sion experiments awaits the undertaking of such experiments.

The programs for the computations performed in this paper were written by Mr Stephen Brenner. I am very grateful for his cooperation.

This research was supported in part by USPHS grant GM30902.

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Rules for Evaluating Triplet Phase Invariants by Use of Anomalous Dispersion Data

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(*Received* 12 *April* 1983; *accepted* 5 *August* 1983)

Abstract

On the basis of some mathematical and physical characteristics of anomalous dispersion experiments, it has been possible to derive simple rules, $R_{\text{ano},1}$, $R_{\text{ano},2}$ and $R_{\text{ano},3}$, that permit the selection of triplet phase invariants, in a single-wavelength experiment, that have values close to $\pi/2$, $-\pi/2$, 0 and other values in the range from $-\pi$ to π. The rules, $R_{\text{ano},1}$, $R_{\text{ano},2}$ and $R_{\text{ano},3}$, apply to the case of a single type of predominant anomalous scatterer. The simple generalization to more than one type of predominant anomalous scatterer is also described. Test examples show that large numbers of invariants may be evaluated by these means with reliabilities that are potentially high, but depend, of course, on the reliability of the experimental data. The only information required besides the measurements of the diffraction intensities is the chemical composition of the anomalously scattering atoms. In some cases, even this information is not required if two alternative sets of estimates of the values of the triplet phase invariants are considered.

Introduction

Anamalous dispersion experiments afford the opportunity to evaluate triplet phase invariants in single-wavelength experiments. Formulas for accomplishing this have already been described by Heinerman, Krabbendam, Kroon & Spek (1978) and by Hauptman (1982). The formulas of Heinerman *et al.* (1978) were derived from probabilistic arguments and give the sines of the invariants. The twofold ambiguity inherent in the sine of an invariant requires auxiliary information for its resolution. The condition used in test calculations was to select the value closest to zero. The formulas of Hauptman (1982) were derived from use of the conditional joint probability distribution and can yield unique estimates for the invariants in the whole interval $-\pi$ to $+\pi$. The method of derivation and type of result to be described in this article are quite different from those in the previous studies. They are based on an analysis of some particular mathematical and physical characteristics of the data from anomalous dispersion experiments, in a fashion that is quite comparable to an analysis recently carried out for isomorphous replacement experiments (Karle, 1983).

The characteristics of interest concern observations related to the differences of the magnitudes of selected types of structure factors and also the expected values of triplet phase invariants associated with the structure of the anomalous scatterers. The only information required of the predominant anomalous scatterers in this approach is their chemical nature. It is not necessary to know the number of positions occupied or the occupancy. The results to be obtained here are simple rules, based on several types of structure-factor magnitudes, for selecting triplet phase invariants whose values are near some particular values.

Test examples performed by Heinerman *et al.* (1978) and Hauptman (1982) show that their formulas have the potential for reliable results. Similarly, it will be seen from the results of test calculations in this article that the rules to be developed here also have the potential for yielding reliable evaluations of very large numbers of triplet phase invariants.

0108-7673/84/010004-08$01.50

Conceptual basis

The concepts that form the basis for the rules of interest are illustrated in Fig. 1. The symbolism represents three different cases, as shown in Table 1. The quantity $F_{\lambda \mathbf{h}}$ is the structure factor associated with a measured intensity and includes the contribution from anomalous dispersion, $F^n_{\mathbf{h}}$ is the corresponding structure factor when the contribution of anomalous dispersion is omitted and $F^a_{\lambda \mathbf{h}}$ is the corresponding structure factor that represents only the contribution from anomalous dispersion. The quantities are related by

$$F_{\lambda \mathbf{h}} = F^n_{\mathbf{h}} + F^a_{\lambda \mathbf{h}}. \tag{1}$$

It follows from (1) that for all the cases in Table 1

$${}_m\mathscr{F}_{1,\mathbf{h}} = {}_m\mathscr{F}_{2,\mathbf{h}} + {}_m\mathscr{F}_{3,\mathbf{h}}. \tag{2}$$

The atomic scattering factor for the pth atom that scatters anomalously is given by

$$f_{p,\mathbf{h}} = f^n_{p,\mathbf{h}} + f'_p + if''_p, \tag{3}$$

where $f^n_{p,\mathbf{h}}$ is the normal atomic scattering factor and f'_p and f''_p are the real and imaginary parts of the anomalous correction, respectively. The quantity δ in Table 1, representing the instance when there is one type of predominant anomalous scatterer, is defined as

$$\delta = \tan^{-1}(f''/f'). \tag{4}$$

The solid lines forming the closed triangle in Fig. 1 represent the vector equation (2) with the presubscript m omitted. Given, for example, the vector $\mathscr{F}_{1,\mathbf{h}}$ as in Fig. 1, the dotted line of radius $|\mathscr{F}_{2,\mathbf{h}}|$ could be a possible location for $\mathscr{F}_{2,\mathbf{h}}$, but not necessarily. It would not be possible if the dotted line connecting this vector with $\mathscr{F}_{1,\mathbf{h}}$ would have to have a magnitude

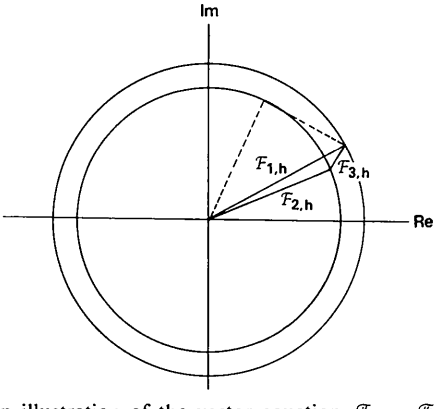

Fig. 1. An illustration of the vector equation, $\mathscr{F}_{1,\mathbf{h}} = \mathscr{F}_{2,\mathbf{h}} + \mathscr{F}_{3,\mathbf{h}}$. The largest magnitude differences, $||\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}||$, are associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$. This case is represented by the triangle formed from the solid lines. The placement of the dotted line representing an alternative position for $\mathscr{F}_{2,\mathbf{h}}$ would not be possible if the magnitude of the dotted lines connecting it to $\mathscr{F}_{1,\mathbf{h}}$ would exceed the maximum possible value. This implies that, for the largest magnitude differences, the phase angles for $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ do not differ by much.

