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A Statistical Method for Selecting Reflections for Bijvoet Difference Measurement in Crystals with Heavy Atoms

BY D. VELMURUGAN AND S. PARTHASARATHY

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras* 600025, *India*

AND V. PARTHASARATHI

Department of Physics, University of Madras, Autonomous Postgraduate Centre, Tiruchirapalli 620020, *India*

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Abstract

The conditional probability distribution of the Bijvoet ratio δ for given $|F_N'|$ and $|F_P'|$ is worked out for a non-centrosymmetric crystal with one species of anomalous scatterers (besides a large number of normal scatterers) in the unit cell. The expression for the conditional probability for $|\delta|$ to be greater than any given value δ_o is then deduced. The use of this expression for testing the suitability of a given Bijvoet pair of a crystal for Bijvoet difference measurement is pointed out. Numerical tables which aid easy implementation of the results to actual crystals are provided. Application of the result in a few actual crystal structures is also discussed.

1. Introduction

The statistical distributions of the normalized Bijvoet differences x and Δ and the Bijvoet ratio δ available in the literature (Srinivasan & Parthasarathy, 1976) are useful for calculating the probable fraction of reflections whose Bijvoet differences could be measured. Though these distributions help in the choice of a suitable heavy-atom derivative for the collection of Bijvoet differences, they cannot be used to judge whether a given Bijvoet pair would exhibit a measurable Bijvoet difference. Since the suitability of a given Bijvoet pair for Bijvoet difference measurement can be decided from the conditional probability distribution of $|\delta|$ for given $|F_N'|$ and $|F_P'|$ (for a definition of these, see § 2), this probability function, denoted by $P(|\delta|; |F_N'|, |F_P'|)$, is derived first. The expression for the conditional complementary cumulative function of δ for given $|F_N'|$ and $|F_P'|$, namely, $N_c(\delta_o; |F_N'|, |F_P'|)$ is then deduced. The latter function denotes the conditional probability that $|\delta|$ takes a value greater than any desired fixed value δ_o for given $|F_N'|$ and $|F_P'|$. The method of implementing the result in actual crystals is discussed in § 3. The application of the result for a few crystal structures is reported in § 4.

2. Derivation of the conditional distribution function of δ

The Bijvoet ratio δ for a given Bijvoet pair **H** and $\bar{\mathbf{H}}$ is defined to be (Zachariasen, 1965)

$$\delta = \frac{I(\mathbf{H}) - I(\bar{\mathbf{H}})}{I} = \frac{\Delta I}{I}, \tag{1}$$

where $I = \frac{1}{2}[I(\mathbf{H}) + I(\bar{\mathbf{H}})]$ is the mean intensity of the Bijvoet pair. For a non-centrosymmetric crystal containing a single species of anomalous scatterer besides a number of normal scatterers, the Bijvoet difference ΔI and the mean intensity I of the Bijvoet pair have been shown to be (Ramachandran & Raman, 1956)

$$\Delta I = 4|F_N'||F_P''| \sin\theta, \quad I = |F_N'|^2 + |F_P''|^2, \tag{2}$$

where F_N' is the contribution to the structure factor of a reflection $\mathbf{H} = hkl$ from the real part of the scattering factor of all the atoms in the unit cell and F_P' that from the anomalous scatterers alone. θ is the angle between the structure factors F_N' and F_P', and iF_P'' is the contribution to the structure factor of the reflection **H** from the imaginary part of the scattering factor of the anomalous scatterers. From (1) and (2) we obtain

$$\delta = \frac{4|F_N'||F_P''| \sin\theta}{|F_N'|^2 + |F_P''|^2} = \frac{4k|F_N'||F_P'| \sin\theta}{|F_N'|^2 + k^2|F_P'|^2}, \tag{3}$$

where we have used the known relation $|F_P''| = k|F_P'|$. As regards the measurability of the Bijvoet difference of a given reflection, only the magnitude of the Bijvoet ratio is relevant. Hence we shall consider $|\delta|$ which from (3) can be written as

$$|\delta| = c|\sin\theta|, \tag{4}$$

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where we have used the abbreviation

