

## The Structure of Triphenylmethyl Perchlorate at 85 °C

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At 85 °C triphenylmethyl perchlorate crystallizes in space group  $F4_132$  with  $Z = 16$  and  $a = 18.91$  Å. Most atoms lie on special positions. The structure was refined by three-dimensional Fourier methods and least-squares techniques.

The carbonium ion is propeller-shaped with three coplanar central bonds (symmetry  $D_3$ ). Adjacent aromatic rings are at angles of 54°. There are two structurally different perchlorate groups; one is disordered, the other is not. The refinement was carried out for two models of disorder, leading to  $R$  values of 9.1 and 8.4% respectively. Neither model is entirely satisfactory. Bond distances and bond angles are reported. It is shown in an appendix that triphenylmethyl tetrafluoroborate at 110 °C is isomorphous with the perchlorate.

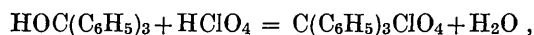
### Introduction

Carbonium ions are of considerable interest as intermediates in numerous organic reactions. Most of these ions are unstable and do not lend themselves to detailed structure analysis. Triarylcarbonium ions,  $[Ar_3C]^+$ , however, are stabilized by resonance in the conjugated  $\pi$ -electron system and seem to occur in reasonably stable solid compounds. To our knowledge only two relevant structure determinations have been reported in the literature.\* Stora (1958) showed from single-crystal X-ray diffraction data that the crystal-violet ion (tri-*p*-dimethylaminophenylcarbonium ion) has threefold symmetry. Sharp & Sheppard (1957) examined the infrared absorption spectra of solid complex fluorides of the triphenylcarbonium ion (TPC) and provided substantial evidence for a propeller-like structure (symmetry  $D_3$ ) with three coplanar central bonds. The present work is an attempt to solve the complete structure of the TPC ion, which was supposed to occur in the coloured perchlorate  $C(C_6H_5)_3ClO_4$ .

### Experimental

#### Preparation

Crystals of octahedral habit were prepared directly by the reaction



\* A third publication appeared during the preparation of this paper (Sundaralingam & Jensen, 1963). It deals with the preliminary results of the structure determination of sym-triphenylcyclopropenium perchlorate.

which was carried out in acetic anhydride at room temperature (Hofmann & Kirmreuther, 1909). The crystals were washed with cold acetic anhydride and anhydrous ether and used for X-ray investigations without further purification.

#### Analyses

The infrared absorption spectrum of a suspension in kerosine was measured; it is virtually identical with the spectrum of the corresponding complex fluorides (Sharp & Sheppard, 1957), except of course for the specific absorption peaks of the respective anions.

By titrimetric analysis the concentration of perchlorate ions was determined to be 102.5% ( $\pm 1.5\%$ ) of the theoretical value (duplicate analysis). This indicates at the same time that the crystals do not contain solvent molecules.

#### Space group and cell dimensions

For reasons that will appear in a following section, the X-ray data were taken of a crystal at 85 °C. At this temperature the Laue symmetry is  $F(4/m)\bar{3}(2/m)$ . With  $a$  (85 °C) =  $18.91 \pm 0.02$  Å as determined from Weissenberg photographs calibrated with aluminum powder lines, and with  $D_m$  (20 °C) =  $1.37$  g.cm<sup>-3</sup> (floatation in a mixture of benzene and carbon tetrachloride) there are 16 formula units in the unit cell.  $D_c$  (85 °C) =  $1.346$  g.cm<sup>-3</sup>.  $F4_132$  is the only space group compatible with the above data as well as with the systematic absence of the reflexions  $hkl$  with mixed indices and  $h00$  with  $h \neq 4n$ .

### Collection and handling of intensity data

An almost spherical crystal with a diameter of about 0.3 mm was obtained by partial dissolution of an octahedral specimen in acetic anhydride. The crystal was mounted in a sealed thin-walled glass capillary and oriented along [110]. In all manipulations care was taken to avoid exposure to air as far as possible, since the formation reaction is readily reversed, even with traces of water vapour. Reflexions  $h+n, h-n, l$  with  $n=0, 1, 2, 3$  were recorded at 85 °C on (equi-inclination) Weissenberg photographs with unfiltered copper radiation. There are 440 non-equivalent reflexions having  $2d_{hkl} < \lambda(\text{Cu } K\alpha)$ . Of these only 186 were actually observed, 20 were experimentally inaccessible, the others (234) were too weak. The intensities were estimated visually by use of the multiple-film technique and corrected for Lorentz, polarization and absorption (Bond, 1959) factors. The atomic scattering factors used throughout this work are those given by Viervoll & Øgrim (1949) for chlorine, and by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon.

### Non-cubic modifications

In a previous publication (Gomes de Mesquita, 1962) a detailed account was given of the phase-transition phenomena in TPC perchlorate, which impose a severe limit on the scope of the present structure investigation. The conclusions of that paper will therefore be summarized here:

Below 5 °C the substance crystallizes in a non-cubic space group. There is strong evidence for tetragonal symmetry ( $c/a=1.011$ ). However, only twinned specimens of this modification were obtained, unsuitable for X-ray structure analysis.

Slightly above 5 °C single crystals were prepared having a complicated modulated structure.\* The sub-cell is tetragonal with  $c'/a'=0.997$  and  $c' \simeq a' \simeq 18.8 \text{ \AA}$ . The modulation extends along the  $c$  axis; it has a period  $c=(9 \pm 1)c'$ ; ( $a=a'$ ). The crystals whose preparation was described above are multiple twins of this modulated structure.