Table 1. *Quantities involved in the three cases leading to rules for selecting triplet phase invariants and the nature of the estimates for each case*

The quantities ${}_m\mathscr{F}_{1,\mathbf{h}}$, ${}_m\mathscr{F}_{2,\mathbf{h}}$, and ${}_m\mathscr{F}_{3,\mathbf{h}}$ are defined by the corresponding entries in columns 2, 3, 4, respectively, for $m = 1, 2, 3$. The estimates are appropriate when one kind of predominant anomalous scatterer is present. More complex circumstances are discussed in the text.

Case, m	${}_m\mathscr{F}_{1,\mathbf{h}}$	${}_m\mathscr{F}_{2,\mathbf{h}}$	${}_m\mathscr{F}_{3,\mathbf{h}}$	Estimates
1	$F_{\lambda \mathbf{h}}$	$F^*_{\lambda \bar{\mathbf{h}}}$ †	$F^a_{\lambda \mathbf{h}} - F^{a*}_{\lambda \bar{\mathbf{h}}}$ †	$\pi/2$ or $-\pi/2$
2	$F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda \mathbf{h}} + F^{a*}_{\lambda \bar{\mathbf{h}}}$	0 or π
3	$F_{\lambda \mathbf{h}}$	$F^n_{\mathbf{h}}$	$F^a_{\lambda \mathbf{h}}$	3δ or $3\delta + \pi$ ‡

† The asterisk denotes complex conjugate.
‡ δ is defined in (4).

that exceeds the maximum possible value for $|\mathscr{F}_{3,\mathbf{h}}|$. The implication of this observation is that if the largest differences $||\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}||$ are selected from a data set, they would be associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$ and $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ would have phases that do not differ greatly. We formalize these observations and their implications, as follows:

1. The largest-magnitude differences, $||\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}||$, are associated with the largest values of the magnitudes $|\mathscr{F}_{3,\mathbf{h}}|$.

2. Triplet phase invariants associated with the largest $|\mathscr{F}_{3,\mathbf{h}}\mathscr{F}_{3,\mathbf{k}}\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ can be expected to have values close to zero, especially for simple heavy-atom structures. [The triplet phase invariants refer to the nonanomalous portion of the scattering, $(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$; additional phase functions arise from the anomalous portion of the scattering and can be readily evaluated from appropriate tables.]

3. For the larger values of $||\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}||$, the phase of $\mathscr{F}_{1,\mathbf{h}}$ will differ little in value from the phase of $\mathscr{F}_{2,\mathbf{h}}$.

Theory

Derivation of $R_{\text{ano},1}$

We are concerned here with case 1 of Table 1. The appropriate equation from (1), since $F^n_{\mathbf{h}} = F^{n*}_{-\mathbf{h}}$, is

$$F_{\lambda \mathbf{h}} - F^*_{\lambda \bar{\mathbf{h}}} = F^a_{\lambda \mathbf{h}} - F^{a*}_{\lambda \bar{\mathbf{h}}}. \tag{5}$$

We form the products

$$\begin{aligned}(F_{\lambda \mathbf{h}} - F^*_{\lambda \bar{\mathbf{h}}})(F_{\lambda \mathbf{k}} - F^*_{\lambda \bar{\mathbf{k}}})(F_{\lambda (\bar{\mathbf{h}}+\bar{\mathbf{k}})} - F^*_{\lambda (\mathbf{h}+\mathbf{k})}) \\ = (F^a_{\lambda \mathbf{h}} - F^{a*}_{\lambda \bar{\mathbf{h}}})(F^a_{\lambda \mathbf{k}} - F^{a*}_{\lambda \bar{\mathbf{k}}})(F^a_{\lambda (\bar{\mathbf{h}}+\bar{\mathbf{k}})} - F^{a*}_{\lambda (\mathbf{h}+\mathbf{k})})\end{aligned} \tag{6}$$

and consider first the interpretation of the right side of (6). We have

$$F^a_{\lambda \mathbf{h}} = \sum_{j=1}^{N_{\text{anom}}} f^a_{\lambda j,\mathbf{h}} \exp(i\delta_{\lambda j,\mathbf{h}}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j), \tag{7}$$

where N_{anom} is the number of anomalously scattering atoms in the unit cell,

$$f^a_{\lambda j,\mathbf{h}} = (f'^2_{\lambda j,\mathbf{h}} + f''^2_{\lambda j,\mathbf{h}})^{1/2}. \tag{8}$$

λ denotes variation with wavelength, $\mathbf{h}$ denotes variation with reciprocal vector, although f' and f'' are usually treated as independent of scattering angle, and δ is defined by (4). Equation (7) can be rewritten in terms of the number of types of anomalous scatterers, q (the subscript 1 is reserved for atoms that essentially do not scatter anomalously):

$$F^a_{\lambda\mathbf{h}} = \sum_{j=2}^{q+1} (f^a_{\lambda j}/f^n_{j,\mathbf{h}}) \exp(i\delta_{\lambda j}) F^n_{j,\mathbf{h}}, \tag{9}$$

where $f^n_{j,\mathbf{h}}$ is the normal atomic scattering factor, $f'_{\lambda j}$ and $f''_{\lambda j}$ are treated as independent of the scattering angle and the $F^n_{j,\mathbf{h}}$ are the structure factors for each type of anomalously scattering atom. We obtain from (9)

$$F^a_{\lambda\mathbf{h}} - F^{a*}_{\lambda\bar{\mathbf{h}}} = 2i \sum_{j=2}^{q+1} (f^a_{\lambda j}/f^n_{j,\mathbf{h}}) \sin\delta_{\lambda j} F^n_{j,\mathbf{h}}. \tag{10}$$

The product on the right side of (6) can now be given in terms of the product of three sums obtainable from the right side of (10). As an approximation, the neglect of cross terms in the latter product gives

$$-8i \sum_{j=2}^{q+1} [(f^{a^3}_{\lambda j})/f^n_{j,\mathbf{h}} f^n_{j,\mathbf{k}} f_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \sin^3\delta_{\lambda j} \times |F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})], \tag{11}$$

where it is expected that, for large values of $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$, the triplet phase invariants $(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$ will have a value close to zero. Although (11) affords the opportunity to analyze the case of several types of anomalous scatterers, as a practical matter there is usually one type of predominant anomalous scatterer. We proceed with this assumption and achieve some simplification.

