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The Stereochemistry of Some Organic Derivatives of Group Vb Elements. IX.* A Study of Three Severely Disordered Molecules: the Crystal and Molecular Structures of the Perchlorate, Chloride and Azide Derivatives, $[(CH_3)_3SbX]_2O$, of μ-Oxo-trimethylantimony(V)

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The structures of the perchlorate(I), chloride(II) and azide(III) derivatives of μ-oxo-trimethylantimony(V) have been investigated by X-ray analysis. The compounds crystallize in the cubic space group *Pa*3 with $a = 11{\cdot}9736$ (5) Å for (I), 11·203 (2) Å for (II), and 11·485 (1) Å for (III). The structures were solved by the heavy-atom method and refined with diffractometer data to $R = 0{\cdot}032$ for 265 intensities considered to be observed for (I), $R = 0{\cdot}030$ for 351 observed intensities for (II) and $R = 0{\cdot}037$ for 113 observed intensities for (III). The molecular symmetry required by the space group is $\bar{3}$; however, the three molecules have no symmetry and are severely disordered. The Sb atoms are five-coordinate, with a distorted trigonal bipyramidal geometry. The Sb–O–Sb angles are 126–129° with Sb–O 2·07–2·12 Å. The ClO_4 group in (I) and the Cl atom in (II) are 'semi-coordinated' with rather long Sb–O(perchlorate) (2·60 Å) and Sb–Cl (2·71 Å) bonds. The Sb–C(methyl) distances range from 2·10–2·14 Å.

Introduction

The compounds $(R_3MX)_2O$ where R is phenyl or methyl, M is Sb or Bi, and X is halide or pseudohalide are inferred from their infrared and conductance data to be non-ionic and to contain five-coordinate Sb and Bi (Kolditz, Gitter & Rösel, 1962; Tranter, Addison & Sowerby, 1968; Doak, Long & Freedman, 1965; Goel & Ridley, 1971). The crystal structure analysis of $(Ph_3SbN_3)_2O$ (Ferguson & Ridley, 1973) showed that coordination about the metal is close to regular trigonal bipyramidal, and the Sb–O–Sb angle is 139·8°, indicating that the oxygen is mainly sp^3 hybridized, the large angle being due primarily to phenyl···phenyl repulsions between the two halves of the molecule. The analogous perchlorates had been thought to be ionic species with four-coordinate, tetrahedral metal atoms (Long, Doak & Freedman, 1964; Doak *et al.*, 1965); however, reinvestigation of their infrared spectra led to the postulate that the metals were also five-coordinate in these compounds. A crystal structure analysis has confirmed this in the case of $(Ph_3BiClO_4)_2O$ (Ferguson, Goel, March, Ridley & Prasad, 1971; March & Ferguson, 1975), and shows that the Bi atom has a similar stereochemistry to the Sb in $(Ph_3SbN_3)_2O$ (angle Bi–O–Bi 142·4°); the perchlorate group is 'semi-coordinated' with a rather long Bi–O(perchlorate) distance of 2·65 Å. It came to our attention that some work had been carried out elsewhere on the related compound $(Me_3SbClO_4)_2O$ (I) (Baird, 1970), which was said to contain four-coordinate, tetrahedral Sb atoms, a linear Sb–O–Sb moiety and an ionic perchlorate group with Sb···O(perchlorate) 2·20 Å. We therefore decided to re-examine the structure of this paragon ourselves. During the course of the structure determination certain problems were encountered, and consequently two supplementary investigations were launched on the compounds $(Me_3SbCl)_2O$ (II) and $(Me_3SbN_3)_2O$ (III). The results of these three structural investigations are given here.

Experimental

Colourless air-stable crystals of (I) and (II) were prepared by recrystallization of powder samples from chloroform–petroleum spirit mixtures and those of (III) from pyridine. The crystal data are summarized in Table 1. The three samples were isomorphous. Precession photographs indicated cubic symmetry, while the systematic absences $0kl$ (k odd), $h0l$ (l odd) and $hk0$ (h odd) indicated space group *Pa*3 uniquely. The cell dimension in each case was obtained from the least-squares refinement of the setting angles of 12 high-order reflexions measured on a Hilger and Watts Y290 four-circle diffractometer. The crystals chosen for data collection for (I) and (III) were small, irregular octahedra with maximum dimensions *ca* 0·20 mm, being bound by the (111) faces. That for (II) was similar but with 12 clearly defined faces and a maximum dimension of 0·24 mm. Intensities were collected on the diffractometer with Zr-filtered Mo $K\alpha$ X-radiation and the $\theta/2\theta$ scan method with a symmetric scan consisting of a number of 0·01° steps. Stationary counter–stationary crystal background counts were made at each end of the integrated scan. Details are given in Table 2. Three standard reflexions of moderate intensity and well separated in reciprocal space were collected at regular intervals. They varied by less than 2%, indicating that in each case both crystal and beam stability were good.

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* Part VIII: March & Ferguson (1975).

Table 1. *Crystal data*

(I) μ-Oxo-bis[trimethylperchloratoantimony(V)], $C_6H_{18}Cl_2O_9Sb_2$
(II) μ-Oxo-bis[trimethylchloroantimony(V)], $C_6H_{18}Cl_2OSb_2$
(III) μ-Oxo-bis[trimethylazidoantimony(V)], $C_6H_{18}N_6OSb_2$

	(I)	(II)	(III)
M	548·7	420·5	433·7
a (Å)	11·9736 (5)	11·203 (2)	11·485 (1)
U (Å^3)	1716·8	1406·1	1514·9
D_m	2·10	1·98	1·91
D_x (Z=4)	2·12	1·99	1·90
F(000)	1048	792	824
$\mu(\lambda=0\cdot71069$ Å) (cm^{-1})	35·2	30·7	30·6

Crystal system: Cubic
Space group: $Pa\bar{3}$, (T_h^6, No. 205)
Molecular symmetry: S_6, $\bar{3}$

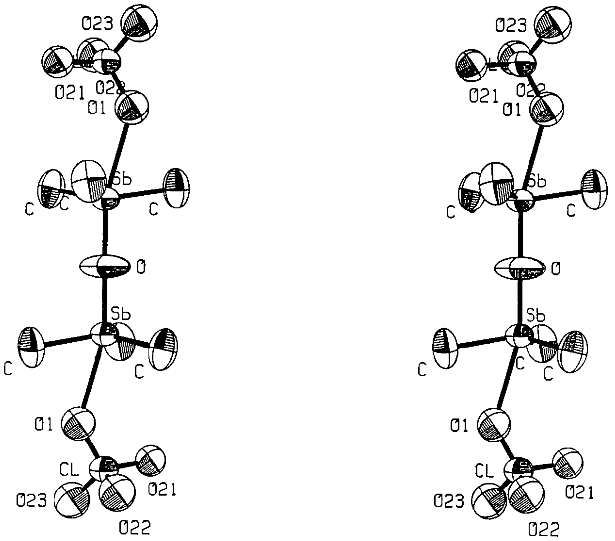

Fig. 1. Stereo view of $[(CH_3)_3SbClO_4]_2O$, showing the positions of the refined atoms and the atomic numbering scheme. The perchlorate groups shown are related by the centre of symmetry at the central oxygen atom. The other orientations of the perchlorate group are generated by the threefold axis which passes through the Sb–O–Sb moiety. N.B. The central oxygen atom is disordered. The ellipsoids in this and other diagrams are at the 50% level.

