BROWN, B. E. (1962). *Norsk Geol. Tidsskr.*, Feldspar Vol., **42**, 25.

COLE, W. F., SÖRUM, H. & KENNARD, O. (1949). *Acta Cryst.* **2**, 280.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

ESKOLA, P. (1951). *Ann. Acad. Sci. Fennicae*, Ser. A. III, **27**, 1.

FERGUSON, R. B. (1960). *Canad. Miner.* **6**, 415.

FERGUSON, R. B., TRAILL, R. J. & TAYLOR, W. H. (1958). *Acta Cryst.* **11**, 331.

FERGUSON, R. B., TRAILL, R. J. & TAYLOR, W. H. (1959). *Acta Cryst.* **12**, 716.

GOLDSCHMIDT, J. R. & LAVES, F. (1954a). *Geochim. Cosmochim. Acta*, **5**, 1.

GOLDSCHMIDT, J. R. & LAVES, J. (1954b). *Geochim. Cosmochim. Acta*, **6**, 100.

GOLDSMITH, J. R. & LAVES, F. (1961). *Cursillos y Conferencias Inst. 'Lucas Mallada'*, **8**, 81.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

JONES, J. B. & TAYLOR, W. H. (1961). *Acta Cryst.* **14**, 443.

KEMPSTER, C. J. E., MEGAW, H. D. & RADOSLOVICH, E. W. (1962). *Acta Cryst.* **15**, 1005.

LAVES, F. (1950). *J. Geol.* **58**, 548.

LAVES, F. (1951). *J. Geol.* **59**, 510.

LAVES, F. & GOLDSMITH, J. R. (161). *Cursillos y Conferencias Inst. 'Lucas Mallada'*, **8**, 71.

MACKENZIE, W. S. & SMITH, J. V. (1959). *Acta Cryst.* **12**, 73.

MACKENZIE, W. S. & SMITH, J. V. (1961). *Cursillos y Conferencias Inst. 'Lucas Mallada'*, **8**, 53.

MEGAW, H. D. (1956). *Acta Cryst.* **9**, 56.

MEGAW, H. D., KEMPSTER, C. J. E. & RADOSLOVICH, E. W. (1962). *Acta Cryst.* **15**, 1017.

NEWNHAM, R. E. & MEGAW, H. D. (1960). *Acta Cryst.* **13**, 303.

RIBBE, P. H. (1963a). *Acta Cryst.* **16**, 426.

RIBBE, P. H. (1963b). Thesis, Cambridge University.

SMITH, J. V. (1954). *Acta Cryst.* **7**, 479.

SMITH, J. V. & BAILEY, S. W. (1963). *Acta Cryst.* **16**, 801.

WEISZ, O., COCHRAN, W. & COLE, W. F. (1948). *Acta Cryst.* **1**, 83.

WILCOX, R. E. (1959). *Amer. Min.* **44**, 1064.

The Probability Distribution of Bijvoet Differences

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The statistical distribution of the difference in intensities between inverse reflexions (Bijvoet difference) in non-centrosymmetric crystals containing atoms, some of which scatter anomalously, has been investigated theoretically. The theory is worked out for structures containing one, two and many anomalous scatterers (all assumed to be alike) in addition to a large number of non-anomalous scatterers. The theoretical results have been tested with calculations based on hypothetical models and also with the observed data from two known structures. The agreement is found to be good. The results suggest that, for observing large Bijvoet differences, a structure containing a large number of anomalous scatterers with a centric configuration is the least favourable as compared with a structure containing either a small number of atoms (one or two) or a large number with an acentric configuration.

1. Introduction

The use of the anomalous dispersion technique in crystal structure analysis, particularly for the determination of the absolute configuration of a structure, was first pointed out by Bijvoet (1954) and the method has since then proved to be one of the most interesting applications of X-ray methods to the elucidation of chemical structure. The full potentialities of the effect came to be realized soon and methods of applying it to actual structure determination were evolved almost simultaneously, but independently, by two groups of workers, namely, Ramachandran & Raman (1956) and Pepinsky and collaborators (Okaya, Saito & Pepinsky, 1955; Pepinsky & Okaya, 1956).

The approach of Ramachandran & Raman was basically from the Fourier-synthesis point of view, whereby the phase angle of a reflexion could be solved for, but for an inherent ambiguity, from the Bijvoet differences.* Of these two possibilities in the phase angle, the one which is closer to the heavy atom phase is taken to be the correct one and a Fourier synthesis, using these phases, would yield the structure. Pepinsky and co-workers have, however, approached the problem from the point of view of the

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* We shall use the term *Bijvoet difference* to denote the difference in intensity between inverse reflexions; that is $I = I(\mathbf{H}) - I(\overline{\mathbf{H}})$. Here $\mathbf{H}$ stands for the reflexion indices hkl and $\overline{\mathbf{H}}$ for $\overline{hkl}$.

Patterson function, using the Bijvoet differences and its deconvolution. Both approaches, in effect, lead to the structure in its absolute configuration.

