angle ω can then be found by fitting the two-dimensional transform — allowing for its elongation by a factor $\sec\varphi$ in a direction at right angles to its axis of tilt — on each of the layers of the reciprocal lattice, with the transform fits identical except for the lateral displacement by $\zeta\tan\varphi$. A knowledge of the direction of the normal may considerably facilitate the fitting of the transform where the tilt, φ, and therefore the elongation of the transform is large (*e.g.* Bolton, 1963*a*,*b*, where the tilts are of the order of 60°).

Where the spikes on the origin peak overlap, the fringe function governing their addition in reciprocal space may suggest the vector separation of their associated centres in real space. In other cases, the method of Taylor & Morley (1959) of plotting $\Sigma||G|-|F_0||$ for selected reflexions may be used to determine the positions in the unit cell of the centres chosen for the calculation of each planar transform. Once the orientation and separation of the planar parts of the molecule are known, the intersection of their transforms with upper layers may be used to determine signs of structure factors, which can then be used either for generalized projections or with direct methods, to find the rest of the cell contents. Phases obtained in this manner from transforms are preferable to those obtained from the direct calculation of structure factors, since doubtful signs are more readily recognized. For the method to be successful, a reasonable proportion of scattering matter must lie in the planar parts of the molecule.

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The Rate of refinement of Coordinates in the Minimum Residual Method

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An investigation is made of the rate at which the residual is reduced as the positional parameters are refined. Good agreement is obtained between theoretical and observed values at the later stages of refinement where the errors are small. Where the errors are large there may be no agreement in spite of the success of the refinement process.

Introduction

The method considered is that proposed by Bhuiya & Stanley (1963) in which each parameter, u_j, is varied individually from $u_j-n\Delta u_j$ to $u_j+n\Delta u_j$ in $2n$ increments of Δu_j. The lowest value of the residual, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ within the range is noted and the corresponding value of u_j is taken as the best value within the permitted range of variation. This method has worked very well with a variety of structures even where other methods have failed. It is interesting to investigate the theoretical rates of refinement by this method and to compare them with those obtained in practice.

The nature of the refinement process

Luzzati (1952), using an elegant statistical method, has obtained details of the variation of the residual, R, as a function of $|\mathbf{s}|$ and of the average error in

a coordinate. He finds that the value of R, at a fixed value of $\sin\theta$, is a monotonic increasing function of the mean error of the coordinates. This implies that, provided that the structure is sufficiently overdetermined, if a coordinate of any atom is varied about its supposed position then in one direction the mean error will be increased and in the other direction it will be reduced. The value of R can then be used to test whether any movement has increased or decreased the mean error.

In the method of Bhuiya & Stanley the procedure adopted was to vary the fractional x parameter of the first atom from $x_1 - n\Delta x_1$ to $x_1 + n\Delta x_1$. The new value of x_1 selected was that giving the lowest value of R. With this new value of x_1 the value of y_1 was varied from $y_1 - n\Delta y_1$ to $y_1 + n\Delta y_1$ in increments of the same absolute length (*i.e.* $b\Delta y = a\Delta x$). If three-dimensional data are being processed the z coordinate of the first atom is similarly treated before moving on to the next atom.

The way in which the refinement progresses can be illustrated in a two-dimensional orthogonal group. It depends on the relative magnitudes of $n\Delta x_j$ (or $n\Delta y_j$) and the magnitude and direction of $\Delta\mathbf{r}_j$, the vector error in $\mathbf{r}_j$, the position of the jth atom. We can visualize three modes of refinement as follows:

(i) If $|\Delta\mathbf{r}_j|\cos\alpha \leq n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha \leq n\Delta y_j$, where α is the angle between $\Delta\mathbf{r}$ and the x axis, the coordinates will refine to the nearest increment of Δx_j and Δy_j in one cycle.

