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Syntheses for the Deconvolution of the Patterson Function. Part V. Test of the Various Syntheses for Centrosymmetric Crystals

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This paper gives an account of the results of testing out the various types of syntheses (the α, β and γ classes in their general and modified forms) which were proposed earlier for the deconvolution of the Patterson function when a part of the structure is known. The tests have been carried out on the centrosymmetric projections of the structures L-tyrosine hydrochloride, L-tyrosine hydrobromide and L-cystine dihydrobromide. As expected from theory, all the syntheses reveal the unknown part of the structure. However, it is rather difficult to decide from the present tests as to which of these is the best.

A modified form of the phase synthesis has also been tested and, as expected from theory, it resembles closely the Fourier synthesis.

1. Introduction

The various theoretical aspects of the problem of developing a structure from its Patterson or vector diagram when a part of the structure is known were discussed in detail in the earlier papers from this laboratory (Ramachandran & Raman, 1959; Raman, 1959, 1961; Srinivasan, 1961). It was shown that there are three classes of syntheses, namely the α, β and γ classes, which could be used for obtaining the unknown part of the structure. There also exists another series namely the α', β' and γ' syntheses which are closely related to the α, β and γ classes. In general, all these syntheses have for their Fourier coefficients a suitable combination of the following information which is available: $|F_N|$, the structure amplitude for the whole structure containing N atoms (say) and $|F_P|$ and $\exp [i\alpha_P]$ the structure amplitude and the phase factor respectively of the known group of P atoms in the structure. In fact, the coefficient used in these syntheses can be put in the general form

$$|F_N|^m |F_P|^n \exp [i\alpha_P] \,.$$

When $m=2$ and $n=1, -1, 0$ we get the α, β and γ classes and when $m=1, n=1, -1, 0$ we get the α', β' and γ' classes respectively. Thus the measured intensities of the reflections given by the crystal are used in the 'undashed' syntheses, while their square roots are used in the 'dashed' syntheses. It will be recognized that the γ' synthesis which uses the quantity $|F_N| \exp [i\alpha_P]$ as coefficient is the well-known heavy atom synthesis in which the structure amplitude of the whole crystal and the phases of the heavy-atom contribution are employed. For the α, β and γ classes it has been shown that it is more advantageous to modify the term $|F_N|^2$ into $(|F_N|^2 - |F_P|^2 - \Sigma^2_{Qj})$ where the f_{Qj}'s refer to the scattering factors of the unknown $Q(=\text{N–P})$ atoms. These quantities are known and the effect is to suppress both the peaks at the known atomic positions and the interactions between them. A similar modification is also possible in the dashed syntheses for centrosymmetric crystals, by taking $(|F_N| - |F_P|)$ instead of $|F_N|$ alone and this eliminates the known atoms.

The theoretical aspects of the application of these syntheses to non-centrosymmetric and centrosymmetric structures, under various situations, as for example when anomalous scatterers are present in the structure or when two isomorphous compounds are available etc., were discussed in the earlier papers. The present paper contains an account of the results of working out the various syntheses for the centrosymmetric projections of some known structures. As will be seen below, all the syntheses reveal the positions of the unknown atoms as expected from theory.

A modified form of the 'phase synthesis' (Ramachandran & Raman, 1959) was also tested on a centrosymmetric projection and this is also discussed in the next section.

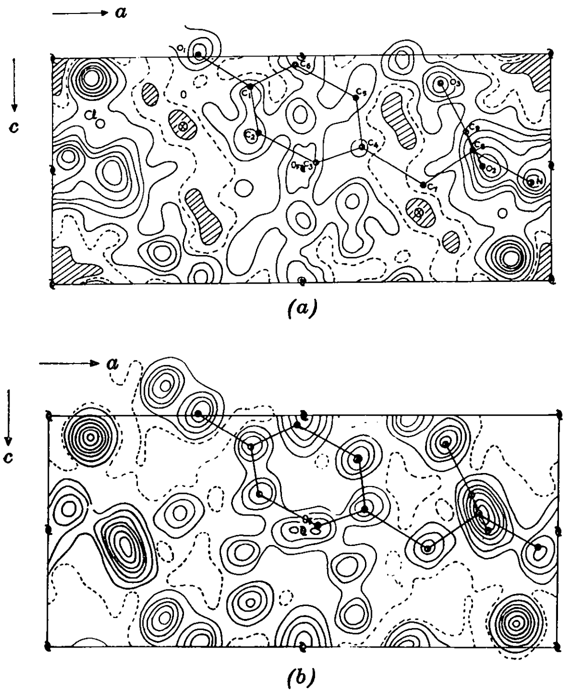
2. Data for the calculation of the syntheses