$$c = \frac{4k|F'_N||F'_P|}{|F'_N|^2 + k^2|F'_P|^2}. \tag{5}$$

Here θ takes values in the interval $-\pi$ to π. From (4) and (5) the conditional p.d.f. $P(\delta; |F'_N|, |F'_P|)$ can be obtained from the conditional p.d.f. $P(\theta; |F'_N|, |F'_P|)$ and the latter is known to be (Srinivasan & Chandrasekharan, 1966)

$$P(\theta; |F'_N|, |F'_P|) = \frac{\exp(2|F'_N||F'_P|\cos\theta/\sigma_Q^2)}{2\pi I_o(2|F'_N||F'_P|/\sigma_Q^2)}, \tag{6}$$

where σ_Q^2 is the sum of the squares of the scattering factors of all the normal scatterers in the unit cell. Since (6) is an even function of θ, the conditional p.d.f. of $|\theta|$ will be given by

$$P(|\theta|; |F'_N|, |F'_P|) = \frac{\exp(2|F'_N||F'_P|\cos\theta/\sigma_Q^2)}{\pi I_o(2|F'_N||F'_P|/\sigma_Q^2)}. \tag{7}$$

The quantity θ in (7) is not convenient since $\sin\theta$ is a double-valued function in the range 0 to π. However, since $\sin\theta$ is symmetrical about $\theta = \pi/2$, $|\delta|$ has the same value for $\theta = \varphi$ and $\theta = \pi - \varphi$, where we define φ to be an acute angle. We can, therefore, restrict the range of the argument of the sine function to 0 to $\pi/2$, provided we take into account the actual probabilities of occurrence for the two events, namely, $\theta = \varphi$ and $\theta = \pi - \varphi$ for which the values of $|\delta|$ are the same. In this context it is found to be convenient to define a new variable φ as

$$\varphi = \begin{cases} \theta & \text{if } 0 \le \theta \le \pi/2 \\ \pi - \theta & \text{if } \pi/2 \le \theta \le \pi. \end{cases} \tag{8}$$

From (7) and (8) we obtain the conditional p.d.f. of φ for a given $|F'_N|$ and $|F'_P|$ to be

$$P(\varphi; |F'_N|, |F'_P|) = P(\theta = \varphi; |F'_N|, |F'_P|) + P(\theta = \pi - \varphi; |F'_N|, |F'_P|) = \frac{2}{\pi}\frac{\cosh(\beta\cos\varphi)}{I_o(\beta)} \tag{9}$$

where we have used the abbreviation

$$\beta = 2|F'_N||F'_P|/\sigma_Q^2. \tag{10}$$

From (4) and (9) the conditional p.d.f. of $|\delta|$ ($= c\sin\varphi$, $0 \le \varphi \le \pi/2$) can be obtained as

$$P(|\delta|; |F'_N|, |F'_P|) = \frac{2}{\pi}\frac{\cosh\frac{\beta}{c}(c^2 - \delta^2)^{1/2}}{I_o(\beta)(c^2 - \delta^2)^{1/2}}.$$

The conditional probability that $|\delta| > \delta_o$ [*i.e.* the complementary cumulative function $N_c(\delta_o; |F'_N|, |F'_P|)$] would therefore be given by

$$\begin{aligned} N_c(\delta_o; |F'_N|, |F'_P|) &= Pr(|\delta| > \delta_o; |F'_N|, |F'_P|) \\ &= 1 - Pr(|\delta| \le \delta_o; |F'_N|, |F'_P|) \\ &= 1 - \int_0^{\delta_o} P(|\delta|; |F'_N|, |F'_P|)\,d\delta \\ &= 1 - \frac{2}{\pi I_o(\beta)}\int_0^{\delta_o}\frac{\cosh\frac{\beta}{c}(c^2 - \delta^2)^{1/2}}{(c^2 - \delta^2)^{1/2}}\,d\delta, \\ &\qquad 0 \le \delta_o \le c. \end{aligned} \tag{11}$$

