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A Study on the Influence of Space-Group Symmetry on the Measurability of Bijvoet Differences

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Values for the mathematical expectation of the normalized Bijvoet difference x are derived for non-centrosymmetric crystals belonging to triclinic, monoclinic and orthorhombic space groups containing a small number (*i.e.* $p=1$ or 2) of anomalous scatterers in the asymmetric unit besides a large number of similar normal scatterers. These results are used to study the influence of space-group symmetry on the measurability of Bijvoet differences.

1. Introduction

The optimum conditions for the measurability of Bijvoet differences and the influence of the number of anomalous scatterers in the unit cell on the measurability were studied earlier by making use of the probability distributions of the normalized Bijvoet differences x and Δ and the Bijvoet ratio δ (Parthasarathy & Srinivasan, 1964; Parthasarathy, 1967; Parthasarathy & Parthasarathi, 1973). These distributions were, however, worked out for triclinic crystals of space group $P1$. Since many organic crystals belong to space groups of higher symmetry (particularly monoclinic and orthorhombic), it would be useful to see whether space-group symmetry influences the measurability of Bijvoet differences. For discussing this the probability distribution of the Bijvoet ratio would be the more relevant quantity, but the derivation of this is complicated. The problem can however be analysed from a knowledge of the expectation value of the normalized Bijvoet difference x. We shall therefore work out this expectation value (denoted by $\langle x\rangle$) which can be evaluated without obtaining the probability distribution of x. The quantity $\langle x\rangle$ will be evaluated under the following conditions: (i) There are either one or two anomalous scatterers (same type) in the asymmetric unit besides a large number of normal atoms of similar scattering power; (ii) All atoms in the asymmetric unit occupy general positions; (iii) Only non-centrosymmetric crystals belonging to triclinic, monoclinic and orthorhombic space groups are considered.

2. Derivation of the expectation value of x

The normalized Bijvoet difference x is defined as (Parthasarathy, 1967)

$$x=|\Delta I|/4k\sigma_Q\sigma'_P=y_Py_Qu\,, \quad (1)$$

where y_P and y_Q are the normalized structure amplitudes due to the real part of the scattering factors of the anomalous scatterers and normal scatterers respectively and $u=|\sin(\alpha'_P-\alpha_Q)|=|\sin\psi|$. Since y_P, y_Q and ψ are independent (Parthasarathy & Srinivasan, 1964), it follows from (1) that

$$\langle x\rangle=\langle y_P\rangle\,\langle y_Q\rangle\,\langle u\rangle\,. \quad (2)$$

Since the Q-atoms (*i.e.* normal scatterers) are assumed to satisfy the requirements of the acentric Wilson distribution, it follows that $\langle y_Q\rangle=\sqrt{\pi}/2$ (Wilson, 1949). Since the angle between F'_P and F_Q is uniformly distributed in the interval $-\pi$ to π, it follows that

$$\langle u\rangle=\frac{2}{\pi}\int_0^{\pi/2}\sin\psi\mathrm{d}\psi=\frac{2}{\pi}\,. \quad (3)$$

We can therefore rewrite (2) as

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\,\langle y_P\rangle\,. \quad (4)$$

From (4) it is clear that $\langle x\rangle$ could be evaluated for crystals of any space group provided $\langle y_P\rangle$ can be obtained. The latter can be evaluated, for crystals of the triclinic, monoclinic and orthorhombic systems by making use of results available in Foster & Hargreaves (1963*a*, *b* – hereafter FH, 1963*a*, *b*).

In FH, 1963*b* it is shown that the values of the moments of the normalized intensity for triclinic, monoclinic and orthorhombic crystals can be calculated from one of only seven categories of expressions. Of these seven categories only categories 1,3,5 and 6 correspond to the non-centrosymmetric case.

