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A Neutron-Diffraction Study of Potassium Hydrogen Bis-Phenylacetate: Part 2

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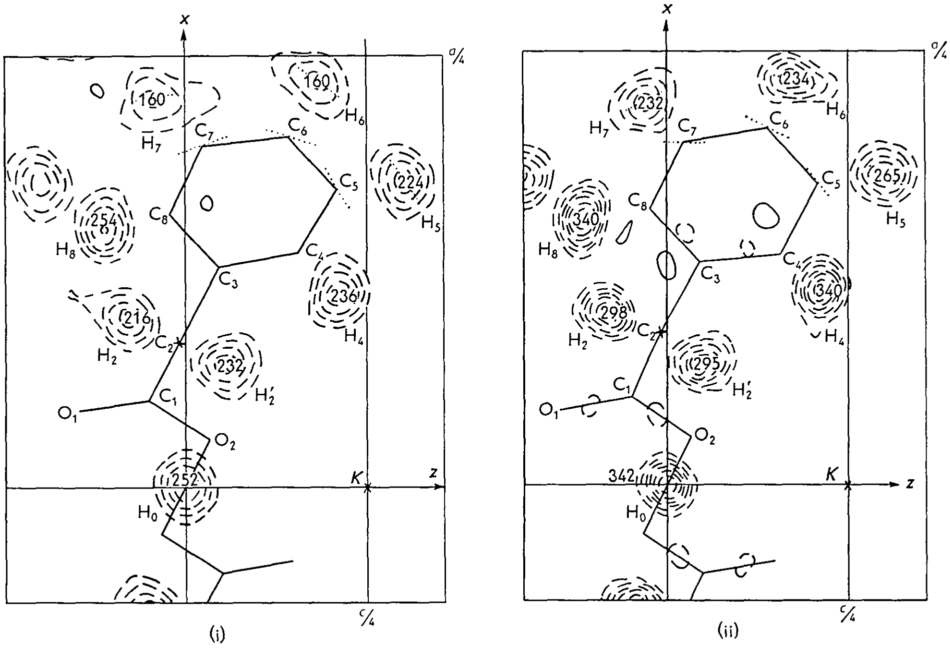
Measurements at 120 °K. lead to the conclusion that the acidic hydrogen takes part in a centred hydrogen bond. A least-squares analysis with anisotropic temperature factors suggests that there is enhanced oscillation of the benzene ring which terminates the molecule and which lies in an open part of the structure.

Introduction

In an earlier paper (Bacon & Curry, 1957) we have described a study of potassium hydrogen bis-phenylacetate by neutron diffraction carried out at room temperature and aimed particularly at detailing the nature of the acidic hydrogen atom at the centre of symmetry. The present paper describes an extension of this work including measurements at a temperature of 120 °K. Again, the main interest has been in the acidic hydrogen atom but in the course of the work some interesting data have been obtained on the atomic and molecular vibrations at both 120 °K. and 293 °K.

Experimental results

The data were obtained with a neutron wavelength of 1·09 Å at the Harwell reactor BEPO using the crystal described in our earlier paper. For the low-temperature measurements the crystal was carried by a goniometer suspended from the inner container of a double-walled Dewar vessel (containing liquid nitrogen) made of aluminium and similar to that described



(i)

(ii)

Fig. 1. The hydrogen atoms in potassium hydrogen bisphenylacetate, as represented by 'difference projections' of the neutron scattering density. These are obtained by Fourier synthesis of the function $(F_o - F_{nH})$, where F_o is the experimentally observed structure factor and F_{nH} is the calculated contribution from all atoms in the structure, other than hydrogen. The relative peak heights of the atoms are indicated in arbitrary units: on the same scale the contours are drawn at intervals of 50 units.

The pattern (i) is for room temperature and (ii) refers to a temperature of 120 °K. Almost all the contours are negative (broken lines) because of the negative scattering amplitude of hydrogen. The rare positive contours are shown by full lines. The dotted lines drawn through the centres of C_5, C_6 and C_7 and H_5, H_6 and H_7 indicate the directions of maximum motion of these atoms as revealed by the least-squares analysis with anisotropic temperature factors.

Table 1. *Atomic parameters and temperature factors at* 293 °K. *and* 120 °K.

