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Crystal Structure of *Cyclo*hexane-1a,3a,5a-thiophosphoric Acid Ester

PER ANDERSEN and K. E. HJORTAAS

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

An X-ray investigation of the thiophosphoric acid α-floroglucitol ester has been carried out. The space group is $Pna2_1$ and the cell dimensions are a 11.45 ± 0.05 Å; b 7.28 ± 0.04 Å; c 9.47 ± 0.05 Å, with 4 molecules in the unit cell. The structure shows that the three ester oxygen atoms are in axial positions in the *cyclo*hexane ring. The space group of the corresponding phosphoric acid ester is Cc with cell dimensions a 11.37 Å; b 6.25 Å; c 11.74 Å; β 118°, and 4 molecules in the cell.

The esters formed by α-floroglucitol and phosphoric acid and thiophosphoric acid, respectively, were synthesised by Stetter and Steinacker in 1951 [1] and the reactions were shown to be:

$$C_6H_9(OH)_3 + OPCl_3 = C_6H_9O_3PO + 3HCl$$

and

$$C_6H_9(OH)_3 + SPCl_3 = C_6H_9O_3PS + 3HCl$$

They assumed configurations as shown in Fig. 1 and could conclude that α-floroglucitol was the *cis* form of *cyclo*-hexane-1,3,5-triol. This had been proved earlier by an X-ray investigation of the dihydrate of α-floroglucitol [2]. The hydroxygroups were in equatorial rather than in axial positions in this crystal structure, however.

The 1,3-carbon-carbon distance in *cyclo*hexane is 2.51 Å and the Cl—Cl distance in both $OPCl_3$ and $SPCl_3$ is 3.23 Å. Even if these distances are somewhat unfavourable the proposed structure is reasonable when compared with the hydroxy-oxygen distances in phosphoric acid [3] which are 2.50—2.52 Å. The proposed structure should therefore be expected to exhibit undistorted axial bonds.

CRYSTALLOGRAPHIC DATA

The X-ray data were obtained from oscillation and Weissenberg photographs using unfiltered Cu$K\alpha$ radiation. Multiple film technique was employed with visual estimation of the intensities using an experimental intensity scale

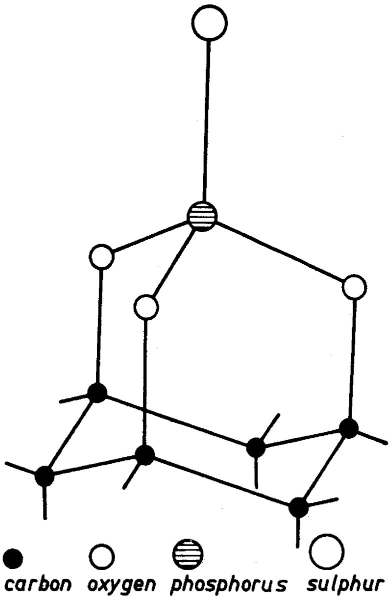

Fig. 1. A model of the molecule.

for comparison. The intensities were corrected in the ordinary way to obtain $|F_o|$ values. The space groups were determined both for the sulphur and oxygen compound, but a structure determination was only carried out for the former.

The thiophosphoric acid ester is orthorhombic with the following unit cell dimensions:

$$a\ 11.45 \pm 0.05\ \text{Å}; \quad b\ 7.28 \pm 0.04\ \text{Å}; \quad c\ 9.47 \pm 0.05\ \text{Å}$$

The experimental density was found equal to 1.64 g cm^{-3} which gives four molecules in the cell. The systematic extinctions show that reflexions in the $(0kl)$ zone are present only when $k + l = 2n$ and in the $(h0l)$ zone when $h = 2n$. The possible space group could therefore be either *Pnam* or $Pna2_1$. Both space groups are equally acceptable as the fourfold positions in *Pnam* require the point symmetry m and the proposed model has the symmetry $3m$. Patterson projections combined with the trial and error computations showed that $Pna2_1$ was the correct space group.