The anomalous dispersion technique has since then proved to be increasingly successful in the determination of the structure of a number of compounds (Raman, 1959; Dale, Hodgkin & Venkatesan, 1963; Kartha, 1963). The success of all these methods depends to a large extent on the possibility of measuring, with considerable accuracy, the Bijvoet differences of a fairly large number of reflexions. Although one would expect that counter techniques would be necessary for such measurements it is interesting to note that even the ordinary photographic technique with visual estimation has proved to be quite successful in certain cases (Dale et al., 1963). However, it is to be mentioned that all the structures that have been solved by this method belong to the space group $P2_1$ with two anomalous scatterers in the unit cell. Although precise information is lacking as to whether this effect is observed to be pronounced in structures containing larger numbers of anomalous scatterers, it appears, at any rate, that the case of two anomalous scatterers in the unit cell is favourable for observing this effect. The present work was undertaken with a view to examine the effect of the number of anomalous scatterers in the unit cell on the statistical distribution of Bijvoet differences. This actually arose out of a remark* by Prof. Ramachandran that the rather marked anomalous dispersion effect observed for the space group $P2_1$ might possibly be due to the rather peculiar nature of the intensity distribution for a two-atom structure (Srinivasan, 1960) and that it would be worth while studying the statistical distribution of Bijvoet differences in relation to the number of anomalous scatterers in the unit cell. We shall therefore consider three cases, namely, structures containing one, two and many anomalous scatterers in the unit cell, in addition to a large number of non-anomalous scatterers. For brevity we shall be referring to these three as the one-, two-, and many-atom cases respectively. In the last case, actually, we shall also have to consider two possibilities, namely when the group of anomalous scatterers takes a centrosymmetric or non-centrosymmetric configuration. For brevity we shall refer to these two as P-centric and P-acentric respectively. The theoretical distribution functions are given in the form of curves for all the cases. They have also been tested with calculations based on hypothetical models and also on a few known structures. The agreement with theory is found to be good.

As to the question of the most favourable case for observing large Bijvoet differences, theory suggests that the one-atom case is the best, followed by the two-atom and many-atom cases (P-acentric) which behave rather closely, and finally by the many-atom case (P-centric). It should be remarked, however, that the differences between all these cases are not so pronounced as to enable us to choose any one in overwhelming preference to another. The choice, therefore, depends on certain other practical factors and these will be discussed in § 5. The next section is devoted to the derivation of the formulae, while § 3 and § 4 will be concerned with the discussion of the nature of the distributions and the testing of the theoretical results respectively.

2. Derivation of the probability distribution of the Bijvoet differences

We assume that a non-centrosymmetric crystal contains P identical anomalous scatterers and a large number (Q) of light atoms (non-anomalous scatterers) in the unit cell, the total number of atoms being $N = P + Q$. We shall represent the atomic scattering factor of the anomalous scatterer as $f_P = f_P^0 + \Delta f_P' + i\Delta f_P'' = f_P' + if_P''$ and that of the non-anomalous scatterer by f_Q. It is convenient to use the Argand diagram to bring out the various relations between the structure factors (Fig. 1). Thus $F_Q(H)$ denotes the contribution to the reflexion H by the light atoms and $F_P'(H)$ and $F_P''(H)$ denote respectively the contributions due to the real and imaginary parts of the atomic scattering factors of the anomalous scatterers. $F_N'(H)$ $(= F_P'(H) + F_Q(H))$ denotes the total contribution to the reflexion H by the real parts of the atomic scattering factors of all the atoms in the unit cell. The corresponding quantities for the inverse reflexions are shown with the symbol $\bar{H}$. Strictly, the various quantities for the reflexion $\bar{H}$ should have been shown in Fig. 1 below the X axis. But in order to bring out
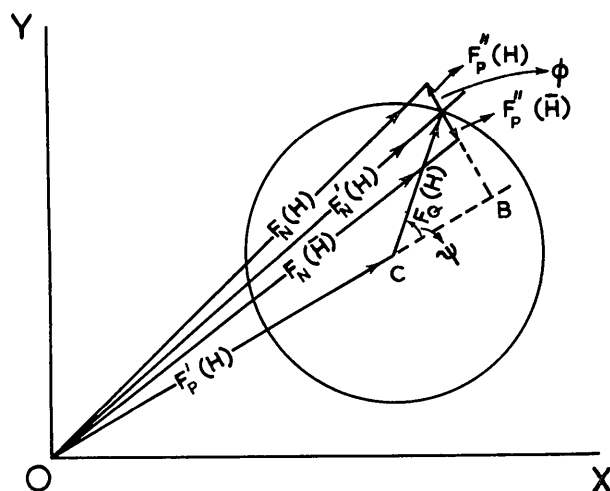

Fig. 1. The relationship between the various components of the structure factor of the inverse reflexions H and $\bar{H}$.