	293 °K.							120 °K.						
Atom	x	z	$\bar{B}$	$B_{\text{max.}}$	$B_{\text{min.}}$	φ	$\overline{u^2}$	x	z	$\bar{B}$	$B_{\text{max.}}$	$B_{\text{min.}}$	φ	$\overline{u^2}$
K	0	0·25	3·8				0·048	0	0·25	1·5				0·019
O_1	0·044	−0·149	3·1				0·039	0·043	−0·149	2·0				0·025
O_2	0·028	0·035	1·7				0·021	0·028	0·033	2·1				0·026
C_1	0·050	−0·049	2·5				0·032	0·051	−0·048	1·5				0·019
C_2	0·087	−0·007	3·5				0·044	0·088	−0·008	2·5				0·031
C_3	0·128	0·046	3·1	(3·7	2·4	−75°)	0·039	0·129	0·046	1·9	(2·3	1·4	81°)	0·024
C_4	0·137	0·157	3·2	(4·1	2·0	5°)	0·040	0·136	0·158	2·3	(2·7	1·8	− 6°)	0·029
C_5	0·174	0·209		5·7	3·4	−32°	0·059	0·175	0·209		4·1	2·2	−40°	0·041
C_6	0·203	0·144		8·3	3·0	−71°	0·078	0·206	0·139		5·2	2·0	−62°	0·049
C_7	0·199	0·026		6·1	4·0	+71°	0·065	0·198	0·024		4·3	2·2	+89°	0·042
C_8	0·159	−0·022	4·7	(5·0	4·1	−88°)	0·059	0·160	−0·024	2·4	(2·7	2·0	49°)	0·030
H_0	0	0		7·0	4·3	0°	0·073	0	0		4·0	1·9	−67°	0·039
H_2	0·098	−0·080		9·0	3·5	−56°	0·086	0·099	−0·083		6·5	3·1	−57°	0·064
H_2'	0·071	0·056		8·3	3·8	85°	0·080	0·071	0·049		5·9	3·5	66°	0·060
H_4	0·113	0·213		8·3	3·6	6°	0·080	0·113	0·212		4·9	2·4	10°	0·049
H_5	0·177	0·304		9·0	4·4	−34°	0·089	0·180	0·301		7·1	5·1	−58°	0·077
H_6	0·234	0·181		16·5	4·1	−53°	0·150	0·233	0·176		10·9	2·9	−75°	0·100
H_7	0·224	−0·033		14·5	7·3	86°	0·144	0·220	−0·030		8·1	5·3	63°	0·085
H_8	0·152	−0·109		8·7	3·4	0°	0·082	0·154	−0·116		6·7	1·7	15°	0·061

The values of x, z are given in decimal fractions of the unit-cell edges. Values of B, $\overline{u^2}$ are in Å². φ is the angle between the axis $0x$ and the direction of maximum displacement, a positive value indicating clockwise rotation away from $0x$.

by Bacon & Pease (1955). The tilt of the crystal was controlled by flexible cables which were connected to the goniometer arcs and brought out to the top of the Dewar. Because of the smaller Debye temperature factors it was possible to measure 164 reflexions at the lower temperature, compared with 118 at room temperature.

The results are summarized pictorially in Fig. 1, which compares Fourier projections of the neutron scattering density on the (010) plane at the two temperatures. The diagrams are difference projections indicating hydrogen atoms only. The function which is synthesised is $(F_o - F_{nH})$, where F_o is the observed structure amplitude factor and F_{nH} is the calculated contribution from all atoms other than hydrogen, the calculation being made on the basis of thermal parameters and atomic co-ordinates secured by a least-squares type of refinement.

The least-squares refinement was carried out using the Harwell Mercury computer and a programme devised by A. R. Curtis. The starting values of the atomic co-ordinates and the thermal parameters were those which resulted from our earlier Fourier synthesis of the room-temperature data. Anisotropic temperature factors were computed for all the hydrogen atoms and for the carbon atoms C_5, C_6 and C_7, making a total of 76 independent parameters. At the end of this stage of refinement, which corresponded to a Discrepancy Index of 0·07 at room temperature and 0·08 at low temperature (ignoring in each case all unobserved reflexions), two further cycles were carried out with anisotropic temperature factors for the carbon atoms C_3, C_4 and C_8 also. It was felt that this was not really justified, involving as it did the determination of 82 parameters, but it was carried out in view of the particular interest in the atomic vibrations in the neighbourhood of carbon C_3 which arose during the work. The above Discrepancy Index of 0·07 obtained with anisotropic temperature factors is to be compared with the value of 0·10, ignoring the unobserved reflexions, when isotropic motion was assumed.

