lumination, so that the resolution in the image is worse than that expected for the aperture size used. These binary oxides of tungsten and niobium, having some quite intense diffraction spots near the periphery of the objective aperture, are rather sensitive to the effect. However, such beams will always be the ones contributing the finer detail in images and, therefore, the effect will always limit resolution to values more than those expected for the size of objective aperture.

The computations show how a decrease in divergence restores the lost detail. We believe that this effect is general, and that the obvious step to improved resolution, apart from reducing the value of $C_S$, is to improve the illuminating system of the microscope to give less divergence without loss of intensity. Fig. 5 shows that to obtain the resolution appropriate to the size of the objective aperture, the divergence should be at most half that used in our experiment, corresponding to the image in Fig. 5(*b*); much detail is still lost in Fig. 5(*c*), where the divergence is reduced by $\frac{2}{7}$.

We wish to thank Dr S. Iijima for providing the electron diffraction pattern and micrograph used in Figs. 1 and 6, and for permission to publish these. Thanks are also due to the members of the Electron Diffraction Section of the CSIRO Division of Chemical Physics, in particular to Dr D. F. Lynch and Mr A. F. Moodie for their theoretical assistance.

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# Probability Distribution Connected with Structure Amplitudes of Two Related Crystals. VII. The Case of an Approximately Centrosymmetric Structure*

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The probability distribution of the structure factors $F_N$ and $F_N^c$ where the former refers to the 'true structure' containing $N$ atoms at locations $\mathbf{r}_{Nj}$ and the latter to the assumed model' with $N$ atoms at locations $\mathbf{r}_{Nj}^c$, is worked out for the situation where the assumed model is exactly centrosymmetric and the true model is approximately centrosymmetric. Other statistical distributions connected with these, such as difference, quotient, reciprocal quotient and the phase-angle difference have also been derived. Also a Booth type of discrepancy index is worked out for such a situation. Theoretical results are verified with a hypothetical model.

## Introduction

In the ealier parts of the series (Part I: Ramachandran, Srinivasan & Raghupathy Sarma, 1963; Part II: Srinivasan, Raghupathy Sarma & Ramachandran, 1963*a*; Part III: Srinivasan, Subramanian & Ramachandran, 1964; Part IV: Srinivasan & Ramachandran, 1965*a*; Part V: Srinivasan & Ramachandran, 1965*b*; Part VI: Srinivasan & Ramachandran, 1966; see also, Srinivasan, Raghupathy Sarma & Ramachandran, 1963*b*; Srinivasan & Chandrasekaran, 1966 – hereafter referred to as SC; Parthasarathy & Srinivasan, 1967 – hereafter referred to as PS) the probability distributions of a pair of structure factors were considered. The results led to various statistical tests such as tests for isomorphism between a pair of crystals, and discrepancy indices for use in crystal structure analysis. The basic problem considered may be stated as the probability distribution of the structure factor of the 'true' structure containing $N$ atoms at locations $\mathbf{r}_{Nj}$ and another 'assumed model' containing a part $P$ of the atoms ($P \leq N$) with coordinate errors. The probability distribution function of the structure factors $F_N$ and $F_P^c$, where $F_N$ corresponds to the true structure

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and $F_P^c$ to the 'assumed model', was established and several statistical results were deduced. Two main cases were considered, namely

(a) case I: when both $F_N$ and $F_P^c$ are non-centrosymmetric;

(b) case II: when both $F_N$ and $F_P^c$ are centrosymmetric.

The cases (III and IV) when one of the two is non-centrosymmetric and the other centrosymmetric were not considered since no immediate practical application was then envisaged. However, it has been realised that a situation of this type could arise in practice and could lead to distributions corresponding to pseudo-symmetric structures. For instance, it is possible that the true structure is 'approximately centrosymmetric' whereas the assumed model is exactly centrosymmetric (case III). The coordinates $\mathbf{r}_{Nj}$ of the true model would then be related to the coordinates $\mathbf{r}_{Nj}^c$ of the assumed model by the shifts $\Delta r_{Nj}$ which would correspond to the perturbation of the centrosymmetric model to yield the non-centrosymmetric one.* This problem has been considered and reported briefly (Srinivasan & Swaminathan, 1975).

The present paper deals with working out in detail the joint probability distribution of the structure factors $F_N$ and $F_N^c$ for such a situation. This enables us to work out several other statistical distributions such as the difference, quotient, reciprocal quotient and phase angle connected with the structure factors $F_N$ and $F_N^c$. Also it is obvious that the converse case of $F_N$ corresponding to a centrosymmetric model and $F_N^c$ to a non-centrosymmetric one, can be deduced from the results of case III.

This type of pseudosymmetric distribution was first considered by Luzzati (1953) who applied his (1952) earlier analysis to the above situation. He deduced the values of a type of discrepancy index involving $F_N$ and $F_N^c$ which would enable one to estimate $\langle|\Delta\mathbf{r}_{Nj}|\rangle$ in a practical situation. Here we treat this problem more systematically following the type of analysis used for cases I and II. In particular, the distributions for the difference, quotient, and reciprocal quotient of the normalized structure factors as well as their phase-angle difference will be arrived at. Since most of the steps for the derivation are common to the earlier parts reference to equations *etc.*, of the earlier parts will be made by a prefix denoting the part concerned.

The treatment of the present problem of the degree of centrosymmetry of a non-centrosymmetric structure arose in another context (Srinivasan & Vijayalakshmi, 1972; Srinivasan, Swaminathan & Chacko, 1972; Srinivasan, Vijayalakshmi & Parthasarathy, 1974).

