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# Discrepancy Indices for Use in Crystal Structure Analysis. V. A Comparative Study of the Normalized and Unnormalized Booth-Type Indices in the Structure Completion Stage*

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A comparative study of the normalized and unnormalized Booth-type *R* indices is carried out in the structure completion stage corresponding to the following cases: (i) Crystals and models satisfying the requirements of the basic Wilson distributions and (ii) Crystals containing a few heavy atoms in the asymmetric unit (as well as a large number of light atoms) and belonging to triclinic, monoclinic and orthorhombic space groups. Indices based on intensity as well as on structure amplitudes are considered. In all cases the normalized index appears to be more powerful than the unnormalized one. Applications of the results to a few actual crystal structures confirm this.

## 1. Introduction

In Part III† a comparative study of six different types of normalized *R* indices has been made for three different crystallographic situations: (i) structure completion; (ii) refinement of an incomplete model and (iii) refinement of a complete model. This investigation has shown that Booth-type indices are preferable to the rest for situations (i) and (ii). The study in Part III was confined to the normalized form of *R* indices owing to the following property‡ noticed by Srinivasan & Ramachandran (1965) for the *unrelated case of the conventional R index* based on structure amplitudes: While $R_1(F)$ is found to be a fixed quantity (*i.e.* independent of the value of $\sigma_1^2$) $R(F)$ is a function of $\sigma_1^2$ [see Figs. 3 and 4 of Srinivasan & Ramachandran (1965)]. The studies in Parts II and IV involving the normalized Booth-type indices have shown that this property is no longer retained in the case of an important class of structures, *viz.* structures with heavy as well as light atoms in the unit cell. The following questions arise naturally now: Even if the property mentioned above does not strictly hold good, does the normalization procedure improve the efficiency of the Booth-type *R* index in the structure completion stage§ in different types of crystals? If there is any such improvement, what is the improvement in quantitative terms? In order to answer these, we shall make a detailed study of the normalized and unnormalized Booth-type indices in different types of crystals for situations (i) and (ii) mentioned above.

In this paper we shall follow the notation employed in Parts I–III. Thus *C* and *NC* are abbreviations for the terms 'centrosymmetric' and 'non-centrosymmetric' and *R* and *UR* for the terms 'related' and 'unrelated'.

## 2. Comparison of the indices in the refinement stage of an incomplete model

$_BR_1(I)$ *vs.* $_BR(I)$

The expressions for $_BR_1(I)$ for the *C* and *NC* cases are available in Table 1 of Part III. The expressions for $_BR(I)$ are to be derived by the procedure used for $_BR(F)$ in Part I. The final expressions thus obtained are [for details see Parthasarathi & Parthasarathy (1975*b*)]

$$\begin{aligned} {}_BR(I) &= 1-\tfrac{2}{3}\sigma_1^2+\sigma_1^4-\tfrac{4}{3}\sigma_1^2\sigma_A^2 \quad \text{for } C \\ &= 1-\sigma_1^2+\sigma_1^4-\sigma_1^2\sigma_A^2 \quad \text{for } NC\,. \end{aligned} \tag{1}$$

The overall value for the *R* index could be obtained by numerical integration with the procedure described in Part III. The variation of the overall values of $_BR_1(I)$ and $_BR(I)$ as a function of $\langle|\Delta \mathbf{r}|\rangle$ for three different values of $\sigma_1^2$, namely, 0·3, 0·5 and 0·7, thus obtained are shown in Fig. 1(*a*) for the *C* case and in Fig. 1(*b*) for the *NC* case. From a study of these figures

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† The papers by Parthasarathy & Parthasarathi (1972), Parthasarathi & Parthasarathy (1975*a*), Parthasarathy & Parthasarathi (1975) and Parthasarathy (1975) will be referred to as Parts I, II, III and IV respectively.