Table 2. *Bond lengths in* Å *at* 293 °K., 120 °K.

	293 °K.	120 °K.		293 °K.	120 °K.
C_3–C_4	1·35	1·35	C_4–H_4	1·11	1·05
C_4–C_5	1·39	1·42	C_5–H_5	1·14	1·11
C_5–C_6	1·34	1·41	C_6–H_6	1·14	1·02
C_6–C_7	1·42	1·37	C_7–H_7	1·16	1·03
C_7–C_8	1·44	1·41	C_8–H_8	1·07	1·11
C_8–C_3	1·40	1·41			

Table 1 lists the data given by the least-squares refinements for the two temperatures. From the atomic co-ordinates given here the sets of bond lengths shown in Table 2 have been calculated. In order to deduce the necessary y co-ordinates we have computed by least-squares methods the equation of a 'plane of best fit' for the benzene ring, using our x and z co-ordinates and the y values at room temperature found by Speakman (1949) using X-rays, for carbon atoms only. The hydrogen atoms and the ring carbons were then assumed to lie in this plane and the y-values deduced for each atom.

Discussion

The standard deviations of the atomic co-ordinates are estimated by Cruickshank's (1949) method to be 0·011 Å for the carbon and oxygen atoms and 0·033 Å for hydrogen. For the thermal parameters the standard deviations in B, the Debye factor in the expression

$F=F_o \exp(-B \sin^2 \theta/\lambda^2)$, are calculated to be 0·5, 0·5 and 0·8 for carbon, oxygen and hydrogen respectively at the low temperature and 0·6, 0·7 and 1·1 at room temperature, using the method of calculation provided in Cruickshank's (1956) paper.

The hydrogen atom H_0

At room temperature the amplitude of displacement of the hydrogen atom at the origin, assuming this to be a single centred atom, is (according to the least-squares analysis) a maximum in the direction of the x axis, with a root-mean-square value $(\overline{u^2})^{\frac{1}{2}}$ of 0·30 Å. The displacement is a minimum along $0z$, where $(\overline{u^2})^{\frac{1}{2}}$ is 0·23 Å. At 120 °K. the direction of maximum displacement is at an angle of $-67°$ to $0x$, which is in a direction roughly normal to the hydrogen bond between the two oxygen atoms. The maximum value of $(\overline{u^2})^{\frac{1}{2}}$ is 0·22 Å, in contrast to a value of 0·16 Å along the hydrogen bond.

It is to be noted that in Fig. 1(i) H_0 is not so circular as in Fig. 1(*b*) of our previous paper, where the difference synthesis was based on values of F_{nH} calculated for purely isotropic atoms. However, the least-squares deduction of maximum displacement along $0x$ appears to be in agreement with the contours of the present Fig. 1(i). At first sight the contours of H_0 in Fig. 1(ii) do not seem to support the least-squares conclusion that the direction of maximum displacement is at $-67°$ to $0x$; but this is due to the distortions in the two lowest contours. The remaining four contours are quite reasonably elliptical in shape and inspection of the plot suggests that the direction of maximum displacement is at $-55°$ to $0x$, in fair agreement with the conclusion from least squares, bearing in mind that the determination of the angle φ by least squares can be very sensitive to random errors.

