

A Tip for Crystallographic Unit Cell Transformation Verified by a Chiral Compound $[C_{24}H_{22}N_4O_4S]_2HCl$

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Chiral Compound $[C_{24}H_{22}N_4O_4S]_2HCl$ 로 確認한 結晶學的 單位胞 變換時의 한 助言

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Abstract

A crystallographic unit cell can be transformed into another one by a 3×3 transformation matrix. If the determinant of the transformation matrix has a negative value, the newly transformed unit cell becomes a left-handed cell. The best way of transforming the left-handed cell to the right-handed one is to multiply each element of the transformation matrix by -1 , and its corresponding transformation matrix must be applied to the atomic coordinates of a noncentrosymmetric crystal so as to maintain the absolute configuration unchanged. The behaviour of absolute configuration caused by transforming the crystallographic unit cell was examined theoretically and experimentally on the compound (S)-(+)-4-phenyl-1-[1-(4-aminobenzoyl) indoline-5-sulfonyl]-4.5-dihydro-2-imidazolone hydrochloride.

1. Introduction

The selection of the alternative unit cell is sometimes motivated by the consequent convenience. For example, while studying solid-state properties of crystals possessing hexagonal system, it is much more convenient to choose an orthorhombic unit cell than the usual crystallographic hexagonal cell. Similarly, considerable convenience results when face-centered cubic cell is described by a primitive rhombohedral unit cell.

Besides, almost two-thirds of the 230 space groups can be expressed in different ways according to the setting of unit-cell axes.¹⁾ If nonstandard space groups are obtained by, for example, X-ray photographic methods or four-circle diffractometry, it is sometimes desirable to transform them into standard space

groups. In the space group No. 5, for instance, there are three different cell choices ($C2$, $A2$, $I2$), and the nonstandard space groups $A2$ and $I2$ can be transformed into the standard one $C2$ by the right-hand rule as shown in International Tables for Crystallography Vol. A.²⁾ The transformation from the $A2$ to $C2$ can also be carried out by means of a noncyclical interchange of a - and c -axes. In all cases, the right-handed system must be maintained. In this paper, a tip necessary for crystallographic unit cell transformation is given.

2. Theory

Five examples of cell transformation are given below. All calculations were carried out with use of a computer program RLVOLUME.³⁾

(1) transformation of the cubic cell to the rhombohedral cell

Input data

a b c : 1.0 1.0 1.0
 al be ga : 90.0 90.0 90.0
 Volume=1.0

Transformation matrix:

$$\begin{pmatrix} 0.5 & 0.5 & 0.0 \\ 0.0 & 0.5 & 0.5 \\ 0.5 & 0.0 & 0.5 \end{pmatrix} \rightarrow \begin{vmatrix} 0.5 & 0.5 & 0.0 \\ 0.0 & 0.5 & 0.5 \\ 0.5 & 0.0 & 0.5 \end{vmatrix} = +\frac{1}{4}$$

Output data

a b c : 0.70711 0.70711 0.70711
 al be ga : 60.0 60.0 60.0
 Volume=+0.25 (right-handed cell)

(2) transformation of the rhombohedral cell to the cubic cell

Input data

a b c : 1.0 1.0 1.0
 al be ga : 60.0 60.0 60.0
 Volume=0.70711

Transformation matrix:

$$\begin{pmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{pmatrix} \rightarrow \begin{vmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{vmatrix} = +4$$

Output data

a b c : 1.41421 1.41421 1.41421
 al be ga : 90.0 90.0 90.0
 Volume=+2.82843 (right-handed cell)

(3) transformation of the hexagonal cell to the orthorhombic cell

Input data

a b c : 1.0 1.0 1.0
 al be ga : 90.0 90.0 120.0
 Volume=0.86603

Transformation matrix:

$$\begin{pmatrix} 2 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \rightarrow \begin{vmatrix} 2 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = +2$$

Output data

a b c : 1.73205 1.0 1.0
 al be ga : 90.0 90.0 90.0
 Volume=+1.73205 (right-handed cell)

(4) transformation of a triclinic cell to a monoclinic cell

Input data

a b c : 6.54730 14.83150 24.66590
 al be ga : 84.45460 82.38300 77.27830
 Volume=2310.15674

