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### References

BRAGG, W. H. & MORGAN, G. T. (1923). *Proc. Roy. Soc. A*, **104**, 437.

COCHRAN, W. (1950). *Acta Cryst.* **3**, 268.

FURNAS, T. C. & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**, 449.

FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.

MORGAN, G. T. & ASTBURY, W. T. (1926). *Proc. Roy. Soc. A*, **112**, 441.

*Acta Cryst.* (1959). **12**, 626

## Basic Beryllium Acetate: Part II. The Structure Analysis\*

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A detailed structure analysis, employing three-dimensional Fourier methods, has been carried out on beryllium acetate. Two sets of independent intensity data were used for this purpose. The observed structure has been approximated through positional parameters, individual and general harmonic thermal vibrations and electron count parameters. The last two were fixed from difference density considerations in non-bonding directions. The final calculated structure agrees well with the observed structures except in certain regions of the acetate groups: there are effects present in the C-C and C-O bonds which suggest chemical bonding and/or anharmonic thermal vibrations; the acetate groups appear to possess a rigid body type angular oscillation about their C-C bonds. Half-weight hydrogen atoms of orientationally disordered methyl groups (two equally probable equilibrium orientations) have been located.

### 1. Structure analysis

#### (i) General atomic arrangement

The point group symmetry of a molecule of beryllium acetate is  $23$  and symmetry requirements fix all but six positional parameters in the asymmetric unit, hydrogen atoms excluded.

Within a molecule, there is a central oxygen atom,  $O_I$ , and it is located at the intersection of three 2-fold rotation axes. Choosing this point as an origin, beryllium atoms surround it on 3-fold rotation axes at  $\bar{u}uu$ ,  $u\bar{u}u$ ,  $uu\bar{u}$  and  $\bar{u}\bar{u}\bar{u}$ . The six acetate groups are arranged octahedrally about the origin, the carbon atoms lying on the 2-fold axes, the carboxyl carbon,  $C_I$ , at  $v$ , the methyl carbon,  $C_{II}$ , at  $w$ . As the acetate groups possess 2-fold symmetry, the carboxyl oxygen atoms,  $O_{II}$ , are equivalent. However, their positions are general. The hydrogen atoms of the methyl groups are also in general positions and if the space group is truly  $Fd\bar{3}$ , their arrangement must satisfy 2-fold symmetry.§ Since methyl groups do not possess such

a symmetry, it becomes clear that they must be orientationally disordered.

Chemical considerations require the carboxyl groups

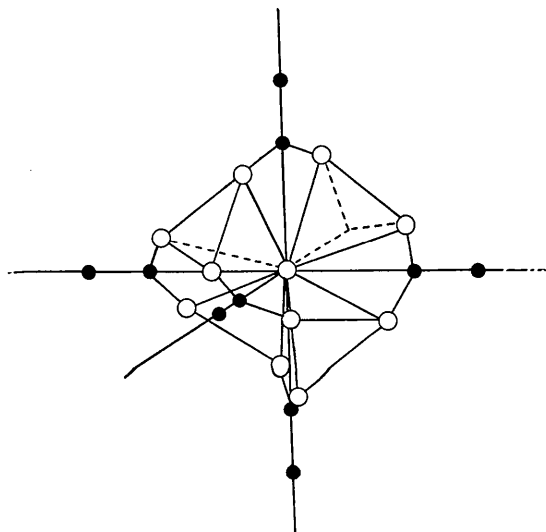


Fig. 1. Atomic arrangement in one molecule, shaded-carbon, circles-oxygen, Be (not shown) near centers of oxygen tetrahedra, one acetate missing.

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§ That the space group is, in fact,  $Fd\bar{3}$  is borne out by the fact that the intensities of reflections of the type  $hkl$  have

been shown to be equivalent to a high degree throughout reciprocal space (Part I).

to be directed toward the origin so that approximate interatomic distances lead to an approximately regular tetrahedral arrangement of oxygen atoms about each beryllium and a regular tetrahedral arrangement of beryllium atoms about the central oxygen. The four  $\text{BeO}_4$  tetrahedra thus formed share a common corner,  $\text{O}_I$ , and the remaining corners of any given tetrahedron are occupied by oxygen atoms from three different acetate groups. The eight molecules in a unit cell are located at the points of a diamond structure and adjacent molecules are related to one another by centers of symmetry at  $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$  and its equivalent positions. A schematic representation of the atomic arrangement in one molecule is shown in Fig. 1.

(ii) *The trial structure, refinement including isotropic thermal motion*

The  $SX$  data were used throughout most of the structure refinement and it was only in the final stages that refinement proceeded against the  $MX$  data.

Structure analysis proper commenced with a trial based upon coordinates proposed by Pauling & Sherman (1934). Structure factors were computed for atoms at rest employing Hartree scattering factors and hydrogen atoms were ignored throughout the early stages of the analysis (for details on all computational phases, see the Appendix). A quantitative comparison of this set of structure factors with intensities on an arbitrary scale (corrected with Lorentz and polarization factors) gave an approximate absolute scale constant together with a mean molecular isotropic temperature factor,  $\langle B \rangle = 3.8 \text{ \AA}^2$ . Scaling the observed data and correcting the calculated structure for an average isotropic thermal motion led to an initial value of  $R = 0.30$ ,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

Refinement proceeded through three-dimensional Fourier methods, electron and difference densities being considered. Three cycles with individual isotropic thermal vibrations brought the structure to  $R = 0.17$ . At this stage, both electron and difference densities showed that individual anisotropic thermal vibrations would have to be included in further refinements. In addition, they also showed that such considerations alone might not be sufficient for completely describing some of the observed atomic electron-density distributions; some of them display effects that can be attributed to chemical bonding or anharmonic thermal vibrations or both. Most impressive are the beryllium atoms which possess a tetrahedral charge distribution, the tetrahedral directions being along bond directions. Other atoms which show effects of a similar type are:  $\text{C}_{II}$ , in the C-C bond and  $\text{C}_I$  and  $\text{O}_{II}$ , in the C-O bond. Such behavior was either not as pronounced or not at all present in the calculated structure.