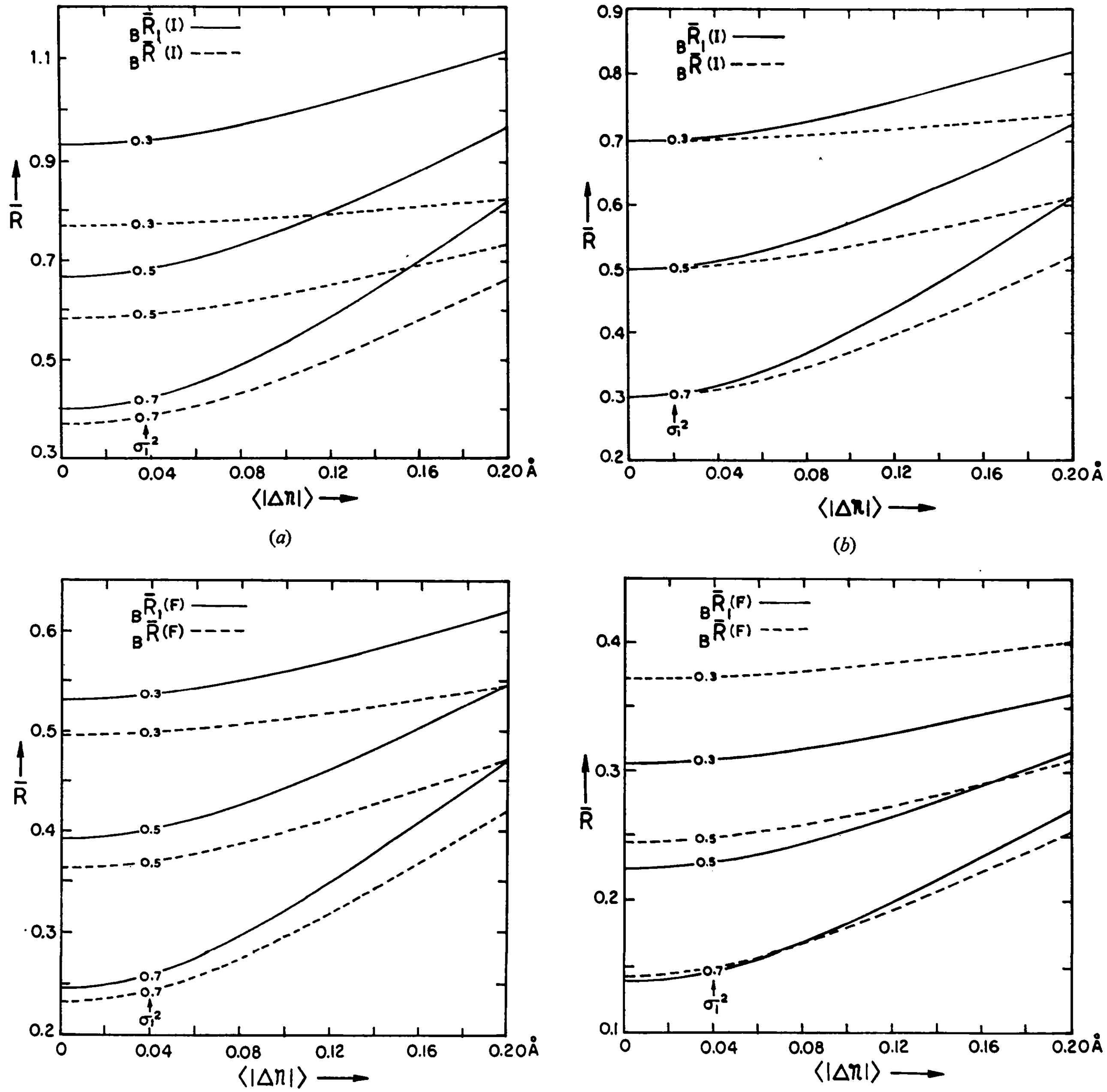
‡ Another advantage possessed by the normalized index is that it can be evaluated even when the correct scale factor for $F_o$ is not known. It may be noted here that the same advantage can be effectively achieved in the case of the unnormalized indices by employing normalized structure amplitudes and normalized intensities in the calculation. Thus, for example, $R(F)$ may be computed as $\sum||F_N|-|F_P||/\sum|F_N|$ when the absolute scale factor is known or as $\sum|y_N-\sigma_1 y_P|/\sum y_N$ when the scale factor is not known.

§ We shall use the term 'structure completion stage' to refer to the following two situations: (i) the structure completion *process* during which more and more atoms are added to the incomplete model and (ii) the refinement of an incomplete model. Note also that in the conventional refinement stage $\sigma_1^2 \simeq 1$ and hence the normalized and unnormalized indices of a given type become equal.

and use of the slope criterion described in Part III, it appears that in the refinement stage of an incomplete model, the normalized index $_BR_1(I)$ would be preferable to the unnormalized index $_BR(I)$ and this is particularly so for medium and low values of $\sigma_1^2$.

### $_BR_1(F)$ *vs.* $_BR(F)$

The expressions for $_BR_1(F)$ for the *C* and *NC* cases are available in Table 1 of Part III and those for $_BR(F)$ in equations (33) and (34) of Part I. The variations of the overall values of these indices obtained by a nu-



(*a*) (*b*)

(*c*) (*d*)

Fig. 1. Representation of the overall values of the normalized and unnormalized Booth-type indices as a function of $\langle|\Delta\mathbf{r}|\rangle$ for the cases $\sigma_1^2=0{\cdot}3$, 0·5 and 0·7. Curves in (*a*) and (*c*) correspond to the *C* case while those in (*b*) and (*d*) correspond to the *NC* case. Curves in (*a*) and (*b*) correspond to the Booth-type indices based on intensity while those in (*c*) and (*d*) to those based on structure amplitude. The broken lines correspond to the unnormalized index and the solid lines to the corresponding normalized index. The number on each curve denotes the value of $\sigma_1^2$.

merical integration method as a function of $\langle|\Delta\mathbf{r}|\rangle$ for the cases with $\sigma_1^2=0{\cdot}3$, $0{\cdot}5$ and $0{\cdot}7$ are shown in Fig. 1(*c*) for the *C* case and in Fig. 1(*d*) for the *NC* case. A study of these figures by the slope criterion indicates the greater efficiency of the normalized index.

### 3. Comparison of the indices during the structure completion process

Owing to theoretical difficulties the studies on ${}_BR_1(F)$ and ${}_BR(F)$ will be confined to triclinic crystals satisfying the requirements of the basic Wilson (1949) distributions and to models for which $P=2$ or many. However, the studies on ${}_BR_1(I)$ and ${}_BR(I)$ will be carried out for crystals containing one or two heavy atoms in the asymmetric unit and belonging to the triclinic, monoclinic and orthorhombic systems. Though, owing to theoretical difficulties, we shall consider only the related (*i.e.* $\langle|\Delta\mathbf{r}|\rangle=0$) and unrelated (*i.e.* $\langle|\Delta\mathbf{r}|\rangle$ large) cases but not the imperfectly related case, this will suffice to answer questions raised in §1.

${}_BR_1(I)$ *vs.* ${}_BR(I)$

(*i*) *Case with one or two heavy atoms per asymmetric unit*: The expressions for ${}_BR_1(I)$ for the related and unrelated cases for crystals containing one or two heavy atoms per asymmetric unit and belonging to the triclinic, monoclinic and orthorhombic space groups as a function of the heavy-atom contribution $\sigma_1^2$ are available in Table 1 of Part II.* These expressions have been derived under the following assumptions: (i) the model is constituted by the heavy atoms in the structure and (ii) the number (*q*, say) of other atoms in the asymmetric unit (which are assumed to be of similar scattering power) are such that the structure factors arising from them obey the basic Wilson distributions. The expressions for ${}_BR(I)$ for the above situations could be derived by the procedure outlined in Part II and hence we shall not give the steps here. The final expressions that can be obtained for ${}_BR(I)$ for the related and unrelated cases for the seven categories of space groups are summarized in Table 1. Making use of the expressions in Table 1 of Part II and those in Table 1 of this paper, the variation of ${}_BR_1(I)$