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the geometrical relations clearly, this part of the diagram has been reflected about the X axis, so that $F'_N(\overline{\mathbf{H}})$ coincides with $F'_N(\mathbf{H})$. The angle between $F'_N(\mathbf{H})$ and $F''_P(\mathbf{H})$ is termed φ and that between $F'_P(\mathbf{H})$ and $F_Q(\mathbf{H})$ is termed ψ.

The Bijvoet difference of the inverse reflexions $\mathbf{H}$ and $\overline{\mathbf{H}}$ can be shown, from simple geometrical considerations, to be (Ramachandran & Raman, 1956; Peerdeman & Bijvoet, 1956)

$$\Delta|F_N(\mathbf{H})|^2 = |F_N(\mathbf{H})|^2 - |F_N(\overline{\mathbf{H}})|^2$$
$$= 4|F''_P||F'_N|\cos\varphi . \qquad (1)$$

It is clear from Fig. 1 that $|F'_N|\cos\varphi = |F_Q|\sin\psi$, using which we get from equation (1)

$$\Delta|F_N|^2 = 4|F''_P||F_Q|\sin\psi . \qquad (2)$$

The reason for recasting the expression (1) into form (2) is that the latter has the advantage that the three quantities on the right hand side are independent random variables. This becomes clear from the fact that, firstly, the contributions to the various reflexions by the atoms P and Q are entirely independent of each other. Also, for a given $|F_Q|$ and $|F_P|$, the vector F_Q can lie anywhere along a circle of radius $|F_Q|$ so that the angle ψ is randomly and uniformly distributed over the range 0 to 2π and is independent of $|F_Q|$. Thus, the distribution of $\Delta|F_N|^2$ can be worked out, since it is expressed as the product of three independent random variables. The distribution of $|F_Q|\sin\psi$ can first be obtained since that of $|F_Q|$ and $\sin\psi$ are known. The distribution of $|F''_P|$ depends on the number of anomalous scatterers and has to be considered separately for the three cases.

For convenience we now define a new variable x by the relation

$$x = \frac{|\Delta|F_N|^2|}{4\sigma_Q\sigma''_P} = \frac{|F''_P|}{\sigma''_P}\frac{|F_Q|}{\sigma_Q}|\sin\psi| ,$$
where $\qquad (3)$
$$\sigma_Q^2 = \sum_{j=1}^{Q} f_{Qj}^2 \quad \text{and} \quad \sigma''^2_P = \sum_{k=1}^{P} f''^2_{Pk} .$$

We shall denote $|F_Q|/\sigma_Q$ and $|F''_P|/\sigma''_P$ by y_Q and y''_P respectively. They are the normalized structure amplitudes corresponding to the contributions from the atomic scattering factors of the Q-atoms and the imaginary part of the atomic scattering factor of the P-atoms respectively. Equation (3) now takes the form

$$x = y''_P y_Q |\sin\psi| . \qquad (4)$$

The advantage of choosing x instead of $\Delta|F_N|^2$ is that it is a normalized statistical variable in the sense that the various theoretical distribution functions turn out to be independent of the parameters σ_Q and σ''_P that characterize a particular crystal.

We shall first obtain the distribution of $|F_Q||\sin\psi|$, since it is common for the three different cases which we shall be considering. Since ψ is uniformly distributed in the range 0 to 2π, the distribution of $|\sin\psi|$, is

$$P_1(|\sin\psi|) = 1/2\pi\sqrt{(1 - \sin^2\psi)} . \qquad (5)$$

The distribution of y_Q for the non-centrosymmetric case is given by (Wilson, 1949; Ramachandran & Srinivasan, 1959)

$$P_2(y_Q) = 2y_Q \exp[-y_Q^2] . \qquad (6)$$

We shall use the well-known theorem in probability that if x and y are independent random variables with probability density functions $P_1(x)$ and $P_2(y)$ respectively, then the probability density function of the variable $z = xy$ is given by

$$P_3(z) = \int_x P_1(x)P_2(z/x)dx/x$$
$$= \int_y P_1(z/y)P_2(y)dy/y . \qquad (7)$$

Using theorem (7), we can write the distribution of $y_Q|\sin\psi| = t$ as

$$P_3(t) = \int_{\psi=0}^{2\pi} P_1(|\sin\psi|)P_2\left(\frac{t}{|\sin\psi|}\right)\frac{d\sin\psi}{|\sin\psi|} ,$$

where $P_1(|\sin\psi|)$ and $P_2(y_Q)$ are given by (5) and (6) respectively. Thus we get

$$P_3(t) = 2\int_0^{\pi}\frac{1}{2\pi\sqrt{(1-\sin^2\psi)}}\frac{2t}{|\sin\psi|}$$
$$\times\exp\left\{-\frac{t^2}{\sin^2\psi}\right\}\frac{d\sin\psi}{|\sin\psi|} . \qquad (8)$$

The factor 2 appears on the right hand side since we are interested only in $|\Delta|F_N|^2|$ and not in $\Delta|F_N|^2$. Equation (8) simplifies to

$$P_3(t) = \frac{2t}{\pi}\int_0^{\pi}\operatorname{cosec}^2\psi\exp[-t^2(1+\cot^2\psi)]d\psi$$
$$= -\frac{2t}{\pi}\exp(-t^2)\int_0^{\pi}\exp(-t^2\cot^2\psi)d(\cot\psi) . \qquad (9)$$

Making the substitution $t\cot\psi = u$ in (9) we obtain

$$P_3(t) = \frac{2}{\pi}\exp(-t^2)\int_{-\infty}^{\infty}\exp(-u^2)du$$
$$= (2/\sqrt{\pi})\exp(-t^2) . \qquad (10)$$

We can now work out the distribution of $x = ty''_P$ where the distribution of t is given by (10). The probability distribution of y''_P depends on the number of anomalous scatterers in the unit cell and it will be worked out for the three different cases respectively.

