TABLE V

COMPOSITION OF EQUILIBRIUM MIXTURES USED IN ABSORBANCE MEASUREMENTS IN 1.000 CM. CELLS AT 25°

	Concentration				
Ratio Br/Se	Br_2		Se_2Br_2		$SeBr_2$
	Formal	Molar	Formal	Molar	Molar
1.431	3.036×10^{-4}	1.94×10^{-5}	7.048×10^{-4}	4.21×10^{-4}	5.68×10^{-4}
2.016	1.068×10^{-3}	2.7×10^{-4}	1.051×10^{-3}	2.5×10^{-4}	1.61×10^{-3}
4.000	3.000×10^{-3}	2.04×10^{-3}	1.000×10^{-3}	4.5×10^{-5}	1.91×10^{-3}
13.06	3.473×10^{-3}	3.19×10^{-3}	2.882×10^{-4}	2×10^{-6}	5.72×10^{-4}

mined, it is possible to compute values of the molar absorptivity for selenium dibromide. These are given in Table IV.

It is interesting to compare the results of the present study with those on related systems and molecules in the literature. The equilibrium

$$2SCl_2 = S_2Cl_2 + Cl_2$$

was studied in the liquid phase, without solvent, by Spong.[8] In this case

$$(S_2Cl_2)(Cl_2)/(SCl_2)^2 = K = 0.013$$

a value which is comparable to that found in the present study.

The spectrum of selenium dibromide in the vapor state has been studied by Wehrli.[9] The strongest band in the vapor was found at 513.8 mμ while the absorption maximum in solution was found in the present study at 507 mμ. The general region of strongest absorption also agrees in the two cases. The spectra found for tellurium dichloride and tellurium dibromide[10] vapor are also similar to that of selenium dibromide in carbon tetrachloride solution.

It is also of interest to note that although $SeBr_4$ exists as a crystalline solid, it does not exist in either the gaseous or the dissolved state. On the other hand, while $SeBr_2$ exists in the gaseous state and in solution, it has not been isolated as a pure phase.

[8] A. H. Spong, *J. Chem. Soc.*, 1547 (1933).

[9] M. Wehrli, *Helv. Phys. Acta*, **9**, 329 (1936).

[10] M. Wehrli, *ibid.*, **9**, 208 (1936).

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Silver Perfluorobutyrate[1]

BY A. E. BLAKESLEE AND J. L. HOARD

RECEIVED AUGUST 9, 1955

The soft waxy crystals of silver perfluorobutyrate are monoclinic with $a = 6.46 \pm 0.01$, $b = 9.01 \pm 0.02$, $c = 13.11 \pm 0.04$ Å., $\beta = 100.2 \pm 0.3°$, space group C2 and two *dimeric* molecules within the unit cell. Spectrometric (MoKα) $h0l$ and $0kl$ intensity data from the best available specimens show that the excessive softness of the crystals arises from extraordinarily large thermal motions, *e.g.*, the anisotropic thermal parameter of the heavy silver atom varies between 3.4 and 7.6 Å.^{2} Dimeric molecules, involving formation of an eight-membered central ring of two silver atoms and two carboxyl groups, exist in the crystal; the central ring approximates to 2/m but the dimer as a whole has only a twofold axis in consequence of twisting within the fluorocarbon groups. Molecular models, the real Fourier synthesis $\rho(x,z)$, and finally the complex synthesis $\rho(y,z)$, give approximate positions of fluorine atoms and provide further support for this interpretation.

Introduction

Examination of the photographic X-ray data afforded by several fluorinated succinates, butyrates and acetates suggested that a determination of structure for silver perfluorobutyrate should be relatively simple. This compound is quite soluble in benzene and in ether, whereas the perfluorobutyrates of sodium, lithium, calcium and lead are but sparingly soluble.[2] Silver perfluorobutyrate is also a good deal less soluble in water and in methanol than are the others but is nearly insoluble in petroleum ether.[2]

Experimental

Silver perfluorobutyrate was prepared by mixing equivalent amounts of freshly precipitated silver oxide and an aqueous solution of perfluorobutyric acid. The material first used was furnished by Dr. Elliot Bergman of this Laboratory. In order to get usable crystals it was necessary to recrystallize from a mixed solvent, roughly one part of benzene to ten parts of petroleum ether. The crystals are typically thin diamond-shaped plates, so soft and fragile as to make them very difficult to handle without injury. They are stable in air except for superficial decomposition apparently produced by the action of ordinary light.

