Table 1. *Results of calculations for selenium*

		Van der Waals diameter in Å from:				
Phase	Temperature °K	Internal pressure *x*	Internal pressure *y*	Internal pressure *z*	Lattice energy	Molecular strain energy
α-Selenium	300	3·96	3·99	4·00	4·04	3·67
	0	3·92	3·94	3·96	3·99	3·63
β-Selenium	300	3·95	3·91	3·99	4·00	3·57
	0	3·92	3·89	3·91	3·95	3·56
Hexagonal selenium	300	3·78	3·77	3·74	3·82	3·49
	0	3·68	3·68	3·65	3·73	3·41

Corner, J. (1939). *Trans. Faraday Soc.* **35**, 711.
Coulson, C. A. (1960). *Rev. Mod. Phys.* **32**, 170.
Kirkwood, J. G. (1932). *Z. Phys.* **33**, 57.
Lennard-Jones, J. E. (1937). *Physica*, **4**, 941.
London, F. (1930). *Z. Phys. Chem.* **B11**, 222.
Marsh, R. E., Pauling, L. & McCullough, J. D. (1953). *Acta Cryst.* **6**, 71.
Milledge, H. J. (1962). *Proc. Roy. Soc.* A**267**, 566.
Newton, C. J. & Colby, M. Y. (1951). *Acta Cryst.* **4**, 477.
Sasada, Y. & Atoji, M. (1953). *J. Chem. Phys.* **21**, 145.
Slater, J. C. & Kirkwood, J. G (1931). *Phys. Rev.* **37**, 682.
Straumanis, M. (1940). *Z. Kristallogr.* **102**, 432.
Strel'tsova, I. N. & Struchkov, Yu. T. (1961). *J. Struct. Chem.* **2**, 296.

Acta Cryst. (1972). A**28**, 426

Discrepancy Factors for Use in Crystal Structure Analysis*

By S. Parthasarathy and V. Parthasarathi

Centre of Advanced Study in Physics, University of Madras, Guindy Campus, Madras-25, India

(*Received* 14 *March* 1972)

Theoretical expressions for two types of discrepancy factors have been obtained for crystals containing both heavy and light atoms in the unit cell. One of the discrepancy factors is defined in terms of the structure amplitude and is called the Booth's reliability index (R_B). The other discrepancy factor (denoted by R_2) is based on intensities. While the expressions for R_2 can be used for crystals of any space group and for crystals containing any number and type of atoms in the unit cell, those for R_B can be used only for crystals in the triclinic and a few monoclinic space groups.

1. Introduction

In this paper we shall obtain theoretical expressions for the discrepancy factors R_B and R_2 [suggested by Booth (1945) and Wilson (1969) respectively] for crystals containing both heavy and light atoms in the unit cell. In the standard notation, these reliability indices can be defined as

$$R_B=\sum_{hkl}(|F_o|-|F_c|)^2/\sum_{hkl}|F_o|^2 \qquad (1)$$

$$R_2=\sum_{hkl}(I_o-I_c)^2/\sum_{hkl}I_o^2\,. \qquad (2)$$

The interest in R_B lies in the fact that it is closely related to the quantity being minimized in the usual least-squares method (Buerger, 1967). The theoretical expressions for R_2 can be obtained under more general conditions than for any other R indices (Wilson, 1969). Owing to the difficulties in the theory, we shall obtain different expressions for the R indices which are applicable under different circumstances.

When the atoms in the model structure† are completely correct we shall call it the *related case* and when all the atoms in the model are completely wrong we shall call it the *unrelated case*. When the model consists of some completely wrong atoms and the rest completely correct, we shall call it the *semi-related case*. When the coordinates of all the atoms in the model suffer finite errors, we shall call it the *imperfectly related case*. For simplicity of notation, we shall use *R*, *UR*, *SR* and *IR* to denote the related, unrelated, semi-related and imperfectly related cases respectively. It is obvious that the *R* and *UR* cases are limiting cases of the *IR* case. We can also think of the *R* and *UR* cases as limiting cases of the *SR* case.

---

* Contribution No. 342 from the Centre of Advanced Study in Physics, University of Madras, Madras, India.

† The model structure need not include all the atoms in the unit cell.

2. Derivation of the theoretical expressions for the R_2 index

(*a*) *SR case when there are no errors in the intensity data*

Consider a crystal (of any space group) containing N atoms in the unit cell. Let the known part consist of P atoms and let $Q(=N-P)$ be the number of unknown atoms. Of the P atoms that constitute the model structure, we shall assume that there are a few wrongly placed atoms (say, Pw in number), so that the number of correctly placed atoms in the model will be $P-Pw(=Pr$, say). With this notation we can write for a given reflexion that

$$F_N=F_P+F_Q \qquad (3)$$

$$F_P^c=F_{Pr}+F_{Pw}\,. \qquad (4)$$

We can now rewrite (2) as

$$R_2^o=\langle(|F_N|^2-|F_P^c|^2)^2\rangle/\langle|F_N|^4\rangle \qquad (5)$$

where the superscript o is used to denote that there are no errors in the observed intensities.* We can simplify (5) to obtain

$$R_2^o=1+[\langle|F_P^c|^4\rangle-2\langle|F_N|^2|F_P^c|^2\rangle]/\langle|F_N|^4\rangle\,. \qquad (6)$$