(a) One-atom case

If the origin is chosen on the anomalous scatterer itself, then we have $|F''_P| = f''_P$ and $\sigma''_P = f''_P$, so that y''_P is a constant equal to unity. Hence $x = t$ and the probability density function of x is given by

$$P(x) = (2/\sqrt{\pi})\exp(-x^2) . \qquad (11)$$

This density function is in the normalized form. It is useful to work out the expectation value of x also. Thus we have, for the present case,

$$\langle x \rangle = (2/\sqrt{\pi}) \int_0^\infty x \exp(-x^2) dx$$

$$= 1/\sqrt{\pi} = 0.5641 .$$

(b) Two-atom case

In this case we can choose the origin midway between the two anomalous scatterers. The distribution of y_P'' is given by (Srinivasan, 1960)

$$P_4(y) = \frac{2}{\pi\sqrt{(2-y_P''^2)}} ; \quad 0 \le y_P'' \le \sqrt{2} . \quad (12)$$

Making use of equations (7), (10) and (12), we get the distribution of $x = t y_P''$ to be

$$P(x) = \int_0^{\sqrt{2}} P_3(x/y_P'')P_4(y_P'')dy_P''/y_P'' . \quad (13)$$

Using the substitution $y_P'' = \sqrt{2} \operatorname{sech} u$, the integral (13) reduces to

$$P(x) = \frac{\sqrt{2}}{\pi\sqrt{\pi}} \exp(-x^2/4) \int_0^\infty \exp\left(-\frac{x^2}{4}\cosh 2u\right) d(2u)$$

$$= (\sqrt{2}/\pi\sqrt{\pi}) \exp(-x^2/4)K_0(x^2/4) , \quad (14)$$

where $K_0(x)$ is the Bessel function of order zero with imaginary argument (Watson, 1944, p. 181).

That the function (14) is correctly normalized can be verified easily by showing that the integral reduces to unity. Thus, if we substitute $x^2/4 = y$ in (14) we get

$$\frac{\sqrt{2}}{\pi\sqrt{\pi}} \int_0^\infty y^{-1/2} \exp(-y)K_0(y) dy ,$$

which, by virtue of the relation (Erdelyi, 1954)

$$\int_0^\infty x^{-1/2} \exp(-x) \cos(4ax^{1/2})K_0(x) dx$$
$$= 2^{-1/2}\pi^{3/2} \exp(-a^2)I_0(a^2) ,$$

reduces to unity.

The expectation value of x for the present case is given by

$$\langle x \rangle = \frac{\sqrt{2}}{\pi\sqrt{\pi}} \int_0^\infty x \exp(-x^2/4)K_0(x^2/4) dx . \quad (15)$$

This integral can be shown to reduce to (Appendix I)

$$\langle x \rangle = (2/\pi)^{3/2} = 0.5029 .$$

(c) Many-atom case

(i) *P-group centric.* — The distribution of y_P'' in this case is (Wilson, 1949; Ramachandran & Srinivasan, 1959)

$$P_5(y_P'') = (2/\pi)^{1/2} \exp(-y_P''^2/2) . \quad (18)$$

Making use of equations (7), (10) and (18), the distribution of x takes the form

$$P(x) = \frac{2\sqrt{2}}{\pi} \int_0^\infty \exp\left[-\frac{y_P''^2}{2} - \frac{x^2}{y_P''^2}\right] \frac{dy_P''}{y_P''} . \quad (19)$$

On substituting $y_P''^2 = \sqrt{2}x \exp(2\theta)$ equation (19) simplifies to

$$P(x) = (2\sqrt{2}/\pi) \int_{-\infty}^\infty \exp[-\sqrt{2}x \cosh(2\theta)]d\theta$$

$$= (2\sqrt{2}/\pi) \int_0^\infty \exp[-\sqrt{2}x \cosh(2\theta)]d(2\theta)$$

$$= (2\sqrt{2}/\pi)K_0(\sqrt{2}x) . \quad (20)$$

This probability density function is in the normalized form and gives the expectation value of x to be (Appendix II)

$$\langle x \rangle = \sqrt{2}/\pi = 0.4502 .$$

(ii) *P-group acentric.** — In this case the distribution of y_P'' is given by

$$P(y_P'') = 2y_P'' \exp(-y_P''^2) . \quad (21)$$

Making use of equations (7), (10) and (21) the distribution of x takes the form

$$P(x) = (4/\sqrt{\pi}) \int_0^\infty \exp[-y_P''^2 - (x^2/y_P''^2)]dy_P'' , \quad (22)$$

which, on integration, gives (see p. 275, equation 427; Hodgman, Weast & Selby, 1958)

$$P(x) = 2 \exp(-2x) . \quad (23)$$

This is obviously in the normalized form. The expectation value of x is given by $\langle x \rangle = \frac{1}{2}$.