With one type of predominant anomalous scatterer, we may replace (11) and avoid the need to make any approximation, with

$$-8i[(f^{a^3}_{\lambda 2}/f^n_{2,\mathbf{h}} f^n_{2,\mathbf{k}} f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}) \sin^3\delta_{\lambda 2} \times |F^n_{2,\mathbf{h}} F^n_{2,\mathbf{k}} F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi^n_{2,\mathbf{h}} + \varphi^n_{2,\mathbf{k}} + \varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})], \tag{12}$$

noting that $f^a_{\lambda 2} \sin\delta_{\lambda 2} = f''_{\lambda 2}$. The left side of (6) may be written

$$\begin{aligned}
&|F_{\lambda\mathbf{h}} F_{\lambda\mathbf{k}} F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})] \\
&- |F_{\lambda\bar{\mathbf{h}}} F_{\lambda\mathbf{k}} F_{\lambda(\mathbf{h}+\mathbf{k})}| \exp[i(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}})] \\
&- |F_{\lambda\mathbf{h}} F_{\lambda\bar{\mathbf{k}}} F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi_{\mathbf{h}} - \varphi_{\bar{\mathbf{k}}} + \varphi_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})] \\
&+ |F_{\lambda\mathbf{h}} F_{\lambda\bar{\mathbf{k}}} F_{\lambda(\mathbf{h}+\mathbf{k})}| \exp[i(\varphi_{\mathbf{h}} - \varphi_{\bar{\mathbf{k}}} - \varphi_{\mathbf{h}+\mathbf{k}})] \\
&- |F_{\lambda\bar{\mathbf{h}}} F_{\lambda\mathbf{k}} F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(-\varphi_{\bar{\mathbf{h}}} + \varphi_{\mathbf{k}} + \varphi_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})] \\
&+ |F_{\lambda\bar{\mathbf{h}}} F_{\lambda\mathbf{k}} F_{\lambda(\mathbf{h}+\mathbf{k})}| \exp[i(-\varphi_{\bar{\mathbf{h}}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}})] \\
&+ |F_{\lambda\bar{\mathbf{h}}} F_{\lambda\bar{\mathbf{k}}} F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(-\varphi_{\bar{\mathbf{h}}} - \varphi_{\bar{\mathbf{k}}} + \varphi_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})] \\
&- |F_{\lambda\bar{\mathbf{h}}} F_{\lambda\bar{\mathbf{k}}} F_{\lambda(\mathbf{h}+\mathbf{k})}| \exp[i(-\varphi_{\bar{\mathbf{h}}} - \varphi_{\bar{\mathbf{k}}} - \varphi_{\mathbf{h}+\mathbf{k}})].
\end{aligned} \tag{13}$$

On the basis of observation 3 above, when the appropriate magnitude differences are large, the triplet phase invariants in (13) may be replaced by some average value $\langle_1\Phi_{\mathbf{h},\mathbf{k}}\rangle$ and then (13) may be rewritten

$$(|F_{\lambda\mathbf{h}}| - |F_{\lambda\bar{\mathbf{h}}}|)(|F_{\lambda\mathbf{k}}| - |F_{\lambda\bar{\mathbf{k}}}|)(|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F_{\lambda(\mathbf{h}+\mathbf{k})}|) \exp(i\langle_1\Phi_{\mathbf{hk}}\rangle). \tag{14}$$

We now compare (14) and (12) representing the left and right sides of (6), respectively. On the basis of observations 1 and 2 above, the triplet phase invariant in (12) can be expected to have a value close to zero so that (12) is essentially a pure imaginary number. In order for (12) and (14) to be approximately equal, the average of the triplet phase invariants, $\langle_1\Phi_{\mathbf{hk}}\rangle$, should have a value close to $\pi/2$ or $-\pi/2$. In fact, given the sign of the triple product of magnitude differences in (14) from experiment and the sign of f'' from tables of f' and f'', it is possible to determine whether $\langle_1\Phi_{\mathbf{hk}}\rangle$ is close to $\pi/2$ or to $-\pi/2$. We can formulate the following rule for the largest triple products of magnitude differences:

$R_{\text{ano},1}$: *If the sign of the product of the largest-magnitude differences,* $(|F_{\lambda\mathbf{h}}| - |F_{\lambda\bar{\mathbf{h}}}|)(|F_{\lambda\mathbf{k}}| - |F_{\lambda\bar{\mathbf{k}}}|)(|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F_{\lambda(\mathbf{h}+\mathbf{k})}|)$, *is the same as the sign of* f'', *the value of the average triplet phase invariant is close to* $-\pi/2$ *and, when the signs are opposite, the value is close to* $\pi/2$.

This rule, in effect, assigns the estimate to all eight triplet phase invariants in (13). As a modification of $R_{\text{ano},1}$, the estimates may be assigned only to those triplet phase invariants that are associated with the larger products of structure-factor magnitudes listed among the eight possibilities given in (13), instead of to all eight of them. Test calculations indicate that improved accuracy may be obtained this way.

If there is more than one type of predominant anomalous scatterer, (11) may be used instead of (12) and compared with (14). In order to use (11), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the $f''_{\lambda j}$ could be obtained from appropriate tables and the values of the $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (6) could be computed from the product of three sums obtainable from the right side of (10).

