The Crystal Structure of Bi-1,3-Dithiacyclopentyl(2)

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The crystal structure of the substance of mp. 135.5° C having the formula $C_6H_{10}S_4$ (a product obtainable from 2,3-dichloro-1,4-dioxan and 1,2-ethanedithiol) has been determined. The substance turned out to be bi-1,3-dithiacyclopentyl(2) and therefore corresponds to the lower melting isomer (111° C) obtained in the reaction between 2,3-dichloro-1,4-dioxan and ethylene glycol.

If ethylene glycol reacts either with 2,3-dichlorodioxan or with glyoxal, two isomeric compounds are obtained. The structure of the lower melting isomer (m.p. 111° C) has been determined¹ and it has been found to be bi-1,3-dioxacyclopentyl(2).

By heating 2,3-dichloro-1,4-dioxan with 1,2-ethanedithiol in anhydrous benzene, Proštenik and Balenović² obtained a compound with the empirical formula $C_6H_{10}S_4$ and m.p. 135.5° C. This compound is identical with glyoxaldiethylenmercaptal already obtained by Fasbender³. They also tried to obtain an isomer, but with negative results. As it could not be determined by the chemical reaction whether $C_6H_{10}S_4$ is bi-1,3-dithiacyclopentyl or *cis*-naphthodithian, the structure has been determined by X-ray diffraction.

EXPERIMENTAL

Bi-1,3-dithiacyclopentyl crystallizes monoclinic, and occurs in different habits. Twinning occurs constantly, especially about (001). Crystals grown from a hot benzene solution are needle-shaped, elongated along the *a*-axis, while crystals grown from a hot saturated solution in acetone are plates with well developed clinopinacoid planes.

A needle-shaped crystal with cross-section $0.24 \times 0.56 \text{ mm}^2$ was used for a series of Weissenberg photographs of the $\{0kl\}$ zone. A tabular crystal with cross-section $0.35 \times 0.25 \text{ mm}^2$ was used for the (*h*0*l*) reflections.

Rotation, oscillation and Weissenberg photographs using $CuK\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) led to the following data for the unit cell:

$a = 4.92 \text{ \AA}$; $b = 13.23 \text{ \AA}$; $c = 6.94 \text{ \AA}$ (all $\pm 1 \%$); $\beta = 96^\circ$

$C_6H_{10}S_4$: Formula weight = 210.3

$V = 454 \text{ \AA}^3$; $D = 1.49 \text{ g/cm}^3$; $Z = 2$ ($Z \text{ calc.} = 1.95$); $F_{000} = 200$

The density D was determined by flotation of some crystals in a $BaBr_2$ solution in water.

Fig. 1. The electron density map of the y - z projection.

Systematic absence of the $h0l$ reflections for $h + l$ odd, and of the $0k0$ reflections for k odd, occurs. Therefore the space group is $P 2_1/n$ and the general positions are

$$x, y, z; \bar{x}, \bar{y}, \bar{z}; 1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z$$

Intensity measurements were carried out visually on Weissenberg photographs, using the multiple film technique. Corrections for the Lorentz polarisation factor were made, whereas corrections for absorption were not thought quite necessary.

A total number of 78 $0kl$ reflections were recorded, about 80 % of those theoretically accessible, and a total number of 24 $h0l$ reflections were recorded, about 69 % of the theoretically accessible.

THE DETERMINATION OF THE STRUCTURE

The a -axis projection. A Patterson F^2 projection along the a -axis gave the coordinates of the sulphur atoms with moderate approximation. However, the phases of numerous observed structure factors were determined, and after successive refinements, the electron-density map shown in Fig. 1 was obtained. The contour line scale corresponds to $2 e \cdot \text{\AA}^{-2}$ for the carbon atoms and the first contour line of the sulphur atoms, whereas the inner contour lines of the sulphur atoms correspond to $4 e \cdot \text{\AA}^{-2}$.

All atoms are well resolved except the carbon C_2 atoms. The sulphur atoms are easily distinguished by the greater height of the peaks. The maximum electronic density reached by the resolved carbon atoms is $6.68 e \cdot \text{\AA}^{-2}$, and for the sulphur atoms $18.56 e \cdot \text{\AA}^{-2}$, which is in good agreement with the theoretical values, (weight of carbon 6, of sulphur 16). No consideration has been given to the hydrogen atoms as they are not expected to show up clearly.

