values from the present study show an improvement over Berman & Kim's values. This improvement in accuracy combined with corrections for thermal motion represents a significant improvement over the earlier geometrical details and has enabled the equivalence of the C–N bonds and the non-equivalence of the two N–C–O angles to be confirmed at a higher level of precision.

Table 12. *Room-temperature* U_{ij} (*w.r.t. reciprocal axis*) ($Å^2 \times 10^2$)

First row: present work. Second row: Larsen & Jerslev (1966). Third row: Berman & Kim (1967).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	3 16	2 69	2·75	0·35	1·59	−0·23
	3·53	1·32	2·30	−0·43	1·74	−0·18
	2·75	2·09	2·53	0·43	1·37	0·22
N(1)	4·72	3·77	2·63	−0·97	2·03	−0·12
	5·20	3·09	2·67	1·18	2·25	0·27
	4·52	3·36	2·38	−1·10	1·81	−0·30
N(2)	4·14	3·40	2·95	−0·85	1·51	−0·13
	4·81	3·00	2·67	0·36	1·53	−0·09
	3·78	3·19	2·67	−0·72	1·35	0·10
O(1)	4·49	3·97	2·11	0·52	1·44	0·13
	4·97	2·99	2·01	−0·48	1·53	−0·14
	4·35	3·36	1·99	0·56	1·37	0·34
O(2)	4·58	3·80	2·40	−0·52	1·58	0·34
	4·91	2·95	2·32	0·33	1·86	−0·27
	4·07	3·47	2·21	−0·20	1·49	0·29

A comparison of the room-temperature thermal parameters from the three studies can be made from Table 12 which shows that those from the present study lie between those of the two earlier studies, but as the early reports do not quote standard deviations for thermal parameters, no statistical comparison can be made.

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The Key Shift Method. II. Application to Superstructures of Molecular Crystals

BY TETSUZO ITO

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama, 351, *Japan*

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The key shift method, a kind of minimum residual method, has been successfully applied to the structure analysis of superstructures, one known and one unknown, of molecular crystals with eight and eleven non-hydrogen atoms respectively in the asymmetric units. In the latter case, symmetry considerations of the substructure–superstructure relationship were important for the solution. In another case of a known superstructure in which there were 30 independent non-hydrogen atoms at the start of the analysis, shifts of rigid-body molecules were found to be more efficient than those of individual atoms.

Introduction

The key shift method for the structure analysis of superstructures was proposed in a previous paper (Ito, 1973; hereinafter called paper I). The computational procedure is analogous to that of the minimum residual method of Bhuiya & Stanley (1963). Two superstructures of mineral crystals, freieslebenite and jordanite, were solved by this method (Ito & Nowacki, 1974*a*, *b*); a successful application to aramayoite has also been reported (Mullen & Nowacki, 1974). The present paper deals with the application of the method to superstructures of molecular crystals.

Application

The key shift method was first applied to a known structure, triclinic quinhydrone (T. Sakurai, 1965), and then to an unknown structure, 3-amino-4,5-dicyano-1-methylpyrazole (ADCMP) (Prusiner, Sundaralingam, Ito & Sakurai, 1976).

(*a*) *Triclinic quinhydrone*

The triclinic modification of quinhydrone, $C_6H_4O_2.C_6H_4(OH)_2$, is a 1:1 molecular complex of quinone and hydroquinone. The space group is $P\bar{1}$, $Z=1$. Since the hydroquinone and quinone molecules of similar shapes are at the origin and $\frac{1}{2},0,0$ respectively, and are almost parallel to each other, the unit cell is approximately halved along the *a* axis (Fig. 1). Because of the approximate halving, the *h* odd reflexions are very weak compared with the *h* even ones; the ratio of the mean F_o values is 0·20. T. Sakurai (1965) solved the complete structure from the P_o function, that is, the Patterson function obtained with only the *h* odd reflexions (K. Sakurai, 1958).

The key shift method started with the atomic coordinates in the substructure with the *a*/2 axial length.* As is evident from Fig. 1, there are eight independent non-hydrogen atoms in the complete cell. At the start, one half of them are related to the other half by a translation of **a**/2. The 100 strongest reflexions were selected from each set of the *h* even and *h* odd reflexions, and these 200 reflexions were used for the analysis. An overall temperature factor of 2·0 Å^2 was assumed. Each coordinate of each atom was independently varied by ±0·1, ±0·2 and ±0·3 Å from the starting value, and the corresponding *R* values were calculated.