Between room temperature and 85 °C a transition takes place whereby the space group changes to  $F4_132$ . At least in those crystals which are twinned at room temperature (these were examined in particular) the transition is a gradual one. In view of this gradual phase change, the X-ray photographs obtained at 85 °C were scrutinized for effects due to possible remnants of a non-cubic structure. The only one found concerned those two reflexions of the form  $\{511\}$  which appeared on a first level photograph;

in one particular crystal their intensities were twice as strong as those of all other reflexions of the same form. It has not been possible to attribute this effect to trivial experimental errors such as inconstancy of the temperature. However, since it could not be reproduced in a second crystal, the effect was neglected.

The X-ray diagrams of twinned modulated crystals at room temperature and those at 85 °C are only slightly different. Initially, these differences were overlooked and room temperature data were used in the earlier stages of the structure investigation. The refinement, however, was carried out with high temperature data.

### Instability of the crystals

Crystals of TPC perchlorate decompose slowly at room temperature (Dauben, Honnen & Harmon, 1960). At 85 °C the decomposition reaction proceeds faster (Gomes de Mesquita, 1962). Nevertheless there are no indications that the X-ray data are particularly unreliable. One crystal specimen was used for recording all the intensities listed in Table 2. During the time needed to make the various exposures a general reduction of all X-ray intensities was noticed. However, except for the above-mentioned  $\{511\}$  reflexions, no difficulties or inconsistencies were encountered in the scaling together of the four layers of observed reflexions assuming cubic symmetry.

### Determination and refinement of the structure

Consideration of the available positions and their point symmetry (*International Tables for X-ray Crystallography*, 1952) shows that  $C(c)$  (Fig. 1) must be either in (c) or (d) with point symmetry  $32(D_3)$ ; the former of these two equivalent positions was

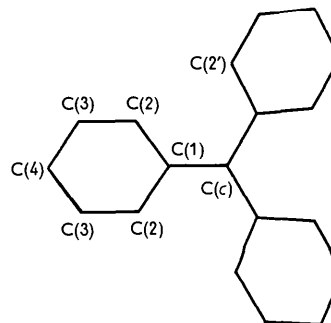


Fig. 1. The triphenylcarbonium ion.

arbitrarily chosen. Then, two positions ( $g$ ) on twofold axes are necessarily occupied by  $C(1)$  and  $C(4)$  respectively, and two general positions ( $h$ ) by  $C(2)$  and  $C(3)$ . The Cl atoms can be located only in (a) and (b). Finally it would seem (see, however, below) that two positions (e) must be occupied by O atoms.

\* Mr A. Kreuger (The Crystallography Laboratory, University of Amsterdam) recently cooled a single crystal of the modulated structure while studying its optical behaviour under the polarizing microscope. He found a sharp transition point at 5 °C.

In all, the values of ten positional parameters are to be determined. It is not difficult to make a reasonable estimate for most of these. However, the twist angle  $\alpha$  (*i.e.* the angle between the plane of the three central C(c)–C(1) bonds and the plane of any of the attached aromatic rings) remains to be found. Furthermore, the orientations of the perchlorate tetrahedra have to be determined, since the space group provides two possibilities for either of the oxygen atoms, O(*a*) and O(*b*), *viz.*  $x_a = \pm|x_a|$  and  $x_b \approx \frac{1}{2} \pm|x_a|$  with  $|x_a| < \frac{1}{8}$ .

The initial value of  $\alpha$  ( $+19^\circ$ ) was somewhat arbitrarily chosen; later on, all other parameters being fairly well determined, a good approximation ( $+35^\circ$ ) was obtained from a direct plot of  $F_c(hkl)$  versus  $\alpha$  for a small number of low-angle reflexions. Whereas the position of O(*b*), about Cl(*b*), was easily established by means of three-dimensional electron-density sections, no ordered model would fit the situation around Cl(*a*). Fair agreement was obtained by assuming a statistical distribution of O(*a*) over the two available positions, and much better agreement when completely spherical disorder was assumed.

After introduction of two isotropic temperature factors, one for the chlorine atoms, the other one for the remainder of the structure, and after application of a few smaller parameter shifts which were suggested in the electron-density maps, the reliability index defined as  $R = \Sigma|F_o - |F_c|| / \Sigma F_o$  was 19.0%. At this stage a complete three-dimensional electron-density synthesis showed no other significant deviations from the assumed structure than a non-uniform distribution of O(*a*) (Fig. 2), for which, however, no interpretation was found in terms of a simple model.

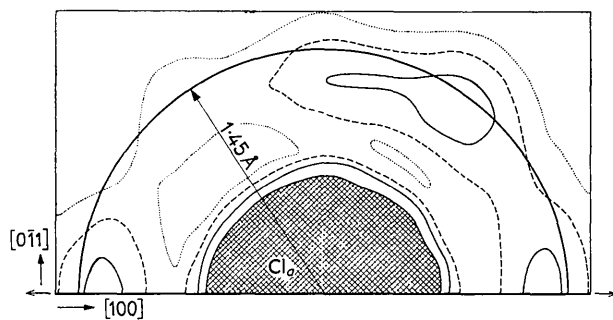


Fig. 2. Section (110) of the three-dimensional electron-density synthesis, cutting through the centre of the disordered perchlorate ion. At this stage  $R = 19.0\%$ . Diffraction data obtained at  $85^\circ\text{C}$ . Dotted contour at  $1.0 \text{ e.}\text{\AA}^{-3}$ , broken contour at  $1.5 \text{ e.}\text{\AA}^{-3}$ , continuous contour at  $2.0 \text{ e.}\text{\AA}^{-3}$ . Centre of Cl(*a*) at  $24 \text{ e.}\text{\AA}^{-3}$ . The Cl–O distance is taken as  $1.45 \text{ \AA}$ .