Transformation matrix:

$$\begin{pmatrix} 1 & -2 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & -1 \end{pmatrix} \rightarrow \begin{vmatrix} 1 & -2 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & -1 \end{vmatrix} = +2$$

Output data

a b c : 28.93481 6.54730 27.52591
 al be ga : 89.99303 117.62186 90.02979
 Volume=+4620.31348 (right-handed cell)

(5) noncyclical axis interchange in a monoclinic cell

Input data

a b c : 27.508 6.54080 28.93400
 al be ga : 90.0 117.58 90.0
 Volume=4614.355

Transformation matrix:

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \rightarrow \begin{vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{vmatrix} = -1$$

Output data

a b c : 28.93400 6.54080 27.50800
 al be ga : 90.0 117.58 90.0
 Volume=-4614.355 (left-handed cell)

As can be seen from the above examples, the determinants of the first four transformation matrices are positive, and therefore the newly transformed unit cell volumes have positive signs meaning the right-handed cells. On the other hand, the determinant of the last transformation matrix is negative, and its transformed cell is left-handed one that must be transformed into right-handed cell.

There are three ways to make a 3×3 determinant change its sign:

(1) an interchange of arbitrary two rows, which means an interchange of two crystallographic axes

(2) multiplication of any one of three rows by -1 , which means a reverse of the sense of the crystallographic axis

(3) multiplication of all the three rows by -1 , which means reverse of the senses of all the three crystallographic axes.

The most suitable way applicable to the triclinic system having minimum symmetry is the last method.

3. Experimental Evidence

For the confirmation of the above theory, the absolute configuration of a chiral compound ((S)-(+)-4-phenyl-1-[1-(4-aminobenzoyl)indoline-5-sulfonyl]-4,5-dihydro-2-imidazolone hydrochloride)(I), whose structural details will be published elsewhere⁴⁾ has been examined here in detail.

The compound (I) was elucidated first with the A2 (space group No. 5) which is not only a noncentric but also a nonstandard space group. Table 1 shows its final crystallographic data, with the standard space group C2, obtained from the least-squares refinement program SHELX97.⁵⁾

Table 2 shows variations of the unit cell parameters, the unit cell's handedness, and the absolute configuration of a chiral group (N13, C117, C118, C119, H118), due to the transformation from a space group A2 to C2 by means of noncyclical axis interchanges.

The data of the initial cell parameters including the chiral group are given in row No. 1 in Table 2. As expected, the initial chiral group has a S-configuration, which is same as that of (S)-phenylglycinol used in the synthesis.⁴⁾ The data in rows No. 1, 2 and 3 are for the space group A2 itself and the rest for the C2. The data from columns 4 to 8 are obtained by the operations of the transformation matrices given in the third column to the initial data, where the handednesses were confirmed by the computer program RLVOLUME³⁾, and the coordinates of the

Table 1. Crystallographic data

Crystal data	
$[C_{24}H_{22}N_2O_4S]_2 \cdot HCl$	MoK $_{\alpha}$ Radiation
$M_r=961.49$	$\lambda=0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
C2	$\theta=9.74-13.52^\circ$
$a=28.934(7) \text{ \AA}$	$\mu=0.237 \text{ mm}^{-1}$
$b=6.5408(7) \text{ \AA}$	$T=293 \text{ K}$
$c=27.508(5) \text{ \AA}$	block
$\beta=117.58(1)^\circ$	$0.3 \times 0.3 \times 0.2 \text{ mm}$
$V=4614(1) \text{ \AA}^3$	pale brown
$Z=4$	
$D_x=1.384 \text{ Mg m}^{-3}$	
D_m not measured	
Data collection	
Enraf-Nonius CAD-4 Diffractometer	$R_{int}=0.0677$ $h=-34 \rightarrow 34$
$\omega/2\theta$ scans	$k=-7 \rightarrow 7$
7756 independent reflections	$l=-32 \rightarrow 17$
$\theta_{max}=25.0^\circ$	3 standard reflections
4072 reflections with $I \geq 2\sigma(I)$	frequency: 300 min
Absorption correction: ⁹⁾ semi-empirical	intensity decay: 1%
ψ scans	
$T_{max}=0.9545$ $T_{min}=0.9328$	
Refinement	
Refinement on I	$(\Delta/\sigma)_{max}=0.001$
$R(F)[I > 2\sigma(I)]=0.0684$	$(\Delta/\rho)_{max}=0.283 \text{ e \AA}^{-3}$
$\omega R(F)=0.1533$	$(\Delta/\rho)_{min}=-0.209 \text{ e \AA}^{-3}$
$S=0.990$	Extinction correction: none
	Scattering factors from
604 parameters	International Tables for
H atoms constrained	Crystallography (Vol. C)
$w=1/[\sigma^2(F_o^2)+(0.0466P)^2+0.00P]$	
where $P=(F_o^2+2F_c^2)/3$	