Table 1. *R maps of key shifts of triclinic quinhydrone* (%)

The *R* value before shifts was 23·4%. The asterisks indicate the key shifts.

	Shift	*R*(*x*)	*R*(*y*)	*R*(*z*)
O(1)	−0·3 Å	20·4	23·9	22·6
	−0·2	16·9*	21·0	18·8
	−0·1	18·5	21·0	18·9
	+0·1	18·5	20·9	19·1
	+0·2	17·5**	20·8	18·2
	+0·3	21·0	23·5	22·1
C(1)	−0·3	19·4	22·1	19·9
	−0·2	19·3	21·8	19·4
	−0·1	20·9	22·2	20·7
	+0·1	20·7	21·8	21·2
	+0·2	19·0	20·9	19·5
	+0·3	19·2	21·2	19·7
C(2)	−0·3	18·7	22·2	20·5
	−0·2	19·5	22·0	20·3
	−0·1	21·4	22·3	21·6
	+0·1	21·5	22·4	21·3
	+0·2	20·0	21·7	19·7
	+0·3	19·7	21·4	19·7
C(3)	−0·3	18·9	21·4	18·5
	−0·2	19·4	21·0	18·9
	−0·1	21·1	21·8	20·7
	+0·1	20·5	22·0	21·0
	+0·2	18·4	21·3	19·4
	+0·3	18·2	21·6	19·5

The *R* maps thus obtained are shown in Table 1. The *R* maps for O(2), C(4), C(5) and C(6) are the same as the corresponding maps in Table 1, because the two molecules were exactly related by a translation of **a**/2 before shifts. As can be seen in Table 1, a −0·2 Å shift in the *x* coordinate of O(1) gave the lowest *R* value of 16·9%, a large 6·5% reduction from the original 23·4%. This was the key shift of the structure. A least-squares refinement which adopted only this one shift converged to an *R* of 12·3% for the 200 reflexions, and the structure reported by T. Sakurai with the origin shifted by **a**/2 was obtained. A second least-squares refinement which adopted a +0·2 Å shift in the *x* coordinate of O(1), corresponding to the second lowest *R* in Table 1, also led to the correct structure with the same origin as defined by T. Sakurai (1965).

(*b*) 3-*Amino*-4,5-*dicyano*-1-*methylpyrazole* (*ADCMP*)

The second example was an unknown structure, ADCMP, $C_3N_2NH_2(CN)_2CH_3$. Since details of the structure analysis are described elsewhere (Prusiner *et al.*, 1976), only important aspects of the key shift method as applied to this structure will be discussed. The crystal is monoclinic, space group $P2_1/c$, with $Z=4$. The unit cell is approximately halved along the *c* axis because the pseudo mirror plane of the molecule (Fig. 2) almost coincides with the *c*-glide plane. The substructure with $\mathbf{c}'=\mathbf{c}/2$ in space group $P2_1/m$ (Fig. 3) was extended to the complete structure by the key shift method. Again, the 100 strongest reflexions with *l* even and *l* odd were used for the analysis. The asymmetric unit of the complete structure consists of one molecule of ADCMP (eleven non-hydrogen atoms). The four NC atoms in Fig. 3, of which the atomic

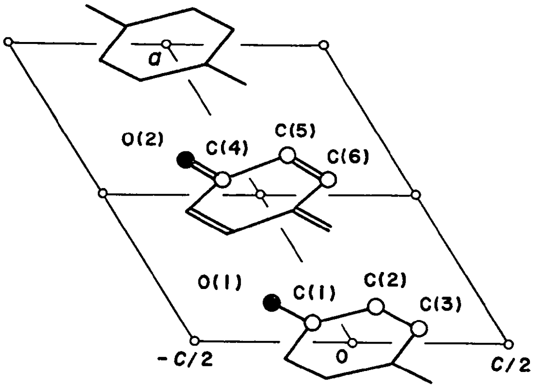

Fig. 1. Triclinic quinhydrone, [010] projection.

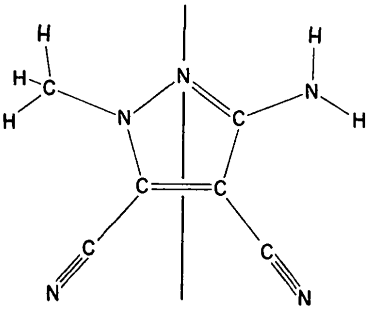

Fig. 2. 3-Amino-4,5-dicyano-1-methylpyrazole (ADCMP). The molecule has a pseudo mirror symmetry.

