

radiation as an intense source of X-rays enables the precise measurement of some of the critical exponents (β and γ). Careful experiments should be performed to understand the nature of the transition discussed here and to gain a better insight into the ordering of intercalated atoms in other dichalcogenide systems. We hope to accomplish a detailed study of this transition in the future.

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SHORT COMMUNICATIONS

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A full-symmetry translation function: the influence of model misorientation. By J. RIUS and C. MIRAVITLLES, *Instituto 'Jaime Almera' CSIC, c/. Martí i Franqués, s/n Box 30, 102 Barcelona, Spain*

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Abstract

A translation function is described which takes into account the full space-group symmetry. It can be easily computed by means of a standard Fourier program with modified coefficients and seems to be applicable if search-model orientation errors are less than 5°. This function has been tested on three structures.

At present most medium-sized molecular crystal structures are solved almost automatically using direct methods. However, if the systematic application of direct methods fails, and if the geometry of the molecule under study is totally or partially known, there exists another possibility for solving the structure. It consists of first obtaining the proper orientation of the molecule using a rotation function. Occasionally, direct methods furnish an *E* map which already reveals a structural fragment properly oriented but misplaced with respect to a permissible origin for the unit cell. The oriented molecule is then positioned with respect to the crystal symmetry elements by means of the so-called translation functions, which work either in intensity space (Tollin & Cochran, 1964; Tollin, 1966; Crowther & Blow, 1967; Karle, 1972; Langs, 1975; Beurskens, 1981; Harada, Lifchitz, Berthou & Jolles, 1981) or in vector space (Huber, 1965; Braun, Hornstra & Leenhouts, 1969; Nordman & Schilling, 1970).

The translation function $\tau(\mathbf{r})$ discussed in this paper is defined as the sum of the products of the observed and calculated cross-Patterson functions over the unit cell, for a given position \mathbf{r} of the input molecule in the unit cell, *i.e.*

$$\begin{aligned}\tau(\mathbf{r}) &= V \int_{\text{unit cell}} \text{cross-}P_o(\mathbf{x}) \times \text{cross-}P_c(\mathbf{x}) d^3\mathbf{x} \\ &= V^{-1} \sum_{\mathbf{h}} |\mathbf{F}'_o(\mathbf{h})|^2 |\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2.\end{aligned}\quad (1)$$

Crowther & Blow (1967) showed that

$$|\mathbf{F}'_o(\mathbf{h})|^2 = |\mathbf{F}_o(\mathbf{h})|^2 - \sum_j |\mathbf{S}_j(\mathbf{h})|^2, \quad (2)$$

where $\mathbf{F}_o(\mathbf{h})$ is the observed structure factor and $\mathbf{S}_j(\mathbf{h})$ [hereafter: $\mathbf{S}_j(\mathbf{h}) = \mathbf{S}_j$ and $\mathbf{F}_o(\mathbf{h}) = \mathbf{F}_o$] is the molecular structure factor computed with the atomic coordinates obtained after applying the rotation matrix R_j to the input oriented molecule, referred to a fixed local origin in the molecule.

The Fourier coefficients of the calculated cross-Patterson expressed as a continuous function of the molecular position \mathbf{r} can be evaluated after Crowther & Blow (1967) and Harada *et al.* (1981) by means of the following expression:

$$\begin{aligned}|\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2 &= \text{Re} 2 \sum_j \sum_{k>j} \mathbf{S}_j \mathbf{S}_k^* \exp[-i2\pi \mathbf{h} \mathbf{t}_{kj}] \\ &\quad \times \exp[-i2\pi \mathbf{h}_{kj} \mathbf{r}]\end{aligned}\quad (3)$$

with $\mathbf{t}_{kj} = \mathbf{t}_k - \mathbf{t}_j$, $\mathbf{h}_{kj} = \mathbf{h}(R_k - R_j)$ and \mathbf{t}_j = translation of the *j*th space-group symmetry operation. Introducing (2) and

Table 1. *Crystal and test data for the three structures*

	(I)	(II)	(III)
Molecular formula	C ₂₈ H ₂₇ NO ₇ · H ₂ O	C ₂₄ H ₃₀ O ₉	C ₂₇ H ₃₂ N ₂ O ₂
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	Pccn
a (Å)	10·239	8·605	18·0616
b (Å)	11·352	15·669	15·5616
c (Å)	22·952	17·117	16·9051
Z	4	4	8
Number observed reflections [F > 3σ(F)]	1836	766	2128
Model size (atoms)	16	14	12
Scattering fraction	0·36	0·36	0·36
σ of refined atom coordinates (Å)	0·007	0·021	0·016