(iii) *Refinement including anisotropic thermal motion*

Individual anisotropic thermal vibrations were included into structure factor computations by a

straightforward treatment of elastic vibrations. If  $\exp(-M_i)$  defines the correction for thermal motion required by the  $i$ th atom, then  $M_i$  in the cubic case is, in general, given by

$$M_i = 2\pi^2/a_0^2 \sum_{j=1}^3 \bar{\mu}_j^2 (h\alpha_{j1} + k\alpha_{j2} + l\alpha_{j3})^2, \quad (1)$$

where  $\bar{\mu}_j^2$  is the mean square displacement of the  $i$ th atom from its equilibrium position along the  $j$ th principal vibration direction and  $a_0$  the length of the cell edge. The  $\alpha_{jk}$  matrix defines the principal axes of the  $i$ th vibration-ellipsoid,  $(X, Y, Z)$ , with respect to the reciprocal axes of the crystal,  $(a^*, b^*, c^*)$ ,

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix} \begin{pmatrix} a^* \\ b^* \\ c^* \end{pmatrix}.$$

Although (1) contains twelve components, only six are independent.

Now, several atoms in beryllium acetate fulfill certain symmetry conditions. In such cases, it is possible to reduce the general expression for  $M_i$ . For example, the central oxygen atom, located at the intersection of three equivalent 2-fold rotation axes, has its principal vibration directions coincident with these axes and its principal mean square displacements are equal. Other restrictions, although less stringent, are imposed upon the carbon and the beryllium atoms. The former possess 2-fold rotational symmetry so that a principal vibration is fixed along this axis; however, there are no conditions on their  $\bar{\mu}_j^2$ 's. The beryllium atoms are similar in that they too have rotational symmetry, 3-fold, and therefore possess a principal vibration along this axis. If this vibration be  $\bar{\mu}_3^2$ , then the higher symmetry of the 3-fold axis requires that  $\bar{\mu}_1^2 = \bar{\mu}_2^2 \neq \bar{\mu}_3^2$ . The vibrations of the carboxyl oxygen and the methyl group hydrogen atoms are general. Thus, only 17 thermal parameters need be considered to describe the thermal motion in a general way, hydrogen atoms excluded.

It has already been stated that the curvatures of some of the observed atomic electron-density distributions differ in bonding and in non-bonding directions in such a way as to suggest chemical bonding and/or anharmonic thermal vibrations.\* In order not to allow for such effects in the calculated structure, a method for the determination of thermal parameters had to be decided upon. The choice made was influenced by symmetry restrictions that are imposed upon some of the vibration-ellipsoids. At the onset, two principal vibrations were fixed along chemical bond directions ( $\text{Be-O}_I$  and C-C). In addition, preliminary considerations showed that a principal vibration of the carboxyl

\* A bond direction is obvious and coincides with the line between two bonded atoms. A non-bonding direction is more difficult to define and depends upon the configuration of an atom's bonds but can usually be taken to be diametrically opposed to a bonding direction.

oxygen atom lay close to the C–O bond direction. Therefore, on the assumption that there was little or no charge redistribution due to chemical bonding in non-bonding directions, it was decided to fix thermal parameters from considerations in these directions. In this way, it was hoped that difference densities between atoms would not be biased and, consequently, would leave open the possibility for differentiating between isolated and chemically bound atoms or determining the degree of anharmonicity of thermal vibration or both, as the case may be.

With the introduction of anisotropic thermal vibrations, thermal parameters were adjusted and fixed making use of special three-dimensional sections that contained the principal vibration directions of the atoms and general surveys of the electron and the difference density were conducted through comprehensive three-dimensional considerations.

Four cycles of refinement including anisotropic thermal vibrations and McWeeny form factors for beryllium and carbon (valence state) reduced  $R$  to 0.12. Hydrogen atoms were still omitted from structure factor computations. Atomic coordinates were fixed accurately, including backshift corrections, from observed and calculated densities assuming a three-dimensional Gaussian charge distribution near atomic centers. At this stage, all serious discrepancies between the observed and the calculated structure had been removed. However, the electron-density distribution of certain atoms, particularly  $O_1$ , Be and  $C_1$ , could not be approximated over reasonably large distances (at least to the  $1.0 \text{ e.}\text{\AA}^{-3}$  contour of the electron density). For these atoms, adjustment of thermal parameters could effect improvement either near atomic centers or in regions further away, but not both. Such behavior implied that these atoms were involved in charge transfer or charge redistribution in non-bonding directions or both. Therefore, it was decided to alter the number of electrons associated with an atom by the removal or addition of outer shell scattering. Before describing the way in which this was approached, the location of the hydrogen atoms will be discussed.

#### (iv) *The location of half-weight hydrogen atoms*

Positive regions of electron density were continually appearing in sections of the electron and difference density expected to be close to hydrogen atom centers (assuming tetrahedral bond angles with C–H  $\sim 1.0 \text{ \AA}$ ). Their serious consideration, however, was postponed until now because the regions were somewhat ambiguous. This, no doubt, was due to the smallness of the effects being sought. It was already known that the methyl carbon atom has an appreciable thermal vibration ( $\langle B \rangle \sim 4.5 \text{ \AA}^2$ ), which, in turn, suggests a large thermal motion for the hydrogen atoms. In addition, the methyl groups are required by symmetry to be orientationally disordered, the best case leading to half-weight hydrogen atoms.

