in character. Hence tautomer IV is the only plausible form for crystalline guanine hydrochloride.

The author is grateful to Professor W. Cochran, F.R.S., for advice and helpful criticism.

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Refinement of the crystal structures of some phosphorus sulphides.

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The crystal structures of P_4S_3 (van Houten, Vos & Wiegers, 1955), P_4S_5 (van Houten & Wiebenga, 1957), P_4S_7 and P_4S_{10} (Vos & Wiebenga, 1955) were determined from three-dimensional Patterson syntheses several years ago. Only for P_4S_3 were all reflexions *hkl* used for a three-dimensional refinement (Leung, Waser, van Houten, Vos, Wiegers & Wiebenga, 1957); P_4S_5, P_4S_7 and P_4S_{10} were refined in projections. The present paper reports the results of a recent three-dimensional refinement of the crystal structures of P_4S_5, P_4S_7 and P_4S_{10} by means of the data collected for the three-dimensional Patterson syntheses. The cell dimensions were redetermined to obtain accurate values for the bond lengths and angles.

The crystallographic data are listed in Table 1. Unit-cell dimensions were measured from zero-level Weissenberg photographs about the crystallographic axes, taken with Ni-filtered Cu radiation [$\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$, $\lambda(\text{Cu } K\alpha_2) = 1{\cdot}5443$ Å]. On the photographs NaCl reflexions were superposed for calibration purposes.

The three-dimensional refinement was carried out by least-squares methods. For P_4S_{10} only 640 of some 900 observed reflexions could be taken into account because of overlap effects on the oscillation photographs used for the intensity measurements (Vos, 1955). As especially high order reflexions had to be excluded from refinement, only isotropic temperature factors were considered. For P_4S_5 and P_4S_7 690 and 1110 reflexions respectively were used. Isotropic refinement of the three compounds was done on the Groningen University computer Zebra with a program devised by Schoone (1961); all reflexions were given equal weight. The anisotropic least-squares analyses of P_4S_5 and P_4S_7 were kindly carried out by Dr J. S. Rollett (1961) on the Mercury computer at Oxford. In the last few cycles the weighting schemes were $w^{-1} = 1 + [(|F| - 18{\cdot}5)/12{\cdot}5]^2$ and $w^{-1} = 1 + [(|F| - 40)/40]^2$ respectively. Prints of the observed and calculated structure factors have been prepared and will be available on request.

Table 1. *Crystallographic data*

	P_4S_5	P_4S_7	P_4S_{10}
Space group	$P2_1$	$P2_1/n$	$P\bar{1}$
a	$6{\cdot}412 \pm 0{\cdot}003$	$8{\cdot}895 \pm 0{\cdot}004$	$9{\cdot}072 \pm 0{\cdot}003$ Å
b	$10{\cdot}903 \pm 0{\cdot}005$	$17{\cdot}44 \pm 0{\cdot}015$	$9{\cdot}199 \pm 0{\cdot}003$
c	$6{\cdot}694 \pm 0{\cdot}003$	$6{\cdot}779 \pm 0{\cdot}004$	$9{\cdot}236 \pm 0{\cdot}003$
α	90	90	$92{\cdot}58 \pm 0{\cdot}07°$
β	$111{\cdot}66 \pm 0{\cdot}1$	$92{\cdot}73 \pm 0{\cdot}1$	$100{\cdot}90 \pm 0{\cdot}1$
γ	90	90	$110{\cdot}18 \pm 0{\cdot}07$

The final parameters are listed in Tables 2, 3 and 4. The atomic coordinates may be compared with the results of the two-dimensional refinements (P_4S_5: van Houten &

Table 2. P_4S_5: *final parameters*

	x	y	z	U_{11}(Å^2)	U_{22}(Å^2)	U_{33}(Å^2)	U_{12}(Å^2)	U_{23}(Å^2)	U_{13}(Å^2)
P(1)	0·6850	0·0033	0·4023	0·0451	0·0233	0·0520	0·0156	0·0012	0·0022
P(2)	0·4628	0·1333	0·4974	0·0296	0·0385	0·0461	0·0205	−0·0040	0·0032
P(3)	0·7583	0·2584	0·5732	0·0223	0·0254	0·0412	0·0086	−0·0019	−0·0001
P(4)	0·4796	0·2393	0·0513	0·0490	0·0284	0·0366	0·0088	−0·0002	0·0015
S(1)	0·6305	0·0654	0·0855	0·0549	0·0320	0·0503	0·0269	0·0005	−0·0052
S(2)	0·2488	0·2085	0·2105	0·0289	0·0461	0·0536	−0·0056	−0·0015	0·0005
S(3)	0·7212	0·3472	0·2868	0·0524	0·0288	0·0423	0·0193	−0·0097	0·0021
S(4)	0·9682	0·1058	0·6196	0·0309	0·0349	0·0661	0·0016	0·0097	−0·0035
S(5)	0·8526	0·3780	0·8033	0·0571	0·0356	0·0454	0·0106	−0·0053	−0·0088