(3) into (1), $\tau(\mathbf{r})$ takes the definitive form

$$\tau(\mathbf{r}) = \text{Re} (2/V) \sum_{\mathbf{h}} \sum_j \sum_{k>j} \{ [F_o]^2 - \sum_l |S_l|^2 \} S_j S_k^* \times \exp [-i2\pi \mathbf{h} \cdot \mathbf{t}_{kj}] \exp [-i2\pi \mathbf{h} \cdot \mathbf{r}_j]. \quad (4)$$

The best fits between observed and calculated cross-Patterson functions are always characterized by a maximum of the $\tau(\mathbf{r})$ function. In general, there will be as many peaks in the τ function as there are permissible origins for the unit cell. The molecular positioning is accomplished by adding the coordinates of the correct solution maximum to the input atomic coordinates. Expression (4) is computed by means of a three-dimensional Fourier synthesis. However, for space groups with the origin having one degree of freedom, only a section is required. Function $\tau(\mathbf{r})$ is equivalent to the Crowther-Blow $T_1(\mathbf{t})$ function for crystal structures containing only one symmetry element. For centrosymmetric space groups, the number of Fourier terms in (4) can be reduced by a factor of $N/(2N-2)$ (N = number of symmetry operations). This modification is given in Appendix 1.

To improve the resolution of the τ function, the $|F_o(\mathbf{h})|^2$ are sharpened, and the molecular structure factors are derived using point atoms with thermal motion.

Test calculations

Several test calculations were done to study the evolution of the position and the height of a correct τ peak towards misorientation errors. Three structures were selected: (I) colchicine benzoate monohydrate (Molins, Rius, Solans, Miravittles, Bladé-Font & Germain, 1985), (II) the natural product 'aupopoline' (Rius, Camps, Coll & Miravittles, 1986), and (III) the synthetic compound 2-(*p*-methoxycarbonylphenyl)-1,3,4,4,5,7,7-heptamethyl-2,4,5,6,7,8-hexahydroindeno[1,2-*c*]pyrrole-5-carbonitrile (Miravittles, Rius, Camps, Coll & Mola, 1986).

Relevant data for these structures are listed in Table 1. Three sets of atom coordinates at different refinement stages (Table 1) were used to build the three search models (Fig. 1).

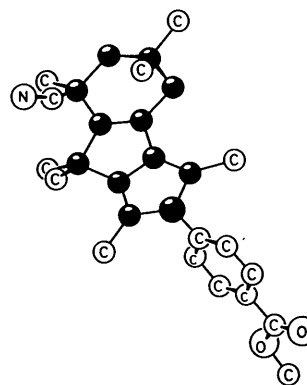
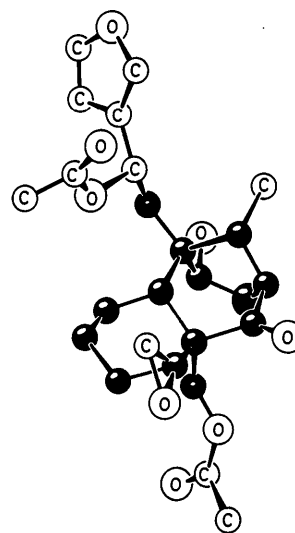
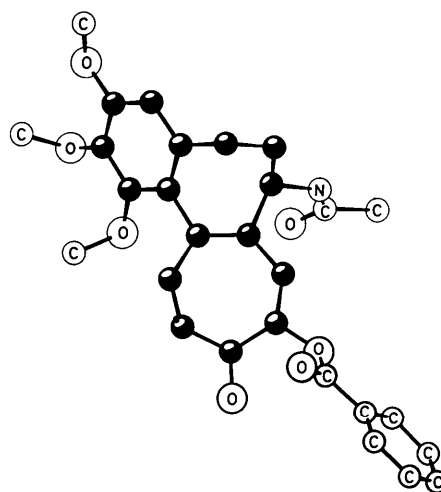


Fig. 1. The molecular conformations for (I) to (III) (H atoms omitted). Full circles define the atoms of the respective search models.

Table 2. Results of the application of the τ function to three test structures

τ_w : height of highest-ranked wrong peak; τ_c : height of correct peak; τ_o : height of correct peak (oriented molecule); s : shift of the correct τ peak from the refined position.