The refinement was first carried out by means of three-dimensional difference syntheses with individual isotropic temperature factors for all atoms. The Cl(*a*)–O(*a*) radius was kept constant at  $1.45 \text{ \AA}$ . In a few cycles the structure refined to  $R = 13.0\%$ . The corresponding difference map showed clear

indications of anisotropic thermal vibrations and of deviations from spherical symmetry of the disordered perchlorate group. All unobserved reflexions were now calculated; without exception their  $F_c$  values were at or below the limit of experimental detectability.

For further refinement use was made of a least-squares program written for the computers STEVIN and PASCAL by Braun & Leenhouts (P. B. Braun & J. I. Leenhouts, unpublished). The program minimizes the function  $\Sigma w(F_o - k|F_c|)^2$ . It assumes no coupling between

- (a) the parameters of different atoms,
- (b) temperature and positional parameters,

and it treats anisotropic temperature factors in the form:

$$\exp\{- (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{31}lh)\}.$$

Unobserved reflexions were omitted from the refinement, and so was the heavily dominant reflexion 422. All other reflexions were given equal weight. Hydrogen atoms were inserted at  $1.084 \text{ \AA}$  from the corresponding carbon atoms; the vibrational and positional parameters of the former were occasionally adapted by hand to those of the latter. The Cl(*a*)–O(*a*) distance was still being kept constant with O(*a*) spherically distributed around Cl(*a*), and both these atoms were given the same isotropic temperature factor. A number of cycles brought the  $R$  value down to  $9.1\%$ . Despite this relatively good result, the difference synthesis showed maxima and minima in the region of the ordered ( $\pm 0.4 \text{ e.}\text{\AA}^{-3}$ ) as well as of the disordered ( $\pm 0.6 \text{ e.}\text{\AA}^{-3}$ ) perchlorate group. These had also been found in the difference map before the least-squares refinement.

The situation about the disordered group in (*a*) with minima in the difference map on (*xxx*) and ( $\bar{x}\bar{x}\bar{x}$ ) and maxima on (*x00*) suggested the following model. This tetrahedral group rotates around any one of its  $\bar{4}$  axes; the rotation axes of all these groups in the crystal are statistically distributed over the four directions of threefold crystal symmetry; the centre of each rotating tetrahedron remains in (000). Actually, the minima at (*xxx*) and at ( $\bar{x}\bar{x}\bar{x}$ ) are not equivalent, one being about 50% deeper than the other. The new model, like the old, takes no account of this difference.

This model, with fixed Cl(*a*)–O(*a*) distance, when fed into the least-squares program, resulted in  $R = 8.4\%$  ( $8.6\%$  including reflexion 422). The quantity to be minimized,  $\Sigma w(F_o - k|F_c|)^2$ , decreased by about 25% owing to the change of model. Nevertheless, the difference map still showed maxima and minima about (*a*) ( $\pm 0.5 \text{ e.}\text{\AA}^{-3}$ ) and (*b*) ( $\pm 0.3 \text{ e.}\text{\AA}^{-3}$ ). At the same time it was found that strong coupling exists between the model used for the disorder of O(*a*) and the temperature parameters of O(*b*); the calculated values of these parameters have therefore little physical significance. The temperature factors of other atoms are also coupled to the model of disorder,

Table 1. *The final parameters after least-squares refinement based on axially disordered ClO<sub>4</sub>(a), uncorrected for oscillational vibrations*

Estimated standard deviations appear in parentheses.  
The values of all temperature parameters have been multiplied by 10<sup>4</sup>

|                       | <i>x</i>       | <i>y</i>       | <i>z</i>       | <i>B</i> <sub>11</sub> | <i>B</i> <sub>22</sub> | <i>B</i> <sub>33</sub> | <i>B</i> <sub>12</sub> | <i>B</i> <sub>13</sub> | <i>B</i> <sub>23</sub> |
|-----------------------|----------------|----------------|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| C(c)                  | 0.1250(0.0000) | 0.1250(0.0000) | 0.1250(0.0000) | 33                     | 33                     | 33                     | -12                    | -12                    | -12                    |
| C(1)                  | 0.1791(0.0007) | 0.1250(0.0000) | 0.0709(0.0007) | 35                     | 42                     | 35                     | -27                    | 45                     | -27                    |
| C(2)                  | 0.2482(0.0006) | 0.1012(0.0006) | 0.0838(0.0006) | 30                     | 56                     | 57                     | 06                     | 01                     | -13                    |
| C(3)                  | 0.2997(0.0006) | 0.0993(0.0007) | 0.0335(0.0006) | 31                     | 80                     | 71                     | 00                     | 23                     | -23                    |
| C(4)                  | 0.2816(0.0019) | 0.1250(0.0000) | 0.9684(0.0019) | 48                     | 94                     | 48                     | -27                    | 30                     | -27                    |
| H(2)*                 | 0.263          | 0.082          | 0.136          | 30                     | 61                     | 59                     | 08                     | -05                    | -21                    |
| H(3)*                 | 0.353          | 0.080          | 0.043          | 36                     | 74                     | 69                     | -03                    | 24                     | -21                    |
| H(4)*                 | 0.322          | 0.125          | 0.928          | 48                     | 88                     | 48                     | -30                    | 20                     | -30                    |
| ClO <sub>4</sub> (a)† | 0.0000(0.0000) | 0.0000(0.0000) | 0.0000(0.0000) | 37                     | 37                     | 37                     | 00                     | 00                     | 00                     |
| Cl(b)                 | 0.5000(0.0000) | 0.5000(0.0000) | 0.5000(0.0000) | 28                     | 28                     | 28                     | 00                     | 00                     | 00                     |
| O(b)                  | 0.5419(0.0009) | 0.5419(0.0009) | 0.5419(0.0009) | 76                     | 76                     | 76                     | -34                    | -34                    | -34                    |

\* All hydrogen parameters have assumed values.