3. Nature of the probability distributions

The probability density functions for the three cases are shown in Fig. 2. The curves for the many-atom case (P-centric) and also for the two-atom case have a singularity at the origin, and this is obvious from the nature of the expressions for them (equations (14) and (20)), which contain the Bessel function $K_0(x)$. It seems to be convenient in such cases to deal with the cumulative function $N(x)$ which is the integral of the probability density function. This function

$$N(x) = \int_0^x P(x) dx$$

has been calculated by graphical integration for the two-atom case and for the many-atom case (P-centric). In the one-atom case $N(x)$ takes the simple form Erf (x) while in the many-atom case (P-acentric) it is given by $1 - \exp(-2x)$. The $N(x)$ curves for all the four cases are shown in Fig. 3.

Our main interest in these curves is to compare their behaviour for fairly large values of x. It may

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* By oversight this case had not been considered by us at first. This was pointed out to us by Prof. G. N. Ramachandran.

be seen from Fig. 2 that the curve for the one-atom case passes well above the others for moderate and large values of x, indicating thereby that it is more
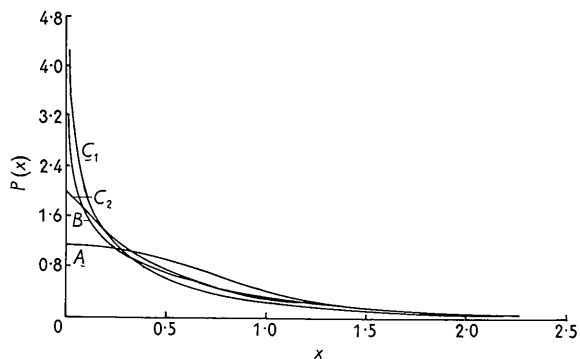

Fig. 2. Theoretical probability density function for the normalized Bijvoet difference x, for (A) one-atom case, (B) two-atom case; (C_1) many-atom case (P-centric), and (C_2) many-atom case (P-acentric).
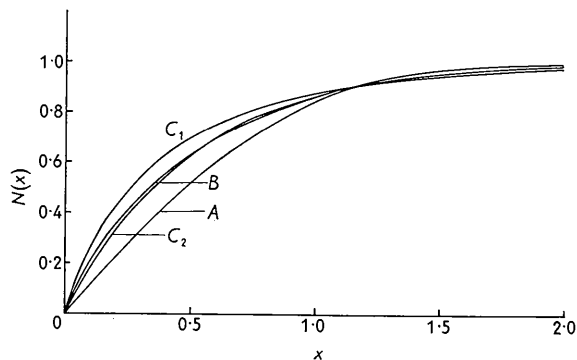

Fig. 3. Theoretical cumulative function for the normalized Bijvoet difference x, for (A) one-atom case, (B) two-atom case, (C_1) many-atom case (P-centric), and (C_2) many-atom case (P-acentric).

favourable than all the other cases for observing large Bijvoet differences. This feature, in general, decreases progressively for increasing values of the number of anomalous scatterers in the unit cell. The curve for the many-atom case (P-acentric) is, however, fairly close to that of the two-atom case even for moderately large values of x, and in fact they become practically indistinguishable for still larger values. The curve for the many-atom case (P-centric) falls below all the others and thus it is the least favourable for observing large Bijvoet differences.

The progressive change in the behaviour of the curves is also reflected in the mean value of x. For instance, the value is maximum for the one-atom case (0·564) while it is minimum for the many-atom (P-centric) case (0·45). The values for the two-atom and many-atom (P-acentric) cases are very close to each other (0·503 and 0·500 respectively). In fact

this is a direct consequence of the difference in the value of $\langle y_P'' \rangle$ for the different cases. For, we can write, since y_P'' and t are independent, $\langle x \rangle = \langle y_P'' t \rangle = \langle y_P'' \rangle \langle t \rangle$ where $\langle t \rangle$ is given by $1/\sqrt{\pi}$ and $\langle y_P'' \rangle$ takes the value $1, 2\sqrt{2}/\pi, \sqrt{(2/\pi)}$ and $\sqrt{\pi}/2$ respectively for the one-, two-, and many-atom (P-centric and P-acentric) cases respectively.