The contribution to the structure factor of a reflexion $\mathbf{H}(\equiv hkl)$ from the real part of the atomic scattering factor of the P-atoms (*i.e.* anomalous scatterers) can be written as:

$$F'_P=sf'_P[\sum_{j=1}^{p}\xi_{pj}+i\sum_{j=1}^{p}\eta_{pj}]=sf'_P[\xi_p+i\eta_p]\,,\ \text{say}, \quad (5)$$

where s is the number of equivalent positions in the unit cell and p is the number of anomalous scatterers in the asymmetric unit. Here ξ_{pj} and η_{pj} are the trig-

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onometric factors of the geometrical structure factor of the jth atom in the asymmetric unit and the other $(s-1)$ atoms equivalent to it. From (5) we have

$$|F'_P| = sf'_P\sqrt{\xi_p^2+\eta_p^2} = sf'_P E, \text{ say,} \tag{6}$$

where

$$E=\sqrt{\xi_p^2+\eta_p^2}\,. \tag{7}$$

From Table 1 of FH (1963*b*) it can be shown that for the present case

$$\langle |F'_P|^2\rangle = \varepsilon s^2 p (f'_P)^2\,, \tag{8}$$

where ε is a constant whose value depends on the space-group category. The values of ε for categories 1, 3, 5 and 6 are given in Table 1. From (6) and (8) we obtain

$$y_p = |F'_P|/\langle |F'_P|^2\rangle^{1/2} = E/\sqrt{\varepsilon p}\,. \tag{9}$$

From (4) and (9) it is clear that

$$\langle x\rangle = \langle E\rangle/\sqrt{\pi\varepsilon p}\,. \tag{10}$$

From Table 1 of FH (1963*b*) the expressions for E for the case of crystals belonging to categories 1, 3, 5 and 6 and containing a single species of p anomalous scatterers at general positions in the asymmetric unit can be obtained and are listed in Table 1. The quantities θ_i, φ_i and ψ_i ($i=1$ to p) are mutually independent random variables uniformly distributed in the interval 0 to 2π (FH, 1963*a*). From Table 1 it follows that $\langle E\rangle$ can be written as

$$\langle E\rangle = \frac{1}{(2\pi)^{3p}}\int_0^{2\pi}\cdots\int_0^{2\pi}\sqrt{\xi_p^2+\eta_p^2}\prod_{i=1}^{p} d\theta_i d\varphi_i d\psi_i\,. \tag{11}$$

Equation (11) requires the evaluation of a $3p$-tuple integral involving the variables $\theta_1,\varphi_1,\psi_1,\ldots,\theta_p$, φ_p and ψ_p. We shall consider the cases $p=1$ and 2 separately.

The case of one anomalous scatterer per asymmetric unit (i.e. $p=1$)

For category 1, it can be shown from Table 1 that $E=1$ and $\varepsilon=1$ so that from (10) we obtain

$$\langle x\rangle = \pi^{-1/2} = 0{\cdot}564\,. \tag{12}$$

For category 3, $\varepsilon=\frac{1}{2}$ and E can be shown to reduce to $|\cos\theta_1|$ (Table 1). Hence we obtain from (10)

$$\begin{aligned}\langle x\rangle &= \left(\frac{2}{\pi}\right)^{1/2}\frac{1}{2\pi}\int_0^{2\pi}|\cos\theta_1|d\theta_1\\ &= \left(\frac{2}{\pi}\right)^{3/2}\int_0^{\pi/2}\cos\theta_1 d\theta_1 = \left(\frac{2}{\pi}\right)^{3/2} = 0{\cdot}508\,.\end{aligned} \tag{13}$$

For category 5, $\varepsilon=\frac{1}{4}$ and E is given by (Table 1)

$$E = (\cos^2\theta_1\cos^2\varphi_1\cos^2\psi_1 + \sin^2\theta_1\sin^2\varphi_1\sin^2\psi_1)^{1/2}\,. \tag{14}$$

Hence we obtain from (10) and (14)

$$\begin{aligned}\langle x\rangle = \left(\frac{2}{\sqrt{\pi}}\right)\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}&[\cos^2\theta_1\cos^2\varphi_1\cos^2\psi_1\\ &+\sin^2\theta_1\sin^2\varphi_1\sin^2\psi_1]^{1/2}d\theta_1 d\varphi_1 d\psi_1\,,\end{aligned} \tag{15}$$

which after the substitution $\theta'_1=\theta_1/2\pi$, $\varphi'_1=\varphi_1/2\pi$ and $\psi'_1=\psi_1/2\pi$ becomes

$$\begin{aligned}\langle x\rangle = \frac{2}{\sqrt{\pi}}\int_0^1\int_0^1\int_0^1&[\cos^2 2\pi\theta'_1\cos^2 2\pi\varphi'_1\cos^2 2\pi\psi'_1\\ &+\sin^2 2\pi\theta'_1\sin^2 2\pi\varphi'_1\sin^2 2\pi\psi'_1]^{1/2}d\theta'_1 d\varphi'_1 d\psi'_1\,.\end{aligned} \tag{16}$$