The phosphoric acid ester is monoclinic and has the cell dimensions:

$$a\ 11.37\ \text{Å}; \quad b\ 6.25\ \text{Å}; \quad c\ 11.74\ \text{Å}; \quad \beta\ 118°$$

The density was found to be 1.60 g cm^{-3} which gives four molecules per unit cell. The systematic extictions show that (hkl) reflexions are present when $h + k = 2n$ and $(h0l)$ reflexions for $l = 2n$. This leads to two possible space groups $C2/c$ and Cc. As the fourfold positions in $C2/c$ has the point symmetry 2 or $\bar{1}$ it must be assumed that Cc is the correct space group.

Table 1. Co-ordinates and temperature factors for the [001] and [010] projection, respectively.

	x	y	B	x	z	B
S	0.227	0.670	3.8	0.226	−0.005	4.1
P	0.341	0.481	3.0	0.341	0	3.1
O_1	0.308	0.310	3.0	0.310	−0.099	3.3
O_2	0.364	0.395	3.0	0.360	0.152	3.3
O_3	0.467	0.540	3.0	0.461	−0.054	3.3
C_1	0.397	0.158	4.0	0.389	−0.090	3.6
C_2	0.406	0.091	4.0	0.410	0.064	3.6
C_3	0.450	0.247	4.0	0.449	0.150	3.6
C_4	0.564	0.324	4.0	0.570	0.095	3.6
C_5	0.560	0.390	4.0	0.552	−0.045	3.6
C_6	0.508	0.239	4.0	0.512	−0.148	3.6
H_1	0.33	0.01	4.0	0.33	0.10	4.0
H_2	0.37	0.05	4.0	0.37	−0.16	4.0
H_3	0.49	−0.02	4.0	0.49	0.06	4.0
H_4	0.46	0.18	4.0	0.46	0.26	4.0
H_5	0.57	0.13	4.0	0.57	−0.16	4.0
H_6	0.50	0.30	4.0	0.50	−0.26	4.0
H_7	0.64	0.23	4.0	0.64	0.09	4.0
H_8	0.59	0.46	4.0	0.59	0.16	4.0
H_9	0.64	0.46	4.0	0.64	−0.09	4.0

It was decided to carry out a structure determination of the sulphur compound because of the higher symmetry in the space group, as in *Cc* not even one projection has a center of symmetry.

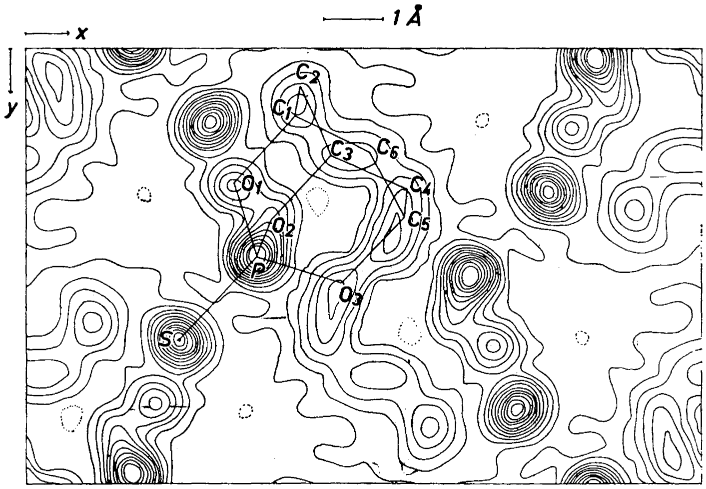

Fig. 2. Projection along [001]. Interval of contour lines 2e Å^{-2}. Zero line dotted.

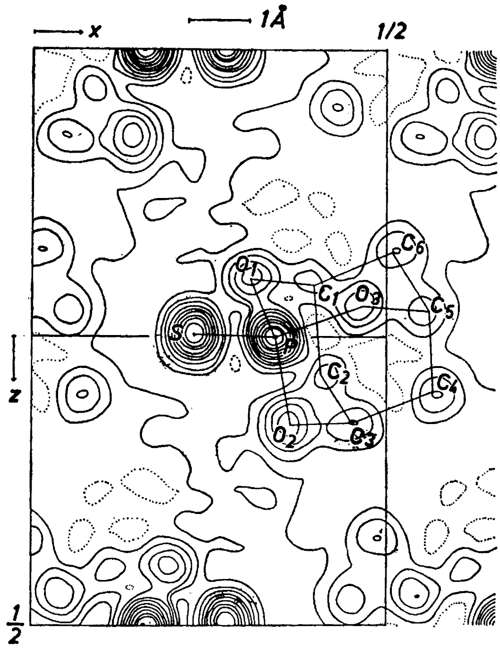

Fig. 3. Projection along [010]. Interval of contour lines 2e Å^{-2}. Zero line dotted.

