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# The Crystal Structure of the 1:1 Addition Compound Formed by Benzyl Sulphide and Iodine

CHR. RØMMING

*Universitetets Kjemiske Institutt, Blindern-Oslo, Norway*

The crystal structure of a compound containing 1 molecule of benzyl sulphide and 1 molecule of iodine has been determined. The space group is *Pnma* with four molecules of $(C_6H_5CH_2)_2S \cdot I_2$ in the unit cell, the dimensions of which are: $a = 9.86$ Å; $b = 16.86$ Å; $c = 9.36$ Å. The investigation reveals a linear sulphur-iodine-iodine arrangement with the observed bond distances 2.78 Å for S-I and 2.82 Å for I-I.

In the course of an investigation of charge transfer complexes in the crystalline state, mainly between halogen molecules and organic electron donor molecules as ethers and amines carried out by Hassel and coworkers, it was found to be of interest to determine whether thioethers form similar compounds with halogen. The 1 : 1 compound benzyl sulphide-iodine was chosen as an object for this investigation. This compound was first prepared by Fromm[1], by whom it was regarded as a compound of quadrivalent sulphur with each of the halogen atoms linked to the sulphur atom. Feigl and Bondi[2], however, investigated further the chemical behaviour of the compound and concluded that it is to be regarded as a polyiodide.

Preliminary results of the present investigation have been reported in a survey article by Hassel[3].

## EXPERIMENTAL

The crystals were prepared according to Feigl and Bondi [2] by mixing hot solutions of benzyl sulphide and iodine in glacial acetic acid and heating the mixture for a quarter of an hour at 120°C. By cooling, small dark red crystals of the addition compound (m.p. 63°C) separated. The crystals were approximately octahedral with the orthorhombic axes along the space diagonals. The dimensions were about 0.15 mm along the axes; the crystals were used without further preparations in the X-ray work.

Integrated Weissenberg photographs were taken with rotation about the three orthorhombic axes. The more intense reflections were measured photometrically; the others were estimated visually by comparison with a standard scale. Cu$K\alpha$-radiation was employed, and of the 114 $h0l$, 91 $0kl$ and 104 $hk0$ reflections attainable, 82, 78, and 51 were actually observed, respectively. The intensities were corrected for Lorentz- and polarisation effects, but no corrections for absorption were applied.

The atomic scattering factor used in the last stages of the calculations are given by the analytical approximation $f = A\exp(-ax^2) + B\exp(-bx^2) + C$ with the constants given by Forsyth and Wells[4].

## CRYSTAL DATA

The crystals were found to be orthorhombic with the unit cell dimensions:
$a = 9.86$ Å ; $b = 16.86$ Å ; $c = 9.36$ Å
The figures given are believed to be accurate to within 0.5 %. By flotation the density was found to be 1.95 g/cm$^3$, while the calculated value with four molecules per unit cell is 2.00 g/cm$^3$.

According to the systematically absent reflections the space group might be either *Pnma* or $Pn2_1a$. The former was assumed to be the correct one, and the structure analysis subsequently confirmed this. Since the number of equivalent positions is eight in the space group *Pnma*, the molecules must posess a center of symmetry or a mirror plane. Only the latter is possible in the present compound.

## STRUCTURE DETERMINATION

The structure analysis was started with projection along the *b*-axis. This is the longest of the axes, but since the mirror planes of the space group are perpendicular to this axis a well resolved Fourier projection could be expected with ideal overlapping of some of the atoms. A Patterson synthesis showed clearly that the iodine atoms lie in a mirror plane. It indicated also strongly that the sulphur atom is lying in the mirror plane with one benzyl group on each side. The parameters of the iodine atoms were determined from the Patterson synthesis and a set of structure factors was calculated. On the basis of signs from these calculations and the observed data a Fourier synthesis (plane group *pgg*) was computed. The Fourier map not only showed the iodine atoms but also indicated the position of the benzyl sulphide molecule. It became quite clear that the S-I-I arrangement is nearly linear, and tentative parameters for the atoms in the benzyl sulphide group could be found. These were now included in the calculations, and a series of Fourier refinements were carried out. At the stage where no more signs shifted the reliability factor *R* had decreased to 20 %. It became obvious from the corresponding Fourier map, however, that the thermal vibrations of the »outer» iodine atom is anisotropic, the peak being elongated in a direction about normal to the I-I bond.

