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Anisotropic Scaling of Three-Dimensional Intensity Data

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Abstract

Three-dimensional diffractometer data collected from single crystals of large and anisotropic mosaic spread were shown to suffer from severe systematic errors. The application of anisotropic scaling of the structure factors in the refinement process proved to be very useful in correcting these errors, yielding more accurate parameters, comparable to those obtained from high-quality crystals.

Introduction

One of the purposes of crystallographic studies of molecular structures is to achieve accurate determination of structure parameters. The result depends on several factors, such as the quality of the crystal, its stability under the measurement conditions, data collection techniques and refinement procedures. Small and medium-size molecules of biological importance are often difficult to crystallize and yield poor-quality specimens of highly anisotropic mosaic spread. When proper scanning modes are not employed due to technical limitations, three-dimensional diffractometer data may suffer from severe systematic errors, which inevitably interfere with structure solution and/or stop the refinement at high R indices, with abnormal anisotropic temperature factors and unsatisfactory geometric parameters. Such effects were observed in the structure analysis of Rb-ADP, (I) (Viswamitra, Hosur, Shakked & Kennard, 1976) and Tris-ADP, (II) (Shakked, Viswamitra & Kennard, 1980).

For both structures, inspection of the data collected on a Syntex $P2_1$ diffractometer by the $\omega/2\theta$ scan technique revealed a systematic discrepancy between observed and calculated structure factors. However, along any given diffracting direction the F_o/F_c ratio was constant, that is independent of either $\sin\theta$ or F_o. The F_o/F_c values for different azimuthal directions varied from 0·7 to 1·4 in (I) and 0·8 to 1·6 in (II). These values were correlated with the large variation in the mosaic spread along these directions as measured by an ω scan of selected reflections; the profile width of these reflections varied from 1·0 to 3·5°. This observation indicated severe losses of the observed intensity measured by the $\omega/2\theta$ scan mode, in directions perpendicular to the longest dimension of the thin plate-like crystals.

An application of a least-squares procedure incorporating anisotropic scaling of the observed structure factors turned out to be most useful in correcting for the observed systematic errors in the data, as reported in a preliminary abstract (Shakked & Rabinovich, 1977).

Results and discussion

In the applied procedure the single scale factor k is replaced by a symmetric tensor (K_{ij}) in the following manner:

$$F_o(\text{scaled}) = F_o/K_H$$

$$K_H = \sum_{i,j=1}^{3} h_i a_i^* h_j a_j^* K_{ij} \Big/ \sum_{i,j=1}^{3} (h_i a_i^*).(h_j a_j^*).$$

h_i and a_i^* are the Miller indices and reciprocal unit-cell vectors respectively. K_{ij} are the components of the symmetric scaling tensor which are refined in the least-squares program together with the usual parameters, where the minimized quantity is

$$\sum_H w|F_o - K_H|F_c||^2.$$

The best refinement strategy turned out to be the following. In the first step the structure is refined isotropically in the usual manner. In the second step, the six components of the scaling tensor are refined in a least-squares program (starting from initial values of 1·0, 1·0, 1·0, $\cos\alpha^*$, $\cos\beta^*$, $\cos\gamma^*$) to obtain the best fit between F_o and F_c. The third step involves the refinement of the usual parameters as well as the scaling tensor. The second step of refinement led to a dramatic decrease of nearly 8% in R for the two structures (Table 1). Only at this stage was it possible to locate the hydrogen atoms by difference Fourier syntheses. In the third step of refinement the components of the scaling tensor were refined together with the atomic coordinates, anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms respectively. A summary of the refinements is given in Table 1.

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Table 1. *Discrepancy* (R) *factors* (%) *and components of the scaling tensor* (K_{ij})

$$R = \sum |F_o - K_H|F_c|| / \sum F_0.$$

	Rb-ADP	Tris-ADP		Perylene*	Perylene†
Isotropic refinement	18	16	Conventional refinement	4·6	1·7
Anisotropic scaling	10	8	Anisotropic scaling	4·0	1·7
Final refinement	8	5			
Number of reflections	1200	1500		2291	2459
K_{11}	0·788 (9)	0·963 (6)		1·068 (7)	0·999 (1)
K_{22}	1·031 (10)	1·719 (11)		1·050 (7)	0·999 (1)
K_{33}	1·587 (20)	0·877 (7)		0·999 (6)	0·999 (1)
K_{23}	−0·002 (9)	−0·201 (7)		0·005 (3)	0·002 (2)
K_{13}	−0·152 (10)	0·028 (5)		0·186 (5)	0·193 (1)
K_{12}	−0·030 (11)	0·009 (5)		−0·021 (5)	0·002 (1)

* $\sin\theta/\lambda < 0·65$ Å^{-1}.
† $\sin\theta/\lambda \geq 0·65$ Å^{-1}.

The possible effects of the scaling tensor on the positional and thermal parameters were examined by using high-quality diffractometer data of perylene measured at liquid-nitrogen temperature (Rabinovich & Hope, 1978). The refinement was carried out for low-order data ($\sin\theta/\lambda < 0·65$ Å^{-1}) and high-order data ($\sin\theta/\lambda \geq 0·65$ Å^{-1}) separately. For the low-order data, significant deviations in the scaling components yielded a significant decrease in the R factor according to Hamilton's (1965) test, whereas no such effects were observed in the refinement of the high-order data (Table 1). These results show that the anisotropic scaling tends to correct for the use of spherical-atom scattering factors in low-order data on one hand, and thus indicating the validity of the spherical-atom approximation for high-order data on the other. For both refinements, the refined atomic parameters were equal within their e.s.d.'s to those obtained in the usual refinement procedure. The anisotropic scaling may also be affected to some extent by absorption effects. However, unlike absorption this scaling is independent of $\sin\theta$.

This procedure has been incorporated in the *SHELX* system (Sheldrick, 1976) and has been applied successfully in other cases (Frolow, Rabinovich & Schurig, 1982).

The anisotropic scaling may be very useful for crystals with large cell dimensions where it is necessary to scan a narrow region of the reflection profile. A combination of an adequate strategy of data collection and refinement procedure may yield accurate data from poor-quality crystals and thus save time and effort in attempts to obtain high-quality crystals.

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