### Basic probability distributions

Let $\mathbf{r}_{Nj}$ denote the coordinates of the structure which is approximately centrosymmetric. This may be considered to have been derived by giving random and independent displacements $\Delta\mathbf{r}_{Nj}$ to the coordinates of a perfectly centrosymmetric assumed model with coordinates $\mathbf{r}_{Nj}$. It is assumed that the shifts $\Delta\mathbf{r}_{Nj}$ and $\Delta\mathbf{r}_{Nj'}$ for the atoms $j$ and $j'$ which are related by a centre of symmetry are random and independent where $n=N/2$. Let $F_N$ and $F_N^c$ denote the structure factors of the true and assumed models, which are considered to consist of a large number of similar atoms. The conditional joint distribution function of $|F_N|$ and $\alpha$ for a given $F_N^c$ can be deduced from equation (A7) of SC by setting $P=N$, $\sigma_Q=0$

$$P(|F_N|,\alpha;\ F_N^c)=\frac{|F_N|}{\pi\sigma_N^2(1-D^2)} \times \exp\left[-\frac{|F_N|^2+D^2|F_N^c|^2-2D|F_N|\,|F_N^c|\cos\alpha}{\sigma_N^2(1-D^2)}\right] \quad (1)$$

where

$$D=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_{Nj}\rangle \quad (1a)$$

and $\alpha$ is the angle between $F_N$ and $F_N^c$. The validity of equation (A7) of SC in the present situation is obvious since the former is deduced from the distribution of $\Delta F$ arising out of $\Delta\mathbf{r}_{Nj}$ for a structure factor with a given $F_N^c$. In terms of the normalized variables, $y_N=|F_N|/\sigma_N$ and $y_N^c=|F_N^c|/\sigma_N$, (1) takes the form

$$P(y_N,\alpha;\ y_N^c)=\frac{y_N}{\pi(1-D^2)} \times \exp\left[-\frac{y_N^2+D^2y_N^{c2}-2Dy_Ny_N^c\cos\alpha}{(1-D^2)}\right]. \quad (2)$$

The conditional distribution of amplitude $y_N$ alone is obtained by integrating (2) with respect to $\alpha$ which yields [equation (A9) of SC, in the normalized form]

$$P(y_N;\ y_N^c)=\frac{2y_N}{(1-D^2)} \times \exp\left[-\frac{y_N^2+D^2y_N^{c2}}{(1-D^2}\right] I_0\left(\frac{2Dy_Ny_N^c}{(1-D^2)}\right). \quad (3)$$

Equation (3) is identical in form with equation (V-9). It is important to note here that for the present case $F_N$ has both phase and magnitude while $F_N^c$ is real since it corresponds to a centrosymmetric model. Thus, although the conditional distribution $P(y_N;\ y_N^c)$ for the present case and case I turns out to be the same, the distinction arises only at the next stage, namely in trying to arrive at the joint distribution $P(y_N,\ y_N^c)$ which needs assumptions about the distribution $P(y_N^c)$. Thus with a centric distribution assumed for $P(y_N^c)$,

$$P(y_N^c)=\sqrt{\frac{2}{\pi}}\exp\left(-\frac{y_N^{c2}}{2}\right), \quad (4)$$

* For convenience we consider only the case when $P=N$.

the joint distribution $P(y_N, y_N^c)$ is deduced to be

$$P(y_N, y_N^c) = P(y_N;\, y_N^c)P(y_N^c) = \sqrt{\frac{2}{\pi}}\,\frac{2y_N}{(1-D^2)} \times \exp\left[-\frac{2y_N^2+(1+D^2)y_N^{c2}}{2(1-D^2)}\right] I_0\left[\frac{2Dy_Ny_N^c}{(1-D^2)}\right]. \quad (5)$$

The distribution of $y_N$ alone can be deduced by integrating (5) with respect to $y_N^c$ with the use of the table of integrals (Gradshteyn & Ryzhik, 1965, p. 710, § 6·618). We get

$$P(y_N) = \frac{2y_N}{\sqrt{1-D^4}} \exp\left(-\frac{y_N^2}{1-D^4}\right) I_0\left(\frac{D^2y_N^2}{1-D^4}\right). \quad (6)$$

**Probability distribution of the phase angle**

Analogously the conditional distribution $P(\alpha;\, y_N^c)$ can be arrived at from (2) by integrating over $y_N$. This turns out to be

$$P(\alpha;\, y_N^c) = \int_0^\infty P(y_N, \alpha;\, y_N^c)\mathrm{d}y_N \quad (7)$$

$$= \int_0^\infty \frac{y_N}{\pi(1-D^2)} \times \exp\left[-\frac{y_N^2+D^2y_N^{c2}-2Dy_Ny_N^c\cos\alpha}{(1-D^2)}\right]\mathrm{d}y_N \quad (8)$$

$$= \frac{1}{\pi(1-D^2)}\int_0^\infty y_N \times \exp\left[-\frac{y_N^2+D^2y_N^{c2}-2Dy_Ny_N^c\cos\alpha}{(1-D^2)}\right]\mathrm{d}y_N\,. \quad (9)$$

Equation (9) can be simplified to (Appendix A)

$$P(\alpha;\, y_N^c) = K\left[\frac{1-D^2}{2} + \frac{Dy_N^c\cos\alpha\sqrt{\pi(1-D^2)}}{2} \times\exp\left(\frac{D^2y_N^{c2}\cos^2\alpha}{1-D^2}\right)\times\left\{1+\operatorname{erf}\left(\frac{Dy_N^c\cos\alpha}{\sqrt{1-D^2}}\right)\right\}\right] \quad (10)$$

where

$$K = \frac{\exp\left[-\dfrac{D^2y_N^{c2}}{1-D^2}\right]}{\pi(1-D^2)}\,.$$

On further simplification (10) takes the form

$$P(\alpha;\, y_N^c) = \frac{1}{2\pi}\exp\left(-\frac{D^2}{1-D^2}\cdot y_N^{c2}\right) + \frac{D}{2\sqrt{\pi}}\,\frac{y_N^c\cos\alpha}{\sqrt{1-D^2}}\times\exp\left(-\frac{D^2y_N^{c2}\sin^2\alpha}{(1-D^2)}\right) \times\left[1+\operatorname{erf}\left(\frac{D}{\sqrt{1-D^2}}\,y_N^c\cos\alpha\right)\right]. \quad (11)$$