† *d*(Cl-O) = 1.45 Å.Table 2. *List of observed and calculated structure factors on an arbitrary scale**F*<sub>ca</sub> corresponds to axial disorder, *F*<sub>cs</sub> to spherical disorder

| <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> <sub>o</sub> | <i>F</i> <sub>ca</sub> | <i>F</i> <sub>cs</sub> | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> <sub>o</sub> | <i>F</i> <sub>ca</sub> | <i>F</i> <sub>cs</sub> | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> <sub>o</sub> | <i>F</i> <sub>ca</sub> | <i>F</i> <sub>cs</sub> | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> <sub>o</sub> | <i>F</i> <sub>ca</sub> | <i>F</i> <sub>cs</sub> |
|----------|----------|----------|-----------------------|------------------------|------------------------|----------|----------|----------|-----------------------|------------------------|------------------------|----------|----------|----------|-----------------------|------------------------|------------------------|----------|----------|----------|-----------------------|------------------------|------------------------|
| 4        | 0        | 0        | 188                   | 183                    | 183                    | 17       | 3        | 1        | 26                    | 29                     | 26                     | 5        | 5        | 3        | 35                    | 34                     | 37                     | 14       | 6        | 6        | 35                    | 38                     | 35                     |
| 8        | 0        | 0        | 109                   | 117                    | 115                    | 5        | 5        | 1        | 16                    | 13                     | 14                     | 16       | 6        | 6        | 73                    | 72                     | 68                     | 16       | 6        | 6        | 32                    | 33                     | 35                     |
| 12       | 0        | 0        | 45                    | 36                     | 28                     | 7        | 5        | 1        | 98                    | 98                     | 98                     | 9        | 5        | 3        | 77                    | 73                     | 73                     | 20       | 6        | 6        | 26                    | 27                     | 29                     |
| 16       | 0        | 0        | 63                    | 61                     | 61                     | 9        | 5        | 1        | 50                    | 53                     | 55                     | 11       | 5        | 3        | 20                    | 18                     | 20                     | 8        | 8        | 6        | 31                    | 34                     | 35                     |
| 20       | 0        | 0        | 32                    | 27                     | 27                     | 11       | 5        | 1        | 18                    | 16                     | 16                     | 13       | 5        | 3        | 40                    | 41                     | 40                     | 10       | 8        | 6        | 49                    | 40                     | 47                     |
| 24       | 0        | 0        | 21                    | 24                     | 24                     | 13       | 5        | 1        | 27                    | 34                     | 31                     | 15       | 5        | 3        | 28                    | 28                     | 27                     | 12       | 8        | 6        | 16                    | 15                     | 16                     |
| 2        | 2        | 0        | 178                   | 184                    | 185                    | 15       | 5        | 1        | 18                    | 26                     | 24                     | 7        | 7        | 3        | 26                    | 25                     | 23                     | 14       | 8        | 6        | 48                    | 43                     | 46                     |
| 4        | 2        | 0        | 278                   | 270                    | 270                    | 17       | 5        | 1        | 18                    | 13                     | 12                     | 9        | 7        | 3        | 41                    | 39                     | 37                     | 18       | 8        | 6        | 22                    | 21                     | 25                     |
| 6        | 2        | 0        | 197                   | 192                    | 187                    | 7        | 7        | 1        | 36                    | 34                     | 34                     | 13       | 7        | 3        | 28                    | 24                     | 25                     | 10       | 10       | 6        | 30                    | 28                     | 27                     |
| 8        | 2        | 0        | 121                   | 117                    | 113                    | 9        | 7        | 1        | 28                    | 23                     | 23                     | 15       | 7        | 3        | 20                    | 20                     | 21                     | 12       | 10       | 6        | 36                    | 34                     | 36                     |
| 10       | 2        | 0        | 52                    | 55                     | 42                     | 9        | 9        | 1        | 48                    | 40                     | 44                     | 9        | 9        | 3        | 13                    | 5                      | 6                      | 16       | 10       | 6        | 18                    | 17                     | 19                     |
| 14       | 2        | 0        | 54                    | 50                     | 45                     | 11       | 11       | 1        | 20                    | 10                     | 13                     | 11       | 11       | 3        | 25                    | 27                     | 27                     | 14       | 12       | 6        | 31                    | 29                     | 30                     |
| 18       | 2        | 0        | 36                    | 24                     | 29                     | 2        | 2        | 2        | 135                   | 129                    | 131                    | 4        | 4        | 4        | 96                    | 107                    | 114                    | 16       | 14       | 6        | 16                    | 20                     | 21                     |
| 22       | 2        | 0        | 15                    | 11                     | 14                     | 4        | 2        | 2        | 402                   | 454                    | 459                    | 6        | 4        | 4        | 92                    | 104                    | 103                    | 7        | 7        | 7        | 74                    | 64                     | 74                     |
| 4        | 4        | 0        | 80                    | 78                     | 85                     | 6        | 2        | 2        | 57                    | 51                     | 53                     | 8        | 4        | 4        | 142                   | 141                    | 148                    | 13       | 7        | 7        | 27                    | 13                     | 13                     |
| 6        | 4        | 0        | 29                    | 30                     | 27                     | 8        | 2        | 2        | 17                    | 16                     | 7                      | 12       | 4        | 4        | 63                    | 59                     | 57                     | 11       | 9        | 7        | 28                    | 33                     | 29                     |
| 8        | 4        | 0        | 47                    | 58                     | 57                     | 10       | 2        | 2        | 15                    | 13                     | 10                     | 14       | 4        | 4        | 19                    | 19                     | 19                     | 13       | 9        | 7        | 20                    | 23                     | 21                     |
| 10       | 4        | 0        | 55                    | 54                     | 50                     | 12       | 2        | 2        | 54                    | 51                     | 44                     | 16       | 4        | 4        | 81                    | 78                     | 79                     | 11       | 11       | 7        | 15                    | 7                      | 8                      |
| 12       | 4        | 0        | 49                    | 52                     | 43                     | 14       | 2        | 2        | 14                    | 11                     | 12                     | 20       | 4        | 4        | 16                    | 16                     | 18                     | 8        | 8        | 8        | 86                    | 75                     | 86                     |
| 20       | 4        | 0        | 28                    | 27                     | 30                     | 16       | 2        | 2        | 56                    | 53                     | 54                     | 6        | 6        | 4        | 44                    | 45                     | 59                     | 12       | 8        | 8        | 23                    | 11                     | 16                     |
| 6        | 6        | 0        | 164                   | 173                    | 173                    | 18       | 2        | 2        | 29                    | 27                     | 27                     | 8        | 6        | 4        | 14                    | 12                     | 13                     | 16       | 8        | 8        | 29                    | 27                     | 28                     |
| 8        | 6        | 0        | 25                    | 16                     | 15                     | 20       | 2        | 2        | 31                    | 27                     | 29                     | 10       | 6        | 4        | 35                    | 32                     | 35                     | 20       | 8        | 8        | 13                    | 13                     | 14                     |
| 10       | 6        | 0        | 55                    | 56                     | 55                     | 24       | 2        | 2        | 11                    | 13                     | 13                     | 14       | 6        | 4        | 28                    | 26                     | 25                     | 10       | 10       | 8        | 63                    | 53                     | 56                     |