As a direct interpretation of the positive regions attributable to hydrogen atoms was still not possible, they were approached through a simple but effective indirect method. As a first approximation, it was assumed that the electron-density distribution of the methyl carbon atom is ellipsoidal. Although this was known not to be strictly correct, it is sufficient for practical purposes in the near vicinity of the atomic center. Given the assumption, the difference in electron density between two equi-spaced planes about the methyl carbon center and parallel to the plane of the hydrogen atoms should contain regions of density accountable to hydrogen atoms. Since the methyl carbon was essentially removed from the difference density at this stage, the difference considered was

$$\rho_H(x, y, z_1) \sim D(x, y, z_1) - D(x, y, z_2),$$

where  $D = \rho_o - \rho_c$ , hydrogens not included, with  $z_1 - z_2 = 0.1574 \text{ \AA}$  so that the two planes are  $\pm 0.0787 \text{ \AA}$  from the methyl carbon center,  $z_1$  being about  $0.32 \text{ \AA}$  from the plane expected to contain the hydrogen atoms. The result is shown in Fig. 2 and although the density is extremely low, because it is so far removed from the plane of the hydrogens, it will be seen that a set of maxima fall on the points of an approximately regular hexagon. This suggests that the disorder is between two equally probable equilibrium orientations separated by  $\pi/3$  and implies half-weight hydrogen atoms.

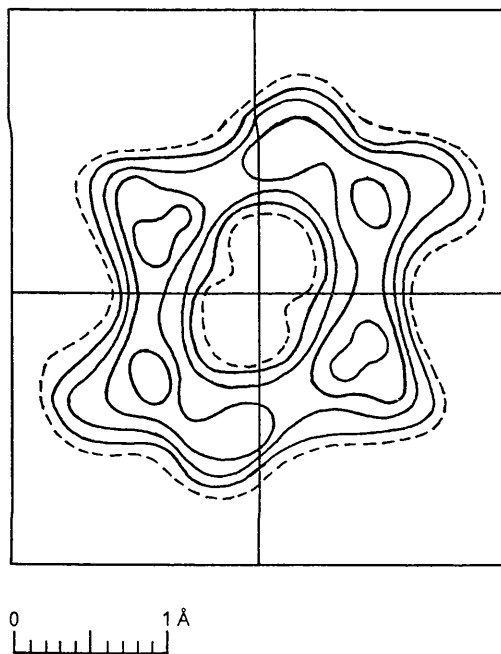


Fig. 2.  $D(x, y, z_1) - D(x, y, z_2)$ ,  $D = \rho_o(SX) - \rho_c$ , hydrogens not included, contours at  $0.01 \text{ e.}\text{\AA}^{-3}$ ,  $0.05 \text{ e.}\text{\AA}^{-3}$  broken.

Half-weight hydrogen atoms undergoing isotropic thermal vibrations were now included into structure factor computations. The temperature factor employed

was the average of the methyl carbon atom. Some significant improvements occurred between observed and calculated low order structure factors and the positive regions attributable to the hydrogen atoms vanished from the difference density when the latter were included. The overall improvement effected was  $\Delta R = -0.02$  so that  $R$  now stood at 0.10. All the foregoing is corroboratory evidence for the original assumption that the disorder is between two equally probable equilibrium orientations.

(v) *Refinement including the adjustment of electron counts*

In the consideration of the number of electrons associated with a given atom, two distinct effects are recognized. One is ordinary charge transfer or ionization. The other is charge redistribution accompanying chemical bond formation (Cochran, 1956). Although the treatment of the former is straightforward, that of the latter is not, since unsymmetrical directional properties are then introduced into the charge distribution.\*

Now, there are several ways of approaching the problem of charge redistribution, but all are more or less arbitrary. The choice made in the present case was influenced by the physical interpretation that could be assigned to it and is as follows. If the electron count of an atom is adjusted, with other atomic parameters, in such a way as to make the difference density vanish in non-bonding directions, then the electron count so determined will be an apparent one,  $n_a$ ,

$$n_a = n + \delta n_i + \delta n_r,$$

where  $n$  is the atomic number of the neutral atom,  $\delta n_i$  the change in count due to ionization and  $\delta n_r$  the change in count due to charge redistribution in non-bonding directions. In general,  $\delta n_r$  will either be zero or negative whereas  $\delta n_i$  can assume positive and negative values depending upon the type of ionization. With covalently bonded atoms,  $n_a$  will always be less than the total electron content of the atom and should represent to some extent the degree of charge redistribution in non-bonding directions. Moreover, in such a treatment, bonding effects appear as positive discrepancies in the difference density.

Now, if the integral over the volume of a bonded atom is essentially the same as that of its isolated counterpart (with the same position, state of ionization and thermal motion), then integration over its volume will lead to a first approximation of its  $\delta n_i$ . If, in addition,  $\delta n_r$  is small, then

$$n_a \sim \int_V \rho_0 dV, \quad (2)$$

\* Anharmonicity of thermal vibration could also result in a similar type of distribution. In what is to follow, such effects will be considered to arise from chemical bonding. In the end, however, they can be interpreted in terms of either or both.

where  $\rho_0$  is the observed electron-density distribution of an atom and the integration extends over the volume of that atom.

