between the trigonal prisms formed by the hydroxyl and oxygen ions of adjacent layers, and escape attention in the electron-density diagram because of its small scattering power. Were this the case, the aluminium layer would be a normal hydrargillite one, and, because of the systematic 'holes', the *b* axis would need to be $3 \times 2\cdot91 = 8\cdot73$ Å. Strongly exposed Weissenberg films taken about the *a* axis give, however, no evidence of a larger unit cell. The same argument proves that the lithium ions cannot occur systematically in sites corresponding to the holes of the hydrargillite layer, but are randomly distributed with the aluminiums over all the sites in a layer of the brucite type.

The manganese–oxygen layer is also composed of octahedra linked together in a closely bonded sheet. This is a most unusual grouping for a tetravalent oxide, and the octahedra, like those comprising the aluminium layer, are grossly distorted owing to the six short edges of each which are shared with its neighbours. The mean lengths of the shared edges, 2·56 Å for each layer, are in good agreement with values found for other compounds in which an O–O pair is shared by two cations of high valency (Pauling, 1940, p. 400).

The hydroxyl bond

An examination of the variations in the OH–OH distances of hydrargillite led Bernal & Megaw (1935) to define the role of hydrogen in intermolecular forces. The characteristic stacking of the $Al(OH)_6$ sheets in hydrargillite was due to the location of hydrogen atoms between the layers to form hydroxyl bonds. The hydrogen atoms themselves were closely associated with oxygen atoms to retain the identity of the (OH) groups.

It has been pointed out above that the stacking of the layers in lithiophorite resembles that of hydrargillite. The distance between adjacent O and (OH) ions is 2·76 Å, in good agreement with the length of the hydroxyl bond given by Bernal & Megaw as 2·7–2·8 Å. It appears, therefore, that the hydrogen atoms of the (Al, Li) layer are directed towards the oxygen ions beneath so as to form hydroxyl bonds, which may be readily disrupted to cause the prominent basal cleavage. The directions of the hydroxyl bonds are given as thick broken lines in Fig. 2.

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An Extension of the Use of Intensity Statistics

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The description, given by Taylor, of the optical basis of Wilson's statistical method for detecting centrosymmetry in a crystal suggests that there are certain conditions under which exceptions may arise. One of these exceptions—a structure with centrosymmetrical molecules arranged centrosymmetrically—gives a more extreme distribution of intensities than does an ordinary centrosymmetrical structure. It is proposed to call this distribution 'hypercentric', and its recognition may lead to useful preliminary information at the outset of a structure determination. The theory of the hypercentric distribution is discussed, and some examples of crystals in which it occurs are given.

1. The hypercentric distribution

The statistical analysis, introduced by Wilson (1949) and developed by Howells, Phillips & Rogers (1950), has provided an extremely powerful addition to the usual methods for determining space groups. As Wilson has pointed out, however, the success of the method depends upon the randomness of the distribution of the atoms within the unit cell; thus it might be expected that the presence of non-crystallographic symmetry in the atomic arrangement might lead to misleading results. A simple illustration of this is provided by consideration of the optical basis of Wilson's theory described by Taylor (1952).

Taylor has shown that the Fraunhofer diffraction pattern of a centrosymmetrical set of holes contains a greater proportion of extreme intensities—high peaks and zeros—than that of a non-centrosymmetrical set. Suppose, however, that a crystal contains centrosymmetrical molecules in general positions in a centrosymmetrical space group. It can easily be seen that such molecules must be exactly parallel, and thus the diffraction pattern of the pair of molecules will be crossed by equally spaced sinusoidal fringes; in other words, an additional set of zeros is superimposed on the zeros present in the diffraction pattern of the single molecule. Thus the intensity distribution would not follow the curve for ordinary centrosymmetrical structures.

This deduction is supported by an analysis of the data from pyrene (Robertson & White, 1947), 1:1:6:6-tetraphenyl hexapentaene, and flavanthrone; the first two crystals have four molecules (Fig. 1(*a*) and 1(*b*)) in the unit cell of space group $P2_1/a$, and, although the latter has only two molecules in the unit cell, each molecule (Fig. 1(*c*)) can be regarded as composed of two centrosymmetrical parts. The *h*0*l* distribution curves for these three crystals are shown in Fig. 2, and it will be seen that the points lie well above the curve for a centric distribution.

