inclined to each other at 1·8°. The effect of non-parallelism is to increase the minimum distance of the fluorine atoms from the plane of the overlapping perylene molecule (in the region of overlap, Fig. 3*c*, *d*) by 0·08 Å to 3·31 Å, and to decrease the corresponding distance for fluoranil carbon atoms by 0·04 Å to 3·19 Å. This result is consistent both with F–C repulsion and C–C attraction. As might be expected, the shortest intermolecular distances are found between overlapping molecules; these have minimum values of 3·29 Å for C–C, 3·34 Å for C–O, and 3·36 Å for C–F. Minimum distances between non-overlapping molecules are 3·39 Å for C–O, 3·45 Å for F–F, 3·46 Å for C–F, and 3·53 Å for C–C.

The specimen material was supplied by Dr W. G. Schneider. All computations for the project were carried out by Dr F. R. Ahmed, using the IBM 650 computer of the Canadian Army Directorate of Personnel Statistics, and the IBM 1620 computer of the National Research Council. Their assistance, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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Probability Distribution Connected with Structure Amplitudes of Two Related Crystals. II. Probability Distribution of the Product

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(*Received* 7 *November* 1962)

The paper deals with the probability distributions connected with the product of the structure amplitudes of a pair of related crystals and they represent, essentially, a generalization of the usual statistics to a pair of crystals. Expressions are derived for the distribution of the normalized 'correlation intensity', $Z=|F_N|\,|F_P|/\sigma_N\sigma_P$, and the 'normalized correlation amplitude', $Y=Z^{\frac{1}{2}}$, where $|F_N|$ and $|F_P|$ are the structure amplitudes of the two crystals containing N and P atoms respectively ($P<N$) and σ_N and σ_P are the root-mean-square values of $|F_N|$ and $|F_P|$. One limiting form of the general distribution characterizes the usual statistics of a single crystal while the other corresponds to the two crystals being independent or 'non-related'. On the basis of these results a statistical criterion is proposed for use as an index to measure the 'degree of relatedness' between two compounds in practice. A critical assessment of the relative merits of the tests developed in this paper and the function $P(w)$ suggested in Part I is also made.

Introduction

In Part I Ramachandran, Srinivasan & Sarma (1963) considered the problem of the probability distribution of the difference in structure amplitudes of two crystals both when they are related to and when they are independent of each other. From the results thus obtained it was suggested that the distribution function could be used in practice for testing the degree of isomorphism of two compounds.

In this paper we shall be mainly concerned with the corresponding problem of the distribution of the product of the two structure amplitudes.* Such a product is in the nature of an intensity and, in fact, the intensity from a single crystal can be considered to be the product of two ideally isomorphous, identical

* The nature of the general assumptions made and also the conditions of applicability *etc.* are the same as in Part I. So also the notation used here follows closely that of Part I.

crystals. Therefore the distribution derived for the product variable should tend, as a limiting case, to that of a single crystal as is in fact shown later to be the case. The other situation when the two crystals are entirely independent of each other will also be considered, and this is found to be another limiting case of the same general distribution. Thus the basic nature of the results obtained in this paper may be described as the generalization of the intensity statistics to a pair of crystals.

In the latter half of the paper a statistical criterion will be developed which can be used in practice as an index to measure the 'degree of relatedness' between two compounds. The test is essentially based on a quantitative evaluation of the 'correlation' between the two structures.

Case of related structure amplitudes

Since we are mainly interested in deriving the distributions connected with the product of two variables, we make use of the following general result from probability theory. If $z=xy$ then

$$P(z)=\int P_2((z/x);x)P_1(x)(dx/x) \quad (1)$$

where $P_2(y;x)$ is the conditional probability density function for y for a given value of x and $P_1(x)$ is the probability density function for the variable x.

We now define the product variable q as

$$q=|F_N||F_P| \quad (2)$$

and use equation (1) to derive the distribution $P(q)$ for different cases.