The distribution of $\alpha$ is then given by

$$P(\alpha) = \int_0^\infty P(\alpha;\, y_N^c)P(y_N^c)\mathrm{d}y_N^c\,. \quad (12)$$

Using (4), (11) and (12), we get

$$P(\alpha) = \int_0^\infty \frac{1}{2\pi}\exp\left(-\frac{D^2y_N^{c2}}{1-D^2}\right)\sqrt{\frac{2}{\pi}}\exp\left(-\frac{y_N^{c2}}{2}\right)\mathrm{d}y_N^c + \int_0^\infty \frac{D}{2\sqrt{\pi}}\,\frac{y_N^c\cos\alpha}{\sqrt{1-D^2}}\exp\left(-\frac{D^2}{1-D^2}y_N^{c2}\sin^2\alpha\right) \times\left[1+\operatorname{erf}\left(\frac{Dy_N^c\cos\alpha}{\sqrt{1-D^2}}\right)\right]\sqrt{\frac{2}{\pi}}\exp\left(-\frac{y_N^{c2}}{2}\right)\mathrm{d}y_N^c\,. \quad (13)$$

Equation (13) can be simplified to (Appendix B)

$$P(\alpha) = \frac{\sqrt{1-D^2}}{2\pi\sqrt{1+D^2}} + \frac{\sqrt{2}}{2\pi}\,\frac{D\sqrt{1-D^2}\cos\alpha}{(2D^2\sin^2\alpha+1-D^2)} \times\left[1+\frac{\sqrt{2}D\cos\alpha}{\sqrt{1+D^2}}\right]. \quad (14)$$

**Probability distribution of the normalized difference**

From previous experience we find that, among several variables connected with the normalized quantities $y_N$ and $y_N^c$ such as sum, difference, product and quotient, it is the difference and the quotient variables which lead to interesting applications. Although the distribution of the difference and quotient variables were derived by Srinivasan & Ramachandran (1965*a*) and Srinivasan, Subramaniam & Ramachandran (1964), this can be done by a slightly different procedure (PS) which also gives the distribution of the sum vaiiable. Thus the joint probability distribution of the variables*

$$y_s = y_N + y_N^c \quad (15)$$

$$y_d = y_N - y_N^c \quad (16)$$

is given by

$$P(y_s, y_d) = \tfrac{1}{2}[P(y_N, y_N^c)]\,,$$

where $\frac{1}{2}$ is the Jacobian of transformation,

$$P(y_s, y_d) = \tfrac{1}{2}\sqrt{\frac{2}{\pi}}\,\frac{(y_s+y_d)}{(1-D^2)}\cdot\exp\left[-\frac{(y_s-y_d)^2}{8}\left(\frac{1+D^2}{1-D^2}\right)\right] \times\exp\left[-\frac{(y_s+y_d)^2}{4(1-D^2)}\right] I_0\left[\frac{D}{2}\cdot\frac{(y_s^2-y_d^2)}{(1-D^2)}\right]. \quad (17)$$

It can be easily shown that the function $P(y_s, y_d)$ is non-zero only in the region

$$-\infty \le y_d \le y_s\,,\quad 0 \le y_s < \infty \quad (18)$$

* We follow uniformly the revised notation for these variables. Thus $s$, $d$, $p$ and $q$ are used as subscripts to denote sum, difference, product and quotient respectively.

and is zero elsewhere. The distributions of $y_d$ can be obtained from (17) and (18) as

$$P(y_d) = \int_{|y_d|}^{\infty} P(y_s,y_d)\mathrm{d}y_s . \tag{19}$$

Substituting for $P(y_s,y_d)$ we have

$$P(y_d)=\tfrac{1}{2}\sqrt{\frac{2}{\pi}}\frac{1}{(1-D^2)}\cdot\exp\left[-\frac{y_d^2}{8}\left(\frac{3+D^2}{1-D^2}\right)\right]$$
$$\times\int_{|y_d|}^{\infty}(y_s+y_d)\exp\left[-\frac{y_s^2}{8}\left(\frac{3+D^2}{1-D^2}\right)\right]$$
$$\times\exp\left(-\frac{y_sy_d}{4}\right)I_0\left[\frac{D}{2}\frac{(y_s^2-y_d^2)}{(1-D^2)}\right]\mathrm{d}y_s . \tag{20}$$

Equation (20) was evaluated by numerical methods.

## Probability distribution of the quotient

As in the earlier treatment (PS) the joint distribution of the product ($y_p$) and quotient ($y_q$) variables, defined as

$$y_p=y_Ny_N^c \tag{21a}$$

$$y_q=y_N/y_N^c \tag{21b}$$

is given by

$$P(y_p,y_q)=\frac{1}{2y_q}P(y_N,y_N^c) , \tag{22}$$

where $1/2y_q$ is the Jacobian of transformation.

It can be easily shown that the function $P(y_p,y_q)$ is non-zero in the domain

$$0\le y_p<\infty;\quad 0\le y_q<\infty \tag{23}$$

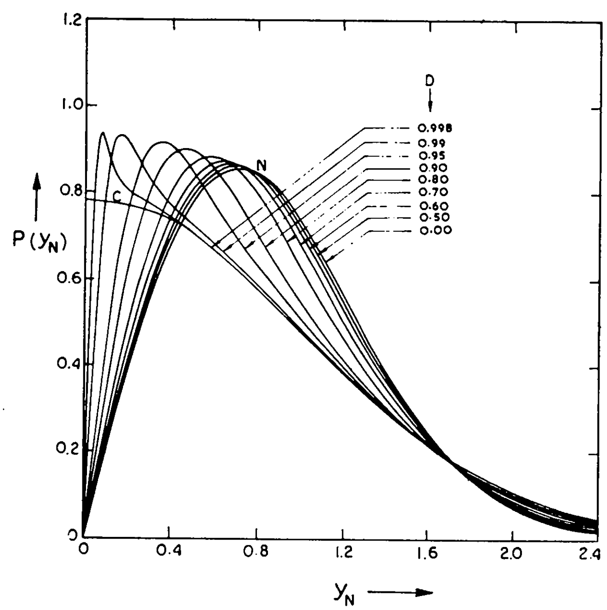


Fig. 1. $P(y_N)$ distribution for an approximately centrosymmetric structure for different $D$ values.

and is zero elsewhere.