chiral group were obtained by the operations of the transpose of the inverse matrix of the crystallographic axial transformation matrix. Fig. 1 drawn by ORTEP⁶⁾ program⁷⁾ illustrates (S)-configuration of the chiral group in the molecule together with

Table 2. Variations of the unit cell parameters, the unit cell's handedness, and the absolute configuration of a chiral group due to the transformation from a space group $A2$ to $C2$ by means of noncyclic axis interchanges. The correct absolute configurations were confirmed by the Fack parameters in the program SHELX97. The unsuitable data are marked by (x)

No.	space group	transformation matrix	unit cell axes	β	handedness	configuration	chiral group			
							atom	x	y	z
1	A2(x)	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	a, b, c	obtuse	right	S	N13	0.7021	0.5045	0.3908
							C117	0.6398	0.5757	0.3053
							C118	0.6925	0.6609	0.3516
							C119	0.7393	0.6818	0.3386
							H118	0.6848	0.7927	0.3630
2	A2(x)	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	a, -b, c	obtuse	left(x)	R(x)	N13	0.7021	-0.5045	0.3908
							C117	0.6398	-0.5757	0.3053
							C118	0.6925	-0.6609	0.3516
							C119	0.7393	-0.6818	0.3386
							H118	0.6848	-0.7927	0.3630
3	A2(x)	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	-a, -b, -c	obtuse	left(x)	R(x)	N13	-0.7021	-0.5045	-0.3908
							C117	-0.6398	-0.5757	-0.3053
							C118	-0.6925	-0.6609	-0.3516
							C119	-0.7393	-0.6818	-0.3386
							H11	-0.6848	-0.7927	-0.3630
4	C2	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	c, b, a	obtuse	left(x)	R(x)	N13	0.3908	0.5045	0.7021
							C117	0.3053	0.5757	0.6398
							C118	0.3516	0.6609	0.6925
							C119	0.3386	0.6818	0.7393
							H118	0.3630	0.7927	0.6848
5	C2	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	-c, b, a	acute(x)	right	S	N13	-0.3908	0.5045	0.7021
							C117	-0.3053	0.5757	0.6398
							C118	-0.3516	0.6609	0.6925
							C119	-0.3386	0.6818	0.7393
							H118	-0.3630	0.7927	0.6848
6	C2	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	c, -b, a	obtuse	right	S	N13	0.3908	-0.5045	0.7021
							C117	0.3053	-0.5757	0.6398
							C118	0.3516	-0.6609	0.6925
							C119	0.3386	-0.6818	0.7393
							H118	0.3630	-0.7927	0.6848
7	C2	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	c, b, -a	acute(x)	right	S	N13	0.390	0.5045	-0.7021
							C117	0.3053	0.5757	-0.6398
							C118	0.3516	0.6609	-0.6925
							C119	0.3386	0.6818	-0.7393
							H118	0.3630	0.7927	-0.6848
8	C2	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	-c, -b, a	acute(x)	left(x)	R(x)	N13	-0.3908	-0.5045	0.7021
							C117	-0.3053	-0.5757	0.6398
							C118	-0.3516	-0.6609	0.6925
							C119	-0.3386	-0.6818	0.7393
							H118	-0.3630	-0.7927	0.6848