Derivation of $R_{\text{ano},2}$

We are concerned now with case 2 of Table 1. The appropriate equation from (1), since $F^n_{\mathbf{h}} = F^{n*}_{-\mathbf{h}}$, is

$$F_{\lambda\mathbf{h}} + F^*_{\lambda\bar{\mathbf{h}}} - 2F^n_{\mathbf{h}} = F^a_{\lambda\mathbf{h}} + F^{a*}_{\lambda\bar{\mathbf{h}}}. \tag{15}$$

We form the products

$$(F_{\lambda\mathbf{h}} + F^*_{\lambda\bar{\mathbf{h}}} - 2F^n_{\mathbf{h}})(F_{\lambda\mathbf{k}} + F^*_{\lambda\bar{\mathbf{k}}} - 2F^n_{\mathbf{k}}) \times (F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F^*_{\lambda(\mathbf{h}+\mathbf{k})} - 2F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}) = (F^a_{\lambda\mathbf{h}} + F^{a*}_{\lambda\bar{\mathbf{h}}})(F^a_{\lambda\mathbf{k}} + F^{a*}_{\lambda\bar{\mathbf{k}}})(F^a_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F^{a*}_{\lambda(\mathbf{h}+\mathbf{k})}) \tag{16}$$

and consider first the interpretation of the right side of (16). We obtain from (9)

$$F^a_{\lambda \mathbf{h}} + F^{a*}_{\lambda \bar{\mathbf{h}}} = 2 \sum_{j=2}^{q+1} (f^a_{\lambda j}/f^n_{j,\mathbf{h}}) \cos \delta_{\lambda j} F^n_{j,\mathbf{h}}. \quad (17)$$

The product on the right side of (16) can now be given in terms of the product of three sums obtainable from the right side of (17). As an approximation, the neglect of cross terms in the latter product gives

$$8 \sum_{j=2}^{q+1} [(f^{a^3}_{\lambda j})/f^n_{j,\mathbf{h}} f^n_{j,\mathbf{k}} f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \cos^3 \delta_{\lambda j} \times |F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp [i(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \quad (18)$$

As in the case of (11), we proceed with the assumption that there is one type of predominant anomalous scatterer and replace (18) with

$$8[(f^a_{\lambda 2})^3/f^n_{2,\mathbf{h}} f^n_{2,\mathbf{k}} f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \cos^3 \delta_{\lambda 2} \times |F^n_{2,\mathbf{h}} F^n_{2,\mathbf{k}} F^n_{2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp [i(\varphi^n_{2,\mathbf{h}} + \varphi^n_{2,\mathbf{k}} + \varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \quad (19)$$

noting that $f^a_{\lambda 2} \cos \delta_{\lambda 2} = f'_{\lambda 2}$.

The left side of (16) is obtained with the use of the notation of Table 1 when $m = 2$. [Note that (13) is equivalent to the case when $m = 1$.] We obtain in general terms

$$\begin{aligned}
&|{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&- |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&- |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&+ |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&- |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&+ |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&+ |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&- |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp [i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \quad (20)
\end{aligned}$$

When $m = 2$, $|{}_2\mathscr{F}_{1,\mathbf{h}}| = |F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}|$, ${}_2\varphi_{1,\mathbf{h}}$ is the phase of $F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}$, $|{}_2\mathscr{F}_{2,\mathbf{h}}| = 2|F^n_{\mathbf{h}}|$ and ${}_2\varphi_{2,\mathbf{h}} = \varphi^n_{\mathbf{h}}$. In the test computations to be described, the $|F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}|$ and ${}_2\varphi_{1,\mathbf{h}}$ were approximated by $|F_{\lambda \mathbf{h}}| + |F^*_{\lambda \bar{\mathbf{h}}}|$ and $(\varphi_{\lambda \mathbf{h}} - \varphi_{\lambda \bar{\mathbf{h}}})/2$, respectively, with small error. There was, in fact, no need to use the approximate form, and in one test calculation it was not used. On the basis of observation 3 above, when the appropriate magnitude differences are large, the triplet phase invariants in (20) may be replaced by some average value $\langle {}_2\Phi_{\mathbf{hk}} \rangle$ and then (20) may be rewritten

$$(|F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}| - 2|F^n_{\mathbf{h}}|)(|F_{\lambda \mathbf{k}} + F^*_{\lambda \bar{\mathbf{k}}}| - 2|F^n_{\mathbf{k}}|) \times (|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F^*_{\lambda(\mathbf{h}+\mathbf{k})}| - 2|F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|) \exp (i\langle {}_2\Phi_{\mathbf{hk}} \rangle). \quad (21)$$

We now compare (21) and (19), representing the left and right sides of (16), respectively. On the basis of observations 1 and 2 above, the triplet phase invariant in (19) can be expected to have a value close to zero so that (19) is essentially a real number. In order for (19) and (21) to be approximately equal, the average of the triplet phase invariants, $\langle {}_2\Phi_{\mathbf{hk}} \rangle$, should have a value close to zero or π. Given the sign of the triple product of magnitude differences in (21) from experiment and the sign of f' from tables of f' and f'', it is possible to determine whether $\langle {}_2\Phi_{\mathbf{hk}} \rangle$ is close to zero or to π. We formulate the following rule for the largest triple products of magnitude differences:

$R_{\text{ano},2}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda \mathbf{h}} + F^*_{\lambda \bar{\mathbf{h}}}| - 2|F^n_{\mathbf{h}}|)(|F_{\lambda \mathbf{k}} + F^*_{\lambda \bar{\mathbf{k}}}| - 2|F^n_{\mathbf{k}}|)(|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F^*_{\lambda(\mathbf{h}+\mathbf{k})}| - 2|F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|)$, *is the same as the sign of* f', *the value of the average triplet phase invariant is close to zero and, when the signs are opposite, the value is close to* π.

In practice, it may not be readily possible to obtain triplet products composed of large-magnitude differences that have a sign different from that of f', so that the opportunity to select triplet phase invariants having values close to π may not arise from use of $R_{\text{ano},2}$.