The distribution of $y_q$ is then given by

$$P(y_q)=\int_0^{\infty}P(y_p,y_q)\mathrm{d}y_p . \tag{24}$$

Substituting for $P(y_p,y_q)$, we have

$$P(y_q)=\sqrt{\frac{2}{\pi}}\cdot\frac{1}{\sqrt{y_q}}\frac{1}{(1-D^2)}\int_0^{\infty}\sqrt{y_p}\exp\left(-\frac{y_py_q}{1-D^2}\right)$$
$$\times\exp\left[-\frac{y_p}{2y_q}\left(\frac{1+D^2}{1-D^2}\right)\right]I_0\left(\frac{2D}{1-D^2}\cdot y_p\right)\mathrm{d}y_p . \tag{25}$$

From the table of integrals (Gradshteyn & Ryzhik, 1965, p. 711, § 6·621) (25) becomes

$$P(y_q)=\frac{2y_q\sqrt{2y_q^2+1+D^2}\sqrt{1-D^2}}{[(2y_q^2+1+D^2)^2-16D^2y_q^2]}$$
$$\times{}_2F_1\left[\tfrac{1}{4},-\tfrac{1}{4};1;\left(\frac{4Dy_q}{2y_q^2+1+D^2}\right)^2\right] . \tag{26}$$

## Probability distribution of the normalized reciprocal quotient

In cases I and II certain symmetry properties of the normalized variables were emphasized. For instance, the function $P(y_d)$ was symmetrical about the origin (Part IV). This was also reflected in the quotient distribution. That is, the distribution of the quotient and its reciprocal were the same (Part III). It turns out that in the present case such symmetry properties are absent. For instance, the distribution of $y_d$ is asymmetric (see next section). This is also reflected in the quotient variable. Thus it becomes necessary to work out the distribution of the reciprocal quotient $u=1/y_q=y_N^c/y_N$. This is readily done by making appropriate transformations in the expression for $P(y_q)$.

We obtain for the distribution of $u$

$$P(u)=\frac{2\sqrt{2+u^2+D^2u^2}\sqrt{1-D^2}}{[(2+u^2+D^2u^2)^2-16D^2u^2]}$$
$$\times{}_2F_1\left[\tfrac{1}{4},-\tfrac{1}{4};1;\left(\frac{4Du}{2+u^2+D^2u^2}\right)^2\right] . \tag{27}$$

The above expression is different from that for $P(y_q)$ except when $D=1$.

## Discussion of the results

The various probability distributions may all be seen to be characterized by a single parameter $D$ defined in (1$a$). It may be noted that $D=0$ when the errors $\Delta\mathbf{r}_j$'s are very large and $D=1$ when all the errors are zero. Physically these two correspond respectively to the true structure being completely non-centrosymmetric and completely centrosymmetric. For intermediate values of $D$ the situation may be described as the true model being approximately centrosymmetric. In essence therefore $D$ is a measure of the degree of centrosymmetry of the true structure.

*Distribution of the normalized amplitude of an approximately centrosymmetric structure*

The way the normalized structure amplitude of an approximately centrosymmetric structure is distributed is readily available in the marginal distribution $P(y_N)$ deduced in (6). As is to be expected this is characterized by the parameter $D$. It is readily shown that (6) reduces to basic acentric and centric distributions respectively for $D=0$ and $D=1$. Fig. 1 gives a family of curves of $P(y_N)$ for different values of $D$ including the limiting cases.

The distribution $P(y_N)$ is identical in form with the distribution of the normalized amplitude for another type of situation which could also be characterized as an approximately centrosymmetric structure. This has been considered earlier (Srinivasan, 1965) (see also Parthasarathy & Parthasarathi, 1974). The situation considered earlier was the distribution of the normalized structure amplitude of a structure in a non-centrosymmetric space group $P1$ containing centrosymmetric ($P$) and non-centrosymmetric ($Q$) groups of atoms. If the ratio of the contribution to the mean intensity by the centrosymmetric group to that of the whole structure is denoted by $\sigma_1^2$ the distribution for such a case turns out to be*

$$P(y_N)=\frac{2y_N}{\sqrt{1-\sigma_1^4}}\exp\left(-\frac{y_N^2}{1-\sigma_1^4}\right)I_0\left(\frac{\sigma_1^2y_N^2}{1-\sigma_1^4}\right). \quad (28)$$

The parallel roles of $\sigma_1$ and $D$ are now obvious. Thus the two limits $D=0$ (or $\sigma_1=0$) and $D=1$ (or $\sigma_1=1$) correspond to acentric and centric distributions. Intermediate values of $D$ (or $\sigma_1$) correspond to different degrees of centrosymmetry of the structure. Physically the two situations are quite different, although one could describe both as approximately centrosymmetric structures. We shall refer to the situation considered in this paper as that of an approximately centrosymmetric structure (distortion type) to distinguish it from the other type referred to earlier. From the above it is also obvious that the parameter $D$ may conveniently replace $\sigma_1$ in other statistical distributions, considered earlier.

*The distribution of the phase-angle difference*

The distribution $P(\alpha)$ available in (14) is exactly the same as the one derived earlier for a noncentrosymmetric crystal [equation (23) of Parthasarathy, (1965)] if $D$ is replaced by $\sigma_1$ and $(1-D^2)$ by $\sigma_2$.† As mentioned in the previous section this is further evidence to indicate the parallel roles of $D$ and $\sigma_1$. The $P(\alpha)$ distribution is given in the form of curves in Fig.