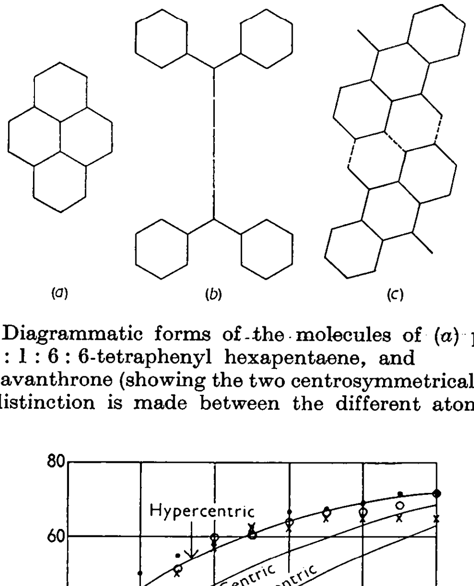

Fig. 1. Diagrammatic forms of the molecules of (*a*) pyrene, (*b*) 1 : 1 : 6 : 6-tetraphenyl hexapentaene, and (*c*) flavanthrone (showing the two centrosymmetrical parts). No distinction is made between the different atoms.

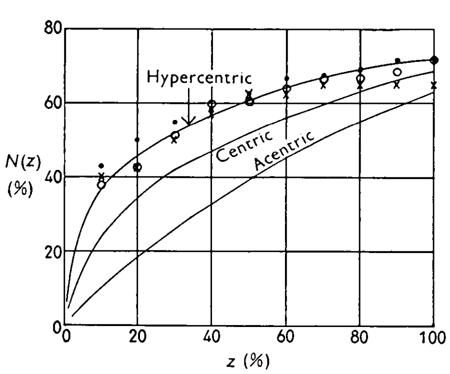

Fig. 2. Intensity distribution curves for pyrene (×), 1 : 1 : 6 : 6-tetraphenyl hexapentaene (○) and flavanthrone (•) (cf. Fig. 1) compared with the curves for acentric, centric and hypercentric zones.

2. Theory of the hypercentric distribution

Consider a crystal with N atoms in sets of four with coordinates $\pm(x+x',\ y+y',\ z+z')$, $\pm(x-x',\ y-y',\ z-z')$, where $\pm(x', y', z')$ are the coordinates of the molecular centres of symmetry relative to that of the unit cell.

The combined contribution of such a set of atoms to the structure factor at any point in the Fourier transform of the pair of molecules is

$$\xi_n = f_n \cos 2\pi\mathbf{s}.\mathbf{r} \times \cos 2\pi\mathbf{s}.\mathbf{r}' \,, \qquad (1)$$

where

$$\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \,,$$
$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \,,$$
$$\mathbf{r}' = x'\mathbf{a} + y\mathbf{b} + z\mathbf{c} \,.$$

The factor $\cos 2\pi\mathbf{s}.\mathbf{r}'$ defines the planes of zero intensity which occur in the transform of a hypercentric structure, as mentioned in § 1.

Within a thin section of the transform for which $\cos 2\pi\mathbf{s}.\mathbf{r}'$ is constant this gives a normal distribution of structure factors about the mean value of zero and with mean square deviation

$$\sigma^2 = \sum_{n=1}^{\frac{1}{4}N} \xi^2 = 2 \cos^2 2\pi\mathbf{s}.\mathbf{r}' \times \Sigma \,,$$

where

$$\Sigma = \sum_{n=1}^{N} f_n^2 \,.$$

The probability, within this section of the transform, that the structure factor at any point lies between F_s and $F_s + dF_s$ is

$$P(F_s)dF_s$$
$$= (4\pi\Sigma)^{-\frac{1}{2}} \exp\left(-F_s^2 \sec^2 2\pi\mathbf{s}.\mathbf{r}'/4\Sigma\right) \sec 2\pi\mathbf{s}.\mathbf{r}' dF_s \,.$$

The probability of finding a structure factor between F and $F+dF$ in the whole transform is

$$P(F)dF$$
$$= \tfrac{1}{2}(4\pi\Sigma)^{-\frac{1}{2}} \int_{-1}^{u=1} \exp\left(-F^2 \sec^2 \tfrac{1}{2}\pi u/4\Sigma\right) \sec \tfrac{1}{2}\pi u \, dF du$$
$$= 2\pi^{-1}(4\pi\Sigma)^{-\frac{1}{2}} \int_{0}^{t=\infty} \exp\left\{-F^2(1+t^2)/4\Sigma\right\}(1+t^2)^{-\frac{1}{2}} dF\, dt \,,$$

where $u = 4\mathbf{s}.\mathbf{r}'$ and $t = \tan \frac{1}{2}\pi u$.

