served reflections were not included in this refinement). The coordinates and temperature factors obtained from this refinement are given in Table 1*.

Table 1. *Coordinates and temperature factors of the atoms*

Atom	x	y	z	B
Cl	0·1646	0·5011	0·9230	3·31
S	0·4885	0·5971	0·6921	3·69
O(1)	0·6511	0·3466	0·6494	4·07
O(2)	0·4654	0·2950	0·8386	3·51
O(3)	0·1876	0·1757	0·4292	4·32
N(1)	0·2972	0·3805	0·4459	2·82
N(2)	0·2065	0·1633	0·8741	3·91
N(3)	0·0251	0·0772	0·6109	3·95
C(1)	0·4812	0·5169	0·4010	2·69
C(2)	0·4451	0·3914	0·4249	2·81
C(3)	0·5210	0·3385	0·6630	1·96
C(4)	0·7424	0·2851	0·8501	6·69
C(5)	0·8609	0·3282	0·8852	13·62
C(6)	0·1366	0·1441	0·6423	3·71

Estimated standard deviations (Å)	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Chlorine and sulfur atoms	0·006	0·007	0·006
Light atoms except C(4) and C(5)	0·02	0·02	0·02
C(4)	0·03	0·03	0·03
C(5)	0·05	0·06	0·05

The crystal is held together mainly by electrostatic attractions and hydrogen bonds between the $-\mathrm{NH}_3^+$ and Cl^- ions and by two other sets of hydrogen bonds: urea-urea and urea–cysteine ethyl ester (Fig. 1). The short c axis allows us to describe the structure as alternating 'layers' of chloride ions and hydrogen-bonded urea–cysteine ethyl ester complexes. Each chloride ion is separated from two neighboring ions in adjacent cells in the **c** direction by four nitrogen atoms, N(3) and N(1) from two urea and two cysteine ethyl ester molecules, respectively. The $\mathrm{CH_2}$–S–H and ethyl ester groups complete the coordination sphere of the chloride ion.

The urea molecules are roughly perpendicular to the (001) plane and form two chains of hydrogen-bonded urea molecules parallel to the c axis; only O(3) and N(2) are involved in the hydrogen bonding scheme, for N(3) coordinates two chloride ions. In addition, O(3) and N(2) are hydrogen-bonded to N(1) and O(2), respectively, of the cysteine ethyl ester molecule. The N(1)–O(3) distance, 2·70 ± 0·03 Å, is the shorter of the two; this is reasonable, since N(1) is positively charged. The N(2)–O(2) hydrogen-bond distance is 3·06 ± 0·03 Å, and O(2) is only 0·14 Å out of the plane of the urea molecule.

The sulfur atom is coordinated by a nitrogen, carbon, and two oxygen atoms in addition to the chloride ion. Little crystallographic information is available for S–H groups, but in view of the fact that none of the sulfur–oxygen or sulfur–nitrogen distances is unusually short, little can be said about specific interactions with the surrounding atoms.

The carbon atoms of the ethyl ester group appear to be in a cavity in which they have some freedom of movement; this is apparent from their high temperature factors. Besides the sulfur atom, no portion of the structure is situated so as to permit suitable stabilization by van der Waals forces for this group.

The bonding between the urea and cysteine ethyl molecule is of interest in that the –NH–C–CO– group is the structural unit of which the α helix is constructed. The present crystal structure shows that urea can be hydrogen-bonded to the charged nitrogen atom the oxygen atom of a single amino acid residue. Its interpretation in terms of protein denaturation, however, must await further experimentation.

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* A 35 mm microfilm containing the observed and calculated structure factors has been deposited as Document Number 8394 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, D.C. Microfilm copies can be obtained by an advance payment of $1·75.

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Location of hydrogen atoms in certain heterocyclic compounds.

By Chatar Singh, *Physics Department, University of Malaya, Kuala Lumpur, Malaysia*

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While the structures of certain pyrimidines were being investigated (Chatar Singh, 1965*a b*), it was noticed that the magnitude of the valence angle of nitrogen atoms in six-membered heterocyclic rings was dependent upon the extra-annular attachment to the nitrogen atom. The valence angle of nitrogen atoms with an extra-annular hydrogen atom was significantly larger than that of nitrogen without any attachment. To substantiate this empirical observation all six-membered heterocyclic compounds reported in *Acta Crystallographica* since 1948 were tabulated (Tables 1 and 2). In all these compounds, the authors have independently established the presence or absence of a hydrogen atom at the ring nitrogen. The histogram in Fig. 1 gives the distribution with respect to the nitrogen valence angle. The weighted mean value, with weight equal to $1/\sigma^2$, of the nitrogen valence angles with an extra-annular hydrogen atom is 125·0° ± 0·2° (from Table 1) whereas that without any attachment is 115·7° ± 0·2° (from Table 2). The differ-