Oscillation and Weissenberg photographs show the X-ray symmetry 2/m, with the longer diagonal of the diamond-shaped plate as the direction of the unique monoclinic axis and the shorter diagonal conveniently chosen as the direction of the secondary axis, a. Lattice constants, as determined with CuKα radiation ($\lambda = 1.5418$ Å.), are $a = 6.46 \pm 0.01$, $b = 9.01 \pm 0.02$, $c = 13.11 \pm 0.04$ Å., $\beta = 100.2 \pm 0.3°$. The systematic vanishings, hkl with $h + k$ odd, are those required by the space groups C2/m, C2 and Cm. The assumption of four (monomeric) molecules within the cell, subsequently confirmed by the analysis of the diffraction data, leads to a calculated density of 2.84 g./cc.

Intensity measurements were carried out on two bar-shaped specimens cut from plates along the principal diagonals, *i.e.*, cut parallel to a and b, respectively. Average dimensions normal to a and b were 0.085 by 0.22 mm. and 0.065 by 0.17 mm. It seemed out of the question to cut specimens down to square cross-section without introducing intolerable distortion. The excessive softness of the crystals doubtless arises from extraordinarily large thermal motions in the crystal, for despite the presence of silver atoms, the range of recordable reflections is limited to $\sin \theta/\lambda \leq 0.72$. A General Electric XRD-3 Geiger Counter Spectrometer, adapted for single crystal work with convergent beam technique by Dr. R. E. Hughes, was used to measure the integrated intensities of all $0kl$ and $h0l$ reflections recordable with MoKα radiation. The most important ad-

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[1] Supported by the Atomic Energy Commission under Contract No. AT(30-1)-878 with Cornell University.

[2] Brochure entitled, "Heptafluorobutyric Acid," Minnesota Mining and Manufacturing Co., St. Paul, Minn.

vantage of using MoKα rather than CuKα radiation lies in the large reduction in the magnitude of the at best rather uncertain absorption corrections which must be applied to the data. The absorption coefficient of silver perfluorobutyrate is 240 cm.$^{-1}$ for CuKα but only 30.4 cm.$^{-1}$ for MoKα.

The intensities of 70 $k0l$ and 99 $h0l$ forms were recorded as above background. These data were reduced to a set of relative $|F|^2$ values through division by the Lorentz and polarization factors and correction for absorption. Transmission normal to the axis of the larger specimen lay in the range $0.50I_0$–$0.80I_0$. Absorption corrections were evaluated for several reflections by the method of Evans[3]; a simplified version of this procedure was used for the remaining data since the maximum deviation in corresponding relative $|F|$ values obtained with the alternative estimates was about 3%. As the specimen was somewhat distorted in cutting and its precise shape could not be exactly determined, it was felt that the more elaborate procedure for making absorption corrections would hardly be justified. The subsequent analysis appeared to support this conclusion.

Two other experimental measurements incidental to the structure determination were carried out. Cryoscopic measurements on solutions of silver perfluorobutyrate in benzene gave a molecular weight for the solute agreeing within 1% with the dimeric formula. A determination of the magnetic susceptibility of crystalline silver perfluorobutyrate showed it to be diamagnetic.

Determination of Structure.—Patterson syntheses of the zonal $|F|^2$ data are immediately interpretable to give four silver atoms the positions $0,\pm0.163,0$ and $1/2,1/2\pm0.163,0$. Thus all silver atoms of the crystal lie in the axial planes, $z = 0,\pm1$, (although c is the longest axis of the cell), and Ag–O bonds are restricted to layers enveloping these axial planes. The grouping of silver atoms into pairs only 2.9 Å. apart along b suggests sequestration of Ag–O bonds within layers to give dimeric molecules; the further analysis directly confirms this tentative conclusion.