| 12       | 6        | 0        | 28                    | 28                     | 28                     | 4        | 4        | 2        | 17                    | 23                     | 22                     | 18       | 6        | 4        | 22                    | 23                     | 24                     | 14       | 10       | 8        | 30                    | 33                     | 34                     |
| 14       | 6        | 0        | 83                    | 94                     | 90                     | 6        | 4        | 2        | 48                    | 56                     | 68                     | 22       | 6        | 4        | 13                    | 18                     | 18                     | 18       | 10       | 8        | 15                    | 14                     | 16                     |
| 18       | 6        | 0        | 44                    | 52                     | 52                     | 8        | 4        | 2        | 47                    | 51                     | 48                     | 8        | 8        | 4        | 31                    | 32                     | 40                     | 12       | 12       | 8        | 54                    | 53                     | 54                     |
| 8        | 8        | 0        | 65                    | 60                     | 62                     | 10       | 4        | 2        | 88                    | 87                     | 85                     | 12       | 8        | 4        | 64                    | 66                     | 67                     | 16       | 16       | 8        | 13                    | 14                     | 15                     |
| 12       | 8        | 0        | 68                    | 71                     | 67                     | 14       | 4        | 2        | 58                    | 57                     | 55                     | 16       | 8        | 4        | 30                    | 32                     | 33                     | 9        | 9        | 9        | 45                    | 40                     | 41                     |
| 10       | 10       | 0        | 55                    | 65                     | 61                     | 16       | 4        | 2        | 25                    | 19                     | 18                     | 10       | 10       | 4        | 103                   | 98                     | 103                    | 11       | 11       | 11       | 20                    | 13                     | 13                     |
| 14       | 10       | 0        | 30                    | 33                     | 25                     | 18       | 4        | 2        | 34                    | 30                     | 31                     | 14       | 10       | 4        | 43                    | 46                     | 46                     | 10       | 10       | 10       | 37                    | 42                     | 44                     |
| 12       | 12       | 0        | 74                    | 76                     | 72                     | 22       | 4        | 2        | 18                    | 17                     | 18                     | 12       | 12       | 4        | 28                    | 19                     | 19                     | 12       | 10       | 10       | 26                    | 19                     | 21                     |
| 16       | 12       | 0        | 20                    | 31                     | 29                     | 6        | 6        | 2        | 37                    | 36                     | 36                     | 16       | 12       | 4        | 19                    | 20                     | 21                     | 16       | 10       | 10       | 24                    | 21                     | 22                     |
| 14       | 14       | 0        | 20                    | 16                     | 16                     | 8        | 6        | 2        | 71                    | 72                     | 77                     | 14       | 14       | 4        | 28                    | 33                     | 31                     | 14       | 12       | 10       | 17                    | 16                     | 16                     |
| 18       | 14       | 0        | 15                    | 23                     | 23                     | 12       | 6        | 2        | 60                    | 59                     | 56                     | 18       | 14       | 4        | 12                    | 13                     | 15                     | 16       | 14       | 10       | 13                    | 18                     | 17                     |
| 16       | 16       | 0        | 19                    | 20                     | 21                     | 16       | 6        | 2        | 37                    | 38                     | 36                     | 5        | 5        | 5        | 44                    | 45                     | 57                     | 12       | 12       | 12       | 16                    | 19                     | 16                     |
| 1        | 1        | 1        | 110                   | 110                    | 110                    | 8        | 8        | 2        | 29                    | 32                     | 30                     | 7        | 5        | 5        | 30                    | 23                     | 31                     | 9        | 9        | 9        | 20                    | 13                     | 13                     |
| 3        | 1        | 1        | 135                   | 124                    | 124                    | 10       | 8        | 2        | 84                    | 84                     | 82                     | 9        | 5        | 5        | 40                    | 44                     | 35                     | 11       | 11       | 11       | 15                    | 22                     | 21                     |
| 5        | 1        | 1        | 27                    | 21                     | 25                     | 14       | 8        | 2        | 45                    | 52                     | 49                     | 11       | 5        | 5        | 29                    | 31                     | 30                     | 14       | 14       | 12       | 15                    | 22                     | 21                     |
| 7        | 1        | 1        | 147                   | 143                    | 134                    | 18       | 8        | 2        | 29                    | 30                     | 30                     | 13       | 5        | 5        | 19                    | 23                     | 20                     | 16       | 14       | 12       | 15                    | 22                     | 21                     |
| 9        | 1        | 1        | 21                    | 25                     | 38                     | 12       | 10       | 2        | 54                    | 53                     | 50                     | 15       | 5        | 5        | 22                    | 10                     | 10                     | 14       | 14       | 12       | 15                    | 22                     | 21                     |
| 11       | 1        | 1        | 38                    | 34                     | 24                     | 16       | 10       | 2        | 42                    | 42                     | 41                     | 17       | 5        | 5        | 15                    | 13                     | 11                     | 16       | 14       | 12       | 15                    | 22                     | 21                     |
| 13       | 1        | 1        | 45                    | 42                     | 35                     | 14       | 12       | 2        | 38                    | 43                     | 41                     | 7        | 7        | 5        | 71                    | 68                     | 58                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 17       | 1        | 1        | 29                    | 30                     | 30                     | 16       | 14       | 2        | 13                    | 15                     | 15                     | 9        | 7        | 5        | 27                    | 28                     | 21                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 19       | 1        | 1        | 21                    | 16                     | 13                     | 3        | 3        | 3        | 186                   | 204                    | 201                    | 13       | 7        | 5        | 24                    | 23                     | 24                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 3        | 3        | 1        | 89                    | 88                     | 89                     | 5        | 3        | 3        | 118                   | 113                    | 112                    | 9        | 9        | 5        | 23                    | 25                     | 18                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 5        | 3        | 1        | 51                    | 51                     | 55                     | 7        | 3        | 3        | 63                    | 68                     | 69                     | 11       | 9        | 5        | 16                    | 15                     | 16                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 7        | 3        | 1        | 55                    | 54                     | 57                     | 9        | 3        | 3        | 83                    | 85                     | 83                     | 6        | 6        | 6        | 18                    | 27                     | 24                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 9        | 3        | 1        | 19                    | 16                     | 13                     | 11       | 3        | 3        | 40                    | 38                     | 34                     | 8        | 6        | 6        | 87                    | 77                     | 90                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 11       | 3        | 1        | 52                    | 52                     | 50                     | 15       | 3        | 3        | 38                    | 44                     | 41                     | 10       | 6        | 6        | 45                    | 43                     | 44                     | 17       | 14       | 12       | 15                    | 22                     | 21                     |
| 15       | 3        | 1        | 33                    | 34                     | 33                     | 17       | 3        | 3        | 21                    | 25                     | 25                     | 12       | 6        | 6        | 106                   | 102                    | 107                    | 17       | 14       | 12       | 15                    | 22                     | 21                     |