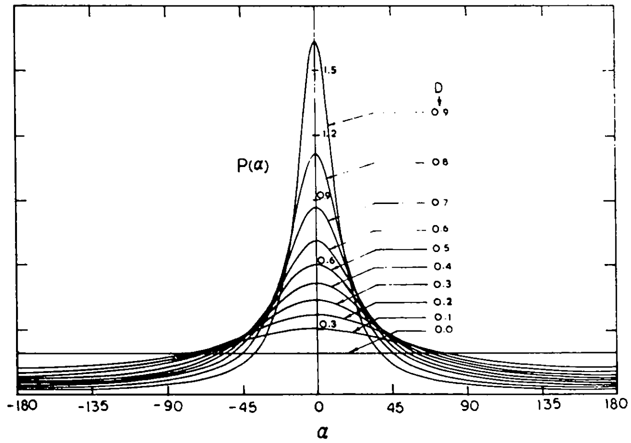


Fig. 2. Theoretical $P(\alpha)$ distribution for different $D$ values.

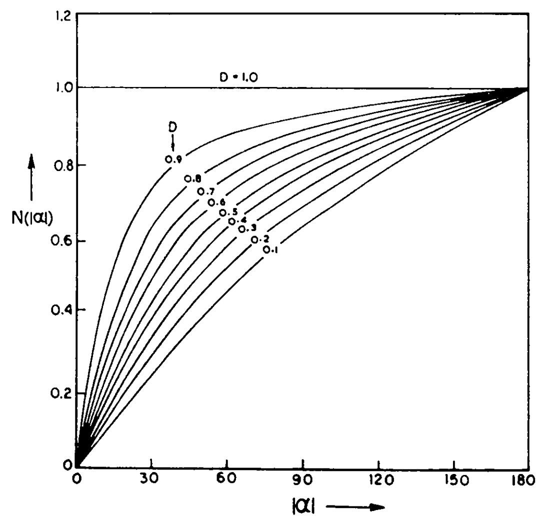


Fig. 3. Theoretical $N(|\alpha|)$ curves for different $D$ values.

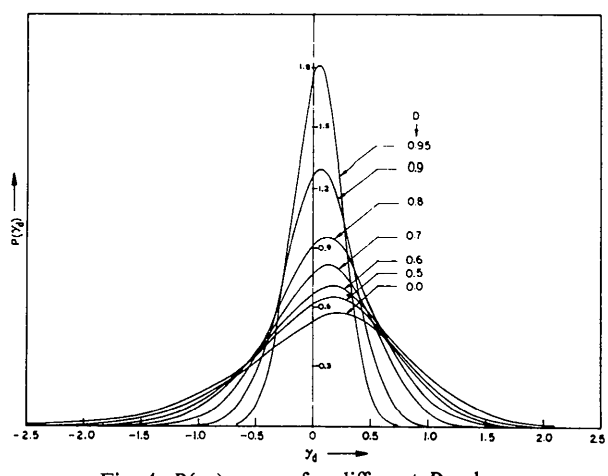


Fig. 4. $P(y_d)$ curves for different $D$ values.

* Although in the reference cited the distribution $P(y_N)$ has been given in the form of an integral it can be reduced to the above from a table of integral transforms (Gradshteyn & Ryzhik, 1965).

† In the reference cited, the distribution is for $|\alpha|$ since the $P(\alpha)$ distribution is symmetrical about the origin $P(|\alpha|)=2P(\alpha)$.

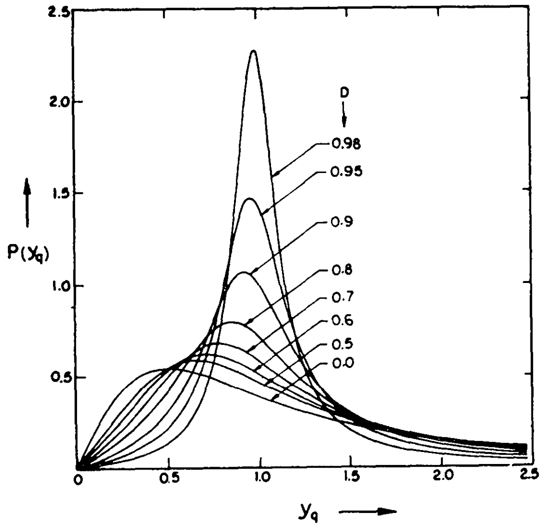


Fig. 5. $P(y_q)$ curves for different $D$ values.

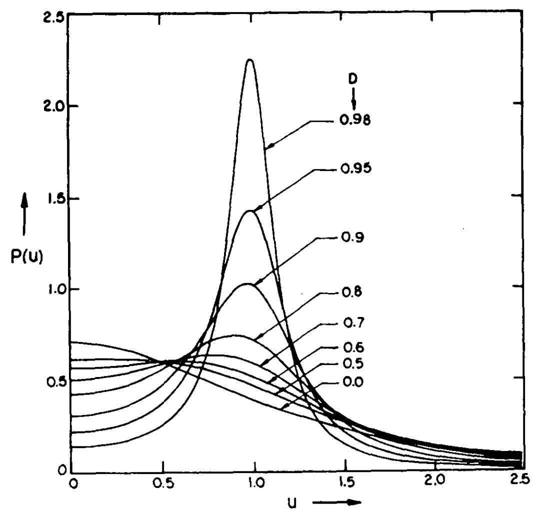


Fig. 6. $P(u)$ curves for different $D$ values.