Silver atoms scatter exactly in phase for all $h0l$ reflections. If the space group be either C2/m or C2, a real Fourier projection of electron density on (010) can be calculated on the basis that silver contributions determine the signs of all important reflections. This Fourier synthesis (Fig. 1) is notably diffuse in consequence of the very large thermal motions in the crystal and shows incomplete resolution of minor peaks. Figure 1, nevertheless, is seen to be incompatible with C2/m: the requirements that the carbon skeleton and one fluorine atom of a butyrate group lie in a mirror plane and that pairs of fluorine atoms occupying general positions and attached to the same carbon be exactly superposed in the projection are clearly not met. However, the prominent minor peak at $x = 0.325$, $z = 0.085$ (or its equivalent through translation at 0.825, 0.085) may very well represent the projection of two oxygen atoms having nearly equal x and z coördinates.

Further analysis must be based upon either C2 or Cm, of which the latter can be definitely eliminated. The intolerably bad packing relations which result if a butyrate group is placed in a position of no symmetry in Cm can be seen in various ways. The four silver atoms in the (001) face of the cell would (most implausibly) be bonded wholly on one side to the terminal oxygen atoms of four butyrate groups. On the average, each such perfluorobutyrate group can be allotted a maximum packing cross-section of $1/4\ ac = 14.6$ Å.^{2}, whereas hydrocarbon chains in parallel alignment are known to require about 20 Å.^{2} per chain. The butyrate groups would not, of course, be required to be in parallel alignment, but a bundle of four would need to be accommodated in the limited cross-section ac.

The alternative possibility based on special positions of Cm would place the carbon skeleton and one fluorine atom of a butyrate group in the mirror plane $y = 0$ and the remaining fluorine atoms equally in the planes $y = \pm y_0$, where $2y_0b$ is the separation of two fluorine atoms attached to the same carbon. On the (complex) Fourier synthesis of $0kl$ amplitudes, $\rho_1(y,z)$, carbon and fluorine atoms would be represented as peaks of electron density distributed along the parallel lines, $y = y_0,0,\bar{y}_0$. Consider now $\rho_0(y,z)$, the apparent electron density resulting from a synthesis of $0kl$ data on the basis of C2/m, *i.e.*, with wholly real amplitudes and signs given by the dominating silver contributions (which last are wholly real in any case). Then, qualitatively and, in favorable cases, semiquantitatively, $\rho_0(y,z)$ is a good substitute for $1/2\{\rho_1(y,z) + \rho_1(y,\bar{z})\}$.[4] In the present case the approximation should be quite good since each real component $|F| \cos \alpha$ used in computing ρ_1 must usually be only slightly smaller than $|F|$ itself. On ρ_0 the carbon and fluorine atoms would still be represented as electron density concentrated along the lines $y = y_0,0,\bar{y}_0$, although attenuated along c as compared with the distribution on ρ_1. $\rho_0(y,z)$ was computed for silver perfluorobutyrate and found to be wholly incompatible (except for oxygen positions) with placement of the butyrate groups in the special positions of Cm.

With the exclusion of Cm and C2/m as possible space groups there remains only C2. The apparent electron density, $\rho_0(y,z)$, is also an approximation to $1/2\{\rho(y,z) + \rho(\bar{y},z)\}$, where $\rho(y,z)$ is the true electron density based upon C2. Any grouping of atoms in general positions of C2 which approximates to the higher symmetry requirements of C2/m will appear on ρ_0 with approximately correct positions and densities. A set of peaks appearing on ρ_0 at $y = \pm0.120$, $z = \pm0.085$ are considerably stronger than any other minor peak but one. In view of their proximity and symmetrical relation to silver peaks on ρ_0, the peaks at ±0.120, ±0.085 are identified as representing oxygen atoms. This identification is greatly strengthened by noting again that $\rho(x,z)$ shows apparently doubled peaks at the same value of z (±0.085). (The general appearance of ρ_0 can easily be visualized if, in Fig. 3, one superposes the mirror image of the lower half of the plot upon the upper half. The consequent enhancement of the oxygen peaks relative to other minor peaks becomes evident.)

The eight oxygen atoms of the unit cell go into two sets of fourfold general positions of C2: xyz; $\bar{x}y\bar{z}$; $1/2 + x$, $1/2 + y,z$; $1/2 - x$, $1/2 + y$, $\bar{z}$. Using $x'y'z'$ for one set of four, we have $x' \cong x$, $y' \cong \bar{y}$, $z' \cong z$. There remains one ambiguity in the choice of parameter values since 0.325, 0.120, 0.085 and −0.175, 0.120, 0.085 are equally consist-

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(3) H. T. Evans, Jr., *J. Appl. Phys.*, **23**, 663 (1952).