3. Discussion of the theoretical results

(11) enables us to calculate the conditional probability that $|\delta|$ will be greater than any specific value (say 0·05) for given values of $|F'_N|$ and $|F'_P|$. This probability for any given reflection of a given crystal is however to be evaluated from (11) by numerical integration after substituting the appropriate values of k, σ_Q^2, $|F'_N|$ and $|F'_P|$. The heavy-atom derivatives met with in organic crystals are such that the heavy atoms could be located from the Patterson synthesis. $|F'_P|$ can hence be calculated for each reflection from the known positions of the P atoms. The values of σ_Q^2 and k for any reflection can be calculated from a knowledge of the unit-cell content and from the known values of the real and imaginary parts of the scattering factor of the P atoms respectively. In the X-ray case the quantity $|F'_N|$ needed for obtaining c and β [see (5) and (10)] could be approximated by the observed value of the structure amplitude of the (*hkl*) reflection under consideration. From the values of k, σ_Q^2, $|F'_P|$ and $|F'_N|$ thus obtained the value of the probability that $\delta > 0{\cdot}05$ could be evaluated from (11). The reflections for which this probability is sufficiently high (>0·75, say) could be expected to be suitable for Bijvoet difference measurement.

The use of (11) requires numerical integration. It would however be useful to have simpler methods for implementing (11). We shall consider this aspect presently. A study of (11) shows that* $N_c(\delta_o; |F'_N|, |F'_P|)$ is an explicit function of c and β which are in turn functions of $|F'_N|$ and $|F'_P|$. The maximum value of c is known to be 2 (Zachariasen, 1965). A study of the numerical value of $N_c(\delta_o)$ as a function of c and β for some fixed value of δ_o (say, 0·1) shows (Table 1) that for any given values of δ_o and c the value of $N_c(\delta_o)$

* In our discussion and the tables we shall also denote this function by $N_c(\delta_o)$ for brevity.

increases as the value of β decreases. If we take the value of $N_c(\delta_o)$ to be fixed (p, say), then we can determine, for any given values of c and δ_o, the value of β which would satisfy the equation,

$$N_c(\delta_o; |F'_N|, |F'_P|) = p. \qquad (12)$$

Taking δ_o to be 0·1 and p to be 0·75 corresponding to each of the values of $c = 0{\cdot}30, 0{\cdot}35, \ldots 2{\cdot}0$, the value of β satisfying (12) was determined. The whole calculation was repeated by taking p to be 0·8, 0·85, 0·9 and 0·95. The results thus obtained are given in Table 2. The corresponding results for $\delta_o = 0{\cdot}05$ are given in Table 3. A study of the values of c and β satisfying (12) shows that for given values of p and δ_o, there is a minimum value of c (denoted by c_m) for which a β (close to zero) exists satisfying (12). Thus, given the values of p and δ_o, the reflections for which $c < c_m$ cannot be expected to show a Bijvoet ratio $|\delta| > \delta_o$ at the probability level of p (or more).

Bijvoet differences have two important uses, (i) for phase determination by the quasi-anomalous method (Ramachandran & Raman, 1956; Peerdeman & Bijvoet, 1956) and (ii) for establishing the absolute configuration of molecules (Bijvoet, 1954). While for the determination of non-centrosymmetric structures with heavy atoms by the quasi-anomalous method one would require Bijvoet differences for as many reflections as possible, for absolute-configuration determination it is sufficient to measure only a few reflections which are expected to exhibit large Bijvoet differences. The simplified procedure that can be followed for selecting reflections suitable for Bijvoet difference measurement for these two applications will now be considered.

(i) *Method of choosing reflections for complete Bijvoet difference data collection*

The procedure to be followed for this case consists of the following steps. (*a*) Collect only the *hkl* intensities and use them to determine the positions of the heavy atoms from the Patterson function. (*b*) Calculate the values of c and β for the various reflections of the crystal from (5) and (10) respectively. Let c_o and β_o denote the observed values of c and β thus obtained. (*c*) Reject the reflections for which $c < c_m$ (= 0·13) corresponding to the probability level* $N_c(0{\cdot}05) = 0{\cdot}75$. (*d*) For the remaining reflections obtain the theoretical value of β (appropriate to the value of c_o) satisfying (12) for $p = 0{\cdot}75$ and $\delta_o = 0{\cdot}05$. This can be done by linear interpolation from Table 3 under the column for which $N_c(0{\cdot}05) = 0{\cdot}75$. Let this value of β be denoted by β_t. (*e*) Check whether $\beta_o < \beta_t$. If this is so, accept the reflection as suitable for Bijvoet difference measurement. Otherwise reject the reflection as unsuitable. (*f*) Now collect the $\bar{h}\bar{k}\bar{l}$ data for the reflections that have been found to be suitable. Use this data and the *hkl* data already collected to obtain the Bijvoet differences.

