ment of these multiple fragments. The A values associated with these triples may be obtained from the magnitude of $E_\mathbf{h}E_\mathbf{k}E_\mathbf{l}$ computed by the chosen phase-invariant equation, where $A = 2\sigma_3/\sigma_2^{3/2}|E_\mathbf{h}E_\mathbf{k}E_\mathbf{l}|$, $\sigma_n = \sum Z_j^n$, Z_j is the atomic number of the jth atom, and the summation is performed over the $m \times n$ atoms in the primitive unit cell. 384 out of the strongest 423 E's had determinable values of $\theta_\mathbf{h}$ for the 31-atom test case, and similarly 359 for the 14-atom example. The accuracy of these initial values given as $\langle\cos(\theta_{\text{true}} - \theta_{\text{calc}})\rangle$ was 0·988 and 0·419 respectively, that is average phase errors of 8·9 and 65°. Out of the initial set of 4930 triples with $A > 1{\cdot}0$ that could be generated by the 423 E's, the 31-atom example produced 3904 accessible triples for which $\langle A\cos(\Phi_{\text{true}} - \Phi_{\text{calc}})\rangle/\langle A\rangle$ was 0·998 by (7) and 0·814 by (3). The 14-atom example accessed 3539 triples for which the corresponding A weighted cosine averages were 0·851 and 0·801. If one considers those triples that have calculated A values greater than 1·0, there are 618 triples computed by (7) with an average cosine discrepancy of 0·933 and 151 triples by (3) with a corresponding value of 0·866. By contrast, there are only 25 unrestricted triples in the original list of 4930 that have A values large enough to warrant an expected cosine exceeding 0·900, and only one that exceeds 0·933. The average error in the estimated values of the phases of the crystal-structure invariants completed by (7) is about ten times better than that produced by (3) in the 31-atom example. Such accuracy is unprecedented for estimates of unrestricted cosine invariants and would appear to be more than adequate to guarantee a structural solution, since, for comparison, it is unlikely that any *ab initio* noncentrosymmetric direct-methods analysis has ever been performed that has had phase relationships approaching this precision. Attempts to improve this accuracy further by quadruple phase refinement (8) with tangent-formula procedures were surprisingly ineffective, in view of the fact that the errors in the estimates of the three-phase invariants were not expected to be interdependently related with those of other triples in a quadrupole relationship. Individual observations indicate that these four triple estimates do not precisely sum to zero, so that the ineffectiveness of this refinement must have some other explanation.

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Note on the Use of Reciprocal-Space Translation Functions for Planar-Molecule Problem Structures

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Abstract

Correlation functions in reciprocal space are applied to 'problem' structures consisting of approximately planar molecules stacked in layers. The relative position of two molecular fragments is determined by a *two-dimensional* translation function. With three-or four-dimensional translation searches two independent fragments can be positioned relative to one another and, simultaneously, relative to a symmetry element.

Introduction

Crystal structures consisting of approximately planar molecules can often be solved by Patterson methods as well as by direct methods. Sometimes direct methods are not successful, and experience has shown that failures more often occur when the planar molecules are stacked in parallel equidistant planes.

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The planar molecules (or fragments) are easily recognized. The problem in such cases is that the positions of the molecules cannot be determined unambiguously.

Different molecules are usually related by space-group symmetry or by a local (pseudo) symmetry element and/or by a translation. (We do not expect direct-methods problems when there are no systematic relations between the molecules.) We can make use of this knowledge to find the positions of the molecules. In this note we show the use of Patterson-type translation functions in reciprocal space.

Method

The family of parallel equidistant planes in which the molecules are stacked is denoted by the indices (HKL). The family (HKL) is defined analogously to Laue indices. A vector $\mathbf{t}$, parallel to (HKL), is given by

$$\mathbf{t} = q_a\mathbf{a}/H + q_b\mathbf{b}/K - (q_a + q_b)\mathbf{c}/L, \qquad (1)$$

where only two independent variables, q_a and q_b, define this three-dimensional vector. Equation (1) describes $\mathbf{t}$ for the general case; simplified expressions for $\mathbf{t}$ can be set up if any of the indices is zero (*i.e.* for a family of planes parallel to one or two unit-cell axes).