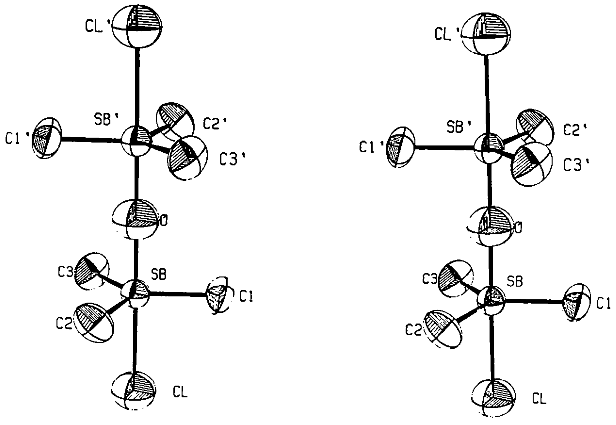

Fig. 2. Stereo view of $[(CH_3)_3SbCl]_2O$ showing the positions of the refined atoms, all of which except C lie on the threefold axis of symmetry (— but this is too simple a representation, see text.)

Table 2. *Data collection statistics* ($\lambda=0\cdot71069$ Å)

Crystal	(I)	(II)	(III)
Scan width	0·80°	0·80°	0·80°
Scan time	60 s	80 s	120 s
Background time	15 s	20 s	30 s
$\theta_{\max}$	25°	30°	23°
Number of intensities	527	673	339
Number of intensities with $I>3\sigma(I)$	265	351	113

Each intensity was corrected for background and the estimated standard deviation was obtained from $\sigma(I)=[\text{scan}+s^2\text{backgrounds}+(0\cdot05\times\text{intensity})^2]^{1/2}$, where s is the ratio of the total background to scan counting times. The octant $+h$, $+k$, $+l$ was collected in each case and corrected for Lorentz and polarization factors. For (I) and (III) no systematic variations in intensity between the three equivalent forms attributable to absorption effects were observed; however, data from (II) were corrected for absorption (Coppens, Leiserowitz & Rabinovich, 1965). Equivalent reflexions were averaged and those with $I>3\sigma(I)$ were regarded as observed and used in the subsequent refinement.

Structure solution and refinement

$[(CH_3)_3SbClO_4]_2O$ (I)

The presence of four molecules in the cell implies a molecular symmetry of $\bar{3}$, with the Sb and Cl lying on the threefold axis along the cell body diagonal. There are two possible sites with $\bar{3}$ symmetry in space group $Pa3$ and the one at the origin was chosen. The coordinates of Sb and Cl were derived from the Patterson function and a subsequent structure-factor calculation yielded a value for R $(=\sum||F_o|-|F_c||/\sum|F_o|)$ and Rw $[=(\sum w(F_o-F_c)^2/\sum wF_o^2)^{1/2}]$ of 0·216. The scattering factors given in *International Tables for X-ray Crystallography* (1962) for Sb, Cl, O, N and C were used. An F_{obs} synthesis, calculated with the phases derived from the positions of these atoms, yielded peaks of electron density close to the Sb and Cl atoms, and a diffuse peak at the origin. There were four unique peaks about Cl, clearly revealing that the perchlorate group was disordered about the threefold axis, and one well resolved unique peak near Sb. Four one-third weight

O atoms were placed on peaks in chemically sensible positions about Cl, and a C atom was placed on the peak near Sb. The structure was refined by full-matrix least-squares calculations, with all atoms constrained to isotropic thermal vibrations, to give $R = 0{\cdot}072$; during the refinement corrections for anomalous dispersion by Sb were included. A further F_{obs} synthesis revealed a strong peak at the origin and an O atom was placed on this position. Further refinement reduced R to 0·054; however the isotropic temperature factor of the O atom was rather large ($U_{\text{iso}} = 0{\cdot}13$ Å^2). Refinement was continued with the Sb, Cl and C atoms allowed anisotropic motion, giving $R = 0{\cdot}035$; however the temperature factor of the O atom increased. Two further cycles with this central O atom allowed anisotropic motion gave convergence with $R = 0{\cdot}032$ and $R_w = 0{\cdot}038$. The maximum shift in any parameter on the last cycle was $0{\cdot}3\sigma$. The shape of the thermal ellipsoid (an oblate spheroid, see Fig. 1) suggested that the central O atom might be disordered and thus lie off the origin on a plane perpendicular to the threefold axis. A difference map calculated from the final parameters listed in Table 3, but with the central O atom assigned a U_{iso} value of 0·065 Å^2, revealed a torus of electron density around the origin in a plane normal to the threefold axis; there were six distinct maxima (*cf.* Fig. 5) (one unique peak (0·8 e Å^{-3}) plus five symmetry-related ones) corresponding to the pattern that would be observed if the O atom lay off the threefold axis. We considered the possibility that these peaks arose because of the anisotropic motion of the bridging O atom but discounted this *inter alia* on consideration of the shapes and distribution of positive and negative regions in the difference map. Further, the perchlorate O atom bonded to Sb lies off the threefold axis and it would not be surprising if the central O also were disordered. The central O was then moved to the position (given in Table 3) indicated by the difference map with the appropriate occupancy factor ($\frac{1}{6}$) and an attempt made to refine its positional and isotropic thermal parameters. While the temperature factor of the atom remained low, the positional coordinates moved randomly and R did not change.

The remote possibility remained that the glide plane absences were accidental, due to the centre-related positions of the majority of the atoms, and that the true space group was $P2_13$ (T^4, No. 198). Therefore an attempt was made to refine the structure in this space group. This had the advantage that the site symmetry of the central oxygen would be reduced to 3, thus lowering the amount of disorder. This attempt yielded a succession of singular matrices and was abandoned.