Table 1. *Final expressions for* ${}_BR(I)$ *for the related* (*R*)*and unrelated* (*UR*) *cases corresponding to the seven categories of space groups belonging to the triclinic, monoclinic and orthorhombic systems when the number* (*p*) *of heavy atoms in the asymmetric unit is one or two*

The heavy-atom part constitutes the model. Here $e_1=1-\sigma_1^2$; $e_2=1-\sigma_1^4$; $e_3=3-2\sigma_1^2-\sigma_1^4$; $e_4=1-\sigma_1^2-\sigma_1^4$; $e_5=3-2\sigma_1^2-3\sigma_1^4$.

| Space-group category number | $p=1$ | | $p=2$ | |
|---|---|---|---|---|
| | *R* case | *UR* case | *R* case | *UR* case |
| 1 | $\frac{2e_1}{\sigma_1^4+2e_2}$ | $\frac{2\sigma_1^4+2e_4}{\sigma_1^4+2e_2}$ | $\frac{4e_1}{3\sigma_1^4+4e_2}$ | $\frac{6\sigma_1^4+4e_4}{3\sigma_1^4+4e_2}$ |
| 2 | $\frac{2e_3}{3\sigma_1^4+6e_2}$ | $\frac{6\sigma_1^4+2e_5}{3\sigma_1^4+6e_2}$ | $\frac{4e_3}{9\sigma_1^4+12e_2}$ | $\frac{18\sigma_1^4+4e_5}{9\sigma_1^4+12e_2}$ |
| 3 | $\frac{4e_1}{3\sigma_1^4+4e_2}$ | $\frac{6\sigma_1^4+4e_4}{3\sigma_1^4+4e_2}$ | $\frac{8e_1}{7\sigma_1^4+8e_2}$ | $\frac{14\sigma_1^4+8e_4}{7\sigma_1^4+8e_2}$ |
| 4 | $\frac{4e_3}{9\sigma_1^4+12e_2}$ | $\frac{18\sigma_1^4+4e_5}{9\sigma_1^4+12e_2}$ | $\frac{8e_3}{21\sigma_1^4+24e_2}$ | $\frac{42\sigma_1^4+8e_5}{21\sigma_1^4+24e_2}$ |
| 5 | $\frac{8e_1}{7\sigma_1^4+8e_2}$ | $\frac{14\sigma_1^4+8e_4}{7\sigma_1^4+8e_2}$ | $\frac{16e_1}{15\sigma_1^4+16e_2}$ | $\frac{30\sigma_1^4+16e_4}{15\sigma_1^4+16e_2}$ |
| 6 | $\frac{8e_1}{9\sigma_1^4+8e_2}$ | $\frac{18\sigma_1^4+8e_4}{9\sigma_1^4+8e_2}$ | $\frac{16e_1}{17\sigma_1^4+16e_2}$ | $\frac{34\sigma_1^4+16e_4}{17\sigma_1^4+16e_2}$ |
| 7 | $\frac{8e_3}{27\sigma_1^4+24e_2}$ | $\frac{54\sigma_1^4+8e_5}{27\sigma_1^4+24e_2}$ | $\frac{16e_3}{51\sigma_1^4+48e_2}$ | $\frac{102\sigma_1^4+16e_5}{51\sigma_1^4+48e_2}$ |

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* Though the expressions in Part IV derived for *any* type of model and crystal are to be used to calculate the values of ${}_BR_1(I)$ for the present case, we have used here only the expressions in Part II, derived under the assumptions (i) and (ii) above. This is because the expressions in Part II conveniently depend on the single *relevant* parameter $\sigma_1^2$ while those in Part IV depend (besides $\sigma_1^2$) on other parameters such as $C_n$ and $C_p$. The authors, however, have carried out numerical studies on hypothetical cases with Cl, Br and I as heavy atoms by using the expressions in both the parts and found that for the present case of heavy-atom structures, the expressions in Part II give accurate results even when *q* is as small as 3. Recently Wilson (1974) has obtained (by statistical methods) certain general expressions for the unnormalized index ${}_BR(I)$. Lenstra (1974) has studied it by employing the Patterson function. These results are also not convenient for our present study for similar reasons.

Table 2. *Values (in %) of the indices $_BR(I)$ and $_BR_1(I)$ for the related (R) and unrelated (UR) cases for the crystals containing $p(=1$ or $2)$ heavy atoms in the asymmetric unit for various categories of space groups belonging to the triclinic, monoclinic and orthorhombic systems*

The ($p$) heavy atoms in the asymmetric unit (assumed to be in general positions) constitute the atoms of the model structure. In part ($A$), since the case $p=1$ in category 1 is trivial (Parthasarathi & Parthasarathy, 1975*a*), the values of the $R$ indices are not given for this case.

(A) CRYSTALS WITH ONE HEAVY ATOM IN THE ASYMMETRIC UNIT (*i.e.* $p=1$)