In order to simplify (6) we must first obtain an expression for the expectation value of $|F_N|^2|F_P^c|^2$ and this calculation is given in Appendix A. Making use of (A7) in (6) we obtain

$$R_2^o=1+[\langle|F_P^c|^4\rangle-2\{\langle|F_{Pr}|^4\rangle+\langle|F_{Pr}|^2\rangle\,\{\langle|F_{Pw}|^2\rangle +\langle|F_Q|^2\rangle\}+\langle|F_{Pw}|^2\rangle\,\langle|F_N|^2\rangle\}]/\langle|F_N|^4\rangle\,. \qquad (7)$$

For further simplification it is convenient to introduce the normalized intensity variables

$$z_P^c=\frac{|F_P^c|^2}{\langle|F_P^c|^2\rangle}\,,\quad z_N=\frac{|F_N|^2}{\langle|F_N|^2\rangle}\,,\quad z_P=\frac{|F_P|^2}{\langle|F_P|^2\rangle}\,. \qquad (8)$$

It is also convenient to make use of the fractional contribution to the local mean intensity from the various groups of atoms and these are defined below

$$\sigma_1^2=\frac{\langle|F_P|^2\rangle}{\langle|F_N|^2\rangle}=\frac{\langle|F_P^c|^2\rangle}{\langle|F_N|^2\rangle}\,,\quad \sigma_2^2=\frac{\langle|F_Q|^2\rangle}{\langle|F_N|^2\rangle}\,, \qquad (9)$$

$$\sigma_{1r}^2=\frac{\langle|F_{Pr}|^2\rangle}{\langle|F_N|^2\rangle}\,,\sigma_{1w}^2=\frac{\langle|F_{Pw}|^2\rangle}{\langle|F_N|^2\rangle}=\frac{\langle|F_{P'r}|^2\rangle}{\langle|F_N|^2\rangle}\,. \qquad (10)$$

It is obvious that

$$\sigma_1^2+\sigma_2^2=1\,,\quad \sigma_{1w}^2+\sigma_{1r}^2=\sigma_1^2\,. \qquad (11)$$

Making use of equations (8) to (11) we can rewrite (7) as

$$R_2^o=1+[\sigma_1^4\langle z_P^{c2}\rangle-2\{\sigma_{1r}^4\langle z_{Pr}^2\rangle+\sigma_{1r}^2(\sigma_{1w}^2+\sigma_2^2) +\sigma_{1w}^2\}]/\langle z_N^2\rangle\,. \qquad (12)$$

Equation (12) holds good when the P group contains any number and any type of atoms. The case when the P group consists of heavy atoms in the unit cell is important in connexion with the heavy atom method and in this case equation (12) takes a simpler form as shown below.

(i) Related case. If the heavy atoms were correctly located, we would have $\sigma_{1w}^2=0$, $\sigma_{1r}^2=\sigma_1^2$ and $z_{Pr}=z_P^c$ so that (12) reduces to

$$R_2^o=1-[\sigma_1^4\langle z_P^{c2}\rangle+2\sigma_1^2\sigma_2^2]/\langle z_N^2\rangle\,. \qquad (13)$$

(ii) Unrelated case. If the heavy atom locations were completely wrong, we would have $\sigma_{1r}^2=0$, $\sigma_{1w}^2=\sigma_1^2$ and $z_{Pw}=z_p^c$ so that (12) reduces to

$$R_2^o=1+[\sigma_1^4\langle z_P^{c2}\rangle-2\sigma_1^2]/\langle z_N^2\rangle\,. \qquad (14)$$

Making use of the values of the higher moments of $\langle z_P^{c2}\rangle$ and $\langle z_N^2\rangle$ (Parthasarathy, 1966) it is easy to obtain the expressions for R_2^0 for the cases $P=2$ and many, and they are summarized in Table 1 for convenience. The graph of R_2^o *vs.* σ_1^2 is also shown in Figs. 1 and 2 for the centrosymmetric and non-centrosymmetric cases respectively.

Table 1. *Final expressions for the R_2^o index for the related and unrelated cases, where there are no errors in the intensity data.*

Number of P atoms	R case	UR case
	I. Centrosymmetric crystal	
2	$\frac{\sigma_2^2(3+\sigma_1^2)}{(1-\frac{\sigma_1^4}{2})}$	$\frac{3-2\sigma_1^2}{3(1-\frac{\sigma_1^4}{2})}$
M	$1-\frac{\sigma_1^2(\sigma_1^2+2)}{3}$	$1+\frac{\sigma_1^2(3\sigma_1^2-2)}{3}$
	II. Non-centrosymmetric crystal	
2	$\frac{\sigma_2^2}{(1-\frac{\sigma_1^4}{4})}$	$\frac{(1-\sigma_1^2+\frac{\sigma_1^4}{2})}{(1-\frac{\sigma_1^4}{4})}$
MC	$\frac{(1-\sigma_1^2)}{(1+\frac{\sigma_1^4}{2})}$	$\frac{(1-\sigma_1^2+2\sigma_1^4)}{(1+\frac{\sigma_1^4}{2})}$
MA	$1-\sigma_1^2$	$1-\sigma_1^2\sigma_2^2$

(*b*) *SR case when there are random errors in the intensity data*

Let I_o be the observed intensity for the reflexion **H**. Let I_P^c be the calculated intensity for the reflexion **H** for the model structure which is assumed to consist of Pr correct atoms and Pw entirely misplaced atoms. Let ε be the error in the observed intensity of the reflexion **H** and let δ be the difference between the true (*i.e.* error-free) intensity of the reflexion and the inten-