The triple integral in (16) can be evaluated numerically to give

$$\langle x\rangle = 0{\cdot}507\,. \tag{17}$$

For category 6, $\varepsilon=\frac{1}{4}$ and E can be shown to reduce to $|\cos\theta_1\cos\varphi_1|$ (Table 1). Hence we obtain from (10)

$$\begin{aligned}\langle x\rangle &= \left(\frac{2}{\sqrt{\pi}}\right)\langle|\cos\theta_1|\rangle\langle|\cos\varphi_1|\rangle\\ &= \frac{2}{\sqrt{\pi}}\left(\frac{2}{\pi}\right)^2 = \frac{8}{\pi^{5/2}} = 0{\cdot}457\,.\end{aligned} \tag{18}$$

The case of two anomalous scatterers per asymmetric unit (i.e. $p=2$)

For category 1, it follows from Table 1 and (10) that

$$\begin{aligned}\langle x\rangle = \frac{1}{\sqrt{2\pi}}\left(\frac{1}{2\pi}\right)^2\int_0^{2\pi}\int_0^{2\pi}&[(\cos\theta_1+\cos\theta_2)^2\\ &+(\sin\theta_1+\sin\theta_2)^2]^{1/2}d\theta_1 d\theta_2\,,\end{aligned} \tag{19}$$

which on simplification yields [see equation (*A*5)]

$$\langle x\rangle = \left(\frac{2}{\pi}\right)^{3/2} = 0{\cdot}508\,. \tag{20}$$

Table 1. *Values of ε and expressions for E $(=\sqrt{\xi_p^2+\eta_p^2})$ for the space-group categories* 1, 3, 5 and 6*

Space-group category number	ε	Expression for E†
1	1	$[(\sum\cos\theta_i)^2+(\sum\sin\theta_i)^2]^{1/2}$
3	$\frac{1}{2}$	$[(\sum\cos\theta_i\cos\varphi_i)^2+(\sum\cos\theta_i\sin\varphi_i)^2]^{1/2}$
5	$\frac{1}{4}$	$[(\sum\cos\theta_i\cos\varphi_i\cos\psi_i)^2+(\sum\sin\theta_i\sin\varphi_i\sin\psi_i)^2]^{1/2}$
6	$\frac{1}{4}$	$[(\sum\cos\theta_i\cos\varphi_i\cos\psi_i)^2+(\sum\cos\theta_i\cos\varphi_i\sin\psi_i)^2)]^{1/2}$

* For the notation see FH (1963*b*). Here $\sum$ denotes the summation over the p atoms in the asymmetric unit.

† As in Table 1 of FH (1963*b*) other combinations for the geometrical structure factors A and B are possible in each category. But these need not be considered in our study since they lead to the same distributions. We have therefore listed the expressions corresponding to only one combination for (A,B).

For category 3, it follows from Table 1 and (10) that

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\left(\frac{1}{2\pi}\right)^4\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}[(\cos\theta_1\cos\varphi_1 +\cos\theta_2\cos\varphi_2)^2+(\cos\theta_1\sin\varphi_1 +\cos\theta_2\sin\varphi_2)^2]^{1/2}d\theta_1 d\theta_2 d\varphi_1 d\varphi_2\,. \quad (21)$$

The quadruple integral in (21) can be reduced to a triple integral [see equation (A9)] so that

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\int_0^1\int_0^1\int_0^1[\cos^2 2\pi\theta'_1+\cos^2 2\pi\theta'_2 +2\cos 2\pi\theta'_1\cos 2\pi\theta'_2\cos 2\pi\omega']^{1/2} \times d\theta'_1 d\theta'_2 d\omega'\,, \quad (22)$$

which on integration by numerical methods yields

$$\langle x\rangle=0{\cdot}507\,. \quad (23)$$

For category 5, we obtain from Table 1 and (10)

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{2\pi}\right)^6\int_0^{2\pi}\cdots\int_0^{2\pi}[(\sum_{i=1}^{2}\cos\theta_i\cos\varphi_i\cos\psi_i)^2 +(\sum_{i=1}^{2}\sin\theta_i\sin\varphi_i\sin\psi_i)^2]^{1/2}\prod_{i=1}^{2}d\theta_i d\varphi_i d\psi_i\,. \quad (24)$$