Table 2. Continued

No.	space group	transformation matrix	unit cell axes	β	handedness	configuration	chiral group			
							atom	x	y	z
9	C2	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	c, -b, -a	acute(x)	left(x)	R(x)	N13	0.3908	-0.5045	-0.7021
							C117	0.3053	-0.5757	-0.6398
							C118	0.3516	-0.6609	-0.6925
							C119	0.3386	-0.6818	-0.7393
							H118	0.3630	-0.7927	-0.6848
10	C2	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	-c, b, -a	obtuse	left(x)	R(x)	N13	-0.3908	0.5045	-0.7021
							C117	-0.3053	0.5757	-0.6398
							C118	-0.3516	0.6609	-0.6925
							C119	-0.3386	0.6818	-0.7393
							H118	-0.3630	0.7927	-0.6848
11	C2	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	-c, -b, -a	obtuse	right	S	N13	-0.3908	-0.5045	-0.7021
							C117	-0.3053	-0.5757	-0.6398
							C118	-0.3516	-0.6609	-0.6925
							C119	-0.3386	-0.6818	-0.7393
							H11	-0.3630	-0.7927	-0.6848

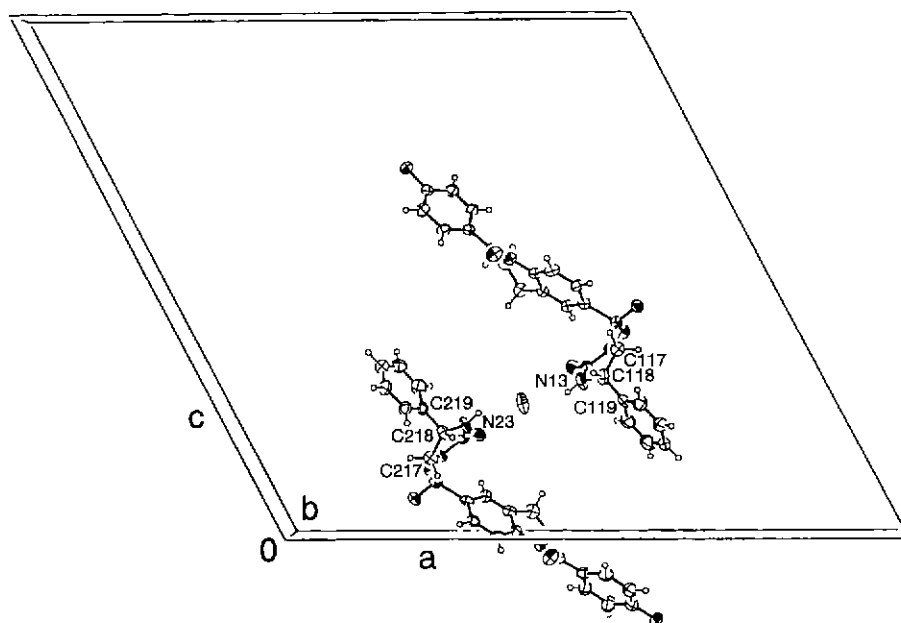


Fig. 1. Only an asymmetric unit (a dimer) of the compound (I) with the standard space group C2 is depicted in a unit cell. Only two chiral groups N13, C117, C118, C119, H118 and N23, C217, C218, C219, H218 in each molecule are labeled and both of them have (S)-configuration. The displacement ellipsoids are drawn at the 36% probability level, and hydrogen atoms are drawn as small circles of arbitrary radii. Hydrogen bonds are not drawn for clarity.

the unit cell, where the absolute configuration was confirmed by the Flack parameters⁸⁾ in the program SHELXL97.⁵⁾

The experimental results in Table 2 make clear that only two transformation matrices given in rows No. 6 and 11 are suitable for the transformation

from A2 to C2. If the compound (I) belonged to a required.

triclinic system, only the last matrix

$$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

must have left, whose determinant is +1.

Therefore it has been confirmed theoretically and experimentally that all elements of the transformation matrix should be multiplied by -1 in case of the noncyclical crystallographic axis interchanges in order to preserve the right-handed cell.

4. Conclusion

If a unit cell is transformed by a 3×3 transformation matrix, it is essential to calculate the determinant of its transformation matrix to make sure whether it is positive. If negative, all terms of the transformation matrix need multiplying by -1 to preserve a right-handed set of axes. Let us say a transformation matrix is P . Then atomic coordinates of a noncentrosymmetric crystal must be transformed by a matrix $[P^T]^{-1}$ to keep up the absolute configuration unchanged, and intensity data must also be transformed by the same matrix P if the crystal structure refinement is

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