(a) Non-centrosymmetric case

When N and P are related the expressions for P_1 and P_2 are (see Part I)

$$P_1(|F_P|)=\frac{2|F_P|}{\sigma_P^2}\exp\left\{-\frac{|F_P|^2}{\sigma_P^2}\right\}. \quad (3)$$

$$P_2(|F_N|;|F_P|)=\frac{2|F_N|}{\sigma_Q^2}\exp\left\{-\frac{|F_N|^2+|F_P|^2}{\sigma_Q^2}\right\}I_0\left(\frac{2|F_N||F_P|}{\sigma_Q^2}\right). \quad (4)$$

Substituting these in (1) and simplifying we get

$$P(q)=\frac{4q}{\sigma_P^2\sigma_Q^2}I_0\left(\frac{2q}{\sigma_Q^2}\right)\int_0^\infty\frac{1}{x}\exp\left[-x^2-\frac{k^2}{x^2}\right]dx, \quad (5)$$

where

$$x=\frac{|F_P|\sigma_N}{\sigma_P\sigma_Q} \text{ and } k=\frac{\sigma_N q}{\sigma_P\sigma_Q^2}.$$

The integral in the above equation and its related forms also appear in other equations to be considered below and they are discussed in Appendix I. By the use of result (A3) of Appendix I the above expression reduces to

$$P(q)=\frac{4q}{\sigma_P^2\sigma_Q^2}I_0\left(\frac{2q}{\sigma_Q^2}\right)K_0\left(\frac{2\sigma_N q}{\sigma_P\sigma_Q^2}\right) \quad (6)$$

where $K_0(x)$ is the Bessel function with imaginary argument (Watson, 1944).

Let us now change the variable to $t=q/\sigma_P\sigma_Q$ and obtain the distribution for t from (6) above. We obtain

$$P(t)=4tI_0(2t\alpha)K_0(2t\sqrt{(1+\alpha^2)}) \quad (7)$$

where $\alpha=\sigma_P/\sigma_Q$. This form is given here since it is used in some calculations to be described later.

However, we are more interested in obtaining the distribution for the normalized product variable, Z, which is defined by

$$Z=|F_N||F_P|/\sigma_N\sigma_P. \quad (8)$$

The use of the symbol Z seems to be natural since, as P tends to N, the right-hand side of (8) tends to $|F_N|^2/\langle I_N\rangle$ which is identical with z, the normalized intensity for a single crystal. Thus Z may be considered as the 'normalized correlation intensity' for a pair of crystals. The distribution for Z can be worked out from (7) by appropriate change of variable, namely by writing $Z=(\sigma_Q/\sigma_N)t$. We thus have

$$P(Z)=4Z(1+\alpha^2)I_0(2Z\alpha\sqrt{(1+\alpha^2)})K_0[2Z(1+\alpha^2)]. \quad (9)$$

This can also be written in another simple form

$$P(Z)=\frac{4Z}{\sigma_2^2}I_0\left(\frac{2Z\sigma_1}{\sigma_2^2}\right)K_0\left(\frac{2Z}{\sigma_2^2}\right), \quad (10)$$

where

$$\sigma_1^2=\sigma_P^2/\sigma_N^2,\ \sigma_2^2=\sigma_Q^2/\sigma_N^2 \text{ so that } \sigma_1^2+\sigma_2^2=1. \quad (11)$$

We now consider another variable, Y, defined by

$$Y=Z^{\frac{1}{2}}=\left(\frac{|F_N||F_P|}{\sigma_N\sigma_P}\right)^{\frac{1}{2}}. \quad (12)$$

It is clear that Y represents the 'normalized correlation amplitude' of the two crystals. It is of interest to consider the distribution for Y. Applying the appropriate rule for transformation of variable, we get from (10)

$$P(Y)=\frac{8Y^3}{\sigma_2^2}I_0\left(\frac{2Y^2\sigma_1}{\sigma_2^2}\right)K_0\left(\frac{2Y^2}{\sigma_2^2}\right). \quad (13)$$

That the expressions derived above for Z, Y, and t all represent real probability density functions can be checked by showing that their integrals reduce to unity. This is demonstrated for one of them in Appendix II.