The advantage of this method is that one can avoid collecting intensities for reflections which may not be expected to have any measurable Bijvoet differences.

(ii) *Method of selecting reflections for absolute configuration determination*

The procedure to be followed for this case consists of the following steps: (*a*) Follow steps (*a*) and (*b*) under

* We have suggested the value of 0·75 for p as suitable from our studies on the Bijvoet difference data of actual crystal structures. One may use a larger value for this probability but this stringent condition would indicate a smaller fraction of reflections as suitable for Bijvoet difference measurement.

Table 1. *Conditional probability* $N_c(0{\cdot}1; |F'_N|, |F'_P|)$ *(in %) as a function of* c *and* β

β \ c →	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
0·0	66·7	78·4	83·9	87·2	89·3	90·9	92·0	92·9	93·6	94·2	94·7	95·1	95·4	95·8	96·0	96·3	96·5	96·6	96·8
1·0	60·7	74·0	80·6	84·5	87·1	88·9	90·3	91·4	92·2	92·9	93·5	94·0	94·3	94·8	95·1	95·4	95·7	95·9	96·1
2·0	49·4	65·6	74·0	79·1	82·6	85·0	86·9	88·3	89·5	90·5	91·3	91·9	92·5	93·0	93·4	93·8	94·2	94·5	94·7
3·0	39·5	57·8	67·8	74·1	78·4	81·4	83·7	85·5	86·9	88·1	89·1	89·9	90·6	91·3	91·8	92·3	92·7	93·1	93·4
4·0	31·9	51·3	62·7	69·8	74·7	78·2	80·9	83·0	84·7	86·1	87·2	88·2	89·0	89·8	90·4	91·0	91·5	91·9	92·3
5·0	26·1	46·2	58·4	66·2	71·6	75·6	78·5	80·9	82·8	84·3	85·6	86·7	87·7	88·5	89·2	89·8	90·4	90·9	91·3
6·0	21·6	41·8	54·6	63·0	68·9	73·2	76·4	79·0	81·1	82·8	84·2	85·4	86·4	87·3	88·1	88·8	89·4	90·0	90·5
7·0	18·0	38·0	51·3	60·2	66·4	71·0	74·5	77·3	79·5	81·3	82·9	84·2	85·3	86·3	87·1	87·9	88·5	89·1	89·7
8·0	15·0	34·7	48·3	57·6	64·2	69·0	72·8	75·7	78·1	80·0	81·7	83·0	84·2	85·3	86·2	87·0	87·7	88·4	88·9
9·0	12·6	31·8	45·6	55·2	62·1	67·3	71·1	74·2	76·7	78·8	80·5	82·0	83·3	84·4	85·3	86·2	87·0	87·6	88·2
10·0	10·6	29·1	43·2	53·0	60·2	65·6	69·6	72·8	75·5	77·6	79·5	81·0	82·4	83·6	84·5	85·4	86·2	86·8	87·4
11·0	9·0	26·7	40·9	51·0	58·4	64·0	68·2	71·6	74·3	76·6	78·5	80·1	81·6	82·7	83·8	84·7	85·5	86·2	86·8