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* Since the complete structure was known in this case, the atomic coordinates in the substructure were obtained as the appropriate means of those in the complete structure.

species were not known, were assumed to be nitrogens. The R value before shifts was 25·0%.

Two settings had to be distinguished in the extension from the substructure to the complete structure: setting A in which the inversion centres in the complete structure coincide with those at $z'=0$ in the substructure, and setting B in which they coincide with those at $z'=\frac{1}{2}$ (Fig. 3). This ambiguity arises because either of the two sets of inversion centres in the substructure becomes pseudo centres in the complete structure. Setting B proved to be the correct setting; after three cycles with four 0·1 Å shifts of atomic coordinates, the R value was 16·7%. In the above analysis, the indicated key shifts multiplied by a damping factor of 0·5 were adopted for the next cycles. An isotropic least-squares refinement converged successfully to an R of 8·2% for the 200 reflexions, and the atomic species of the four NC atoms were readily known from comparison of the refined B values. It was found later that a least-squares refinement which adopted only the first key shift, a 0·1 Å shift in y of N(1) ($R=21·8$%), also led to the correct structure.

Discussion

Practical suggestions

For an efficient use of the key shift method, several practical suggestions may be added to those given in paper I.

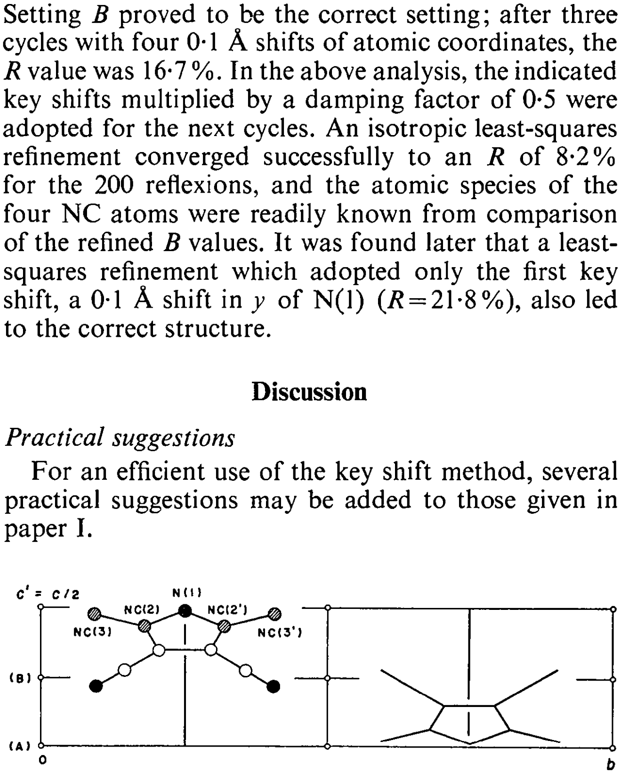

Fig. 3. Substructure of ADCMP in space group $P2_1/m$. (A) and (B) indicate the two sets of inversion centres at $z'=0$ and $\frac{1}{2}$ respectively.

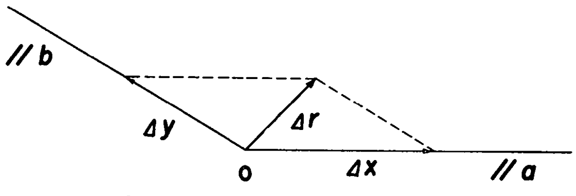

Fig. 4. Key shift in the case of a large interaxial angle. The key shift, $\Delta\mathbf{r}(\Delta x,\Delta y)$, may not be apparent from independent shifts of x and y.

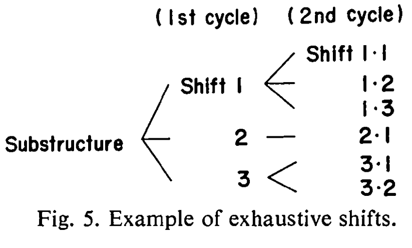

Fig. 5. Example of exhaustive shifts.

(1) Correct space groups must be assigned to the substructure as well as to the superstructure. The substructure–superstructure relationship can then be clearly defined. Furthermore, information on the substructure such as electron density maps and thermal parameters obtained in a correct space group will facilitate the subsequent analysis.

(2) All the different settings must be examined as illustrated in the case of ADCMP. Only one of the two settings was examined in triclinic quinhydrone because the space group $P\bar{1}$ with $Z=1$ required both the hydroquinone and quinone molecules to be on special positions, that is, on inversion centres. Different settings can also arise from symmetry elements other than inversion centres. For example, if a structure in a non-centrosymmetric space group $P2_1$ has a pseudo translation of $\mathbf{c}/2$, two settings similar to the settings A and B in ADCMP must be examined in the extension from the substructure (also in space group $P2_1$) to the complete structure.

