

## 2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

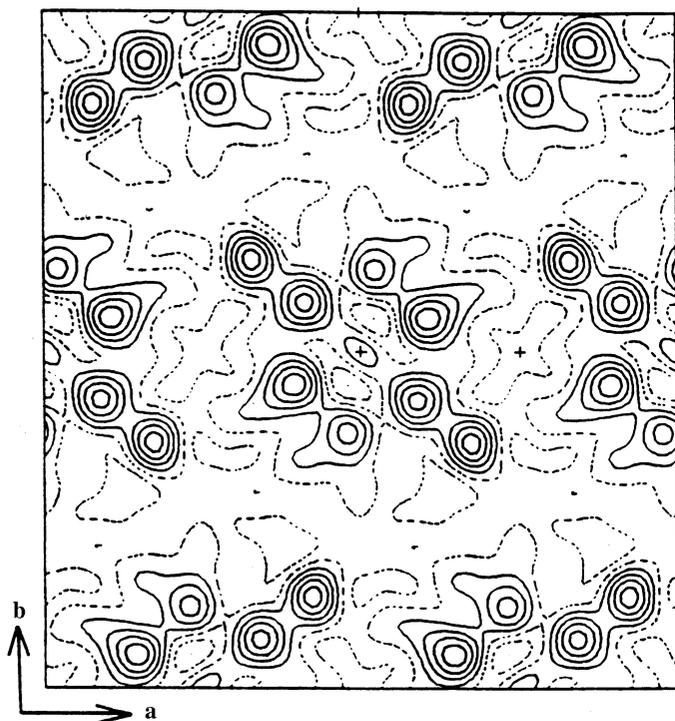


Fig. 2.5.8.1. Potential map for diketopiperazine ([001] projection) after a direct phase determination with texture electron-diffraction intensity data obtained originally by Vainshtein (1955).

can be particularly effective for structure analysis. Of particular importance historically have been the  $\Sigma_2$ -triple invariants where  $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0$  and  $\mathbf{h}_1 \neq \mathbf{h}_2 \neq \mathbf{h}_3$ . The probability of predicting  $\psi = 0$  is directly related to the value of

$$A = (2\sigma_3/\sigma_2^3)|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|,$$

where  $\sigma_{\mathbf{h}} = \sum_{j=1}^N Z_j^n$  and  $Z$  is the value of the scattering factor at  $\sin \theta/\lambda = 0$ . Thus, the values of the phases are related to the measured structure factors, just as they are found to be in X-ray crystallography. The normalization described above imposes the point-atom structure (compensating for the fall-off of an approximately Gaussian form factor) often assumed in deriving the joint probability distributions. Especially for van der Waals structures, the constraint of positivity also holds in electron crystallography. (It is also quite useful for charged atoms so long as the reflections are not measured at very low angles.) Other useful phase invariant sums are the  $\Sigma_1$  triples, where  $\mathbf{h}_1 = \mathbf{h}_2 = -1/2\mathbf{h}_3$ , and the quartets, where  $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 + \mathbf{h}_4 = 0$  and  $\mathbf{h}_1 \neq \mathbf{h}_2 \neq \mathbf{h}_3 \neq \mathbf{h}_4$ . The prediction of a correct phase for an invariant is related in each case to the normalized structure-factor magnitudes.

The procedure for phase determination, therefore, is identical to the one used in X-ray crystallography (see Chapter 2.2). Using vectorial combinations of Miller indices, one generates triple and quartet invariants from available measured data and ranks them according to parameters such as  $A$ , defined above, which, as shown in Chapter 2.2, are arguments of the Cochran formula. The invariants are thus listed in order of their reliability. This, in fact, generates a set of simultaneous equations in crystallographic phase. In order to begin solving these equations, it is permissible to define arbitrarily the phase values of a limited number of reflections (three for a three-dimensional primitive unit cell) for reflections with Miller-index parity  $hkl \neq ggg$  and  $\sum_i h_i k_i l_i \neq ggg$ , where  $g$  is an even number. This defines the origin of a unit cell. For noncentrosymmetric unit cells, the condition for defining the origin, which depends on the space group, is somewhat more

complicated and an enantiomorph-defining reflection must be added.