SPACE GROUP CATEGORY NUMBER

| $\sigma_1^2$ ↓ | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ |
| 0.00 | R | 100.0 | 83.3 | 100.0 | 75.0 | 100.0 | 108.3 | 100.0 | 87.5 | 100.0 | 112.5 | 100.0 | 145.8 |
| | UR | 100.0 | 83.3 | 100.0 | 75.0 | 100.0 | 108.3 | 100.0 | 87.5 | 100.0 | 112.5 | 100.0 | 145.8 |
| 0.10 | R | 93.5 | 79.9 | 90.2 | 69.9 | 93.2 | 100.0 | 90.1 | 80.0 | 89.9 | 100.0 | 92.9 | 130.0 |
| | UR | 93.8 | 83.2 | 90.7 | 74.9 | 94.1 | 108.4 | 90.9 | 87.5 | 91.1 | 112.5 | 94.5 | 145.8 |
| 0.20 | R | 87.1 | 76.2 | 80.8 | 64.6 | 86.2 | 91.6 | 80.4 | 72.4 | 79.6 | 87.6 | 84.9 | 114.1 |
| | UR | 88.4 | 83.0 | 82.8 | 74.7 | 89.6 | 108.4 | 83.4 | 87.4 | 84.6 | 112.4 | 91.2 | 145.6 |
| 0.30 | R | 80.6 | 72.1 | 71.6 | 59.1 | 78.8 | 82.9 | 70.8 | 64.6 | 69.2 | 75.3 | 76.1 | 98.4 |
| | UR | 83.8 | 82.5 | 76.2 | 74.4 | 86.4 | 108.5 | 77.6 | 87.4 | 80.3 | 112.4 | 90.2 | 145.3 |
| 0.40 | R | 73.9 | 67.4 | 62.5 | 53.1 | 70.8 | 74.0 | 61.2 | 56.6 | 58.8 | 63.2 | 66.7 | 82.8 |
| | UR | 79.7 | 81.9 | 70.8 | 74.0 | 84.7 | 108.7 | 73.5 | 87.2 | 78.4 | 112.3 | 91.5 | 144.9 |
| 0.50 | R | 66.7 | 61.9 | 53.3 | 46.7 | 62.2 | 64.4 | 51.6 | 48.4 | 48.5 | 51.5 | 56.6 | 67.7 |
| | UR | 76.2 | 81.0 | 66.7 | 73.3 | 84.4 | 108.9 | 71.0 | 87.1 | 78.8 | 112.1 | 94.9 | 144.4 |
| 0.60 | R | 58.5 | 55.3 | 44.0 | 39.6 | 52.7 | 54.2 | 41.9 | 39.8 | 38.3 | 40.2 | 45.9 | 53.0 |
| | UR | 73.2 | 79.7 | 63.7 | 72.5 | 85.7 | 109.2 | 70.2 | 86.9 | 81.3 | 112.0 | 100.5 | 143.9 |
| 0.70 | R | 49.0 | 47.0 | 34.2 | 31.6 | 42.2 | 43.0 | 32.0 | 30.8 | 28.3 | 29.3 | 34.9 | 38.8 |
| | UR | 70.6 | 77.9 | 62.1 | 71.5 | 88.7 | 109.5 | 71.1 | 86.7 | 86.0 | 111.8 | 108.0 | 143.2 |
| 0.80 | R | 37.3 | 36.3 | 23.8 | 22.6 | 30.2 | 30.6 | 21.7 | 21.2 | 18.5 | 19.0 | 23.5 | 25.2 |
| | UR | 68.6 | 7[illegible].5 | 61.9 | 70.2 | 93.7 | 109.9 | 73.9 | 86.4 | 92.6 | 111.6 | 117.3 | 142.4 |
| 0.90 | R | 21.8 | 21.6 | 12.5 | 12.2 | 16.3 | 16.4 | 11.1 | 11.0 | 9.1 | 9.2 | 11.8 | 12.2 |
| | UR | 67.2 | 72.0 | 63.3 | 68.7 | 100.9 | 110.4 | 78.7 | 86.1 | 101.0 | 111.4 | 128.3 | 141.6 |
| 1.00 | R | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | UR | 66.7 | 66.7 | 66.7 | 66.7 | 111.1 | 111.1 | 85.7 | 85.7 | 111.1 | 111.1 | 140.7 | 140.7 |

(B) CRYSTALS WITH TWO HEAVY ATOMS IN THE ASYMMETRIC UNIT (*i.e.* $p=2$)

