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## De kristalstructuur van P4S3 en P4S5

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## S U M M A R Y

In this thesis the crystal structure determinations of two phosphorus sulphides,  $P_4S_3$  and  $P_4S_5$ , are described. A short introduction, dealing with the history, the preparation and the most important properties and applications of the phosphorus sulphides, may be found in chapter 1. A survey of the structure models suggested for the phosphorus sulfides  $P_4S_3$ ,  $P_4S_5$ ,  $P_4S_7$  and  $P_4S_{10}$  is given. The crystal structures of the latter two compounds were recently determined (Vos, 1955); the X-ray investigation of the crystal structures of  $P_4S_3$  and  $P_4S_5$  is described in the chapters 2 and 3 of this thesis.

$P_4S_3$  has a transition point at 39 °C; the heat of transition amounts to ca 3.4 kcal/mol. Only the crystal structure of the low-temperature modification was investigated. This modification belongs to the space-group  $Pmnb$ . With a special back-reflexion camera, the following values for the lattice parameters were obtained:

$a = 9.660 \text{ \AA}$ ;  $b = 10.597 \text{ \AA}$ ;  $c = 13.671 \text{ \AA}$ ; eight molecules per unit cell.

The intensities of 954 independent reflexions  $hkl$  were measured on integrated equi-inclination Weissenberg photographs about the  $a$  axis, taken with Ni-filtered Cu radiation. The structure was deduced from a three-dimensional Patterson synthesis; the coordinates were refined by calculating successive Fourier syntheses of the three projections. More accurate values for the coordinates were obtained from a three-dimensional least-squares refinement, which was carried out with our intensity data by Dr. Jürg Waser, Chemistry Department, Houston, Texas, U.S.A. The final coordinates are listed in table 2.1. The disagreement index  $R$  for the observed reflexions  $hkl$  amounts to 0.16, the temperature factor  $\exp(-3.83 \sin^2\theta/\lambda^2)$  being used.

The crystal consists of molecules  $P_4S_3$  (fig. 2.7). The structure of these molecules is identical with the structure of the molecules in gaseous  $P_4S_3$  (Hassel and Pettersen, 1941). The bond lengths and angles are listed in table 2.3. The average P-S and P-P distances are respectively 2.090 Å and 2.235 Å; the estimated standard deviation in these mean values is 0.005 Å. Fig. 2.8

shows the arrangement of the molecules in the crystal. One of the symmetry planes of the molecule coincides with a mirror plane of the unit cell.

$P_4S_5$  belongs to space-group  $P2_1$ . The lattice parameters were measured on Weissenberg and oscillation photographs about the three axes. In this way the following values were found:  $a = 6.41 \text{ \AA}$ ;  $b = 10.94 \text{ \AA}$ ;  $c = 6.69 \text{ \AA}$ ;  $\beta = 111.7^\circ$ ; two molecules per unit cell.

The intensities of 738 independent reflexions  $hkl$  were visually estimated on equi-inclination Weissenberg photographs about the  $a$  axis, taken with Ni-filtered Cu radiation. Since the crystals were twinned, either across the plane (001) or with respect to the line [100], two independent sets of reflexions  $hkl$ , with the exception of  $h = 0$ , were available.

After some unsuccessful attempts to solve the structure by means of inequalities, a three-dimensional Patterson synthesis was calculated, from which it was possible to deduce an approximate structure. The coordinates so obtained were refined by computing successive Fourier syntheses of the three projections; "backshift" corrections were applied in the later stages of the refinement. The final coordinates are given in table 3.1. The standard deviation in these coordinates is estimated at  $0.015 \text{ \AA}$ . The temperature parameters  $B$  and the disagreement indices  $R$  of the three projections have the following values:

projection	$B$	$R$
[001]	$2.37 \text{ e\AA}^{-2}$	8 %
[010]	$2.69 \text{ e\AA}^{-2}$	12 %
[100]	$2.88 \text{ e\AA}^{-2}$	7 %

The observed and calculated  $F$  values are compared in table 3.3.

The crystal consists of molecules  $P_4S_5$  (fig. 3.6). The structure of these molecules is completely asymmetric;  $P_4S_5$  is therefore optically active. The bond lengths and angles are listed in table 3.2. The P-S distances vary from  $2.08 - 2.19 \text{ \AA}$ , the average value for the P-P bond lengths is  $2.21 \text{ \AA}$  and the P=S distance is  $1.94 \text{ \AA}$ . The intramolecular distance between the non-bonded atoms  $P_2$  and  $P_4$  is very short,  $3.01 \text{ \AA}$ . The arrangement of the molecules in the crystal is shown in fig. 3.7.

In chapter 4 the molecular structures of the four known phos-

phorus sulphides  $P_4S_3$ ,  $P_4S_5$ ,  $P_4S_7$  and  $P_4S_{10}$  are compared with each other and with the structure of the  $P_4$  molecule. A survey of the bond lengths and angles found in these and in other phosphorus and sulphur compounds is given.