Now a least squares refinement was carried out, using a Ferranti Mercury computer[5]. Two cycles were computed with variation of the parameters with isotropic temperature functions, then a few cycles with an anisotropic temperature function for the »outer» iodine atom. During the first step the reliability factor decreased from 20 % to 15 %, after the anisotropic temperature function was introduced it dropped to 10.5 %. The positional parameters changed very little during the last cycles, however. The direction of the maximum vibration amplitude of the iodine atom in question as calculated from the constants in the expression for the temperature factor $\exp(-uh^2-vhk-wk^2)$ was found to be within 2° perpendicular to the direction of the I—I bond.

Table 1. Observed and calculated structure factors.

| $h\,k\,l$ | $F_o$ | $F_c$ | $h\,k\,l$ | $F_o$ | $F_c$ | $h\,k\,l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 0 0 2 | 81 | 73 | 5 0 7 | <30 | −11 | 12 0 2 | 19 | 24 |
| 0 0 4 | <18 | −9 | 5 0 8 | <28 | −18 | 0 2 0 | 211 | 277 |
| 0 0 6 | 112 | 114 | 5 0 9 | <26 | −11 | 0 4 0 | 470 | 482 |
| 0 0 8 | 80 | 81 | 5 0 10 | 35 | −32 | 0 6 0 | 346 | 348 |
| 0 0 10 | <26 | 10 | 6 0 0 | 34 | 24 | 0 8 0 | 266 | 252 |
| 1 0 1 | 92 | 117 | 6 0 1 | 35 | −31 | 0 10 0 | 320 | 277 |
| 1 0 2 | 171 | 221 | 6 0 2 | 137 | 128 | 0 12 0 | 240 | 209 |
| 1 0 3 | <18 | 8 | 6 0 3 | 47 | −44 | 0 14 0 | 212 | 201 |
| 1 0 4 | 41 | 37 | 6 0 4 | 166 | 174 | 0 16 0 | 152 | 136 |
| 1 0 5 | 62 | 65 | 6 0 5 | <27 | −11 | 0 18 0 | 122 | 120 |
| 1 0 6 | 21 | 10 | 6 0 6 | <28 | −11 | 0 20 0 | 112 | 96 |
| 1 0 7 | 70 | 76 | 6 0 7 | 39 | 23 | 0 1 1 | 104 | −54 |
| 1 0 8 | 60 | 59 | 6 0 8 | <27 | 18 | 0 3 1 | 87 | −83 |
| 1 0 9 | 44 | 41 | 6 0 9 | <27 | −20 | 0 5 1 | 86 | −84 |
| 1 0 10 | 31 | 40 | 6 0 10 | 28 | 35 | 0 7 1 | 45 | −39 |
| 1 0 11 | <20 | −6 | 7 0 1 | 50 | 39 | 0 9 1 | 92 | −63 |
| 2 0 0 | 114 | 90 | 7 0 2 | 56 | −52 | 0 11 1 | <33 | −11 |
| 2 0 1 | 30 | −9 | 7 0 3 | 109 | 105 | 0 13 1 | <40 | −14 |
| 2 0 2 | 140 | −137 | 7 0 4 | 56 | 48 | 0 15 1 | <40 | 3 |
| 2 0 3 | 103 | 103 | 7 0 5 | 51 | 54 | 0 17 1 | <39 | −14 |
| 2 0 4 | 104 | −97 | 7 0 6 | 66 | 53 | 0 19 1 | <30 | 12 |
| 2 0 5 | 21 | −16 | 7 0 7 | 33 | 27 | 0 2 2 | 190 | −185 |
| 2 0 6 | <23 | −8 | 7 0 8 | <24 | 10 | 0 4 2 | 126 | −116 |
| 2 0 7 | <27 | 16 | 7 0 9 | 27 | 36 | 0 6 2 | 85 | −95 |
| 2 0 8 | <28 | −11 | 7 0 10 | 11 | 11 | 0 8 2 | 95 | −112 |
| 2 0 9 | 58 | 73 | 8 0 0 | <27 | −16 | 0 10 2 | 101 | −93 |
| 2 0 10 | <26 | −23 | 8 0 1 | 46 | −39 | 0 12 2 | 102 | −93 |
| 2 0 11 | 34 | 46 | 8 0 2 | <28 | 8 | 0 14 2 | 105 | −97 |
| 3 0 1 | 154 | −156 | 8 0 3 | <28 | −11 | 0 16 2 | 78 | −63 |
| 3 0 2 | 178 | 179 | 8 0 4 | <28 | 8 | 0 18 2 | 81 | −70 |
| 3 0 3 | 143 | −152 | 8 0 5 | 29 | 43 | 0 20 2 | 49 | −50 |
| 3 0 4 | 51 | −45 | 8 0 6 | 30 | −32 | 0 1 3 | <20 | −5 |
| 3 0 5 | 58 | −53 | 8 0 7 | 48 | 53 | 0 3 3 | 64 | 53 |
| 3 0 6 | 76 | −60 | 8 0 8 | <21 | 1 | 0 5 3 | 61 | 41 |
| 3 0 7 | 100 | −84 | 9 0 1 | 52 | −51 | 0 7 3 | 33 | 21 |
| 3 0 8 | 54 | 56 | 9 0 2 | 54 | −49 | 0 9 3 | 41 | 42 |
| 3 0 9 | 53 | −53 | 9 0 3 | 53 | −45 | 0 11 3 | <36 | −14 |
| 3 0 10 | <24 | 11 | 9 0 4 | 38 | 41 | 0 13 3 | <39 | −5 |
| 3 0 11 | 18 | −26 | 9 0 5 | 66 | −68 | 0 15 3 | <40 | 1 |
| 4 0 0 | 204 | −189 | 9 0 6 | 38 | 42 | 0 17 3 | <37 | −13 |
| 4 0 1 | 46 | 47 | 9 0 7 | 22 | −27 | 0 19 3 | <30 | 16 |
| 4 0 2 | 92 | −87 | 10 0 0 | <25 | −7 | 0 2 4 | 39 | −34 |
| 4 0 3 | 38 | 28 | 10 0 1 | 31 | −26 | 0 4 4 | 31 | 34 |
| 4 0 4 | <22 | −13 | 10 0 2 | 54 | −58 | 0 6 4 | <30 | 10 |
| 4 0 5 | 72 | −61 | 10 0 3 | <24 | −9 | 0 8 4 | <34 | 0 |
| 4 0 6 | 97 | −93 | 10 0 4 | 80 | −78 | 0 10 4 | 59 | 60 |
| 4 0 7 | 53 | −50 | 10 0 5 | <23 | 14 | 0 12 4 | <39 | 5 |
| 4 0 8 | 49 | −41 | 10 0 6 | 31 | −30 | 0 14 4 | 40 | 39 |
| 4 0 9 | 32 | −11 | 10 0 7 | 21 | −15 | 0 16 4 | 57 | 50 |
| 4 0 10 | <23 | −7 | 11 0 1 | <23 | 9 | 0 18 4 | 32 | 27 |
| 5 0 1 | 70 | −63 | 11 0 2 | <23 | −7 | 0 1 5 | 118 | 142 |
| 5 0 2 | <21 | 10 | 11 0 3 | 19 | −26 | 0 3 5 | 111 | 134 |
| 5 0 3 | 82 | 75 | 11 0 4 | 10 | −10 | 0 5 5 | 115 | 110 |
| 5 0 4 | 61 | −59 | 11 0 5 | <18 | −18 | 0 7 5 | 84 | 75 |
| 5 0 5 | 84 | 85 | 12 0 0 | 59 | 67 | 0 9 5 | 93 | 95 |
| 5 0 6 | 95 | −83 | 12 0 1 | <18 | −2 | 0 11 5 | 93 | 79 |

