The Structure of Mercuri-iodide Ions
II. Bistrimethylsulphonium Mercuritetraiodide [(CH₃)₃S]₂HgI₄

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Bistrimethylsulphonium mercuritetraiodide, [(CH₃)₃S]₂HgI₄, crystallizes in space group $Pna2_1$ with cell dimensions $a = 13 \cdot 22 \pm 0 \cdot 05$, $b = 16 \cdot 69 \pm 0 \cdot 04$, $c = 9 \cdot 13 \pm 0 \cdot 05$ Å and four molecules per cell. The X-ray diffraction data were collected using a Buerger precession camera and Ag $K\alpha$ radiation with a crystal ground into a sphere. The structure was solved by Patterson and Fourier syntheses with least-squares refinement. The HgI_4^{2-} ion is approximately tetrahedral.

Introduction

As described in the previous paper, mercuri-iodide ions have provided useful derivatives of many proteins for use in the isomorphous replacement method of protein structure analysis. The present structure determination was principally undertaken to find the conformation of the mercuritetraiodide ion.

Experimental

The compound was prepared by the method of Rây & Adhikary (1930). Crystals, which had the form of thick plates, were grown by slow evaporation of a solution in acetone. Oscillation, Weissenberg and precession photographs showed that the crystal system is orthorhombic with reflexions $0kl$ present only when $(k+l)$ is even and reflexions $h0l$ present only when h is even. Thus the space group is either $Pnam$ or $Pna2_1$: the structure analysis has shown that the crystal is most probably non-centrosymmetric with space group $Pna2_1$.

Two cell dimensions were determined by superimposing a powder pattern from sodium chloride on a zero-level Weissenberg photograph, and the remaining cell dimension was determined from a precession photograph in which a correction for film shrinkage was made using the fiducial holes in the cassette. In each dimension an error of $0 \cdot 1 \%$ was allowed for the miscentering of the crystal. The cell dimensions are

$$a = 13 \cdot 22 \pm 0 \cdot 05 \text{ Å}$$
$$b = 16 \cdot 69 \pm 0 \cdot 04$$
$$c = 9 \cdot 13 \pm 0 \cdot 05$$

The density was measured by flotation in a mixture of Rohrbach's solution and alcohol and found to be $2 \cdot 81 \pm 0 \cdot 05$ gm.cm⁻³. Thus there are four molecules per cell which gives a calculated density of $2 \cdot 85 \pm 0 \cdot 02$ g.cm⁻³.

A crystal containing such a large proportion of heavy atoms is highly absorbing to X-rays, and in order

to remove the absorption errors from the diffraction data as much as possible, a crystal was ground into an approximately spherical shape for which the absorption corrections are readily obtained. The crystal used for data collection had diameters in three mutually perpendicular directions equal to $0 \cdot 0327$, $0 \cdot 0386$ and $0 \cdot 0336$ cm giving a 'sphere' of mean radius $R = 0 \cdot 0175$ cm.

Data collection

In order to reduce the absorption of X-rays by the crystal it was decided to use silver radiation to collect the diffraction data, Ag $K\bar{\alpha}$ having a wavelength of $0 \cdot 5608$ Å. For this wavelength the linear absorption coefficient of the crystal, μ, equals 75 cm⁻¹ so that for a crystal with the dimensions given above, the μR value varies from $1 \cdot 23$ to $1 \cdot 45$ with a mean value of $1 \cdot 31$. Thus the absorption factor A for $\theta = 0$ varies from $1 \cdot 36$ to $1 \cdot 82$ with the mean sphere having a value of $1 \cdot 62$ (*International Tables for X-ray Crystallography*, Vol.II).

The sphere was orientated using copper radiation and oscillation methods and then transferred to the precession camera. A palladium filter was used to remove the Ag $K\beta$ radiation. The rating of the tube did not allow it to be used at the voltage required to produce the maximum possible ratio of intensities of characteristic to background radiation but the highest permissible value, 50 kV, was used.

The data collection was made by a series of zero and upper level precession photographs and 85% of data within the sphere corresponding to $1 \cdot 2$ Å were collected. As the quantum efficiency of the emulsion and celluloid of the film is very small for silver radiation, a piece of shim steel of thickness $0 \cdot 0051$ cm was inserted between two films in the cassette to give effective reduced exposure to the second film. With a precession angle of 15°, no splitting of spots was observed on the films and the second film had a uniform background intensity which indicated that the shim steel was of uniform thickness.