Table 1. *Six-membered heterocyclic compounds with extra-annular hydrogen attached to the ring nitrogen*

Compound	Angle C–N–C (°)	σ (°)	References
Adenine hydrochloride	123·0	0·7	Cochran (1951
α-Pyridone	125·1	0·8	Penfold (1953*b*)
α-Thiopyridone	122	2·0	Penfold (1953*a*)
6-Amido-3-pyridazone	126	1·0	Cucka & Small (1954)
Uracil	124·7 123·6	0·7	Parry (1954)
Indanthrone	125·0 125·0	0·5	Bailey (1955)
Dialuric acid monohydrate	122 118	2·0	Alexander & Pitman (1956)
Diketopiperazine	126·0 126·0	0·3	Degeilh & Marsh (1959)
Thymine monohydrate	126·3 122·8	0·4	Gerdil (1961)
Barbituric acid dihydrate	124·8 125·5	0·7	Jeffrey, Ghose & Warwicker (1961)
Calcium thymidylate	125·7	1·4	Trueblood, Horn & Luzzati (1961)
Cytosine-5-acetic acid	122·0 121·9	0·3	Marsh, Bierstedt & Eichhorn (1962)
Pyridine hydrochloride	128	2·0	Rérat (1962)
Thiamine hydrochloride	120·7	0·4	Kraut & Reed, (1962)
1-Methylcytosine hydrobromide	127	2·0	Bryan & Tomita (1962)
Cytosine monohydrate	121·3	0·4	Jeffrey & Kinoshita (1963)
1-Methylthymine	126·3	0·2	Hoogsteen (1963)
Anhydrous barbituric acid	128·1 124·8	0·4	Bolton (1963*a*)
Anhydrous dilituric acid	126·9 124·0	0·3	Bolton (1963*b*)
1-Methyluracil hydrobromide	120·1	2·0	Sobell & Tomita (1964*a*)
9-Methylguanine hydrobromide	126·5	2·0	Sobell & Tomita (1964*b*)
Anhydrous alloxan	126·2 126·2	0·5	Bolton (1964)
Ammonium barbiturate	125·2 125·7	0·8	Craven (1964)
Alloxan	125·9 126·7	0·3	Chatar Singh (1965*a*)
Alloxantin	125·0 123·9	0·8	Chatar Singh (1965*b*)

Table 2. *Six-membered heterocyclic compounds without extra-annular attachment to the ring nitrogen*

Compound	Angle C–N–C (°)	σ (°)	References
2-Amino-4-methyl-6-chloropyrimidine	114 114	1·2	Clews & Cochran (1948)
2-Amino-4,6-dichloropyrimidine	114 114	1·2	Clews & Cochran (1948)
4-Amino-2,6-dichloropyrimidine	110·2 115·0	1·2	Clews & Cochran (1949)
5-Bromo-4,6-diaminopyrimidine	112 114	1·2	Clews & Cochran (1949)
Cytidine	116	2·0	Furberg (1950)
Adenine hydrochloride	112·5	0·7	Cochran (1951)
Nicotinic acid	117·5	1·1	Wright & King (1953)
6-Amido-3-pyridazone	118	1·0	Cucka & Small (1954)
Nicotinamide	118·4	1·5	Wright & King (1954)
s-Triazine	113·2 113·2	0·4	Wheatley (1955)
α-Phenazine	116·6 116·6	0·6	Herbstein & Schmidt (1955)
Acridine III	117·2	0·3	Phillips (1956)
s-Tetrazine	116·3 116·3 115·6 115·6	0·7	Bertinotti, Giacomello & Liquori (1956)
4,5-Diamino-2-chloropyrimidine	118·0 112·5	0·9	White & Clews (1956)
2,2′-Bipyridine	116·7	1·4	Merritt & Schroeder (1956)
Pyrazine	115·1 115·1	0·3	Wheatley (1957)
Pyrimidine	115·2 115·1	0·5	Wheatley (1960)

Compound	Angle C–N–C (°)	σ (°)	References
α-Pyrazinamide	115·4 116·0	0·6	Takaki, Sasada & Watanabe (1960)
2,2′-Pyridil	116·5 120·5	1·8	Hirokawa & Ashida (1961)
Thiamine hydrochloride	118·8	0·4	Kraut & Reed (1962)
1-Methylcytosine hydrobromide	114	2·0	Bryan & Tomita (1962)
Cytosine monohydrate	118·9	0·4	Jeffrey & Kinoshita (1963)
9-Methylguanine hydrobromide	112·3	2·0	Sobell & Tomita (1964*b*)

