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The Effect of Heavy Atoms on the Wilson-Ratio Test for Distinguishing between Centrosymmetric and Non-centrosymmetric Structures

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On the basis of the probability distributions of structure factors for unit cells containing heavy atoms, values of $\varrho = \langle|F|\rangle^2/\langle|F|^2\rangle$ have been derived in terms of $r = (\Sigma_H/\Sigma_L)^{\frac{1}{2}}$, where $\Sigma = \Sigma f_i^2$, and the summations are respectively over all the heavy atoms (H) and the light atoms (L) in the unit cell. In some circumstances values of ϱ very different from those given by Wilson are obtained.

1. Introduction

In the first of many papers on the probability distributions of X-ray intensities Wilson (1949) derived by means of the central limit theorem (Cramér, 1937, pp. 56–60), the distributions corresponding to a large number of atoms arranged randomly in centrosymmetrical and non-centrosymmetrical unit cells, subject to the condition that no one part of the structure dominates the scattering. From the derived distributions Wilson showed that the ratio ϱ, defined by

$$\varrho = \langle|F|\rangle^2/\langle|F|^2\rangle ,$$

assumed the values $2/\pi = 0{\cdot}6366$ and $\pi/4 = 0{\cdot}7854$ for centrosymmetrical and non-centrosymmetrical structures respectively, and suggested that this ratio could be used to differentiate between the two types of structure.

In a later paper Howells, Phillips & Rogers (1950) showed that a number of structures gave experimental values for ϱ in good agreement with the theoretical values, though it was recognized that the values given by Wilson are ideal limiting values and that in real crystals, especially when heavy atoms dominating the scattering are present, significant deviations from these values can occur. In the case of the centrosymmetrical (010) projection of *l*-ephedrine hydrobromide, $C_{10}H_{16}ONBr$, for example, a value of 0·695 was obtained for ϱ, whereas in the case of the hydrochloride a value of 0·647, which is considerably nearer to the theoretical value, was obtained.

As an alternative to the ratio test, these authors suggested the use of the integral distribution function $N(z)$, defined as the fraction of reflexions with $I/\langle I\rangle$ less than or equal to z, and derived expressions for this function for both the centrosymmetrical and non-centrosymmetrical cases.

The question of the effect on the expected $N(z)$ distributions of the presence of atoms of large atomic number in a structure composed largely of atoms of smaller atomic number has been discussed by a number of later authors. The important cases for consideration are those in which the asymmetric unit contains one heavy atom or less, and there are then three cases, corresponding to the heavy-atom contribution taking one of the forms

$$(1)\ f_H,\quad (2)\ f_H\cos\varphi_H,\quad (3)\ f_H\cos\varphi_H\cos\theta_H .$$

Hargreaves (1955) has derived $N(z)$ distributions corresponding to these cases for structures containing one atom only in the asymmetric unit, and has denoted them by ${}_{\max.}N(z)$, ${}_{c}N(z)$, ${}_{cc}N(z)$. Collin (1955) and Sim (1958) have discussed the case of heavy atoms in fixed positions, and the latter has given a table of $N(z)$ distributions for a triclinic cell containing one heavy atom and a number of light atoms, in terms of the parameter r defined by

$$r = f_H/\Sigma_L^{\frac{1}{2}} ,$$

where

$$\Sigma_L = \sum_{i=1}^{m} f_i^2$$

is a summation over the m light atoms in the unit cell.

In the present paper the effect of heavy atoms on the Wilson-ratio test is considered for both the oblique and rectangular plane groups, and a table of values of ϱ for the various cases is given. Where the unit cell contains more than one heavy atom the parameter r is defined by

$$r = (\Sigma_H/\Sigma_L)^{\frac{1}{2}} ,$$

where

$$\Sigma_H = \sum_{j=1}^{n} f_j^2$$

is a summation over the n heavy atoms in the unit cell.