The various syntheses were tested mainly on the centrosymmetric b-axis projection of L-tyrosine hydrochloride (Srinivasan, 1959*a*) though, however, the results of the application of one or two of these syntheses to two other structures, namely L-tyrosine hydrobromide (Srinivasan, 1959*b*) and L-cystine dihydrobromide (Ananthakrishnan & Srinivasan, 1960) also proved useful in testing the theory. Actually, the β_{mod} synthesis for L-cystine dihydrobromide was calculated during the analysis of its structure and was found to be very helpful for working out one of its projections. The crystallographic data for these compounds are briefly given below for reference.

	L-Tyrosine hydrobromide ($C_9H_{11}O_3N.HBr$	L-Tyrosine hydrochloride ($C_9H_{11}O_3N.HCl$)	L-Cystine dihydrobromide ($C_6N_2O_4S_2.2HBr$)
a	11·38 Å	11·07 Å	17·91 Å
b	9·12 Å	9·03 Å	5·35 Å
c	5·18 Å	5·09 Å	7·48 Å
β	91·2°	91·8°	—
Sp. gr.	$P2_1$	$P2_1$	$P2_12_12_1$
Z	2	2	2

3. The phase synthesis

The close resemblance of the phase synthesis $\exp[i\alpha]$ to the Fourier synthesis, $|F|\exp[i\alpha]$, has already been pointed out by Ramachandran & Raman (1959), when discussing the nature of the various standard syntheses such as $|F|$, $1/|F|$, $\exp[i\alpha]$ etc. Though, in a way, this seems to stress the importance of the phase angles, a test of the relative importance of the phase angles and the structure amplitudes was thought worthwhile. In order to study this a modified form of the phase synthesis was devised. The modification consisted in not using unit amplitudes for all reflections as in our $\exp[i\alpha]$ synthesis but a value equal to $\sqrt{(\Sigma f_j^2)}$, which is the mean for all reflections having the same value of $(\sin\theta/\lambda)$. The consequence of this will be that the peaks will not be sharp, but will have a width corresponding to an average atom in the structure. Thus, in effect, the magnitudes of the geometrical structure factors of all reflections are made equal, but all of them are multiplied by a mean atomic scattering factor. However, the phases were taken to be the same as those calculated for the structure. We shall call this synthesis the 'normalised phase synthesis', the normalisation being such that $\Sigma|F|^2$ is the same for both the Fourier synthesis and the phase synthesis.



(a)

(b)

Fig. 1.* (a) The normalized phase synthesis and (b) the Fourier synthesis of L-tyrosine hydrochloride projected along the b axis. Contours at intervals of 1 e.Å^{-2}. The dashed contour corresponds to 1 e.Å^{-2}. Shaded areas correspond to troughs.

This synthesis was computed for the centrosymmetric b-axis projection of L-tyrosine hydrochloride. For each reflection the sign of the calculated structure factor (Srinivasan, 1959a) was used along with the value of $\sqrt{(\Sigma f_j^2)}$ at the value of $(\sin\theta/\lambda)$ corresponding to the particular reflection, which could be obtained easily from a graph. The resultant synthesis is shown in Fig. 1(a) which compares extremely well with the full Fourier synthesis (Fig. 1(b)). It will be noticed that although all the $|F|$'s in a small range of $(\sin\theta/\lambda)$ were made equal, the atoms are not equal in strength in the synthesis. The chlorine atom, in particular, has come out quite strongly, and the relative heights of the other peaks also agree closely with those in the Fourier synthesis. There are also practically no large spurious peaks in the map. The existence of a negative peak at $\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Pk}$ as demanded by theory is also noteworthy.