The rule $R_{\text{ano},2}$ in effect assigns the estimate to all eight triplet phase invariants in (20). As a modification of $R_{\text{ano},2}$, the estimates may be assigned to only those triplet phase invariants that are associated with the larger products of magnitudes listed among the eight possibilities given in (20), instead of to all eight of them.

Similarly to case 1, if there is more than one type of predominant anomalous scatterer, (18) may be used instead of (19) and compared with (21). In order to use (18), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the $f'_{\lambda j}$ could be obtained from appropriate tables and the values of the $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (16) could be computed from the product of the sums obtainable from the right side of (17).

Derivation of $R_{\text{ano},3}$

We are concerned now with case 3 of Table 1. The appropriate equation is (1) which we rewrite as

$$F_{\lambda\mathbf{h}} - F^n_{\mathbf{h}} = F^a_{\lambda\mathbf{h}}. \tag{22}$$

We form the products

$$(F_{\lambda\mathbf{h}} - F^n_{\mathbf{h}})(F_{\lambda\mathbf{k}} - F^n_{\mathbf{k}})(F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} - F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}) = F^a_{\lambda\mathbf{h}} F^a_{\lambda\mathbf{k}} F^a_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})} \tag{23}$$

and consider first the interpretation of the right side of (23) which can be expressed in terms of the product of three sums of the type given in (9). As an approximation, the neglect of cross terms in the latter product gives

$$\sum_{j=2}^{q+1} [(f^a_{\lambda j})^3 / f^n_{j,\mathbf{h}} f^n_{j,\mathbf{k}} f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \exp(i3\delta_{\lambda j}) \times |F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \tag{24}$$

We proceed with the assumption that there is one type of predominant anomalous scatterer and replace (24) with

$$[(f^a_{\lambda 2})^3 / f^n_{2,\mathbf{h}} f^n_{2,\mathbf{k}} f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \exp(i3\delta_{\lambda 2}) \times |F^n_{2,\mathbf{h}} F^n_{2,\mathbf{k}} F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \exp[i(\varphi^n_{2,\mathbf{h}} + \varphi^n_{2,\mathbf{k}} + \varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \tag{25}$$

The left side of (23) may be obtained from (20) when $m = 3$ in the notation of Table 1. In this case, $|{}_3\mathscr{F}_{1,\mathbf{h}}| = F_{\lambda\mathbf{h}}$, ${}_3\varphi_{1,\mathbf{h}}$ is the phase of $F_{\lambda\mathbf{h}}$, $|{}_3\mathscr{F}_{2,\mathbf{h}}| = |F^n_{\mathbf{h}}|$ and ${}_3\varphi_{2,\mathbf{h}} = \varphi^n_{\mathbf{h}}$. On the basis of observation 3 above, when the appropriate magnitude differences are large, the triplet phase invariants in (20) may be replaced by some average value, $\langle {}_3\Phi_{\mathbf{hk}} \rangle$ and then (20) may be rewritten

$$(|F_{\lambda\mathbf{h}}| - |F^n_{\mathbf{h}}|)(|F_{\lambda\mathbf{k}}| - |F^n_{\mathbf{k}}|) \times (|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|) \exp(i\langle {}_3\Phi_{\mathbf{hk}} \rangle). \tag{26}$$

We now compare (26) and (25), representing the left and right sides of (23), respectively. On the basis of observations 1 and 2 above, the triplet phase invariant in (25) can be expected to have a value close to zero so that (25) is essentially a real positive number multiplied by the function $\exp(i3\delta_{\lambda 2})$. In order for (25) and (26) to be approximately equal, the average of the triplet phase invariants, $\langle {}_3\Phi_{\mathbf{hk}} \rangle$, should have a value close to 3δ or $3\delta + \pi$, where δ is defined by (4). We formulate the following rule for the largest triple products of magnitude differences:

$R_{\text{ano},3}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda\mathbf{h}}| - |F^n_{\mathbf{h}}|)(|F_{\lambda\mathbf{k}}| - |F^n_{\mathbf{k}}|)(|F_{\lambda(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|)$, *is positive, the value of the average triplet phase invariant is close to* 3δ *and when the sign is negative, the value is close to* $3\delta + \pi$.

The rule $R_{\text{ano},3}$ in effect assigns the estimate to all eight triplet phase invariants in (20). As a modification of $R_{\text{ano},3}$, the estimates may be assigned to only those triplet phase invariants that are associated with the larger products of magnitudes listed among the eight possibilities given in (20), instead of to all eight of them.

Similarly to cases 1 and 2, if there is more than one type of predominant anomalous scatterer, (24) may be used instead of (25) and compared with (26). In order to use (24), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the $\delta_{\lambda j}$ could be obtained from appropriate tables and the values of the $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (23) could be computed from the product of the sums obtainable from the right side of (9).

The effect of rescaling the $\mathscr{F}$ to represent approximately structure factors from point atoms on the application of $R_{\text{ano},1}$, $R_{\text{ano},2}$ and $R_{\text{ano},3}$ has not yet been investigated.

Interpretation of the triplet products of magnitude differences

We investigate

$$(|{}_m\mathscr{F}_{1,\mathbf{h}}| - |{}_m\mathscr{F}_{2,\mathbf{h}}|)(|{}_m\mathscr{F}_{1,\mathbf{k}}| - |{}_m\mathscr{F}_{2,\mathbf{k}}|) \times (|{}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |{}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|) \equiv T, \tag{27}$$

where $m = 1$, 2 or 3, as in Table 1. It is assumed that the differences are of large magnitude and the contributions, ${}_m\mathscr{F}_{3,\mathbf{t}}$, of the anomalously scattering atoms are much smaller in magnitude than the contributions from the essentially nonanomalously scattering atoms, ${}_m\mathscr{F}_{2,\mathbf{t}}$. This is ordinarily appropriate with macromolecules.