Table 3. P_4S_7: *final parameters*

	x	y	z	U_{11}(Å^2)	U_{22}(Å^2)	U_{33}(Å^2)	U_{12}(Å^2)	U_{23}(Å^2)	U_{13}(Å^2)
P(1)	0·2839	0·3793	0·7067	0·0434	0·0464	0·0270	−0·0023	−0·0065	−0·0013
P(2)	0·3550	0·2939	0·4645	0·0347	0·0384	0·0378	0·0024	−0·0142	0·0022
P(3)	0·2718	0·4610	0·2724	0·0334	0·0368	0·0353	−0·0001	0·0034	0·0006
P(4)	−0·0023	0·3332	0·4106	0·0330	0·0346	0·0339	−0·0025	−0·0084	0·0005
S(1)	0·0459	0·4252	0·2217	0·0336	0·0404	0·0384	0·0092	−0·0161	0·0001
S(2)	0·3066	0·5447	0·0974	0·0485	0·0442	0·0533	0·0177	0·0118	−0·0014
S(3)	−0·2102	0·3065	0·3619	0·0331	0·0511	0·0524	−0·0031	−0·0079	−0·0011
S(4)	0·3059	0·4869	0·5699	0·0450	0·0404	0·0399	−0·0113	−0·0013	−0·0013
S(5)	0·4145	0·3677	0·2360	0·0355	0·0425	0·0365	0·0009	0·0070	0·0023
S(6)	0·1482	0·2447	0·3652	0·0399	0·0320	0·0415	−0·0083	−0·0042	0·0003
S(7)	0·0481	0·3640	0·7024	0·0432	0·0426	0·0300	−0·0048	0·0081	−0·0013

Table 4. P_4S_{10}: *final parameters*

	x	y	z	B
P(1)	0·2569	0·0859	−0·1881	2·42 Å^2
P(2)	−0·0924	0·1616	−0·2855	2·37
P(3)	0·2698	0·4391	−0·2984	2·09
P(4)	0·1801	0·3482	0·0373	2·41
S(1)	0·3449	−0·0724	−0·1933	4·09
S(2)	0·0094	−0·0134	−0·2882	3·22
S(3)	0·3699	0·2687	−0·3032	2·69
S(4)	0·2861	0·1760	0·0327	2·06
S(5)	−0·3163	0·0671	−0·3735	4·05
S(6)	0·0278	0·3410	−0·4027	2·66
S(7)	−0·0655	0·2471	−0·0656	2·53
S(8)	0·3703	0·6055	−0·4057	3·15
S(9)	0·2920	0·5279	−0·0805	2·63
S(10)	0·2064	0·4281	0·2388	3·25

Table 5. P_4S_5: *bond angles*

S(1)–P(4)–S(2)	100·3°	S(3)–P(3)–P(2)	106·0°
S(1)–P(4)–S(3)	103·9	S(3)–P(3)–S(4)	110·8
S(2)–P(4)–S(3)	99·6	S(3)–P(3)–S(5)	108·4
P(1)–S(1)–P(4)	107·2	S(5)–P(3)–S(4)	115·0
P(2)–S(2)–P(4)	100·4	S(5)–P(3)–P(2)	125·5
P(3)–S(3)–P(4)	103·4	P(1)–P(2)–P(3)	83·0
S(1)–P(1)–P(2)	101·1	P(2)–P(3)–S(4)	89·6
S(1)–P(1)–S(4)	107·0	P(3)–S(4)–P(1)	88·7
S(2)–P(2)–P(1)	104·9	S(4)–P(1)–P(2)	87·0
S(2)–P(2)–P(3)	100·7		

Wiebenga, 1957, Table 1; P_4S_7: Vos & Wiebenga, 1955, Table 2; P_4S_{10}: Vos & Wiebenga, 1955, Table 1). The molecules and the bond lengths and angles are shown in Fig. 1 and in Tables 5, 6 and 7.