This diagram thus confirms the great importance of the phase angles in a Fourier synthesis, as was deduced from a theoretical study of the phase synthesis.

4. The other syntheses

The various other syntheses mentioned earlier were evaluated with the idea of testing how well they reveal the rest of the atoms in a structure when the positions of some are known. This was done for the centrosymmetric projections of three compounds and is discussed below.

Since all the projections on which calculations were made were centrosymmetric, the various syntheses reduce to the following.

$$\alpha_{\text{gen}} = |F_o|^2|F_P|\exp[i\alpha_P] = S|F_o|^2|F_P| \tag*{(1}$$

$$\alpha_{\text{mod}} = S(|F_o|^2-|F_P|^2-\sum_j f_{Qj}^2)|F_P| \tag{2}$$

$$\beta_{\text{mod}} = \alpha_{\text{mod}}/|F_P|^2 \tag{3}$$

$$\gamma_{\text{mod}} = \alpha_{\text{mod}}/|F_P| \tag{4}$$

$$\gamma' = S|F_o| \tag{5}$$

$$\gamma'_{\text{mod}} = S(|F_o|-|F_P|)\ . \tag{6}$$

In the above formulae S refers to the sign of the structure factor F_P. Also, $|F_o|^2$ stands for the observed intensity which was used instead of $|F_N|^2$, the intensity calculated from the whole structure, in order to see the effects, if any, of the small errors in the observed data.

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* In all the Figures (1) to (4) the origin of the Fourier synthesis is marked O_F.