---

* Unless stated explicitly, it will be assumed in general that the errors of observation in the intensity data are negligible.

sity due to the atoms in the model structure. That is

$$\varepsilon = I_o - I_N \text{ and } \delta = I_N - I_P^c \tag{15}$$

where

$$I_N = |F_N|^2 \text{ and } I_P^c = |F_P^c|^2 \,. \tag{16}$$

Making use of (15), (2) can be written as

$$\begin{aligned} R_2 &= \langle (I_o - I_c)^2 \rangle / \langle I_o^2 \rangle \\ &= \langle (\varepsilon + \delta)^2 \rangle / \langle (I_N + \varepsilon)^2 \rangle \,. \end{aligned} \tag{17}$$

We shall assume that the errors in the intensity are normally distributed with parameters (0, σ_ε) and that there is no correlation between the error and the intensity (see Wilson, 1969). Since ε arises from inaccuracy in the data and δ from that in the model, we can treat ε and δ as independent random variables. Equation (17) therefore leads to

$$R_2 = [\sigma_\varepsilon^2 + \langle \delta^2 \rangle] / [\langle I_N^2 \rangle + \sigma_\varepsilon^2] \,. \tag{18}$$

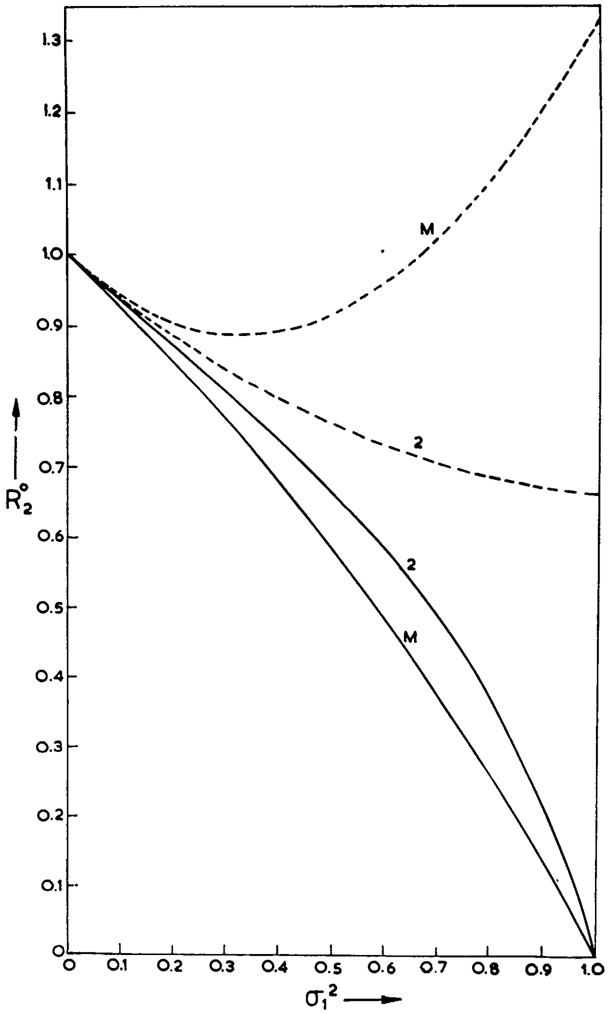

Fig. 1. The variation of the R_2^o index as a function of the fractional heavy-atom contribution σ_1^2 for the centrosymmetric crystal. The solid lines are for the related case while the dotted lines are for the unrelated case. The symbols 2 and *M* near the curves denote the number of *P* atoms in the unit cell.

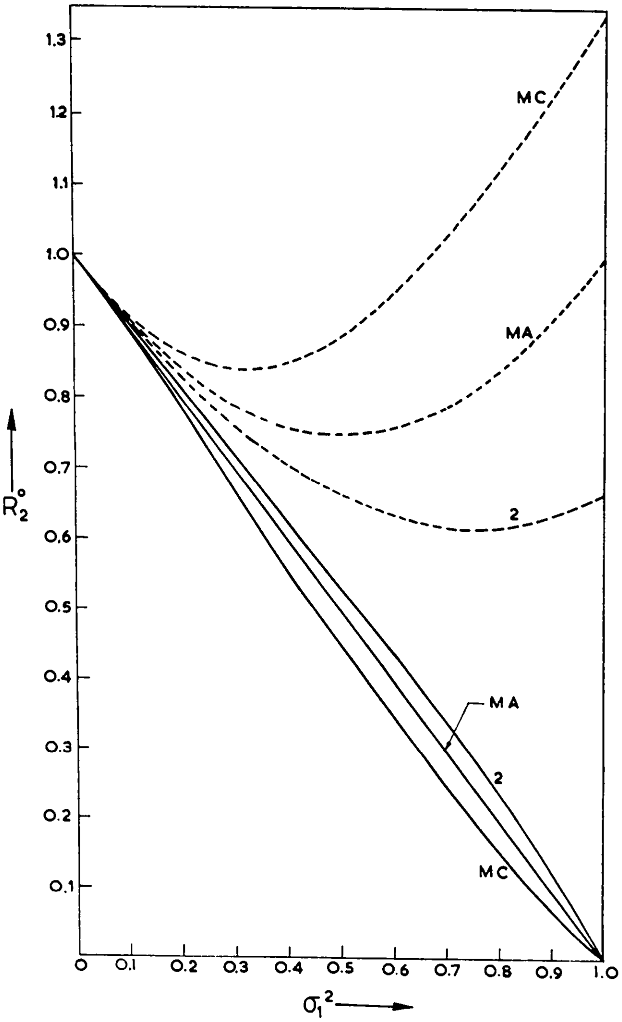

Fig. 2. The variation of the R_2^o index as a function of σ_1^2 for the non-centrosymmetric crystal.