STRUCTURE DETERMINATION

The Patterson projections $P(u, v)$ and $P(u, w)$ did not give any conclusive indications as to the position or orientation of the molecule. The assumption that the molecule as a whole is roughly spherical (except for the sulphur atom) combined with trial and error computations and informations from the Patterson projections finally lead to a structure which could be refined. One could thus unequivocally exclude the more symmetrical space group *Pnam*.

Table 2. Standard deviation of co-ordinates expressed in Å for the [001] and [010] projection, respectively.

	$\sigma(x)$	$\sigma(y)$	$\sigma(x)$	$\sigma(z)$
S	0.005	0.006	0.007	0.013
P	0.005	0.005	0.006	0.007
O	0.015	0.017	0.022	0.027
C			0.026	0.032

Table 3. Bond lengths (Å), bond angles and standard deviations.

						S.d.
S–P	1.90					0.01
P–O_1	1.60	P–O_2	1.59	P–O_3	1.56	0.02
O_1–C_1	1.47	O_2–C_3	1.48	O_3–C_5	1.52	0.04
C_1–C_2	1.55	C_2–C_3	1.48	C_3–C_4	1.54	
C_4–C_5	1.42	C_5–C_6	1.56	C_6–C_1	1.56	0.04
S–P–O_1	113°	S–P–O_2	114°	S–P–O_3	114°	0.9°
O_1–P–O_2	105°	O_2–P–O_3	106°	O_3–P–O_1	103°	1.1°
P–O_1–C_1	114°	P–O_2–C_3	112°	P–O_3–C_5	114°	1.7°

The structure was refined in the [001] and the [010] projection using ($F_o - F_c$) difference syntheses. The hydrogens were introduced in the final stage for reflexions with ξ values less than about 0.6 and by assuming the C—H bond to be 1.09 Å. In the [001] projection the R factor in the end was 0.13 with an isotropic temperature factor $B = 3.2$ Å^2 for all atoms. The corresponding values for the [010] projection were $R = 0.14$ and $B = 3.6$ Å^2. In calculating R the (002) and (201) reflections are omitted because of extinction. In calculating $\Sigma||F_o|-|F_c||$ unobserved reflections are given the minimum observable value $|F'_o|$ when $|F_c| > |F'_o|$, but are omitted when $|F_c| < |F'_o|$. In either case they are excluded from $\Sigma\ |F_o|$. The difference syntheses in both projec-

Table 4. Shortest intermolecular distances (Å).

$O-CH_2$	3.40	4.18	4.85
$O-S$	3.78	4.00	
CH_2-CH_2	3.75	5.21	
$S-CH_2$	3.89	4.16	4.40

Table 5. Observed and calculated structure factors and phase angles.

h k l	F_{calc}	$\lvert F_{\text{obs}}\rvert$	*h k l*	F_{calc}	$\lvert F_{\text{obs}}\rvert$	*h k l*	F_{calc}	$\lvert F_{\text{obs}}\rvert$
0 2 0	−8	9	3	−18	20	4	−6	4
4	7	7	4	4	6	5	13	15
6	24	25	5	3	4	6	2	<2
8	0	<2	6	4	4	7	−4	2
1 1 0	64	58	7	−20	20	9 1 0	−35	32
2	−28	30	8	−7	8	2	4	4
3	22	24	5 1 0	15	14	3	7	8
4	24	24	2	−62	62	4	8	8
5	8	8	3	15	14	5	−15	12
6	9	10	4	0	<2	6	−6	6
7	4	5	5	4	6	7	−6	7
8	−3	3	6	−11	12	10 0 0	−15	16
9	2	4	7	1	<2	1	12	11
2 0 0	17	14	8	−9	10	2	−17	14
1	59	55	6 0 0	10	10	3	0	<3
2	4	5	1	8	9	4	−8	9
3	17	17	2	29	31	5	−15	14
4	11	11	3	−33	33	6	3	<2
5	2	<2	4	34	32	11 1 0	−5	4
6	−28	28	5	−11	12	2	−1	<3
7	7	8	6	1	<3	3	−9	8
8	6	7	7	5	4	4	−9	9
9	3	4	8	6	9	5	10	10
3 1 0	−25	24	7 1 0	31	31	12 0 0	2	<2
2	−17	16	2	16	14	1	−4	4
3	−20	22	3	5	6	2	7	7
4	−12	14	4	−14	16	3	−1	<2
5	−13	16	5	6	7	4	6	7
6	−2	<3	6	5	7	5	−3	2
7	−3	4	7	7	8	13 1 0	2	<2
8	4	4	8 0 0	−4	6	2	−1	<2
4 0 0	0	<1	1	−21	19	3	11	11
1	−47	51	2	1	<2	14 0 0	3	2
2	−46	48	3	1	<2	1	2	2