Structure (I)	Oriented	Model Rotated by 5° about the		
		a axis	b axis	c axis
τ_w/τ_c	0.90	0.88	0.92	0.82
Rank number correct peak	1	1	1	1
τ_c/τ_o	—	0.94	0.84	0.86
s (Å)	0.12	0.10	0.14	0.14
Structure (II)				
τ_w/τ_c	1.20	1.45	1.31	1.30
Rank number of correct peak	3	4	3	3
τ_c/τ_o	—	0.87	0.91	0.90
s (Å)	0.09	0.16	0.18	0.15
Structure (III)				
τ_w/τ_c	0.88	0.88	0.89	0.85
Rank number of correct peak	1	1	1	1
τ_c/τ_o	—	0.88	0.91	0.81
s (Å)	0.09	0.09	0.09	0.10

The highest ($\sin \theta/\lambda$) value for the included reflections in the τ synthesis depends on the size and the degree of misorientation of the search model, as well as on the number of grid points in the Fourier map. To determine its optimum value for a medium-sized model misoriented by 5°, a number of preliminary τ syntheses (grid size = 0.3 Å) with the two ($\sin \theta/\lambda$)_{max} values 0.32 and 0.45 Å⁻¹ were performed. Under the same conditions, the best results were always reached for ($\sin \theta/\lambda$)_{max} = 0.45 Å⁻¹, i.e. better resolution and better peak-to-background ratio. Consequently, this was the value employed in the test calculations (Table 2).

The data in Table 2 can be summarized as follows:

(1) With increasing model misorientation, the absolute height of the correct peak decreases; e.g. for an error of 5°, an observed average ratio of 0.88 (4) is found.

(2) Even for properly oriented models (scattering fraction = 0.36), the model position determined with the τ synthesis can show errors of 0.10 Å.

(3) Misorientation errors of 5° can produce positional errors up to approximately 0.20 Å, so that the subsequent structure expansion should not be disturbed.

Although three test structures are by no means sufficient to arrive at a general conclusion, these results seem to indicate that the τ function can be applied successfully in those cases where the model is slightly misoriented (error < 5°).

APPENDIX 1

Simplification of the Fourier expansion of $|\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2$ due to the presence of a symmetry center:

$$|\mathbf{F}_o(\mathbf{h})|^2 = \left\{ \sum_j^N \mathbf{S}_j \exp [i2\pi \mathbf{h} \mathbf{r}_j] \right\} \times \left\{ \sum_j \mathbf{S}_j^* \exp [-i2\pi \mathbf{h} \mathbf{r}_j] \right\},$$

where N is the number of space-group symmetry operations.

Since $\mathbf{S}_j = \mathbf{S}_j^*$ and $\mathbf{S}_j^* = \mathbf{S}_{j'}$ for the j th and j' th molecules related by a symmetry center, then

$$\begin{aligned} |\mathbf{F}'_c(\mathbf{h})|^2 &= |\mathbf{F}_o|^2 - 2 \sum_j^{N/2} |\mathbf{S}_j|^2 \\ &= \text{Re } 2 \sum_j^{N/2} \mathbf{S}_j^* \mathbf{S}_j \exp [-i4\pi \mathbf{h} \mathbf{r}_j] \\ &\quad + \text{Re } 4 \sum_j^{N/2} \sum_{k>j}^{N/2} \mathbf{S}_j^* \mathbf{S}_k^* \exp [-i2\pi \mathbf{h}(\mathbf{r}_k + \mathbf{r}_j)] \\ &\quad + \text{Re } 4 \sum_j^{N/2} \sum_{k>j}^{N/2} \mathbf{S}_j \mathbf{S}_k^* \exp [-i2\pi \mathbf{h}(\mathbf{r}_k - \mathbf{r}_j)]. \end{aligned}$$

If all the molecular position vectors are expressed in terms of one only, and with the following abbreviations,

$$\mathbf{h}_{kj}^+ = \mathbf{h}(\mathbf{R}_k + \mathbf{R}_j); \quad \mathbf{h}_{kj}^- = \mathbf{h}(\mathbf{R}_k - \mathbf{R}_j);$$

$$\mathbf{t}_{kj}^+ = \mathbf{t}_k + \mathbf{t}_j; \quad \mathbf{t}_{kj}^- = \mathbf{t}_k - \mathbf{t}_j,$$

it follows that

$$\begin{aligned} |\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2 &= \text{Re } 2 \sum_j^{N/2} \mathbf{S}_j^* \mathbf{S}_j \exp [-i4\pi \mathbf{h} \mathbf{t}_j] \\ &\quad \times \exp [-i4\pi \mathbf{h} \mathbf{r}] + \text{Re } 4 \sum_j^{N/2} \sum_{k>j}^{N/2} \mathbf{S}_j^* \mathbf{S}_k^* \\ &\quad \times \exp [-i2\pi \mathbf{h} \mathbf{t}_{kj}^+] \exp [-i2\pi \mathbf{h} \mathbf{r}_{kj}^+] \\ &\quad + \text{Re } 4 \sum_j^{N/2} \sum_{k>j}^{N/2} \mathbf{S}_j \mathbf{S}_k^* \exp [-i2\pi \mathbf{h} \mathbf{t}_{kj}^-] \\ &\quad \times \exp [-i2\pi \mathbf{h} \mathbf{r}_{kj}^-]. \end{aligned}$$

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