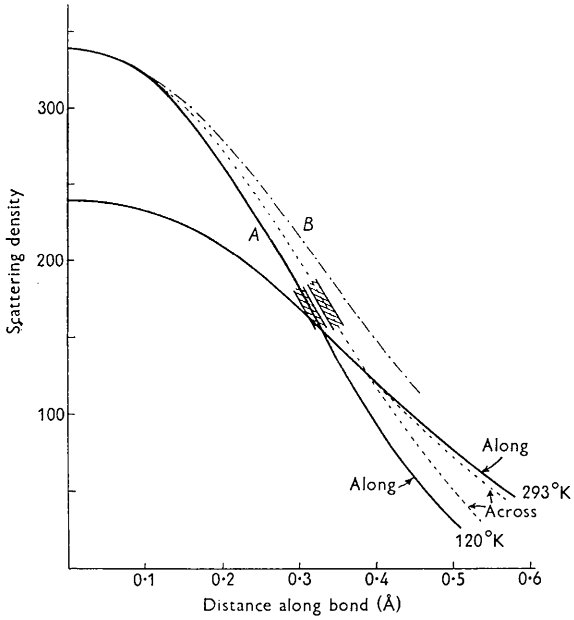


Fig. 2. A summary of the information about the contours of the acidic hydrogen atom at the origin of the unit cell. The full lines and dotted lines show respectively the shape contours along and across the hydrogen bond, at 120 °K. and at 293 °K. The shaded areas on the curves for 120 °K. represent the standard deviation of error in the determination of the curves. The chain-dotted curve B is a calculated curve for two half-hydrogen atoms placed, at ±0·20 Å, on each side of the centre of symmetry. It is concluded that the increased width of shape B in comparison with A rules out the 'two-position' model in favour of a single centred hydrogen atom.

The significance of these values of the apparent thermal displacements, in the light of the experimental accuracy of determination of the B values and with reference to the rival theories of a centred or a two-position hydrogen atom, can be appreciated from Fig. 2. The sets of curves in the figure represent the widths of this hydrogen atom both along and across the bond as represented by the contours in the Fourier projections in Fig. 1. Particular attention is drawn to the 'along' and 'across' bond contours at 120 °K. on which have been drawn small shaded areas to indicate the standard deviation applicable to the determination of the thermal parameters by least squares, and representing, in turn, the accuracy of the contours of the Fourier projection. These two curves are to be contrasted with the chain-dotted curve which is an assessment of what the along-the-bond contour would be if the true structure were represented by two half-hydrogen atoms arranged on either side of the centre of symmetry in such a way as to give conventional O–H distances of 1·07 Å. This chain-dotted curve was arrived at by summing the contours of two half-hydrogens, having the 'across-the-bond' contour which was observed experimentally, placed with a separation of 0·40 Å. Thus a comparison of the two significant curves, A and B in Fig. 2, leads to the very plausible conclusion that the hydrogen atom H_0 is a single hydrogen atom located at the origin and not a pair of half-hydrogen atoms (corresponding to either static or dynamic ordering) either side of the centre of symmetry. In view of the limited experimental accuracy it must be acknowledged that this is not an indisputable conclusion.

The atomic and molecular motions

The information on the variation of the directionally-averaged B values with temperature is summarized in Fig. 3 from which it is clear that the atoms which show the largest vibrations are C_5, C_6, C_7 and their associated hydrogen atoms H_5, H_6 and H_7 at the free end of the molecule. It is also plain that these atoms show the largest variation of B with temperature. These same conclusions are also reached by a general inspection of the difference projections in Fig. 1 which show very markedly the increasing diffuseness of the hydrogen atoms at the end of the molecule. On this figure are marked the directions of maximum displacement of these atoms, as given by the least-squares analysis, and from these it appears that the benzene ring which terminates the molecule is in oscillation about some point near to C_3 whereas the portion of the molecule between C_3 and the centre of symmetry is relatively stationary. This suggestion is supported to some extent by the curves in Fig. 4 in which $\overline{u^2}$, the mean-square thermal displacement for an atom, is plotted against d^2, where d is the distance of the atom from the origin in projection. These curves, particularly the low temperature data for which the internal consistency is better, suggest that $\overline{u^2}$ is largely independent of d^2 until C_3 is reached, after which there is a steady increase in magnitude. To a first approximation therefore the molecular motion can be regarded as an oscillation of the ring at the end of the molecule, superimposed upon a general translation motion of the whole molecule. The latter motion is represented by the 'background levels' in Fig. 4 which correspond to values of $\overline{u^2}$ of 0·025 and 0·037 Å^2 at low temperature and room temperature respectively. These displacements are equivalent to Debye temperatures of about 47 °K. and 60 °K. and the equivalent B values are 2·0 and 3·0 Å^2. They refer only to the directionally-averaged translation motion of the whole molecule. It seems likely from a close inspection of the B values that this translation motion is slightly anisotropic in the plane of the projection with a larger motion at right angles to the length of the molecule than along it.