SPACE GROUP CATEGORY NUMBER

| $\sigma_1^2$ ↓ | | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ |
| 0.00 | R | 100.0 | 75.0 | 100.0 | 108.3 | 100.0 | 87.5 | 100.0 | 120.8 | 100.0 | 93.8 | 100.0 | 106.3 | 100.0 | 139.6 |
| | UR | 100.0 | 75.0 | 100.0 | 108.3 | 100.0 | 87.5 | 100.0 | 120.8 | 100.0 | 93.8 | 100.0 | 106.3 | 100.0 | 139.6 |
| 0.10 | R | 90.2 | 69.9 | 93.2 | 100.0 | 90.1 | 80.0 | 93.1 | 110.0 | 90.1 | 85.0 | 89.9 | 95.0 | 92.9 | 125.0 |
| | UR | 90.7 | 74.9 | 94.1 | 108.4 | 90.9 | 87.5 | 94.2 | 120.9 | 90.9 | 93.7 | 91.1 | 106.2 | 94.4 | 139.6 |
| 0.20 | R | 80.8 | 64.6 | 86.2 | 91.6 | 80.4 | 72.4 | 85.8 | 99.2 | 80.2 | 76.2 | 79.8 | 83.8 | 85.1 | 110.4 |
| | UR | 82.8 | 74.7 | 89.6 | 108.4 | 83.4 | 87.4 | 90.1 | 120.9 | 83.7 | 93.7 | 84.3 | 106.2 | 90.9 | 139.5 |
| 0.30 | R | 71.6 | 59.1 | 78.8 | 82.9 | 70.8 | 64.6 | 77.9 | 88.2 | 70.4 | 67.3 | 69.6 | 72.7 | 76.6 | 95.9 |
| | UR | 76.2 | 74.4 | 86.4 | 108.5 | 77.6 | 87.4 | 87.7 | 121.1 | 78.3 | 93.7 | 79.7 | 106.2 | 89.6 | 139.4 |
| 0.40 | R | 62.5 | 53.1 | 70.8 | 74.0 | 61.2 | 56.6 | 69.4 | 77.0 | 60.6 | 58.3 | 59.4 | 61.6 | 67.3 | 81.4 |
| | UR | 70.8 | 74.0 | 84.7 | 108.7 | 73.5 | 87.2 | 87.1 | 121.3 | 74.7 | 93.7 | 77.2 | 106.2 | 90.4 | 139.2 |
| 0.50 | R | 53.3 | 46.7 | 62.2 | 64.4 | 51.6 | 48.4 | 60.2 | 65.6 | 50.8 | 49.2 | 49.2 | 50.8 | 57.4 | 67.2 |
| | UR | 66.7 | 73.3 | 84.4 | 108.9 | 71.0 | 87.1 | 88.2 | 121.5 | 73.0 | 93.7 | 76.9 | 106.2 | 93.3 | 139.0 |
| 0.60 | R | 44.0 | 39.6 | 52.7 | 54.2 | 41.9 | 39.8 | 50.3 | 53.8 | 40.9 | 39.9 | 39.1 | 40.1 | 46.9 | 53.1 |
| | UR | 63.7 | 72.5 | 85.7 | 109.2 | 70.2 | 86.9 | 91.1 | 121.8 | 73.1 | 93.6 | 78.7 | 106.1 | 98.3 | 138.7 |
| 0.70 | R | 34.2 | 31.6 | 42.2 | 43.0 | 32.0 | 30.8 | 39.4 | 41.4 | 30.9 | 30.4 | 29.1 | 29.7 | 35.9 | 39.4 |
| | UR | 62.1 | 71.5 | 88.7 | 109.5 | 71.1 | 86.7 | 96.0 | 122.2 | 75.2 | 93.6 | 82.6 | 106.1 | 105.2 | 138.4 |
| 0.80 | R | 23.8 | 22.6 | 30.2 | 30.6 | 21.7 | 21.2 | 27.5 | 28.4 | 20.8 | 20.6 | 19.2 | 19.5 | 24.4 | 25.9 |
| | UR | 61.9 | 70.2 | 93.7 | 109.9 | 73.9 | 86.4 | 102.9 | 122.6 | 79.2 | 93.5 | 88.5 | 106.0 | 114.1 | 138.1 |
| 0.90 | R | 12.5 | 12.2 | 16.3 | 16.4 | 11.1 | 11.0 | 14.5 | 14.7 | 10.5 | 10.5 | 9.5 | 9.6 | 12.4 | 12.8 |
| | UR | 63.3 | 68.7 | 100.9 | 110.4 | 78.7 | 86.1 | 112.1 | 123.2 | 85.2 | 93.4 | 96.3 | 105.9 | 124.8 | 137.7 |
| 1.00 | R | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | UR | 66.7 | 66.7 | 111.1 | 111.1 | 85.7 | 85.7 | 123.8 | 123.8 | 93.3 | 93.3 | 105.9 | 105.9 | 137.3 | 137.3 |

and $_BR(I)$ as a function of $\sigma_1^2$ could be studied. The relevant numerical results are summarized in Table 2(*A*) for crystals with one and in Table 2(*B*) for crystals with two heavy atoms per asymmetric unit. From Table 2 we can state the following: (i) Since the distinction between the *R* and *UR* cases is more marked for the normalized index than for the unnormalized, $_BR_1(I)$ would be preferable to $_BR(I)$ in testing for the correctness of the heavy-atom positions. (ii) For a given value of $\sigma_1^2$ the *R* indices become more efficient for space groups of higher category number.

(ii) *Triclinic crystals with many heavy atoms in the unit cell*: We shall assume that the *P* atoms constituting the model structure obey the requirements of the basic Wilson distributions. If the crystal is centrosymmetric we shall denote the situation by writing

Table 3. *Values (in %) of the indices $_BR(I)$, $_BR_1(I)$, $_BR(F)$ and $_BR_1(F)$ for the related (R) and unrelated (UR) cases corresponding to triclinic crystals with two or many heavy atoms in the unit cell (i.e. M, MN and MC cases)*

The heavy-atom part constitutes the model. The values of $_BR(I)$ and $_BR_1(I)$ for the case $P=2$ in space group $P\bar{1}$ are nothing but those given for category 2 of Table 2(*A*). Similarly for the case $P=2$ in space group $P1$ the values correspond to those given for category 1 of Table 2(*B*). Hence these are not given here.