but to a much lesser extent. The shifts of the positional parameters — in going from one model to the other — were very small and in most cases much smaller than the estimated standard deviations; only the *z* parameters of C(2) and C(3) shifted by about 1.5 times the e.s.d.

Table 1 contains the final parameters after the last refinement. Standard deviations of positional parameters were estimated from the inverses of the normal-equation matrices. Standard deviations of temperature parameters were not computed at all. A list of observed and calculated structure factors is given in Table 2.

It includes the final values computed both for spherical and for axial disorder.

### Discussion

The temperature parameters of the carbon atoms have been interpreted in terms of rigid-body movements (Cruickshank, 1956*a*). The displacive vibration is almost isotropic, having an r.m.s. amplitude of 0.26 ± 0.03 Å along the threefold axis and of 0.24 ± 0.02 Å along directions perpendicular to it. At the same time the r.m.s. librational amplitude is 5.3° ± 0.6°

about the threefold axis, and  $2.8^\circ \pm 0.9^\circ$  about any axis perpendicular to it. Following common practice, the bond distances and bond angles shown in Tables 3 and 4 are corrected accordingly (Cruickshank, 1956*b*), although the meaning of such corrections is somewhat obscure (Kay & Behrendt, 1963).

Table 3. Bond distances in the carbonium ion corrected for oscillational vibrations (deduced from the parameters of Table 1)

| Bond      | Length  | e.s.d.  |
|-----------|---------|---------|
| C(c)-C(1) | 1.454 Å | 0.018 Å |
| C(1)-C(2) | 1.408   | 0.014   |
| C(2)-C(3) | 1.364   | 0.016   |
| C(3)-C(4) | 1.372   | 0.028   |

Table 4. Bond angles in the carbonium ion corrected for oscillational vibrations (deduced from the parameters of Table 1)

|                | e.s.d. in parentheses |        |
|----------------|-----------------------|--------|
| C(2)-C(1)-C(2) | 115.3°                | (1.6°) |
| C(1)-C(2)-C(3) | 123.5                 | (1.1)  |
| C(2)-C(3)-C(4) | 116.1                 | (2.0)  |
| C(3)-C(4)-C(3) | 125.3                 | (3.7)  |

Most distances agree fairly well with previously published results (Gomes de Mesquita, 1962), but  $d(C(2)-C(3))$  is significantly shorter. The aromatic ring shows no significant deviations from planarity: C(2) and C(3) are at a distance of 0.013 Å from the best plane through the ring, one at either side. The angle between the plane of the three central C(c)-C(1) bonds and the plane of C(2)-C(1)-C(2) is  $32.4^\circ$ ; this last plane and the plane of C(3)-C(4)-C(3) are at an angle of  $1.2^\circ$ . The twist angle  $\alpha$  may therefore be taken as  $31.8^\circ \pm 0.6^\circ$ ; this corresponds to an angle of  $54.3^\circ$  between adjacent aromatic rings. A value of  $47^\circ$ - $54^\circ$  was estimated on the basis of steric considerations (Deno, Jaruzelski & Schriesheim, 1954). The shortest distance between hydrogen atoms of neighbouring rings is 2.6 Å; this must be twice the van der Waals radius of the hydrogen atom. There is no evidence that the carbonium ion would rather have a pyramidal configuration: from the values of the temperature parameters it is computed that C(c) and C(4) are not smeared out along the direction parallel to the threefold axis.