12·0	7·8	24·7	38·8	49·1	56·7	62·4	66·8	70·3	73·2	75·5	77·5	79·2	80·7	81·9	83·0	84·0	84·9	85·7	86·4
13·0	6·8	22·7	36·8	47·3	55·1	60·9	65·5	69·1	72·1	74·5	76·6	78·3	79·9	81·2	82·3	83·4	84·2	85·1	85·8
14·0	5·5	21·0	35·0	45·6	53·5	59·5	64·2	68·0	71·0	73·6	75·7	77·5	79·1	80·5	81·7	82·7	83·7	84·5	85·3
15·0	4·7	19·4	33·3	44·0	52·0	58·2	63·1	66·9	70·1	72·7	74·9	76·8	78·4	79·8	81·0	82·1	83·1	84·0	84·8
16·0	4·0	18·0	31·7	42·5	50·7	57·0	61·9	65·9	69·2	71·8	74·1	76·0	77·7	79·2	80·4	81·5	82·5	83·3	84·1
17·0	3·4	16·6	30·2	41·1	49·4	55·8	60·8	64·9	68·2	71·0	73·3	75·3	77·0	78·5	79·8	80·9	82·0	82·9	83·8
18·0	2·9	15·3	28·8	39·8	48·2	54·7	59·8	63·9	67·3	70·2	72·5	74·5	76·3	77·9	79·2	80·4	81·5	82·4	83·3
19·0	2·5	14·3	27·5	38·4	46·9	53·6	58·8	63·0	66·5	69·4	71·8	73·9	75·7	77·3	78·7	79·9	81·0	82·0	82·9
20·0	2·1	13·3	26·3	37·2	45·7	52·5	57·8	62·1	65·6	68·6	71·1	73·2	75·1	76·7	78·1	79·4	80·5	81·5	82·4
22·0	1·6	11·5	24·0	34·9	43·5	50·4	55·9	60·4	64·1	67·1	69·7	72·0	73·9	75·6	77·1	78·4	79·6	80·6	81·6
24·0	1·2	9·9	21·9	32·7	41·5	48·5	54·2	58·8	62·6	65·7	68·4	70·8	72·8	74·5	76·1	77·4	78·7	79·8	80·7
26·0	0·9	8·6	20·1	30·8	39·6	46·7	52·5	57·2	61·1	64·4	67·2	69·6	71·7	73·5	75·1	76·5	77·8	78·9	80·0
28·0	0·6	7·5	18·4	29·0	37·8	45·1	50·9	55·8	59·8	63·2	66·0	68·5	70·7	72·5	74·2	75·7	77·0	78·2	79·2
30·0	0·5	6·5	16·9	27·3	36·2	43·6	49·5	54·4	58·5	62·0	64·9	67·4	69·7	71·6	73·3	74·8	76·2	77·4	78·5
32·0	0·4	5·7	15·6	25·7	34·6	42·0	48·0	53·1	57·3	60·8	63·8	66·4	68·7	70·7	72·5	74·0	75·4	76·7	77·8
34·0	0·3	4·9	14·3	24·3	33·1	40·5	46·7	51·8	56·1	59·7	62·8	65·5	67·8	69·8	71·6	73·2	74·7	76·0	77·1
36·0	0·2	4·3	13·2	22·9	31·7	39·2	45·4	50·6	54·9	58·6	61·8	64·5	66·9	69·0	70·9	72·5	74·0	75·3	76·5
38·0	0·1	3·8	12·2	21·7	30·4	37·9	44·2	49·4	53·8	57·6	60·8	63·6	66·1	68·2	70·1	71·8	73·3	74·6	75·9
40·0	0·1	3·3	11·2	20·5	29·2	36·7	43·0	48·3	52·8	56·6	59·9	62·7	65·2	67·4	69·3	71·1	72·6	74·0	75·3
42·0	0·1	2·9	10·3	19·4	28·0	35·5	41·8	47·2	51·8	55·7	59·0	61·9	64·4	66·6	68·6	70·4	72·0	73·4	74·7
44·0	0·1	2·5	9·6	18·4	26·9	34·3	40·7	46·2	50·8	54·7	58·1	61·1	63·6	65·9	67·9	69·7	71·3	72·8	74·1

