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# The Interpretation of Patterson Functions: An Application of the Superposition Method

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The superposition method of solving Patterson functions was applied, without any prior identification of the nature of any of the Patterson peaks, to the (*hk*0) projection of nitroguanidine. After preliminary considerations concerning the molecular orientation, the correct structure was quickly obtained without any additional assumptions. The method should be of use generally for crystals in which the orientation, but not the position, of a group of atoms of known structure, such as a benzene ring or a carboxyl group, can be deduced.

## Introduction

Recent contributions to the interpretation of Patterson functions have included the vector convergence method of Beevers & Robertson (1950), the vector set and image-seeking methods of Buerger (1951), and the superposition method due to V. Schomaker (Shoemaker, Barieau, Donohue & Lu, 1953). The vector convergence method was statedby its authors to depend upon the presence of a heavy atom; although this restriction is unnecessary (Donohue & Trueblood, 1952) the presence of a heavy atom makes the interpretation of vector convergence diagrams more straightforward. The vector set and image-seeking method, as described by Buerger (1951), depends on the prior identification of the nature of at least three peaks in the Patterson function. In the simple example of $FeSb_2S_4$ used by Buerger, this identification was easy, but in a more complicated structure such Patterson peaks between atoms related by symmetry elements are usually swamped by more general interactions. The superposition method, in its most general form, is subject to no prior information whatever, except knowledge of the numbers, kinds, and shapes of atoms present. It depends solely upon the obvious property of the Patterson function that if its origin is placed at any atom, then all other atom centers must lie either on resolved peaks or in regions of relatively high vector density. Consequently, if the origin of the Patterson function is placed at more than one atom, all atom centers must lie on peaks in all of the Patterson functions. Possible atomic positions accordingly may be located at the coincidences of peaks in the superposition of the several Patterson functions. The superpositions may be initiated by choosing first a peak which appears to be resolved in the original Patterson function and proceeding from promising coincidences, or by making use of such additional structural knowledge as may be available.

In the determination of the structure of nitroguanidine (Bryden, Donohue, Burkhardt & Hughes, 1955) use was made of the superposition method in a way which should be capable of further application. It is particularly interesting that after the failure of Harker–Kasper inequalities to solve the structure—a situation due in part to an overestimation of the scale factor by 30%—the subsequent use of the superposition method led quickly to the correct structure.

## Experimental

The usual experimental procedures are described in the paper concerned with the results of the complete structure determination (Bryden *et al.*, 1955). Results pertinent to the present problem are that nitroguanidine crystals are orthorhombic, with

$$a_0 = 17{\cdot}58,\ b_0 = 24{\cdot}83,\ c_0 = 3{\cdot}58\ \text{Å}.$$

The space group is *Fdd*2, and there are 16 molecules in the unit cell. The projection on (001) is centrosymmetric, and, since $c_0$ is so small, is expected to be fully resolved. Of the 144 (*hk*0) reflections accessible to Cu $K\alpha$, 113 were observed. These were placed on an absolute scale by the method of Wilson (1942). A Patterson projection on (001), shown in Fig. 1(*a*), was then prepared from these data. Since the resolution was so poor, two procedures first suggested by Patterson (1935), namely sharpening and removing the peak at the origin, were then applied. This projection, shown in Fig. 1(*b*), did not appear to have any serious diffraction effects even though no convergence function had been employed. As may be seen, the resolution was greatly improved.