Corresponding to the three types of heavy-atom contribution, the test ratio ϱ will be denoted by

$$(1)\ {}_{\max.}\varrho_{1,r} \text{ and } {}_{\max.}\varrho_{\bar{1},r},\quad (2)\ {}_{c}\varrho_{1,r} \text{ and } {}_{c}\varrho_{\bar{1},r},$$
$$(3)\ {}_{cc}\varrho_{\bar{1},r} ,$$

where 1 and $\bar{1}$ refer to non-centrosymmetric and centrosymmetric structures respectively.

2. Oblique projections containing one heavy atom

2·1. *Plane group p*1

Let the unit cell contain one heavy atom (H) and a number m of light atoms (L), and choose the origin on the heavy atom so that

$$F(hk) = x+iy ,$$

where

$$x = f_H+\sum_{i=1}^{m} f_i \cos 2\pi(hx_i+ky_i) ,$$

$$y = \sum_{i=1}^{m} f_i \sin 2\pi(hx_i+ky_i) .$$

The probability $p(|F|)d|F|$ of obtaining a value of $|F|$ between $|F|$ and $|F|+d|F|$ is then (Sim, 1958),

$$p(|F|)d|F| = 2|F|(\Sigma_L)^{-1} \exp [-(|F|^2+f_H)^2/\Sigma_L] \times I_0(2f_H|F|/\Sigma_L)d|F| .$$

The average value of $|F|$, denoted by $\langle|F|\rangle$, is (cf. Rice, 1954, p. 251),

$$\begin{aligned}\langle|F|\rangle &= \int_0^\infty |F|p(|F|)d|F| \\ &= \Sigma_L^{\frac{1}{2}}\Gamma(3/2) \exp [-f_H^2/2\Sigma_L] \\ &\quad \times [(1+f_H^2/\Sigma_L)I_0(f_H^2/2\Sigma_L) \\ &\quad + (f_H^2/\Sigma_L)I_1(f_H^2/2\Sigma_L)] \\ &= \tfrac{1}{2}(\pi\Sigma_L)^{\frac{1}{2}} \exp (-r^2/2)[(1+r^2)I_0(r^2/2) \\ &\quad + r^2 I_1(r^2/2)] .\end{aligned}$$

In the above equations $I_0(x)$ and $I_1(x)$ are respectively the zero-order and first-order Bessel functions with imaginary argument (Watson, 1922, p. 77).

Since

$$\langle|F|^2\rangle = \Sigma_L+f_H^2 ,$$

it follows that

$$_{\max.}\varrho_{1,r} = \langle|F|\rangle^2/\langle|F|^2\rangle$$

is given by

$$_{\max.}\varrho_{1,r} = \tfrac{1}{4}\pi(1+r^2)^{-1} \exp (-r^2)[(1+r^2)I_0(r^2/2) + r^2 I_1(r^2/2)]^2 .$$

When $r = 0$, $_{\max.}\varrho_{1,r} = \frac{1}{4}\pi = 0{\cdot}7854$.

When $r \to \infty$, $_{\max.}\varrho_{1,r} \to 1$.

Values of $_{\max.}\varrho_{1,r}$ for various values of r are listed in Table 1.

2·2. *Plane group p*2

The unit cell contains one heavy atom (H) and m light atoms (L) so that the heavy atom must be placed on the centre of symmetry at the origin, there are $m/2$ light atoms in the asymmetric unit and

$$F(hk) = f_H+2\sum_{i=1}^{m/2} f_i \cos 2\pi(hx_i+ky_i) .$$

Table 1. *Values of the test ratio* ϱ *as a function of* r

r	$_{\max.}\varrho_{\bar{1},r}$	$_{\max.}\varrho_{1,r}$	$c\varrho_{\bar{1},r}$	$c\varrho_{1,r}$	$cc\varrho_{\bar{1},r}$
0·0	0·6366	0·7854	0·6366	0·7854	0·6366
0·5	0·6417	0·7899	0·6403	—	—
1·0	0·6805	0·8217	0·6660	0·7993	—
1·5	0·7475	0·8685	0·7040	—	—
2·0	0·8137	0·9076	0·7356	0·8171	—
2·5	0·8648	0·9343	0·7572	—	—
3·0	0·9005	0·9517	0·7712	0·8197	—
4·0	0·9412	0·9711	0·7871	0·8189	—
5·0	0·9615	0·9810	0·7952	0·8177	—
∞	1·0000	1·0000	0·8106	0·8106	0·6570