The spots on the film due to the characteristic Ag $K\alpha$ radiation were superimposed on continuous streaks and so the films were measured with a microdensitometer

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scanning radially along the streaks. Four quadrants of data were measured on four films and Lp factors applied to the average intensities. The scale factors required to put the various zones of data on a common scale were obtained from the sums of common rows as described by Rollett & Sparks (1960). The absorption corrections for a sphere published by W. L. Bond in *International Tables for X-ray Crystallography* (Vol. II) were applied to the scaled data.

Structure determination

A three-dimensional Patterson synthesis was calculated. With the space group ambiguity mentioned above and four formula units per cell, the structure either consists of one formula unit in a general position per asymmetric unit of $Pna2_1$ or, if the space group is $Pnam$, then the formula unit must itself possess a mirror plane with the mercury atom situated on the mirror plane at $z = \frac{1}{4}$.

The approximate positions of one mercury and four iodine atoms were determined from the Patterson synthesis, but from this solution it was not possible to distinguish between the two space groups, as the solution could be interpreted in terms of $Pnam$ with the ion precisely located about the mirror plane or in terms of $Pna2_1$ with the ion approximately in the symmetrical position.

The positions and isotropic temperature factors of these five atoms were initially refined with respect to the non-centrosymmetric space group by a least-squares method, and subsequently anisotropic factors were included. The result of the refinement gave atomic pos-

Table 1. *Observed and calculated structure factors*

itions close to an ion on a mirror plane. The five atoms were then refined in the centrosymmetric space group in which the ion was forced to possess mirror symmetry. The residual achieved was as low as when a greater degree of freedom was allowed but one atom had an abnormally high temperature factor perpendicular to the mirror plane, suggesting that its true position was out of this plane. The true space group thus is probably $Pna2_1$.

A difference Fourier synthesis from the non-centrosymmetric structure factors revealed the sulphur atoms; one peak appeared near the pseudo-mirror plane and two others appeared symmetrically on either side of this plane. Each of the latter two peaks was included in turn in the subsequent refinement but no choice could be made between the two positions for the second sulphur atom. Further refinement was carried out with a half-sulphur in each position on the assumption that the second trimethylsulphonium ion is statistically distributed in two sites related by the pseudo-mirror plane. The residual fell to 0·09 but no significant indications of the methyl groups could be found. A list of observed and calculated structure factors is given in Table 1.

Description of structure

The parameters at the end of the refinement process are shown in Table 2 where $T1$ and $T2$ are the two half-sulphurs. The temperature factor is given by exp $\{-(B \sin^2\theta/\lambda^2)\}$ or exp $\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{31}lh+B_{12}hk)\}$. The values of the temperature fac-

tors of all atoms are high but this is consistent with the fact that there are no observable diffraction data from either ground or unground crystals corresponding to planes of spacing smaller than 1·2 Å.

Table 2. *Parameters of mercury, iodine and sulphur atoms*

Positions

Atom	x/a	y/b	z/c
Hg	0·251	0·096	−0·001
I(1)	0·460	0·105	0·043
I(2)	0·168	0·174	0·232
I(3)	0·193	0·941	0·000
I(4)	0·192	0·164	0·747
S(1)	0·038	0·655	0·007
$T(1)$	0·377	0·384	−0·083
$T(2)$	0·379	0·386	0·081

Vibrations

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Hg	0·015	0·008	0·038	−0·003	−0·002	0·001
I(1)	0·014	0·017	0·084	−0·010	0·001	0·003
I(2)	0·023	0·017	0·052	−0·020	−0·005	0·006
I(3)	0·038	0·010	0·089	0·005	0·008	−0·014
I(4)	0·037	0·024	0·036	0·013	−0·011	−0·001