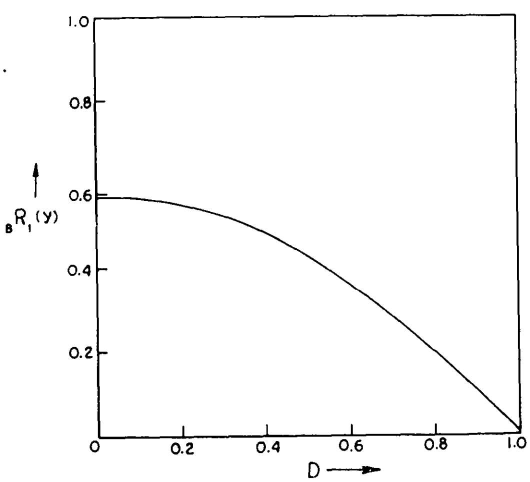


Fig. 7. Variation of ${}_BR_1(y)$ with $D$.

2. The limiting values of $P(\alpha)$ are $1/2\pi$ (for $D=0$) and $\delta(\alpha)$ (for $D=1$). The cumulative function of $|\alpha|$ given by $N(|\alpha|)=2\int_0^{|\alpha|} P(\alpha)\mathrm{d}\alpha$ for different values of $D$ is shown in Fig. 3.

*Distribution of the difference*

The distributions of the difference variable $y_d$ for different values of $D$ are shown in Fig. 4. Unlike cases I and II the $P(y_d)$ distribution for the present case is asymmetric. The maxima of $P(y_d)$ occur on the positive side of $y_d$. The asymmetry is maximum for $D=0$ and it vanishes at $D=1$ when the $P(y_d)$ function is a delta function at the origin. Physically these features are understandable. For example, the maximum asymmetry for $D=0$ corresponds to the true model being completely non-centrosymmetric while the assumed model is centrosymmetric. For the general case the lack of symmetry may be seen to be a consequence of the fact that $y_N$ and $y_N^c$ correspond to approximately noncentrosymmetric and centrosymmetric structures respectively.

The curves in this form are useful in a situation when the true structure is approximately centrosymmetric, while the trial model is assumed to be centrosymmetric. One would then expect that the $y_d$'s will not be as often negative as positive. The proportion of positive and negative values of $y_d$ may be calculated from the curves in Fig. 4 by working out the area under the curve for $y_d>0$ and $y_d<0$. These are given in Table 1 as a function of $D$. The difference $(y_N^c-y_N)$ will obviously be related to the above curves $P(y_d)$ by a mirror at $y_d=0$.

Table 1. *Ratio of the area $A_+$(for $y_d>0$) to $A_-$ (for $y_d<0$) under the $P(y_d)$ curve*

| $D$ | $A_+$ | $A_-$ | $A_+/A_-$ |
|---|---|---|---|
| 0·0 | 0·577 | 0·423 | 1·364 |
| 0·2 | 0·577 | 0·423 | 1·364 |
| 0·4 | 0·577 | 0·423 | 1·364 |
| 0·5 | 0·577 | 0·423 | 1·364 |
| 0·6 | 0·576 | 0·424 | 1·358 |
| 0·7 | 0·575 | 0·425 | 1·352 |
| 0·8 | 0·572 | 0·428 | 1·336 |
| 0·9 | 0·565 | 0·435 | 1·298 |
| 0·95 | 0·557 | 0·443 | 1·257 |
| 0·99 | 0·538 | 0·462 | 1·164 |

*Distribution of the quotient*

The quotient distributions $P(y_q)$ for different values of $D$ are shown in Fig. 5. For the limit $D=1$ we obtain a delta function at $y_q=1$ and for $D=0$ we obtain a distribution similar to the acentric distribution $P(y)$. The symmetry property associated with the quotient distribution for cases I and II is absent here. Thus for cases I and II both $P(y_q)$ and $P(1/y_q)$ had identical forms. However, for the present case the reciprocal $u(=1/y_q)$ of $y_q$ has a distribution different from that of $y_q$. The $P(u)$ curves are given in Fig. 6. Here again for $D=1$ we get a delta function at $u=1$ and for $D=0$

we get a distribution somewhat similar to the centric distribution $P(y)$.

*Discrepancy index*

Several types of discrepancy index can be deduced from the distributions $P(y_d)$, $P(y_q)$ *etc.* (for a recent account see Srinivasan & Parthasarathy, 1975). We shall adopt here for convenience the Booth type of index in the normalized form defined by

$$_BR_1(y) = \frac{\sum (y_N - y_N^c)^2}{\sum y_N^2}$$

or equivalently

$$_BR_1(y) = \frac{\langle (y_N - y_N^c)^2 \rangle}{\langle y_N^2 \rangle} = \langle y_d^2 \rangle .$$

This index has the advantage in the present case that the denominator is the same whether the model is centrosymmetric or non-centrosymmetric or approximately centrosymmetric and is equal to unity. The various values of $_BR_1(y)$ for different $D$ values are shown in Fig. 7.

*Test of the theoretical curves*

The theoretical distributions $P(y_d)$, $P(y_q)$, $P(u)$ and $P(\alpha)$ have been tested with the hypothetical model shown in Fig. 8. The molecules (1) and (2) form the asymmetric unit in the two-dimensional plane group $P1$. To start with, the molecules (1) and (2) were assumed to be exactly related by a centre of inversion. With one molecule fixed, small shifts were given to the atoms of the other to yield an approximately centrosymmetric structure. Care was taken to ensure that the shifts were randomly distributed. The tests were carried out for $D=0{\cdot}9$ and $0{\cdot}6$. The results are given in Figs. 9–12. The agreement with theory is reasonable.