(ii) If $|\Delta\mathbf{r}_j|\cos\alpha > n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha < n\Delta y_j$ the error in y_j will be reduced to zero (to the nearest increment of Δy_j) in the first cycle and subsequent cycles will be concerned only with the reduction of the error in x_j.

(iii) If $|\Delta\mathbf{r}_j|\cos\alpha > n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha > n\Delta y_j$ the first and subsequent cycles will reduce the error in $\mathbf{r}_j$ by refining along the direction at 45° to the x and y axes until one axis is reached. After this refinement will be concerned with one coordinate only.

The three processes are illustrated in Fig. 1.

Initially most of the atoms will have large errors and the second or third mode of refinement would be expected. Consequently the value $|\Delta\mathbf{r}_j|$ will, in general, change by an amount somewhere between the limiting values of $n\Delta x_j$ when the error in y_j is zero and $\sqrt{(2)}n\Delta x_j$ when the error in $\mathbf{r}_j$ is along the line at 45° to the axes. It is possible to evaluate a proper average in any particular case but the variation is quite small and a reasonable value for the average would be of the order $1{\cdot}2n\Delta x_j$. The way in which the change in $|\Delta\mathbf{r}_j|$ varies with the angle $\Delta\mathbf{r}_j$ makes with the axes is shown in Fig. 2. This argument can be extended to three dimensions without difficulty. The maximum change in $|\Delta\mathbf{r}_j|$ then becomes $n\sqrt{(3)}\Delta x_j$ when $\mathbf{r}_j$ is along the direction equally inclined to the three axes. In all cases the variation in the change in $|\Delta\mathbf{r}_j|$ is relatively small.

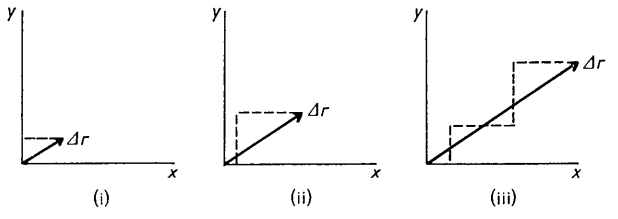

Fig. 1. The possible modes of refinement.

(i) $|\Delta\mathbf{r}_j|\cos\alpha < n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha < n\Delta y_j$.
(ii) $|\Delta\mathbf{r}_j|\cos\alpha > n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha < n\Delta y_j$.
(iii) $|\Delta\mathbf{r}_j|\cos\alpha > n\Delta x_j$ and $|\Delta\mathbf{r}_j|\sin\alpha > n\Delta y_j$.

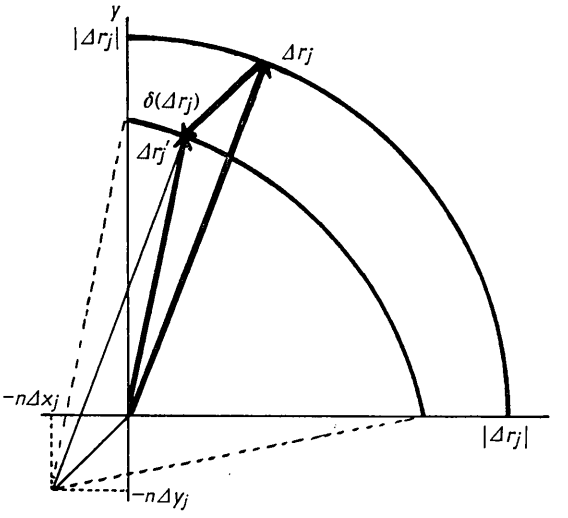

Fig. 2. The locus of $\Delta\mathbf{r}_j' = \Delta\mathbf{r}_j - \delta(\Delta\mathbf{r}_j)$.