(b) Centrosymmetric case

The expressions for P_1 and P_2 for this case are (see Part I)

$$P_1(|F_P|)=\sqrt{(2/\pi\sigma_P^2)}\exp\{-|F_P|^2/2\sigma_P^2\}. \quad (14)$$

$$P_2(|F_N|;|F_P|)=\frac{1}{\sqrt{(2\pi\sigma_Q^2)}}\left\{\exp\left[-\frac{(|F_N|+|F_P|^2)}{2\sigma_Q^2}\right]+\exp\left[-\frac{(|F_N|-|F_P|)^2}{2\sigma_Q^2}\right]\right\}. \quad (15)$$

When substituted in (1) these lead to

$$P(q)=\frac{2}{\pi\sigma_P\sigma_Q}\cosh\left(\frac{q}{\sigma_Q^2}\right)\int_0^\infty\frac{1}{x}\exp\left[-x^2-\frac{q^2\sigma_N^2}{4\sigma_P^2\sigma_Q^2x^2}\right]dx \quad (16)$$

where $x=|F_P|\sigma_N/\sigma_P\sigma_Q\sqrt{2}$. Using (A3) of Appendix I, we obtain

$$P(q)=\frac{2}{\pi\sigma_P\sigma_Q}\cosh\left(\frac{q}{\sigma_Q^2}\right)K_0\left(\frac{\sigma_N q}{\sigma_P\sigma_Q^2}\right). \quad (17)$$

Similar to expression (7) for the non-centrosymmetric case, we now have

$$P(t)=\frac{2}{\pi\sigma_P\sigma_Q}\cosh(\alpha t)K_0(t\sqrt{(1+\alpha^2)}). \quad (18)$$

The expressions for the normalized product variable Z thus take the forms

$$P(Z)=\frac{2}{\pi}\sqrt{(1+\alpha^2)}\cosh(Z\alpha\sqrt{(1+\alpha^2)})K_0[Z(1+\alpha^2)] \quad (19)$$

or

$$P(Z)=\frac{2}{\pi\sigma_2}\cosh\left(\frac{Z\sigma_1}{\sigma_2^2}\right)K_0\left(\frac{Z}{\sigma_2^2}\right). \quad (20)$$

It follows that the distribution for Y is

$$P(Y)=\frac{4Y}{\pi\sigma_2}\cosh\left(\frac{Y^2\sigma_1}{\sigma_2^2}\right)K_0\left(\frac{Y^2}{\sigma_2^2}\right). \quad (21)$$

Case of unrelated structure amplitudes

(a) Non-centrosymmetric case

When N and P are independent of each other, $P_1(|F_P|)$ is given by equation (3) while $P_2(|F_N|;|F_P|)$ is given by

$$P_2(|F_N|;|F_P|)=P_2(|F_N|)=\frac{2|F_N|}{\sigma_N^2}\exp\left\{-\frac{|F_N|^2}{\sigma_N^2}\right\}. \quad (22)$$

Substituting these in equation (1) we get

$$P(q)=\frac{4q}{\sigma_P^2\sigma_N^2}\int_0^\infty\exp\left\{-\frac{|F_P|^2}{\sigma_P^2}-\frac{q^2}{\sigma_N^2|F_P|^2}\right\}\frac{d|F_P|}{|F_P|}.$$