In the ordered perchlorate group the Cl(b)-O(b) bond distance, as found from the least-squares refinement, is  $1.37 \pm 0.03$  Å. The correction for oscillational vibrations is easily computed (0.05 Å), but in view of the coupling that exists between the parameters of the ordered and the disordered group, it has no real significance. It must be noted that the least-squares technique does not yield the same Cl(b)-O(b) distance as the refinement by means of difference syntheses: the latter method leads to a bond length which is longer by as much as 0.08 Å. This effect was not found in the determination of the carbon positions.

None of the disorder models described in this paper is entirely satisfactory. It seems possible that the ClO<sub>4</sub>(a) groups in the crystal are statistically distributed over 12 general positions, or even that experimentally unobserved deviations from space-group symmetry occur. However, the difference maps do not seem to give a clue to a better interpretation of the intensity data.

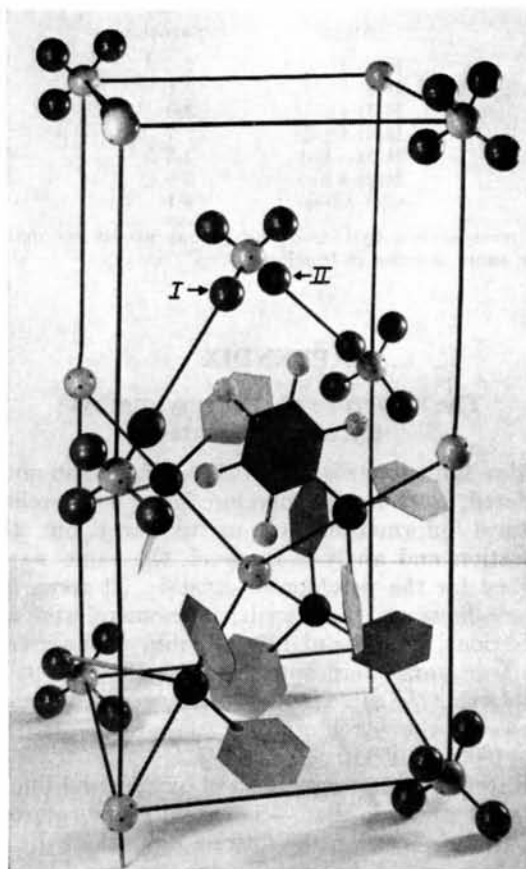


Fig. 3. Simplified model of one quarter of the unit cell. The complete cell is obtained by application of the face-centring operation. Disordered perchlorate groups are represented by a single central atom. The size of the hexagons corresponds to the carbon positions. For clarity, hydrogen atoms are attached to one aromatic ring only. The 'empty' upper half is actually filled with carbon and hydrogen atoms belonging to twelve propeller blades, only two of which are shown. The numbers I and II refer to Table 5.

A much simplified model of the structure is shown in Fig. 3, where the face-centring operation is left out; moreover, the disordered group is represented by a single atom at its centre, and hydrogen atoms are attached to one aromatic ring only. As to the stacking of the ions the structure is analogous to KAlO<sub>2</sub> and KFeO<sub>2</sub>: ClO<sub>4</sub>(a) corresponds to Al or Fe, the carbonium ion to O, and ClO<sub>4</sub>(b) to K.

The central part of the carbonium ion is 'sandwiched' between two equidistant disordered perchlorate

groups; the peripheral parts are nearer to the ordered perchlorate ions. The disordered group is tetrahedrally surrounded by four carbonium ions, whereas the ordered perchlorate group is enclosed by twelve 'propeller-blades', only two of which are shown in the figure. Some short non-bonding distances are given in Table 5.

Table 5. *Some short non-bonding distances*

| Atoms       | Separation |
|-------------|------------|
| H(2)–H(2')* | 2.6 Å      |
| H(4)–O(bI)  | 3.1        |
| H(3)–O(bII) | 3.0        |
| H(3)–O(bI)  | 2.7        |
| H(3)–Cl(b)  | 3.3        |
| H(2)–Cl(a)  | 3.9        |
| C(c)–Cl(a)  | 4.1        |

\* Corresponding hydrogen and carbon atoms are denoted by the same number in brackets.

## APPENDIX

### The structure of triphenylmethyl tetrafluoroborate

The idea that crystals of  $C(C_6H_5)_3BF_4$  might not be disordered, and would therefore give more reliable structural information, led us to carry out their preparation and analysis in much the same way as described for the perchlorate crystals. At room temperature, however, the disorder phenomena were even more serious, and only at 110 °C, again after a gradual phase transition, were apparently single crystals obtained having the same Laue symmetry and systematic absences as the perchlorate crystals at 85 °C;  $a = 18.87 \pm 0.03$  Å at 110 °C.

The atomic scattering factors of oxygen and fluorine are almost equal, so that — in case of isomorphism — the difference between the diffraction data of the two compounds would be mainly due to the difference between the chlorine and boron scattering factors. Because of their special positions in the unit cell, the Cl atoms contribute fully to reflexions  $hkl$  with  $h+k+l=4n$ , and hardly at all to any other reflexion. (If the temperature factors of Cl(a) and Cl(b) were equal, their contribution to reflexions having  $h+k+l \neq 4n$  would even be strictly zero.)

A comparison of  $F_o(hkl)$  values ( $l \neq 4n$ ) of the two compounds (Table 6) already provides convincing evidence for isomorphism. Moreover, the signs of the structure factors  $F(hkl)$  with  $l=4n$  were determined according to the isomorphous replacement method: the results were in complete agreement with those of the perchlorate structure determination.