(i). (*b*) Reject the reflections for which $c < c_m$ (= 0·26) corresponding to the probability level $N_c(0{\cdot}1) = 0{\cdot}75$. (*c*) Find the value of β_t appropriate to the value of c_o satisfying (12) for $p = 0{\cdot}75$ and $\delta_o = 0{\cdot}1$. This can be done by linear interpolation from Table 2. (*d*) Select the reflections for which $\beta_o < \beta_t$. (*e*) For these few reflections calculate (from Table 1) the actual probability values $N_c(0{\cdot}1)$ by a bivariate interpolation method (Abramovitz & Stegun, 1965). This is much simpler than evaluating $N_c(0{\cdot}1)$ directly from (12). (*f*) Order these reflections with decreasing probability values and choose the top few (say 10) reflections as the optimum reflections for Bijvoet difference measurement.

The advantage of this method is that one can predict suitable Bijvoet pairs at the beginning of a structure determination, and thus avoid the necessity of keeping the crystal for Bijvoet difference measurement till the crystal structure is refined.

4. Test of the theoretical result

(11) has been tested for three actual crystal structures,* L-ephedrine hydrochloride (Ramachandran & Raman, 1956), L-tyrosine hydrochloride (Parthasarathy, 1962) and L-lysine hydrochloride dihydrate (Raman, 1959). For the lysine derivative the measured Bijvoet differences are available for the *hk*0 and 0*kl* reflections while for the other two the differences for *hk*0 reflections alone are available. For each crystal the value of the conditional probability $N_c(0{\cdot}1)$ for each

* All these belong to the space group $P2_1$.

Table 2. *β as a function of c satisfying the equation* $N_c(0{\cdot}1) = p$ *for different fixed values of p*

	Value of β for which $N_c(0{\cdot}10)$ is				
c	0·75	0·80	0·85	0·90	0·95
0·30	0·97				
0·35	1·40	0·69			
0·40	1·86	1·11			
0·45	2·32	1·49	0·47		
0·50	2·82	1·85	0·99		
0·55	3·35	2·22	1·22		
0·60	3·93	2·60	1·48		
0·65	4·56	3·00	1·76	0·19	
0·70	5·24	3·43	2·02	0·75	
0·75	5·98	3·90	2·30	0·99	
0·80	6·77	4·39	2·59	1·12	
0·85	7·61	4·92	2·88	1·32	
0·90	8·50	5·48	3·20	1·49	
0·95	9·44	6·08	3·53	1·67	
1·00	10·43	6·70	3·88	1·85	
1·05	11·47	7·36	4·24	2·02	
1·10	12·57	8·05	4·63	2·21	
1·15	13·72	8·78	5·03	2·39	
1·20	14·91	9·54	5·45	2·58	
1·25	16·16	10·32	5·89	2·78	
1·30	17·46	11·15	6·34	2·98	0·25
1·35	18·81	12·00	6·82	3·19	0·57
1·40	20·21	12·89	7·31	3·41	0·78
1·45	21·66	13·81	7·83	3·64	0·93
1·50	23·17	14·76	8·36	3·87	1·00
1·55	24·72	15·74	8·90	4·11	1·03
1·60	26·33	16·76	9·47	4·36	1·14
1·65	27·98	17·80	10·05	4·62	1·24
1·70	29·69	18·88	10·66	4·88	1·33
1·75	31·45	20·00	11·28	5·15	1·42
1·80	33·26	21·14	11·92	5·44	1·50
1·85	35·12	22·32	12·57	5·73	1·59
1·90	37·03	23·53	13·25	6·02	1·68
1·95	39·00	24·77	13·94	6·33	1·77
2·00	41·01	26·04	14·65	6·64	1·86

Note: The lowest values of *c* for which β tends to zero are 0·26, 0·32, 0·43, 0·64 and 1·26 when $N_c(0{\cdot}1) = 0{\cdot}75$, 0·80, 0·85, 0·90 and 0·95 respectively.

Table 3. *β as a function of c satisfying the equation* $N_c(0{\cdot}05) = p$ *for different fixed values of p*

	Value of β for which $N_c(0{\cdot}05)$ is				
c	0·75	0·80	0·85	0·90	0·95
0·20	1·86	1·11			
0·25	2·82	1·85	0·99		
0·30	3·93	2·60	1·48		
0·35	5·24	3·43	2·02	0·75	
0·40	6·77	4·39	2·59	1·12	
0·45	8·50	5·48	3·20	1·49	
0·50	10·43	6·70	3·88	1·85	
0·55	12·57	8·05	4·63	2·21	
0·60	14·91	9·54	5·45	2·58	
0·65	17·46	11·15	6·34	2·98	0·25
0·70	20·21	12·89	7·31	3·41	0·78
0·75	23·17	14·76	8·36	3·87	1·00
0·80	26·33	16·76	9·47	4·36	1·14
0·85	29·69	18·88	10·66	4·88	1·33
0·90	33·26	21·14	11·92	5·44	1·50
0·95	37·03	23·53	13·25	6·02	1·68
1·00	41·01	26·04	14·65	6·64	1·86
1·05	45·19	28·69	16·13	7·30	2·04
1·10	49·57	31·46	17·67	7·98	2·22
1·15	54·16	34·37	19·29	8·70	2·41
1·20	58·95	37·40	20·99	9·44	2·60
1·25	63·95	40·56	22·75	10·23	2·80
1·30	69·15	43·85	24·59	11·04	3·00
1·35	74·55	47·27	26·49	11·88	3·21
1·40	80·16	50·82	28·47	12·76	3·43
1·45	85·97	54·49	30·53	13·67	3·66
1·50	91·99	58·30	32·65	14·61	3·89
1·55	98·21	62·23	34·85	15·58	4·14
1·60	104·63	66·30	37·12	16·59	4·39
1·65	111·26	70·49	39·46	17·62	4·64
1·70	118·09	74·82	41·87	18·69	4·91
1·75	125·13	79·27	44·35	19·79	5·19
1·80	132·37	83·85	46·91	20·92	5·47
1·85	139·81	88·56	49·54	22·09	5·76
1·90	147·46	93·40	52·24	23·28	6·06
1·95	155·31	98·36	55·01	24·51	6·37
2·00	163·36	103·46	57·86	25·77	6·68