| | | CENTROSYMMETRIC | | NON-CENTROSYMMETRIC | | | | CENTROSYMMETRIC | | | | NON-CENTROSYMMETRIC | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\sigma_1^2$ | P → | M | | MN | | MC | | 2 | | M | | 2 | | MN | | MC | |
| ↓ | | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(I)$ | $_BR_1(I)$ | $_BR(F)$ | $_BR_1(F)$ | $_BR(F)$ | $_BR_1(F)$ | $_BR(F)$ | $_BR_1(F)$ | $_BR(F)$ | $_BR_1(F)$ | $_BR(F)$ | $_BR_1(F)$ |
| 0.0 | R | 100.0 | 133.3 | 100.0 | 100.0 | 100.0 | 158.0 | 100.0 | 56.3 | 100.0 | 72.7 | 100.0 | 40.4 | 100.0 | 42.9 | 100.0 | 58.6 |
| | UR | 100.0 | 133.3 | 100.0 | 100.0 | 100.0 | 150.0 | 100.0 | 56.3 | 100.0 | 72.7 | 100.0 | 40.4 | 100.0 | 42.9 | 100.0 | 58.6 |
| 0.1 | R | 93.0 | 120.0 | 90.0 | 90.0 | 89.6 | 129.9 | 63.8 | 53.8 | 67.7 | 66.3 | 58.7 | 37.6 | 59.0 | 38.7 | 63.1 | 52.7 |
| | UR | 94.3 | 133.3 | 91.0 | 100.0 | 91.5 | 149.8 | 64.5 | 56.2 | 69.7 | 72.7 | 59.5 | 40.4 | 60.3 | 42.9 | 65.3 | 58.7 |
| 0.2 | R | 85.3 | 106.7 | 80.0 | 80.0 | 78.4 | 109.8 | 53.3 | 50.8 | 57.3 | 59.7 | 46.0 | 34.6 | 46.0 | 34.6 | 50.7 | 45.1 |
| | UR | 90.7 | 133.3 | 84.0 | 100.0 | 86.3 | 149.0 | 55.6 | 55.9 | 63.1 | 72.7 | 48.5 | 40.2 | 49.8 | 42.9 | 56.9 | 58.9 |
| 0.3 | R | 77.0 | 93.3 | 70.0 | 70.0 | 67.0 | 90.4 | 46.4 | 47.3 | 49.5 | 53.1 | 37.6 | 31.3 | 37.2 | 30.6 | 41.7 | 38.8 |
| | UR | 89.0 | 133.3 | 79.0 | 100.0 | 84.2 | 147.8 | 50.8 | 55.3 | 60.3 | 72.7 | 42.3 | 39.9 | 44.0 | 42.9 | 53.0 | 59.4 |
| 0.4 | R | 68.0 | 80.0 | 60.0 | 60.0 | 55.6 | 72.2 | 40.8 | 43.2 | 42.8 | 46.2 | 31.0 | 27.6 | 30.3 | 26.5 | 34.2 | 32.7 |
| | UR | 89.3 | 133.3 | 76.0 | 100.0 | 85.2 | 146.3 | 47.9 | 54.4 | 59.5 | 72.7 | 38.5 | 39.5 | 40.7 | 42.9 | 51.5 | 60.1 |
| 0.5 | R | 58.3 | 66.7 | 50.0 | 50.0 | 44.4 | 55.6 | 35.7 | 38.4 | 36.3 | 39.3 | 25.3 | 23.6 | 24.4 | 22.4 | 27.5 | 26.8 |
| | UR | 91.7 | 133.3 | 75.0 | 100.0 | 88.9 | 144.4 | 46.1 | 53.1 | 60.0 | 72.7 | 36.2 | 39.0 | 38.9 | 42.9 | 51.7 | 60.9 |
| 0.6 | R | 48.0 | 53.3 | 40.0 | 40.0 | 33.9 | 40.7 | 30.4 | 32.7 | 29.9 | 32.1 | 20.1 | 19.3 | 19.2 | 18.2 | 21.4 | 21.1 |
| | UR | 96.0 | 133.3 | 76.0 | 100.0 | 94.9 | 142.4 | 44.7 | 51.2 | 61.4 | 72.7 | 34.8 | 38.4 | 38.3 | 42.9 | 53.2 | 62.1 |
| 0.7 | R | 37.0 | 40.0 | 30.0 | 30.0 | 24.1 | 27.7 | 24.4 | 26.0 | 23.3 | 24.7 | 15.0 | 14.7 | 14.3 | 13.9 | 15.7 | 15.6 |
| | UR | 102.3 | 133.3 | 79.0 | 100.0 | 102.8 | 140.2 | 43.4 | 48.7 | 63.5 | 72.7 | 34.3 | 37.8 | 38.6 | 42.9 | 55.8 | 63.6 |
| 0.8 | R | 25.3 | 26.7 | 20.0 | 20.0 | 15.2 | 16.7 | 17.3 | 18.1 | 16.3 | 17.0 | 10.0 | 9.9 | 9.6 | 9.4 | 10.3 | 10.3 |
| | UR | 110.7 | 133.3 | 84.0 | 100.0 | 112.1 | 137.9 | 41.9 | 45.6 | 66.1 | 72.7 | 34.4 | 37.2 | 39.5 | 42.9 | 59.7 | 65.5 |
| 0.9 | R | 13.0 | 13.3 | 10.0 | 10.0 | 7.1 | 7.5 | 9.2 | 9.4 | 8.7 | 8.9 | 5.0 | 5.0 | 4.8 | 4.8 | 5.1 | 5.1 |
| | UR | 121.0 | 133.3 | 91.0 | 100.0 | 122.4 | 135.6 | 40.0 | 41.9 | 69.2 | 72.7 | 35.4 | 37.0 | 41.0 | 42.9 | 64.8 | 68.1 |
| 1.0 | R | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | UR | 133.3 | 133.3 | 100.0 | 100.0 | 133.3 | 133.3 | 37.9 | 37.9 | 72.7 | 72.7 | 37.9 | 37.9 | 42.9 | 42.9 | 72.7 | 72.7 |

Table 4. *Theoretical expressions of the index $_BR_1(F)$ for the related (R) and unrelated (UR) cases corresponding to triclinic crystals with two or many heavy atoms in the unit cell (i.e. M, MN and MC cases)*

The heavy atoms constitute the model. Here $a=1+\sigma_1^2$ and $r=\sigma_1/\sigma_2$.

| *P* | Related case | Unrelated case |
|---|---|---|
| | (*a*) Centrosymmetric crystal | |
| 2 | $2-\frac{8\sigma_2}{\pi^{3/2}}\,{}_2F_2(-\frac{1}{2},1;\frac{1}{2},\frac{3}{2};-r^2)$ | $2-\frac{8}{\sigma_2\pi^{3/2}}\exp(-r^2/2)[I_0(r^2/2)+\sigma_1^2I_1(r^2/2)]$ |
| *M* | $2-\frac{4}{\pi}[\sigma_2+\sigma_1\sin^{-1}(\sigma_1)]$ | $2-\frac{4}{\pi}$ |
| | (*b*) Non-centrosymmetric crystal | |
| 2 | $2-\left(\frac{1+3\sigma_1^2}{2\sigma_1}\right)\mathrm{erf}\,(\sqrt{2}r)-\sqrt{\frac{2}{\pi}}\,\sigma_2\exp\,(-2r^2)$ | $2-\frac{2\sqrt{2}}{\sqrt{\pi}}\,\sigma_2\,{}_2F_2(-\frac{1}{2},\frac{1}{2};1,1;-2r^2)$ |
| *MN* | $2-2E(\sigma_1)+\sigma_2^2K(\sigma_1)$ | $2-\frac{\pi}{2}$ |
| *MC* | $2-\sqrt{2a}$ | $2-\frac{2\sqrt{2}}{\pi}\sqrt{a}E\left(\sqrt{\frac{2\sigma_1^2}{a}}\right)$ |