In an effort to approximate the various  $n_a$ 's, (2) was evaluated by numerical integration, but the results proved to be unsatisfactory because the electron count of an atom is a function of its assumed atomic radius and the number of data used to represent it. Consequently, the problem reduces to the definition of a bound within which all of an atom's electrons can be considered to be located. Although the radius of this bound is intimately related with the minimum observed spacing, if it is chosen at a region where the observed atomic density distribution no longer decays in a systematic manner and is apparently beginning to fluctuate in a random background, then the electron count determined is invariably low. For example, the central oxygen atom of beryllium acetate reaches background (approximately  $\pm 0.25 \text{ e.}\text{\AA}^{-3}$ ) at about 0.8 Å from its center. However, only 7.8 electrons are contained within this region although the electron count finally determined was 10.0 electrons. Employing an arbitrary procedure to extrapolate the observed atomic electron-density distribution to vanishingly small values increased the radius to about 1.0 Å, but the increase in count was only 0.6 of an electron.

In passing, it should be mentioned that the arbitrary nature of assumed atomic volumes in electron counting procedures has already been recognized in the literature and that extraordinarily large counting radii are continually being used in electron counting (C, N, O  $\sim 1.5$  Å, H  $\sim 1.1$  Å with Cu radiation). Although such radii lead to expected results, the validity of the procedure must be doubted, since an appreciable amount of the counting volume is at background level. Therefore, it is tacitly assumed that background fluctuation is equal and opposite in these regions so that there is no net spurious contribution to the electron count. However, it would seem to be difficult to satisfy such an assumption in the small volume that is concerned.

In an effort to avoid the difficulties inherent in electron counting of observed atomic electron-density distributions, recourse was made to counting the difference density. Once again, the results were low. The calculated central oxygen contained 6.6 electrons within a radius of 0.8 Å and 7.2 electrons within 1.0 Å, whereas an eight electron oxygen atom had been used in structure factor computations. This was again attributable to the fact that counting in regions fluctuating within background level was avoided. However, counting of the difference density did prove to be useful in a qualitative sense. Differences in electron counts indicated in which direction adjustment should proceed, although direct quantitative estimates as to the magnitude of the change remained in doubt. Initially, the changes implied by the difference density were used to approximate the various  $n_a$ 's. Afterward, electron counts were adjusted by trial, in con-

junction with other atomic parameters, from difference density considerations in non-bonding directions.

Atomic scattering factors were corrected for changes in  $L$  electron scattering in the following manner. For the oxygen atoms, the scattering form of an atom containing  $n_a$  electrons was taken to be

$$f_{n_a} = f_0 + (n_a - n)(f_{0-2} - f_0)/2,$$

where  $f_{0-2}$  and  $f_0$  are Hartree scattering factors for a doubly ionized and a neutral oxygen atom, respectively, both scattering factors being for atoms at rest. The difference ( $f_{0-2} - f_0$ ) extends out to about  $2\theta = 60^\circ$ . The beryllium atom scattering factor was changed in a similar way except that the difference between the neutral and the ionized state, ( $f_{\text{Be}} - f_{\text{Be}^{+2}}$ ), was obtained from Hartree curves and was used with a neutral McWeeny beryllium atom. In this case, the two form factors merge near  $2\theta = 44^\circ$ , which, of course, makes the determination of the electron count of the beryllium atoms less reliable. The carbon atoms were corrected directly since McWeeny gives scattering forms for a  $2p$  electron. The average curve was used and it extends out to about  $2\theta = 70^\circ$ .

The initial results obtained from counting the difference density indicated that  $O_I$ , Be and  $C_I$  required changes in electron content. An extra electron was implied for  $O_I$  and a deficiency of about an electron for Be and  $C_I$ . Introducing these changes into structure factor computations reduced  $R$  to 0.087, a significant improvement.

#### (vi) *The final refinement*

From this point, refinement of the structure proceeded against the  $MX$  data. Six more cycles were carried out, electron counts and thermal parameters constituting the principal parameter adjustments. The structure converged slowly because of its sensitivity in the very final stages. The final values of  $R$  for the two sets of data are: all reflections included, hydrogens excluded,  $R_{MX} = 0.074$ ,  $R_{SX} = 0.079$ ; the contribution of half-weight hydrogen atoms reduces these values to  $R_{MX} = 0.054$  and  $R_{SX} = 0.058$ .

#### (vii) *Refinement of the half-weight hydrogen atoms*

As the half-weight hydrogen atoms had a relatively small effect on the agreement between the observed and the calculated structure, refinement of their parameters did not advance with each cycle, but rather, at  $R = 0.087$  and at the very end. Refinement proceeded through the consideration of difference densities, half-weight hydrogen included, and also, through parameter variation investigations. In the latter, four parameters were chosen which defined the plane containing the half-weight hydrogens, the C-H distance, the orientation of a regular hexagonal arrangement of half-weight hydrogens and an isotropic temperature factor. The parameters were varied systematically from values deduced from difference density

considerations and the agreement between observed and calculated structure factors was used as a criterion for the amount of improvement effected. This turned out to be rather insensitive and some twenty variations were performed before deciding upon a final set of atomic parameters.

During the course of the parameter variation investigations, several dodecagonal arrangements of quarter-weight hydrogen atoms were considered. In all cases, the overall agreement decreased with respect to the agreement with half-weight hydrogens. Moreover, the difference density approximated the difference between a hexagonal and dodecagonal arrangement of partial-weight hydrogen atoms. All of this, of course, lends further support for disorder between two equilibrium positions.