Hartree's model of the atomic scattering function f was used for the calculation of the structure amplitudes F . The theoretical f -curves were multiplied by the temperature factor $e^{-B\sin^2\Theta/\lambda^2}$ where the constant B was determined by comparison between the calculated and the observed structure factors F . B was found to equal $3.9 \text{ \AA}^2$.

The agreement between calculated and observed amplitudes is given by $R = \frac{F_{\text{calc}} - F_{\text{obs}}}{F_{\text{obs}}}$ where the F_{calc} corresponding to observed values too weak to be detected, were taken in the summation with half of their value. The result obtained was $R = 0.21$. The final y and z coordinates are determined from the map, and given with three significant figures (Table 1). A detailed consideration of the error has not been attempted, but the coordinates are probably reliable to $\pm 0.002 \text{ \AA}$, with exception of C_2 which may be less certain. (The numbering of atoms is given in Fig 1.) In Table 3 the structure factors calculated from the y and z coordinates are compared with the observed structure amplitudes.

Table 1.

	x/a	y/b	z/c	x	y	z
S_1	0.23	0.996	0.292	1.13 $\text{\AA}$	-0.053 $\text{\AA}$	2.026 $\text{\AA}$
S_3	0.22	0.147	0.988	1.08 »	1.945 »	-0.014 »
C_3	0.15	0.013	0.026	0.74 »	0.172 »	0.180 »
C_4	0.42	0.194	0.218	2.07 »	2.567 »	1.513 »
C_5	0.27	0.131	0.379	1.33 »	1.733 »	2.630 »

The b-axis projection. The knowledge of the z -coordinates and the generally accepted bond lengths made it possible to work out this projection. The positions of the sulphur atoms were found from a Patterson projection. Once the positions of these atoms were established, a change in the x -coordinates of the carbon atoms to any acceptable position did not change the sign of calculated structure factors corresponding to any measurable amplitude, and the electron density map shown in Fig. 2 was obtained after only two refinements. As the peaks overlap extensively, it is not possible to derive accurate coordinates from this map. Table 1 gives the x -coordinates found by means of numerous successive calculations of the correlation factor. These calculations were made following the same procedure as before, but a better agreement between the observed and the calculated amplitudes was obtained in this case by choosing a B value of 2.5 in the temperature factor $e^{-B\sin^2\Theta/\lambda^2}$. In the a -axis projection B had a considerably higher value 3.9. This may indicate an oriented thermal vibration of the molecules.

A further study of the variation of B -values has not been attempted, but while bi-1,3-dioxacyclopentyl seems to vibrate chiefly in a direction normal to $(100)^1$ in our case the thermal vibration seems rather to take place in the (100) plane. Keeping in mind that the a -axis chosen in this projection is a diagonal axis, the disagreement may be apparent.

It is also of interest to point out that the c -axis of bi-1,3-dioxacyclopentyl(2) is the longest one, the cell dimensions are $a = 4.46 \text{ \AA}$, $b = 7.76 \text{ \AA}$, $c = 11.64 \text{ \AA}$, $\beta = 121.5^\circ$, while the cell dimensions of bi-1,3-dithiacyclopentyl show that

Fig. 2. The electron density map of the x - z projection. Full lines indicate structure I, dotted lines structure II.

the b -axis is the longest one. The different orientation of thermal vibrations which the B value in the temperature factor seems to indicate, may be related to this difference in the cell dimensions. The x coordinates in Table 1 are given with only three significant figures because no greater accuracy can be expected with the unsatisfactory procedure in their determination.

The structure factors calculated from the xz -coordinates in Table 1 are compared with the observed amplitudes in Table 4. The correlation factor obtained is $R = 0.23$.

MOLECULAR DIMENSIONS AND DISCUSSION

The electron density map represented in Fig. 1 gives a good determination of the structure as far as the y and z coordinates are concerned, and there can be no doubt concerning the question whether the compound studied is bi-1,3-dithiacyclopentyl or *cis*naphthodithian.

Fig. 3. The x - z projection of structure I.

Table 2.