$P=M$. In a non-centrosymmetric crystal the $P$ group can be either centrosymmetric (denoted by $P=MC$) or non-centrosymmetric (denoted by $P=MN$). The expressions for ${}_BR(I)$ for the cases $P=M$, $MN$ and $MC$ are available in Table 1 of Part I and those for ${}_BR_1(I)$ for the cases $P=M$ and $MN$ could be deduced from Table 1 of Part III and the results thus obtained are:

Related case:

$$\begin{aligned} {}_BR_1(I) &= 1-\sigma_1^2 \quad \text{for } P=MN \\ &= \tfrac{4}{3}(1-\sigma_1^2) \quad \text{for } P=M; \end{aligned} \tag{2}$$

Unrelated case:

$$\begin{aligned} {}_BR_1(I) &= 1 \quad \text{for } P=MN \\ &= \tfrac{4}{3} \quad \text{for } P=M\,. \end{aligned} \tag{3}$$

The expressions of ${}_BR_1(I)$ for the $R$ and $UR$ cases when $P=MC$ could be derived by the method outlined in Part II. We can show that for this case (note the crystal is $NC$)

$$\begin{aligned} {}_BR_1(I) &= \frac{3-4\sigma_1^2+\sigma_1^4}{2+\sigma_1^4} \quad \text{for the } R \text{ case} \\ &= \frac{3+\sigma_1^4}{2+\sigma_1^4} \quad \text{for the } UR \text{ case}\,. \end{aligned} \tag{4}$$

From these expressions, the numerical values of ${}_BR_1(I)$ and ${}_BR(I)$ as a function of $\sigma_1^2$ can be obtained and these are given in Table 3. This table shows that the normalized index is more powerful for this case as well.

### ${}_BR_1(F)$ *vs.* ${}_BR(F)$

The expressions for ${}_BR(F)$ for the $R$ and $UR$ cases when $P=2$, $M$, $MN$ and $MC$ are available in Table 2 of Part I and those for ${}_BR_1(F)$ are to be derived by the procedure followed for ${}_BR(F)$ in Part I. Owing to the similarity of the method of derivation the steps are not given here. The final expressions for the various cases are summarized in Table 4. The numerical values of these indices as a function of $\sigma_1^2$ for the various cases are given in Table 3. From this table it is seen that the normalized index is more powerful for these cases also.

## 4. Studies of the indices ${}_BR_1(I)$ and ${}_BR(I)$ in some actual crystals containing heavy atoms

In order to study how the indices behave in practical situations, they were computed in the case of a number of actual crystal structures containing heavy atoms

Table 5. *Comparative study of the indices ${}_BR_1(I)$ and ${}_BR(I)$ in a few actual crystal structures*

Crystals (1) to (7) belong to the $NC$ space group $P2_1$ while the rest belong to the $C$ space group $P2_1/c$. Each crystal contains one heavy atom per asymmetric unit and the heavy atom part is taken to be the trial model. $E$ denotes experimental value. $R$ and $UR$ denote the theoretical values for the related and unrelated cases respectively. $B$ = Overall isotropic temperature factor.

| No. | Crystal | Molecular formula | $B$ (Å²) | $\langle\sigma_1^2\rangle$ | | ${}_BR_1(I)$ | ${}_BR(I)$ | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | L-Tyrosine hydrochloride | $C_9NO_3H_{12}Cl$ | 3·0 | 48·2 % | $E$ | 54·4 % | 60·5 % | Srinivasan (1959*b*) |
| | | | | | $R$ | 47·9 | 55·0 | |
| | | | | | $UR$ | 73·5 | 67·3 | |
| 2 | 1-(1-Methyl-2-phenylethyl)-2-methyl-3-hydroxyazetidinium hydrochloride | $C_{13}NOH_{20}Cl$ | 3·0 | 48·9 | $E$ | 51·2 | 64·3 | Wetherington & Moncrief (1974) |
| | | | | | $R$ | 47·4 | 54·4 | |
| | | | | | $UR$ | 73·4 | 67·1 | |
| 3 | Glycyl-L-alanine hydrochloride | $C_5N_2O_3H_{11}Cl$ | 3·0 | 52·1 | $E$ | 49·0 | 63·9 | Naganathan & Venkatesan (1972) |
| | | | | | $R$ | 45·2 | 51·4 | |
| | | | | | $UR$ | 73·2 | 65·9 | |
| 4 | L-α-γ-Diaminobutyric acid hydrochloride | $C_4N_2O_2H_{11}Cl$ | 3·0 | 58·2 | $E$ | 40·8 | 47·0 | Naganathan & Venkatesan (1971) |
| | | | | | $R$ | 40·9 | 45·7 | |
| | | | | | $UR$ | 72·7 | 64·2 | |
| 5 | L-Valine hydrochloride | $C_5NO_2H_{12}Cl$ | 3·0 | 59·2 | $E$ | 40·4 | 45·3 | Parthasarathy (1966) |
| | | | | | $R$ | 40·1 | 44·7 | |
| | | | | | $UR$ | 72·6 | 63·9 | |
| 6 | L-Tryptophan hydrobromide | $C_{11}N_2O_2H_{12}Br$ | 3·0 | 84·6 | $E$ | 16·4 | 20·4 | Ramachandra Ayyar & Chandrasekharan (1967) |
| | | | | | $R$ | 18·0 | 18·7 | |
| | | | | | $UR$ | 69·5 | 62·3 | |
| 7 | L-Tyrosine hydrobromide | $C_9NO_3H_{12}Br$ | 2·5 | 85·5 | $E$ | 19·4 | 19·4 | Srinivasan (1959*a*) |
| | | | | | $R$ | 17·1 | 17·8 | |
| | | | | | $UR$ | 69·4 | 62·5 | |
| 8 | 5-Methyl-2,2,4-triacetyl-1,3-oxathiole | $C_{10}O_4H_{12}S$ | 3·0 | 43·5 | $E$ | 69·2 | 79·9 | Ruben, Kaplan, Zalkin & Templeton (1974) |
| | | | | | $R$ | 70·7 | 67·9 | |
| | | | | | $UR$ | 108·7 | 84·5 | |
| 9 | 2-Aminoadamantane-2-carboxylic acid hydrobromide | $C_{11}NO_2H_{18}Br$ | 2·88 | 85·5 | $E$ | 22·3 | 27·9 | Chacko & Zand (1973) |
| | | | | | $R$ | 23·0 | 22·8 | |
| | | | | | $UR$ | 110·2 | 97·3 | |
| 10 | DL-Ornithine hydrobromide | $C_5N_2O_2H_{14}Br$ | 2·65 | 88·7 | $E$ | 20·5 | 29·9 | Kalyanaraman & Srinivasan (1971) |
| | | | | | $R$ | 18·4 | 18·2 | |
| | | | | | $UR$ | 110·4 | 99·8 | |