The authors are greatly indebted to Mr A. Kreuger of the University of Amsterdam for his skilful assistance in the experimental work and to Mr J. I. Leenhouts of the Philips Research Laboratories, who

Table 6. *List of observed structure factors  $hkl(2h+l \neq 4n)$  of triphenylmethyl perchlorate (85 °C) and tetrafluoroborate (110 °C) on the same arbitrary scale*

| h  | l  | $F_o(BF_4)$ | $F_o(ClO_4)$ |
|----|----|-------------|--------------|
| 1  | 1  | 120         | 110          |
|    | 3  | 130         | 135          |
|    | 5  | 25          | 27           |
|    | 7  | 147         | 147          |
|    | 9  | 13          | 21           |
|    | 11 | 39          | 38           |
|    | 13 | 45          | 43           |
|    | 17 | 29          | 29           |
| 2  | 2  | 128         | 135          |
|    | 6  | 62          | 57           |
|    | 10 | 15          | 15           |
|    | 18 | 26          | 29           |
| 3  | 1  | 94          | 89           |
|    | 3  | 194         | 186          |
|    | 5  | 116         | 118          |
|    | 7  | 66          | 63           |
|    | 9  | 92          | 83           |
|    | 11 | 43          | 40           |
|    | 15 | 37          | 38           |
|    | 17 | 23          | 21           |
| 4  | 2  | 15          | 17           |
|    | 6  | 95          | 92           |
| 5  | 1  | 20          | 16           |
|    | 3  | 35          | 35           |
|    | 5  | 51          | 44           |
|    | 7  | 30          | 30           |
|    | 9  | 41          | 40           |
|    | 11 | 24          | 29           |
|    | 13 | 17          | 19           |
| 6  | 2  | 37          | 37           |
|    | 6  | 15          | 18           |
|    | 10 | 50          | 45           |
|    | 14 | 30          | 35           |
| 7  | 1  | 42          | 36           |
|    | 3  | 25          | 26           |
|    | 5  | 70          | 71           |
|    | 7  | 73          | 74           |
|    | 13 | 24          | 27           |
| 8  | 2  | 27          | 29           |
|    | 6  | 32          | 31           |
| 9  | 1  | 41          | 48           |
|    | 5  | 24          | 23           |
|    | 9  | 38          | 43           |
| 10 | 6  | 27          | 30           |
|    | 10 | 33          | 37           |
| 11 | 3  | 21          | 25           |

expertly carried out the computational part of this structure analysis.

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## The Surface Re-Orientation Caused by Unidirectional Abrasion on Polycrystalline Antimony

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Electron diffraction is used to examine the surface re-orientation produced on a polycrystalline antimony surface by unidirectional abrasion. The immediate surface region is randomly disoriented, but at a few hundred to  $\sim 10,000$  Å depth the main feature of the re-orientation is a large azimuthal spread about a [111] trigonal axis which is forwardly inclined from the outward specimen normal towards the direction in which the abrasive particles travel. This azimuthal range extends to at least  $\pm 30^\circ$  from the mean, which is such that a [1 $\bar{1}$ 0] or [110] direction is normal to the abrasion direction; and it may possibly be up to  $\pm 60^\circ$ , although it is suggested that the latter may be due to pseudo-octahedral twinning (relative to the f.c. rhombohedral pseudo-cubic cell). This abrasion texture is completely analogous, in respect of type of orientation axis and sense of its inclination, to that produced by abrasion on zinc and cadmium. However, additional evidence leads to the conclusion that the above structure is a secondary, though prominent, modification of an initially produced, backwardly inclined (110) (f.c. rhombohedral axes) orientation, analogous to that observed in the case of the f.c. cubic metals.

### 1. Introduction

Recent results from this laboratory (see Goddard, Harker & Wilman, 1962; King & Wilman, 1961, 1962; Dobson & Wilman, 1962*a, b*) have shown the nature of the preferred orientation of the surface regions of metals and inorganic non-metallic materials abraded unidirectionally on emery papers. In general, materials of the same structure type show the same type of orientation, and this is closely similar in type and azimuthal preference to the rolling texture.

In all the materials examined, except zinc and cadmium, the orientation axis is inclined backward from the outward specimen normal, towards the direction from which the abrasive particles come; and the angle of tilt can be accounted for in relation to the coefficient of friction for the ploughing abrasive particles. However, in zinc and cadmium the orientation axis, [0001], is inclined forwards by 10 to 15° (Avient, 1961), in contrast to the backwardly tilted [0001] orientation observed for the hexagonal metals beryllium and magnesium (Scott & Wilman, 1958; Levin, 1960), but agreeing with the known rolling texture of zinc and cadmium (*cf.* Barrett, 1953).

In connection with our experiments on friction and wear during abrasion of antimony and bismuth (Stroud & Wilman, 1963), we have investigated by electron diffraction the surface structure (down to 2 microns depth) of antimony after unidirectional abrasion on 0000 emery paper wet with propyl alcohol, at a load of 1 kg. Our wear and friction results, and optical microscopy, showed that brittle fracture (cleavage) of the antimony surface regions occurs prominently during abrasion, and contributes much to the wear. Notwithstanding this, however, the results presented below show that much plastic flow also occurs and leads to a well-defined re-orientation of at least much of the surface region. The orientation developed is [0001] as for all the hexagonal metals, but this axis is tilted slightly forward, like that in zinc and cadmium. There is in addition marked azimuthal preference of the orientation, about this axis.

The crystal lattice of antimony is most simply described as rhombohedral with axial length  $a_r = 4.9762$  Å (at 25 °C), and rhombohedral angle  $\alpha = 57^\circ 6.6'$  (Wyckoff, 1948), with two atoms per unit cell, in the positions  $uuu$ ,  $\bar{u}\bar{u}\bar{u}$ , where  $u = 0.233$