$$p(|F|)d|F| = (2\pi\Sigma_L)^{-\frac{1}{2}} \{\exp [-(|F|-f_H)^2/2\Sigma_L] + \exp [-(|F|+f_H)^2/2\Sigma_L]\} d|F| .$$

$$\begin{aligned}\langle|F|\rangle &= \int_0^\infty |F|p(|F|)d|F| \\ &= (2\pi\Sigma_L)^{-\frac{1}{2}} \int_{-r}^{\infty} (\Sigma_L^{\frac{1}{2}}x+f_H)\Sigma_L^{\frac{1}{2}} \exp (-x^2/2)dx \\ &\quad + (2\pi\Sigma_L)^{-\frac{1}{2}} \int_r^\infty (\Sigma_L^{\frac{1}{2}}x-f_H)\Sigma_L^{\frac{1}{2}} \exp (-x^2/2)dx \\ &= 2(\Sigma_L/2\pi)^{\frac{1}{2}} \exp (-r^2/2)+2f_H\varphi(r) ,\end{aligned}$$

where

$$\varphi(r) = (2\pi)^{-\frac{1}{2}} \int_0^r \exp (-u^2/2)du .$$

Since

$$\langle|F|^2\rangle = f_H^2+\Sigma_L ,$$

it follows that the test ratio $\langle|F|\rangle^2/\langle|F|^2\rangle$ is given by

$$_{\max.}\varrho_{\bar{1},r} = 4[(2\pi)^{-\frac{1}{2}} \exp (-r^2/2)+r\varphi(r)]^2[1+r^2]^{-1} .$$

When $r = 0$, $_{\max.}\varrho_{\bar{1},r} = 2/\pi = 0{\cdot}6366$.

When $r \to \infty$, $_{\max.}\varrho_{\bar{1},r} \to 1$.

Values of $_{\max.}\varrho_{\bar{1},r}$ are given in Table 1.

3. Oblique projections containing two heavy atoms

3·1. *Plane group p*1

Let the unit cell contain two heavy atoms (H) and m light atoms (L), and choose the origin midway between the heavy atoms so that

$$F(hk) = x+iy ,$$

where

$$x = 2f_H X+\sum_{i=1}^{m} f_i \cos 2\pi(hx_i+ky_i) ,$$

$$y = \sum_{i=1}^{m} f_i \sin 2\pi(hx_i+ky_i) ,$$

$$X = \cos 2\pi(hx_H+ky_H) .$$

The probability $p(X)dX$ of obtaining a value of X between X and $X+dX$ is

$$p(X)dX = dX/\pi(1-X^2)^{\frac{1}{2}} ,$$

and the probability $p_X(|F|)d|F|$ of obtaining a value of $|F|$ between $|F|$ and $|F|+d|F|$ for fixed X is

$$p_X(|F|)d|F| = 2|F|(\Sigma_L)^{-1}\exp[-(|F|^2+4f_H^2X^2)/\Sigma_L] \times I_0(4f_H X|F|/\Sigma_L)d|F| .$$

Since

$$p(|F|)d|F| = \int_{X=-1}^{1} p_X(|F|)d|F|p(X)dX$$

and

$$\langle|F|\rangle = \int_0^\infty |F|p(|F|)d|F| ,$$

it follows that

$$\langle|F|\rangle = \int_{X=-1}^{1}\int_{|F|=0}^{\infty} |F|p_X(|F|)p(X)dX\,d|F| .$$

