treated as a linear vibration imposed on a spherically symmetrical vibration, and the effects of both are considered separately. This limitation was imposed so that the final result could be used in a practical case by a simple graphical interpretation.

For the sake of simplicity of explanation the formula will be deduced for a monoclinic crystal, but it may easily be generalized to the triclinic case. Only the linear vibration is considered.

Fig. 1(a) shows the basal plane of a monoclinic unit cell and Fig. 1(b) is the corresponding reciprocal-lattice plane in its proper orientation. Let OQ (shown on both figures) be the direction of linear vibration of a particular atom or set of atoms and let OM be its projection on to the basal plane. We require to find the angle β_{hkl} between OQ and the normal to the crystallographic plane (hkl), i.e. the angle between OQ and the line joining O to the reciprocal-lattice point P_{hkl}. Choose axes Ox, Oz in the plane a^*Oc^* such that Ox lies along OM and Oz is perpendicular to OM. The third axis is coincident with the ζ axis of reciprocal space and we have $y = \zeta$ and $\xi = \sqrt{(x^2+z^2)}$.

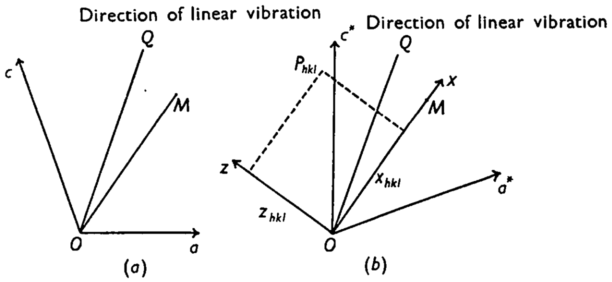

Fig. 1. (a) Real space. (b) Reciprocal space.

Let the direction cosines of OQ be $p_x, p_y, 0$ (p_z is zero by the choice of axes).

The direction cosines of OP_{hkl} are $x_{hkl}/2\sin\theta_{hkl}$, $\zeta_k/2\sin\theta_{hkl}$, $z_{hkl}/2\sin\theta_{hkl}$, where θ_{hkl} is the Bragg angle for the (hkl) reflexion, ζ_k is the ζ value for the kth layer line,

and
$$\cos\beta_{hkl} = \frac{p_y\zeta_k + x_{hkl}p_x}{2\sin\theta_{hkl}}\,. \qquad (1)$$

The angle β may be required as the inclination of the scattering normal to a molecular orbital in McWeeny's treatment of the modifications to scattering curves demanded by the asymmetric electron clouds of real atoms (McWeeny, 1951). The evaluation of β_{hkl} for each reflexion requires only the measurement of x_{hkl}, the x coordinate of the point P_{hkl}, on the zero layer of the reciprocal lattice; x_{hkl} is of course independent of layer line for monoclinic or higher symmetries, p_y and p_x are calculated once and for all when the direction of linear vibration is decided upon, and ζ and $\sin\theta_{hkl}$ are usually known from previous measurements for other purposes.

Let a particular atom A have a mean-square displacement $\overline{u_q^2}$ in the direction OQ.

Then the mean-square displacement of $A(\overline{u_s^2})$ in a direction perpendicular to the plane (hkl) is given by

$$\overline{u_s^2} = \overline{u_q^2}\cos^2\beta_{hkl}\,. \qquad (2)$$

The result given by James (1948, equation $1{\cdot}33$) states that an (hkl) structure factor is reduced by thermal vibrations by an amount $\exp[-M]$,

where
$$M = 8\pi^2\overline{u_s^2}\,(\sin^2\theta_{hkl})/\lambda^2\,. \qquad (3)$$

Thus we have

$$M = 8\pi^2\overline{u_q^2}\cos^2\beta_{hkl}\,(\sin^2\theta_{hkl})/\lambda^2\,, \qquad (4)$$

or, substituting for $\cos\beta$,

$$M = 2\pi^2\frac{\overline{u_q^2}}{\lambda^2}\,(p_y\zeta_k + x_{hkl}p_x)^2\,. \qquad (5)$$

This may be simplified to

$$M = D(p_y\zeta_k + x_{hkl}p_x)^2\,, \qquad (6)$$

where D is a constant having the value $2\pi^2\overline{u_q^2}/\lambda^2$.

If, as often happens, the direction of linear vibration lies in the basal plane, then $p_y = 0$ and the expression is further simplified to

$$M = Dx_{hkl}^2p_x^2\,. \qquad (7)$$

In this special case all reflexions with the same h and l values are reduced by the same amount, regardless of their k indices (i.e. of the layer line on which they fall).

Equation (7) represents the asymmetric part of the temperature factor given by Cochran (1951a, equation (3)). The difference in the treatment given above is that the isotropic temperature factor (depending only on $\sin\theta$) has been ignored and that now the expression for the asymmetric temperature factor applies to all layer lines for monoclinic or higher symmetries.

In the general triclinic case the same procedure is followed and axes Ox, Oz, are always chosen in the zero layer of the reciprocal lattice such that the plane yOx contains the direction of linear vibration. In this case the reducing factor for a structure factor is

$$\exp\left[-2\pi^2\overline{u_q^2}(p_y\zeta_k + p_xx_{hkl})^2\right]; \qquad (8)$$

p_x, p_y and 0 are the direction cosines of the direction of maximum vibration, ζ_k is the height in the reciprocal lattice of the kth layer line and x_{hkl} is the x co-ordinate of the hkl lattice point. Once again the x's may be measured on the zero layer of the reciprocal lattice but they will have to be increased by a constant $k\alpha$ for the kth layer to allow for the shift in the layer origin (see Bunn, 1945, for the evaluation of α).

The method has been applied by the author in the evaluation of the three-dimensional structure factors of polycaproamide. The structure, which will be fully described in a later paper, is monoclinic and consists of hydrogen bonded sheets of long-chain molecules, and, as might be expected, the thermal vibrations are anisotropic, the direction of maximum vibration being perpendicular both to the plane of the sheets and to the b axis. The reducing factors for 115 structure factors distributed on eight layer lines were calculated in two hours with the use of a zero-layer reciprocal lattice, square and exponential tables and a multiplying machine.

References

Bunn, C. W. (1945). *Chemical Crystallography*. Oxford: Clarendon Press.

Cochran, W. (1951a). *Acta Cryst.* **4**, 81.

Cochran, W. (1951b). *Acta Cryst.* **4**, 408.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.