Putting $|F_P|/\sigma_P=x$, this takes the form

$$P(q)=\frac{4q}{\sigma_P^2\sigma_N^2}\int_0^\infty\exp\left\{-\left(x^2+\frac{k^2}{x^2}\right)\right\}\frac{dx}{x}. \quad (23)$$

where $k=q/\sigma_N\sigma_P$. By the use of result (A3) of Appendix I, this gives

$$P(q)=\frac{4q}{\sigma_P^2\sigma_N^2}K_0\left(\frac{2q}{\sigma_P\sigma_N}\right). \quad (24)$$

For the normalized variable Z we thus obtain

$$P(Z)=4ZK_0(2Z). \quad (25)$$

It is interesting to note that $P(Z)$ is independent of σ_1^2. Now, when $\sigma_1^2\to 0$, the related and the unrelated cases should lead to the same distribution. Hence equation (25) for $P(Z)$ for the unrelated case should be obtained on putting $\sigma_1^2\to 0$ in the distribution function for the related case, namely (10). This is readily verified to be the case.

From equation (25) the expression for $P(Y)$, is obtained in the form

$$P(Y)=8Y^3K_0(2Y^2). \quad (26)$$

(b) Centrosymmetric case

For this case $P_1(|F_P|)$ is given by (14) and, since N and P are independent,

$$P_2(|F_N|;|F_P|)=P_2(|F_N|)=\sqrt{(2/\pi\sigma_N^2)}\exp\left\{-\frac{|F_N|^2}{2\sigma_N^2}\right\}. \quad (27)$$

Substituting these in (1) we obtain

$$P(q)=\frac{2}{\pi\sigma_P\sigma_N}\int_0^\infty\exp\left\{-\left[\frac{|F_P|^2}{2\sigma_P^2}+\frac{q^2}{2|F_P|^2\sigma_N^2}\right]\right\}\frac{d|F_P|}{|F_P|} \quad (28)$$

$$=\frac{2}{\pi\sigma_P\sigma_N}\int_0^\infty\exp\left\{-\left(x^2+\frac{q^2}{4\sigma_P^2\sigma_N^2x^2}\right)\right\}\frac{dx}{x}. \quad (29)$$

where $|F_P|/\sqrt{(2)}\sigma_P=x$. By result (A3) this reduces to

$$P(q)=\frac{2}{\pi\sigma_N\sigma_P}K_0\left(\frac{q}{\sigma_N\sigma_P}\right). \quad (30)$$

We thus have finally

$$P(Z)=\frac{2}{\pi}K_0(Z). \quad (31)$$

$$P(Y)=\frac{4y}{\pi}K_0(Y^2). \quad (32)$$

In this case also we see that $P(Z)$ is independent of σ_1^2 and the expressions (31) and (32) are obtained by setting $\sigma_1^2=0$ in equations (20) and (21).

Limiting forms of the general case

We have already seen that in the limiting case when $\sigma_1^2=0$ the general expression yields the distribution corresponding to the unrelated structure amplitudes. It is of interest to see what happens to the general expression in the other limiting case, namely when $\sigma_1^2\to 1$. Since, physically, this situation is equivalent to $P\to N$, the variables Z and Y become z and y, the normalized intensity and normalized amplitude, respectively, for a single crystal. Thus we should expect that the general expression given by equations (13) and (21) would reduce to the familiar functions ${}_NP(y)$ and ${}_CP(y)$ (Ramachandran & Srinivasan, 1960) which are given by

$${}_NP(y)=2y\exp\{-y^2\}. \quad (33)$$

$${}_CP(y)=\sqrt{(2/\pi)}\exp\{-\tfrac{1}{2}y^2\}. \quad (34)$$

This can be proved easily as follows. Firstly we observe that when σ_1^2 tends to 1, σ_2^2 tends to 0 and both $I_0(x)$ and $K_0(x)$ in expression (13) can be replaced by their asymptotic expansions, since x is large. Thus, using the results

$$I_0(x) = \frac{e^x}{\sqrt{(2\pi x)}}\left\{1+\frac{1^2}{1!\,8x}+\ldots\right\}. \quad (35)$$

$$K_0(x) = \frac{e^{-x}\pi^{\frac{1}{2}}}{\sqrt{(2x)}}\left\{1-\frac{1^2}{1!\,8x}+\ldots\right\}. \quad (36)$$

in (13) and simplifying we get

$$P(y) = \frac{2Y}{\sqrt{(\sigma_1)}}\exp\left\{-\frac{2Y^2(1-\sigma_1)}{\sigma_2^2}\right\}. \quad (37)$$