Substitute $X = \sin\alpha$ and

$$\langle|F|\rangle = (4/\pi\Sigma_L)\int_0^{\pi/2}\int_0^\infty |F|\exp[-|F|^2+4f_H^2\sin^2\alpha)/\Sigma_L] \times I_0(2f_H|F|\sin\alpha/\Sigma_L)d\alpha\,d|F| .$$

$$= (\Sigma_L/\pi)^{\frac{1}{2}}\int_0^{\pi/2} R_1(\alpha)d\alpha ,$$

where

$$R_1(\alpha) = \exp(-r^2\sin^2\alpha)[(1+2r^2\sin^2\alpha)I_0(r^2\sin^2\alpha) + (2r^2\sin^2\alpha)I_1(r^2\sin^2\alpha)] .$$

As

$$\langle|F|^2\rangle = 2f_H^2+\Sigma_L ,$$

$$_c\varrho_{1,r} = [\pi(1+r^2)]^{-1}\left[\int_0^{\pi/2} R_1(\alpha)d\alpha\right]^2 .$$

When $r = 0$, $_c\varrho_{1,r} = \pi/4 = 0{\cdot}7854$.

When $r \to \infty$, $_c\varrho_{1,r} \to 8/\pi^2 = 0{\cdot}8106$.

Values of $_c\varrho_{1,r}$ for various values of r are given in Table 1.

3·2. *Plane group p2*

Following the methods used in §§ 2·2 and 3·1, there is obtained

$$_c\varrho_{\bar{1},r} = (4/\pi)^2(1+r^2)^{-1}\left[\int_0^{\pi/2} R_2(\alpha)d\alpha\right]^2 ,$$

where

$$R_2(\alpha) = (2\pi)^{-\frac{1}{2}}\exp(-r^2\sin^2\alpha) + (\sqrt{2}.r\sin\alpha)\varphi(\sqrt{2}.r\sin\alpha) .$$

When $r = 0$, $_c\varrho_{\bar{1},r} = 2/\pi = 0{\cdot}6366$.

When $r \to \infty$, $_c\varrho_{\bar{1},r} \to 8/\pi^2 = 0{\cdot}8106$.

Values of $_c\varrho_{\bar{1},r}$ are given in Table 1.

4. Rectangular projections

4·1. *Plane groups pm, pg, cm*

For the case of one heavy atom in the asymmetric unit the analysis given in § 3·1 and the results tabulated under $_c\varrho_{1,r}$ apply.

4·2. *Plane groups pmm, pmg, pgg, cmm*

With one heavy atom in the asymmetric unit

$$F = 4(8)f_H\begin{matrix}\cos\\ \sin\end{matrix}hx_H\begin{matrix}\cos\\ \sin\end{matrix}ky_H + 4(8)\sum_{i=1}^{m/4(8)} f_i\begin{matrix}\cos\\ \sin\end{matrix}hx_i\begin{matrix}\cos\\ \sin\end{matrix}ky_i ,$$

where the value 8 corresponds to *cmm* and the value 4 to the other plane groups.

In the limiting case when $r = \infty$

$$F = 4(8)f_H X ,$$

where

$$X = \begin{matrix}\cos\\ \sin\end{matrix}hx_H\begin{matrix}\cos\\ \sin\end{matrix}ky_H ,$$

and

$$p(|X|)d|X| = (4/\pi^2)K(1-|X|^2)^{\frac{1}{2}}d|X| ,$$

where K is the complete elliptic integral of the first kind. Values of K are tabulated by, among others, Flügge (1954, pp. 84–109).

$$\langle|X|\rangle = \frac{4}{\pi^2}\int_0^1 |X|K(1-|X|^2)^{\frac{1}{2}}d|X| = 4/\pi^2 .$$

Since

$$\langle|X|^2\rangle = \tfrac{1}{4} ,$$

it follows that

$$_{cc}\varrho_{\bar{1},r=\infty} = 4(4/\pi^2)^2 = 0{\cdot}6570 .$$

When $r = 0$

$$_{cc}\varrho_{\bar{1},r} = 0{\cdot}6366 ,$$

so that as r varies over the range $0 \le r \le \infty$, $_{cc}\varrho_{\bar{1},r}$ varies only slightly from the value given by Wilson. Accordingly, results for intermediate values of r have not been calculated.