A difference map, calculated from the atomic parameters listed in Table 3, revealed a number of small peaks. The highest of these (0·5 e Å^{-3}) occurred in positions close to the C atom and possibly corresponded to methyl H atoms. However, the peaks were poorly defined and no attempt was made to include the H atoms in any calculations. The final error in an ob-

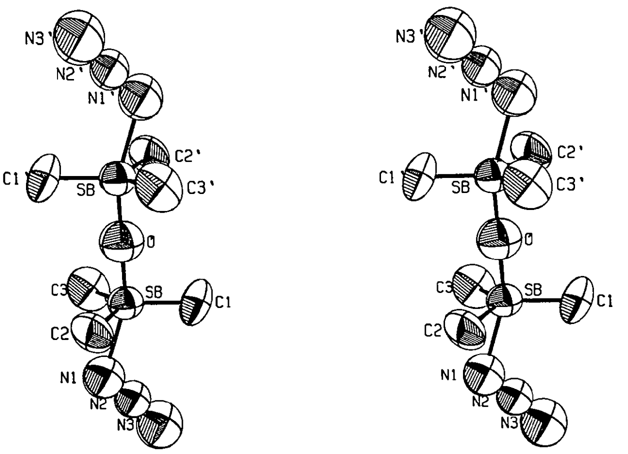

Fig. 3. Stereo view of $[(CH_3)_3SbN_3]_2O$. The azide groups shown are related by the centre of symmetry at the central oxygen atom and the threefold axis passes through the Sb–O–Sb moiety. (As in Fig. 2 this is an oversimplification of the true structure.)

Table 3. *Final positional and thermal parameters for* $[(CH_3)_3SbClO_4]_2O$ (I)

	x/a	y/b	z/c	U_{iso}
Sb	0·08976 (15)	0·08976	0·08976	*
Cl	0·2710 (7)	0·2710	0·2710	*
C	0·0216 (10)	0·0499 (9)	0·2465 (10)	*
O(1)	0·199 (2)	0·1754 (18)	0·2568 (19)	0·090 (8)
O(21)	0·334 (2)	0·291 (2)	0·169 (2)	0·077 (8)
O(22)	0·208 (3)	0·378 (3)	0·286 (3)	0·098 (10)
O(23)	0·332 (3)	0·251 (2)	0·370 (3)	0·103 (10)
O	0·0	0·0	0·0	*
O(*d*)	0·0225	−0·0615	0·0390	

* Anisotropic thermal parameters

The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0·0587 (12)	0·0587	0·0587	−0·0076 (11)	−0·0076	−0·0076
Cl	0·064 (4)	0·064	0·064	−0·007 (4)	−0·007	−0·007
C	0·102 (9)	0·095 (8)	0·068 (6)	0·012 (8)	0·032 (7)	0·016 (7)
O	0·15 (3)	0·15	0·15	−0·06 (3)	−0·06	−0·06

servation of unit weight calculated over all the observed data was 1·01, indicating that the weighting scheme is satisfactory.

$[(CH_3)_3SbCl]_2O$ (II)

The coordinates of the Sb and Cl atoms were determined from a Patterson synthesis. An electron density distribution phased with the Sb and Cl contributions revealed an O at the origin and the methyl C atoms. With all non-hydrogen atoms included in the structure-factor calculations R was 0·21. Two cycles of full-matrix least-squares refinement with isotropic thermal parameters for these atoms reduced R to 0·078. After a further six cycles of full-matrix refinement with all the non-hydrogen atoms allowed anisotropic thermal parameters and with Sb corrected for anomalous dispersion, convergence was achieved, at which point the shift/e.s.d. ratio was 0·13; $R=0{\cdot}030$ and $R_w=0{\cdot}026$. The final error in an observation of unit weight calculated over all the observed data is 1·60. A difference synthesis computed with the coordinates listed in Table 4 but with artificially small values of U_{iso} (0·063 Å^2) for O and Cl showed six distinct maxima around O and three distinct maxima around Cl in planes normal to the threefold axis. Their positions (Table 4) correspond to the disorder pattern which would arise if the O and Cl atoms lay off the threefold axis (see Figs. 5 and 6). An attempt to refine these disordered atoms resulted in the positional coordinates of the O atom moving randomly, while the Cl atom tended to move back towards the threefold axis, and refinement thus was abandoned.

$[(CH_3)_3SbN_3]_2O$ (III)

The coordinates of the Sb atom were derived from the Patterson function. An electron density map phased with Sb contributions showed peaks of electron density at the origin, close to the position of the Sb atom, and near $\frac{1}{4},\frac{1}{4},\frac{1}{4}$. An O atom was placed at the origin and a C atom on the unique peak near Sb. The diffuse electron density peak near $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ was due to the azide group but individual atoms were not discernible. A structure-factor calculation based on Sb, O, C and an N atom at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ yielded $R=0{\cdot}25$ and a subsequent difference synthesis revealed a possible position for the terminal azide atom N(3) off the threefold axis indicating that the N_3 group was disordered over at least three sites. Two cycles of full-matrix least-squares refinement with N(3) included but not refined and with the Sb, O and C atoms allowed isotropic motion, reduced R to 0·063. Subsequent difference syntheses failed to reveal unique positions for N(1) and N(2). These atoms appeared as a diffuse peak of electron density on the threefold axis near $\frac{1}{4},\frac{1}{4},\frac{1}{4}$. The coordinates of N(1) and N(2) were calculated assuming a linear azide group with N–N 1·20 Å, Sb–N 2·24 Å and Sb–N–N 118°, the distances and angle found for $[(C_6H_5)_3SbN_3]_2O$ (Ferguson & Ridley, 1973). Two cycles of refinement with anisotropic Sb, O and C atoms and with the azide atoms treated as a rigid group with individual isotropic thermal parameters, reduced R to 0·040; no further refinement of the N_3 group was undertaken because, although the thermal parameters, the Sb–N(1) distance and the Sb–N–N angle were reasonable, a study of the N atom shifts showed that the group was, in effect, rotating round the threefold axis. The 'final' coordinates listed in Table 5 for the N atoms are from this stage of refinement. Four further cycles with the Sb, O, and C atoms vibrating anisotropically and Sb corrected for anomalous dispersion reduced R to its final value of 0·037 and R_w to 0·043. The final parameters are in Table 5. The maximum ratio of shift/e.s.d. on the last cycle was 0·25. The final error in an observation of unit weight is 2·54.