Table 5. Continued.

$h\,k\,l$	$\lvert F_{calc}\rvert$	$\lvert F_{obs}\rvert$	α°	$h\,k\,l$	$\lvert F_{calc}\rvert$	$\lvert F_{obs}\rvert$	α°
0 0 2	151	72	354	6 0 5	22	22	95
4	44	42	278	6	16	19	18
6	36	36	334	7	18	16	76
8	24	24	5	8	12	11	22
10	12	6	342	9	10	9	63
2 0 0	14	14	0	10	4	6	45
1	84	54	277	8 0 0	8	8	180
2	40	38	174	1	42	43	283
3	18	18	174	2	8	8	180
4	42	42	180	3	30	32	266
5	16	18	192	4	6	4	63
6	30	30	200	5	34	34	242
7	22	24	325	6	12	12	18
8	28	27	197	7	24	24	261
9	14	13	342	8	4	<3	11
10	22	18	180	9	12	10	270
11	8	10	233	10 0 0	18	20	180
4 0 0	3	<2	180	1	18	21	73
1	22	23	52	2	18	18	221
2	34	35	283	3	20	22	85
3	8	7	304	4	16	16	150
4	18	18	354	5	18	20	114
5	8	6	225	6	20	18	139
6	6	6	315	7	12	12	99
7	6	8	104	8	6	4	180
8	14	14	270	12 0 0	2	<3	0
9	12	12	81	1	10	12	239
10	4	6	225	2	6	7	34
11	6	8	104	3	10	9	243
6 0 0	12	12	0	4	12	12	59
1	30	31	101	5	4	6	90
2	16	16	270	6	6	6	45
3	22	23	121	14 0 0	2	<2	0
4	8	8	297	1	2	3	315
				2	6	6	90

tions indicated that individual damping should be used. The phosphorus atom should be damped less and the sulphur atom more. This is also what one should expect from an inspection of the structure.

A least squares refinement carried out on a Ferranti Mercury computer for the two projections in question gave the correlation factors $R = 0.09$ and $R = 0.07$, respectively, for the [001] and [010] projection. The contribution from the hydrogen atoms is here included in all structure factors. The coordinates and the individual isotropic temperature factors are listed in Table 1. Figs. 2 and 3 show the two Fourier projections based on the phases calculated from these parameters. The standard deviations calculated from the equation derived by Cruickshank[4] are listed in Table 2, the values are doubled in the non-centrosymmetrical projection[5]. The interatomic distances and valency angles within the molecule and their standard deviations are listed in Table 3.

DISCUSSION

Orientation of the molecule in the cell is such that the S—P bond lies approximately in the *xy* plane and the axial bonds of the *cyclo*hexane ring are roughly parallel to this plane which is not far from being a plane of symmetry. The closest intermolecular approaches are listed in Table 4. They have all values which are compatible with accepted van der Waals radii.

The structure determination shows that the configuration proposed by Stetter and Steinacker is the correct one, and all distances and angles are within the limits of error those to be expected from an ideal model. The three oxygen atoms are in axial positions and the O—O distances are in good agreement with those computed for axial positions. Both the P—O distance and the O—P—O angle are in good agreement with those found in phosphoric acid[3].

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