(It may be mentioned here that the test ratio in the case of the plane group $p2$ with two heavy atoms in the asymmetric unit is also described by the function $_{cc}\varrho_{\bar{1},r}$.)

For the case of one-half heavy atom in the asymmetric unit special positions must be occupied, and, depending on whether the heavy atoms lie on centres of symmetry or mirror planes, values of $_{\max.}\varrho_{\bar{1},r}$ or $_c\varrho_{\bar{1},r}$ apply. Care must be exercised in this situation, for in, for example, the plane group *pgg* the heavy atoms occupy the positions (0, 0) and $(\frac{1}{2}, \frac{1}{2})$ and so contribute only to the reflexions for which $h+k = 2n$. For these reflexions the appropriate value of $_{\max.}\varrho_{\bar{1},r}$ should be used, whereas for the reflexions with $h+k = 2n+1$ the value for $r = 0$, i.e. Wilson's value of 0·6366, applies.

5. Discussion

Table 1 shows that large deviations from the values of the test ratio given by Wilson can occur for structures containing heavy atoms, and that in this circumstance a simple application of Wilson's test-ratio values could be misleading, the largest effect being

produced when the heavy atoms are in special positions.

The acid salt rubidium hydrogen di-*o*-nitrobenzoate provides such an example, being triclinic with one molecule in the unit cell. The experimentally determined value of ϱ is 0·76 (Speakman, 1957), suggesting that the space group is $P1$. Interpolation in Table 1, however, for $r = 1{\cdot}77$ (Sim, 1958) gives

$$\max.\varrho_{\bar{1},r=1.77} = 0{\cdot}784\ ,$$
$$\max.\varrho_{1,r=1.77} = 0{\cdot}892\ ,$$

indicating that the space group is really $P\bar{1}$.

It is also obvious from Table 1 that for large values of r it may be difficult to distinguish between a centrosymmetric and non-centrosymmetric structure, even when accurate intensity measurements are available. For triclinic cells containing one or two heavy atoms the value of r at which this difficulty arises is about $r \approx 2{\cdot}5-3{\cdot}0$.

If we consider as an example a molecule consisting of M carbon atoms (hydrogen atoms may safely be neglected), and a halogen atom, then this limiting value of r corresponds approximately to the following numbers of carbon atoms:

Halogen	M
Cl	2
Br	6
I	12

In the case of rectangular projections this difficulty should arise only for cells containing fewer than four heavy atoms (or eight in the case of the choice between *cmm* and *cm*).

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The Crystal Structure of 1:14-Benzbisanthrene

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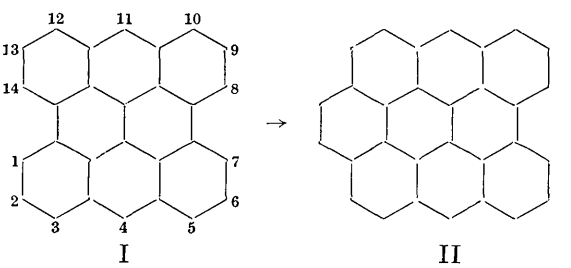
The crystal structure of the aromatic hydrocarbon 1:14-benzbisanthrene, $C_{30}H_{14}$, has been determined from the projection down the short crystal axis ($c = 4{\cdot}68$ Å) by use of the Patterson synthesis and trial methods. The structure is rather unusual in having two molecules in the asymmetric unit. All the atoms are well resolved in projection, and the measured bond lengths compare well with those predicted by superposition of Kekulé structures.

Introduction

Bisanthrene (I) readily adds maleic anhydride to form an adduct, which yields 1:14-benzbisanthrene (II) on decarboxylation (Clar, 1957), exactly analogous to the conversion of perylene into 1:12 benzperylene. However, while benzperylene can be converted into



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