A difference synthesis calculated from the atomic parameters listed in Table 5 for the Sb, C and N atoms and with a small isotropic thermal parameter $U_{\text{iso}}=0{\cdot}065$ Å^2 assigned to the central O atom at the origin, showed ill defined maxima near the azide group and six distinct maxima around the origin as for (I) and (II). The coordinates of the unique 'disordered oxygen' peak are also listed in Table 5. In view of our previous experiences, no refinement of this position was undertaken.*

Table 4. *Final positional and thermal parameters for* $[(CH_3)_3SbCl]_2O$ (II)

	x	y	z	U_{iso}
Sb	0·09826 (11)	0·09826 (11)	0·09826 (11)	*
O	0·0	0·0	0·0	*
O(*d*)	0·063	−0·012	−0·051	–
Cl	0·2334 (6)	0·2334 (6)	0·2334 (6)	*
Cl(*d*)	0·184	0·263	0·253	–
C	0·0296 (8)	0·0211 (9)	0·2552 (7)	*

* Anisotropic thermal parameters

Table 4 (*cont.*)

The anisotropic thermal parameters are of the form given in Table 3.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0·00537 (6)	0·00537	0·00537	−0·00017 (6)	−0·00017	−0·00017
O	0·0118 (14)	0·0118	0·0118	−0·0025 (15)	−0·0025	−0·0025
Cl	0·0135 (5)	0·0135	0·0135	−0·044 (4)	−0·0044	−0·0044
C	0·0110 (8)	0·0132 (10)	0·0080 (6)	−0·0013 (5)	0·0020 (5)	0·0013 (6)

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* A list of structure factors for the three molecules (I), (II), and (III) is available from the authors and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30831 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

The structures of the species $(Me_3SbX)_2O$, where $X = ClO_4$ (I), Cl (II), and N_3 (III), show that they are correctly formulated as well separated $X–Me_3Sb–O–SbMe_3–X$ molecules with two five-coordinate Sb atoms, each having a distorted trigonal bipyramidal geometry, with equatorial methyl groups, and bridged by an O atom, which occupies an apex common to both trigonal bipyramids. The space group $Pa\bar{3}$ with $Z = 4$ requires the molecules to lie on the body diagonal of the cell and implies a molecular symmetry $\bar{3}$; however in each of the three structures this symmetry results from disorder in the crystal and the correct molecular symmetry for the species is lower. The nature of this disorder will be discussed below.

The final coordinates are listed for (I), (II) and (III) in Tables 3–5 respectively. In each of these tables, the coordinates of the unique disordered O atom near the origin are labelled O(*d*) and in (II) the coordinates of the unique residual peak near the Cl atom are labelled Cl(*d*). The molecular dimensions for the three structures are given in Tables 6–8 and the atomic labelling and views of the molecules are given in Figs. 1–3.

μ-Oxo-bis(trimethylperchloratoantimony) (I)

As in the analogous phenyl derivative $(Ph_3BiClO_4)_2O$ (IV) (March & Ferguson, 1975) the coordination geometry about the metal atom is intermediate between the tetrahedral configuration that was predicted if the ClO_4^- ion was not coordinated, and the regular trigonal bipyramid which would be expected if the O atoms at the apices of the bipyramid were equivalent. Thus C–Sb–C is 117·6 (5)° and the Sb atom lies 0·33 Å off the plane formed by the three equivalent methyl C atoms, displaced towards the central O atom. These are similar to the analogous angle and distance in (IV): 118·5° and 0·27 Å. As in (IV) the perchlorate group in (I) is weakly coordinated, with Sb–O(perchlorate) = 2·60 (2) Å, *cf.* Bi–O 2·65 Å. In the present structure, although the crystallographic symmetry would imply a linear Sb–O–Cl moiety, the structure is disordered, with the O(perchlorate) atom lying off the threefold axis, giving rise to a threefold disorder of the perchlorate group. The angle Sb–O–Cl is 136 (1)°, *cf.* Bi–O–Cl = 132·4° in (IV). The dimensions (Table 6) of the disordered perchlorate group [Cl–O 1·41–1·50 (4) Å, O–Cl–O 103–118 (1)°] are in accord with what is commonly found for disordered perchlorate ions. The other important molecular features are common to all three structures and will be compared later.

μ-Oxo-bis(trimethylchloroantimony) (II)

The coordination geometry about Sb deviates slightly from a regular trigonal bipyramid with C–Sb–C = 119·6 (1)° and a displacement of the Sb atom towards

Table 5. *Final positional and thermal parameters for* $[(CH_3)_3SbN_3]_2O$ (III)

	x	*y*	*z*	U_{iso}
Sb	0·0941 (3)	0·0941 (3)	0·0941 (3)	*
O	0·0	0·0	0·0	*
O(*d*)	−0·066	0·045	0·021	–
C	0·0307 (18)	0·2502 (22)	0·0230 (27)	*
N(1)	0·2123	0·1470	0·2518	0·178 (30)
N(2)	0·2356	0·2488	0·2545	0·140 (14)
N(3)	0·2589	0·3506	0·2572	0·225 (35)

* Anisotropic thermal parameters

The anisotropic thermal parameters are of the form given in Table 3.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0·0112 (4)	0·0112	0·0172	−0·0015 (4)	−0·0015	−0·0015
O	0·017 (4)	0·017	0·017	−0·002 (5)	−0·002	−0·002
C	0·018 (1)	0·008 (1)	0·021 (3)	0·001 (2)	0·002 (2)	0·003 (2)

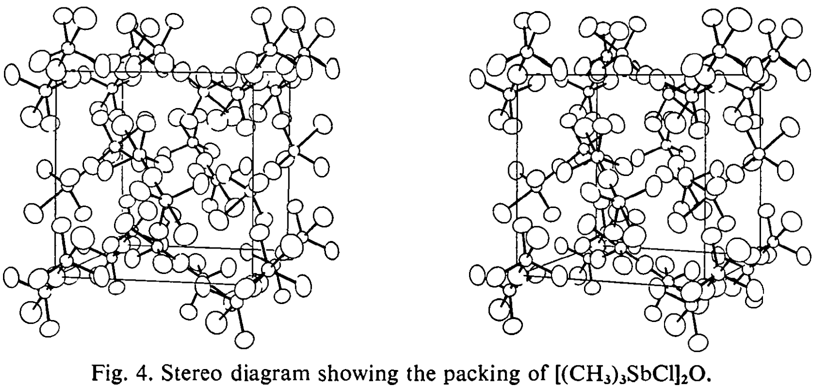

Fig. 4. Stereo diagram showing the packing of $[(CH_3)_3SbCl]_2O$.

the central O atom out of the plane of the methyl groups by 0·10 Å. No evidence for disorder of the Cl atom has been observed from Fourier maps, as was the case for the coordinated ligand in (I). However the r.m.s. displacement of the Cl atom perpendicular to the threefold axis is large (Table 9) and a difference map computed through the atom in the plane perpendicular to the threefold axis, with the Cl atom assigned a small isotropic thermal parameter ($U_{\text{iso}}=0{\cdot}063$ Å^2) reveals one unique peak 0·68 Å off the axis (Fig. 5).