It follows from (2) that

$$|{}_m\mathscr{F}_{1,\mathbf{h}}|^2 = |{}_m\mathscr{F}_{2,\mathbf{h}}|^2 + |{}_m\mathscr{F}_{3,\mathbf{h}}|^2 + 2|{}_m\mathscr{F}_{2,\mathbf{h}}|\,|{}_m\mathscr{F}_{3,\mathbf{h}}| \times \cos({}_m\varphi_{2,\mathbf{h}} - {}_m\varphi_{3,\mathbf{h}}). \tag{28}$$

Since it is assumed that $|{}_m\mathscr{F}_{2,\mathbf{h}}| \gg |{}_m\mathscr{F}_{3,\mathbf{h}}|$, we have to good approximation

$$|{}_m\mathscr{F}_{1,\mathbf{h}}| - |{}_m\mathscr{F}_{2,\mathbf{h}}| \simeq |{}_m\mathscr{F}_{3,\mathbf{h}}| \cos({}_m\varphi_{2,\mathbf{h}} - {}_m\varphi_{3,\mathbf{h}}). \tag{29}$$

If the product in (27) is formed from (29), we obtain the factor

$$\cos({}_m\varphi_{2,\mathbf{h}} - {}_m\varphi_{3,\mathbf{h}}) \cos({}_m\varphi_{2,\mathbf{k}} - {}_m\varphi_{3,\mathbf{k}}) \times \cos({}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} - {}_m\varphi_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}) \equiv P_3. \tag{30}$$

It has been shown (Karle, 1983) that such a product of cosines, when the magnitudes of the differences in (27) are large, is given to good approximation by the left side of (31) and when this is combined with (27) and (29), we obtain

$$\cos({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} - {}_m\varphi_{3,\mathbf{h}} - {}_m\varphi_{3,\mathbf{k}} - {}_m\varphi_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$$

Table 2. *Estimates of values of triplet phase invariants from anomalous dispersion of* Cr $K\alpha$ *radiation by sulfur in quinidine sulfate*

Number of independent data	Number of invariants	Case, m	Estimate	Actual average value	Invariant selection*	Average error (rad)
4708	46	1	$-\pi/2$	−1·59	*L*	0·37
4708	54	1	$\pi/2$	1·60	*L*	0·35
824	49	1	$-\pi/2$	−1·51	*L*	0·68
824	51	1	$\pi/2$	1·46	*L*	0·68
4708	100(×8)†	2	0	0·00	*A*	0·30‡
4708	100(×8)†§	2	0	−0·06	*A*	0·61‡
4708	50	3	−2·52	−2·50	*L*	0·38
4708	49	3	0·62	0·65	*L*	0·27
3988	54	3	−2·52	−2·52	*L*	0·33
3988	46	3	0·62	0·60	*L*	0·28
4708	55	3¶	−2·52	−2·57	*L*	0·36
4708	45	3¶	0·62	0·61	*L*	0·30
4708	81§	3	−2·52	−1·95	*L*	0·64
4708	19§	3	0·62	1·21	*L*	0·62

* *L* means errors and averages are based on the value of the triplet phase invariant associated with the largest product of structure-factor magnitudes and *A* means that they are based on the average values of the eight possible invariants formed for a given $\mathbf{h}, \mathbf{k}, \bar{\mathbf{h}}+\bar{\mathbf{k}}$.

† Phases, $\varphi_{\mathbf{h}}$, for which $|F_{\mathbf{h}}| < 10$ were omitted from the invariants.

‡ Invariants based on writing $F_{\lambda\mathbf{h}} + F^*_{\lambda\bar{\mathbf{h}}} \simeq (|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}|) \exp[i(\varphi_{\lambda\mathbf{h}} - \varphi_{\lambda\bar{\mathbf{h}}})/2]$.

§ $|F^n_{\mathbf{h}}|$ was estimated from $|F^n_{\mathbf{h}}| \simeq 0{\cdot}5\,W(|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}|)$.

¶ Invariants composed from differences numbered 301–600 in order of decreasing magnitude rather than the top 300 differences.

$$\simeq \frac{T}{\left|{}_m\mathscr{F}_{3,\mathbf{h}}\ {}_m\mathscr{F}_{3,\mathbf{k}}\ {}_m\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}\right|}. \tag{31}$$

In the case of one predominant anomalous scatterer, (31) leads to $R_{\text{ano},1}$, $R_{\text{ano},2}$ and $R_{\text{ano},3}$ by use of (12), (19) and (25), respectively, if it is assumed that the cosine function is equal to +1 or −1 depending upon whether the triplet product T is positive or negative. We can obtain, in principle, more information concerning ${}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$ from (31) if we are able to evaluate ${}_m\varphi_{3,\mathbf{h}} + {}_m\varphi_{3,\mathbf{k}} + {}_m\varphi_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$ and the denominator of (31). If we know the structure of the anomalously scattering atoms, then it is straightforward to obtain this needed information from (9), (10) and (17). If we know the chemical nature and amounts of the anomalous scatterers but do not know their atomic positions, it may be possible to obtain the needed information from (11), (18) and (24). In addition to setting the triplet phase invariants, $\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$, equal to zero in (11), (18) and (24), it would be necessary to make an estimate, on some basis such as the largest possible values or some fraction thereof, of the $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$.

Test calculations

Model calculations were performed on quinidine sulfate, $(C_{20}H_{25}N_2O_2)_2SO_4.2H_2O$, (Karle & Karle, 1981) which crystallizes in space group $P2_1$. In the test calculations, the source of anomalous dispersion was considered to be solely the sulfur atom with Cr $K\alpha$ radiation, a relative amount of anomalous scattering power comparable to that of heavy atoms in macromolecules. Products of magnitude differences, as appear in (14), (21) and (26), were generally composed from the 300 largest-magnitude differences and ordered with the largest product first. Hundreds of triplet phase invariants were estimated to be $+\pi/2$ or $-\pi/2$ by use of $R_{\text{ano},1}$, 0 by use of $R_{\text{ano},2}$ and 3δ or $3\delta + \pi$ by use of $R_{\text{ano},3}$, as shown in Table 2. The factor (×8) implies that all eight triplet phase invariants, as appear, for example, on the right side of (20) when $m = 2$, are evaluated by the estimates. This is also indicated by the letter *A* which implies that the average values of the sets of eight invariants are used to estimate the average errors.