(3) The same number of sub- and superstructure reflexions were used in the two examples. This choice will be justified from the following considerations. Let F_1 and F_2 be partial structure factors of the two halves, $0\le x<\frac{1}{2}$ and $\frac{1}{2}\le x<1$ respectively, of a complete structure approximately halved along the a axis. Then, the structure factors of the complete structure are given by: $F(h\text{ even})=F_1+F_2$ and $F(h\text{ odd})=F_1-F_2$. These expressions show that information on the complete structure is contained equally in the h even and h odd reflexions. Similarly, if the complete structure is to be derived from a $\frac{1}{3}$ structure with $\mathbf{a}'=\mathbf{a}/3$, use of approximately the same number of $h=3n$, $3n+1$ and $3n+2$ reflexions will be appropriate.

(4) Since shifts in this method are diagonal, key shifts may not be apparent in R maps if one or more of the unit-cell angles deviates much from $\pi/2$, as shown in Fig. 4. In such cases, shifts along a new set of orthogonal axes will be preferable.

(5) Because of the diagonal approximation, systematic consecutive shifts such as are shown in Fig. 5 will be safer, at least in earlier cycles, if more than one key shift competes in the same cycle.

(6) In the case of a molecular crystal, key shifts indicated by lowest R values are usually overestimates of the correct shifts because atomic shifts are usually correlated strongly with those of adjacent atoms. Damping factors of 0·5–0·7 will be useful.

(7) One or two key shifts are often sufficient for least-squares and Fourier methods of refinement. However, it would be safer, especially for non-centrosymmetric structures, to continue key shifts until most of the subsequent shifts become unambiguous in the R maps; that is, until lower R values are indicated only in either of the plus or minus directions for most of the parameters.*

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* In the first R maps of triclinic quinhydrone (Table 1), lower R values are indicated in both the plus and minus directions for all parameters.

Key shifts of rigid-body molecules

In some superstructures of molecular crystals which consist of many (for example, more than 20) independent non-hydrogen atoms, shifts of rigid-body molecules or fragments of a molecule may be more efficient than those of individual atoms. In fact, key shifts of rigid-body molecules were found to be useful when applied to a known structure, the 1:2 molecular complex of phloroglucinol and *p*-benzoquinone, $C_6H_3(OH)_3.2C_6H_4O_2$ (Sakurai & Tagawa, 1971). The crystal is triclinic, space group $P\overline{1}$, with $Z=1$. The complete structure is a multi-superstructure of a $\frac{1}{6}$ structure with $\mathbf{b}'=\mathbf{b}/3$ and $\mathbf{c}'=\mathbf{c}/2$.

The $\frac{1}{6}$ structure was first doubled along the c axis into a $\frac{1}{3}$ structure by key shifts of individual atoms. There were 12 independent non-hydrogen atoms at the start. Only one key shift of a site occupancy of an O atom from two to unity, which reduced the R value from the original 32·6 to 26·4%, was sufficient to solve the $\frac{1}{3}$ structure. In the extension from the $\frac{1}{3}$ structure to the complete structure, however, reduction of R due to a parameter shift of one atom among 30 starting atoms was so small (about 2% compared with the original R of 42·2%) that the correct structure was obtained only after four cycles with five shifts.

A Fortran program of rigid-body shifts was written and applied. The computational procedure of translational and rotational shifts of rigid-body molecules is analogous to those used in the minimum residual analysis of molecular crystals (Milledge, 1962; Damiani, Giglio, Liquori & Ripamonti, 1967; Sakurai, Ito & Kobayashi, 1968). In the first R maps of rigid-body shifts of the molecules in the extension from the $\frac{1}{3}$ structure to the complete structure, a translational shift of 0·3 Å along the c axis of a quinone molecule gave the lowest R of 34·1% with a large 8·1% reduction. A least-squares refinement which adopted only this one shift led to the complete structure reported by Sakurai & Tagawa (1971).

Although the discussions in paper I and in this article are confined mainly to superstructures of the integer ratio type, the unit-cell translations of which are linear combinations with integer coefficients of those of the substructures (T. Sakurai, 1973), the key shift method may also be useful for superstructures of other types.

The numerical calculations were performed on the FACOM 230/75 computer of this Institute. The author thanks Dr T. Sakurai for his encouragement throughout the work.

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