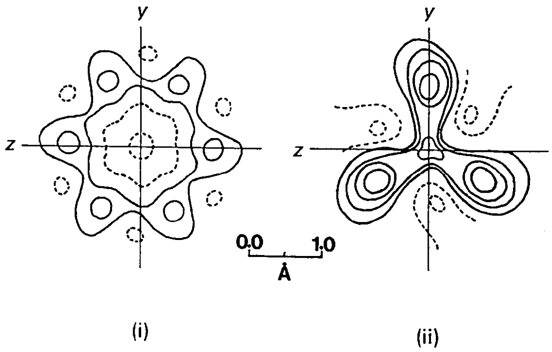

Fig. 5. Difference synthesis perpendicular to, and in the region of, the threefold axis (X) for $[(CH_3)_3SbCl]_2O$, with the bridging oxygen and Cl atoms included on the axis, with $U_{\text{iso}}=0{\cdot}063$ Å^2. Coordinate axes X, Y and Z are related to the unit-cell axes x, y and z by the relation: $X=(x+y+z)$, $Y=-x/\sqrt{2}-y\sqrt{2}+\sqrt{2}z$, $Z=(\sqrt{3}/\sqrt{2})\,(x-y)$. (i) Section at $X=0$. (ii) Section at $X=0{\cdot}233$. Contours are at intervals of approximately 0·35 e Å^{-3} starting at +0·35 e Å^{-3}. Dotted lines represent regions of zero and negative electron densities.

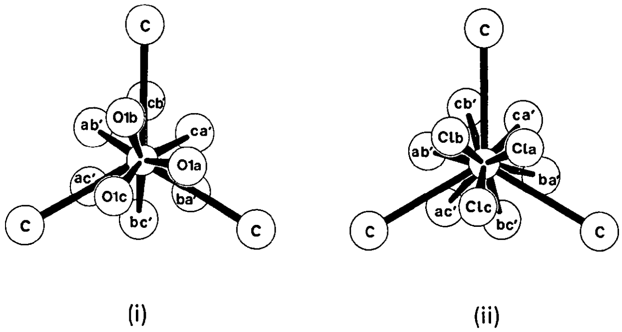

Fig. 6. Views down the threefold axis for (i) $[(CH_3)_3SbClO_4]_2O$ and (ii) $[(CH_3)_3SbCl]_2O$. In (i) for clarity only one set of disordered (perchlorate) oxygen atoms (labelled O1*a*, O1*b*, O1*c*) and bonded to one antimony (unlabelled) is shown. The methyl carbon atoms (labelled C) are bonded to the same antimony as O1*a*, O1*b*, O1*c*. The six disordered oxygen atoms bridging the two Sb atoms are labelled *ab'*, *ac' etc.* The labelling of these bridging oxygens is according to the O(perchlorate) atom with which they make the O(bridge)–Sb–O(perchlorate) angle nearest to 180°. Thus bridge oxygen *ab'* makes an angle close to 180° with the Sb atom shown and O1*a* (hence the *a* in the label); the *same* bridging atom *ab'* also makes an angle close to 180° with the centre of symmetry-related atoms Sb' and O1*b'* (hence the *b'* in the label). A similar description holds for (ii) with the disordered Cl*a*, Cl*b*, Cl*c* replacing O1*a*, O1*b*, O1*c*.

Table 6. *Distances* (Å) *and angles* (°) *for* $[(CH_3)_3SbClO_4]_2O$ (I)

Intramolecular distances and angles for the refined atomic positions

Sb–O	1·862 (2)	Sb—O(1)–Cl	134·7 (13)
Sb–C	2·102 (12)	O(1)—Cl—O(21)$^{\mathrm{I}}$	110·0 (14)*
Sb–C	2·127 (13)†	O(1)—Cl—O(21)$^{\mathrm{III}}$	83·9 (14)
Sb–O(1)	2·601 (23)	O(1)—Cl—O(21)$^{\mathrm{IV}}$	59·6 (13)
Cl–O(1)	1·443 (24)	O(1)—Cl—O(22)$^{\mathrm{I}}$	113·1 (17)*
Cl–O(21)	1·455 (25)	O(1)—Cl—O(22)$^{\mathrm{III}}$	76·9 (17)
Cl–O(22)	1·498 (37)	O(1)—Cl—O(22)$^{\mathrm{IV}}$	123·2 (17)
Cl–O(23)	1·413 (37)	O(1)—Cl—O(23)$^{\mathrm{I}}$	105·9 (18)*
		O(1)—Cl—O(23)$^{\mathrm{III}}$	128·7 (18)
Sb$^{\mathrm{I}}$–O–Sb$^{\mathrm{II}}$	180	O(1)—Cl—O(23)$^{\mathrm{IV}}$	153·0 (18)
O—Sb–C	99·2 (3)		
O—Sb–O(1)	164·2 (5)	O(21)–Cl—O(22)$^{\mathrm{I}}$	102·8 (17)*
C$^{\mathrm{I}}$–Sb–C$^{\mathrm{III}}$	117·5 (2)	O(21)–Cl—O(23)$^{\mathrm{I}}$	117·6 (18)*
C—Sb–O(1)$^{\mathrm{I}}$	66·3 (6)	O(22)–Cl—O(23)$^{\mathrm{I}}$	107·7 (21)*
C—Sb–O(1)$^{\mathrm{III}}$	93·5 (6)		
C—Sb–O(1)$^{\mathrm{IV}}$	83·0 (6)		

Selected distances and angles involving the disordered oxygen atom [O(*d*)]

Sb—O(*d*)	2·07	C$^{\mathrm{I}}$—Sb–O(*d*)	85
		C$^{\mathrm{III}}$–Sb–O(*d*)	87
Sb$^{\mathrm{I}}$—O(*d*)–Sb$^{\mathrm{II}}$	128	C$^{\mathrm{IV}}$–Sb–O(*d*)	125
O(1)–Sb—O(*d*)$^{\mathrm{II}}$	167		
O(1)–Sb—O(*d*)$^{\mathrm{IV}}$	164		

Selected non-bonded contacts

C$^{\mathrm{I}}\cdots$C$^{\mathrm{V}}$	4·79 (2)
C$^{\mathrm{I}}\cdots$O(23)$^{\mathrm{VI}}$	2·92 (2)
C$^{\mathrm{I}}\cdots$O(21)$^{\mathrm{VII}}$	3·25 (4)
C$^{\mathrm{I}}\cdots$O(22)$^{\mathrm{VII}}$	3·35 (4)
C$^{\mathrm{I}}\cdots$O(22)$^{\mathrm{VIII}}$	3·41 (4)

The roman numerals after the atom label represent the symmetry transformations listed below. Where this is not specified, symmetry I is implied.