Making use of (5), we can rewrite (18) as

$$R_2 = \left[R_2^o + \frac{\sigma_\varepsilon^2}{\langle z_N^2 \rangle \langle I_N \rangle^2} \right] \Big/ \left[1 + \frac{\sigma_\varepsilon^2}{\langle z_N^2 \rangle \langle I_N \rangle^2} \right] \tag{19}$$

where R_2^o stands for the reliability index when there are no errors in the intensity data, *viz.* that given by (12).

(*c*) *IR case when there are random errors in the intensity data*

Consider a crystal belonging to the triclinic system. Let the model structure consist of a large number of atoms in the *P* group with similar scattering power, so that F_P^c obeys Wilson's (1949) distribution. Let $\Delta \mathbf{r}j$ be the error in the coordinates of the atom j ($j = 1, 2, \ldots P$) of the model structure. It is clear that (18) holds good in this case also. In order to simplify (18) to obtain a convenient expression for the R_2 index we must first obtain a suitable expression for $\langle \delta^2 \rangle$ and this can be done as follows: From (15) we obtain

$$\langle \delta^2 \rangle = \langle I_N^2 \rangle + \langle I_P^{c2} \rangle - 2 \langle I_N I_P^c \rangle \,. \tag{20}$$

Since $F_N = F_P + F_Q$ we can write

$$\langle I_N I_P^c \rangle = \langle (I_P + I_Q + 2\sqrt{(I_P I_Q)}\, \varepsilon_{P,Q}) I_P^c \rangle = \langle I_P I_P^c \rangle + \langle I_Q \rangle \langle I_P^c \rangle \,. \quad (21)$$

Making use of (21) in (20) and further employing the normalized intensity variables we can rewrite (18) as

$$R_2 = \frac{[\langle z_N^2 \rangle + \sigma_1^4 \langle z_P^{c2} \rangle - 2\sigma_1^2\sigma_2^2 - 2\sigma_1^4 \langle z_P z_P^c \rangle + \sigma_\varepsilon^2 / \langle I_N \rangle^2]}{\langle z_N^2 \rangle + (\sigma_\varepsilon^2 / \langle I_N \rangle^2)} \,. \quad (22)$$

It is known that $\langle z_N z_P^c \rangle$ has values $1+2D^2$ and $1+D^2$ for the centrosymmetric and non-centrosymmetric crystals respectively (Parthasarathy & Srinivasan, 1967). The quantity D is defined (Luzzati, 1952) by

$$D = \langle \cos 2\pi \mathbf{H} \,.\, \Delta \mathbf{r}_j \rangle_P \,.$$

It may be noted here that D is a measure of the r.m.s. error in the coordinates of the atoms in the P group. It is also well known that

$$\langle z_N^2 \rangle = \langle z_P^{c2} \rangle = \begin{cases} 3 \text{ for space group } P\bar{1} \\ 2 \text{ for space group } P1 \end{cases} \quad (23)$$

$$\langle I_N \rangle = \sum_{j=1}^{N} f_j^2 = \Sigma, \text{ say} \,. \quad (24)$$

Making use of these results in (22) we obtain

$$R_2 = \begin{cases} \dfrac{3 + \sigma_1^4 - 2\sigma_1^2\sigma_2^2 - 4\sigma_1^4 D^2 + (\sigma_\varepsilon^2/\Sigma^2)}{3 + (\sigma_\varepsilon^2 \Sigma/^2)} \text{ for } P\bar{1} & (25) \\[2ex] \dfrac{2(1 - \sigma_1^2\sigma_2^2 - \sigma_1^4 D^2) + (\sigma_\varepsilon^2/\Sigma^2)}{2 + (\sigma_\varepsilon^2/\Sigma^2)} \text{ for } P1 \,. & (26) \end{cases}$$

3. Derivation of theoretical expressions for the R_B index

(*a*) *Related and unrelated cases*

In this section, we shall consider a crystal belonging to the triclinic system with P heavy atoms of similar scattering power in the unit cell. Making use of the normalized structure amplitude variables, (1) can be rewritten as

$$R_B^o = 1 + \sigma_1^2 - 2\sigma_1 \langle y_N y_P^c \rangle \,. \quad (27)$$

In the R case* y_N and y_P^c are dependent random variables while in the UR case they are independent. Hence we have

$$\langle y_N y_P^c \rangle = \begin{cases} \displaystyle\int_{y_P^c} \langle y_N ; y_P^c \rangle\, y_P^c P(y_P^c) \mathrm{d}y_P^c \quad \text{for the } R \text{ case} & (28) \\[2ex] \langle y_N \rangle \langle y_P^c \rangle \quad \text{for the } UR \text{ case.} & (29) \end{cases}$$

In (28), $\langle y_N ; y_P^c \rangle$ is the conditional expectation of y_N for a given y_P^c. It is clear from (27) and (28) that the value of R_B^o depends on the number of P atoms and we shall consider here two cases, $P=2$ and many. The expressions for $\langle y_N y_P^c \rangle$ for these cases are worked out in Appendix B. Making use of (B7), (B9), (B11), (B12) and (B14) in (27) we can obtain the final expressions for R_B^o for the R case. The expressions for R_B^o for the UR case can easily be obtained by making use of the expression for $\langle y_N \rangle$ as obtained by Parthasarathy (1966). These results are summarized in Table 2 for convenience. The graph of R_B^o *vs.* σ_1^2 is shown in Figs. 3 and 4 for the centrosymmetric and non-centrosymmetric cases respectively.