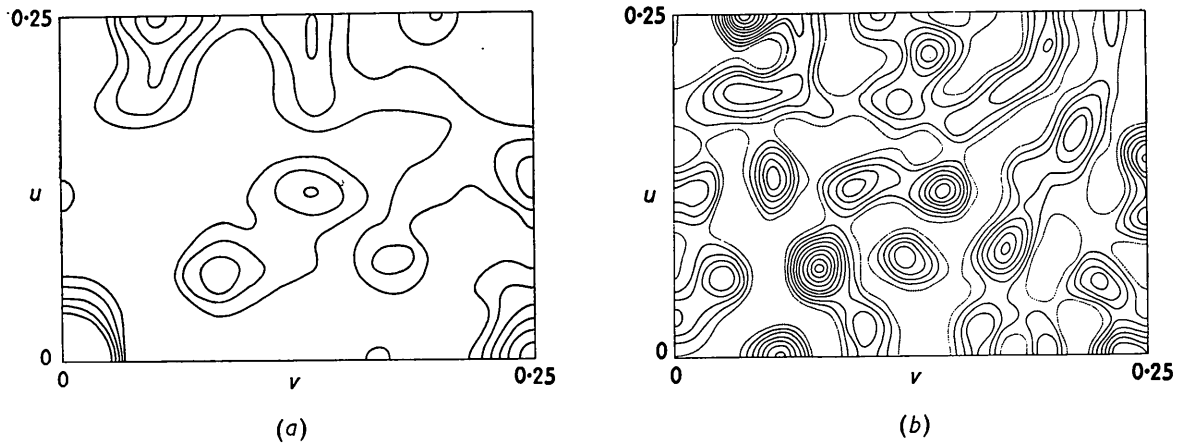
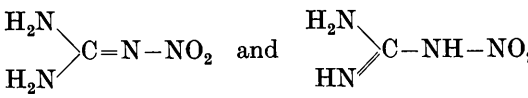


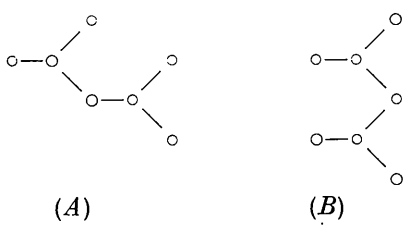

Fig. 1. (*a*) Unsharpened Patterson projection down the *c* axis for nitroguanidine. (*b*) Sharpened Patterson projection down the *c* axis for nitroguanidine. The peak at the origin has been removed.

## Interpretation

There are two possible chemical formulas for nitroguanidine,




At this stage these two may be considered indistinguishable, and, moreover, the two ends of the molecule may also be considered the same because of the similarity in scattering factors of carbon, nitrogen and oxygen. Also, as a first approximation, a reasonable trial structure is one in which all bonds are about 1·35 Å and all bond angles are 120°. The hexagonal array of the peaks near the origin of the Patterson projection suggests a molecular orientation in which one or more of the covalent bonds are parallel to $b_0$. There are then only two unique possibilities, *A* and *B*:




The six remaining orientations are derived from either *A* or *B* by the operations of the space group. Considering only intramolecular interatomic vectors in equivalent molecules, these orientations give different sets of interactions, as shown in Fig. 2. Comparison with Fig. 1(*b*) shows that orientation *A* is obviously the correct one.

With the orientation of the molecules fixed, an attempt was then made to locate the position of the molecules relative to the origin of the unit cell, but no unique solution could be found.

A superposition plot was then prepared. The atom positions in a reasonable molecular model placed in orientation *A* were taken as the origins in seven successive overlaps of the Patterson projection. The resulting plot is shown in Fig. 3; the contours enclose regions which are positive in all seven projections, the origins of which lie at the seven atoms of molecule *M* in the lower left-hand corner. Since one-quarter of the projected unit cell contains four molecules, two of which are related to molecule *M* by the *d* glide planes,

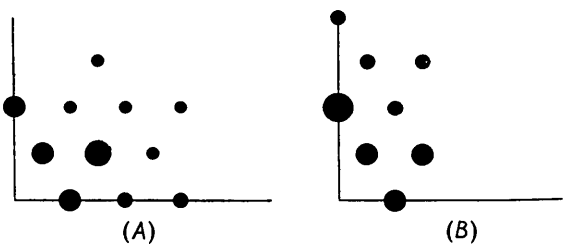



Fig. 2. Intramolecular interactions for orientations *A* and *B* for nitroguanidine. The sizes of the circles are proportional to the number of interactions per peak.