(4) *Cf.* J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

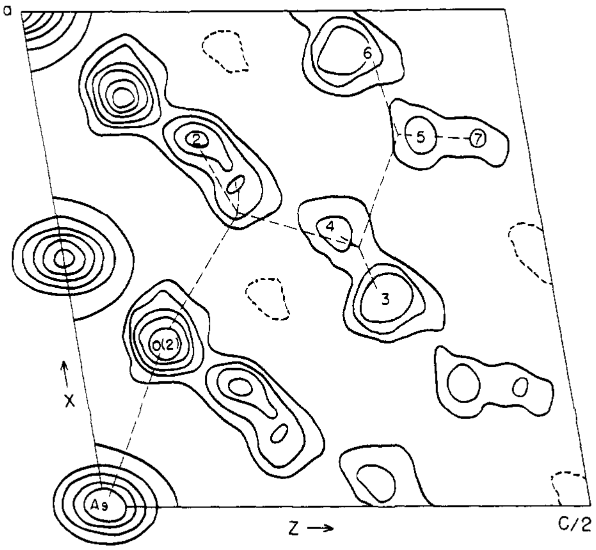
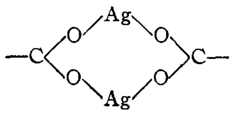


Fig. 1.—Fourier synthesis of *h0l* amplitude data. Fluorine peaks are numbered to agree with Fig. 2. The indicated bond diagram for half a dimeric molecule is not intended to imply that carbon positions are determined from the data. The density interval for silver contours is ten times that for minor peaks.

ent with the analysis of $\rho(x,y)$ and $\rho_0(y,z)$. Using the nearest silver atom (0,0.163,0), Ag–O separations of 2.24 and 1.78 Å. are obtained. In cubic Ag_2O, the bond distance is accurately 2.04 Å., but in silver oxalate, involving bonds between silver and carboxyl oxygen, larger values of 2.17 and 2.30 Å. are reported.[5] Thus the choice of oxygen parameters (0.325, 0.120, 0.085) giving Ag–O = 2.24 Å. appears much more probable and is supported by the further analysis.

The separation of two oxygen atoms at 0.325, 0.120, 0.085 and 0.325, −0.120, 0.085 is 2.16 Å., about that expected with a carboxyl group of standard dimensions; it is, of course, much too small for an O–O separation between different carboxyls. At this point we conclude that the characteristics species in the crystal is the dimeric molecule, itself characterized by an eight-membered central ring



approximating to 2/m, although required to have only a twofold axis. It is further to be noted that this conclusion is deduced from the structural evidence independently of the observation that silver perfluorobutyrate exists as the dimer in benzene solution and that it would still hold even if the alternative choice of oxygen parameters were correct.

With the configuration and orientation of the central ring system known, the prospects for making a fairly detailed interpretation of $\rho(x,z)$ are greatly improved. Scaled models of the dimer were put together using the data cited for the central ring system and, in addition, C–O = 1.25, C–C = 1.54, C—F = 1.33 Å.,[6] and regular tetrahedral bond angles within the perfluoropropyl radical. As it then appears that dimeric molecules having the full symmetry of 2/m could pack together satisfactorily within the lattice, the failure of the molecule to retain a mirror plane is to be ascribed to intramolecular causes. Steric repulsions between fluorine atoms attached to different carbon atoms in the skeleton of a flat zig-zag chain are eased if the chain is twisted by a regular increment from carbon to carbon[7]; according to Bunn and Howells[7] a complete turn of 360° is made in polytetrafluoroethylene during an advance of 26 carbon atoms along the chain. This twisting, moreover, is accompanied by an expansion of the C–C–C bond angle to about 116°. The particular helix best suited to an extended chain need not be established in a chain as short as perfluoropropyl, but we were prepared to find that both a twisting of the skeleton and an alteration in C–C–C bond angles might be required to fit our data. We did assume that the F–C–F bond angle would remain near 109.5°; this is indicated for octafluorocyclobutane[6] and for the Cl–C–Cl angle in octachlorocyclobutane,[8] despite marked departure from planarity of the carbon skeleton presumably arising from steric repulsion between halogen atoms attached to adjacent carbons.