Table 8 shows the disagreement indices R for the reflexions used in the refinement, and the estimated values for the standard deviations in the bond lengths and angles. For P_4S_5 and P_4S_7 the standard deviations were estimated from the standard deviations in the atomic coordinates, as calculated by Rollett's least-squares program; for P_4S_5 the calculated values were multiplied by 1·5 as for some atoms shifts comparable with the e.s.d. were observed when changing the weighting scheme. Comparison of the standard deviations in the individual bond lengths with those estimated after the two-dimensional refinement (0·025 Å), shows that the three-dimensional refinement has increased the accuracy of the structure determinations considerably. For P_4S_{10} the greater accuracy is reflected by a smaller variation in the lengths of the chemically equivalent bonds, the maximum observed difference has decreased from 0·11 to 0·05 Å. The standard deviations for P_4S_{10} were estimated by comparing the lengths of the equivalent bonds.

For P_4S_7 the results of the present more accurate structure determination suggest (Fig. 1) that the lengths of the chemically non-equivalent P–S single bonds, which were assumed to be equal after the two-dimensional refinement, are slightly different. For P–S bonds of type P(3)–S(4), P(3)–S(1) and P(1)–S(4) respectively average values of 2·079, 2·114 and 2·108 Å are found. A similar, although not significant, variation in bond length has been observed in the sulphur-deficient modification of P_4S_7 (β-$P_4S_7 = P_4S_{6\cdot5}$), for molecules of P_4S_7 type in which the atoms S(2) and S(3) are partially lacking (Dixon, Einstein & Penfold, 1965). The average values corresponding to those mentioned above for the present compound (α-P_4S_7), are 2·065, 2·12 and 2·105 Å. An interesting difference has been observed, however, between the two types of P_4S_7 molecule. In α-P_4S_7 the P–P bond is unusually long, 2·326 Å, whereas the observed value for P–P in β-P_4S_7, 2·26 Å (s.d. 0·02 Å), is not significantly different from those in the remaining phosphorus sulphides, *viz.* 2·24 Å in P_4S_3 and 2·25 Å in P_4S_5. More accurate structure determinations of the two types of P_4S_7 molecule are worth while, to check whether the observed difference is real. For β-P_4S_7 the symmetry of the molecule is *mm*2 within the experimental error. For α-P_4S_7 a slight deviation from this symmetry is found; the difference between the related non-bonded distances S(4)···S(7) = 3·294 Å and S(5)···S(6) = 3·343 Å is about five times its e.s.d., for the distances S(3) · · · S(6) = 3·365 Å and S(3) · · · S(7) = 3·333 Å the difference is just significant.

As in P_4S_7, unequal values have been measured for the single P–S bonds in the asymmetric molecule of P_4S_5. A theoretical explanation of the observed variation in the lengths of the single P–S bonds has not yet been given.

Comparison of the results of the two- and three-dimensional refinements shows that in P_4S_{10} and P_4S_7 the observed lengths of the double P–S bonds have become smaller, whereas the single P–S bonds have become longer, on the average. The shortening of the double bonds is from 1·950 to 1·918 Å in P_4S_7 and from 1·955 to 1·908 Å in P_4S_{10}, the lengthening of the single bonds is from 2·080 to 2·097, and from 2·085 to 2·097 Å respectively. Therefore, the average lengths observed in the two-dimensional refinement for the single and double P–S bonds respectively are apparently affected by rather large errors, in spite of the good agreement between the average values obtained for the two compounds.

Table 6. P_4S_7: *bond angles*

Angles within a group are equivalent for *mm*2 symmetry

		Average			Average
S(2)–P(3)–S(1)	107·7°	107·7°	S(4)–P(3)–S(5)	102·9°	102·8°
S(1)–P(4)–S(3)	107·6		S(7)–P(4)–S(6)	102·8	
P(3)–S(1)–P(4)	110·1	110·1	P(3)–S(4)–P(1)	102·8	
			P(3)–S(5)–P(2)	102·4	102·4
S(2)–P(3)–S(4)	114·6		P(4)–S(6)–P(2)	102·1	
S(2)–P(3)–S(5)	113·9	114·0	P(4)–S(7)–P(1)	102·4	
S(3)–P(4)–S(6)	114·6				
S(3)–P(4)–S(7)	112·9		S(4)–P(1)–P(2)	103·0	
			S(7)–P(1)–P(2)	102·3	102·7
S(4)–P(3)–S(1)	108·4		S(5)–P(2)–P(1)	102·4	
S(5)–P(3)–S(1)	109·2	109·1	S(6)–P(2)–P(1)	102·9	
S(7)–P(4)–S(1)	109·9				
S(6)–P(4)–S(1)	108·9		S(4)–P(1)–S(7)	102·7	103·9
			S(5)–P(2)–S(6)	105·1	