Note: The lowest values of *c* for which β tends to zero are 0·13, 0·16, 0·21, 0·32 and 0·64 when $N_c(0{\cdot}05) = 0{\cdot}75$, 0·80, 0·85, 0·90 and 0·95 respectively.

Table 4. *Test of the statistical method of selecting the optimum reflections for absolute configuration determination*

h k l	$N_c(0{\cdot}1)$	δ_{obs}	*h k l*	$N_c(0{\cdot}1)$	δ_{obs}
L-Ephedrine hydrochloride			L-Tyrosine hydrochloride		
3 4 0	90·3%	44%	4 4 0	88·9%	41%
3 2 0	89·8	54	1 9 0	81·8	59
7 3 0	89·0	12	5 4 0	78·8	19
5 2 0	82·5	19	2 9 0	78·4	20
9 3 0	81·9	5*	5 6 0	78·4	21
6 3 0	78·9	27	10 6 0	78·4	13
3 5 0	78·7	24	8 5 0	78·1	7*
7 1 0	78·4	1*	2 5 0	77·3	17
7 4 0	77·3	54	5 2 0	75·1	14
11 3 0	77·1	9*	9 3 0	74·1	34
L-Lysine hydrochloride dihydrate: *hk*0 data			L-Lysine hydrochloride dihydrate: 0*kl* data		
1 2 0	93·9	42	0 8 0	91·5	58
2 8 0	91·4	7*	0 0 5	89·4	13
4 6 0	90·4	36	0 2 5	86·8	26
3 4 0	90·3	42	0 1 4	79·0	1*
4 8 0	89·7	0*	0 2 2	77·5	4*
5 6 0	87·4	13	0 3 4	77·2	7*
1 4 0	87·2	6*	0 1 3	76·0	11
5 8 0	86·5	15	0 5 2	74·7	32
1 12 0	80·5	21	0 12 3	73·1	25
1 8 0	78·4	2*	0 11 1	71·8	12

Table 5. *Test of the statistical method for selecting reflections for Bijvoet differences for phase determination*

Crystal	N_t	N_o	Success of prediction (%)
L-Ephedrine hydrochloride	24	20 (49)	83·3
L-Tyrosine hydrochloride	42	33 (84)	78·6
L-Lysine hydrochloride dihydrate			
0*kl* data	28	17 (65)	60·7
*hk*0 data	27	21 (68)	77·8

Note: N_t denotes the number of Bijvoet pairs for which the theoretical value of $N_c(0{\cdot}05) > 0{\cdot}75$ and N_o denotes those for which the observed value of $\delta > 0{\cdot}05$. The numbers in parentheses denote the total number of reflections for which the Bijvoet difference measurements are reported.

observed reflection was calculated and the various reflections were arranged in decreasing order of the probability values. The top ten reflections with the highest probabilities are given in Table 4. The last column of Table 4 also contains the corresponding observed values of the Bijvoet ratio. For each crystal, the cases for which the prediction is wrong are shown with an asterisk. Table 4 shows that the present method is successful in 73% of the cases on average.

The result was also tested for its use in selecting reflections for Bijvoet difference data collection for phase determination. For the above three crystals, for each reflection for which the Bijvoet differences have been reported, the value of the probability $N_c(0{\cdot}05)$ was calculated. Corresponding to each crystal the number of reflections for which this probability $>0{\cdot}75$ is shown in Table 5. The number of reflections in which the prediction is correct and the percentage of success of this method for the three crystals are also shown. It can be seen that the present method is successful in 75% of the cases on average.

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