Table 2. *Final expressions for the R_B^o index for the related and unrelated cases, when there are no errors in the intensity data*

Number of P atoms	R case	UR case
	I. Centrosymmetric crystal	
2	$a - \dfrac{8\sigma_1\sigma_2}{\pi^{3/2}}\, {}_2F_2(-\frac{1}{2}, 1; \frac{1}{2}, \frac{3}{2}; -r^2)$	$a - \dfrac{8r}{\pi^{3/2}} \exp\left(-\dfrac{r^2}{2}\right) \left[I_o\left(\dfrac{r^2}{2}\right) + \sigma_1^2 I_1\left(\dfrac{r^2}{2}\right)\right]$
M	$a - \dfrac{4}{\pi}\, \sigma_1[\sigma_2 + \sigma_1 \sin^{-1}(\sigma_1)]$	$\left(a - \dfrac{4\sigma_1}{\pi}\right)$
	II. Non-centrosymmetric central	
2	$a - \frac{1}{2}(1 + 3\sigma_1^2)\, \mathrm{erf}\,(\sqrt{2}r) - \sqrt{\dfrac{2}{\pi}}\, \sigma_1\sigma_2 \exp(-2r^2)$	$a - \dfrac{2\sqrt{2}}{\sqrt{\pi}}\, \sigma_1\sigma_2 {}_2F_2(-\frac{1}{2}, \frac{1}{2};\ 1, 1;\ -2r^2)$
MC	$a - \sqrt{(2a\sigma_1^2)}$	$a - \dfrac{2}{\pi} \sqrt{(2a\sigma_1^2)} E \sqrt{\left(\dfrac{2\sigma_1^2}{a}\right)}$
MA	$a - 2\sigma_1 \left[E(\sigma_1) - \dfrac{\sigma_2^2}{2} K(\sigma_1)\right]$	$a - \dfrac{\pi\sigma_1}{2}$

Where $a = (1 + \sigma_1^2)$ and $r = \sigma_1/\sigma_2$

---

* For the R case y_P^c tends to y_P^n.

(*b*) *IR case when there are no errors in the intensity data*

We shall consider the case when P = many, so that F_P^c satisfies Wilson's distribution. It is clear that equation (27) holds good in this case also. Making use of the results in equations (*A*13) and (*A*19) of Parthasarathy & Srinivasan (1967) and following the method outlined in Appendix *B*, it is possible to show that

$$\langle y_N y_P^c \rangle = \begin{cases} \dfrac{2}{\pi}[\sigma_B + \sigma_A \sin^{-1}(\sigma_A)] & \text{for } C \quad (30) \\ E(\sigma_A) - \dfrac{\sigma_B^2}{2} k(\sigma_A) & \text{for } NC \quad (31) \end{cases}$$

where $\sigma_A = \sigma_1 D$ and $\sigma_B = \sqrt{(1-\sigma_A^2)}$. (32)

Making use of (30) and (31) in (27) we obtain

$$R_B^o = \begin{cases} 1+\sigma_1^2 - \dfrac{4\sigma_1}{\pi}[\sigma_B + \sigma_A \sin^{-1}(\sigma_A)] & \text{for } C \quad (33) \\ 1+\sigma_1^2 - 2\sigma_1 \left[E(\sigma_A) - \dfrac{\sigma_B^2}{2} k(\sigma_A)\right] & \text{for } NC\,. \quad (34) \end{cases}$$

It is easily seen that equations in the rows (2) and (5) of Table 2 follow from (33) and (34) as particular cases if we put $D=1$ and 0 (*i.e.* *R* and *UR* cases) respectively.

4. Discussion of the theoretical results

It is easy to show that equations (16) and (37) of Wilson (1969) follow from (12) as particular cases. The expressions (12), (13), (14) and (19) hold good for any space group while (25) and (26) hold good only for triclinic space groups. For a numerical evaluation of the R_2 index from these expressions we must first evaluate the second-order moments of the normalized intensity variables. These moments actually depend on the space group symmetry of the crystal and by making use of the results of Foster & Hargreaves (1963*a*,*b*) it is possible to evaluate these moments for crystals belonging to the triclinic, monoclinic and orthorhombic systems. For the theoretical evaluation of the R_2 index from (19) we must of course know the standard deviation of the errors in the measurement of the intensity data. Equations (25) and (26) hold good for space groups $P\bar{1}$ and $P1$ respectively and can be applied only to models which satisfy Wilson statistics. Making use of equations (25) and (26) [(33) and (34)] and the experimental value of the R_2 index (R_B index) it is possible to obtain the value of D for any given model structure. From the value of D thus obtained it is possible to estimate the r.m.s. error $\langle|\Delta \mathbf{r}_j|^2\rangle_P^{1/2}$ in the coordinates of the atoms in the model. Since the procedure for obtaining the r.m.s. error in the coordinates of the P atoms from the value of D has already been described by Srikrishnan and Srinivasan (1968), we shall not describe it here.

One of the authors (V.P.) thanks the University Grants Commission, India, for financial support.