S_1-S_3	2.86 Å	S_3-C_4	1.84 Å
S_1-C_4	1.86	C_4-C_5	1.52
S_1-C_5	1.89	C_4-C_3	1.52
S_3-C_5	1.82		

Angles

$$\begin{aligned} S_1C_4S_3 &= 104^\circ \\ C_4S_1C_5 &= 102^\circ \\ C_5S_3C_4 &= 109^\circ \\ S_1C_5C_4 &= 109^\circ \end{aligned}$$

$$\begin{aligned} C_5C_4S_3 &= 100^\circ \\ C_4C_5S_3 &= 112^\circ \\ C_4C_3S_1 &= 107^\circ \end{aligned}$$

The electron density map represented in Fig. 2 does not give so unquestionable results; a second structure (dotted on Fig. 2) is considered possible. In this case the x coordinates of the C_4 and C_5 are $x_4 = 0.30$ Å and $x_5 = 1.13$ Å. However, the refinement could not be improved beyond $R = 0.28$ in structure II whereas a value $R = 0.23$ was reached if the calculations were based upon structure I. Fig. 3 represents the zx projection of structure I. The bond lengths and angles calculated from the coordinates in Table 1 corresponding to structure I are given in Table 2. The four independent determinations of the C—S bond, agree within the limits of error with the generally accepted value⁴, 1.81 Å. By using electron diffraction the single bond length C—S is found⁵ within the range 1.78 to 1.90 Å. The C—C bond lengths are in close agreement with the accepted value of 1.54 Å. A detailed consideration of the errors has not been attempted, but on account of the very unsatisfactory determination of the x coordinates no greater accuracy than $\pm 4\%$ can be expected. The deviation of the bond angles from 109° are also within the limits of error.

A plane containing the three atoms S_1 C_2 S_3 will pass between the two carbon atoms C_4 and C_5 and the distance from these atoms to the plane is 0.47 Å for C_4 and for C_5 —0.32 Å. The minus sign for the distance means that the atom is on the same side of the plane as origo.

The shortest intermolecular distances are those between C_4-S_3 (3.13 Å) and C_5-S_3 (3.71 Å). The C_4S_3 distance is shorter than the generally accepted value of 3.4 to 3.7 Å between a methylene group and a sulphur atom^{6,7}. Recently however, shorter CH_3-S intermolecular distances have been found *e.g.* in the crystal structure of metanethiosulphonates, a CH_2-S distance as low as about 3.1 Å was obtained⁸ which is identical with the corresponding distance found in this structure.

CHEMICAL ASPECTS

On heating 2,3-dichloro-1,4-dioxan with 1,2-ethanedithiol in anhydrous benzene no compound was obtained which contained oxygen, but only bi-1,3-dithiacyclopentyl(2). The first reaction mechanism mentioned by Furberg and Hassel and based on hydrogen bonds is of course not possible when ethylene glycol is replaced by the corresponding dithiol. The second alternative, however, also discussed by Proštenik and Balenović appears possible: 2,3-di-

Table 3.