| $h k l$ | $F_o$ | $F_c$ | $h k l$ | $F_o$ | $F_c$ | $h k l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 0 13 5 | 61 | 57 | 0 10 8 | 57 | 77 | 4 13 0 | 144 | −130 |
| 0 15 5 | 72 | 70 | 0 12 8 | 52 | 64 | 4 14 0 | 114 | 106 |
| 0 17 5 | 37 | 31 | 0 14 8 | 43 | 50 | 4 15 0 | 118 | 100 |
| 0 2 6 | 164 | −171 | 0 1 9 | 56 | 35 | 4 16 0 | 112 | − 98 |
| 0 4 6 | 139 | −150 | 0 3 9 | $<39$ | 14 | 4 17 0 | 96 | − 90 |
| 0 6 6 | 137 | −151 | 0 5 9 | 59 | 58 | 4 18 0 | 70 | 80 |
| 0 8 6 | 134 | −150 | 0 7 9 | 37 | 27 | 4 19 0 | 70 | 72 |
| 0 10 6 | 86 | −109 | 0 9 9 | 41 | 47 | 4 20 0 | 56 | − 66 |
| 0 12 6 | 81 | −106 | 2 1 0 | 92 | − 60 | 8 1 0 | 194 | 182 |
| 0 14 6 | 85 | − 82 | 2 3 0 | 62 | 40 | 8 3 0 | 204 | −190 |
| 0 16 6 | 80 | − 82 | 2 5 0 | 30 | − 28 | 8 5 0 | 190 | 168 |
| 0 18 6 | 68 | − 73 | 2 7 0 | 58 | 56 | 8 7 0 | 184 | −174 |
| 0 1 7 | 94 | −110 | 4 1 0 | 238 | −266 | 8 9 0 | 150 | 140 |
| 0 3 7 | 101 | −114 | 4 2 0 | 200 | 228 | 8 11 0 | 138 | −134 |
| 0 5 7 | 93 | −105 | 4 3 0 | 194 | 214 | 8 13 0 | 112 | 108 |
| 0 7 7 | 79 | − 87 | 4 4 0 | 222 | −220 | 8 15 0 | 110 | − 98 |
| 0 9 7 | 88 | − 96 | 4 5 0 | 228 | −218 | 12 1 0 | 70 | − 60 |
| 0 11 7 | 60 | − 82 | 4 6 0 | 230 | 220 | 12 2 0 | 82 | − 68 |
| 0 13 7 | 59 | − 64 | 4 7 0 | 218 | 212 | 12 3 0 | 72 | 60 |
| 0 15 7 | 57 | − 71 | 4 8 0 | 200 | −176 | 12 4 0 | 70 | 70 |
| 0 2 8 | 89 | 95 | 4 9 0 | 182 | −148 | 12 5 0 | 52 | − 56 |
| 0 4 8 | 73 | 87 | 4 10 0 | 174 | 148 | 12 6 0 | 58 | − 60 |
| 0 6 8 | 102 | 122 | 4 11 0 | 182 | 160 | | | |
| 0 8 8 | 64 | 78 | 4 12 0 | 138 | −118 | | | |