## 2. Results\*

The final electron-density distribution ( $MX$  data) in the plane of the acetate group is shown in Fig. 3. The

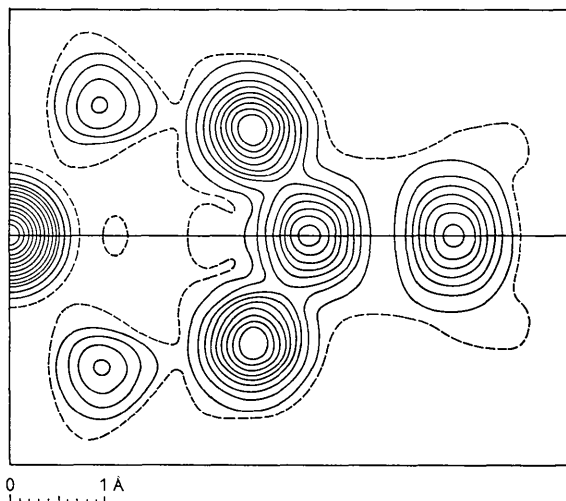


Fig. 3.  $\rho_o(MX)$  in the plane of an acetate group, contours at  $1 \text{ e.}\text{\AA}^{-3}$ ,  $0.5 \text{ e.}\text{\AA}^{-3}$  broken.

main points of interest are the shape of the beryllium atoms and the electron-density distribution in the bonds of the acetate group. The shape of the beryllium atoms (located  $0.24 \text{ \AA}$  above and below the plane of the acetate) suggests a tetrahedral charge distribution. This was verified from a general three-dimensional survey which also showed that the tetrahedral directions correspond closely to bond directions. A detailed examination of the electron-density distribution in the bonds of the acetate group reveals a small excess of density between  $C_I$  and  $O_{II}$  and peculiar behavior in the C-C bond. In the latter, the distribution of  $C_I$

\* A record of the observed and calculated structure factors has been deposited as Document No. 5998 with ADI Auxiliary Publications project, Photo-duplication Service, Library of Congress, Washington 25, D.C., U.S.A.

falls off more rapidly in the bond direction whereas that of  $C_{II}$  does not.

The final difference density distribution ( $MX$  data) in the plane of the acetate group is shown in Fig. 4. A cursory look is sufficient to show that the observed structure has been approximated closely and in addi-

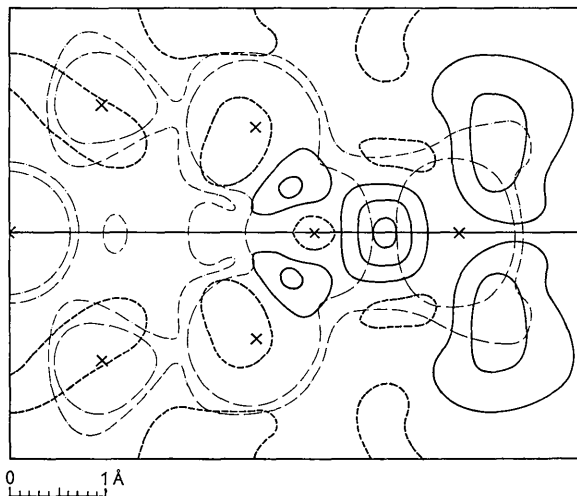


Fig. 4.  $\rho_o(MX) - \rho_c$  in the plane of an acetate group, hydrogens not included, contours at  $0.1 \text{ e.}\text{\AA}^{-3}$ , solid-positive, broken-zero, chain- $0.5$  and  $1.0 \text{ e.}\text{\AA}^{-3}$  contours of corresponding  $\rho_o(MX)$ , crosses indicate atomic positions.

tion, that there are effects present that can be interpreted in terms of chemical bonding or anharmonic thermal vibrations or both. Specifically, there are relatively large concentrations of electron density between the carbon atoms (peak height  $\sim 0.40 \text{ e.}\text{\AA}^{-3}$ ) and between  $C_I$  and  $O_{II}$  (peak height  $\sim 0.26 \text{ e.}\text{\AA}^{-3}$ ). Another feature of interest, which came as a surprise, is that the tetrahedral charge distribution of the beryllium atoms has been removed in the difference density, this being accomplished with merely an isotropic scattering form and harmonic anisotropic thermal vibrations. In general, the final difference density fluctuates between  $\pm 0.1 \text{ e.}\text{\AA}^{-3}$ .

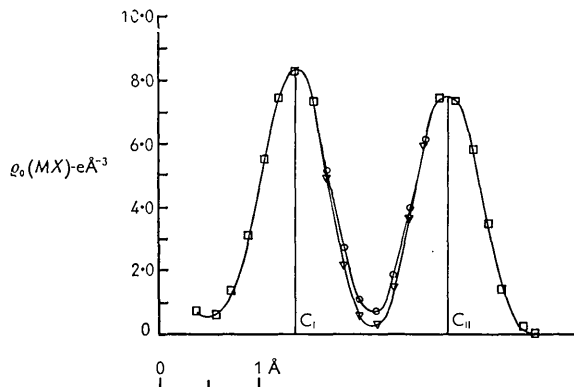


Fig. 5. Line section of  $\rho_o(MX)$  and  $\rho_c$  along a 2-fold axis, circles  $-\rho_o(MX)$ , triangles  $-\rho_c$ , squares  $-\rho_o(MX)$  and  $\rho_c$ .

With the knowledge of the difference density, the behavior of the charge distribution in the C-C bond becomes more understandable. This can be seen from the line section (part of a 2-fold axis) shown in Fig. 5. The points shown are equi-spaced about the carbon atom centers so that it is clear that the curvature of  $C_I$  is greater in the direction of  $C_{II}$ . However, it will be seen that the calculated structure behaves similarly. In fact, the difference in curvatures of  $C_I$  to and from  $C_{II}$  is greater in the case of the calculated structure.