Since σ_2^2 tends to zero we may substitute $\sigma_1=\sqrt{(1-\sigma_2^2)} = 1-\frac{1}{2}\sigma_2^2$ in (37) which immediately gives expression (33). A corresponding result can be shown for the centrosymmetric case also.

Nature of the distributions*

Let us now study the nature of the distribution derived in the earlier sections. We shall, however, consider in detail only the $P(Y)$ curves since they seem to be more useful from a practical point of view than the $P(Z)$ curves.

The distributions $P(Y)$ are given in Fig. 1 and Fig. 2 for the non-centrosymmetric and centrosymmetric cases respectively. In addition to the two limiting forms, curves are also given for values of σ_1^2 equal to 0·5 and 0·8. It can be seen from Fig. 1 that for a non-centrosymmetric crystal, the curve for the unrelated case ($\sigma_1^2=0$) has properties similar to the ${}_NP(y)$ curve ($\sigma_1^2=1$) in that its maximum occurs away from the origin. The curves for other intermediate values of σ_1^2 fall in between these two curves.

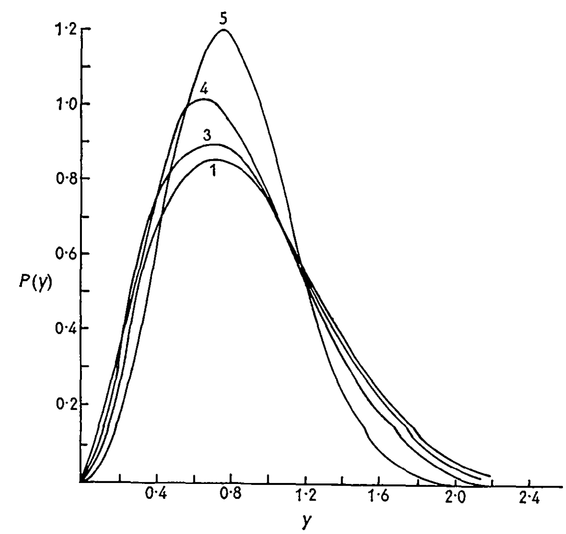

Fig. 1. Probability distribution function $P(y)$, for the non-centrosymmetric case, corresponding to $\sigma_1{}^2 = 1.0$ (1); $\sigma_1{}^2=0{\cdot}8$ (3); $\sigma_1{}^2=0{\cdot}5$ (4); and $\sigma_1{}^2=0$ (5).

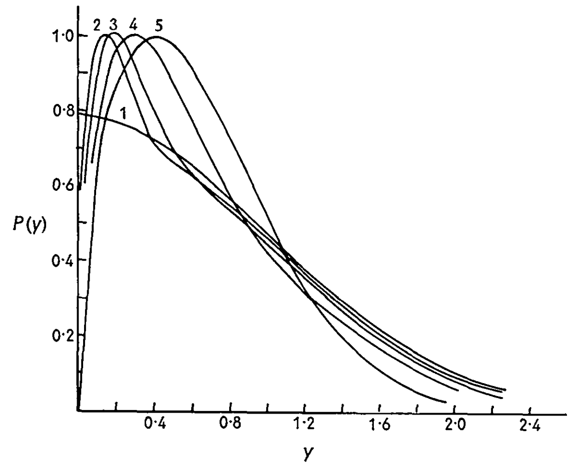

Fig. 2. Probability distribution function $P(y)$, for the centrosymmetric case, corresponding to $\sigma_1{}^2=1{\cdot}0$ (1); $\sigma_1{}^2=0{\cdot}9$ (2); $\sigma_1{}^2=0{\cdot}8$ (3); $\sigma_1{}^2=0{\cdot}5$ (4) and $\sigma_1{}^2=0$ (5).