A Fourier map of the projection along the *b*-axis based on the signs arrived at with the final set of parameters is reproduced in Fig. 1. Observed and calculated structure factors are listed in Table 1.

From a model of the benzyl sulphide molecule the *y*-coordinates could be estimated, the sulphur and iodine atoms lying in mirror planes.

A set of structure factors was then calculated for the 0*kl*-zone and the corresponding Fourier synthesis was worked out. The plane group of this projection is *cmm*, the origin being in (1/4, 1/4) relative to the origin of the original unit cell. The iodine peaks were found at the expected positions in the mirror plane at $y = 0$, and the benzyl sulphide molecule showed up clearly in the map. Some atoms from different molecules overlapped, however. After a few Fourier refinements the parameters of this projection were subjected to at least squares refinement. The »outer» iodine atom was not corrected for anisotropic thermal vibrations in this projection, this not being possible for an atom in a mirror plane with the present computer program. The discrepancies of the common parameters of the heavy atoms found in the (010)- and (100)-projections were 0.0005 for $I_1$, 0.0019 for $I_2$, and 0.004 for S. The final *R*-factor for the (100)-projection was 13.8 %; the corresponding Fourier map is shown in Fig. 2 and the observed and calculated structure factors (origin in (1/4, 1/4) of the cell given in *International Tables*) are listed in Table 1.

In the *hk*0-zone very few reflections other than the ones with $h = 4n$ were observed. The reason for this is of course the rather special positions of the iodine atoms in this projection, the projection having a pseudo translation 1/4 along the *a*-axis. One iodine atom overlaps with the sulphur atom in this projection, consequently rather few informations is to be had from these

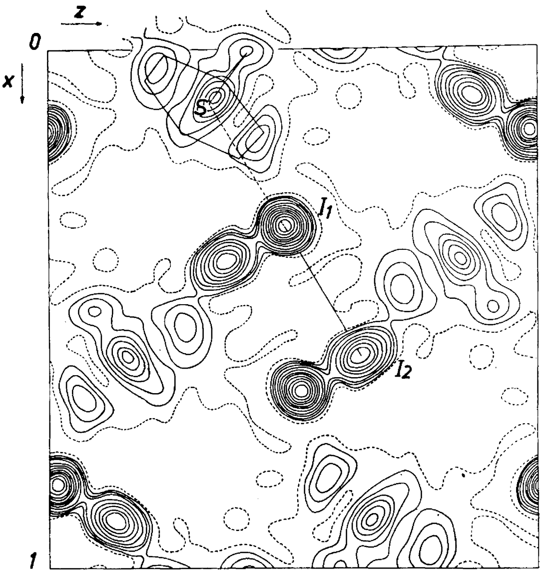

*Fig. 1.* Electron density projection along the *b*-axis. Contour intervals of 5 e.Å$^{-2}$ up to 20 e.Å$^{-2}$ and of 10 e.Å$^{-2}$ from 30 to 100 e.Å$^{-2}$.

data. Only the *x*-parameter of the iodine atom nearest the sulphur atom was determined from this projection and it showed good agreement with the one found in the projection along *b*. The final *R*-factor for the *hk*0-zone was 10.4 %. The observed and the corresponding calculated structure factors are listed in Table 1.