Returning to Fig. 4, two half-weight hydrogen atoms can be seen, but only partially, since their centers are not contained by the section ( $0.32 \text{ \AA}$  above and below). They are the two positive regions in the proximity of the swells in the  $0.5 \text{ e.}\text{\AA}^{-3}$  contour of the electron density of  $C_{II}$ . The difference density distribution in the plane containing the half-weight hydrogen centers is shown in Fig. 6. Also shown is the plane of the acetate group. The methyl groups are oriented in such a way that the projection of the  $C_{II}-H_I$  line on a plane perpendicular to the C-C bond makes an angle of  $+20.5^\circ$  with the plane of the acetate group. Therefore, the methyl hydrogen atoms lie approximately between a *cis* and a *trans* configuration with respect to the carboxyl oxygen atoms.

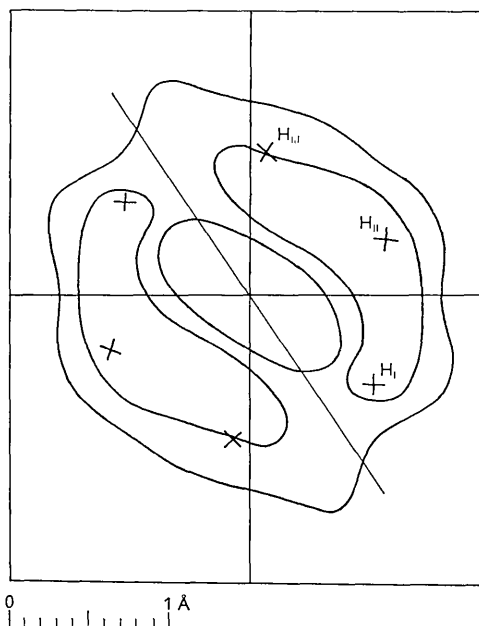


Fig. 6.  $\rho_o(MX) - \rho_c$  in the plane of the hydrogen atoms, hydrogens not included, contours at  $0.1 \text{ e.}\text{\AA}^{-3}$  beginning with  $0.2 \text{ e.}\text{\AA}^{-3}$ , crosses indicate proposed atomic positions.

The two observed structures, *MS* and *SX*, are compared in Fig. 7, which is their difference in the plane of the acetate group. It will be seen that the agreement is generally good. This can also be said of the complete three-dimensional distribution. Increasing the scale of the *SX* data by about 1% can improve the situation in the vicinity of  $O_I$  and the Be's without

essentially altering the character of the remaining distribution. In either case, it will be seen that the major effects present in the final difference density (Fig. 4) are common to both sets of data.

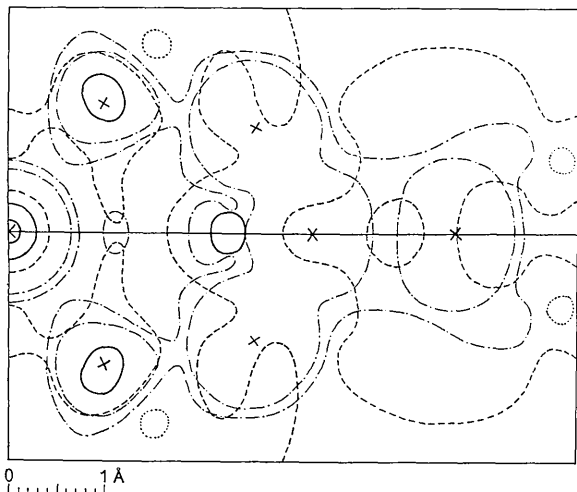


Fig. 7.  $\rho_0(MX) - \rho_0(SX)$  in the plane of an acetate group, contours at  $0.1 \text{ e.}\text{\AA}^{-3}$ , solid-positive, dotted-negative, broken-zero, chain- $0.5$  and  $1.0 \text{ e.}\text{\AA}^{-3}$  contours of corresponding  $\rho_0(MX)$ , crosses indicate atomic positions.

Hitherto, the effects present in the final difference density and certain aspects of the observed electron-density distribution have been considered in terms of chemical bonding or anharmonic thermal vibrations or both, primarily because the latter are physically interpretable phenomena. However, it is also possible that such effects arise from errors in the observed data, either from systematic errors and/or from an accumulation of random errors in certain regions. The last three possibilities will be considered in detail in Part III of this series of communications.

The final atomic parameters are given in Table 1, where those fixed by symmetry are represented by

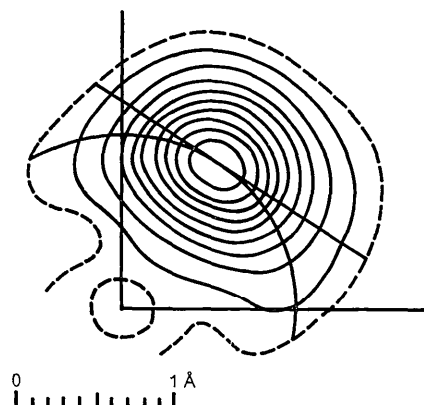


Fig. 8.  $\rho_0(MX)$  in the plane at right angles to a 2-fold axis and passing through the center of  $O_{II}$ , contours at  $1.0 \text{ e.}\text{\AA}^{-3}$ ,  $0.5 \text{ e.}\text{\AA}^{-3}$  broken.