Using Luzzati's figures for the variation of R as a function of the mean error in $|\mathbf{r}_j|$, when the values of $|\Delta\mathbf{r}_j|$ are distributed normally, and $|\mathbf{s}|$, we can evaluate the actual values of R for any type of scattering curve by evaluating

$$R = \frac{\int_0^{s_{\max}} sR(s,\sigma)\langle|F|\rangle ds}{\int_0^{s_{\max}} s\langle|F|\rangle ds}$$

where $\langle|F|\rangle$ is the mean value of $|F|$ and $R(s,\sigma)$ is the value of R for a standard deviation of coordinates of σ at the value of s. (These values are given by Luzzati as a function of $|\overline{\Delta\mathbf{r}}|$ and s). Although the value of this integral will depend on the types of atom involved and on the value of $s_{\max}$ it is worth while evaluating it for what is probably the most common case, that of carbon atoms and the limit of $s_{\max}$ as the limit of the sphere of reflexion for Cu $K\alpha$ radiation. Tables 1 and 2 give the values of R as a function of $\sigma(r)$ and B, the temperature coefficient,

Table 1. *Values of* $(\bar{1})R$ *as a Function of* $\sigma(r)$ *and* B.

B	0·0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0
$\sigma(r)$											
0·00	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·02	0·094	0·089	0·083	0·079	0·074	0·070	0·066	0·063	0·060	0·057	0·055
0·04	0·181	0·171	0·161	0·152	0·144	0·136	0·129	0·123	0·117	0·112	0·108
0·06	0·262	0·248	0·234	0·221	0·209	0·198	0·188	0·179	0·171	0·164	0·158
0·08	0·334	0·317	0·300	0·284	0·269	0·256	0·243	0·232	0·222	0·213	0·205
0·10	0·399	0·379	0·359	0·341	0·324	0·308	0·294	0·281	0·270	0·259	0·250
0·12	0·455	0·434	0·412	0·393	0·374	0·357	0·341	0·327	0·314	0·302	0·291
0·14	0·504	0·481	0·459	0·438	0·419	0·400	0·383	0·368	0·354	0·342	0·330
0·16	0·546	0·523	0·501	0·479	0·459	0·440	0·422	0·406	0·392	0·378	0·366
0·18	0·582	0·559	0·536	0·514	0·494	0·475	0·457	0·440	0·425	0·412	0·399
0·20	0·612	0·589	0·567	0·545	0·525	0·506	0·488	0·472	0·456	0·443	0·430
0·22	0·637	0·615	0·594	0·573	0·553	0·534	0·516	0·499	0·484	0·471	0·458
0·24	0·658	0·637	0·617	0·596	0·577	0·559	0·541	0·525	0·510	0·496	0·484
0·26	0·676	0·656	0·637	0·617	0·598	0·581	0·564	0·548	0·533	0·520	0·507
0·28	0·691	0·673	0·654	0·635	0·617	0·600	0·584	0·569	0·554	0·541	0·529
0·30	0·704	0·686	0·668	0·651	0·634	0·618	0·602	0·587	0·573	0·561	0·549
0·32	0·715	0·699	0·682	0·665	0·649	0·634	0·619	0·605	0·591	0·579	0·567
0·34	0·724	0·709	0·693	0·677	0·662	0·647	0·633	0·620	0·607	0·595	0·583
0·36	0·733	0·718	0·703	0·689	0·674	0·660	0·646	0·634	0·621	0·610	0·599
0·38	0·740	0·727	0·712	0·699	0·685	0·672	0·659	0·646	0·635	0·624	0·613
0·40	0·747	0·734	0·721	0·708	0·695	0·682	0·670	0·658	0·647	0·637	0·626
0·42	0·753	0·741	0·728	0·716	0·703	0·691	0·679	0·668	0·658	0·648	0·638
0·44	0·758	0·746	0·735	0·722	0·711	0·699	0·689	0·678	0·668	0·658	0·649
0·46	0·763	0·752	0·741	0·730	0·719	0·708	0·697	0·687	0·677	0·668	0·659
0·48	0·767	0·757	0·747	0·736	0·726	0·715	0·705	0·695	0·686	0·677	0·669
0·50	0·771	0·761	0·751	0·741	0·731	0·721	0·712	0·703	0·694	0·685	0·677

Table 2. *Values of* $(1)R$ *as a function of* $\sigma(r)$ *and* B.