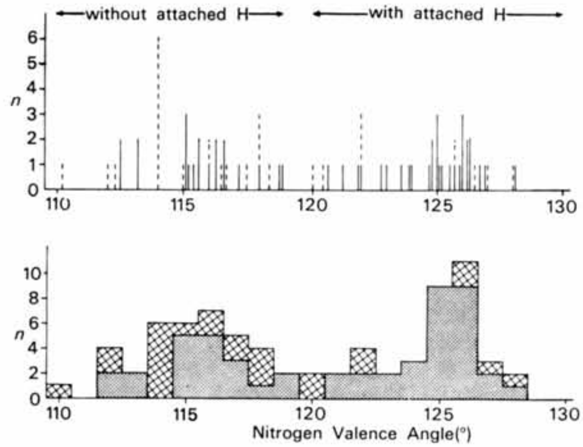

Fig. 1. The distribution with respect to the nitrogen valence angle for heterocyclic compounds with and without an extra-annular hydrogen atom attached to the ring nitrogen. *n* is the number of angles in the angular range. Angles with standard deviations of less than 1° are represented by dotted rectangles (lower figure) and continuous lines (upper figure).

ence of 9·3° between these two values is indeed very significant. Taking the spread to be ±3° leaves a three-degree gap which is very significant; since a reasonably well-refined structure should have an angular standard deviation of less than 2°. The above observation contradicts that made by Hameka & Liquori (1956) who stated that in heterocyclic rings the bond angle of nitrogen is less than 120°. The observation makes it possible to decide whether or not a nitrogen atom in a six-membered ring has an extra-annular hydrogen atom attached to it – if the angle lies within the range (125 ± 3)° it indicates that a hydrogen atom is bonded to the nitrogen and if it lies within the range (116 ± 3)° then no hydrogen is attached to the nitrogen.

As an example, consider guanine hydrochloride (Fig. 2) in which the hydrogen atom positions were not determined in the structure analysis (Broomhead, 1951). Broomhead reduced the fourteen possible tautomers to four which she stated were indistinguishable. The valence angles of the nitrogen atoms N(1) and N(3), are 126° and 113° respectively. Application of the empirical observation rules out the possibility of a hydrogen at N(3) thereby eliminating the possible existence of tautomers I and II. Tautomer III can next be eliminated by consideration of the magnitude of the C(6)–O bond of length 1·20 Å, which is double-bond

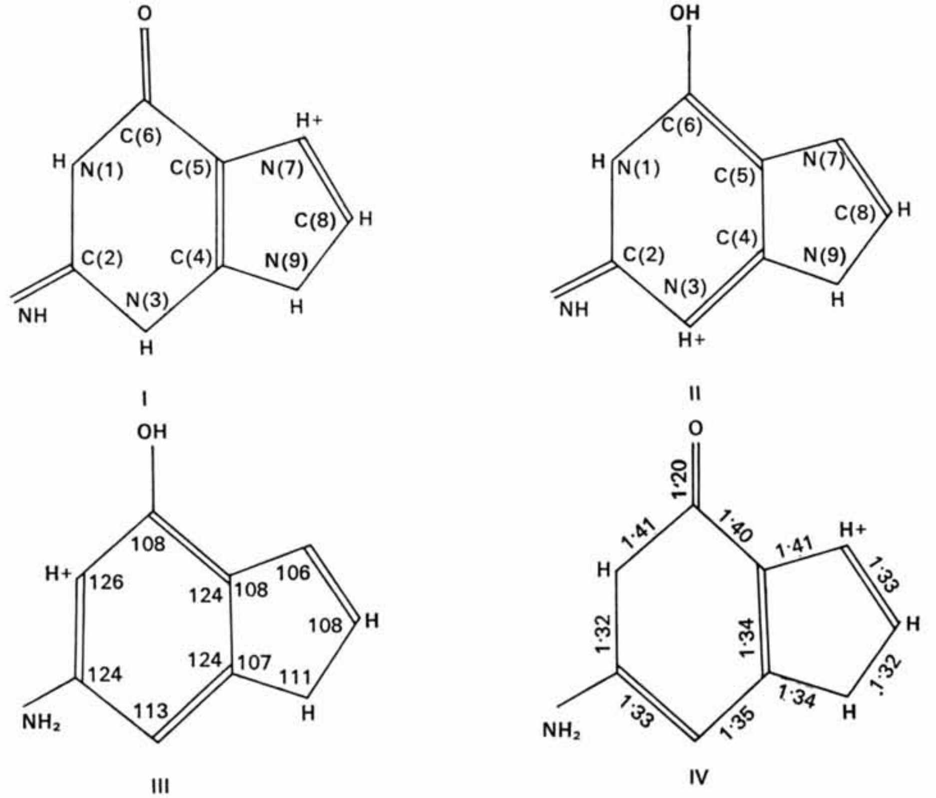

Fig. 2. Guanine hydrochloride tautomers (Broomhead, 1951).

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

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Refinement of the crystal structures of some phosphorus sulphides.

By AAFJE VOS, ROELI OLTHOF, F. VAN BOLHUIS and RIEMKE BOTTERWEG, *Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Bloemsingel* 10, *Groningen, The Netherlands*

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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.

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 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.

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 &