In the evaluation of phase-invariant sums above a certain probability threshold, phase values are determined algebraically after origin (and enantiomorph) definition until a large enough set is obtained to permit calculation of an interpretable potential map (*i.e.* where atomic positions can be seen). There may be a few invariant phase sums above this threshold probability value which are incorrectly predicted, leading either to false phase assignments or at least to phase assignments inconsistent with those found from other invariants. A small number of such errors can generally be tolerated. Another problem arises when an insufficient quantity of new phase values is assigned directly from the phase invariants after the origin-defining phases are defined. This difficulty may occur for small data sets, for example. If this is the case, it is possible that a new reflection of proper index parity can be used to define the origin. Alternatively,  $\phi_n = a, b, c \dots$  algebraic unknowns can be used to establish the phase linkage among certain reflections. If the structure is centrosymmetric, and when enough reflections are given at least symbolic phase assignments,  $2^n$  maps are calculated and the correct structure is identified by inspection of the potential maps. When all goes well in this so-called 'symbolic addition' procedure, the symbols are uniquely determined and there is no need to calculate more than a single map. If algebraic values are retained for certain phases because of limited vectorial connections in the data set, then a few maps may need to be generated so that the correct structure can be identified using the chemical knowledge of the investigator. The atomic positions identified can then be used to calculate phases for all observed data (*via* the structure-factor calculation) and the structure can be refined by Fourier (or, sometimes, least-squares) techniques to minimize the crystallographic  $R$  factor.

The first actual application of direct phasing techniques to experimental electron-diffraction data, based on symbolic addition procedures, was to two methylene subcell structures (an  $n$ -paraffin and a phospholipid; Dorset & Hauptman, 1976). Since then, evaluation of phase invariants has led to numerous other structures. For example, early texture electron-diffraction data sets obtained in Moscow (Vainshtein, 1964) were shown to be suitable for direct analysis. The structure of diketopiperazine (Dorset, 1991a) was determined from these electron-diffraction data (Vainshtein, 1955) when directly determined phases allowed computation of potential maps such as the one shown in Fig. 2.5.8.1. Bond distances and angles are in good agreement with the X-ray structure, particularly after least-squares refinement (Dorset & McCourt, 1994a). In addition, the structures of urea (Dorset, 1991b), using data published by Lobachev & Vainshtein (1961), paraelectric thiourea (Dorset, 1991b), using data published by Dvoryankin & Vainshtein (1960), and three mineral structures (Dorset, 1992a), from data published by Zvyagin (1967), have been determined, all using the original texture (or mosaic single-crystal) diffraction data. The most recent determination based on such texture diffraction data is that of basic copper chloride (Voronova & Vainshtein, 1958; Dorset, 1994c).

Symbolic addition has also been used to assign phases to selected-area diffraction data. The crystal structure of boric acid (Cowley, 1953) has been redetermined, adding an independent low-temperature analysis (Dorset, 1992b). Additionally, a direct structure analysis has been reported for graphite, based on high-voltage intensity data (Ogawa *et al.*, 1994). Two-dimensional data from several polymer structures have also been analysed successfully (Dorset, 1992c) as have three-dimensional intensity data (Dorset, 1991c,d; Dorset & McCourt, 1993).

Phase information from electron micrographs has also been used to aid phase determination by symbolic addition. Examples include the epitaxially oriented paraffins  $n$ -hexatriacontane (Dorset & Zemlin, 1990),  $n$ -tritriacontane (Dorset & Zhang, 1991) and a 1:1 solid solution of  $n$ -C<sub>32</sub>H<sub>66</sub>/ $n$ -C<sub>36</sub>H<sub>74</sub> (Dorset,