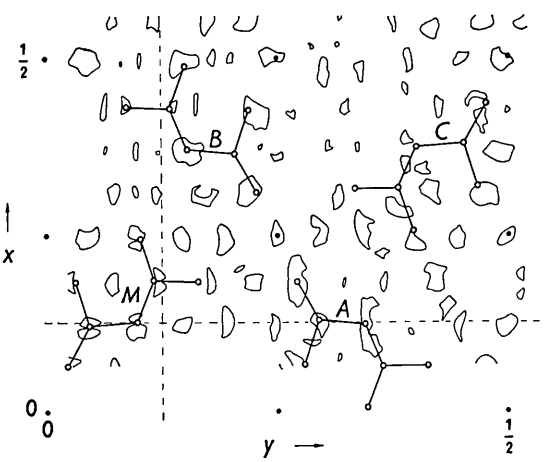



Fig. 3. Sevenfold superposition plot for the (*hk*0) zone of nitroguanidine, prepared from the sharpened Patterson projection down the *c* axis (Fig. 1(*b*)).

the location of molecule $M$ with respect to the origin is accomplished by locating, in the superposition plot, positions for the molecule for which the atoms lie in (or near) regions enclosed by the contours. This procedure is aided by consideration of the symmetry operations. Molecule $A$, which is related to $M$ by a $d$ glide parallel to the $y$ axis, must lie $\frac{1}{4}b$ along $y$ from $M$, in a reflected orientation. The location of $A$ in Fig. 3 is the only reasonable one for a molecule related to $M$ in this way. Thus the origin with respect to the $x$ axis is fixed. Similar considerations locate molecule $B$, and thus the origin with respect to the $y$ axis. This fixes the position of the fourth molecule in the quarter-cell, $C$, which is related to $M$ by a 2 or $2_1$ axis. The agreement in the case of molecule $C$ is not too good, and recourse was made to several incomplete superposition diagrams, which were prepared with less than the full number of seven overlapping Patterson projections. It was noted that good agreement with the postulated origin could be obtained from these incomplete diagrams, and, moreover, that a sevenfold overlap of positive regions was in some cases quite sensitive to the dimensions of the molecular model chosen. After preliminary adjustment of some of the parameters with Bragg–Lipson charts of the structure factors of 15 low-order reflections, the positions of the atoms as shown in Fig. 3 were then used as the start in successive Fourier projections. During the course of the Fourier refinement of this zone, the ambiguity with respect to which end of the molecule was the nitro group, and which the guanidine group, was easily resolved and the ultimate Fourier projection was calculated. These procedures, together with the determination of the $z$ parameters and a discussion of the results, are described fully elsewhere (Bryden *et al.*, 1955).

Table 1. *Initial and final atomic parameters*

| Atom | Parameter | Superposition | Final Fourier |
|---|---|---|---|
| C | $x$ | 0·182 | 0·1981 |
| | $y$ | 0·115 | 0·1176 |
| $N_1$ | $x$ | 0·242 | 0·2578 |
| | $y$ | 0·098 | 0·0932 |
| $N_2$ | $x$ | 0·182 | 0·1961 |
| | $y$ | 0·163 | 0·1721 |
| $N_3$ | $x$ | 0·123 | 0·1361 |
| | $y$ | 0·097 | 0·0968 |
| $N_4$ | $x$ | 0·117 | 0·1306 |
| | $y$ | 0·042 | 0·0420 |
| $O_1$ | $x$ | 0·180 | 0·1773 |
| | $y$ | 0·030 | 0·0114 |
| $O_2$ | $x$ | 0·058 | 0·0748 |
| | $y$ | 0·022 | 0·0255 |

It is of interest to compare the parameters obtained from the superposition plot with those obtained from the final Fourier analysis. This is done in Table 1. The average shift in a parameter from the trial structure was 0·19 Å, and the maximum shift was 0·45 Å.

## General conclusions

Since the accuracy of the trial parameters depends in large part on the exact dimensions and orientation chosen for the starting molecule, it seems highly likely that an even better set of trial parameters could be obtained in the case where the dimensions of the molecule, or part of a molecule, could be predicted with more confidence than in the present example. Such would be the case with a benzene ring, a peptide residue, or a carboxyl group (including the $\alpha$-carbon atom), providing, of course, the orientations of these groups could be fixed with narrow limits. There remains also the unfortunate circumstance that it is not always to be expected that interatomic interactions will lie within positive regions of the Patterson function (Donohue & Trueblood, 1952). For this reason, cautious use of incomplete superposition plots should also be made before rejecting a particular trial structure.

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