From extensive trials carried out with systematic variations in the shape and orientation of the model, we arrived at a fairly satisfactory interpretation of $\rho(x,z)$. Projected positions of fluorine atoms on $\rho(x,z)$ are indicated (Fig. 1) by numbers corresponding to those employed on the diagram of the molecular model (Fig. 2). The marked positions are those finally selected following calculation (Fig. 3) of the complex synthesis, $\rho(y,z)$. The (mean) principal axis of the butyrate group

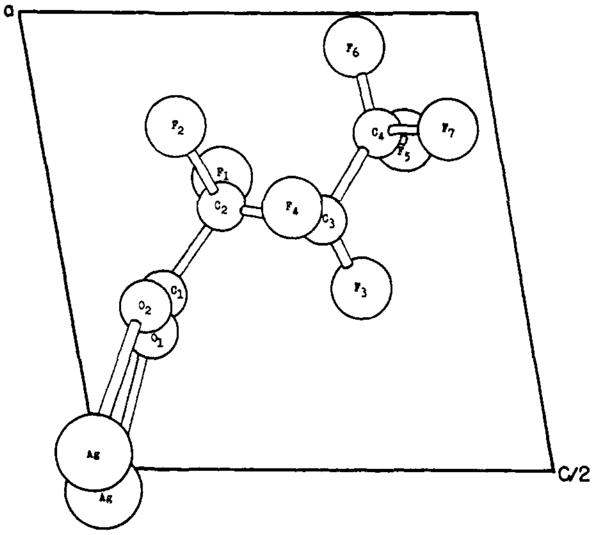


Fig. 2.—Oriented model for half a dimeric molecule shown in perspective. The mean principal axis of the molecule lies nearly in $y = 0$.

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(5) R. L. Griffith, *J. Chem. Phys.*, **11**, 499 (1943).

(6) H. P. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 (1952).

(7) C. W. Bunn and E. R. Howells, *Nature*, **174**, 549 (1954).

(8) T. B. Owens and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

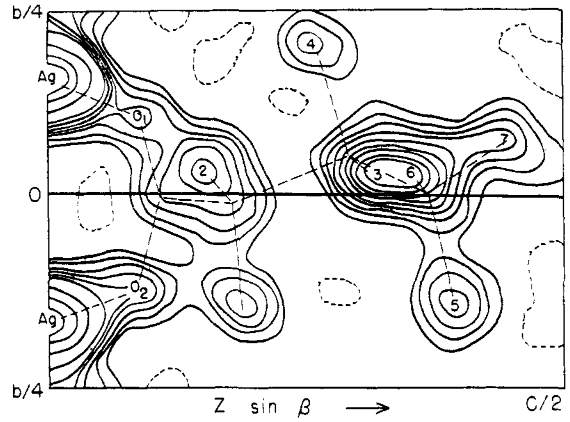

Fig. 3.—Fourier synthesis of 0*kl* amplitude data. Numbering scheme as in Fig. 1.

lies nearly in the plane $y = 0$ and is otherwise oriented as shown in Fig. 2. We could find no alternative interpretation differing grossly from that shown in Figs. 1–3 which seemed at all promising; in particular, use of the alternative set of oxygen parameters gave no slightest prospect of a reasonable interpretation of fluorine positions.

Quantitatively, however, the interpretation of $\rho(x,z)$ leaves much to be desired. The apparently unsystematic variations in the densities and shapes of fluorine peaks and the indecisive indications of carbon positions would seem to show that, despite the care with which they were taken, the experimental data lack the accuracy required to give a highly precise picture of electron density. On the other hand, $\rho(x,z)$ must be diffuse in consequence of the excessively large and complex thermal motions executed by the molecules within the crystal. There is little hope of making a convincing analysis of thermal motions for the lighter atoms, but presumably lower limits for the molecule as a whole are set by a determination of the very large and highly anisotropic thermal parameters for silver atoms.