In terms of intensity

$$P(I)dI$$
$$= \pi^{-1}(4\pi\Sigma I)^{-\frac{1}{2}} \int_{0}^{t=\infty} \exp\left\{-I(1+t^2)/4\Sigma\right\}(1+t^2)^{-\frac{1}{2}} dI dt \,.$$

From (1) it is easily deduced that the mean intensity $\langle I \rangle$ of the transform is

$$2\Sigma \times \text{ mean value of } \cos^2 2\pi \mathbf{s}.\mathbf{r}'\,.$$

Hence

$$\langle I \rangle = \Sigma\,.$$

If we put $I/\langle I \rangle = z$,

$$P(z)dz = \pi^{-1}(4\pi z)^{-\frac{1}{2}} \int_0^{t=\infty} \exp\{-\tfrac{1}{4}z(1+t^2)\}(1+t^2)^{-\frac{1}{2}}dt\,dz\,.$$

The proportion of intensities lower than z is

$$N(z) = \pi^{-1}(4\pi)^{-\frac{1}{2}} \int_0^{z=z} \int_0^{t=\infty} z^{-\frac{1}{2}} \exp -\{\tfrac{1}{4}z(1+t^2)\}(1+t^2)dt\,dz\,.$$

Let $z = 2\alpha^2/(1+t^2)$, then

$$N(z) = \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_0^{\alpha=\{\frac{1}{2}z(1+t^2)\}^{\frac{1}{2}}} \int_0^{t=\infty} \exp(-\tfrac{1}{2}\alpha^2)(1+t^2)^{-1}dt\,dz\,.$$

We may put $\dfrac{1}{\sqrt{(2\pi)}}\displaystyle\int_0^K \exp(-\tfrac{1}{2}\alpha^2)d\alpha = \varphi(K)$, which is a common statistical integral and well tabulated (e.g. Weatherburn, 1947, p. 46). Then

$$N(z) = \frac{4}{\pi}\int_0^\infty \varphi\{\tfrac{1}{2}z(1+t^2)\}^{\frac{1}{2}}(1+t^2)^{-1}dt\,.$$

This function is shown graphically in Fig. 2 and it will be seen that the points for the three crystals mentioned in § 1 lie reasonably close to the curve.

It should be noted that the above treatment applies strictly to the intensity distribution of the transform of a single unit cell and applies to the intensities of reciprocal-lattice points only when these are a fair sample of the whole transform. In the special case of a glide plane parallel to the plane of projection, for example, the distribution of the transform intensity will be that of the normal hypercentric case. The reciprocal lattice, however, samples the transform in a very special way, namely, at points on the planes defined by $\cos 2\pi\mathbf{s}.\mathbf{r}' = \pm 1$ or 0 and the distribution for these points does not follow the hypercentric theory. The systematic absences should be ignored and the remaining points give the normal centric distribution (Howells, Phillips & Rogers, 1950).

3. Causes of departure from ordinary distribution

The above results suggest that the acentric, centric and hypercentric distributions are special cases of a family of curves which correspond to different 'degrees' of symmetry. Thus it may still be possible to extract some information from a zone of intensities even if it gives no clear indication of the space group; the approach to one or other of the different curves may be due to molecular, rather than crystallographic, symmetry. For example, the $0kl$ intensities for di-*p*-anisyl nitric oxide (Hanson, Taylor & Lipson, 1952) give the distribution curve shown in Fig. 3, and this suggests that the projection is centrosymmetrical. Systematic absences show that the space group is either *Abam* or *Aba*2, and since there are only four molecules (Fig. 4) in the unit cell, the former is impossible, since it would require the molecule to have symmetry $2/m$. The latter space group, however, has not a centrosymmetrical projection on (100). The simulation of the higher symmetry is largely due to the fact that the molecule may be considered to consist approximately of two centrosymmetrical parts.

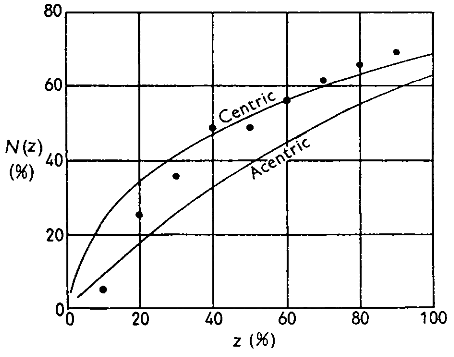

Fig. 3. Distribution curve for di-*p*-anisyl nitric oxide.

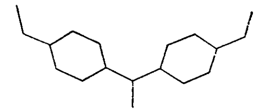

Fig. 4. Diagrammatic form of the molecule of di-*p*-anisyl nitric oxide.

If considerations of this sort are borne in mind, it is possible that the use of intensity statistics will have as great an importance in the study of the atomic positions in a structure as they have already been shown to have in distinguishing between space groups.

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