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## APPENDIX A

Equation (9) can be written as

$$P(\alpha; y_N^c) = \frac{\exp\left(-\frac{D^2}{1-D^2}\cdot y_N^{c2}\right)}{\pi(1-D^2)} \times \int_0^\infty \exp\left(-\frac{y_N^2}{1-D^2} + \frac{2Dy_N^c}{1-D^2}\cdot y_N \cos\alpha\right) y_N \mathrm{d}y_N \quad \text{(A1)}$$

$$= K\int_0^\infty \exp(-\mu y_N^2 - 2\nu y_N) y_N \mathrm{d}y_N \quad \text{(A2)}$$

where

$$K = \frac{\exp\left(-\frac{D^2 y_N^{c2}}{1-D^2}\right)}{\pi(1-D^2)} ; \quad \mu = \frac{1}{(1-D^2)}$$

and

$$\nu = -\frac{Dy_N^c \cos\alpha}{(1-D^2)} .$$

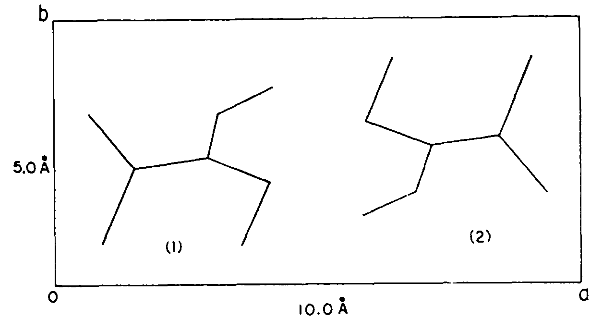


Fig. 8. Hypothetical model used for testing the theoretical distributions.

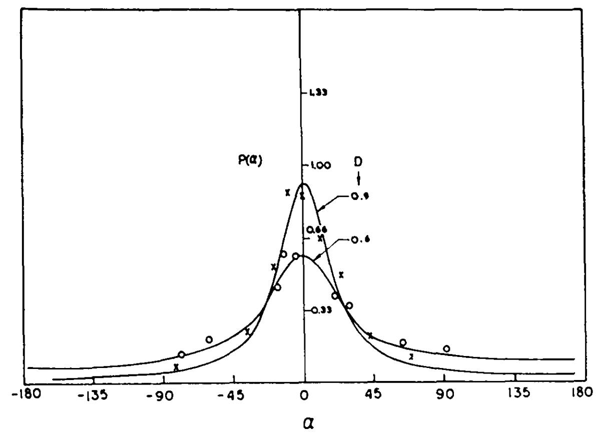


Fig. 9 $P(\alpha)$ curves for $D=0{\cdot}6$ and $0{\cdot}9$. Experimental values are marked by crosses and circles.

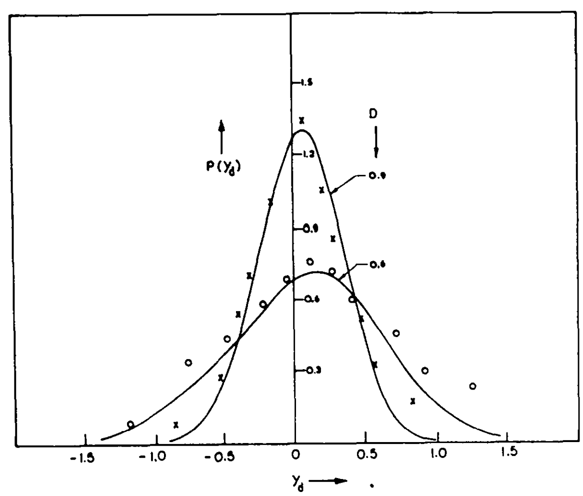


Fig. 10. $P(y_d)$ curves for $D=0{\cdot}6$ and $0{\cdot}9$. Experimental values marked by crosses and circles.

(A2) is further simplified to

$$P(\alpha;\, y_N^c)=K\left[\frac{1}{2\mu}+\frac{1}{2\mu}\int_0^\infty \exp\,(-\mu y_N^2-2\nu y_N)\mathrm{d}y_N\right]. \tag{A3}$$

From the table of integral transforms [Gradshteyn & Ryzhik, 1965, p. 307, 3·322(2)], A3 is simplified to

$$P(\alpha;\, y_N^c)=K\left[\frac{1}{2\mu}-\frac{\nu}{2\mu}\sqrt{\frac{\pi}{\mu}}\exp(\nu^2/\mu)\left(1+\operatorname{erf}\frac{\nu}{\sqrt{\mu}}\right)\right]. \tag{A4}$$

Substituting for $\mu$ and $\nu$ we get (10).

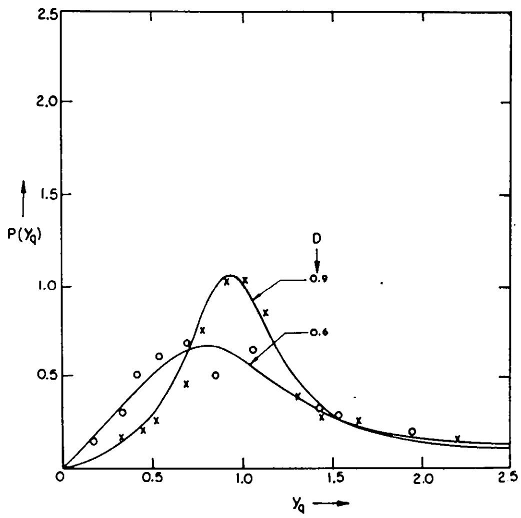


Fig. 11. $P(y_q)$ curves for $D=0{\cdot}6$ and $0{\cdot}9$. Experimental values are marked by circles and crosses.

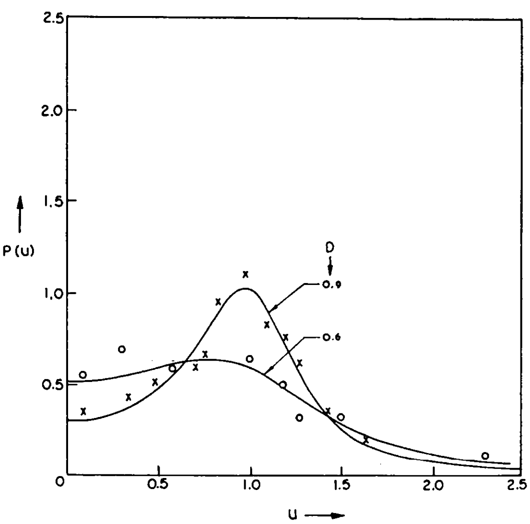


Fig. 12. $P(u)$ curves for $D=0{\cdot}6$ and $0{\cdot}9$. Experimental values are given by circles and crosses.