The first four rows of Table 2 indicate that a major decrease in the number of data used in the calculations is accompanied by a modest increase in the average error. Table 2 also shows that the use of

$$|F^n_{\mathbf{h}}| \simeq 0{\cdot}5\,W(|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}|), \tag{32}$$

where

$$W = \left\{ \frac{\sum_{j=1}^{N_{\text{non}}} f^2_{j\mathbf{h}} + \sum_{j=1}^{N_{\text{ano}}} (f^n_{j\mathbf{h}})^2}{\sum_{j=1}^{N_{\text{non}}} f^2_{j\mathbf{h}} + \sum_{j=1}^{N_{\text{ano}}} [(f^n_{j\mathbf{h}} + f'_j)^2 + f''^2_j]} \right\}^{1/2}, \tag{33}$$

instead of a precisely known value for $|F^n_{\mathbf{h}}|$ effects a modest increase in the average error. Rows 11 and 12 of Table 2 show that there is a much larger number of invariants amenable to accurate evaluation than is displayed in the Table. The calculation in the fifth row of Table 2 was repeated with the function $|F_{\lambda\mathbf{h}} + F^*_{\lambda\bar{\mathbf{h}}}| - 2|F^n_{\mathbf{h}}|$ instead of the approximation to it, namely, $|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}| - 2|F^n_{\mathbf{h}}|$ with essentially indistinguishable results. The actual average value for 100 invariants was −0·01 rad instead of 0·00 and the average error was 0·29 rad instead of 0·30.

A calculation was made for the case of $m = 3$ to explore the use of a formula such as (24) in estimating

Table 3. *Estimates of values of triplet phase invariants from anomalous dispersion of* Cu $K\alpha$ *radiation by* Pt, Fe, Cl *and* S *in cytochrome* $c550.PtCl_4^{2-}$

Resolution of data (Å)	Number of invariants	Case, m	Estimate	Actual average value	Average* error (rad)
2·5	246	1	$-\pi/2$	−1·55	0·64
2·5	254	1	$\pi/2$	1·58	0·69
5·0	262	1	$-\pi/2$	−1·61	0·77
5·0	238	1	$\pi/2$	1·59	0·77
2·5	71	2†‡	π	3·03	0·46
2·5	343	2†	0	−0·03	0·51
2·5	240	2	0	0·10	1·18
2·5	163	3†	0·26	−0·29	0·74
2·5	190	3†	−2·88	−3·25	0·69
2·5	160	3	0·26	−1·13	1·48
2·5	242	3	−2·88	−3·84	1·07

* All calculations of error are based on the known average value of eight invariants, as occur in (20), for cases $m = 1, 2, 3$.

† All $|F_{\mathbf{h}}^n|$ required for cases $m = 2$ and 3 were computed from (32). In these particular calculations, the $|F_{\mathbf{h}}^n|$ were computed from data obtained from Mo $K\alpha$ radiation rather than Cu $K\alpha$.

‡ For $m = 2$, $|F_{\lambda\mathbf{h}} + F_{\lambda\bar{\mathbf{h}}}^*|$ has been replaced by $|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}|$.

triplet invariants when there is more than one predominant anomalous scatterer. The value of 3δ for one of the scatterers was −2·52 rad and for the other it was −0·81 rad. The weighted contribution from use of (24) put the expected value for the triplets at −1·09 rad for positive triple products and at 2·05 rad for negative products. To make the calculation, it was assumed that $(F_{j\mathbf{h}}^n / f_{j\mathbf{h}}^n n_j^{1/2})$, where n_j is the number of atoms of type j, is approximately the same for all j. Expected values computed from known values for the coordinates of the anomalously scattering atoms by use of (9) were −1·14 for positive triplet products and 2·00 for negative ones. For comparison, the actual average values of the triplet phase invariants were −1·31 and 1·95 rad, respectively, as computed from the values of the triplet phase invariants associated with the largest product of structure-factor magnitudes for each given $\mathbf{h}, \mathbf{k}, \bar{\mathbf{h}} + \bar{\mathbf{k}}$. The average error of the estimates for 100 of the largest triple products was 0·71 rad. It is seen that this is about twice as great as the best average errors reported in Table 2 and implies that the presence of different types of anomalous scatterers with considerably disparate values for 3δ is associated with greater uncertainty in the estimates.

Model calculations were also performed on exact data computed from the coordinates for cytochrome $c550.PtCl_4^{2-}$ from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976). Calculations had already been made of triplet phase invariants for this substance by use of probability theory (Hauptman, 1982) and, although the nature of the calculations performed here is rather different, some insight concerning the relative accuracies available from the two techniques can be obtained. The calculations were performed with data at 2·5 Å resolution and some at 5·0 Å resolution and the results are shown in Table 3 for cases $m = 1, 2, 3$.

All reported average errors in Table 3 are based on the known average values of sets of eight invariants as occur in (20). For $m = 2$, $|F_{\lambda\mathbf{h}} + F_{\lambda\bar{\mathbf{h}}}^*|$ has been replaced by $|F_{\lambda\mathbf{h}}| + |F_{\lambda\bar{\mathbf{h}}}|$ and all $|F_{\mathbf{h}}^n|$ required for $m = 2$ and 3 were computed from (32) and (33).