B	0·0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0
$\sigma(r)$											
0·00	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·02	0·060	0·056	0·053	0·049	0·046	0·044	0·041	0·039	0·037	0·036	0·034
0·04	0·119	0·112	0·105	0·099	0·093	0·088	0·083	0·079	0·075	0·072	0·069
0·06	0·176	0·166	0·156	0·147	0·139	0·131	0·124	0·118	0·112	0·107	0·103
0·08	0·228	0·215	0·203	0·192	0·181	0·172	0·163	0·155	0·148	0·142	0·136
0·10	0·274	0·259	0·246	0·233	0·221	0·209	0·199	0·190	0·182	0·174	0·167
0·12	0·314	0·299	0·284	0·269	0·256	0·244	0·232	0·222	0·213	0·205	0·197
0·14	0·350	0·333	0·318	0·302	0·288	0·275	0·263	0·252	0·242	0·233	0·225
0·16	0·381	0·364	0·348	0·332	0·317	0·304	0·291	0·279	0·269	0·259	0·251
0·18	0·406	0·390	0·373	0·358	0·343	0·329	0·316	0·304	0·293	0·283	0·274
0·20	0·428	0·412	0·396	0·380	0·365	0·351	0·338	0·327	0·316	0·306	0·296
0·22	0·446	0·430	0·415	0·399	0·385	0·371	0·359	0·347	0·336	0·356	0·317
0·24	0·461	0·446	0·431	0·417	0·403	0·389	0·377	0·365	0·354	0·344	0·335
0·26	0·474	0·460	0·446	0·432	0·418	0·405	0·393	0·382	0·371	0·361	0·352
0·28	0·485	0·472	0·458	0·445	0·432	0·419	0·408	0·397	0·386	0·377	0·368
0·30	0·494	0·481	0·469	0·456	0·444	0·432	0·421	0·410	0·400	0·391	0·382
0·32	0·502	0·490	0·478	0·466	0·455	0·443	0·433	0·422	0·413	0·404	0·395
0·34	0·509	0·498	0·486	0·475	0·464	0·453	0·443	0·433	0·424	0·415	0·407
0·36	0·515	0·505	0·494	0·483	0·473	0·463	0·453	0·443	0·435	0·426	0·418
0·38	0·520	0·510	0·500	0·490	0·480	0·471	0·462	0·453	0·444	0·436	0·429
0·40	0·525	0·516	0·507	0·497	0·488	0·478	0·470	0·461	0·453	0·445	0·438
0·42	0·529	0·521	0·512	0·503	0·494	0·485	0·477	0·469	0·461	0·453	0·447
0·44	0·533	0·525	0·516	0·508	0·500	0·491	0·483	0·476	0·468	0·461	0·454
0·46	0·537	0·529	0·521	0·513	0·505	0·497	0·489	0·482	0·475	0·468	0·462
0·48	0·540	0·532	0·525	0·517	0·510	0·502	0·495	0·488	0·481	0·475	0·469
0·50	0·543	0·536	0·528	0·521	0·514	0·507	0·500	0·493	0·487	0·481	0·475

for, respectively, centric and acentric distributions of intensities assuming carbon atoms of the type suggested by Vand, Eiland & Pepinsky (1957). This table is interesting in itself since it shows clearly how the value of R for accurate $|F_o|$ depends on both the values of $\sigma(r)$ and on B and on the symmetry. For example a centrosymmetric projection with $\sigma(r)$ 0·04 Å would give R values of 0·18 and 0·14 for values of B of 0 and 5·0 respectively. The corresponding values for a non-centrosymmetric projection are 0·12 and 0·09. It is also of interest to note that the gradient $dR/d\sigma$ is greatest at the origin.