APPENDIX *A*

Simplification of $\langle|F_N|^2|F_P^c|^2\rangle$

Here $|F_N|$ and $|F_P^c|$ are correlated random variables. To obtain a suitable expression for the expectation value of $|F_N|^2\,|F_P^c|^2$ it is convenient to think of the P group in the actual crystal structure as made up of two groups of atoms, *viz.* (i) the *Pr* atoms of the model structure and (ii) the rest of the atoms in the *P* group (of the crystal structure) which we shall call the *P′r* atoms. We can write

$$F_P = F_{Pr} + F_{P'r}\,. \qquad (A1)$$

Making use of (4), (5) and (*A*1) we obtain

$$\begin{aligned}\langle|F_N|^2|F_P^c|^2\rangle &= \langle|F_{Pr}+F_{P'r}+F_Q|^2\,|F_{Pr}+F_{Pw}|^2\rangle \\ &= \langle(|F_{Pr}|^2+|F_{P'r}|^2+|F_Q|^2+2|F_{Pr}|\,|F_{P'r}|\varepsilon_{Pr,P'r} \\ &\quad +2|F_{P'r}|\,|F_Q|\varepsilon_{P'r,Q}+2|F_{Pr}|\,|F_Q|\varepsilon_{Pr,Q}) \\ &\quad \times(|F_{Pr}|^2+|F_{Pw}|^2+2|F_{Pr}|\,|F_{Pw}|\varepsilon_{Pr,Pw})\rangle\,. \end{aligned} \qquad (A2)$$

Here $\varepsilon_{i,j}$ stands for the cosine of the angle between the structure factor F_i and F_j (of a given reflexion) if they are complex or for the product of the signs of F_i and F_j if they are real. Since all the quantities in the right-hand side of (*A*2) are independent random variables it is obvious that

$$\langle\varepsilon_{i,j}\rangle = 0 \text{ if } i \neq j \text{ for all } i,j = Pr, P'r, Q, Pw\,. \qquad (A3)$$

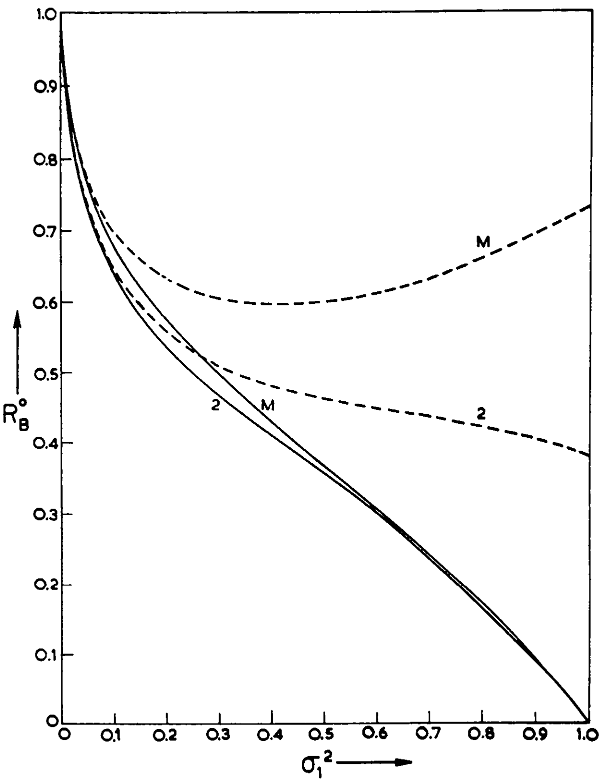

Fig. 3. The variation of the R_B^o-index as a function of σ_1^2 for the centrosymmetric crystal.

It is also obvious that

$$\langle \varepsilon_{Pr,P'r}\varepsilon_{Pr,Pw}\rangle = \langle \varepsilon_{Q,Pr}\varepsilon_{Pr,Pw}\rangle = \langle \varepsilon_{Q,P'r}\varepsilon_{Pr,Pw}\rangle = 0\,, \quad (A4)$$

since these are the products of the cosines of the angles which F_{Pr} makes with the independent structure factors $F_{P'r}$, F_Q and F_{Pw}. Further since $F_N = F_{Pr} + F_{P'r} + F_Q$ it follows that

$$\langle |F_{Pr}|^2\rangle + \langle |F_{P'r}|^2\rangle + \langle |F_Q|^2\rangle = \langle |F_N|^2\rangle\,. \quad (A5)$$

Since the number and nature of atoms in the $P'r$ group and Pw group are the same it follows that

$$\langle |F_{P'r}|^2\rangle = \langle |F_{Pw}|^2\rangle\,. \quad (A6)$$

Making use of ($A3$) to ($A6$) we can simplify ($A2$) to obtain

$$\begin{aligned}\langle |F_N|^2 |F_P^c|^2\rangle = {} & \langle |F_{Pr}|^4\rangle + \langle |F_{Pr}|^2\rangle \{\langle |F_{Pw}|^2\rangle + \langle |F_Q|^2\rangle\} \\ & + \langle |F_N|^2\rangle \langle |F_{Pw}|^2\rangle\,. \quad (A7)\end{aligned}$$

APPENDIX *B*

Derivation of expressions for $\langle y_N y_P^c\rangle$ for the related case

We know that (Parthasarathy, 1966)

$$\langle y_N ; y_P^c\rangle = \begin{cases} \dfrac{\sqrt{\pi}}{2}\sigma_2\, {}_1F_1\left(-{}^1/_2; 1; -\dfrac{\sigma_1^2 y_P^{c2}}{\sigma_2^2}\right) & \text{for } NC \quad (B1) \\ \sqrt{\dfrac{2}{\pi}}\sigma_2\, {}_1F_1\left(-\tfrac{1}{2}; \tfrac{1}{2}; -\dfrac{\sigma_1^2 y_P^{c2}}{2\sigma_2^2}\right) & \text{for } C \quad (B2) \end{cases}$$