<i>h k l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h k l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
0 2 0	43.9	43.8	0 0 4	32.7	41.7
0 4 0	5.2	7.9	0 1 4	10.6	-11.4
0 6 0	64.9	72.1	0 2 4	9.8	8.2
0 8 0	38.1	40.4	0 3 4	0	-1.7
0 10 0	5.0	5.1	0 4 4	4.4	2.9
0 12 0	9.8	10.4	0 5 4	7.5	6.3
0 14 0	16.0	18.3	0 6 4	20.3	26.4
			0 7 4	0	-3.8
			0 8 4	10.6	10.9
0 1 1	27.2	30.7	0 9 4	2.6	3.0
0 2 1	20.4	18.0	0 10 4	0	-0.8
0 3 1	27.4	35.7	0 11 4	0	-0.5
0 4 1	14.8	-14.8	0 12 4	5.8	6.5
0 5 1	7.1	2.4			
0 6 1	0	-1.1	0 1 5	0	-0.9
0 7 1	21.9	21.1	0 2 5	10.6	-8.1
0 8 1	6.0	-5.6	0 3 5	25.8	-36.6
0 9 1	11.0	-11.5	0 4 5	0	2.3
0 10 1	4.9	-2.4	0 5 5	12.1	13.4
0 11 1	9.6	-10.0	0 6 5	7.8	8.2
0 12 1	0	-0.4	0 7 5	0	2.0
0 13 1	7.3	7.6	0 8 5	3.7	-4.4
0 14 1	4.8	-5.8	0 9 5	10.1	-12.0
			0 10 5	3.5	-1.9
			0 11 5	9.9	-12.2
0 0 2	0	6.5			
0 1 2	9.1	-9.6	0 0 6	9.8	13.7
0 2 2	19.3	27.2	0 1 6	0	1.0
0 3 2	12.4	-9.1	0 2 6	0	-0.3
0 4 2	46.5	-53.8	0 3 6	0	-0.1
0 5 2	17.0	14.5	0 4 6	7.6	-6.5
0 6 2	0	-0.7	0 5 6	6.5	4.5
0 7 2	10.5	7.5	0 6 6	5.2	7.9
0 8 2	0	-0.1	0 7 6	2.5	2.6
0 9 2	6.8	-5.8	0 8 6	4.2	4.9
0 10 2	24.6	-30.7	0 9 6	0	2.2
0 11 2	0	3.9	0 10 6	4.2	-6.2
0 12 2	7.0	-6.4	0 11 6	5.1	5.8
0 13 2	5.0	5.1			
			0 1 7	8.8	13.9
0 1 3	46.1	54.5	0 2 7	4.4	-6.8
0 2 3	4.2	-3.5	0 3 7	5.6	5.7
0 3 3	4.0	1.3	0 4 7	2.5	3.3
0 4 3	14.4	11.4	0 5 7	7.2	6.9
0 5 3	11.0	15.9	0 6 7	5.5	4.5
0 6 3	5.7	-1.0	0 7 7	9.4	13.8
0 7 3	37.0	44.2	0 8 7	3.9	-2.7
0 8 3	0	2.3			
0 9 3	8.0	8.6	0 0 8	0	3.9
0 10 3	6.4	6.0	0 1 8	4.5	-4.4
0 11 3	0	-2.0	0 2 8	3.5	-4.4
0 12 3	6.8	2.6	0 3 8	0	-0.4
0 13 3	12.1	14.4	0 4 8	5.8	-8.4
			0 5 8	3.4	3.4

Table 4.

<i>h k l</i>	<i>F</i> _{obs}	<i>F</i> _{calc.}	<i>h k</i>	<i>F</i> _{obs}	<i>F</i> _{calc.}
0 0 2	0	1.59	3 0 $\bar{1}$	10.45	-10.52
0 0 4	13.35	11.57	3 0 1	0	0
0 0 6	4.82	4.28	3 0 3	9.24	-7.55
1 0 $\bar{5}$	0	-0.56	3 0 5	1.98	-2.20
1 0 $\bar{3}$	5.32	-1.82	3 0 7	3.90	-2.79
1 0 $\bar{1}$	15.90	20.05	4 0 $\bar{6}$	2.97	-3.34
1 0 1	10.80	-11.24	4 0 $\bar{4}$	2.86	2.03
1 0 3	10.35	11.00	4 0 $\bar{2}$	0	-0.12
1 0 5	2.21	2.04	4 0 0	5.12	7.95
2 0 $\bar{6}$	3.70	-5.27	4 0 2	0	-0.80
2 0 $\bar{4}$	7.27	-4.14	4 0 4	2.87	2.94
2 0 $\bar{2}$	2.72	-3.38	4 0 6	0	0.04
2 0 0	18.63	-19.78	5 0 1	3.53	6.58
2 0 2	0	-1.17	5 0 1	0	-0.54
2 0 4	8.40	-8.56	5 0 3	4.07	5.5
2 0 6	0	-1.98			
3 0 $\bar{5}$	0	0.74	6 0 0	1.000	-2.99
3 0 $\bar{3}$	2.58	-2.39			

chloro-1,4-dioxan by mild hydrolysis gives (besides glycol) a quantity of glyoxal equivalent to the amount of water originally present. Bi-1,3-dithiacyclopentyl(2) will then be formed by the reaction between glyoxal and 1,2-ethanedithiol since this process again yields water, thus enabling the reaction to continue.

I am indebted to the *American Association of University Women* which gave me a fellowship thus making it possible for me to begin my work in the field of structure determination by X-ray diffraction. Thanks are due to professor M. Proštenik and K. Balenović for sending to professor O. Hassel the compound to be determined. I will also express my gratitude to professor O. Hassel for suggesting this problem and giving me possibilities of working at his institute. Finally I will thank professor H. Haraldsen for giving me all possibilities to continue and finish the work at his institute.

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Received March 1, 1954.