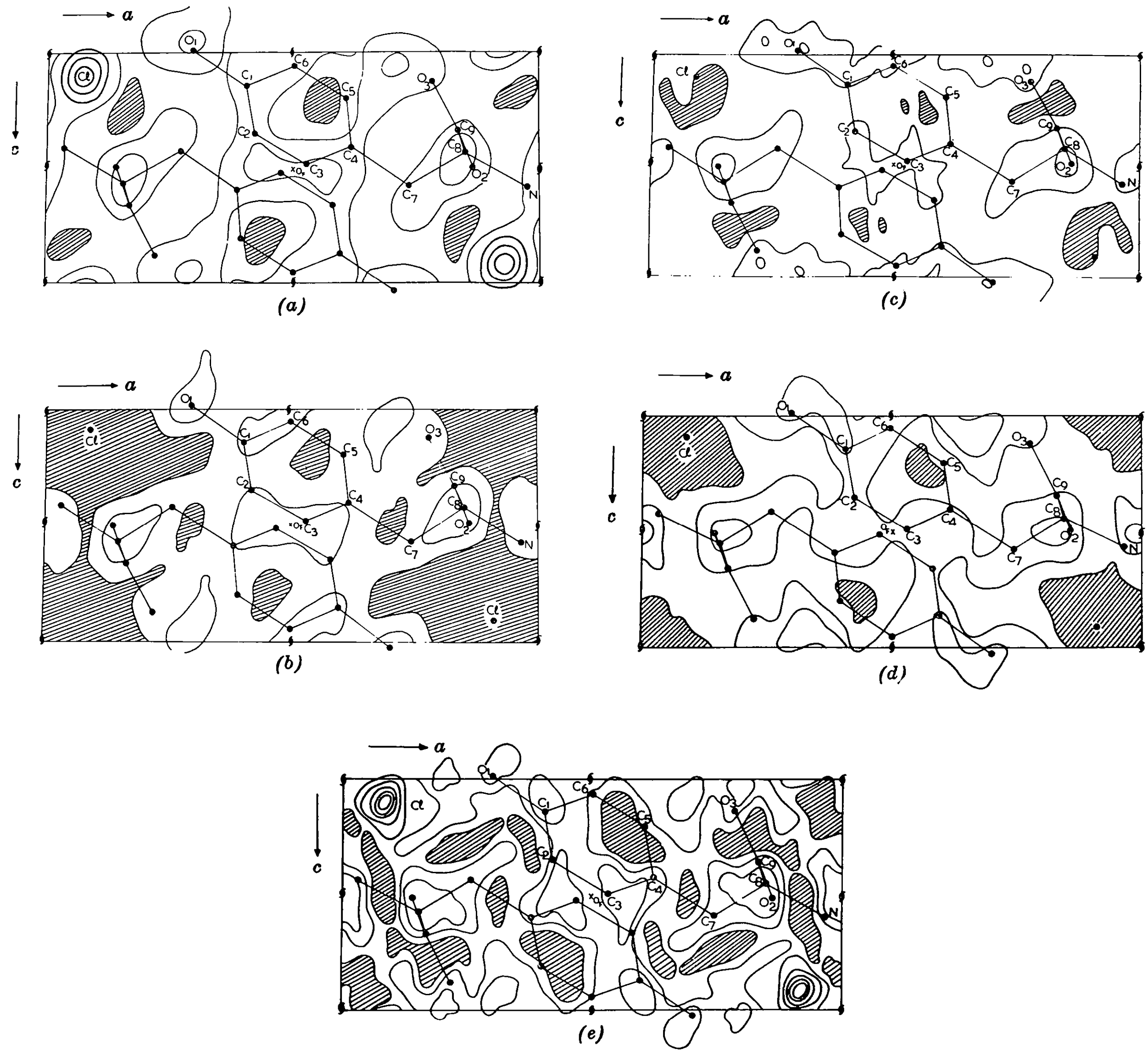
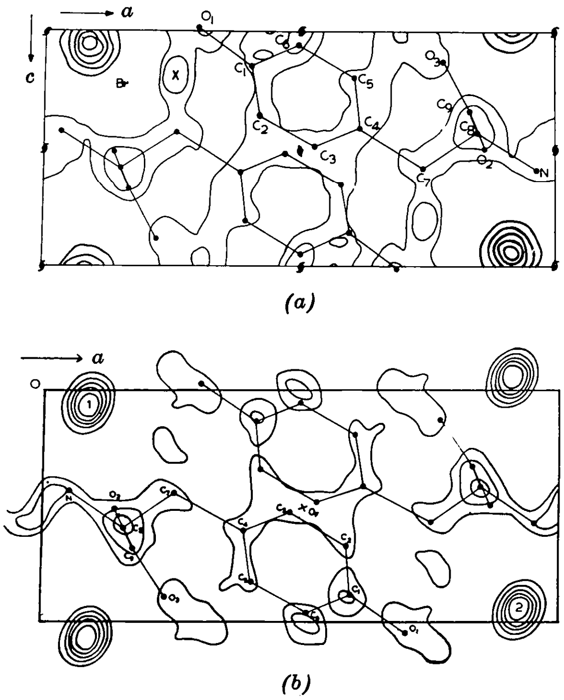


Fig. 2. (*a*) α_{gen}, (*b*) α_{mod}, (*c*) β_{mod}, (*d*) γ_{mod} and (*e*) γ' (heavy-atom) synthesis of L-tyrosine hydrochloride projected along the *b* axis. Shaded areas correspond to troughs.

The first five syntheses, (1) to (5), were calculated for the centrosymmetric *b*-axis projection of L-tyrosine hydrochloride where the chlorine atom was chosen as the known group of *P* atoms, so that all the other atoms (9 carbons, 3 oxygens and 1 nitrogen) formed the unknown group of *Q* atoms. These syntheses are shown in Figs. 2(*a*) to 2(*e*).

For L-tyrosine hydrobromide (which is isomorphous with the hydrochloride) α_{gen} was calculated (Fig. 3(*a*)) and it can be compared with the minimum function (Fig. 3(*b*)) which had been computed earlier during the structure analysis of this compound. In this case the two bromine atoms were chosen for the known group *P*. The minimum function was also obtained using the Br–Br vector in the projection of the Patterson function.