I	x,	y,	z	V	$-y$,	$-z$,	$-x$
II	$-x$,	$-y$,	$-z$	VI	$\frac{1}{2}-z$,	$x-\frac{1}{2}$,	y
III	z,	x,	y	VII	$y-\frac{1}{2}$,	z,	$\frac{1}{2}-x$
IV	y,	z,	x	VIII	$\frac{1}{2}-y$,	$z-\frac{1}{2}$,	x.

* Unique set.

† Corrected for thermal motion based on the riding motion model.

Attempts to refine the positional coordinates of a disordered atom were unsuccessful as the atom tended to refine to the threefold axis. However the above evidence strongly suggests that, as for (I), the ligand is also disordered.

The nature of this disorder, and that of the bridging O atom, is discussed in detail below. The Sb–Cl distance (with the Cl atom positioned on the threefold axis) is 2·622 (6) Å, which is rather larger than has been reported for a number of other Sb–Cl bonds, *e.g.* $(CH_3)_3SbCl_2$, 2·49 Å (Wells, 1938); $(C_6H_5)_3SbCl_2$, 2·458 (4) and 2·509 (4) Å (Polynova & Porai-Koshits, 1966). The disordered model suggested would increase this distance considerably, with a maximum distance of 2·71 Å when the atom is 0·68 Å from the axis. The Sb–Cl bond would seem to be too long for a normal single bond and may be only partly covalent as for the 'semi-coordinated' perchlorate group in (I).

Table 7. *Distances* (Å) *and angles* (°) *for* $[(CH_3)_3SbCl]_2O$ (II)

Intramolecular distances and angles for the refined atomic positions

Sb–O	1·907 (1)	Sb$^{\mathrm{I}}$–O –Sb$^{\mathrm{II}}$	180
Sb–C	2·067 (9)	O—Sb–C	93·8 (3)
Sb–C	2·103 (9)*	C$^{\mathrm{I}}$—Sb–C$^{\mathrm{III}}$	119·6 (8)
Sb–Cl	2·628 (6)	O—Sb–Cl	180

Selected distances and angles involving the disordered oxygen [O(*d*)] and chlorine [Cl(*d*)] atoms

Sb–O(*d*)	2·12		
Sb–Cl(*d*)	2·71		
Sb$^{\mathrm{I}}$—O(*d*)–Sb$^{\mathrm{II}}$	129	O(*d*)–Sb–C$^{\mathrm{I}}$	112
Cl(*d*)$^{\mathrm{I}}$–Sb—O(*d*)$^{\mathrm{I}}$	166	O(*d*)–Sb–C$^{\mathrm{III}}$	69
Cl(*d*)$^{\mathrm{I}}$–Sb—O(*d*)$^{\mathrm{IV}}$	164	O(*d*)–Sb–C$^{\mathrm{V}}$	100
		Cl(*d*)–Sb–C$^{\mathrm{I}}$	82
		Cl(*d*)–Sb–C$^{\mathrm{III}}$	101
		Cl(*d*)–Sb–C$^{\mathrm{V}}$	77

Selected non-bonded contacts

C$^{\mathrm{I}}$···C$^{\mathrm{IV}}$	4·58 (2)
C$^{\mathrm{I}}$···C$^{\mathrm{VI}}$	3‘82 (2)
C$^{\mathrm{I}}$···C$^{\mathrm{VII}}$	4·06 (2)
C$^{\mathrm{I}}$···Cl$^{\mathrm{VIII}}$	4·11 (1)
C$^{\mathrm{I}}$···Cl$^{\mathrm{IX}}$	4·17 (1)

The roman numerals after the atom label represent the symmetry transformations listed below. Where this is not specified symmetry I is implied.

I	$x,$	$y,$	z	VI	$\frac{1}{2}-z,$	$-x,$	$\frac{1}{2}+y$
II	$-x,$	$-y,$	$-z$	VII	$y,$	$\frac{1}{2}-z,$	$\frac{1}{2}+x$
III	$z,$	$x,$	y	VIII	$\frac{1}{2}-x,$	$y-\frac{1}{2},$	z
IV	$-z,$	$-x,$	$-y$	IX	$x-\frac{1}{2},$	$y,$	$\frac{1}{2}-z$
V	$y,$	$z,$	x				

* Corrected for thermal motion based on the riding motion model.

Table 8. *Distances* (Å) *and angles* (°) *for* $[(CH_3)_3SbN_3]_2O$ (III)

Intramolecular distances and angles for the refined atomic positions

Sb–O	1·872 (3)	Sb$^{\mathrm{I}}$–O—Sb$^{\mathrm{II}}$	180
Sb–C	2·100 (26)	O—Sb—C	93·9 (8)
Sb–C*	2·140 (29)	C$^{\mathrm{I}}$—Sb—C$^{\mathrm{III}}$	119·5 (2)
Sb–N(1)	2·344	O—Sb—N(1)	158·5 (9)
		Sb–N(1)–N(2)	117·3

Selected distances and angles involving the disordered oxygen [O(*d*)]

Sb—O(*d*)	2·10	C$^{\mathrm{I}}$—Sb–O(*d*)	77
		C$^{\mathrm{III}}$–Sb–O(*d*)	85
Sb$^{\mathrm{I}}$—O(*d*)–Sb$^{\mathrm{II}}$	126	C$^{\mathrm{V}}$ –Sb–O(*d*)	120
N(1)–Sb—O(*d*)$^{\mathrm{III}}$	159		
N(1)–Sb—O(*d*)$^{\mathrm{IV}}$	173		

Selected non-bonded contacts

C$^{\mathrm{I}}$···C$^{\mathrm{III}}$	4·54 (5)
C$^{\mathrm{I}}$···N(3)$^{\mathrm{VI}}$	3·25
C$^{\mathrm{I}}$···N(3)$^{\mathrm{VII}}$	3·27
C$^{\mathrm{I}}$···N(3)$^{\mathrm{VIII}}$	3·46
C$^{\mathrm{I}}$···C$^{\mathrm{IX}}$	4·02 (5)

The roman numerals after the atom label represent the symmetry transformations listed below. Where this is not specified symmetry I is implied.

I	$x,$	$y,$	z	VI	$x-\frac{1}{2},$	$z,$	$\frac{1}{2}-y$
II	$-x,$	$-y,$	$-z$	VII	$z,$	$\frac{1}{2}-x,$	$y-\frac{1}{2}$
III	$z,$	$x,$	y	VIII	$z-\frac{1}{2},$	$x,$	$\frac{1}{2}-y$
IV	$-z,$	$-x,$	$-y$	IX	$\frac{1}{2}-y,$	$\frac{1}{2}+z,$	x
V	$y,$	$z,$	x				

* Corrected for thermal motion based on the riding motion model.