Comparison of theoretical and observed rates of refinement

The question arises of what is meant by a change in $\sigma(r)$ of $\delta\sigma(r)$.

If

$$\sigma(r) = \left\{\frac{\sum_{j=1}^{j=N} (|\Delta \mathbf{r}_j|)^2}{N}\right\}^{\frac{1}{2}}$$

and

$$\sigma(r)' = \left\{\frac{\sum_{j=1}^{j=N-1} (|\Delta \mathbf{r}_j|)^2 + (|\Delta \mathbf{r}_N| - \delta|\Delta \mathbf{r}_N|)^2}{N}\right\}^{\frac{1}{2}}$$

$$= \left\{\sigma^2(r) - \frac{\delta|\Delta \mathbf{r}_N|\{2|\Delta \mathbf{r}_N| - \delta|\Delta \mathbf{r}_N|\}}{N}\right\}^{\frac{1}{2}}$$

$$\simeq \sigma\left\{1 - \frac{\delta|\Delta \mathbf{r}_N|\{2|\Delta \mathbf{r}_N| - \delta|\Delta \mathbf{r}_N|\}}{2N\sigma^2}\right\}$$

provided

$$\delta|\Delta \mathbf{r}_N|\{2|\Delta \mathbf{r}_N| - \delta|\Delta \mathbf{r}_N|\} \ll 1 .$$

The change in $\sigma(r)$ is given by

$$\delta\sigma(r) = \sigma(r) - \sigma(r)' = \frac{\delta|\Delta \mathbf{r}_N|\{2|\Delta \mathbf{r}_N| - \delta|\Delta \mathbf{r}_N|\}}{2N\sigma} .$$

If $\delta|\Delta \mathbf{r}_N| \ll |\Delta \mathbf{r}_N|$

$$\delta\sigma(r) \simeq \frac{|\Delta \mathbf{r}_N|\delta|\Delta \mathbf{r}_N|}{N\sigma} \qquad (1)$$

and

$$\overline{\delta\sigma(r)} \simeq \sqrt{\frac{\pi}{2}}\,\frac{\delta|\Delta \mathbf{r}_N|}{N}$$

since

$$\overline{|\Delta \mathbf{r}_N|} = \sigma\sqrt{\frac{\pi}{2}} \text{ (Luzzati, 1952).}$$

But if $\delta|\Delta \mathbf{r}_N| = |\Delta \mathbf{r}_N|$

$$\delta\sigma(r) \simeq \frac{|\Delta \mathbf{r}_N|^2}{2N\sigma} . \qquad (2)$$

We can compare the observed rates of refinement with those calculated from the values of $\delta\sigma$ and $dR/d\sigma$.

(i) *Naphthocinnoline*, [001]. The structure of this material has been determined by Bhuiya & Stanley (to be published). The [001] projection is centrosymmetric and the asymmetric unit contains sixteen carbon atoms and two nitrogen atoms. The initial R value was 0·37 and the general temperature factor was 3·5 Å^2. From Table 1 the value of $\sigma(r)$ corresponding to $R=0{\cdot}37$ is 0·11. In fact during refinement the total shifts had a value $\sigma(r)$ of 0·5 Å which corresponds to a value of $R \sim 0{\cdot}73$. This very large discrepancy is presumably because the displacements of the atoms are not random. In the first cycle of refinement, details of which are given in Table 3, the value of R fell from 0·37 to 0·29. All the atoms were shifted to the extreme end of their permitted range of movement in at least one direction. (In this case $na\Delta x = nb\Delta y = 0{\cdot}1$ Å.) Using (1) to calculate the value of $\overline{\delta\sigma}$ we obtain the value 0·008 Å and, taking the value of $(dR/d\sigma)_{R=0{\cdot}73}$ as 0·25 Å^{-1} from Table 1, the expected rate of refinement would be 0·002 per atom. If, on the other hand, we take $(dR/d\sigma)_{R=0{\cdot}37}$ as 2·5 from Table 1 the expected rate of refinement would be ten times as great at 0·02 per atom. The average rate observed from the values given in Table 3 is 0·005 per atom. It is probable that the structure was already in a minor minimum condition so far as R was concerned and the fact that it found its way into the correct minimum is an indication of the strength of the method. In these circumstances however one would hardly expect any agreement with the calculated rates of refinement.

