

SHORT COMMUNICATIONS

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Recognition and use of systematically aberrant phase relationships. By DOYLE BRITTON* and JACK D. DUNITZ. *Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland*

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Abstract

Conventional application of direct methods sometimes fails because of systematically aberrant triples. The structure of 8-nitro-1-naphthonitrile, $C_{11}H_6N_2O_2$, provides an example. Here the procedure of Thiessen & Busing [*Acta Cryst.* (1974), **A30**, 814–821] could be used to identify such aberrant triples. The trial structure could then be found straightforwardly. Some situations where aberrant triples may cause trouble are discussed.

8-nitro-1-naphthonitrile is monoclinic, space group $P2_1/c$, $Z = 8$. An attempt to find a trial structure with the centric direct methods subroutine in *SHELX* (Sheldrick, 1976) was unsuccessful. A similar attempt with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) gave two parallel planar fragments each consisting of three six-membered rings fused around a central atom. Attempts to improve the situation with Fourier maps were unsuccessful.

The Patterson map showed the pattern of a benzene ring in the peaks about the origin. This confirmed the *MULTAN* result that all the six-membered rings had the same orientation. Thiessen & Busing (1974) have recognized that this situation leads to systematically aberrant phase relationships, where $S_h S_k S_{h+k} \approx -1$ rather than $+1$. They pointed out that unless aberrant triples are recognized as such and allowed for, the phase-determining process will go wrong. Thiessen & Busing (1974) made some tests on a structure that had already been solved, but, as far as we know, their approach has not been used to solve an unknown structure. Here we report an example.

The main idea is indicated by the following quotation from Thiessen & Busing (1974): 'To the extent that any crystal structure is dominated by a system of similarly oriented benzene rings occupying the same or parallel planes, its phase relationships with large values of $|E(-h) E(k) E(h-k)|$ will be normal or aberrant depending on whether the corresponding relationships in the correctly oriented benzene transform are normal or aberrant.' This is illustrated in Fig. 1 where the zeros in the Fourier transform of a benzene ring have been superimposed on the distribution of strong

reflections ($|E| \geq 1.48$) in the reciprocal lattice of our crystal, projected in a direction normal to the molecular plane. The transform is positive with maximum value 6 within the nearly circular regions, and negative with minimum value -2 between the positive regions. Triples involving three reciprocal-lattice points from the positive regions (+++) or one from a positive region and two from negative regions (+--) are normal. Triples involving three reciprocal lattice points from the negative regions (---) are aberrant. The pattern is such that strong triples involving a single reciprocal lattice point from a negative region (-++) are rare. A convergent, but wrong, solution is obtained by assuming all the triples to be normal. In general, the transforms of structures containing parallel benzene rings are more complex, but normal and aberrant triples remain the same as would be produced by the simple benzene transform.

With the use of a local program, the signs of about 70 reflexions were found unambiguously from normal triples

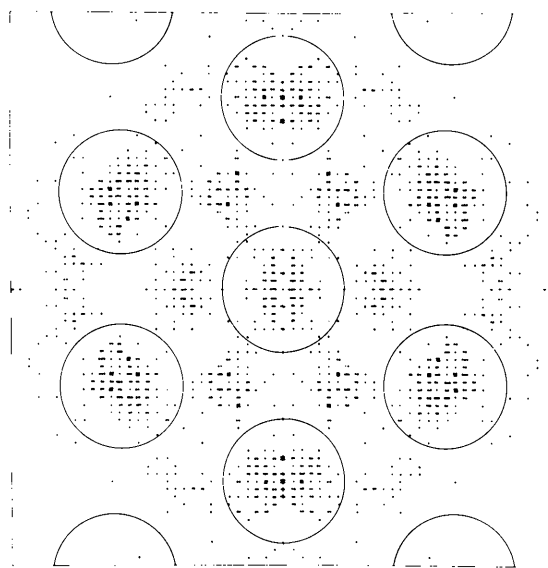


Fig. 1. A view of the Bragg reflexions having $|E| > 1.48$ seen along the normal to the plane of the molecules. The circles show the zeros for the Fourier transform of an isolated benzene ring.