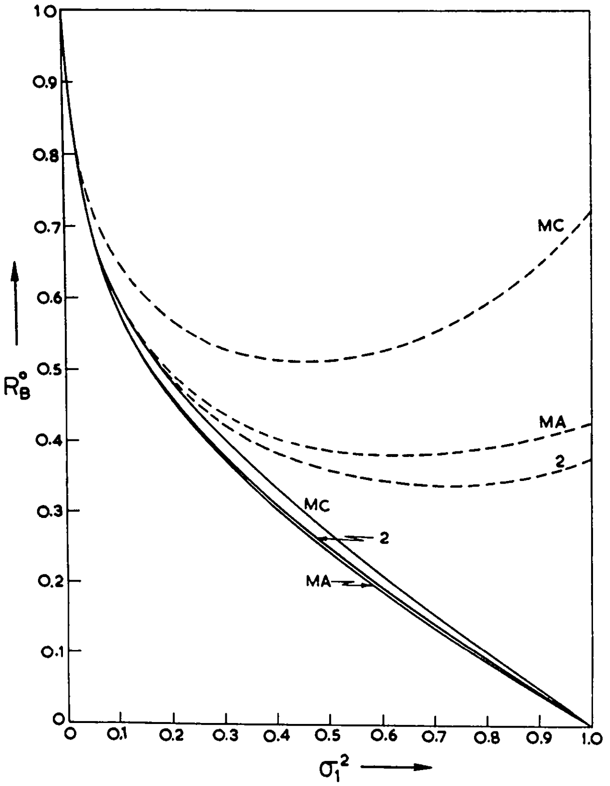

Fig. 4. The variation of the R_B^o-index as a function of σ_1^2 for the non-centrosymmetric crystal.

where NC and C stand for non-centrosymmetric and centrosymmetric crystals respectively. The probability density function of y_P^c when $P=2$ and many are well known and they are

$$P(y_P^c) = \begin{cases} \dfrac{\sqrt{2}}{\pi}(1 - y_P^{2c}/2)^{-1/2}, \; 0 \le y_P^c \le \sqrt{2} \quad \text{for } P=2 & (B3) \\ \sqrt{\left(\dfrac{2}{\pi}\right)} \exp\,(-y_P^{c2}/2), \; 0 \le y_P^c < \infty \text{ for } P=MC\,. & (B4) \end{cases}$$

(a) Non-centrosymmetric crystal

Making use of ($B3$) and ($B1$) in (28) and then using the substitution that $y_P^{c2} = 2x$ we obtain the expression for $(y_N y_P^c\rangle$ for the two-atom case as

$$\langle y_N y_P^c\rangle = \frac{\sigma_2}{\sqrt{2}\pi}\int_0^1 (1-x)^{-1/2}{}_1F_1\left(-\tfrac{1}{2}; 1; \frac{-2\sigma_1^2}{\sigma_2^2}x\right) \mathrm{d}x\,. \quad (B5)$$

Making use of equation (16) on page 47 of Sneddon (1961) in ($B5$) it is easy to show that

$$\langle y_N y_P^c\rangle = \sqrt{\left(\frac{2}{\pi}\right)}\,\sigma_2\, {}_1F_1\left(-\tfrac{1}{2}; \tfrac{3}{2}; \frac{-2\sigma_1^2}{\sigma_2^2}\right)\,. \quad (B6)$$

Making use of equations (2.2.1) on page 19 of Slater (1960) and (11.iii) in page 46 of Sneddon (1961) and the result that $\sigma_1^2 + \sigma_2^2 = 1$ we can simplify ($B6$) to give

$$\langle y_N y_P^c\rangle = \frac{\sigma_2}{2\pi}\exp\left(\frac{-2\sigma_1^2}{\sigma_2^2}\right) + \frac{(1+3\sigma_1^2)}{4\sigma_1}\operatorname{erf}\left(\frac{\sqrt{2}\sigma_1}{\sigma_2}\right)\,. \quad (B7)$$

Putting $n=\frac{1}{2}$ in equation ($A19$) of Parthasarathy & Srinivasan (1967) we can obtain the expression for $\langle y_N y_P^c\rangle$ for the $P=MA$ case as

$$\langle y_N y_P^c\rangle = \frac{\pi}{4}\sigma_2^4\, {}_2F_1(\tfrac{3}{2}, \tfrac{3}{2}; 1; \sigma_1^2)\,. \quad (B8)$$

Making use of equations 3(ii) on page 43 and equations 1(viii) and 1(ix) on page 42 of Sneddon (1961) we can simplify ($B8$) to obtain

$$\langle y_N y_P^c\rangle = E(\sigma_1) - \frac{\sigma_2^2}{2}k(\sigma_1)\,. \quad (B9)$$

Making use of ($B4$) and ($B1$) in (28) and then using the substitution that $y_P^{c2} = x$ we can obtain an expression for $\langle y_N y_P^c\rangle$ for the $P=MC$ case:

$$\langle y_N y_P^c\rangle = \frac{\sigma_2}{2\sqrt{2}}\int_0^\infty {}_1F_1\left(-\tfrac{1}{2}; 1; \frac{-\sigma_1^2}{\sigma_2^2}x\right)\exp -(x/2)\mathrm{d}x\,. \quad (B10)$$