Table 9. *Root-mean-square amplitudes of thermal vibration for the anisotropic atoms*

R.m.s. amplitudes are given along the principal axes of the thermal ellipsoids in Å. For an atom on the threefold axis *R*1 and *R*2 are perpendicular and parallel to the axis respectively.

		*R*1	*R*2	*R*3
(I)	Sb	0·258 (3)	0·208 (4)	0·258 (3)
	Cl	0·265 (15)	0·225 (13)	0·265 (15)
	O	0·45 (5)	0·20 (9)	0·45 (5)
	C*	0·22 (3)	0·36 (2)	0·29 (3)
(II)	Sb	0·236 (2)	0·224 (2)	0·236 (2)
	Cl	0·428 (9)	0·227 (13)	0·428 (9)
	O	0·38 (3)	0·26 (4)	0·38 (3)
	C*	0·255 (13)	0·344 (11)	0·372 (12)
(III)	Sb	0·356 (2)	0·285 (2)	0·356 (2)
	O	0·437 (13)	0·348 (12)	0·437 (13)
	C*	0·26 (7)	0·48 (4)	0·41 (5)

* For the methyl group carbon atoms *R*1 and *R*2 are the principal axes of the thermal ellipsoid most nearly perpendicular and parallel to the threefold axis. Thus *R*1 corresponds to the r.m.s. thermal displacement in the approximate direction of the Sb-C bond, and *R*2 makes an angle with the threefold axis of 12 ± 13° for (I), 30 ± 17° for (II), and 21 ± 16° for (III).

μ-Oxo-bis(trimethylazidoantimony) (III)

The structure is analogous to that of $(Ph_3SbN_3)_2O$ (V) (Ferguson & Ridley, 1973). The coordination geometry at Sb deviates slightly from an ideal trigonal bipyramid with C–Sb–C = 119·5 (2)°, and with the Sb atom displaced towards the central O atom by 0·11 Å from the plane formed by the three equivalent methyl groups, *cf.* mean values for this angle and distance of 119·7° and 0·11 Å for (V). The azide group is disordered as was the perchlorate group in (I) but little structural

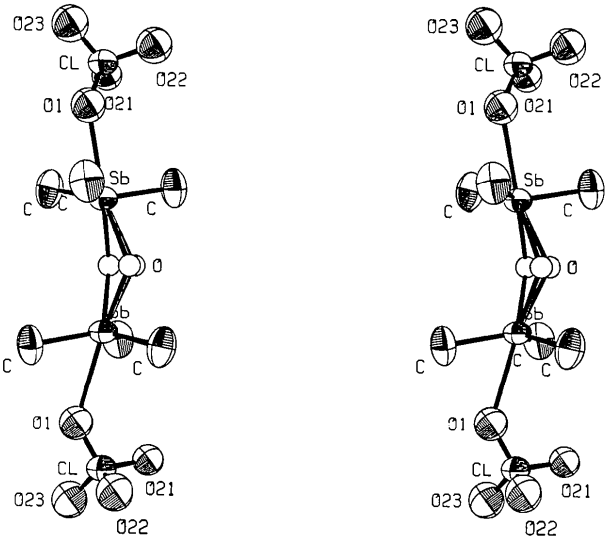

Fig. 7. Stereo view of a molecule of $[(CH_3)_3SbClO_4]_2O$ showing the 'best' arrangement which gives O–Sb–O angles nearest 180°. For each (disordered) Sb–O(perchlorate) moiety there are *two* equally probable bridging oxygen atoms but only one of the pair is common to both antimony trigonal bipyramids; hence three bridging oxygens are shown (with arbitrary isotropic thermal parameters).

information about it has been obtained, since refinement of this azide group did not lead to convergence.

The molecular disorder

The main problem is to distinguish between peaks in a difference synthesis which would arise if genuine anisotropic thermal movement were not allowed for properly, and those which would arise from disorder. In all three structures the bridging O atom when refined anisotropically at the origin, shows anomalously large r.m.s. amplitudes of vibration perpendicular to the threefold axis. This would be unexpected in view of the fact that it is tightly bound to two heavy metal atoms. In addition, in order to explain the 'linear' Sb–O–Sb system and the anomalously short Sb–O bridge bonds (range 1·862–1·907 Å for O at origin) it is necessary to invoke *sp* hybridization of the O atom. This seems highly unlikely in view of the established structures of $(Ph_3SbN_3)_2O$ and $(Ph_3BiCl_4)_2O$. A much more satisfactory explanation is that the bridging O atom lies off the threefold axis equidistant from the two metal atoms. This is borne out by the nature of the residual peaks on the difference maps.

The nature of the disorder of the O atom about the origin of the cell and its relationship to the disorder of the ligand at the other apex of the bipyramid about the Sb atom is shown in Figs. 5 and 6. Fig. 5 (i) is drawn from a difference map obtained for (II), but is illustrative of the patterns found for (I) and (III). The distance of the unique peak from the origin was approximately the same (0·9 Å) for each of the three structures. These positions are approximate since they were determined from difference syntheses and have not been refined. Distances and angles for the Sb–O–Sb bridge derived from the coordinates of the disordered O atoms are given in Tables 6–8 and give a range of 2·07–2·12 Å for Sb–O(bridge) and 126–129° for Sb–O–Sb. These compare well with the corresponding distances and angles for (IV) and (V) (2·065 (10) Å, 142·4 (7)°; 1·985 (3) Å, 139·8 (4)° respectively), and indicate that, despite the imprecise data, the Sb–O–Sb angle in these compounds is substantially greater than the tetrahedral value, but is certainly much smaller than 180°.

A similar analysis of a section of the difference map through the Cl atom for (II) reveals three peaks 0·68 Å from the threefold axis. The positions of these maxima are shown in Fig. 5 (ii). Fig. 6 shows the relationship between the disordered atoms at the apices of the trigonal bipyramid for (I) and (II), with the bridging O atoms labelled to indicate the ligand atom [O(perchlorate) or Cl] which makes an angle O(bridging)–Sb–X closest to 180°. To achieve this, the ligands, X, at each end of the molecule are related by inversion through the symmetry centre and rotation of 120° about the threefold axis. For each disordered Sb–X moiety there are two equally probable bridging O atom positions available to complete the fifth site of the trigonal bipyramid at the Sb atom. The situation is further complicated because, of necessity, only one of the pair of disordered O atom positions is common to both Sb trigonal bipyramids. This is also shown diagrammatically in Fig. 7. The position of the coordinated N atom in (III) has not been precisely determined, because it probably has an even higher degree of disorder than threefold. The O–Sb–X angles which result from the disorder are given for the three structures in Tables 6–8.