After the substitution

$$\theta'_i=\theta_i/2\pi,\ \varphi'_i=\varphi_i/2\pi,\ \psi'_i=\psi_i/2\pi,\ i=1,2\,, \quad (25)$$

(25) can be conveniently rewritten as

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\int_0^1\cdots\int_0^1[(\sum_{i=1}^{2}\cos 2\pi\theta'_i\cos 2\pi\varphi'_i\cos 2\pi\psi'_i)^2 +(\sum_{i=1}^{2}\sin 2\pi\theta'_i\sin 2\pi\varphi'_i\sin 2\pi\psi'_i)^2]^{1/2}\prod_{i=1}^{2}d\theta'_i d\varphi'_i d\psi'_i\,. \quad (26)$$

The sextuple integral in (26) was evaluated by the Monte Carlo method (Demidovich & Maron, 1973) to give

$$\langle x\rangle=0{\cdot}500\,. \quad (27)$$

For category 6, we obtain from Table 1 and (10)

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{2\pi}\right)^6\int_0^{2\pi}\cdots\int_0^{2\pi}[(\sum_{i=1}^{2}\cos\theta_i\cos\varphi_i\cos\psi_i)^2 +(\sum_{i=1}^{2}\cos\theta_i\cos\varphi_i\sin\psi_i)^2]^{1/2}\prod_{i=1}^{2}d\theta_i d\varphi_i d\psi_i\,. \quad (28)$$

The sextuple integral can be reduced to a quintuple integral [see equation (A12)]

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\int_0^1\cdots\int_0^1[\cos^2 2\pi\theta'_i\cos^2 2\pi\varphi'_i +\cos^2 2\pi\theta'_2\cos^2 2\pi\varphi'_2 +2\cos 2\pi\theta'_1\cos 2\pi\theta'_2\cos 2\pi\varphi'_1\cos 2\pi\varphi'_2 \times\cos 2\pi\omega']^{1/2}d\theta'_1 d\theta'_2 d\varphi'_1 d\varphi'_2 d\omega'\,, \quad (29)$$

which was evaluated by the Monte Carlo method, yielding

$$\langle x\rangle=0{\cdot}487\,. \quad (30)$$

3. Discussion of the theoretical results

From a study of the above results we see: (i) Among the commonly-arising case of crystals containing one anomalous scatterer per asymmetric unit (*i.e.* $p=1$), the triclinic crystal (space group $P1$) is best suited for Bijvoet difference measurements, and the orthorhombic crystal of category 6 is the least favourable, other conditions such as the complexity of the asymmetric unit, the type of anomalous scatterer *etc.*, being the same. (ii) For crystals containing two anomalous scatterers per asymmetric unit, though the orthorhombic crystal of category 6 is the least favourable, the distinction between the various categories becomes less marked.

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APPENDIX

Expanding the square terms in the integrand of (19) and simplifying we obtain

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\left(\frac{1}{2\pi}\right)^2\int_0^{2\pi}\int_0^{2\pi}[1+\cos(\theta_1-\theta_2)]^{1/2}d\theta_1 d\theta_2\,. \quad (A1)$$

Making the substitution $\theta_1-\theta_2=\omega$, we can rewrite (A1) as

$$\langle x\rangle=\frac{1}{4\pi^{5/2}}\int_0^{2\pi}d\theta_2\int_{-\theta_2}^{2\pi-\theta_2}(1+\cos\omega)^{1/2}d\omega\,. \quad (A2)$$

Since the integrand is periodic with period 2π, we can rewrite (A2) as

$$\langle x\rangle=\frac{1}{4\pi^{5/2}}\int_0^{2\pi}d\theta_2\int_0^{2\pi}(1+\cos\omega)^{1/2}d\omega\,. \quad (A3)$$

Interchanging the order of integrations in (A3), we obtain

$$\langle x\rangle=\frac{1}{2\pi^{3/2}}\int_0^{2\pi}(1+\cos\omega)^{1/2}d\omega =\frac{1}{\pi^{3/2}}\int_0^{\pi}(1+\cos\omega)^{1/2}d\omega\,. \quad (A4)$$

Using the result $\cos\omega=2\cos^2(\omega/2)-1$, and changing the variable of the integration to $\omega/2=\omega'$ we can show that (A4) yields