The largest common divisor of H, K and L is denoted by m. When $m = 1$, the vector function $\mathbf{t}(q_a, q_b)$ spans all planes (HKL). For $m > 1$, vectors $\mathbf{u}$ may be added to reach other parallel planes. A vector $\mathbf{u}$ is a fixed interlayer vector; for instance, an integer multiple of $\mathbf{a}/H$.

Assume that we have found and identified (for instance, from a direct-methods E map) two molecular fragments, denoted ρ_1 and ρ_2. The fragments may be on the same plane or on neighbouring planes. Partial structure factors for reflections $\mathbf{h}$, calculated from these fragments, are $F_{1\mathbf{h}}$ and $F_{2\mathbf{h}}$, respectively.

If ρ_1 and ρ_2 are symmetry related, then $F_{2\mathbf{h}}$ is directly related to the calculated $F_{1\mathbf{h}}$ values. Otherwise, no symmetry is used in the following argument.

In the present notation ρ_1 is kept fixed, and ρ_2 is allowed to shift on different planes of the family (HKL). Thus shift vectors $\mathbf{t}+\mathbf{u}$ are applied to fragment ρ_2. The partial structure factor for the sum of the two fragments is

$$F_{p\mathbf{h}} = F_{1\mathbf{h}} + F_{2\mathbf{h}} \exp\,[2\pi i\mathbf{h}(\mathbf{t}+\mathbf{u})], \qquad (2)$$

where $\mathbf{t} = \mathbf{t}(q_a, q_b)$ is a two-dimensional variable, and $\mathbf{u}$ are m fixed vectors. Thus we can determine the position of ρ_2 in three-dimensional space by at most m two-dimensional translation searches.

Table 1. *Crystal data of examples*

	FOC1	LU17
	$C_{17}H_{16}N_2O_2$	$C_8H_{10}N_4O_2$
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	8·0164 (5)	15·11 (1)
b (Å)	10·6705 (8)	13·606 (3)
c (Å)	17·5227 (19)	19·877 (6)
α (°)	77·08 (1)	90
β (°)	101·24 (1)	111·92 (3)
γ (°)	99·28 (1)	90
Z	4	16
Reflections	4952	1671
Final R	0·058	0·079

References: FOC1: Beurskens, Beurskens, Apreda, Foces-Foces, Cano & Garcia-Blanco (1984); LU17: Stalhandske, Bruins Slot & Beurskens (1985).

As search function we use the correlation function (Tollin, 1966; Beurskens, 1981, and references therein)

$$Q_{\mathbf{u}}(\mathbf{t}) = \langle |E_{\mathbf{h}}|^2 |E_{p\mathbf{h}}(\mathbf{t}+\mathbf{u})|^2 \rangle_{\mathbf{h}}, \qquad (3)$$

where $|E_{\mathbf{h}}|$ is the observed normalized structure factor and $|E_{p\mathbf{h}}|$ is the normalized equivalent of (2); the average is taken over the reflections with $|E_{\mathbf{h}}|$ greater than a threshold $E_{\min}$.

The function $Q_{\mathbf{u}}(\mathbf{t})$ is easily programmed, and the result is plotted as a function of the parameters q_a and q_b. Maxima in this function correspond to probable positions of ρ_2.

Application

The method allows the positioning of two planar fragments relative to one another. When the two fragments are symmetry related, the method is equivalent to a conventional translation search, except that for space group $P\bar{1}$ a three-dimensional problem is now solved by a two-dimensional search. The resulting reduction of computer time involved allows the expansion of the method to include the simultaneous positioning of two fragments relative to one another *and* to symmetry-related fragments.

Examples

The present procedure was tested on a known structure, code name FOC1, and was used to solve an unknown structure, code name LU17, see Table 1.

The test structure FOC1 has molecules stacked on (024) planes. The molecules are nearly planar: ring D is not completely planar, but in a poorly phased E map this ring will show up as part of a planar ring system.

MULTAN (Main *et al.*, 1980) and some *DIRDIF* runs (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens, Parthasarathi, Bruins Slot & Haltiwanger, 1984) led to the so-called chicken-wire pattern (Fig. 1). The structure was solved in several parallel *DIRDIF* runs by manually breaking the manyfold positional and rotational ambiguities. It was found that symmetry-independent molecules are rotated by a local rotation of 60° around an axis perpendicular to the molecular planes.