## APPENDIX B

Equation (13) can be written as

$$P(\alpha)=I_1+I_2 \tag{B1}$$

where

$$I_1=\frac{1}{2\pi}\int_0^\infty \exp\left(-\frac{D^2}{1-D^2}\cdot y_N^{c2}\right)\sqrt{\frac{2}{\pi}}\exp\left(-\frac{y_N^{c2}}{2}\right)\mathrm{d}y_N^c \tag{B2}$$

$$=\frac{\sqrt{2}}{2\pi^{3/2}}\int_0^\infty \exp\left[-\frac{y_N^{c2}}{2}\left(\frac{1+D^2}{1-D^2}\right)\right]\mathrm{d}y_N^c\,. \tag{B3}$$

For convenience put

$$\frac{1}{\varrho^2}=\frac{(1+D^2)}{2(1-D^2)}\,;$$

B3 can be written as

$$I_1=\frac{\sqrt{2}}{2\pi^{3/2}}\int_0^\infty \exp\left(-\frac{y_N^{c2}}{\varrho^2}\right)\mathrm{d}y_N^c$$

$$=\frac{\sqrt{2}}{2\pi^{3/2}}\cdot\varrho\int_0^\infty \exp\left(-\frac{y_N^{c2}}{\varrho^2}\right)\mathrm{d}\left(\frac{y_N^c}{\varrho}\right) \tag{B4}$$

$$=\frac{\sqrt{2}}{2\pi^{3/2}}\cdot\varrho\cdot\frac{\sqrt{\pi}}{2}=\frac{\sqrt{1-D^2}}{2\pi\sqrt{1+D^2}}\,. \tag{B5}$$

$$I_2=\frac{\sqrt{2}\,D}{2\pi\sqrt{1-D^2}}\cdot\int_0^\infty y_N^c\cos\alpha$$
$$\times\exp\left(-\frac{D^2}{1-D^2}\cdot y_N^{c2}\sin^2\alpha\right)\exp\left(-\frac{y_N^{c2}}{2}\right)$$
$$\times\left[1+\operatorname{erf}\left(\frac{D}{\sqrt{1-D^2}}\cdot y_N^c\cos\alpha\right)\right]\mathrm{d}y_N^c \tag{B6}$$

$$=\frac{\sqrt{2}}{2\pi}\frac{D}{\sqrt{1-D^2}}\cdot\int_0^\infty y_N^c\cos\alpha$$
$$\times\exp\left[-\frac{(2D^2\sin^2\alpha+1-D^2)}{2(1-D^2)}y_N^{c2}\right]$$
$$\times\left[1+\operatorname{erf}\left(\frac{D}{\sqrt{1-D^2}}\cdot y_N^c\cos\alpha\right)\right]\mathrm{d}y_N^c\,. \tag{B7}$$

For convenience put

$$\frac{1}{\varrho_1^2}=\frac{2D^2\sin^2\alpha+1-D^2}{2(1-D^2)}$$

$$I_2=\frac{\sqrt{2}}{2\pi}\frac{D}{\sqrt{1-D^2}}\cdot\int_0^\infty y_N^c\cos\alpha\exp\left(-\frac{y_N^{c2}}{\varrho_1^2}\right)$$
$$\times\left[1+\operatorname{erf}\left(\frac{D}{\sqrt{1-D^2}}\,y_N^c\cos\alpha\right)\right]\mathrm{d}y_N^c\,. \tag{B8}$$

This on integration by parts gives

$$I_2=\frac{\sqrt{2}}{2\pi}\frac{D\sqrt{1-D^2}\cos\alpha}{(2D^2\sin^2\alpha+1-D^2)}\left[1+\frac{\sqrt{2}D\cos\alpha}{\sqrt{1+D^2}}\right] \quad \text{(B9)}$$

$$P(\alpha)=I_1+I_2=\frac{\sqrt{1-D^2}}{2\pi\sqrt{1+D^2}}+\frac{\sqrt{2}}{2\pi}\frac{D\sqrt{1-D^2}\cos\alpha}{(2D^2\sin^2\alpha+1-D^2)}\left(1+\frac{\sqrt{2}D\cos\alpha}{\sqrt{1+D^2}}\right).$$

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# Etude Expérimentale des Susceptibilités Diamagnétiques Moléculaires. III. Stéroïdes $C_{21}$

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Within the framework of the research undertaken in the authors' laboratory, the magnetic anisotropy of some corticosteroids $C_{21}$ has been studied. The diamagnetic molecular tensors are deduced from the measured crystal tensors by an original method. The orientation of the principal molecular axes with regard to the steroid skeleton is given.

## Introduction

Si, depuis de nombreuses années déjà, des chercheurs se penchent sur les propriétés diamagnétiques des molécules, ce sont les composés organiques et même, plus spécialement, les aromatiques qui constituent le terrain de prédilection aussi bien des expérimentateurs que des théoriciens.

Le manque presque total d'informations sur les propriétés diamagnétiques de l'importante famille que constituent les stéroïdes, nous a incités à explorer ce domaine. Notre but est de tenter d'obtenir des renseignements sur la conformation des molécules des stéroïdes et plus particulièrement sur celle des molécules de corticostéroïdes $C_{21}$, composés qui exercent sur l'organisme deux types très importants d'activité, d'une part, une activité minéralocorticoïde et, d'autre part, une activité glucocorticoïde. Ces renseignements pourront se révéler d'une grande utilité lorsque nous serons en mesure d'étudier les interactions au niveau moléculaire entre les corticostéroïdes et les macromolécules réceptrices.

## Résultats

Dans l'optique décrite dans l'introduction, nous avons entrepris la mesure et l'interprétation des propriétés diamagnétiques d'un certain nombre de corticostéroïdes $C_{21}$. En effet, si nous parvenons à déterminer le tenseur attaché à la molécule à partir du ten-