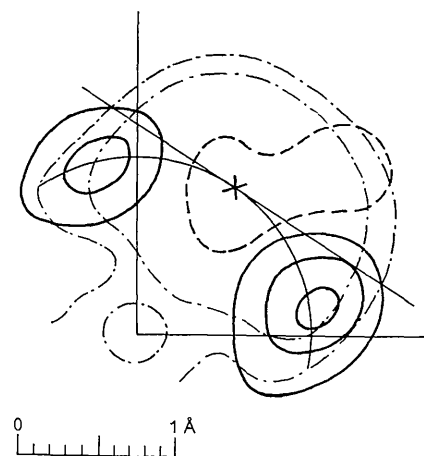


Fig. 9.  $\rho_0(MX) - \rho_c$  in the plane at right angles to a 2-fold axis and passing through the center of  $O_{II}$ , contours at  $0.1 \text{ e.}\text{\AA}^{-3}$ , solid-positive, broken-zero, chain- $0.5$  and  $1.0 \text{ e.}\text{\AA}^{-3}$  of corresponding  $\rho_0(MX)$ , cross indicates atomic position.

Table 1. *Final atomic parameters\**

Atom	O <sub>I</sub>	O <sub>II</sub>	C <sub>I</sub>	C <sub>II</sub>	Be	H <sub>I</sub>	H <sub>II</sub>	H <sub>III</sub>
$n_a$ electrons	10.0	8.0	4.3	5.8	2.0	0.5	0.5	0.5
$x$	0	-0.0386	0	0	-0.0611	-0.038	0.025	0.065
$y$	0	0.1617	0.1997	0.2950	0.0611	0.052	0.061	0.008
$z$	0	0.0576	0	0	0.0611	0.317	0.317	0.317
$\overline{\mu_1^2} \text{ \AA}^2$	0.0304	0.0922	0.0552	0.0920	0.0462	0.060	0.060	0.060
$\overline{\mu_2^2} \text{ \AA}^2$	0.0304	0.0345	0.0364	0.0433	0.0462	0.060	0.060	0.060
$\overline{\mu_3^2} \text{ \AA}^2$	0.0304	0.0493	0.0314	0.0335	0.0360	0.060	0.060	0.060
$\alpha_{11}$	1	0.866	-0.574	-0.682	0	1	1	1
$\alpha_{12}$	0	-0.151	0.819	0.731	$\sqrt{2}/2$	0	0	0
$\alpha_{13}$	0	0.477	0	0	$-\sqrt{2}/2$	0	0	0
$\alpha_{21}$	0	-0.121	0	0.731	$\sqrt{6}/3$	0	0	0
$\alpha_{22}$	1	0.862	0	0.682	$\sqrt{6}/6$	1	1	1
$\alpha_{23}$	0	0.493	1	0	$\sqrt{6}/6$	0	0	0
$\alpha_{31}$	0	-0.486	0.819	0	$-\sqrt{3}/3$	0	0	0
$\alpha_{32}$	0	-0.486	0.574	0	$\sqrt{3}/3$	0	0	0
$\alpha_{33}$	1	0.729	0	1	$\sqrt{3}/3$	1	1	1

\* The limits of error of these quantities will be given in Part III.

exact numbers. However, the final electron and difference densities indicate that the atoms of the acetate group have an additional degree of freedom. The acetate group seems to be undergoing a rigid body type of angular oscillation about its C-C bond. This is suggested in Fig. 8 and is supported in Fig. 9. The arc shown passes through the  $O_{II}$  center and is itself centered on the 2-fold axis. The direction of maximum vibration of  $O_{II}$  is also shown. The intermediate vibration is in the C-O bond.

The central oxygen atom has the smallest overall thermal disorder,  $O_{II}$  the largest, followed by  $C_{II}$ . The direction of maximum vibration of  $C_{II}$  is  $+13.7^\circ$  out of the plane of the acetate group and the minimum direction lies in the C-C bond. The direction of maximum vibration of  $C_I$  is  $+21.7^\circ$  out of the plane of the acetate and the minimum vibration is perpendicular to it and to the C-C bond. The 3-fold axis is the direction of minimum vibration for the Be atom.

The apparent electron counts of  $O_I$  and Be in conjunction with the final difference density would seem to indicate that these atoms are essentially ionized. If the  $O_{II}$ 's were ionized  $-\frac{1}{2}$ , then the  $BeO_4$  tetrahedra would be ionic. Now, although the electron count of  $O_{II}$  has been found to be 8.0 electrons, considering the large thermal disorder of these atoms, it is doubtful whether the two possibilities (8.0 and 8.5 electrons) can be distinguished. The count determined for  $C_I$  suggests partial ionization plus an appreciable amount of charge redistribution. This is compatible with the fact that the carboxyl carbon is involved in a particularly complex bonding system.

The principal interatomic distances and interbond angles are given in Table 2. The C-O distance has been

Table 2.\* *Interatomic distances and interbond angles*

$C_I-C_{II}$	1.500 Å	$\angle O_{II}-C_I-O_{II}$	123.4°
$C_I-O_{II}$	1.264	$\angle O_I-Be-O_{II}$	115.2
$Be-O_I$	1.666	$\angle O_{II}-Be-O_{II}$	102.7
$Be-O_{II}$	1.624		
$C_{II}-H$	1.1		

\* The limits of error of these quantities will be given in Part III.

corrected for the angular oscillation of  $O_{II}$ ; this correction amounts to about 0.02 Å and corresponds to a r.m.s. amplitude of angular oscillation of about  $11^\circ$ . From the Be-O interatomic distances and interbond angles, it will be seen that the  $BeO_4$  tetrahedra are elongated along the 3-fold axes. Three edges are 2.778 Å, while the other three are 2.536 Å, the longer edges extending from  $O_I$  to  $O_{II}$ .