4. Test of the theoretical curves

The theoretical curves given in Figs. 2 and 3 have been tested mainly with a hypothetical model and in a few cases with known structures for which experimentally observed data for the Bijvoet differences were available. The hypothetical structure for the many-atom case (P-group acentric) was based on a two-dimensional unit cell in the plane group symmetry pg (Fig. 4) with 6 chlorine atoms as anomalous scatterers (for Cu $K\alpha$, $\Delta f_{Cl}' = 0\cdot23$ and $\Delta f_{Cl}'' = 0\cdot69$) and 18 carbon atoms. For the two-atom case the same unit cell was used except that the chlorine atoms marked a, a', c and c' were removed. For the one-atom case the rectangle marked $AEFD$ was used except that the chlorine atoms marked a and c were removed.
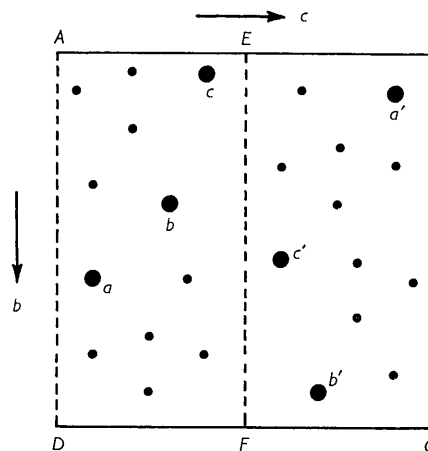

Fig. 4. Hypothetical structure in the plane group symmetry pg for the many-atom case. Unit-cell dimensions are $10\ \text{Å} \times 10\ \text{Å}$. ● Chlorine, • Carbon.

The values of x for the various reflexions in these hypothetical cases were calculated from the formula (Appendix III)

$$x = (a_P b_Q - b_P a_Q)/\sqrt{(PQ)} . \tag{21}$$

These values of x which we shall call the 'experimental values' were used to obtain the data shown in Fig. 5. It may be seen that the points representing experimental values follow closely the theoretical curves $N(x)$ for all the cases. Only in the many-atom case (P-acentric) there appears to be initially a slight deviation of the experimental points from the

theoretical curve. This might probably be due to the fact that the value 6 used for the number of anomalous scatterers in this case was not large enough. It appears that a value $P > 10$ would give a close approximation to the asymptotic distribution (Slack, 1946).* In the centrosymmetric case, however, it appears that even three pairs of atoms is a sufficient approximation to the asymptotic distribution (Qurashi, 1953).

The theoretical curves were also tested with the actually observed Bijvoet differences in two crystals.
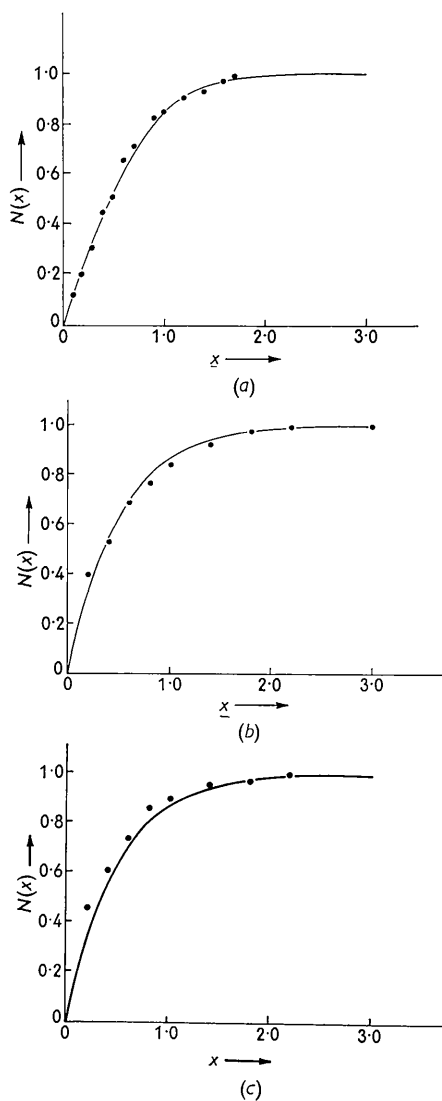

(a)

(b)

(c)

Fig. 5. Comparison of experimental data with the theoretical cumulative distribution of normalized Bijvoet difference for (A) one-atom case, (B) two-atom case, and (C) many-atom case (P-acentric). The solid lines are theoretical curves and dots represent experimental values.

* We wish to thank the referee for bringing this reference to our notice.

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The data were available only for the two-atom case, namely L(+)-lysine hydrochloride dihydrate (Raman, 1959) and L-tyrosine hydrochloride (Parthasarathy, 1962; Srinivasan, 1959) both of which belong to the space group $P2_1$. The experimental points for these two cases are shown along with the theoretical $P(x)$ curve in Fig. 6 and there is seen to be good agreement between the two.
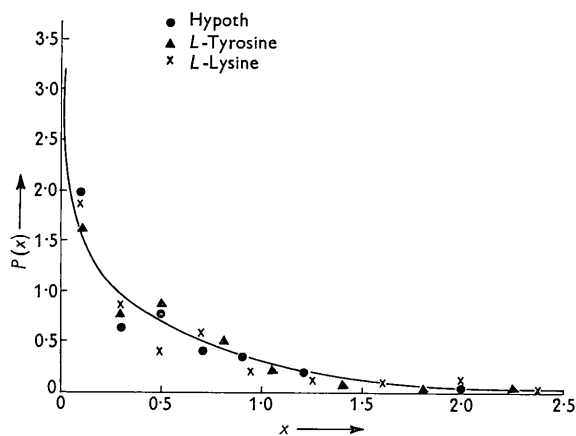

Fig. 6. Comparison of experimental data with the theoretical probability density function of the Bijvoet difference, for the two-atom case.