## DISCUSSION OF THE STRUCTURE

Benzyl sulphide-iodine crystallizes with a nearly linear S-I-I arrangement with a mirror plane through the sulphur and iodine atoms and between the benzyl groups. Figs. 1 and 2 show the electron density projections along the *b* and *a* axes, respectively. For the final parameters listed in Table 2, values from the projections along *b* were used for the sulphur and iodine atoms, whereas a mean value from all projections were used for the lighter atoms.

The distance between the iodine atoms in the iodine molecule is found to be 2.819 Å and between the sulphur atom and the nearest iodine atom 2.78 Å. The standard deviations[6] for these distances are 0.009 Å and 0.02 Å, respectively. The sulphur and iodine atoms are within the accuracy of the investigation lying on a straight line, the S-I-I angle being found equal to 179°.

The sulphur-methylene carbon distance was found to be 1.82 Å, in good agreement with the normal single bond value[7]. The distances between carbon atoms in the benzene ring are of course not well determined in a structure with heavy atoms like the present one, the mean value was found to be 1.38 Å for the nearest C-C distance with deviations of up to 0.1 Å. There is an angle

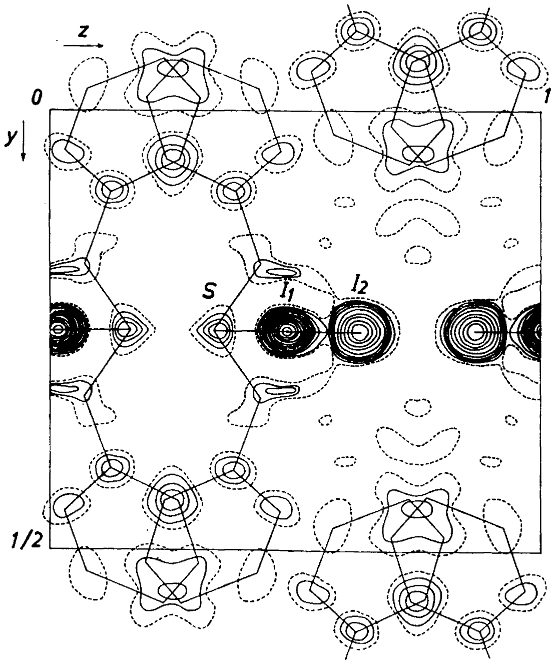

*Fig. 2.* Electron density projection along the *a*-axis. Contour intervals as in Fig. 1.

of 93° between the two sulphur-methylene carbon directions; the angle between the sulphur-iodine and the sulphur-methylene carbon directions is found to be 100°.

The nearest iodine-iodine approach between the molecules was 4.33 Å, corresponding closely to the van der Waals' distance given by Pauling[7]. The fact that the direction of maximum vibration of the »outer» iodine atom as observed in the projection along the *b*-axis is normal not only to the intramolecular I-I bond but also to the loose intermolecular I-I interaction in the mirror plane suggests that the anisotropy has some structural significance.

*Table 2.* Atomic coordinates as fractions of the cell edges.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| $I_1$ | 0.3428 | 0.2500 | 0.4849 |
| $I_2$ | 0.5893 | 0.2500 | 0.6374 |
| S | 0.1025 | 0.2500 | 0.3298 |
| $C_{methyl}$ | 0.009 | 0.328 | 0.422 |
| $C_1$ | 0.062 | 0.426 | 0.369 |
| $C_2$ | 0.002 | 0.459 | 0.237 |
| $C_3$ | 0.074 | 0.524 | 0.196 |
| $C_4$ | 0.164 | 0.554 | 0.270 |
| $C_5$ | 0.223 | 0.526 | 0.409 |
| $C_6$ | 0.151 | 0.458 | 0.454 |

The investigation shows that organic sulphur compounds may act as electron donors to form molecular addition compounds in the same way as amines. The lengthening of the I-I bond (0.17 Å relative to the sum of the normal covalent radii [7]) is the same as found where an amine act as the electron donor [8]. It agrees also fairly well with the value given by McCullough *et al.* in the compound dithiane · $2I_2$. The lengthening of the S-I bond relative to the covalent bond distance is consistent with the corresponding values in compounds between amines and halogen, it is in very good agreement with the value given by McCullough.

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