### 3. Discussion

All the principal interatomic distances and interbond angles in beryllium acetate, with the exception of the C-C distance, are quite normal. The beryllium-oxygen distances can be compared with those found in hex-

agonal beryllium oxide, which also contains beryllium-oxygen tetrahedra (Jeffrey, Parry & Mozzi, 1956). Like beryllium acetate, beryllium oxide possesses two different beryllium-oxygen distances (1.655 and 1.647 Å). Although these differ somewhat from one of those found in beryllium acetate, this should be expected as the two structures differ somewhat in type. The variation between the distances in beryllium oxide is less, probably because of the smaller contrast in its environment. The  $C_I-O_{II}$  distance is in qualitative agreement with the host of other determinations of the carbon-oxygen distance in a carboxyl group. Only the  $C_I-C_{II}$  distance appears to be abnormal by being only 1.500 Å. However, since it is adjacent to a double bond, the methyl group hydrogen atoms can enter into hyperconjugation. The net effect of this would be to shorten the  $C_I-C_{II}$  distance.

### APPENDIX

All computations were performed at IBM's Watson Scientific Computing Laboratory\* with an IBM Type 650 Magnetic Drum Data Processing Machine. The programs were written specifically for space group  $Fd\bar{3}$  so that computational times would be at a minimum.

Three-dimensional Fourier series were synthesized with a program based upon principles described elsewhere (Tulinsky, 1957). An intersection of three 2-fold rotation axes was employed as an origin putting summations involving sectional coefficients into a particularly suitable form. The summations were carried out at intervals of  $\frac{1}{100}$ th of the cell edge (0.1574 Å), the most convenient asymmetric unit being chosen to be  $\pm\frac{1}{8} \times \frac{1}{4} \times \frac{1}{2}$ . The program evaluated series containing up to 1,100 coefficients, at 676 points, in 45 min. (one three-dimensional section).

Three programs were written to compute structure factors: the first included individual isotropic while the second included individual anisotropic thermal vibrations and the third computed isotropic hydrogen atom contributions. The first was written to avoid the general case, thereby decreasing computational time by a factor of ten. The other two were written to consider the general case, finite storage capacity preventing the accomplishment of this with one program. Provisions were included so that the output from either program served as input for the other. This enabled the computation of two sets of structure factors in one machine pass, one set including the hydrogen atom contributions.

A center of symmetry was naturally chosen as an origin in structure factor computations. However, atomic coordinates were referred to an intersection of three 2-fold rotation axes since this is the natural molecular origin and since a considerable simplification in formulae occurred, especially when considering only isotropic thermal vibrations. Cosines of arguments to

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one ten-thousandth of the cell edge were formed by linear interpolation of a table in thousandths. Strictly isotropic structure factors were computed at the rate of 25 per min., as were the hydrogen contributions, while general structure factors were computed at 3 per min. With the latter, 48 general atoms had to be considered since storage facilities were not available for including special cases. Even so, the program required 1,987 storage locations out of a possible 2,000.

In all, a total of approximately 450 hr. machine time was consumed by this analysis. This represents 15 cycles of three-dimensional refinement.

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### References

- COCHRAN, W. (1956). *Acta Cryst.* **9**, 924.  
 JEFFREY, G. A., PARRY, G. S. & MOZZI, R. L. (1956). *J. Chem. Phys.* **25**, 1024.  
 PAULING, L. & SEERMAN, J. (1934). *Proc. Nat. Acad. Sci., Wash.* **20**, 340.  
 TULINSKY, A. (1957). *Acta Cryst.* **10**, 745.

*Acta Cryst.* (1959). **12**, 634

## Basic Beryllium Acetate: Part III. Evidence for Chemical Bonding; Assessment of Accuracy\*

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Anharmonic thermal vibrations, systematic errors in the data and the systematic accumulation of random errors have been considered as possible sources for the excess positive density observed in the C-C and C-O bonds of the acetate group (Part II). None were found to account for this density completely and satisfactorily. An assessment of the accuracy of the structure determination has been made by averaging over the cell. The advantages of atoms in special positions are discussed.

### 1. Introduction

It has been mentioned in Part II that the discrepancies between the observed and calculated structures in the bonds of the acetate group could arise from one or more of four effects: chemical bonding, anharmonic thermal vibrations, systematic errors, accumulation of random errors. The last three will now be considered in some detail.

### 2. Anharmonic thermal vibrations

Fundamentally, there is a clear distinction between chemical bonding and anharmonic thermal vibrations. Anharmonicity of thermal vibration would be expected to affect both inner and outer shell electrons whereas chemical bonding involves only the outer shell. Therefore, in principle, the two can be differentiated by

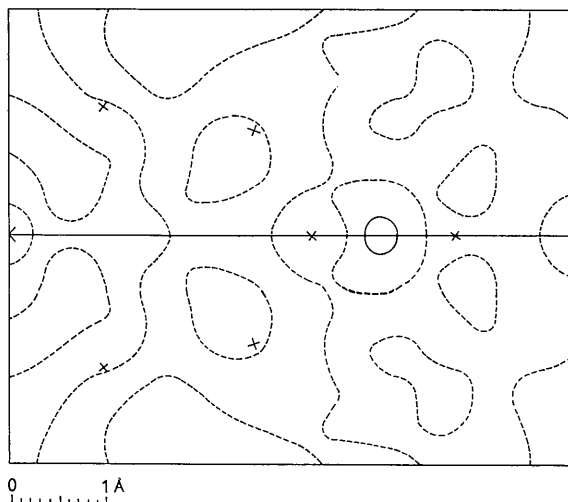


Fig. 1. High order  $\rho_o(MX) - \rho_c$  in the plane of the acetate group,  $(F_o - F_c)$  in the range  $2\theta \leq 83^\circ$  omitted, contours at  $0.1 \text{ e.}\text{\AA}^{-3}$ , solid positive, broken zero, crosses indicate atomic positions.

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