On an absolute basis the experimental amplitudes per monomeric molecule lie in the range 2.2–58.6, with all values near the observational limit of $\sin \theta/\lambda$ only slightly above the background equivalent of the Geiger counter and almost wholly attributable to silver scattering. The effective form factor for silver must then fall off to about 2 at the limit of observation. The principal axes of the thermal parameter ellipsoid are *b* and, at least very nearly, *c* and *a** (Figs. 1 and 3). Using a hybrid Thomas–Fermi with Pauling–Sherman form factor and employing successive approximations which permitted small adjustments in the scale factor for experimental amplitudes, the following values for the thermal parameters of silver were obtained: $B_c = 7.6$, $B_b = 3.6$, $B_{a*} = 3.4$ Å.^{2}. For *h*0*l* reflections having $\sin \theta/\lambda = 0.40$, values of $F - F_{Ag}$ were then generally small and essentially randomly distributed about zero. Over the whole range $\Sigma|F| - |\Sigma F_c| \cong 0$, where F_c is the calculated amplitude including contributions of the light atoms based on the parameter data of Table I. In this and all later calculations of F_c we have used for all atoms the thermal parameters evaluated for silver. We would expect that the average thermal parameter for a fluorine atom would be larger than that of silver though not necessarily showing the same degree of anisotropy. However, the irregular contours and lack of precise definition of the minor peaks in Fig. 1 indicates that a further attempt to evaluate thermal parameters for individual light atoms, necessarily would be largely on an arbitrary trial and error basis. While we might hope to achieve a moderate improvement in the degree of agreement between calculated and observed amplitudes, it is quite certain that the data at hand are incapable of yielding a sufficiently accurate determination of light atoms positions for significant quantitative comparison of bond distances and angles with those given by other studies. Nevertheless, the conclusions already stated as to the general character of the dimeric molecule can be further strengthened.

TABLE I

PARAMETER DATA FOR SILVER PERFLUOROBUTYRATE

(Values rounded off to 0.005 for fluorine atoms)

Atom	*x*	*y*	*z*
Ag	0	0.161	0
O_1	0.325	− .120	0.083
O_2	.325	.110	.089
F_1	.650	− .140	.190
F_2	.740	.040	.155
F_3	.410	.035	.325
F_4	.550	.205	.260
F_5	.740	− .135	.395
F_6	.930	.030	.360
F_7	.740	.080	.440

For *h*0*l* reflections, the value of $R = (\Sigma||F| - |F_c||>/\Sigma|F|$ is found to be 0.24 with F_c approximated by F_{Ag} and 0.18 with F_c based upon the parameter data of Table I. Large differences, in $F - F_{Ag}$, are limited to small $\sin \theta/\lambda$, and for such reflections the inclusion of light atoms contributions in F_c yields substantial improvements. For reflections having $\sin \theta/\lambda > 0.40$ the total contribution to *R* is not very different whether F_c or F_{Ag} be used. This clearly indicates the limited accuracy of the parameter data. For the most part the calculated contributions of light atoms have correct signs but are rather too large on the average; the desirability of using somewhat larger thermal parameters for light atoms is thus indicated. It may be noted also that the initial set of *x* and *z* parameters, derived for best average fit of $\rho(x,z)$ by the (internally twisted) model held to the previously specified bond distances and angles, lead to the significantly lower value of 0.155 for *R*.[9]

The difference synthesis, $1/A\ \Sigma\Sigma(F - F_{Ag}) \cos 2\pi\,(hx + lz)$ was computed and found not to differ materially from $\rho(x,z)$ as regards resolution and positions of the minor peaks. The additional uncertainties in the difference synthesis arising from

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(9) Amplitude data for *h*0*l* and 0*kl* reflections have been deposited as Document No. 4787 with the ADI auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress

uncertainties in F_{Ag} were thought to be more important for our data than any small errors in $\rho(x,z)$ arising from finite termination of series. We chose, therefore, to rely on the complete synthesis.

The original fitting of $\rho(x,z)$ with the model involved also consideration of the (easy) packing relations and provided trial values for y as well as x and z parameters. Using phases calculated from this structure, the complex synthesis of $0kl$ amplitudes was computed. The result was in gratifyingly good agreement with the trial structure while indicating some small changes in parameters. Phases were recalculated and the final synthesis, $\rho(y,z)$, computed (Fig. 3). When considered in conjunction with $\rho(x,z)$, reasonable estimates (Table I) could be made for all parameter values of fluorine and oxygen atoms as indicated on Figs. 1 and 3. No carbon positions can be read directly from the projections. The value of R is 0.16 for $0kl$ reflections.