Table 3. *First cycle of refinement of naphthocinnoline*, [001]

Atom No.	$\lvert\Delta x\rvert$	$\lvert\Delta y\rvert$	R	ΔR
1	0·10 Å	0·10 Å	0·3651	0·0051
2	0·10	0·10	0·3593	0·0058
3	0·06	0·10	0·3549	0·0044
4	0·10	0·10	0·3497	0·0052
5	0·10	0·10	0·3449	0·0048
6	0·10	0·02	0·3425	0·0024
7	0·10	0·10	0·3376	0·0051
8	0·10	0·10	0·3323	0·0053
9	0·08	0·10	0·3277	0·0046
10	0·06	0·10	0·3233	0·0044
11	0·10	0·10	0·3185	0·0048
12	0·10	0·10	0·3138	0·0047
13	0·08	0·10	0·3091	0·0047
14	0·08	0·10	0·3045	0·0046
15	0·10	0·10	0·2994	0·0051
16	0·10	0·10	0·2947	0·0047
17	0·10	0·10	0·2898	0·0049
18	0·10	0·10	0·2850	0·0048

(ii) *Triphenyl phosphate*, [001]. The structure of

Table 4. *Final cycle of refinement of triphenyl phosphate*, [001]

Atom No.	$\lvert\Delta x\rvert$ (Å)	$\lvert\Delta y\rvert$ (Å)	R	ΔR (obs.)	ΔR (calc.)
3	0·00	0·01	0·1084	0·0002	0·00025
2	0·00	0·00	0·1084	0·0000	0·00000
3	0·00	0·01	0·1076	0·0008	0·00025
4	0·01	0·00	0·1075	0·0001	0·00025
5	0·00	0·01	0·1073	0·0002	0·00025
6	0·01	0·02	0·1064	0·0009	0·00125
7	0·01	0·02	0·1055	0·0009	0·00125
8	0·00	0·01	0·1053	0·0002	0·00025
9	0·00	0·01	0·1051	0·0002	0·00025
10	0·01	0·00	0·1050	0·0001	0·00025
11	0·00	0·00	0·1050	0·0000	0·00000
12	0·00	0·00	0·1050	0·0000	0·00000
13	0·00	0·00	0·1050	0·0000	0·00000
14	0·01	0·01	0·1046	0·0004	0·00050
15	0·01	0·00	0·1045	0·0001	0·00025
16	0·01	0·01	0·1043	0·0002	0·00050
17	0·01	0·01	0·1037	0·0006	0·00050
18	0·01	0·00	0·1035	0·0002	0·00025
19	0·00	0·03	0·1024	0·0011	0·00225
20	0·00	0·00	0·1024	0·0000	0·00000
21	0·00	0·00	0·1024	0·0000	0·00000
22	0·00	0·00	0·1024	0·0000	0·00000
23	0·00	0·01	0·1024	0·0000	0·00025

this material has been determined by Davies & Stanley (1962). This second example is of a centrosymmetric projection in the final stage of refinement. There are twenty-three atoms in the asymmetric unit including one phosphorus atom and four oxygen atoms. The details of this cycle of refinement are given in Table 4. The value of R is 0·105 with an average temperature factor of 4·5 Å^2 corresponds to a value of $\sigma(r)$ of 0·03 Å. None of the shifts were to the limit of the permitted range of movement in either direction. (In this case $na\Delta x = nb\Delta y = 0{\cdot}05$ Å.) The appropriate value of $\delta\sigma$ is obtained from (2) and in this case is $|\Delta \mathbf{r}_N|^2/1{\cdot}38$. The value of $(dR/d\sigma)_{R=0{\cdot}105}$ is 3·5 Å^{-1}. From these figures the expected value of R can be calculated for each shift. The observed and calculated values of ΔR given in the last two columns of Table 4 are in good agreement.