Table 7. P_4S_{10}: *intramolecular bond lengths and angles*

Bonds or angles within a group are equivalent for $\bar{4}3$m symmetry

P(1)–S(1)	1·89 Å	S(2)–P(1)–S(1)	108·1°	S(2)–P(2)–S(7)	108·7
P(2)–S(5)	1·91	S(3)–P(1)–S(1)	111·1	S(6)–P(2)–S(7)	110·7
P(3)–S(8)	1·92	S(4)–P(1)–S(1)	110·1	S(3)–P(3)–S(6)	108·5
P(4)–S(10)	1·91	S(2)–P(2)–S(5)	107·8	S(3)–P(3)–S(9)	110·9
Mean value	1·908	S(6)–P(2)–S(5)	112·2	S(6)–P(3)–S(9)	109·5
		S(7)–P(2)–S(5)	108·8	S(4)–P(4)–S(7)	109·0
P(1)–S(2)	2·11	S(3)–P(3)–S(8)	110·7	S(4)–P(4)–S(9)	109·2
P(1)–S(3)	2·10	S(6)–P(3)–S(8)	107·6	S(7)–P(4)–S(9)	108·8
P(1)–S(4)	2·10	S(9)–P(3)–S(8)	109·5	Mean value	109·3
P(2)–S(2)	2·12	S(4)–P(4)–S(10)	109·1		
P(2)–S(6)	2·11	S(7)–P(4)–S(10)	110·5	P(1)–S(2)–P(2)	109·0
P(2)–S(7)	2·08	S(9)–P(4)–S(10)	110·1	P(1)–S(3)–P(3)	110·4
P(3)–S(3)	2·07	Mean value	109·6	P(1)–S(4)–P(4)	109·7
P(3)–S(6)	2·08			P(2)–S(6)–P(3)	109·7
P(3)–S(9)	2·08	S(2)–P(1)–S(3)	109·5	P(2)–S(7)–P(4)	110·1
P(4)–S(4)	2·12	S(2)–P(1)–S(4)	109·5	P(3)–S(9)–P(4)	110.0
P(4)–S(7)	2·10	S(3)–P(1)–S(4)	108·6	Mean value	109·8
P(4)–S(9)	2·09	S(2)–P(2)–S(6)	108·6		
Mean value	2·097				

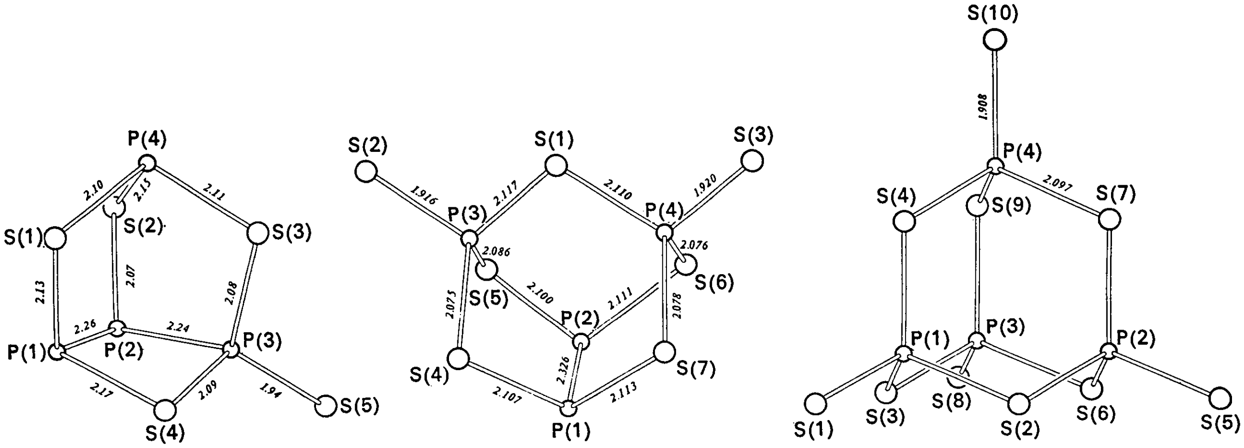

Fig. 1. From left to right: molecules of P_4S_5, P_4S_7 and P_4S_{10} with bond lengths in Å. For P_4S_{10} average values are given for bonds which are equivalent for the assumed $\bar{4}3m$ symmetry.