In the case of L-cystine dihydrobromide the β_{mod} and γ'_{mod} syntheses and the minimum function were calculated for the *b* axis projection at a stage when, during the structure analysis, only the positions of the bromine and sulphur atoms had been determined from the Patterson function. For the calculation of the β_{mod} and γ'_{mod} syntheses the known group of *P* atoms was therefore taken as bromine and sulphur. The minimum function plot was, however, calculated using only a single Br–Br vector deduced from the Patterson function. These syntheses are shown in Figs. 4(*a*) to 4(*c*).



(a)

(b)

Fig. 3. (a) α_{gen} synthesis and (b) minimum function diagram of L-tyrosine hydrobromide projected along the b axis.

The calculation of the syntheses, α_{gen} and γ' does not require a knowledge of the scale factor, but the maps contain the known atoms in addition to certain unwanted and rather strong interactions between them. In the modified syntheses, these are eliminated but one then requires a knowledge of the scale factor. In the case of L-tyrosine hydrochloride and L-tyrosine hydrobromide, since the structure analysis had been completed, the correct scale factor could be used for the calculation of these syntheses. For L-cystine dihydrobromide, however, we used the scale factor determined from a Wilson plot.

All the observed reflections could be included in the syntheses of the α and γ classes whether of the modified or unmodified types. However, in the β class, (e.g., β_{mod} Figs. 2(c), 4(a) above) coefficients with small values of $|F_P|$ had to be omitted (see Ramachandran & Raman, 1959). In the β_{mod} synthesis we omitted those reflections for which $|F_P|$ was small but the numerator, $(|F_N|^2-|F_P|^2-\Sigma f_{Qj}^2)$ was large, so that the coefficient β_{mod} was significantly larger than the average value for the particular range of $(\sin\theta/\lambda)$. A better criterion would be to omit all those reflections for which $|F_P|$ was less than one fifth the root mean square value for the particular range of $(\sin\theta/\lambda)$, i.e., the value of $|F_P|^2$ is less than 4% of its mean. Actually, an examination of the data used for calculation showed that this criterion was approximately satisfied.

Of the dashed syntheses, only the γ' was evaluated, since it corresponded to the usual heavy-atom synthesis.

5. Discussion

An examination of the various diagrams in Figs. 2, 3 and 4 reveal the following facts. (a) For L-tyrosine hydrochloride, all the syntheses seem to be nearly as good as one another, the only difference being that, in the modified syntheses, the known chlorine atoms are absent. It may be mentioned that the mean contribution of chlorines (namely, $2f_{\text{Cl}}^2$) forms 55% of the total intensity $|F_N|^2$. This corresponds to the ratio S_P^2/S_N^2 of the earlier papers, which was shown there to determine the strengths of the unknown peaks. We shall denote the ratio by σ_P^2, the notation being similar to that adopted by the author in connection with the statistical distribution of intensities (Srinivasan, 1960). However, a number of spurious peaks as well as distortions of the electron density distribution do occur in all the syntheses as may be seen by comparing them with Fig. 1(b), the final Fourier synthesis. However, the atoms in the unknown part occur mainly in regions of high density and it is not at all difficult to fit a model of the structure to any one of the syntheses. (b) In L-tyrosine hydrobromide, since the bromines are much stronger scatterers than chlorines, the ratio σ_P^2 is nearly 85%. Consequently, the unknown structure comes out much more strongly in the α_{gen} synthesis. The existence of the bromine atoms themselves and a false peak at $\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Pk}$ as given by theory is noteworthy (marked in Fig. 3(a)). The close similarity of this diagram to the minimum function shows that the sum function which is α_{gen} is not much inferior to the minimum function in working out the atomic positions from the Patterson function. The false peak at $\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Pk}$ is present in the minimum function also.* (c) The case of L-cystine dihydrobromide is particularly interesting since the syntheses were worked out in this case during the structure analysis and before the structure was known. However, the four bromines and four sulphur positions had been worked out from the Patterson diagram itself to a good degree of accuracy and the ratio σ_P^2 was almost 90% in this case. Therefore it is not surprising that both β_{mod} and γ'_{mod} (heavy-atom synthesis with heavy atom removed) give the rest of the structure to a good degree of accuracy. This may be seen from Fig. 4 where the final atomic co-ordinates have been marked.