(iii) *Naphthocinnoline*, [010]. This is a non-centrosymmetric projection of the same structure as (i). During the course of refinement in one typical cycle the value of R fell from 0·27 to 0·24. The details of this cycle are given in Table 5. The average value of R during this cycle was 0·26 corresponding to a value of $\sigma(r)$ (from Table 2) of 0·12 Å. The corresponding value of $(dR/d\sigma)_{R=0{\cdot}026}$ is 1·75 Å^{-1}. Using the expression (2) to evaluate $\delta(\sigma)$ for each atomic shift the values of R were calculated as above. The agreement between the observed and the calculated values of R given in the last two columns of Table 5 is fairly good.

Table 5. *One cycle of refinement of naphthocinnoline*, [010]

Atom No.	$\lvert\Delta x\rvert$ (Å)	$\lvert\Delta y\rvert$ (Å)	R	ΔR (obs.)	ΔR (calc.)
1	0·00	0·02	0·2743	0·0003	0·0002
2	0·06	0·00	0·2723	0·0020	0·0018
3	0·02	0·00	0·2719	0·0004	0·0002
4	0·00	0·00	0·2719	0·0000	0·0000
5	0·02	0·00	0·2717	0·0002	0·0002
6	0·10	0·00	0·2652	0·0065	0·0050
7	0·04	0·00	0·2647	0·0005	0·0008
8	0·06	0·00	0·2627	0·0020	0·0018
9	0·04	0·02	0·2616	0·0011	0·0010
10	0·02	0·00	0·2613	0·0003	0·0002
11	0·04	0·00	0·2603	0·0010	0·0008
12	0·04	0·02	0·2587	0·0016	0·0010
13	0·08	0·02	0·2531	0·0056	0·0034
14	0·06	0·00	0·2504	0·0027	0·0018
15	0·00	0·02	0·2492	0·0012	0·0002
16	0·04	0·00	0·2461	0·0031	0·0008
17	0·02	0·00	0·2436	0·0025	0·0002
18	0·00	0·02	0·2429	0·0007	0·0002

Conclusions

The rates of refinement observed during the application of the minimum residual method are in good agreement with the rates calculated on the basis of the figures given by Luzzati in the later stages of refinement. The fact that $(dR/d\sigma)$ is greatest at the origin suggests that the method should become more efficient as the refinement progresses. This should certainly be true with an ideal structure where there are no errors in the intensities, all the corrections are known and where all the scattering curves are known precisely and the accessible value of R is zero. Quite what the situation will be when the accessible value of R is much larger than zero is difficult to predict but from the values obtained from the fully refined [001] zone of triphenyl phosphate quoted above it appears that the rate of refinement is determined by the value of $(dR/d\sigma)$ at the appropriate value of R irrespective of the value of the accessible minimum. It is rather as though the origin is shifted to the value of $\sigma(r)$ corresponding to the accessible minimum value of R.

The case of the [001] projection of naphthocinnoline given in the first example is interesting. This structure, at the stage where refinement by this method was started, was obviously in some minor minimum region with an R value of 0·37. (Least-squares refinement reduced R to 0·33 in two cycles but failed to refine the structure further.) In spite of this the structure was successfully refined by the new method. The lack of agreement between the theoretical and the observed rates of refinement is not unexpected. It is interesting to note that the observed rate is in rather better agreement with that calculated from the value of $(dR/d\sigma)$ corresponding to $\sigma(r)$ rather than that corresponding to the accidentally low value of R.

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