Making use of equations 17(i) on page 48 and 1(i) on page 42 of Sneddon (1961) in ($B10$), we obtain

$$\langle y_N y_P^c\rangle = [(1+\sigma_1^2)/2]^{1/2}\,. \quad (B11)$$

(*b*) *Centrosymmetric crystal*

Making use of (B2) and (B3) in (28) and then using the substitution that $y_P^{c^2}=2x$ we obtain for the two-atom case

$$\langle y_N y_P^c\rangle=\frac{2\sigma_2}{\pi^{3/2}}\int_0^1(1-x)^{-1/2}\,{}_1F_1\left(-\tfrac{1}{2};\tfrac{1}{2};\frac{-\sigma_1^2}{\sigma_2^2}x\right)\mathrm{d}x$$

$$=\frac{4\sigma_2}{\pi^{3/2}}\,{}_2F_2\left(-\tfrac{1}{2},1;\tfrac{1}{2},\tfrac{3}{2};\frac{-\sigma_1^2}{\sigma_2^2}\right) \qquad (B12)$$

where we have made use of equation (16) on page 47 of Sneddon (1961). Putting $n=\frac{1}{2}$ in equation (A13) of Parthasarathy & Srinivasan (1967) we obtain for the many-atom case that

$$\langle y_N y_P^c\rangle=\frac{2}{\pi}\,{}_2F_1\,(-\tfrac{1}{2},-\tfrac{1}{2};\tfrac{1}{2};\sigma_1^2)\,. \qquad (B13)$$

Making use of equation (7.4) on page 24, equations 4(ii) on page 44 and 1(vii) on page 42 of Sneddon (1961) we can simplify (B13) as

$$\langle y_N y_P^c\rangle=\frac{2}{\pi}\,[\sigma_2+\sigma_1\sin^{-1}(\sigma_1)]\,. \qquad (B14)$$

In obtaining (B14) we have also made use of the result that

$$\tan^{-1}(x)=\sin^{-1}\left(\frac{x}{\sqrt{(1-x^2)}}\right).$$

References

BOOTH, A. D. (1945). *Phil. Mag.* **36**, 609.
BUERGER, M. J. (1967). *Crystal Structure Analysis*, p. 589. New York: John Wiley.
FOSTER, F. & HARGREAVES, A. (1963*a*). *Acta Cryst.* **16**, 1124.
FOSTER, F. & HARGREAVES, A. (1963*b*). *Acta Cryst.* **16**, 1133.
LUZZATI, V. (1952). *Acta Cryst.* **5**, 802.
PARTHASARATHY, S. (1966). *Z. Kristallogr.* **123**, 27.
PARTHASARATHY, S. & SRINIVASAN, R. (1967). *India J. Pure Appl. Phys.* **5**, 502.
SLATER, L. J. (1960). *Confluent Hypergeometric Functions.* Cambridge Univ. Press.
SNEDDON, I. N. (1961). *Special Functions of Mathematical Physics and Chemistry.* London: Oliver & Boyd.
SRIKRISHNAN, T. & SRINIVASAN, R. (1968). *Z. Kristallogr.* **127**, 427.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.
WILSON, A. J. C. (1969). *Acta Cryst.* **B25**, 1288.

Acta Cryst. (1972). A**28**, 432

The Molecular Packing of Solid II Cyclobutane by Means of Spectroscopic Data and Potential Energy Calculations

BY E. CASTELLUCCI, M. G. MIGLIORINI AND P. MANZELLI

Istituto di Chimica Fisica, Università di Firenze, Via G. Capponi 9, 50121-*Firenze, Italy*

(*Received* 6 *March* 1972)

The molecular packing of solid II cyclobutane has been calculated starting from the knowledge of the site symmetry (point group D_2) and of two possible symmetries of the primitive unit cell (D_2 and D_{2h} factor group symmetry), derived from analysis of the infrared and Raman spectra. Crystal potential energy has been calculated for 13 orthorhombic space groups using the packing program written by Williams. The calculation was based on a pairwise potential of Buckingam type, widely tested on a large number of hydrocarbon crystal structures and properties. The energy was calculated as a function of the unit cell parameters (length of the cell edges), considering the molecules as rigid bodies and leaving the crystal symmetry unchanged. The results show the packing corresponding to space group *Ccca* to have the lowest calculated potential energy. The spectroscopic results allowed some changes to be made in the previous assignment of the fundamental frequencies of cyclobutane and cyclobutane-d_8.

Introduction

Several low temperature infrared and Raman studies on molecular crystals have been carried out in recent years with the aim of determining the crystal structure when X-ray data were not available. In order to restrict the choice of the possible structures compatible with the spectral data, simple closest-packing arguments and, when available, the comparison between calculated and observed density, have often been used.

A different approach to this problem concerns the calculation of the structure using the structural information obtained from the analysis of the crystal spectra. At any given temperature and pressure the most stable structure is governed by the arrangement of molecules that has the lowest free energy. Assuming the zero point lattice energy to be comparable for a number of possible close-packed structures, one can reasonably assume that the most probable structure is the one with the lowest calculated lattice energy.

Cyclobutane offers an attractive possibility for this kind of investigation since: (i) the molecular geometry has been widely investigated; (ii) the molecule possesses only C and H atoms; (iii) infrared spectra in polarized