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and the phases of about 70 more were found in terms of a symbolic sign A . The value of A was then determined from 53 aberrant triples with about 85% consistency. A much higher level of consistency is not expected since the three E 's in each aberrant triple are seldom very large (the negative regions in the benzene transform reach only one-third the height of the positive regions). One *MULTAN* cycle based on these 140 reflexions with fixed signs led to an E map in which we could easily identify all 30 non-hydrogen atoms in the two molecules.

In retrospect, the structure could probably have been determined from the initial *MULTAN* E map with a little more persistence on our part, since 20 of the 30 highest peaks turned out to be correct in the end. However, most of the atoms belonging to the ring substituents were missing and, moreover, the false peaks allowed three possible orientations of each naphthalene group. The eventual solution would not have been so straightforward.

We have seen here an example of planar, parallel, similarly oriented, six-membered rings giving rise to aberrant triples at a troublesome level. The question arises: are all these conditions (planar, parallel, similarly oriented, six-membered, ring) necessary for the same difficulty to arise? If we restrict our attention to planar rings it would appear that the only other essential feature is that the rings must be parallel. It is well known that the Fourier transform of a circle (*i.e.* the limit of an n -membered ring) is a zeroth-order Bessel

function. This has a negative annulus of depth 0.4 times the magnitude of the origin peak, *i.e.* this trough is relatively even deeper than in the benzene transform and it will produce aberrant triples in just the same way. The arguments of Thiessen & Busing (1974), that pairs of such rings give rise to more complex transforms but to the same aberrant triples, still hold. If rings with equal numbers of atoms lie in parallel planes but in dissimilar orientations, the transform will be complex, in general, but the real part will be similar to the Bessel function, and aberrant triples will still occur. Hence aberrant triples can be a problem when a structure is dominated by similar, parallel, planar rings. Three- and four-membered rings are too far from circular for our argument to apply.

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A varying-step algorithm for the numerical integration of Takagi-Taupin equations. By Y. EPELBOIN, *Laboratoire de Minéralogie-Cristallographie, associé au CNRS, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris CEDEX 05, France*

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Abstract

A varying-step algorithm is presented which allows the automatic selection of the step for the integration of Takagi-Taupin equations.

Takagi-Taupin equations may be solved analytically only in a few cases. Various methods have been suggested for numerical integration (Taupin, 1964; Authier, Malgrange & Tournarie, 1968). More recently Petrashen (1976) has suggested a varying-step algorithm to take into account the fast oscillations of the amplitude of the wave fields near the edges of the Borrmann fan. The main difficulty is in finding a method of adapting the local integration step to its best value. We have developed an algorithm in which this step is automatically chosen throughout the numerical integration.

This new algorithm permits either faster calculations by a factor of two to three without increasing the precision of the integration or a much better accuracy in all details of simulated images of Lang section topographs.

It is based upon the following three considerations:

- (1) Choosing of integration step is dependent upon the local value of the extinction distance (Epelboin, 1977).
- (2) The interaction of a defect with the wave fields is weaker near the reflected edge of the Borrmann fan.
- (3) The amplitude of the wave fields increases tremendously in the direction of the direct image of a defect whenever it exists.

Firstly, the integration network is established according to the above ideas.

For this purpose the zeros of the J_0 Bessel functions are calculated and the horizontal integration step is chosen in such a way that between two zeros at least five steps are calculated (Fig. 1). It is thus possible to calculate the amplitudes of the wave fields near the edges of the Borrmann fan without losing any oscillation.

To decrease the computation time the integration step may be increased wherever the amplitudes of the wave fields vary more slowly. Moreover, the integration step may be larger near S_n than near S_0 , due to the weak interaction of any defect with the wave fields.