With the present procedure, this structure could be solved easily. One fragment, ρ_1, is a planar fragment: rings *A*, *B* and *C* and the two oxygen atoms. The second fragment, ρ_2, is the inverse of ρ_1. The aim of this application is to determine the position of the center of symmetry by a two-dimensional search. The position of the center of symmetry is either on or between the (024) planes (*i.e.* $\mathbf{u} = \mathbf{0}$ or $\mathbf{u} = \mathbf{b}/2$). Therefore, two parallel searches are needed. Structure factors for fragment ρ_1 are calculated, while structure factors for fragment ρ_2 are their complex conjugates.

The highest maximum in one of the two $Q_\mathbf{u}(\mathbf{t})$ maps appeared to be correct, and a single subsequent *DIRDIF* run in space group $P\bar{1}$ with the shifted fragment ρ_1 as input revealed all non-H atoms of both independent molecules.

The unknown structure, LU17, consists of molecules stacked on the (006) planes. Only four of the six (006) planes through the unit cell contain the enprofylline molecules; this, however, was not known at the outset of the present investigation. The molecules are planar with the exception of the *n*-propyl chains.

From *MULTAN E* maps, as well as from *DIRDIF* Fourier maps based on the correct orientation of one enprofylline molecule, in which many well defined molecules could be recognized, the following problems arose. Equally oriented symmetry-independent molecules were recognized in different layers, molecules in one layer were related to one another by a local rotation of 60°, additional local symmetry elements were found, the center of symmetry could be either on or between the (006) planes and an unequal distribution of the sixteen molecules over the six planes in the unit cell was required.

The present procedure was applied to solve the structure. The correct orientation of a rigid fragment from the literature ($C_5N_4O_2$, Mercer & Trotter, 1978) was found with the orientation search program *ORIENT*, which is a part of the *DIRDIF* system. This fragment, ρ_1, was fixed on one of the (006) planes. A second, equally oriented fragment, ρ_2, was allowed to shift on an adjacent (006) plane and both fragments were positioned relative to the *c*-glide plane. Thus, a three-dimensional search, with two parameters for the positioning of ρ_2 relative to ρ_1 and one parameter for the positioning of the *c*-glide plane, was performed, in which four fragments contributed to the calculation of E_{ph}. The $Q_\mathbf{u}(\mathbf{t})$ map did not show any outstanding peak, but a large number of tentative positions of ρ_1 and ρ_2 relative to the *c*-glide plane was obtained. They were tested, subsequently, with *DIRDIF* in space group *Pc*. The fourth peak yielded a Fourier map that revealed all non-H atoms and the space-group symmetry, $P2_1/c$, was confirmed by this solution. [In case of failure, we would have tried to position the second fragment on another (006) plane!]

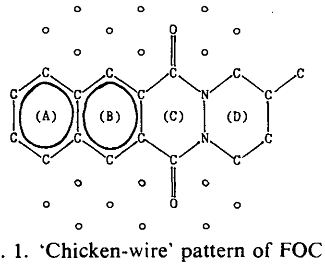

Fig. 1. 'Chicken-wire' pattern of FOC1.

Discussion

The two examples clearly show the advantages of reciprocal-space translation functions based on Patterson methods. Direct-methods approaches to solve structures consisting of approximately planar molecules stacked in layers sometimes fail because of the existence of positional (and sometimes also rotational) ambiguities. The expansion and refinement of phases by the tangent formula is strongly influenced by these ambiguities. It is not generally understood that this problem is related to failure of origin and/or enantiomorph fixation. The phases, calculated for a known fragment, may fix the origin and enantiomorph in the 'direct-methods' terminology but not in reality and tangent expansion will lead to multiple images. The present procedure to overcome these problems is intrinsically better because the correct positions of fragments are always present, although they might be hidden in a large number of possible peaks in the $Q_\mathbf{u}(\mathbf{t})$ map. When the present method finds the relative position of fragments, and if the resulting collection of fragments defines a unique part of the structure, the origin and enantiomorph ambiguities are solved.

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