● Hypothetical two-atom case.
▲ L-tyrosine hydrochloride.
× L(+)-lysine hydrochloride dihydrate.

5. Conclusion

The results of the foregoing sections indicate that in order to observe fairly large Bijvoet differences one should choose, in order of preference, a structure containing one, two or many anomalous scatterers with an acentric configuration and lastly many anomalous scatterers with a centric configuration. This is, however, based purely on probability considerations. But there are certain other factors that have to be considered in applying the results to actual structure analysis. Thus it is well-known that the determination of phases by the anomalous dispersion method has a twofold inherent ambiguity. One method of resolving this ambiguity is to use both the phases, which is what is done effectively in the β-anomalous synthesis (Ramachandran & Raman, 1959). The nature of the resultant map depends to a large extent on the anomalous scatterers. If the P-atoms have a centre of symmetry, as is necessarily the case for the one- and two-atom cases, there is a duplication of the structure about the centre of symmetry of the P-group; the inverse peaks have, however, negative strengths. If the P-group is acentric, the concentration of the negative peaks does not occur, but diffuses into a negative background. It would appear therefore

that the case of many anomalous scatterers with an acentric configuration is to be preferred. At any rate the many-atom case with the P-group having a centric configuration seems to be the least preferable in view of the duplication of the peaks and also the rather low probability of occurrence of large Bijvoet differences.

In the case of one and two anomalous scatterers in the unit cell it is, however, a point to be examined whether the occurrence of duplication is such a real disadvantage as to offset the other favourable feature, namely that they have a fairly high probability of exhibiting large Bijvoet differences. In fact, the duplication of peaks in these cases is not a real disadvantage as one might be tempted to assume initially. It can probably be taken to be more of an advantage because it helps the interpretation of the map in terms of peaks of equal but opposite strengths related by an inversion about the apparent centre of symmetry introduced by the P-group. The only difficulty that may arise is that there may be partial cancellation of peaks due to overlap resulting from atoms which are nearly centric with reference to the centre of inversion of the P-group of atoms.

Instead of using both the possible phases in the Fourier synthesis, one may adopt a different procedure. This arises from the fact that the anomalous scatterers are invariably heavy atoms and the phase of a reflexion is in general dominated by the phase of these heavy atoms. Since the contribution of the heavy atom to the phase of a reflexion will in general be known, one might choose, out of the two possible phases, the one that is nearer the phase of the anomalous group and use it in the Fourier synthesis. The duplication of the peaks will not be present in such a map. This procedure has been adopted successfully in a recent structure determination (Dale *et al.*, 1963). Thus, it appears that, in order to have larger Bijvoet differences, it will be profitable to look for crystals containing one or two anomalous scatterers in the unit cell or many anomalous scatterers with an acentric configuration. Such an attempt is likely to be more rewarding with the two-atom case, in view of the rather high frequency of occurrence of the monoclinic space group $P2_1$.

APPENDIX I

If we use the substitution $x^2/4 = y$, the integral (15) reduces to

$$\langle x \rangle = (2/\pi)^{3/2} \int_0^\infty \exp(-y) K_0(y) dy . \quad \text{(A1)}$$

Using the integral definition of the Bessel function $K_0(y)$, namely,

$$K_0(y) = \int_0^\infty \exp(-y \cosh t) dt$$

the integral (A1) becomes

$$\langle x \rangle = (2/\pi)^{3/2} \int_{t=0}^\infty \int_{y=0}^\infty \exp[-y(1+\cosh t)] dt\, dy . \quad \text{(A2)}$$

Performing the integration with reference to y first, the integral (A2) becomes

$$\langle x \rangle = (2/\pi)^{3/2} \int_{t=0}^\infty dt \int_{y=0}^\infty \exp[-y(1+\cosh t)] dy$$

$$= (2/\pi)^{3/2} \int_{t=0}^\infty \frac{dt}{1+\cosh t}$$

If we put $t/2 = u$, the above integral becomes

$$\langle x \rangle = (2/\pi)^{3/2} \int_0^\infty \text{sech}^2 u\, du$$

$$= (2/\pi)^{3/2} = 0.5079 . \quad \text{(A3)}$$

APPENDIX II

To see that the density function (20) is in the normalized form, consider the integral

$$\int_0^\infty P(x) dx = (2\sqrt{2}/\pi) \int_0^\infty K_0(\sqrt{(2)}x) dx . \quad \text{(A4)}$$