For a majority of the minor peaks, $\rho(y,z)$ seems to show rather better definition than does $\rho(x,z)$. This may be partly a fictitious effect resulting from the use of too small thermal parameters for the light atoms in calculating phases, thus tending to make imaginary components in $\rho(y,z)$ somewhat large on the average. In view of this artificial enhancement of imaginary components and the fact that accurate evaluation of light atom positions is not feasible with the data at hand, it would perhaps have been just as well to have stopped with the first calculation of $\rho(y,z)$. However, the differences between the two approximations are too small to affect the general conclusions.

Discussion of the Structure

The general character of the dimeric molecule of symmetry 2, with an eight-membered central ring approximating to 2/m, is readily visualized from Fig. 2. The lowering of the symmetry of the dimer from 2/m to 2 results from twisting of the fluorocarbon skeletons. These conclusions follow unambiguously from the analysis of the data. The quantitative aspects of the results are much less satisfactory.

The only accurately determined distance within the dimer is the Ag–Ag separation of 2.90 ± 0.02 Å. As this is nearly identical with the bond distance in metallic silver, a bridging across the ring may be indicated. The diamagnetism of the crystal shows that any such bridging does not involve unpairing of electrons in the silver core.

Within the accuracy of the determination of oxygen positions, the Ag–O bond distances are equal at about 2.25 Å., in essential agreement with the probably no more accurate values of 2.17 and 2.30 Å. reported[5] for silver oxalate. The O_1–O_2 separation of about 2.08 Å. is roughly 0.10 Å. smaller than the average value found for carboxyl in more accurate studies; such a variation is doubtless within the accuracy of our determination.

In view of the easy packing relations, the twisting of the fluorocarbon chain about its long axis presumably arises from intramolecular repulsions, most strikingly exemplified in the continuous helical twisting observed for polytetrafluoroethylene molecules.[7] However, we find no convincing evidence that the C–C–C bond angle in the perfluorobutyrate group must be appreciably larger than 109.5°.

There are two interesting aspects of the packing relations. The plane $z = 1/2$ is a median plane of contact between fluorocarbon ends of two distinct layers of dimeric molecules. In addition to forming two bonds to oxygen atoms within a dimeric molecule each silver atom is about 2.6 Å. from two oxygen atoms of two neighboring molecules. The group of five atoms comprises a distorted tetrahedron of symmetry 2 with silver at the center. The bond angle within the dimer is about 160°, and the O–Ag–O angle involving atoms from three different molecules is about 83°. The only moderately close intermolecular contact otherwise is between O_2 and F_1 at about 2.9 Å. Calculated intermolecular separations involving fluorine atoms range upward from 3.4 Å.

In view of the very limited accuracy of the parameter data, a full presentation of calculated interatomic distances and angles within the perfluorobutyrate group is hardly justified. The following comparisons should serve to indicate the general character of the results. It was pointed out in the preceding section that the trial structure derived for the best average fit of the model with $\rho(x,z)$ with simultaneous regard for packing relations actually gave significantly better agreement between calculated and observed amplitudes than did any subsequent refinement. On this basis the trial structure may well be a better approximation to the actual structure than is given by the data of Table I; in any case the trial structure employed "standard" bond angles and bond distances and is useful for comparison. The mean deviation in the positions of O_1, O_2, F_1 and F_2, as given by the two structures, is about 0.05 Å., but is about 0.20 Å. for the remaining fluorine atoms. The effective length of the molecule is not significantly different in the two structures. The final structure does, however, attribute a significantly smaller effective diameter, particularly toward the ends, to the molecule. As we doubt either that the C–F distance can be much less than 1.33 Å.[6] or that it decreases toward the ends of the molecule, we conclude that this result is rather an indication of the errors inherent in the final parameter values for fluorine atoms. The reading of the Fourier projections probably makes insufficient allowance for incomplete resolution of minor peaks, and it certainly does not include allowance for libratory twisting motion about the long axis of the molecule.[7] Thus the at best uncertain reading of the projections is likely to give an underestimate of the size of the butyrate group.

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