The nature of the distribution for the centrosymmetric case is rather interesting. For $\sigma_1^2=1$, we have the usual ${}_CP(y)$ curve, which has its maximum value at the origin and which slowly decreases as Y increases. On the other hand, for $\sigma_1^2=0$, the nature of the curve is completely different. It starts with a value zero at the origin (unlike the ${}_CP(y)$ curve) and has a maximum away from the origin (at $Y\simeq 0{\cdot}5$). For intermediate values of σ_1^2, the behaviour of the curve is somewhat peculiar. Until about $\sigma_1^2=0{\cdot}8$ the curve remains more or less similar in its shape to that for $\sigma_1^2=0$ excepting for a shift in the position of the maximum towards the origin. For large values of σ_1^2, the curve is close to the ${}_CP(y)$ curve except in the region near the origin. It is clear from the curves that as σ_1^2 increases further the region of dissimilarity will be confined more and more to the vicinity of the origin while, away from the origin, the curve will approach more closely the ${}_CP(y)$ curve.

Parameter defining the degree of relatedness of two structures

The distribution functions considered in the earlier sections might prove useful as qualitative tests for relatedness in actual practice. However, it seems desirable to have a quantitative measure for this purpose. In this section we shall develop a statistical criterion which has the required property. Define a parameter γ by

$$\gamma = \frac{\langle Z\rangle_{\rm obs}-\langle Z\rangle_{\rm unrel}}{\langle Z\rangle_{\rm rel}-\langle Z\rangle_{\rm unrel}}, \quad (38)$$

* The calculations were all done on EDSAC II with a single program to handle both centrosymmetric and non-centrosymmetric cases. The forms of the functions used were equations (7) and (18) and both $P(Z)$ and $P(Y)$ were obtained from these by simple hand calculation.

where $\langle Z \rangle$ is the expectation value of Z and the different subscripts have the following meanings. $\langle Z \rangle_{\text{rel}}$ refers to the theoretical value of $\langle Z \rangle$ for the particular value of σ_1^2 for a pair of related crystals; $\langle Z \rangle_{\text{unrel}}$ refers to the case when the two structures are completely independent and $\langle Z \rangle_{\text{obs}}$ is the observed value of $\langle Z \rangle$. This last quantity can be calculated from the observed structure amplitudes of the two crystals since, by definition,

$$\langle Z \rangle = \left\langle \frac{|F_N|\,|F_P|}{\sigma_N \sigma_P} \right\rangle = \frac{\Sigma |F_N|\,|F_P|}{\sqrt{(\Sigma |F_N|^2)}\sqrt{(\Sigma |F_P|^2)}} \,. \quad (39)$$

It can be seen from the above relation that $\langle Z \rangle$ can also be described as the 'direct correlation coefficient' between the two structure amplitudes (Srinivasan, 1961).

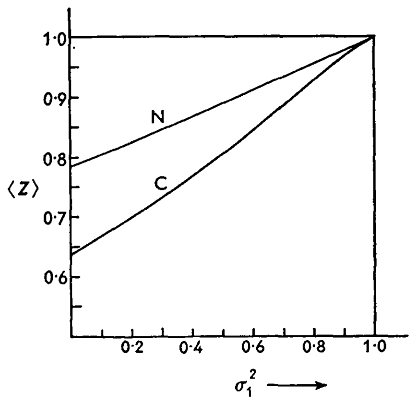

Fig. 3. Graph of $\langle Z \rangle$ as a function of $\sigma_1{}^2$ for non-centrosymmetric (N) and centrosymmetric case (C).