Table 8. *Estimated values for the standard deviations in bond lengths* (σ_1) *and valence angles* (σ_2), *and indices R*

	P_4S_5	P_4S_7	P_4S_{10}
σ_1(Å)	0·011	0·007	0·015
σ_2(°)	0·45	0·3	0·7
R	0·073	0·078	0·087

We wish to thank Professor E. H. Wiebenga for his interest throughout the course of this investigation. The anisotropic least-squares analyses were kindly carried out by Dr J. S. Rollett; the further calculations were done at the Groningen University computing centre. One of us (R.O.) acknowledges support from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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Crystal data for sodium thymidylyl-(5′ → 3′)-thymidylate-(5′).

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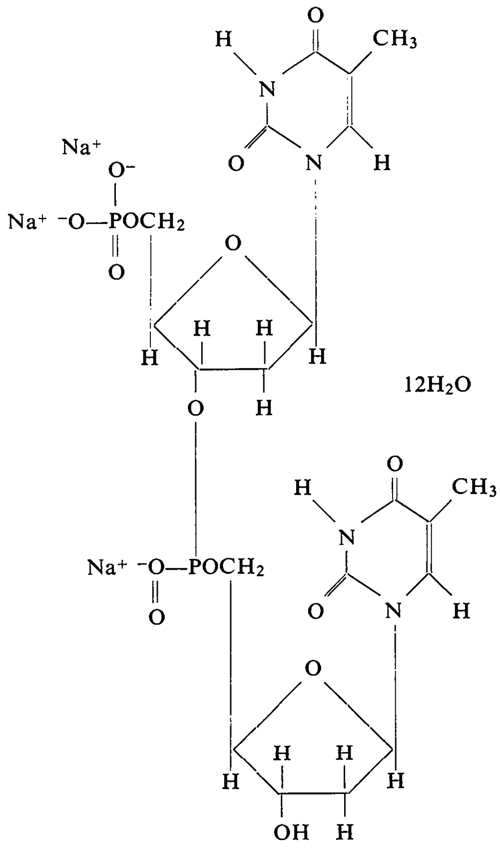

(I)

Crystals of the dinucleotide, sodium thymidylyl-(5′ → 3′)-thymidylate-(5′) (see I), prepared by the method of Gilham & Khorana (1958) and crystallized from 50% ethanol-water, are colorless plates elongated along *a* with (001) developed. The density was measured by flotation in $CHCl_3$–$CHBr_3$, and the unit-cell dimensions and space group were determined from various rotation, Weissenberg and precession photographs, and on the General Electric Spectrogoniometer.

Crystal data (λ, Cu $K\alpha$ = 1·5418 Å; λ, Mo $K\alpha$ = 0·7107 Å).

Sodium thymidylyl-(5′ → 3′)-thymidylate-(5′),
$C_{20}H_{25}N_4O_{15}P_2Na_3$, M.W. 692·4
(with $12H_2O$, M.W. 908·6).
Orthorhombic, $a = 16·06 \pm 0·04$, $b = 15·13 \pm 0·04$, $c = 15·65 \pm 0·04$ Å.
$U = 3803$ Å^3.
$D_m = 1·588$ g.cm^{-3}, $Z = 4$, $D_x = 1·209$ g.cm^{-3}. With $12H_2O$ of hydration per molecule of dinucleotide $D_x = 1·587$ g.cm^{-3}.
Absorption coefficient for Cu $K\alpha$ X-rays, $\mu = 23$ cm^{-1}.
$F(000) = 1904$.
Absent spectra: $h00$ when h is odd, $0k0$ when k is odd. Space group is $P2_12_12$ (D_2^3).

Gilham & Khorana (1958) reported $13H_2O$ of hydration on the basis of chemical analysis, but our measured density (1·588 g.cm^{-3}) corresponds closely to $12H_2O$ per molecule of dinucleotide ($D_x = 1·555$, 1·587, 1·618 g.cm^{-3} for 11, 12, and $13H_2O$ respectively).

The intensities of all reflexions out to $d = 1·2$ Å were measured with a scintillation counter and Cu $K\alpha$ radiation, by our usual techniques (see, *e.g.*, Camerman & Trotter, 1965). 953 reflexions (70% of the total) had intensities above