Changing the variable to $v = \sqrt{(2)}x$, the above integral becomes (Watson, 1944, p. 388)

$$(2/\pi) \int_0^\infty K_0(v) dv = 1 . \quad \text{(A5)}$$

The expectation value of x is given by

$$\langle x \rangle = (2\sqrt{2}/\pi) \int_0^\infty x K_0(\sqrt{2}x) dx . \quad \text{(A6)}$$

Using the same substitution $v = \sqrt{2}x$ we get (Watson, 1944, p. 388)

$$\langle x \rangle = (\sqrt{2}/\pi) \int_0^\infty v K_0(v) dv$$

$$= \sqrt{2}/\pi = 0.4502 . \quad \text{(A7)}$$

APPENDIX III

We have in an obvious notation

$$F(\mathbf{H}) = \sum_{j=1}^N f_j \exp(i\theta_j)$$

where $\theta_j = 2\pi \mathbf{H} . \mathbf{r}_j$. Separating $F(\mathbf{H})$ into two parts

corresponding to the contributions from the P and Q atoms, we have

$$F(\mathbf{H}) = \sum_{j=1}^{P} f_P \exp(i\theta_{Pj}) + \sum_{k=1}^{Q} f_Q \exp(i\theta_{Qk}) . \quad (A8)$$

Here we have omitted the subscripts j and k in f_P and f_Q respectively, since the P atoms are all chlorine and the Q atoms are all carbon in our hypothetical model. For convenience we denote

$$\sum_{j=1}^{P} \cos\theta_{Pj} \text{ by } a_P \text{ and } \sum_{j=1}^{P} \sin\theta_{Pj} \text{ by } b_P .$$

Using a similar notation for the Q atoms, we have

$$F(\mathbf{H}) = (f_P' + if_P'')(a_P + ib_P) + f_Q(a_Q + ib_Q)$$
$$= (f_Q a_Q + f_P' a_P - f_P'' b_P) + i(f_Q b_Q + f_P' b_P + f_P'' a_P) .$$

Similarly, for the structure factor of the inverse reflexion $\overline{\mathbf{H}}$ we have

$$F(\overline{\mathbf{H}}) = (f_Q a_Q + f_P' a_P + f_P'' b_P) - i(f_Q b_Q + f_P' b_P - f_P'' a_P) .$$

Hence we get, for the Bijvoet difference

$$\Delta|F|^2 = |F(\mathbf{H})|^2 - |F(\overline{\mathbf{H}})|^2$$
$$= 4 f_P'' f_Q (a_P b_Q - b_P a_Q) .$$

It is easy to see that $\sigma_Q \sigma_P'' = \sqrt{(PQ)} f_P'' f_Q$. Thus, we have finally

$$x = \frac{\Delta|F|^2}{4\sigma_Q \sigma_P''} = \frac{a_P b_Q - b_P a_Q}{\sqrt{(PQ)}} .$$

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References

BIJVOET, J. M. (1954). *Nature, Lond.* **173**, 888.

DALE, D., HODGKIN, D. C. & VENKATESAN, K. (1963). In *Crystallography and Crystal Perfection.* p. 237. Ed. RAMACHANDRAN, G. N. London: Academic Press.

ERDELYI, A. (Ed.) (1954). *Tables of Integral Transforms.* Vol. II p. 369. New York: McGraw-Hill.

HODGMAN, C. D., WEAST, R. C. & SELBY, S. M. (1959). *Handbook of Chemistry and Physics.* p. 275. Cleveland: Chemical Rubber Publishing Co.

KARTHA, G. (1963). Personal Communication.

OKAYA, Y., SAITO, Y. & PEPINSKY, R. (1955). *Phys. Rev.* **98**, 1957.

PEERDEMAN, A. F. & BIJVOET, J. M. (1956). *Acta Cryst.* **9**, 1012.

PEPINSKY, R. & OKAYA, Y. (1956). *Proc. Nat. Acad. Sci. Wash.* **42**, 286.

PARTHASARATHY, R. (1962). Ph. D. Thesis, University of Madras.

QURASHI, M. M. (1953). *Acta Cryst.* **6**, 577.

RAMAN, S. (1959). *Z. Kristallogr.* **111**, 301.

RAMACHANDRAN, G. N. & RAMAN, S. (1956). *Curr. Sci.* **25**, 348.

RAMACHANDRAN, G. N. & RAMAN, S. (1959). *Acta Cryst.* **12**, 957.

RAMACHANDRAN, G. N. & SRINIVASAN, R. (1959). *Acta Cryst.* **12**, 410.

SLACK, M. (1946). *J. Inst. Elec. Eng.* **93**, 76.

SRINIVASAN, R. (1959). *Proc. Indian Acad. Sci.,* A **50**, 19.

SRINIVASAN, R. (1960). *Acta Cryst.* **13**, 388.

WATSON, G. N. (1944). *A Treatise on the Theory of Bessel Functions.* Cambridge Univ. Press.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.