The value of $\langle Z \rangle_{\text{rel}}$ has been calculated for different values of σ_1^2 by numerical integration and the results are shown in Fig. 3. It is of some interest to discuss the form of the two curves. Though for any general value of σ_1^2 the calculation has to be done by numerical integration, the limiting cases can be dealt with by the following simple argument purely from a physical point of view. When σ_1^2 tends to unity we know that the normalized correlation intensity Z tends to z, the normalized intensity for a single crystal, and we know that $\langle z \rangle$ equals unity both for centrosymmetric and non-centrosymmetric cases. On the other hand when σ_1^2 tends to 0, the two structures are independent and we can therefore write

$$\langle Z \rangle = \left\langle \frac{|F_N|}{\sigma_N} \right\rangle \left\langle \frac{|F_P|}{\sigma_P} \right\rangle . \quad (40)$$

Since each one of the quantities on the right hand side of the above equation represents the expectation value of the normalized structure amplitude of a single crystal, the value of $\langle Z \rangle$ becomes $\pi/4$ for the non-centrosymmetric and $2/\pi$ for the centrosymmetric case respectively. A direct calculation of $\langle Z \rangle$ by means of expressions (25) and (31) also gives the same values (Appendix III) which only proves the essential correctness of the above procedure.

The curve thus starts with the value 0·637 at the origin for the centrosymmetric and 0·785 for the non-centrosymmetric case. The increase in its value is more rapid for the former than for the latter and both curves reach unity as σ_1^2 tends to unity.

Returning to the parameter γ as defined by (38) we see that when there is complete lack of relatedness, γ should be equal to zero and when there is 'perfect relatedness', its value should be equal to unity. In practice it would have a value in between 0 and 1, and its actual value can be taken as a measure of the 'degree of relatedness' between the two compounds.

Discussion

It is interesting to compare the statistical tests suggested in this paper (in particular the value of γ) with the $P(w)$ function considered in Part I.

The nature of the $P(Y)$ curves suggests that they are not likely to be very useful as a practical test for isomorphism. As compared with this the function $P(w)$ seems to be powerful especially when σ_1^2 is large since, then, the theoretical curve has a pronounced maximum at the origin.

However, there is one difficulty that is likely to be met with in practice while applying the $P(w)$ test. The observed structure amplitudes are always subject to errors, and since we take their *difference* for obtaining the $P(w)$ curve these errors might introduce large fluctuations in the experimental curve. This might become particularly serious when σ_1^2 is large precisely in the region when the $P(w)$ curves are most effective. This difficulty will not be present to the same degree with the $P(Y)$ curves, but on the other hand there is not sufficient dissimilarity between the plots of the $P(Y)$ functions in the related and the unrelated cases to make the test particularly efficient.

As compared with these, the γ test appears to have certain distinct features which would make it more useful than the others. Firstly, the calculation of γ can be done very quickly. Secondly it is not as susceptible to errors in the observed intensities as $P(w)$, since it is the product of the structure amplitudes that enters its calculation. It is also independent of scaling errors as can be seen by the nature of the expression (39). In other words, γ is relatively more stable as a statistical criterion. Finally it has the additional advantage that it gives a quantitative estimate of the 'degree of relatedness' as contrasted with the other functions, which give results only in a qualitative way.

The applicability of any of these tests rests primarily on the assumption that the usual conditions of statistics hold good. However, the use of γ seems to be justifiable even under quite different conditions provided it is interpreted in a more general sense based on its definition (equation (38)). Thus, for instance, when the asymmetric unit contains dissimilar atoms or a pseudosymmetric molecule, even though the value of $\langle Z\rangle_{\text{unrel}}$ can no longer be taken to be the ideal value for a random structure, it can still be calculated for the particular structure under consideration since, by definition, $\langle Z\rangle_{\text{unrel}}$ is only the average value of Z for two structures when they are independent. Thus, structure factors can be calculated for any two random orientations of the molecules in the two structures and these can be used to evaluate $\langle Z\rangle_{\text{unrel}}$ by relation (39). An exactly similar manipulation simulating 'relatedness' in the two structures will give the value of $\langle Z\rangle_{\text{rel}}$. In this way it will be possible to eliminate whatever disturbing features that may exist as a result of the asymmetric unit not satisfying the usual conditions.