The values of the estimated angles in Table 3 for $m = 3$, 0·26 and −2·88, are very close to the values 0·32 and −2·82, respectively, that would be obtained if the only anomalous scatterer present were the Pt atom. This demonstrates the predominance of the Pt atom as an anomalous scatterer. The values used were obtained from (24) in which the triplet phase invariants for the heavy atoms were set equal to zero and the ratios $|F_{j\mathbf{h}}^n F_{j\mathbf{k}}^n F_{j(\bar{\mathbf{h}}+\bar{\mathbf{k}})}^n| / [n_j^{3/2} f_{j\mathbf{h}}^n f_{j\mathbf{k}}^n f_{j(\bar{\mathbf{h}}+\bar{\mathbf{k}})}^n]$ for the heavy atoms were assumed, in some average sense, to be equal, where n_j is the number of atoms of type j present in the structure. This gave for (24) (except for a proportionality constant),

$$\sum_{j=2}^{q+1} n_j^{3/2} (f_{\lambda j}^a)^3 \exp(i3\delta_{\lambda j}). \qquad (34)$$

The estimated angles for $m = 3$ were obtained by evaluating the arctangent of the ratio of the imaginary part to the real part. The latter arctangent is the estimate associated with a positive value for the triple product of magnitude differences in (26) and the estimate plus π is associated with a negative value for the triple product. In computing (34), the contributions from the S and Cl atoms as anomalous scatterers were found to be negligible, and, as noted, the Fe atom had only a minor effect.

Results of the calculations are shown in Table 3. For case $m = 1$, it is seen that use of data with 5·0 Å resolution causes only a slight increase in error for the 500 invariants having the largest triplet product of magnitude differences over that obtained for the 500 invariants having the largest triple product of magnitude differences at 2·5 Å resolution.

All the $F_{\lambda\mathbf{h}}$ and $F_{\lambda\bar{\mathbf{h}}}^*$ used for Table 3 were computed with Cu $K\alpha$ radiation. The values of the $|F_{\mathbf{h}}^n|$ required for cases $m = 2$ and 3 were computed by use of (32).

Some $|F_{\mathbf{h}}^n|$ were computed from (32) with data obtained from Cu $K\alpha$ radiation and some with data obtained from Mo $K\alpha$ radiation, as indicated in the footnotes to Table 3. Use of Mo $K\alpha$ radiation for data collection should be feasible for many proteins. An example of a good diffraction photograph with Mo $K\alpha$ radiation is the one published for crambin (Teeter & Hendrickson, 1979).

The accuracy of the $|F_{\mathbf{h}}^n|$ computed from (32) with data from Mo $K\alpha$ radiation is greater than that obtained with data from the longer Cu $K\alpha$ radiation. This can be accounted for by the increasing magnitude of the real correction for the atomic scattering factor for Pt as the wavelength becomes longer. It is evident from Table 3 that the accuracy of the calculations of the values of the triplet invariants is enhanced significantly with use of Mo $K\alpha$ radiation to obtain the $|F_{\mathbf{h}}^n|$. In case $m=2$, the average error is less than half that obtained when $|F_{\mathbf{h}}^n|$ is derived from data computed for Cu $K\alpha$ radiation. For case $m=3$, the use of shorter wavelengths than Cu $K\alpha$ to obtain $|F_{\mathbf{h}}^n|$ for this example is virtually required because the errors are otherwise potentially quite large.

A rather different type of evaluation is obtained in the sampling described here as compared to the results of the probability theory described by Hauptman (1982). Good accuracy is obtained here for regions other than in the vicinity of $\pm\pi/2$ only if $|F_{\mathbf{h}}^n|$ is obtained from data at a smaller wavelength than Cu $K\alpha$, *e.g.* Mo $K\alpha$. The advent of synchrotron X-ray radiation facilities should facilitate greatly the collection of multiple-wavelength data. The estimates from the probability theory seem to cluster in the vicinity of about $\pm 1{\cdot}2$ and $\pm 2{\cdot}6$ rad (Hauptman, 1982), maintaining about the same accuracy in each region, an average magnitude of error of about 0·5–0·6 rad for many thousands of invariants. The average error of the better results in Table 3 is of the same magnitude, but the comparison is limited because the errors from the probability theory are based on the values of individual invariants and not on the average values of sets of eight, as occur in (20). As carried out, the calculations in the probability theory represent the values of individual triplet phase invariants whereas the calculations here represent the values for the eight invariants that occur in (20). An individual value could have been assigned only to the triplet phase invariant in (20) associated with the largest triple product of structure-factor magnitudes, as was the case for many entries in Table 2. Although calculations have shown that this may improve the accuracy somewhat, it would seem that in practice there would be no real advantage to proceeding in this way.

Concluding remarks

The opportunity to estimate the values of triplet phase invariants by probability methods, $R_{\text{ano},1}$, $R_{\text{ano},2}$ and $R_{\text{ano},3}$ and generalizations of the rules for more than one type of predominant anomalous scatterer gives rise to questions concerning possible applicability. Much depends upon the accuracy with which intensity data can be measured and its relationship to the formulas of interest, a matter for detailed study. It seems probable that the accuracy achieved in the case of macromolecules will usually not permit the application of a stepwise phase-determination procedure as is used for small structures. It is possible that the tangent formula and a variety of least-squares methods that have been developed could be used in procedures for phase determination and refinement that make use of estimated values for the triplet phase invariants. Such procedures should also take into account the many established procedures for applying anomalous dispersion data and new ones, as yet untested, such as the exact algebraic analysis of multi-wavelength anomalous dispersion experiments (Karle, 1980).

A particular feature of the results of this paper is that, for one type of predominant anomalous scatterer, it is only necessary to know the chemical identity of the anomalous scatterer. In fact, for cases 1 and 2 of Table 1, it is not even necessary to know the chemical identity of the anomalous scatterer if one is willing to consider the two alternative possibilities for cases 1 and 2 that would then arise, because the signs of f' and f'' would not be known, and pursue them to a sensible conclusion. In the case of more than one type of predominant anomalous scatterer, it is also necessary to have an estimate of the amount of each anomalous scatterer. Again, for cases 1 and 2 of Table 1, this information is not required if the chemical identity is known for all anomalous scatterers and the signs of all f' are the same and the signs of all f'' are also the same. If they are not all the same, two alternative possibilities in the estimates of the triplet phase invariants in cases 1 and 2 would arise and those would have to be alternately pursued until an acceptable structure is obtained.

I wish to thank Mr Stephen Brenner for making the computations reported here.

This research was supported in part by USPHS grant GM30902.

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