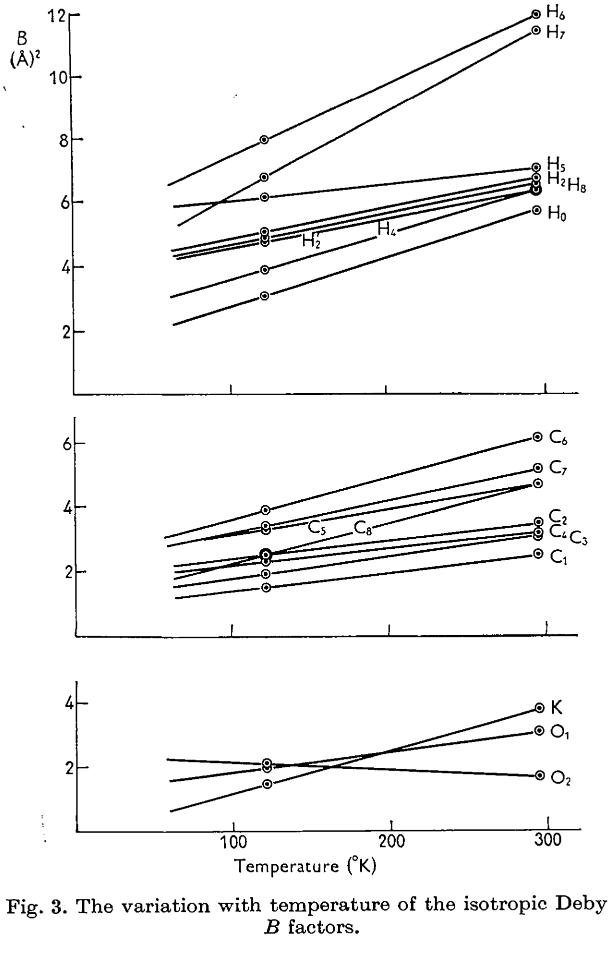


Fig. 3. The variation with temperature of the isotropic Debye B factors.

It is of interest to pursue our interpretation of enhanced movement about C_3 to the extent of working out the amount of angular motion. At low temperature the values of $B_{\text{min.}}$ for C_5, C_6 and C_7 are 2·2, 2·0 and 2·2, in good agreement with our value of 2·0 for the B value due to translational motion of the whole molecule. It seems justifiable therefore, bearing in mind the directions found for $B_{\text{max.}}$, to take the value of $(B_{\text{max.}}-B_{\text{min.}})$ as due to the rotation about C_3. At room temperature the values of $B_{\text{min.}}$ are 3·4, 3·0 and 4·0, in comparison with our deduction of 3·0 for the molecular translational motion. Proceeding, therefore, with the values of $(B_{\text{max.}}-B_{\text{min.}})$ as representative of the oscillational motion and assuming that the oscillation is in the plane of the ring, rather than in the plane of the projection, we find that the root-mean-square amplitude is about 5° of angle at room temperature and 4° at 120 °K. This conception of a heavy 'wagging tail' at the end of the molecule is very similar to what we concluded for dichloro di-phenyl sulphone, (Bacon & Curry, 1960). In the present case it seems quite reasonable physically if we look at an extended projection of the structure as seen along the y-axis. Such a view is provided by Fig. 5 which

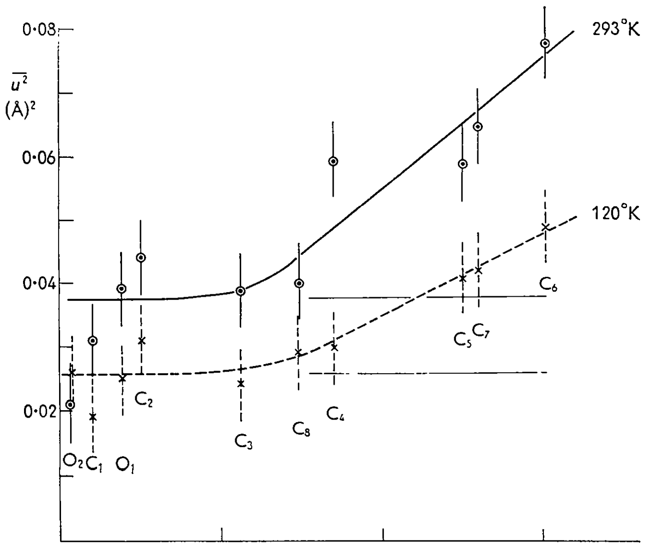


Fig. 4. The dependence of the mean-square atomic displacement $\overline{u^2}$ for the carbon and oxygen atoms on their distance d from the centre of symmetry at the origin. The individual atoms can be identified from Fig. 1. The limiting 'background levels', indicated by the horizontal lines, represent the directionally-averaged displacements of the whole molecule.