by taking the heavy-atom part as the model. Details of the results obtained are summarized in Table 5. In each crystal, the structure factors were calculated from the published coordinates of the atoms and with an overall isotropic temperature factor as shown in Table 5. For structures (1) and (7), the $B$ values correspond to those given. For structures (9) and (10), the $B$ values in our calculation correspond to the mean of the individual atom isotropic temperature factor of the light atoms. For the other structures individual atom anisotropic thermal parameters were used and the $B$ values chosen in our calculations are set as 3 Å$^2$. Further, the H atoms are excluded in the structure-factor calculations. The structure factors thus obtained were treated as the $F_o$ data and this evidently corresponds to an ideal case involving no errors of observation.* The ${}_BR_1(I)$ values for each crystal were then computed from equation (2) of Part II and the ${}_BR(I)$ values from equation (2) of Part I. In the computation only general *hkl* reflexions which satisfy the relation $1/a_{\min} \le (\sin\theta)/\lambda \le 0{\cdot}5$ (where $a_{\min}$ is the shortest cell dimension of the crystal) were included. The values thus computed are entered against row $E$ (*i.e.* experimental) in Table 5. The mean value of the heavy-atom contribution $\sigma_1^2$ obtained for each case is also given, as well as the values for the $R$ and $UR$ cases corresponding to this value of $\sigma_1^2$. Table 5 shows that in all cases the normalization procedure leads to better results.

From the present study it appears that the normalized index is more powerful than the unnormalized index in the structure completion stage (see foot-note ‡ on p. 529). This seems to be plausible from the following physical considerations: The normalized index ${}_BR_1(I)$, for example, could be defined in two equivalent forms, namely,

$$
\begin{aligned}
{}_BR_1(I) &= \langle (I_N - I_P^C/\sigma_1^2)^2 \rangle / \langle I_N^2 \rangle && (5a)\\
&= \langle (z_N - z_P^C)^2 \rangle / \langle z_N^2 \rangle\,. && (5b)
\end{aligned}
$$

Equation (5*b*) shows that ${}_BR_1(I)$ could be interpreted to correspond to the $R$ value for a point-atom structure in an equal-atom structure and to a structure with atoms in which the electron density is more concentrated (*i.e.* an approximation towards the point-atom situation) in other cases. This might be responsible for the greater efficiency of the normalized $R$ indices.

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* When there are random errors in the intensities both ${}_BR_1(I_{\rm obs})$ and ${}_BR(I_{\rm obs})$ differ from ${}_BR_1(I_N)$ and ${}_BR(I_N)$ respectively by the same amount, *viz.* $\sigma_e^2/\langle I_N^2\rangle$ [see equations (54) and (55) of Parthasarathy (1975)]. The present ideal procedure was adopted to test the efficiency of the results under identical conditions.

## References

CHACKO, K. K. & ZAND, R. (1973). *Acta Cryst.* **B29**, 2681–2686.

KALYANARAMAN, A. R. & SRINIVASAN, R. (1971). *Acta Cryst.* **B27**, 1420–1427.

LENSTRA, A. T. H. (1974). Private communication.

NAGANATHAN, P. S. & VENKATESAN, K. (1971). *Acta Cryst.* **B27**, 2159–2164.

NAGANATHAN, P. S. & VENKATESAN, K. (1972). *Acta Cryst.* **B28**, 552–556.

PARTHASARATHI, V. & PARTHASARATHY, S. (1975*a*). *Acta Cryst.* **A31**, 38–41.

PARTHASARATHI, V. & PARTHASARATHY, S. (1975*b*). *Indian J. Pure Appl. Phys.* To be submitted.

PARTHASARATHY, R. (1966). *Acta Cryst.* **21**, 422–426.

PARTHASARATHY, S. (1975). *Acta Cryst.* **A31**, 375–380.

PARTHASARATHY, S. & PARTHASARATHI, V. (1972). *Acta Cryst.* **A28**, 426–432.

PARTHASARATHY, S. & PARTHASARATHI, V. (1975). *Acta Cryst.* **A31**, 178–185.

RAMACHANDRA AYYAR, R. & CHANDRASEKHARAN, R. (1967) *Curr. Sci.* **36**, 139–143.

RUBEN, H., KAPLAN, D., ZALKIN, A. & TEMPLETON, D. H. (1974). *Acta Cryst.* **B30**, 547–549.

SRINIVASAN, R. (1959*a*). *Proc. Indian Acad. Sci.* **A49**, 340–373.

SRINIVASAN, R. (1959*b*). *Proc. Indian Acad. Sci.* **A50**, 19–50.

SRINIVASAN, R. & RAMACHANDRAN, G. N. (1965). *Acta Cryst.* **19**, 1003–1007.

WETHERINGTON, J. B. & MONCRIEF, J. W. (1974). *Acta Cryst.* **B30**, 534–537.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

WILSON, A. J. C. (1974). Private communication.