	B
S(1)	25
$T(1)$	16
$T(2)$	18

The bond lengths and angles of the mercuritetraiodide ion together with their standard deviations, which were obtained from the least-squares process, are given in Table 3. The distances between these ions and the
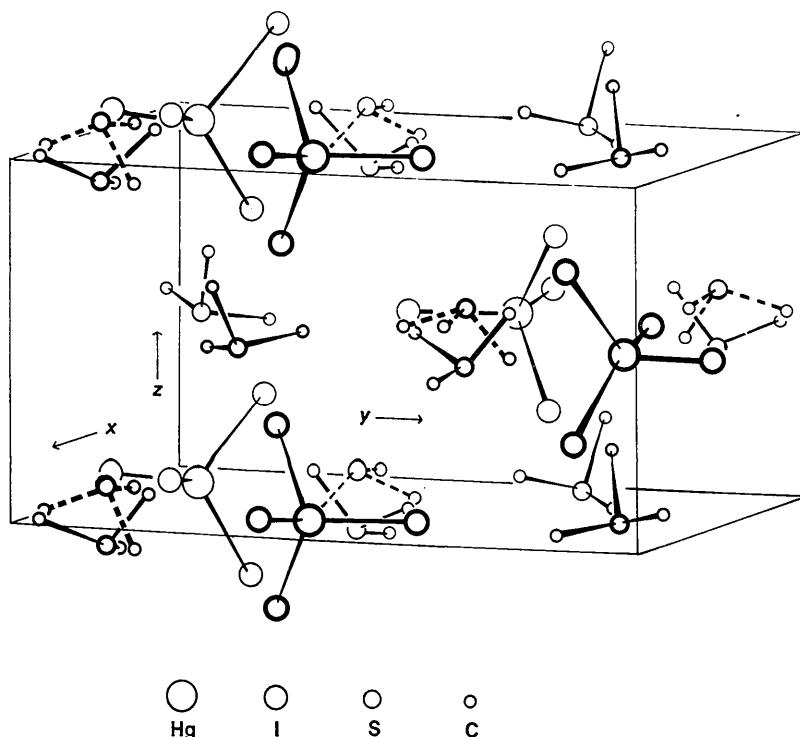

Fig. 1. Clinographic projection of structure including possible carbon positions. One of the statistically distributed trimethyl-sulphonium ions is shown with broken lines

distances between the sulphurs and these atoms are all greater than 4 Å. The mercuritetraiodide ion is approximately tetrahedral.

Table 3. *Bond lengths and angles in the mercuritetraiodide ion and their standard deviations*

Bonds		σ			σ
Hg–I(1)	2·80 Å	0·01 Å	Hg–I(3)	2·69 Å	0·01 Å
Hg–I(2)	2·73	0·02	Hg–I(4)	2·68	0·02

Angles		σ			σ
I(1)–Hg–I(2)	105·2°	0·2°	I(2)–Hg–I(3)	119·8°	0·2°
I(1)–Hg–I(3)	109·3	0·2	I(2)–Hg–I(4)	110·3	0·3
I(1)–Hg–I(4)	113·1	0·2	I(3)–Hg–I(4)	108·9	0·4

Lopez-Castro & Truter (1964) have determined the conformation of the sulphonium ion to be pyramidal with carbon–sulphur distances 1·82 Å and carbon–sulphur–carbon angles 103°. A test was made to ensure that there is sufficient space in the proposed structure for such an ion in each of the proposed positions.

For the sulphonium ion about S(1), an orientation was found for which the minimum carbon–iodine distance was 3·5 Å; for the sulphonium ion about $T(1)$, an orientation was found for which the minimum carbon–iodine distance was 3·7 Å, and for an orientation about $T(2)$ the minimum carbon–iodine distance was 3·8 Å.

This investigation showed that there is adequate space between the mercuritetraiodide ions for a sulphonium ion centered on S(1) and either of $T(1)$ or $T(2)$ and there is no evidence from spatial considerations against the distribution of the second ion between the two latter positions. With these orientations, the minimum distance between the carbons bonded to S(1) and those around either $T(1)$ or $T(2)$ is 3·5 Å.

The structure including the possible carbon positions is illustrated in Fig. 1.

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The Crystal and Molecular Structure of 2,5-Dimethyl-7,7-dicyanonorcaradiene*

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The substituted norcaradiene, $C_{11}H_{10}N_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a cell having $a = 11·044$, $b = 7·126$, $c = 12·113$ Å. Copper $K\alpha$ diffraction data measured by scintillation counter gave an R of 3·9 % when fit by least squares to a model including σ bonds. The molecule has nearly exact C_s symmetry; the cyclopropane ring is inclined at about 73° to the approximately planar C_6 ring. Bonds adjacent to the C_3 ring are shortened by 0·02–0·03 Å from corresponding unstrained values; cyclopropane C–C bonds are 1·558, 1·553, and 1·500 Å. The experimental electron density is matched much better by a 'bent' bond cyclopropane model than the straight-bond model; the angle of bending is roughly 20°.

Introduction

Cyclopropane rings present opportunities to study carbon in unusual hybridization states for which little accurate geometrical information is available. The present study was undertaken with the additional purpose of

confirming the bicyclic nature of the material $C_{11}H_{10}N_2$, one of the simplest containing the norcaradiene skeleton (Ciganek, 1965).

Experimental data

Clear, block-like crystals of $C_{11}H_{10}N_2$, 2,5-dimethyl-7,7-dicyanonorcaradiene, and of $C_9H_6N_2$, 7,7-dicyanonorcaradiene, were supplied by Dr Ciganek. On Cu

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