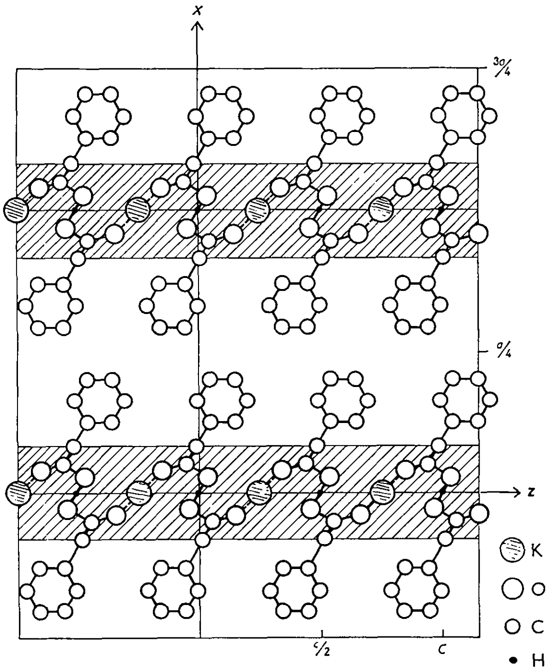


Fig. 5. An extended view of the structure along the y axis, indicating the molecular environment and emphasising the tightly bound layers (shown shaded) held together by the potassium and hydrogen atoms, in contrast to the open arrangement at the ends of the molecules, i.e. at $x=a/4$, $3a/4$ etc.

emphasises a point made originally by Speakman (1949) in his description of the structure as revealed by X-ray analysis. The structure is really of a layer type with pairs of layers of phenylacetate residues sandwiched between infinite layers of potassium ions and hydrogen atoms. The potassium and hydrogen atoms are interlinked via the carboxyl groups of the phenylacetate in such a way as to give an octahedral grouping of oxygen atoms about the potassium ion and a strong, short, hydrogen bond across the centre of symmetry. In contrast to the strength within these layers, which are shown shaded in the figure, the layers of benzene rings will be quite open and loosely held, with only weak intermolecular forces and the restraining influence of the bond C_2–C_3 to retain them in position.

The C–H *bonds*

The standard deviation of the measurement of each C–H bond is 0·034 Å and the differences in the individual values found at room temperature and 120 °K. are not significant. It is appropriate at this stage in our general studies of C–H bonds to the benzene ring to summarize the data which we have obtained from various compounds. These are

α-resorcinol, 4 readings	$1{\cdot}08 \pm 0{\cdot}04$ Å
4,4′ di-chloro diphenyl sulphone, 4 readings	$1{\cdot}05 \pm 0{\cdot}02$
KH, phenylacetate	
290 °K., 5 readings	$1{\cdot}12 \pm 0{\cdot}02$
120 °K., 5 readings	$1{\cdot}06 \pm 0{\cdot}02$

giving an overall mean value of 1·08 Å.

The large standard deviations of error of 0·8 and 1·1 in the determination of our B values for hydrogen must limit the significance of any detailed examination which we may make of the motion of individual hydrogen atoms. It may, however, be worth recording that the motion of the hydrogen atoms H_5, H_6 and H_7 relative to their associated carbon atoms C_5, C_6 and C_7 is larger than would be expected from ordinary considerations of the bending and stretching of C–H bonds. These hydrogen atoms seem to be extraordinarily diffuse at both temperatures. The significance of this impression must await the attainment of improved accuracy in determining the thermal parameters. It may be noted, in accordance with the large motions parallel to $0z$ of these peripheral atoms, that there is an observable increase in the c-dimension of the unit cell of 0·1 Å in going from a temperature of 120 °K. to 293 °K. but no noticeable change in the value of a. It is clearly of great importance to carry out at least three-plane projections, and preferably full three-dimensional analyses, of structures of this kind as soon as possible, in order to have a more favourable ratio of the number of reflexions measured to the number of parameters which have to be determined.

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