A further implication of this disorder model is that the methyl groups are also disordered; however no direct evidence is found for this. Analysis of the thermal ellipsoids of the methyl groups in each structure reveals a large component of the r.m.s. amplitude of vibration parallel to the threefold axis (Table 9). Any slight disorder of these groups will be accounted for in this apparent motion. The Sb–C distances found in each structure are similar, with values of 2·127 (13) for (I), 2·103 (9) for (II) and 2·140 (29) Å for (III). These are not significantly different from values observed for Sb–C(phenyl) bonds, *e.g.* in (V) Sb–C(phenyl) = 2·115 (9) Å and in dimethoxytriphenylantimony the distance is 2·120 (12) Å (Shen, McEwen, La Placa, Hamilton & Wolf, 1968).

All three structures have similar packing diagrams. The simplest, that for $[(CH_3)_3SbCl]_2O$, is shown in Fig. 4 with molecules having $\bar{3}$ symmetry. Several of the intermolecular contacts listed in Tables 6, 7 and 8 are shorter than the sums of the appropriate van der Waals radii. These distances involve the methyl C atoms which we have implied to be slightly disordered.

We are grateful to the National Research Council for Canada for financial support *via* operating and computing grants (to GF) and a postgraduate scholarship (to DRR). The calculations were performed on the University IBM 370/155 computer with local versions of Zalkin's Fourier program (*FORDAP*), the Busing–Levy full-matrix least-squares (*ORFLS*) and function and error (*ORFFE*) programs, originally supplied to us by the crystallography group at the University of Canterbury, New Zealand. The diagrams were prepared with the aid of Johnson's (1965) *ORTEP* program.

References

BAIRD, H. W. (1970). *J. Elisha Mitchell Sci. Soc.* **86**, 173.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
DOAK, G. O., & LONG, G. G. FREEDMAN, L. D. (1965). *J. Organometal. Chem.* **4**, 82–91.
FERGUSON, G., GOEL, R. G., MARCH, F. C., RIDLEY, D. R. & PRASAD, H. S. (1971). *Chem. Commun.* pp. 1547–1548.
FERGUSON, G. & RIDLEY, D. R. (1973). *Acta Cryst.* **B29**, 2221–2226.
GOEL, R. G. & RIDLEY, D. R. (1971). *Inorg. Nucl. Chem. Lett.* **7**, 21–23.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
KOLDITZ, L., GITTER, M. & RÖSEL, E. (1962). *Z. anorg. allgem. Chem.* **316**, 270–277.
LONG, G. G., DOAK, G. O. & FREEDMAN, L. D. (1964). *J. Amer. Chem. Soc.* **86**, 209–213.
MARCH, F. C. & FERGUSON, G. (1975). *J. Chem. Soc. Dalton.* Submitted for publication.
POLYNOVA, T. N. & PORAI-KOSHITS, M. A. (1966). *Zh. Strukt. Khim.* **7**, 742–751.
SHEN, K., MCEWEN, W. E., LA PLACA, S. J., HAMILTON, W. C. & WOLF, A. P. (1968). *J. Amer. Chem. Soc.* **90**, 1718–1723.
TRANTER, G. C., ADDISON, C. C. & SOWERBY, D. B. (1968). *J. Organometal. Chem.* **12**, 369–376.
WELLS, A. F. (1938). *Z. Kristallogr.* **99**, 367–377.

Acta Cryst. (1975). B**31**, 1268

Refinement of *trans*-Stilbene: a Comparison of Two Crystallographic Studies

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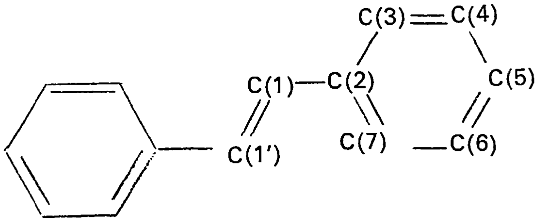
The recently reported improved structure of *trans*-stilbene, based on data collected on a Nonius CAD-4 diffractometer [Finder, Newton & Allinger. *Acta Cryst.* (1974). B30, 411–415], is compared with a refinement based on data from a Syntex $P\bar{1}$ diffractometer. The two studies are in excellent agreement, especially with regard to the unusually short ethylene double-bond lengths, which are probably due to disorder.

Finder, Newton & Allinger (1974) (FNA) recently published the results of an improved structure of *trans*-stilbene (I). We were in the final stages of a similar investigation when their report appeared. The results of FNA show remarkable agreement with those from this laboratory, and in view of some of the rather unusual features of the molecular geometry found in both determinations and the somewhat differing methods of data collection and refinement, we felt that a comparison of the two refinements would be of interest to crystallographers.



(I)

The crystal data are compared in Table 1. Our space group assignment and cell constants follow the original ones of Robertson & Woodward (1937) (RW), while the parameters of FNA involve a change in space group to the more conventional one ($P2_1/c$ instead of $P2_1/a$) and a different choice of **a**. For ease of comparison we have also refined our cell constants in the FNA space group.

Table 1. *Comparison of crystallographic constants*

	RW	This work	This work*	FNA
a (Å)	12·35	12·382 (6)	15·679 (5)	15·710 (4)
b	5·70	5·720 (1)	5·720 (1)	5·723 (1)
c	15·92	15·936 (4)	12·382 (6)	12·381 (3)
β (°)	114·0	114·15 (2)	111·96 (3)	111·89 (4)
Radiation	Cu $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Cu $K\bar{\alpha}$
Number of reflexions in LS		14	14	28
ϱ_c(g cm^{-3})	1·161	1·162	1·162	1·156
ϱ_m(g cm^{-3})	1·159	1·160†	1·160†	1·164
V (Å)^3	1023	1029·9	1029·9	1033

* Least-squares refinement according to choice of cell of Finder, Newton & Allinger (1974).

† Flotation, aqueous potassium iodide.

Table 2. *Comparison of methods of data collection*

	This work	FNA
Instrument	Syntex $P\bar{1}$	Nonius CAD-4
Radiation	Mo $K\alpha$	Cu $K\bar{\alpha}$
Monochromator	Graphite	Graphite
Scan technique	ω–2θ	ω–2θ
Interval for monitor reflexions	50	51
Total measured	2453	2366
Total observed	1689	1685
Criterion for unobserved	$F<2·5\sigma(F)$	$I<2\sigma(I)$

Very well formed crystals were grown by slow evaporation of an ethanolic solution in a refrigerator. Data were collected on a crystal approximately 0·3 mm on a side. Details of the data collection (Table 2) are similar to those of FNA, except for the difference in diffractometers. Hence these two determinations offer one of the first comparisons between the Nonius CAD-4 and the Syntex $P\bar{1}$ diffractometers. In contrast to FNA we observed a deterioration of the crystal which led to a