Detailed tests of these ideas are in progress and will be reported in due course.

APPENDIX I

We are interested in the integrals of the type

$$\int_0^\infty \frac{1}{x}\exp -\left(x^2+\frac{k^2}{x^2}\right)dx \qquad \text{(A1)}$$

where k is a constant. Substituting $x=\sqrt{(k)}e^\theta$, the above integral reduces to

$$\int_{-\infty}^\infty \exp -2k\,(\cosh 2\theta)\,d\theta \qquad \text{(A2)}$$

$$=\int_0^\infty \exp -2k\,(\cosh\varphi)\,d\varphi = K_0(2k)\,. \qquad \text{(A3)}$$

Also from the above result we get

$$\int_0^\infty \frac{1}{x}\exp -\left(x-\frac{k}{x}\right)^2 dx = e^{2k}K_0(2k)\,. \qquad \text{(A4)}$$

APPENDIX II

That the various functions derived in the text are real probability density functions can be checked by showing that their integrals are equal to unity. We make use of the following result (Watson, 1944, p. 410):

$$\int_0^\infty K_\mu(at)J_\nu(bt)t^{\mu+\nu+1}dt=\frac{(2a)^\mu(2b)^\nu\Gamma(\mu+\nu+1)}{(a^2+b^2)^{\mu+\nu+1}}\,. \qquad \text{(A5)}$$

Consider the expression for $P(t)$ for the non-centrosymmetric case (equation (7)). A comparison with the above result (A5) shows that we should substitute $\mu=0$, $\nu=0$, $b=ib'$ where $b'=2\alpha$, $a'=2\sqrt{(1+\alpha^2)}$. The integral of $P(t)$ then proves to be unity. It has not been possible to prove the corresponding result for the general expression of the centrosymmetric case. However, it is possible to do it for the limiting case when $\sigma_1^2=0$ (expression (31)). We make use of the following formula (Watson, 1944, p. 388):

$$\int_0^\infty K_\nu(t)t^{\mu-1}dt = 2^{\mu-2}\Gamma\left(\frac{\mu-\nu}{2}\right)\Gamma\left(\frac{\mu+\nu}{2}\right)\,. \qquad \text{(A6)}$$

Substitution of $\nu=0$, $\mu=1$ gives the desired result.

APPENDIX III

The expectation values of Z for $\sigma_1^2=0$ can be worked out directly since we have the required distribution functions (expressions (25) and (31)). We thus have, for the centrosymmetric case,

$$\langle Z\rangle_{\text{unrel}}=\frac{2}{\pi}\int_0^\infty ZK_0(Z)\,dZ\,. \qquad \text{(A7)}$$

Using formula (A6) this gives immediately $\langle Z\rangle_{\text{unrel}}=2/\pi$. So also for the non-centrosymmetric case,

$$\langle Z\rangle_{\text{unrel}}=\int_0^\infty 4Z^2K_0(2Z)\,dZ \qquad \text{(A8)}$$

which, again by using (A6), reduces to $\pi/4$.

One of the authors (R. S.) wishes to thank Prof. Sir Nevill Mott and Dr W. H. Taylor for provision of facilities and Dr M. V. Wilkes for permission to use the EDSAC. His thanks are also due to Dr J. C. P. Miller for helpful discussions regarding numerical integration and to Miss J. C. Ward for assistance with the computer. He also wishes to thank the Commonwealth Scholarship Commission for the award of a scholarship, during the tenure of which part of the present work was done.

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