The β_{mod} synthesis contains more false detail, but this is partly due to the fact that no great care was exercised in choosing the terms for the summation. This aspect is being examined further.

The minimum function in this case was worked out using only one Br–Br vector for the shift vector, but it has nevertheless revealed the structure fairly accurately. It will be noticed that the diagram (Fig. 4(c))

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* Fig. 3(b) differs from the one given earlier (Srinivasan, 1959a). The false peak at $(\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Pk})$ had escaped notice earlier and only a subsequent close examination of the map revealed its existence.

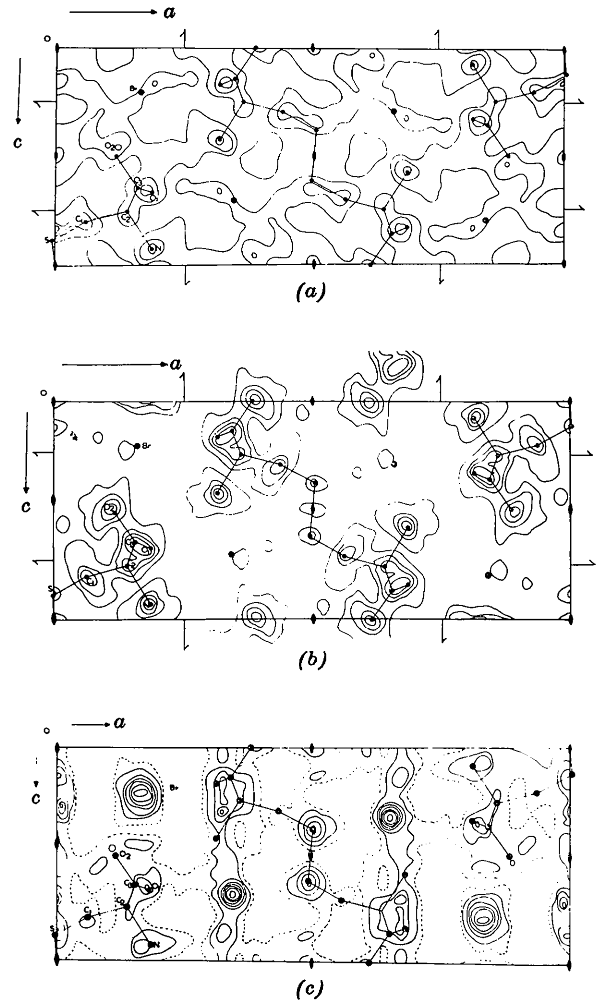

Fig. 4. (a) β_{mod}, (b) γ'_{mod} and (c) minimum function of L-cystine dihydrobromide projected along the b axis.

does not have the space group symmetry of the crystal, in spite of which the co-ordinates of the remaining atoms could be obtained. This indicates the great power of vector shift methods, particularly if a heavy atom is present.

Although the calculation of the various syntheses in the above cases has clearly established their usefulness for revealing the positions of the unknown atoms, it is difficult to say which of them has come out best. This is mainly because the known group of atoms used for the deconvolution of the Patterson contains a major part of the total scattering power of the unit cell (the quantity σ_P^2 is about 55% for L-tyrosine hydrochloride, about 85% for the hydrobromide and more than 90% for the cystine compound). It would be worthwhile trying the tests with a smaller value of σ_P^2, say in the range 30 to 50% and also with a larger number of atoms in the P group. This is being carried out. Also, an exact comparison between theory and experiment, as regards the relative strengths of the peaks in the different syntheses becomes difficult because of the varying background. Consequently, the values of ϱ, the ratio of the strengths of the unknown atoms to those of the known atoms, which have been worked out in Part IV could not be tested here. It is probable that the test could be carried out with three-dimensional calculations. However, since with the facilities available in the laboratory calculations could be made only on projections, this was not attempted.

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