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{3/2}. \quad (A5)$$

Expanding the square terms in the integrand of (21) and simplifying we obtain

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\left(\frac{1}{2\pi}\right)^4\int_0^{2\pi}\ldots\int_0^{2\pi}[\cos^2\theta_1+\cos^2\theta_2+2\cos\theta_1\cos\theta_2\cos(\varphi_1-\varphi_2)]^{1/2}\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\varphi_1\mathrm{d}\varphi_2\,. \quad (A6)$$

Making the substitution $\varphi_1-\varphi_2=\omega$, we can rewrite ($A6$) as

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\left(\frac{1}{2\pi}\right)^4\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\varphi_2\times\int_{-\varphi_2}^{2\pi-\varphi_2}[\cos^2\theta_1+\cos^2\theta_2+2\cos\theta_1\cos\theta_2\cos\omega]^{1/2}\mathrm{d}\omega\,. \quad (A7)$$

Making use of the arguments employed in obtaining ($A4$) from ($A2$) we can simplify ($A7$) to obtain

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}[\cos^2\theta_1\cos^2\theta_2+2\cos\theta_1\cos\theta_2\cos\omega]^{1/2}\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\omega\,. \quad (A8)$$

Making the substitution

$$\omega'=\omega/2\pi,\ \theta'_i=\theta_i/2\pi,\ i=1,2\,,$$

we can rewrite ($A8$)

$$\langle x\rangle=\frac{1}{\sqrt{\pi}}\int_0^1\int_0^1\int_0^1[\cos^2 2\pi\theta'_1+\cos^2 2\pi\theta'_2+2\cos 2\pi\theta'_1\cos 2\pi\theta'_2\cos 2\pi\omega']^{1/2}\mathrm{d}\theta'_1\mathrm{d}\theta'_2\mathrm{d}\omega'\,. \quad (A9)$$

Expanding the square terms in the integrand of (28) and simplifying we obtain

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{2\pi}\right)^6\int_0^{2\pi}\ldots\int_0^{2\pi}[\cos^2\theta_1\cos^2\varphi_1+\cos^2\theta_2\cos^2\varphi_2+2\cos\theta_1\cos\theta_2\cos\varphi_1\cos\varphi_2\cos(\psi_1-\psi_2)]^{1/2}\times\prod_{i=1}^{2}\mathrm{d}\theta_i\mathrm{d}\varphi_i\mathrm{d}\psi_i\,. \quad (A10)$$

Making the substitution $\psi_1-\psi_2=\omega$ we can rewrite ($A10$) as

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{2\pi}\right)^6\int_0^{2\pi}\ldots\int_0^{2\pi}\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\varphi_1\mathrm{d}\varphi_2\mathrm{d}\psi_2\times\int_{-\psi_2}^{2\pi-\psi_2}[\cos^2\theta_1\cos^2\varphi_1+\cos^2\theta_2\cos^2\varphi_2+2\cos\theta_1\cos\theta_2\cos\varphi_1\cos\varphi_2\cos\omega]^{1/2}\,\mathrm{d}\omega. \quad (A11)$$

Making use of the arguments employed in obtaining ($A4$) for ($A2$) we can rewrite ($A11$) as

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{2\pi}\right)^5\int_0^{2\pi}\ldots\int_0^{2\pi}[\cos^2\theta_1\cos^2\varphi_1+\cos^2\theta_2\cos^2\varphi_2+2\cos\theta_1\cos\theta_2\cos\varphi_1\cos\varphi_2\cos\omega]^{1/2}\times\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\varphi_1\mathrm{d}\varphi_2\mathrm{d}\omega\,,$$

which, after the substitution,

$$\omega'=\omega/2\pi,\ \theta'_i=\theta_i/2\pi,\ \varphi'_i=\varphi_i/2\pi,\ i=1,2\,,$$

can be rewritten as

$$\langle x\rangle=\left(\frac{2}{\pi}\right)^{1/2}\int_0^1\ldots\int_0^1[\cos^2 2\pi\theta'_1\cos^2 2\pi\varphi'_1+\cos^2 2\pi\theta'_2\cos^2 2\pi\varphi'_2+2\cos 2\pi\theta'_1\cos 2\pi\theta'_2\cos 2\pi\varphi'_1\cos 2\pi\varphi'_2\times\cos 2\pi\omega']^{1/2}\mathrm{d}\theta'_1\mathrm{d}\theta'_2\mathrm{d}\varphi'_1\mathrm{d}\varphi'_2\mathrm{d}\omega'\,. \quad (A12)$$

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